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Studies of the Molecular Dynamics, Transport Properties, and Thermal Degradation of PVC

by

Theodore Radiotis

A thesis submitted to the Faculty of Graduate Studies in partial fulfillment of the requirements of the degree of Doctor of Philosophy

Department of Chemistry McGill University Montreal, Quebec, Canada

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Chemistry

Theodore Radiotis

Studies of the Molecular Dynamics, Transport Properties, and Thermal Degradation of PVC

Abstract

This thesis concentrates on three main areas of research in the field of poly(vinyl chloride), PVC: (1) microstructure determination and local chain motions of PVC in a plasticized system, (2) permeability of PVC and plasticized PVC to gases, and (3) computer modeling of the thermal degradation of PVC.

A quantitative carbon-13 NMR spectrum of PVC in 1,1,2,2-tetrachloroethane- d_2 (TCE- d_2) was recorded. Theoretical predictions using Bernoullian statistics permitted the reassignment of several resonances. Carbon-13 spin-lattice relaxation times and NOE values were measured as a function of temperature at two magnetic fields for PVC in two solvents, di-butyl phthalate (DBP) and TCE- d_2 . The difference found in the simulation parameters, from the Dejean-Lauprêtre-Monnerie model, for PVC in the two solvents were rationalized by assuming a specific interaction between DBP and the CHCl group of PVC and to the relative solvent quality.

The permeability coefficients, P, of PVC films to oxygen were measured as a function of temperature and plasticizer type and concentration. The plasticizers used were di-(2-ethylhexyl) phthalate (DOP), tri-butyl phosphate (TBP), and a binary mixture of the two with a concentration of $\phi_{DOP} = 0.6$. The effect of plasticizer type on the permeation coefficients of oxygen followed the trend: P(TBP) > P($\phi_{DOP} = 0.6$) > P(DOP). Arrhenius plots of the permeability coefficients showed that the unplasticized and plasticized PVC films of low concentration of plasticizer ($\phi_{plas} < 0.2$) displayed a discrete change in the slope, in the vicinity of the glass transition temperature, that reflected changes in the activation energy for permeation. In addition, the permeation and diffusion coefficients of oxygen and hydrogen chloride gases in an unplasticized PVC film were measured as a function of temperature. The permeation coefficient of hydrogen chloride gas, at a given temperature, was *ca*. 80 times higher than that for oxygen and the diffusivity *ca*. 8 times lower. The activation energies for diffusion above the T_g were about 47% larger than

those below the T_g and were accounted for by the ratio of the thermal expansion coefficients of PVC above and below the T_g . The activation energies for diffusion were found to be smaller for O_2 than HCl which was justified from differences in their molecular diameters. The activated entropies for diffusion, for both gases, were lower in the glassy state as compared with the rubbery state. These results suggest that the increase in segmental mobility of the polymer chains above the T_g increases the diffusivity as well as the zone of activation for diffusion leading to the increase in both energy and entropy of activation.

A computer program has been written which simulates, according to Bernoullian statistics, the relative handedness of successive monomer units during polymerization and calculates the probabilities of configurational sequences before and after a specified degradation mechanism. At levels of degradation that are accessible to experimental verification by solution NMR (<2%), the changes in isotacticity that are predicted by these simulations are at (or under) the limits of experimental error. Furthermore, the simulations indicate that for the degradation to result in double bond lengths that correspond to experimentally determined values requires that the dehydrochlorination also include some atactic and syndiotactic sequences which, in turn, reduces the changes in P_{mm} . As a result it is unlikely that direct verification of the preferential initiation of degradation at isotactic sequences can be achieved by NMR techniques.

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Chimie

Theodore Radiotis

Etude du mouvement moléculaire, des propriétés de transport, et de la dégradation thermique du PCV

Résumé

Cette thèse se concentre sur trois domaines de recherche du polychlorure de vinyle, PCV: (1) la détermination de la microstructure et les mouvements locaux d'une chaine de PCV dans un système plastifié, (2) la perméabilité des gaz dans le PCV et les PCV plastifiés, et (3) la simulation par ordinateur de la dégradation thermique du PCV.

Des spectres RMN¹³C quantitatifs ont été obtenus pour le PCV dans le tetrachlorure-1,1,2,2 d'éthane deutéré (ETC-d₂) avec une résolution uniquement augmentée. Les calculs statistiques de Bernoulli ont permis une réévaluation de certaines résonnances. Le temps de relaxation spin-réseau et le facteur d'intensification d'Overhauser ont été mesurés en fonction de la température dans deux champs magnétiques pour le PCV en solution dans le dibutyl phthalate (DBP) et l' ETC-d₂. La différence dans les paramètres de simulations, d'après le modèle de Dejean-Lauprêtre-Monnerie, provient d'une intéraction spécifique entre le solvant DBP et le groupe CHCl du PVC et de l'effet la qualité du solvant utilisé.

Les coefficients de perméabilités, P, de l'oxygène dans des pellicules de PCV ont été mesurés en fonction de la température, du type de plastifiant, et de leur concentration. Les plastifiants utilisés etaient di(éthyl-2-hexyl) phthalate (DOP), tributyle phosphate, (TBP), et un mélange des deux à concentration de $\phi_{DOP} = 0.6$. L'effet du type de plastifiant sur les coefficients de perméabilité de l'oxygène suivent l'ordre: P(TBP) > P($\phi_{DOP} = 0.6$) > P(DOP). La courbe d'Arrhénius des coefficients de perméabilité pour des systèmes plastifiés et non plastifiés indique, à basse concentration de plastifiant ($\phi_{plas} < 0.2$), un changement de pente dans les environs de la transition vitreuse indiquant un changement dans l'énergie d'activation. Les coefficients de perméabilité et de diffusion de l'oxygène et du gaz hydrochlorique ont aussi été mesurés en fonction de la température. Le coefficient de perméabilité du gaz hydrochlorique, à n'importe quelle temperature, est 80 fois plus haut que celui de l'oxygène, tandis que celui de la diffusion est 8 fois plus bas. L'énergie d'activation pour la diffusion à des températures plus hautes que la transition vitreuse est 47% plus élevée que celle à des températures inférieures à la transition vitreuse. La différence est reliée au ratio des coefficients d'expansion thermique du PCV au dessus et en dessous de la transition vitreuse. Les énergies d'activatrion pour la diffusion sont plus petites pour l'oxygène que pour le gaz hydrochlorique. Cette différence est reliée aux différents diamètres moléculaires. L'entropie d'activation pour la diffusion des deux gaz est plus basse pour l'état vitreux que pour l'état élastique. Ces résultats suggèrent que l'augmentation de mobilité dans les chaînes du polymère, aux températures plus élevées que celle de la transition vitreuse, augmente la diffusion ainsi que la zone d'activation pour la diffusion, qui elle entraine une augmentation de l'entropie et l'énergie d'activation.

Un logiciel à été développé pour simulé, d'après les statistiques de Bernoulli, la polymérisation des chaînes de PCV et calculer les probabilités configurationelles avant et après une dégradation spécifique. Aux niveaux des dégradations qui sont accessibles à la vérification par RMN en solution (<2%), les changements dans les séquences isotactiques prédits par ces simulations sont dans les limites permises de l'incertitude expérimentale. De plus, les simulations indiquent que pour obtenir des séquences dégradées qui sont observables par détermination expérimentale, il est nécessaire d'inclure les séquences syndiotactiques et atactiques lors de l'élimination de l'hydrochlorure. Ces séquences permettent ainsi de réduire les changements dans la valeur P_{mm} . Donc, l'observation de l'initiation préférentielle de dégradation des séquences isotactiques ne peut être accomplie par RMN.

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List of Symbols

$\rightarrow \rightarrow \rightarrow \rightarrow \rightarrow$ a, b, c, or d	vectors describing the four directions found in a tetrahedral lattice	
A	area of film	
Ad	a parameter used in the free volume theory of diffusion	
A _∞	maximum amplitude of a signal in an NMR spectrum	
b	the logarithmic base in the log χ^2 distribution model	
b _v	the molar volume constant of the van der Waals equation of state for gases	
b _{ha}	the hole affinity constant	
B _d	parameter that characterizes the efficiency of use of the available free volume fraction in the diffusion process	
B _{loc}	local magnetic field	
B ₀	static magnetic field strength	
B ₁	alternating magnetic field orthogonal to the static field	
c	concentration	
∂с/∂х	concentration gradient	
c ₁	the concentration of the permeant in the face adjacent to chamber 1	
С	total concentration of penetrant in a polymer	
C _H	the concentration of permeant sorbed in holes (Langmuir sorption)	
Ċ _Ħ	the hole saturation constant	
C _{plas}	concentration of plasticizer	
đ	diameter of a cylinder produced by four adjacent and roughly parallel chain segments	
d _b	molecular diameter calculated from the van der Waals constant	
D	the diffusion coefficient	
Do	pre-exponential factor for diffusion	
ΔE	energy separating the nuclear spin states	
Ea	apparent activation energy calculated from correlation times	

Ed	activation energy for diffusion
Ep	activation energy for permeation
Eη	activation energy of the solvent viscosity
f	the fractional free volume of a system
f_1, f_2	fractional free volumes of components 1 and 2
f _{g1} , f _{g2}	fractional free volumes of components 1 and 2 at their respective glass transition temperature
F	flux, <i>i.e.</i> , the amount of substance diffusing across unit area in unit time
F _d	sum of the squares of the relative deviations between the experimental and calculated T_1 and NOE values
F _x	flux in the x-direction
<i>g</i> ⁺	gauche ⁺ conformation, <i>i.e.</i> , the rotation angle ϕ equals +120°
8-	gauche ⁻ conformation, <i>i.e.</i> , the rotation angle ϕ equals -120°
ΔG_m	free energy of mixing
C(t)	time-dependent correlation function
Ğ(τ)	correlation function for a distribution of correlation times
h	Planck constant
ΔH_{m}	heat of mixing
ΔH _s	heat of solution
ΔH _υ	molar heat of fusion of a polymer repeat unit
$\Delta \bar{H}_{cond}$	the molar heat of condensation
$\Delta \bar{H}_1$	the partial molar heat of mixing
I	nuclear spin angular-momentum quantum number
I ₀	modified Bessel function of order zero
I _{NMR}	experimental intensities determined by the NMR integrator
I _{CA}	experimental intensities determined by a curve analysis program
J(ω)	spectral density function
k	the plasticizer efficiency parameter

k _b	Boltzmann constant	
k _d	diffusion-controlled rate constant for a type 1 transition	
k _H	Huggins constant	
k _K	Kraemer constant	
1	membrane thickness	
М	angular momentum	
M ₀	magnetization at equilibrium	
M ₁	molecular weight of the diluent	
Mz	magnetization along the z-axis	
M _{xy}	magnetization along the x-y plane	
M _y .	magnetization along the y' axis	
\overline{M}_n	number average molecular weight	
Mw	weight average molecular weight	
N(n _i)	number fraction of isotactic sequences containing exactly n _i units	
W(n _i)	weight fraction of isotactic sequences containing exactly n _i units	
m	meso configuration	
m	magnetic states	
m _b	number of bonds involved in the cooperative motion	
m _d	mobility for the diffusant molecule	
n _H	number of directly bonded protons	
n _i	number of repeat units in an isotactic sequence	
<n<sub>i></n<sub>	average length of isotactic sequences	
n _s	number of repeat units in a syndiotactic sequence	
<n<sub>s></n<sub>	average length of syndiotactic sequences	
n	length of polyene sequence	
ni	minimum isotactic length for degradation	
N	number of molecules	
N _A	Avogadro's constant	
N_, N_	populations of the upper and lower magnetic states	

Nni	number of isotactic sequences containing n _i isotactic repeat units	
N _{ns}	number of syndiotactic sequences containing n _s syndiotactic repeat units	
р	parameter that is related to the width of the distribution of correlation times in the log- χ^2 model	
P1. P2	the ambient pressures on the opposite sides of the film	
P	the permeation coefficient	
Pa	the partial pressure of the permeant	
P _i	internal pressure	
P _m	probability of generating a meso configuration	
Pr	probability of generating a racemic configuration	
Po	pre-exponential factor for permeation	
P _{mm}	probability of an mm triad sequence	
P _{mr}	probability of an mr triad sequence	
P _{rr}	probability of an rr triad sequence	
P _{HH}	probability of obtaining two heads	
P _{mmmm}	probability of an mmmmm pentad sequence	
Pmmmr	probability of an mmmmr pentad sequence	
Prmmr	probability of an rmmmr pentad sequence	
Q	total amount of permeant	
r	racemic configuration	
R	the gas constant	
r _i	distance of atom i from the rotation axis in a Type 1 motion	
^г С-Н	¹³ C-H internuclear distance	
r/n	relative frequency when n trials are made and a given event occurs r times	
S	the solubility coefficient	
So	pre-exponential factor for solubility	
∆S _m	entropy of mixing	
ΔS^{\ddagger}	the entropy of activation for a diffusion jump	

۸S [‡]	activated entropy of the diffusing molecule
	activated entropy of the solution
ΔS polymer	activated entropy of the porymer
t	ŭme
t	trans conformation, <i>i.e.</i> , the rotation angle ϕ equals 0°
t _l	the time lag in diffusion studies
^t р	duration of the radio frequency irradiation
^t d	delay time between pulses
Т	temperature
T ₁	spin-lattice relaxation time
T ₂	spin-spin relaxation time
T _b	the boiling temperature of a gas
T _c	the critical temperature of a gas
T _f	final temperature in the apparent melting of a PVC particle
Tg	glass transition temperature
T _m	mid-point temperature in the apparent melting of a PVC particle
T _m o	melting temperature of the pure polymer
Τ _o	onset temperature in the apparent melting of a PVC particle
T_{g1}, T_{g2}	glass transition temperature of components 1 and 2
T _{g,PVC}	glass transition temperature of PVC
T _{flow}	flow temperature
T _{break}	temperature at which a break occurs in the Arrhenius plots of the transport coefficients
vo	blank voltage reading from oxygen sensor
V _u , V ₁	molar volumes, at T_m , of the polymer repeat unit and diluent
V _∞	final voltage from oxygen sensor
w ₃	characteristic frequency or rate of occurrence of a three bond jump
wplas	the weight fraction of the plasticizer
W	waiting time before the sequence is repeated
W ₀	zero-quantum process arising from a mutual spin flip

W ₂	double quantum process which corresponds to the simultaneous
	relaxation of both spins.
$w_{\alpha\beta}$	transition probability for an $\alpha \rightarrow \beta$ transition
w_{1H}	single quantum transition probability for a hydrogen nucleus
w _{1C}	single quantum transition probability for a carbon-13 nucleus
x	x-direction

Greek letters

α_{g}, α_{r}	the expansion coefficients in the glassy and rubbery states
α ₁	coefficient of thermal expansion for the diluent
$\Delta \alpha_1, \Delta \alpha_2$	thermal coefficients of expansion of components 1 and 2.
α_A, α_B	quadratic force constants in the initial and final states of a type 1 motion
Г(р)	gamma function of p
γ	magnetogyric ratio
γ _C . γ _H	the magnetogyric ratios of ¹³ C and ¹ H nuclei
ε/k	the force constant in the Lennard-Jones 6-12 potential
η _r	relative viscosity
[η]	intrinsic viscosity
η _{sp}	specific viscosity
θ	angle between the moment and B ₀
θι	half angle of the librational motion of the C-H bond in the DLM model
θν	bond valence angles
θ _{CH}	half angle of the librational motion of the C-H bond in the methine group
θ_{CH_2}	half angle of the librational motion of the C-H bond in the methylene group
θ _{C-H}	the angle of the ¹³ C-H bond with the magnetic field
θ	theta solvent

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λ	the length of a unit diffusion jump	
μ	magnetic moment	
μ ₀	vacuum magnetic permeability	
v ₀	resonance frequency	
v ₁	frequency of alternating magnetic field	
ξ _i	friction constant for atom i in the mobile unit	
ρ	density of the diluent at 25 °C	
σ	root mean square of the relative deviations between the experimental and calculated T_1 and NOE values	
- T	average correlation time that defines the center of the distribution of correlation times in the log- χ^2 model	
τ _C	molecular correlation time	
τ _h	harmonic mean correlation time	
τ _R	correlation time for the overall tumbling of the entire polymer chain	
τ ₀	correlation time for an isolated transition	
τι	correlation time for a correlated pair transition	
τ_2	correlation time for the librational motion	
φ	the angle of rotation about each bond of the chain	
φ ₁ , φ ₂	volume fraction of components 1 and 2	
фдор	volume fraction of DOP in a binary mixture of DOP and TBP	
χ	Flory-Huggins interaction parameter	
ω _C , ω _H	¹³ C and ¹ H Larmor frequencies	

Abbreviations

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Ar	argon
AT	acquisition time
A/D	analog to digital
CED	cohesive energy density of the polymer
Cl ₂	chlorine
CH4	methane

CO	carbon monoxide	
CO ₂	carbon dioxide	
CSA	chemical shift anisotropy	
DCB	dichlorobenzene	
DD	dipole-dipole interaction	
DP	degree of polymerization	
DBP	di-butyl phthalate	
DLM	Dejean, Lauprêtre, and Monnerie conformational model	
DOA	di-octyl adipate	
DOP	di-octyl phthalate	
H ₂	hydrogen	
Не	helium	
H ₂ O	water	
HWH	Hall, Weber, and Helfand conformational model	
IR	infrared spectroscopy	
JS	Jones and Stockmayer conformational model	
Kr	krypton	
NMR	nuclear magnetic resonance	
nt	number of transients	
NOE	nuclear Overhauser effect	
N ₂	nitrogen	
Ne	neon	
NH4	ammonia	
O ₂	oxygen	
PEMA	poly(ethyl methacrylate)	
PMA	poly(methyl acrylate)	
PVA	poly(vinyl acetate)	
PVC	poly(vinyl chloride)	
RD	the total time between sequences or the recovery delay $(= W + AT)$	

- SC scalar coupling
- SR spin rotation
- THF tetrahydrofuran
- TBP tri-butyl phosphate
- TCE 1,1,2,2-tetrachloroethane
- TCP tri-cresyl phosphate
- TMS tetramethylsilane
- STP standard temperature and pressure
- VCM vinyl chloride monomer
- ¹³C carbon-13 nucleus
- %deg percent degradation

CHAPTER 1 INTRODUCTION TO POLY(VINYL CHLORIDE)

1.1 GENERAL

Polymerization of vinyl chloride by free-radical initiation generates poly(vinyl chloride), PVC, which is converted by compounding and fabrication into a great variety of plastic articles and devices. The polymer alone is difficult to process (it cannot be molded without thermal decomposition) and the resulting products are rigid and unusually tough. However, its response to ready chemical additives has permitted the generation of both rigid and flexible products which, in turn, has allowed PVC to become a worldwide, multibillion-pound industry.

The two major drawbacks that are inherent to PVC are (1) its vulnerability to photo and thermal degradation; and (2) its rigid and tough characteristics which severely limit the useful end-products, except when plasticizers are added. In contrast to the orderly technical development of other polymers, PVC has developed in a largely unplanned fashion. Only in recent years have scientific efforts been made in developing an understanding of the formulations and fabrication of PVC. The two main areas of research that form the basis of this thesis are: (1) the plasticizer and the diffusion of gases through PVC and plasticized PVC films; and (2) the photo and thermal degradation of PVC.

When a small amount of plasticizer is added to PVC, the resin can be molded to form semi-rigid to very flexible products, depending on the amount of plasticizer added. Hence, a plasticizer is incorporated into a resin to increase its workability and its flexibility. As a result the physical properties of the polymer are altered tremendously. For example, the glass transition temperature is lowered and the permeation coefficient, *i.e.*, the rate at which a gas that can pass through the resin, is increased. This property has very important industrial applications. For example, the controlled permeation of oxygen through a film is vital if it is to be used as a food packaging material (topic of Chapter 3). The compatibility of PVC with plasticizers is not well understood at the molecular level. interactions, the functional group of PVC which is actually interacting with the plasticizer has been a matter of controversy (topic of Chapter 2).

The thermal and photo degradation of PVC has been considered by most experts to be a major disadvantage of this material. Upon exposure to temperatures as low as 100 to 120 °C, it undergoes a degradation reaction that results in the release of hydrogen chloride gas and the formation of long polyene sequences. This instability is surprising because low-molecular-weight model compounds for PVC are relatively stable organic compounds. Hence, over the years many studies have been made to develop a better understanding of the reason for its poor thermal stability (topic of Chapter 4).

Prior to probing further into the problems and advancements in these areas of research, a brief summary of the historical aspects of PVC, the role of PVC in the market, environmental and safety issues, and the structure of PVC will be presented.

1.1.1 Historical Aspects of PVC

The vinyl chloride monomer (VCM) was first synthesized by von Liebig and Regnault in 1835. It was about forty years later that Baumann discovered that when vinyl chloride is exposed to sunlight a white solid (PVC) is formed. From the early 1900's to about the mid 1930's several discoveries were made, *e.g.*, (1) the production of VCM by the addition of hydrogen chloride to acetylene; (2) the use of organic peroxides to initiate the polymerization to PVC; (3) the use of plasticizers, by Simon, who noted that boiling PVC in tri-cresyl phosphate (TCP) or di-butyl phthalate (DBP) produced a highly elastic polymer; and (4) the stabilization of PVC with earth soaps. However, it was not until 1936 that Union Carbide opened the first PVC homopolymer plant. Its great demand during World War II for use as wire insulation in military applications further enhanced the success of PVC. By 1950 five U.S companies were producing PVC and this increased to 20 by the 1960's. Today, it is has become an international multibillion-pound business.

1.1.2 Role of PVC in the Market

Even though all sorts of problems have beset the PVC industry, for instance, the finding that VCM vapor may cause liver cancer, it is still among the most frequently used thermoplastics. A recent survey indicates, Table 1.1, that in the U.S. market PVC ranked third among major plastics in terms of pounds of resin sold in the year 1993. Building and construction applications overshadow other PVC uses, accounting for nearly 70% of its use, followed by consumer and institutional, packaging, and electrical and electronic

Table 1.1

volume, in billion pounds, of major plastics used in U.S. for various
applications in 1993 (from Chemical and Engineering News ¹).

• • • •

Plastic	Volume	
Low-density polyethylene ^a	11.50	
High-density polyethylene	9.38	
Polyvinyl chloride	9.17	
Polypropylene	8.15	
Polystyrene	5.15	
Thermoplastic polyester	2.17	

^aLow density and linear low density polyethylene

applications at about 7% each. The current growth of PVC consumption is attributed mainly to construction codes that have allowed its use in place of copper or cast iron pipes.

1.1.3 Environmental and Safety Aspects

A major problem that the PVC industry faced in the early 1970's resulted from studies which indicated that inhalation of vinyl chloride vapors could cause rare angiosarcoma liver cancer. PVC makers were forced to lower substantially (1 ppm limit) the residual VCM in the resin, which they did efficiently.

Today, the new battle over the future of PVC is the global debate concerning the industrial use of chlorine, *i.e.*, is PVC a polymer that is generating an ecological time bomb that should be banned or are the hazards overstated (or at least unproven) so that a ban is unwarranted. These issues were most recently debated in Toronto by Fred Krause, director and in charge of environmental solutions for the PVC-supplier Geon Co., and Charlie Cray, a midwest toxics campaigner for the advocacy group Greenpeace.² The major point that was addressed was the dioxin levels that are emitted when PVC is fed into incinerators. Due to a limited number of studies, the debate did not resolve anything nor was it expected to. What it did was bring forth the environmental issues so that the industry can better address this matter. Undoubtedly this will continue to be a major issue of debate in the foreseeable future.
1.2 STRUCTURE OF PVC

1.2.1 Particle Morphology

Poly(vinyl chloride) is polymerized from vinyl chloride through a free-radical mechanism, generally by suspension or emulsion polymerization methods. It is insoluble in its monomer and precipitates from the monomer phase at about 0.1% conversion.^{3,4} This phase separation affects both the polymerization kinetics and particle morphology of the resin.

The aggregation process within the monomer plays an important role in establishing the morphological character of the resin. Knowledge of the particle structure is important in both rigid and flexible PVC applications. In the case of flexible PVC, which is pertinent to this study, the particles must be capable of ingesting large quantities of plasticizer during powder mixing. The particle structure, undoubtedly, plays a major role in this plasticizer uptake. A summary of the nomenclature often found in the literature to describe the PVC particle regions along with a description of their origin is given in Table 1.2.^{5,6}

The average grain size of PVC resins normally manufactured is between 50 and 250 μ m in diameter. A sliced PVC particle shows that the interior comprises agglomerates of many small, *ca.* 1 μ m, particles called primary particles. It is the space between these primary particles that gives PVC its porosity, which in turn allows it to be easily compounded with plasticizers, stabilizers, and lubricants.

1.2.2 Polymer Chain Structure

A variety of analytical techniques have been employed to study the effects of polymerization conditions on the polymer chain structure. At the molecular level, poly(vinyl chloride) can be depicted as having the following chemical structure:

This representation implies that all chains are initiated by an active site I, with the monomer units placed in a head-to-tail arrangement and terminated by a species X. As it

Term	Size (µm)	Origin or description		
Microdomain	0.01-0.02	Aggregation of about 50 polymer chains (occurs at $< 1\%$ conversion).		
Domain	0.1-0.2	Aggregation of about 1000 micro-domains to form the nucleus of the primary particle.		
Primary particle	0.6-0.8	Growth of a domain that is formed at low conversions ($< 2\%$).		
Agglomerate	1-10	Formed during the early stages of polymerization by aggregation of primary particles (occurs at 4-10% conversion).		
Subgrain	10-150	Growth of the agglomerates. Polymerized monomer droplet.		
Grain	50-250	Visible, free-flowing powder that is made up of more than one subgrain.		

 Table 1.2

 Poly(vinyl chloride) nomenclature used to describe the particle regions.

will become apparent later, this simple representation does not portray accurately the actual situation in vinyl chloride polymerizations. During the past decade, extensive efforts have been made to better understand the chemical structure of the PVC chain. Studies in the areas of thermal stability and stereoregularity have played major roles in shedding new light on the structure of PVC.

1.2.2.1 Chain Defect Sites

In the last twenty years, a vast amount of evidence has been accumulated about the defect structures of PVC. These studies involved the reductive dehydrochlorination of PVC, followed by 13 C NMR analysis of the resulting polyethylene. The following structures have been reported:

(1) Chloromethyl branches, in the range of 2 to 4 per 1000 monomer units⁷⁻⁹

(Scheme 1.2)

(2) Saturated end groups, of about 0.8 to 0.9 per molecule⁷⁻¹²

$$\sim CH_2 - CH - CH_2 \qquad (Scheme 1.3)$$

(3) Unsaturated end groups, with a 0.7 content per molecule⁷⁻¹¹

$$\sim CH_2 - CH = CH - CH_2 CI \qquad (Scheme 1.4)$$

(4) Longer branches consisting of butyl (1.8 branches per 1000 monomer units) and longchain branches (0.6 branches per 1000 monomer units).¹³ The question of whether branch points have a tertiary hydrogen (Scheme 1.5(a)) or tertiary chlorine (Scheme 1.5(b)) has been the subject of some controversy. From the work of Hjertberg and Sorvik⁹ it now seems to be resolved in favor of tertiary chlorine.



(5) In commercial manufacturing of PVC, complete elimination of oxygen is difficult. As a consequence, the oxygen interacts with the growing polymer radical to form an internal carbonyl structure.

(6) In Scheme 1.4, a representation of unsaturated end groups is given. However, unsaturation can also occur along the chain. The chlorine adjacent to the double bond is termed an allylic chlorine. Studies have shown that PVC contains between 0.1 and 0.2 internal double bonds per 1000 monomer units.¹⁴⁻¹⁷

1.2.2.2 Introduction to Tacticity (Configurations)

The structure in Scheme 1.1 is a simple planar representation of the threedimensional PVC structure. As is discussed in detail later, the addition of each monomer occurs in a manner such that there is free rotation around the terminal carbon-carbon bond. As a consequence, the polymer chain can take on several possible configurations. Before discussing these configurations, a general introduction to stereoregularity is desirable. This will not only develop a clearer understanding of stereoregularity, but is essential background to Chapters 2 and 4. In this section, a statistical description of stereoregularity is given. The discussion of stereoregularity includes references to the application of high resolution nuclear magnetic resonance (NMR) techniques for the quantitative determination of configurational sequence distributions which can be used to test theoretical predictions. A brief review is also given on the following topics: Elementary statistical analysis (probability); Bernoullian statistics; average lengths and size distributions of isotactic and syndiotactic sequences.

1.2.2.2.1 Nomenclature and Application of NMR to Synthetic Vinylic Polymers

The use of ¹H NMR in studying stereochemical configurations was pioneered and developed to a high degree of sophistication by Bovey and his colleagues.¹⁸⁻²⁰ In the last two decades, this has been facilitated by tremendous advancements in the development of superconducting magnets with increased field strength as well as of new techniques²¹⁻²³, such as ¹³C and 2D NMR. The theory of NMR is discussed in detail in Chapter 2.

For this discussion, the polymerization of a monosubstituted vinyl monomer will be considered:



(Scheme 1.6)

For vinyl chloride monomer R = CL Assuming only a head-to-tail addition, the monomer can attach to the growing chain with either of two forms of relative handedness,



In Scheme 1.7 structures (I) and (II) will not superimpose; hence they are nonequivalent structures. Although the methine carbon atoms are not truly asymmetric centers, and are more accurately described as pseudoasymmetric, the difference is found in the

stereochemical configuration of these carbon atoms because they provide a local symmetry.

Tacticity is the term used to describe this stereochemical regularity. The three possible configurations of a monosubstituted vinyl polymer chain are most readily seen when the molecule is drawn in its fully extended (all trans) planar zigzag conformation, as shown in Figure 1.1. Depending on whether the substitute R group of successive repeat units lies on the same side, alternating sides or at random with respect to the backbone, these configurations are called isotactic, syndiotactic, or atactic, respectively.

In discussing tacticity at a molecular level, it has become conventional to refer to two, three, four or five **monomer** units on a polymer chain as a dyad, triad, tetrad, or pentad, respectively. In addition, a dyad is designated *racemic* (r) if the two repeat units have opposite configurations, or *meso* (m) if the configurations are the same. This terminology is best conveyed by focusing attention on the methylene group of the vinyl polymer. When this group lies in a plane of symmetry in an isotactic chain it defines a meso structure



(Scheme 1.8)

On the other hand, a CH_2 group that lies in syndiotactic environment is defined as a racemic structure



(Scheme 1.9)

Because of the two-fold axis of symmetry of the r-dyad, the methylene protons are magnetically equivalent, *i.e.*, they resonate at the same frequency and appear as a singlet in a ¹H NMR spectrum. In the m-dyad, which lacks an axis of symmetry, the two methylene protons are in different chemical environments and consequently show different chemical shifts. Furthermore, due to strong geminal coupling each of the two protons will split the resonance of the other into a doublet. In addition to this coupling there is also vicinal coupling that makes the proton spectrum considerably more complex.²⁴



Figure 1.1 • Isotactic (a), syndiotactic (b), and atactic (c) configurations of a monosubstituted vinyl polymer.

In a triad attention is focused on the central methine which has two neighboring monomer units. These neighboring monomers can be of the same or opposite configurations. It follows that in a triad the following possibilities exist:

(1) An isotactic triad (mm) that is generated by two successive meso additions:



(2) A syndiotactic triad (rr) that is generated by two successive racemic additions:



(3) An atactic triad that is generated by opposite additions, *i.e.*, a meso followed by a racemic addition (mr), or a racemic followed by a meso addition (rm):



In an NMR experiment, the two atactic triads, mr and rm, are indistinguishable, hence a single peak is observed and their probabilities are grouped together. Table 1.3 shows the various distinguishable stereochemical sequences for the methylene (dyad and tetrad) and the methine groups (triads and pentads). As a result of improved NMR techniques and instrument design, resolution of resonances corresponding to longer configurational sequences, *e.g.*, hexads and heptads, has become possible.^{21,23} Although protons initially served as the spin probe in NMR studies of polymers, the spectra suffered from extensive ¹H-¹H spin-spin coupling and a narrow dispersion of chemical shifts which resulted in extensive overlapping of resonances belonging to different stereosequences. Consequently, ¹³C NMR spectroscopy, which does not suffer from these shortcomings,

methine (CH)			methylene (CH ₂)		
Designation		Bernoullian	Designation		Bernoullian
		Probability	<u> </u>		Probability
Triad	mm	P_m^2	Dyad	m	P_m
	mr+rm	$2P_mP_r$		r	Pr
	rr	P _r ²			
Pentad	mmm	P _m ⁴	Tetrad	mmm	P _m ³
	mmmr+rmmm	$2P_m^3P_r$		mmr+rmm	$2P_m^2P_r$
	rmmr	$P_m^2 P_r^2$		rmr	$P_m P_r^2$
	mmrm+mrmm	$2P_m^3P_r$		mrm	$P_m^2 P_r$
	mmrr+rrmm	$2P_m^2P_r^2$		• rrm+mrr	$2P_mP_r^2$
	rmrm+mrmr	$2P_m^2P_r^2$		LLL	Pr ³
	IMIL+LIMI	$2P_mP_r^3$			
	mrrm	$P_m^2 P_r^2$			
	rrrm+mrrr	$2P_mP_r^3$			
	rrrr	P_r^4			

Designation and Bernoullian probabilities for dyad, triad, tetrad and pentad sequences (from Bovey²⁴).

Table 1.3

has become the method of choice for determining the microstructure of synthetic polymers.^{25,26} Its sensitivity to molecular structure can be demonstrated by the 75.4 MHz ¹³C spectrum of PVC, Figure 1.2, where heptad fine structure is observed in the methine region and all six tetrad resonances are observed in the methylene region. Provided that the peaks in the NMR spectrum of a polymer can be assigned to the various configurational sequences, the areas under the peaks can then be measured by integration or deconvolution to determine their relative abundances (fractions). These fractions provide a measure of the probabilities of configurational sequences and can be used in conjunction with statistical models to gain insight into the propagation mechanism of polymerization. Before discussing such models a brief introduction to elementary statistics is warranted.



Figure 1.2 \blacklozenge Expanded portion of the methine (CH) and methylene (CH₂) regions of a proton-decoupled carbon-13 NMR spectrum of 5% (wt/v) poly(vinyl chloride) in 1,1,2,2-tetrachloroethane-d₂ recorded at a magnetic field of 75.4 MHz and a temperature of 114 °C.

1.2.2.2.2 Elementary Statistical Analysis (Probability)

Probability is best introduced by considering the number of possible outcomes for . a given situation. The simplest way to visualize this is to consider the tossing of a balanced coin. For example, in tossing a single coin, there are two possible outcomes either a head (H) or a tail (T). In tossing two coins, there are four possible outcomes -TT, TH, HT, HH. In general, the number of possible outcomes in tossing n coins, where n is greater than or equal to 1, is given by 2^n .

The probability of any particular outcome is given by the reciprocal of the total number of outcomes, *i.e.*, $1/2^n$. For example, in tossing two coins the probability of any particular outcome, HH, HT, TH, or TT, is ¹/₄. This probability can also be obtained by applying the multiplication theorem of probability which states that the probability of the joint occurrence of two or more independent events is the product of their separate probabilities, *i.e.*, the probability of obtaining two heads (HH), P_{HH}, is given by the probability that the first coin will be heads, P_H, multiplied by the probability that the second coin will be heads, *i.e.*, P_{HH} = (P_H)(P_H) = ($\frac{1}{2}$)($\frac{1}{2}$) = $\frac{1}{4}$.

Another approach to calculating probabilities, which is particularly useful in computer simulations is to take into consideration the relative frequencies, *i.e.*, if n trials are made and a given event occurs r times, then the relative frequency is given by r/n. For reasonably high values of n, the relative frequency can be considered as a good estimate of the probability P, where P is defined as the limit approached by the relative frequency as n approaches infinity.²⁷

1.2.2.2.3 Bernoullian Statistics

The two mathematical models used most frequently to describe a stochastic process, such as the distribution of configurational sequences in a polymeric chain, are the Bernoulli-trial and Markov chain models.²⁸ For simplicity only the Bernoulli model will be considered in this discussion. In this model, the probability of various outcomes at a particular step in the process is independent of what has occurred previously and does not affect what happens later. The building of a polymer chain by Bernoulli-trial steps can be described as a process of reaching into a large jar containing balls marked with one of the two configurations, meso (m) or racemic (x). Hence the probabilities are similar to those described in flipping a coin, except that this may be an unfair coin since the number ratio of the two types of balls need not be unity.

The probability of generating a meso sequence when a new monomer is added to the chain is generally denoted as P_m . Since there are only two possible outcomes, m or r, it follows that $P_m + P_r = 1$. As discussed above, for a triad sequence there are four possible outcomes: nm, mr, rm and rr. Since the mr and rm triads are indistinguishable in an NMR experiment, their probabilities are grouped together; therefore, the probabilities of the nm, mr, and rr triads are given by P_m^2 , $2P_mP_r$, and P_r^2 , respectively. These probabilities are obtained by application of the multiplication theorem of probability, which has also been applied to calculate the relative concentrations of the longer configurational sequences shown in Table 1.3. These relations are best represented by plotting the normalized probability of the n-ad as a function of P_m , as shown in Figures 1.3 and 1.4 for triad and tetrad sequences, respectively.²⁹ A polymer conforms to Bernoullian statistics when the isotactic (mm), syndiotactic (rr), and atactic (mr) triad probabilities, as obtained from the relative areas of the appropriate peaks of an NMR spectrum, lie on a single vertical line in Figure 1.3, *i.e.*, they correspond to a single value of P_m .



Figure 1.3 \blacklozenge Normalized probabilities, as described in Table 1.3, of isotactic, mm (solid line), syndiotactic, rr (dotted line), and atactic, mr+rm (dashed line) triads as a function of P_m (from Bovey²⁴).



Figure 1.4 \blacklozenge Normalized tetrad probabilities, solid line for mmm (rrr), dotted line for mmr (rrm), and dashed line for mrm (rmr) sequences, as described in Table 1.3, as a function of P_m . The bottom scale is used for sequences in parentheses (from Bovey²⁴).

1.2.2.3 Configurational Studies of PVC

Numerous studies have shown that free radical polymerization of poly(vinyl chloride) generates polymeric chains that conform to Bernoullian statistics. In early studies, before the appearance of NMR, the tacticity of PVC was generally determined from infrared spectroscopy using the 1428 cm⁻¹ and 1434 cm⁻¹ bands.³⁰⁻³² These studies showed that PVC tends to have a syndiotactic character with P_m values ranging from 0.49 for a polymerization temperature of 90 °C to about 0.20 at -75 °C polymerization temperature. Nowadays, ¹³C NMR has totally replaced infrared spectroscopy and, as discussed above, has become the accepted method for determining tactic structure because it is self-calibrating and it has a higher sensitivity, allowing higher order stereosequences to be observed. Consequently, NMR data have made possible the testing of Bernoullian and other statistical models.

The studies of Carman, *et al.*³³⁻³⁵ were the first to correctly assign the stereosequences of PVC found in a proton-decoupled ¹³C NMR spectrum. Furthermore, they showed that PVC polymerized by free radical initiation at 50 °C conforms to Bernoullian statistics with a P_m value of about 0.45. Later Pham, *et al.*³⁶ used ¹³C NMR to study the effect of polymerization temperature on tacticity. Their results, shown in Table 1.4, were in good agreement with the results obtained by infrared spectroscopy with the exception of polymers polymerized at low temperatures which were found to be less syndiotactic than indicated by the infrared results.

The effect of polymerization temperature on tacticity (from Pham, et al. ³⁶).		
Polymerization Temperature (°C)	Isotactic fraction (P _m)	
55	0.45	
25	0.43	
0	0.40	
-30	0.36	
-50	0.34	
-76	0.32	

 Table 1.4

 The effect of polymerization temperature on tacticity (from Pham, et al.³⁶).

In summary, PVC produced by a free radical polymerization is slightly syndiotactic and conforms to Bernoullian statistics with P_m values between 0.32 and 0.48, depending on the reaction temperature. An increase in polymerization temperature results in a lower syndiotactic content. Commercial PVC that is suspension and mass polymerized in the usual temperature range of 40 to 70 °C has a P_m value between 0.44 and 0.48.

1.2.2.4 Conformational Analysis of PVC

To this point the various possible configurations of PVC, as represented in Figure 1.1, have been discussed. These representations fail to convey what is perhaps one of the most significant structural features of a polymeric chain, namely, its ability to assume an enormous array of conformations. This conformational versatility is a consequence of the considerable degree of rotational freedom about single bonds on the chain. For example, the polymer shown in Figure 1.1 expresses only one conformation, the fully extended one, out of a great number of possible ones. An enormous number of irregular shapes may be realized by performing rotations about the bonds of the chain.

To specify the spatial relationships between the segments of a polymer chain, the bond lengths, the bond valence angles, θ_v , and the angle of rotation, ϕ , about each bond in the chain must be known (see Figure 1.5). For carbon-backbone polymers, all bond lengths are generally fixed at 1.54 Å and all valence angles at 112°. However, the rotations about the C-C bonds retain a certain degree of freedom in polymers. Studies of low-molecular-weight compounds have shown the existence of potentials hindering rotations about the chemical bonds. The rotation potential is threefold with three energy minima at $\phi = 0^\circ$, +120°, and -120°. A rotation angle of 0° is described as a *trans* (t) conformation and the angles ±120° as *gauche* (g⁺ and g⁻) conformations. This is more readily seen in Newman projections as illustrated in Figure 1.6.



Figure 1.5 \diamond Schematic representation of a small portion of a simple singly bonded carbon chain (from Flory³⁷).

For each of the isotactic and syndiotactic configurations, there are nine possible conformations. However, the number of different conformations is reduced considerably, since some of the combinations are the same while others are sterically not possible due to severe steric hindrance. Initial studies concentrated mainly in determining the possible structural conformations of PVC. From NMR, IR, and dipole moment studies³⁸⁻⁴³ several authors concluded that in the meso dyad the *trans-gauche (tg)* and *gauche-trans (gt)* conformations occur while in the racemic dyad essentially only the



Figure 1.6 \blacklozenge Newman projections of a simple bonded carbon chain in the (a) trans ($\phi = 0^{\circ}$), (b) gauche⁺ ($\phi = +120^{\circ}$), and (c) gauche⁻ ($\phi = -120^{\circ}$) conformations.

trans-trans (tt) conformation is allowed. Of the techniques mentioned above, the most valuable tool for investigating conformations in PVC has been vibrational spectroscopy. IR studies have established that in the isotactic, heterotactic, and syndiotactic triads the following conformations are predominant: g^+ttg^- and g^+tg^+t (or its mirror image tg^+tg^+), $tttg^+$, and tttt, respectively, as shown in Figure 1.7.



Figure 1.7 \diamond The most frequent conformations of isotactic, heterotactic, syndiotactic triads found in PVC.⁴⁴

1.3 THERMAL DEGRADATION OF PVC

1.3.1 Introduction

It is well known that poly(vinyl chloride) cannot be processed or put to end use applications without the incorporation of additives such as stabilizers, plasticizers, antioxidants, etc. Most experts consider the thermal degradation of PVC to be a major disadvantage of this material. Its thermal and photochemical instability has restricted its use in many applications. Upon exposure to temperatures as low as 100 to 120 °C^{45,46}, it undergoes a degradation reaction that releases hydrogen chloride and forms long polyene sequences of conjugated double bonds. The dehydrochlorination reaction can be represented as follows:

$$\begin{array}{cccc} H & CI & H & CI \\ I & I & I \\ -(C - C)_{n} & \longrightarrow & -(CH = CH)_{m} (C - C)_{n-m} + mHCI & (Scheme 1.13) \\ I & I & I \\ H & H & H \end{array}$$

A few long polyene sequences can make the polymer appear black and result in a breakdown of its physical properties, *i.e.*, loss of mechanical, electrical, and optical characteristics. It is generally accepted that polyenes result from a zipper mechanism, *i.e.*, the first double bond activates the formation of the second conjugated double bond, and so on, until long polyenes are formed. The two preferred mechanisms that have been proposed to account for this zipper reaction are the ion-pair mechanism^{47.49} and the free-radical mechanism.^{50,51} The ion-pair mechanism is represented in Scheme 1.14 and the free-radical mechanism in Scheme 1.15.

This instability is surprising because low-molecular-weight model compounds for PVC, such as 2,4-dichloropentane or 2,4,6-trichloroheptane, are relatively stable organic compounds (HCl elimination takes place at temperatures above 300 °C) with dehydrochlorination rates that are much slower than that those for PVC.^{45,46,49,52,53} Hence, over the years many studies have been made to develop a better understanding of the source of its poor thermal stability. The two competing theories that have been proposed to rationalize the instability of PVC are: (1) Initiation due to the presence of a few abnormal or irregular structures in the polymer, the so called 'labile sites'; and (2) initiation due to the occurrence of some local conformations that are related to isotacticity. Authors do



(Scheme 1.14)



(to be repeated)

(Scheme 1.15)

(to be repeated)

20

not agree as to which of the two sites is more important in initiating the zipper reaction. Pin pointing the sites that initiate the dehydrochlorination reaction could ultimately lead to an improved and more controlled stabilization of the polymer.

