ISOTHERMAL GROWTH OF LOW MOLECULAR WEIGHT POLYETHYLENE SINGLE CRYSTALS FROM SOLUTION

٠

by

WING-MAN LEUNG

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements of the degree of

Doctor of Philosophy

Department of Chemistry McGill University Montreal, Quebec Canada

(

October, 1982

G

ABSTRACT

The linear growth rates of solution grown low molecular weight polyethylene single crystals have been investigated as a function of crystallization temperature, molecular weight and solution concentration. Sharp fractions were used covering the molecular weight range from 3100 to 11600. The crystals were characterized by studying (1) the equilibrium melting/dissolution temperature as a function of the molecular weight, (2) the lamellar thickness as a function of the crystallization temperature and (3) the fusion/dissolution behavior as a function of crystallization temperature.

The most interesting results are as follows: (a) The lamellar thickness varies continuously with crystallization temperature. This behavior has been interpreted to provide information on the important question of the location of the chain ends in the crystals. (b) For the higher molecular weight fractions the growth rate decreases monotonically with the crystallization temperature. In contrast for fractions in the molecular weight range of 3000 to 4000 the growth rate versus crystallization temperature curves show a notched appearance in which two branches can be distinguished. These branches intersect at a transition temperature where the temperature coefficient of the growth This behavior is interpreted to mean rates changes discontinuously. that the transition temperatures correspond to changes in the conformation of the molecules deposited on the growth faces. The growth rate data have been analyzed using current kinetic theories of polymer crystal growth. Basal surface free energies thus obtained are compared

with the estimates from the relations between lamellar thickness and supercooling and melting/dissolution temperature and lamellar thickness. These results are discussed in relation to the molecular structure of the crystals.

- 11 😓

7

RESUME

- iii -

Les taux de croissance linéaire de monocristaux de polyéthylène de faible poids moléculaire obtenus à partir de solutions dans le xylène ont été étudiés en fonction de la température de cristallişation, du poids moléculaire et de la concentration de la solution. A cette fin des fractions ayant une distribution étroite du poids moléculaire ont été utilisées. Ces poids moléculaires variaient de 3100 à 11600. Les cristaux ont été caracterisés par l'étude de: l) la température de dissolution et de fusion, à l'équilibre, en fonction du poids moléculaire; 2) l'épaisseur des monocristaux lamellaires en fonction de la température de cristallisation et 3) le comportement du polymère lors de la fusion et de la dissolution en fonction de la température de cristallisation.

Parmi les résultats les plus intéressants on notera que: a) l'épaisseur des lamelles varie de façon continue en fonction de la température de cristallisation. L'interprétation de ce phénomène a donné certaines informations quant à la position des bouts de chaine dans les cristaux. b) Dans le cas des fractions des plus hauts poids moléculaires le taux de croissance diminue de façon monotone avec la température de cristallisation. Par contre dans le cas des fractions dont le poids moléculaire se situe entre 3000 et 4000 des discontinuités ont été observées dans les courbes donnant le taux de croissance en fonction de la température de cristallisation. Sur ces courbes on distingue deux branches se rejoignant à une température, dite température de transition, et à laquelle il y a discontinuité pour le coefficient de température des vitesses de croissance des cristaux. Cette discontinuité a été interprétée comme correspondant à des modifications de la conformation des molécules déposées sur les surfaces croissantes. Les résultats des études de taux de croissance ont été analysés à l'aide des théories cinétiques actuelles sur la croissance des cristaux polymériques. Les valeurs obtenues des énergies libres de surface des plans de base ont été comparées à celles estimées à l'aide des corrélations entre l'épaisseur des lamelles et la surfusion, et entre la température de dissolution et de fusion et l'épaisseur des lamelles. Ces résultats ont été discutés en fonction de la structure moléculaire des cristaux.

PREFACE

The work described in this thesis was carried out under the supervision of Dr. K. St. John Manley as part of the postgraduate research program conducted in the Department of Chemistry in cooperation with the Pulp and Paper Research Institute of Canada at McGill University. The general aim of the research is to study the properties and crystallization kinetics of low molecular weight solution grown polyethylene single crystals. The thesis is presented in the following format. First there is a general introduction in which the properties of polymer crystals and theories of polymer crystallization are reviewed. The "Scope and Aims" of the thesis are also included in this chapter as the concluding section.

The main body of the thesis is presented in three chapters which follow the Introduction. These chapters have been written in the form of self-contained scientific papers which may be submitted for publication with minor changes. Chapter II deals with the variation of the lamellar thickness with crystallization temperature and the measurement of the equilibrium melting and dissolution temperature as a function of molecular weight. Chapter III deals with the melting and dissolution temperatures and the heats of fusion of crystals grown at various temperatures. Chapter IV describes the kinetics of isothermal growth of the crystals from solution as a function of molecular weight, solution

The thesis concludes with claims to original research and suggestions for further research.

ACKNOWLEDGEMENTS

vi

The author wishes to express his deep appreciation all those who have given their assistance to this project. Special thanks go to:

Dr. R. St. John Manley, my research director, for his invaluable guidance and constant enthusiasm throughout this work and thesis preparation.

Dr. J.-F. Revol, for teaching me the techniques of X-ray diffraction and electron microscopy, for his interest and stimulating discus-

Dr. P. Smith, for his useful suggestions in the studies of fusion behavior of single crystals.

Dr. M. Tsuji, for his help in the operation of the microdensitometer and his timely comments and discussions about this work.

Mr. F. St-Germain, for translating the abstract into French.

Drs. D.A.I. Goring and D.G. Gray, for their encouragement, helpful advice and good senses of humor.

Drs. J.M. Yang, L. Larrondo, S.-L. Tseng, R. Werbowyj, P. Whiting, J. Abbot, B. Favis, R. Mbachu, S. Saka, Mr. W.Q. Yean, G. Laivins, G. Suranyi, S.J. Kuang and Ms. B. Brown, M. Mary for making my life at McGill enjoyable.

The Department of Chemistry, McGill University, for teaching fellowship in 1978-79.

The Pulp and Paper Research Institute of Canada, for the use of their facilities and services and for the award of the Otto Maass Memorial Fellowship during 1979-80, 1980-81 and 1981-82.

cont'd.

Finally, I wish to express my sincere thanks to my late grandmother, my parents and brothers for their spiritual support, my wife, Choi-Man, my son, Fung-Hwa, for their infinite patience and understanding.

[]

بخنكر:

2	TABLE OF CONTENTS	•	2
		Page	
	CHAPTER I		-Lan
	INTRODUCTION	بر	ø
1.	MORPHOLOGY OF SYNTHETIC CRYSTALLINE POLYMERS	2	4
۲	Prerequisites for Crystallization	3	•
	Polymer Crystal Structures	. 6	٥
	Fringed Micelle Model	8	
	Spherulites	10	
,	Lamellar Single Crystals 🗋	11	
	Variation of the Long Period in Polyethylene Single		
-	Crystals	13	ų
*	The Equilibrium Melting and Dissolution Temperature of	-	
ŀ	Polymer Crystals	16	,
2.	THEORIES OF CRYSTALLIZATION	18	
	Nucleation	20	
	A. Primary Nucleation	20	
	B. Secondary Nucleation	24	
	Regime I and Regime II Crystallization	26	
,	Sanchez-DiMarzio Theory for Crystallization of Finite		
	Molecular Weight Polymers from Dilute Solution	34	
	Recent Development of the Kinetic Theories of Polymer		
	Crystal Growth	44	,
	• A. General Description ,	44	
3	B. Theoretical	45	
	C. Comparison with Experiment	49	

(

-viii -

SCOPE AND AIMS OF THE THESIS 54 REFERENCES 57 SELECTED BIBLIOGRAPHY 62

CHAPTER II

ISOTHERMAL GROWTH OF LOW MOLECULAR WEIGHT POLYETHYLENE

SINGLE CRYSTALS FROM SOLUTION. I. VARIATION OF EQUILIBRIUM DISSOLUTION TEMPERATURE WITH MOLECULAR WEIGHT AND LAMELLAR THICKNESS WITH CRYSTALLIZATION TEMPERATURE

ABSTRACT	-65
INTRODUCTION	66
EXPERIMENTAL	68
Materials	68
Measurement of the Equilibrium Dissolution Temperature	69 [.] *
Preparation of Crystals and Measurement of Lamellar	
. Thickness	71
RESULTS AND DISCUSSION	^t 72 •
a Equilibrium Melting and Dissolution Temperatures	72
Variation of Lamellar Thickness with Crystallization	,
Temperature	83
The Basal Surface Free Energy	90
CONCLUSIONS	93
REFERENCES	95
¥	

- ix -

CHAPTER III

ISOTHERMAL GROWTH OF LOW MOLECULAR WEIGHT POLYETHYLENE

SINGLE CRYSTALS FROM SOLUTION. II. MELTING AND

DISSOLUTION BEHAVIOR

ABSTRACT	9 8
INTRODUCTION	99
EXPERIMENTAL .	101
RESULTS AND DISCUSSION .	103
Melting and Dissolution Behavior	103
Surface Free Energies and Equilibrium Melting/Dissolution	
Temperatures	113
Enthalpies of Fusion	120
CONCLUSIONS	129
REFERENCES	131

CHAPTER IV.

