POLYMERIZATION OF ACRYLONITRILE BY n-BUTYLLITHIUM

Patel

Chemistry

Raman Patel

POLYMERIZATION OF ACRYLONITRILE BY n-BUTYLLITHIUM

ABSTRACT

The polymerization of acrylonitrile by anionic initiation with n-butyllithium was investigated. The polymer yield and the molecular weights of the polymer samples obtained by varying the reaction time, acrylonitrile concentration, n-butyllithium concentration and polymerization temperature were determined and related to the polymerization conditions.

Both the polymer yield and molecular weight increased with time. Variation in the temperature of polymerization affected polymer yield, molecular weight, molecular weight distribution, structure and coloration in polyacrylonitriles. The kinetic molecular weight of a polymer was much lower than the viscosity average molecular weight.

An attempt was made to determine the order of the reaction with respect to monomer and to calculate the difference between the activation energy for propagation and termination. The observed low efficiency of n-butyllithium in chain initiation, the possibility of side reactions and the stability of the propagating centers during polymerization of acrylonitrile are discussed.

POLYMERIZATION OF ACRYLONITRILE BY n-BUTYLLITHIUM

by

Raman Patel, M.Sc. (Gujarat)

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

Department of Chemistry, McGill University, Montreal, Que., Canada

٢

March, 1968

ACKNOWLEDGEMENTS

The author wishes to acknowledge his indebtedness to:

Dr. R.F. Robertson

for guidance and assistance throughout this work;

Dr. D.A.I. Goring

for helpful suggestions;

Mr. H.G. Sanderson

for ultracentrifuge data.

The author is grateful to the National Research Council of Canada for a studentship (1964-67); to McGill University for a Graduate Fellowship (1963-64) and demonstratorships (1962-66); to the Chemistry Department for laboratory accommodation and use of its services and facilities.

TABLE OF CONTENTS

1 GENERAL INTRODUCTION Radical polymerization 2 4 Coordinate polymerization Cationic polymerization 5 7 Anionic polymerization 7 I. General 9 Initiation by electron transfer mechanism II. Initiation by nucleophilic attack of the III. 10 anion IV. Relative reactivity of the monomers, initiators and polymeric anions in 12 polymerization v. Effect of solvents on polymerization 15 16 VI. Propagation VII. Chain propagation and ion-pair formation 18 VIII. Chain termination in anionic polymerization .. 20 Stereospecific polymerization by anionic initiators 23 25 Equilibrium thermodynamics of polymerization Kinetics of polymerization and molecular weight 28 distribution Effect of impurities on molecular weight distribution 34 in polymers Chain initiation by n-butyllithium 37 44 Polymerization of acrylonitrile 44 Radical polymerization of acrylonitrile I. II. Radiation induced polymerization 45 46 III. The anionic polymerization of acrylonitrile ... IV. Polymerization of acrylonitrile with 50 n-butyllithium 54 The molecular weight averages The molecular weight distribution from sedimentation 58 velocity measurements 60 EXPERIMENTAL 60 A-I Treatment of glassware 60 The vacuum apparatus A-II 63 Removal of air from liquids A-III 64 A-IV Materials

page

TABLE OF CONTENTS (cont'd)

	A-V	n-Butyllithium	70
		a. Preparation of n-butyllithium	70
		b. Subdivision of n-butyllithium solution	72
		c. The analysis of n-butyllithium solution	73
	A-VI	Polymerization procedure	75
R	ESULTS .	• • • • • • • • • • • • • • • • • • • •	79
P	OLYMERIZA	TION OF ACRYLONITRILE	79
	B-I	Reproducibility of polymerization data	79
	B-II	Effect of different variables on polymerization	81
		a. Effect of time on polymerization	81
	•	b. Effect of initiator concentration on polymerization	81
		c. Effect of monomer concentration on	
		polymerization	84
		d. Effect of long reaction time on polymerization .	87
		e. Effect of temperature on polymerization	91
	ים דד י	I. Effect of solvents on polymerization	95
	B-111	The order of reaction with respect to monomer	95
	₽ - 1¥	The polymerization at different initiation and propagation temperatures	100
	BV	Formation of by-products during polymerization	100
	B-VI	The kinetic molecular weight, Mk	103
	B-VII	Comparision of experimental degree of polymerization, (DP), with theoretical degree of polymerization, $(DP^n) \exp t$	103
	B-VIII	The initiator efficiency in initiation reaction	106
CH	IARACTERI	ZATION OF POLYACRYLONITRILES	108
	C-I	Viscosity measurements	108
		a. Procedure	108
		b. Results	112
	C-II	Sedimentation velocity measurements	11 6
		a. Determination of sedimentation coefficients	11 6
		b. Inter dependence of sedimentation coefficient and intrinsic viscosity	122
		c. Branching in polyacrylonitriles	124

page

TABLE OF CONTENTS (cont'd)

· · · · · · · · · · · · · · · · · · ·	
d. The molecular weight distribution in polyacrylonitriles	126
C-III The spectroscopic measurements	136
a. Infrared	136
b. Ultraviolet	140
DISCUSSION	143
The time dependence of polymerization at -78° C.	143
Variation of percent yield of polymer with monomer concentration and the order of reaction at -78°C.	148
The effect of initiator concentration and $[M]_{o}/[I]_{o}$ on the yield and molecular weight of	150
polyacryionitriles obtained at -70 C.	150
The stability of a propagating center in polymerization	155
acrylonitrile polymerization	157
Effect of polymerization temperature	167
a. The dependence of yield and molecular weight on temperature	167
b. Heterogeneity in polymers prepared at different temperatures	170
c. Discussion on spectroscopic measurements on polyacrylonitriles	173
d. Color and branching in polyacrylonitriles	179
APPENDIX	185
A. Polymerization and viscosity data	- 185
B. Temperature dependence of polymerization in toluene and viscosity data on polyacrylonitriles	193
C. Sedimentation velocity data corrected for pressure effects	197
SUMMARY	200
CLAIMS TC ORIGINAL RESEARCH	204
SUGGESTIONS FOR FURTHER WORK	206
BIBLIOGRAPHY	208

page

LIST OF TABLES

TABLE	pa pa	ge
G-I	Rate propagation constant, k	17
G-II	Viscosity average molecular weights of polymers formed in the three day polymerization experiments	53
G-III	Comparision of the Mark-Houwink constants for PAN solution in DMF	57
I	Rate of polymerization at high initiator concentration - reproducibility	80 ⁻
II	Rate of polymerization at low initiator concentration - reproducibility	82
III	Effect of time on conversion and molecular weight	83
IV	Polymerization data for various initiator concentrations	85
v	Polymerization data - 50 hour experiments	90
VI	Temperature dependence of polymer yield	94
VII	Difference in activation energy (EE_)	97
VIII	Effect of different hydrocarbon solvents on polymerization and properties of the resulting polyacrylonitriles	98
IX	Rate propagation constant, k 1	01
X	Polymerization at different initiation and propagation temperatures	.02
XI	Kinetic molecular weight of polyacrylonitriles 1	.05
XII	Flow time of polyacrylonitrile solution	.09
XIII	Viscosity and molecular weight of polyacrylcnitriles . 1	15
XIV	Solution properties of polyacrylonitriles obtained at different temperatures	.23
xv	Degree of branching in polyacrylonitriles 1	27
xvi	H(Z) for different sedimentation times and H(Z) 1	30
XVII	Molecular weight averages and the heterogeneity index	.38
XVIII	The absorption coefficients of polyacrylonitriles 1	42
XIX	Degree of polymerization (constant $[M]_0/[I]_0)$ 1	52
APPEN	DIX	
A	Polymerization and viscosity data 1	85
В	Temperature dependence of polymerization in toluene and viscosity data of polyacrylonitriles	93
C	Sedimentation velocity data corrected for pressure effects 1	97

. .

LIST OF FIGURES

FIGUR		page
l	Ampoules	61
2	The vacuum apparatus	62
3	Unit for preparation of sodium dispersion	65
4	Solubility of water in acrylonitrile	67
5	Apparatus for drying acrylonitrile	68
6	Apparatus for preparation of n-butyllithium	71
7	Apparatus for subdivision of n-butyllithium solution	74
8	Apparatus for analysis of n-butyllithium	76
· 9	The polymerization apparatus	77
10	Effect of initiator concentration on polymerization	86
11 .	Effect of monomer concentration on polymerization (constant initiator concentration)	88
12	Effect of monomer concentration on polymerization (constant monomer to initiator ratio)	89
13	Conversion as a function of initiator concentration	92
14	Conversion as a function of monomer to initiator ratio	93
15	Semilogarithmic plots of molecular weight versus reciprocal of polymerization temperature	96
16	Semilogarithmic plots of polymerization rate data	99
17	Infrared spectrum of by-products obtained during polymerization	104
18	Plots of reduced viscosity against concentration for different polyacrylonitriles	111
19	Variation of molecular weight with percent conversion	114
20	Schlieren photographs of sedimentation velocity gradients	118
21	Sedimentation coefficients as a function of concentration	121
22	Log S ^o versus log[η]	125
23	Plot of data of Table XVI	132
24	Plot of $H(Z) = f(Z)$	133
25	Differential molecular weight distribution function	
	against molecular weight for polyacrylonitriles	137
26	Infrared spectra of polyacrylonitriles	139
- 27	Ultraviolet spectra of polyacrylonitriles	141

LIST OF SYMBOLS

Symbol	Meaning
a	Exponent in the empirical relationship between intrinsic viscosity and molecular weight
AN	Acrylonitrile
b .	Exponent in the empirical relationship between sedimentation coefficient and molecular weight
С	Concentration, gm/100 ml
C	Concentration, gm/1000 ml
(DP _n) _{calc}	Theoretical degree of polymerization
(DPn)expt	Experimental degree of polymerization
DMF	N,N'-dimethyl formamide
dx _i	Distance between a point, i, and the reference hole on the Schlieren photographs
Ε	Optical density
E p	Activation energy for propagation
E_t	Activation energy for termination
f	Fraction of initiator consumed in chain initiation
ΔF _p	Free energy change for polymerization
f(M)dM	Fraction of a polymer sample with molecular weight between M and $M+dM$
g'	Ratio of the intrinsic viscosity of a nonlinear to a linear polymer molecule of same molecular weight
g*(S)dS	Fraction of polymer with sedimentation coefficient between S and S+dS
∆ ^H p	Enthalpy change for polymerization
[1]	Initiator concentration, mole/liter
[I]°	Initial initiator concentration, mole/liter
k	Constant in the empirical relationship between intrinsic viscosity and molecular weight

k' Huggin

Kd

Ke

k.

k_s

M sv

 $\overline{\mathtt{M}}_{w}$

M_z

 $\overline{M}_{w}/\overline{M}_{n}$

Huggin's constant

K₁,K₂ Equilibrium constants

k Constant in the empirical relationship between sedimentation coefficient and molecular weight

k₃ Proportionality constant

K Rate constant for association of the ion-pairs

Rate constant for dissociation of the ion-pairs

Thermodynamic equilibrium constant for polymerization

Rate constant for initiation reaction

k Rate constant for propagation reaction

Arbitrary constant in empirical relation for concentration dependence of sedimentation coefficient

^k t	Rate constant for termination reaction						
k _{tr,M}	Rate constant for chain transfer to monomer						
^k tr,P	Rate constant for chain transfer to polymer						
^k tr,S	Rate constant for chain transfer to solvent						
יו	Thickness of the cell, cm						
[M]	Monomer concentration, mole/liter						
[M] _e	Equilibrium monomer concentration, mole/liter						
[M] ₀	Initial monomer concentration, mole/liter						
[M] _t	Monomer concentration (mole/liter) at time, t						
^M k	Kinetic average molecular weight						
M _n	Number average molecular weight						

Sedimentation viscosity average molecular weight

Weight average molecular weight

z-Average molecular weight

Heterogeneity index

MA Methacrylate

MAN Methacrylonitrile

MMA Methyl methacrylate

m Pressure dependence parameter

m Number of branched units per polymer molecule

m Number of moles of monomer that would react with one mole of monofunctional initiator

N Avogadro's number

PAN Polyacrylonitrile

PVC Polyvinyl chloride

P* Living j mer

R Gas constant

r Distance from center of rotation

 \overline{r}_i Distance from the maximum of the refrective index gradient curve to the center of rotation at time t.

S Sedimentation coefficient

S^o Sedimentation coefficient corrected for pressure effects

Sedimentation coefficient corrected for both pressure and concentration effects

T Temperature(^oK)

so

t

Temperature(^CC)

t Time, Sec or min.

T Ceiling temperature

T_f Floor temperature

THF Tetrahydrofuran

THP Tetrahydropyran

Y Distance parameter

 $Y_i(x)$ Height of the refrective index gradient curve at a distance x_i from the center of rotation

· .		
ightarrow	æ	kg.C
	б	Derived constant
	η	Viscosity of the solution
	η	Viscosity of the solvent
	η	Relative viscosity
• •	η _{εν}	Specific viscosity
	[ŋ] ⁻	Intrinsic viscosity
	[11] _b	Intrinsic viscosity of branched molecules
	[Ŋ] ₁	Intrinsic viscosity of linear molecules
	0	Phase plate angle
	ų	Pressure dependence constant
	H	Wavelength
	ν	Number of monomer molecules reacting with each initiator molecule
	$\overline{\mathcal{V}}$	Partial specific volume
	Σ	Summation sign
	Po	Density of the solvent medium
	P	Density of the solution
	ф.	- ^C 6 ^H 5
	Ŵ	Angular velocity, radian/sec.

· .

GENERAL INTRODUCTION

With the realization that anionic polymerization involving stable propagation centers could be used to prepare polymers having very narrow molecular weight distributions and stereoregular structures, much research has been conducted in this branch of polymer chemistry. The polymerization data collected to date indicate that a good number of unsaturated monomers (e.g. containing vinyl, diene or carbonyl type unsaturation) and cyclic ethers could be polymerized by the anionic mechanism, but it is not always easy to obtain polymers with a low heterogeneity index.

There are other types of mechanisms, namely radical, cationic and coordinate, by which a vinyl type monomer may be polymerized. Often a given monomer may be polymerized by more than one of these mechanisms. Styrene for example has been shown to polymerize by all the four mechanisms (1-4). A common feature of all these polymerization mechanisms is that a propagating center of a kinetic chain is retained by a single polymer molecule throughout the course of its growth (5). A complete description of such an addition system consists of four steps: initiation, propagation, termination and chain transfer. In some systems depropagation also plays an important role (6).

Before discussing the anionic polymerization at length, it would be desirable to discuss briefly other mechanisms which operate in the polymerization of vinyl monomers.

-1-

RADICAL POLYMERIZATION

- 2 -

The radical polymerization is characterized by the fact that the propagating center is a radical introduced in a variety of ways. An organic peroxide (e.g. benzoyl peroxide), an aliphatic azobisnitrile (e.g. azo-bis-isobutyronitrile) etc. which produce radicals upon decomposition may be used as initiators (7). The radicals interact with the monomer to produce propagating radical centers. Radicals produced by light, X-rays (5) or other high energy radiation (8) have also been found to initiate polymerization of some monomers.

Propagation occurs by the successive addition of a monomer to a growing radical center while the activity of the propagating center is preserved. At any stage during polymerization, the reaction mixture contains unreacted monomer, inactive high polymer and a very low concentration of the propagating radicals (often of the order of $\sim 10^{-8}$ mole). The propagating centers are very short-lived and may be destroyed by transferring their reactivity to a solvent, monomer, polymer or an impurity. If a newly produced radical center initiates a polymeric chain, then the transfer process is known as a chain transfer. Thus compounds known as 'chain transfer agents' may be added to control the molecular weight of polymers. If two growing polymeric radicals interact to terminate polymer chains, the interaction may be by a combination of the two radicals to give one polymeric molecule or by a disproportionation mechanism to give two polymer molecules, one with an unsaturated end group.

At any stage during reaction a polymerization mixture contains

a polymer the molecular weight of which depends upon the initial experimental conditions and does not vary appreciably with conversion. An exception to this may be found if polymerization is allowed to reach a high conversion. Under these conditions the active radicals may become trapped, reducing the rate of termination, while still possessing an appreciable propagation rate. As an example of this, North et al. (9) observed that the propagation rate constant, k_p , was independent of the viscosity of the reaction medium but the termination rate constant, k_t , decreased with increase in viscosity.

The polymerization involving a radical mechanism has been studied in greater detail than the other mechanisms of vinyl polymerization. Flory (5) has reviewed the methods of determining the various rate constants in radical polymerization and the interpretation of these measurements.

Polymers obtained by the radical mechanism are usually characterized by a most probable molecular weight distribution (i.e. $\overline{M}_w/\overline{M}_n = 2$), but polymers having both a broad and a narrow molecular weight distribution have been produced (10,11) by this mechanism. In 1944, Huggins (12) predicted on theoretical grounds that at lower temperatures radical polymerization should favor stereospecific placements. This was supported by the experimental findings of Fox and coworkers (13,14). That the radical polymerization at lower temperatures, favors syndiotactic placements has been realized both theoretically and practically (15).

- 3 -

COORDINATE POLYMERIZATION

The reaction product of a metal (group I to III) alkyl or aryl and a transition metal (group IV to VI) halide or ester, acts as an initiator for coordinate polymerization (16). The reaction product of triethyl aluminum with titanium tetrachloride is an example of an initiator which promotes this type of polymerization. The various initiators used for coordinate polymerization have been discussed by Stille (17).

In the coordinate polymerization, initiation and propagation mechanisms may be of the radical, cationic or anionic nature depending upon the ability of the propagating end to stabilize a radical, a cation or an anion (18). A common feature of all the coordinate propagation mechanisms is the ability of the initiator to ccordinate with the monomer and present it to the growing center to obtain a specific type of The decrease in the number of ways of approach of a monomer addition. to the propagating center increases the isotacticity of the resulting polymer (18). As a result of investigations with several coordinate type initiators, it has been realized that stereoregular polymers could be prepared with both homogeneous and heterogeneous initiators. The influence of heterogeneity on steric control can only be rationalized if a detailed characterization of the configuration of the active sites and the structures of the surface were possible. Surface chemistry has not yet advanced sufficiently to make the requisite information available (18). The influence of ionic factors on the steric control during polymerization has been discussed by Roha (19).

Termination may occur by the abstraction of a hydride ion from the last ligand of the propagating chain. However in a particular case of ethylene polymerization with bis-cyclopentadienyl titanium dichloride-dimethyl aluminum chloride complex (20), termination involved the reduction of two Ti^{+4} to Ti^{+3} proceeding simultaneously with the disproportion of two propagating chains.

There is little information in the literature on the molecular weights and the molecular weight distributions of polymers obtained by the coordinate mechanism. Using Gralen's method of analysis (21), Dawes (22) found that the heterogeneity index of polybutadienes obtained by the coordinate mechanism was between 1.03 and 1.16. Sakurada (23) studied the polymerization of \propto -methyl styrene with triethyl aluminum-titanium tetrachloride complex and found that the heterogeneity index of the polymer obtained was affected by the initiator aging temperature. When the initiator was aged at -78° C., the polymer obtained had a low heterogeneity index, but the use of the initiator aged at 0° C., gave a polymer having a broad molecular weight distribution.

CATIONIC POLYMERIZATION

Cationic polymerization may be propagated by a carbonium ion, an oxonium ion or any other ion carrying a positive charge. Isobutylene, vinyl ethers and other monomers which are basic in nature have been found to polymerize by this mechanism. The cationic polymerization may be affected by either of the following two types of the initiators:

- 5 -

(i) sulfur dioxide and highly polar organic compounds, e.g. triphenyl methyl chloride (24) which dissociate easily in ions, or
(ii) aluminum trichloride, boron trifluoride (25) etc., which are acids in the Lewis definition.

An appropriate coinitiator is always required with an initiator of the second type. Traces of water, alcohol, acetic acid etc. have been found to act as coinitiators. The exact role of a coinitiator in cationic polymerization is still unexplained. It might be to enhance the availability of a proton for initiation. This may be achieved by complexing with a gegenion, by self ionization or by solvation (18).

The addition of a proton or other cation to the monomer to convert it to an active propagation site characterizes a cationic initiation process. The ease with which a proton can be made available will determine the relative effectiveness of an initiator. The anion acts as the gegenion and remains in the vicinity of the propagating The repetitive addition of the monomer to the active center center. characterizes propagation. As in radical polymerization, chain termination does not occur when two propagating centers approach each other, since both have a similar positive charge. However a chain transfer to monomer, solvent or impurity might terminate a growing polymeric chain. The gegenion might abstract a proton from the propagating chain end to give an inactive polymer molecule with an unsaturated end group. The presence of terminal unsaturation has been confirmed by infrared measurements on polyisobutylenes obtained with boron trifluoride monohydrate (25).

- 6 -

In cationic polymerization, a low polymerization temperature and a reaction medium with high dielectric constant increase both the propagation rate and the polymer yield. Because of the dominant chain transfer mechanism, monomers polymerized by a cationic mechanism, usually give polydispersed polymers. Both the optically active polymers (26) and stereoregular polymers (27) have been prepared by using cationic initiators. In 1947-48 Schildknecht and coworkers (27) were the first to prepare stereospecific polyvinyl ethers with cationic initiators.

ANIONIC POLYMERIZATION

I. General

In studies on anionic polymerization, Ziegler (28) noted that it was necessary to consider only a two-step mechanism: initiation and propagation, to explain the polymerization of dienes initiated by alkali metals and alkyls of sodium and lithium. Further, in metal alkyl initiated polymerization, the propagation occurred at one end of a polymeric chain, whereas in alkali metal initiation, propagation occurred on both ends of the polymeric chains. It has been recognized that the initiation of anionic polymerization is accompanied by a color characteristic of the growing anion. Further the color would persist as long as the anion is not destroyed. In 1948, Robertson and Marion (29) were the first workers to report a characteristic red color in the sodium metal initiated polymerization of styrene. Upon addition of carbon dioxide to the reaction mixture, the polystyryl anions were destroyed and the color disappeared.

- 7 -

Evans, Higginson and Wooding (30) reported the first quantitative kinetic study on anionic polymerization of styrene initiated at -33°C., by potassium amide in liquid ammonia. They proposed a termination by chain transfer to ammonia in agreement with their data on the molecular weight and nitrogen content of the polymer. Higginson and Wooding (31) studied the polymerization of methyl methacrylate, acrylonitrile and styrene by a variety of basic initiators and correlated the pK value of the base with its ability to initiate the polymerization of vinyl monomers.

If the polymerization is initiated by alkali metals or organometallics of alkali and alkaline earth metals in an ether (at low temperature) or in a hydrocarbon solvent, the termination step may be eliminated and the propagating centers would continue to add all the available monomer. If more monomer is added to a reaction mixture containing the active anionic centers, the polymerization would be resumed again. Szwarc (32) labelled this type of polymer as 'Living Polymer'. Since the propagation is by the addition of monomer molecules to the ionic centers carrying a negative charge, the polymerization is also known as an 'Anionic Polymerization'.

Vinyl monomers having electrophilic substituent groups, e.g. ester (methacrylate), phenyl (styrene), nitrile (acrylonitrile), vinyl (butadiene), ketone (acetone), etc., and cyclic ethers have been polymerized by the anionic mechanism. The propagating center carrying a negative charge may be a carbanion, an alkoxide ion, an imine ion or other anion.

- 8 -

II. Initiation by Electron Transfer Mechanism

Alkali metals and alkali metal complexes with aromatic hydrocarbons initiate anionic polymerization by either a homogeneous or a heterogeneous electron transfer mechanism. Aromatic hydrocarbon-metal complexes in ether and alkali metals dissolved in liquid ammonia have been reported to initiate polymerization by a homogeneous electron transfer mechanism. Chain transfer to solvent (30) invariably occurs in alkali metal initiated polymerization in ammonia.

$$\sim CH_2 - CH_K^+ + NH_3 \xrightarrow{k_{tr,S}} \sim CH_2 - CH_2 + K^+ NH_2$$

The amide ion produced may or may not initiate the polymerization. The polymerization by alkali metal dispersion in hydrocarbon solvent is by a heterogeneous electron transfer mechanism.

The electron transfer mechanism which explains the sodium naphthalene initiated polymerization of styrene in tetrahydrofuran, and which has been generalized to explain the initiation by alkali metals (33,34), was proposed by Szwarc, Levy and Milkovitch (32).



- 9 -



where i and j are variables.

The radical end of a radical-ion usually disappears by dimerization (35), producing a dianion, which then propagates at both the ends by an anionic mechanism. However, from the analysis of styrene-methyl methacrylate copolymer obtained using lithium as an initiator, Tobolsky et al. (33) showed that propagation occurred at both anionic as well as radical ends. Szwarc et al. (36) have discussed in detail the problem of the formation and stability of radical-ions.

III. Initiation by Nucleophilic Attack of the Anion

Various covalent or ionic (alkali or alkaline earth) organometallic compounds (e.g. metal alkyl, alkoxide, amide, ketyl etc.) have been reported to initiate polymerization by nucleophilic attack of the anion on one end of the double bond. As a result of this attack, an anionic propagation center is formed which adds further monomer to give a high polymer. In the sodiomalonic ester initiated polymerization of acrylonitrile (37), the experimental findings could be explained by the following anionic mechanism:

(i) initiation:



- 10 -

(ii) propagation:





^{CH}2⁻

C2H500C





 Na^+ $\xrightarrow{\text{CH}_2-C-CH_2-CH-CH_2-CH-CH_2-CH-1}_{I}$ CH2 I CN $\sim CH_2-C=CH_2 + \sim CH-CH_2-CH_Na^+$

CN

CN

CN



In the above scheme, $k_{tr,M}$ and $k_{tr,P}$ are rate constants for chain transfer to monomer and polymer respectively.

The degree of polymerization calculated from this kinetic scheme would be given as,

$$\overline{DP} = \frac{k_p[M]}{k_{tr,M}[M] + k_{tr,P}[P]}$$

If \underline{x} is the fraction of monomer converted to polymer, one obtains

$$\overline{DP} = k_{p} / \{k_{tr,M} + k_{tr,P}(x/l-x)\}$$

The degree of polymerization so obtained was observed to be independent of monomer concentration but decreased with increasing polymer conversion.

IV. <u>The Relative Reactivity of Monomers, Initiators, and Polymeric</u> <u>Anions in Polymerization</u>

From a comparison of the reactivity ratios of different monomers in ionic copolymerization, Mayo and Walling (38) observed that the reactivity of monomers in anionic polymerization decreased in the following order:

vinylidene cyanide > acrylonitrile > methacrylonitrile > methyl methacrylate > styrene > butadiene.

Since these monomers have different substituent groups, they possess different polarities. If the same monomers are arranged according to increasing polarity (38,39) then,

vinylidene cyanide > acrylonitrile > methacrylonitrile > methyl methacrylate > styrene ≈ butadiene. The similarity between the order of variation of reactivity and polarity of the monomer leads one to conclude that the polarity and reactivity of a monomer are closely related in ionic polymerization. However other factors (e.g. dielectric constant of the reaction medium, solvation, side reactions, temperature etc.) affect the polymerization rate. Therefore it may not be always experimentally possible to find a variation in reactivity clearly related to polarity.

There seems to be a reciprocal relation between the reactivity of a monomer in initiation and the reactivity of the anion produced. A monomer which is more reactive in the initiation reaction produces a less reactive anion. Methyl methacrylate is found to be more reactive than styrene but less reactive than acrylonitrile (38). The relation between the reactivity of a monomer and an anion leads one to conclude that the styryl anion should be more reactive than an acrylonitrile or a methyl methacrylate anion. When 9-fluorenyllithium, which does not initiate the polymerization of styrene, was used to polymerize a mixture of styrene and methyl methacrylate, only the homopolymer of methyl methacrylate was obtained (40). The absence of styrene-methyl methacrylate copolymer proves that the polymerization of styrene cannot be initiated by methyl methacrylate anion. It has been reported (41,42) that styryl anion is sufficiently basic to initiate the polymerization of methyl methacrylate and acrylonitrile. When a mixture of styrene and acrylonitrile is polymerized with monofunctional anionic initiators, only homopolymer of acrylonitrile is obtained (43). However, if electron transfer anionic initiators are used, a small amount of copolymer is formed, probably by styrene addition on the radical end (44). Graham et al. (45) studied the polymerization of polar monomers initiated by polymeric carbanions in tetrahydrofuran and observed a qualitative relation between the initiation by a polymeric anion and the 'e' value (Alfrey-Price Q-e scheme) of a monomer.

The problem of the reactivity of the growing ion in ionic polymerization has been considered by Okamura and coworkers (46). Using the molecular orbital approach, the results of measurements of the propagation rate constant and a comparison of the ratios of chain transfer constants in polymerization, it was shown that the ion produced from the more reactive monomer was stable, but less reactive.

In a review article, comparing the reactivity of acrylonitrile, methyl methacrylate and styrene in initiation, Szwarc (47) concluded that acrylonitrile required a less basic and styrene a more basic initiator than that required for methyl methacrylate.

When different alkoxides with the same counterion were used as initiators in the polymerization of acrylonitrile, the reactivity of the alkoxide was found to increase with a decrease in the acidity of parent alcohol (48). The basic strength of anionic initiators derived from hydrocarbons has been shown to vary in the order (49): butyllithium > phenyllithium > 9-fluorenyllithium > cyclopentadienyllithium.

During the polymerization of dienes, Hsieh (50) found that the rate of initiation of polymerization with different butyllithiums varied with the structure of the butylanion in the order:

sec-butyllithium >tert-butyllithium >i-butyllithium >n-butyllithium.

Goode, Snyder and Fettes (51) studied the polymerization of methyl methacrylate in liquid ammonia. The rate of polymerization and percent conversion were found to decrease, with change in the counterion of the amide initiator in the order:

 $\operatorname{KNH}_2 > \operatorname{NaNH}_2 > \operatorname{LiNH}_2 > \operatorname{Si}(\operatorname{NH}_2)_2.$

V. Effect of Solvent on Polymerization

In the polymerization of butadiene and isoprene by butyllithium the rate of initiation was higher in toluene and followed the order (50):

toluene \gg n-hexane > cyclohexane.

From the experimental data, on n-butyllithium initiated polymerization of styrene in benzene at 0° C., Worsfold and Bywater (52) showed that the rate of initiation was low. At high initiator concentration, the polymerization was complete and the initiator was not completely consumed.

The absorption spectra of polystyryl ion with different counterions (e.g. Na⁺, K⁺, Ii⁺) were measured in benzene, n-hexane and tetrahydrofuran. From the close similarities in the spectra obtained, Bywater, Johnson and Worsfold (53) concluded that the alkali metal-carbon bond had the same structure, and appeared to be independent of counterion or solvent. Similar results were obtained from spectroscopic measurements on polybutadienyl and polyisoprenyl anions (53).

VI. Propagation

A propagation step is characterized by the repeated addition of the monomer while the reactivity of the growing center is maintained. The counterion remains in the vicinity of the anion and may be very closely associated with it. The extent to which association affects the rate of propagation is governed by the degree of association which in turn is determined by the counterion, solvent, temperature and the presence of other electrolytes. Solvents influence the propagation through their different dielectric constants and their tendencies to solvate an ion to varying degrees.

Data on the propagation rate constant, k_p , at 25°C., for styrene addition to styryl anions with different counterions in different reaction media (54-56) have been collected in Table G-I. From these data it is seen that k_p varies with both the solvent and the counterion. The difference in dielectric constants and the capacity of solvents to solvate different ions to different extent cou'd lead to these results (Table G-I). The Li⁺ might be highly solvated in THF while poorly solvated in dioxane. The charge separation would obviously be influenced by the different degrees of solvation.

For a given counterion and solvent, styrene was found to be approximately 100-fold more reactive than \ll -methyl styrene. The combined electronic and steric effects of the methyl group (55) seem to cause \ll methyl styrene to be less reactive.

- 16 -

TABLE G-I

Rate Propagation Constant, k

Solvent:	THF (56)*	THP (55)*	Dioxane (55)*	Dioxane (56)*	Benzene (54)*	
Counter Ion	k_p (l. mole ⁻¹ sec ⁻¹)					
Li ⁺	160.0	-	-	0.9	23.0	
Na	80.0	13.0	6.5	3.5	-	
к+	50.0	68.0	28.0	19.8	47.0	
Rb ⁺	50.0	76.0	34.0	21.5	24.0	
Cs ⁺	25.0	49.0	15.0	24.5	18.0	

* Reference numbers

THF - Tetrahydrofuran

THP - Tetrahydropyran

VII. Chain Propagation and Ion-pair Formation

Medvedev et al. (57) have shown from conductometric studies that the ion pair dissociation constant, K_d , for the reaction,

 $\sim M^{-}C^{+}$ $\xrightarrow{K_{d}}$ $\sim M^{-} + C^{+}$

where \underline{M}^+ represents a polystyryl or polybutadienyl ion was highest when the gegenion (C^+) was $\underline{\text{Li}}^+$, and decreased in the order:

$$\text{Li}^+ > \text{Na}^+ > \text{K}^+$$

The value of K_d was higher in dimethoxy ethane than in tetrahydrofuran. This was probably a reflection of the increased dissociation of the ion pair with solvation of the cation.

Geacintov, Smid and Szwarc using a flow technique (58), which allowed the study over a short reaction interval (\ll 1 sec), observed that the polymerization reaction was first order in styrene in THF at 25°C., but the value of the rate constant, k_p , decreased with increasing the concentration of the living ends. This was later found to reflect the existence of different types of propagation centers on which the rate of addition of monomer could vary by a factor of 10³ (56,59). Typically, polystyryl sodium has been shown to exist as $\sim M^{-}Na^{+}$ (closely associated ion pair) and $\sim M^{-}//Na^{+}$ (solvent separated ion pair) or $-M^{-} + Na^{+}$, (free ions), all of which propagate at different rates. The rate propagation constants for $-M^{-}M^{-1}$ respectively (60) (where VM⁻ represents vinyl mesitylenyl anion). The different forms of a propagating center satisfy the equilibrium:



where K_d and K_a are the dissociation and association constants respectively. On the addition of an electrolyte (e.g. sodium tetraphenyl boron, NaBPh₄) which does not react with the cation or polymeric anion and for which the dissociation constant, K_d , is high, the equilibrium should shift to the left, decreasing the concentration of $\sim M^- + Na^+$, by the common ion effect. The rate constant K_a and K_d can be determined (61) from the overall propagation rate constants and the molecular weight distribution of polymers obtained at different electrolyte concentrations.