1.3.2 Role of Defect Structures

As discussed previously, numerous studies47,54-56 have sought to determine the irregular structures in a poly(vinyl chloride) chain. These structures, e.g., head-to-head structures, branch points containing a tertiary chlorine, internal and chain end unsaturation (allylic chloride), and groups containing oxygen, some of which were depicted in Schemes 1.2 to 1.5, have been identified as being responsible for the initiation of the dehydrochlorination reaction. It is important to recognize the difficulty in identifying which defect structures are responsible for initiating the dehydrochlorination reaction and to correlate these defect structures with the low thermal stability of PVC. This difficulty stems from the fact that these defect sites are few and their dependence on the polymerization conditions altimately brings about structural changes that differ from polymer to polymer.⁵⁷ Therefore, there has been considerable controversy concerning the nature, concentration, and relative importance of these irregular structures in the polymer. For example, Hjertberg and co-workers^{9,17,58} have shown that the tertiary chlorine is the most important labile structure in PVC. On the other hand, Minsker, et al.59 have claimed that internal unsaturation is the most important defect in initiating the thermal degradation of PVC. The effects of these anomalous structures are many and their discussion is beyond the scope of this chapter. For a more detailed discussion on the structural defects and their origin reference can be made to the review article by Braun and Bezdadea.⁶⁰

1.3.3 Role of Tacticity

Recently, strong support has developed for the existence of random dehydrochlorination, *i.e.*, initiation at local conformations in stereosequences which were previously considered as normal units.^{58,61-64} The recent systematic studies of Millan and co-workers⁶⁵⁻⁷⁵, on the influence of tacticity on the thermal degradation of PVC brought to light the possibility that such normal structures are responsible for initiating the dehydrochlorination reaction. From their work, which is reviewed in detail in Chapter 4, these authors concluded that the labile structures in PVC are chlorine atoms located mainly at g^+ag^- isotactic triad conformation, shown in Figure 1.7.

1.4 PLASTICIZATION OF PVC

1.4.1 Introduction

Plasticizers are added to PVC primarily to convert the rigid PVC resin into workable and flexible compounds that exhibit a wide range of properties with many versatile applications. One of the main disadvantages of PVC is that when used without additives it is difficult to process. For example, when a high molecular weight PVC homopolymer is fluxed on a hot roll mill, at 160 °C, the resin particles pour unchanged, like sand, between the rolls. If the temperature is increased, the resin softens and eventually forms a tough sheet around one of the rolls. While it is softening and "sheeting out" on the mill, it decomposes to an extent that renders it a worthless, brown to black, horny to brittle, relatively tough plastic. However, if a small amount of plasticizer is added, the resin softens and fuses onto the roll mill at 160 °C. Upon removal, the sheet is clear, colorless to faint yellow, and semi-rigid to very flexible, depending on the amount of plasticizer added.

By definition⁷⁶ a plasticizer is a material, frequently solvent-like, that is incorporated into a resin to increase its workability and its flexibility or distensibility (elongation). Addition of a plasticizer may lower the melt viscosity, the temperature of the second-order transition, and the elastic modulus of the plastic.

The most common plasticizers for PVC are esters of carboxylic acids or phosphoric acid. Other types include ethers, hydrocarbons, halogenated hydrocarbons, polyglycols, and sulfonamides. In order for a plasticizer to be of industrial importance, the following properties are essential: (1) compatibility with the resin, (2) high molecular weight, 300 to 600 g mol⁻¹, (3) viscosities of 50 to 450 cP, (4) flash points greater than 200 °C, and (5) vapor pressures of less than 3.0 torr at 200 °C.⁷⁷ These properties assure that the plasticizer does not separate from the polymer into a discrete phase. This separation may be as an "exudation", which is the formation of liquid droplets at the surface of the film, and is sometimes called "sweat out". Because of the loss of plasticizer such separations result in the loss of the desired properties of the plastic. Out of the thousands of patented plasticizers only a few have good all-round properties and sufficiently low production costs to make them useful in industrial applications.

1.4.2 Compatibility of Plasticizer with Resin

By definition compatibility is the ability of two or more substances to mix with each other to form a homogeneous composition of useful plastic properties. According to thermodynamics, two substances will be miscible when the free energy of mixing, ΔG_m , is negative;

$$\Delta \mathbf{G}_{\mathbf{m}} = \Delta \mathbf{H}_{\mathbf{m}} - \mathbf{T} \Delta \mathbf{S}_{\mathbf{m}} \tag{1.1}$$

where ΔH_m is the heat of mixing, ΔS_m the entropy of mixing, and T the temperature. Application of the theory to real solutions has led to the formulation of several parameters to characterize the compatibility between resin and plasticizer. Of particular importance is the Flory-Huggins interaction parameter, χ , which corrects for nonideality of both heat and entropy of mixing. This interaction parameter is concentration dependent. Values of χ lower than 0.5 indicate compatibility of high molecular weight polymers with low molecular weight plasticizers.

A simplified technique to measure the χ parameter for PVC-plasticizer systems is the technique developed by Anagnostopoulos, *et al.*⁷⁸ The method involves determining optically the temperature at which complete dissolution of a grain of resin in a drop of plasticizer occurs. This method is described in Chapter 2.

The compatibility between PVC and plasticizers is generally attributed to the presence of specific interactions, at the molecular level, between the plasticizer and the PVC chain. Infrared spectroscopy studies of ester-containing plasticizers with PVC have strongly suggested that the carbonyl group of the plasticizer is involved in a specific interaction. However, the functional group of PVC with which it is actually interacting is a matter of controversy. The following specific interactions of the carbonyl group have been suggested: (1) a hydrogen bond with the hydrogen attached to the methine carbon⁷⁹⁻⁸³, (2) a hydrogen bond with the hydrogens on the methylene carbon⁸⁴, and/or (3) dipole-dipole interactions with the chlorine atom.⁸⁵⁻⁸⁷ These interactions will be further described in Chapter 2.

1.4.3 General Theories Concerning the Mechanism of Plasticizer Action

Four major theories, the gel, lubricity, mechanistic, and free volume, have been proposed to account for the main effects produced by plasticizers.⁸⁸ The lubricity theory views the resistance of a polymer to deformation to be a result of intermolecular friction, *i.e.*, the plasticizer acts as a lubricant which facilitates the movement of the polymer

chains. The gel theory, which applies to the amorphous portion of the resin, assumes that the chains form a three dimensional honeycomb structure, or gel. The plasticizer breaks the points of attachment by selectively solvating the polymers at these points.

More realistically, the mechanistic theory assumes that plasticizers of different types are attracted to polymer chain sites by forces of different magnitude and none of them are bound permanently. Rather, there is a continuous exchange whereby one plasticizer molecule becomes attached to a given active group to be dislodged and replaced by another.

The free volume theory gained much attention because it added a mathematical perspective to plasticization and clarified the mechanisms of the earlier theories. This theory assumes there is nothing but free space between atoms and molecules. Thus, any material is composed of space occupied by the atoms, the "occupied volume", and unoccupied space, the "free volume". The total volume of a plasticizer or a polymer increases with temperature. Since no mass is added, this increase is the result of an increase in free volume. Other factors affect the free volume, *e.g.*, the free volume of a polymer increases with increasing molecular motion, decreasing molecular weight, and addition of small molecules with flexible ends.

A molecule cannot move into a new position unless it finds sufficient free volume to accommodate the movement of a molecule or chain segment. Increasing the free volume of a polymer results in plasticization, *i.e.*, its glass transition temperature, modulus and tensile strength decrease while its elongation and impact strength increase. Free volume has been measured and used in thermodynamic equations. The most important application of the theory in polymer science has been to explain the lowering of the glass transition by a plasticizer. This application has become standard material in almost all introductory polymer science books and is discussed below.

1.4.4 Effect on Physical Properties

The effect that a plasticizer has on the physical properties of the plastic depends mainly on two important factors: (1) the type of plasticizer used and (2) its concentration. Of the many properties⁸⁹ that are altered by the addition of a plasticizer, only the glass transition temperature and the diffusion coefficients are considered in this thesis.

1.4.4.1 Glass transition temperature

In general, plasticizers lower the glass transition temperature T_g more than the flow temperature, T_{flow} ; therefore, the overall effect is that the elastomeric range between

 T_g and T_{flow} is increased. The first theory of the T_g of polymers was based on the concept of free volume, which was developed by Eyring and others⁹⁰⁻⁹² and was successfully applied by Flory and Fox.⁹³ The rubber-to-glass transition occurs at what has been called an 'iso-free volume' condition, *i.e.*, at the T_g and temperatures below the T_g , the free volume is assumed to be constant and the same for all polymers.

As noted above, the most important application of the theory has been to explain the lowering of the glass transition by a plasticizer. The plasticizer is generally composed of molecules that are much smaller than the polymer. Hence, the free volume of the plasticizer, relative to that of the polymer, is large. As a result, the addition of small amounts of plasticizer gives a large excess free volume and can lower the T_g by 40 to 5^{10} °C.

The theoretical treatment of Kelly and Bueche⁹⁴ which describes the compositional dependence of T_g for polymer-diluent systems is based on the hypothesis that the fractional free volume of the binary mixture (f) is given by the weighted sum of the fractional free volumes of the pure components, f_i ,

$$\mathbf{f} = \boldsymbol{\phi}_1 \mathbf{f}_1 + \boldsymbol{\phi}_2 \mathbf{f}_2 \tag{1.2}$$

where ϕ_i is the concentration (volume fraction) of the components and f_1 and f_2 at any temperature T are given by:

$$\mathbf{f_1} = \mathbf{f_{g1}} + \Delta \alpha_1 (\mathbf{T} - \mathbf{T_{g1}}) \tag{1.3}$$

$$\mathbf{f_2} = \mathbf{f_{g2}} + \Delta \alpha_2 (\mathbf{T} - \mathbf{T_{g2}}) \tag{1.4}$$

where f_{gi} are the fractional free volumes of pure components at their respective glass transition temperature T_{gi} (assumed to be 0.025) and $\Delta \alpha_i$ are the coefficients of thermal expansion. Substituting equations (1.3) and (1.4) into eq. (1.2), the total fractional free volume of the mixture (f) becomes:

$$\mathbf{f} = \phi_1 \big(\mathbf{0.025} + \Delta \alpha_1 (\mathbf{T} - \mathbf{T}_{g1}) \big) + \phi_2 \big(\mathbf{0.025} + \Delta \alpha_2 (\mathbf{T} - \mathbf{T}_{g2}) \big)$$
(1.5)

At $T = T_g$ (for the mixture), f becomes 0.025 and rearrangement of eq. (1.5) leads to

$$T_{g} = \frac{\phi_{1} \Delta \alpha_{1} T_{g1} + \phi_{2} \Delta \alpha_{2} T_{g2}}{\phi_{1} \Delta \alpha_{1} + \phi_{2} \Delta \alpha_{2}}$$
(1.6)

On this basis, the glass transition temperature of the mixture can be predicted by eq. (1.6), for any volume fraction of plasticizer under the condition that the T_g and $\Delta \alpha$ of the pure components are known. This treatment has been used with a considerable, but not universal, degree of success. From a theoretical point of view, there are several other factors that should be taken into consideration, such as the polymer-plasticizer specific interactions and excess volumes of mixing. Other equations that take these factors into account have been proposed and are described elsewhere.⁹⁵

1.4.4.2 The permeability of PVC to gases

The complete process of a gas diffusing through a solid is termed permeation, and the property of the solid which permits this is its permeability. Gas molecules diffusing through a polymeric solid may be visualized as jumping into holes which form and disappear as a result of the thermal motion of polymer segments. The addition of a plasticizer increases the free volume of the system allowing the permeant to diffuse at a faster rate. Therefore, as the concentration of plasticizer increases the permeability coefficient of the polymer also increases. In addition, the permeability of PVC varies considerably depending on the structure of plasticizer used. For example, Deeg and Frosch⁹⁶ studied the permeability of PVC plasticized with tri-cresyl phosphate (TCP), methyl phthalyl ethyl glycolate, di-2-ethylhexyl phthalate (DOP), and tri-ethylene glycol di-(2-ethyl butyrate) and showed that: (1) all four plasticizers increased the water permeability of the resin, and (2) of the four, the resin plasticized with TCP gave the lowest permeability while the PVC containing tri-ethylene glycol di(2-ethyl butyrate) lead to the highest permeability.

Above the T_g , the free volume of PVC and plasticized PVC increases with temperature and as a consequence so do the permeation rates of gases and vapors. Using PVC films plasticized with various concentrations of DOP, Lelchuk and Sedlis⁹⁷ studied their permeability to water as a function of temperature. These workers showed that above the T_g the activation energy for permeation was much higher than that below the T_g . A similar study was performed by Eustache and Jacquot⁹⁸ where the permeation of carbon dioxide (CO₂) and oxygen (O₂) through a plasticized PVC was studied as a function of temperature. They found that permeability, at a given temperature, was higher for CO₂ than O₂. In addition, the activation energy for permeation above the T_g was much higher than that below T_g and the breaks in the permeability curves for both CO_2 and O_2 were slightly above 52 °C, which is close to the glass transition temperature of the film as determined by traditional methods. These studies report a higher barrier to diffusion above the T_g , suggesting the involvement of segmental motions, contrary to only vibrational motions below the T_g .

The effect of the glass transition temperature on the transport properties of gases in polymers has been studied previously. In 1954, Meares⁹⁹ was the first to measure gas transport parameters in a polymer above and below the glass transition temperature. He measured the sorption of a number of gases in poly(vinyl acetate), both directly and from the quotient of permeation and diffusion coefficients. For all the gases investigated, a change of slope in the Arrhenius plots was observed at the glass transition temperature, suggesting that the activation energies in the glassy state differed from those in the rubbery state. For the larger gas molecules, a somewhat flatter part of the curve was found in the vicinity of the T_g. However, similar measurements were later repeated by Stannett and Williams¹⁰⁰ and only a clean break was observed. The activation energies calculated from the Arrhenius plot of the data were always higher above the glass transition temperature. At that time the data could not be readily explained. Therefore, explanations for the data in his pioneering work were based on the presumption that the mechanism for the diffusion of small molecules was different in the two states.

Meares suggested that the measured sorption and diffusion properties reflected changes in the segmental mobility of the polymer chains as the T_g was traversed. Based on the experimental activation energies for diffusion and heats of solution in the two regions and application of the activation zone theory, Meares^{99,101} proposed the following idealized concept of the gaseous diffusion and sorption process in polymers. In the rubbery state gas molecules which dissolve in the polymer must create their own holes by separating the interchain contacts. The penetrant then diffuses along the cylindrical voids that are created by the synchronized rotation of the polymer segments about the backbone bonds. In the glassy state, the gas sorbs and diffuses between holes which already exist in the polymer matrix due to the disordered arrangement of chains. This mode of diffusion, unlike that for the rubbery state, does not create long cavities, hence, the zone of chain activation is much larger in the rubbery state. Above the T_g , the heat of solution for the sorption of gases must include a heat of interaction between the penetrant and polymer. In addition it must include the energy for separating the polymer chains, an endothermic process. Therefore, the sum accounts for the observed endothermic or slightly exothermic

heats of solution. Diffusion in the rubbery state requires a larger zone of activation, which is consistent with the observation that the energy of activation is higher above the T_g .

Michaels, *et al.*^{102,103} observed similar behavior for the sorption and diffusion data of He, O₂, N₂, Ar, CO₂, and CH₄ in poly(ethylene terephthalate), *i.e.*, a break was observed in the Arrhenius plot at the glass transition temperature, *ca*. 67 °C, and the activation energy for diffusion in the rubbery state was greater than for that in the glassy state. Barrer, *et al.*¹⁰⁴ studied the sorption and diffusion of H₂ and Ne in PVC films, unplasticized and plasticized with tri-cresyl phosphate. Changes in the slopes of the Arrhenius plots were observed for the diffusion of both gases in the unplasticized and plasticized films, at the respective glass transition temperatures.

In 1961, Kumins and Roteman¹⁰⁵ reported data for the diffusion of several gases through vinyl chloride-vinyl acetate copolymer films. The main goal of their work was to study the effect of penetrant diameter on the nature of the discontinuity of the Arrhenius plots at Tg. Of the gases studied, He, H2, Ne, NH4, O2, CO, CO2, Kr, and water vapor, only CO₂ and H₂O displayed a change in slope at the T_g . Their work suggested that a critical zone of activation size is necessary to observe the break in the Arrhenius plots. In other words, penetrant molecules smaller than this zone obey the same mechanism both in the rubbery and glassy states. Stannett and Williams¹⁰⁰ extended the work on the effect of penetrant size by studying the transport properties of various gases in poly(ethyl methacrylate), PEMA, membranes. A break was not observed in the Arrhenius plots of the transport properties, even for large penetrants. In collaboration with Tikhomirov and Hopfenberg¹⁰⁶ these workers extended their study further, by studying the diffusion properties of gases in unplasticized PVC films. They found that PVC exhibited transitional behavior that was dependent upon penetrant size. Of the gases studied, He, Ne, N₂, O₂, CO₂, CH₄, Kr, and Ar, the break in the Arrhenius plot was only found for the larger penetrants, i.e., Ar and Kr. Burgess, Hopfenberg, and Stannett¹⁰⁷ studied the permeability, diffusivity, and solubility of He, Ne, Ar, and Kr in poly(methyl acrylate), PMA, and poly(vinyl acetate), PVA, and found that the activation energies for diffusion, for all four gases, were higher above T_g than below.

From this short literature survey, it is evident that based on the presence or absence of a break in the Arrhenius plots, three types of polymers with different transport behavior exist: (1) Polymers which display a break for all penetrants; (2) polymers that display a break for penetrants of size above a certain critical diameter; (3) polymers that do not display this effect with any gas penetrants. A detailed description of the diffusion process of gases through PVC films, which includes definitions and basic equations,

measurements and calculations, temperature and concentration dependence, effects of penetrant size and shape, and models for diffusion is the main topic of Chapter 3.

1.5 PRESENT INVESTIGATION

In the present investigation, three main areas of research in PVC are addressed. These include studies on (1) the microstructure determination and dynamics of PVC in a plasticizer and in a non interacting solvent (Chapter 2), (2) the diffusion of gases through PVC and plasticized PVC films (Chapter 3), and (3) a computer simulation of the thermal degradation of PVC (Chapter 4).

1.5.1 Microstructure Determination and Dynamics of PVC in a Plasticizer and Non Interacting Solvent

The plasticization of PVC is important from an academic as well as an industrial point of view. As discussed previously, primary plasticizers are used extensively to convert the rigid PVC resin into workable and flexible compounds that exhibit a wide range of properties depending on the type and concentration of plasticizer. Although the technology of plasticization is well developed^{108,109}, the mechanism of plasticization of PVC and its interactions with the plasticizer are not well understood at the molecular level. In this study, described in Chapter 2, the microstructure and dynamics of PVC in a plasticizer (di-butyl phthalate, DBP) were determined by carbon-13 NMR spectroscopy. For comparison, a parallel study was made for solutions of PVC in a non-interacting solvent (1,1,2,2-tetrachloroethane-d₂, TCE-d₂), which may give some insight into the specific interactions between plasticizer and PVC. The goal was to obtain, from NMR studies, a molecular description of the effects of plasticization on the motions of PVC.

1.5.2 Diffusion of HCl and O₂ Gases Through Plasticized PVC Films

The permeability of PVC increases as a consequence of the incorporation of plasticizer into the resin matrix. This easy control of oxygen permeation has major advantage especially in meat packaging, where the high permeability of plasticized PVC keeps the red color of meat two to three days longer than in other packaging materials. However, diffusion of gases is not only important in the performance of the final products but also in the choice of processing methods and conditions. For example, a slow diffusion rate of hydrogen chloride can lead to auto-catalysis of the thermal degradation.¹¹⁰ Although PVC is one of the most frequently used polymers, relatively few

investigations have been carried out on the transport properties of small gas molecules through a PVC film. In Chapter 3 a detailed examination is presented of (1) the dependence on temperature and plasticizer type and concentration of the permeation of oxygen through PVC films; (2) the temperature dependence of the permeability, diffusion, and solubility coefficients of oxygen and hydrogen chloride gases in rigid PVC. In the former study the plasticizers used were binary mixtures of di-(2-ethylhexyl) phthalate, DOP, and tri-butyl phosphate, TBP, with concentrations of $\phi_{\text{DOP}} = 0$, $\phi_{\text{DOP}} = 0.6$, and $\phi_{\text{DOP}} = 1.0$. The temperature range used provided data above and below the glass transition temperature of PVC.

1.5.3 Computer Simulations of the Thermal Degradation Process

Recent studies of the dehydrochlorination of PVC in the solid state offer convincing indirect evidence in support of a mechanism that involves initiation at local configurations in stereosequences which were previously considered to be normal units. Indeed, attempts have been made, using NMR, to verify such a mechanism by direct measurements of the changes in tacticity that result from the degradation.¹¹¹ In this study, described in Chapter 4, results are reported from computer simulations that use Monte Carlo methods to simulate preferential degradation at isotactic sequences of various minimum lengths. The predicted changes in tacticity are then compared to (1) the experimental results obtained by ¹³C NMR spectroscopy measurements of thermally degraded PVC in solution and (2) the tacticity changes reported by Millan, *et al.*¹¹¹ and Velazquez¹¹² for the thermal degradation of PVC in the solid state. Such studies give insight into the role that tacticity plays in the initiation of the dehydrochlorination reaction at the molecular level.

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CHAPTER 2

CARBON-13 NUCLEAR MAGNETIC RELAXATIONS AND CHAIN LOCAL MOTIONS OF POLY(VINYL CHLORIDE) IN DI-BUTYL PHTHALATE AND TETRACHLOROETHANE SOLUTIONS

2.1 INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy is one of the most effective and powerful methods employed in polymer science to study the structure and dynamics of the polymer chain, both in solution and in the solid state. In the solid state, the resonances are quite broad due to the relatively slow motions of the chains which cause the dipole-dipole (DD) interaction to be static and the chemical shift anisotropy (CSA) no longer averages to its isotropic value. By comparison, in solution the chain motions are fast enough to eliminate such effects and spectra with clearly resolved resonances can be obtained for structurally distinct nuclei. This chapter deals with the use of solution NMR spectroscopy, specifically ¹³C NMR, to investigate the structure and dynamics of PVC. The detailed structural information obtained for polymers in solution makes it by far the method of choice to determine microstructure. In the study of dynamics, solid state and solution NMR both offer unique advantages. Since synthetic polymers are useful mainly because of their physical and mechanical properties in the solid state, studying the dynamics in the same state can be justifiably argued as having greater practical importance. On the other hand, dilute solution measurements offer their own advantage in the sense that interchain entanglements are alleviated thus allowing the roles played by intramolecular steric effects and solvent viscosity to be elucidated.

The most fundamental and usually the first information that is sought in a polymer is its microstructure. The concepts related to the configurational placement of monomer units in a polymer chain are fundamental to an understanding of its physical properties. Until the development of techniques of high resolution NMR, there were no methods, aside from x-ray diffraction studies (only applicable to stereoregular, crystallizable

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polymers), for direct experimental determination of polymer microstructure. The advent of proton-decoupled spectra recorded in the Fourier-transform mode has quickly made ¹³C NMR spectroscopy the method of choice for determining the microstructure of polymers.

In recent years carbon-13 nuclear magnetic relaxations have been employed in observing molecular motion and understanding the complex dynamic problems presented by polymer chains. The main advantage of this method is that it provides detailed information on molecular motion at the atomic level. Segmental motions play an important role since they influence many macroscopic properties of polymeric systems. In particular, the effect of the chemical structure of polymers on their viscous or viscoelastic response is controlled by characteristics of their segmental dynamics, such as frequency, activation energy, *etc.* Several reviews¹⁻⁵ are available which describe the various models developed for the interpretation of nuclear spin relaxation data for polymers in solution.

Initial attempts to quantitatively interpret polymer dynamics led to the use of distribution models, especially the so-called $\log_2 \chi^2$ distribution of Schaefer.⁶ This model utilizes a broad asymmetric distribution of correlation times for the molecular motions, with a tail towards the high end of the scale; however, it lacks a detailed insight into the nature of the chain motions. More promising models have been developed which are based on a molecular description of segmental motions. These include the three-bond jump model developed by Jones and Stockmayer⁷ (JS model) and the conformational jump model of Hall, Weber, and Helfand^{8,9} (HWH model). Lately Dejean, Lauprêtre, and Monnerie¹⁰ (DLM model) modified the HWH model by taking into consideration a fast libration of the C-H vectors in addition to segmental motion.

On the basis of relaxation data for PVC in di-butyl phthalate (DBP) and in 1,1,2,2tetrachloroethane- d_2 (TCE- d_2) obtained in this study, a critical evaluation of these four models is made regarding their ability to describe the local motions of the PVC chain. In addition, a comparison of the dynamics of PVC in the two solvents is made in search of discernible differences in local motion, apart from the effects of solvent viscosity.

The goals of this study were to investigate the microstructure of PVC and to obtain insight into the chain local motions of PVC dissolved in DBP. The latter studies are important from an academic as well as an industrial point of view since phthalates are used extensively as primary plasticizers, to convert the rigid PVC resin into workable and flexible compounds that exhibit a wide range of properties depending on the type and concentration of plasticizer. Although the technology of plasticization is well developed^{11,12}, the mechanism of plasticization of PVC and its interactions with the

plasticizer are not well understood at the molecular level. For comparison, a parallel study was made for solutions of PVC in TCE- d_2 .

2.2 THEORETICAL BACKGROUND

The purpose of this section is to provide a brief introduction to: (1) the physics and measurements of the nuclear magnetic resonance (NMR), and (2) the use of carbon-13 nuclear relaxation parameters to study macromolecular dynamics. Part 1 provides a basis for understanding two applications of major interest of polymer NMR spectroscopy: (1) the determination of microstructure using ¹³C NMR spectroscopy and (2) the use of ¹³C relaxation parameters for studying the chain local motions of synthetic polymers. For a deeper understanding and appreciation of the NMR phenomenon, the reader is encouraged to consult a number of text books and review articles.¹³⁻²⁰

2.2.1 Basic NMR Theory

2.2.1.1 Nuclear Spin and Magnetic Moment

Only atomic nuclei possessing a nuclear spin angular-momentum quantum number (or simply nuclear spin), I, that is determined by the number of protons and neutrons, are suitable probes for nuclear magnetic resonance spectroscopy. As a result of this spin a nucleus possesses angular momentum, M, given by $I(h/2\pi)$, where h is Planck's constant, and a magnetic moment, μ , which is taken parallel to the angular momentum vector. The ratio of the magnetic moment to the angular momentum is called the magnetogyric ratio, γ , and is given by

$$\gamma = \frac{\mu}{M} = \frac{2\pi\mu}{hI}$$
(2.1)

This ratio is characteristic for a given nucleus, as shown in Table 2.1 for nuclei of major interest to polymer NMR spectroscopy.

Two approaches are used to describe the interaction of the magnetic moment with an applied magnetic field: (a) The quantum mechanical and (b) the classical treatment. Each has its advantages and is used accordingly in describing the various NMR techniques.
Table 2.1

Natural abundance, spin quantum number (I), resonance frequency (v_0) in a 1 T field, and magnetogyric ratio (γ) of nuclei of major interest to polymer NMR spectroscopy.²¹

Isotope	Abundance (%)	v ₀ (MHz)	I	γX 10 ⁻⁶ (s ⁻¹ T ⁻¹)
¹ H	99.9844	42.577	1/2	267.43
² H	0.0156	6.536	1	41.05
¹³ C	1.108	10.705	1/2	67.24
¹⁴ N	99.635	3.076	1	19.32
15 _N	0.365	4.315	1/2	-27.102
¹⁹ F	100	40.055	1/2	251.59
²⁹ Si	4.7	8.460	1/2	-53.14
³¹ P	100	17.235	1/2	108.25

2.2.1.2 Quantum Mechanical Description of NMR

Elementary quantum treatment of nuclear spin predicts that the magnetic nucleus has 2I+1 distinct spin states in which the component of angular momentum will have values from +I to -I in integral or half-integral multiples of $h/2\pi$. In the absence of an external magnetic field, the various spin states are degenerate. However, when placed in a magnetic field B₀ the interaction of μ and B₀ removes the degeneracy and results in 2I+1 equally spaced nuclear spin energy levels with separation

$$\Delta \mathbf{E} = \gamma \frac{\mathbf{h}}{2\pi} \mathbf{B}_{\mathbf{o}} \tag{2.2}$$

referred to as the nuclear Zeeman splitting. This is shown schematically in Figure 2.1 for nuclei with a spin I = 1/2, *e.g.*, proton (¹H) or carbon (¹³C), that are characterized by two magnetic states, m = +1/2 and m = -1/2. The energy levels may be thought of as arising from different orientations of μ with respect to the external magnetic field B₀, *i.e.*, in the direction of the field vector B₀ (+1/2) and in the opposite direction (-1/2). The direct relationship between ΔE and the magnetic field strength is illustrated in Figure 2.2, where the energy separation is plotted at six commonly employed commercial spectrometer field strengths.



Figure 2.1 \diamond Nuclear magnetic energy levels for nuclei with a spin of 1/2 in a magnetic field B₀.



Figure 2.2 \blacklozenge The splitting of magnetic energy levels of protons as a function of spectrometer field strength B₀ (in tesla).

The relative population of the upper and lower states is given by a Boltzmann distribution:

$$\frac{N_{+}}{N_{-}} = \exp\left(-\frac{\Delta E}{k_{b}T}\right) = \exp\left(-\frac{2\mu B_{0}}{k_{b}T}\right)$$
(2.3)

where N_+ and N_- are the populations of the upper and lower states, respectively, and k_b is Boltzmann's constant. The population difference is dependent on both the magnetic field strength and the properties of the nuclear species under observation. There is a small excess population of spins in the lower state. For example, for protons at room temperature in a 2.34 T field, this excess is *ca.* 1.6 X 10⁻⁵, *i.e.*, for every million spins in the upper state there is an excess of 16 spins in the lower energy state. For an assemblage of nuclei, this difference in spin population leads to a bulk magnetization which can be measured directly.

The basis of NMR experiments is to induce transitions between adjacent spin states by absorption and emission of energy quanta. This is accomplished by applying an alternating magnetic field B₁ orthogonal to the static field with a radio frequency v_1 equal to the frequency of radiation required to induce transitions between adjacent spin states, v_0 , known as the Larmor frequency. This frequency can be obtained by substituting the relation $\Delta E = hv_0$ into eq. (2.2)

$$v_0 = \frac{\gamma}{2\pi} B_0 (\text{Hz}) \quad \text{or} \quad \omega_0 = \gamma B_0 (\text{radians s}^{-1})$$
 (2.4)

As seen from this equation, the Larmor frequency is proportional to the magnetic field strength, B_0 , and the magnetogyric ratio, which is a characteristic property of the nucleus. For typical laboratory magnetic fields, v_0 is in the radio frequency range, *e.g.*, magnetic field strengths of 1-11.75 T correspond to $v_0 = 42-500$ MHz, for proton resonance. The Larmor frequency of common nuclei, in a 1 T magnetic field, are shown in Table 2.1.

2.2.1.3 Classical Mechanical Description of NMR

According to the classical theory of electromagnetism, in a magnetic field the magnetic moment experiences a torque that tends to tip the moment toward B_0 ; however, the angle θ between the moment and B_0 does not change because it is counterbalanced by the rate of change of its angular momentum. This causes the magnetic moment to precess

about the direction of the field vector \mathbf{B}_0 , as indicated by the path traced out by the end of the vector μ in Figure 2.3. This figure depicts the nuclear precession in a perpendicular x,y,z coordinate system where the direction of the field vector \mathbf{B}_0 is defined along the z axis.



Figure 2.3 \blacklozenge Nuclear magnetic moment μ in the presence of an applied magnetic field B₀ acting along the z-axis of the coordinate system.

The frequency of precession is the Larmor frequency v_0 , as described previously by eq. (2.2). Thus, the nuclear moment precesses about B_0 with a frequency that is proportional to the magnetic field strength and the magnetogyric ratio. A significant feature of eq. (2.2) is that the frequency is independent of the angle θ . On the other hand, the energy of the spin system is given by

$$\mathbf{E} = -\mu \mathbf{B}_{\mathbf{0}} \cos \theta \qquad (2.5)$$

which depends on the angle θ . When a small magnetic field B_1 is placed orthogonal to B_0 , and is made to rotate about B_0 at a frequency v_0 (see Figure 2.3), the angle θ can be changed because μ experiences the combined effects of B_0 and B_1 . Under these conditions, energy is absorbed from the B_1 field into the nuclear spin system. However, if B_1 rotates at a frequency other than v_0 then it will be in and out phase with μ , and no net energy will be absorbed. Hence, the absorption of energy is a resonance phenomenon that is sharply tuned to the precession frequency of the observable nucleus. Therefore, by varying the frequency of B_1 through the Larmor frequency, energy from B_1 will be transferred to the spinning nucleus tipping the precession angle θ to a new angle closer to the x-y plane. This will cause the magnetic moment to have a larger component along the x-y plane which can be detected by placing a receiver coil in this plane. This component will be a rotating magnetic field which will induce a current in the receiver coil which can be amplified and plotted, indicating that resonance has occurred.

Nuclear magnetic resonance experiments can be simplified by considering a rotating frame of reference rather than a fixed laboratory frame of reference. In a rotating reference frame, the x and y axes rotate about the z axis at the Larmor frequency, thus producing a x',y',z' coordinate system. The effect is to produce a standing picture where the magnetization M_0 , at equilibrium, is directed along the z' axis and perpendicular to x', as shown in Figure 2.4a. The B_1 vector now rotates with the x' axis and its frequency deflects the M_0 vector along the y'-z' plane (Figure 2.4b), hence building up the transverse magnetization $M_{y'}$. The angle of deflection, θ , through which the magnetization M_0 is tipped from the field or z'-axis, depends upon the duration of the radio frequency irradiation, t_p , called the pulse width, given by

 $\boldsymbol{\theta} = \boldsymbol{\gamma} \boldsymbol{B}_1 \boldsymbol{t}_p \tag{2.6}$

The radiation can be kept on long enough such that the magnetization M_0 is deflected by 90° or $\pi/2$ radians (Figure 2.4c) thus causing all the magnetization to lie along the y' axis, *i.e.*, $M_{y'} = M_0$. The term used for such a pulse is a 90° or $\pi/2$ pulse. Since it is more convenient to discuss NMR experiments in the rotating frame, the axis primes will be dropped and, for the remainder of the text, x, y and z refer to the rotating rather than the laboratory reference frame.

2.2.1.4 Relaxation of Nuclear Spins

The relative populations of spins, as described by the Boltzmann distribution given by eq. (2.3), may be equalized or inverted upon application of an appropriate pulse of rf energy. Relaxation from upper level spin states to their lower energy level is made possible because each spin is not completely isolated from the rest of the molecules in the sample, called the lattice. The spins and the lattice may be thought as separate systems that are weakly coupled, thus providing a means by which thermal energy can be exchanged. Molecular motions of neighboring nuclei in the lattice provide the mechanism



Figure 2.4 \blacklozenge Influence of an alternating magnetic field B₁ on the motion of the magnetization vector M₀, in a rotating coordinate system, at (a) equilibrium, (b) start of deflection, and (c) 90° deflection ($\pi/2$ pulse)

for transferring thermal energy between the spins and their surroundings. These motions generate fluctuating magnetic fields that have a broad range of frequencies and, relative to the observed nucleus, are nearly random. Components of the fluctuating magnetic fields that have a frequency v_0 and lie orthogonal to the applied field B_0 will, like B_1 , induce transitions between the magnetic energy levels of the observed nuclei.

The process of returning from an excited state to the equilibrium state is termed spin-lattice relaxation, characterized by a time T_1 which is the time required for the spin populations to be relaxed by a factor of e. For liquids T_1 is usually in the range 10^{-2} to 10^2 s. Spin-lattice relaxation produces a change in energy by which the magnetic moments with components along the B_0 field are redistributed. Since it is associated with a decay of the macroscopic nuclear moment along the direction of the applied field, T_1 is often called the longitudinal relaxation time. A second mode by which nuclear magnetic moments may interact is shown in Figure 2.5. As the pair of magnetic moments precess about the axis of the B_0 field each will have a rotating component in the x-y plane and a static component along B_0 . If the rotating components of both nuclear moments precess at the same frequency this will constitute the right sort of field to induce a transition and result in a spin exchange. Such mutual spin exchange or flip-flop occurs without any change in the overall energy of the system but clearly shortens the lifetimes of the interacting spins. This causes a broadening of the resonance of similar magnitude to the dipolar broadening. Both effects are included in the characteristic time T_2 which describes the spin-spin relaxation. The time T_2 is also referred to as the transverse relaxation time because it is concerned with the rate of change of magnetization in the x-y plane which is transverse to the direction of the B_0 field.



Figure 2.5 \blacklozenge Interaction between a pair of precessing nuclear moments via the rotating component of their nuclear moments, **a**, resulting in a spin exchange.

2.2.1.5 Chemical Shift

NMR is a useful spectroscopic tool for the study of molecular structure because even for nuclei of the same type resonance occurs at slightly different frequencies depending on the chemical environment. Different resonance frequencies result from changes in the electronic environment about each nucleus, which may shield (greater electron density) or deshield the nucleus relative to the applied magnetic field thus requiring a slightly lower or higher, respectively, value of v_0 to achieve resonance. For example, protons attached to or near electronegative groups such as halogens, OH, OR, CO₂R, and OCOR experience a lower density of shielding electrons and resonate at a higher frequency. When these protons are removed from such groups and placed into a hydrocarbon chain they will resonate at a lower frequency. Such variations are termed chemical shifts and are customarily reported relative to the resonance of tetramethylsilane (TMS) where the chemical shifts of both the ¹H and ¹³C nuclei are taken as zero. The chemical shift is expressed in parts per million (ppm) of the total applied magnetic field. Because of the direct relation between v_0 and B_0 (eq. (2.2)) this conveniently allows the chemical shift to have a constant value that is independent of the radio frequency and the magnetic field that the NMR spectrometer employs.

For proton chemical shifts in organic compounds, the total range is only of the order of 10 ppm, that is about 1 kHz in a magnetic field of 2.34 T. On the other hand, ¹³C nuclei have a range that is much greater (over 200 ppm), which is one of the principal reasons that ¹³C NMR has received great attention in the study of structure of polymers.

2.2.1.6 Nuclear Coupling

In addition to the slight correction of electronic screening of the local field, each nucleus will also experience the effects of its magnetic neighbors. Two important modes of nuclear spin-spin coupling are dipolar and scalar coupling.

In dipolar coupling, a local field, B_{loc} , is produced by a proton directly attached to a ¹³C nucleus which is given by

$$B_{loc} = \pm \frac{h}{2\pi} \gamma_{\rm H} \frac{(3\cos^2\theta_{\rm C-H} - 1)}{r_{\rm C-H}^3}$$
(2.7)

where \pm sign indicates that the local magnetic field may add to or subtract from B₀, depending whether the magnetic dipole of the neighboring nucleus is aligned with or against the magnetic field, r_{C-H} is the ¹³C-H internuclear distance, and θ_{C-H} is the angle of the ¹³C-H bond with the magnetic field, as shown in Figure 2.6. This form of spin-spin coupling broadens the resonance line of a nucleus. In polymer samples, which are in the glassy state, a summation over many values of θ_{C-H} and r_{C-H} is obtained and results in a dipolar broadening of many kHz. However, as the rate of molecular motion begins to exceed the linewidth, *i.e.*, the C-H vectors assume all angles in a time shorter than the dipolar coupling, the resonance begins to narrow.



Figure 2.6 \diamond A ¹³C-H bond of internuclear distance r_{C-H} making an angle θ_{C-H} with the magnetic field.

The second mode by which magnetic nuclei may transmit information concerning spin states is through the intervening covalent bonds. If a nucleus of spin 1/2 has a equivalently coupled neighbors, also of spin 1/2, its resonance will be split into n+1 peaks. The value n+1 corresponds to the number of spin states of the neighboring group of spins, *i.e.*, for a single neighboring spin, the probabilities of finding it with (n = +1/2) or against $(m = -1/2) B_0$ are nearly equal. Simple statistical considerations describe the intensities of the peaks which are proportional to the coefficients of the binomial expansion. For two neighboring spins, the observed resonance is split into a 1:2:1 triplet (++, +-(-+), and -- spin orientations). The strength of the coupling is expressed in Hz and denoted by J. Nuclear coupling between ¹³C nuclei and directly bonded protons is strong and in the range of 125-250 Hz. The splitting of the resonance is spectrum and is undesirable.

2.2.1.7 Decoupling in ¹³C Spectra

The ¹³C isotope has a natural abundance of only 1.1% and is referred to as a 'rare' spin. This relatively low natural abundance assures that the ¹³C spectrum of a low molecular weight compound can be considered as a mixture of molecules each containing a single ¹³C atom. In other words, in unenriched samples coupling between adjacent carbons is rare. However, substantial coupling occurs between carbons and their attached hydrogens as well as more distant hydrogens, which makes the ¹³C spectra of organic molecules quite complex. This problem is readily solved by decoupling the proton spins

from the carbon spins, which is accomplished by irradiating the entire range of ¹H chemical shifts in the form of *white noise* such that all of the proton lines are decoupled at once. In addition to the collapse of multiplets from the ¹³C-¹H coupling, there is a substantial increase in the signal. This effect is caused by the transfer of spin polarization to the carbons during the decoupling process and is termed the *nuclear Overhauser effect*, or NOE, which will be discussed in detail later.

The absence of coupling between adjacent carbons and decoupling of proton spins from carbon spins are further important advantages of using ¹³C NMR as opposed to ¹H NMR. These advantages have made ¹³C NMR spectroscopy the method of choice for determining the structure and studying the local motions of synthetic polymers.

2.2.2 Carbon-13 Nuclear Relaxation Parameters

2.2.2.1 Description of Spin-Lattice and Spin-Spin Relaxation

With the aid of magnetic energy levels, a brief qualitative description of the relaxation processes was given in section 2.2.1.4. In this section, the use of magnetic vectors will be employed to formalize these processes.

After application of a 90° pulse, the recovery processes regenerate the nuclear spin equilibrium state which is characterized by the re-establishment of equilibrium magnetization M_0 along the z-axis and complete absence of the transverse magnetization $(M_y = 0)$, *i.e.*, in going from Figures 2.4c to 2.4a. The spin-lattice relaxation time T_1 governs the return of the magnetization along the z-axis, M_z , while the spin-spin relaxation time T_2 governs the return of the x, y magnetization, M_{xy} , to its equilibrium value of zero. These relaxation processes are best described in a rotating coordinate system, as shown in Figure 2.7.

The spin-spin relaxation (Figures 2.7b-e) is the decay of the transverse magnetization M_v which is assumed to occur continuously as a single exponential

$$\frac{dM_y}{dt} = -\frac{M_y}{T_2}$$
(2.8)

The precessing magnetic vectors lose their phase coherence and re-adopt the regular distribution over the precession cone. This process can be characterized by a time



Figure 2.7 \blacklozenge Magnetization vector, in a rotating coordinate system, at a) equilibrium, b) after application of a $\pi/2$ pulse, b) to e) during spin-spin relaxation, *i.e.*, the decay of the transverse magnetization, and f) to g) during spin-lattice relaxation, *i.e.*, re-establishment of equilibrium magnetization along the z-axis.

constant T_2 of the exponential decay of the nuclear induction current as recorded by the receiver of an NMR spectrometer. Thus, the spin-spin relaxation time T_2 indicates the time required for the nuclear induction current to drop to 36.8% (1/e) of its original value.

During spin-lattice relaxation, the nuclear spins in the excited state return to the more stable state. The Boltzmann distribution of nuclear spins, which was disrupted by excitation, is re-established and the magnetization along the z-axis resumes its equilibrium value M_0 . This process is depicted schematically in Figures 2.7f-g and can be described by

$$\frac{\mathrm{d}M_z}{\mathrm{d}t} = -\frac{M_z - M_0}{T_1} \tag{2.9}$$

where the spin-lattice relaxation is assumed as a continuous increase in the magnetization along the z-axis, M_z , to the equilibrium value M_0 with a time constant T_1 , the spin-lattice relaxation time. Physically, T_1 represents the time that is required after the perturbation to recover 1-1/e, or 63.2 %, of the magnetization lost as a result of the perturbation.

For a given type of nucleus, the spin-spin and spin-lattice relaxations can proceed at different rates. In the solid state or with macromolecules in solution, the spin-lattice relaxation is slower than the spin-spin relaxation, *i.e.*, $T_1 > T_2$. In small and medium sized molecules in solution, both processes proceed at the same rate, *i.e.*, $T_1 = T_2$. The spinspin relaxation time can be obtained as the inverse of the linewidth; however, laboratory field inhomogeneity contributes to line broadening making it difficult to measure T_2 accurately. Therefore, the relaxation parameters that will be considered in this study are T_1 and NOE.