	ISOTHERMAL GROWTH OF LOW MOLECULAR WEIGHT ROLYETHYLENE						
	SINGLE	CRYSTALS	FROM	SOLUTION.	111.	KINETIC STUDIES	
ABSTRACT	[c •			134
INTRODUC	CTION						136
EXPERIME	ENTAL			• •			. 138
RESULTS	AND DISC	CUSSION			,		143
C .			f . 1	1 am tladahd	Denem	damage of the	

Concentration and Molecular Weight Dependence of the

Growth Rate

4

(

(

· ALANA ALANA

Page

interaction of a second second

143

	Page
Temperature Variation of the Growth Rate	158
Basal Surface Free Energies	166
CONCLUSIONS	177
REFERENCES	1 79
CLAIMS TO ORIGINAL RESEARCH	. 181
SUGGESTIONS FOR FURTHER RESEARCH	184
٨	Ξ _γ

8

4

ž

(

(

- xi -

- xii -

┍

LIST OF FIGURES

Figure

Ċ

(

Page

\$

CHAPTER I

1.1	The Chain Configuration in (a) Isotactic, (b) Syndio-	
	tactic, and (c) Atactic Polymers.	5
[•] 1.2	The Orthorhombic Unit Cell of Polyethylene.	7
1.3	The Helical Conformation of Isotactic Polypropylene	
	Chains	7
1.4	Fringed-Micelle Model:	9
1.5	Lamellar Chain-Folded Polymer Crystal.	12
1.6	Variation of Long Period with Crystallization Tempe-	
\rangle	rature for Polyethylene Single Crystals Grown from	
	Several Different Solvents.	15
1.7	Primary Folded-Chain Crystal Nucleus.	22
1.8	Variation of the Free Energy of Formation of a Primary	
	Nucleus as a Function of Nucleus Size and Fold	
	Period.	22
1.9	Model for Surface Nucleation and Growth of Chain-	
	Folded Crystal.	25
1.10	Free Energy of Formation of a Chain-Folded Surface	
	Nucleus.	27
1.11	Schematic Representation of Growth Front Morphology	,
	for Regime I and Regime II Growth.	28
1.12	Schematic Representation of the "Self-Nucleating"	
	Mechanism.	35

Figure		Page
1.13	Schematic Representation of Primary and Secondary Cilia	
	Formation.	37
1.14	Cilia Nucleation: Effect of Crystallization Tempera-	
	ture on Concentration Dependence.	40
1.15	Cilia Nucleation: Effect of Molecular Weight on Con-	
	centration Dependence.	40
1.16	Nucleation of Molecules from Solution: Effect of Mole-	
	cular Weight.	42
1.17	Effects of Concentration as a Function of Molecular	
4	Weight on S ^S and S ^C .	42
1.18	Crystal Growth Rate vs. Temperature for Low Molecular	
·	Weight Fractions of Poly(ethylene Oxide).	46
1.19	Crystallographic Deposition of a Single Stem onto the -	
	Growth Face.	46
	` · ·	
	CHAPTER II	
2.1	DSC Fusion Thermograms for Samples PE11600 and PE4050.	75
2.2.	DSC Dissolution Thermograms of Single Crystals of	
	PE4050 in the Presence of Xylene at Various Concen-	
	trations.	76
2.3	Dissolution Temperature as a Function of Concentration.	77
2.4	Comparison of the Molecular Weight Dependence of T_m°	
	and T° with the Relationship Estimated from the	
	Flory-Vrij Equation, the Pennings Equation and the	

n

- xiji -

C

(

Sanchez-DiMarzio Equation.

82

-

i

Figure		Page
2.5-	Lamellar Thickness as a Function of Crystallization	
2.6	Temperature.	84
2.7	Lamellar Thickness as a Function of Supercooling.	87
2.8	Lamellar Thickness as a Function of Reciprocal Super-	
	cooling	92

-xiv -

(

CHAPTER III

L

3.1	Melting Peak Temperature as a Function of Heating Rate	
	for Adipic and Benzoic Acid.	104
3.2	Melting Endotherms for Fraction PE6750 crystal aggre-	
J	gates.	105
3.3	Melting Peak Temperature as a Function of Heating Rate	
	for Sample PE6750.	106
3.4	Melting Endotherms for PE3100 Crystals.	109
3.5	Melting Peak Temperature as a Function of Heating Rate	
	for PE4050 Crystals.	110
3.6	Melting Peak Temperature as a Function of Heating Rate \hat{r}	
	for PE2000 Crystals.	110
3.7	Melting Endotherms for PE4050 Crystals in the Presence	
	of Xylene.	111
3.8	Melting Peak Temperatures in the Presence of Xylene as a	
	Function of Heating Rate for Crystals of PE2000 and	
•	PE4050.	112
3.9-	Melting and Dissolution Temperature as a Function of	
3,10	Reciprocal Lamellar Thickness.	116

i

Figure		Page
3.11	Enthalpy of Fusion as a Function of Crystallization	
<u>`</u>	, Temperature.	122
3.12	Enthalpy of Fusion as a Function of Reciprocal Lamellar	

XV

Thickness.

(

4

ŗ.

ÿ

CHAPTER IV

124

4.1-4.2 Growth Rate as a Function of Concentration.	149
4.3 Concentration Exponent as a Function of Concentration.	152
4.4 Concentration Exponent as a Function of Molecular	
Weight.	153
4.5 Growth Rate as a Function of Molecular Weight.	157
4.6-4.7 Temperature Dependence of the Growth Rate.	159
4.8 Bright and Dark Field Electron Micrographs of PE3100	
Crystals Grown at 81° C and 55° C.	163
4-9-4.10 Plots of log g vs $1/T(\Delta T)f$.	169

LIST OF TABLES

- xvi -

CHAPTER II

*

2.1	Characteristics of the Polyethylene Fractions Studied.	69
2.2	Crystallization Condition and Lamellar Thickness of Low	
	Molecular Weight Polyethylene Single Crystals.	73
2.3	List of the Calculated and Experimental T_m° and T_d°	
	Values for Various Low Molecular Weight Polyethylene)
	Samples.	78
2.4	Lamellar Thickness of Low Molecular Weight Polyethylene	
	Single Crystals at Various Crystallization Tempera-	
•	tures. K	86
2.5	Values of the Basal Surface Free Energy σ_{e} and the	X
	Intercept Obtained from the Plots of 2 vs 1/AT.	93
2	,	

CHAPTER III

3.1	Melting/Dissolution Temperature and the Reciprocal of		
	the Lamellar Thickness of Polyethylene Single Cry-		
	stals Grown at Various Temperatures T.	114	
3.2	Basal Surface Free Energy σ_e and the Equilibrium		
	Melting/Dissolution Temperature $(T_m^{\circ}/T_d^{\circ})$ Obtained		
	From a Plot of T_m (or T_d) vs. 1/2.	118	
3.3	Enthalpy of Fusion of Polyethylene Single Crystals.	121	
3.4	Surface Enthalpy and Entropy of the Polyethylene Single	•	
	Crystal.	127	

Table

----- T ----

Surrow of

C

Ĵ,

(

Page

K.a.	Table		Page
	4.1	Characteristic of the Polyethylene Fractions.	139
•	4.2-	Growth Rate Data for the {110} Faces of Polyethylene	
	4.5	Single Crystals from Xylene Solution.	144
-	4.6	Values of the Concentration Exponent as a Function of	
$\left(- \right)^{2}$	ı	Crystallization Temperature.	148
	4.7	Values of K Calculated from Plots of ln G vs.	-
•	•	$1/T(\Delta T)f$.	171
	4.8	Values of the Surface Free Energy Product and the	
•		Basal Surface Energies.	174
•		• •	
		•	
		. بالا م الم	

¢.

67

•

- xvii -

.