The overall propagation rate constant, k_p , for the addition of styrene to polystyryllithium in benzene was measured by Bywater et al. (52) and found to be first order in monomer and half order in living ends. This indicates that the polystyryl ions were associated as dimers. Viscosity (3) and light scattering measurements (62) on living and dead polymer obtained in hydrocarbon solvents led to the same conclusion. On the other hand, with THF as a solvent for this reaction, association in the living polymers was negligible or absent (63).

The propagation rate constant of styrene in benzene increases with increase in temperature (52). In the alkyllithium initiated polymerizations, Lewis acids or bases probably form complexes with the growing ends. In hydrocarbon solvents, the addition of a Lewis acid decreases the rate of polymerization whereas the addition of a Lewis base increases the rate (64-68).

- 19 -

Zilkha et al. (69-71) have investigated the effect of solvents on the lithium-organyl initiated polymerization of styrene, acrylonitrile and methyl methacrylate and observed the marked influence of solvents on the molecular weights of the polymers obtained.

VIII. Chain Termination in Anionic Polymerization

The propagation process ceases if the supply of monomer is exhausted or if an event occurs in which the growing center loses its activity. The anionic center may lose its activity with or without generation of a new active center. If a new active center is generated with the loss of activity of an existing propagation center, then the process is known as a chain transfer. In anionic polymerization termination may be by a chain transfer to monomer, polymer, or solvent. Termination is also possible by isomerization of the growing anionic end or a reaction of the active center with an impurity present in the reaction mixture. In anionic polymerization termination by combination or disproportionation does not occur. The collision between two anionic ends does not lead to termination because of repulsion. Overberger et al. (72) and Szwarc (47) have discussed in detail the different modes of termination.

Oxygen, carbon dioxide, or any proton-donating impurity, if present in the system, can terminate the polymerization. For example, if water is added to the reaction mixture, it will react with a carbanion as follows:

 \sim CH₂-CH Na⁺ + H₂O \sim CH₂-CH₂ + OH⁺ Na⁺

If the polymerization is conducted in such solvents as ammonia, proton transfer from ammonia to carbanion terminates the growing chain. A new carbanion may be generated by the amide ion (31).



In polymerization of vinyl mesitylene in tetrahydrofuran (THF) proton transfer from the monomer with the generation of an inert ion (I) was shown to terminate polymerization (60) through the following proposed mechanism:



Spectroscopic measurements on the reaction mixture supported this mode of termination.

A chain transfer to solvent was shown to occur in the polymerization of butadiene and isoprene in tetrahydrofuran (73). In the biphenyl sodium initiated polymerization of acrylonitrile in a mixture of (1:1) DMF and THF at -78° C., it has been suggested (74) that a chain transfer to polymer occurs by abstraction of a proton. The experimental evidence for this chain transfer mechanism can be found in a comparison of the number and viscosity average molecular weights and an examination of IR spectra of the polyacrylonitriles obtained.



The anion II would add more monomer to give a branched polymer. Since the polymer was soluble in DMF, the possibility of a three-dimensional network is eliminated. Polystyryl anions, on standing, show changes in the UV spectra and become incapable of adding further monomer (75). This was explained by the following reactions of polystyryl anions (76):





The carbanion (III) produced is incapable of adding styrene. A hydride transfer has been proposed as a mode of termination in the formation of polyacrylonitrile by sodiomalonic ester (37) and sodium triethyl thioisopropoxy aluminate (77) in DMF.

In the methyl methacrylate polymerization, a carbanion may be terminated if a carbonyl addition occurs instead of vinyl addition (51):



Pseudo-termination of the growing carbanion to form a cyclic complex (IV) has been proposed to explain data obtained from the 9-fluorenyllithium initiated polymerization of methylmethacrylate (78): OMe 0



Szwarc (47) has proposed the following isomerization mechanism in acrylonitrile polymerization:



The weak imine ion (V) is considered to be incapable of adding monomer.

STEREOSCOPIC POLYMERIZATION BY ANIONIC INITIATORS

When alkyllithiums or aryllithiums were used as initiators in toluene, acrylic esters were polymerized to give isotactic polymers. The addition of THF to the reaction mixture was found to decrease the iso-
tactic placements in polyacrylates. Polymers prepared in 1,2-dimethoxy ethane or THF were characterized by a highly syndiotactic structure (79-81).

To relate the stereoregularity of the polymers with the different experimental conditions Tsuruta and Furukawa (82) have polymerized acrylic esters by a variety of organo-metallic initiators in different solvents.

Lithium or organolithium initiators in hydrocarbon media have been shown to produce highly cis-1,4-polyisoprene with some 3,4-addition but no trans-1,4- or 1,2-addition (83,84). The use of sodium or potassium as the counterion in hydrocarbon solvents gives 45-60% trans-1,4-polyisoprene, 37-49% cis-1,4-polymer and the remainder 3,4- and 1,2-polyisoprene. If ethers or amines are used as the solvents, 1,4-isoprene addition decreases to zero, while the proportion of 3,4-addition increases with all the counterions noted above. Stearns and Forman (83) in a study of the lithium catalyzed polymerization of isoprene, noted that a specific solid surface was not necessary to produce a stereoregular polymer structure. Rather the electronic structure of the lithium atom, the molecular structure of isoprene and their proper interaction would lead to stereoregular placements.

From a study of butadiene polymerization Hsieh (84) showed that 1,4-addition decreased with a rise in the polymerization temperature. In hydrocarbon solvents butadiene polymerized to give 50% cis-1,4-addition, $9 \sim 10\%$ 1,2-addition and the remainder trans-1,4-addition polymer (84).

During studies on polymerization of 4-methyl-1,3-pentadiene with radical and anionic initiators, Livshits and Stepanova (85) observed that about 88% polymer had 1,4-placement with n-butyllithium.

- 24 -

Each of these examples leads to the conclusion that under the proper experimental conditions, the propagation step in anionic polymerization can be controlled to produce a specific type of monomer addition.

EQUILIBRIUM THERMODYNAMICS OF POLYMERIZATION

In the absence of chain termination, a growing active center may bring about the depropagation reaction:

$$P_{j}^{*} + M \xrightarrow{k_{p}} P_{j}^{*} \qquad (1)$$

where \underline{M} and \underline{P}_{k}^{*} are the monomer and the living \underline{j} mer, and k and k are j the rate constants for propagation and depropagation respectively.

From (1) the equilibrium constant, K_{e} , is given as,

$$K_{e} = k_{p}/k_{d}$$
 (2)

In relation (1) for large <u>j</u>, K_e and the monomer concentration at equilibrium, $[M]_e$ can be expressed as (86):

$$K_{e} = 1/[M]_{e}$$
(3)

At equilibrium, the rate of propagation and depropagation would be equal and the free energy change for the polymerization reaction would be zero. The equilibrium constant K and the standard free energy change, ΔF_{p}^{0} , are related in,

$$\Delta F_{p}^{o} = -RT \ln K_{e} \qquad (4)$$

By determining K_e at different temperatures the enthalpy change, ΔH_p , and entropy change, ΔS_p , for the polymerization could be calculated

from

$$\frac{d\ln K_e}{dT} = \Delta H_p / RT^2$$

 $\Delta F_{p} = \Delta H_{p} - T \Delta S_{p}$ (5)

A basic approach to the thermodynamics of addition polymerization was presented by Dainton and Ivin (6). A method of determining the ceiling temperature, a temperature above which polymerization does not occur, was described by these authors.

For a propagation to occur, the free energy change, ΔF_p , must be negative. As discussed by Szwarc (87), depending upon the sign of ΔH_p and ΔS_p in a polymerization reaction, the following four possibilities could be encountered.

(i) In most polymerization systems, ΔH_p and ΔS_p have been found to be negative. Under these conditions when the polymerization temperature reaches a ceiling temperature, T_c , given by

$$T_{c} = \Delta H_{p} / \Delta S_{p}$$
 (6)

the value of ΔF_p would be zero. No polymerization would occur above the ceiling temperature since ΔF_p becomes positive. (ii) When ΔH_p and ΔS_p are both positive, polymerization would be possible only above the floor temperature, T_f , defined by

$$T_{f} = \Delta H_{p} / \Delta S_{p}$$
(7).

(iii) If $\Delta H_p < 0$, $\Delta S_p > 0$ then ΔF_p would be negative at all reaction temperatures. The polymerization reaction would thus be favored at all temperatures.

(iv) If $\Delta H_p > 0$ and $\Delta S_p < 0$, ΔF_p would be positive at all temperatures

and depropagation would become the spontaneous process.

In a study of the polymerization of \ll -methyl styrene initiated by sodium naphthalene, Worsfold and Bywater (86) established that only a small amount of monomer could be converted to polymer even though the polymeric chains were active and still capable of adding further monomer. When polymerization experiments were made at 0°C., equilibrium was reached within 16 hours and no further increase in polymer yield was possible even after a reaction time of 124 hours. The equilibrium constants, obtained in three different laboratories (86,88,89) for sodium naphthalene initiated polymerization of \approx -methyl styrene, were plotted against 1/T by Szwarc (87). From the mean plot the values of ΔH_p and ΔS_p were calculated as -7.5 K.cal/mole and -26.5 e.u. respectively.

Eisenberg et al. (90,91) showed that the experimental data from the equilibrium polymerization of \propto -methyl styrene, could be treated by a more general theory of equilibrium polymerization. Good agreement was obtained between the theoretical calculations and the experimental results when both the initiation and the propagation equilibria were considered.

A spectroscopic method has been used to determine the concentration of monomer at equilibrium, if it is too low to be estimated accurately by other analytical methods. The concentration of styrene in equilibrium with living polymer at room temperature is too low to be estimated even by spectroscopy. Therefore to study the equilibrium,

$$\begin{array}{c} R-(CH_2-CH_-)CH_2-CH_- + CH_2=CH_{k_1} & R-(CH_2-CH_-) & CH_2-CH_{k_2} \\ \hline & & & & & \\ \Phi & & & & & \\ \end{array}$$

- 27 -

in styrene polymerization spectroscopically, Bywater et al. (92) conducted experiments in the temperature range ~ 100 to 115° C. with benzene and cyclohexane as solvents. The restrictions in the use of solvents and possible side reactions e.g. isomerization, have also been discussed in this paper.

The existence of a floor temperature has been suggested in the polymerization of t-butyl vinyl ketone (93) since both ΔH_p and ΔS_p were found to be positive. Further, a floor temperature has been reported for the equilibrium polymerization of sulfur (94).

An increase in the pressure of a reaction system has been reported to elevate the ceiling temperature for polymerization (95). This may prove useful in the study of anionically polymerizable monomers (e.g. 1,1-diphenyl ethylene) which are difficult to polymerize because of steric hindrance (87).

KINETICS OF POLYMERIZATION AND THE MOLECULAR WEIGHT DISTRIBUTION

When there is no termination mechanism in polymerization, the propagation would cease if the supply of monomer was exhausted. Under these circumstances, only two steps, initiation and propagation need to be considered. The initiation step may be represented by

$$A^{-}B^{+} + M \xrightarrow{k} AM_{1}^{-}B^{+}$$
(8)

and the propagation step by

$$AM_{\overline{j}}B^{+} + M \xrightarrow{k_{p}} AM_{\overline{2}}B^{+}$$
$$AM_{\overline{j}-1}B^{+} + M \xrightarrow{k_{p}} AM_{\overline{j}}B^{+}$$
(9)

where AB and \underline{M} are the initiator and monomer respectively, and where $k_{\underline{i}}$ and $k_{\underline{o}}$ are the rate constants for initiation and propagation.

The absence of termination in a polymerization system, leads to a number average degree of polymerization, $(DP_n)_{calc.}$ given by (32):

$$(DP_n)_{calc} = N / k_3 \cdot n$$
 (10)

where \underline{N} is the total number of monomer molecules, \underline{n} is the number of propagating centers and k_3 is a proportionality constant with a value of unity or one half depending upon whether the propagating centers are located on one or both ends of the polymeric chains. An intermediate value of k_3 would indicate the presence of polymeric anions in the reaction mixture with propagation center at one and both ends of the polymeric chain.

In the absence of termination the degree of polymerization determined experimentally, $(DP_n)_{expt}$ would be equal to $(DP_n)_{calc}$ and should be independent of polymerization temperature, rate of initiation and of propagation.

Over a temperature range 0 to -78° C., Szwarc et al. (96) observed $(DP_n)_{calc} \approx (DP_n)_{expt}$ for the sodium naphthalene initiated polymerization of styrene in THF. Morton et al. (3) determined the viscosity average molecular weights of polystyrene prepared using ethyllithium and butyllithium and found them to be approximately equal to the number average molecular weights calculated from the initiator concentrations and polymer yield. Worsfold and Bywater (52,66) have reported similar results in studies of the anionic polymerization of styrene.

Tsukamoto (74) polymerized acrylonitrile with biphenylsodium in a mixture of DMF and THF at -78° C. The $(DP_n)_{expt}$ determined from osmotic measurements on the polyacrylonitriles obtained were shown to be equal to the value of $(DP_n)_{calc}$.

If all the initiator participates in the initiation reaction, the number of propagating centers, n, would be equal to the number of initiator molecules. In actual practice the residual impurities would destroy an equivalent amount of the initiator, and prevent production of an equivalent number of active centers. This would lead to an increase In a similar way if an initiator is not consumed completely in (DP_n)_{expt}. in the initiation reaction, a higher $(DP_n)_{expt}$ would be obtained than that calculated from the initial initiator concentration and the polymer yield. The incomplete consumption of the initiator may be due to a slow initiation rate compared to the propagation reaction or a side reaction of the initiator with monomer or with polymer. Molecular weights and therefore $({
m DP}_n)_{
m expt}$ determined for polymers prepared with anionic initiators have been found, in the polymerization of styrene (97), methylmethacrylate (78), acrylonitrile (43), and isoprene (65), to be higher than the $(DP_n)_{calc}$ obtained from equation (10). The deviation in $(DP_n)_{expt}$ could be either the result of incomplete participation or the occurrence of side reactions, or both.

From equations (8) and (9) the rate of disappearance of initiator and monomer can be given as:

$$-d[I]/dt = k_i[M][I]$$
(11)

$$-d[M]/dt = k_{i}[M][I] + k_{p}[M]([I]_{o} - [I])$$
$$= (k_{i} - k_{p})[M][I] + k_{p}[M][I]_{o} \qquad (12)$$

In these equations [I] and [M] are the initiator and monomer concentrations at time, \underline{t} , and [I]_o is the initial initiator concentration.

Bauer and Magat (98) have numerically integrated equations (11) and (12) to give

$$\frac{\left[M\right]_{o} - \left[M\right]}{\left[I\right]_{o}} = \frac{k_{p}}{k_{i}} \left\{ \ln(1-f)^{-1} - f \right\} + f \qquad (13)$$

where <u>f</u> is the fraction of the initiator consumed in the initiation reaction and $[M]_{o}$ is the initial monomer concentration.

Szwarc (47) calculated values of \underline{f} for different values of k_p/k_i and $(\underline{M}_o - \underline{M})/[\underline{I}_o$ and showed that for $k_p \gg k_i$ some of the initiator would remain unreacted after all the monomer has been polymerized. This could be related to competition between the initiator and the living \underline{j} mer, for the monomer. The \underline{j} mers would compete more efficiently with the progress of the polymerization reaction. This has been confirmed experimentally in studies of sodium naphthalene (99) and butyllithium (97) initiated polymerization of styrene.

For a polymerization system, in which all the growing chains have an equal opportunity to add monomer and in which initiation is only slightly slower than propagation, Flory (100) has derived the relation,

$$\overline{M}_{w}/\overline{M}_{n} = 1 + \frac{\nu}{(1+\nu)^{2}}$$
(14)

where $\underline{\mathcal{V}}$ is the number of monomer molecules reacting with each molecule of initiator.

This relation assumes termination to be absent. For larger values of $\underline{\mathcal{V}}$ in equation (14), the heterogeneity index would be very close to unity. In actual investigations, low values (close to unity) of the heterogeneity index have been obtained. These will be discussed shortly.

Gold (101) has derived relations to calculate molecular weight distributions from kinetic data and showed the nature of the molecular weight distribution to be dependent on $[I]_o$, $[M]_o$ and k_p/k_1 . Further for $k_p/k_1 \gg 1$, the heterogeneity index was shown to approach a value 1.4. For $k_p = k_1$, the derivation by Gold (101) was identical with equation $(\underline{14})$ above. Glusker et al. (78) have showed that in a non-terminating polymerization, when $k_p \gg k_1$, the value of $\overline{M}_w/\overline{M}_n$ was equal to or less than 4/3.

Cowie, Worsfold and Bywater (102) analyzed polystyrenes obtained by butyllithium initiation and found the osmotically determined number average molecular weight, \overline{M}_n , to be approximately equal to the weight average molecular weight, \overline{M}_w , determined by light scattering. The value of the heterogeneity index was found to be between 1.02 and 1.06 for different samples of anionic polystyrenes. McCormick (103) estimated the heterogeneity for polystyrene from sedimentation velocity data and found the value to be in the range 1.02 to 1.09. Morton and coworkers (104) also reported the preparation of polystyrenes with a narrow molecular weight distribution, in THF at -78° C., and in benzene at 0°C. By fractionation of polyacrylonitriles obtained with n-BuLi, at -78°C., Miller (105) showed that the heterogeneity index was 1.2 to 1.3. No heterogeneity indices have been reported in the literature for polyacrylonitriles obtained with anionic initiators at other temperatures.

If $k_i < k_p$, the molecular weight distribution would be broad. However if a seeding technique is used, a narrow molecular weight distribution may be obtained. In the seeding technique, a small portion of the monomer is added to the initiator solution at higher temperatures. The reaction is allowed to proceed until all the initiator is consumed. The reaction mixture is then cooled to a desired temperature, more monomer is added and the polymerization is allowed to go to completion. By employing this technique Morton et al. (3,67) obtained, in hexane with alkyllithium initiators, polyisoprene having a heterogeneity index of 1.20. The polyisoprene prepared without the use of the seeding technique had a heterogeneity index of 1.70 to 2.10. The seeding technique cannot be used if the initiator reacts with the functional group of the monomer to give by-products or if a carbanion produced is unstable. For example, in potassium amide initiated polymerization of methacrylonitrile, the anion has been shown to react with the nitrile group of the polymer or monomer (34). In a similar way phenyllithium has been found to react with the ester group of the methyl methacrylate (106).

Hsieh and McKinney (107) have determined the molecular weight distribution in polymers of styrene, isoprene and butadiene prepared with butyllithium (108). The heterogeneity indices calculated from analysis of these polymers were found to be less than 1.12 for $k_i/k_p \ge 1$. For $k_i/k_p < 1$, the polymers were more heterogeneous.

A similar finding has been reported by Brower and McCormick (109), who observed that polystyrenes obtained from different solvents with different anionic initiators had different values of the heterogeneity indices. When toluene was used as a solvent, the anionically prepared polymethyl methacrylate had a heterogeneity index of about 55 (78). The addition of THF (20%) to toluene reduced the heterogeneity index of the polymer to 27. It is evident that in actual practice the experimental values of the heterogeneity index for $k_i/k_p < 1$ are in poor agreement with the theoretical relations (78,101,107,109).

EFFECT OF IMPURITIES ON MOLECULAR WEIGHT DISTRIBUTION IN POLYMERS

When a solvent and an initiator are mixed, the impurities present in the solvent might react with the initiator to destroy an equivalent amount of the initiator. If a monomer free from impurities is added to the reaction mixture and if the solvent-initiator interaction products do not interfere with the polymerization, a polymer having a low heterogeneity index but $(DP_n)_{expt} > (DP_n)_{calc}$ would be obtained. If a monomer containing impurities is added to the reaction mixture, a small portion of the impurities would react with initiator and the remaining portion of the impurities would react with the growing polymeric chains to produce a polymer having a broader molecular weight distribution. If the solvent and monomer are first mixed and the initiator is subsequently added, impurities from both the solvent and the monomer would contribute to the termination of the growing chains and consequently the molecular weight distribution in the resulting preparation would be broader. The effect of impurities on the molecular weight distribution in anionic polymerization has been considered by Szwarc and Litt (110) and in greater detail by Wenger et al. (111). By considering the probability of the reaction of an impurity with the growing anion at a particular impurity level, Wenger et al. (111) showed that the heterogeneity index deviated from unity to a greater extent for anionic chains propagating at one end than for those propagating at both ends. By carefully removing impurities from the reactants Wenger (112) prepared polystyrene having a heterogeneity index of 1.02 and poly \propto -methyl styrene having a heterogeneity index of 1.05-1.06.

When propagation occurs at both ends of polymeric chains, the impurities present may terminate some of the chains at one end only, without affecting the propagation reactivity of the other end. The molecular weight of polymeric chains propagating at one end would be one half the value of those propagating at both ends. Polymers prepared with bifunctional initiators (e.g. electron-transfer type initiators) have been found to have this bimodal molecular weight distribution (112).

From a study on the polymerization of styrene in different solvents Brower and McCormick (109) concluded that solvents promoting rapid initiation and relatively slow propagation gave a polymer having a low heterogeneity index. The solvents arranged in the order of promotion of rapid initiation and slow propagation would form the series: dioxane > THF > ethylene glycol dimethyl ether > diethylene glycol dimethyl ether.

Litt and Szwarc (113) have considered the effect of chain

- 35 -

transfer to monomer on the molecular weight distributions in polymers prepared by the anionic mechanism. From probability considerations, the degree of polymerization, $(\overline{\rm DP}_n)$, and weight average degree of polymerization, $(\overline{\rm DP}_w)$, were given as

$$\overline{DP}_{n} = [p/m + (1 - p)]^{-1}$$
 (15)

$$\overline{DP}_{w} = [(1+p)/(1-p)] - [2p(1-p^{m})/(1-p)^{2}m] \quad (16).$$

In these equations \underline{m} is the number of moles of monomer that would react with each mole of monofunctional initiator. \underline{p} and $\underline{l-p}$ represent the probability that the monomer undergoes polymerization and chain transfer with the carbanion. When $\underline{p} = 1$, equations (15) and (16) would give

$$\overline{\mathrm{DP}}_{\mathrm{n}} = \overline{\mathrm{DP}}_{\mathrm{w}} = \mathrm{m}$$

and a monodisperse polymer would be obtained. For values of $m(1-p) \gg 0.1$, equation (16) has been approximated (112) as

$$\overline{\rm DP}_{\rm W} = 2/(1-{\rm p})$$
 (17).

A chain transfer to monomer has been reported for the anionic polymerization of acrylonitrile (42).

Various authors have given theoretical treatments to different aspects of anionic polymerization. Figini and Schulz (114) have reported that improper mixing could contribute to the inhomogeneity in the molecular weight distribution of polymers obtained by anionic initiators. An expanding drop model of mixing was used as a basis for deriving the mathematical relations. Litt (115) has used a laminar flow model to explain the effect of improper mixing on the molecular weight distributions in the polymers. Zilkha and coworkers (42) have shown that the yield and molecular weight of the polymer depended upon the rate of monomer addition to the initiator solution.

By assuming initiation to be instantaneous and the initiator to be monofunctional, Coleman (116) has mathematically correlated irreversible termination with the chain length distribution. Stockmayer (117) has considered the polymerization system where the contribution from the depropagation reaction is too large to be neglected in the derivation of the kinetic relations. The effect of delayed addition of the initiator has been discussed by Eisenberg and McQuarrie (118) and relations have been derived for the calculation of the heterogeneity index and molecular weight distribution in the polymer.

In summary, one can conclude that the probability of obtaining polymers having a low heterogeneity index depends directly upon the attainment of the following experimental conditions: (i) absence of chain termination - incidental or otherwise, (ii) absence of chain transfer reactions, (iii) rate of propagation to be slower than the rate of initiation, (iv) negligible depropagation under experimental conditions, (v) uniform mixing of the reactants, and (vi) uniform conditions with regard to polymerization temperature.

CHAIN INITIATION BY n-BUTYLLITHIUM

In 1917, Schlenk and Holtz (119) prepared simple alkyls of

lithium from the reaction of the organomercury compounds with lithium metal. These alkyllithiums have been known to initiate the polymerization of dienes since 1928 (28). However it was not realized until 1956-57 (120,121) that dienes polymerized by lithium and its alkyl compounds give highly ordered structures. Since then the detailed polymerization of alkyl vinyl ketones, acrylic esters, dienes, vinyl nitriles, styrenes, etc., have been studied using these organometallics as initiators.

In a kinetic study on the polymerization of non-polar monomers with n-Buli in hydrocarbon media, a plot of the overall rate of monomer consumption was found to have the S-shape, characteristic of slow initiation (122,68). O'Driscoll and Tobolsky (68) suggested that a small fraction of monomeric n-Buli, in equilibrium with the associated form of n-Buli, was an active initiator. The degree of polymerization calculated from the known concentrations of the monomer and the initiator was lower than that of the polystyrene actually obtained (97). This was taken to indicate that even at the conclusion of polymerization, some of the initiator remained unreacted.

Worsfold and Bywater (52), in a study of the polymerization of styrene, followed spectroscopically the rate of initiation and the rate of disappearance of monomer and interpreted the results in terms of the following scheme:

Initiation:

-d[BuLi] /dt = k_[BuLi]^{0.15}[styrene]

Propagation:

$$-d[styrene] / dt = k_p[polystyryllithium]^{0.5}[styrene] total$$

This scheme would suggest a mechanism of the type:

Initiation:

Buli + M
$$\xrightarrow{k_1}$$
 Bu M Li

Propagation:

$$(\operatorname{Bu}(M)_{j}Li^{+}) \cdot (\operatorname{Bu}(M)_{j}Li^{+}) \stackrel{K_{2}}{=} \operatorname{Bu}(M)_{j}Li^{+} + \operatorname{Bu}(M)_{j}Li^{+}$$
$$\operatorname{Bu}(M)_{j}Li^{+} + M \stackrel{k_{p}}{\longrightarrow} \operatorname{Bu}(M)_{j+1}Li^{+}$$

That the n-BuLi is associated as a hexamer has been shown from measurements, in hydrocarbon solvents, of molecular weights by osmotic techniques (122). The viscosity and light scattering measurements before and after the termination of polymerization showed the polystyryllithium to be associated in dimers (3,62). Morton et al. (3,63) noted that polyisoprenyllithium and polybutadienyllithium were also associated as dimers. Worsfold et al. (62,65) and Spirin et al. (123) found that polyisoprenyllithium was associated as a tetramer and polybutadienyllithium was associated as a hexamer.

O'Driscoll et al. (124) studied the polymerization of styrene at 25°C. in benzene and showed the initiation to be one-third order in [BuLi] and first order in [styrene]. This indicates that n-BuLi exists as a trimeric isomer. By gas chromatographic measurements Hsieh (50)

estimated unreacted butyllithium for different reaction times and showed that in hydrocarbon solvents the rate of initiation was first order in [initiator] for styrene, isoprene and butadiene. At 50°C., the rate of propagation of styrene was one-half order in [polystyryllithium] and first order in [styrene] (125). For the dienes the rate of propagation was one-half order at high concentration of active ends ($>10^{-2}$ mole/liter) and one-third order at low concentration (125). Thus, in diene polymerization, the value of the association number reported from different laboratories lacks agreement. Further clarification of this point should prove useful. In alkyllithium initiated polymerizations conducted in hydrocarbon media, the addition of a catalytic amount of a basic compound (ether, amine, etc.) to the reaction mixture increased the rate of initiation, while the addition of a Lewis acid (Bu₂Zn) retarded the rate of initiation (64). The variation of the rate of polymerization of styrene in the presence of varying amounts of THF, has been shown to be due to the formation of mono- and dietherate complexes of variable reactivity (66,67).

When polar monomers (e.g. methyl methacrylate, acryl amides) are polymerized with organometallics, polymerization is often accompanied by side reactions, which complicate the interpretation of the polymerization data and the postulation of a reaction mechanism.

Zilkha et al. (126) have studied the heterogeneous polymerization of methacrylonitrile in petroleum ether. At 0° C. the degree of polymerization increased with increase in the monomer to initiator ratio without regard to the order of the addition of monomer or n-BuLi to the solvent. If initiator association is assumed, at a fixed initiator concentration, the initiator efficiency should increase slightly or remain constant with an increase in the monomer concentration and hence in the dielectric constant of the medium. From the data reported in this paper (126) the initiator efficiency appeared to decrease to 25%when the monomer concentration was increased from 0.24 mole/liter to 1.9 mole/liter. The overall efficiency of the initiator was found to be less than 7%. The molecular weight and conversion were found to be independent of temperature between 10° and -30° C. A low initiator efficiency was explained by assuming association of n-BuLi and by assuming the monomer to add to the growing chains rather than to the unreacted initiator.

Buli initiated polymerization of vinyl chloride (127) was found essentially to be unaffected by air and $(DP_n)_{expt}$ was found to be much higher than $(DP_n)_{calc}$. Some polar monomers, (e.g. vinyl acetate, methyl acrylate, dimethyl maleate, allyl acetate) have been reported to give a low polymer yield with n-BuLi (42). n-BuLi adds to the carbonyl group of a ketone, which by repeated carbonyl additions yields a polymer. For example, infrared measurements on polyacetone suggest the following structure (128).



The chlorine content of polyvinylidine chloride (129) was found to be independent of the temperature of polymerization but did decrease with an increase in the butyllithium concentration in the reaction mixture. This is probably due to side reactions between initiator and monomer or In fact n-BuLi has been found to react with polymers. In THF, polymer. polyvinyl chloride (PVC) reacts with n-Buli to give a gradual color change from deep purple to blue, green and pale yellow. Butylation, dehydrochlorination or partial lithiation were considered among the possible reactions (130) between PVC and n-BuLi. Polyisoprene reacted with n-Buli lowering both the molecular weight and unsaturation (131). By employing labelled terminators in 9-fluorenyllithium initiated polymerization of methyl methacrylate (MMA), Glusker et al. (78) showed 98% of the initiator to be consumed in reactions with MMA in five seconds and about 80% of the total propagating centers to be still capable of adding monomer at the end of polymerization. Cottam, Wiles and Bywater (132) also showed that n-BuLi was consumed rapidly in the initiation reaction with MMA. Korotkov et al. (133) further studied the kinetics of the n-Buli initiated polymerization of MMA in toluene between -50° and -80°C., and pointed out that three modes of n-BuLi addition to MMA (1,2; 3,4 and 1,4) were possible. The usual polymerization proceeds by 1,2 addition. The carbanions obtained by 1,2 addition may however react with the monomer to give the 1,4 or 3,4 adducts.

Wiles and Bywater (134) investigated the polymerization of MMA with n-BuLi in toluene at -5° and -30° C. The polymer contained a low molecular weight component, the proportion of which increased with an increase in the initiator concentration, and with the temperature. The first order reaction plots for this polymerization were not linear. The initiator could not be completely accounted for in the initiation reaction. Some of the initiator was seemingly consumed in a side reaction with the

ester group as:



A similar reaction may also occur between the growing carbanion and an ester group of monomer or polymer. The lithium methoxide would react with acetic acid to give methanol.

CH3OLT + CH3COOH ---- CH3OH + CH3COOLT

After the reaction was terminated, methanol was detected by gas chromatographic analysis of the reaction mixture (135).

The effect of Lewis bases on the molecular weight of methyl methacrylate polymerized in toluene by n-BuLi was investigated by Zilkha and coworkers (70). The value of \overline{M}_{W} reached a minimum when the concentration of Lewis base was twice the n-BuLi concentration. A further increase in the Lewis base concentration did not affect the molecular weight.

Kawabata and Tsuruta (136) have studied the reaction mode of n-BuLi in the initiation step of the polymerization of methyl acrylate, (MA), methyl methacrylate (MMA), acrylonitrile, (AN), and methacrylonitrile, (MAN), in both n-hexane at 30°C., and THF at -78°C. Butane formation represented the major side reaction. Nitrile or carbonyl addition also occurred to varying degrees. The relative reactivities of monomers were in the order:

> MMA > MA > AN > MAN in hexane and MA > AN > MMA > MAN in THF.

The n-Buli initiated polymerization of acrylonitrile has been investigated in petroleum ether (42), dimethyl formamide (69), toluene (105), tetrahydrofuran (69), etc., and will be discussed in detail in the following section.

POLYMERIZATION OF ACRYLONITRILE

Although Moureu (137) first prepared acrylonitrile by the dehydration of ethylene cyanohydrin and acrylamide with phosphorus pentoxide in 1893, acrylonitrile is manufactured today from propylene, ethylene oxide, acetylene, acetaldehyde, etc. (138). Chemically, acrylonitrile is a very reactive compound capable of undergoing many reactions involving either the vinyl double bond or the nitrile triple bond (138). Although the polymerization does not occur in the absence of radiation or initiators, radiation and initiators seem to polymerize acrylonitrile by a radical or anionic mechanism (139,140). The radical mechanism of acrylonitrile polymerization is probably better understood than the anionic mechanism and the kinetics of the radical polymerization seems to have been studied in greater detail.

I. Radical Polymerization of Acrylonitrile

The polymerization of acrylonitrile by radical initiators has been studied under both homogeneous and heterogeneous conditions. With ethylene carbonate as solvent, the initial rate of polymerization (at $50-60^{\circ}C.$) was found to be proportional to the monomer concentration and was approximately 0.6 order in initiator (azo-bis-isobutyronitrile) concentration (141). The solvent acted as a diluent and a transfer agent. A first order dependence of the polymerization rate on the monomer concentration was satisfied to a reasonably high conversion, implying the viscosity of the medium to have no effect on the polymerization rate. Further, the mechanism of the chain transfer to monomer or polymer under conditions of homogeneous polymerization seemed to be negligible. Polymeric radicals have been found to undergo chain termination by both recombination (142) and a chain transfer (143) in homogeneous polymerization.