2.2.2.2 Measurement of Spin-Lattice Relocation Time

The most frequently employed method for measuring spin-lattice relaxation times is the inversion recovery method'. In this method, the spin-lattice relaxation is initiated by a pulse whose duration is sufficiently long to rotate the magnetization through 180°, or π radians, which inverts the Bultzmann distribution of nuclear spins and hence the magnetization from its equilibrium value M₀. After a perfect π pulse, all the magnetization lies along the z-axis, hence no signal appears on the receiver coil. To monitor the magnetization, a $\pi/2$ pulse is applied which rotates the remaining z magnetization onto the y axis producing a signal of amplitude A that depends on the magnitude of the remaining z magnetization. If the $\pi/2$ pulse is applied immediately after the π pulse, the magnetization



Figure 2.8 • Vector diagram of the inversion recovery pulse sequence.²²

will not have recovered to any significant extent, hence the magnetization will lie along the -y axis thus producing an inverted signal, Figures 2.8b-c. If, in a separate experiment, a slightly longer delay is applied, the magnetization will have recovered to a point just below the origin, thus after application of a $\pi/2$ pulse a smaller but still inverted signal will be produced, Figures 2.8d-e. If a slightly longer delay time is chosen prior to the $\pi/2$ pulse, the magnetization will pass through the origin thereby generating a +y magnetization and hence a positive signal, Figures 2.8f-g. Choosing a sufficiently long delay between pulses will allow the magnetization to be relaxed to its equilibrium value of M₀, Figures 2.8h-i.

By running a series of separate experiments in which the delay times are varied, a magnetization anywhere between $-M_0$ to M_0 can be produced, corresponding to spectra

with a signal amplitude ranging from $-A_{\infty}$ to $+A_{\infty}$, as shown in Figure 2.9 for a series of proton-decoupled ¹³C spectra of the methine and methylene regions of PVC in TCE-d₂ with delay times ranging from 0.01 to 2.5 s recorded with the sample at a temperature of 101 °C and a magnetic field strength of 75.4 MHz. The pulse sequence for such experiments can be written as:

$$\left(\pi - t_{d} - \pi/2 - AT - W\right)_{nt}$$
(2.10)

where t_d is the operator controlled delay time, AT is the acquisition time, W is a suitable waiting time before the sequence is repeated, and *nt* denotes the number of transients or repetitions. This sequence is represented schematically in Figure 2.10. If the total time between sequences or the recovery delay (= W + AT) is sufficiently long, $\geq 5T_1$, to allow the magnetization to recover fully to its equilibrium value then the time-dependent signal, can be described by:

$$\mathbf{A}_{\mathbf{t}_{\mathbf{d}}} = \mathbf{A}_{\infty} \left(1 - 2\mathbf{e}^{-\mathbf{t}_{\mathbf{d}}/\mathbf{T}_{\mathbf{l}}} \right) \tag{2.11}$$

Data reduction can be achieved in two ways: (1) semilogarithmic plot or (2) an iterative exponential fit.

2.2.2.3 Mechanism of ¹³C Spin-Lattice Relaxation

As discussed previously, in spin-lattice-relaxation the spin system returns from a disturbed state to its equilibrium state by transferring its excitation energy to the surroundings. The link by which thermal energy is exchanged is provided by nolecular motion. Each carbon-13 nucleus experiences fluctuating local fields, that originate mainly in the same molecule. Potentially these fields can develop via four mechanisms: (1) Chemical shift anisotropy (CSA) that arises from the anisotropic (*i.e.*, directional) nature of the magnetic shielding of nuclei; (2) scalar coupling (SC) in which spins of two proximate nuclei in a molecule undergo coupling; (3) spin rotation (SR) that originates from the fact that molecules are rotating charge systems; and (4) dipole-dipole interaction (DD) whereby each nuclear spin generates a local magnetic field, as described formally by eq. (2.7).

For carbon-13 nuclei in organic molecules, especially those linked to protons, the only significant mechanism is the dipole-dipole interaction with neighboring magnetic



Figure 2.9 \blacklozenge A series of proton-decoupled carbon-13 spectra displaying the effect of altering the operator controlled delay time t_d on the signal amplitude of the methine and methylene regions of PVC in TCE-d₂ recorded at a magnetic field strength of 75.4 MHz and at T = 101 °C.



Figure 2.10 \blacklozenge The inversion recovery pulse sequence, where AT is time for the spectrometer to acquire the data and W is a waiting period before the next sequence is repeated which allows the magnetization to reach its equilibrium value M₀, usually of length equal to 5T₁. 54

nuclei, mainly protons. The preponderance of dipole-dipole relaxation relative to other mechanisms has been examined previously by Cutnell and Glasel.²³ Molecular motions and rotation of the ¹³C-¹H bonds are fast and the orientations of these bonds relative to B_0 will be changing constantly. Such constantly imposed magnetic re-orientations generate fluctuating local fields which, given sufficient strength and frequency, will contribute to the relaxation of the nuclear spin.

To explore further the dipolar induced relaxation process, the translational and reorientational modes of molecular motion must be described formally and in physical terms. Due to the complexity of the random process, it is not possible to describe all of these processes in causal terms and one must resort to a statistical description of the motion.²⁴ A description of such random time processes is best given through the medium of timecorrelation functions²⁵ that describe the persistence of convolation in a sequence of timeordered events. Assuming that the molecules can be described as Brownian particles, the local dipole field has the following properties:

- 1. The average value of B_{loc} over time is zero, *i.e.*, $\langle B_{loc}(t) \rangle = 0$.
- 2. The mean square average value of B_{loc} over time is non-zero, *i.e.*, $\langle B_{loc}^2(t) \rangle \neq 0.$
- 3. The value of B_{loc} at time t+ τ does not in any manner depend on the value at time t, provided that τ is sufficiently long, *i.e.*,

 $\langle B_{loc}(t+\tau) \cdot B_{loc}(t) \rangle = 0$, at long τ values.

At sufficiently short τ values, the quantity is expected to have a finite value.

These characteristics are embodied mathematically in the so-called time-dependent correlation function G(t) of B_{loc} which, at a reference time of zero, is given by the ensemble average

$$\mathbf{G}(\mathbf{t}) = \left\langle \mathbf{B}_{\mathbf{loc}}(\mathbf{0}) \cdot \mathbf{B}_{\mathbf{loc}}(\mathbf{t}) \right\rangle_{\mathbf{0}}$$
(2.12)

The time dependence is produced by the natural molecular motion in the system. Qualitatively, this function describes the persistence of a dynamical property before being averaged to zero by molecular motions and is particularly useful for describing weakly coupled systems, as is the case for a nuclear spin system and its lattice.²⁶ In other words, this function describes the time scale for decay of inherent motional order in the system. Information on the molecular system depends on the value of G(t), and as G(t) decays towards zero so does the knowledge of the dynamical processes.²⁴ In simplistic terms, G(t) provides information concerning the orientation of a collection of internuclear vectors - in particular the ¹³C-¹H internuclear vector - in the laboratory frame.²⁷

Since the time correlation function embodies all of the information about mechanisms and rates of motions, obtaining this function is crucial for a quantitative interpretation of the relaxation data. The Fourier transformation of G(t), the spectral density function $J(\omega)$, given by,

$$J(\omega) = \int_{-\infty}^{+\infty} G(t) e^{i\omega t} dt$$
(2.13)

provides a means of characterizing the *frequency distribution* and *magnitude* of the fluctuations in B_{loc} . Thus, $J(\omega)$ simply represents a transformation from the time to the frequency domain and may be thought of as the power available, at a frequency ω , to relax the spins in question. If G(t) decays to zero quickly, information about the system is lost quickly and the frequency spectrum is narrow, *i.e.*, molecules have only a short memory of their previous state of motion. However, if G(t) decays slowly information persists and the frequency spectrum is broad.²⁴

2.2.2.4 Quantum-Mechanical Treatment of Bloc

We now focus our attention on the derivation of expressions for the T_1 and NOE of a ¹³C nucleus relaxing purely by a dipolar interaction with a proton. For a more detailed and rigorous treatment, reference can be made to the excellent review article of the theory of ¹³C relaxation by Lyerla and Levy.²⁸ Since spin-lattice relaxation involves the transition between energy levels brought about by a fluctuating magnetic field, such that $B_{loc} \ll B_0$, the spin-lattice process can be treated via time-dependent perturbation theory. Figure 2.11 shows the energy levels and associated transition probabilities for a ¹³C-¹H dipolar relaxation mechanism. The ¹H spectrum consists of a doublet from the corresponding 1,3 and 2,4 transitions, where relaxation is characterized by the single quantum transition probability W_{1H} . Similarly, the ¹³C spectrum consists of a doublet



Figure 2.11 \blacklozenge Energy level diagram for a two-spin system, ¹³C and ¹H, with transition probabilities denoted as W_i, where i refers to the total change in spin quantum number and the first sign of a particular state denotes the spin of ¹H.

corresponding to the transitions 1,2 and 3,4 with a transition probability W_{1C} . W_0 is a zero-quantum process arising from a mutual spin flip and W_2 is a double quantum process which corresponds to the simultaneous relaxation of both spins.

Taking into consideration the properties of B_{loc} and the treatment of an $\alpha \rightarrow \beta$ transition, the transition probability $W_{\alpha\beta}$ is given as

$$\langle W_{\alpha\beta} \rangle = \int_{-\infty}^{+\infty} G(t) e^{i\omega_{\alpha\beta}t} dt$$
 (2.14)

which by analogy to eq. (2.13) is equal to $J_{\alpha\beta}(\omega_{\alpha\beta})$. Hence, the transition probability $W_{\alpha\beta}$ is directly related to the spectral density function at frequency $\omega_{\alpha\beta}$ and this relation is the link between T_1 and information concerning molecular dynamics. For a dipolar mechanism, the perturbing Hamiltonian can be written as a product of a spin operator and

second-order spherical harmonics thus allowing the determination of the transition probabilities, specified in Figure 2.11,

$$W_{0} = \frac{1}{20} K^{2} J_{0} (\omega_{H} - \omega_{C})$$

$$W_{1C} = \frac{3}{40} K^{2} J_{1} (\omega_{C})$$

$$W_{1H} = \frac{3}{20} K^{2} J_{1} (\omega_{H})$$

$$W_{2} = \frac{3}{10} K^{2} J_{2} (\omega_{H} + \omega_{C})$$
(2.15)

where $\omega_{\rm C}$ and $\omega_{\rm H}$ are the ¹³C and ¹H Larmor frequencies, respectively, the subscript for each J refers to the total change in spin quantum number upon a transition, $\mathbf{K} = \gamma_{\rm H} \gamma_{\rm C} \hbar / r_{\rm C-H}^3$ where $\gamma_{\rm C}$ and $\gamma_{\rm H}$ are the magnetogyric ratios of ¹³C and ¹H nuclei, respectively, $r_{\rm C-H}$ is the C-H internuclear distance, and $\hbar = h/2\pi$ where h is Planck's constant.

Through the differential equation describing the rate at which the z-magnetization for a ¹³C nucleus approaches its equilibrium value in a two spin system, Solomon²⁹ has shown that under random noise proton decoupling conditions, the ¹³C spin-lattice relaxation rate is given by

$$\frac{1}{T_1} = W_0 + 2W_{1C} + W_2 \tag{2.16}$$

Solving the differential equation under steady state conditions leads to the familiar nuclear Overhauser enhancement value

NOE = 1 +
$$\frac{\gamma_{\rm H}}{\gamma_{\rm C}} \frac{(W_2 - W_0)}{(W_0 + 2W_{1\rm C} + W_2)}$$
 (2.17)

By substituting the various transition probabilities, described by eq. (2.15), into the expressions for T_1 (eq. (2.16)) and NOE (eq. (2.17)), the spin-lattice relaxation time and the nuclear Overhauser enhancement can be expressed in terms of the spectral density function, $J_i(\omega_i)$, and in the SI system^{30,31} they are given as follows:

$$\frac{1}{T_1} = \frac{n_H}{10} \left(\frac{\mu_0 \hbar \gamma_H \gamma_C}{4\pi r_{C-H}^3} \right)^2 \left[J_0(\omega_H - \omega_C) + 3J_1(\omega_C) + 6J_2(\omega_H + \omega_C) \right] (2.18)$$

$$NOE = 1 + \frac{\gamma_{\rm H}}{\gamma_{\rm C}} \left[\frac{6J_2(\omega_{\rm H} + \omega_{\rm C}) - J_0(\omega_{\rm H} - \omega_{\rm C})}{J_0(\omega_{\rm H} - \omega_{\rm C}) + 3J_1(\omega_{\rm C}) + 6J_2(\omega_{\rm H} + \omega_{\rm C})} \right]$$
(2.19)

where μ_0 is the vacuum magnetic permeability and n_H is the number of directly bonded protons.

2.2.2.5 Experimental Approach

Thus far it has been shown that a random process is best described by the timecorrelation function whose Fourier transformation is the spectral density function. In addition, the transition probabilities that in turn determine the value, of T_1 and NOE are also directly related to the spectral density function. Therefore, obtaining the spectral density, actually its Fourier inverse, the correlation function, is the ultimate objective of relaxation studies. Unfortunately, at a given magnetic field strength, measurements of relaxation parameters respond to values of $J(\omega)$ at a limited number of frequencies. Hence it is impractical to obtain $J(\omega)$ over a wide frequency range and in sufficient detail to derive G(t). Under these circumstances, the most promising approach is to:

- (1) Derive an adjustable form of the correlation function based on a physically reasonable dynamical model for the polymer molecule;
- (2) measure several relaxation parameters at different resonance frequencies so that J(ω) can be sampled discretely at several frequencies giving some insight into the form of G(t); and
- (3) use the experimental data as a sound basis for critically testing the theories of polymer chain motions.

This approach is useful in several ways: (1) By suggesting a functional form of the correlation function, experimental data can be fitted and relevant parameters can be extracted; and (2) a good fit of the data to the theoretical model serves as an experimental verification of the proposed mechanism.

2.2.2.6 Models

Single correlation time model. The simplest model views the polymer chain as a rigid sphere immersed in a viscous continuum. The macromolecule reorientates by small, random diffusive jumps, *i.e.*, by isotropic rotational diffusion. The time correlation function, or the loss of memory of the previous motional state, is a single exponential function of time decaying with a time constant, τ_C , the molecular correlation time

$$\mathbf{G}(\mathbf{t}) \equiv \mathbf{e}^{-\mathbf{t}/\tau_{\mathbf{C}}} \tag{2.20}$$

The correlation time may be thought of as the time involved between diffusive steps in the state of motion of the molecule. Substituting eq. (2.20) into eq. (2.13) and integrating yields the familiar expression for the spectral density

$$\mathbf{J}(\boldsymbol{\omega}) \equiv \frac{\tau_{\mathbf{C}}}{1 + \omega^2 \tau_{\mathbf{C}}^2} \tag{2.21}$$

With a quick glance at this equation three characteristics of $J(\omega)$ readily become apparent: (1) It reaches a maximum value when $\omega = 0$; (2) in the range $\omega \ll 1/\tau_C$, it is approximately constant; and (3) it decreases with increasing frequency as $\omega \rightarrow 1/\tau_C$. Additionally, the condition that

$$\int_{0}^{\infty} J(\omega) d\omega = \pi/2$$
(2.22)

indicates that the total spectral density is constant and independent of $\tau_{\rm C}$. In other words, variation in $\tau_{\rm C}$ does not change the available molecular power, it merely changes the distribution of the spectral density over the frequency spectrum. This is conveniently displayed in Figure 2.12 which shows the spectral density function as a function of resonance frequency for three values of $\tau_{\rm C}$:

- (1) At large values of $\tau_{\rm C}$, corresponding to *slow motions* that are generally found in large molecules, stiff chains, or viscous solvents;
- (2) at small t_C values corresponding to *fast motions* such as those found in small molecules, or very flexible chains; and
- (3) an intermediate case when $\tau_C \equiv 1/\omega_0$, where ω_0 is the resonance frequency of the observed nucleus.



Figure 2.12 • The spectral density function (motional frequency) as function of frequency for three values of the correlation time τ_C , long, medium, and short (ω_0 , corresponds to the nuclear Larmor frequency).

As discussed previously, for an efficient spin-lattice relaxation sufficient power must be available at the Larmor frequency. In the case where the correlation time is long, the component at ω_0 is weak, as is readily seen from the dashed vertical line seen in Figure 2.12. In the short τ_C case, the frequency spectrum is broad and none of the components is very intense. Whereas at intermediate correlation times, the resonance component is maximum. This result indicates that the T_1 will be relatively small or a minimum at the intermediate case, where $\tau_C \equiv 1/\omega_0$, and large for the relatively short and long correlation times, *i.e.*, the value of T_1 as a function of τ_C goes through a minimum.

For the single rotational model, T_1 and NOE values can be calculated by substituting the corresponding spectral density function, described by eq. (2.21), into equations (2.18) and (2.19), respectively. As shown in Figure 2.13, a plot of the T_1 values, calculated for a magnetic field strength of 50.3 MHz, as a function of τ_C illustrates that the T_1 does indeed go through a minimum. This figure also illustrates the behavior of the NOE as function of τ_C . It shows that at short correlation times, *i.e.*, fast motions, the NOE has a maximum value of 2.988 and as molecular motions become slow it decreases very sharply in the vicinity of the T_1 minimum, reaching its minimum value which is slightly larger than unity (1.154).

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Figure 2.13 \diamond Calculated T₁ and NOE curves, using the single correlation model, for a ¹³C nucleus relaxed, via the dipolar relaxation mechanism, by a single directly bonded proton at magnetic field strength of 50.3 MHz.

Since $J_i(\omega_i)$, in eq. (2.18), is magnetic field strength dependent it follows that both T_1 and NOE are also frequency dependent. The frequency dependence of T_1 and NOE is illustrated in Figures 2.14 and 2.15, respectively. From Figure 2.14, it is readily seen that as the magnetic field strength increases the value of T_1 at the minimum increases and shifts to smaller values of τ_C . Similarly, in the NOE field dependence, the point of inflection occurs at smaller values of τ_C as the magnetic field strength is increased, as is shown in Figure 2.15. At very fast motions, *i.e.*, when $\omega_0 \tau_C \ll 1$, better known as the extreme narrowing condition, all $J_i(\omega_i)$ become equal to τ_C and the equation for T_1 and NOE simplify to

$$\frac{1}{T_{I}} = n_{H} \tau_{c} \left(\frac{\mu_{o} \hbar \gamma_{H} \gamma_{c}}{4 \pi r_{c-H}^{3}} \right)^{2}$$
(2.23)

$$NOE = 1 + \frac{1}{2} \frac{\gamma_{\rm H}}{\gamma_{\rm C}}$$
(2.24)

Under this condition T_1 and NOE become frequency invariant; however, the higher the magnetic field strength the more rapid is the motion necessary to satisfy this condition.

Due to the constraints imposed on the chain from its connectivity, it seems reasonable that the motions that are responsible for the spin-lattice relaxation are too complicated to be described by an isotropic rotational model. The two main pieces of evidence that support the idea that the segmental or local motions are responsible for the T_1 relaxation as opposed to a simple rotation are: (1) T_1 values have been found to be independent of chain length when the degree of polymerization is higher than 100;^{32,33} (2) fluorescence depolarization experiments that measure directly the autocorrelation function have unambiguously shown that experimental data cannot be described by this simple model.^{34,35}

In addition to local conformational changes, a polymer chain can experience a variety of motions, such as rotation of the whole chain or tumbling of large segments of the chain at much lower frequencies than the backbone local rearrangements, as well as motions of pendent groups, *e.g.*, methyl or phenyl. In view of the wide variety of motions with different rates and mechanisms, it is not surprising that eq. (2.20) is an unrealistic model for describing the actual spectral density function for a flexible polymer chain, as is well documented in the literature.^{1-3,5,36} Nonetheless, $J(\omega)$ still has the form of eq. (2.21)



Figure 2.14 \bullet A log-log plot of T_1 , for ¹³C nucleus relaxed by a single proton, as a function of correlation time, τ_C , at four magnetic field strengths, expressed in tesia.



Figure 2.15 \blacklozenge Nuclear Overhauser enhancement, NOE, as function of the logarithm of the correlation time, τ_C , at three magnetic field strengths, expressed in tesla.

and the behaviors of T_1 and NOE are similar to those shown in Figure 2.13, with the exception that a raised and broadened T_1 minimum as well as broadened NOE transitions are generally observed.

Since the models describing segmental dynamics in flexible polymer chains have been reviewed very comprehensively by Heatley¹⁻³, only a short description of the models and the associated correlation functions and spectral densities are given below.

Log- χ^2 distribution model. The simplest approach to dealing with the complex motions of a flexible polymeric chain is to analyze the experimental data in terms of a distribution of correlation times. With such models one expects that if the distribution is physically reasonable then trends in the distribution parameters as a function of temperature, solvent, etc., can provide some insight regarding the polymer motions. The spectral density function, in eq. (2.21), is easily modified to accommodate a distribution of correlation times, $\tilde{G}(\tau)$, for isotropic reorientations, and is given by

$$\mathbf{J}(\boldsymbol{\omega}) = \int_{0}^{\infty} \widetilde{\mathbf{G}}(\tau) \frac{\tau}{1 + \boldsymbol{\omega}^{2} \tau^{2}} d\tau$$
(2.25)

For practical purposes, it is convenient to define the density function on a logarithmic scale because the polymeric motions cover a wide range of frequencies so that the correlation time τ generally covers several orders of magnitude. Generally, a variable s is used which is a function of log τ . Hence, the distribution function $\tilde{G}(\tau)$ is replaced by F(s), a density function which is a function of s, *i.e.*,

$$\mathbf{G}(\tau)\,\mathbf{d}\tau = \mathbf{F}(\mathbf{s})\,\mathbf{d}\mathbf{s} \tag{2.26}$$

The function adopted by Schaefer⁶ is an extension of a logarithmic scale of the χ^2 distribution and hence is referred to as the log- χ^2 distribution model. The choice of this function is based on the fact that it has a skewed distribution with a tail towards longer correlation times. This is in accordance with the argument that polymeric motions should be dominated by high frequency local motions but the final loss of correlation should be attained by low frequency cooperative motions. The log- χ^2 distribution is one of the earliest models used in interpreting polymeric relaxation data in terms of a distribution of correlation times associated with correlated interactions between repeat units, as well as correlation times in the extreme narrowing region. The normalized distribution function is given by

$$\mathbf{F}(\mathbf{s}) = \frac{\mathbf{p}}{\Gamma(\mathbf{p})} (\mathbf{p}\mathbf{s})^{\mathbf{p}-1} \mathbf{e}^{-\mathbf{p}\mathbf{s}}$$
(2.27)

where the parameter p is related to the width of the distribution and $\Gamma(p)$ is the gamma function of p and represents a normalization factor. The variable s is defined by

$$s = \log_{b} \left(1 + (b-1)\frac{\tau}{\tau} \right)$$
(2.28)

where τ is the average correlation time that defines the center of the distribution and the logarithmic base is described by the parameter b.

The effect of the width parameter p on the normalized distribution function is best illustrated in a plot of F(s) as function of s, shown in Figure 2.16. At low values of p, the



Figure 2.16 \blacklozenge The log- χ^2 distribution of correlation times, F(s), proposed by Schaefer⁶, for three values of the width parameter, where the variable s is defined in eq. (2.28).

distribution function is asymmetric having a greater density for long correlation times. As p increases the distribution becomes narrower, inevitably approaching a δ function as $p \rightarrow \infty$. In fact, when $p \ge 100$ this model reduces to the single correlation time model.

The spectral density function for this model is given by⁶

$$J_{i}(\omega_{i}) = \int_{0}^{+\infty} \frac{F(s)\bar{\tau}(b^{s}-1)}{(b-1)\left(1+\omega_{i}^{2}\bar{\tau}^{2}\left[\frac{b^{s}-1}{b-1}\right]^{2}\right)} ds$$
(2.29)

By substituting this expression into equations (2.18) and (2.19), T_1 and NOE can be numerically calculated as a function of τ , p, and b. Although b is an adjustable parameter it is generally fixed at 1000. Therefore, in practice, the $\log_2 \chi^2$ distribution is a twoparameter model. Figure 2.17 shows the effect of the $\log_2 \chi^2$ distribution of correlation times on T_1 for two values of the width parameter p. *i.e.*, for a narrow (p = 100) and b = 1000) and a wider (p = 8 and b = 1000) distribution. For the narrow distribution, the calculation yields a T_1 curve that is identical with the prediction of the single correlation model. On the other hand, the distribution that is relatively broad yields a shallower, flatter, and asymmetric T_1 curve. In addition, there is an upward shift of about 30 ms in the T_1 minimum. Examples of calculated NOE values as a function of $\log(\tau)$ for four values of the width parameter are shown in Figure 2.18. As seen from these plots, for p < 20 and τ < 10⁻⁹, the NOE values can be substantially less than the theoretical maximum of 2.988 and the NOE shows a more gradual dependence on τ .

In summary, as the width of the distribution increases, *i.e.*, as p decreases, the T_1 minimum is raised and broadened. The NOE shows a more gradual dependence on τ and has a value that is substantially less than the theoretical maximum of 2.988, which is in fact the behavior displayed by most polymeric systems. As discussed previously, the major drawback of the use of distribution functions is that they are curve-fitting techniques and lack detailed insight into the nature of chain motions. More attractive theories based on a molecular description of segmental motions have been developed.

Although it has been shown that conformational jumps are responsible for the local chain dynamics, the precise nature of these jumps remains to be defined. Initially, when



Figure 2.17 • Plots of calculated T_1 , for a ¹³C nucleus with a single attached proton at a magnetic field strength of 22.6 MHz, for two values of the width parameter of the log- χ^2 distribution model, *i.e.*, a narrow (p = 100 and b = 1000) and wider (p = 8 and b = 1000) distribution.⁶



Figure 2.18 \blacklozenge Sample calculations of the nuclear Overhauser enhancement, NOE, at a magnetic field strength of 22.6 MHz, for four values of the width parameter p of the log- χ^2 distribution model.⁶

conformational transitions of a flexible chain were considered one was faced with the conceptual difficulty that when a rotation is restricted about a single bond without any conformational changes occurring in the remainder of the chain, then a large part of the chain must move through the viscous medium with a prohibitively large dissipation of energy, as shown in Figure 2.19a. Intuitively, this difficulty was circumvented by suggesting³⁷⁻⁴¹ that two rotations occur simultaneously so that only a small portion of the chain moves through the medium (Figure 2.19b). This is often referred to as a 'crankshaft-like motion'.



Figure 2.19 \blacklozenge Schematic representation of two possible conformational transitions that can occur in a polymer chain: (a) a single rotation about a single bond in the backbone; (b) a crankshaft-like motion which is characterized by the simultaneous rotation about two bonds in such a manner that the chain ends remain undisturbed during the transition.⁴²

Later, Helfand⁴³ classified segmental motions of polymers into three general types, that differed according to the relative positions in the initial and final states of the tails attached to the mobile segment:

Type 1 motion: Type 1 motions are characterized by the fact that they leave the tails, attached on either side of the segment undergoing the motion, in the same position during the transition, *i.e.*, transitions of the 'crankshaft' type. The conformational changes that occur in such a transition are illustrated in Figure 2.20 where a short sequence located in the middle of the polymer chain that has an initial conformation of Pttg+ttQ will, at the end of the transition, have the conformational sequence Pg+tg-tg+Q, where t and g denote 'trans' and 'gauche' bond conformations, respectively, and P and Q denote the tails on either side of the sequence undergoing the transition.



Figure 2.20 • Schematic representation of a typical type 1 transition, *i.e.*, a three bond motion which is characterized by the conformational sequence transition: $Pttg^+ttQ \rightarrow Pg^+tg^-tg^+Q$.

Type 2 motion. In this motion the chain ends suffer a translational motion such that the angular orientation of the two is unaffected. Two examples of this motion which, according to computer simulations, occur readily are illustrated in Figure 2.21 and are known as gauche migration, $Pg^+ttQ \rightarrow Pttg^+Q'$, and pair gauche production, $PtttQ \rightarrow Pg^+tg^-Q'$.

Type 3 motion. A type 3 motion alters the orientation of one tail relative to the other, *i.e.*, the orientation of P relative to Q changes. A simple example is a single bond rotation which can be characterized with the following conformational sequence reaction,

$PtQ \xrightarrow{\rightarrow} Pg^+Q'.$

Intuitively, one would expect type 1 transitions to be most favored since these minimize solvent friction. Using a modification of Kramer's theory of the rate of passage over a potential barrier, E^* , Helfand has shown that the diffusion-controlled rate constant (k_d) for a type 1 transition, is given by

$$\mathbf{k}_{d} = \left[\frac{\left(\alpha_{A}\alpha_{B}\right)^{1/2}}{2\pi\sum_{i}\xi_{i}r_{i}^{2}}\right] \exp(-\mathbf{E}^{*}/\mathbf{k}_{B}T)$$
(2.30)



Figure 2.21 • Schematic representation of two examples of a type 2 transition, (a) a gauche migration, $Pg^+ttQ \xrightarrow{\rightarrow} Pttg^+Q'$, and (b) a pair gauche production, $PtttQ \xrightarrow{\rightarrow} Pg^+tg^-Q'$.

where ξ_i is the friction constant for atom i in the mobile unit located at a distance r_i from the rotation axis, α_A and α_B are quadratic force constants in the initial and final states, respectively, k_B is Boltzmann's constant and T is the temperature. Increasing the number of bonds that undergo a transition will increase E* whereas an increase in the size of the kinetic unit will increase the frictional forces between the kinetic unit and viscous medium, *i.e.*, the $\sum \xi_i r_i$. Assuming that ξ_i is proportional to the solvent viscosity, and α_A , α_B and E* are independent of solvent, eq. (2.30) indicates that $k_d \propto \eta^{-1}$ and since $\tau \propto k_d^{-1}$ it follows that $T_1 \propto \eta^{-1}$. Although the concept of type 1 transitions was originally intended to apply to conformational transitions of polymers in the bulk, it was later used in consideration of the conformational mobility of flexible-chain molecules in highly dilute solutions. As a matter of fact, type 1 transitions formed the basis of the early models of polymer motion for relaxation analysis.

Jones-Stockmayer (JS) model. The JS model originates from the general "tetrahedral or diamond lattice" model first proposed by Valeur and collaborators (VJGM model).⁴⁴ The VJGM model is based on three and four-bond motions, *i.e.*, "crankshaft" motions which are allowed to occur in a polymer chain embedded in a tetrahedral lattice, where each bond can occupy one of the four directions, $\vec{a}, \vec{b}, \vec{c}, \text{or } \vec{d}$, as shown in Figure 2.22. As a result of the chain connectivity and the restriction imposed by the lattice, *i.e.*, coincidence of the bonds with the direction of the lattice, the smallest group that can move is composed of three bonds and corresponds to a $g^+ \rightarrow g^-$ conformational change. In terms of the evolution of the orientation of the vectors, the orientation of the first and third bonds have been interchanged.



Figure 2.22 \blacklozenge Representation of a three-bond motion of a chain embedded on a diamond lattice. This motion corresponds to a $g^+ \rightleftharpoons g^$ conformational change or to the following evolution $\vec{b}, \vec{a}, \vec{c} \rightleftharpoons \vec{c}, \vec{a}, \vec{b}$ of the orientation vectors of the bonds 3-4-5-6 \rightleftharpoons 3-4'-5'-6.

In solving the lattice equation which describes the three-bond motion, Valeur, *et al.*⁴⁴ used a continuous limit approximation that led to an expression with an unrealistic infinite slope of the resulting time correlation function at t = 0 and a slow decay, proportional to $t^{-1/2}$ at long times. Jones and Stockmayer⁷ overcame these shortcomings

by introducing an arbitrary truncation of the conformational coupling of the motion along the chain. According to this refined model, in the absence of overall tumbling and internal rotations of pendent groups, the correlation function is given by a discrete distribution of exponential functions, *i.e.*,

$$G(t) = \sum_{k=1}^{s} B_k \exp(-t/\tau_k)$$
 (2.31)

and the spectral density function by

$$J_{i}(\omega_{i}) = 2 \sum_{k=1}^{s} G_{k} \frac{\tau_{k}}{1 + \omega_{i}^{2} \tau_{k}^{2}}$$
(2.32)

$$(\tau_k)^{-1} = w_3 \lambda_k$$
; $s = (m_b + 1)/2$

The values of λ_k and G_k are found from the sharp cut-off solution of the three-bond jump equation as

$$\lambda_{k} = 4\sin^{2}\left(\frac{(2k-1)\pi}{2(m_{b}+1)}\right)$$
 (2.33)

$$G_{k} = \frac{1}{s} + \frac{2}{s} \sum_{q=1}^{s-1} 9e^{-q} \cos\left(\frac{(2k-1)\pi q}{2s}\right)$$
(2.34)

The two adjustable parameters in this model are w_3 , the characteristic frequency or rate of occurrence of a three bond jump, that is usually expressed as the harmonic mean correlation time, $\tau_h = (2w_3)^{-1}$, and m_b , the number of bonds involved in the cooperative motion, or the quantity, $2m_b - 1$, which stands for the chain segment expressed in bonds that are coupled to the central bonds. No correlated motions are assumed outside that segment. The parameter $2m_b - 1$ represents the breadth of the distribution of correlation times and ensures the aforementioned truncation.

Although the displacement of the chain ends involved in a type 2 motion makes it less favorable than a type 1 motion, a smaller activation energy is associated with the former. In fact, the activation energy for a type 2 motion is only slightly greater than the barrier separating the trans and gauche states (*ca.* 10 kJ mol⁻¹).⁴⁵⁻⁵⁰ Even though a type 1 motion does not induce any displacement of the ends of the sequence undergoing the motion, hence the viscous friction is limited to the group of moving atoms and is very weak, it does however, require the simultaneous orientational change of two bonds. This implies that two energy barriers have to be crossed corresponding to an activation energy *ca.* 20 kJ mol⁻¹, *i.e.*, twice the energy barrier for the trans-gauche transition.

Based on experimental findings^{42,51-57} and theoretical calculations⁵⁸⁻⁶¹, the existence of crankshaft-like motions has been questioned. For example, experimental data obtained by Morawetz and co-workers^{42,56,57} showed that the temperature dependence of excimer fluorescence in polymeric systems is virtually identical to that in their small molecule analogs, containing the same chromophore, proving that conformational transitions of polymer chains cannot involve two simultaneous rotations. Furthermore, observed activation energies are considerably lower than those expected for crankshaft-like motions.⁵¹ That is, assuming that the activation energy for correlation times or the apparent activation energy can be written as $E_a = E^* + E_{\eta}$, where E_{η} is the viscosity activation energy of the solvent, observed values of E^* were found to be about 10 kJ mol⁻¹ which is more consistent with just one rotation about a single bond.⁶²

Hall-Weber-Helfand (HWH) model. At that time, two issues had to be resolved. Firstly, it appears that the possibility of two simultaneous hindered rotations has to be excluded. Secondly, a single bond rotation is difficult to justify since the attached end would undergo a large swinging motion thus creating an enormous frictional resistance which would cause the rate of the motion to be exceedingly slow and dependent on the chain length, in contradiction to the experimental fact that relaxation times are independent of molecular weight. To obtain some insight concerning these problems, theoretical calculations and kinetic theory analysis of conformational transitions were performed.

The theoretical calculations, in the form of Brownian motion computer simulations, by Helfand, Wasserman, and Weber^{58,59}, showed that the rate-controlling step is the surmounting of a single internal rotational barrier with an activation energy approximately equal to one barrier height between the trans and gauche states. These simulations also revealed another important feature: following the transition of a single bond there is a strong increase in the transition rate of its second neighbor bond. The transitions described previously as the gauche migration and gauche production, as shown in Figure 2.21, were found to dominate, accounting for about 80% of all of the pair transitions. Since these frequently observed pair transitions can occur without involving the rotation of the entire chain end, but only a small translation of part of the chain end, this greatly reduces the frictional resistance.

In addition, kinetic theory analysis by Skolnick and Helfand⁶⁰ revealed that the reaction coordinate is always a localized mode, *i.e.*, as rotation of the first bond occurs the movement of the remote carbon atoms falls off exponentially with distance along the chain. Therefore, individual transitions are justified by the fact that they are accompanied by librational fluctuations in neighboring bonds, which are denied in a strict lattice model, in such a manner as to localize the motion. In pair transitions, before the distortion has had an opportunity to spread, the counter-rotation of the second-neighbor bond is brought to the point of its own transition, as the first transforming bond continues to the bottom of its new conformational energy well. Since the activation energy is one barrier height, this suggests that the two processes occur in a coherent, sequential fashion.

Hall, Weber, and Helfand^{8,9} used this information to develop a model which takes into account correlated pair transitions and isolated transitions occurring with correlation times τ_1 and τ_0 , respectively. The pair transitions ensure the propagation along the chain, while isolated, *i.e.*, single bond transitions, are responsible for damping. Analytically, the motions are represented by the following correlation function

$$G(t) = \exp(-t/\tau_0)\exp(-t/\tau_1)I_0(-t/\tau_1)$$
(2.35)

where I_0 is the modified Bessel function of order zero. Fourier transformation yields the following spectral density function

$$\mathbf{J}_{i}(\boldsymbol{\omega}_{i}) = 2\left(\alpha^{2} + (-\beta)^{2}\right)^{-\frac{1}{4}} + \cos\left(\frac{1}{2}\arctan\left(-\frac{\beta}{\alpha}\right)\right)$$
(2.36)

where
$$\alpha = \frac{1}{\tau_0^2} + \frac{2}{\tau_0 \tau_1} - \omega_i^2$$
 and $\beta = -2\omega_i \left(\frac{1}{\tau_0} + \frac{1}{\tau_1}\right)$.

Dejean-Lauprêtre-Monnerie (DLM) model. While the HWH model represented a significant advance in describing polymer chain local motions, in many cases it underestimated the value of T_1 at the minimum. Furthermore, it could not account for the different local dynamics observed at different carbon sites of a polymer chain.⁶³ The model proposed by Dejean, Lauprêtre, and Monnerie (DLM)¹⁰ is a clever modification of
the HWH model which corrects for these deficiencies by introducing an additional independent motion with a correlation time that differs from the correlation time for orientational diffusion along the chain. This motion is superimposed on the backbone rearrangement and has been attributed to molecular librations, of limited extent, of the C-H vector inside a cone of half angle, θ_{l} , the axis of which is the rest position of the C-H bond (Figure 2.23). This type of librational motion which must be faster, as supported by results derived from fluorescence anisotropy decay⁶⁴ and NMR^{65,66}, and more local than the orientational diffusion along the chain, has been described independently by Howarth.⁶⁷



Figure 2.23 \diamond Depiction of the librational motion as described in terms of a random, anisotropic fast reorientation of the C-H vector, with a characteristic correlation time τ_2 , inside a cone of half-angle, θ_1 , the axis of which is the rest position of ¹³C-¹H bond.

Hence, in this model the local chain motions consist of conformational jumps and bond librations. Assuming that these motions occur independently, Dejean-Lauprêtre-Monnerie¹⁰ used the HWH correlation function to describe the effect of conformational jumps and the Howarth description of bond libration, to obtain the following correlation function

$$G(t) = (1 - A)\exp(-t/\tau_0)\exp(-t/\tau_1)I_0(-t/\tau_1) + A\exp(-t/\tau_2) \quad (2.37)$$

where τ_2 is the correlation time for the librational motion, τ_1 and τ_0 are the correlation times for pair transitions and isolated transitions, respectively, as described previously for the HWH model, and

$$1 - A = \left[\frac{\cos\theta_1 - \cos^3\theta_1}{2(1 - \cos\theta_1)}\right]^2$$
(2.38)

The Fourier transform of eq. (2.37) yields the following composite spectral density

$$J_{i}(\omega_{i}) = \frac{1 - A}{(\alpha + i\beta)^{1/2}} + \frac{A\tau_{2}}{1 + \omega_{i}^{2}\tau_{2}^{2}}$$
(2.39)

where the parameters α and β have been defined in the HWH model.

These authors have shown that the height of the T_1 minimum is highly dependent on the conic half angle, *i.e.*, as the half angle increases the T_1 minimum increases in value. In addition, the τ_1/τ_2 ratio influences only the T_1 values in the long term or slow motion part of the curve, *i.e.*, a smaller ratio produces a broader T_1 curve.

2.3 EXPERIMENTAL SECTION

2.3.1 Polymer

The poly(vinyl chloride) used in this study was an Esso 366 industrial resin for which the following characteristics were quoted: $\overline{M}_n = 46\ 000$; $\overline{M}_w = 83\ 000$; density = 1.39 g cm⁻³ and $[\eta] = 0.98$ dL g⁻¹ in chlorobenzene at 25 °C. The glass transition temperature, T_g, as determined by a Perkin Elmer DSC-2C was 87 °C. Prior to use the PVC sample was dissolved in THF and precipitated with cold methanol in order to remove impurities and low molecular weight species. Previous studies^{68,69} by ¹³C NMR indicated that it is an essentially atactic polymer with P_m = 0.45, as determined from the methine triad sequence distribution.

2.3.2 Viscosity

Viscosity measurements were carried out by means of calibrated Ubbelodhe-type viscometers having various capillary sizes (SGA Scientific Inc.) immersed in a

thermostated water bath, regulated to ± 0.02 °C. Dilute solutions of PVC in DBP (0.06 to 0.20 g dL⁻¹) and in TCE (0.04 to 0.20 g dL⁻¹) were prepared with solvents purchased from Aldrich Co. All viscosity measurements were repeated at least twice. The effect of concentration on the viscosity of dilute polymer solutions was described by Huggins:⁷⁰

$$\frac{\eta_{sp}}{c} = [\eta] + k_{H}[\eta]^{2}c \qquad (2.40)$$

and by Kraemer:71

$$\frac{\ln(\eta_r)}{c} = [\eta] + k_K [\eta]^2 c \qquad (2.41)$$

where η_{sp} is the specific viscosity, η_r is the relative viscosity, and c is the concentration in g dL⁻¹. The values of intrinsic viscosity, [η], Huggins, k_H, and Kraemer, k_K, constants for PVC in DBP and for PVC in TCE at 30.0 °C, were obtained from the intercept and slope of plots of η_{sp}/c and $\ln(\eta_r)/c$ as a function of c. As seen from Figure 2.24, the Huggins and Kraemer plots for PVC in DBP have a common y-intercept that corresponds to an intrinsic viscosity of 0.89 dL g⁻¹. Similarly, for PVC in TCE, [η] was found to be 0.74 dL g⁻¹. Intrinsic viscosities along with values of k_H and k_K as well as activation energies for the solvent viscosity, E_{η} , obtained from the slopes of the plots of ln (η) as a function of 1/T (Figure 2.25), are listed in Table 2.2.

2.3.3 Determination of Interaction Parameter

Apparatus: The apparatus used in this study was a modified version of that described previously.^{72,73} The viewing apparatus consisted of a Leitz HM-LUX binocular light microscope equipped with a polarizer/analyser accessory that was used at 250X magnification. A DC-powered fiber optic light source was used for transmittance illumination. In addition, the optical microscope was equipped with a high-speed response silicon photodiode with a photosensitive effective surface area of 1.6 mm² and a spectral response range between 320 and 730 nm (peak wavelength at 560±20 nm). The photodiode analog signal was conditioned using a non-inverting operational amplifier circuit, converted to digital format via a Techmar A/D board, and the data were acquired with an AT computer using a Pascal program specifically written for this application. A



Figure 2.24 • Plots of η_{sp}/c (open symbols) and $\ln(\eta_r)/c$ (closed symbols) as a function of concentration, c, for the determination of Huggins and Kraemers coefficients for PVC in DBP (circle) and TCE (triangle) at 30.0°C.



Figure 2.25 \blacklozenge Arrhenius plot for the determination of activation energy of solvent viscosity, E_{η} , for DBP (circle) and TCE (triangle).

Table 2.2

Experimental values of intrinsic viscosity, [η], Huggins, k_H, and Kraemer, k_K, constants for PVC in DLP and PVC in TCE at 30.0 °C as well as activation energies for the solvent viscosity, E_n.

Solvent	[η] (dL g ⁻¹)	k _H	k _K	$E_{\eta} (kJ mol^{-1})^a$
DBP	0.89	0.36	-0.13	24.2 (24)
TCE	0.74	0.74	0.19	10.2 (12)

^a Values in parentheses correspond to literature values of E_{η} for DBP⁷⁴ and TCE.⁷⁵

Mettler FP52 hot stage with an FP5 temperature controller was used to heat the samples, at a constant heating rate, in the temperature range between 30 and 120°C. Temperature calibration was performed using thermometric standards.

Method: The method employed to determine the Flory-Huggins interaction parameter of PVC with DBP and TCE is a variation⁷⁶ of the technique described by Anagnostopoulos, et al.⁷⁷, and involves the microdetermination of the temperature at which a PVC particle in excess plasticizer undergoes an apparent phase change. The particle was observed through the microscope, with the polars positioned at ca. 15° from cross polarization, while the temperature was raised from 30 °C, at a constant heating rate of 1 °C/min, until an apparent phase change occurred. Within this temperature region, the photodiode detected the total light transmitted through a fixed viewing area including a single PVC particle in excess solvent. An AT computer recorded all changes in total light transmitted, thus allowing a reproducible determination of the temperature range in which the phase change occurred. The observed change was always gradual, occurring over several degrees.