' ر

×

ŧ

,

۲

, AT

د م

(

.

,

. .

/ 、 、

Ċ



· · ·

おおおん きょうしょう ひかっ シュー・ショ

C

(

チン

CHAPTER I .

INTRODUCTION

1. MORPHOLOGY OF SYNTHETIC CRYSTALLINE POLYMERS

A polymer is a large molecule built up by the repetition of small chemical units (monomers) held together by covalent bonds. The repeating units may be simple or quite complex. They can link together linearly or interconnectedly to form three-dimensional networks. Many polymers, in spite of the fact that they may contain thousands of repeating units, are partially crystalline. The X-ray diffraction patterns of crystalline polymers show both, sharp features associated with regions of three-dimensional order, and more diffuse features characteristic of molecularly disordered regions. The co-existence of the ordered and disordered regions in most crystalline polymers is one of the characteristics of crystalline polymers.

An understanding of the crystallization process is important in order to control the properties of a polymer in the solid state. The density or relative amorphous to crystalline content, crystallite size, arrangement and distribution of crystallites, and the crystalline form (spherulites, dendrites, etc.) all characterize the super-molecular level of ordering in polymers, which in turn dictates the solid state properties. The morphological features may be modified by varying the molecular weight, the molecular weight distribution, the crystallization conditions (e.g., temperature), the degree of molecular branching, and by annealing the sample.

• The following sections will consider the requirements for crystallization in polymers and general aspects of polymer morphology.

-

Prerequisites for Crystallization

It is well known that the crystallinity of a polymer is directly related to the regularity of its molecular structure. Occasional irregularities, such as chain branching in polyethylene, hinder the extent of crystallization but do anot prevent its occurrance. On the other hand, polymers with irregular structures such as copolymers with significant amounts of two or more quite different monomer constituents, or atactic polymers cannot crystallize.

There are two types of regularities: chemical regularity and stereoregularity.

(A) Chemical Regularity:

When a linear polymer chain has identical repeating units, then complete chemical regularity exists. This kind of polymer is called a homopolymer. Many important polymers, however, have two or more monomers polymerized together and are therefore called gopolymers. If the argangement of the monomer units is random, they are called random . copolymers. If the polymer chain is made up of subchains of A units and B units linked at their ends, such as A-A-A-A-A-A-A-B-B-B-B-A-A-A-A-A, it is called a block copolymer. While random copolymers have no chemical regularity, block copolymers would appear superficially to have all the chemical regularity necessary for crystallization. This would be true only if all the A subchains were of the same length and , all the B subchains were of the same length. If A and B subchains are not completely monodisperse, irregularity in these polymers still exists due to the various lengths of the A and B subchains in the total chains.

Some polymers such as polyethylene, have side branches and may be represented schematically by the sequence



where the B units are chemically different pendent groups such as CH_3 , C_2H_5 , C_3H_7 , etc. The amount of such irregularity depends very much on the polymerization process and has a very pronounced effect on the crystallinity. Crystallinity decreases from 90% to 40% for polyethylene as the side groups increase from about three per 1000 chain units to three per 100 chain units (1).

Another type of chemical irregularity arises from the 'head-tohead' as compared to 'head-to-tail' sequences in addition polymers. It usually occurs in the free-radical polymerization, but the fraction of head-to-head as compared to head-to-tail sequences is generally small and cannot prevent the crystallization from occurring.

(B) Stereoregularity:

When the polymers contain side groups, the carbon atom to which the side group is attached is an asymmetric carbon atom, and the possibility of stereo-isomerism occurs. In order that these polymers can crystallize they must, generally speaking, be stereoregular. The backbone carbon stems which are arranged in zigzag conformation defines a plane. The side groups may be attached either to the right or the left of the plane (Figure 1.1). If these groups are randomly placed to the left or the right of the backbone carbon plane, the structure is

0,



FIGURE 1.1

Ć

An illustration of the chain configuration in (a) isotactic, (b) syndiotactic, and (c) atactic polymers. irregular and is called atactic. Polymer chains with such an irregular configuration do not crystallize. If all the pendent groups are on one side, the structure is called isotactic. If the pendent groups are alternately left and right of the backbone plane, the structure is called syndiotactic. Both isotactic and syndiotactic have the necessary configurational regularity for crystallization.

Polymer Crystal Structures

Analysis of the diffraction patterns of crystalline polymers revealed that the chain molecules are in parallel alignment within the crystals. The atoms along the chain are in register and define a three-dimensional lattice repeating indefinitely. The atoms along a given chain are held together by valence forces as opposed to atoms belonging to adjacent chains where lesser forces of, for instance, the van der Waals type are in effect. This means that the periodicity along the chains will be closely linked to the structure of the molecules.

The process of crystal structure analysis in polymers can be divided into two stages: (i) the conformation of the chain molecule and (ii) the packing of the chains. The chain conformation is the most important and is characteristic of the polymer. Thus the chain can be a planar zigzag of carbon atoms as in polyethylene or polyamides (Figure 1.2) or can be a helix as in polypropylene (Figure 1.3), the type of helicity depending on the chemical constitution of the chain in the different polymers.

- 6 -



FIGURE 1.2

The orthorhombic unit cell of polyethylene.

- (a) General view showing the planar zig-zag form.
- (b) Projection along c axis (chain direction).



FIGURE 1.3

ĺ

The helical conformation of isotactic polypropylene chains. Small and large circles are the backbone carbon atoms and the methyl branches respectively. The chain packing is less intrinsic unless some specific interchain forces are operative, as for example, the hydrogen bonds in polyamides. In most cases the chains will pack in some hexagonal or pseudohexagonal pattern. A variety of closely similar packing requirements can exist which is the origin of polymorphism of some polymer crystal structures.

Fringed Micelle Model

(

In the 1920s, about the same time that chemists recognized that polymers were long-chain covalently bonded molecules, rather than colloidal aggregates, X-ray diffraction studies demonstrated that many polymers yielded a few broad Bragg diffraction peaks superimposed on a diffuse, liquid-like scattering pattern. From the width of the diffraction rings and the diffuse, liquid-like scattering background, it was concluded that polymeric substances contain relatively perfect crystals (with size rarely exceeding a few hundred angstroms) in an amorphous matrix. This conclusion led to the concept of the 'fringed micelle' as the primary crystalline or morphological form (2,3). The idea of this model was that the chain molecules were in crystallographic alignment over distances corresponding to the dimension of the crystallites while other segments were constituents of amorphous regions. A given molecule was thought to pass through several crystalline and amorphous regions. This model is illustrated in Figure 1.4.

This model enjoyed widespread recognition and popularity for many years, mainly because it led to simple and appealing consequences such

- 8 -



FIGURE 1.4

į

ĺ

An illustration of the fringed micelle structure of a semi-crystalline polymer. The molecules pass alternately through several crystalline and amorphous regions.

Ĵ

as the strong bonding of crystalline and amorphous regions into a composite structure of good mechanical properties, and the simple interpretation of degree of crystallinity in terms of the percentages of well-defined crystalline and amorphous regions. However, dt was recognized as an oversimplification by many investigators (4). The detailed observations of polymer morphology of the past several decades have shown that the fringed micellar model gives little insight into the structures of larger entities such as spherulites and draws attention away from the fine structure of polymer crystals.

Spherulites

Spherulites, as suggested by their name, are spherical aggregates of crystals. It is the dominant morphological entity formed when polymers crystallize from the melt. They were first observed in polyethylene by Bunn and Alcock (5) and Bryant (6). The size of the spherulites may range from submicroscopic to millimeters in diameter, depending on the magnitude of the supercooling. Each spherulite exhibits an extinction cross centered at the spherulite center with the arms of the cross oriented parallel to the vibration directions of the polarizer and analyzer of the microscope.

From the birefringence measurement, the molecular chains were found to be aligned tangentially to the spherulite, which obviously, cannot be interpreted by the fringed micelle model. No satisfactory explanation of spherulitic growth could be found until the chain folding phenomenon in polymer crystallization and the lamellar morphology had been recognized.