The bulk polymerization of acrylonitrile is autocatalytic and can be explosive (144). During bulk or suspension polymerization, polyacrylonitrile precipitates together with some active radicals. The burying of radicals reduces the apparent polymerization rate, but the intrinsic reactivity of the trapped radicals seems to be unchanged. Peelbes (145) has discussed the heterogeneous polymerization of acrylonitrile and noted that under these conditions polymerization occurs at three different sites: (i) in solution, (ii) at the surface of the precipitated polymer, and (iii) in the interior of the polymer. Each site had its own characteristic rate of polymerization.

II. Radiation Induced Polymerization

Polymerization by radiation seems to occur by both a radical and an anionic mechanism. Copolymers of styrene and acrylonitrile obtained at -78° C. by γ -radiation contained only a small fraction of styrene, but those obtained at 0°C. contained more styrene than acrylonitrile. Since the radical mechanism leads to a copolymer rich in styrene, it can be concluded that polymerization occurs by anionic mechanism at low temperature and by radical mechanism at high temperature (146,147). On irradiating acrylonitrile at -78°C. in ethylene, Sobue et al. (146) observed that polymerization occurred by a vinyl and a nitrile addition. This indicated that the polymerization proceeded by the radical and anionic mechanism concomitantly. Chapiro et al. (148) have found polymerization in solid acrylonitrile to proceed by a different mechanism than in liquid acrylonitrile.

In DMF, γ -ray initiated polymerization of acrylonitrile gave a colored, DMF-soluble polymer but in water, the monomer was converted to a white, crosslinked product only partially soluble in DMF (149).

III. The Anionic Polymerization of Acrylonitrile

Acrylonitrile is an acidic monomer, which can be polymerized anionically by basic initiators. Beaman (150) reported the anionic polymerization of acrylonitrile initiated by butyl magnesium bromide in ether to give a low molecular weight polymer. In the polymerization initiated with potassium metal in liquid ammonia, the molecular weight of the polymer obtained varied inversely with temperature (30). Termination was by chain transfer to the solvent. The polyacrylonitrile was yellow and soluble in acetone and ammonia. The color formation in the polymer was related to a conjugated structure resulting from the polymerization of the nitrile group (30).

In the sodium or potassium alkoxide initiated polymerization in DMF or petroleum ether, a reproducible induction period was observed

- 46 -

(48). The induction period increased with the free alcohol concentration in the reaction mixture and was shown to be related to a cyanoethylation reaction (48). In petroleum ether the molecular weight of the polymer increased with monomer concentration but decreased with alcohol concentration indicating that termination was by chain transfer to the alcohol. The molecular weight varied with the nature of the counterion and with the temperature (48). In DMF the molecular weight of polyacrylonitrile was shown to be independent of monomer concentration, reaction temperature, the counterion (Na⁺, K⁺, Li⁺) and the conversion.

Zilkha and coworkers (43) found metal ketyls of the sodium benzophenone type to initiate the polymerization of acrylonitrile and other monomers in THF. The molecular weight of the polyacrylonitriles was found to be independent of monomer and initiator concentration while that of polystyrene and polymethyl methacrylate was found to vary inversely with the initiator concentration and directly with the monomer concentration. Neither a homopolymer nor a copolymer of styrene was obtained when styrene was added to a reaction mixture of acrylonitrile, monosodium benzophenone and THF (43). Apparently all the initiator was consumed in chain initiation and side reactions with acrylonitrile over a very short reaction interval. The termination process was explained by a chain transfer to acrylonitrile. This agrees with the observation that the polymer molecular weight was independent of the monomer concentration. Further evidence of a chain transfer mechanism in termination was found in the infra-red absorption at $5.9 \sim 6.1 H$ (assigned to =CH₂) (43).



polymer

Furukawa et al. (151) observed that lithium benzophenone does not initiate polymerization of acrylonitrile but sodium and potassium benzophenone does.

In the presence of water acrylonitrile was polymerized with quaternary ammonium hydroxides in dimethyl formamide to give a low molecular weight product, where termination was shown to be by a chain transfer to monomer (152). The molecular weight of the polyacrylonitrile obtained varied with different quaternary ammonium hydroxides in the following order:

$(CH_3)_4 NOH > (C_2H_5)_4 NOH > (CH_3)_3C_6H_5CH_2NOH$

No explanation for chain transfer to monomer in the presence of water has been offered but a cyanoethylation reaction between water and acrylonitrile (138) in the presence of base might explain this chain transfer.

Cundall et al. (37) followed dilatometrically the kinetics of acrylonitrile polymerization initiated by disodiomalonic ester in DMF. At -40°C., the rate of disappearance of monomer was found to be proportional to $[M]^2[I]$. The molecular weight was independent of the monomer or the initiator concentration, but decreased with an increase in the conversion. The extent of unsaturation in the polymer was found to be one double bond per polymer molecule. Termination by chain trans-

fer to monomer and random splitting of the polymer chains by the growing carbanions were proposed to explain these findings (37).

In another investigation (77), acrylonitrile was polymerized in DMF with sodium triethylthioisopropoxyaluminate. The molecular weights calculated from light scattering measurements and from the sulfur content of the polymers (assuming one sulfur atom per polymer molecule) were approximately equal for polymers obtained at -78° C. For polymerization at -30° C., the molecular weight based on sulfur content was higher than the experimentally determined value. This was taken to imply that more than one polymeric chain was produced per initiator molecule. Since the sulfur content of the polymer was less than that of the initiator some of the initiator was consumed in reactions other than the chain initiation. The polymerization never went to completion at -30° C. because of the short life time of the carbanions at this temperature. At -78° C., the carbanions were found to be stable for days, suggesting a negligible participation of carbanions in chain transfer or chain termination reactions.

In THF, the molecular weight of polyacrylonitrile obtained with sodium and lithium aryl type initiators was independent of initiator concentration at higher initiator concentrations, but varied inversely with the initiator concentration at low initiator concentration (44,49). The conversion was found to increase with initiator concentration. The polymerization with lithium as the counterion gave a polymer with higher molecular weight than that obtained with sodium as the counterion. A decrease in the reaction temperature (0 to -50° C.) increased both the polymer yield and the molecular weight, implying that the carbanion stability varied inversely with temperature. Further, the polymers prepared at 0°C. contained less nitrogen than the theoretical nitrogen content of the polyacrylonitrile.

Since the viscosity average molecular weight of polyacrylonitrile obtained with biphenyl sodium, at -78° C., in DMF, THF or in a mixture (1:1) of both, was lower than both the kinetic and the number average molecular weight, the polymer was assumed to be branched (74). The polymer obtained from a DMF, THF-mixture was white and gave an IR-spectrum similar to that obtained from a polymer prepared by a radical mechanism. The polymer obtained in DMF alone was colored probably because of participation of the nitrile group in the reaction. Acrylonitrile, when polymerized with aryl and alkyl compounds of lithium and sodium in THF, THF + DMF, toluene (at -78° C.) and DMF (at -50° C.), gave a branched polymer (153). The degree of branching was found to be affected by both the solvents and the initiators.

That the cyclopentadienyl sodium and lithium act as a polyfunctional initiator was shown by the ozonolysis of the polyacrylonitriles produced by these initiators in THF (49). Isolation and characterization of the cyanoethylation products from the reaction mixture supported further the polyfunctionality of the cyclopentadienyl anion (154).

IV. Polymerization of Acrylonitrile with n-Butyllithium

When acrylonitrile was polymerized with n-Buli in different solvents, the molecular weight of the polymer increased as the dielectric constant of the solvent decreased (69). This has been related to an increased initiator efficiency with dielectric constant. An increased rate of chain transfer or chain termination with dielectric constant could also explain this behavior.

In the heterogeneous n-Buli initiated polymerization of acrylonitrile in petroleum ether at 0°C., the molecular weight of polymer depended upon the momentary concentration of the monomer in the reaction mixture and the relative order of addition of monomer and initiator (42). A two stage propagation mechanism, in which the growing carbanion of AN, ~CH2-CH Ii, was solvated by the monomer, was proposed to explain these findings. Under identical experimental conditions, the molecular weight was higher, the lower the monomer concentration at a given [M]/[I] ratio. The molecular weight of the polymer increased with a decrease in initiator concentration or reaction temperature (0°C to -50°C.), indicating an increase in carbanion stability at lower temperatures. The molecular weight of polymer obtained under homogeneous conditions (in DMF) was independent of the monomer and initiator concentration at high initiator concentration, but increased with decrease in temperature of polymerization (155). Although the degree of polymerization calculated from viscosity measurements was found to be higher than $(DP_n)_{calc}$, a chain transfer to monomer was considered to be the termination mechanism. The chain transfer mechanism was supported by the infrared measurements on polyacrylonitriles where the absorption at 6.03μ was related to terminal unsaturation. To account for all the initiator it was necessary to assume that the initiator was highly associated and that only dissociated n-BuLi participated in chain initiation while the associated form remained

unreacted (42,155). At low initiator concentrations the molecular weight increased directly with monomer concentration and inversely with the initiator concentration (155). The variation of temperature (0° to -50° C.) had essentially no effect on the molecular weight of polyacrylonitrile (155). For polymerization at low initiator concentrations a monomolecular chain termination mechanism was proposed in which the carbanion was shown to cyclize to an imine ion incapable of adding a monomer molecule. The lowering of the reaction temperature should increase the stability of the anion which in turn should give a higher polymer yield. However at low initiator concentrations a decrease in the reaction temperature lowered the polymer yield (155).

Miller (105) found, at initiator concentrations in excess of 2.4 meq./liter at -78°C. in toluene, the percent polymerization to be independent of initiator concentration and to vary inversely with the monomer concentration. The molecular weights of polyacrylonitriles, formed over a three-day reaction period at -78°C., as reported by Miller (105) are given in Table G-II. This table demonstrates that there is actually little experimental evidence of any relation existing between molecular weight and monomer or initiator concentration. In polymerization experiments of short reaction times, the percent conversion was independent of monomer concentration up to 13% acrylonitrile. A polymer obtained after 24 hours had a low heterogeneity index. However the molecular weight distribution plot of the polymer sample indicated the presence of a small amount of low and a high molecular weight fraction. The polymer cbtained by reaction termination immediately after the monomer addition showed a bimodal molecular weight distribution. These

TABLE G-II

Viscosity Average Molecular Weights of Polymers Formed in the Three Day Polymerization Experiments*

Initiator concentration	· · ·	Monomer, volume - %			
(mole/liter) x 100	27	13	5.7		
0.24	125	1150	1350		
0.49	-	1300	940		
1.01	725	720			
1.48	780	564	_		

Molecular Weight x 10^{-3}

* Reference 105.

molecular weight distribution data suggested a slow initiation of new polymeric chains and a slow chain growth. Gradual chain termination by impurities present in the monomer may be an alternate explanation for the observed molecular weight distributions.

In all the work reported on n-BuLi initiated acrylonitrile polymerization, the observed low initiator efficiency has been explained by assuming n-BuLi to be associated and by assuming monomer addition to the active carbanions in preference to the n-BuLi molecules.

The polymerization of acrylonitrile, at different temperatures (0 to -78°C.) in toluene, with n-Buli as the initiator, is reported in the present thesis. The object was to study the effect of time, temperature, monomer concentration, and initiator concentration on polymerization and molecular weights of polyacrylonitriles. An attempt has also been made to trace the initiator unaccounted for in initiation. The effect of temperature on polymer structure and molecular weight distribution is investigated.

THE MOLECULAR WEIGHT AVERAGES

Since the polymer molecules in a given preparation cover a large range of molecular weights, the entire distribution of molecular weights would be required for the complete description of the polymer sample. This is usually not done. In practice molecular weight averages are employed.

If f(M)dM represents the fraction of the material having a

molecular weight between \underline{M} and M + dM, some of the molecular weight averages are given as,

$$\overline{M}_{n} = \int_{0}^{\infty} f(M) \, dM / \int_{0}^{\infty} (f(M)/M) \, dM$$

$$\overline{M}_{w} = \int_{0}^{\infty} f(M)M \, dM / \int_{0}^{\infty} f(M) \, dM$$

$$\overline{M}_{z} = \int_{0}^{\infty} f(M)M^{2} dM / \int_{0}^{\infty} f(M)M \, dM$$

$$\overline{M}_{v} = \left[\int_{0}^{\infty} f(M)M^{1+a} dM / \int_{0}^{\infty} f(M)M \, dM\right]^{1/a}$$

where \overline{M}_n , \overline{M}_w , \overline{M}_z , and \overline{M}_v are the number average, weight average, zaverage and the viscosity average molecular weights respectively; <u>a</u> is a constant.

A most convenient method of measuring an average molecular weight of a polymer is based on viscosity. For this purpose the Mark-Houwink (156) relation is used.

$$[\widehat{\Pi}] = k \, \widetilde{M}^{a} \qquad (18')$$

In this relation \underline{k} is a constant for a given solvent-polymer system at a given temperature. The coefficient \underline{a} is conveniently taken as a constant in the range of molecular weights usually studied, although the value of \underline{a} for a given system varies from 0.5 to 1.0 as the molecular weight increases from zero to infinity (157). The above relation was derived theoretically by Kirkwood and Riseman (158), Buche et al. (159) and Brinkman (160) from models of polymeric chains in solution. In actual practice \underline{k} and \underline{a} are evaluated from intrinsic viscosity measurements on a series of monodisperse fractions of known molecular weights. The experimental values of \underline{k} and \underline{a} for polyacrylonitriles are collected in Table G-III. Since the polyacrylonitrile obtained by radical initiators may differ in structure and molecular weight distribution and since the fractionation of polyacrylonitrile is often poor (ll,l61) the values of \underline{k} and \underline{a} show poor correlation. The values of the constants determined by Stockmayer et al. (l61) appear to be the most reliable (140). A relation equivalent to that of Stockmayer et al. (l61) was derived by Miller et al. (l62) from light-scattering and viscosity measurements on high molecular weight polyacrylonitriles at 29.9° C. This relation has the form

$$[\eta] = 2.27 \times 10^{-4} \overline{M}_{v}^{0.75}$$
(18)

This relation would not hold if the polymer structure is branched as is sometimes the case for polyacrylonitriles prepared anionically (74,153).

A relation between the sedimentation coefficient and molecular weight (163) can be derived in a manner analogous to the relation between intrinsic viscosity and molecular weight. For a given polymersolvent system at a given temperature the relation has the form,

$$s_{o}^{o} = k_{2}\overline{M}^{b}$$
 (19)

where S_0° is the sedimentation coefficient corrected for pressure and concentration effects. The constants k_2 and <u>b</u> can be evaluated from the known values of <u>k</u> and <u>a</u>. Elimination of <u>M</u> from the equations (18) and (19) gives the relation:

$$s_{o}^{o} = k_{2}[\eta]^{b/a}/k^{b/a}$$
 (20)

A plot of log S_0^o against log[η] should be a straight line with a slope equal to b/a and an intercept equal to log $k_2 - \frac{b}{a} \log k$. From the known

Author	k x 10 ³	<u>a</u>	10 ⁻³ x Molecular weight range	Method
Houtz	1.750	0.660	18-135	0 . f
Frind	2.500	0.660	9- 69	0.p
Bisschops	0.166	0.810	48-270	S.f
Stockmayer	0.243	0.750	15-132	L.p
Onyon	1.970	0.625	177-1000	0 . p
Ciampa	0.040	1.000	12- 61	0.p
Kobayashi	0.278	0.770	28-575	Dv.f
Miller***	0.227	0.750	65–202	L.f

Comparison of Mark-Houwink Constants for PAN Solution in DMF**

TABLE G-III

Abbreviations: 0 : Osmometry; S : Sedimentation velocity; L : Light scattering; Dv : Diffusion and viscometry; f : fractionated polymer; p : Polydisperse polymer.

** Taken from Kawai, T and Ida, E., Kolloid. Zeit & Zeit Polymer 194, 40 (1964).

**** Reference (162).

¥

values of <u>a</u> and <u>k</u>, the constants <u>b</u> and k_2 can be evaluated. Once the constants k_2 and <u>b</u> are known, the molecular weights could be calculated from the sedimentation coefficients.

THE MOLECULAR WEIGHT DISTRIBUTION FROM SEDIMENTATION

VELOCITY MEASUREMENTS

If for a given polymer sample the distribution of sedimentation coefficients can be determined, the molecular weight for each sedimentation coefficient and hence the molecular weight distribution can be calculated. Baldwin et al. (163,164) have discussed the evaluation of the sedimentation coefficient distribution from the measurements of sedimentation velocity gradient curves and the requisite corrections for diffusion, concentration and pressure effects. Gupta, Robertson and Goring (165) have evaluated the sedimentation coefficient distributions for alkali lignin fractions. McCormick (103) has studied the molecular weight distributions in anionically prepared polystyrenes using the sedimentation velocity method. The concentration effects were minimized by working under theta conditions.

The compressibility of the organic liquids under pressure leads to a change in the density and viscosity of the solvent. A detailed experimental treatment of this pressure effect on the observed sedimentation coefficients is not yet possible. A correction for pressure can be made by applying the relations of Fujita (166) or Oth and Desreux (167) but such corrections are difficult to apply experimentally. Billick (168) showed that a least square method could be used to eliminate the pressure effects by evaluating the S^O from the relation,

$$\ln r_{i} = \ln r_{o} + S^{o} \omega^{2} t_{i} + B(\omega^{2} t_{i})^{2}$$
(21)

in which r_i is the position of the maximum at time t_i (sec.), S^o is the sedimentation coefficient corrected for the pressure effects and $\underline{\omega}$ is the angular velocity (radian/sec.). The parameter <u>B</u> was shown to be related to the pressure dependence parameter (168). Blair and Williams (169) showed that the value of S^o calculated by using the least square technique was not affected by any small inaccuracies in the measurements of time.

Wales and Rehfeld (170) have developed a method of calculating the molecular weight distribution which corrects for diffusion, concentration and pressure effects. The procedure for pressure effect corrections involves the calculation of the pressure parameter by evaluating the sedimentation coefficient at a series of angular velocities. For each given polymer concentration the pressure parameter can be determined by Billick's method (168) and can be substituted in the equations derived by Wales et al. (170) to calculate the molecular weight distributions. This method was used in the present work. Neither sedimentation coefficient distributions nor the molecular weight distributions from them are available in the literature for polyacrylonitriles.
EXPERIMENTAL

A-I TREATMENT OF GLASSWARE:

All the glassware (reaction flasks, ampoules, round bottom flasks etc.), employed in this study, was cleaned with chromic acid solution, rinsed several times with water followed by distilled water and dried for 15 to 20 hours at 2000C. The standard-taper round bottom flasks and tubes were transferred while hot to a vacuum desiccator, evacuated for 30 minutes and flushed with dry nitrogen. The object of this treatment was to remove surface films of water, gases, etc., which are usually adsorbed on the glass. In the present work, round bottom flasks treated in this manner will be referred to as 'dry nitrogen flushed flasks'. The graduated ampoules, equipped with break-seals shown in Figure 1, and reaction flasks were attached, before use, to the appropriate sections of the vacuum line described in Figure 2, evacuated overnight, heated gently with a hand torch for about 15 minutes and allowed to cool under continuous evacuation.

A-II THE VACUUM APPARATUS:

It is now well recognized that anionic initiators (e.g. compounds of hydrocarbons with alkali metals) and polymeric anions are quite sensitive to traces of oxygen, carbon dioxide, water and to the impurities containing active hydrogen. The vacuum apparatus illustrated in Figure 2 was used to minimize such impurities. The apparatus consisted of an oil pump (Fig.2,A) which in combination with the mercury

AMPOULES

- A Monomer ampoule
- B Initiator ampoule
- C Solvent ampoule
- D Di-n-butylmercury ampoule



THE VACUUM APPARATUS

I	Monomer degassing and distillation section			
II.	Solvent degassing and distillation, initiator preparation and dilution section			
III	Polymerization reactors evacuation section			
A	Vacuum pump			
Β.	Diffusion pump			
C	Liquid air trap			
D	Monomer ampoules			
Е	Monomer container			
F	n-Hexane container			
G	Toluene container			
J	McLeod gauge			
K	Solvent ampoules			
R	Pressure release			

Silica gel trap

Т



0

ness and a stranger of the second stranger of the second stranger of the second stranger of the second stranger



diffusion pump (B) reduced the pressure in the system to 10^{-5} to 10^{-6} mm Hg as measured by the McLeod gauge (J). The liquid air cooled trap (C) was used to remove condensable gases from the manifold and to prevent contamination of the manifold by mercury vapor from the diffusion pump. The main manifold was divided into three sections: section I was used to degas and distill the monomer; section II to degas and distil the solvents, to prepare the initiator and to dilute the initiator solution; and section III, to evacuate the reaction flasks. The pressure release (R) prevented excess helium pressure build-up. Condensables from helium gas were removed by the dry silica gel trap (T) immersed in liquid air.

A-III <u>REMOVAL OF AIR FROM LIQUIDS</u>:

The flask containing the material to be degassed was connected to an appropriate outlet on the vacuum line. The manifold was evacuated to 10^{-6} mm Hg. The contents of the flask were frozen by a liquid air cooling bath, and the flask was evacuated by opening the stopcock to the vacuum line. After 10 to 15 minutes this stopcock was closed, the bath removed and the frozen liquid was allowed to attain room temperature. The liquid was degassed again after 15 to 20 minutes of stirring. The freezing, evacuating, thawing and stirring cycle was repeated until a pressure of 10^{-5} mm Hg was attained with the material in the frozen state. The degassed liquid was flash distilled into graduated ampoules equipped with break-seals.

A-IV MATERIALS:

<u>Toluene</u> (Fisher - Certified Reagent) was refluxed over sodium metal for more than 24 hours. It was distilled fractionally, under slightly positive nitrogen pressure, into a dry nitrogen flushed flask containing sodium metal. This flask was attached to the refluxing system, shown in Figure 2, which had been previously flushed with dry nitrogen. The contents of the flask were boiled gently for two hours, the heater was removed, and the mixture was stirred vigorously to disperse the liquid sodium (m.p. 97.5°C.) as fine particles. The stirring was stopped after the temperature dropped to 90°C. These operations were performed under positive nitrogen pressure. The cool flask containing sodium dispersed in toluene was attached to an outlet of the vacuum apparatus (Fig. 2,G). The toluene, degassed as described above, was vacuum distilled into evacuated ampoules.

<u>n-Hexane</u> (B.D.H. - AR) was refluxed over sodium metal, distilled fractionally under nitrogen into a flask coated with a sodium mirror, degassed by freezing-thawing and distilled into ampoules or a reaction vessel.

Benzene (Fisher - Certified Reagent) was purified in the same manner as n-hexane.

Diethyl ether (Matheson Coleman and Bell) was purified in the same manner as n-hexane.

<u>Benzyl chloride</u> (Fisher) was dried over phosphorus pentoxide, distilled under reduced pressure from P_2O_5 , degassed and collected into ampoules. <u>Di-n-butyl mercury</u> (Eastman Kodak) was distilled under reduced pressure. The middle fraction was collected in a dry nitrogen flushed flask, and

UNIT FOR PREPARATION OF SODIUM DISPERSION

G Toluene container



was stored under nitrogen until used.

<u>N.N.-dimethyl formamide (DMF)</u> (Matheson Coleman and Bell) was distilled azeotropically from benzene and further distilled under reduced pressure. <u>Nitrogen</u> (Linde - Dry) and <u>Helium</u> (Matheson of Canada Ltd.) were each dried by passing them through a dry silica gel trap immersed in liquid air.

Acrylonitrile (AN) (Matheson Coleman and Bell - Technical Grade) was used in the present work. The main impurities in the acrylonitrile were acetone, acetonitrile, aldehydes, water and inhibitor (hydroquinone monomethyl ether). Most of the acetonitrile was removed from acrylonitrile by washing with distilled water. Acetone and aldehyde distilled over first and were rejected with the forerun during the azeotropic distillation of acrylonitrile with water (171). The portion left in the distillation flask contained traces of acetonitrile, inhibitor, water and a portion of acrylonitrile and was rejected. The azeotrope (b.p. 70.7°C.) containing 85.7% acrylonitrile and 14.3% water was collected in a round bottom flask, cooled to -10°C., and decanted to remove the ice phase separating at this temperature. The acrylonitrile so treated contained about 1.5% water. The solubility of water in acrylonitrile as a function of temperature is plotted in Figure 4 (138). By reference to this plot approximately 0.02% water is soluble in acrylonitrile at -80°C. Obviously most of the water could be removed from AN upon cooling to this temperature. The apparatus used for this purpose and to avoid contamination of other volatiles from the atmosphere during cooling is shown in Figure 5. A liquid air-cooled silica gel trap (D) was used to remove traces of moisture present in nitrogen. An adjustable pressure

- 66 -

SOLUBILITY OF WATER IN ACRYLONITRILE (138)



APPARATUS FOR DRYING ACRYLONITRILE

A	Acrylonitrile container
В	Acrylonitrile receiver
С	Oil trap
D	Silica gel trap
Е	Fritted disc
F	Pressure regulator
G,H,J	Stopcocks
К	Transfer tube



release (F) allowed the pressure in the system to be varied. The fritted disc (E) was used to prevent contamination of AN with solids during the transfer. After flushing the system with nitrogen, AN was transferred to flask (A). The stopcock (G) was closed and (J) and (H) were opened. The AN flask was maintained at -78°C. by an ethanol-dry ice bath, for an hour to attain equilibrium. Then (G) was opened and the direction of flow through stopcock (H) was changed to connect flask (B) to the oiltrap (C). By increasing the nitrogen pressure, the acrylonitrile was transferred to flask (B) leaving behind the ice in (A). Once AN had attained the room temperature, the flask (B) was transferred to a fractional distillation unit. The acrylonitrile was distilled under nitrogen and the distillate was collected in dry nitrogen flushed containers. These fractions were analyzed for water by Karl Fischer Reagent. Only when the analysis showed the water content to be less than 15 ppm, was the distillate collected in bulk. This fraction was further degassed by freezing and thawing under vacuum. The degassed monomer (AN) was vacuum distilled in an ampoule and analyzed for water. This gave a double check on the purity of the monomer. For polymerization experiments, the monomer thus purified was distilled as required into the graduated ampoules as shown in Figure 1,A.

<u>Ethyl alcohol</u> (95% Commercial), <u>Acetone</u> (Fisher - Reagent), <u>Hydrochloric</u> <u>acid</u> (Baker - Reagent), <u>Sodium metal</u> (B.D.H. - Lumps), <u>Lithium wires</u> (Lithium Corporation of America), <u>Methanol</u> (Fisher - Spectranalyzed), <u>Pyridine</u> (Fisher - Reagent), <u>Iodine</u> (Fisher - Reagent), <u>Zinc chloride</u> (Fisher - Reagent), <u>Sulfur dioxide</u> (Matheson of Canada Ltd.) were used without further purification.

A-V n-BUTYLLITHIUM (n-BuLi):

a. Preparation of n-Butyllithium

The procedure described here is a slightly modified version of that employed by Morton et al. (104). The flask (D), shown in Figure 1, was connected to the vacuum line (Fig. 2, sect. II), evacuated and flushed The desired amount of vacuum-distilled di-n-butyl mercury with helium. was added to the flask (D) by opening the side arm (G). The helium flow was stopped when (G) was closed. The contents of the flask were evacuated and degassed. The flask was sealed off the vacuum line after 70 to 80 ml. of dry, thoroughly degassed, n-hexane was collected. The flask (D) containing di-n-butyl mercury solution was sealed to the apparatus, shown in Figure 6, for the preparation of n-BuLi. The apparatus was connected to the vacuum line through (H:), evacuated to 10⁻⁶ mm Hg, flamed gently, cooled and flushed with helium. Lithium, cut in very small pieces under paraffin, was transferred to flask (A), by opening the side arm at (B). The helium flow was stopped after the side arm was resealed. The apparatus was then evacuated overnight to 10^{-5} mm Hg and 40 to 50 ml. of degassed, anhydrous n-hexane was introduced by flash distillation. After removing the apparatus from the vacuum line, the contents of the flask (A) were stirred for some time to dissolve the petrolatum coating from the lithium This solution was transferred to (E), leaving lithium behind in metal. (A). n-Hexane was flash distilled into (A) to repeat the cycle until the lithium was clean. The flask (E), containing petrolatum solution in nhexane, was then sealed off the apparatus. The lithium metal pieces were transferred to side arm (H), and the di-n-butyl mercury solution from flask (D) was added to reaction flask (A). A small portion of lithium

APPARATUS FOR PREPARATION OF n-BUTYLLITHIUM

A	Reaction flask
В	Side arm end
C	n-Butyllithium receiver
D	Di-n-butylmercury solution
D ı	Fritted disc
Е	Receiver for lithium washings
H	Side arm
Hŧ	Vacuum outlet



was added to (A) and the contents were stirred continuously by a magnetic stirrer. As the reaction

$$(n-C_{4}H_{9})_{2}Hg + 2Ii - 2n-C_{4}H_{9}Ii + Hg$$
 (XI)

proceeded at room temperature, the mercury liberated formed an amalgam, with lithium, coating the lithium surface and hindering its reactivity. The amalgam coated lithium being heavier, settled out. At this point a second portion of lithium was added to the solution from the side arm, with continuous stirring, until the amalgam coated lithium again settled out. The addition of lithium was repeated until no further amalgam formation occurred as indicated by the lithium metal remaining for 7 to 8 hours on the surface of the solution. Additional lithium was added and the reaction mixture was stirred for another 12 hours to insure completion of the reaction. The n-BuLi solution was collected in flask (C) by filtration through the fine porosity disc (D⁺). The flask (A) was rinsed three times by back distillation to insure quantitative transfer. Flask (C) was cooled in an ethanol-dry ice bath and sealed off the apparatus.

When all the lithium metal was added in one portion as suggested by Morton et al. (104), the reaction was not complete even after 4 days and gave a yield of 80 to 85 percent n-BuLi. The modification of this method used in the present work gave yields of more than 99 percent n-BuLi (in both cases the percent yield is based on di-n-butyl mercury).

b. Subdivision of n-Butyllithium Solution

Since n-Buli is very reactive, and the reaction products of n-Buli with impurities may also react directly or indirectly with active

propagating centers during polymerization, it is essential to handle n-BuLi solution in the absence of oxygen, moisture, carbon dioxide and any impurities containing active hydrogen.

The solutions of n-Buli of known volume and concentration were sealed in calibrated ampoules and preserved in a deep freeze until used in the polymerization work. The apparatus employed to fill the ampoules is shown in Figure 7. In this figure the flask (C) containing n-Buli solution was connected to the manifold (T), which in turn was sealed to the vacuum line at (V). The manifold was evacuated to 10^{-6} mm Hg with thorough outgassing and was finally sealed off. The break seal of the flask (C) was opened to allow the solution to enter the tube (T) which was aligned and clamped in a horizontal plane. After a 15-minute interval (to attain equilibrium), the tube (T) was rotated to allow the solution to flow and to be divided uniformly among the ampoules. After two hours at room temperature the ampoules were cocled in an ethanol-dry ice bath, and finally sealed off the main manifold (T). The volume of n-Buli solution in each ampoule was determined at room temperature.

c. The Analysis of n-Butyllithium Solution

The solution of n-BuLi was analyzed by the double titration method of Gilman et al. (172). In this double titration technique the total hydrolyzable lithium is determined by direct hydrolysis and subsequent titration with standard HCl solution. The hydrolyzable lithium not bonded to carbon is then determined by the hydrolysis and titration of the products from the reaction of n-BuLi with benzyl chloride in diethyl ether. The difference between the results of the two analyses represents

APPARATUS FOR SUBDIVISION OF n-BUTYLIITHIUM SOLUTION

- C n-Butyllithium container
- T Main manifold
- V Vacuum outlet



•

.

the amount of n-BuLi. The reaction

 $3 n-C_4H_9Li + 3 \bigcirc -CH_2Cl \longrightarrow n-C_4H_9.C_4H_9 + \bigcirc CH_2.H_2C \bigcirc$

- $\mathbf{O}_{5}^{H_{11}} + 3$ LiCl (XII)

is rapid and quantitative at room temperature.

Despite all the precautions taken, the complete exclusion of impurities was never attained when a dry nitrogen glove box was used to establish an inert atmosphere. The results were inconsistent and only 65 to 70 percent of Li was found as n-BuLi. To improve the technique, the apparatus described in Figure <u>8</u> was employed. This apparatus was connected to the vacuum line at (V), evacuated to 10^{-6} mm Hg, degassed <u>in vacuo</u> and sealed off. The n-BuLi solution (C) was added to flask (A), cooled to -78° C., and benzyl chloride and cold (-78° C.) diethyl ether (E) were added to (A). The reactants were allowed to attain room temperature and were stirred. The flask was opened, the contents were hydrolyzed and titrated with standard hydrochloric acid to determine hydrolyzable lithium other than n-BuLi. The total hydrolyzable Li was determined from direct hydrolysis and titration with standard acid. The n-BuLi used in the present work contained more than 97% C-Li bonds.

A-VI POLYMERIZATION PROCEDURE:

In the present polymerization study, toluene, n-BuLi, and acrylonitrile were used as the solvent, initiator (I) and monomer (M) respectively. The monomer was polymerized in 300 or 500 ml. round bottom flasks, equipped with five outlets, as shown in Figure 2. A

APPARATUS FOR ANALYSIS OF n-BUTYLLITHIUM

A	Reactor
В	Benzyl chloride ampoule
C	n-Butyllithium ampoule
E	Di-ethyl ether ampoule
V	Vacuum outlet



1

.

THE POLYMERIZATION APPARATUS

Reactor

A

D

.