A typical photodiode response curve of the light transmitted through a fixed viewing area that includes a PVC particle in DBP is presented in Figure 2.26. Superimposed on it are photomicrographs of the PVC particle that show the physical changes that occur as the temperature is raised from 30 to 95 °C, at a heating rate of 1.0 °C/min. A sudden, sharp increase in light transmission is observed in the region between 70 and 85 °C. It is apparent from photographs d and e that this change reflects an expansion, as well as an increase in the clarity, of the PVC particle. However, it still



Figure 2.26 \blacklozenge A typical photodiode light transmission curve for a single PVC particle in DBP recorded at a heating rate of 1 °C/min. Superimposed are photomicrographs of the PVC particle at selected temperatures of a) 35, b) 57, c) 60, d) 70, and e) 81 °C.

retains its distinct outline. The shape of the light transmission curve suggests the occurrence of a phase change that can be characterized by three temperatures: The onset (T_0) , the mid-point (T_m) and the final (T_f) temperatures.

Determination of Interaction Parameter: The calculation of the Flory-Huggins interaction parameter, χ , for the PVC-plasticizer systems is based on Flory's⁷⁸ theory of the melting point depression for a polymer-diluent system that was adapted to the microtechnique by Anagnostopoulos, *et al.*⁷⁷ From Flory's theory

$$\frac{1}{T_{m}} = \frac{1}{T_{m}^{o}} + \frac{R V_{u} \left(\phi_{1} - \chi \phi_{1}^{2}\right)}{\Delta H_{u} V_{1}}$$
(2.42)

where, T_m^o is the melting temperature of the pure polymer, T_m is the melting temperature of the mixture, ΔH_u is the molar heat of fusion of a polymer repeat unit, V_u and V_1 are the molar volumes at T_m of the polymer repeat unit and diluent, respectively, and ϕ_1 is the volume fraction of the diluent. With the assumption that the volume fraction of polymer in excess plasticizer is negligible, *i.e.*, $\phi_1 = 1$, and substitution of the values for ΔH_u , V_u and T_m^o , 656 cal mol⁻¹, 44.6 cm³ and 449 K, respectively, into eq. (2.42) yields

$$\frac{1}{T_{m}} = 0.002226 + \frac{0.1351(1-\chi)}{V_{1}}$$
(2.43)

The molar volume of the diluent can be calculated using the relation

$$\mathbf{V}_{1} = \frac{\mathbf{M}_{1}}{\rho} \left[1 + \alpha_{1} \left(\mathbf{T}_{m} - 25 \right) \right]$$
(2.44)

where M_1 is the molecular weight, α_1 is the coefficient of thermal expansion, and ρ is the density, at 25 °C, for the diluent. Using the final temperature, T_f , as the apparent melting temperature, in conjunction with the molar volumes determined from eq. (2.44), the χ parameters for the PVC/diluent systems were calculated using eq. (2.43) and are given in Table 2.3.

Table 2.5
Apparent melting temperatures and χ values for various PVC/solvent systems
at a heating rate of 1 °C/min.

T-11- 7 7

Solvent	V ₁ (cm ³)	T _f (°C)	χ
DBP	277.9	81	-0.23
TCE	109.4	56	+0.34

2.3.4 NMR Experiments

In the NMR experiments, the polymer was studied as 5% w/v solutions in both DBP (Aldrich Co.) and TCE-d₂ (MSD Isotopes). The lock signal for the PVC solution in the protonated DBP solvent was obtained either by using an external tube containing a solution of DBP in TCE-d₂, or by placing a co-axial tube containing deuterated solvent inside the 10 mm tube. No differences in relaxation parameters were observed using these two techniques.

Carbon-13 spin-lattice times, T_1 , and nuclear Overhauser enhancement, NOE, values were measured using Varian XL-200 and XL-300 spectrometers operating at 50.3 and 75.4 MHz, respectively, for the carbon nucleus. The temperature was controlled to within ± 0.5 °C as indicated by a precalibrated copper-constantan thermocouple in the probe insert. Spin-lattice relaxation times were measured by the standard inversion recovery method, eq. (2.10), with a repetition time longer than ST_1 . A total of 500-2000 transients, depending on solvent and temperature, was accumulated for each set of 12-14 "arrayed" t_d values. Values of T_1 were determined by a three parameter nonlinear procedure with an rms uncertainty of less than $\pm 5\%$. The ¹³C NOE experiments were carried out by reverse gated decoupling, at least three experiments being performed at each temperature. Delays of at least 10 times the longest T_1 were used between the 90° pulses.

The quantitative carbon-13 NMR spectrum of PVC in TCE-d₂ was recorded on a Varian XL-300 at a temperature of 114 °C. Instrument conditions used to record the spectrum in Figure 1.2 were: spectral width 16 501 Hz, acquisition time 3.9 sec, 18.5 μ s (90°) pulse, 12 416 transients, and NOE suppressed by gated decoupling. Chemical shifts were measured relative to the solvent peak and converted to δ (TMS) according to the relationship δ (TMS) = δ (TCE) + 75.50 ppm.

2.3.5 Numerical Analysis

The correlation times were calculated using a modified^{79,80} version of the MOLDYN⁸¹ program which includes the JS, HWH, and DLM motional models. Experimental relaxation data (T₁ and NOE values) for the methine, CH, and/or methylene, CH₂, carbons of PVC, determined at both field strengths for a given temperature, were used as the input data. Using a Simplex routine, the best fit relaxation data were calculated by varying one or more simulation parameters, depending on the model, until the target function, F_d, described by eq. (2.42) as the sum of the squares of the relative deviations between the experimental and calculated T₁ and NOE values was a minimum

$$F_{d} = \sum_{i=1}^{n} \left[\frac{S_{i,cal} - S_{i,exp}}{S_{i,exp}} \right]^{2}$$
(2.42)

where $S = T_1$ and/or NOE, and n represents the number of experimental relaxation parameters. Throughout this discussion differences between the experimental and calculated values are described by the function, σ , defined as the root mean square of the relative deviations,

$$\sigma = \frac{\sqrt{F_d}}{n}$$
(2.43)

The initial calculations, using the $\log \chi^2$ distribution, were performed by entering the relaxation data for the methine carbon, determined at both field strengths, for the temperature where the T₁ exhibits a minimum value. The optimum correlation time $\bar{\tau}$ was determined by varying the distribution width p, in steps of unity, until a minimum F value was obtained. The methylene relaxation data were then calculated using the optimized values of $\bar{\tau}$ and p calculated from the data for the methine carbon. In the HWH and JS models, the T₁ and NOE values of the CH and CH₂ carbons, for both field strengths at a temperature corresponding to the T₁ minimum, were entered simultaneously through a geometry file that included a nonbonded dipolar relaxation mechanism. In the HWH model, τ_0 and τ_1 were optimized simultaneously, while for the JS model w₃ was optimized while the parameter $2m_b - 1$ was varied manually in steps of unity until a minimum F value was obtained. No significant deviations between experimental and calculated relaxation data were found when the data for CH and CH_2 carbons were entered separately or using a geometry file which embodied nonbonded $^{13}C^{-1}H$ dipolar interactions.

For the DLM model, relaxation data for the CH carbon at the minimum of the plot of T₁ as a function of 1/T were used as input values and the optimized values for the correlation time for cooperative motion τ_1 and the angle θ_{CH} (half angle of the librational motion of the C-H vector for the carbon in the methine group) were determined by varying τ_0/τ_1 and τ_1/τ_2 manually in steps of 1 and 10 units, respectively, until a minimum F value was obtained. The factors θ_{CH} , τ_0/τ_1 , and τ_1/τ_2 were then kept constant over the whole temperature range while τ_1 was optimized. The half angle, θ_{CH_2} , of the C-H vector for the CH₂ carbon was calculated from experimental relaxation data at the minimum and τ_1 , τ_0/τ_1 , and τ_1/τ_2 values from the CH carbon. Calculations of the T₁ and NOE values for the CH₂ carbon at both field strengths over the whole temperature range were performed by entering the angle θ_{CH_2} and the τ_1 , τ_0/τ_1 , and τ_1/τ_2 parameters obtained for the CH carbon at a given temperature.

2.4 RESULTS AND DISCUSSION

2.4.1 Microstructure Determination

Figure 1.2 shows expanded portions and stereosequence assignments of the methine and methylene regions of a carbon-13 spectrum of PVC in TCE-d₂ recorded at a magnetic field strength of 75.4 MHz and at a temperature of 114 °C. As reported earlier by others^{82,83}, both the methine and methylene regions exhibit tacticity effects. Examination of the methine carbon signal reveals that peaks for all ten possible pentads are present with some heptad fine structure. In the methylene region, peaks for the six possible tetrads are visible with some hexad fine structure.

Table 2.4 gives the ¹³C chemical shifts of the methine and methylene resonances, their respective experimental relative areas and calculated relative areas assuming Bernoullian statistics with $P_m = 0.431$. Good agreement between observed and calculated areas indicates that the stereochemistry of the propagation step conforms to Bernoullian statistics. The assignments of the peaks were, with a few exceptions, obtained from a study of Elgert, *et al.*⁸⁴, in which was reported a ¹³C NMR spectrum of PVC in 1,4dioxane-d₈ recorded at a magnetic field strength of 125.8 MHz and a temperature of 97 °C. The differences in the stereosequence assignments are based on two exceptions:

Table 2.4

Carbon-13 chemical shift^a assignments, and observed and calculated relative areas for poly(vinyl chloride) in TCE-d₂ at a magnetic field of 75.4 MHz and at a temperature of 114 °C.

Assignment	δ(¹³ C)	Obs. rel. area	Cal. ^b rel. area
rmrrmr	58.72	0.024	0.019
rmrrmm	58.67	0.025	0.029
mmrrmm rrrmm rrrmr	58.61	0.112	0.102
mrrrmm mrrrmr	58.56	0.061	0.068
rrrr	58.48	0.101	0.105
mmrm mmrr	57.75	0.220	0.211
rimimi	57.63	0.065 -	0.068
mrmrmm mrmrmm	57.57	0.206	0.211
mmmm	56.89	0.039	0.035
numr	56.74	0.086	0.091
THEAT	56.58	0.060	0.060
rrr	49.14	0.176	0.184
rmr	48.73	0.137	0.140
rrm	48.34	0.281	0.279
maarr naarr	47.77	0.094	0.091
rmmrm	47.71	0.117	0.120
mrm	47.58	0.117	0.106
mmm	46.92	0.077	0.080

^a measured relative to solvent peak and converted to δ (TMS) according to the relationship δ (TMS) = δ (TCE) + 75.50 ppm.

b assuming Bernoullian statistics with $P_m = 0.431$.

(1) Due to the use of a higher magnetic field and a different solvent, Elgert, *et al.* obtained a higher quality spectrum whereby higher order stereosequences were observed; (2) large deviations between experimental and calculated peak areas and a recent⁸⁵ assignment of poly(vinyl chloride) based on a 2D-INADEQUATE spectrum led to the reassignment of several peaks.

The discrepancies that arise from differences in spectral quality are the mmmm and mmmr peaks located at 56.89 and 56.74 ppm, respectively. For these peaks Elgert. *et al.* observed a higher order of stereosequences. For the mmmn peak they observed all three possible mmmm centered heptads and, beginning from the downfield peak, assigned them to rmmmmr, mmmmmr, and mmmmmn. For the mmmr peak two clearly resolved peaks were observed and were assigned to the following combinations of mmmr centered heptads: rmmmrr + mmmmrm and rmmmrm.

The second exception, which is more serious, deals with the assignments of several peaks. Firstly, in the methylene region all six possible tetrads are observed with a small shoulder peak at 47.77 ppm indicating hexad fine structure. This peak was also observed by Elgert, et al., but they made no attempt to assign it. According to the calculated relative areas the peaks at 47.77 and 47.71 ppm can be assigned as mmmrm + xmmry and ymmrx + rmmrr, respectively, where x is either an m or r placement and y is dependent on the x placement, taking an opposite designation, *i.e.*, if x = m then y = r. In other words, the stereosequences rmmrm and mmmrr are interchangeable since it is not possible by this method (Bernoullian statistics) to unambiguously assign resonance signals with equal numbers of m and r monomer placements. However, recent ¹³C NMR chemical shift assignments of poly(vinyl chloride), by Nakayama, et al.⁸⁵, based on carbon-carbon connectivities revealed by a 2D-INADEQUATE spectrum, attributed the peaks at 47.77 and 47.71 ppm to mammum + manarr and ramarm + ramarr, respectively. Since the method of the 2D experiment is correct, this assignment has been used in this study also. As shown in Table 2.4, excellent agreement between calculated and experimental area is obtained for this assignment, i.e., deviations of only 0.003 for both peaks.

Secondly, the peaks located at 57.63 and 57.57 ppm have been assigned by Elgert, et al., as mmrr and rmrr, respectively. They reported that the calculated peak areas are 0.100 and 0.183, assuming a P_m value of 0.423. With this P_m value the calculated areas should be 0.119 and 0.163. A comparison of the correctly calculated areas with their reported experimental areas of 0.087 and 0.204 corresponds to even larger deviations than those reported, *i.e.*, 0.032 compared to a reported deviation of 0.013 for the peak at 57.63 ppm and 0.041 compared to 0.021 for the peak at 57.57 ppm. The corresponding experimental relative peak areas obtained in the present study are 0.065 and 0.206 which strongly suggests that these peaks share the heptad fine structure containing mmrr or rmrm centers. Since these centers contain the same number of m and r placements it is not possible to unambiguously assign these peaks. However, 2D experiments have shown that the peak at 57.63 ppm contains rmrm centered heptads. Based on these arguments, the peaks at 57.63 and 57.57 ppm have been reassigned to rrmrmr + rrmrmm and mrmrmr + mrmrmm + rmrr, respectively. As shown in Table 2.4, this assignment yields deviations between calculated and experimental areas of 0.003 and 0.005 for the peak at 57.63 and 57.57 ppm, respectively.

The methine peak at 57.75 ppm with its two neighboring peaks, one downfield and one upfield, appearing only as shoulders, have been assigned to a combination of the mmrm and mmrr pentads, whereas, Elgert, *et al.*, observed three resolved peaks which, beginning from the downfield peak, were assigned to mmmrmm + mmmrmr, mmmrmm + mmrmr + mmmrm + mmrmr, and mmrr + mmmrm heptads. It is certain that the mmr centered heptads should be mmrr centers. In addition, attempts to perform deconvolution of the resonance observed at 57.75 ppm, into three peaks yielded peaks with areas of 0.032, 0.149, and 0.039. When these areas are compared to their calculated values of 0.039, 0.104, and 0.068, assuming a $P_m = 0.431$, considerable discrepancy is obtained, especially for the last two peaks. This may be due either to improper assignment or inaccurate deconvolution of the peaks, the latter being more probable since the peaks in this region appear as small shoulders.

2.4.2 Relaxation Studies

Figure 2.27 shows a series of proton-decoupled ¹³C NMR spectra of a 5% solution of PVC in TCE-d₂ recorded at a field strength of 75.4 MHz in the temperature range -19 to 114 °C. At all temperatures tacticity effects are apparent for both the methine and methylene carbons. At the lower temperature (T<20) the molecular motions are not fast enough to effectively average out the line broadening resulting from dipolar interaction and chemical shift anisotropy. In this temperature range, the lines are much broader which is evidence for an increase in the natural line width $(1/\pi T_2)$ of the carbon-13 nuclei. As the temperature is increased, the peaks become much sharper, improving resolution and allowing finer microstructure to be observed.



Figure 2.27 \blacklozenge Series of ¹³C NMR spectra of 5% (wt/v) PVC in TCE-d₂ recorded at a magnetic field of 75.4 MHz in the temperature range -19 to 114 °C.

Although the chemical shifts of the stereosequences of the methine resonance are unaffected by changes in temperature, those of the methylene resonances show a definite temperature dependence, *i.e.*, as the temperature is increased both m and r centered tetrads are shifted downfield. Also the chemical shift differences between the m-centered tetrads decreases almost equally, whereas the r-centered tetrads show an unequal decrease as the temperature is increased. As the temperature is increased, the combination of these effects results in increases in the chemical shift differences between rrr and rmr, rrm and mmr and mmm, while decreasing the chemical shift differences between rrr and rmr, T = 114 °C the mrm peaks, such that at T = 61 °C these peaks are well resolved and at T = 114 °C the mrm peak appears as a shoulder of the mmr peak.

Since no dependence of T_1 values on stereosequences was found in either solvent and overlapping peaks were observed at low temperatures, the average values of T₁ and NOE for the methine and methylene resonances are reported. Table 2.5 summarizes the T_1 and NOE values for the methine and methylene carbons of PVC in DBP and TCE-d₂ as a function of temperature as determined at the two magnetic fields. Plots of T_1 and NOE values as a function of 1/T, shown in Figure 2.28 for PVC in DBP and in Figure 2.29 for PVC in TCE-d₂, display, as discussed previously, five characteristics that are commonly observed in the relaxation data for polymeric materials: (1) As the temperature decreases the T₁ values decrease monotonically, in both fields, reaching a minimum which is followed by an increase in T_1 with further decrease in temperature; (2) At a given temperature, T_1 values increase with increasing magnetic field. The difference in T_1 values between the two magnetic fields becomes more pronounced as the temperature decreases (slow motion regime); (3) The NOE values decrease with increasing magnetic field at all temperatures; (4) Both the NOE and T_1 transitions are much broader than for small molecules; (5) At high temperatures (extreme narrowing condition), the NOE values are substantially less than the theoretical maximum and a residual NOE is observed at low temperatures (slow motion regime).

An interesting feature of the data in Table 2.5 is that the ratio of T_1 values of the CH and CH₂ groups, $T_1(CH)/T_1(CH_2)$, as determined in both magnetic fields, in both solvents is fairly constant at 1.80 ± 0.04 throughout the temperature range studied. This value is different from the value 2 which is expected from the number of directly bonded protons and suggests different local motions for the C-H internuclear vectors associated with the CH and CH₂ groups.

Table 2.5

Experimental carbon-13 spin-lattice relaxation times(T_1 , in ms) and NOE values^a of methine and methylene carbons of PVC in DBP and TCE-d₂ as a function of temperature at two magnetic fields.

	50.3 MHz		75.4 MHz					
Temp, °C	CH	CH ₂	CH	CH ₂				
	PVC in DBP							
20	160 (1.43)	83 (1.38)	307 (1.31)	167 (1.28)				
41	132 (1.56)	71 (1.50)	226 (1.36)	127 (1.43)				
61	136 (1.75)	77 (1.72)	202 (1.54)	114 (1.50)				
82	165 (2.06)	92 (2.10)	219 (1.77)	126 (1.79)				
91	181 (2.18)	99 (2.16)	241 (1.85)	133 (1.84)				
114	264 (2.45)	149 (2.46)	325 (2.16)	183 (2.11)				
137	389 (2.54)	222 (2.50)	432 (2.33)	243 (2.23)				
· _ ·		PVC in TCE-d ₂						
-19	182 (1.49)	100 (1.55)	290 (1.48)	163 (1.47)				
-1	147 (1.55)	81 (1.61)	235 (1.47)	131 (1.49)				
20	147 (1.72)	81 (1.71)	214 (1.59)	115 (1.58) ⁺				
41	172 (1.93)	95 (1.95)	221 (1.66)	124 (1.71)				
61	211 (2.18)	115 (2.18)	255 (1.89)	142 (1.96)				
81	275 (2.44)	155 (2.51)	315 (1.99)	179 (2.12)				
101	374 (2.61)	215 (2.70)	415 (2.18)	232 (2.33)				
114	464 (2.65)	266 (2.65)	498 (2.44)	285 (2.47)				

•

^a Values in parentheses.



Figure 2.28 \blacklozenge Carbon-13 spin-lattice relaxation times, T₁, and NOE values for methine (circle) and methylene (triangle) carbons of PVC in DBP as a function of reciprocal temperature at field strengths of 50.3 (solid symbols) and 75.4 MHz (open symbols). The solid lines represent the best fit values calculated by the DLM model.



Figure 2.29 \diamond Carbon-13 spin-lattice relaxation times, T₁, and NOE values for methine (circle) and methylene (triangle) carbons of PVC in TCE-d₂ as a function of reciprocal temperature at field strengths of 50.3 (solid symbols) and 75.4 MHz (open symbols). The solid lines represent the best fit values calculated by the DLM model.

In modeling the dynamics of PVC two types of motion are considered: (1) The overall tumbling of the entire, or large segments, of the chain, and (2) segmental backbone rearrangements. Assuming that these motions act as independent sources of motional modulation of the dipole-dipole interaction, the composite autocorrelation function can be written as a product of the correlation functions associated with each motion. In the event that the overall motion is much slower than the chain local motions, which is usually the case for sufficiently high molecular weight polymers, it makes a negligible contribution to the relaxation of the backbone carbons.

The correlation time for the overall tumbling of the entire PVC chain, τ_R , at infinite dilution can be estimated from knowledge of the molecular weight, \overline{M}_w , and the intrinsic viscosity, [η], of the polymer solution in a given solvent with viscosity η_0 through the hydrodynamic equation^{86,87}

$$\tau_{\rm R} = 2 \, M_{\rm w} \, [\eta] \, \eta_{\rm o} / 3 \, {\rm R} \, {\rm T}$$
 (2.44)

This calculation gives correlation times of 2.5×10^{-5} s for PVC in DBP and 2.4×10^{-6} s in TCE, at 30 °C. Such long correlation times guarantee that the local segmental motions are the major source of relaxation for the protonated carbons of PVC in both solvents.

Backbone rearrangement is the second type of motion that modulates dipolar interaction which, as discussed previously, can be modeled by the log- χ^2 distribution, HWH, JS, and DLM correlation functions. These four models are evaluated below as to their ability to describe the local motions of the PVC chain.

2.4.2.1 Comparison of Relaxation Data at the T_1 Minimum with Predictions of Motional Models

The first criterion for the validity of any model is the existence of a good fit of the relaxation data at the minimum of the curve of T_1 plotted as a function of 1/T. This minimum occurs at temperatures of 61 and 20 °C for PVC in DBP (Figure 2.28) and PVC in TCE-d₂ (Figure 2.29), respectively. Table 2.6 shows the experimentally determined relaxation data for PVC in DBP and TCE-d₂, for the two magnetic fields at a temperature where T_1 exhibits a minimum value, and the calculated relaxation data derived by using the log- χ^2 , HWH, JS and DLM correlation functions. The simulation parameters for the four models that best reproduce the relaxation data for both solvents at these temperatures are summarized in Table 2.7.

Experimental and calculated ^a (log- χ^2 , HWH, JS and DLM models) carbon-
13 spin-lattice relaxation times (T_1 , in ms) and NOE values ^b of methine and
methylene carbons of PVC in DBP and TCE-d ₂ for two magnetic fields at a
temperature in which T_1 exhibits a minimum value.

Table 2.6

	50.3 MHz		75.4				
	CH	CH ₂	CH	CH ₂	σ(%)		
		PVC in D	BP, 61 °C				
Exp't	136 (1.75)	77 (1.72)	202 (1.54)	114 (1.50)			
log-χ ²	135 (1.68)	68 (1.68)	206 (1.61)	103 (1.61)	2.3		
HWH	106 (1.82)	54 (1.82)	154 (1.61)	79 (1.61)	6.8		
JS	107 (1.83)	55 (1.83)	154 (1.62)	79 (1.62)	6.7		
DLM	136 (1.74)	77 (1.74)	202 (1.55)	114 (1.55)	0.4		
PVC in TCE-d ₂ , 20 °C							
Exp't	147 (1.72)	81 (1.71)	214 (1.59)	115 (1.58)			
$\log-\chi^2$	143 (1.69)	72 (1.69)	218 (1.63)	109 (1.63)	1.7		
HWH	109 (1.91)	56 (1.91)	156 (1.71)	80 (1.71)	7.6		
JS	107 (1.81)	55 (1.81)	154 (1.60)	79 (1.60)	7.6		
DLM	<u>146 (1.75)</u>	80 (1.75)	215 (1.57)	117 (1.57)	0.5		

^a Refer to Table 2.7 for simulation parameters.

b Values in parentheses.

Table 2.7

Simulation parameters for the log- χ^2 , HWH, JS and DLM models which best reproduce the relaxation data of the CH carbon of PVC in two solvents at temperatures corresponding to the T₁ minimum.

	log-χ ²		H	HWH		JS		DLM	
Solvent	р	τ (ns)	^т о (µs)	τ ₁ (ns)	2m _b -1	τ _h (ns)	τ_0/τ_1	τ_1/τ_2	
DBP, 61 °C	11	3.125	10	3.215	7	1.20	7	600	
TCE-d ₂ , 20 °C	9	3.475	10	1.002	7	1.25	7	· 200	

As seen in Table 2.6, for the log- χ^2 distribution σ values of 2.3 and 1.7% are obtained for PVC in DBP and in TCE-d₂, respectively. Although these σ values suggest a good fit, a closer examination reveals that this model is unable to simultaneously account for the relaxation data of both the CH and CH₂ carbons. For example, for PVC in DBP a distribution width of p = 11 yields good agreement between the experimental and calculated data for the T_1 of the CH group whereas the $T_1(CH_2)$ values are underestimated. On the other hand, a distribution width of p = 10 results in a better fit for the CH₂ group at the expense of a worse fit for the CH data. This pattern is also followed for the relaxation data of PVC in TCE-d₂. To obtain a good fit for both the CH and CH₂ groups different p values must be used. This corresponds to a slightly different breadth of correlation times for the CH and CH₂ groups, and is the only way that this model can account for the fact that $T_1(CH)/T_1(CH_2)$ ratio is less than 2. Although this is not a recommended method for fitting the data, it does suggest that these groups may be experiencing different local dynamics. Since this model cannot account for the fact that the $T_1(CH)/T_1(CH_2)$ ratio is less than 2 and it does not provide a precise description of the phenomena involved, it will not be investigated further.

The high σ values obtained with the HWH and JS models clearly show that these are inadequate in describing the segmental motion of PVC. These high σ values arise from the fact that the HWH and JS models grossly underestimate the value of T₁ at the minimum. It was mainly for this reason that the DLM model was developed.

The DLM model gives an excellent fit ($\sigma = 0.5\%$) between experimental and calculated T₁ and NOE values for both the CH and CH₂ groups at both fields, making it the best model, by far, in describing the dynamics of PVC in the two solvents. Hence, this model will be used for all further calculations of the relaxation data over the whole temperature range.

2.4.2.2 PVC Motions According to the DLM Model

The best fit to the T_1 and NOE data over the whole temperature range for the CH and CH₂ carbons of PVC in DBP and in TCE-d₂ are shown graphically in Figures 2.28 and 2.29, respectively. It is clear from these plots that very good agreement between experimental and calculated values is obtained throughout the entire temperature range by use of this model. As shown in Table 2.7 the values of the fitting parameter τ_1/τ_2^{88} were found to be 600 and 200 for PVC in the DBP and TCE-d₂ solutions, respectively. These ratios indicate that the correlation time for librational motion of the C-H vector of PVC in

DBP is 600 times shorter than the correlation time for diffusive chain motions, whereas in TCE- d_2 it is only 200 times shorter.

The best fit half-angles of the librational motion of the C-H vector for the methine carbon, θ_{CH} , and methylene carbon, θ_{CH_2} , were found to be 27° and 32° for PVC in DBP and 30° and 33° for PVC in TCE-d₂. In both solvents θ_{CH} is less than θ_{CH_2} which explains the fact that $T_1(CH)/T_1(CH_2) < 2$ and supports the previous suggestion that the C-H internuclear vectors at the methine and methylene groups experience different local dynamics. The smaller θ_1 value for the CH group indicates a greater steric hindrance to the librational motion of the C-H vector relative to that of the CH₂ group. The methine carbon has a directly attached chlorine atom which, because of its size, can physically restrict the amplitude of the local libration. This observation is in agreement with earlier findings for poly(β -hydroxybutyrate)^{80,89} and other polymeric systems^{10,90} that have been summarized by Monniere.⁹¹

As seen above, the half-angle of the C-H vector for the methine carbon is smaller for PVC in DBP than in TCE-d₂, *i.e.*, θ_{CH} (in DBP) < θ_{CH} (in TCE-d₂). This result is in agreement with the τ_1/τ_2 ratio in the two solvents; in other words, a smaller half-angle should correspond to a shorter correlation time for the librational motion.

It is of interest to note that the values of θ_{CH_2} obtained for PVC in DBP and TCE d_2 are approximately the same (32° and 33°), whereas those for θ_{CH} (27° and 30°) are quite different. The effects on the quality of the fit for such differences in the librational angle can be seen by comparing the calculated values of T_1 and NOE using the DLM model for the two solvents (Table 2.6). Examination of these data reveals that the changes in the half-angles do not affect the NOE values, however the T₁ values for the methine carbon change by ca. 7% whereas the T_1 values for the methylene carbon change by only ca. 3%. While the percent difference in the T_1 values for the methine carbon are above the usual experimental uncertainty ($\leq 5\%$), that for the methylene carbon is within this error limit. A smaller half-angle for the methine group in DBP indicates a greater steric hindrance to the librational motion of the C-H vector relative to that of the methine carbon of PVC in TCE-d₂. Such a change in angle could reflect differences in coil dimensions, depending on the solvent quality, or a specific interaction between DBP and the CHCl group of PVC. The latter appears to be more likely since the former should affect the angles of the methine and methylene groups equally. The reduction in θ_{CH} implies that a greater steric hindrance is imposed to the librational motion of the C-H bond, as might be expected from a specific interaction between DBP and the chlorine atom of the PVC chain.

The compatibility of binary mixtures of PVC and plasticizers is generally attributed to the presence of a specific interaction between the carbonyl group of the ester and PVC, although the precise nature of this interactions is still a matter of controversy. Infrared spectroscopy studies of blends of ester-containing polymers with PVC or of solutions of small molecules containing a carbonyl group with PVC or low molecular weight chlorinated molecules have strongly suggested, with general agreement, that the carbonyl group is involved in a specific interaction. However, there has been some debate as to the functional group of PVC with which it is actually interacting. The following specific interactions of the carbonyl group have been suggested:

(1) A hydrogen bond with the α -hydrogen⁹²⁻⁹⁶, *i.e.*, the hydrogen attached to the methine carbon,

(2) A hydrogen bond with the β -hydrogens⁹⁷,

and (3) A dipole-dipole interaction with the chlorine atom.98-100

A hydrogen bond interaction involves a heavy moiety (DBP) being directly attached to the proton of the ¹³C-¹H vector (Figure 2.23) resulting in an increase in the half-angle and in a longer correlation time for the librational motion, which is contrary to the experimental observation of a lower value of θ_{CH} and a shorter correlation time (Table 2.7) obtained for PVC in DBP relative to PVC in TCE-d₂ solution. The differences in half-angles are, however, in keeping with the formation of a complex of the type C=O----Cl-C, *i.e.*, between the carbonyl group of DBP and the chlorine atom of PVC.

Additional support for this type of interaction has recently been given by Millan and co-workers.¹⁰¹ Using FTIR spectroscopy, the molecular interactions of poly(vinyl chloride) with some solvents (cyclohexanone, methyl ethyl ketone and N-methylpyrrolidone), esters (di-octyl phthalate and butyl stearate), and polyesters (poly(ethylene adipate) and poly(ε -caprolactone)) were investigated. Changes in both the carbonyl absorption frequencies and the C-Cl stretching bands of PVC as well as previous work^{102,103} on the thermal degradation of PVC in blends of different compatibility, led these workers to suggest an interaction that is of a local conformational nature, *i.e.*, the interacting chlorine of PVC is located in a $g^+\pi g^-$ conformation of an -mmr-sequence.

The τ_1 values derived from fitting the experimental relaxation data for PVC in both solvents using the DLM model are compiled in Table 2.8. A plot of the logarithm of these values as a function of 1/T shows linear correlations, in the temperature ranges studied, yielding apparent activation energies, E_a , of 33.4 and 23.9 kJ mol⁻¹ for PVC in DBP and TCE-d₂, respectively. The activation energy, E*, of the conformational transitions associated with the τ_1 correlation time can be estimated from the relation¹⁰⁴

 $\mathbf{E}^* = \mathbf{E}_a - \mathbf{E}_\eta \tag{2.45}$

where E_{η} is the activation energy for solvent viscosity, which were found to be 24.2 and 10.2 kJ mol⁻¹ for DBP and TCE (Table 2.2), respectively. This leads to values of E* of 9.2 ± 0.9 kJ mol⁻¹ for PVC in DBP and 13.7 ± 0.9 kJ mol⁻¹ for PVC in TCE-d₂.

The difference in E* for PVC in the two solvents is in agreement with earlier findings for other polymers reported by Ediger and co-workers.^{105,106} For polyisoprene and polystyrene they found that the activation energies were higher for Θ solvents than for good solvents, and that local segmental dynamics are slower in Θ solvents. In a Θ solvent the polymer coil exists in its unperturbed dimensions, *i.e.*, long-range forces between polymer segments which cause the chain to contract are balanced by an expansion caused by polymer-solvent interactions. They suggested that the activation energy obtained for the segmental motions of a polymer in a good solvent represents the "true" activation energy associated with rotational barriers traversed in a local conformational change. The local density of segments is higher for a polymer in a Θ solvent which leads to slower local dynamics because the rigid environment inhibits local conformational transitions. It also was pointed out that near the Θ temperature the local segment concentration changes significantly with temperature which adds to the barrier for local chain motions obtained for a good solvent. This is reflected by an increase in the apparent activation energy.

The lower E* value for PVC in DBP than in TCE is consistent with the fact that DBP is a better solvent. Moreover, the correlation times, τ_1 , from the DLM model describing segmental motion (Table 2.8), scaled by the viscosities of the solvent are longer for TCE than in DBP (Figure 2.30). This is in agreement with increasing local segment concentration in the poorer TCE solvent. This relative quality of the solvents is also

PVC i	n DBP	PVC in	TCE-d ₂
Temp (°C)	$\tau_1 \ge 10^9 (s)$	Temp (°C)	$\tau_1 \ge 10^9 (s)$
20	6.241	-19	6.241
41	2.411	-1	2.186
61	1.431	20	1.414
82	0.656	41	0.901
91	0.472	61	0.423
114	0.217	81	0.249
137	0.125	101	0.149
		114	0.109
E _a , kJ mol ⁻¹	33.4		23.9
10 ¹⁵ t _w ,s	7.294		72.0
corr. coeff. (r)	0.998		0.994

Calculated correlation times $(\tau_1, \text{ in s})$ using the DLM model to describe segmental motion for the backbone carbons of PVC in DBP and in TCE-d₂.

Table 2.8

^a Refer to Table 2.7 for simulation parameters.

b Values in parentheses.



Figure 2.30 Arrhenius plots of reduced correlation times, τ_1/η , for local segmental motions of PVC in DBP (circle) and in TCE-d₂ (triangle). τ_1 is expressed in nanoseconds and η in centipoise.

consistent with the values of the Huggins constant, $k_{\rm H}$, obtained in this study. These are 0.36 and 0.74 for PVC in DBP and TCE, respectively. Polymers in theta solutions exhibit values of $k_{\rm H}$ close to 0.7, whereas in good solvents the values are much lower. 0.2 to 0.4.¹⁰⁷ Additional evidence for the solvent quality is offered by apparent melting point depression measurements⁷⁷ which yielded Flory-Huggins interaction parameters, χ , of -0.22 and +0.34 for PVC with DBP and TCE (Table 2.2), respectively.

While the differences in E* can be accounted for satisfactorily by consideration of solvent quality, the possibility remains that the nature of the local chain motions is different in the two solvents. As discussed previously, a type 1 motion is a crankshaft conformational motion about two collinear bonds in which the positions of the chain ends remain unchanged during the transition, while a type 2 motion results in a translational motion of the chain ends, the angular orientation of the two being unaffected.⁴⁰ Although the displacement of the chain ends involved in a type 2 motion makes it less favorable than a type 1 motion, a smaller activation energy is associated with the former. In fact the activation energy for a type 2 motion is only slightly greater than the barrier separating the trans and gauche states (ca. 10 kJ mol⁻¹). A type 1 motion requires simultaneous rotations about two coaxial backbone bonds, involving on average two barrier crossings (ca. 20 kJ mol⁻¹), *i.e.*, twice the energy barrier for the trans-gauche transition. The present experiments yielded an activation energy of 9.2 kJ mol⁻¹ for the segmental motion of PVC in DBP, corresponding to a single barrier crossing and indicating that in this solvent type 2 motions predominate. The higher activation energy (13.7 kJ mol⁻¹) for PVC in TCE opens up the possibility that in this solvent type 1 motion may also occur to some degree. Since type 2 motions involve translation of segment ends, they are expected to be more difficult for a contracted coil due to congestion of chain segments than under conditions where the chain dimensions increase, e.g., PVC in DBP. The observed differences in activation energy would then reflect differences in the nature of the chain motions that result from changes in coil dimensions rather than added hindrance to barrier crossing due to local chain interactions. In both cases solvent quality is directly involved. Unfortunately, there is insufficient evidence to choose between these alternative explanations.

2.5 SUMMARY

A quantitative carbon-13 NMR spectrum of PVC in TCE-d₂ was recorded at a field strength of 75.4 MHz and at a temperature of 114 °C. The methine carbon signal

displayed a resolution whereby all ten possible pentads with some heptad fine structure was observed. In the methylene region, all six tetrads as well as some hexad fine structure, for the mmr tetrad, were observed. Excellent agreement between observed and calculated relative areas indicates that the stereochemistry of the propagation step conforms with Bernoullian statistics with a P_m value of 0.431. Analysis using Bernoullian statistics along with recently published carbon-13 chemical shift assignments of PVC based on a 2D NMR spectrum permitted a reassignment of several resonances. More specifically, in the heterotactic region of the methine resonance, the peak 57.75 ppm has been assigned to mmrm + mmrr pentads and those at 57.63 and 57.57 ppm to rrmmmr + rmmrm and mmmmr + mmrr pentads in the mmr region have been assigned to mmmrm + mmrr hexads.

Carbon-13 relaxation data of the methine and methylene carbons of PVC in DBP and TCE-d₂ have been modeled by using four different correlation functions describing segmental motion in polymer chains. Among these the $\log_2 \chi^2$ failed to account for both the methine and methylene relaxation data and the JS and HWH models failed to account for the T₁ minimum in the curve of T₁ as a function of 1/T. The DLM model proved to be the superior model and was able to account for the relaxation data of both the methine and methylene carbons of PVC at both field strengths throughout the temperature range studied.

The simulation parameters from this model were found to differ in the two solvents. Firstly, the activation energies for cooperative segmental motion, E*, in the PVC chain were found to be 9.2 and 13.7 kJ mol⁻¹ in DBP and TCE-d₂, respectively. The difference in E* for PVC in the two solvents indicates that DBP is a better solvent for PVC than TCE. Secondly, the half-angle of the C-H vector for the methine carbon is smaller in DBP than in TCE-d₂, reflecting a greater steric hindrance to the librational motion of this vector in DBP. This is rationalized by assuming a specific interaction between the carbonyl of the plasticizer and the chlorine atom of PVC, *i.e.*, C=O----Cl-C.

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CHAPTER 3

TRANSPORT PROPERTIES OF GASES IN PLASTICIZED AND UNPLASTICIZED POLY(VINYL CHLORIDE) FILMS

3.1 INTRODUCTION

3.1.1 Historical aspects

In this section the early history of gas transport studies will be reviewed briefly. For a more complete description reference may be made to the works of Stannett¹ and Felder and Huvard.² The first observations of the transport of gases in membranes were those of Graham³ in 1829. He reported that when a wet pig bladder was placed into an atmosphere of carbon dioxide it inflated to the bursting point. In 1831, Mitchell^{4,5} reported values for the rates of permeation of ten different gases through natural rubber. The rates varied one hundred fold, carbon monoxide being the slowest and ammonia the most rapid.

The next major breakthrough was a remarkable paper by Graham⁶ in 1866. Many of his concepts and ideas are still used today. Graham devised an apparatus, having a vacuum on one side, to measure the gas permeation through a flat membrane by the displacement of a mercury column. He postulated that the movement of gases through polymer membranes occurs by the following process: solution (condensation and mixing) of the gas at one surface, migration through the membrane to the opposite surface under a concentration gradient, followed by evaporation of the gas from that surface into the ambient phase. That was the basis of the so-called solution-diffusion model which, in various forms, is still used today. Graham made several observations which are still useful and tenable today: (1) Gases which are easily condensable penetrate more rapidly; (2) there is a correlation between the solubility of the gas in rubber and its rate of passage through the film; (3) the permeability increases with increasing temperature even though the solubility decreases, which was correctly attributed to the increasing softness and more liquid-like nature of the rubber at high temperatures; and (4) crosslinking of the rubber reduces the sorption and the permeability of the gas. In 1855, Fick proposed his law of mass diffusion which states that the flux, F (the rate at which a substance diffuses through a section of unit area), in a given direction is proportional to the concentration gradient. In 1879, Wroblewski⁷ showed that the permeation of gases in rubber is proportional to the product of the solubility and the diffusion coefficients. In addition, he showed that the solution of gases in rubber follows Henry's law and he defined the solubility coefficient as the amount of gas (in cm³ at STP) that is dissolved in one cm³ of polymer at one atmosphere of pressure. Combining this observation with Fick's law, Wroblewski showed that the steady state flux through a membrane of thickness l is given by

$$\mathbf{F} = \frac{\mathbf{DS}(\mathbf{p}_2 - \mathbf{p}_1)}{\mathbf{l}} \tag{3.1}$$

where D is the diffusion coefficient, S is the solubility coefficient, and p_2 and p_1 are the ambient pressures on the opposite sides of the film.

Although several papers appeared after this period, they only provided further support of the existing theories. It was not until 1920 that Daynes⁸ achieved the next major breakthrough in the field of gas and vapor transport in polymer membranes. He realized that steady state permeability measurements could only lead to the determination of the product of D and S, and not their separate values. His analyses of the non-steady state kinetics, using a flat membrane, showed that the value of D can be determined by the time taken to reach the steady state. Since the product D S can be obtained from the steady state rate of permeation and D from the non-steady state, S can also be calculated readily. This is the so called "time lag" method which is still used today for gas and some vapor transport studies. This method did not get much attention until it was fully developed by Barrer⁹ in 1939. His major contribution was to show that the permeabilities and diffusivities follow the Arrhenius equation and that the activation energies for both processes can be determined. It was left to van Amerongen¹⁰ in 1946 to show that, for various gases in rubber, the solubility coefficients measured directly are the same as those obtained from the quotient of the permeabilities and the time lag diffusivities.

Fundamental studies of the transport properties of gases in polymers, rather than rubbers, began in 1954 with the work of Meares.¹¹ He demonstrated the break in the Arrhenius plots at the glass transition temperature and speculated on the existence of two modes of sorption in the glassy state. Subsequently, the need for materials with improved

permeation properties led to an ever increasing number of studies involving various gases and polymers.

3.1.2 Current research in membrane technology

Today the transport properties of gases and vapors in polymeric materials is a topic of interest in many fields of science and technology. The selection or development of polymeric materials requires knowledge and appreciation of the many factors that affect the solution and transport behavior. Such studies have gained importance in recent years due to the accelerating demands related to separation membranes, pharmaceutical interests, diverse applications that require exposure to various environmental agents, and highly impermeable, selectively permeable or barrier films used for packaging.

In membrane separation, polymers with extended lifetimes which display selectivity, *i.e.*, different permeability rates for different gases, are ideal candidates. The advantages of membrane systems over conventional methods of separation include low capital investment, ease of operation, and low energy consumption. Membranes that are used for gas separation include cellulose derivatives, polyimides, polyamides, and polysulphones. This technique is relatively young and research in this area is mainly concerned with improvement of membranes by chemical modification, novel polymers, or morphological changes.