Lamellar Single Crystals

In 1938, Storks (7) prepared thin films of gutta percha [trans-1,4-poly(2-methylbutadiene)] by evaporation from a dilute solution in chloroform. Based on the electron diffraction studies, he concluded: "Films of gutta percha are found to be composed of relatively large crystallites which are precisely oriented with their fiber axis direction normal to the film surface. It is presumed that the macromolecules are folded back and forth upon themselves in such a way that adjacent sections remain parallel." Unfortunately, this report was virtually neglected for many years. A major advance in the understanding of the crystallite structure only came seventeen years later when platelets or lamella-like crystallites grown from solution for linear polyethylene in several laboratories (8-11) were reported. Typically such crystals are composed of lamellae with 1 - 50 µm in lateral dimension and with a thickness on the order of 100 - 200 Å. Electron diffraction patterns revealed that the molecular chains were oriented perpendicular to the upper and lower surfaces of the lamellae (10, 11). Since the molecules are thousands of angstroms long, the only plausible explanation of these apparently paradoxical observations is that the molecules are folded back and forth within the crystal with a fold period corresponding to the thickness of the lamellae. This is schematically shown in Figure 1.5.

For the sake of simplicity, the monolayered crystal shown in Figure 1.5 depicts the molecular axis as being normal to the upper and lower surfaces (fold surfaces). In actuality, polymer single crystals



FIGURE 1.5

.

ĺ.

An idealized lamellar chain-folded polymer crystal. The lines on the surface of the crystal delineate four sectors or domains. The arrows in each sector indicate the orientation of the planes along which the molecules are folded (the fold planes). In this model the folds are considered to be sharp and regular. アーニュー

are seldom planar as grown. Polyethylene crystals are usually found to be hollow pyramidal structures (12). The polymer chains are oriented parallel to the pyramid axis and thus are not exactly normal to the fold surfaces. It should be noticed that polymer molecules fold up and down along planes which are parallel to the growth faces of the crystal. As a result, the lamellae are subdivided into a number of distinguishable sectors. In each sector, the molecules are folded along the fold planes parallel to the particular lateral crystal face that subtends the sector. This sectorization of lamellar polymer crystals is shown in Figure 1.5.

Normal paraffins whose chain lengths are less than 100 Å usually form crystals without chain folding. These extended chain crystals are usually flat and without sectors. It is thus suggested that sectorization and pyramidal geometry are the direct consequences of folding (14).

Temperature Variation of the Long Period in Polyethylene

The long period is the distance between the folds in a polymer single crystal and hence is the approximate thickness of the crystal. Following the discovery of chain folding in polymer crystals, much work was done on the variation of the long period of crystals as a function of crystallization temperature. The results demonstrated a general increase of the long period with increase of the crystallization temperature (15-19). Fischer and Lorenz (20) reported that the change of the long period with the crystallization temperature was the same for

- 13 -

polyethylene single crystals formed from several solvents. However, later data (21-29) indicated that there was a variation with solvent and the long period was dependent on the supercooling rather than the absolute temperature of crystallization (Fig. 1.6).

The variation of the long period with molecular weight is less well documented. Early data (13,30) showed that at a given crystallization temperature the long period does not vary with molecular weight. However, Kawai et al (31) did observe a variation of long period of polyethylene with molecular weight in the low molecular weight range. By using sharp fractions of low molecular weight polyethylene in the present work, it was shown clearly that the long period decreases with increasing molecular weight at any one crystallization temperature (see Chapter II of this thesis). As predicted by Sanchez and DiMarzio (32), the equilibrium dissolution temperature T_d° , and hence the supercooling, decreases with molecular weight when the molecular weight is below 10^5 . Thus the dependence of long period on molecular weight is really a relation between the long period and the supercooling.

Finally, it should be mentioned that unlike polyethylene, poly-(ethylene oxide) crystals do not show a gradual increase in long period with increasing crystallization temperature. Instead, their thickness increases step-wise according to the reduction in the number of folds per molecule (33,34). This is probably due to the presence of the hydrogen bonding between the hydroxyl end groups of the polymer.

- 14 -



FIGURE 1.6

(

Variation of long period with crystallization temperature for polyethylene single crystals grown from several different solvents. Curve (1) decalin; (2) toluene, xylene and tetralin; (3) n-octane; (4) n-hexadecane; (5) diphenylether. [From Nakajima et al (23)]. x

The Equilibrium Melting and Dissolution Temperature of Polymer Crystals

Ű.

The driving force of the crystallization of polymer molecules from solution/melt is the free energy difference between the supercooled solution/melt and the equilibrium crystal. The free energy difference in turn is a sensitive function of the supercooling (ΔT) of the system. Supercooling is defined as $\Delta T = T_m^{\circ} - T$, where T_m° is the equilibrium melting temperature and T is the temperature at which crystallization is studied. In crystallization from solution, $\Delta T = T_d^{\circ} - T$, where T_d° is the equilibrium dissolution temperature. Thus it is critically important to obtain precise values of T_m° or T_d° in the analysis of the growth rate data of polymer crystals.

 T_m° may be defined as the temperature at which a large perfect crystal (consisting of extended chain molecules) is in thermal equilibrium with the surrounding pure liquid polymer, whereas T_d° is defined as the temperature at which a large perfect crystal is in equilibrium with the polymer solution. Both T_m° and T_d° depend on the molecular weight of the polymer (32). A widely used method to determine T_m° or T_d° is to measure melting/dissolution temperatures (T_m/T_d) at various ~lamellar thickness (1) and extrapolate the data to infinite lamellar thickness, according to the relation (35)

$$T_{m}(or T_{d}) = T_{m}^{\circ}(or T_{d}^{\circ}) [1 - 2\sigma_{e}/(\Delta h_{f})!]$$
 (1.1)

1

where σ_e is the basal surface free energy and Δh_f is the heat of fusion. However, it has been pointed out that these kinds of experiments may not be sensitive enough to evaluate T_m° (T_d°) as a function

- 16 -

of molecular weight (32) and the validity of applying this relation to low molecular weight polymers has been questioned (64). Flory and Vrij (69) have derived a relation which allows one to calculate T_m° theoretically at various molecular weights. Sanchez and DiMarzio (32) also proposed a semi-empirical equation for T_a°

$$T_{d}^{*} = [T_{m}^{*} - 29 + \tau_{d}^{*}]/2$$
 (1.2)

where T_m° and τ_d° are respectively the Flory-Vrij (69) and Pennings (72) estimates for the equilibrium melting temperature and the equilibrium dissolution temperature. Unfortunately this equation does not give reliable results for low molecular weight polymers as will be discussed in this thesis.

17

- 17 -

2. THEORIES OF CRYSTALLIZATION

The classical concept of crystal nucleation for small molecules was developed by Gibbs (36), Volmer (37) and Kossel (38) and has been applied successfully to polymer crystallization. It is based on the consideration of heterophase fluctuations about the thermodynamic state of equilibrium at the crystal growth face caused by the repeated deposition and remelting of molecules. A' stable nucleus is first required on which growth may occur. When several molecules spontaneously crystallize together, the chemical potential of the system is reduced by the molecular interactions created, but the net reduction in Gibbs free energy is modified by the energy expended in creating the crystal surfaces. At temperatures below the melting point the net free energy change is positive and unfavourable for the stabilization of very small nuclei, passing over a maximum at a certain critical nucleus size. If the nuclei are larger than this critical size they are stable and growth may occur on them.

However, there are many differences between the crystallization of small molecules and polymers that the theories of crystallization of polymers should account for. Small molecules are incorporated one after another into molecular crystals, producing entities of macroscopic size in three dimensions. In contrast, under many conditions linear polymer molecules crystallize by forming platelets of the order of 50 - 200 Å thick and the remaining two dimensions are very large in comparison with this thickness. The thickness of the crystals usually does not change at a given crystallization temperature but varies with

- 18 -
the supercooling in a reciprocal manner. The fold surfaces are the highest energy surfaces in the crystal, yet it is just these surfaces that do not grow at all. In addition, polymers, especially when crystallized from the melt, exhibit a persistent amount of noncrystalline material even after prolonged storage at a temperature where crystallizátion was initially quite rapid. This is not a result of impurities and has no analog in molecular crystals consisting of small molecules. All these peculiarities arise from the long-chain character of the polymer molecule.

Two main classes of theory have been proposed in order to account for the phenomena of polymer crystallization. They are equilibrium and kinetic theories. The equilibrium theory (39-42) suggests that the thermal longitudinal and torsional oscillations of the chain tend to smear out the lattice potential energy field and hence increase the free energy density of the crystal. This effect increases with increasing length of the crystallized polymer chain segment. The fold surface would, in contrast, contribute a constant positive free energy to the overall free energy of the crystal. Combining these factors could lead to a minimum free energy of the crystal at a finite chain length. According to the kinetic theories (32,43-53), chains are regularly folded in crystallites because of a nucleation requirement. The observed chain-folded crystals correspond to the structure with maximum crystallization rate rather than maximum thermodynamic stability. Crystals with extended chains should be in the lowest state of free energy. The equilibrium theory will not be detailed here because in

- 19

its present form it does not adequately account for the experimental observations that have been made. For instance, it does not account for the observed dependence of the fold length on supercooling rather than on temperature of crystallization. Also, reversibility with temperature would be expected from the theory, but is definitely not observed with chain-folded single crystals. This need not mean that a thermodynamic criterion does not exist by which the stablest crystal is of finite thickness, but according to available evidence this does not seem to govern the folding behavior of the crystals which appears to be of kinetic origin.