- B Solvent ampoule
- C Initiator ampoule
 - Monomer ampoule
- E Acidified acetone ampoule



teflon coated magnetic stirring bar (inert to n-BuLi solution at low temperature (173)) was used to stir the reaction mixture in flask (A). The reactor was connected to the vacuum line, evacuated overnight, degassed under vacuum and sealed off. The initiator and the solvent were added to the flask (A) from (C) and (B) respectively, and maintained at a desired temperature. After 15 minutes the monomer at the same temperature was added to the initiator solution from (D) with stirring. The reaction was instantaneous as evidenced by the yellow color characteristic of the carbanions derived from acrylonitrile. The reaction was stopped by the addition of the acidified acetone from (E) to the reaction mixture with rapid shaking of the flask to mix the contents.

The polymer was separated from the reaction mixture by filtration through a fritted disc, washed several times with ethanol until free of hydrochloric acid, and dried under vacuum to a constant weight. The percent yield was calculated from the known weight of acrylonitrile and the polymer obtained.

The kinetic molecular weight, \overline{M}_k , was calculated from the relation,

 \overline{M}_{k} = Weight of the polymer obtained/number of moles of k initiator taken.

- 78 -

RESULTS

POLYMERIZATION OF ACRYLONITRILE

B-I REPRODUCIBILITY OF POLYMERIZATION DATA:

In the present work, the reproducibility of the polymerization data depended upon the initiator concentration, monomer concentration, the rate of addition of the monomer to the reaction mixture and the reaction time. The reproducibility was poor at high initiator and monomer concentration. At high initiator and monomer concentration, the reaction mixture became highly viscous or almost solid, before complete addition of the monomer. This led to difficulties in stirring and in some cases to complete separation of a solid phase in contact with a clear supernatent liquid phase of the monomer. Under such conditions the addition of acidified acetone to the reaction mixture did not lead to instantaneous deactivation of the propagating centers and consequently the time of reaction could only be estimated approximately. Occasionally the reaction mixture was so dense, that the propagation centers remained active (as evidenced by the yellow color of the active carbanions) until the reaction mixture was removed from the flask and stirred vigorously in more ethanol. The time for monomer addition was not constant, but usually varied between 20 to 50 seconds, depending upon the amount of monomer and the size of the orifice obtained on opening the break-seal of the monomer ampoule. The results presented in Table \underline{I} illustrate the low reproducibility obtained at relatively high initiator concentration.

TABLE I

Rate of Polymerization at High Initiator Concentration - Reproducibility

Temperature: - 78° C. Solvent : Toluene Initiator Concentration = 20 x 10^{-4} Mole/Liter Monomer Concentration = 1 Mole/Liter

	Reaction time (Minutes)	Polymer Yield (Per Cent)
., ·	2	31
· · ·	5	30
	5	32
	10	38
	20	28
	60	37
	60	41
	240	39
	300	35
	1200	50
	1500	33
	7200	45

In the initial stages of polymerization at low initiator concentration the liquid reaction mixture was less viscous. It was thus possible to attain proper mixing of the monomer or the terminator to obtain better reproducibility, as seen in Table <u>II</u>. In the major portion of the kinetic studies made, the initiator concentration was very low and the reproducibility was better than $\pm 2\%$ from the arithmetic mean.

B-II EFFECT OF DIFFERENT VARIABLES ON POLYMERIZATION:

a. Effect of Time on Polymerization

The polymerization was studied over intervals of five minutes to fifty hours at -78° C. and at varying levels of monomer and initiator concentrations. The yellow color of the carbanions persisted throughout the reaction period. The conversion and viscosity average molecular weight (\overline{M}_{v}) increased with time as seen in Table <u>III</u>. As the reaction proceeded, the reaction medium became highly viscous or solid. As a result of this the rate of propagation which was rapid in the early stages of polymerization, levelled off gradually. The detailed data on polymerization experiments are presented in Tables <u>A-I</u> to <u>A-IV</u> of Appendix <u>A</u>.

b. Effect of Initiator Concentration on Polymerization

In the present study, the initiator concentration was varied from 0.167 to 2.0 meq/liter of the reaction mixture at four different monomer concentrations. The percent conversion data, as a function of

TABLE II

Rate of Polymerization at Low Initiator Concentration - Reproducibility

Temperature: -78°C. Solvent : Toluene

Reaction time (Minutes)	Initiator Conc. , (Mole/Liter) x 10 ⁴	Monomer Conc. (Mole/Liter)	Polymer yield (Per Cent)
5	10.00	l	28
11	tr i	11	31
tt .	5.00	. 11	11 ,
TT	11	11	13
t II	2.50	11	. 7
11	11	11	8
11	1.67	11	5
Tt	1t	11	6
10	10.00	2	25
11. · · ·	11	11	27
20	5.00	11	15
TT	tt	11	18
60	2.50	1	_ 10
11	11	12	12
300	5.00	18	24
1t	tt	11	27

TABLE III

Effect of Time on Conversion and Molecular Weight

Temperature: -78° C. Solvent : Toluene Initiator = 20 x 10⁻⁴ Mole/Liter Monomer = 0.5 Mole/Liter

Expt. No.	Reaction time (Minutes)	Polymer yield (Per Cent)	Molecular weight $(\overline{M}_v) \ge 10^{-5}$
Av-1	5	28	1.72
Av-2	10	30	2.19
Av-3	20	33	2.93
Av-4	60	36	3.82
Av-5	300	40	4.50
Av-6	3000	50	5.70

time at different initiator concentrations but a constant monomer concentration of 0.5 mole/liter, given in Table <u>IV</u>, are plotted in Figure <u>10A</u> to illustrate the effect of the initiator concentration on the rate of polymerization. For a fixed reaction interval, the percent conversion increased with increase in the initiator concentration, but there was no simple relation between percent conversion and initiator concentration, over the concentration range investigated. Using the polymerization data from Appendix <u>A</u>. the percent polymerization versus time is plotted in Figures <u>10B,C,D</u> for 1, 2 and 4 mole/liter monomer respectively. A similar time dependence of polymerization rate is found in these plots. From these results (Appendix <u>A</u>) it could be noted that the percent conversion decreases less rapidly than the decrease in the initiator concentration (Table I).

- 84 -

Miller (105) using the same toluene-n-BuLi-acrylonitrile system observed that below 1 meq/liter of initiator concentration no polymerization occurred. He studied the effect of varying the initiator concentration (from 2.4 to 10.0 meq/liter) on polymerization and found a similar time dependence on polymerization rate. In the present study the polymerization data were not reproducible in this range of initiator concentration.

c. Effect of Monomer Concentration on Polymerization

(i) Constant initiator concentration:

The polymerization data from Appendix <u>A</u> have been used to compare the variation in percent conversion at different reaction intervals, with change in monomer concentration. Polymerization data for 0.5, 1.0, 2.0 and 4.0 mole/liter monomer and 1.0 meq/liter initiator

TABLE IV

Polymerization Data for Various Initiator Concentrations

Temperature: -78°C. Solvent: Toluene Monomer concentration = 0.5 Mole/Liter

Reaction time		Conversion %				
(Minutes)	2.00	Initiator Co 1.00	ncentration 0:50	(Meq /Liter) 0.25	0.166	
5	28.2	18.8	13.7	11.1	3.4	
10	30.0	21.9	16.4	12.3	-	
20	33.0	24.5	18.5	16.6	-	
40	35.9	-	-	16.5		
60	40.3	26.6	22.8	18.6	-	
120	-	-	-	· · · ·	8.9	
300	49.9	32.5	24.1	21.7	11.1	
EFFECT OF INITIATOR CONCENTRATION ON POLYMERIZATION

	Temper	78 ⁰ C.		
	Solven	t: To	luene	
Figure:	A	В	C	D
Monomer (mole/liter):	0.5	1.0	2.0	4.0

LEGEND:

	Initiator (meq /liter)
Δ	0.167
	0.250
	0.333
0	0.500
	0.667
0	1.000
	2.000

1.120

<u>.</u>::







are plotted in Fig. <u>11A</u>. If the reproducibility is taken in the present study as approximately $\pm 2\%$, the percent conversion at a particular initiator concentration, seems to be independent of monomer concentration. Thus when the monomer concentration is varied from 0.5 to 4.0 mole/liter the rate of polymerization is proportional to monomer concentration, indicating a first-order reaction in monomer. Similar results were obtained at other initiator concentrations and are plotted in Figures <u>11B-11D</u>. As seen From Figure <u>11D</u>, the plot of conversion against time for 0.5 mole/liter monomer concentration deviates more than $\pm 2\%$ at long reaction intervals.

(ii) Constant monomer to initiator ratio $([M]_o / [I]_o)$:

Polymerization data (Appendix <u>A</u>) obtained by varying the monomer concentration at constant $[M]_0/[I]_0$ are plotted in Figure 12A. These data indicate that the percent conversion increases with the monomer concentration at a fixed ratio. This was found to be the case when the ratio $[M]_0/[I]_0$ was varied from 500 to 12000 at four different monomer concentrations as shown in Figures <u>12B-12F</u>.

d. Effect of Long Reaction Time on Polymerization

These experiments were formed by varying the initiator and the monomer concentration at -78° C. in toluene. In all except two to three long polymerization experiments, the reaction mixture was in the form of a solid gel, yellow in color. The exceptions were noted at low initiator and low monomer concentrations. The color of the carbanions indicated that most of the propagating centers were active and capable of adding monomer. The polymer yield obtained from these experiments is given in Table <u>V</u>. From these data it is apparent that

an an tha an the state of the state of the

EFFECT OF MONOMER CONCENTRATION ON POLYMERIZATION (constant initiator concentration)

	Temp	Temperature: -78°C.			
	Solvent:		Toluene		
Figure:	A	B	C	D	
Initiator (meq /liter):	1.00	0.50	0.25	0.167	

LEGEND:

Monomer (mole/liter) ○ 0.5 ○ 1.0 □ 2.0 △ 4.0





EFFECT OF MONOMER CONCENTRATION ON POLYMERIZATION (constant monomer to initiator ratio)

	Tempera	ature:	-78°	С.			
	Solvent:		Toluene				
Figure:	A	В	C	, D	E	F	
[M] _° /[I]°:	500	1000	2000	4000	6000	12000	

IEGEND:

	Monomer (mole/liter)
0	0.5
Δ	1.0
	2.0
0	4.0



.







.

Polymerization Data - 50-Hour Experiments

Temperature-78°C.Reaction time:50 Hrs.Solvent:Toluene

Expt. No.	Initiator Conc.	Monomer Conc.		Polymer Yi	eld
	(Mole/Liter)x104	(Mole/Liter)	[++]o/ [+]o	(Per Cent)	(MPL)
h (00.00	0 5	250		0 250
AV-0	20.00	0.5	290	47.7	0.200
Au-6	10.00	0.5	2000	27.J	0.197
A s- 6	5.00	0.5	1000	27.0	0.149
A q- 6	2.50	0.5	2000	28.1	0,140
Bv-6	20,00	1.0	500	45.0	0.450
Bu-6	10.00	1.0	1000	36.5	0.365
Be-6	5,00	1.0	2000	29.6	0.296
Ba-6	2 50	10	1,000	20.4	0.204
Dy-0 Pr 4	2.00	1.0	6000	10 0	0 100
ър 0	1.07		0000	17.0	0.1/0
Cs-6	5.00	2.0	4000	33.5	0.670
Cr=6	3,33	2.0	6000	29.0	0.580
Ca-6	2.50	2.0	8000	26.0	0.520
Cn-6	1 67	2.0	12000	19.9	0.398
00-00	T •01	2.0		_/•/	
Du-6	10.00	4.0	4000	29.7	1.188
Dt-6	6.67	4.0	6000	28.6	1.414
De-6	5 00	1.0 1.0	8000	26.4	1.056
D6	3 33	· · · ·	12000	19.8	0.792
DT.=0	2.22	4.0	12000	_ 720	~ • [/~

the percent conversion is not independent of monomer concentration within the limits of reproducibility ($\pm 2\%$). From a plot of percent conversion as a function of initiator concentration given in Figure <u>13A</u>, it is evident that the deviation from $\pm 2\%$ reproducibility is irregular and independent of monomer concentration. In Figure <u>13B</u>, the data of Table <u>V</u> are plotted as conversion (mole/liter) against initiator concentration. At a particular $[M]_{O}/[I]_{O}$ ratio the percent conversion increases with the monomer concentration, but tends to approach the same percent conversion at lower $[M]_{O}/[I]_{O}$ ratios (≤ 250) as seen from Figure <u>14</u>.

e. Effect of Temperature on Polymerization

The effect of temperature on polymerization was studied over the range -78° to 0° C., for a fixed reaction time of one hour. The results of these experiments, given in Table <u>VI</u>, show that the percent conversion at a particular monomer and initiator concentration varies inversely with the temperature. At any temperature between 0 and -78° C., under identical conditions, the percent conversion increases with the initiator concentration but is independent of monomer concentration. Detailed results of these experiments are tabulated in Appendix <u>B</u>. As seen from these data the percent conversion in a few cases changes in an irregular fashion with respect to monomer concentration.

At all the polymerization temperatures investigated, before termination, the reaction mixture was yellow in color. Upon terminating the reaction, the color disappeared at -78° and -60° C. and a white polymer was obtained. Since the polyacrylonitrile (PAN) obtained at

CONVERSION AS A FUNCTION OF INITIATOR CONCENTRATION

	Temperature:	-78 ⁰ C.	
	Solvent:	Toluene	
	Reaction time:	50 Hours	
Figure:	А		В
Conversion:	percen	t	mole/liter

LEGEND:

Monomer (mole/liter) ○ 0.5 ○ 1.0 □ 2.0 △ 4.0



,

CONVERSION AS A FUNCTION OF MONOMER TO INITIATOR RATIO

Temperature:	-78°C.
Solvent:	Toluene
Reaction time:	50 Hours

LEGEND:

(m	Monomer ole/liter)
O	0.5
0	1.0
	2.0
Δ	4.0

TABLE VI

Temperature Dependence of Polymer Yield

Reaction time: 60 minutes Solvent: Toluene

Reaction Temp.	Initiator Conc.	Monomer Conc.	Polymer Yield
(°C.)	(Mole/Liter)x104	(MOLe/Liter)	(Per Cent)
-78	10	2.0	28.2
-60	10	2.0	14.4
-40	10	2.0	6.8
-20	10	2.0	3.8
0	10	2.0	3.5
-78	5	0.5	22.8
-60	5	0.5	12.9
-40	5	0.5	5.0
-20	5	0.5	3.5
. O	5	0.5	3.0
-40	20	0.5	9.9
-40	20	1.0	10.5
-40	20	2.0	8.0
-40	20	4.0	9.4
0	40	4.0	6.9
0	20	4.0	4.3
0	10	4.0	2.3

-40° to 0°C. was yellow, it was impossible to decide by visual inspection whether or not the propagating carbanions at higher polymerization temperatures were active before the reaction was terminated.

The difference in activation energy between propagation and termination could be evaluated from the slope of the semilogarithmic plot of molecular weight, \overline{M}_v , against 1/T, where <u>T</u> is the temperature in ^OK. These plots for PAN are given in Figures <u>15A-15D</u>. The activation energy data calculated from the slopes of the plots are given in Table <u>VII</u>.

f. Effect of Solvents on Polymerization

During the preliminary studies on polymerization, different hydrocarbon solvents were used as diluents. The observations from these experiments are recorded in Table <u>VIII</u>. It can be seen from these data that the polymers obtained using different diluents differ in yield, color and molecular weight.

B-III THE ORDER OF THE REACTION WITH RESPECT TO MONOMER:

The logarithm of monomer concentration $[M]_t$ against time, \underline{t} , is a non-linear function as given in Figures <u>16A-16D</u>. It does, however, approach linearity with time. Further, these semilogarithmic plots cannot be extrapolated back to initial monomer concentration. For a first-order polymerization reaction, log $[M]_t$ against \underline{t} plots should be linear (provided side reactions are absent). Therefore it is not possible to calculate the overall propagation rate constant, k_p , from

SEMILOGARITHMIC PLOTS OF MOLECULAR WEIGHT VERSUS

RECIPROCAL OF POLYMERIZATION TEMPERATURE (°K)

	Solvent:	Toluer	ıe	• .
Figure:	A	В	C	D
Monomer (mole/liter):	0.5	1.0	2.0	4.0

LEGEND:

Initiator (meq /liter)

4.0 0 2.0 Δ 1.0 0 0.5





(Mole/Liter) x 10^4 (Mole/Liter)AB200.52.767.6310n3.433.435n2.972.97201.03.242.0110n4.480.585n2.610.57202.02.871.9910n4.981.565n4.821.46204.02.490.2910n2.690.13	Initiator Concentration	Monomer Concentration	E _p -E _t * (K.Cal/Mole)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	(Mole/Liter) x 10^4	(Mole/Liter)	A	В
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	20	0.5	2.76	7.63
5 $"$ 2.97 2.97 20 1.0 3.24 2.01 10 $"$ 4.48 0.58 5 $"$ 2.61 0.57 20 2.0 2.87 1.99 10 $"$ 4.98 1.56 5 $"$ 4.82 1.46 20 4.0 2.49 0.29 10 $"$ 2.69 0.13	10	11	3.43	3.43
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5	11	2.97	2.97
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	20	1.0	3.24	2.01
5" 2.61 0.57 20 2.0 2.87 1.99 10 " 4.98 1.56 5 " 4.82 1.46 20 4.0 2.49 0.29 10 " 2.69 0.13	10	n	4.48	0.58
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5	rt .	2.61	0.57
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	20	2.0	2.87	1.99
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	20	11	4,98	1.56
5 n 4.82 1.40 20 4.0 2.49 0.29 10 n 2.69 0.13	10	•••	1 00	1 1.6
20 4.0 2.49 0.29 10 n 2.69 0.13	5		4.0%	1.40
20 4.0 2.49 0.29 10 n 2.69 0.13				
10 n 2.69 0.13	20	4.0	2.49	0.29
	10	n	2.69	0.13

Difference	in A	ctivation	Energy	(<u>EE_</u>)

* The values listed under A and B are calculated from higher and lower temperature parts respectively of the semilogarithmic plots (Fig. 15 -A to D).

		·			
Hydrocarbon solvent	Mon ome r Conc. (Mole/Liter)	Initiator Conc. (Mole/Liter)x10 ³	Polymer yield (%)	[1] ₂₅	Color
Benzene	2.00	40.0	41.7	0.415	Bright yellow
Benzene	2.00	4.0	6.6	0.562	Yellow
n-Hexane	2.00	4.0	25.0	1.427	Very pale yellow
Toluene	2.00	4.0	13.2	1.126	Pale yellow
Toluene	2.00	20.0	35.5	0.622	Bright yellow

Effect of Different Hydrocarbon Solvents on Polymerization, and Properties of the Resulting Polyacrylonitriles*

TABLE VIII

* The reaction temp. was 2°C. ; Reaction time was one hour.

SEMILOGARITHMIC PLOTS OF POLYMERIZATION RATE DATA

· .	Temper	ature: -	-78 ⁰ C.	
	Solver	nt: To	oluene	
Figure:	A	В	C	D
Monomer (mole/liter):	0.5	1.0	2.0	4.0

LEGEND:

	Initiator (meq /liter)
Δ	0.167
	0.250
	0.333
O	0.500
0	1.000
	2.000
•	0.667



:



the semilogarithmic plots obtained in the present work (Fig. 16). A propagation rate constant over a particular reaction time interval might be calculated. The propagation rate constants calculated for a time interval between 5 to 10 minutes are presented in Table <u>IX</u> for four different initial monomer concentrations. However the propagation rate constants thus calculated are of little value, as their magnitude may vary with the rate of monomer addition and the monomer mixing, both of which were beyond control in the present study.

B-IV POLYMERIZATION AT DIFFERENT INITIATION AND PROPAGATION TEMPERATURE:

In a few experiments the polymerization was initiated at higher temperatures (-40° or 0°C.). After a short time interval, t_1 , the reaction mixture was cooled to -78°C., and the reaction was continued, at -78°C., for a time interval, t_2 . The results of these experiments are presented in Table <u>X</u>. Also given in this table, for purposes of comparison, are the data on polymerization at 0° and -40°C. without a subsequent change in temperature to -78°C. and for -78°C alone.

B-V FORMATION OF BY-PRODUCTS DURING POLYMERIZATION:

The filtrate and washings from the polymerization experiments at each temperature were collected and evaporated to dryness at room temperature. The white, soluble residues from the filtrate of the experiments at -60° and -78° C. were identified as lithium chloride. The residues from the filtrate and washings of the experiments at -40° , -20° and 0° C.

TABLE IX

The Rate Propagation Constant, $k_p \ge 10^3 \text{ min}^{-1}$ (Reaction Interval 5 to 10 Minutes)

Initiator Concentration]	$k_{\rm p} \ge 10^3$	Av. k x 10 ³		
(Mole/Liter)x10 ⁴	Monomer Concentration (Mole/Liter)				(min. ⁻¹)
	0.5	<u> </u>	2	4	
20.00	5.15	4.05		• • —	4.60
10.00	6.95	1.52	-	10.59	6.18
5.00	6 .3 5	5.52	4.60	5.06	5.38
3.33	-	—	3.68	5.52	4.60
2.50	2.85	5 .43	5.52	-	4.60
1.67	-	3.68	2.76	-	3.22

TABLE X

Polymerization at Different Initiation and Propagation Temperatures

Expt. No.	Initiation Temp. (^o C)	Propagation Temp. (^o C)	React: (Min t	ion time nutes) ^t 2	Monomer (Mole/Liter)	Initiator (Mole/Liter)x10 ⁴	Polymer yield (Per Cent)
6	0	-78	5	120	l	20	7.6
7	0	-78	5	120	1	20	4.5
10	0	- 78	l	600	1	20	4.0
156	0	0	60	-	1	20	7.0
12	-40	-78	5	600	1	20	8.6
9	- 40	-40	60	—	1	20	10.5
27	-78	-78	60	-	1	20	37.6
13	-40	-78	5	600	2	40	6.7
15	-40	-78	5	960	2	40	8.6
162	-40	-40	60	· - .	2	40	8.0
109	-78	-78	60	-	2	40	23.4

- 102

1

.

were yellow and contained water-soluble lithium chloride and trace amounts of polymer. The infrared spectrum of the water-insoluble residue is given in Figure <u>17</u>. A very small, absorption peak at 2242 cm⁻¹ in the IR spectrum of the residue compared to that in an IR spectrum of the polyacrylonitrile (Fig. 26A), indicates that during polymerization the nitrile group participated in the reactions.

The polymer obtained at -78° and -60° C. was white in color and insoluble in acetone. The polymer obtained at -40° to 0° C., was yellow in color and partially soluble in acetone. A visual examination indicated that under otherwise similar experimental conditions, the color was more intense at higher initiator concentration and higher polymerization temperature.

B-VI THE KINETIC MOLECULAR WEIGHT, M.:

The kinetic molecular weights calculated from the polymerization data obtained at -78°C. are tabulated in Appendix <u>A</u>. A comparison between the viscosity average molecular weight, \overline{M}_{v} , and \overline{M}_{k} show that the former is always higher than the latter, and both increase with polymerization time. In general the kinetic molecular weight is found to increase with an increase in monomer concentration or decrease in an initiator concentration as given in Table <u>XI</u>.

B-VII <u>COMPARISON OF EXPERIMENTAL DEGREE OF POLYMERIZATION, (DP_n)_{expt}, WITH THEORETICAL DEGREE OF POLYMERIZATION, (DP_n)_{calc}:</u>

During a study on anionic polymerization of acrylonitrile with

INFRARED SPECTRUM OF BYPRODUCTS OBTAINED DURING POLYMERIZATION

.

low, being in the range of 2 to 4 percent for 0.5 mole/liter monomer; 3 to 5 percent for 1.0 mole/liter monomer; 4 to 7 percent for 2.0 mole/ liter monomer; and 6 to 10 percent for 4.0 mole/liter monomer. Although the percent initiator consumed in the initiation reaction is small, it increases with an increase in monomer concentration. The quantity of the initiator does not vary regularly with a change in the initiator concentration, but depending upon the monomer concentration, fluctuates over a narrow range.

The data for other temperatures have not been treated by these calculations, since the assumption $\overline{M}_n \approx \overline{M}_v$ will no longer hold and, as will be seen later, the polyacrylonitriles obtained at other temperatures are branched as well as polydispersed.

THE CHARACTERIZATION OF POLYACRYLONITRILES

C-I VISCOSITY MEASUREMENTS:

a. Procedure

The polymer solution was prepared with freshly vacuum distilled, N,N-dimethyl formamide (DMF). The solution was filtered through a medium porosity fritted disc. The disc was washed with pure DMF to insure the quantitative transfer of polymer (174). The filtrate and washings were collected in a stoppered flask. As DMF is very hygroscopic, all solutions and solvent were stored over silica gel in a desiccator. Following the technique employed by LeBel et al. (175) for their work with dimethyl sulfoxide, the DMF used in the present work contained 0.1% water.

Although as shown in Table <u>XII</u> the viscosity measurements made at intervals over a period of one week indicated the viscosity of the solution to be constant within experimental error, all the viscosity measurements were made within 48 hours of the time the polymer was completely dissolved in DMF. Viscosity measurements were made at $25 \pm$ 0.05°C. with the Utbelohde type viscometer described by Graig and Henderson (176). Exactly 20 ml. of polymer solution at 25°C. were added to the viscometer and allowed to stand for five minutes. The solution was then drawn above the mark in the capillary and the efflux time noted. This process was repeated four times and an average time was recorded. The same procedure was repeated for three to four additional dilutions. The flow time for the DMF solvent was checked at the end of each set of measurements. The initial concentration was established by freeze-

TABLE XII

Flow Time of Polyacrylonitrile Solution

Time (hours)		Flow time (se	Av. Flow time (seconds)	
:				
0	210.4	210.5	210.2	210.36
28	210.3	210.2	210.4	210.30
46	210.4	210.4	210.5	210.43
74	210.2	210.4	210.5	210.37
125	210.5	210.3	210.4	210.40
169	210.2	210.2	210.4	210.27

drying a known volume of the initial solution to a constant weight. The validity of the dilution procedure was found to be within $\pm 1\%$ as determined from the solids content of the final solution by the freeze-dry method.

The particular viscometer used had a flow time of 138.9 seconds for DMF. The dependence of viscosity on shear rate was not investigated and the kinetic energy correction was not applied (177).

If η_{o} and t_{o} are the viscosity and the flow time of the solvent through the viscometer, $\underline{\eta}$, \underline{t} and \underline{C} are respectively the viscosity, flow time and concentration in gm/100 ml(dl) of the polymer solution, then the relative viscosity, η_{r} , specific viscosity, η_{sp} , and reduced viscosity, $\eta_{sp/C}$, are given as,

 $\eta_{r} = \frac{\eta}{\eta_{o}} = \frac{t}{t_{o}}$ $\eta_{sp} = \frac{t}{t_{o}} - 1 = \eta_{r} - 1$ $\eta_{sp/c} = (\eta_{r} - 1)/c.$

The reduced viscosity can then be plotted against C to give a typical Huggin's plot, following the relation,

$$\eta_{\rm sp/C} = [\eta] + \kappa [\eta]^2 C \qquad (22)$$

Such plots of $\gamma_{sp/C}$ versus C are given in Figure <u>18</u> for different polyacrylonitriles. The intercept of the plot, at C = O, is called the intrinsic viscosity [7], and represents the contribution of the polymer to the solution viscosity. The parameter k', known as the Huggins interaction parameter, can be evaluated from the slope as

PLOTS OF REDUCED VISCOSITY AGAINST CONCENTRATION

FOR

DIFFERENT POLYACRYLONITRILES


$$k^{\dagger} = \text{slope}/\left[\eta\right]^2 \tag{23}$$

Using the equation (24) for the temperature dependence of of polyacrylonitrile solution (178), the value of $[\eta]$ at 25°C. was corrected to the appropriate value at 30°C.

 $\partial \ln [\eta] / \partial t = 0.0019$ (24)

where t, is the temperature in degrees centigrade.

Molecular weights can be calculated from viscosity measurements using an empirical relation of the Mark-Houwink (156) type, generally represented as

$$[\eta] = k \overline{M}_{v}^{a}$$
(25)

where <u>k</u> and <u>a</u> are constants for a given temperature, polymer and solvent. This equation has been found to be generally applicable over a large range of molecular weights. The molecular weight, \overline{M}_{v} , for polyacrylonitrile was determined from the relation (162),

 $[\eta]_{30} = 2.27 \times 10^{-4} M_v^{0.75}$ (18)

b. Results

Under the various conditions of polymerization, employed in the present work, the polymers obtained had intrinsic viscosities as low as 0.2 dl/gm and as high as ll.0 dl/gm. The initiator concentration, the monomer concentration, reaction temperature and other variables, affected the intrinsic viscosities of the polymers.

(i) Effect of monomer concentration at -78°C.:

The results of viscometry on these polymers presented in

Tables <u>A-I</u> to <u>A-IV</u> of Appendix <u>A</u>, indicate that although under identical conditions $[\eta]$ and hence \overline{M}_{v} increases with monomer concentration, there is no apparent simple relation between the molecular weight and the monomer concentration. At constant initiator concentration, if a definite percent conversion is considered, then theoretically an x-fold increase in monomer concentration should lead to an x-fold increase in the molecular weight.

(ii) Effect of initiator concentration at -78°C.:

Results of molecular weight measurements from Appendix <u>A</u> are plotted in Figures <u>19A-19D</u>. These figures show that the molecular weight increases with a decrease in initiator concentration at any conversion obtained during the reaction.

(iii) Variation of molecular weight with polymerization:

The molecular weight as a function of percent conversion plotted in Figures <u>19A-19D</u> shows the molecular weight to increase with conversion in a linear fashion. In some cases deviation from linearity is found to occur at higher conversions, which corresponds to a reaction period between five and fifty hours. As seen from Figure <u>19D</u>, the deviation is maximum for polymers obtained with 4.0 mole/liter monomer concentration. In the case of polymers obtained using 0.5 mole/liter monomer and 2.0 meq/liter initiator concentration, the molecular weight increases less rapidly than the corresponding conversion (Fig. 19A) at longer reaction intervals.

(iv) Effect of long polymerization time on viscosity (intrinsic) and molecular weight of polymers:

The intrinsic viscosity and molecular weight data for polyacrylonitriles formed over a 50-hour reaction period are given in Table XIII.

VARIATION OF MOLECULAR WEIGHT WITH PERCENT CONVERSION

Figure:	A	В	C	D
Monomer (mole/liter):	0.5	1.0	2.0	4.0

LEGEND:

	Initiator (meq /liter)
	2.000
0	1,000
\bullet	0.667
0	0.500
	0.333
	0.250
Δ	0.167





TABLE XIII

Viscosity and Molecular Weight of Polyacrylonitriles

Initiato r Conc. (Mole/Liter)xl0 ⁴	Monomer Conc. (Mole/Liter)	[1] ₂₅	$\overline{M_v} \ge 10^{-5}$
20.00	0.5	4.765	5.70
10.00	11	4.970	6.04
5.00	tt	4.873	5.90
2.50	11	4.940	6.00
20.00	1.0	5.045	6.08
10.00	ft .	6.070	8.00
5.00	11	5.580	7.10
2.50	TT	7.010	9.61
1.67	**	7.952	11.40
5.00	2.0	8.140	11.75
3.33	11	8.210	11.80
2.50	tt	9.100	13.70
1.67	17	11.050	17.50
10.00	4.0	7.150	9.80
6.67	11	8.880	13.20
5.00	11	10.260	16.00
3.33	tt	10.020	15.50

(50-HOUR POLYMERIZATION AT -78°C.)

The $[\eta]$ and therefore \overline{M}_{v} are higher than for polyacrylonitriles obtained from shorter reaction periods (Appendix A). Under similar experimental conditions, the molecular weight increases with a decrease in initiator concentration or an increase in monomer concentration. In a few experiments at 0.5 and 1.0 mole/liter monomer concentration, the molecular weight of polymer obtained did not increase with decrease in the initiator concentration.

(v) Effect of varying polymerization temperature on $[\eta]$ and \overline{M}_v of polymers:

The data in Appendix <u>B</u>, Tables <u>B-I</u> to <u>B-IV</u> give the effect of reaction temperature on molecular weight. When the other variables are held constant, the molecular weight of the polyacrylonitrile obtained increases with increase in monomer concentration or decrease in temperature and/or initiator concentration, but there does not seem any simple quantitative relation to express this variation.

C-II THE SEDIMENTATION VELOCITY MEASUREMENTS:

a. Determination of Sedimentation Coefficients

The sedimentation velocity measurements were made on a Beckman Spinco E Ultracentrifuge equipped with rotor temperature indicator and control unit, (ETIC), and Wölter phase plate Schlieren optics. In the sedimentation velocity experiments the rotor speed was 56100 RPM, temperature $25 \pm 0.5^{\circ}$ C. and the phase plate angle was 50, 55 or 60°. Kel-F coated double sector, 12 mm cells were used for all sedimentation studies. The solutions employed for these experiments were from 0.1% to 0.8% (w/v) of polyacrylonitrile in DMF. At least six pictures were taken at 16 or 32 minutes intervals, after the boundary had moved away from the meniscus. Assuming the acceleration of the rotor to be a linear function of time, the usual correction for equivalent time at speed was applied (179).

Typical Schlieren tracings are given in Figure 20. In these tracings the image of the opaque element was always sharp except after very long time intervals at low concentrations. For polymers prepared at -40° C. and at higher temperatures, the tracings were usually less sharp. These tracings were magnified five times and printed. From this the position of the maximum of the ordinate was measured with respect to the position of the reference hole on the rotor, and was related to the center of rotation after correcting for the magnification of the enlarger and the camera lens. The distance between the center of rotation of the ordinate was taken as the position of the maximum of the ordinate was taken as the position of the maximum of the ordinate was taken as the position of the maximum of the ordinate was taken as the position of the moving boundary, r.