Polymer permeability plays many important roles in various areas of pharmaceutical interest. These include the uptake of preservatives, such as cleansing and soaking solutions for soft contact lenses, tablet coatings, and hemodialysis. In addition to these applications, a considerable amount of research and development has been concerned with the use of polymers as agents for controlling the release of drugs from various types of formulated products, *e.g.*, tablets, implants, injectables, and topically applied adhesive strips.¹²

Polymeric coatings are widely encountered in a many aspects of life. For example, they are used for coatings of devices that span the range from the largest bridges and ships, by paint, to the smallest electronic circuits, by specially formulated epoxides and silicones. The main purpose of these coatings is to protect the substrate from various environmental agents, such as moisture, oxygen or other gases which can lead to degradation and shorten the service lifetime. Unfortunately, there is no ideal polymeric coating which excludes all environmental agents. Generally polymeric coatings transport liquids, gases, and vapors to a greater or lesser extent and this permeability is one of the most important factors in determining whether a particular polymer is suitable for a specific application.¹³

In the food industry, the packaging material is selected mainly for its barrier properties. The packaging material must provide an environment that is suitable to the product and maintain an adequate barrier against external deteriorative influences. Hence, the package must protect the product against physical hazards and atmospheric environmental influences, such as rain, water vapor, gases, and odors, as to maintain food quality. Materials are chosen for their resistance to gases and vapors, usually oxygen and water vapors.¹⁴

3.2 THEORETICAL CONSIDERATIONS

3.2.1 Definitions and Basic Equations

The mathematical theory of diffusion in isotropic substances is based on Fick's first law of diffusion. It states that the flux in the x-direction, F_x , which is the amount of substance diffusing across unit area in unit time, is proportional to the concentration gradient, $\partial c / \partial x$,

$$\mathbf{F}_{\mathbf{x}} = -\mathbf{D}(\partial \mathbf{c} / \partial \mathbf{x}) \tag{3.2}$$

This law can only be directly applied to the diffusion in the steady state, *i.e.*, where the concentration does not vary with time. Non-steady state diffusion can be described by Fick's second law of diffusion

$$(\partial \mathbf{c}/\partial \mathbf{t}) = \mathbf{D} \left(\partial^2 \mathbf{c}/\partial \mathbf{x}^2 \right) \tag{3.3}$$

This equation describes the unidirectional diffusion in an isotropic continuum where the diffusion coefficient is independent of x, t or c. Comparable equations and solutions describing the multidirectional fluxes and cylindrical or spherical geometries are given in Crank's book.¹⁵

3.2.2 Measurements and calculations

As discussed previously, permeation through polymers is explained in terms of a solution-diffusion model. The permeability coefficient is given as a combination of the
diffusivity of the gas dissolved in the polymer and its concentration gradient, which is related to the solubility coefficient.

A wide variety of techniques^{2,16} have been developed to measure these coefficients. The simplest and most frequently used technique is the "time lag" method. For a film of area A and thickness l, separating two chambers containing the permeation gas at fixed pressures, the gas will permeate from the high pressure chamber to the low pressure chamber. The total amount of permeant, Q, that passes through the membrane in a time t is given by

$$\frac{Q}{lc_1} = \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-Dn^2 \pi^2 t/l^2\right)$$
(3.4)

where c_1 is the concentration of the permeant in the face adjacent to chamber 1. A plot of eq. (3.4) shows that there is an initial build-up period but eventually a linear relationship develops as t $\rightarrow\infty$. Under these conditions eq. (3.4) simplifies to

$$\mathbf{Q} = \frac{\mathbf{D}\mathbf{c}_1}{\mathbf{l}} \left(\mathbf{t} - \frac{\mathbf{l}^2}{\mathbf{6}\mathbf{D}} \right)$$
(3.5)

which has an intercept on the time-axis known as the time lag, t_l . The diffusion coefficient can be evaluated from the following relation

$$\mathbf{D} = \frac{\mathbf{l}^2}{\mathbf{6t_l}} \tag{3.6}$$

At sufficiently low penetrant concentration, which is usually the case for permanent gases, the concentration is proportional to the partial pressure of the gas P_a , *i.e.*, $c = S P_a$, where S is a proportionality constant, called Henry's law solubility coefficient. In this case, the flux is given by eq. (3.1) and rearrangement of this equation leads to the following expression for the total amount of permeant to have passed through the film after a time t

$$Q = DSAt(p_2 - p_1)/l$$
 (3.7)

Since the permeability coefficient, P, is given as the product of the diffusion and solubility coefficients, *i.e.*,

$$\mathbf{P} = \mathbf{D} \mathbf{S} \tag{3.8}$$

it can be determined from the slope at steady state, as described by eq. (3.7). In addition, knowledge of P and D permits the solubility coefficient to be calculated readily from the relation given in eq. (3.8).

3.2.3 Temperature and concentration dependence

The movement of the penetrant can be viewed as a sequence of unit diffusion jumps during which a particle passes over a potential barrier separating one position from the next. Physically, the unit jump involves a cooperative rearrangement of the penetrant molecule and the surrounding polymer chain segments. The two most important factors that affect polymer chain segmental motion, hence permeation properties, are the temperature and concentration of sorbed penetrant within the polymer. An increase in temperature provides energy to the polymer which causes an increase in the segmental motion. If the temperature range encompasses structural transitions, such as the glass or melting transitions, the solution and diffusion processes display further effects. Furthermore, the presence of sorbed penetrant increases the free volume. Hence, segmental motions are enhanced to the same extent that they would be by a corresponding increase in temperature and this leads to an equivalent increase in free volume.

3.2.3.1 Sorption

Sorption is a general term that is used to describe the initial penetration and dispersal of penetrant molecules in a polymeric matrix to form a mixture. It includes adsorption, absorption, incorporation into micro-voids, cluster formation, solvation-shell formation and other modes of mixing.¹⁸ The permeant may undergo several modes of sorption simultaneously. The amount of penetrant sorbed and the mode of sorption in a polymer are governed by the thermodynamics of the system, *i.e.*, sorption depends upon the enthalpy and entropy of polymer-permeant mixing.

Different types of sorption behavior have been classified on the basis of the relative strengths of the interactions between the polymer and the permeant molecules or between the permeant molecules themselves. Three general types of sorption isotherms are observed in the sorption of gases in polymers: Henry's law sorption, Langmuir-type sorption, and dual-mode sorption.

The simplest type of sorption, described as a type I or Henry's law, arises when ideal solution behavior occurs, *i.e.*, when Henry's law is obeyed. Since the polymerpenetrant and penetrant-penetrant interactions are weak, the sorbed gas is said to be randomly dispersed within the polymer. In this case the solubility coefficient, at a given temperature, is independent of the sorbent concentration and the sorption isotherm is a linear relation of concentration with pressure. This behavior is generally observed when permanent gases are sorbed by rubbery and often glassy polymers, provided that the gas pressure does not exceed one atmosphere.

The second type of sorption behavior is the Langmuir sorption which is seen when significant amounts of sorption occur at relatively low pressures. Physically, this represents sorption in some type of specific site or immobilization of the permeant molecule in microvoids. Once all the sites have been filled, a small amount of permeant begins to dissolve the polymer. The concentration of permeant sorbed in these holes, C_{H} , is given by the Langmuir equation

$$C_{H} = \frac{C_{H} b_{ha} p}{1 + b_{ha} p} \tag{3.9}$$

where C_{H} is a hole saturation constant and b_{ha} is the hole affinity constant.

Dual-mode sorption, which is a combination of Henry's law sorption with that of the Langmuir type, was first proposed by Michaels, *et al.*¹⁹ Recently, this model has achieved great attention for its ability to explain the isotherms observed in the sorption of substantially soluble gases in glassy polymers. Initially, the model assumed that the gas molecules that are sorbed according to Henry's law are free to move down the concentration gradient while the remaining gas molecules are immobilized at a fixed number of adsorption sites or holes within the polymer. The bound and mobile gas molecules are in equilibrium with the total concentration, C, given by

$$C = Sp + \frac{C_H b_{ha} p}{1 + b_{ha} p}$$
(3.10)

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This model was subsequently modified to allow the immobilized permeant molecules a limited mobility.^{20,21}

The temperature dependence of the sciubility coefficient, of a given polymerpenetrant system can be described in the form of a van't Hoff relation

$$\mathbf{S} = \mathbf{S}_{\mathbf{o}} \exp(-\Delta \mathbf{H}_{\mathbf{s}} / \mathbf{RT}) \tag{3.11}$$

which allows the heat of solution, ΔH_s , to be estimated. The heat of solution can be expressed as

$$\Delta \mathbf{H}_{s} = \Delta \, \bar{\mathbf{H}}_{cond} + \Delta \, \bar{\mathbf{H}}_{1} \tag{3.12}$$

where ΔH_{cond} is the molar heat of condensation and ΔH_1 is the partial molar heat of mixing.

3.2.3.2 Diffusion and permeation

The dependence of the diffusivity on sorbed penetrant concentration is empirical and beyond the scope of this study. Suffice it to say that the presence of permeant molecules within the polymer weakens the interactions between adjacent polymer chains which leads to the commonly observed effects of plasticization.

As for the temperature dependence, the diffusion and permeability coefficients can be described as activated processes and thus an activation energy for diffusion, E_d , and for permeation, E_p , can be determined from an Arrhenius-type relation^{9,22},

$$\mathbf{\dot{p}} = \mathbf{D_o} \exp(-\mathbf{E_d} / \mathbf{RT}) \tag{3.13}$$

$$\mathbf{P} = \mathbf{P}_{\mathbf{o}} \exp\left(-\mathbf{E}_{\mathbf{p}} / \mathbf{RT}\right) \tag{3.14}$$

where D_0 and P_0 are the pre-exponential factors for diffusion and permeation, respectively, R is the gas constant, and T the temperature. Using the relation P = DS and combining equations (3.11), (3.13) and (3.14), it follows that E_p is simply the sum of E_d and ΔH_s

$$\mathbf{E}_{\mathbf{p}} = \mathbf{E}_{\mathbf{d}} + \Delta \mathbf{H}_{\mathbf{s}} \tag{3.15}$$

3.2.4 Penetrant Size and Shape

In general, for a series of chemically similar penetrants an increase in size (average diameter or molar volume) leads to an increase in solubility and a decrease in the diffusion coefficient. Since the permeability is the product of the two, its variation with size is often less dramatic. However, for permanent gases the solubility often plays a minor role and penetrant size dependence of the permeation coefficient follows the trends observed for diffusivity.

Since the interactions between permanent gases and polymers are weak, the main factor controlling sorption is the ease of condensation of the gas. Numerous approximately linear relations have been proposed²²⁻²⁷ to describe the relationship between log S and either the boiling temperature, T_b , or the critical temperature, T_c , or the force constant in the Lennard-Jones 6-12 potential, ε/k , or other parameters which measure the condensability of a gas or vapor. In the absence of strong specific polymer-gas interactions, all these parameters increase as the size of the penetrant increases.

The diffusivity has been shown to decrease enormously with increasing permeant size, up to ten orders of magnitude for glassy polymers.²⁸ In addition, flattened or elongated molecules diffuse about 1000 times more rapidly than spherical molecules of equivalent molecular weight.^{22,28,29} The higher diffusivity implies that the polymer chains are disturbed to a lesser extent by anisotropic molecules which can be rationalized by assuming that the anisotropic molecules diffuse along their narrow axis.

The activation energy for diffusion is found to be proportional to the penetrant diameter raised to a power intermediate between one and two. As pointed out by Berens and Hopfenberg²⁸, this range is partly due to the significant uncertainty and discrepancies that exist from the choice of method to be used to determine the diameter of the penetrant.

Both sorption and diffusion are more dependent on penetrant size and shape for polymer membranes in the glassy state as compared to the rubbery state. This can be ascribed to a change in the process, *i.e.*, from a one site generation, above T_g , to an effective filling of pre-existing sites found in the more rigid glassy polymer.

3.2.5 Models for Diffusion

Over the years a number of theories have been proposed in order to model the variation of the diffusion coefficient with concentration, temperature, and penetrant size. These are cast in terms of either the energy required for a critical volume disturbance or the availability of a favorable distribution of localized excess volume (free volume) to

allow a diffusive jump. They can be classified as molecular theories or free volume theories. Since these models have been reviewed elsewhere³⁰, only the main features are discussed here.

3.2.5.1 Molecular models

In these models statistical mechanics is used to calculate thermodynamic parameters based on specific relative molecular motions of penetrant and polymer. Relevant structure, energy, volume, and pressure parameters are introduced. It is proposed that the energy of activation for diffusion arises from the need to separate the polymer matrix sufficiently to allow the penetrant to make a unit diffusional jump.

In one of the earlier models, Meares¹¹ considered the activation energy for diffusion as the energy required to separate, by thermally induced segmental motion, four adjacent and roughly parallel chain segments so as to produce a cylindrical volume $(d^2 \lambda \pi/4)$, where d is the diameter of the cylinder) with a cross-section that will allow the penetrant molecule to make a unit jump of length λ . This approach, effectively equates the activation energy for diffusion with the product of the cohesive energy density of the polymer, CED, and the activated volume, $(\pi/4) d^2 \lambda$,

$$\mathbf{E}_{\mathbf{d}} = (\pi/4) \, \mathbf{d}^2 \, \lambda \, \mathbf{N}_{\mathbf{A}} \, \mathbf{CED} \tag{3.16}$$

where N_A is Avogadro's constant and d can be taken as the collision diameter of the penetrant molecule. This equation correctly describes the size dependence for most small molecule gas-polymer systems and allows the calculation of the jump distance λ .

Other molecular theories have been proposed: (1) Brandt³¹ considered E_d as the energy required to bend polymer chains and overcome the forces between them so as to allow the diffusion jump; (2) DiBenedetto and Paul³²⁻³⁵ proposed that a gas molecule residing in an equilibrium sorbed cage behaves as a three-dimensional harmonic oscillator; and (3) Pace and Daytner³⁶⁻⁴⁰ combined the features of these two models and assumed that the penetrant molecules move through the polymer matrix along the axis of a tube formed by four adjacent parallel chains and periodically executes jumps perpendicular to this axis. Although the resulting equations correctly describe the variation of E_d with temperature and permeant size, they incorporate a number of adjustable parameters which do not have a closely defined physical meaning.

3.2.5.2 Free volume model

The basic idea of this model is that in a polymer-penetrant mixture the mobilities of polymer and diffusing molecule are determined primarily by the amount of free volume in the system. Considering the case of substantial concentrations of penetrant, Fujita⁴¹ defined a mobility for the diffusant molecule, m_d (= D/RT), which depends on the free volume of the system through a Doolittle type expression

$$\mathbf{m}_{\mathbf{d}} = \mathbf{A}_{\mathbf{d}} \exp(-\mathbf{B}_{\mathbf{d}} / \mathbf{f}) \tag{3.17}$$

where f is the fractional free volume of the system, A_d is a parameter that is dependent on the size and shape of the penetrant, and B_d is a parameter that characterizes the efficiency of use of the available free volume fraction f in the diffusion process.

Molecular models have several advantages over the free volume theories. They are more realistic since they describe specific molecular motions. Furthermore, the necessary parameters are generally predictable from the inherent properties of the penetrant and polymer. However, the shortfall of the more recent models is that they generally have more than one adjustable parameter and the expressions are more complex so that they require considerable parameter input.

3.2.6 Present Work

In spite of the fact that PVC is one of the most frequently used commercial plastics, relatively few investigations have been made of the transport properties of gas molecules through PVC and plasticized PVC films. In this chapter a detailed investigation is presented of (1) the dependence of the permeability coefficient for the penetration of oxygen through PVC films on temperature and plasticizer concentration, including a binary mixture; (2) the temperature dependence of the permeability, diffusion, and solubility coefficients of oxygen and hydrogen chloride gases in PVC. The temperature range was selected such that it provided data above and below the glass transition temperature.

Such studies are important both from an industrial as well as an academic point of view. If films are to be used for packaging applications often a low diffusion rate of oxygen is a requirement, especially for food containers, so that detrimental oxidative changes are kept to a minimum. However, for PVC the easy control of oxygen permeation, by addition of plasticizers, has a major advantage especially in meat packaging, where the high permeability of plasticized PVC keeps the red color of meat

two to three days longer than in other packaging materials. But the diffusion of gases is not only important in the performance of the final products but also in the choice of processing methods and conditions. For example, a slow diffusion rate of hydrogen chloride can lead to auto-catalysis of the thermal degradation.⁴²

3.3 EXPERIMENTAL

3.3.1 Materials

The PVC used in this study was an Esso 366 commercial resin for which the manufacturer quoted characteristics were listed on page 77. Studies by ¹³C NMR, using a Varian XL-300 spectrometer, indicated an essentially atactic polymer with $P_m = 0.45$, as determined from the methine triad sequence distribution. The plasticizers, tri-butyl phosphate, TBP, and di-octyl phthalate, DOP, were purchased from Aldrich. The thermal stabilizer, T-35 (alkyl tin mercaptan ester), was obtained from Elf Atochem Canada, Inc. The gases, hydrogen chloride (semi conductometric grade), extra dry oxygen, and nitrogen, used in the transport experiments were purchased from Matheson Gas Products. The extra dry oxygen was used as received, whereas the hydrogen chloride gas was further purified by removal of water.

3.3.2 Film Preparation

The unplasticized and plasticized PVC films were prepared in the following manner: (1) PVC powder and the appropriate amount and type of plasticizer with 1 phr of T-35 thermal stabilizer was blended for several minutes in an industrial Warren blender; (2) Further blending and fusing of the material was obtained by milling the mixture on a two roll mill at a temperature of 165 °C for several minutes; (3) A small sample was then compression molded to ensure a film of appropriate dimensions, *i.e.*, having a surface area greater than 5 cm² and a uniform thickness between 0.01 and 0.04 cm with a standard deviation of less than 4%. The film thicknesses were determined with an MDC Series 293 Digimatic micrometer with a precision of ± 0.001 mm. The compositions of the films used in this study are given in Table 3.1 along with their glass transition temperatures, as determined by use of a differential scanning calorimeter (Perkin Elmer, Model DSC-2C). The compression molded films were then annealed at 90 °C for 30 minutes to remove any

Glass transition temperature, T_g (in °C), of the various plasticized PVC films
used in the permeation studies, where the concentration of plasticizer is
expressed as a volume fraction, ϕ_{plas} .

Table 3.1

Plasticizer	\$ plas	T _g (°C)	
none	0	87	
	0.094	68	
TBP	0.168	48	
	0.407	-11	
DOP/TBP	0.100	63	
$(\phi_{\rm DOP} = 0.60)$	0.200	41	
	0.402	-6	
	0.101	65	
DOP	0.217	38	
	0.400	-4	

residual effects due to pressure.⁴³ After this thermal treatment, measurements of the permeation at room temperature, with either gas, were identical before and after the measurements at temperatures above the glass transition temperature, *i.e.*, they did not exhibit any thermal hysterisis effects.

It was found that this method of film preparation yielded the most reliable results. Other methods of film preparation, such as solution casting, yielded variable permeabilities that depended upon the solvent (poor solvents tend to yield films of higher permeability) and drying technique, as is well documented in the literature.⁴⁴ Preliminary work with films cast from tetrahydrofuran (THF) solution indicated that extended, harsh thermal conditions⁴⁵ are required to remove the residual solvent. Since such conditions in effect also resulted in the loss of some of the plasticizer, this method was impractical.

3.3.3 Apparatus

Permeation measurements for oxygen gas: A coulometric oxygen detector (Mocon Modern Controls Inc.) incorporated into a device similar to the Ox-Tran Model 100, as shown in Figure 3.1, was used to detect the amount of oxygen permeating through the polymer film. This device consisted of a cell separated into two chambers by the sample



Figure 3.1 \blacklozenge A simplified diagram of the coulometric system used in the measurement of the transport coefficients of oxygen gas.

film. One side of the sample was flushed continuously with extra dry oxygen. On the other side, dry nitrogen carrier gas containing 3% hydrogen swept the permeating oxygen molecules to the sensor, where an electrochemical reaction produced a current which is a linear function of the mass flow rate of oxygen into the sensor. The nitrogen gas used contained 3% hydrogen which when passed through a platinum catalyst caused the hydrogen to react with any residual oxygen that might have been in the system.

The operational principles of the sensor are as follows: As an oxygen molecule enters the sensor it reacts at the surface of the graphite cathode to capture 4 electrons

 $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

The hydroxide ions then reacts at the porous Cd anode to release electrons and form cadmium hydroxide

 $2Cd + 4OH^- \rightarrow 2Cd(OH)_2 + 4e^-$

Since each oxygen molecule causes the transfer of four electrons, one mole of oxygen is equivalent to four Faradays. From Faraday's relations it can be shown that the current produced is directly proportional to the rate of oxygen flow entering the sensor. Hence, the sensor is a constant-current source which can be converted into a d.c. voltage by placing an appropriate load resistor into the circuit. This yields a convenient relationship between voltage and the transmission rate of oxygen, *i.e.*, for a 5.03 ohm resistor a one millivolt reading corresponds to transmission rate of 100 cc(STP) m⁻² day⁻¹. Therefore, as oxygen diffuses through the barrier and enters the sensor, the sensor current rises and finally levels off at a value representative of the equilibrium transmission rate of oxygen through the barrier. Using the final voltage, V_{∞} , and taking into account the area (5 cm²) and thickness of the film, 1, and the partial pressure of the permeant, P_a, the permeation coefficient can be calculated from the following relation

$$P = \frac{2.28 \times 10^{-13} (V_{\infty} - V_0) \text{ (transmission rate) } l}{P_a}$$
(3.18)

where V_0 corresponds to the blank voltage reading and the constant 2.28 X 10⁻¹³ is a conversion factor that yields a P value in units of cc(O₂ @ STP) cm cm⁻² s⁻¹ Pa⁻¹ when the values of V_{∞} , transmission rate, l, and P_a are entered with units of mV, cc m⁻² day⁻¹, cm, and atm, respectively.

Diffusion studies for oxygen: The above apparatus was initially designed solely for measurement of a permeation coefficient from the final voltage reading (equilibrium method). For the purpose of this study it was modified by interfacing it to a computer equipped with a program that was developed, using Turbo Pascal, to automatically acquire the voltage as a function of time. The signal from the sensor was conditioned by, firstly, amplifying it from a programmable gain circuitry whose amplifier was built directly on the A/D board (National Instruments). Secondly, the voltage was converted to digital format via the A/D board so that the data could be acquired by the computer. Figure 3.2

shows a typical trace for the permeation of oxygen through a 0.027 cm thick PVC film maintained at a temperature of 92 °C. As oxygen diffuses through the barrier and is carried to the sensor by the purge gas, the sensor current rises and finally levels off to an equilibrium value. As will be seen later, both the diffusion and permeation coefficients can be obtained from this curve (transient method).



Figure 3.2 \diamond Typical trace of voltage as a function of time obtained with a 0.027 cm PVC film at a temperature of 92 °C.

Diffusion studies for hydrogen chloride gas: The apparatus used to measure the transport coefficients of hydrogen chloride gas, shown schematically in Figure 3.3, incorporated a glass cell that was separated into two chambers by the PVC film. The glass cell was placed into a constant temperature oven and a steady flow of hydrogen chloride gas passed through the upper chamber while the bottom chamber was continuously purged with nitrogen. As the hydrogen chloride permeated through the PVC film it was carried by the nitrogen stream into 100 ml of deionized water, thermostated in a bath at 25.0 °C. The conductance of the resulting solution was monitored continuously using dipping platinum electrodes connected to a Model 35 conductance meter (YSI Scientific) interfaced to an Apple II microcomputer, which allowed automatic acquisition and processing of a large number of data points.



Figure 3.3 \blacklozenge A detailed schematic diagram of the experimental assembly used in the measurement of the transport coefficients of hydrogen chloride gas through a PVC film.

3.3.4 Experimental Technique

The voltage, in the case of oxygen permeation, or the conductance, in the permeation experiments with hydrogen chloride, was converted to amount of gas, Q, which was plotted as function of time (transient method). A typical plot for the amount of oxygen gas permeating through a PVC film is shown in Figure 3.4. From such plots the diffusion coefficient was calculated using the relation given in eq. (3.6) where the time lag t_1 is taken as the intercept on the time axis of the extrapolated linear steady state portion of the plot, as indicated in Figure 3.4. The permeation coefficient was calculated, using a rearranged form of the relation given in eq. (3.7), *i.e.*,

$$\mathbf{P} = (\Delta \mathbf{Q} / \Delta t) (\mathbf{U} / \mathbf{A} \mathbf{P}_{\mathbf{a}}) \tag{3.19}$$

where ΔQ is the quantity of gas which has permeated in the time interval Δt during steady state flow (*i.e.*, the slope of the linear portion of the plot), A is the effective film area, and P_a is the partial pressure of permeant. The solubility coefficient was calculated from the relation given in eq. (3.8) which, assuming that Henry's Law is obeyed, states that the solubility coefficient is given as the ratio of the permeability and diffusion coefficients.



Figure 3.4 \blacklozenge Typical plot for the amount of oxygen gas, Q (in cm³(@ STP)), permeating through a PVC film as function of time at a temperature of 92 °C, where t₁ is the lag time.

3.4 RESULTS AND DISCUSSION

3.4.1 Oxygen Permeation Through Plasticized PVC Films

3.4.1.1 Oxygen permeation results

The permeation coefficients, at various temperatures, for oxygen in the various PVC films were obtained from the measured values of the equilibrium voltage, V_{∞} , by use of eq. (3.18). As an example, Table 3.2 shows these values for the unplasticized PVC in the temperature range that includes data above and below the glass transition temperature. The data follow a trend that is generally observed, *i.e.*, as the temperature is raised the permeation coefficients increase. This behavior can be clearly seen in Figure 3.5 where the permeation coefficient P is plotted as a function of temperature. In addition, this plot reveals that the rate of change in the permeation coefficient increases dramatically as the glass transition temperature, *ca.* 80 °C, is traversed.