Nucleation

According to the kinetic theories of crystallization, two nucleation steps are necessary in the growth of a crystal. A stable threedimensional nucleus has to be formed first. This is called a primary nucleus. Then a two-dimensional secondary nucleus is required to form on a smooth crystal face before another molecular layer can be added. These nucleation processes are the rate-determining steps in crystallization. The primary nucleation rate determines the induction time while the formation of stable secondary nuclei controls the rate of growth of the crystals.

(A) Primary Nucleation:

Consider a crystalline cluster of polymer molecules that is formed at a temperature below the melting point (Figure 1.7). The free energy of formation of this cluster, or the primary nucleus, may be expressed as (44,45)

$$\Delta \phi = 4 \mathbf{x} l \sigma + 2 \mathbf{x}^2 \sigma - \mathbf{x}^2 l (\Delta f) \qquad (1.3)$$

where $\Delta \phi$ is the change of the free energy during the formation of a nucleus, 1 is the thin dimension of the crystal, x is the large dimension, σ is the lateral surface free energy representing the interfacial energy due to the interfacial surface tensions between the liquid and solid, σ_e is the fold surface free energy consisting of interfacial energy and strain energy of the folds and Δf is the free energy of fusion which is the difference in chemical potential of the liquid and solid. Near the melting point Δf can be approximated by assuming that the heat of fusion (Δh_f) is independent of temperature (54)

$$\Delta f = \Delta h_f - T \Delta S_f = \Delta h_f - T (\Delta h_f) / T_m^\circ = \Delta H_f \Delta T / T_m^\circ \sqrt{1.49}$$

where T $\overset{\circ}{m}$ is the equilibrium melting temperature and ΔT is the supercooling.

The positive energy change caused by the creation of surfaces is balanced by the reduction in bulk free energy. A plot of the free energy of formation as a function of l and x is a saddle shaped surface, the lowest barrier corresponding to the saddle point (Figure 1.8). The dimensions of a nucleus at the saddle⁴ point can be obtained by equating to zero the derivative of $\Delta \phi$ with respect to l and x in turn. The critical parameters for the primary nucleus are then

(`,

- 21 -



1

FIGURE 1.7

3

C.

Primary folded-chain crystal nucleus.



FIGURE 1.8 "

Variation of the free energy of formation of a primary nucleus as a function of nucleus size and fold period.

$$l^* = 4\sigma_e / \Delta f \qquad (1.5a)$$

$$x^* = 4\sigma_e / \Delta f \qquad (1.5b)$$

$$\Delta \phi^* = 32\sigma_e \sigma^2 / (\Delta f)^2$$
 (1.5c)

Thus the most probable value of the thickness of the primary nuclei, corresponding to the lowest free energy barrier at a given temperature, is l^* . The free energy of a nucleus with such a fold period will decrease and the nucleus becomes stable when $x > x^*$. It has been shown that the probability of finding a nucleus of length l compared to that of finding one of length l^* is (43)

$$P = \exp - \left[\Delta \phi - \Delta \phi^{*}\right]/kT \qquad (1.6)$$

For polyethylene the distribution in ℓ is sharp, and the dispersion about the mean of 1.12 ℓ^* is small. All stable nuclei then have very nearly the same length. Once a stable nucleus has been formed more molecules can add on with folding to length ℓ . Thus the thickness of the developing platelet will remain quite constant and close to the critical nucleus length ℓ^* .

It appears that the constant thickness (and its temperature dependence) of single crystals of high polymers results directly from a nucleation-controlled growth wherein growth of nuclei is inhibited in directions normal to the plane of the folds. The critical nucleus sizes as a function of crystallization temperature demonstrates that the polymer molecular weight just sufficient to form the nuclei by intramolecular crystallization increases markedly as the supercooling decreases. The logarithms of the nucleation induction times (62) were shown to be proportional to $1/T_{c}\Delta T$ demonstrating how sensitive nucleation is to supercooling.

(B) Secondary Nucleation:

Lauritzen and Hoffman (55) have proposed a theory of the secondary nucleation. The model used is shown in Figure 1.9. A polymer molecule from the solution or supercooled melt is considered to be physically adsorbed onto the surface of the crystal and then comes into crystallographic register with the substrate, forming the first stem. The molecule then folds back on itself and crystallizes in a position adjacent to the first stem. By repeating this procedure, the surface nucleus of molecular width a, thickness b and height ℓ that is fixed at a specified supercooling grows along the g direction and the overall growth of the crystal is in the G direction. The free energy of formation when ν stems and $\nu_f = \nu - 1$ folds have been formed (ignoring chain-end effects) is

9**9**

ş

$$\Delta \phi_{ij} = .2bl\sigma + 2v_{f}ab\sigma_{j} - vabl\Delta f \qquad (1.7)_{ij}$$

When v = 1, the free energy of formation is increased by $(2bl\sigma - abl\Delta f)$ because of the formation of two new surfaces and the increase of the crystal volume. Formation of a second stem by folding will cost $2ab\sigma_p$

- 24 -



FIGURE 1.9

ĺ.

Model for surface nucleation and growth of chain-folded crystal. A surface nucleus composed of stems of length ℓ , width a, and thekness b, with folds, forms on the substrate and spreads in the direction g. The surface nucleus then completes a layer of thickness b by spreading to the crystal width L, causing the crystal to grow in the G direction. The lateral and fold surface free energies σ and σ_{e} are also shown. [From Hoffman et al (59)].

because a fold surface is created. No new lateral surface is formed at this time and the bulk free energy is decreased again by $abl \Delta f$. Successive crystallization as the surface nucleus spreads in the direction g will eventually lead the system to attain the region of stability. The change of the free energy of formation of a chain-folded surface nucleus as a function of number of stems is shown schematically in Figure 1.10.

Calculation of the rate constants leads to estimates of the mean fold period and the lateral growth rate G which in turn gives information about the fold surface free energy of the crystal.

Regime I and Regime II Crystallization

ø

Lauritzen and Hoffman et al (55,56) considered that there are two means by which a growth strip might fill in. In the first case, which they refer to as Regime I, they assume that nucleation is the rate determining step. Each nucleation act once accomplished, quickly completes the growth strip of length L, adding a complete layer of thickness b before a new nucleation act occurs (Figure 1.11). The growth rate can be described as (55)

where i is the rate of deposition of chain-folded nuclei on a unit length of a substrate, L the length of the side of the crystal and can be expressed as $L = n_s a$, n_s is the number of sites where surface nuclei

- 26 -



FIGURE 1.10

Free energy of formation of a chain-folded surface nucleus. The diagram shows the relationship of the rate constants A_0 , B_1 , A and B to the free energy of the processes involved in the formation and growth of the surface nucleus as it spreads in the g direction. The rate constants of forward and backward reactions between the state v = 0 and v = 1 are A_0 and B_1 , respectively, and all the subsequent forward and backward reactions are given by A and B, ψ is a parameter, ranging from zero to unity and is related to the fraction of the polymer segments which is crystallographically attached onto the substrate. [From Hoffman et al (59)].

- 27 -

FIGURE 1.11

Ć

- Se dell' Statistica

Schematic representation of growth front morphology for regime I and regime II growth.

Regime I: Diagrams at left. Single nucleus forms on surface, rapidly completes new layers. Folds are parallel to edge of crystal.

Regime II: Diagrams at right. Many new surface nuclei form before previous layer is complete, leading to reentrant or creneleated growth frong. Some folds are parallel to direction of overall growth. [From Hoffman et al (59)].

(

.

3





G

Ś

¢

can be initiated on the substrate and a is the width of the molecule. One readily finds in cases where $G \propto i$ that (55)

$$G = G_{o} \exp[-U^{*}/R(T - T_{w})] \exp[-4b\sigma\sigma_{e}/(\Delta f)KT] \quad (1.9)$$

where the factor $\exp[-U^*/R(T - T_{\infty})]$ represents the temperature dependence of the segmental jump rate in polymers. Factors not strongly dependent on temperature are collected into the pre-exponential term G_0 . T_{∞} is a hypothetical temperature where all motion associated with viscous flow ceases and is generally taken to be about 50° C below the glass transition temperature of the polymer, T_g . For dilute solutions, $\exp[-U^*/R(T - T_{\infty})]$ is replaced by $\exp(-\Delta H^*/RT)$. Here ΔH^* is the acti-vation energy of diffusion in solution, which is usually small, $\sim 1 - 3$ Kcal/mole.