The sedimentation coefficient, S, is usually defined as

$$S = \frac{1}{\omega 2} \cdot \frac{d \ln r}{dt}$$
(26)

where <u>r</u> is the position of the moving boundary from center of rotation, expressed in centimeters, <u>t</u>, is the corrected time in seconds, and $\underline{\omega}$ represents the angular velocity of the rotor in radians/second.

Generally in organic solvents, under non-theta conditions, the value of the sedimentation coefficient is a function of both concentration and pressure. A correction for concentration can be made using one of the empirical relations (164)

SCHLIEREN PHOTOGRAPHS OF SEDIMENTATION VELOCITY GRADIENTS

#	PAN No.	Polymerization temperature (°C.)	Polymer concentration (gm /dl)
A	17	` –78	0.2727
В	214	-60	0.2484
C	261	0	0.2220



ф





A

р

υ

ř

$$S = S_{0}/(1 + k_{s}C)$$
 (27)

$$S = S_0(1 - k_s^{C})$$
 (28)

where S_0 is the value of sedimentation coefficient corrected for concentration, k_s is an empirical constant and <u>C</u> is the concentration of the polymer solution (gm/dl).

From equation (27) the concentration dependence of polyacryloin nitrile could be corrected for by plotting 1/S against <u>C</u> and extrapolating the plot to zero concentration to give $(1/S)_{C=0} = 1/S_0$. The constant k_s could then be calculated from the slope of this plot from the simple relation,

If the pressure dependence of the viscosity (η_0) and density (P_0) of the solvent is known, then the effect of pressure on <u>S</u> could be corrected for by the method of Oth and Desreux (167), provided the variation of the partial specific volume, \overline{U} , of the polymer is constant or assumed to be so. Since these requisite data for DMF are not available, the least square technique of Billick (168) was used to calculate the pressure corrected sedimentation coefficient, S^o. The quantity $1/S^{\circ}$ was plotted versus <u>C</u>, to give on extrapolation to zero concentration, $(1/S^{\circ})_{C=0} = 1/S_0^{\circ}$. Using the value of pressure and concentration coefficient, k_s was calculated as

$$k_s = slope.S_o^o$$
 (29)

The relation derived by Billick (168) for pressure correction of the sedimentation coefficient is given as

$$\ln r_{i} = \ln r_{o} + S^{o} \omega^{2} t_{i} + B(\omega^{2} t_{i})^{2}$$
(21)

where r_i is the position of the maximum of the ordinate of the boundary at time t_i , and

$$B_{5}^{2} = -\frac{m(2\alpha+1) - \alpha}{1 + \alpha}$$
(30)

where $\mathbf{x} = \mathbf{k}_{\mathbf{s}} \mathbf{x} \mathbf{C}$

1

$$n = 1/2 \rho_0 r_0^2 \omega^2 \mathcal{A}$$
(31)

and where \mathcal{H} is a constant characteristic of a given solvent-polymer system. The equation (21) was solved numerically by computer using the following relations to calculate r_0 , S^0 and <u>B</u>.

$$nr_{o} + S^{o} \sum_{i=1}^{n} \omega^{2} t_{i} + B \sum_{i=1}^{n} (\omega^{2} t_{i})^{2} = \sum_{i=1}^{n} \ln r_{i}$$

$$r_{o} \sum_{i=1}^{n} \omega^{2} t_{i} + S^{o} \sum_{i=1}^{n} (\omega^{2} t_{i})^{2} + B \sum_{i=1}^{n} (\omega^{2} t_{i})^{3} = \sum_{i=1}^{n} \ln r_{i} \omega^{2} t_{i}$$

$$r_{o} \sum_{i=1}^{n} (\omega^{2} t_{i})^{2} + S^{o} \sum_{i=1}^{n} (\omega^{2} t_{i})^{3} + B \sum_{i=1}^{n} (\omega^{2} t_{i})^{4} = \sum_{i=1}^{n} \ln r_{i} (\omega^{2} t_{i})^{2}$$

where $\underline{n} = 6$

Taking ρ_{o} (DMF) = 0.9445 gm/ml at 25°C. (180), $\underline{\mathcal{H}}$ was calculated.

The pressure corrected sedimentation coefficients, obtained at different concentrations for different polyacrylonitriles are tabulated in Appendix <u>C</u> along with the values of S_0^0 , k_s , <u>m</u>, <u>H</u> etc. Sample plots of $1/S^0$ versus <u>C</u> for four different polyacrylonitriles are plotted in Figure <u>21</u>. These plots are straight lines whose slope increases with

SEDIMENTATION COEFFICIENT AS A FUNCTION OF CONCENTRATION (cf. Appendix C)

LEGEND:

Polyacrylonitrile sample No.

89
▲ 152
● 214
■ 261

increase in the magnitude of sedimentation coefficients. As shown in Appendix <u>C</u>, the value of <u>m</u> which depends on concentration, pressure and interaction between solvent and polymer is different in each case. The value of <u>H</u>, which is a characteristic of a solute-solvent system, has approximately the same order of magnitude $\sim 10^{-9}$ for all polymer solutions. The average value of <u>H</u> was found to be $1.36_{30} \times 10^{-9}$.

b. <u>Interdependence of Sedimentation Coefficient and Intrinsic</u> <u>Viscosity</u>

The viscosity and sedimentation data for polyacrylonitriles obtained at different temperatures are given in Table <u>XIV</u>. By reference to this table the sedimentation coefficients for polyacrylonitriles, prepared at -78° C., increase with [7] and hence with the molecular weight. The value of k_s also increases with S₀^o. From the theories of Flory (181) and Burgers (182), Wales et al. (183) have derived a theoretical relation between [7] and k_s,

$$k_{s} = 1.66 [\eta]$$
 (32)

The experimental results of others (184,185) cast considerable doubt on the general applicability of this relation. In the present work the product 1.66 $\boxed{1}$ given in Table <u>XIV</u> is larger than the experimental value of k_s for polyacrylonitrile prepared at -78°C., but the product is smaller than k_s for polymer prepared at -60° to 0°C.

In the case of polyacrylonitriles obtained at different temperatures and having approximately the same $[\eta]$, the value of S_o^o is found to increase with increase in temperature of polymerization (Table XIV).

TABLE XIV

Solution Properties of Polyacrylonitriles Obtained at Different Temperatures

PAN #	Polymerization temperature (°C.)	[1] ₂₅	Log[IJ]	so	Log S _o	1.66[1]	, k _s
1	-78	3.480	0.5416	3.92	0.5933	5.777	3.714
17	ŦŦ	5.020	0.7007	4.84	0.6848	8.333	6.822
21	TT	3.723	0.5708	3.96	0.5977	6.180	5.923
89	11	8.620	0.9355	6.61	0.8203	14.309	10.856
152	11	2.320	0.3655	3.19	0.5038	3.851	3.504
214	-60	2.450	0.3874	4.01	0.6030	4.067	4.445
217	-40	2.300	0.3617	3.98	0.5999	3.818	5.009
261	0	2.300	0.3617	10.04	1.0017	3.818	13.636

For polyacrylonitriles prepared at $-78^{\circ}C.$, the plot of log S₀^o versus log[] is linear as seen in Figure <u>22</u>. The data of Bisschops (177) and Krigbaum et al. (186) are recorded in this figure for comparison.

Using the data of Figure 22, the dependence of S_0° on $[\eta]$ could be given as,

$$s_{o}^{o} = 1.95 \left[\Pi \right]^{0.564}$$
 (33)

which upon substituting for $[\eta]$ gives,

$$s_o^o = 1.72 \times 10^{-2} M^{0.423}$$
 (34)

This is an empirical relation of the type, $S_0^o = k_2 M^b$ (19).

c. Branching in Polyacrylonitriles

For a linear polymer fraction, Flory (181) has derived the relation, $\overline{\nu}^2/3$

$$s_{o} \left[\eta\right]^{1/3} = \frac{\overline{M}_{sv}^{2/3} (1 - \overline{\mathcal{V}}_{o})^{\beta}}{N\eta_{o}} \cdot \qquad (35)$$

where \underline{N} , $\underline{\beta}$ and \overline{M} are respectively Avogadro's number, the universal constant and sedimentation viscosity average molecular weight.

The value of $\underline{\rho}$ is found to vary with several polymer-solvent systems under non-theta conditions (187,188).

Senti et al. (189) have shown from their experiments on branched dextrans that the value of \underline{P} does not vary with branching. The additional assumption could be made that \underline{V} does not vary with branching

LOG SO VERSUS LOG [7]

LEGEND:

0	Data	of	the present work (Table XIV)
	Data	of	Krigbaum and Kotliar (186)
Δ	Data	of	Bisschops (177)



for a particular polymer-solvent system. Using the above relation (35), one can derive a further relation for two polymer samples of identical molecular weight, but one having a linear and the other having a branched structure.

$$s_{01}^{\circ}[\eta]_{1}^{1/3} = \frac{M_{sv}^{2/3}(1-\bar{\nu}\rho_{0})\beta}{\eta_{0}N} = s_{0b}^{\circ}[\eta]_{b}^{1/3}$$
(36)

where the subscripts $\underline{1}$ and \underline{b} refer to the linear and branched forms respectively.

Substituting equation (33) for linear polyacrylonitrile in relation (36) one obtains,

1.95
$$[\eta]_{1}^{0.897} = s_{o_b}^{o}[\eta]_{b}^{1/3}$$
 (37)

From relation (37), using known values of $[\eta]_b$ and S_{ob}^o , a value of $[\eta]_1$ for non-linear polymer could be determined. Once this is done, the number of branched units per polymer molecule, <u>m</u>, could be evaluated using the relation of Zimm et al. (190), which is given as,

$$[\eta]_{b} / [\eta]_{1} = g' = [(1 + m/7)^{1/2} + 4m/9\pi]^{-1/4}$$
 (38)

The present data were treated in the above manner and the results of the calculations are given in Table <u>XV</u>. These calculations indicate that the number of branched units per polymer molecule, <u>m</u>, increases with increase in the polymerization temperature.

d. The Molecular Weight Distribution in Polyacrylonitriles

Following a velocity ultracentrifugation method proposed by Wales et al. (170), the molecular weight distribution in polyacrylonitriles obtained

Degree of Branching in Polyacrylonitriles

Polymerization temperature	[1] _b	s°[1] _b ^{1/3}	[1],	<u>ព្]_b ក្រា</u>	No. of branched units per molecule
(°C.)			<u> </u>	(g [†])	m
-60	2.45	5.397	3.111	0.7875	8
-40	2.30	5.251	3.017	0.7623	10
0	2.30	13.253	8.422	0.2731	89 ?

at different temperatures was computed. To make this calculation, the concentration gradient $(dc/dx)_i$ was calculated at each point from the relation, valid for a Schlieren optical system:

$$\left(\frac{dc}{dx}\right)_{i} = \frac{Y_{i}(x) \cdot \tan \Theta}{m_{1} \cdot E \cdot a \cdot L} / \frac{dn}{dc} = A_{k} Y_{i}(x) \cdot \tan \Theta \qquad (39)$$

where

m is the magnification by the cylindrical lens= 3.416lEis the magnification by the enlarger= 5.000a is the cell thickness (cm.)= 1.200

<u>L</u> is the length of the optical level arm (cm.) = 57.860dn/dc is the refractive index increment for polymer

solution (0.083 ml/9m) (161).

Therefore $A_{k} = 1.0159 \times 10^{-2}$.

 \underline{o} is the phase plate angle (50, 55 or 60°).

 $Y_{i}(x)$ is the height of the refractive index gradient curve at i

a distance x, from the center of rotation.

The Y values were measured at 1 mm intervals along the X-axis i (distance from center of rotation) on the enlarged photographic prints of the refractive index gradient curves recorded during sedimentation velocity experiments.

The dx was converted to \underline{x} , the distance from center of rotation, using the relation,

$$x_{i} = 7.3 - dx_{i}/m_{2}$$
.E.

where m_0 is magnification by the camera lens

The sedimentation coefficients at each point x_i were calculated using the following relation derived by Wales (170).

$$s_{i}^{o} = \frac{1}{2\omega^{2}t(1+\infty)} \left[\frac{1}{1+m} \left(1 + \frac{2m\alpha}{(1+m)^{2}} \right) \ln \frac{Y_{i}}{1+m-mY_{i}} + \frac{\alpha}{(1+m)^{2}} \left(1 - m - \frac{1+m-2mY_{i}}{Y_{i}(1+m-mY_{i})} \right) \right]$$
(40)

where the values of \propto and \underline{m} used are from Appendix \underline{C} , and $\underline{Y} = (\underline{x}_i / \underline{x}_i)^2$. where \underline{x}_i is the position of the meniscus with respect to the center of rotation.

> The function $g^{*}(S)$ was calculated from the relation, $g^{*}(S) = \frac{\omega^{2} t x_{i}^{3} (dc/dx)_{i} (1+m-mY_{i})^{2} (1+\infty)}{c_{o} x_{o}^{2} (1+\infty/Y_{i}(1+m-mY_{i}))}$ (41)

Where $g^*(S)dS$ is the fraction of the material having sedimentation coefficient between <u>S</u> and S + dS.

Further the functions \underline{Z} and H(Z) were calculated from equations (42) and (43) respectively as,

$$Z_{i} = S_{i}^{o}/S_{max}^{o}$$
(42)
$$H_{i}(Z) = g_{i}^{*}(S)/g^{*}(S_{max})$$
(43)

The above calculations were made on IBM 7090 computer. The values of $H_i(Z)$ were plotted against Z_i for each tracing. For each concentration of the polymer solution six plots were obtained for six different time intervals. From these plots the values of H(Z) at fixed values of Z were tabulated. A typical set of data is given in Table <u>XVI</u>. The value of H(Z), as given in Table <u>XVI</u> should be corrected for diffusion, but this was not possible since the variation in H(Z) from

H(Z) for Different* Sedimentation Times and H(Z) av

		H(Z)					
_			Time in	minutes			H(Z)
<u></u> Z	56.4	72.4	88.4	104.4	120.4	136.4	av
0.350	0.003	_	-		-	-	-
0.400	0.006	0.002	-	-	_	_	_
0.450	0.011	0.004	0.003	-	_	-	0,003
0.500	0.021	0.010	0.009	0.006	0.002	-	0.008
0.550	0.029	0.022	0.018	0.015	0.012	0.008	0.017
0.600	0.038	0.037	0.030	0.029	0.022	0.020	0.029
0.650	0.059	0.045	0.052	0.050	0.042	0.036	0.047
0.700	0.076	0.062	0.066	0.067	0.056	0.050	0.063
0.750	0.102	0.130	0.095	0.090	0.076	0.075	0.095
0.800	0.145	0.160	0.130	0.130	0.132	0.130	0.138
0.850	0.220	0.230	0.177	0.200	0.180	0.208	0.202
0.900	0.350	0.370	0.320	0.310	0.255	0.370	0.329
0.925	0.485	0.522	0.450	0.435	0.430	0.510	0.472
0.950	0.655	0.705	0.675	0.615	0.625	0.670	0.657
0.975	0.830	0.855	0.870	0.835	0.800	0.840	0.838
1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
1.025	0.815	0.820	0.795	0.805	0.785	0.790	0.802
1.050	0.650	0.625	0.580	0.555	0.575	0.615	0.600
1.075	0.510	0.425	0,385	0.350	0.300	0.370	0.390
1.100	0.345	0.180	0.185	0.225	0.190	0.210	0.222
1.150	0.160	0.117	0.090	0.080	0.040	0.100	0.083
L.200	0.087	0.072	0.060	0.045	0.012	0.005	0.047
1.250	0.050	0.045	0.035	0.027	0.004	-	0.027
1.300	0.030	0.025	0.017	0.014	-	- ,	0.014
L.35U	0.018	0.011	0.005	0.005	-	-	0.006
1.400	0.010	0.003	-	-	-	-	-

* PAN 17; polymer concentration = 0.2727 gm/dl.

diffusion is less than the precision with which the (refractive index) gradient curves can be located. Consequently six values of $H_i(Z)$, determined at each Z_i were averaged. The $H_i(Z)_{av}$ was then plotted against Z_i as given in Figure 23. Four plots were made at the four different polymer solution concentrations for each polymer sample. From a set of four such plots, the values of \underline{Z} for fixed values of H(Z) were tabulated. These values of \underline{Z} at each H(Z) were plotted against \underline{C} to correct for concentration dependence of \underline{Z} . The value of H(Z) at zero concentration, $H(Z_0)$, was then plotted as a function of Z_0 as illustrated by the solid line curve in Figures <u>24A,B</u> for two different polymer samples. The magnitude of the correction due to concentrations, included in these plots. From the solid lines of these plots (Fig. 24A,B), the values of $H(Z_0)$ were tabulated at different Z_0 .

Using the values of Z_0 and $H(Z_0)$, for four polymer samples, the differential molecular weight distribution function f(M) and various molecular weight averages were computer calculated using the following relations:

$$\boldsymbol{\delta} = \frac{\eta_{o}^{N}}{p(1-\overline{\mathcal{V}}p)} = \frac{10^{13}}{k^{1/3} \cdot k_{2}} = 9.47 \times 10^{15}$$

where \underline{k} and \underline{k}_2 are the coefficients in the empirical equations relating viscosity and sedimentation coefficient respectively to molecular weight.

The sedimentation-viscosity average molecular weight, \overline{M}_{sv} , is given by the relation,

PLOT OF DATA OF TABLE XVI

 $H(Z)_{av} = f(Z)$

۰.



FIGURE 24A

$$\frac{PLOT \text{ OF } H(Z) = f(Z)}{(polyacrylonitrile # 261)}$$

LEGEND:

• • •

	Concentration of polymer solution (gm/100 ml.)
Q	0.0000 (extrapolation)
	0.1997
Δ	0.2379
0	0.3808



FIGURE 24B

 $\frac{PIOT OF H(Z) = f(Z)}{(polyacrylonitrile # 17)}$

LEGEND:

	Concentration of polymer solution (gm/100 ml.)
0	0.0000 (extrapolation)
	0.1887
Δ	0.4912
0	0.7674



$$\overline{M}_{sv} = \left(\frac{\eta_{o}^{N}}{(1-\eta_{o}^{N})\beta}\right)^{3/2} [\eta]^{1/2} s_{o}^{3/2} = \sigma_{s}^{3/2} [\eta]^{1/2}$$
(44)

The molecular weight, \underline{M} , for each value of Z_0 , and a fraction of a polymer sample, $f(\underline{M})d\underline{M}$, having the molecular weight between \underline{M} and $\underline{M} + d\underline{M}$ were calculated from,

$$M = Z_{o}^{3/(2-a)} \cdot \overline{M}_{sv} \cdot \left[\frac{\int_{o}^{\sigma} H_{o} dZ_{o}}{\int_{o}^{\sigma} Z_{o}^{3a/2-a} H_{o} dZ_{o}} \right]^{1/2}$$
(45)

$$f(M) = \frac{2-a}{3} \cdot \frac{H_{o}}{Z_{o}^{(a+1)/(2-a)}} \cdot \frac{1}{M_{sv}} \cdot \frac{\left[\int_{a}^{\infty} Z_{o}^{3a/2-a} H_{o} dZ_{o}\right]^{1/2}}{\left[\int_{a}^{\infty} H_{o} dZ_{o}\right]^{3/2}}$$
(46)

Where $\underline{a} = 0.75$ for polyacrylonitrile in DMF at 25° C. (162).

The number average molecular weight, \overline{M}_n , was calculated from,

$$\overline{M}_{n} = \frac{\overline{M}_{sv} \left[\int_{0}^{\infty} (H_{o} dZ_{o})^{3/2} \right]}{\left[\int_{0}^{\infty} Z_{o}^{-3/(2-a)} H_{o} dZ_{o} \right] \left[\int_{0}^{\infty} Z_{o}^{3a/(2-a)} H_{o} dZ_{o}^{1/2} \right]}$$
(47)

where the weight average molecular weight, $\overline{\mathrm{M}}_{\mathrm{W}}$, was calculated from,

$$\overline{M}_{W} = \frac{\overline{M}_{sv} \left[\int_{0}^{\infty} Z_{o}^{3/(2-a)} H_{o} dZ_{o} \right]}{\left(\int_{0}^{\infty} H_{o} dZ_{o} \right)^{1/2} \left(\int_{0}^{\infty} Z_{o}^{3a/(2-a)} H_{o} dZ_{o} \right)^{1/2}}$$
(48)

From the calculated values of \overline{M}_w and \overline{M}_n , the heterogeneity index, $(\overline{M}_w/\overline{M}_n)$, was calculated.

The values of the differential molecular weight distribution

function, f(M), are plotted against molecular weight, <u>M</u>, calculated from equations (45) and (46). The four molecular weight distribution curves given in Figures <u>25A-25D</u> for polymers obtained at different temperatures, show the heterogeneity in molecular weight of a polymer to increase with an increase in polymerization temperature. The molecular weight distribution is narrow in a polyacrylonitrile obtained at -78° C. The different molecular weight averages and heterogeneity indices for these polymers are tabulated in Table <u>XVII</u>. It can be seen from this table that the heterogeneity index, $\overline{M}_w/\overline{M}_n$, for polymer obtained at -78° C. is very low (1.08), and increases with the polymerization temperature. The value of $\frac{\overline{M}_w}{\overline{M}_n}$ at 0°C. corresponds to the most probable distribution.

C-III THE SPECTROSCOPIC MEASUREMENTS:

a. Infrared (IR)

The IR spectra of polyacrylonitriles were measured by the KBr disc technique. Approximately 3 to 4 mg of polymer sample was ground intimately with KBr and transformed to a semitransparent disc in the press, under vacuum. The IR spectrum of this disc was measured on a Perkin Elmer Model 137 or Model 257 spectrophotometer. Typical spectra of the polyacrylonitriles prepared at different temperatures are given in Figures <u>26A-26C</u>. An IR spectrum of PAN prepared using a radical initiator (191) is given in Figure <u>26D</u>.

The absorption bands, at 2.85-3.25µ and 5.70-6.60µ present in the spectra of anionically prepared PAN (Fig. 26A-26C) seem to be absent in the polymer prepared with a radical initiator (Fig. 26D).

DIFFERENTIAL MOLECULAR WEIGHT DISTRIBUTION FUNCTION

AGAINST MOLECULAR WEIGHT FOR POLYACRYLONITRILES

Figure	Sample No.	Polymerization temperature (°C.)
A	17	-78
В	214	- 60
C	217	-40
D	261	0








TABLE XVII

Molecular Weight Averages and the Heterogeneity Index

Polymer #	Polymerization temperature (°C.)	Molecular weight x 10 ⁻⁵				
		M _v	M _{sv}	M _w	M _n	M _w ∕M _n
17	-78	6.10	6.95	6.71	6.21	1.08
214	– 60	2.42	3.66	3.51	2.72	1.29
217	- 40	2.17	3.51	3.53	1.97	1.79
261	0	2.17	1 3. 97	13.23	6.12	2.16

FIGURE 26

INFRARED SPECTRA OF POLYACRYLONITRILES

Diagram	Polymerization <u>temperature (°C.)</u>	Nature of <u>initiation</u>
A	-78	Anionic
В	-40	. 11
C	0	**
D	60	Radical (191)



Upon examination of these spectra, of polymers obtained with n-BuLi, the presence of structural units such as $-C=C-(\sim 5.9-6.1\mu)(43)$, $-(C=N)_n -(\sim 6.25\mu)(192)$, $>C=N-(\sim 6.0\mu)$, $>C=O(\sim 5.85\mu)$, =NH $(\sim 3.08\mu; 6.00\mu)(193)$ could be detected over and above the usual, H $-C-(\sim 3.38\mu, 3.5\mu, 6.88\mu)$, $-C=N(\sim 4.42\mu)$ and $-C-(\sim 3.41\mu, 7.35\mu)$ H (191) units encountered in polyacrylonitriles in the absence of structural irregularity.

b. <u>Ultraviolet</u> (UV)

For the measurements, PAN was dissolved in 63% aqueous zinc chloride solution. The UV spectra of these solutions were measured against a $2nCl_2$ solution on a Unicam SP500 spectrophotometer. Fused silica cells with 1 mm and 10 mm path lengths were used for the measurements. The measured optical density of the solution, <u>E</u>, at a chosen wavelength, was used to calculate the absorption coefficient, <u>k</u>, from the equation $E = kcl^{\dagger}$.

where \underline{c} is the concentration of polymer solution in gm/liter and l^{*} is the path length in centimeters. The plots of the UV spectra of PAN solutions treated in this manner and given in Figure <u>27</u> show an absorption maximum at about 265-270 mµ. The magnitude of this absorption maximum varies with the polymerization conditions. The concentration of the monomer, the concentration of the initiator and the temperature of polymerization, affect the absorption maxima, as shown by the absorption coefficient values given in Table <u>XVIII</u> for several PAN samples.

FIGURE 27

ULTRAVIOLET SPECTRA OF POLYACRYLONITRILES

LEGEND:

Figure	Polymerization temperature (°C.)		
А	-78		
В	-40		
C	0		



TABLE XVIII

The Absorption Coefficients of Polyacrylonitriles

Solvent:

aq. ZnCl₂ (63% w/v)

= 268 m*H*

,		Absorption co	efficient, k	
Polymerization	Mono	omer concentra	tion (mole/lit	er)
temperature	·			
(°C.)	0.5	1.0	2.0	4.0
(i) Initiator co	ncentration = 4 3	c 10 ⁻³ mole/li	ter	
-78	-		-	0.4735
-60	-	-	· · · · · · · · · · · · · · · · · · ·	1.3760
-40	2 - A		-	3.6577
-20	-	—	-	4.4440
. 0	· • ·	-	. -	4.9179
(ii) Initiator c	oncentration = 2	x 10 ⁻³ mole/1	iter	
-78	0.4493	0.3506	0.1032	0.2895
-60	1.2660	1.0820	0.7517	0.5465
-40	4.7370	4.0820	2.5130	1.4927
-20	5.3101	4.6290	4.4759	2.8224
0	7.0000	5.3960	4.8730	4.4540
(iii) Initiator	concentration 1	x 10 ⁻³ mole/li	ter	
-78	0.4038	0.2612	0.1982	0.1707
-60		0.62/18	0.4281	0.2949
-40	2 0950	1,6110	1.3458	1,1512
-20	1, 1,210	1.0770	3.8620	2,6860
0	5.6461	5.2690	3.2520	3.0304
(iv) Initiator c	concentration 0.5	x 10 ⁻³ mole/1	iter	
-78	0.3520	0.1849	0.1085	-
-60	0.7272	0.3472	0.2238	-
-40	2.3350	1.2550	1.3806	— •
-20	4.4020	2,0920	3,2910	_
0	3.9387	2.9680	2.5105	-
(v) Initiator co	mcentration 20 \mathbf{x}	10 ⁻³ mole/lit	er	
0	-	8,3700	7.3330	_

DISCUSSION

TIME DEPENDENCE OF POLYMERIZATION AT -78°C .:

In the present work the polymer yield was found to increase with time over a reaction period of five minutes to fifty hours. The polymerization data plotted in Figures <u>10</u> to <u>12</u> indicate that the variation in percent conversion which is rapid in the beginning gradually slows down with time. These findings agree with those of Miller (105) for somewhat higher initiator concentrations. At any time before termination of the reaction, the characteristic yellow color of the polyacrylonitrile carbanions persisted in the reaction mixture indicating that the chain termination was negligible or absent. Even though polyacrylonitrile, PAN, is insoluble in toluene at room temperature, it was found that the growing polymeric species do not precipitate from the reaction mixture. Rather the polymeric species remain in solution as the reaction proceeds and contribute to the solution viscosity, until the solution phase solidifies to a highly swollen gel.

The observed variation in percent conversion with time might be due to any or all of the following: a decrease in monomer concentration with time, a gradual approach to a thermal equilibrium, a gradual deactivation of the carbanions, and a gradual decrease in accessibility of the monomer to the propagating centers. Each of these will be discussed in order.

The gradual decrease in monomer concentration with time

A decrease in monomer concentration with time would decrease

the rate of polymerization, but this decrease would not be the sole reason for the observed marked decrease in the conversion rate. The independence of percent conversion of the monomer concentration illustrated in Figure <u>ll</u> for several initiator concentrations suggests a first order reaction with respect to monomer. In a first order reaction, the decrease in monomer concentration would be logarithmic with time. Reference to Figure <u>16</u> shows that this is not the case.

The gradual approach to a thermal equilibrium

As discussed earlier, a monomer would not polymerize below a floor temperature or above a ceiling temperature. Between these two temperatures the conversion would increase until the rate of propagation and the rate of depropagation would be equal and an equilibrium is attained. Acrylonitrile has been reported to polymerize at temperatures as low as -196° C., and as high as 70° C. (140). The polymerization temperature under discussion (-78° C.) is far from either the floor temperature or the ceiling temperature for polymerization of acrylonitrile. Thus, at -78° C., the equilibrium monomer concentration should be very low favoring high polymer yield. Further in biphenyl sodium initiated polymerization at -78° C., PAN was obtained in quantitative yield (74), indicating that the equilibrium concentration of acrylonitrile was indeed low at -78° C.

The gradual deactivation of the carbanions

A gradual deactivation mechanism by which the propagating centers could be rendered inactive might also lead to a decrease in the propagation rate. An active center may lose its reactivity by an isomerization reaction, an interaction with a functional group of a monomer or polymer, or by a chain transfer to a polymer, a monomer, an impurity or a solvent. Of these reactions, only those which give products incapable of adding further monomer might contribute to the observed decrease in the polymerization rate. A chain transfer to toluene, acrylonitrile or PAN would not destroy but merely transfer the activity of the propagating centers. Since the system used in the present work was carefully purified, the destruction of the initiator by the impurities would account for only a small portion of the total initiator present.

The deactivation of the carbanions by isomerization to give an inactive anion, or the interaction of carbanions with a functional group have been found to occur in the polymerization of methyl methacrylate (134) and allyl acrylate (194). However there seems to be no support for the existence of these termination mechanisms in the present polymerization work at -78°C. The molecular weight data plotted in Figure 19 clearly imply that \overline{M}_{v} increases linearly with conversion over a reaction period of 50 hours. Further for a PAN sample prepared at -78°C., the heterogeneity index, $\overline{M}_w/\overline{M}_n$, was found to have a low value Many of the PAN samples were examined by the of 1.08 (Table XVII). sedimentation velocity method at about 0.2 to 0.3 percent concentration. Those obtained at -78°C. were found to sediment in a sharp boundary as indicated by the refractive index gradient curve without any discrete fractions appearing on either side of the boundary (Figure 20). The linear relation between the molecular weight and percent conversion, as well as the narrow molecular weight distributions in the polymers obtained at -78°C., seem to rule out any possibility of the decrease in the

polymerization rate with time resulting from a gradual termination of the carbanions. Therefore a gradual decrease in the ability of the propagating centers to acquire the necessary monomer for propagation seems to be a reasonable explanation.

The gradual decrease in the accessibility of the monomer to the propagating centers

An increase in conversion and molecular weight with time would cause the viscosity of the medium to increase continuously until the reaction mixture becomes a gel. The solidification of the reaction mixture to a gel often occurred within minutes of the acrylonitrile addition to the reaction flask.

In a set of two experiments with a 50 hour overall reaction period, the temperature was allowed to rise to -20° C. (from -78° C.) after 40 hours in one experiment, but was maintained at -78° C. for the whole reaction period in the other. The polymer yield obtained in the experiment maintained at -78° C. was 26 percent compared to 34 percent in the other in which the temperature was raised to -20° C. The polymer obtained at -20° C. was not completely soluble in DMF indicating the presence of branching coupled with a high molecular weight.

A solid gel specimen, of yellow colored active reaction mixture, when placed in acetone acidified with hydrochloric acid, was not deactivated immediately as judged by the color change. The color faded slowly from the surface of the specimen. Only when the specimen was broken into small pieces did the central part show a color change. In fluid reaction mixtures obtained at short reaction intervals the color of the carbanions was discharged immediately upon addition, with mixing, of acidified acetone.

The above results clearly show that the carbanions were active, capable of adding acrylonitrile, but the monomer was prevented from approaching the carbanions by the gelation of the reaction mixture.

In the polymerization of acrylonitrile, initiated by n-Buli at -78°C. in toluene, Rempp et al. (153) observed that the molecular weight of polymer did not increase and that the polymerization did not go to completion on further addition of the monomer. These observations led the authors to conclude that 'when polymerization is conducted in toluene the living polyacrylonitrile probably commits suicide very rapidly'. However, it might be noted that an approach of the monomer to the propagating center and not the mere addition of the monomer to the reaction mixture would lead to further polymerization. The results reported by Rempp et al. (153) might be rationalized if the monomer has difficulty in approaching the active centers.

An increase in the viscosity of the reaction medium has been reported to decrease the rate of termination through a decrease in the mobility of the polymeric radicals (9). It is known that the half-life time of the active radicals is usually of the order of a fraction of a second. As mentioned earlier in the heterogeneous polymerization of acrylonitrile the newly formed polymer precipitates over active radicals burying them and rendering them apparently inactive (144). The trapped radicals were found to be stable, for a period of about a week, if stored at -80° C. in the absence of small molecules (e.g. 0_2). In a similar way it is quite possible that carbanions are trapped and though their intrinsic reactivity is unaffected, their apparent reactivity is decreased since the monomer is largely prevented from reaching these centers which are tightly coiled in the gel. When the temperature of the reaction is increased the mobility of the monomer is also increased leading to a higher conversion. This same increase in reaction temperature will, however, lead to an increase in the side reactions related to branching and coloration.

VARIATION OF PERCENT YIELD OF POLYMER WITH MONOMER CONCENTRATION AND THE ORDER OF REACTION AT -78°C.:

The polymerization data plotted in Figure <u>ll</u> show the percent conversion to be generally independent of monomer concentration. Some deviation from this relationship occurs however at low initiator concentrations. This deviation does not seem to be related to a change in order of reaction in monomer but seems rather to be related to the destruction of a relatively large fraction of carbanions by the residual impurities present in the monomer. Since, in the present work, the percent polymer yield is found to be independent of monomer concentration, the reaction might be first order in monomer. However the polymerization data when plotted as the logarithm of the monomer concentration, $[M]_t$, at time <u>t</u>, against <u>t</u> as given in Figure <u>l6</u>, failed to give the linear graphs which should have been obtained if the reaction was first order in monomer. The deviation from linearity of these plots seems to be related to a gradual decrease in the ability of the monomer to reach the carbanions as the reaction mixture became more dense with time. Other factors (e.g. a gradual decrease in the population of the carbanions, slow rate of initiation etc.) do not seem to contribute to the deviation of the plots from linearity.