Ta	ble	3.2
		~~~

Temperature (°C)	P X 10 ¹⁴ Temperature (°C)		P X 10 ¹⁴	
8.0	0.122	74.0	2.05	
17.5	0.211	77.0	2.51	
25.3	0.342	81.5	3.35	
32.4	0.489	84.0	3.99	
37.1	0.494	85.1	4.34	
46.4	0.777	87.9	5.07	
54.0	1.05	90.5	6.08	
59.0	1.13	91.5	6.69	
65.0	1.60	97.6	9.49	
67.4	1.63	102.2	12.8	
73.5	2.09			

Oxygen permeation coefficient, P (in cc cm cm 2  s 1  Pa 1 ), for an unplasticized PVC film at temperatures above and below its glass transition temperature.



Figure 3.5  $\blacklozenge$  The effect of temperature on the permeation coefficient, P, of oxygen passing through an unplasticized PVC film.

This behavior is not surprising considering the features of the two principal microstructural conditions of the polymeric material, *i.e.*, the glassy and rubbery states. In the glassy state, PVC is hard and brittle, a consequence that is intimately related to the restricted polymer chain mobility. Rotations about the chain axis are limited and motions within the structure are largely vibrational. In this state the polymer has a very dense structure with very little internal void space. Therefore, the permeation of the gases through this structure is low. In contrast, a polymer in its rubbery state is generally tough and flexible; such properties are associated with freer chain motion. In this state, the diffusion process involves larger chain segments due to the internal micromotions of the chain rotation and translation, as well as vibration. Basically, as the temperature is increased, or more specifically as the glass transition temperature is traversed, the chain motions increase in frequency and amplitude and hence a larger amount of free volume is more readily accessible. This allows the permeant to diffuse at a fast rate.⁴⁶

The permeability coefficients of oxygen in PVC films plasticized with TBP, a binary DOP/TBP mixture with concentration  $\phi_{\text{DOP}} = 0.6$ , and DOP are shown in Figures 3.6, 3.7, and 3.8, respectively, as a function of temperature and plasticizer content. For each film the temperature range was selected such that, whenever possible, it included temperatures above and below the glass transition temperature. For comparison, each figure also includes the permeation data for the unplasticized PVC film. These plots contain a substantial amount of information about the transport properties of plasticized PVC films that is addressed below, *i.e.*, (1) the relationship between the glass transition temperature and the temperature at which the Arrhenius plots display a break; (2) the activation energies for permeation; and (3) the dependence of plasticizer type and concentration.

# 3.4.1.1.1 Relationship between the glass transition temperature and the temperature at which the Arrhenius plots display a break

As discussed previously in Chapter 1, Section 1.4.4.2, the transport behavior of polymers can be categorized into three types: (1) polymers which display a break for all penetrants; (2) polymers that display a break for penetrants of size above a certain critical diameter; (3) polymers that do not display this effect with any gas penetrants. An explanation that has been proposed⁴⁷ for the lack of effect is based on the size of the penetrants and the relative extent and nature of the change in the coefficients of thermal expansion above and below the T_g. Kumins and Roteman⁴⁸ argued that at temperatures



**Figure 3.6** Arrhenius-type plots for the permeation coefficients of oxygen through PVC films plasticized with TBP, where the symbols represent different concentration of plasticizer:  $\phi_{plas} = 0$  (circle),  $\phi_{plas} = 0.094$  (triangle),  $\phi_{plas} = 0.168$  (square),  $\phi_{plas} = 0.407$  (diamond).



Figure 3.7 • Arrhenius-type plots for the permeation coefficients of oxygen through plasticized (DOP/TBP mixture with  $\phi_{DOP} = 0.6$ ) PVC films, where the symbols represent different concentration of plasticizer:  $\phi_{plas} = 0$  (circle),  $\phi_{plas} = 0.100$  (triangle),  $\phi_{plas} = 0.200$  (square),  $\phi_{plas} = 0.402$  (diamond).



**Figure 3.8**  $\blacklozenge$  Arrhenius-type plots for the permeation coefficients of oxygen through PVC films plasticized with DOP, where the symbols represent different concentration of plasticizer:  $\phi_{plas} = 0$  (circle),  $\phi_{plas} = 0.101$  (triangle),  $\phi_{plas} = 0.217$  (square),  $\phi_{plas} = 0.400$  (diamond).

above the  $T_g$  the number of holes does not change, only their size, *i.e.*, there is a change in the amplitude of the segmental oscillations or rotations. For small penetrant molecules only minor changes should be displayed since the probability of encountering a hole is about the same. However, for the larger penetrants molecules, the size becomes important and an effect of the glass transition temperature can be observed. Stannett and Williams⁴⁷ suggested that the difference in the thermal expansion coefficients above and below the  $T_g$  is related to the degree of change in slope in the Arrhenius plots at the  $T_g$ . This is supported by the fact that polymers, such as PEMA, that exhibit a rather small difference in thermal expansion coefficients do not display a break in the Arrhenius plots of the transport properties. On the other hand, PVC which has a change of intermediate value and PVA with a rather larger difference display a break only for larger penetrants.

For the polymer-penetrant systems that display this effect, it is generally accepted that the temperature at which the polymers exhibit a break represents the glass transition temperature. As a matter of fact, in recent studies Compan and co-workers⁴⁹ have used oxygen permeability measurements as a means of determining the glass transition temperature of poly(cyclohexyl acrylate). Their measurements were within  $\pm 1$  °C of the values obtained by differential scanning calorimetry and specific volume dilatometry.

In this study Figures 3.6, 3.7, and 3.8 show that the unplasticized and plasticized PVC films of low concentration of plasticizer ( $\phi_{plas} < 0.2$ ) display a discrete change in the slope, regardless of the plasticizer system. The temperatures at which a break in the Arrhenius plots occurs, Tbreak, for the various films are given in Table 3.3. A plot of these temperatures along with the glass transition temperatures, as measured by DSC, as a function of the weight fraction of plasticizer is shown in Figure 3.9. This plot also includes data for the films with volume fraction of plasticizer of about 0.20. Although the temperature at which the break occurs, at this concentration, is difficult to distinguish in Figures 3.7 and 3.8, it is readily apparent in more expanded plots and continues on the same linear relationship as that for the other plasticized films. The temperature at which this break occurs is consistently lower, by ca. 15 °C, than the glass transition temperature as determined by DSC. This difference may be due to the different heating rates - for the DSC measurements a heating rate of 20 °C/min was used while the permeation measurements take several hours which corresponds to a very slow heating. An alternative explanation is that oxygen as a probe molecule, because of its size, detects segmental motions of PVC with a shorter number of units than that observed in differential scanning calorimetry.

## Table 3.3

Activation energy for permeation^a,  $E_p$  (in kJ mol⁻¹), pre-exponential factor^a,

 $P_o$  (in cc cm cm⁻² s⁻¹ Pa⁻¹) and temperature at which a break in the permeation data occurs,  $T_{break}$  (in °C) for the various plasticized PVC films, where the concentration of plasticizer is expressed as a volume fraction,  $\phi_{plas}$ .

Plasticizer	$\phi_{plas}$	Ep	Po	Tbreak
none	0	34	2.6 X 10 ⁻⁹	75
		(69)	(5.1 X 10 ⁻⁴ )	
	0.094	31	2.0 X 10 ⁻⁹	55
		(55)	(1.7 X 10 ⁻⁵ )	
ТВР	0.168	28	2.1 X 10 ⁻⁹	33
		(47)	(4.3 X 10 ⁻⁶ )	
	0.407	(24)	(1.3 X 10 ⁻⁸ )	
DOP/TBP	0.100	32	3.2 X 10 ⁻⁹	50
$(\phi_{\rm DOP}=0.6)$		(56)	(2.3 X 10 ⁻⁵ )	
	0.200	(51)	(1.9 X 10 ⁻⁵ )	
	0.402	(37)	(1.1 X 10 ⁻⁶ )	
	0.101	35	7.6 X 10 ⁻⁹	48
DOP		(58)	(4.6 X 10 ⁻⁵ )	
	0.217	(52)	(3.1 X 10 ⁻⁵ )	
	0.400	(43)	(6.4 X 10 ⁻⁶ )	

^a Values in parentheses correspond to temperatures above the glass transition temperature.



Figure 3.9  $\blacklozenge$  Glass transition temperature, T_g, as measured by DSC (dashed lines), and the temperature at which the plots of ln P as a function of 1/T show a break, T_{break} (solid lines), for PVC films plasticized with TBP (circle), a DOP/TBP mixtures with  $\phi_{DOP} = 0.6$  (square), and DOP (triangle), as a function of weight fraction of plasticizer, w_{plas}.

A very common feature⁵⁰⁻⁵⁸ that is also exhibited in Figure 3.9 is that at low plasticizer concentrations the glass transition decreases linearly as the concentration of plasticizer increases. A well known measure of plasticizer effectiveness for PVC is the extent to which the glass transition temperature of PVC ( $T_{g,PVC}$ ) is depressed by incorporation of a given amount of plasticizer. Both the  $T_g$  and  $T_{break}$  as a function of weight fraction of plasticizer fit well, with correlation factors greater than 0.99, to the linear equation of Mauritz and Storey⁵⁹⁻⁶¹, *i.e.*,

$$T_{g} = T_{g,PVC} - kw_{plas}$$
(3.20)

where  $T_g$  is the glass transition temperature as measured by DSC or the temperature at which a break in the Arrhenius plots occurs,  $w_{plas}$  is the weight fraction of the plasticizer, and k is the plasticizer efficiency parameter which is uniquely defined at low-to-moderate plasticizer concentrations. From DSC measurements k values of 303, 286, and 285 °C were obtained for PVC films plasticized with TBP, a DOP/TBP mixtures with  $\phi_{DOP} = 0.6$ , and DOP, respectively, while the permeation measurements yielded values of 331, 329, and 318 °C. These values follow the trend k(TBP) > k( $\phi_{DOP} = 0.6$ ) > k(DOP) which implies that TBP is a more effective plasticizer than DOP.

## 3.4.1.1.2 Activation energy for permeation

According to eq. (3.14), the slopes and intercepts of the linear portions of the plots shown in Figures 3.6, 3.7, and 3.8 correspond to the activation energies for permeation,  $E_p$ , and the pre-exponential factors,  $P_o$ , respectively. As discussed above, for PVC films with low plasticizer concentration ( $\phi_{plas} < 0.2$ ) there is a discrete change of slope, in the vicinity of the glass transition temperature which reflects a change in the activation energy for permeation. The various activation energies and pre-exponential factors are given in Table 3.3.

The effect of plasticizer type and concentration on the activation energy for permeation is best seen in Figure 3.10. In all cases, the activation energy above the glass transition temperature has a greater value than that below the  $T_g$ . This difference decreases as the concentration of plasticizer increases. At temperatures above the glass transition temperature, the activation energies decrease monotonically as the concentration of plasticizer in the film is increased and tends towards a limiting value at high plasticizer concentrations. The activation energies below the  $T_g$  appear to decrease to a lesser extent with increase in plasticizer concentration except for DOP which indicates a slight increase. Above the  $T_g$ , differences in activation energies are observed amongst the various plasticizers and the following trend is observed  $E_p(DOP) > E_p(\phi_{DOP} = 0.6) > E_p(TBP)$ . This trend becomes more pronounced as the plasticizer concentration increases.

The effects of plasticizer type and concentration on the pre-exponential factor,  $P_0$ , shown in Figure 3.11, exhibit similar features.

Florianczyk and Dahlig⁶² performed similar experiments in which the permeability coefficients of CO₂, O₂ and N₂ were determined in the temperature range 22 to 64 °C as

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**Figure 3.10** • Activation energy,  $E_p$ , for oxygen permeation through plasticized PVC films as a function of volume fraction of plasticizer,  $\phi_{plas}$ , at temperatures above (dashed lines) and below (solid lines) the glass transition temperature, where the plasticizers used are TBP (circle), a DOP/TBP mixture with  $\phi_{DOP} = 0.6$  (square), and DOP (triangle).



Figure 3.11  $\blacklozenge$  Pre-exponential factor, P_o, for oxygen permeation through plasticized PVC films as a function of volume fraction of plasticizer,  $\phi_{plas}$ , at temperatures above (dashed line) and below (solid line) the glass transition temperature, where the plasticizers used are TBP (circle), a DOP/TBP mixture with  $\phi_{DOP} = 0.6$  (square), and DOP (triangle).

a function of plasticizer concentration (2.5-35 wt%) for PVC plasticized with di-octyl adipate (DOA), di-butyl phthalate (DBP), DOP, or TCP. Thus, their studies were confined to a smaller temperature range and the films used were prepared by casting from THF/ethyl acetate (50/50) solution. In no case can a break be detected when their permeation data are plotted in the form of Arrhenius plots. This can be attributed, in part to insufficient data, *i.e.*, the temperature range covered in their experiments was too narrow (22-64 °C) and permeation coefficients were measured at only four temperatures which is often insufficient to reach the T_g.

Activation energies calculated from the data of Florianczyk and Dahlig⁶² are displayed as a function of plasticizer concentration in Figure 3.12. At low plasticizer concentrations (< 10 wt%),  $E_p$  increases as  $C_{plas}$  increases. For the temperature range used in their study, these activation energies should correspond to values below the glass transition temperature, provided that solvent removal is adequate, and are in fair agreement with present results, as seen by the comparison given in Figure 3.13. However, there is no discontinuity with increase in plasticizer concentration in spite of the fact that



Figure 3.12  $\diamond$  Activation energy, E_p, for permeation of oxygen through plasticized PVC film as a function of plasticizer concentration, C_{plas}.⁶² DOA(open circle); DOP(filled circle); DBP(open triangle); TCP(filled triangle).



Figure 3.13 • Activation energy,  $E_p$ , for permeation of oxygen through DOP plasticized PVC films as a function of DOP concentration,  $C_{plas}$ (wt. %). Florianczyk and Dahlig⁶² (filled circle); present work for  $E_p$ above  $T_g$  (open triangle and dashed line); present work for  $E_p$  below  $T_g$ (open triangle and solid line).

at plasticizer concentrations >10 wt. % the  $E_p$  values must be activation energies above the glass transition temperature. Instead, the values continue to decrease and level off to about 17 kJ mol⁻¹ for all plasticizer systems. These values of E_p are at least 35 kJ mol⁻¹ lower than the present results. Furthermore, our results indicate that the activation energies tend to level off at Ep values that are different for the three plasticizer systems (Figure 3.10). Although the differences in activation energies can probably be accounted for, in part, by differences in sample preparation, further work is needed to determine the causes. Certainly, a strong case can be made for the validity of the values obtained in the present study since for the PVC film plasticized with DOP the activation energy tends towards ca. 40 kJ mol⁻¹, compared to ca. 17 kJ mol⁻¹ in the work of Florianczyk and Dahlig, which corresponds well to the activation energy for viscosity for DOP63, ca. 36 kJ mol⁻¹. Similarly, for TBP⁶⁴ the activation energy for viscosity is 15 kJ mol⁻¹. Assuming that these activation energies are additive, the activation energy for DOP/TBP mixture with concentration  $\phi_{DOP} = 0.6$  should be about 28 kJ mol⁻¹, in good agreement with activation energies obtained in the present study for permeation at high plasticizer concentrations. This is expected if the diffusion of oxygen through a highly plasticized PVC film occurs mainly via the least tortuous path which is the plasticizer matrix.

## 3.4.1.1.3 Plasticizer type and concentration dependence

Figures 3.6, 3.7, and 3.8 show that, regardless of the plasticizer system, the permeation coefficients increase as the concentration of plasticizer is increased. The effect of plasticizer type on the permeation coefficients of oxygen is more readily seen by constructing plots of ln P as a function of temperature for films of similar plasticizer content, as shown in Figure 3.14 for the plasticized PVC films with  $\phi_{plas} \equiv 0.4$ . This figure reveals the following trend in permeation coefficients:  $P(TBP) > P(\phi_{DOP} = 0.6) > P(DOP)$ . In other words, the barrier properties of the plasticized films improve as the concentration DOP increases in the plasticizer mixture.



Figure 3.14 • Arrhenius-type plots for the permeation coefficient of oxygen through plasticized PVC films of similar plasticizer content ( $\phi_{\text{plas}} \equiv 0.4$ ), where the different symbols refer to the plasticizers used, *i.e.*, TBP (circle), a DOP/TBP mixture with  $\phi_{\text{DOP}} = 0.6$  (square), and DOP (triangle).

Because of insufficient experimental data for plasticized films of similar concentration, it is not possible to determine whether this trend is generally observed at all plasticizer concentrations. However, from the linear portions of the plots in Figures 3.6, 3.7, and 3.8, interpolated values of the permeation coefficient, at a given temperature, can be obtained. Plots of these as a function of plasticizer concentration at temperatures of 20 °C and 60 °C, Figure 3.15, reveal that: (1) the permeation coefficients increase logarithmically as the concentration of plasticizer is increased; and (2) the same trend in plasticizer type is followed, *i.e.*, P(TBP) > P( $\phi_{DOP} = 0.6$ ) > P(DOP). Furthermore, at the higher temperature, T = 60 °C, the trend in plasticizer type is discernible only when the volume fraction of plasticizer is greater than 0.1, whereas, at the low temperature, T = 20 °C, the effect is more pronounced and is observed even at low plasticizer concentrations.



**Figure 3.15** • Plots of the natural logarithm of the permeation coefficient of oxygen through plasticized PVC films as a function of volume fraction of plasticizer,  $\phi_{plas}$ , where the different symbols represent the interpolated values of the different plasticizers used: TBP (circle),  $\phi_{DOP} = 0.6$  (square), DOP (triangle), at temperatures of 20 °C (solid symbols) and 60 °C (open symbols).

Although the permeation coefficients of oxygen through plasticized PVC films have been analyzed in some detail, various questions remain. For example, according to eq. (3.8) the permeation coefficient is given as the product of the diffusion and solubility coefficients. However, thus far no information is given as to the relative importance of the two parameters in the transport of oxygen. To investigate these questions, the permeation apparatus was modified, as discussed in the Experimental section, in order to be able to measure the diffusion and, from the relation given in eq. (3.8), the solubility coefficients. As a first approach these coefficients were measured for oxygen through an unplasticized PVC film. Furthermore, the break observed in the Arrhenius-type plots is related to the size of permeant used. As discussed above, depending on the size of the permeant a break may or may not be observed. In search for such differences as well as its importance to the processing and thermal degradation of PVC, hydrogen chloride gas was used as a second probe molecule.

## 3.4.2 Transport Properties of Oxygen and Hydrogen Chloride Gases Through an Unplasticized PVC Film

## 3.4.2.1 Permeability coefficients for $O_2$ and HCl gases determined by the time-lag method

The permeation coefficients of oxygen and hydrogen chloride gases in the unplasticized PVC film were determined, as a function of temperature, from the slope of the linear portion of the plot of Q as a function of time, as described in the Experimental section by eq. (3.19). Figure 3.16 shows good agreement between the permeation coefficients of oxygen as measured by the equilibrium and transient method. When the data obtained from this transient method, better known as the "time-lag" method, for both gases are plotted as a function of temperature, Figure 3.17, it is apparent that: (1) for both gases, as the temperature is increased the permeation coefficients increase; and (2) the permitivity increases at a rate that is substantially higher as the glass transition is exceeded. In addition, the permeation coefficient of HCl gas, at a given temperature, is *ca.* 80 times higher than that for O₂. For example, the permeability coefficient of HCl, at 89 °C, is  $38.19 \times 10^{-13}$  compared to 0.46  $\times 10^{-13}$  cc cm cm⁻² s⁻¹ Pa⁻¹ for O₂.

The permeation coefficients, for both gases, in the form of an Arrhenius-type plot, Figure 3.18, display an abrupt change of slope in the vicinity of the glass transition



Figure 3.16  $\diamond$  Comparison of the permeation coefficients, P, of oxygen, through an unplasticized PVC film as determined by the equilibrium (triangle) and transient method (circle).



Figure 3.17  $\blacklozenge$  Permeation coefficient, P, of oxygen (open circle) and hydrogen chloride (solid circle) gases through an unplasticized PVC film as a function of temperature.



Figure 3.18  $\blacklozenge$  Arrhenius plots of the permeation coefficient, P (cc cm cm⁻²s⁻¹Pa⁻¹), for oxygen (open circle) and hydrogen chloride (solid circle) gases in an unplasticized PVC film.

temperature. The temperatures at which a break in the plot occurs,  $T_{break}$ , for the two gases are given in Table 3.4 along with the activation energies for permeation above and below the glass transition temperature. What is surprising with these results is that, although the permeation coefficients are significantly different for the two gases, the activation energies for permeation are identical. Comparison between the oxygen permeation results,  $E_p$  and  $T_{break}$ , from the equilibrium method (Table 3.3) and the transient method (Table 3.4) reveals that these values agree within experimental error.

## 3.4.2.2 Diffusion coefficients for $O_2$ and HCl gases by the time-lag method

The diffusion coefficients of oxygen and hydrogen chloride gases at various temperatures were calculated using the intercept on the time axis that results from the extrapolation of the linear steady state portion of the plot of Q as a function of time, as indicated in Figure 3.4, in eq. (3.6). The Arrhenius plot, Figure 3.19, reveals that as the temperature is increased the diffusion coefficients increase, for both gases, with a distinct change in the slope in the vicinity of the glass transition temperature. Furthermore, the diffusivity, at a given temperature, is higher for oxygen than for hydrogen chloride.

### Table 3.4

Temperatures at which the Arrhenius plots of the permeation, diffusion, and sorption coefficients display a break,  $T_{break}$ , as well as their corresponding activation energies (in kJ mol⁻¹) and pre-exponential factors for the transport of oxygen and hydrogen chloride gases through PVC at temperatures above and below  $T_{g}$ .

Method	Gas	Activation Energy		Pre-exponential factor		T _{hreak}
		Below Tg	Above T _g	Below T _g	Above T _g	(°C)
Permeation	0 ₂	34 (34) ^a	70 (70) ^a	2.5 X 10 ⁻⁹	4.9 X 10-4	78
	HCl	33 (29) ^a	70 (62) ^a	1.3 X 10-7	4.7 X 10 ⁻²	78
Diffusion	0 ₂	36 (54) ^b	74	1.0 X 10 ⁻²	4.6 X 10 ³	78
	HCl	44 (63) ^b	99	3.0 X 10 ⁻²	6.3 X 10 ⁶	71
Sorption	0 <u>2</u>	-2	-4	2.3 X 10 ⁻⁷	1.1 X 10-7	77
	HCl	-15	-37	1.4 X 10 ⁻⁶	5.1 X 10 ⁻¹⁰	66

^a Values in parentheses represent calculated values from  $E_p = E_d + \Delta H_s$ 

^b Literature values from Tikhomirov, et al.⁶⁵ for O₂ and Imoto and Ogo⁶⁶ for HCl.

The lower diffusivity of HCl compared to  $O_2$  is an expected result that can be accounted by the differences in the size of the penetrant molecules, as reported by Berens and Hopfenberg.²⁸ In their study, diffusion coefficients of various C₁ to C₆ organic vapors, determined by gravimetric sorption rate measurements⁶⁷⁻⁶⁹, were used in conjunction with the published data of Tikhomirov, *et al.*⁶⁵ on diffusivities of permanent gases to show that the diffusivities are a strong function of the molecular size of the penetrant. That is, the diffusivities for gases in PVC at 30 °C define a continuous curve when plotted as a function of the molar volume constant, b_v, of the van der Waals



Figure 3.19  $\diamond$  Arrhenius plots of the diffusion coefficient, D (cm² s⁻¹), for oxygen (open circle) and hydrogen chloride (solid circle) gases in an unplasticized PVC film.

equation of state for gases and vapors, as shown in Figure 3.20. The diffusivities (7.42 X  $10^{-10}$  for HCl and 5.81 X  $10^{-9}$  cm² s⁻¹ for O₂ at 30 °C) of the present work closely follow this continuous curve indicating that the larger b_v constant for HCl (0.04081 L mol⁻¹)⁷⁰ compared to O₂ (0.03183 L mol⁻¹)⁷⁰ leads to a smaller diffusion coefficient. Berens and Hopfenberg went one step further and showed that despite the uncertainties in penetrant dimensions, which are related to the method by which they are determined, the diffusivities decrease exponentially with increasing diameter of the penetrant molecules, Figure 3.21. The increase in the diffusivity in going from HCl (3.19 Å) to O₂ (2.94 Å) coincides with the decrease in molecular diameter calculated from the van der Waals constant b_v, as described by Barrow.⁷¹

The temperatures at which a breaks occur in the Arrhenius plot of the diffusion coefficient,  $T_{break}$ , for the two gases are given in Table 3.4 along with the activation energies for diffusion above and below the glass transition temperature. For both gases, the activation energy above the glass transition temperature has a greater value than that below the T_g, as observed by other workers⁷², and is considered in detail later. The



Figure 3.20  $\diamond$  Diffusivities in PVC at 30 °C as a function of the molar volume constant, b_v, of the van der Waals equation of state for gases and vapors, where the symbols denote the source of the data: Tikhomirov, *et al.*⁶⁵ (solid circle), Berens and Hopfenberg²⁸ (solid square), and present work (open triangle).

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Figure 3.21  $\diamond$  Diffusivities in PVC at 30 °C as a function of penetrant mean diameter, where the symbols denote the source and type of diameter used: Data from Tikhomirov, *et al.*⁶⁵ with diameters determined from the Lennard-Jones force constants from gas viscosity measurements (solid circle), Berens and Hopfenberg²⁸ with diameter from density measurements (solid square), and present work with diameter calculated from the van der Waals molar volume⁷⁰ (open triangle).

temperature at which a break occurs in the plot of  $\ln D$  as a function of 1/T is 7 °C lower for hydrogen chloride than for oxygen. A possible explanation of this effect is that HCl, because of its higher solubility, depresses the glass transition temperature of PVC, *i.e.*, it behaves like a plasticizer.

## 3.4.2.3 Gas sorption results for $O_2$ and HCl gases by the time-lag method

The effects of temperature on the solubilities of  $O_2$  and HCl gases in the unplasticized compression molded PVC film are shown in the form of Arrhenius type plots in Figure 3.22. At a given temperature, the solubility of HCl is much higher than that of  $O_2$ , probably due to specific interactions with the polymer. The solubilities follow a similar trend, *i.e.*, as the temperature increases the solubility decreases, indicating a negative heat of solution. The effect of temperature is more dramatic for the PVC-HCl system, in keeping with a larger heat of solution as expected for specific interactions. The solubility coefficients, for both gases, display an abrupt change of slope in the vicinity of the glass transition temperature.



Figure 3.22  $\blacklozenge$  Arrhenius plots of the solubility coefficient, S (cc cc⁻¹ atm⁻¹), for oxygen (open circle) and hydrogen chloride (solid circle) gases in an unplasticized PVC film.
The temperatures at which a breaks occur in the plots of ln S as a function of 1/T,  $T_{break}$ , are given for the two gases in Table 3.4 along with the heats of solution, above and below the glass transition temperature. (Although it is not apparent from Figure 3.22, as shown, that a break exists in Arrhenius plot for oxygen, it becomes apparent upon expansion of the ordinate.) The lower  $T_{break}$  observed for the PVC-HCl system compared to the PVC-O₂ system is probably due to the higher solubility of HCl, *i.e.*, the higher solubility of the gas in the polymer increases the free volume of the system thus causing a decrease in T_g. This is in keeping with the results of several workers who have observed⁷³⁻⁷⁵ and set out to measure experimentally^{73,75} depressions in the T_g due to higher absorption of gas.

Table 3.4 also shows that the heats of solution, above and below the  $T_g$ , are negative for both gases, indicating an exothermic process. However, as seen in this table the difference between the heats of solution, for oxygen, above and below the  $T_g$  are quite small. Such a magnitude for  $\Delta H_S$  is typical for processes involving the physical sorption of gases in polymers and rubbers.⁷⁶ By comparison, the values and differences between the heats of solution above and below the  $T_g$ , for HCl, are quite large.

It is generally accepted^{77,78} that the sorption process can be viewed as taking place in two stages: (i) the formation of a hole of molecular size in the polymer, an endothermic process, and (ii) the transfer of a molecule from the gas phase into the hole with concomitant interaction with the surrounding segments (condensation), an exothermic process. In other words, the heat of solution is the sum of the work required to create the hole to accommodate the penetrant gas and the interaction energy between the gas and the polymer. The energy required to make a hole of molecular size in the polymer will depend upon the molecular volume of the gas and CED of the polymer. The energy evolved in the second stage is governed by the strength of van der W: is interactions of the sorbed gas molecules with the surrounding polymer, which increases with the polarizability and complexity of the gas molecule and is relatively insensitive to the details of the structure of different polymers.

These considerations are clearly reflected in the present data. Since the heats of solution, for both gases, above and below the  $T_g$  are exothermic, this suggests that the energy of the second process outweighs that of the first. Furthermore, the heats of solution of HCl, below the  $T_g$ , are more exothermic than those for  $O_2$  ( $\Delta H_s = -15$  for HCl and -2 kJ mol⁻¹ for  $O_2$ ). The difference in  $\Delta H_s$  is more pronounced at temperatures above the  $T_g$  ( $\Delta H_s = -37$  for HCl compared to -4 kJ mol⁻¹ for  $O_2$ ). As expected the energy of the second stage, which is governed by strength of van der Waals interactions of the

sorbed gas molecules with the surrounding polymer, is greater for HCl, which is more polarizable than  $O_2$ . Furthermore, for both gases the heats of solution are larger above the  $T_g$ .

The lower solubility of oxygen compared to that of hydrogen chloride can be rationalized by differences in the Lennard-Jones constant and the critical temperature. Michaels and Bixler²⁷ proposed a correlation between the solubility coefficient in polyethylene with the Lennard-Jones force constant, *i.e.*, S increases as the Lennard-Jones constant increases. Later, Durrill and Griskey⁷⁹ and Stern, *et al.*⁸⁰ developed correlations using the critical temperature instead of the Lennard-Jones force constant. These correlations predict well the sorption data of the present work. For example, the critical temperature⁷¹ of O₂, 154.4 K, is much lower than that of HCl, 324.6 K.

#### 3.4.2.4 Activation energies for permeation and diffusion of $O_2$ and HCl in PVC

As stated previously, the Arrhenius plots of the permeation and diffusion coefficients, Figures 3.18 and 3.19, respectively, display an abrupt change of slope, for both  $O_2$  and HCl, in the vicinity of the glass transition temperature. That is, the diffusion coefficients are lower below the  $T_g$  but not as low as expected from a linear extrapolation of the plots of ln P as a function of 1/T from above the  $T_g$ . The same holds true for the specific volumes. Such a break was not detected by Tikhomirov, *et al.*⁶⁵, for the PVC- $O_2$  system, nor by Imoto and Ogo⁶⁶, for the PVC-HCl system.

The values of  $E_p$  and  $E_d$  for both gases above and below the  $T_g$ , obtained from the linear portion of the Arrhenius plots in Figures 3.18 and 3.19, along with literature values are summarized in Table 3.4. For both gases the  $E_d$  values are about 20 kJ mol⁻¹ lower than reported previously. This difference may be attributed to, in part, to differences in sample preparation. Imoto and Ogo for the PVC-HCl system used films that were cast from THF solution and Tikhomirov, *et al.* for PVC-O₂ system used commercial calendered films. On the other hand, it also possible that the differences are related to the smaller temperature range, with fewer data points, explored in the previous studies. In addition, the data in this Table reveal that above the  $T_g$  the activation energies,  $E_p$  and  $E_d$ , are about 50% larger than those below the  $T_g$ . This behavior is predicted by Brandt's theory³¹ which predicts that the ratio of activation energies for diffusion above and below the  $T_g$  should be given by

$$\frac{\mathbf{E}_{d}(\mathbf{T} > \mathbf{T}g)}{\mathbf{E}_{d}(\mathbf{T} < \mathbf{T}g)} \equiv \mathbf{0.8} \frac{\alpha_{g}}{\alpha_{r}}$$
(3.21)

where  $\alpha_g$  and  $\alpha_r$  are the expansion coefficients in the glassy and rubbery states, respectively. For poly(vinyl chloride)⁸¹  $\alpha_g$  is 6.6-7.3 X 10⁻⁵ and  $\alpha_r$  is 17-17.5 X 10⁻⁵, so that  $E_d(T>T_g)/E_d(T<T_g) = 2.3 - 2.6$  is predicted by eq. (3.21) compared to experimental ratios of the activation energies of 2.05 to 2.25.

As discussed previously, when Henry's law is obeyed  $E_p$  is given as a simple sum of  $E_d$  and  $\Delta H_s$ , eq. (3.15). The values of  $E_p$  above and below the  $T_g$  for both gases, obtained by summing  $E_d$  and  $\Delta H_s$ , are also given Table 3.4. For O₂ these values are in good agreement with the experimental results; however, for HCl a small deviation is observed. Perhaps, because of its high solubility, Henry's law does not apply and a secondary mechanism is operative.

The difference in the activation energies for diffusion between  $O_2$  and HCl can be accounted for on the basis of differences in molecular diameter, d_b, calculated from the van der Waals constant, by (2.94 Å for O2 and 3.19 Å for HCl).82 However, when Lennard-Jones diameters (3.487 Å for O2 and 3.305 Å for HCl)83 are used, as proposed by Berens and Hopfenberg²⁸, the opposite effect is observed, *i.e.*, E_d decreases with the diameter of penetrant. Berens and Hopfenberg²⁸ combined the data of Berens⁷⁵⁻⁷⁷ for a number of organic vapors with previously published values for gases⁶⁵ and demonstrated that the activation energy for diffusion, below the Tg, increases as the molecular diameter increases, as shown in Figure 3.23. The  $E_d$  values for  $O_2$  and HCl in the present study follow this trend when the molecular diameters calculated from the van der Waals constant are used. However, this is by no means universally true. Recently, Wachi and co-workers studied the transport properties of 1-butene⁸⁴ and Cl₂⁸⁵ in PVC and found a contradiction to the correlation proposed by Berens and Hopfenberg, i.e., the activation energies decreased with the molecular diameter. Although not discusted in their paper, this may be attributed to the shape of the molecule, *i.e.*, butene is perhaps diffusing along its long axis. Nonetheless, the purpose of this discussion is to show that, as pointed out by Berens and Hopfenberg, the limiting factor in correlating the activation energies with molecular diameters is the method used to determine the diameters.

From Meares model, eq. (3.16), the activation energy for diffusion of  $O_2$  is expected to be smaller than HCl, simply on the basis of the relative values of their collision diameters (2.94 Å for  $O_2$  and 3.19 Å for HCl).⁸² This is in agreement with the present results, as shown in Table 3.4. As pointed out by Muller, *et al.*⁸², a test of the validity of eq. (3.16) for a polymer with data for at least two gases is to verify that the ratio of molecular diameters of the two gases is equal to the ratio of the respective activation energies and diffusion coefficients, at a given temperature, as described by eq. (3.22)



Figure 3.23 • Activation energy for diffusion,  $E_d$ , in PVC at temperatures below the glass transition temperature as a function of penetrant mean diameter, where the symbols denote the source of the data: Tikhomirov, *et al.*⁶⁵ (solid circle), Berens and Hopfenberg²⁸ (solid square), and present work (open triangle).

$$\left[\frac{\mathbf{d}_{\mathbf{b}}^{\mathbf{HCI}}}{\mathbf{d}_{\mathbf{b}}^{\mathbf{O}_{2}}}\right] = \left[\frac{\mathbf{E}_{\mathbf{d}}^{\mathbf{HCI}}}{\mathbf{E}_{\mathbf{d}}^{\mathbf{O}_{2}}}\right]^{1/2} = \left[\frac{\log(\mathbf{D}^{\mathbf{HCI}}/\mathbf{D}_{\mathbf{o}}^{\mathbf{HCI}})}{\log(\mathbf{D}^{\mathbf{O}_{2}}/\mathbf{D}_{\mathbf{o}}^{\mathbf{O}_{2}})}\right]^{1/2}$$
(3.22)

These ratios, calculated from the present data, are given in Table 3.5 and support the use of eq. (3.16) for PVC-HCl and PVC-O₂ systems.

From eq. (3.16) the diffusional jump length can be calculated, provided that the cohesive energy density of the polymer is known. The internal pressure,  $P_i = (\partial E/\partial V)_T$ , of the polymer is a good estimation of its cohesive energy density.¹⁸ The effect of temperature on the internal pressure⁸⁷ of PVC was studied by Turturro and Bianchi.⁸⁸

#### Table 3.5

Ratio of molecular diameters^a, activation energies and diffusion coefficient of oxygen and hydrogen chloride in PVC sample.

$d_b^{HCl}/d_b^{O_2}$	$\left(E_{d}^{HCl}/E_{d}^{O_{2}}\right)^{1/2}$		$\left[\frac{\log(D^{HCl}/I)}{\log(D^{O_2}/I)}\right]$	$ \begin{bmatrix} \mathbf{D}_{\mathbf{o}}^{\mathrm{HCl}} \\ \mathbf{D}_{\mathbf{o}}^{\mathrm{O}_{2}} \end{bmatrix}^{1/2} $
	below Tg	above T _g	below T _g	above T _g
1.09	1.10	1.16	1.10	1.16

 a  molecular diameter:  $d_b{}^{HCl} = 3.19$  Å and  $d_b{}^{O2} = 2.94$  Å

They found that at temperatures below the  $T_g$  the internal pressure increased linearly with temperature followed by a sharp rise as the glass transition was traversed. For example, typical internal pressure values of 234 and 477 J cm⁻³ were reported for temperatures of 25 and 90 °C, respectively. Based on these values, eq. (3.16) qualitatively indicates that the activation energy below the  $T_g$  should be smaller than  $E_d$  above the  $T_g$ , in keeping with the present results. Using this expression and the  $P_i$  values, the unit diffusion jump lengths,  $\lambda$ , were calculated for a temperature below (25 °C) and above (90 °C) the  $T_g$ , as shown in Table 3.6. These results show that the unit diffusion jump length for oxygen, 38 Å, is the same above and below the  $T_g$ . By comparison the data for hydrogen chloride gas show a slight increase of  $abc_{vi} 4$  Å in going from a temperature of 25 to 90 °C. These values are much longer than the jumps, *ca.* 2-5 Å, that are thought to produce diffusion in solution.⁷⁷

#### Table 3.6

Activation energies,  $E_d$ , pre-exponential factor,  $D_o$ , entropies of activation,  $\Delta S^{\dagger}$ , and jump length,  $\lambda$ , for the diffusion of oxygen ( $O_2$ ) and hydrogen chloride (HCl) gases in PVC at a temperature above (90 °C) and below (25 °C)

				the T _g .				
Gas	E	d	D	 ) ₀		λ	Δ	S [‡]
	kJ n	nol-1	$\mathrm{cm}^2$	² s ⁻¹	, i i i i i i i i i i i i i i i i i i i	Å.	J mol	-1 K-1
	< T _g	$> T_g$	< T _g	> T _g	25 °C	90 °C	25 °C	90 °C
0 ₂	36	74	1.0X10-2	4.6X10 ³	38	38	-45	61
HCl	44	99	<u>3.0X10-2</u>	6.3X10 ⁶	39	43	-37	119

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#### 3.4.2.5 Pre-exponential factor for diffusion, $D_{o}$ for $O_2$ and HCl in PVC

The interpretation of the constant  $D_0$  is less complete. The first descriptive efforts that are still used today center around the hole theory, popularized by Barrer.⁸⁹ The theory employs the conceptual model of discrete holes, or cavities, dispersed throughout the polymer matrix. These are created by Brownian movement of the molecular segments of the polymeric chain. When the fluctuations are sufficiently large to create a hole that can contain the diffusant, movement occurs. Table 3.4 shows that the  $D_0$  values are smaller for  $O_2$  than HCl, the effect being more pronounced at temperatures above the  $T_g$ . *i.e.*,  $D_0$  for HCl is three times larger than  $D_0$  for  $O_2$  at temperatures below the  $T_g$  compared to a difference of three orders of magnitude above the  $T_g$ . A smaller  $D_0$  value for  $O_2$ , compared to HCl, is consistent with the work of Meares¹¹ who noted that in polyvinyl acetate the values of  $D_0$  increased by seven orders of magnitude by increasing the size of the penetrant from krypton to helium.

Since  $O_2$  is a smaller molecule than HCl, the observation that  $D_0$  increases with the size of the diffusing molecule implies that the entropy of activation for a diffusion jump increases. This reflects the greater disturbance of the surrounding molecules which is required to free the larger diffusate particles. This is also consistent with the fact that  $D_0$  is larger for branched gases than for linear ones, as reported by others.⁷⁷

By use of the assumption that the activation energy is the energy required to create a hole of proper dimensions, Glasstone, Laidler, and Eyring⁹⁰ applied the theory of absolute reaction rates to diffusion and showed that  $D_0$  relates to the entropy of activation for a diffusion jump,  $\Delta S^{\ddagger}$ , through the following relation,

$$\mathbf{D}_{\mathbf{a}} = (\mathbf{e}\lambda^2 \mathbf{k}_{\mathbf{b}} \mathbf{T}/\mathbf{h}) \, \mathbf{e}^{(\Delta \mathbf{S}^*/\mathbf{R})} \tag{3.23}$$

where  $\lambda$  is the length of a unit diffusion jump,  $k_b$  and h are the Boltzmann and Planck constants, respectively, T is the temperature, and R is the gas constant. Thus, the entropies of activation for diffusion may be obtained from the D_o values and use of eq. (3.23). The values in Table 3.6 were calculated using the appropriate lengths for a unit diffusion jump, as calculated by eq. (3.16). The values of  $\Delta S^{\ddagger}$ , both above and below the T_g, and larger for HCl than for O₂. As mentioned above, this suggests that a greater disturbance of the surrounding molecules is required to free the larger HCl diffusate molecule.

Below the  $T_g$  negative  $\Delta S^{\ddagger}$  values are obtained for both gases. Several authors⁹¹⁻⁹³ have argued that a negative entropy change should not be considered as an

indication that a more ordered state is obtained as a result of diffusion. Rather, the results should be considered only in a relative manner and negative values for a given polymergas system should be taken to imply that less disorder is necessary for diffusion than in a system for which the entropy change is positive. On this basis, the negative  $\Delta S^{\ddagger}$  values obtained for both gases for diffusion below the  $T_g$  may be interpreted as meaning that less additional disorder is produced by diffusion than at temperatures above the  $T_g$ . This is entirely reasonable considering the physical orientation and greater restriction of the chain motions in the glassy state. Below the transition the polymer consists of regions of densely packed and arranged chains, separated by less dense regions of disordered chains which are the 'holes' in which sorption takes place. Presumably, in this state diffusion occurs through these pre-existing holes. On the other hand, at temperatures above the  $T_g$  the amplitude of the segmental oscillation or rotations of the polymer increases thus allowing for a larger zone of activation, thereby leading to the observed increase in entropy of activation.

According to Meares¹¹,  $\Delta S^{\ddagger}$  contains two contributions: one stemming from the freeing of the gas molecule and the other from the disturbance of the surrounding polymer. Meares calculated the entropy of the diffusing molecule from its vibrational frequency. At 300 K,  $\Delta S^{\ddagger}_{gas}$  for hydrogen was found to be -9.2 J mol⁻¹ K⁻¹ and for argon it was -32.6 J mol⁻¹ K⁻¹. Hence, knowing the  $\Delta S^{\ddagger}$  of the system, the  $\Delta S^{\ddagger}_{polymer}$  for the two gases were calculated readily. The values were 4.2 and 109.6 J mol⁻¹ K⁻¹ when hydrogen and argon gases, respectively, were used as the penetrant molecules. It was concluded that the diffusion of very small molecules causes little disturbance of the polymeric chains, whereas for the larger ones, such as argon, the production of a cavity for diffusion involves a large zone of activation. In the present study,  $\Delta S^{\ddagger}_{gas}$  for O₂ and HCl were estimated at -28 and -44 J mol⁻¹ K⁻¹. Therefore, the entropies of activation of the polymeric medium are -17 and 7 J mol⁻¹ K⁻¹ when oxygen and hydrogen chloride gases, respectively, were used as the penetrant in the diffusion of the polymeric medium are -17 and 7 J mol⁻¹ K⁻¹ when oxygen and hydrogen chloride gases, respectively, were used as the penetrant molecules. It is clear that in the diffusion of the polymeric molecule less disturbance of the polymeric chains is required for the smaller oxygen molecule less disturbance of the polymeric chains is required for the production of a cavity.

## 3.5 SUMMARY

The permeation coefficients of oxygen through PVC and plasticized PVC films were measured as a function of temperature and plasticizer concentration using an equilibrium method. The plasticizers used were TBP, a binary mixture of DOP and TBP

with volume fraction 0.6 ( $\phi_{DOP} = 0.6$ ), and DOP. Regardless of the plasticizer system, the permeability coefficients increased with plasticizer concentration. The effect of plasticizer type on the permeability coefficients followed the trend: P(TBP) > P( $\phi_{DOP} = 0.6$ ) > P(DOP). In other words, the barrier properties of the plasticized films improved as the concentration of DOP increased in the plasticizer mixture.

Arrhenius plots of the permeability coefficients showed that the unplasticized and plasticized PVC films with low concentration of plasticizer ( $\phi_{plas} < 0.2$ ) displayed a discrete change in the slope, in the vicinity of the glass transition temperature, that reflected changes in the activation energy of permeation. The temperature at which a break in the plots of ln P as a function of 1/T occurred for the various films were consistently about 15 °C below their glass transition temperature measured by differential scanning calorimetry. This deviation was rationalized by differences in the heating rates used in the two experiments and the possibility that oxygen as a probe molecule, because of its size, detects segmental motions of PVC with a shorter number of units than that observed by differential scanning calorimetry. In all cases the activation energies were higher above the glass transition temperature than below the Tg, the difference decreasing with plasticizer concentration. Moreover, for temperatures above the  $T_g$  the activation energies decreased monotonically as the concentration of plasticizer was increased and, at high plasticizer concentrations, appeared to level off towards values corresponding to the activation energy of plasticizer viscosity. For the plasticized films the activation energies above the T_g followed the trend:  $E_p(DOP) > E_p(\phi_{DOP} = 0.6) > E_p(TBP)$ , the trend becoming more pronounced as the plasticizer concentration was increased.

The permeation apparatus was modified to accommodate measurements using the "time lag" method to enable the permeability as well as the diffusion coefficients of oxygen in an unplasticized PVC film to be measured as a function of temperature. In addition, transport coefficients were also measured for hydrogen chloride gas. The permeation coefficient of hydrogen chloride gas, at a given temperature, was *ca.* 80 times greater than that for oxygen, but the diffusivity was *ca.* 8 times smaller for hydrogen chloride than for oxygen. Since the permeability is given as the product of diffusion and solubility coefficients, the higher permeability of HCl in the unplasticized PVC film must be due to a substantially higher solubility of HCl in the polymer. The lower diffusion of hydrogen chloride to oxygen was readily account by differences in the size of the penetrant molecules. The higher solubility of HCl was explained by specific interactions and its inherently higher critical temperature.

Arrhenius type plots of the permeabilities and diffusivities of both gases showed an almost discontinuous dependence on temperature characterized by an abrupt change in slope at the glass transition temperature of PVC, in keeping with discrete changes in activation energy. Such changes for the PVC-O₂ and PVC-HCl systems have not been reported previously. The temperature at which this break in the Arrhenius plot of diffusion coefficients occurred is about 7 °C lower for hydrogen chloride than for oxygen. This difference was attributed to the higher solubility of HCl in PVC, resulting in a depression of its glass transition temperature. In other words, HCl behaves like a plasticizer for PVC.

The heats of solution of both gases, above and below the  $T_g$ , were negative indicating an exothermic process. This suggests that the energy released by the transfer of a molecule from the gas phase into a hole with concomitant interactions with the surrounding segments outweighs the energy required to make a hole of molecular size in the polymer matrix. The higher heat of solution of HCl compared to  $O_2$  indicates that the strength of van der Waals bonds formed between the sorbed gas molecules and the PVC chain is greater for HCl than for  $O_2$ .

The activation energies for diffusion above the  $T_g$  were about 47% larger than those below the  $T_g$ . This conformed to Brandt's theory which relates the ratio of activation energies for diffusion above and below the  $T_g$  to the ratio of thermal expansion coefficients of the polymer. The activation energies for diffusion were found to be smaller for  $O_2$  than HCl, in keeping with the differences in their molecular diameters.

Calculated values of the unit diffusion jump length for  $O_2$  and HCl above and below the  $T_g$  were found to be *ca.* 38 Å. However,  $D_0$  values, both above and below the  $T_g$ , were larger for HCl than  $O_2$  and which to larger  $\Delta S^{\ddagger}$  values. This reflected a greater disturbance of the surrounding molecules to free the larger HCl diffusate molecule. The larger negative  $\Delta S^{\ddagger}$  values below the  $T_g$  compared to the positive values above the  $T_g$  were interpreted as meaning that less additional disorder is produced by diffusion below the  $T_g$ . This was rationalized by assuming that in the glassy state diffusion occurs through pre-existing holes. On the other hand, above the  $T_g$  the amplitude of the segmental oscillation or rotations increases to allow for a larger zone of activation, leading to the observed increase in entropy of activation.

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# **CHAPTER 4**

## COMPUTER SIMULATIONS OF MICROSTRUCTURAL CHANGES RESULTING FROM THERMAL DEGRADATION OF POLY(VINYL CHLORIDE)

## 4.1 INTRODUCTION

#### 4.1.1 General Considerations of the Thermal Degradation of PVC

Most experts consider the thermal and photochemical instability of PVC to be a major disadvantage of this material. As a result, its use has been restricted in a number of applications. As discussed in Chapter 1, upon exposure to temperatures as low as 100 to 120  $^{\circ}C^{1,2}$ , this polymer undergoes a degradation reaction that releases hydrochloric acid and forms long polyene sequences of conjugated double bonds (Scheme 1.13).

The degradation process involves two basic steps, namely, initiation and propagation or build up of polyene sequences. It is generally accepted that polyenes result from a "zipper" mechanism, *i.e.*, the first double bond activates the formation of the second conjugated double bond, and so on, until long polyenes are formed. However, there is much controversy about the initiation mechanism and over the years many studies have been made to better understand this process. The two competing theories that have been proposed to rationalize the instability of PVC are: (1) the presence of a few abnormal or irregular structures in the polymer, the so called 'labile sites' (Section 1.3.2); and (2) the occurrence of some local conformations that are related to isotacticity (Section 1.3.3). Pinpointing the sites that initiate the dehydrochlorination reaction will ultimately lead to an improved and more controlled stabilization of the polymer.

In this chapter only the role of labile chlorines located at various configurations within a specific conformation will be considered as possible initiating sites. This should in no way be taken to imply a preference of one initiating site over the other.

#### 4.1.1.1 Role of Tacticity

As discussed in Chapter 1, strong support has developed recently for the existence of random dehydrochlorination, i.e., initiation at local conformations which were previously considered normal units.³⁻⁷ Initial studies⁸⁻¹² concentrated, in the main, in determining the structural conformations of PVC. NMR studies showed that alongside the normal trans-trans (tt) conformations there exist numerous trans-gauche (tg) and gauche-trans (gt) linkages. In addition, several authors concluded that for the meso dyads the (tg) and (gt) conformations occur while for the racernic dyad essentially only the (tt)conformation is allowed. However, it was the systematic studies of Millan and coworkers¹³⁻²³ on the influence of tacticity on the thermal degradation of PVC which are responsible for enlightening and addressing the possibility that such normal structures are responsible for the initiation of the dehydrochlorination reaction. Their work, which will be reviewed here, includes studies on; (i) the degradation of PVC samples of different tacticities; (ii) the degradation of PVC after modification by stereoselective nucleophilic substitution; (iii) the influence of temperature on the kinetics of degradation and the polyene distribution in degraded samples; and (iv) changes in the highly resolved ¹³C NMR spectrum as a result of thermal degradation. Recently, Millan, et al. reviewed their most notable results, published and unpublished.²⁴ The review concluded that "the very labile structures in PVC are some chlorine atoms located mainly at the normal but little frequent  $g^+\pi g^-$  isotactic triad conformation".

#### 4.1.2 Review of the Work of Millan and co-workers

In a number of publications^{13-15,18,21}, Millan and co-workers have shown that the rate of thermal degradation of PVC depends on its isotactic content, as shown in Figure 4.1. Since the polymerization of PVC leads to polymers with a  $P_m$  value between 0.36 and 0.46, the notation used by Millan will also be used here, *i.e.*, when  $P_m = 0.46$  the polymer can be considered as "isotactic",  $P_m = 0.41$  as "Bernoullian" polymer, and  $P_m = 0.36$  as a "syndiotactic" polymer. According to the data shown in Figure 4.1, the polymer becomes more stable as the isotactic content increases up to a certain extent beyond which it begins to lose stability. The minimum in the curve, which corresponds to the most stable polymer, agrees with the so-called "Bernoullian" distribution of tacticity. This work clearly suggests that the instability is associated with the presence of tactic ("isotactic" or syndiotactic") units. In addition, the higher slope of the right side of the curve suggests that this effect is more pronounced for the isotactic sequences.



Figure 4.1  $\blacklozenge$  Dependence of degradation rate on isotactic content of PVC as reported by Millan, *et al.*²⁴ (degradation experiments performed in an inert atmosphere at 180 °C).

Another feature that has been extensively studied by this group is the type and distribution of polyenes formed during the degradation. It has been shown that the thermal degradation of the so-called "isotactic" and "syndiotactic" polymers gives rise to longer polyene sequences than the "Bernoullian" polymers. However, the "isotactic" polymers exhibit a narrow distribution in polyene sequence length in which the most frequent polyenes are between 7 and 9 double bonds. On the other hand, the "syndiotactic" polymers develop a much broader polyene distribution with long polyenes, up to 16 double bonds as well as short ones similar to those observed for the "Bernoullian" polymer. They suggested that this indicates the existence of two competing processes; one pertains to the dehydrochlorination of the syndiotactic sequences and the other from the remaining parts of the chain that are Bernoullian in character.

From these results they concluded that various tactic sequences, whether isotactic or syndiotactic, are involved in an enhanced propagation of dehydrochlorination with the effect being more marked for isotactic sequences. In addition, comparison of the degradation rates of the "isotactic" and "syndiotactic" polymers, shown in Figure 4.1, suggests that the labile sites must be related to the isotactic structure.

More conclusive evidence of the role played by isotactic triads as initiating sites was obtained from degradation studies of PVC after nucleophilic substitution with sodium benzenethiolate.^{16,17,25-27} These studies showed that: (1) regardless of the experimental conditions, whenever an isotactic triad in  $g^+trg^-$  conformation is present the substitution reaction occurs exclusively at the central chlorine atom. More specifically, carbon-13 NMR studies showed the mmmmrx heptad appears to be the only reactive sequence during the initial stages of substitution (0 to 7%). (2) For a PVC sample with  $P_m = 0.46$ , the degradation rate decreases dramatically with increasing degree of substitution¹⁹, up to about 0.8% conversion, which agrees well with the content of  $g^+\pi g^-$  conformers in the original polymer. At higher conversions the degradation rate tends to either stabilize or decrease. (3) The polyene distribution resulting from thermal degradation was also found to be strongly dependent upon the degree of substitution. The UV-visible spectra for degraded PVC samples of various degree of substitution were similar to those observed with polymers of different tacticities. For example a 0.8% substituted PVC sample  $(P_m = 0.46)$  that was degraded to 0.3% at 180 °C, displayed a UV-visible spectrum similar to that for the degraded "Bernoullian" polymer ( $P_m = 0.41$ ). This suggests that the disappearance of the isotactic  $g^+ttg^-$  conformations, as a consequence of substitution, causes the polymer to behave as though it were "Bernoullian". Such a process accounts for both the observed increase in thermal stability and the broader polyene distribution.

In another study²⁸, the kinetics of degradation were studied at temperatures between 110 and 190 °C to obtain further support for the existence of two degradation processes, *i.e.*, initiation at the labile  $g^+ttg^-$  isotactic conformation or random degradation at any stable chlorine atom along the chain. In keeping with the hypothesis, Arrhenius plots indicated two well differentiated slopes with corresponding activation energies of 29 (at the lower temperatures) and 84 kJ mol⁻¹. Therefore, there appear to be two different initial processes, depending on the reaction temperature. Additionally, it was found that the break in the Arrhenius plot occurs at a lower temperature for the PVC sample with a lower isotactic content (P_m = 0.41) compared to the one with a higher isotactic content (P_m = 0.47). This suggests that the low activation energy must correspond to degradation of labile chlorines located at  $g^+ttg^-$  isotactic triad conformation.

In a recent approach, Millan, et al.²⁴ reported some "tentative" tacticity changes as a result of thermal degradation. The degraded PVC sample was dissolved in dioxane so that highly resolved ¹³C NMR spectra could be obtained allowing a very accurate determination not only of the mm, mr and rr triad content but also the mmmm, mmmr, and rmmr pentad content. The reported areas, integrated from the spectra prior to and after 0.8% degradation at 180 °C, are compiled in Table 4.1. These workers claim that there is no change in the syndiotactic or the heterotactic triad content. However, the decrease of the isotactic triads appears to be appreciable, even though the observed changes lie at the limit of experimental uncertainty. For the isotactic pentads, the decrease in the isotactic triad content is shared by the mmmr and rmmr pentads while the mmmm pentad remains unchanged. From these results, and the indications from previous work that the chlorines located at the -mmr- sequence with a  $g^+ng^+$  conformation are labile, Millan and coworkers²⁴ concluded that the labile chlorines are those of the mmmr and rmmr pentads.

Table 4.1
Tacticity changes in triad and isotactic pentad probabilities as a consequence
of thermal degradation of PVC up to 0.8% at 180 °C as reported by Millan, et
aL ²⁴

_	n	mr	rr	mmmm	mmmr	rmmr
initial	0.204	0.493	0.303	0.043	0.098	0.063
degraded	0.197	0.492	0.302	0.043	0.094	0.060
change	007	001	001	0	004	003

## **4.1.3 Present Investigation**

In this chapter, computer simulations of the configurational placement of monomer units in a vinyl polymer chain formed according to Bernoullian statistics are reported. The program then simulated the dehydrochlorination of randomly selected isotactic stereosequences using various degradation mechanisms. These studies were carried out to determine the tacticity changes that should occur from a theoretical point of view. The results were then compared to: (1) tacticity changes resulting from the thermal degradation of PVC in solution; (2) tacticity changes as reported by Velazquez²⁹ and Millan and co-workers.²⁴

### 4.2 EXPERIMENTAL

#### 4.2.1 NMR and Degradation Experiments

The poly(vinyl chloride) used in this study was an Esso 366 industrial resin with manufacturer quoted characteristics given on page 77. Prior to use the PVC sample was dissolved in THF and precipitated with cold methanol in order to remove impurities and low molecular weight species.

Even though, the most common test of heat stability is to measure the amount of HCl evolved from a known amount of solid sample, in the present experiments the thermal degradation of the purified PVC sample was studied as a 4% w/w solution in 1,2-dichlorobenzene-d₄, 1,2-DCB-d₄ (Aldrich Co.). The major disadvantages of solid state studies are: (1) the HCl released can act as a catalyst³⁰; (2) the diffusion of HCl away from the sample is an important complication; (3) the morphology of the resin plays an important role; and (4) a high degree of degradation leads to cross-linking that renders the polymer insoluble, hence useless for solution NMR studies. By comparison, in solution the polymer chains are presumably further apart such that degradation can occur without considerable cross-linking. Although solution degradation overcomes some of these complications, the solvent, impurities, and HCl build up in the solution can be important factors in this method.