Regime II growth considers the case where surface nuclei form in large numbers on the substrate at a rate i and spread slowly at a velocity g. According to Sanchez and DiMarzio (57), the crystal growth rate in this case is proportional to the square root of the surface nucleation rate, i.e., $G = b(ig)^{\frac{1}{2}}$, where i is the surface nucleation rate and g is the spreading rate on the lateral surface. The following equation can then be derived (57):

$$G = G_{o} \exp[-U^{*}/R(T - T_{o})] \exp[-2b\sigma\sigma_{e}/(\Delta f)KT]$$
 (1.10)

A general expression for the crystal growth rate for both regimes may now be formulated

$$G_{a} = G_{o} \exp[-U^{*}/R(T - T_{o})]\exp[-K_{g}/T(\Delta T)f] \qquad (1.11)$$

where ΔT is the supercooling, f a factor near unity that accounts for the slight diminution of the heat of fusion as the temperature falls below T_m° . For dilute solutions, $\exp[-U^*/R(T - T_m)]$ is replaced by $\exp[-\Delta H^*/RT]$ as described before.

By comparison with equations 1.9, 1.10 and 1.11, it is seen that for regime I

$$K_{g(I)} = 4b\sigma\sigma_{e}T_{m}^{o}/(\Delta h_{f})K \qquad (1.12)$$

while for regime II

$$K_{g(II)} = 2b\sigma\sigma_{e}T_{m}^{o}/(\Delta h_{f})K \qquad (1.13)$$

The growth rate G for regime II differs from that for regime I by a factor of one-half in the nucleation exponent. This arises fundamentally from the fact that $G_{(I)} \propto i$, while $G_{(II)} \propto i^{\frac{1}{2}}$. Regime II would be expected to lead to a rough growth front, for many new surface nuclei form before the previous layer is complete. In addition many folds would be parallel to the direction of overall growth as depicted in Figure 1.11.

Lauritzen (58) has shown that a dimensionless quantity $Z = iL^2/4g$ governs the distinction between regime I and regime II behavior. If Z \leq 0.01, regime I behavior is expected. If Z = 0.1 regime I behavior is

- 31 -

approximated within about 10%. When Z > 1, regime II is approached. The test for regime I and regime II is as follows. The value of K is obtained from the analysis of experimental data. Z can be approximated as (55)

$$Z = iL^{2}/4g = 10^{3}(L/2a)^{2}exp[-X/T(\Delta T)] \qquad (1.14a)$$

X = K for test of regime I with Z < 0.01 (1.14b)

 $X = 2K_g$ for test of regime II with Z > 1 (1.14c)

From equation 1.14, it is possible to estimate the range of L values consistent with regime I or regime II behavior. What frequently happens is that this procedure suggests a reasonable value of L for one regime, and an unrealistic value for the other. Thus a correct choice may be made between them.

Hoffman et al (59) analyzed the data of Holland and Lindenmeyer (60) for the growth of polyethylene single crystals from xylene and found that the growth rate data were just on the border of regime I type crystallization. Cooper and Manley (61) reported the growth rates for polyethylene fractions of molecular weight 25200 and 83900 in xylene at a somewhat larger supercooling than Holland et al and suggested that the data were on the border of regime I and regime II ($K_g \approx 3b\sigma\sigma_eT_d^{\circ}/(\Delta h_f)K$). It appears then that polyethylene, as crystallized

- 32 -

from dilute solution, may pass from regime I to regime II behavior on increasing the supercooling. This transition is much more clear in polyethylene grown from the melt as reported by Hoffman et al (56). A transition temperature at about 127° C was detected, above which only axialites were observed and regime I behavior was obtained, and below which spherulitic morphology and regime II behavior was indicated. A number of other polymers, such as poly(chlorotrifluoroethylene), are also found to give regime I growth at high temperature, while others, such as isotactic polystyrene, fall almost entirely into regime II (55).

In summary, the theory emphasizes the details of how the first step element and fold go on the substrate. It is apparent from the theory that the rate of formation of a chain-folded surface nucleus simultaneously governs the crystal growth and the initial thickness of the chain-folded crystal. The restriction of the crystals to a finite thickness is fundamentally a result of kinetic considerations. The surface free energies σ and σ_e control the thickness while the product of σ and σ_e governs the temperature dependence of the growth rate.

The theory has been widely applied and is supported by a large amount of kinetic data on polymers. However, certain fundamental concepts of the theory are still under debate. The theory is based on the model of chain folding with adjacent reentry in the crystal. It describes a highly restricted form of growth. Once a single unit of a chain is attached to the interface, the final position of any other unit in the molecule is almost predetermined. Such a process seems

- 33 -

likely in the crystallization from dilute solution where the density of chains in the liquid is low and competition between chains for the growth sites is infrequent. In growth from the melt, however, much more competition between chains or different parts of the same chain for growth sites is expected, since the densities of molecular units in the melt and crystal are nearly the same. Moreover, the model only considers infinite molecular weight polymer chains with many folds. Chain end and concentration effects are not included. It is apparent that the theory cannot be used in its present form to predict the variation of the growth rate of polyethylene single crystals from dilute solution with molecular weight and concentration.

Sanchez-DiMarzio Theory for Crystallization of Finite Molecular Weight Polymers From Dilute Solution

(A) General Description:

Sanchez and DiMarzio published a dilute solution theory for polymer single crystals (32,53) in 1971, in which they attempted to predict the effects of molecular weight and concentration on the growth rate. The basic postulate of the theory is self-nucleation by cilia (Figure 4.12). Cilia are the dangling ends of molecules that are partially incorporated into the crystal lattice. They are formed in the following manner. The first segment of a solution molecule to deposit on a crystal growth strip would likely be not an end portion but some more central region of the molecule. When these first segments have attached to the crystal the two ends of the molecule are left dangling



- 35 -

FIGURE 1.12

4

、「見る思想はいい」

()

Schematic representation of the "self-nucleating" mechanism. A cilium formed in an underlying growth strip nucleates a new growth strip. [From Sanchez and DiMarzio (53)].

in solution. If the long chain portion begins folding, the shorter one will be left dangling in solution as a primary cilium, and if the process of chain folding is interrupted by the incorporation of a new chain from solution or a previously formed cilium into the growing strip, then a secondary cilium is formed. This is illustrated in Figure 1.13. In dilute solution crystallization, secondary ciliation will be less important than primary ciliation simply because of the sparsity of polymer molecules in solution around the growing face and the lengths of the secondary cilia are usually a fractional number of stem lengths. It is the primary cilia which may nucleate the following growth strip. Making what is considered to be a reasonable assumption, that once a new growth strip is nucleated then filling in by chain folding of molecules is a rapid process (45,46,48,49). Sanchez and DiMarzio studied theoretically the effects of molecular weight and temperature on the concentration dependence of crystal growth rates.

Two models were considered in the theory. In the first model, primary cilia are not allowed to reenter the crystal, whereas in the second model, primary cilia are allowed to reincorporate in the next growth strip. The total nucleation rate S can be expressed as a linear combination of the cilia nucleation rate S^c and the nucleation rate S^s for solution molecules:

$$s = w_1 s^c + w_2 s^s$$
 (1.15)

where W_1 and W_2 are weighting constants. Sanchez and DiMarzio were not

- 36 -



FIGURE 1.13

1

Schematic representation of primary and secondary cilia formation. In (a) a chain molecule attaches in the growth niche at some arbitrary place along its contour length. One of the dangling chain portions proceeds to fold (b) until it completes folding or until a new molecule interrupts its growth (c). [From Sanchez and DiMarzio (53)]. able to estimate the values of W_1 and W_2 , however, they pointed out that W_1 is proportional to 1/MW since the shorter the molecular length the greater the number of cilia present per unit length of growth strip.

(B) Behavior of S^S and S^C

The reader is referred to the original papers for details concerning the derivations of the theory. Some important predictions from the theory for the behavior of S^{S} and S^{C} for polyethylene as crystallized from xylene solution are summarized below:

(1) S^S is generally found to be proportional to the concentration raised to the first power. The first order kinetics indicates that the rate of nucleation is directly dependent on the number of molecules in solution. At very low molecular weights this proportionality tends to exceed unity indicating that one molecule is of insufficient length to stabilize itself by chain folding; several more stems from other molecules are needed to stabilize the nucleus.