By confining their experiments to a reaction period of one hour, Zilkha and coworkers (49) found the percent polymerization to be independent of acrylonitrile concentration in agreement with the findings of the present work. Miller (105) observed that, at -78°C., for two mole per liter or less acrylonitrile concentrations, the percent conversion was independent of monomer concentration. At higher monomer concentration the rate of polymerization increased more rapidly than the monomer concentration. The increased rate of polymerization with monomer concentration is rather difficult to explain, since an increase in the monomer concentration would lead to more difficulties in mixing the monomer with the initiator solution and the reaction mixture would solidify more rapidly.

The n-BuLi has been shown to exist as a hexamer in equilibrium with a small concentration of monomeric n-BuLi. The dielectric constants of toluene and acrylonitrile are 2.4 and 38.0 respectively. An increased proportion of acrylonitrile in the reaction mixture would increase the dielectric constant of the medium, which in turn would increase the proportion of monomeric n-BuLi in the reaction mixture. If it is assumed that this increased amount of monomeric initiator would initiate an increased number of polymeric chains, the percent polymerization should . increase gradually with monomer concentration and not suddenly as reported by Miller (105).

. 149 _

Semilogarithmic plots with characteristics similar to those of Figure <u>16</u> have been reported for the n-Buli initiated polymerization of allyl acrylate (194). The fractionation of the polyallyl acrylates obtained showed the presence of a low molecular weight and a high molecular weight fraction suggesting a deactivation of the carbanions during the early stages of polymerization. The molecular weight distribution in polyacrylonitrile obtained at -78° C. as given in Figure <u>25A</u> shows no evidence of the presence of a low molecular weight fraction. Further the filtrate from the polymerization experiments at -78° C. gave on evaporation a water soluble residue (LiCl) and no low molecular weight polymer. Therefore it can be concluded that at -78° C. deactivation of the carbanions does not occur to any great extent.

THE EFFECT OF INITIATOR CONCENTRATION AND [M] / [I] ON THE YIELD AND MOLECULAR WEIGHT OF POLYACRYLONITRILES OBTAINED AT -78°C.:

Since an increase in the initiator concentration would increase the number of propagating centers, the polymer obtained at high initiator concentration would have a lower degree of polymerization and a lower molecular weight. Although as given in Table XIII, the molecular weight of polyacrylonitriles varied inversely with initiator concentration, the decrease in molecular weight was less rapid than the increase in the initiator concentration. Further the \overline{M}_v was much higher than the kinetic molecular weight, \overline{M}_k , obtained by assuming one initiator molecule per polymeric chain. The initiator efficiency in chain initiation does not seem to be quantitative. Rather a small fraction of the initiator participates in a chain initiation reaction. The fraction, which initiates the polymerization, seems to be affected by the nature and concentration of the reactants, and reaction temperature. For these reasons the correlation between polymer yield, molecular weight and initial concentration of reactants can be interpreted only in a qualitative manner. The assumed low initiator efficiency in chain initiation and the possible fate of the initiator will be dealt with at a later stage.

By simultaneously varying both the monomer and initiator concentration but with the ratio $[M]_{o}/[I]_{o}$ maintained constant, the degree of polymerization calculated from the molecular weight of the polymer should be constant, provided that the chain deactivation is absent. The values of $(DP_n)_{expt}$, calculated from \overline{M}_v , are presented in Table XIX for different $[M]_{o}/[I]_{o}$ ratios. The value of $(DP_{n})_{expt}$ appears to increase with an increase in $[M]_{o}$ and $[I]_{o}$ at constant $[M]_{o}/[I]_{o}$. At higher monomer concentrations, however, the increase in $(DP_n)_{expt}$ no longer shows this behavior, probably since the accessibility of the monomer to the carbanions is lowered by the increased extent of gelation of the reaction mixture. Both the efficiency of n-Buli in chain initiation and the percent polymerization increase with $[M]_{O}$ and $[I]_{O}$ at a given $[M]_{O}/[I]_{O}$ (Table XIX). However, the polymer yield seems to increase more rapidly than the initiator efficiency. This irregular variation in both the conversion and initiator efficiency could explain the observed dependence of the $(DP_n)_{expt}$ on $[M]_o$ and $[I]_o$ at a given $[M]_o/[I]_o$

In the polymerization of acrylonitrile with n-BuLi at -78° C., the percent conversion was found (105) to be independent of the initiator concentration at $[I] \ge 5 \text{ meq /liter}$. At $[I] \le 1 \text{ meq /liter}$, no polymerization occurred possibly because of the impurities present in the reaction mixture. Degree of Polymerization (Constant $[M]_{o}/[I]_{o}$)

Solvent:	Toluene
Reaction time:	60 Minutes
Temperature:	-78°C.

Monomer Conc.	[M]。/[I]。	Polymer yield	$10^3 \times (DP_n)_{expt}$.	Initiator	
(Mole/Liter)		(Per Cent)		(Per Cent)	
			1		
0.5	1000	22.8	7.15	3.2	
1.0	1000	30.3*	7.83	3.9	
0.5	2000	18.6	7.92	4.7	
1.0	2000	23.1	9.37	4.9	
2.0	2000	29.6	15.09	3.9	
1.0	4000	16.3*	11.81	4.2	
2.0	4000	21.5	17.17	5.0	
4.0	4000	29.1	15.66	7.4	
1.0	6000	11.8	12.73	5.6	
2.0	6000	21.0	17.26	7.3	
4.0	6000	24.7	16.41	9.1	
2.0	8000	16.4	21.88	6.0	
4.0	8000	20.5	18.30	8.9	
2.0	12000	11.0	19.06	6.9	
4.0	12000	16.0	20.19	9.5	

* Reaction time was 40 minutes.

Further the molecular weights of the polymers obtained by varying both the monomer concentration and the initiator concentration (Table G-II) showed very little correlation to the experimental conditions. The presence of impurities in the reaction mixture and probably a lack of proper mixing could have contributed to the lack of correlation in the results given in Table <u>G-II</u> (105). In the present work experiments with $[n-Buld] \ge 2.0 \text{ meq}$ /liter did lead to poor reproducibility in the polymer yield as given in Table <u>I</u>. The percent conversion was independent of AN concentration and decreased with a decrease in initiator concentration, while the molecular weight increased with monomer concentration and decreased with an increase in the initiator concentration (Appendix A).

An increase in the percent conversion with initiator concentration has been reported in n-BuLi, phenyllithium, and 9-fluorenyllithium initiated polymerization of acrylonitrile at 0° C. (42,49) in agreement with the results of the present work (Appendix B). The molecular weights of the polymers, however, were found to be independent of initiator and AN concentration (42,49) indicating a chain transfer to monomer. Both the use of high initiator concentration and high polymerization temperature rather than the chain transfer mechanism may be taken into consideration to explain the results.

THE STABILITY OF A PROPAGATING CENTER IN POLYMERIZATION

Both the increase in the value of the heterogeneity index of polyacrylonitriles (Table XVII) and the decrease in the yield and molecular weight of the polymers (Appendix B) with increase in reaction temperature

- 153

suggest a low stability of the propagating centers at the high temperatures investigated in the present work. Since the benzyl $(C_6H_5CH_2^-)$ and acrylonitrile (CH_3-CH^-) or $CH_2=C^-)$ anions obtained by a chain transfer to toluene and acrylonitrile are basic enough to add more monomer, the chain transfer mechanism would not account for the observed temperature dependence of the polymer yield.

If a decrease in polymer yield is caused by the thermodynamic equilibrium,

$$P_j^* + M \xrightarrow{k_p}_{k_d} P_{j+1}^*$$

the polymer yield might be improved by lowering the temperature of the reaction mixture. To check this possibility polymerization was initiated in a series of experiments at 0 or -40°C. After maintaining at this temperature for five minutes, the reaction mixture was cooled to -78°C., and the reaction was allowed to continue at -78°C. for at least $t_{\rm two}$ hours. The results of these experiments and of the experiments performed under otherwise identical conditions at 0, -40 and -78°C. are given in Table X. A comparison between the polymer yields obtained under different temperature conditions shows that chain initiation and propagation at higher temperatures ($\geq -40^{\circ}$ C.) for five minutes followed by continued chain propagation at -78°C. does not increase the polymer yield. Therefore under the experimental conditions used in the present work at or above -40°C., most of the carbanions were destroyed within five minutes after the initiation of the polymerization. Since the monomer and solvent were carefully purified, total termination within a short time could not be due

to the presence of excessive amounts of the contaminants. Further the n-BuLi was found to initiate the polymerization of acrylonitrile at -78° C. in the present work and in published work (105,153). If any n-BuLi is left unreacted during the reaction at or above -40° C., this active residue should initiate polymerization of acrylonitrile when the reaction mixture was cooled to -78° C. and increase the polymer yield. From the data of Table <u>X</u>, it is evident that no increase in the polymer yield occurs. Obviously in the absence of chain initiation all the initiator must have been used up instantly in some other reactions.

There are three sets of experimental evidence in the present work which suggest that most of the carbanions produced and maintained at -78°C. were stable. This evidence can be found in (a) the linear dependence of molecular weight on percent conversion as given in Figure 19, (b) the gradual increase in the polymer yield with time as given in Table <u>III</u> and (c) the narrow molecular weight distribution in a polyacrylonitrile prepared at -78°C. Undoubtedly some of the carbanions would undergo reaction with impurities but the amount must be negligibly small.

Zilkha et al. (42) found 78% yield for the n-BuLi initiated polymerization of acrylonitrile in petroleum ether at -15°C. when the monomer was added gradually to the reaction mixture. The polymer yield was 90% when the monomer was added in one portion. In both cases the molecular weight was independent of the monomer concentration. Consequently, termination was assumed to proceed through a mechanism of chain transfer to the monomer. The validity of this mechanism was

- 155 -

supported by the infrared spectral data cited in the paper. However, if this mechanism of chain transfer was operative the observed decrease in the percent conversion with a rate of monomer addition would be difficult to explain. A chain termination by some other mechanism, that would not lead to regeneration of the propagation centers, might be better to explain the short life of the carbanions.

During the polymerization of the non-polar monomers e.g. styrene, isoprene, etc., the carbanions have been shown to be stable at temperatures as high as 50°C. (195). In the polymerization of polar monomer methyl methacrylate in toluene the stability of the carbanions was found to vary inversely with the polymerization temperature when either n-BuLi or diphenyl hexyllithium was employed as the initiator (135,196). Further at low temperatures, some of the initiator was found to react with the carbonyl group of the monomer. In another report (78) polymethyl methacrylate anion was shown to be terminated by cyclization.

It is quite likely that the variation in the stability of a carbanion of the acrylonitrile with temperature could have occurred by cyclization of the growing end,



or by a reaction of the nitrile group of a polymer or a monomer molecule with the carbanion,

- 156 -



The imine ion, > C = N Li⁺, is not basic enough to add more monomer.

THE EFFICIENCY OF n-Buli AS AN INITIATOR IN ACRYLONITRILE POLYMERIZATION:

Polyacrylonitrile is soluble in highly polar solvents (e.g. dimethyl sulfoxide) and concentrated aqueous salt solutions (e.g. ZnCl₂) all of which react with organometallics. Polymerizations in these solvents could be induced by the initiator itself or by a reaction product of the initiator with the solvent. Consequently the interpretation of the data on polymerization of acrylonitrile obtained in these reaction media will be difficult, particularly at higher polymerization temperatures. In hydrocarbon solvents, in which carbanions and organometallics have been shown to be stable, polyacrylonitrile is insoluble. During polymerization the polymer precipitates and propagation occurs in different phases each with a different propagation rate (145). This also complicates the interpretation of the data obtained in the polymerization experiments.

The bulk of the data on the polymerization of acrylonitrile

with lithium organometallics reported to date have been obtained with the initiator concentration sufficiently high for the initiator to be considered highly associated. Consequently the low efficiency of the initiator has been explained assuming the inability of the associated initiator to participate in the polymerization (42,105,155). An explanation of the low initiator efficiency based upon the associated state of alkyllithiums might be justified in non-polar solvents. However in THF and other polar solvents, in the polymerization of both polar and non-polar monomers at temperatures as low as -78°C., the initiation reaction has been shown to be very rapid and complete in a short time (78,122). In the polymerization of acrylonitrile at or about O°C. in THF or DMF, the efficiency of lithium organometallics in chain initiation has been reported to be low (49,69,155). This fact brings into question the soundness of any explanation of the initiator efficiency based upon associated state of the initiator alone, and therefore makes questionable the interpretation of the polymerization data. In the discussion that follows, an attempt will be made to trace the fate of the initiator in accordance with the polymerization data obtained in the present work as well as those available in the literature.

If all the initiator is consumed in the chain initiation reaction and if there is one initiator molecule per polymeric chain, then for a monofunctional chain initiator, the polymer obtained would satisfy the condition:

$$(DP_n)_{expt} = (DP_n)_{calc}$$

A chain transfer to a monomer, a solvent or an impurity, with the generation

. 158

of a new propagating center would lead to a value of $(DP_n)_{calc}$ which is higher than that of $(DP_n)_{expt}$. If the $(DP_n)_{calc}$ is lower than $(DP_n)_{expt}$, it is doubtful that all the initiator would be consumed in chain initiation.

The low efficiency of n-Buli in chain initiation can be seen by comparing the kinetic molecular weight, \overline{M}_k , with viscosity average molecular weight, \overline{M}_v , given in Appendix <u>A</u> for polymers prepared at -78°C. The efficiency of n-BuLi as an initiator, as recorded in the last column of Appendix <u>A</u>, is between 2% and 10% depending upon the monomer and the initiator concentration. The molecular weight distribution plots given in Figure <u>25</u> for polyacrylonitriles prepared at different temperatures do not show the presence of a low molecular weight fraction in the polymers. Therefore the slow chain initiation process usually observed in non-polar monomers (35,122) and also presumed to be present in acrylonitrile polymerization (105) does not seem to occur under the conditions employed in the experiments being reported in this investigation. One might conclude that the initiator was destroyed during the initial short period in the reactions other than chain initiation.

A very low initiator efficiency has been reported in the n-BuLi initiated polymerization of acrylonitrile (42,105,155), methacrylonitrile (126) and methyl methacrylate (70). Miller (105) noted that in acrylonitrile polymerization experiments only 1 to 5 percent of the initiator could be accounted for in the chain initiation process.

The n-Buli has been shown to be associated as a hexamer and the

rate of chain initiation of non-polar monomers in hydrocarbon solvents has been shown to be 1/6th order in n-BuLi (52). It has been assumed that the low efficiency of n-BuLi in the polymerization of acrylonitrile could be related to the associated state of the initiator (42,105,155). In the polymerization of methacrylonitrile the low efficiency of n-Buli was thought to result both from the associated state of n-BuLi and from a preferential addition of the monomer to the propagating centers rather than n-Buli (126). If either the preferential addition of the monomer to the propagating centers or the associated state of the initiator are responsible for the low initiator efficiency, an increase in initiator concentration in the reaction mixture would decrease the efficiency of the initiator. An analysis of the data reported on the n-Buli initiated polymerization of methacrylonitrile shows the initiator efficiency to increase with an increase in n-Buli concentration. This contradicts both the assumption of a preferential addition of monomer to the carbanions and the assumption of incomplete participation of n-Buli in the chain initiation of polar monomers because of associated state. Since acrylonitrils and methacrylonitrile are acidic monomers, the anions obtained from them would be less active in monomer addition than butyl anion (e.g. butyl anion is capable of adding styrene while the acrylonitrile anion is not). Therefore if a preferential addition of a monomer occurs it should be to n-butyl anion rather than to a polyacrylonitrile or to a polymethacrylonitrile anion.

About 98.5% of 9-fluorenyllithium has been shown to disappear during the first five minutes of polymerization of methyl methacrylate in toluene-diethyl ether mixture (9:1) at -78° C. (78). Acrylonitrile and n-BuLi are more reactive than methyl methacrylate and 9-fluorenyllithium respectively (47,49). Therefore it is rather difficult to understand how n-BuLi could remain unreacted in the reaction mixture for the long periods of reaction time considered in the polymerization of acrylonitrile and methacrylonitrile. Recently Kawabata and Tsuruta (136) have shown in n-hexane at 30°C. and in THF at -70° C., that n-BuLi reacts very rapidly with acrylonitrile, methacrylonitrile, methyl methacrylate and methyl acrylate.

Since the efficiency of n-Buli as an initiator based on one initiator molecule per polymeric chain was low in both the present work and in the work reported elsewhere (42,105), and since as discussed above the initiator would not remain unreacted for any prolonged period, the initiator must have been consumed in reactions other than the chain initiation. Some examples of the possible reactions between n-BuLi and acrylonitrile or polyacrylonitrile are given below:





If the polymerization occurs rapidly, reactions XXIII and XXIV are also possible with a polymer molecule as given in reactions XXV and XXVI respectively.

Reaction XXI followed by the successive 1,2 addition of acrylonitrile to carbanion (A) would give the normal polymerization process:

 $C_{4}H_{9}-CH_{2}-CH^{-}Li^{+} + CH_{2}=CH \xrightarrow{k_{p}} C_{4}H_{9}-CH_{2}-CH-CH_{2}-CH^{-}Li^{+} CN \xrightarrow{k_{p}} CAH_{9}(-CH_{2}-CH) \xrightarrow{k_{p}} CAH_{9}(-CH_{2}-$

XXVII

Acrylonitrile undergoes a cyanoethylation reaction with compounds possessing a reactive hydrogen atom (symbolized below by HA). The reaction is believed to occur by an attack of the anion A^- on the positively polarized β -carbon atom (138):

$$CH_2=CH-C=N$$
 \rightarrow $CH_2-CH=C=N$

 $\begin{array}{c} d'_{+} & d'_{-} \\ CH_{2}-CH=CH=N & + A & \longrightarrow (A-CH_{2}-CH=C=N & A-CH_{2}-CH-C=N) \\ & & & & \\ & &$

It has never been established either that the proton adds to the nitrogen atom followed by a rearrangement or that the proton adds directly to the \propto -carbon atom. If an analogy is drawn with the cyancethylation reaction the anion obtained in reaction XXII would rearrange as:



If (B) adds monomer without undergoing a rearrangement, then the spectrum of a polyacrylonitrile obtained should give an absorption band in the IR region at 4.8-5.0µ, characteristic of a >C=C=N group. The absorption band at 4.8-5.0µ was absent from the IR spectra of the polymers

obtained in the present work (Fig. 26). Therefore the monomer addition to (B) did not occur. If (B) is rearranged to anion (A), propagation would occur by the reaction XXVII by a 1,2-addition. The initiator efficiency observed in the present work could then be accounted for by reactions XXI and XXII. The possibility that (B) was not converted to (A) and hence could not propagate the polymerization cannot be ruled out. On termination with acidified acetone this would give (F):

$$C_4H_9-CH_2-CH=C=N^{-}Li^+$$
 + HCl --- $C_4H_9CH_2-CH=C=NH$ + LiCl
 $C_4H_9CH_2-CH_2-CH$ (F)

Since the filtrate and washings obtained after removal of PAN were not analyzed chemically, the presence of (F) could not be confirmed.

A reaction of n-Buli with monomer to give (C) or a similar reaction with a polymer (XXVI) would account for the contribution of the initiator to the side reaction. The imine ion produced is considered to be too weak to add monomer. It may however react with the nitrile group on the polymer to give a cyclic structure (34) with the development of a color. The intensity of the color would depend upon the number of consecutive cyclic units along a polymeric chain.



- 164 -

The polyacrylonitrile obtained at -78° C. is white, indicating that a cyclization reaction as described above does not occur or occurs to a very small extent. At or above -40° C., the polymer was colored, the intensity of which depended upon the polymerization conditions (e.g. monomer concentration, initiator concentration, reaction temperature, etc.).

Upon termination of the reaction the imine ion would be converted to an imine group (>C=NH), which may be hydrolyzed to a carbonyl group:

>C=NH + H₂O ---- >C=O + NH₃

The presence of $-\dot{C}=N-$, $-(\dot{C}=N)_n-$, and $\dot{C}=0$ have been indicated by the infrared measurements on the polyacrylonitriles obtained at different temperatures (Fig. 26).

Therefore it may be concluded that reaction XXIII and XXVI compete with the chain initiation reaction by n-Buli in acrylonitrile polymerization and they seem to be partly responsible for decreased efficiency of n-Buli in chain initiation.

In a study of the potassium amide initiated polymerization of methacrylonitrile, a colored polymer was obtained (34). An attack of an amide anion on the nitrile group followed by cyclization of the polymeric chain by the attack of the imine ion on the neighboring nitrile groups was proposed to explain the coloration in the polymer (34). Further, n-Buli has been found to attack the carbonyl group of allyl acrylate and methyl methacrylate (133,194). Tsuruta et al. (136) have showed that in n-hexane at 30°C., and in THF at -78°C., only the reactions XXI and XXIV occur to a large extent between n-Buli and acrylonitrile. Reaction XXIII accounted for about 1% initiator in n-hexane. Depending upon the concentration of n-Buli and acrylonitrile in THF, the nitrile addition (XXIII) accounted for 3 to 10 percent of the initiator. The anion (D) produced in the reaction XXIV has also been postulated to form during a chain transfer to monomer and to propagate polymerization by monomer addition (42,155):



(D)





- 166 -

Although the reaction (XXV) was definitely absent at -78°C., it might have contributed to the observed branching at higher temperatures. The exact contribution to the polymerization process of reaction (XXV) is difficult to establish from the present work.

From the above discussion it could be concluded that a small fraction of the initiator initiates the polymerization by the reactions XXI and/or XXII. Reactions XXIII and XXVI account for the consumption of the initiator in the side reactions. Reaction XXIV does not occur with the monomer. However reaction XXV might be occurring with the polymer to a varying extent, particularly at higher temperatures.

EFFECT OF POLYMERIZATION TEMPERATURE:

In the formation of polyacrylonitriles the temperature of polymerization was found to affect the polymer yield, the molecular weight, the molecular weight distribution, the absorption bands in the spectra, the color and the extent of branching.

a. The dependence of yield and molecular weight on temperature

If the stability of the carbanion is independent of temperature, the propagation should continue as long as monomer is available. This would lead to a quantitative polymer yield independent of temperature and the molecular weight of the polymer would be equal to the molecular weight of the monomer times the monomer-to-initiator ratio. The data on the polymer yield and the molecular weight given in Appendix <u>B</u> show that in the present work both the percent conversion and the molecular weight decreased with an increase in polymerization temperature. This would seem to imply that the stability of the carbanions is temperature dependent.

In hydrocarbon solvents n-Buli has been shown to exist as a hexamer in equilibrium with a low concentration of a monomeric n-Buli (35,122). Therefore it is quite reasonable to assume that with an increase in the reaction temperature the concentration of monomeric n-Buli would increase, a higher number of polymeric chains would be initiated and the molecular weight of the polymer would decrease. However an increase in the number of polymeric chains should increase the polymer yield. In the present work the percent conversion was found to decrease with an increase in the polymerization temperature.

In the polymerization of styrene, a non-polar monomer, the conversion and molecular weight of the polymer were found to be independent of the temperature (96). Among polar monomers, the temperature dependence of yield and molecular weight of polyacrylonitrile has been reported by Zilkha and coworkers (42,43,49), and appears to agree with the present work.

The carbanions seem to be stable below -60° C., but the gel formation in the reaction mixture complicates the progress of the reaction. Therefore the conversion was never quantitative. Both the instability of the carbanions at higher temperatures and the gel formation at lower temperatures led to difficulties in measuring the propagation rate constant as a function of a temperature. Therefore the activation energy for propagation, E_p , was difficult to determine.

- 168 -
Flory (197) has used a semilogarithmic plot of a molecular weight against 1/T to obtain a value of the difference in the activation energy between propagation and termination, (E_p-E_t) . Further, the plots of log \overline{M}_v against 1/T for polyacrylonitriles obtained with anionic initiators have been reported to be linear in the temperature range of 20 to -60°C. (42,43,49). When the molecular weight data of the present work (Appendix B) are plotted in this manner as in Figure <u>15</u>, a deviation from linearity appears for polymers prepared at or below -60°C., with the deviating points falling below the straight line.

Either 100% conversion or complete deactivation of the propagating centers can be taken to indicate the completion of the reaction. At or above -40° C., the reaction was completed in a very short time (< 5 minutes). Below -60° C., the conversion and molecular weight increased gradually with time and the reaction was incomplete after one hour. If the molecular weights obtained after the completion of the reaction at or below -60° C. are plotted (Fig. 15), the points may lie on or above the linear plot obtained for polymers prepared at or above -40° C.

The values of (E_p-E_t) for the polymerization of acrylonitrile calculated from the semilogarithmic plots have been found to lie between 2.0 and 5.2 k.cal/mole (43,48). This compares with the values of (E_p-E_t) between 2.5 and 5.0 k.cal/mole for polymerization between 0 and -60°C. (Table VII). The values calculated from the molecular weight data on polymers obtained at -60°C. and -78°C. are also recorded in this table but are of doubtful significance.

The polyacrylonitrile prepared at -78°C. in THF, THF + DMF and

at -50°C. in DMF with alkyllithiums and other initiators were shown to possess a branched structure (74,153). In the present work also the polymers were found to contain a branched structure, the degree of which increased with temperature (Table XV). Therefore the molecular weights calculated from viscosity measurements using the Mark-Houwink relation (156) would be in error. In all the semi-logarithmic plots of molecular weight against 1/T thus reported, \overline{M}_v has been used without regard to the presence of branching. Therefore it seems reasonable to conclude that the values of (E_p-E_t) reported in this thesis and in the literature are open to serious question both in their significance and in the applicability of the method used for their determination.

b. Heterogeneity in polymers prepared at different temperatures

The molecular weight distributions determined by a method based upon the analysis of progressive boundary spreading in the sedimentation velocity experiments, although tedious and time-consuming, appear to be reasonably accurate. This method does not seem to have been applied to determine molecular weight distributions in polyacrylonitriles. Usually the molecular weight distributions, reported for PAN samples, are determined from the molecular weight data, measured on fractions obtained by the fractional precipitation technique. Unfortunately this technique gives a poor separation of PAN fractions (161,186).

An analysis of the sedimentation velocity experiments on a mixture of two uniform polystyrene samples showed the resolution efficiency of different molecular weights to be quite good (103). Scholtan (198) analyzed polyvinyl pyrrolidone by sedimentation velocity analysis, fractionation and turbidimetric titration and observed good agreement in the results obtained. Wales and Rehfeld (170) observed good agreement between the molecular weight distributions determined by sedimentation velocity analysis and precipitation chromatography. Gupta, Robertson and Goring (165) have shown that alkali lignin samples had a continuous sedimentation coefficient distribution ranging from 0.5 to 400 <u>S</u>. The sedimentation coefficient distribution curves computed from the sedimentation velocity analysis studies on fractionated and unfractionated polymer samples showed fairly good correlation.

On the basis of the findings of these workers on the application of this technique to other polymer systems and the generally low reliability of other techniques used for determining the molecular weight distribution in PAN samples, it was decided to apply the sedimentation velocity analysis method in the present work.

The differential molecular weight distribution data calculated from the sedimentation velocity analysis of polyacrylonitrile samples prepared at different temperatures are plotted in Figure <u>25</u>. The values of the heterogeneity indices determined from the molecular weight distribution data are given in Table <u>XVII</u>. From these plots it appears that the polymer samples contained no low molecular weight material. The samples did however contain a high molecular weight fraction in varying amounts. The absence from the polymer samples at -78° C. of a low or a high molecular weight fraction (Fig. 25A) and a low value of the heterogeneity index (1.08) suggest a uniform chain propagation and the absence of a slow chain initiation or chain termination. The fraction of high molecular weight material (Figs. 25B to 25D) and the heterogeneity indices (Table XVII) increase with the temperature of polymerization. These data suggest that the rate of both chain initiation and chain termination increased with the temperature of polymerization.

Non-polar monomers have been polymerized by the anionic mechanism to give polymers having a very narrow molecular weight distribution and a low heterogeneity index (112). The presence of a functional group in a polar monomer often complicates the polymerization mechanism and leads to polymers having a broad molecular weight distribution. In 9-fluorenyllithium initiated polymerization of methyl methacrylate for example, the value of the heterogeneity index was 20 (199). In another report Bywater et al. (132) found that polymethyl methacrylate obtained with n-Buli had a bimodal molecular weight distribution. From these data it was concluded that a rapid termination of most of the carbanions occurred. The literature has only one report on the molecular weight distribution in the polyacrylonitriles obtained with anionic initiators. By fractionation of the polyacrylonitriles prepared at -78°C., Miller (105) showed the polymers to have a narrow molecular weight distribution. The heterogeneity index of the polyacrylonitrile was reported to be between 1.2 and 1.3 compared to a value of 1.08 reported in the present work (Table XVII). The molecular weight distribution obtained by Miller (105) showed the presence of a low and a high molecular weight fraction in the polymer. This experimental finding caused Miller to conclude that the polymerization proceeded through a slow initiation and slow propagation of the polymeric chains.

c. <u>Discussion on spectroscopic measurements on polyacrylonitriles</u>(i) The infrared spectra of polyacrylonitriles

The presence of absorption bands between 5.5 and 6.5µ in the IR spectra of PANs given in Figures <u>26A</u> and <u>26C</u> clearly indicates that the polymer structure is composed of more than mere $-CH_2$ -CH units joined together in a head to tail fashion.

The IR spectrum of PAN prepared at -78° C. (Fig. 26A) is virtually identical with that reported for PAN prepared by a radical initiation (Fig. 26D). The only observable difference between the spectra is in the weak but distinct absorption bands at about 5.8, 6.0 and 6.1µ. These absorption bands are absent in the IR spectra of the radical polymer. The absorption bands at 5.8 and 6.0µ could be assigned to the presence of >C=O and >C=N- respectively (193). The absorption bands at 6.1µ could be assigned to the presence of >C=C<, $-(\dot{C}=N)_n$ - or to the traces of water (43,200,201).

If during polymerization, polymeric chains are terminated by a chain transfer to monomer, the presence of >C=C< in the polymer may be by either of the following reactions:



- 173 -

The anion (D) is also produced by the interaction of n-BuLi with acrylonitrile:

$$n-C_{4}H_{9}Li + CH_{2}=CH - C_{4}H_{10} + CH_{2}=C_{1i}^{+}$$

$$CN CN CN CN$$
(D)

The -CH=CH- end group, if present in the polymer, should give absorption bands at 13.7 - 15.0µ (cis position) or at 10.2 - 10.4µ (trans position) and at 6.1 μ . The >C=CH₂ end group, on the other hand, should give absorption bands at 6.1µ and at 11.15 - 11.30µ (193). Since no absorption bands but the 6.1µ band were observed in the spectrum of PAN (Fig. 26A), >C=C< was absent. The absence of >C=C< from the polymer was also indicated by the bromination test. Since the polymer is white in color, the presence of the conjugated structure to any significant extent is questionable. However the presence of a few $-(\dot{C}=N)_n$ - conjugated units at random in the polymer might have contributed to the observed weak absorption band at 6.1µ. The presence of water in the KBr disc could be inferred from the absorption bands at 2.75 - 2.83µ and at 6.1µ. The absorption band at 6.1 was stronger in the spectra of those PAN samples which showed stronger absorption bands around 2.75 - 2.83µ when the moisture content in the KBr of the discs was higher. Therefore the 6.1µ absorption band in the spectra of polymers could be assigned to the presence of water and possibly $-(C=N)_n$ -.

The IR spectra of PAN samples prepared at higher temperatures such as given in Figures <u>26B,C</u> differ remarkably from that of PAN prepared by a radical initiator (Fig. 26D). The absorption bands between

5.5 and 6.5µ are stronger and more in number than those in polymers prepared at -78°C. Moreover, above 6.5µ several new absorption bands are also observed in these spectra (Figs. 26B,C). The presence of an amide group $(-CONH_2)$ in these polymers is suggested by the absorption bands at 2.96, 3.07, 6.00, 6.25 and 7.05µ in the spectra of these polymers (202). Further the absorption bands at 5.8 and 6.00u could be assigned to the presence of >C=0 and >C=N- groups respectively (193). It is well known that the systems which contain conjugated unsaturated groups, such as $-(\dot{C}=\dot{C})_n$ and $-(\dot{C}=N)_n$, form colored species. In the IR spectra of compounds containing these groups an absorption band is observed around 6.1µ. Thus the broad absorption band observed near 6.1µ could be assigned to either one or both of these groups in the polymer. The inability of these polymers to add bromine and the absence of bands at 13.7 - 15.00µ, 10.2 - 10.4µ, or at 11.15 - 11.30µ from the spectra of polymers suggest the absence of >C=C< structural units from these polymers. Therefore the absorption bands in the spectra around 6.1µ and the color of the polymer could be considered to reflect the presence of $-(C=N)_n - in$ the polymer.

Tsukamoto (74) observed that the polymerization of AN in DMF + THF as a solvent at -78° C. gave a white polymer having an IR spectrum very similar to that of the polymer prepared by radical initiation. In DMF alone at -55° C., the polymer obtained was yellow. The spectrum of the polymer was not reported however. In DMF, n-BuLi initiated polymerization gave a white PAN (155). The presence of the cyclic keto group was established in this polymer from an absorption band at 5.8µ. If, during polymerization, propagation ceases by monomolecular termination of the polymeric chains to give an imine ion as: CH_2 CH_2 CH_2 CH_2 CH_2

on termination of polymerization with an acid the imine ion gives the $\zeta = NH$ group which hydrolyzes to the $\zeta = 0$ group.