The quantitative carbon-13 NMR spectra of non-degraded and degraded PVC in 1,2-DCB-d₄ at a temperature of 120 °C were recorded on a Varian Unity 500 spectrometer operating at a frequency of 125.7 MHz for the ¹³C nucleus. Isothermal degradation experiments were performed with the sample inside the NMR cavity at a temperature of 160 °C. The sample was allowed to degrade for a given time after which the temperature was lowered to 120 °C for spectral recording and then increased again to 160 °C for further degradation. Instrument conditions used to record the spectra were: spectral width 30 000 Hz, 15  $\mu$ s (90°) pulse, acquisition time of 1.08 sec, delay time of 5.5 sec, and 9 600 transients. The delay time was chosen such that the total delay time (acquisition time plus delay time) corresponded to value greater than 5T₁. The T₁ values for the methine and methylene carbons were found to be 0.66 and 0.35 sec, respectively, as measured by the inversion recovery method.

#### 4.2.2 Description of Computer Simulation Program

The simulations were made using a Pascal program which uses Monte Carlo methods to simulate first the polymerization of vinyl chloride to produce a PVC of specified  $P_m$  and then its random dehydrochlorination, according to specified parameters. Specifically, it performs the following main tasks:

- (1) It generates Bernoullian chains according to entered values of  $P_m$ , the degree of polymerization, DP, and the number of molecules, N.
- (2) It determines the dyad, triad, tetrad and pentad probabilities.
- (3) It counts the number of isotactic and syndiotactic sequences containing exactly n_i and n_s repeat units, respectively.
- (4) According to entered values of a minimum isotactic length, n_i, and percent degradation, it randomly locates and degrades isotactic sequences that contain n_i or higher repeat units.
- (5) It calculates average values of the dyad, triad, tetrad and pentad probabilities after the degradation.
- (6) It counts the number of double bonds of various sequence lengths (n₋ repeat units) and calculates the average double bond length that resulted from degradation.

As shown in Appendix A, the program consists of fifteen sections: the main body and fourteen procedures. Its logic is better understood by following the program structure illustrated by the flowchart shown in Figure 4.2. The program commences by allowing the user to enter the desired value of P_m, the degree of polymerization, DP, and the number of molecules, N, to be generated, the percent degradation, %deg, and the minimum isotactic length to be degraded, ni. Random numbers ranging from 0 to 1 are then generated and, according to the entered P_m value, are rounded off to integral values of 0 or 1 and stored in a one-dimensional array called configuration. This mimics a polymerization reaction where a 0 denotes a unit in the chain with one configuration and a 1 denotes a unit of the opposite configuration. The random number generator continues until the designated degree of polymerization has been attained. Once the chain has been polymerized to the desired degree of polymerization, the contents of the array configuration are examined and, accordingly, the character m or r is stored in a new one-dimensional array called configuration_m_r. Whether a unit will be designated as an m or r sequence is better understood by considering the chain in terms of doublets. Since two adjacent units of a doublet are said to form a meso configuration if both units have the same handedness,



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Figure 4.2  $\blacklozenge$  Illustration of the computer program structure by means of a flowchart.

units of two adjacent zeros (00) or ones (11) are designated as an m configuration (isotactic sequence). Similarly, units of opposite handedness, (01) or (10), are designated as an r configuration (syndiotactic sequence). It should be noted that the array configuration_m_r will have one less element than the array configuration.

The program then examines the array configuration to find isotactic sequences equal to or greater than the minimum limit set by the user. These units are degraded by replacing the numerical values by the number 2. Degradation continues until the desired percent degradation, also entered by the user, has been attained. The contents of the array configuration are examined and, accordingly, the character m, r or = is in a one-dimensional array called configuration_m_r. The contents of this array are examined and the number dyads and distinguishable triads, tetrads, and pentads are counted as well as the number of double bonds containing exactly n_ repeat units.

The main program continues to call these procedures until the specified number of molecules have been generated. The summations of all dyad and distinguishable triad, tetrad, and pentad sequences are then passed to the procedure AVERAGE_PROBABILITIES which calculates and prints out the average values (or relative frequencies) of the various stereosequences before and after degradation. The total number of isotactic, syndiotactic, and double bond sequences containing exactly n repeat units are then printed out.

## **4.3 RESULTS AND DISCUSSION**

## 4.3.1 Verification that Computer Simulation Results Conform to Bernoullian Statistics

The program was tested stringently for effects of sample size on the conformation to Bernoullian statistics. Firstly, appropriate values for the degree of polymerization and the number of molecules had to be chosen so as to avoid the effects of sample size and chain-end effects. After careful analysis of the results it was found³¹ that the effect of sample size could be conveniently eliminated by keeping the product of DP and number of molecules (DP x N) to a value of 1 000 000. Although this value appears high one has to take into account the P_m dependency, *i.e.*, the more the P_m value deviates from randomness (P_m = 0.5), the larger the product must be. For example, for a P_m value of 0.5 the product DP x N must be greater than 50 000, whereas, for P_m = 0.9 the product must be greater than 400 000. Secondly, the data from the computer simulation were tested to verify that it conformed to Bernoullian statistics. This was achieved by collecting data, relative frequency of dyad, triad, tetrad, and pentad sequences as well as the total number of isotactic and syndiotactic sequences containing n units, for various values of  $P_m$  (0.1, 0.2, 0.4, 0.5, 0.6, 0.8, and 0.9) and by keeping the number of molecules and the degree of polymerization (DP) at a fixed value of 1 000. For the available data, the following three tests are a good criteria for assessing Bernoullian statistics:

(1) The average probabilities can be used to construct plots of normalized dyad, triad, tetrad, and pentad probabilities as a function of P_m. Good agreement between theory (solid lines) and simulation (points) was obtained, as shown in Figures 4.3 and 4.4 for triad and tetrad probabilities, respectively.³²



Figure 4.3  $\blacklozenge$  Normalized probabilities of isotactic (nm), syndiotactic (rr), and atactic (mr+rm) triads as a function of  $P_m$ . The solid curves are theoretical, as described in Table 1.3, and the points are obtained from the computer simulation.



Figure 4.4  $\blacklozenge$  Normalized tetrad probabilities as a function of  $P_m$ . The solid curves are theoretical, as described in Table 1.3, and the points are obtained from the computer simulation. The bottom scale is used for sequences in parentheses.

(2) If the number of isotactic sequences containing  $n_i$  isotactic repeat units,  $N_{n_i}$ , and the number of syndiotactic sequences containing  $n_s$  syndiotactic repeat units,  $N_{n_s}$ , are known for all values of  $n_i$  and  $n_s$ , then the average lengths of isotactic,  $\langle n_i \rangle$ , and syndiotactic;  $\langle n_s \rangle$ , sequences can be obtained from the following relations

$$<\mathbf{n}_{i} > = \frac{\sum_{n=1}^{N} \mathbf{N}_{n_{i}}(\mathbf{n}_{i})}{\sum_{n=1}^{N} \mathbf{N}_{n_{i}}}$$
(4.1)  
$$<\mathbf{n}_{s} > = \frac{\sum_{n=1}^{N} \mathbf{N}_{n_{s}}(\mathbf{n}_{s})}{\sum_{n=1}^{N} \mathbf{N}_{n_{s}}}$$
(4.2)

Through various mathematical manipulations³³ it can be shown that

$$< n_i > = \frac{1 - (P_{mm}/P_{rr})}{1 - (P_{mm}/P_{rr})(P_r/P_m)}$$
(4.3)

$$\langle \mathbf{n}_{s} \rangle = \frac{1 - (\mathbf{P}_{mm}/\mathbf{P}_{rr})}{(\mathbf{P}_{m}/\mathbf{P}_{r}) - (\mathbf{P}_{mm}/\mathbf{P}_{rr})}$$
(4.4)

Substitution of the isotactic and syndiotactic triad probabilities, *i.e.*  $P_{mm} = P_m^2$  and  $P_{rr} = P_r^2$ , into equations (4.3) and (4.4), yields the following simple relations:

$$\langle \mathbf{n}_{\mathbf{i}} \rangle = \mathbf{1}/\mathbf{P}_{\mathbf{r}} \tag{4.5}$$

$$\langle \mathbf{n}_{\mathbf{s}} \rangle = 1/\mathbf{P}_{\mathbf{m}} \tag{4.6}$$

Using data from the computer simulation, the calculated average lengths of isotactic and syndiotactic sequences from equations (4.1), (4.3), and (4.5) and equations (4.2), (4.4), and (4.6), respectively, are shown in Table 4.2 which display excellent agreement, usually to the third decimal place.

#### Table 4.2

Calculated average lengths of isotactic (equations (4.1), (4.3), and (4.5)) and syndiotactic (equations (4.2), (4.4), and (4.6)) sequences of a polymer chain for various values of  $P_{m}$ .

•		<1;>				
P_m	eq. (4.1)	eq. (4.3)	eq. (4.5)	eq. (4.2)	eq.(4.4)	eq. (4.6)
0.1	1.112	1.112	1.111	9.956	10.046	10.033
0.2	1.245	1.246	1.248	4.996	5.017	5.028
0.4	1.670	1.671	1.668	2.497	2.500	2.496
0.5	2.000	2.002	2.002	1.997	1.999	1.998
0.6	2.498	2.500	2.502	1.663	1.664	1.666
0.8	4.961	4.981	4.977	1.252	1.253	1.252
0.9	9.907	9.998	9.980	1.113	1.113	1.111

(3) The expressions given above describe only the average sequence lengths. A more complete description should include the number and weight fractions of all isotactic and syndiotactic sequence lengths. The calculation of the number fraction (probability) of an isotactic sequence of a given length, using the m and r notation³⁴, is a straightforward application of the multiplication theorem of probabilities once it is recognized that a isotactic block sequence must be terminated at both ends by a syndiotactic dyad, *i.e.*, r(m)_{ni}r. Hence, the number fraction, N(n_i), and weight fraction, W(n_i), of isotactic sequences containing exactly n_i units are given by

$$\mathbf{N}(\mathbf{n}_{\mathbf{i}}) = \mathbf{P}_{\mathbf{r}} \left( \mathbf{P}_{\mathbf{m}} \right)^{\mathbf{n}_{\mathbf{i}}} \mathbf{P}_{\mathbf{r}}$$
(4.7)

and

$$\mathbf{W}(\mathbf{n}_{\mathbf{j}}) = (\mathbf{n}_{\mathbf{j}}) \mathbf{P}_{\mathbf{r}} (\mathbf{P}_{\mathbf{m}})^{\mathbf{n}_{\mathbf{j}}} \mathbf{P}_{\mathbf{r}}$$
(4.8)

Similar arguments can be used to derive equations for the syndiotactic sequence lengths. The effect of varying  $n_i$  and  $P_m$  on the number and weight fraction of isotactic sequences is best illustrated by constructing plots of as function of  $n_i$  for  $P_m$  values of 0.1, 0.5, and 0.9, as shown in Figures 4.5 and 4.6, respectively. The solid lines represent theoretical curves as described by equations (4.7) and (4.8) and the points are simulation values that were converted to number fractions by use of

$$N(n_i) = Nn_i / v_{tot.dvads}$$
(4.9)

and weight fractions by use of

$$W(n_i) = Nn_i n_i / v_{tot.dvads}$$
(4.10)

Once again excellent agreement is displayed between theoretical values and values obtained from the computer simulation. These plots show that the number fraction decreases monotonically with  $n_i$  while the weight fraction goes through a maximum. In both cases, the effect of increasing  $P_m$  is to broaden the distributions and to produce longer isotactic sequences.



Figure 4.5  $\blacklozenge$  The number fraction of isotactic sequences, N(n_i), as a function of the length of isotactic sequences for P_m values of 0.1 (circle), 0.5 (square), and 0.9 (triangle). The solid curves are theoretical and the points are obtained from the computer simulation.



Figure 4.6  $\diamond$  The weight fraction of isotactic sequences, W(n_i), as a function of the length of isotactic sequences for P_m values of 0.1 (circle), 0.5 (square), and 0.9 (triangle). The solid curves are theoretical and the points are obtained from the computer simulation. The vertical dashed lines represent the average length of isotactic sequence, <n_i>, as described by eq. (4.5).

#### 4.3.2 Tacticity Changes Resulting from Thermal Degradation of PVC

#### 4.3.2.1 NMR

In the present work, the thermal degradation of PVC was studied in solution rather than in the solid state. The sample, a 4% w/w of PVC in 1,2-DCB-d₄, was degraded at T=160 °C for various times (4, 8, 14 and 20 hours) inside the NMR cavity and the spectra were recorded at T=120 °C. Figure 4.7 shows a typical ¹³C NMR spectrum of the methine and methylene carbons of the PVC sample prior to degradation as recorded at a magnetic field strength of 125.7 MHz. The assignment of the various stereosequences, with the exception of several minor resolution effects, are similar to those given in Figure 1.2 (Chapter 1), for PVC in TCE-d₂ that was recorded at a lower temperature (114 °C) and a lower magnetic field strength (75.4 MHz). The major differences are mainly a consequence of the different solvent used with minor effects due to the differences in temperature and magnetic field strength. The effect of solvent on the stereosequence is more pronounced in the methylene carbon, as observed by other workers.³⁵⁻³⁷ For example, in the methylene region not only is there reversal of the mrm and mmr tetrads but the isotactic tetrad (mmm) is clearly resolved into all three isotactic hexads, mmmmm, mmmmr, and rmmmr. Whereas, the methine carbon displays only a slightly better resolution in the syndiotactic and atactic triads. Although higher stereosequences (pentads) are observed, the peaks are not clearly resolved.

The areas for the methine carbon stereosequences, for both degraded and nondegraded PVC samples, were carefully determined using the NMR integrator and a curve analysis program purchased from Jandel Scientific (PeakFit). For the curve analysis program, the best fits were obtained by use of a Voigt line shape. An example of this fit is displayed in Figure 4.8 for the non-degraded PVC sample. In all cases, the calculated results obtained by addition of constituent peaks are in excellent agreement with the experimental points ( $r^2 > 0.9994$ ). The experimental relative areas, as determined by both methods, for the non-degraded PVC sample and the 4, 8, 14, and 20 hours degraded samples are given in Tables 4.3 to 4.7, respectively. These data reveal no significant differences between the two methods of area determination.

Prior to discussing the tacticity changes that occurred to the PVC sample as a consequence of thermal degradation, tests were made for conformity to Bernoullian statistics. This was achieved by comparing the experimental areas with calculated values of the relative areas which are also given in the tables. These values were calculated assuming Bernoullian statistics with a  $P_m$  value as determined by the following relation



Figure 4.7  $\diamond$  Expanded portion of the methine (CH) and methylene (CH₂) region of a proton-decoupled carbon-13 NMR spectrum of 4% (wt/wt) poly(vinyl chloride) in 1,2-dichlorobenzene-d₄ recorded at a magnetic field of 125.7 MHz and at a temperature of 120 °C.



Figure 4.8  $\blacklozenge$  Typical diagram showing the deconvolution of the syndiotactic (rr), atactic (mr), and isotactic (mm) stereosequences of the methine region of PVC. The points represent the experimental data and the solid line the fitted results from the constituent peaks (dashed line).

#### Table 4.3

Experimental intensities, as determined by the NMR integrator  $(I_{NMR})$  and curve analysis program  $(I_{CA})$ , and calculated^{a)} intensities of the methine stereosequences of non-degraded PVC sample.

Assignment	I _{NMR} (Exp.)	I _{NMR} (Calc.)	I _{CA} (Exp.)	I _{CA} (Calc.)
rr	0.315	0.319	0.315	0.317
mr	0.498	0.492	0.497	0.492
mm	0.187	0.190	0.189	0.191
mmmm	0.036	0.036	0.036	0.037
mmr	0.090	0.093	0.089	0.094
rmmr	0.061	0.060	0.064	0.061

a) Assuming Bernoullian statistics with  $P_m = 0.436$  for data using the NMR integrator and  $P_m = 0.437$  for data obtained from the curve analysis program.

#### Table 4.4

Experimental intensities, as determined by the NMR integrator  $(I_{NMR})$  and curve analysis program  $(I_{CA})$ , and calculated^{a)} intensities of the methine stereosequences of PVC after 4 hours of thermal degradation at a temperature of 160 °C.

Assignment	I _{NMR} (Exp.)	I _{NMR} (Calc.)	I _{CA} (Exp.)	I _{CA} (Calc.)
rr	0.314	0.317	0.313	0.316
mr	0.497	0.492	0.497	0.492
mm	0.189	0.191	0.190	0.192
manm	0.037	0.037	0.037	0.037
mmmr	0.091	0.094	0.094	0.095
rmmr	0.061	0.061	0.059	0.061

a)Assuming Bernoullian statistics with  $P_m = 0.437$  for data using the NMR integrator and  $P_m = 0.438$  for data obtained from the curve analysis program.

#### Table 4.5

Experimental intensities, as determined by the NMR integrator $(I_{NMR})$ and curve
analysis program ( $I_{CA}$ ), and calculated ^{a)} intensities of the methine stereosequences
of PVC after 8 hours of thermal degradation at a temperature of 160 °C.

Assignment	I _{NMR} (Exp.)	I _{NMR} (Calc.)	I _{CA} (Exp.)	I _{CA} (Calc.)
rr	0.316	0.319	0.316	0.317
mr	0.497	0.492	0.495	0.492
mm	0.187	0.190	0.190	0.191
mmmm	0.036	0.036	0.035	0.037
mmmr	0.092	0.093	0.094	0.094
rmmr	0.059	0.060	0.061	0.061

^{a)}Assuming Bernoullian statistics with  $P_m = 0.436$  for data using the NMR integrator and  $P_m = 0.437$  for data obtained from the curve analysis program.

#### Table 4.6

Experimental intensities, as determined by the NMR integrator (I_{NMR}) and curve analysis program (I_{CA}), and calculated^a) intensities of the methine stereosequences of PVC after 14 hours of thermal degradation at a temperature of 160 °C.

Assignment	I _{NMR} (Exp.)	I _{NMR} (Calc.)	I _{C.A} (Exp.)	I _{CA} (Calc.)
rr	0.315	0.318	0.314	0.316
mr	0.498	0.492	0.498	0.492
mm	0.187	0.190	0.189	0.192
mmm	0.036	0.036	0.036	0.037
mmr	0.091	0.093	0.092	0.094
rmmr	0.061	0.060	0.060	0.061

^{a)}Assuming Bernoullian statistics with  $P_m = 0.436$  for data using the NMR integrator and  $P_m = 0.438$  for data obtained from the curve analysis program.

#### Table 4.7

Assignment	I _{NMR} (Exp.)	I _{NMR} (Calc.)	I _{CA} (Exp.)	I _{CA} (Calc.)
rr	0.319	0.322	0.315	0.318
mr	0.497	0.491	0.497	0.492
mm	0.184	0.187	0.188	0.191
mmmm	0.036	0.035	0.035	0.036
mmr	0.089	0.092	0.091	0.094
rmmr	0.060	0.060	0.062	0.061

Experimental intensities, as determined by the NMR integrator  $(I_{NMR})$  and curve analysis program  $(I_{CA})$ , and calculated^{a)} intensities of the methine stereosequences of PVC after 20 hours of thermal degradation at a temperature of 160 °C.

^{a)}Assuming Bernoullian statistics with  $P_m = 0.433$  for data using the NMR integrator and  $P_m = 0.437$  for data obtained from the curve analysis program.

$$P_{m} = (mm) + 1/2(mr)$$
 (4.11)

The excellent agreement between experimental and calculated intensities, to the third decimal place, confirms that this polymer conforms to Bernoullian statistics, as has been observed by other workers.^{29,38} Further support that the polymer conforms to Bernoullian statistics is the fact that the ratio  $4(mm)(rr)/(mr)^2 \approx 1$ . Using the intensities obtained from the NMR integrator and curve analysis program, these ratios for the non-degraded PVC sample were found to be 0.95.

As seen in Tables 4.3 to 4.7, the tacticity changes ¹¹ at occurred as a consequence of thermal degradation are small, generally lying within the differences between experimental and calculated intensities. For example, for the data determined by the NMR integrator, the differences between non-degraded PVC and the sample that was degraded for 20 hours were -0.003, -0.001, +0.004 for the mm, mr, and rr triad probabilities, respectively, and 0, -0.001, and -0.001 for the mmmr, and rmmr isotactic centered pentad probabilities. Even when the tacticity changes are plotted as a function of degradation time, the variation in the slope for the mmmr pentad, for example, is in disagreement between the two methods of area determination. These plots, of the triads and isotactic centered pentads, for areas determined by the NMR integrator, are shown in Figures 4.9 and 4.10, respectively, and for areas determined by the curve analysis program in Figures 4.11 and 4.12, with their appropriate slopes given in Table 4.8. The data reveal, for both methods, that the mm triad decreases while the mr and rr triad probabilities increase. However, for the isotactic centered pentads the data as determined by the NMR integrator indicates a decrease in all three stereosequences, whereas, data from the curve analysis program indicates that the mmmr stereosequence should increase.

In conclusion it is apparent that the tacticity changes that occur as a consequence of thermal degradation are small and fall within the limits of experimental error. To probe further into this matter, computer simulations were carried out by selectively degrading isotactic units and noting changes in these stereosequences.

#### 4.3.2.2 Computer simulations of selective degradation of isotactic units

Computer simulated degradations were carried out by selectively degrading isotactic units of a minimum length and noting the changes in stereosequences before and after degradation. The initial chains were simulated in such a manner as to mimic the properties of a typical commercial PVC sample (e.g., Esso 366 industrial resin) with DP = 600 and  $P_m = 0.45$ .

In the first set of simulations, degradation of the isotactic sequences was unconstrained by the sequence length. The program randomly selected a site for elimination to occur provided it appeared in an isotactic (m) environment, irrespective of length. The elimination proceeded in both directions from the random site and was terminated when it encountered a syndiotactic dyad (r). In other words, this is equivalent to a random degradation of isotactic sequences of any length. Typical results are shown in Figure 4.13, which shows a plot of the difference in probabilities for the triad stereosequences, P(degraded) - P(non-degraded), as a function of the percent degradation. The most striking feature is that in spite of the selective elimination of isotactic sequences the relative changes in the probabilities of the mm triad sequence are small. For example, even at 10% degradation the changes in the mm probabilities are ca. 0.01. Furthermore, for this type of degradation mechanism, the probabilities of both isotactic (mm) and atactic (mr) triads decrease while the syndiotactic triads (rr) actually increase.



Figure 4.9  $\diamond$  Changes in triad probabilities (as obtained from NMR integrator), mm (square), mr (circle), and rr (triangle), as a function of isothermal (T = 160 °C) degradation time.


Figure 4.10 Changes in pentad probabilities of isotactic centered triads (as obtained from NMR integrator), mmmm (square), mmmr (circle), and rmmr (triangle), as a function of isothermal (T = 160 °C) degradation time.







Figure 4.11  $\blacklozenge$  Changes in triad probabilities (obtained from the curve analysis program), mm (square), mr (circle), and rr (triangle), as a function of isothermal (T = 160 °C) degradation time.



Figure 4.12  $\blacklozenge$  Changes in isotactic pentad probabilities of isotactic centered triads (as obtained from the curve analysis program), mmmm (square), mmmm (circle), and mmmr (triangle), as a function of isothermal (T = 160 °C) degradation time.

Slopes^{a)} obtained from plots of triad and isotactic centered pentad probabilities, measured using the NMR integrator (NMR) or curve analysis program (CA), as a function of degradation time.

Stereosequence	NMR	CA
mm	-0.00017	-0.00007
mr	+0.00002	+0.00003
rr	+0.0019	+0.00002
mmmm	-0.00002	-0.00006
mmmr	-0.00005	+0.00002
rmmr	-0.00003	-0.00004

a) A negative slope indicates a decrease in the stereosequence probability.



Figure 4.13  $\blacklozenge$  Changes in triad probabilities, mm (square), mr (circle), and rr (triangle), resulting from the elimination of isotactic dyads and longer sequences, as a function of percent degradation.

At first this is an unexpected result, *i.e.*, if the simulation degrades only isotactic units, why should there be any changes in the atactic and syndiotactic triads? By definition and according to the constraints chosen for the simulation, each isotactic sequence is terminated by a syndiotactic dyad at both ends. As a result of the elimination of the isotactic units these syndiotactic dyads loose their designation. For example, the degradation of an isotactic triad shown in Figure 4.14 results in the elimination of two meso and two racemic dyads. However, as a result of the decrease in the total number of dyads, the values of  $P_m$  and  $P_x$  remain unchanged. For the triads a total of five stereosequences are lost, *i.e.*, xx, rm, mm, mr, and rx, where x can be either an m or r. For simplicity, if  $P_m = 0.5$  the two xr triads will on average correspond to one syndiotactic (rr) and one atactic (rm) triad. Therefore, selective degradation of isotactic triads involves the removal of 1 mm, 3 mr, and 1 rr sequences, *i.e.*, when the decrease in total number of triads is taken into account it results in an increase in  $P_{mm}$  and  $P_{rr}$  and a decrease in  $P_{mr}$ . Similar considerations can be made for the selective elimination of longer



Figure 4.14  $\blacklozenge$  A simplified schematic diagram of the dehydrochlorination reaction of an isotactic triad (mm) sequence in PVC, where m denotes a meso dyad, r denotes a racemic dyad, x can be either an m or r dyad, and 0 denotes an assignment that differs from the m/r assignments.

isotactic units. These results are summarized in Table 4.9 for the changes in dyad and triad probabilities for the selective degradation of isotactic dyads (rmr), triads (rmmr), tetrads (rmmr), pentads (rmmr), hexads (rmmmr), or heptads (rmmmr). The data reveal that there is a turning point in trends for the degradation of isotactic tetrads, *i.e.*, both  $P_m$  and  $P_{mm}$  begin to decrease,  $P_r$  and  $P_{rr}$  have commenced to increase while  $P_{mr}$  remains invariant, however, begins to increase for degradation of isotactic pentads and above.

Table 4.9

Changes ^{a)} in dyad and triad probabilities as a consequence of degrading						
Units degraded	P _m	P _r	P _{mm}	P _{mr}	P _{rr}	•
rmr	+		+	-	=	
rnmr	=	=	+	-	+	
rmmr	-	+	-	=	+	
rmannr	-	+	-	+	+	
THERMOMET	-	+		+	+	
rnammanr	-	+	-	+	+	

a) The changes in probability are denoted by +, -, or = which indicates an increase, decrease, or identical probabilities, respectively.

With this information at hand, the computer simulated results can be more readily understood. Obviously, the results of the computer simulation that were presented above refer to a somewhat more complicated situation. For example, the  $P_m$  value was not 0.5 nor was the simulated degradation restricted to isotactic units of a specific length. Hence, as shown in Figure 4.13, the random degradation of isotactic sequences of any length results in a decrease in  $P_{mm}$  and  $P_{mr}$  while  $P_{rr}$  increases. Comparison of these changes with the predictions given in Table 4.9 suggests that this type of behavior corresponds, on the average, to degradation of isotactic units between triads and tetrads. Indeed, the resulting average double bond length was computed to be 3.3.

Changes in the triad stereosequences resulting from computer simulations of degradation mechanisms that involve the degradation of isotactic units greater than or equal to triads, tetrads and pentads are shown in Figures 4.15, 4.16, and 4.17,



Figure 4.15  $\diamond$  Changes in triad probabilities, mm (square), mr (circle), and rr (triangle), resulting from the elimination of isotactic triads and longer sequences, as a function of percent degradation.



Figure 4.16  $\diamond$  Changes in triad probabilities, mm (square), mr (circle), and rr (triangle), resulting from the elimination of isotactic tetrads and longer sequences, as a function of percent degradation.



Figure 4.17  $\blacklozenge$  Changes in triad probabilities, mm (square), mr (circle), and rr (triangle), resulting from the elimination of isotactic pentads and longer sequences, as a function of percent degradation.

respectively. It should be noted that in Figure 4.17 the percent degradation, unlike Figures 4.13, 4.15, and 4.16, does not exceed four percent because statistically not all chains have isotactic units of sufficient length to cause a higher degradation. These plots display several features and trends that need to be brought forth. Firstly, for mechanisms involving the degradation of isotactic units, irrespective of minimum length, the value of  $P_{mr}$  decreases while the value of  $P_{rr}$  increases. Secondly, the value of  $P_{mr}$  which decreased for random elimination of dyads and higher sequences (Figure 4.13) commences to increase for degradations involving isotactic triads and above (Figure 4.15). Thirdly, the changes that occur are small, *e.g.*, a 2% degradation, for degradation of isotactic pentads and higher sequences, results in a change in the mm triad that is less than 0.008 (the value decreases as the minimum isotactic length decreases).

Similar plots were constructed, Figures 4.18 to 4.21, for the changes in the pentad stereosequences with isotactic centered triads, *i.e.*, mmm, mmmr, and mmmr pentads. These plots reveal that for degradations involving isotactic dyads, Figure 4.18, and triads, Figure 4.19, all three isotactic pentads decrease with percent degradation. However, for



Figure 4.18  $\blacklozenge$  Changes in the isotactic pentad probabilities, mmmm (square), mmmr (circle), and mmmr (triangle), after degradation of isotactic dyads and longer sequences, as a function of percent degradation.



Figure 4.19  $\blacklozenge$  Changes in the isotactic pentad probabilities, mmmm (square), mmmr (circle), and mmmr (triangle), after degradation of isotactic triads and longer sequences, as a function of percent degradation.



Figure 4.20  $\blacklozenge$  Changes in the isotactic pentad probabilities, mmmm (square), mmmr (circle), and mmmr (triangle), after degradation of isotactic tetrads and longer sequences, as a function of percent degradation.



Figure 4.21 • Changes in the isotactic pentad probabilities, mmmm (square), mmmr (circle), and rmmr (triangle), after degradation of isotactic pentads and longer sequences, as a function of percent degradation.

degradation involving isotactic tetrads and above, the rmmr pentad increases. These trends are more readily seen and additional information is revealed by combining these plots as shown in Figure 4.22. These graphs reveal that in each of the simulations, regardless of minimum sequence length, the probability of mmmm sequences diminishes with increased extent of degradation. However, a greater decrease is observed as the minimum sequence length for degradation increases. A similar pattern is seen for the mmmr sequences up to a minimum specification of tetrads; the reduction in  $P_{mmmr}$  is less



Figure 4.22  $\blacklozenge$  The effects of changes in minimum isotactic sequence length on the changes in various pentad probabilities: dyads and longer (circle), triads and longer (square), tetrads and longer (triangle), pentads and longer (diamond).

when the minimum sequence length is a pentad than when it is a tetrad. For degradation involving isotactic dyads and triads, the value of  $P_{rmmr}$  decreases. However, when the minimum length corresponds to tetrads and longer, the probability of the rmmr pentad shows a sharp increase as a result of degradation and then remains relatively unchanged for pentads and longer. This is as expected, since they are of shorter length than the specified minimum.

#### 4.3.2.3 Comparison of experimental and simulation results

From the experimental degradation results of PVC in the present study, it was concluded that the tacticity changes that occurred as a consequence of thermal degradation were quite small and within or at the limit of experimental uncertainty. For the triad probabilities, tacticity changes of less than 0.004 were observed and about 0.001 for the pentad stereosequences. Taking into account that the extent of degradation was at most 2%, it is now obvious from the computer simulations that such degradations should correspond to small tacticity changes.

Nonetheless, comparisons can be made between the *trends* observed in the computer simulated degradations and experimental degradations, which are conveniently summarized in Table 4.10. For the triad changes, these trends suggest that the observed experimental changes can be justified by assuming a mechanism in which isotactic triads

#### **Table 4.10**

Computer simulated changes^{a)} in triad and pentad probabilities as a consequence of degrading isotactic units above a minimum limit along with experimentally observed changes.

Units degraded	mm	mr	rr	mmm	mmmr	rmmr
dyad	-	-	+	-	<u> </u>	
triad	-	+	+	-	-	-
tetrad	-	÷	+	-	-	+
pentad		+	+	-	-	+
experimental results	• •	+	+	-	-/+	-

a)An increase in probability is denoted by a + sign and a decrease by a - sign.

and higher sequences are degraded. Furthermore, the computer simulated results reveal that an increase in the mmmr pentad is not possible with this type of degradation mechanism, as was reported for the data measured by the curve analysis program. Therefore, assuming that the mmmr pentad decreases (NMR integrator result) then a possible mechanism is degradation of isotactic dyads or triads.

Recently, Millan, et al.²⁴ reported some "tentative" tacticity changes as a result of thermal degradation in the solid state. The degraded PVC sample was dissolved in dioxane thus obtaining a highly resolved ¹³C NMR spectrum that allowed them to very accurately determine not only the mm, mr and rr triad content but also the mmmm, mmmr, and rmmr pentad content. The reported areas as integrated from the spectra prior to and after a 0.8% degradation at 180 °C were shown previously in Table 4.1. These workers claim that neither the syndiotactic nor the heterotactic triads change. However, the decrease in the isotactic triad appears to be appreciable even if the observed changes lie at the limit of experimental uncertainty. For the changes in the isotactic pentads, the decrease in the isotactic triad content is shared by the mmmr and rmmr pentads while the mmmm pentad remains unchanged. From these results and the indication from previous work that the chlorines located at the -mmr- sequence with a  $g^+ttg^-$  conformation are labile, they concluded that the labile chlorines are those of the mmmr and rmmr pentads.

To generate data which could be meaningfully compared to those of Millan, et  $al.^{24}$ , computer simulations of similar extent of degradation (0.85 to 1.01%) were performed. The results for the selective degradation of isotactic dyads, triads, tetrads, and pentads and above (Table 4.11) indicate that: (1) the changes in the triad probabilities are small and become measurable after degradation of isotactic triads and higher sequences. (2) The large decrease in the mm triad (-0.007) reported by Millan, et al. is not possible for this type of degradation mechanism. For the simulated results, the largest decrease in the mm triad was -0.0042, which was obtained for the degradation of isotactic pentads and higher sequences. However, for this degradation mechanism the atactic and syndiotactic triads should increase, in contradiction with their results. (3) For the pentad probabilities, a decrease in all three pentads is only possible when isotactic units of smaller length (dyads or triads and above) are degraded. For the degradation of higher isotactic units (tetrad or pentads and above), the mmm shows signs of an increase. Furthermore, for neither degradation mechanism does the mmmm pentad remain constant while the mmmm and mmmm decrease, as reported by Millan, *et al.* 

Computer simulated tacticity changes in triad and isotactic pentad probabilities as a result of degrading isotactic units above a minimum length

Stereosequence	non-degraded	degraded	difference			
0.92% degradation of isotactic dyads and above						
Pmr	0.4951	0.4944	-0.0007			
Pmm	0.2024	0.2016	-0.0008			
P _{rr}	0.3025	0.3040	+0.0015			
Pmmmm	0.0409	0.0407	-0.0002			
Pmmmr	0.1001	0.0998	-0.0003			
P _{rmmr} ·	0.0613	0.0612	-0.0001			
1.0	0% degradation of iso	ptactic triads and at	bove			
Pmr	0.4948	0.4952	+0.0004			
P _{mm}	0.2025	0.2003	-0.0022			
Prr	0.3026	0.3045	+0.0019			
Pmmmin	0.0411	0.0404	-0.0007			
P _{mmmr}	0.1003	0.0991	-0.0012			
Prnanz	0.0612	0.0608	-0.0004			
0.85% degradation of isotactic tetrads and above						
P _{mr}	0.4951	0.4962	+0.0011			
P _{mm}	0.2025	0.1997	-0.0028			
Prr	0.3024	0.3042	+0.0018			
Pmmm	0.0411	0.0398	-0.0013			
Pmmmr	0.1002	0.0981	-0.0021			
Prome	0.0612	0.0618	+0.0006			
1.01% degradation of isotactic pentads and above						
Pmr	0.4953	0.4972	+0.0019			
Pmm	0.2025	0.1983	-0.0042			
P _{rr}	0.3022	0.3045	+0.0023			
Pmmmm	0.0408	0.0380	-0.0028			
Pmmmr	0.1003	0.0983	-0.0020			
P _{rmmr}	0.0613	0.0620	+0.0007			

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Obviously there are two possible explanations to this discrepancy: (1) the results of Millan, *et al.* are within experimental uncertainty and they have reported trends that are perhaps erroneous; or (2) the degradation mechanism chosen for the simulation does not accurately reflect the events that occur experimentally. Undoubtedly, the latter possibility is true since it is well known from UV-visible spectra that the average double bond sequences should contain between 7 and 9 double bonds.²⁴ The average double bond sequence obtained in the simulation results for the degradation of dyads, triads, tetrad and pentads and higher sequences contained 3.3, 4.2, 5.1, and 6.1 double bonds, respectively. However, it should be pointed out that although the average double bond sequences are not in agreement, this type of degradation mechanism produces the largest changes in the mm triad.

To justify this point, the computer simulation program was modified to perform simulated degradations via two other mechanisms: (1) locating isotactic sequences above a minimum length and degrading eight units beginning at the mmr sequence (Table 4.12); (2) locating isotactic sequences above a minimum length and degrading eight units beginning at the center of the isotactic sequence and degrading equally in both directions (Table 4.13). These degradation mechanisms are closer to the proposed mechanism of Millan, et al., i.e., degradation is initiated at an -mmr- sequence, and a little more realistic since it takes into account the observed average double bond sequence length.³⁹ Even though a higher extent of degradation (1.33%) was obtained using these mechanisms, a comparison of these results (Tables 4.12 an 4.13) with those from the degradation mechanism involving the degradation of isotactic units only (Table 4.11) indicates smaller relative changes. This might be expected since these longer sequences inevitably include r placements. Secondly, the observed trends are the same. Therefore, it can be concluded that the results reported by Millan, et al. cannot be matched by the present simulated degradation mechanisms and are perhaps not accurate since they lie within experimental uncertainty.

Previously, Velazquez²⁹ in this laboratory followed the changes in tacticity during the degradation reaction of a PVC sample heated under vacuum at 150 °C. The experimental triad and pentad probabilities at various degradation times, Table 4.14, were calculated from the methine carbon region of a ¹³C NMR spectrum recorded at a magnetic field strength of 75.4 MHz. From these data, the author concluded that the isotactic (mm) and heterotactic (mr) triads decreased while the syndiotactic (rr) triads

Computer simulated tacticity changes in triad and isotactic pentad probabilities by locating isotactic units above a minimum length and degrading eight units beginning at an mmr sequence

Stereosequence	non-degraded	degraded	difference		
location of isotactic triads and above with a 1.34% degradation					
mr	0.4948	0.4950	+0.0002		
P _{mm}	0.2022	0.2007	-0.0015		
P _{rr}	0.3031	0.3044	+0.0013		
Pmmm	0.0409	0.0406	-0.0003		
Pmmmr	0.0999	0.0990	-0.0009		
Prmmr	0.0613	0.0610	-0.0003		
location o	f isotactic tetrads and	above with a 1.34%	degradation		
o mr	0.4947	0.4955	+0.0008		
mm	0.2019	0.1993	-0.0026		
rr	0.3034	0.3052	+0.0018		
mmmm	0.0410	0.0398	-0.0012		
) mmmr	0.0997	0.0976	-0.0021		
	0.0613	0.0618	+0.0005		
location o	f isotactic pentads and	above with a 1.34%	degradation		
mr	0.4954	0.4972	+0.0018		
> mm	0.2018	0.1983	-0.0035		
rr	0.3029	0.3045	+0.0016		
) Immmm	0.0406	0.0381	-0.0025		
	0.0997	0.0977	-0.0020		
<b>)</b>	0.0616	0.0621	+0.0005		

Computer simulated tacticity changes in triad and isotactic pentad probabilities as a consequence of degrading eight units beginning at the center of an isotactic sequence and degrading equally in both directions

Stereosequence	non-degraded	degraded	difference			
location of isotactic triads and above with a 1.33% degradation						
P _{mr}	0.4944	0.4947	+0.0003			
P _{mm}	0.2028	0.2011	-0.0016			
P _{rr}	0.3028	0.3041	+0.0013			
Pmmmm	0.0411	0.0406	-0.0005			
Pmmmr	0.1005	0.0996	-0.0008			
P _{rmmr}	0.0613	0.0609	-0.0003			
location	n of isotactic tetrads and	above with a 1.33%	degradation			
Pmr	0.4945	0.4955	+0.0010			
P _{mm}	0.2021	0.1993	-0.0028			
P _{rr}	0.3034	0.3052	+0.0018			
Pmmmm	0.0410	0.0398	-0.0012			
P _{mmmr}	0.1000	0.0979	-0.0022			
P _{rmmr}	0.0611	0.0617	+0.0006			
location	location of isotactic pentads and above with a 1.33% degradation					
P _{mr}	0.4948	0.4966	+0.0018			
P _{mm}	0.2022	0.1982	-0.0040			
P _{rr}	0.3030	0.3053	+0.0022			
P _{mmmm}	0.0407	0.0380	-0.0027			
Pmmmr	0.1001	0.0981	-0.0020			
Prmmr	0.0614	0.0621	+0.0007			

Tacticity changes in triad and isotactic pentad probabilities during thermal degradation of PVC at 150 °C as reported by Velazquez²⁹

Time	mm	mr	rr	mmmm	mmr	rmmr
(min)		· · · ·		_		
0	0.200	0.494	0.306	0.056	0.085	0.059
15	0.199	0.491	0.310	0.052	0.084	0.064
150	0.195	0.484	0.321	0.046	0.087	0.062
180	0.188	0.472	0.340	0.044	0.085	0.059

decreased while the syndiotactic (rr) triads increased. For the pentad probabilities, the mmmm pentad decreased while the mmmr and rmmr stereosequences remained essentially unchanged.

The changes, reported by Velazquez²⁹, in the experimental triad and pentad probabilities are quite large. For example, for the 180 minutes degradation time, the changes in the nun, mr, rr triads, and mmmm pentad are -0.012, -0.022, +0.034, and -0.012, respectively. As seen from the computer simulations, such large changes in tacticity require a large extent of degradation (>5%) where the polymer forms crosslinks and no longer amenable to solution studies. Therefore, these results should be looked at with caution. A possible explanation of such large differences is that the data were calculated using the NMR integrator and the spectra were recorded with an instrument having lower magnetic field strength effectively leading to a larger experimental uncertainty. This is readily seen by examining closely the experimental probabilities, *i.e.*, from the triad probabilities a  $P_m$  value of 0.447 is obtained, hence the calculated values of the mmmm and mmmr pentads are 0.040 and 0.099, respectively. This corresponds to differences between calculated and experimental values of 0.016 and 0.014, which are quite large when compared to the differences of the present results or those of Millan, *et al.* 

#### 4.4 SUMMARY

In this chapter, studies that probe into the thermal degradation mechanism of PVC at the molecular level have been presented. Such attempts proved to be unsuccessful because the tacticity changes were small and either within or at the limit of experimental uncertainty. To better understand the tacticity changes that can occur from a theoretical point of view a computer program was written that uses Monte Carlo methods to simulate the relative handedness of successive monomer units as they appear along a Bernoullian polymer chain.

Computer simulated degradations were, firstly, carried out by selectively degrading isotactic units above a given minimum length in PVC chains of similar properties to the Esso 366 sample, *i.e.*, DP = 600 and  $P_m = 0.45$ . The resulting changes in stereosequences were noted. As a consequence of this type of degradation mechanism, the value of  $P_{mm}$ decreased while the value of Prr increased, independently of the minimum length of the isotactic unit. By comparison, the changes in Pmr were sensitive to the length of the isotactic unit that was degraded, i.e., for degradations involving short isotactic units (dyads) Pmr decreased while for higher isotactic units (above triads) it increased. For degradations where the minimum isotactic units were dyads or triads, all three pentad stereosequences, mmmm, mmmr, and rmmr, decreased with extent degradation. However, for degradations involving isotactic tetrads and above, the rmmr pentad began to increase. In addition, the most striking feature is that, regardless of the minimum length of isotactic sequences to be degraded, the resulting changes in the probabilities are very small, at the levels of degradation (<2%) that are accessible to experimental verification using solution NMR. For example at a 2% extent of degradation for the mechanism involving degradation of isotactic pentads and higher sequences the resulting changes in the mm triad is less than 0.008 (the value decreases as the minimum isotactic length decreases).

The simulation results were compared with experimental ones obtained in the present study (solution degradations) and with the work of Velazquez²⁹ and Millan, *et al.*²⁴ It was concluded that for small extents of degradation that are experimentally attainable for PVC, the tacticity changes are quite small and within or at the limit of experimental uncertainty.

From experimental findings it appears that the degradation of purely isotactic sequences does not represent accurately the mechanism for the degradation PVC. The computer simulation program was therefore modified to take into account the 7 to 9 average double bond length found in thermally degraded PVC. The results from these simulations indicated similar trends but the changes in tacticity were, as suspected, much lower. From this study it can be concluded that, firstly, in order to observe changes in tacticity a higher extent of degradation must be attained. Secondly, a more realistic mechanism should be considered whereby not only the average double bond sequence length is taken into account but the distribution of double bonds as obtained from UV-visible experiments. In addition, the mechanism should also incorporate not only initiation

at the -mmr sequence but also random degradation due to initiation of other labile chlorines.

#### 4.5 REFERENCES AND NOTES

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## **CHAPTER 5**

## CONTRIBUTIONS TO ORIGINAL KNOWLEDGE AND SUGGESTIONS FOR FUTURE WORK

#### 5.1 CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

In this thesis contributions were made to a better understanding at the molecular level of two fundamental aspects of PVC, namely, the plasticization and the thermal degradation of PVC. This included studies in: (1) the microstructure determination and chain local motions of PVC in a plasticizer by carbon-13 NMR spectroscopy; (2) the diffusion of gases through PVC and plasticized PVC films; and (3) computer simulations of the thermal degradation of PVC. Pertinent results and the contributions to original knowledge are summarized below.

#### 5.1.1 Microstructure Determination and Carbon-13 Nuclear Magnetic Relaxations and Chain Local Motions of PVC in DBP and TCE

It is well known that the relative peak positions of the various stereosequences in carbon-13 NMR spectra of PVC are solvent dependent. The microstructure of PVC in a solvent, 1,1,2,2-tetrachloroethane- $d_2$  (TCE- $d_2$ ), that was not previously studied, was determined from a quantitative ¹³C NMR spectrum. With this solvent, the resolution of the methine carbon signal was such that all ten possible pentads, as well as some heptad fine structure, were observed. In the methylene region, all six tetrads as well as some hexad fine structure, for the mmr tetrad, were observed. Analysis using Bernoullian statistics and recent carbon-13 chemical shift assignments of PVC based on a 2D NMR spectrum permitted a reassignment of several resonances.

Carbon-13 spin-lattice relaxation times and NOE values for PVC were measured as a function of temperature at two magnetic fields for the first time using two solvents, di-butyl phthalate (DBP) and TCE- $d_2$ . The relaxation data were interpreted in terms of chain local motions by using various models to describe the dynamics. This analysis yielded the following results:

- Among the various models used to test the relaxation data, it was found that the Dejean-Lauprêtre-Monnerie (DLM) correlation function is the most appropriate in describing the chain segmental motions of PVC.
- (2) The simulation parameters obtained from the best fit to this model were found to differ for PVC in the two solvents, *i.e.*, the half-angles of the librational motion of the C-H vector for the methine carbon were found to be 27° and 30° in DBP and in TCE-d₂, respectively. This was used to develop an argument for a specific interaction between the carbonyl group of the DBP and the chlorine on the methine carbon of PVC, hence partly resolving the controversy as to which functional group of PVC is actually interacting with the plasticizer site.
- (3) The activation energies for cooperative segmental motions were found to be  $9.2 \text{ kJ} \text{ mol}^{-1}$  for PVC in DBP as compared to  $13.7 \text{ kJ} \text{ mol}^{-1}$  when the polymer is in the TCE-d₂ solvent. This difference was attributed to effects that arise from the relative solvent quality, *i.e.*, the local density of segments is higher when the polymer is dissolved in a  $\Theta$  solvent, TCE-d₂, and this leads to slower local dynamics because the rigid environment inhibits local conformational transitions compared to DBP, which is a good solvent for PVC.

### 5.1.2 Permeation of $O_2$ Gas through Plasticized PVC and Transport Properties of HCl and $O_2$ Gases Through Rigid PVC Films

The permeability coefficients of plasticized PVC films were measured for the permeation of oxygen where the plasticizers used were DOP, TBP, and for the first time a DOP/TBP mixture with  $\phi_{DOP} = 0.6$ . The permeabilities were measured as a function of temperature and plasticizer concentration. The following observations were made:

- (1) The effect of plasticizer type on the permeation coefficients of oxygen followed the trend:  $P(TBP) > P(\phi_{DOP} = 0.6) > P(DOP)$ .
- (2) Arrhenius plots of the permeation coefficients showed that the unplasticized and plasticized PVC films of low concentration of plasticizer ( $\phi_{plas} < 0.2$ ) displayed a discrete change in the slope, in the vicinity of the glass transition temperature, that reflected changes in the activation energy of permeation. The activation energies above the glass transition temperature were greater than those below the T_g. Furthermore, as the concentration of plasticizer in the film was increased the activation energies above the T_g decreased monotonically and leveled off to value

that corresponded to the activation energy associated with the plasticizer viscosity, a feature that was not previously reported.

For the second part of this study, the instrument was modified so as to provide data which permitted the permeability coefficient to be separated into the diffusion and solubility coefficients. The temperature dependence of the permeability, diffusion, and solubility coefficients of oxygen and hydrogen chloride gases in rigid, molded PVC film were determined. The results showed that:

- The permeation coefficient of hydrogen chloride gas, at a given temperature, is ca.
   80 times higher than that for oxygen and the diffusivity ca. 8 times lower. This reflects a higher solubility for HCl, as a result of strong van der Waals interactions with PVC.
- (2) The permeabilities and diffusivities of both gases showed an almost discontinuous dependence on temperature characterized by an abrupt change in slope at the glass transition temperature of PVC that results in discrete changes in activation energy. The activation energies for diffusion were found to be smaller for  $O_2$  than HCl, as expected from differences in their molecular diameters. Furthermore, the activation energies for diffusion above the  $T_g$  are about 47% larger than those below the  $T_g$ ; this can be accounted for on the basis of the ratio of the thermal expansion coefficients of PVC above and below the  $T_g$ . These results suggest that the increase in segmental mobility of the polymer chains at temperatures above the  $T_g$  increases the diffusivity as well as the zone of activation for diffusion leading to the increase in both energy and entropy of activation.

#### 5.1.3 Computer Simulations of the Thermal Degradation Process

An original computer program was written which simulates, according to Bernoullian statistics, the relative handedness of successive monomer units during polymerization and calculates the probabilities of configurational sequences before and after a specified degradation mechanism.

Computer simulated degradations were, firstly, carried out by selective dehydrochlorination of isotactic units of length greater than or equal to a specified minimum length. This type of degradation mechanism showed that:

(1) For the triads, the value of  $P_{nm}$  decreased while the value of  $P_{rr}$  increases, independently of the minimum length of the isotactic unit. By comparison, the changes in  $P_{mr}$  are sensitive to the length of the isotactic unit that is degraded, *i.e.*,

for degradations involving short isotactic units (dyads) the  $P_{mr}$  decreases while for longer isotactic units (above triads) it increases.

- (2) For isotactic-centered pentads, the three stereosequences mmmm, mmmr, and rmmr all decreased in percentage with extent degradation when it was restricted to isotactic units of dyads and triads as the minimum isotactic length. However, for degradations involving isotactic tetrads and above, the rmmr pentad began to increase. The most striking feature is that the changes in sequence population are small, e.g., a 2% degradation with degradation of isotactic pentads and above results in a change in the mm triad fraction that is less than 0.008 (the value decreases as the minimum isotactic length decreases).
- (3) The results of the simulations were compared with experimental results of the present study (solution degradations), the work of Millan, et al., and Velazquez. In all three comparison it was concluded that for the extent of degradation, at levels that are accessible to experimental verification by solution NMR (<2%), the tacticity changes are quite small and within or at the limit of experimental uncertainty.</p>

It was realized that the dehydrochlorination of purely isotactic sequences does not accurately simulate the mechanism for the degradation mechanism of PVC in that it fails to produce average double bond length in accord with experimentally determined values (7 to 9 bonds). Thus the computer simulation program was modified in such a manner that polyene sequences of expected length were produced. However, this requires that the dehydrochlorination also include some atactic and syndiotactic sequences. As suspected, this left the trends unchanged but the changes in tacticity as were much lower. From this study it was concluded that:

- Direct observation changes in tacticity by ¹³C NMR requires that a higher extent of degradation be attained than is experimentally possible.
- (2) A more realistic mechanism should be considered whereby not only the average double bond length is taken into account but the distribution of double bonds as obtained from UV-visible experiments. Furthermore, the mechanism should also incorporate not only initiation at the -mmr- sequence but also random degradation due to initiation of other labile chlorines as is well documented.

#### 5.2 SUGGESTIONS FOR FUTURE WORK

# 5.2.1 Carbon-13 Nuclear Magnetic Relaxations and Chain Local Motions of PVC

After submitting the results in Chapter 2 for publication it was suggested¹ that another possibility exists in describing the results. This suggestion deals with the nonapplicability of Kramers' theory in the high friction limit^{2,3} for polymers without large and rigid side groups. That is the activation energies for conformational transitions, E^{*}, derived from eq. (2.45) are based on Kramers' theory. This theory assumes that the correlation time for conformational transitions is inversely proportional to the rate constant for isomerization which allows the temperature and viscosity dependence of the correlation time to be predicted by

$$\tau_{c} = A\eta e^{(E^{*}/RT)}$$
(5.1)

where the pre-factor A is a viscosity independent constant. This equation predicts a linear dependence of  $\log(\tau_{C})$  vs.  $\log(\eta)$  with a slope equal to one. Substituting into eq. (5.1) the temperature dependence of the solvent viscosity as described by an Arrhenius type relation

$$\eta = \eta_0 e^{(E_{\eta}/RT)}$$
(5.2)

leads to

$$\tau_{c} = \mathbf{A}' \eta e^{(\mathbf{E}^{*} + \mathbf{E}_{\eta} / \mathbf{RT})}$$
(5.3)

where A' is a constant. Hence, the experimental (apparent) activation energy obtained from a plot of  $\ln(\tau_C)$  as a function of 1/T is the sum of the barrier for conformational transitions and the activation energy for the viscous flow as described by eq. (2.45). Any deviation from linearity in the  $\log(\tau_C)$  versus  $\log(\eta)$  plot indicates that Kramers' expression, eq (5.3), is insufficient in describing the experimental relaxation rates. Ediger and co-workers suggested the following empirical relation

$$\tau_{\mathbf{C}} = \mathbf{A}' \eta^{\alpha} \mathbf{e}^{(\mathbf{E}^* + \mathbf{E}_{\eta} / \mathbf{RT})}$$
(5.4)

The exponent  $\alpha$  takes values in the range 0.1 to 1. Hence, the apparent activation energy is given as

$$\mathbf{E}_{\mathbf{a}} = \mathbf{E}^* + \alpha \mathbf{E}_{\eta} \tag{5.4}$$

The correlation times from the DLM model yield  $\alpha = 0.73$  and  $E^* = 16.5$  kJ mol⁻¹. However, to test this more solvents have to be tried of various solvent quality and viscosity.

#### 5.2.2 Transport Properties of Gases Through Plasticized PVC Films

As described in Chapter 3, the oxygen permeation apparatus was modified to allow the determination of both the permeation and diffusion coefficients. This in turn opens up the possibility of a more complete analysis of the transport properties of films. Plasticized PVC films can be studied by varying the type and concentration of the plasticizer.

Furthermore, the dual-mode sorption has recently achieved great attention in its ability to explain the isotherms observed in the sorption of substantially soluble gases in glassy polymers. Sorption isotherms of various gases can be obtained in order to test the validity of this model with rigid and plasticized PVC films.

#### 5.2.3 Computer Simulations of the Thermal Degradation Process

Indeed, further improvements in the quality of the NMR data, either by devising a means of extending the accessible range of dehydrochlorination or by obtaining improved spectral resolution, can perhaps solve this dilemma. However, there are inherent limitations to the changes in the values  $P_{mm}$ ,  $P_{rr}$  and  $P_{mr}$ . These limitations are intrinsically linked to the statistical distributions of configurational sequences in a Bernoullian polymer. To obtain experimentally accessible changes in  $P_{mm}$  requires the exclusive degradation of isotactic sequences. However, there are not enough isotactic sequences of sufficient length to yield the experimentally determined double bond sequence lengths. For degradation to result in double bond lengths that correspond to experimentally determined values requires the dehydrochlorination also include some atactic and syndiotactic sequences which, in turn, reduces the changes in  $P_{mm}$ . Therefore, it is possible that confirmation of the role of tacticity in the thermal degradation by NMR methods may be unwarranted.

Realizing that the degradation of purely isotactic sequences is not an accurate mechanism for the degradation mechanism of PVC, the computer simulation program

should be modified to take into account not only the average double bond length but the distribution of double bonds as obtained from UV-visible experiments in thermally degraded PVC. Secondly, the mechanism should also incorporate not only initiation at the -mmr- sequence but also random degradation due to initiation of other labile chlorines as is well documented.

#### **5.3 REFERENCES AND NOTES**

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## **APPENDIX** A

PROGRAM PVCDEG:	
CONST	
$MAX_DEG_POLYM = 1000;$	
TYPE	
TYPEOFARRAY = ARRAY[1MAX_DEG_POLYM]	OF INTEGER;
TYPEOFARRAY_M_R = ARRAY[1MAX_DEG_POLY]	M] OF CHAR:
VAR	
CONFIGURATION : TYPEOFARRAY;	
CONFIGURATION_M_R: TYPEOFARRAY_M_R;	
COUNTM.	
COUNTR,	
TOTAL_COUNTM,	
TOTAL_COUNTR.	
COUNT_DOUBLE_BONDS : ARRAY[1MAX_DEG_P	OLYM] OF REAL:
NUMBER_OF_M,	
NUMBER_OF_R,	
NUMBER_OF_MRs.	
COUNTMM.	
COUNTRR.	
COUNTMR,	
COUNTMMM,	
COUNTMMR.	
COUNTMRR.	
COUNTMRM,	
COUNTRMR.	
COUNTRRR.	
COUNTMMMM,	
COUNTMMMR,	
COUNTMMRM,	
COUNTMMRR,	
COUNTMRMR.	
COUNTMRRM.	
COUNTMRRR,	

.

COUNTRMMR. COUNTRMRR. COUNTRRRR. TCOUNT. STOPPER. STOP_PRINT : REAL; L . J, ĸ : INTEGER; COUNTMOLECULES, ni, MOLECULES : INTEGER: T_CHECKCOUNT, CHECKER, DEG_POLYM, FRACTION_DEGRADATED. TOTAL_FRACTION. AVG_DEGRAD, FAVORABILITY, SUM_m, SUM_r, SUM_mr. SUM_mm, SUM_II, SUM_mmm, SUM_mmr. SUM_mm, SUM_mmr, SUM_mrr, SUM_m, SUM_mmm, SUM_mmmr, SUM_mmm. SUM_mmr, SUM_mmr, SUM_mmm,

.



SUM_mrit, SUM_rmmr, SUM_rmit, SUM_rttt, SUMD_m,

SUMD_r.

SUMD_mr,

SUMD_mm.

SUMD_n,

SUMD_mmm.

SUMD_mmr,

SUMD_mm.

SUMD_rmr,

SUMD_mr.

SUMD_rrr,

SUMD_mmmm,

SUMD_mmmr,

SUMD_mmm,

SUMD_mmm,

SUMD_mmr,

SUMD_mmm,

SUMD_mm,

SUMD_mmr,

SUMD_rmm,

SUMD_mm,

TOTALDYADS,

TOTALTRIADS,

TOTALTETRADS,

TOTALPENTADS, TOTALDYADS_D,

TOTALTRIADS_D.

TOTALTETRADS_D,

TOTALPENTADS_D,

total_double_bonds,

avg_bonds : REAL;

(-----) { THE FOLLOWING PROCEDURE PRINTS OUT A BOX OF ASTERISKS AROUND THE AREA SPECIFIED BY TWO POINTS, (x1,y1) to (x2,y2)* } • procedure put_in_box(x1,y1,x2,y2: integer); var index, i : integer; begin for index := y1 to y2 do begin if ((index = y1) or (index = y2))then for i := x1 to x2 do begin gotoxy(i,index); write('*'); end else begin gotoxy(x1,index); write('*'); gotoxy(x2,index); write('*'); end end end;{end of procedure put_in_box} {-----} { THE FOLLOWING PROCEDURE PRINTS A MESSAGE TO THE USER AND WAITS FOR 3. ( HIM/HER TO STRIKE THE ENTER KEY IN ORDER TO CONTINUE } {-----}

procedure wait_for_user;

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var index : integer; begin delay(1500); for index := 1 to 50 do begin gotoxy(20,25); chreol; gotoxy(20,25); write('<Strike the ENTER key to continue>'); end; readln; chrscr; end; {end of procedure wait_for_user}

**{-----**} ( THE FOLLOWING PROCEDURE PRINTS THE TITLE PAGE FOR THE PROGRAM } Procedure title_page_introduction; var index : integer; begin clrscr; delay(1500); for index := 1 to 11 do begin gotoxy(2*index - 1, index); write('COMPUTER GENERATED POLY (VINYL) CHLORIDE'); gotoxy((21-index)*2 + 1, 22-index);write('COMPUTER GENERATED POLY(VINYL) CHLORIDE'); delay(100); end; delay(500); for index := 1 to 10 do begin

gotoxy(2*index-1,index):
clreol:
gotoxy((20-index)*2 + 1, 22-index):
clreol:
delay(100):
end:
gotoxy(21,13):
write('WRITTEN BY : Theodore Radiotis'):
gotoxy(21,15):
write('Version 2.0 (1990)'):
put_in_box(15,9,65,17): { CALLS PROCEDURE TO PUT INFO IN BOX }
wait_for_user: { CALLS PROCEDURE TO WAIT FOR USER TO
STRIKE THE ENTER KEY }

end; {End procedure title_page_introduction}