(2) S^C is proportional to the concentration raised to a power less than one (Figure 1.14). This indicates that although solution molecules are not being used in nucleating a growth strip directly, they are usually required to stabilize the nuclei formed by cilia which are too short to stabilize themselves by chain folding. As the crystallization temperature increases, the long period increases and the number of stems that a cilium can contribute to stabilize the nucleus decreases. The nucleus becomes increasingly dependent on solution molecules as the supercooling decreases and the concentration exponent then increases slightly with T_c . As the molecular weight increases up to about MW ~ 10⁵ the cilia are of sufficient length to stabilize themselves and therefore there is no change of S^C with concentration (Figure 1.15).

(3) The dependence of S^8 on molecular weight at various crystallization temperatures is shown in Figure 1.16. The _nucleation rate first increases with molecular weight, passes through a broad maximum and then decreases slightly. The increase of the nucleation rate with molecular weight is of course due to the increase of supercooling. This effect is opposed by the localization free energy (53) which increases with molecular weight and causes the maximum in the curve. No maximum is predicted in the relation between S^c and molecular weight. S^c increases monotonically with molecular weight (Figure 1.17).

(4) The effects of concentration on S^8 and S^C are shown in Figure 1.17. As expected, S^8 increases proportionally with concentration over the molecular weight range while S^C increases with concentration at low molecular weight but becomes independent of concentration at molecular weights above ~ 10^5 .

Recently, Cooper and Manley (63) have shown that the predictions of the theory can be readily checked by studying the behavior of S^{C} and S^{S} individually under varying conditions of molecular weight, temperature and concentration. The results were found to be compatible with the self-nucleation mechanism.

- 39 -

Ĩ.

FIGURE 1.14

The effect of crystallization temperature T_c on the concentration dependence of the isothermal cilia nucleation rate S^c . The concentration dependence increases slightly as T_c increases. [From Sanchez and DiMarzio (32)].

FIGURE 1.15

The effect of molecular weight on the concentration dependence of the isothermal cilia nucleation rate S^{c} . The concentration dependence decreases as the molecular weight increases. [From Sanchez and DiMarzio (32)].





(`·

41

FIGURE 1.16

あつ たいこうちょう

The isothermal nucleation rate for solution molecules S^5 versus molecular weight. The isotherms pass through a shallow maximum which shifts to higher molecular weights as the crystallization temperature increases. [From Sanchez and DiMarzio (32)].

FIGURE 1.17

The relative effect of concentration on solution molecule and cilium isothermal nucleation rates S^{s} and S^{c} , as a function of molecular weight. [From Sanchez and DiMarzio (32)].

< تې

C



\$,

ł,

C

(

- 43 -

5

7 V

÷.

Recent Development of the Kinetic Theories of Polymer Crystal Growth (A) General Description:

As mentioned above, kinetic theories based on coherent surface nucleation have been proposed (45,48) to account for the folded conformation of polymer chains during/crystallization. A direct means to test the validity of the theories and probe the origin of the chain folding in polymer crystallization is to study the crystallization of low molecular weight polymers in the region of molecular weight and supercooling where the transition from extended-chain to folded-chain crystal growth can be observed. By far the most exhaustive set of data which has been obtained is that for low molecular weight hydroxyl terminated poly(ethylene oxide) (PEO) single crystals grown from bulk by Kovacs and co-workers (64-66). They investigated the growth kinetics, melting and thickening behavior of bulk samples of PEO single crystals systematically in the molecular weight and supercooling region where the polymer chains are either folded a small number of times or extended. It has been shown (33) that the lamellar thickness 1 of PEO is an integral submultiple of the overall chain length L. This indicates that each molecule is folded exactly a small number of times n, with chain ends rejected on the surface layers of the crystalline lamellae and the chain folds are tight with adjacent re-entry. The growth rate data of PEO show distinct branches corresponding to each integral value of n (64) (see Figure 1.18). Each branch has the quantitative shape of log G vs T curves for a typical high molecular weight polymer, includ-

ing giving approximately the characteristic linear relation between

¢:::

- 44 -

log G vs $1/T(\Delta T)$. The current kinetic theories, which assume molecular weight to be infinite, do not permit a consistent analysis of the kinetic data on the low molecular weight poly(ethylene oxide) samples.

Recently, Point and Kovacs (67) and Buckley (68) had extended the existing kinetic theories to short chain polymers, particularly to the low molecular weight PEO system. Basically, the extended theory is similar to the current kinetic theories patterned after Hoffman and Lauritzen (45); it is still based on coherent surface nucleation and the formation of the surface nucleus is assumed to be a sequential process. What is new is that the chain end effects are taken into consideration in a consistent manner.

(B) Theoretical:

On the attachment of the first stem of a short chain molecule onto a crystal surface, the variation of the free energy of formation is

 $\Delta \phi_{0} = 2b \Re \sigma + \alpha 2ab \sigma_{e} - \phi \Delta F_{c}(\Re, T) \qquad (1.16)$

where a, b and ℓ are the geometrical dimensions of the stem, σ and σ_{e} are the lateral surface free energy and the excess free energy associated with the two dangling chain ends respectively (Figure 1.19), α is a factor ranging from zero to unity and is used here to account for a possible asymmetry of the activation barrier associated with $2ab\sigma_{e}$. The parameter ψ , also ranging from zero to unity, is related to whether or not the polymer molecule is physically absorbed on the surface prior



FIGURE 1.18

L

Crystal growth-rate G versus temperature T for four low MW fractions of PEO: A, $M_n = 1890$; B, $M_n = 3900$; C, $M_n = 5970$; D, $M_n = 7760$ and one high MW sample: E, $M_n = 152$ 000 after Kovacs and coworkers (64-66). Parameter shown is n, the number of folds per molecule. [From Buckley (68)].



FIGURE 1.19

Crystallographic deposition of a single stem onto the growth face. [From Point and Kovacs (67)]. to actual crystallographic attachment onto the substrate. Thus the first and second terms of $\Delta\phi_0$ are positive and correspond to the crea tion of the new surface and the excess free energy created by the cilia, respectively. The third term represents the decrease in the bulk free energy of crystallization relevant to the stem of length l. It should be noticed that $\Delta\phi_0$ must be positive in order to prevent the nucleation frequency, and thus the growth rate from increasing with l.

Under steady state conditions, the flux S(l) over the nucleation barrier to generate a monomolecular layer of length l can be expressed by (55):

$$S(l) = N_{0}A_{0}(A - B)/(A - B + B_{1})$$
 (1.17)

where A_0 and B_1 are the rate of deposition and full detachment of the first stem, respectively. They can be written as

A = $\beta \exp(-\Delta \phi_0/KT)$

= $\beta \exp[(-2bl\sigma - \alpha^2ab\sigma + \psi\Delta F_c)/KT]$

(1,18)

- $B_1 = A_o \exp[(2bl\sigma + 2ab\sigma_e \Delta F_c)/KT]$
 - = $\beta \exp \left\{ \left[-(1 \psi) \Delta F_{c} + (1 \alpha) 2 a b \sigma_{e} \right] / KT \right\}$ (1.19)

A and B are the forward and backward reaction rates for the attachment of additional stems of length & in an adjacent position to the first.

- 47 -

They can be expressed by

$$A = \beta \exp[(\psi \Delta F_c - \alpha' 2ab\sigma_e)/KT] \qquad (1.20)$$

where σ_e represents the average value of the basal surface free energy per stem. This is because for short chains the additional stems may include either chain ends or folds or other types of crystal defects. The factor α' associated with $\overline{\sigma}_e$ is generally assumed to be equal to unity (48,55). The total flux S_T which controls the growth rate is given by integrating over all possible values of 1, ranging from a minimum to L, viz.,

$$S_{T} = \sum_{\substack{k \in S(k) \\ lmin}} L = k_{u}^{-1} \int_{u} S(k) dk \qquad (1.22)$$

where λ_u is the length of one repeating unit. This is one of a major departure from the infinite molecular weight approximation in which the upper limit of the integration is infinity.