Zilkha and coworkers (43) have assigned to $>C=CH_2$ groups the 6.lµ absorption band observed in the spectra of PANs prepared with anionic initiators. However no reference has been made to any absorption around 11.15 - 11.30µ in the spectra. Worrall et al. (37) did observe an absorption around 11.11µ in the IR spectra of PANs prepared with sodiomalonic ester and this was assigned to the presence of terminal methylene, (>C=CH₂), groups in the polymer.

In the γ -ray initiated polymerization of acrylonitrile in ethylene, Sobue and coworkers (146) showed that the polymerization of both vinyl and nitrile groups occurred. Further the polymerization of the nitrile group was by an anionic mechanism giving a colored polymer with an absorption band around 6.0 - 6.25 μ . During studies on the potassium amide initiated polymerization of methacrylonitrile in ammonia, the observed color of the polymer and an absorption around 6.00 μ in the IR spectra were assigned to the presence of conjugated $-(\dot{C}=N)_n$ - units in the polymer (34). The amide ion was considered to attack the nitrile group to give an imine ion, followed by propagation via neighboring nitrile groups, the propagation being limited to the isotactic sequence in a polymeric chain.

The heat and alkali treatment of PAN has been long known to give a colored product having an absorption band around 6.Qu (203,204). Any agreement on the exact origin of this band is still lacking, but it has been considered to be a characteristic of either conjugated $-(\dot{c}=\dot{c})_n$ or conjugated $-(\dot{c}=N)_n$ - groups (192,205). Recently Peebles (200) has shown that the observed color and infrared absorption in heat and alkali treated PANs could be better explained by assuming the presence of conjugated $-(\dot{c}=N)_n$ - in the polymer.

The IR spectra and the bromination test with PANs prepared at different temperatures does not indicate the presence of any >C=C< groups in the polymers. Hence it is quite reasonable to consider the observed color and IR absorption bands of PAN as having their origin in the presence of $-(\dot{C}=N)_n$ in the polymer. If the butyl anion attacks the nitrile group, the subsequent nitrile addition to the imine ion so obtained would explain the presence of conjugated $-(\dot{C}=N)_n$ units in the polymer.

The IR spectrum of the residue from the filtrate and washings of the polymerization experiments above -40° C., given in Figure <u>17</u>, has a small absorption band at 4.42µ compared to that in the spectra of PAN samples given in Figure <u>26</u>. This indicates that the nitrile group participates in reactions during polymerization

$$\begin{array}{c} -CH_{2} - CH - CH_{2} - CH - CH_{2} - CH_{2} - CH_{2} \\ CN & CN \\ \end{array}$$
Buli

$$\begin{array}{c} -CH_{2} - CH - CH_{2} - CH - CH_{2} - CH_{2} \\ \hline \\ -CH_{2} - CH - CH_{2} - CH - CH_{2} - CH_{2} \\ \hline \\ Bu - C - H \\ \end{array}$$
Propagation:

$$\begin{array}{c} -CH_{2} - CH - CH_{2} - CH - CH_{2} - CH_{2} \\ \hline \\ Bu - C - H \\ \end{array}$$
Propagation:

$$\begin{array}{c} -CH_{2} - CH \\ \hline \\ Bu - C \\ \end{array}$$

$$\begin{array}{c} -CH_{2} - CH \\ \hline \\ Bu - C \\ \end{array}$$

$$\begin{array}{c} -CH_{2} - CH \\ \hline \\ CH_{2} - CH \\ \hline \\ CH_{2} - CH \\ \end{array}$$

$$\begin{array}{c} -CH_{2} - CH \\ \hline \\ CH_{2} - CH \\$$

The presence of amide groups in the IR spectra of PANs arises from the partial hydrolysis of nitrile groups in these samples (202).

- 178 -

(ii) The ultraviolet spectra of polyacrylonitriles

The spectroscopic measurements on a number of compounds containing >C=C=N showed an absorption band at 4.8 - 5.0µ in the IR region and at 286 - 294 mu in the UV region in the spectra (206). Both of these absorption bands were missing from the spectra of PANs obtained in the present work. Beevers (207) has studied the IR and UV spectra of PAN films and concluded that the UV absorption band at 270 mu observed in those films could not be explained by the presence of ketene-imine groups in the polymers. Schurz and coworkers (208) have studied the UV absorption spectra of several compounds containing carbonyl and imine functional groups. In n-hexane, iminobutyronitrile was shown to have an absorption maxima around 259 mu. Thus, it is very likely that the UV absorption observed in PANs at-268 mu as shown in Figure 27 could be due to the presence of =NH groups in the polymers. Infrared measurements on PANs as given in Figures <u>26A</u> to <u>26C</u> do confirm the presence of =NH groups in the polymers. However it could not be established definitely that the absorption at 268 mµ was caused by the presence of =NH alone. A variety of factors (decrease in monomer concentration, increase in initiator concentration and increase in polymerization temperature), which favor increased participation of the initiator in side reactions, were also found to give polymers with increased absorption at-268mu, as seen in Table XVIII.

d. Color and branching in polyacrylonitriles

During the polymerization of acrylonitrile initiated by organometallics, in addition to a chain initiation and a chain propagation

- 179 -

reaction, other reactions occur which often lead to a yellow branched polymer.

In the present work acrylonitrile was polymerized to give a white polymer below -60° C. and to give a yellow polymer at higher temperatures. During the polymerization, an anion A⁻ derived from the initiator or the propagating center may attack a nitrile group of a polymeric chain at random to give an imine ion (XXVIII):



Depending upon the spatial arrangement of the neighboring nitrile groups, the imine ion might undergo further reaction with the nitrile groups to give a cyclic structure:



The presence of the conjugated imine groups in polyacrylonitriles prepared at or above -40°C. was indicated by IR measurements on the polymers (Fig. 26). Further, the coloration in heat and alkali treated polyacrylonitriles has been explained by the presence of cyclic structures in the polymers (192, 205). Therefore it is reasonable to conclude that the nitrile group of the polymer was attacked by the butyl (C_4H_9) or the polyacrylonitrile (-CH₂-CH⁻) anion, and the imine ion was further cyclized to give a colored product. Since the polymer was white at or below -60°C., the cyclization reaction did not occur to any marked degree. Overberger et al. (34) explained the coloration in polymers by postulating an attack of the amide ion on the nitrile group of the polymethacrylonitrile followed by the cyclization through successive nitrile additions to the imine ion. Further the coloration in the disodiomalonic ester initiated polymerization of acrylonitrile has been explained by assuming the presence of a cyclic structure in the polymer (37).

For polymers having the same molecular weight, the intrinsic viscosity, $[\eta]$, will decrease while the sedimentation coefficient, s_o^o , will increase with increase in the number of branched units per polymeric chain. A logarithmic plot of $[\eta]$ against S^o should be non-linear and have a negative slope. For polyacrylonitriles prepared at -78°C., the two quantities $[\eta]$ and S_o^o (which vary opposite to each other with variation in branching in polymers) were related linearly on a logarithmic scale, with a positive slope, as given in Figure 22. Therefore one can conclude that the reactions leading to a branched structure in the polymer were minimal at -78°C. At other temperatures, the reactions contributing to branching were significant, as seen from Table XV. The degree of branching in a polymer sample obtained at O^OC. (PAN # 261) is rather high and probably in error. Since the sample was polydispersed, the sedimentation coefficient determined from the maxima of the velocity gradient curves might be higher than the actual value. It is also possible that equation (36), used to convert S_0^o to $[n]_1$, may not hold for a highly branched polymer.

In PAN branching is possible by an attack of butyl ion on a tertiary carbon atom or a nitrile group of the polymer followed by the usual chain propagation:



The anion obtained in XXV has been considered to be reactive enough to add more monomer to give a branched polymer (74).



The basicity of the imine ion obtained in XXVI is considered to be insufficient to add monomer (47). Recently it has been shown that acrylonitrile does not add the imine ion (153). Moreover a carbanion of the growing chain may interact with the tertiary hydrogen, or with a nitrile group, to produce a branched structure as given by reaction XXX:



Therefore the reaction XXX or the monomer addition to the carbanion (G) would lead to branching in PAN.

In a solvent consisting of DMF and THF (1:1) mixture, at -78° C., the PAN obtained with several sodium and lithium organometallic compounds was shown to have a branched structure (74,153). The presence of branching in the PAN was explained by assuming the attack of the carbanion on the polymeric chain as given by the reaction XXV, followed by the propagation reaction. Tsuruta et al. (136) have shown that in hexane at 30° C. and in THF at -78° C., an attack upon the tertiary hydrogen atom of AN and PAN is the major reaction that n-Buli would undergo to give $CH_2=C_{CN}^{-1}$ and (G) together with n-butane.

The formation of $CH_2=\overline{C}$ given by the reaction XXIV does not seem to be indicated from the data of the present work (monomer addition to $CH_2=\overline{C}$ would give polymer with terminal vinyl group). Since the carbanion (G) has been produced by either reaction XXV or XXIX and, further, since (G) has been found to propagate at $-78^{\circ}C$., the PAN obtained at $-78^{\circ}C$. should have a highly branched structure. Since more than 90 percent of the initiator has been consumed in reactions other than chain initiation, a larger portion of the initiator might have contributed in a reaction to produce (G). However the polymer obtained in the present work at $-78^{\circ}C$. had a linear structure. Therefore the reaction to produce (G) and its subsequent propagation at $-78^{\circ}C$. does not seem to occur under the polymerization conditions used in the present work.

It should be noted that in the n-BuLi initiated polymerization of acrylonitrile, at $0^{\circ}C.$, in DMF, THF and petroleum ether (42,155), or

at -78, -40 and 0° C. in toluene (105), no mention has been made of the presence of branching in the polymers. Only in one recent paper has it been claimed that, at -78°C. in toluene, n-Buli initiated polymerization of acrylonitrile produces a branched polymer (153). In this same publication the molecular weight has been reported to decrease with increase in conversion. This would be possible if the polymer is being degraded during the polymerization as reported by Worrall et al. (37). No evidence for degradation was found in the present work and the molecular weight of PAN (obtained at -78°C.) was found to increase with conversion.

In the n-Buli and the 1,1-diphenyl hexyllithium initiated polymerization of allyl acrylate (containing a tertiary hydrogen atom similar to acrylonitrile) Bywater et al. (194) have shown that the initiator attacks the ester group in preference to the tertiary hydrogen atom of the monomer or the polymer. Since the butyl anion is more reactive than the polyacrylonitrile anion it seems more reasonable to conclude that the polyacrylonitrile anion would not attack the tertiary hydrogen atom, rather the initiator and the carbanions would react with the nitrile group. The imine ion produced by these reactions adds to nitrile groups to further the cyclization to give a colored polymer. The interaction of the carbanion with the nitrile group followed by the cyclization reaction would lead to a colored polymer having a branched structure.

APPENDIX A

TABLE A-I

<u>Acrylonitrile Polymerization and Viscosity Data</u> Initial Monomer Concentration, $[M]_{o} = 0.5$ Mole/Liter (Polymerization in Toluene at -78°C. Viscosity measured in Dimethyl formamide at 25°C.)

Reaction time, t (Minutes)	Polymer yield (%)	Monomer conc. at t [M] _t	[1] ₂₅	M _v x10 ⁻⁵	M _k x10 ⁻³	$\frac{(DP_n)_{expt}}{(DP_n)_{calc}}$	Initiator consumed (Mole/Liter)x10 ⁵	(%)
Set (a) Init	iator conce	ntration = 1.0	x 10 ⁻³	Mole/Liter;	[M]^(I]	o = 500		· ·
5 10 20 60 300	18.8 21.9 24.5 26.6 32.5	0.406 0.390 0.377 0.367 0.337	2.300 2.851 3.130 3.602 4.220	2.16 2.90 3.28 3.96 4.90	4.99 5.81 6.50 7.06 8.62	43.30 49.91 50.46 56.11 56.83	2.31 2.00 1.98 1.78 1.76	2.3 2.0 2.0 1.8 1.8
Set (b) Init	iator conce	entration $= 5 x$	10 ⁻⁴ M	ole/Liter; [N	i]_/[I]_	= 1000		
5 10 20 60 300	13.7 16.4 18.5 22.8 24.1	0.432 0.418 0.407 0.386 0.379	2.100 2.637 2.880 3.491 3.070	1.93 2.60 2.92 3.79 3.20	7.25 8.70 9.81 12.10 12.79	26.63 29.88 29.75 31.33 25.03	1.88 1.67 1.68 1.60 2.00	3.8 3.4 3.4 3.2 4.0

(continued)

- 185

TABLE A-I (continued)

Reaction time, t (Minutes)	Polymer yield (%)	Monomer conc. at t [M] ₊	[ŋ] ₂₅	M _v x10 ⁻⁵	M _k x10 ⁻³	$\frac{(DP_n)_{expt}}{(DP_n)_{calc}}$	Initiator consumed	
Set (c) Init	iator conce	entration = 2.5	5 x 10 ⁻⁴	Mole/Liter;	[M]°\[I]	o = 2000	(Mole/Liter)x10 ²	(%)
5 10 20 40 60 300	11.1 12.3 16.6 16.5 18.6 21.7	0.444 0.438 0.417 0.417 0.407 0.391	2.950 3.070 3.263 3.320 3.678 4.340	3.03 3.20 3.46 3.55 4.20 5.08	11.78 13.05 17.60 17.51 19.74 23.03	25.72 24.51 19.66 20.27 21.28 22.06	0.97 1.02 1.27 1.23 1.18 1.13	3.8 4.1 5.1 4.9 4.7 4.5
Set (d) Init	iator conce	entration $= 1.6$	6 x 10 ⁻¹	Mole/Liter	; [M] ₀ /[I]	o = 3000		
5 120 300	3.4 8.9 11.1	0.483 0.455 0.444	2.450 3.130 4.110	2.37 3.29 4.70	5.43 14.18 18.15	43.66 23.20 25.90	0.38 0.72 0.64	2.3 4.3 3.8

APPENDIX A

TABLE A-II

Acrylonitrile Polymerization and Viscosity Data

Initial Monomer Concentration, $[M]_{o} = 1.0 \text{ Mole/Liter}$

(Polymerization in Toluene at -78⁰C. Viscosity measured in Dimethyl formamide at 25°C.)

Reaction time, t (Minutes)	Polymer yield (%)	Monomer conc. at t [M] ₊	[1] ₂₅	₩ _v x10 ⁻⁵	M _k x10 ⁻³	$\frac{(DP_n)_{expt}}{(DP_n)_{expt}}$	Initiator consumed	
Set (e) Init	iator conce	ntration = 1.0) x 10 ⁻³ M	lole/Liter;	[M]°\[I]°	h care = 1000	(Mole/Liter)x10	<u>(%)</u>
1 5 10 20 40 300	25.7 28.3 26.8 28.3 30.3 34.7	0.743 0.717 0.732 0.717 0.697 0.653	5.280 4.470 3.700 3.680 3.750 5.260	6.45 5.30 4.10 4.08 4.15 6.50	13.64 15.02 14.22 15.02 16.08 18.41	47.30 35.29 28.83 27.17 25.81 35.30	2.09 2.83 3.47 3.68 3.87 2.83	2.0 2.8 3.5 3.7 3.9 2.8
Set (f) Init	iator conce	ntration = 5 x	. 10 ⁻⁴ Mol	e/Liter; [M] _o /[I] _o =	2000		·
5 10 20 40 60 300	13.3 15.6 17.2 20.1 23.1 27.6	0.867 0.844 0.828 0.799 0.769 0.724	3.860 4.093 4.190 4.276 4.278 4.970	4.34 4.70 4.81 4.95 4.97 6.05	14.11 16.55 18.25 21.33 24.51 29.29	30.75 28.39 26.35 23.20 20.27 20.65	1.62 1.76 1.89 2.15 2.47 2.42	3.2 3.5 3.8 4.3 4.9 4.8

(continued)

TABLE A-II (continued)

Reaction time, t (Minutes)	Polymer yield (%)	Monomer conc. at t	[1] ₂₅	M _v x10 ⁻⁵	M _k x10 ⁻³	$\frac{(DP_n)_{expt}}{(DP_n)_{celc}}$	Initiator consumed	
		t				<u>II Carc</u>	<u>(Mole/Liter)x10²</u>	_(%)_
Set (g) In	nitiator conce	entration = 2.5	x 10 ⁻⁴	Mole/Liter;	[M] ₀ /[I] ₀	= 4000		
2	5.2	0.948	3.630	4.00	11.04	36.24	0.69	
5	8.0	0.920	3.952	4.45	16.98	26.21	0.95	35
10	11.0	0.892	5.310	6.60	22.92	28.79	0.87	3.5
20	12.9	0.871	5.015	6.10	27.42	22.24	1.12	4.5
40	16.3	0.837	6.260	8.25	34.59	23.84	1.05	Б. 2
300	18.7	0.813	6.545	8.80	39.68	22.17	1.13	4.5
Set (h) Ir	itiator conce	entration = 1.6	67 x 10	-4 Mole/Liter	r; [M] ₀ /[I]_ = 6000		
5	5.8	0.942	4.050	4.62	18.46	25.02	0.67	1.0
10	8.1	0.919	4.560	5.40	25.79	20.94	0.80	1, g
20	9.1	0.909	4.870	5.90	28.97	20.36	0.82	4.9
60	11.8	0.882	5.372	6.75	37.57	17.97	0.93	5.6
240	16.1	0.839	6.800	8.15	51.26	15.90	1.05	6.3

APPENDIX A

TABLE A-III

Acrylonitrile Polymerization and Viscosity Data

Initial Monomer Concentration, $[M]_{o} = 2.0$ Mole/Liter

(Polymerization in Toluene at -78⁰C. Viscosity measured in Dimethyl formamide at 25^oC.)

Reaction time, t (Minutes)	Polymer yield (%)	Monomer conc. at t [M] _t	[Ŋ] ₂₅	\overline{M}_{v} x10 ⁻⁵	M _k x10 ⁻⁴	$\frac{(DP_n)_{expt}}{(DP_n)_{calc}}$	Initiator consumed (Mole/Liter)x10 ⁵	(%)
Set (i) Init	ciator conce	entration = 1.0) x 10 ⁻³	Mole/Liter;	[M] ₀ /[I]] _o = 2000		· ·
5	35.4	1.292	4.930	6.00	3.76	15.97	6.26	6.3
10	25.4	1.492	6.070	8.00	2.69	29.68	3.37	3.4
20	27.4	1.452	5.554	7.05	2.90	24.25	4.12	4.1
60	29.6	1.408	6.080	8.00	3.14	25.47	3.92	3.9
300	30.9	1.381	6.300	8.30	3,28	25.27	3.95	3.9
Set (j) Init	ciator conce	entration $= 5.0$) x 10 ⁻⁴	Mole/Liter;	[M]_/[I]	o = 4000		
2	11.3	1.774	4,950	6.02	2.40	25.06	2.00	4.0
5	14.5	1.711	5.450	6.85	3.07	22.32	2.24	4.5
10	20.2	1;596	6.160	8.07	4.28	18.33	2.66	5.3
20	18.5	1.631	5.960	7.70	3.92	19.66	2.54	5.1
40	21.3	1.574	6.250	8.27	4.52	18.30	2.73	5.5
60	21.5	1.569	6.720	9.10	4.56	19.95	2.51	5.0
300	26.8	1.464	7.160	9.80	5.69	17.23	2.90	5.8

(continued)

- 189

TABLE A-III (continued)

Reaction time, t (Minutes	Polymer yield (%)	Monomer conc. at t [M] _t	[1] ₂₅	M _v x10 ⁻⁵	M _k x10 ⁻⁴	$\frac{(DP_n)_{expt}}{(DP_n)_{calc}}$	Initiator consumed	
Set (k) Ini	tiator conce	entration $= 3$.	33 x 10 ⁻¹	+ Mole/Liter;	; [M] ₀ /[I]	o = 6000	(Mole/ Liter)x10°	(%)
5 10 20 60 300	14.2 15.6 17.2 21.0 23.9	1.716 1.688 1.656 1.580 1.522	5.923 6.110 6.300 6.760 7.260	7.65 8.02 8.32 9.15 10.00	4.52 4.97 5.46 6.69 7.61	16.92 16.15 15.24 13.69 13.14	1.97 2.06 2.19 2.43 2.54	5.9 6.2 6.6 7.3 7.6
Set (1) Ini	tiator conce	ntration = 2.	5 x 10 ⁻⁴	Mole/Liter;	[M]^(I]°	= 8000		
5 10 20 60 300	10.8 13.8 15.0 16.4 20.9	1.784 1.725 1.700 1.672 1.582	6.320 6.800 7.800 8.100 8.400	8.35 9.25 11.00 11.60 12.20	4.58 5.84 6.36 6.96 8.87	18.21 15.83 17.27 16.66 13.75	1.37 1.58 1.44 1.50 1.82	5.5 6.3 5.8 6.0 7.3
Set (m) Ini	tiator conce	ntration = 1.	66 x 10 ⁻⁴	Mole/Liter;	[M]_/[I]	o = 12000		
5 10 20 60 300	3.2 .4.8 .6.7 11.0 14.2	1.936 1.904 1.866 1.780 1.716	4.740 5.579 6.540 7.320 7.800	5.70 7.10 8.80 10.10 11.00	2.04 3.06 4.27 7.00 9.04	27.98 23.23 20.63 14.42 12.16	0.60 0.72 0.81 1.15 1.37	3.6 4.3 4.8 6.9 8.2

- 190

.

APPENDIX A

TABLE A-IV

Acrylonitrile Polymerization and Viscosity Data

Initial Monomer Concentration, $[M]_0 = 4.0$ Mole/Liter

(Polymerization in Toluene at -78°C. Viscosity measured in Dimethyl formamide at 25°C.)

Reaction time, t (Minutes)	Polymer yield (%)	Monomer conc. at t [M] _t	[ŋ] ₂₅	M _v x10 ⁻⁵	M _k x10 ⁻⁴	$\frac{(DP_n)_{expt}}{(DP_n)_{calc}}$	Initiator consumed (Mole/Liter)x10 ⁵	(4)
Set (n) Init	iator conce	ntration = 1.0	x 10 ⁻³	Mole/Liter;	[M] ₀ /[I]	o = 4000		
5 10 20 60 300	18.3 22.5 25.2 29.1 29.4	3.267 3.100 2.892 2.836 2.824	5.650 5.950 6.042 6.282 6.530	7.05 7.70 7.90 8.30 8.80	3.89 4.78 5.35 6.18 6.24	18.13 16.12 14.77 13.44 14.10	5.52 6.20 6.77 7.44 7.09	5.5 6.2 6.8 7.4 7.1
Set (o) Init	iator conce	ntration = 6.6	6 x 10 ⁻¹	Mole/Liter;	[M]_/[I] _o = 6000		
5 10 20 60 300	12.2 17.0 21.3 24.7 26.4	3.512 3.320 3.148 3.012 2.944	5.020 5.950 6.110 6.520 7.040	6.10 7.70 8.00 8.70 9.62	3.88 5.41 6.78 7.86 8.40	15.71 14.23 11.80 11.06 11.45	4.25 4.69 5.65 6.03 5.82	6.4 7.0 8.5 9.1 8.7

(continued)

-161

Reaction time, t	Polymer yield	Monomer conc. at t	[ŋ] ₂₅	M _v x10 ⁻⁵	M _k x10 ⁻⁴	$\frac{(DP_n)_{expt}}{(DP_n)}$	Initiator consumed	
	(%)		····	······································		n'calc	(Mole/Liter)x10 ²	» (%)
Set (p) Init	tiator conce	entration $= 5.0$	0×10^{-4}	Mole/Liter;	[M] / [I]	, = 8000		· .
5	11.4	3.544	5.680	7.22	4.84	14.92	3.35	6.7
10	14.2	3.432	6.280	8.30	6.03	13.77	3.63	7.3
20	16.3	3.348	7,020	9.61	6.92	13.89	3.60	7.2
40	18.5	3.260	6.220	8.22	7.85	10.47	4.78	9.5
60	20.5	3.180	7:080	9.70	8.70	11.15	4.48	8.9
300	25.0	3.002	7.500	10.40	10.59	9.82	5.09	10.2
Set (r) Init	tiator conce	entration $= 3.3$	33 x 10 ⁻⁴	Mole/Liter	; [M] ₀ /[I]) _o = 12000		· · .
5	10.1	3.596	6.340	8.40	6.43	13.06	2.55	7.7
10	14.5	3.420	6.940	9.40	9.23	10.18	3.28	9.8
20	14.6	3.416	7.160	9.80	9.30	10.54	3.15	9.5
60	16.0	3.360	7.610	10.70	10.19	10.50	3.18	9.5
120	16.9	3.324	7.940	11.30	10.76	10.50	3.18	9.5
300	18.2	3.272	8.720	12.80	11.59	11.05	3.02	9.1

TABLE B-I

Temperature Dependence of Polymerization in Toluene and Viscosity Data of Polyacrylonitriles

Initial Monomer Concentration, $[M]_0 = 0.5$ Mole/Liter

Reaction temp. (°C.)	Initiator concentration (Mole/Liter)xl0 ⁴	[M]。 [I]。	Polymer yield (%)	[1] ₂₅	k' (slope/[ነ] ²)	M _v x10 ⁻⁴
-78	20	250	35.9	3.520	0.350	38.20
11	10	500	26.6	3.602	0.347	39.60
11	5	1000	22.8	3.491	0.360	37.90
-60	20	250	32.7	1.620	0.267	13.50
11	10	500	17.3	1.780	0.309	15.40
11	5	1000	12.9	2.450	0.323	24.20
-40	20	250	9.9	0.847	0.524	5.70
11	10	500	8.2	1.402	0.410	11.15
11	5	1000	5.0	1.473	0.276	11.20
-20	20	250	9.2	0.600	0.222	3.60
11	10	500	7.6	0.771	0.210	5.05
11	5	1000	3.5	0.852	0.338	5.74
0	20	250	8.1	0.435	0.195	2.35
11	10	500	5.1	0.560	0.478	3.30
11	5	1000	3.0	0.765	0.232	5.00

TABLE B-II

Temperature Dependence of Polymerization in Toluene and Viscosity Data of Polyacrylonitriles

Initial Monomer Concentration, $[M]_0 = 1.0 \text{ Mole/Liter}$

Reaction temp. (°C.)	Initiator concentration (Mole/Liter)x10 ⁴	[M] [I]。	Polymer yield (%)	[Ŋ] _{25 ,} (k' slope/[ŋ] ²)	M_x10 ⁻⁴
-78 "	20 10 5	500 1000 2000	37.6 34.9 23.1	3.600 3.935 4.276	0.369 0.390 0.331	39.50 44.40 49.50
-60 11 11	20 10 5	500 1000 2000	19.5 16.6 15.9	2.573 3.578 3.917	0.423 0.328 0.339	25.30 39.00 44.20
-40 11	20 10 5	500 1000 2000	10.5 8.0 5.0	1.510 2.300 2.865	0.306 0.324	12.30 21.70 29.00
-20 11	20 10 5	500 1000 2000	7.9 4.0 3.2	0.981 1.266 2.030	0.403 0.240 0.654	6.95 9.75 18.20
0 11 17 17	20 10 5 200	500 1000 2000 50	7.0 3.4 3.0 42.9	0.743 0.764 1.530 0.208	0.272 0.770 0.303	4.80 5.00 12.50 0.84

TABLE B-III

Temperature Dependence of Polymerization in Toluene and Viscosity Data of Polyacrylonitriles

Initial Monomer Concentration, $[M]_0 = 2.0 \text{ Mole/Liter}$

· ·			· ·			
Reaction temp. (°C.)	Initiator concentration (Mole/Liter)x10 ⁴	[M] <u>。</u> [I]。	Polymer yield (%)	[ŋ] _{25 ,}	k' (slope/[ŋ] ²)	M _v x10 ⁻⁴
-78 "	20 10 5	1000 2000 4000	22.4 28.2 21.5	4.710 6.080 6.720	0.384 0.348 0.363	56.20 80.00 91.00
-60 ""	20 10 5	1000 2000 4000	16.5 14.4 12.0	3.370 4.762 5.326	0.387 0.355 0.381	36.00 57.00 66.40
-40 11 11	20 10 5	1000 2000 4000	8.0 6.8 3.4	2.230 3.495 3.685	0.452 0.323 0.420	20.80 38.00 40.80
-20 "	20 10 5	1000 2000 4000	5.5 3.8 1.8	1.524 1.802 1.981	0.353 0.277 0.315	12.50 15.60 17.60
0 17 17 17 17	20 10 5 40 200	1000 2000 4000 500 100	5.5 3.5 1.4 13.2 35.5	1.146 1.670 1.129 1.126 0.622	0.381 0.283 0.205 0.564 0.434	8.58 14.20 8.15 8.40 3.80

TABLE B-IV

Temperature Dependence of Polymerization in Toluene and Viscosity Data of Polyacrylonitriles

Initial Monomer Concentration, $[M]_0 = 4.0$ Mole/Liter

Reaction temp. (°C.)	Initiator concentration (Mole/Liter)x10 ⁴	[M] <u>。</u> [I]。	Polymer yield (%)	[1] _{25 ,}	k' (slope/[ŋ] ²)	M_x10 ⁻⁴
-78 " " -60	40 20 10 40 20	1000 2000 4000 1000 2000	24.5 23.1 29.1 12.9 12.6	4.630 5.282 6.282 3.642 5.021	0.302 0.337 0.375 0.379 0.387	55.00 65.00 83.00 40.00 61.00
-40 "" "" -20	40 20 10 40	1000 2000 4000	9.4 8.0 4.6 6.7	2.070 3.910 4.320 1.597	0.377 0.245 0.379 0.324 0.431	78.00 18.70 44.00 50.00 13.30
17 0 17 17	20 10 40 20 10	2000 4000 1000 2000 4000	5.1 2.6 6.9 4.3 2.3	2.960 2.993 2.030 2.083 2.301	0.259 0.385 0.567 0.299 0.423	30.30 31.00 18.30 19.00 21.5

APPENDIX C

TABLE C-I

Sedimentation Velocity Data Corrected for Pressure Effects

 $\omega^2 = 3.4513 \times 10^7 (rad^2/sec^2); \rho_0 IMF = 0.9445 gm/ml.$

Concentration (gm/dl)	S ^o (Svd)	1/s°	В	B/S ^{o²}	æ	'n	r _o (cm.)	$\frac{1}{2}r_{o}^{2} \rho_{o} \omega^{2}$	<i>4</i> /x10 ⁹
<u>#17</u>				· · · · · ·	•• •••••••••••••••••••••••••••••••••••			<u>x 10</u>	
0.7674 0.4912 0.3825 0.2659 0.1887	0.7796 1.0991 1.3384 1.7428 2.5674	1.2827 0.9098 0.7472 0.5738 0.3895	0.2265 1.7434 1.5027 1.1977 6.6949	0.3727 1.4432 0.8388 0.3943 1.0156	5.2356 3.3512 2.6096 1.8141 1.2874	0.6590 1.2503 0.9065 0.6317 1.0097	6.2333 6.1570 6.1115 6.1163 6.1062	6.3326 6.1786 6.0877 6.0972 6.0679	1.0406 2.0236 1.4670 1.0361 1.6640
$S_0^{\circ} = 4.84_{14}$			k _s =	6.8225					
<u>#152</u>		•						· · · · ·	
0.5165 0.4253 0.3307 0.2292	1.1084 1.2755 1.3543 1.7686	0.9022 0.7840 0.7383 0.5654	0.2030 0.8244 0.8534 4.0295	0.1652 0.5067 0.4651 1.2881	1.8098 1.4902 1.1587 0.8031	0.4901 0.6913 0.6519 1.1992	6.1422 6.0866 6.1923 6.0954	6.1490 6.0382 6.2497 6.0556	0.7970 1.1448 1.0430
$s_0^0 = 3.19_{40}$			$k_s = 2$	3.504 ₀			·		1.7005
#214								•	
0.6721 0.5245	1.0134 1.1920	0.9868 0.8389	0.8760 1.0015	0.8530 0.7048	2.9876 2.3315	0.9159 0.8263	6.1735 6.1128	6.1617 6.0903 (continued)	1.4864 1.3567

I 197

		•							
Concentration (gm/dl)	s°	1/s°	В	B/S ^{o²}	×	m	ro	$\frac{1}{2}r_{o}^{2}\boldsymbol{\rho}_{o}\boldsymbol{\omega}^{2}$	#x10 ⁹
							(cm,)	x 10 ⁻⁸	•
<u>#214</u> (cont ! d.)									•
0.4189 0.2382	1.3854 1.9734	0.7218 0.5067	1.0010 3.5077	0.5214 0.8911	1.8621 1.0588	0.7100 0.9280	6.1087 6.1106	6.0820 6.0859	1.1673 1.5248
S ₀ ^o = 4.01 ₀₀			$k_s = 4$	•4452					
<u>#217</u>									
0.4250 0.3588 0.2828 0.2324	1.5088 1.5908 1.8929 2.0555	0.6628 0.6286 0.5283 0.4865	1.6189 1.4102 3.5750 3.5952	0.7115 0.5572 0.9699 0.8508	2.1288 1.7972 1.4165 1.1641	0.8281 0.7304 0.9810 0.9093	6.2387 6.1192 6.0884 6.1119	6.3437 6.1031 6.0418 6.0885	1.3053 1.1967 1.6236 1.4934
$S_0^0 = 3.97_{80}$			$k_s = 5$.0090				•	:
<u>#261</u>									
0.3808 0.2713 0.2379 0.1997	1.6240 2.1485 2.2144 2.8963	0.6158 0.4654 0.4516 0.3453	1.3070 4.8093 1.0524 7.6760	0.4956 1.0418 0.2146 0.9150	5.1927 3.6995 3.2440 2.7231	0.7256 1.0233 0.5262 0.9509	6.1504 6.1319 6.1254 6.1208	6.1654 6.1283 6.1154 6.1062	1.1769 1.6697 0.8604 1.5572
$S_0^0 = 10.04_{00}$	•		k _s = 1	3.6360		•			

TABLE C-I (continued)

Av. $\mathcal{A} = 1.3630 \times 10^{-9}$

(continued)

1 **36T**

t

TABLE C-I (continued)

Concentration (gm/dl)	s ^o	1/5°
<u># 1</u>		
0.6734 0.4489 0.3367 0.2245	1.1364 1.5547 1.6177 2.2884	0.8800 0.6432 0.6182 0.4370
$s_{0}^{0} = 3.92_{34}$ #21	$k_{s} = 3.714_{2}$	
0.5366 0.4349 0.3210 0.1929	0.9660 1.0928 1.3024 1.9357	1.0352 0.9151 0.7678 0.5166
s ^o = 3.95 ₆₄ <u>#89</u>	$k_{s} = 5.923_{1}$	
0.4139 0.3104 0.2069 0.1035	1.2574 1.5423 2.0775 3.5133	0.7953 0.6484 0.4813 0.2846
$S_0^0 = 6.61_{06}$	$k_{s} = 10.855_{9}$	

- 199

SUMMARY

- 200 -

A new method was developed for the purification of acrylonitrile. An apparatus was designed to handle the material and to eliminate the contamination by atmospheric impurities during the cooling process. Acrylonitrile purified by this method contained less than 15 ppm water.