```
( THE FOLLOWING PROCEDURE INITIALIZES THE RELEVANT COUNTERS
                                                            }
PROCEDURE INITIALIZE_COUNTERS;
BEGIN
SUM_m := 0; SUMD_m := 0;
SUM_r := 0; SUMD_r := 0;
SUM_mr := 0; SUMD_mr := 0;
SUM_mm := 0; SUMD_mm := 0;
SUM_{\pi} := 0; SUMD_{\pi} := 0;
SUM_mmm := 0; SUMD_mmm := 0;
SUM_mmr := 0; SUMD_mmr := 0;
SUM_mm := 0; SUMD_mm := 0;
SUM_rmr := 0; SUMD_rmr := 0;
SUM_mrr := 0; SUMD_mrr := 0;
SUM_m := 0; SUMD_m := 0;
SUM_mmm := 0; SUMD_mmmm := 0;
SUM_mmmr := 0; SUMD_mmmr := 0;
SUM_mmrm := 0; SUMD_mmrm := 0;
SUM_mmr := 0; SUMD_mmr := 0;
```

```
SUM_mrmr := 0; SUMD_mrmr := 0;
SUM_mrmr := 0; SUMD_mrmr := 0;
SUM_mrmr := 0; SUMD_mrmr := 0;
SUM_rmmr := 0; SUMD_rmmr := 0;
SUM_rmmr := 0; SUMD_mmr := 0;
SUM_mrmr := 0; SUMD_mrmr := 0;
TOTAL_FRACTION := 0;
FOR J := 1 TO ROUND(DEG_POLYM) DO
BEGIN
TOTAL_COUNTM[J] := 0;
TOTAL_COUNTR[J] := 0;
COUNT_DOUBLE_BONDS[J] := 0;
END;
```

END;

```
_____
                                                   -----}
{-----
{ THE FOLLOWING PROCEDURE ASKS THE OPERATOR TO INPUT THE FOLLOWING
                                                             }
( PARAMETERS: (1) NUMBER OF MOLECULES,
                                                        .
                                                             }
           (2) DEGREES OF POLYMERIZATION
{
                                                             }
{
           (3) THEORETICAL Pm,
                                                             }
           (4) PERCENT DEGRADATION, AND
{
                                                             }
           (5) MINIMUM ISOTACTIC LENGTH TO BE DEGRADED.
£
                                                             }
{------
                 ______
PROCEDURE SET_PVC_INFO;
VAR
DUMMY: REAL:
BEGIN
REPEAT
 CLRSCR:
 PUT_IN_BOX(5,10,70,14);
 GOTOXY(10,12);
 WRITE(HOW MANY PVC MOLECULES WOULD YOU LIKE TO GENERATE? );
 READLN(DUMMY);
 MOLECULES := ROUND(DUMMY)
UNTIL ((DUMMY >= 1) AND (DUMMY \leq 30000));
```

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REPEAT

CLRSCR;

PUT_IN_BOX(5,10,75,14);

GOTOXY(10,12);

WRITE(ENTER THE DEGREES OF POLYMERIZATION FOR PVC (10 TO

',MAX_DEG_POLYM,')');

READLN(DEG_POLYM);

UNTIL (DEG_POLYM >= 10) OR (DEG_POLYM <= MAX_DEG_POLYM);

REPEAT

CLRSCR;

PUT_IN_BOX(5,10,75,15);

GOTOXY(15,12);

WRITE (ENTER THE PROBABILITY OF GENERATING A );

GOTOXY(20,13);

WRITE('MESO SEQUENCE, Pm (0 TO 1): ');

READLN(FAVORABILITY);

FAVORABILITY := 1-FAVORABILITY;

```
UNTIL (FAVORABILITY >= 0) AND (FAVORABILITY <= 1);
```

REPEAT

CLRSCR;

PUT_IN_BOX(5,10,75,14);

GOTOXY(10,12);

WRITE('ENTER THE DESIRED FRACTION OF DEGRADATION (O TO 1): ');

READLN(FRACTION_DEGRADATED);

UNTIL ((FRACTION_DEGRADATED >= 0) OR (FRACTION_DEGRADATED <= 1)); REPEAT

. .

CLRSCR;

PUT_IN_BOX(5,10,75,15);

GOTOXY(15,12);

WRITE(ENTER THE MINIMUM LENGTH OF ISOTACTIC );

GOTOXY(20,13);

WRITE('UNITS TO BE DEGRADED : ');

READLN(ni);

ni := round(ni);

UNTIL (ni >= 1) AND (ni <= 10);

CLRSCR;

END;

```
(-----)
{ THE FOLLOWING PROCEDURE GENERATES A PVC MOLECULE ACCORDING TO
                                                           }
{ THE ENTERED DEGREES OF POLYMERIZATION AND TACTICITY.
                                                           }
( AT THE END OF THE PROCEDURE VALUES OF 0 AND 1 ARE STORED IN A
                                                          )
             2-DIMENSIONAL ARRAY CALLED CONFIGURATION
(
                                                           }
(-----)
PROCEDURE SET_RANDOM_MOLECULES;
VAR
 NUMBER : REAL:
BEGIN
 NUMBER := RANDOM;
 IF NUMBER >= 0.5
 THEN
   CONFIGURATION[1] := 1
 ELSE
   CONFIGURATION[1] :== 0;
 FOR J := 2 TO round(DEG_POLYM) DO
 BEGIN
  NUMBER := RANDOM;
  IF CONFIGURATION[J-1] = 0
  THEN
    IF NUMBER <= FAVORABILITY + (1 - (FAVORABILITY*2))
    THEN
      CONFIGURATION[J] := 0
    ELSE
      CONFIGURATION[J] := 1
  ELSE
    IF NUMBER <= FAVORABILITY
    THEN
      CONFIGURATION[J] := 0
    ELSE
      CONFIGURATION[J] := 1
  END:
```

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### END; {SFT_RANDOM_MOLECULES}

```
{-----
                     { ACCORDING TO THE DATA FROM THE ARRAY CONFIGURATION, THE FOLLOWING
                                                                  )
{ PROCEDURE SETS UP AN ARRAY CALLED CONFIGURATION_M_R THAT CONSISTS
                                                                  }
{ OF M'S AND R'S. TWO ADJECENT ONES (11) OR ZEROS (00) ARE SAVED
                                                                  )
       AS AN M, WHEREAS A (10) OR (01) ARE DENOTED AS AN R.
ſ
                                                                  }
{-----}
PROCEDURE SET_M_R;
BEGIN
CASE CONFIGURATION[1] OF
  0: CONFIGURATION_M_R[1] := '0';
  1: CONFIGURATION_M_R[1] := '1';
  2: CONFIGURATION_M_R[1] := '=';
END;
FOR J := 2 TO ROUND(DEG_POLYM) DO
 CASE CONFIGURATION[J] OF
   0: CASE CONFIGURATION[J-1] OF
      0: CONFIGURATION_M_R[J] := 'M';
      1: CONFIGURATION_M_R[J] := 'R';
      2: CONFIGURATION_M_R[J] := '0';
     END;
   1: CASE CONFIGURATION[J-1] OF
      0: CONFIGURATION_M_R[J] := 'R';
      1 : CONFIGURATION_M_R[J] := 'M':
      2 : CONFIGURATION_M_R[J] := '1';
     END:
   2: CASE CONFIGURATION[J-1] OF
      0: CONFIGURATION_M_R[J] := '=';
```

1 : CONFIGURATION_M_R[J] := '=';

2 : CONFIGURATION_M_R[J] := '='; END;

END;

{------}
{ THE FOLLOWING PROCEDURE COUNTS THE NUMBER OF M'S AND R'S IN THE }
{ ARRAY CONFIGURATION_M_R. }
}

PROCEDURE COUNT_NUMBER_OF_M_R( VAR NUMBER_OF_M,

NUMBER_OF_R : REAL);

VAR

PROBABILITY_M,

PROBABILITY_R,

NUMBER_OF_MRs: REAL;

BEGIN

NUMBER_OF_M := 0;

NUMBER_OF_R := 0;

FOR J := 1 TO ROUND(DEG_POLYM) DO

BEGIN

CASE CONFIGURATION_M_R[J] OF

'M' : BEGIN

```
NUMBER_OF_M := NUMBER_OF_M + 1;
```

END:

'R' : BEGIN

```
NUMBER_OF_R := NUMBER_OF_R + 1;
```

END;

END;

END;

NUMBER_OF_MRs := NUMBER_OF_M + NUMBER_OF_R;

PROBABILITY_M := NUMBER_OF_M / NUMBER_OF_MRs;

PROBABILITY_R := NUMBER_OF_R / NUMBER_OF_MRs;

```
END;{COUNT_NUMBER_OF_M_R}
```

CHECKCOUNT,

```
COUNT
        : INTEGER;
CH
       : CHAR;
NOTDONE : BOOLEAN;
BEGIN
  FOR J := 1 TO round(DEG_POLYM) DO
    BEGIN
     COUNTM[J] := 0;
     COUNTR[J] := 0;
    END;
  J := 2:
  NOTDONE := TRUE;
  WHILE J <= DEG_POLYM DO
   BEGIN
     COUNT := 0:
     CH := CONFIGURATION_M_R[J];
     WHILE ((CH = CONFIGURATION_M_R[J]) AND NOTDONE) DO
      BEGIN
       COUNT := COUNT + 1;
       J := J + 1;
       IF J > DEG_POLYM THEN NOTDONE := FALSE;
      END;
     IF CH = 'M' THEN COUNTM[COUNT] := COUNTM[COUNT] + 1;
     IF CH = 'R' THEN COUNTR[COUNT] := COUNTR[COUNT] + 1 ;
    END;
   J := 1;
   CHECKCOUNT := 0;
   FOR J := 1 TO round(DEG_POLYM) DO
    BEGIN
     TOTAL_COUNTM[J] := TOTAL_COUNTM[J] + COUNTM[J];
     TOTAL_COUNTR[J] := TOTAL_COUNTR[J] + COUNTR[J];
    END;
```

END; {END OF PROCEDURE}

```
{-----}
( THE FOLLOWING PROCEDURE COUNTS THE NUMBER OF ISOTACTIC (MM),
                                                              }
{
        ATACTIC (MR), AND SYNDIOTACTIC (RR) TRIADS.
                                                              }
(-----)
PROCEDURE PROBABILITY_MM_RR_MR(VAR COUNTMM,
             COUNTRR,
              COUNTMR : real );
VAR
PROB_MR_RM.
PROB_MM,
PROB_RR.
TCOUNT : REAL;
BEGIN
 COUNTMM := 0;
 COUNTMR := 0;
 COUNTRR := 0;
 FOR J := 2 TO round(DEG_POLYM - 1) DO
 CASE CONFIGURATION_M_R[J] OF
   'M': CASE CONFIGURATION_M_R[J+1] OF
      M : COUNTMM := COUNTMM + 1;
      R': COUNTMR := COUNTMR + 1;
     END;
   'R': CASE CONFIGURATION_M_R[J+1] OF
      \mathbf{R}': \mathbf{COUNTRR} := \mathbf{COUNTRR} + 1;
      M : COUNTMR := COUNTMR + 1;
     END:
 END:
 TCOUNT := COUNTRR + COUNTMM + COUNTMR:
 PROB_MR_RM := COUNTMR / TCOUNT;
 PROB_MM := COUNTMM / TCOUNT;
```

PROB_RR := COUNTRR / TCOUNT;

{ THE FOLLOWING PROCEDURE COUNTS ALL THE DISTINGUISHABLE TETRADS (MMM, MMR, MRR, MRM, RRR) { {-----} PROCEDURE PROBABILITY_MMM_RRR( VAR COUNTMMM, COUNTMMR, COUNTMRR, COUNTMRM. COUNTRMR. COUNTRRR : real); VAR PROB_MMM, PROB_MMR, PROB_MRR, PROB_MRM. PROB_RMR. PROB_RRR. TOTALCOUNT : real; BEGIN COUNTMMM := 0; COUNTMMR := 0; COUNTMRR := 0; COUNTMRM := 0; COUNTRMR := 0; COUNTRRR := 0; FOR J := 2 TO round(DEG_POLYM - 2) DO CASE CONFIGURATION_M_R[J] OF 'M': CASE CONFIGURATION_M_R[J+1] OF 'M': CASE CONFIGURATION_M_R[J+2] OF 'M' : COUNTMMM := COUNTMMM + 1; 'R': COUNTMMR := COUNTMMR + 1; END: 'R': CASE CONFIGURATION_M_R[J+2] OF 'M': COUNTMRM := COUNTMRM + 1; 'R' : COUNTMRR := COUNTMRR + 1; END;

}

)

END;

'R': CASE CONFIGURATION_M_R[J+1] OF

```
'M': CASE CONFIGURATION_M_R[J+2] OF
```

```
M': COUNTMMR := COUNTMMR + 1;
```

```
'R' : COUNTRMR := COUNTRMR + 1;
```

```
END;
```

```
'R': CASE CONFIGURATION_M_R[J+2] OF
```

```
'M': COUNTMRR := COUNTMRR + 1;
```

```
'R': COUNTRRR :=COUNTRRR + 1;
```

END;

END;

END;

```
TOTALCOUNT := COUNTMMM + COUNTMMR + COUNTMRM + COUNTMRR + COUNTRRR
```

## + COUNTRMR;

```
PROB_MMM := COUNTMMM / TOTALCOUNT;

PROB_MMR := COUNTMMR / TOTALCOUNT;

PROB_MRM := COUNTMRM / TOTALCOUNT;

PROB_RMR := COUNTMRR / TOTALCOUNT;

PROB_MRR := COUNTMRR / TOTALCOUNT;

PROB_RRR := COUNTRRR / TOTALCOUNT;
```

END;

PROCEDURE PROBABILITY_MMMM_RRRR(VAR COUNTMMMM,

COUNTMMR, COUNTMMRM, COUNTMMRR, COUNTMRRM, COUNTMRRR, COUNTMRRR, COUNTRMRR, COUNTRMRR, VAR

COUNTRRRR : real);

AR

PROB_MMMM. PROB_MMMR.

PROB_MMRM.

PROB_MMRR.

PROB_MRMR.

PROB_MRRM.

PROB_MRRR.

PROB_RMMR.

PROB_RMRR.

PROB_RRRR.

TOTALCOUNT : real;

BEGIN

COUNTMMMM := 0;

COUNTMMMR := 0;

COUNTMMRM := 0;

COUNTMMRR := 0;

COUNTMRMR := 0;

COUNTMRRM := 0;

COUNTMRRR := 0;

```
COUNTRMMR := 0;
```

COUNTRMRR := 0;

```
COUNTRRRR := 0;
```

FOR J := 2 TO round(DEG_POLYM - 3) DO

CASE CONFIGURATION_M_R[J] OF

'M': CASE CONFIGURATION_M_R[J+1] OF

'M': CASE CONFIGURATION_M_R[J+2] OF

```
M: CASE CONFIGURATION_M_R[J+3] OF
```

M : COUNTMMMM := COUNTMMMM + 1;

'R' : COUNTMMMR := COUNTMMMR + 1;

END;

'R': CASE CONFIGURATION_M_R[J+3] OF

```
'M' : COUNTMMRM := COUNTMMRM + 1;
```

```
'R': COUNTMMRR := COUNTMMRR + 1;
```

END:

'R': CASE CONFIGURATION_M_R[J+2] OF

```
'M' : CASE CONFIGURATION_M_R[J+3] OF
```

```
'M' : COUNTMMRM := COUNTMMRM + 1;
```

```
'R' : COUNTMRMR := COUNTMRMR + 1;
```

```
END;
```

'R' : CASE CONFIGURATION_M_R[J+3] OF

```
'M' : COUNTMRRM := COUNTMRRM + 1;
```

```
'R' : COUNTMRRR := COUNTMRRR + 1;
```

END:

END;

END;

```
'R' : CASE CONFIGURATION_M_R[J+1] OF
```

```
'M': CASE CONFIGURATION_M_R[J+2] OF
```

```
'M': CASE CONFIGURATION_M_R[J+3] OF
```

```
'M': COUNTMMMR := COUNTMMMR + 1;
```

R': COUNTRMMR := COUNTRMMR + 1; END:

'R' : CASE CONFIGURATION_M_R[J+3] OF

```
'M': COUNTMRMR := COUNTMRMR + 1;
```

```
'R': COUNTRMRR := COUNTRMRR + 1;
```

```
END;
```

END;

'R': CASE CONFIGURATION_M_R[J+2] OF

'M' : CASE CONFIGURATION_M_R[J+3] OF

```
'M': COUNTMMRR := COUNTMMRR + 1;
```

```
R': COUNTRMRR := COUNTRMRR + 1;
END;
```

'R': CASE CONFIGURATION_M_R[J+3] OF

```
'M : COUNTMRRR := COUNTMRRR + 1;
```

```
'R' : COUNTRRRR := COUNTRRRR + 1;
```

END;

END;

END;

TOTALCOUNT := COUNTMMMM + COUNTMMMR + COUNTMMRM + COUNTMMRR +

COUNTMRMR + COUNTMRRM + COUNTMRRR + COUNTRMMR + COUNTRMRR + COUNTRRRR;

PROB_MMMM := COUNTMMMM / TOTALCOUNT:

PROB_MMMR := COUNTMMMR / TOTALCOUNT;

PROB_MMRM := COUNTMMRM / TOTALCOUNT;

PROB_MMRR := COUNTMMRR / TOTALCOUNT:

PROB_MRMR := COUNTMRMR / TOTALCOUNT;

PROB_MRRM := COUNTMRRM / TOTALCOUNT:

FROB_MRRR := COUNTMRRR / TOTALCOUNT;

PROB_RMMR := COUNTRMMR / TOTALCOUNT;

PROB_RMRR := COUNTRMRR / TOTALCOUNT;

PROB_RRRR := COUNTRRRR / TOTALCOUNT;

END;

```
{------
            _____
                                                -----}
{ THE FOLLOWING PROCEDURE FINDS AND DEGRADES ISOTACTIC SEQUENCES.
                                                        }
{ THE LENGTH MUST BE ABOVE A MINIMUM LIMIT THAT IS SET BY THE
                                                        }
{ OPERATOR. DEGRADATION SEIZES ONCE AN UPPER LIMIT OF DEGRADATION
                                                        )
        IS REACHED (ALSO ENTERED BY THE USER)
{
                                                        }
PROCEDURE DEGRADATION(VAR TOTAL_FRACTION : REAL);
VAR
POSITION.
START_POSITION,
COUNTER,
TEMPORARY : INTEGER;
NOT_FINISHED,
NOTCOMPLETE : BOOLEAN;
FRACTION : REAL;
BEGIN
FRACTION := 0:
REPEAT
 NOT_FINISHED := TRUE;
 REPEAT
  REPEAT
```

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POSITION := RANDOM(round(DEG_POLYM)) + 1

UNTEL POSITION >= 1

UNTIL ((CONFIGURATION[POSITION] = 1) OR (CONFIGURATION[POSITION] = 0));

TEMPORARY := CONFIGURATION[POSITION];

WHILE ((POSITION >= 1) AND NOT_FINISHED) DO

IF CONFIGURATION[POSITION] = TEMPORARY

THEN POSITION := POSITION - 1

ELSE NOT_FINISHED := FALSE;

POSITION := POSITION + 1;

START_POSITION := POSITION;

COUNTER := 0;

```
NOTCOMPLETE := TRUE;
```

WHILE ((POSITION <= (DEG_POLYM - 1)) AND NOTCOMPLETE) DO

IF CONFIGURATION[POSITION] = TEMPORARY

THEN

BEGIN

**CCUNTER** := COUNTER + 1;

```
POSITION := POSITION + 1;
```

END

ELSE NOTCOMPLETE := FALSE;

```
IF COUNTER >= (ni+1)
```

THEN

BEGIN

```
FRACTION := FRACTION + COUNTER/DEG_POLYM;
```

POSITION := START_POSITION;

```
COUNT_DOUBLE_BONDS[COUNTER] := COUNT_DOUBLE_BONDS[COUNTER] + 1;
```

REPEAT

```
CONFIGURATION[POSITION] := 2;
```

**POSITION := POSITION + 1** 

UNTIL ((CONFIGURATION[POSITION] - TEMPORARY) <> 0);

END

UNTIL FRACTION >= FRACTION_DEGRADATED;

TOTAL_FRACTION := TOTAL_FRACTION + FRACTION;

### PROCEDURE

AVERAGE_PROBABILITTES(SUM_m.SUM_r,SUM_mr,SUM_mm,SUM_rr,SUM_mmm,

SUM_mmr,SUM_mm.SUM_rmr,SUM_mrr,SUM_rrr,

SUM_mmmn,SUM_mmmr,SUM_mmrm,SUM_mmrr,SUM_mrmr,

SUM_mrnn,SUM_mrrr,SUM_rmmr,SUM_rmrr,SUM_rrrr,

TOTALDYADS, TOTALTRIADS, TOTALTETRADS,

TOTALPENTADS : REAL);

### VAR

AVG_Pm,

AVG_Pr,

AVG_Pmr,

AVG_Pmm,

AVG_Pn,

AVG_Pmmm,

AVG_Pmmr,

AVG_Pmm,

AVG_Prmr,

AVG_Pmrr,

AVG_Pm,

AVG_Pmmmm,

AVG_Pmmmr,

AVG_Pmmm,

AVG_Pmmr,

AVG_Pmrmr,

AVG_Pmm,

AVG_Pmrn,

AVG_Prmmr,

AVG_Primit,

AVG_Pmr : REAL;

BEGIN

AVG_Pm := SUM_m /TOTALDYADS; AVG_Pr := SUM_r /TOTALDYADS;



```
AVG_Pmr := SUM_mr / TOTALTRIADS;
```

AVG_Pmm := SUM_mm / TOTALTRIADS;

AVG_Prr := SUM_rr / TOTALTRIADS;

AVG_Pmmm := SUM_mmm / TOTALTETRADS;

AVG_Pmmr := SUM_mmr / TOTALTETRADS;

AVG_Pmrm := SUM_mrm / TOTALTETRADS;

AVG_Prmr := SUM_rmr / TOTALTETRADS;

AVG_Pmrr := SUM_mrr / TOTALTETRADS;

AVG_Pmr := SUM_mr / TOTALTETRADS;

AVG_Pmmmm := SUM_mmmm / TOTALPENTADS;

AVG_Pmmmr := SUM_mmmr / TOTALPENTADS;

AVG_Pmmrm := SUM_mmrm / TOTALPENTADS;

```
AVG_Pmmrr := SUM_mmrr / TOTALPENTADS;
```

AVG_Pmrmr := SUM_mrmr / TOTALPENTADS;

AVG_Pmrm := SUM_mrm / TOTALPENTADS;

AVG_Pmmr := SUM_mmr / TOTALPENTADS;

AVG_Pmmr := SUM_mmr / TOTALPENTADS;

AVG_Prmrr := SUM_rmrr / TOTALPENTADS;

AVG_Pmr := SUM_mr / TOTALPENTADS;

WRITELN(LST);

WRITELN(LST, 'AVERAGE Pm = ',AVG_Pm:1:5);

WRITELN(LST,'AVERAGE Pr = ',AVG_Pr:1:5);

WRITELN(LST);

WRITELN(LST,'AVERAGE Pmr+rm = ',AVG_Pmr:1:5); WRITELN(LST,'AVERAGE Pmm = ',AVG_Pmm:1:5);

WRITELN(LST,'AVERAGE Prr = ',AVG_Prr:1:5);

WRITELN(LST);

WRITELN(LST,'AVERAGE Pmmm = ',AVG_Pmmm:1:5); WRITELN(LST,'AVERAGE Pmmr+mmm = ',AVG_Pmmr:1:5); WRITELN(LST,'AVERAGE Pmm = ',AVG_Pmm:1:5); WRITELN(LST,'AVERAGE Pmmr = ',AVG_Pmmr:1:5); WRITELN(LST,'AVERAGE Pmmr+mmm = ',AVG_Pmm:1:5); WRITELN(LST,'AVERAGE Pmmmm = ',AVG_Pmmm:1:5); WRITELN(LST,'AVERAGE Pmmmmm = ',AVG_Pmmm:1:5); WRITELN(LST,'AVERAGE Pmmmmmm = ',AVG_Pmmm:1:5);

WRITELN(LST,'AVERAGE Pmmrm+mrmm = ',AVG_Pmmrm;1;5); WRITELN(LST,'AVERAGE Pmmrt+rmm = ',AVG Pmmrt,1;5); WRITELN(LST,'AVERAGE Pmrmr+rmrm = ',AVG_Pmrmr;1:5); WRITELN(LST, 'AVERAGE Pmrm = 'AVG_Pmrm;1:5); WRITELN(LST,'AVERAGE Pmrrr+mrm = 'AVG Pmrrr:1:5); WRITELN(LST, 'AVERAGE Prmmr = ',AVG_Prmmr:1:5); WRITELN(LST,'AVERAGE Prmrt+rrmr = ',AVG_Prmrt,1:5); WRITELN(LST,'AVERAGE Pmr =',AVG_Pmr:1:5); END:

# BEGIN

TITLE_PAGE_INTRODUCTION; SET_PVC_INFO; WRITELNILST.'------'): WRITELN(LST, NUMBER OF MOLECULES = ', MOLECULES); WRITELN(LST, DEGREES OF POLYMERIZATION = 'DEG POLYM:5:0); WRITELN(LST, THEORETICAL Pm = ',1-FAVORABILITY:1:4); WRITELN(LST, DESIRED PERCENT DEGRADATION = 'FRACTION_DEGRADATED*100:2:2,'%'); WRITELN(LST, MINIMUM LENGTH OF ISOTACTIC UNT'S THAT WILL BE DEGRADED = ',ni); WRITELN(LST.'--------'); INITIALIZE COUNTERS: FOR COUNTMOLECULES := 1 TO MOLECULES DO BEGIN SET_RANDOM_MOLECULES; SET M R: COUNT_CONSECUTIVE_M_Rs; COUNT_NUMBER_OF_M_R(NUMBER_OF_M,NUMBER_OF_R);  $SUM_m := SUM_m + NUMBER_OF_M;$  $SUM_r := SUM_r + NUMBER_OF_R;$ PROBABILITY_MM_RR_MR(COUNTMM,COUNTRR,COUNTMR); SUM_mr := SUM_mr + COUNTMR; SUM_mm := SUM_mm + COUNTMM;  $SUM_{\pi} := SUM_{\pi} + COUNTRR;$ 

SUM_mmm := SUM_mmm + COUNTMMM;

SUM_mmr := SUM_mmr + COUNTMMR;

SUM_mm := SUM_mm + COUNTMRM;

SUM_rmr := SUM_rmr + COUNTRMR;

SUM_mrr := SUM_mrr + COUNTMRR;

SUM_m := SUM_m + COUNTRRR;

PROBABILITY_MMMM_RRRR(COUNTMMMM,COUNTMMMR,COUNTMMRR,

### COUNTMRMR, COUNTMRRM, COUNTMRRR, COUNTRMMR,

COUNTRMRR,COUNTRRRR);

SUM_mmmm := SUM_mmmm + COUNTMMMM;

SUM_mmmr := SUM_mmmr + COUNTMMMR;

SUM_mmm := SUM_mmm + COUNTMMRM;

SUM_mmrr := SUM_mmrr + COUNTMMRR;

SUM_mmr := SUM_mmr + COUNTMRMR;

SUM_mrm := SUM_mrm + COUNTMRRM;

SUM_mmr := SUM_mmr + COUNTMRRR;

SUM_mmr := SUM_mmr + COUNTRMMR;

SUM_mmr := SUM_mmr + COUNTRMRR;

SUM_mm := SUM_mm + COUNTRRRR;

DEGRADATION(TOTAL_FRACTION);

SET_M_R;

COUNT_NUMBER_OF_M_R(NUMBER_OF_M,NUMBER_OF_R);

 $SUMD_m := SUMD_m + NUMBER_OF_M;$ 

SUMD_r := SUMD_r + NUMBER_OF_R;

PROBABILITY_MM_RR_MR(COUNTMM,COUNTRR,COUNTMR);

SUMD_mr := SUMD_mr + COUNTMR;

SUMD_mm := SUMD_mm + COUNTMM;

SUMD_n := SUMD_n + COUNTRR;

# PROBABILITY_MMM_RRR(COUNTMMM,COUNTMMR,COUNTMRR,COUNTMRM,COUNTRMR, COUNTRRR):

SUMD_mmm := SUMD_mmm + COUNTMMM; SUMD_mmr := SUMD_mmr + COUNTMMR; SUMD_mrm := SUMD_mrm + COUNTMRM; SUMD_rmr := SUMD_rmr + COUNTRMR; SUMD_mrr := SUMD_mrr + COUNTMRR; SUMD_rmr := SUMD_mr + COUNTRRR;

### PROBABILITY_MMMM_RRRR(COUNTMMMM,COUNTMMMR,COUNTMMRM,COUNTMMRR,

### COUNTMRMR, COUNTMRRM, COUNTMRRR, COUNTRMMR,

### COUNTRMRR,COUNTRRRR);

SUMD_mmmm := SUMD_mmmm + COUNTMMMM;

SUMD_mmmr := SUMD_mmmr + COUNTMMMR;

SUMD_mmm := SUMD_mmm + COUNTMMRM;

SUMD_mmrr := SUMD_mmrr + COUNTMMRR;

SUMD_mrmr := SUMD_mrmr + COUNTMRMR;

SUMD_mrm := SUMD_mrm + COUNTMRRM;

SUMD_mrrr := SUMD_mrrr + COUNTMRRR;

SUMD_mmr := SUMD_mmr + COUNTRMMR;

SUMD_mmr := SUMD_mmr + COUNTRMRR;

SUMD_mr := SUMD_mr + COUNTRRRR;

end;

TOTALDYADS := SUM_m + SUM_r;

TOTALTRIADS := SUM_mr + SUM_mm + SUM_rr;

TOTALTETRADS := SUM_mmm + SUM_mmr + SUM_mrm + SUM_mrr + SUM_rmr;

```
TOTALPENTADS := SUM_mmm + SUM_mmm +
```

TOTALDYADS_D := SUMD_m + SUMD_r;

TOTALTRIADS_D := SUMD_mr + SUMD_mm + SUMD_rr;

```
TOTALTETRADS_D := SUMD_mmm + SUMD_mmr + SUMD_mm + SUMD_mrr + SUMD_rrr + SUMD_rmr;
```

TOTALPENTADS_D := SUMD_mmmm + SUMD_mmmr + SUMD_mmrm + SUMD_mmrr + SUMD_mrmr + SUMD_mrrm + SUMD_mrrr + SUMD_mmrr +

SUMD_mm + SUMD_mm;

AVG_DEGRAD := TOTAL_FRACTION * 100/MOLECULES;

AVERAGE_PROPABILITIES(SUM_m,SUM_r,SUM_mr,SUM_mm,SUM_r,SUM_mmr,

SUM_mrm,SUM_rmr,SUM_mrr,SUM_rrr,SUM_mmmm,SUM_mmmr,

SUM_mmrm,SUM_mmrr,SUM_mrmr,SUM_mrrn,SUM_mrrr,SUM_rmmr,

# SUM_mmr,SUM_mm,TOTALDYADS,TOTALTRIADS,TOTALTETRADS, TOTALPENTADS):

WRITELN(LST);

wRITELN(LST, AVERAGE DEGRADATION PER PVC MOLECULE = ',AVG_DEGRAD:3:3,'%'); wRITELN(LST);

AVERAGE_PROBABILITIES(SUMD_m,SUMD_r,SUMD_mr,SUMD_mm,SUMD_rr,SUMD_mmm,

SUMD_mmr, SUMD_mrm,SUMD_rmr,SUMD_mrr,SUMD_rrr, SUMD_mmmm,SUMD_mmmr,SUMD_mmrm,SUMD_mmrr,

SUMD_mmr,SUMD_mm,SUMD_mmr,SUMD_mmr,SUMD_rmm,

SUMD_mm,TOTALDYADS_D,TOTALTRIADS_D,TOTALTETRADS_D,

```
TOTALPENTADS_D);
```

CHECKER := MOLECULES * (DEG_POLYM - 1);

T_CHECKCOUNT := 0;

J := 1;

REPEAT

WRITELN(LST);

.

```
WRITELN(Ist, TOTAL NUMBER OF ', J, ' CONSECUTIVE Ms = ',TOTAL_COUNTM[J]:6:0);
WRITELN(Ist, TOTAL NUMBER OF ', J, ' CONSECUTIVE Rs = ',TOTAL_COUNTR[J]:6:0);
T_CHECKCOUNT := T_CHECKCOUNT + J*TOTAL_COUNTM[J] + J*TOTAL_COUNTR[J]:
```

J:=J+1

UNTIL T_CHECKCOUNT >= CHECKER;

WRITELN(LST,

WRITELN(LST,' TOTAL Ms AND Rs = ', T_CHECKCOUNT:6:0);

-----"):

J := I;

 $STOP_PRINT := 0;$ 

total_double_bonds := 0;

REPEAT

WRITELN(LST, TOTAL NUMBER OF ', J,' CONSECUTIVE DOUBLE BONDS THAT WERE DEGRADED

=', COUNT_DOUBLE_BONDS[J]:5:0);



STOP_PRINT := STOP_PRINT + (J*COUNT_DOUBLE_BONDS[J]): STOPPER := STOP_PRINT * 100 /(MOLECULES*DEG_POLYM): total_double_bonds := total_double_bonds + count_double_bonds[j]: J := J + 1 UNTIL STOPPER >= AVG_DEGRAD; writeln(lst); avg_bonds := stop_print / total_double_bonds; writeln(lst,'Average bond degradation = ',avg_bonds:3:3); END,

.