The procedure for preparing n-butyllithium from di-n-butyl mercury and lithium was modified for optimum n-BuLi yield. The apparatus units were designed for quantitative subdivision and analysis of the n-BuLi solution. The analytical apparatus proved convenient for the analysis of the small quantity of n-BuLi solution usually employed in laboratory scale polymerizations and eliminated the need for a dry nitrogen box.

Polymerization of acrylonitrile by n-BuLi in toluene was investigated over a temperature range from -78°C. to 0°C. The molecular weights of polyacrylonitriles were calculated from the viscosity measurements on the polymer solutions in DMF.

At -78°C. the characteristic yellow color of the carbanions persisted until the polymerization was terminated by the acidified acetone. The percent polymer yield was independent of monomer concentration but increased with an increase in the initiator concentration. Though the rate of polymerization was rapid in the beginning, it decreased rapidly with time. The semilogarithmic plot of monomer concentration against time was nonlinear. This was attributed to a decrease in the ability of the carbanions to acquire enough monomer for propagation. At or above -40° C., the carbanions were deactivated before the reaction was terminated. The polymer yield was independent of the monomer concentration and decreased with a decrease in the initiator concentration and/or an increase in the polymerization temperature.

The molecular weights of polyacrylonitriles obtained at -78°C. increased with an increase in polymerization time, an increase in monomer concentration or a decrease in initiator concentration. The molecular weights of polyacrylonitriles obtained at a given composition of the reaction mixture were linearly related to the polymer yield. The increase in the temperature of polymerization decreased the molecular weights of the polymers.

The sedimentation coefficients corrected for pressure and concentration effects were determined for several polyacrylonitrile samples. For polymer samples prepared at -78° C., the plot of log S_{o}° against log $[\eta]$ was a straight line. Deviation from linearity occurs, for polymer samples prepared at other temperatures, with the deviating points falling above the straight line. The constants in the empirical relation between the sedimentation coefficient and the molecular weight were determined.

The stability of the carbanions decreased and the reactions other than the chain initiation and propagation increased with the polymerization temperature. The extent of branching, molecular weight, molecular weight distribution and coloration observed in polyacrylonitriles depended upon the polymerization temperature. The coloration observed in polymers prepared at higher temperatures could be explained by assuming the presence of conjugated $-(\dot{C}=N)_n^{-1}$ structural units. The linear white polyacrylonitrile obtained at $-78^{\circ}C$. had a narrow molecular weight distribution.

The UV absorption maxima at 266 - 270 mµ of polyacrylonitriles seem to be due to the products of side reactions taking place during polymerization. Though the exact origin of this absorption could not be determined, it was shown that the factors governing increased side reactions during polymerization led to polymers having stronger UV absorption at 266 - 270 mµ.

The observed low efficiency of n-BuLi in chain initiation could not be explained by assuming the low reactivity of associated n-BuLi or by the addition of the monomer to a propagating center in preference to a butyl anion. In the n-BuLi initiated polymerization of acrylonitrile, the chain initiation is a rapid process. Most of the initiator is destroyed in simultaneous side reactions during early stages of polymerization.

The kinetic molecular weight was higher than the viscosity average molecular weight.

The values of $E_p - E_t$ reported in the present thesis and in the literature are open to serious question regarding the applicability of the method used in calculation and the accuracy of these values.

The chain termination reaction appears to be absent at -78° C. At higher temperatures carbanions are terminated probably by an isomerization reaction, by an interaction with the nitrile group or both. The occurrence of a chain transfer to a monomer or a polymer molecule to give an active site for propagation could not be supported by the present work.

By carefully excluding the impurities from the reactants it is possible to prepare linear white polyacrylonitrile having a narrow molecular weight distribution and molecular weight as high as 1.7 million.

Since the extent of the initiator consumed in side reactions could not be controlled or determined in advance, polyacrylonitriles with predetermined molecular weights could not be prepared.

CLAIMS TO ORIGINAL RESEARCH

 A new method was developed for purification of acrylonitrile.
 An apparatus was designed for handling the material during the cooling process involved.

2. The apparatus units were designed for the quantitative subdivision and the analysis of n-Buli solution.

3. The polyacrylonitrile anions were stable at -78° C. in toluene. The rapid gelation of the reaction mixture decreased the propagation rate.

4. The stability of the carbanions was temperature dependent and affected both the polymer yield and the molecular weight.

5. The molecular weight of polyacrylonitriles obtained at -78°C. was linearly related to the polymer yield obtained over a reaction period of 50 hours. The molecular weight of polymers increased with an increase in a monomer concentration or a decrease in an initiator concentration.

6. The polymer samples obtained at -78° C. had a linear structure. The polymer samples prepared at higher temperatures contained a branched structure and probably cyclic units with conjugated $-(\dot{C}=N)_n$ groups. The extent of branching and cyclization was temperature dependent.

7. The constants in the empirical relation between the sedimentation coefficient and the molecular weight were determined for polyacrylonitriles in N,N'-dimethyl formamide.
8. The molecular weight distributions in polymer samples prepared at different temperatures were determined by an analysis of the sedimentation velocity data.

9. The observed low efficiency of n-BuLi in initiating acrylonitrile polymerization could be explained by its simultaneous reaction with the nitrile group.

10. Termination by chain transfer to monomer, polymer or solvent could not be supported by the present work. At or above $-40^{\circ}C.$, the polymeric chains were terminated by either a monomolecular isomerization process or an interaction of the carbanions with the nitrile groups.

11. A polymer sample obtained at -78° C. had a very low value for the heterogeneity index (1.08).

12. Polyacrylonitrile samples prepared at -78° C. had molecular weights as high as 1.7 million.

SUGGESTIONS FOR FURTHER WORK

The information regarding polymer yield, molecular weight, molecular weight distribution, structural variations and coloration in polyacrylonitriles obtained in the present work indicates the presence of side reactions during the course of polymerization. In some cases it was difficult to decide between the alternate course of reactions. To arrive at a better understanding of the mechanisms further work is desirable.

In view of the foregoing, the following suggestions are made for future investigations. It is hoped that from the information so collected it would be possible to arrive at a better understanding of the mechanisms operative in anionic polymerization of acrylonitrile.

(1) Some knowledge could be gained in the relative reactivity of n-BuLi for 1,2-, 1,4-, 3,4-additions and for the reaction of n-BuLi with tertiary hydrogen of monomer or polymer by studying polymerization of acrylonitrile with C^{14} labelled n-BuLi and examination of the polymer and the filtrate for C^{14} content.

(2) Branching and molecular weight distribution in polyacrylonitriles obtained at different initiator concentration and monomer concentration should be investigated.

(3) With the help of model compounds the origin of the UV absorption of polyacrylonitriles could be investigated. Such a work should prove helpful in deciding between the alternate paths of the reactions. (4) A study of stereoregularity in polyacrylonitriles obtained under different polymerization conditions should prove helpful in gaining some knowledge of the reactivity of the $>C=N^-$ anion as a function of temperature.

(5) The effect of time on polymer yield and molecular weight over a temperature range -40° to -60° C. should throw some light on the stability of the carbanion.

(6) The linear narrow dispersed polyacrylonitriles prepared at -78° C. could be used to determine the constants in the Mark-Houwink empirical equation, $[\gamma] = k M_{v}^{a}$.

REFERENCES

- 208 -

- 1. Schulz, G.V. and Husemann, E., Z. Physik. Chem. B39, 246 (1938).
- 2. Colclough, R.O. and Dainton, F.S., Trans. Faraday Soc. 54, 901 (1958).
- 3. Morton, M., Bostick, E.E. and Livigni, R., Rubber and Plastics Age 42, 397 (1961).
- 4. Burnett, G.M. and Tait, P.J.T., Polymer 1, 151 (1960).
- 5. Flory, P.J., Principles of Polymer Chemistry, Cornell Univ. Press, Ithaca, New York. Ch. IV (1953).
- 6. Dainton, F.S. and Ivin, K.J., Nature 162, 705 (1948); Quart. Rev. 12, 61 (1958).
- 7. Baysal, B. and Tobolsky, A.V., J. Polymer Sci. 8, 529 (1952).
- Bainton, F.S., Nature 160, 268 (1947); J. Phys. Colloid. Chem. 52, 490 (1948).
- 9. North, A.M. and Reed, G.A., Trans. Faraday Soc. 57, 859 (1961).
- 10. Bianchi, J.P., Price, F.P. and Zimm, B.H., J. Polymer Sci. 25, 27 (1957).
- 11. Peebles, L.H. Jr., J. Am. Chem. Soc. 80, 5603 (1958).
- 12. Huggins, M.L., J. Am. Chem. Soc. 66, 1991 (1944).
- 13. Fox, T.G., Garrett, B.S., Goode, W.E., Gratch, S., Kincaid, J.F., Spell, A. and Stroupe, J.D., J. Am. Chem. Soc. 80, 1768 (1958).
- 14. Fox, T.G., Goode, W.E., Gratch, S., Huggett, C.M., Kincaid, J.F., Spell, A. and Stroupe, J.D., J. Polymer Sci. 31, 173 (1958).
- 15. Coleman, B.D., J. Polymer Sci. 31, 155 (1958).
 - Fordham, J.W.L., Burleigh, P.H. and Sturm, C.L., J. Polymer Sci. 41, 73 (1959).
- 16. Bawn, C.E.H. and Ledwith, A., Quart. Rev. 16, 361 (1962).
- 17. Stille, J.K., Chem. Rev. 58, 541 (1958).
- 18. Kennedy, J.P. and Langer, A.W. Jr., Fortschr. Hochpolymer.-Forsch. 3, 508 (1964).

- 19. Roha, M., Fortschr. Hochpolymer.-Fortsch. 4, 353 (1965).
- 20. Chien, J.C.W., J. Am. Chem. Soc. 81, 86 (1959).
- 21. Schachman, H.K., Ultracentrifugation in Biochemistry, Academic Press, New York. Ch. IV (1959).
- 22. Dawes, D.H., Ph.D. Thesis, McGill University (1962).
- 23. Sakurada, Y., J. Polymer Sci. 1A, 2407 (1963).
- 24. Tokura, N., Matsuda, M., Shirai, I., Shiina, K., Ogawa, Y. and Kondo, Y., Bull. Chem. Soc. (Japan), 35, 1043 (1962).
 - Eley, D.D. and Richards, A.W., Trans. Faraday Soc. 45, 436 (1949).
- 25. Dainton, F.S. and Sutherland, G.B.B.M., J. Polymer Sci. 4, 37 (1949).
- 26. Pino, P., Lorenzi, G.P. and Previtera, S., Rend. Acc. Naz. Lincei 29, 562 (1960).
- 27. Schildknecht, C.E., Zoss, A.O. and McKinley, C., Ind. Eng. Chem. 39, 180 (1947).

Schildknecht, C.E., Gross, S.T., Davidson, H.R., Lambert, J.M. and Zoss, A.O., ibid. 40, 2104 (1948).

28. Ziegler, K. and Bahr, K., Ber. 61, 253 (1928).

Ziegler, K., Jakob, L., Wollthan, H. and Wenz, A., Ann. 511, 64 (1934).

Ziegler, K., Angew. Chem. 49, 499 (1936).

- 29. Robertson, R.E. and Marion, L., Can. J. Research 26B, 657 (1948).
- 30. Evans, N.G., Higginson, W.C.E. and Wooding, N.S., Rec. Trav. Chim. 68, 1069 (1949).

Higginson, W.C.E. and Wooding, N.S., J. Chem. Soc. (London) 760 (1952).

- 31. Higginson, W.C.E. and Wooding, N.S., J. Chem. Soc. (London) 774 (1952).
- 32. Szwarc, M., Levy, M. and Milkovitch, R., J. Am. Chem. Soc. 78, 2656 (1956).

Szwarc, M., Nature 178, 1168 (1956).

- O'Driscoll, K.F. and Tobolsky, A.V., J. Polymer Sci. 31, 115, 123 (1958).
- 34. Overberger, C.G., Pearce, E.M. and Mayes, N., J. Polymer Sci. 31, 217 (1958); ibid. 34, 109 (1959).
- 35. Bywater, S., Adv. Polymer Sci. 4, 66 (1965).
- 36. Szwarc, M., Adv. Chem. Phys. 2, 147 (1959).

Lee, C.L., Smid, J. and Szwarc, M., J. Phys. Chem. 66, 904 (1962).

- 37. Cundall, R.B., Eley, D.D. and Worrall, J.W., J. Polymer Sci. 58, 869 (1962).
- 38. Mayo, F.R. and Walling, C., Chem. Rev. 46, 191 (1950).
- Price, C.C., Faraday Soc. Discussions 2, 304 (1947); J. Polymer Sci.
 3, 772 (1948).
- 40. Graham, R.K., Dunkelberger, D.L. and Goode, W.E., J. Am. Chem. Soc. 82, 4000 (1960).
- 41. Szwarc, M. and Rembaum, A., J. Polymer Sci. 22, 189 (1956).
- 42. Frankel, M., Ottolenghi, A., Albeck, M. and Zilha, A., J. Chem. Soc. (London) 3858 (1959).

Feit, B., Mirelman, D. and Zilkha, A., J. Appl. Polymer Sci. 9, 2459 (1965).

- 43. Zilkha, A., Neta, P. and Frankel, M., J. Chem. Soc. (London) 3357 (1960); Bull. Res. Council, Israel 9A, 185 (1960).
- 44. Zilkha, A. and Anvy, Y., J. Polymer Sci. 1A, 549 (1963).
- 45. Graham, R.K., Panchak, J.R. and Kampf, M.J., J. Polymer Sci. 44, 411 (1960).
- 46. Higashimura, T., Imanishi, Y., Yonezawa, T., Fukui, K. and Okamura, S., Polymer 3, 167 (1962).
- 47. Szwarc, M., Fortschr. Hochpolymer.-Forsch. 2, 275 (1960).
- 48. Zilkha, A., Feit, B. and Frankel, M., J. Chem. Soc. (London) 928 (1959).

Zilkha, A. and Feit, B., J. Appl. Polymer Sci. 5, 251 (1961); ibid. 7, 287 (1963).

49. Ottolenghi, A., Barzakay, S. and Zilkha, A., J. Polymer Sci. 1A, 3643 (1963).

- 50. Hsieh, H.L., J. Polymer Sci. 3A, 163 (1965).
- 51. Goode, W.E., Snyder, W.H. and Fettes, R.C., J. Polymer Sci. 42, 367 (1960).
- 52. Worsfold, D.J. and Bywater, S., Can. J. Chem. 38, 1891 (1960).
- 53. Bywater, S., Johnson, A.F. and Worsfold, D.J., Can. J. Chem. 42, 1255 (1964).
- 54. Roovers, J.E.L. and Bywater, S., Trans. Faraday Soc. 62, 701 (1966).
- 55. Dainton, F.S., East, G.C., Harpell, G.A., Hurworth, N.R., Ivin, K.J., LaFlair, R.T., Pallen, R.H. and Hui, K.M., Macromol. Chem. 89, 257 (1965).
- 56. Bhattacharyya, D.N., Lee, C.L. Smid, J. and Szwarc, M., Polymer 5, 54 (1964); J. Phys. Chem. 69, 612, 624 (1965).
- 57. Arest-Yakubovich, A.A., Gantmakher, A.R. and Medvedev, S.S., Dokl. Akad. Nauk S.S.S.R. 167, 1069 (1966).
- 58. Geacintov, C., Smid, J. and Szwarc, M., J. Am. Chem. Soc. 83, 1253 (1961); ibid. 84, 2508 (1962).
- 59. Hostalka, H., Figini, R.V. and Schulz, G.V., Macromol. Chem. 71, 198 (1964).
- Bhattacharyya, D.N., Smid, J. and Szwarc, M., J. Polymer Sci. 3A, 3099 (1965).
- 61. Figini, R.V., Lohr, G. and Schulz, G.V., Poly. Letters 3, 985 (1965).
- 62. Johnson, A.F. and Worsfold, D.J., J. Polymer Sci. 3A, 449 (1965).
- 63. Morton, M., Eostick, E.E., Livigni, R.A. and Fetters, L.J., J. Polymer Sci. 1A, 1735 (1963).
- 64. Welch, F.J., J. Am. Chem. Soc. 81, 1345 (1959); ibid. 82, 6000 (1960).
- 65. Worsfold, D.J. and Bywater, S., Can. J. Chem. 42, 2884 (1964).
- 66. Bywater, S. and Worsfold, D.J., Can. J. Chem. 40, 1564 (1962).
- 67. Morton, M., Fetters, L.J. and Bostick, E.E., J. Polymer Sci. 1C, 311 (1963).
- 68. O'Driscoll, K.F. and Tobolsky, A.V., J. Polymer Sci. 35, 259 (1959).
- 69. Zilkha, A. and Katz, Y., J. Polymer Sci. 62, 153 (1962).
- 70. Tahan, M., Ottolenghi, A. and Zilkha, A., J. Eur. Polymer 2, 199 (1966).

- 71. Zilkha, A., Barzakay, S. and Ottolenghi, A., J. Polymer Sci. 1A, 1813 (1963).
- 72. Mulvaney, J.E., Overberger, C.G. and Shiller, A.M., Fortschr. Hochpolymer.-Forsch. 3, 106 (1962).
- 73. Fetters, L.J., Poly. Letters 2, 425 (1964).
- 74. Tsukamoto, A., J. Polymer Sci. 3A, 2767 (1965).
- 75. Levy, M., Szwarc, M., Bywater, S. and Worsfold, D.J., Polymer 1, 515 (1960).
- 76. Spach, G., Levy, M. and Szwarc, M., J. Chem. Soc. (London) 355 (1962).
- 77. Chiang, R. and Friedlander, H.N., J. Polymer Sci. 4A-1, 2857 (1966). Chiang, R., Rhodes, J.H. and Evans, R.A., ibid. 4A-1, 3089 (1966).
- 78. Glusker, D.L., Stiles, E. and Yoncoskie, B., J. Polymer Sci. 49, 297 (1961).

Glusker, D.L., Lysloff, I. and Stiles, E., ibid. 49, 315 (1961).

- 79. Goode, W.E., Owens, F.H., Fellmann, R.P., Snyder, W.H. and Moore, J.E., J. Polymer Sci. 46, 317 (1961).
- Glusker, D.L., Galluccio, R.A. and Evans, R.A., J. Am. Chem. Soc. 86, 187 (1964).
- 81. Wiles, D.M. and Brownstein, S., Poly. Letters 3, 951 (1965).
- 82. Tsuruta, T. and Furukawa, J., Bull. Inst. Chem. Research, Kyoto Univ. (Japan) 40, 151 (1962).
- 83. Stearns, R.S. and Forman, L.E., J. Polymer Sci. 41, 381 (1959).
- 84. Hsieh, H.L., J. Polymer Sci. 3A, 181 (1965).
- 85. Livshits, I.A. and Stepanova, V.I., Vysokomol. Soedin. 8, 1773 (1966).
- 86. Worsfold, D.J. and Bywater, S., J. Polymer Sci. 26, 299 (1957); Can. J. Chem. 36, 1141 (1958).
- 87. Szwarc, M., Fortschr. Hochpolymer.-Forsch. 4, 457 (1967).
- 88. McCormick, H.W., J. Polymer Sci. 25, 488 (1957).
- 89. Vrancken, A., Smid, J. and Szwarc, M., Trans. Faraday Soc. 58, 2036 (1962).

- 213 -

- 90. Tobolsky, A.V., Rembaum, A. and Eisenberg, A., J. Polymer Sci. 45, 347 (1960).
- 91. Tobolsky, A.V. and Eisenberg, A., J. Am. Chem. Soc. 82, 289 (1960); J. Colloidal Sci. 17, 49 (1962).
- 92. Bywater, S. and Worsfold, D.J., J. Polymer Sci. 58, 571 (1962).
- 93. Overberger, C.G. and Schiller, A.M., J. Polymer Sci. 1C, 325 (1963).
- 94. Tobolsky, A.V. and Eisenberg, A., J. Am. Chem. Soc. 81, 780 (1959).
- 95. Kilroe, J.G. and Weale, K.E., J. Chem. Soc. (London) 3849 (1960).
- 96. Waack, R., Rembaum, A., Coombes, J.D. and Szwarc, M., J. Am. Chem. Soc. 79, 2026 (1957).
- 97. Cubbon, R.C.P. and Margerison, D., Proc. Royal Soc. A268, 260 (1962).
- 98. Bauer, E. and Magat, M., J. Chim. Phys. 47, 841 (1950).
- 99. Lyssy, T., Helv. Chim. Acta. 42, 2245 (1959).
- 100. Flory, P.J., J. Am. Chem. Soc. 62, 1561 (1940).
- 101. Gold, L., J. Chem. Phys. 28, 91 (1958).
- 102. Cowie, J.M.G., Worsfeld, D.J. and Bywater, S., Trans. Faraday Soc. 57, 705 (1961).
- 103. McCormick, H.W., J. Polymer Sci. 36, 341 (1959); ibid. 41, 327 (1959).
- 104. Morton, M., Rembaum, A.A. and Hall, J.L., J. Polymer Sci. 1A, 461 (1963).
- 105. Miller, M.L., J. Polymer Sci. 56, 203 (1962).
- 106. Schreiber, H., Macromol. Chem. 36, 86 (1959).
 - 107. Hsieh, H.L. and McKinney, O.F., Poly. Letters 4, 843 (1966).
 - 108. Hsieh, H.L., J. Polymer Sci. 3A, 191 (1965).
 - 109. Brower, F.M. and McCormick, H.W., J.Polymer Sci. 1A, 1749 (1963).
 - 110. Szwarc, M. and Litt, M., J. Phys. Chem. 62, 568 (1958).
 - 111. Orofino, T.A. and Wenger, F., J. Chem. Phys. 35, 532 (1961).Wenger, F., J. Polymer Sci. 60, 99 (1962).

- 112. Wenger, F., Macromol. Chem. 36, 200 (1960); ibid. 64, 151 (1963);
 J. Am. Chem. Soc. 82, 4281 (1960).
- 113. Litt, M. and Szwarc, M., J. Polymer Sci. 42, 159 (1960).
- 114. Figini, R.V. and Schulz, G.V., Z. Physik. Chem. 23, 233 (1960); Macromol. Chem. 41, 1 (1960).
- 115. Litt, M., J. Polymer Sci. 58, 429 (1962).
- 116. Coleman, B.D., J. Chem. Phys. 39, 3233 (1963).
- 117. Miyake, A. and Stockmayer, W.H., Am. Chem. Soc. Preprints, Vol. 6, 273 (1965).
- 118. Eisenberg, A. and McQuarrie, D.A., J. Polymer Sci. 4A-1, 737 (1966).
- 119. Schlenk, W. and Holtz, J., Ber. 50, 262 (1917).
- 120. Stavely, F.W. and co-workers, Ind. Eng. Chem. 48, 778 (1956).
- 121. Hsieh, H. and Tobolsky, A.V., J. Polymer Sci. 25, 245 (1957).
- 122. Cubbon, R.C.P. and Margerison, D., Progress in Reaction Kinetics, Pergamon Press, London. 3, 405 (1965).
- 123. Spirin, Yu. L., Gantmakher, A.R. and Medvedev, S.S., Vysokomol. Soedin 1, 1258 (1959).
- 124. O'Driscoll, K.F., Ricchezza, E.N. and Clark, J.E., J. Polymer Sci. 3A, 3241 (1965).
- 125. Hsieh, H.L., J. Polymer Sci. 3A, 173 (1965).
- 126. Feit, B., Heller, E. and Zilkha, A., J. Polymer Sci. 4A-1, 1151 (1966).
- 127. Furukawa, J., J. Chem. Soc. (Japan) 63, 645 (1960).
- 128. Kawai, W., Bull Chem. Soc. (Japan) 35, 516 (1962).
- 129. Konishi, A., Bull. Chem. Soc. (Japan) 35, 197 (1962).
- 130. Shiina, K. and Minoura, Y., J. Polymer Sci. 4A-1, 1069 (1966).
- 131. Harada, H., Shiina, K. and Minoura, Y., Kogyo Kagaku Zasshi 69, 337 (1966).
- 132. Cottam, B.J., Wiles, D.M. and Bywater, S., Can. J. Chem. 41, 1905 (1963).

- 215 -

- 133. Korotkov, A.A., Mitsengendler, S.P. and Krasulina, V.N., J. Polymer Sci. 53, 217 (1961).
- 134. Wiles, D.M. and Bywater, S., Polymer 3, 175 (1962).
- 135. Wiles, D.M. and Bywater, S., Chem. and Ind. (London) 1209 (1963); J. Phys. Chem. 68, 1983 (1964).
- 136. Kawabata, N. and Tsuruta, T., Macromol. Chem. 86, 231 (1965); ibid. 98, 262 (1966).
- 137. Moureu, C., Bull. Soc. Chim. (France) 9, 424 (1893).
- 138. The Chemistry of Acrylonitrile, 2nd Ed., American Cyanamid Co., U.S.A. (1959).
- 139. Kern, W. and Fernow, H., J. Prakt. Chem. 160, 281 (1942).
- 140. Thomas, W.M., Fortschr. Hochpolymer.-Forsch. 2, 401 (1961).
- 141. Peebles, L.H., J. Polymer Sci. 3A, 341, 353 (1965).
- 142. Bamford, C.H., Jenkins, A.D. and Johnston, R., Trans. Faraday Soc. 55, 179 (1959).
- 143. Ulbricht, J., Faserforsch. u Textiltech. 10, 115 (1959); ibid. 10, 166 (1959).
- 144. Bamford, C.H. and Jenkins, A.D., Proc. Royal Soc. (London) A216, 515 (1953).
- 145. Peebles, L.H., Copolymerization, Interscience Publishers, New York. (ed. by G.E. Ham). Ch. IX (1964).
- 146. Sobue, H. and Tabata, Y., J. Polymer Sci. 43, 459 (1960).

Tabata, Y., Hara, K. and Sobue, H., ibid. 2A, 4077 (1964).

- 147. Mezhirova, L.P., Smigasevich, Z., Sheinker, A.P. and Abkin, A.D., Vysokomol. Soedin 5, 473 (1963).
- 148. Amagi, Y. and Chapiro, A., J. Chem. Phys. 59, 537 (1962).
- 149. Arthur, J.C. Jr., Demint, R.J. and Pittman, R.A., J. Phys. Chem. 63, 1366 (1959).
- 150. Beaman, R.G., J. Am. Chem. Soc. 70, 3115 (1948).
- 151. Inoue, S., Tsuruta, T. and Furukawa, J., Macromol. Chem. 42, 12 (1960).

- 152. Zilkha, A., Feit, B. and Frankel, M., J. Polymer Sci. 49, 231 (1961).
 153. Parrod, J., Rempp, P., Rosset, J. and Galin, J.C., C.R. Ac. Sci. 260, 1651 (1965).
 Galin, J.C., Herz, J., Rempp, P. and Parrod, J., Bull. Soc. Chim. (France) 1120 (1966).
 154. Zilkha, A. and Ottolenghi, A., J. Polymer Sci. 56, 539 (1962).
 155. Ottolenghi, A. and Zilkha, A., J. Polymer Sci. 1A, 687 (1963).
- 156. Mark, H., Der feste Korper. Hirzel, Leipzig (1938) p. 103.
 - Houwink, R., J. Prakt. Chem. 157, 15 (1940).
- 157. Peterlin, A., J. Colloid Sci. 10, 587 (1955).
- 158. Kirkwood, J.G. and Riseman, J., J. Chem. Phys. 16, 565 (1948).
- 159. Debye, P. and Bueche, A.M., J. Chem. Phys. 16, 573 (1948).
- 160. Brinkman, H.C., Appl. Sci. Res. A-1, 27 (1947).
- 161. Cleland, R.L. and Stockmayer, W.H., J. Polymer Sci. 17, 473 (1955).
- 162. Miller, M.L., Button, P.A., Stamm, R.F., Rapoport, L. and Gleason, E.H., Paper presented at the Meeting-in-Miniature of the New York Section of A.C.S., 1956.
- 163. Baldwin, R.L. and van Holde, K.E., Fortschr. Hochpolymer.-Forsch. 1, 451 (1960).
- 164. Williams, J.W., van Holde, K.E., Baldwin, R.L. and Fujita, H., Chem. Rev. 58, 715 (1958).
- 165. Gupta, P.R., Robertson, R.F. and Goring, D.A.I., Can. J. Chem. 38, 259 (1960).
- 166. Fujita, H., J. Am. Chem. Soc. 78, 3598 (1956).
- 167. Oth, J. and Desreux, V., Bull. Soc. Chim. Belges 63, 133 (1954).
- 168. Billick, I.H., J. Phys. Chem. 66, 565, 1941 (1962).
- 169. Blair, J.E. and Williams, J.W., J. Phys. Chem. 68, 161 (1964).
- 170. Wales, M. and Rehfeld, S.J., J. Polymer Sci. 62, 179 (1962).
- 171. Horsley, L.H., Anal. Chem. 19, 508 (1947).

- 172. Gilman, H. and Haubein, A.H., J. Am. Chem. Soc. 66, 1515 (1944).
- 173. Dezmelyk, E.W. and Reed, R.S., Ind. Eng. Chem. 53, 68A (1961).
- 174. Goring, D.A.I. Private communication.
- 175. LeBel, R.G. and Goring, D.A.I., J. Chem. & Eng. Data 7, 100 (1962).
- 176. Craig, A.W. and Henderson, D.A., J. Polymer Sci. 19, 215 (1956).
- 177. Bisschops, J., J. Polymer Sci. 17, 81 (1955).
- 178. Fujisaki, Y. and Kobayashi, H., Kobunshi Kagaku 19, 81 (1962).
- 179. Trautman, R., J. Phys. Chem. 60, 1211 (1956).
- 180. E.I. du Pont de Nemours, Product Information Bulletin on N,N-Dimethyl Formamide.
- 181. Flory, P.J., Principles of Polymer Chemistry, Cornell Univ. Press, Ithaca, New York. Ch. XIV (1953).
- 182. Burgers, J.M., Proc. Ned. Akad. Wet. 45, 9 (1945).
- 183. Wales, M. and van Holde, K.E., J. Polymer Sci. 14, 81 (1954).
- 184. Cheng, P.Y. and Schachman, H.K., J. Polymer Sci. 16, 19 (1955).
- 185. Blachford, J. Ph.D. Thesis, McGill University (1963).
- 186. Krigbaum, W.R. and Kotliar, A.M., J. Polymer Sci. 32, 323 (1958).
- 187. Kurata, M. and Yamakawa, H., J. Chem. Phys. 29, 311 (1958).
- 188. Stockmayer, W.H. and Albrecht, A.C., J. Polymer Sci. 23, 215 (1958).
- 189. Senti, F.R., Hellman, N.N., Ludwig, N.H., Babcock, G.E., Tobin, R., Glass, C.A. and Lamberts, B.L., J. Polymer Sci. 17, 527 (1955).
- 190. Zimm, B.H. and Kilb, R.W., J. Polymer Sci. 37, 19 (1959).
- 191. Yamadera, R., Todokoro, H. and Murahashi, S., J. Chem. Phys. 41, 1233 (1964).
- 192. Grassie, N. and McNeill, I.C., J. Polymer Sci. 27, 207 (1958).
- 193. Cross, A.D., An Introduction to Practical Infrared Spectroscopy, Butterworths, London. p. 57 (1960).
- 194. Bywater, S., Black, P.E. and Wiles, D.M., Can. J. Chem. 44, 695 (1966).

196. Wiles, D.M. and Bywater, S., Trans. Faraday Soc. 61, 150 (1965).

- 197. Flory, P.J., Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York. Ch. V (1953).
- 198. Scholtan, W., Macromol. Chem. 36, 162 (1960).
- 199. Goode, W.E., Ovens, F.H. and Myers, W.L., J. Polymer Sci. 47, 75 (1960).
- 200. Peebles, L.H. Jr. and Brandrup, J., Macromol. Chem. 98, 189 (1966).
- 201. Skoda, W., Schurz, J. and Bayzer, H., Z. Physik. Chem. 210, 35 (1959).
- 202. Overberger, C.G., Yuki, H. and Urakawa, N., J. Polymer Sci. 45, 127 (1960).
- 203. Houtz, R.C., Textile Res. J. 20, 786 (1950).
- 204. LaCombe, E.M., J. Polymer Sci. 24, 152 (1957).
- 205. Berlin, A.A., Dubinskaya, A.M. and Moshkovski, Yu.S., Vysokomol. Soedin. 6, 1938 (1964).
- 206. Stevens, C.L. and French, J.C., J. Am. Chem. Soc. 75, 657 (1953); ibid. 76, 4398 (1954).
- 207. Beevers, R.B., J. Phys. Chem. 66, 1271 (1962).

208. Schurz, J., Treiber, E. and Tcplak, H., Z. Electrochem. 50, 67 (1956).