From these basic equations, Point and Kovacs (67) obtained, growth rate expressions for extended chain crystals corresponding to the case of PEO.

$$G_{i}(0, p) \propto \beta(p) \exp\left(-\frac{2ibL\sigma}{kT}\right) \exp\left[\frac{\psi a bL\Delta h_{f}\Delta T}{kT_{m}(\infty)T} - \frac{a^{2}ab\sigma}{kT}\right] \left\{1 - \exp\left[\frac{2ab\sigma}{kT} - \frac{\Delta F_{c}(L,T)}{kT}\right]\right\}$$
(1.23)

where $\sigma_{e,e}(0)$ is the surface free energy contribution of one free energy contribution of one chain end in a surface involving n = 0 and i _____ = 1 for regime I growth and i = $\frac{1}{2}$ for regime II growth. Similarly, the general growth rate expression for folded chain PEO crystals is given by the equation:

$$G_{i}(n, T) \propto A[1 - (\beta/A)] \exp\left\{-[2bl_{n}\sigma + \alpha^{2}ab(\sigma_{e} - \overline{\sigma_{e}})](i/KT)\right\}$$
 (1.24)

where it is assumed that (i) the length l_n of the growth nuclei is always an integer submultiple of the chain length, i.e., $l_n = L/(1+n)$, and its value increases step-wise with T corresponding to the change of n, and (ii) B = B₁, thus $\alpha = \alpha'$.

(C) Comparison with Experiment:

1

A STATE A STATE

()

In order to avoid the arbitrary assignment of the unknown parameters such as ψ and α , Point and Kovacs (67) expressed G in terms of an appropriate reduced variable enabling direct comparison of the data obtained for any pair of PEO fractions investigated. For extendedchain crystal growth, the expression

$$\frac{G_{i}(0, p_{1})}{G_{i}(0, p_{2})} \simeq (p_{1}/p_{2})^{-(\gamma + \psi')} exp\left[\frac{2iblu\sigma}{KT_{m}(\infty)}(p_{1} - p_{2})\right] (1.25)$$

can be obtained for any two fractions of PEO from equation 1.23 and the relation $\beta(p) = JP^{-\gamma}$ (70) in which p is the degree of polymerization of a fraction, J is the frequency factor which is insensitive to small temperature changes and the value of the exponent γ ranges from zero to unity. Note that the right hand side of this expression is independent of both T and the reduced supercooling $\theta = (P/T)[T_m(\infty) - T]$. Thus they deduced the following reduction rule:

"The logarithmic growth rate branches G(o, p) of extended chain crystals, obtained with low molecular weight PEO fractions (or similar materials), plotted against the reduced undercooling θ , are superposable within a fair accuracy by means of vertical shifts, except in the vicinity of the relevant melting temperatures $T_m(0, p)$, where G(0, p)vanishes."

Point and Kovacs found that the reduction rule is well supported by the experimental data. However, when they rearranged equation 1.25 to the expression

$$i\sigma = \frac{2.303 kT_{m}(\infty)}{2b l_{u}(p_{2} - p_{1})} \left[\log \frac{G(o, p_{1})}{G(o, p_{2})} \right|_{\theta} - (\gamma + \psi') \log \frac{P_{2}}{P_{1}} \right] (1.26)$$

and attempted to estimate the lateral surface free energy σ by assuming upper and lower limits to the unknown parameters, they noticed that the σ values are much smaller than those usually reported (59). Actually, they are too low to have any physical meaning for characterizing the

(:

, **1**

ちょううち

- 50 -

sharp boundary between a crystalline substrate and the melt. Furthermore, the apparent i σ value is reciprocally related to the chain length. This is inconsistent with the theoretical model, implying σ to be independent of the chain length.

Similarly, for the growth of n times folded crystals, by defining

$$\phi(n, T) \equiv \{\psi \Delta F_{c}[L(1 + n)^{-1}, T] - \alpha 2ab\sigma_{a}(n)\}(KT)^{-1}$$
 (1.27)

one can express the ratio of the growth rates observed at any two corresponding temperatures T_n , involving the same value of ϕ , by

$$\frac{G_{i}(n, T)}{G_{i}(n', T)} \bigg|_{\phi} \simeq \exp \bigg\{ - \frac{2ibL\sigma}{k} \bigg[\frac{1}{(n+1)T} - \frac{1}{(n'+1)T'} \bigg] \bigg\} (1.28)$$

Note also that the right hand side of this equation is independent of ϕ and depends only slightly upon T. Thus a similar rule can be stated: The various G(n, T) growth paranches plotted against ϕ/ϕ should be superposable merely by vertical shift over the entire overlapping ϕ range. This theoretical requirement was found approximately fulfilled. However, the apparent values of io derived from equation 1.28 are very low at values of n and increase rapidly with decreasing n, attaining acceptable values at relatively large supercooling.

When plotting $G(n, T_m)$ against T_c , the theory predicts the existence of discrete growth branches for integral values of n. Reasonable quantitative agreement with experiment is found for high values of n.

For low values of n and small supercooling, however, there is a large quantitative discrepancy between the predicted and observed G values. Moreover, the theory predicts a dramatic increase for both 1 and G (which has been referred to as the $\delta \ell$ catastrophe (55)) when $\Delta \phi_{a}$ becomes negative, i.e., when $\psi \Delta F_c > 2bl\sigma + \alpha 2ab\sigma_c$. This may arise when the crystallization temperature is low enough. Experimental results show a levelling off for both ℓ and G at low temperature (T < 300 K) rather than an increase. Point and Kovacs have concluded that the nature of the failure of the theoretical predictions reveals a series of fundamental discrepancies contradicting the model of coherent surface nucleation resulting in a sequential deposition of chain segment of fixed length. These discrepancies may originate from the incorrect evaluation of the free energy barrier $\Delta \phi_0$ (equation 1.16) which opposes the crystallographic attachment of the first stem. The failure of the postulate of the sequential deposition of the consecutive stems of fixed length (i.e., the use of equation 1.17) cannot be ruled out. Recent data on the chain conformation in polymer crystals as revealed by neutron scattering shows that the chain conformations in solution and melt-crystallized polymers are (not alike (71) and that melt crystallization does not alter significantly the radius of gyration of the chains from that in the liquid state, where they have a random coil This suggests that crystal growth may not involve a conformation. unique process as set out in the kinetic theory.

It is not, however, certain whether the behavior of poly(ethylene oxide) is typical of low molecular weight crystalline polymers in general or associated with end group pairing, due to hydrogen bonding between the terminal hydroxyl groups. Thus in order to further our understanding of the onset of chain folding in polymers, a polymer should be used in which there are no strong attractive forces between the end groups.

ĺ.

し、これないのないまでものないである

()

SCOPE AND AIMS OF THE THESIS

Although the phenomenon of chain folding in polymers has been extensively investigated during the past twenty-five years, it is still not completely understood. Recent studies of the melt crystallization of low molecular weight hydroxyl terminated poly(ethylene oxide) show that the lamellar thickness varies with the crystallization temperature in a step-wise manner, corresponding to an integral change in the num-, ber of folds per chain (n) in the crystals. Growth rate data show branches corresponding to each integral value of n. .Systematic analysis of the growth rate data has revealed a number of inconsistencies and led to the claim that there is a fundamental conceptual failure in the current kinetic theories of polymer crystal growth. It is not clear, however, whether the results are of general validity or associated with hydrogen bonding between the hydroxyl end groups in the special case of poly(ethylene oxide) chains.

In order to further our understanding of the crystallization of low molecular weight polymers and more generally of the origins of the chain folding phenomenon, the following questions need to be answered:

(1) Is the step-wise variation of lamellar thickness with crystallization temperature in poly(ethylene oxide) a general phenomenon in low molecular weight polymers?

(2) Are the distinct branches that are observed in the growth rate-temperature curves in poly(ethylene oxide) a general phenomenon in low-molecular weight polymers?

- 54 -
(3) Is the current kinetic theory, which is modelled on infinitely long polymer chains, still valid for low molecular weight polymers?

(4) Is there any difference in the growth mechanism of folded and extended chain crystals? If so, will it be reflected in the growth rate?

The work presented in this thesis is designed to provide answers to these questions. Lamellar thickness, fusion behavior, crystal morphology and growth rates of solution grown polyethylene single crystals were studied as a function of crystallization temperature, molecular weight and solution concentration. The regions of molecular weight and supercooling that have been chosen are such that the transition for extended chain to folded chain crystal growth can be observed. The main reason for choosing polyethylene is that strong attractive forces do not exist between the end groups, thus it should be possible to test the generality of the results previously obtained with poly(ethylene oxide). Furthermore the decision was taken to study solution crystallization since it would permit a wider range of supercoolings to be encompassed than would be possible in melt crystallization.

Finally, it may be noted that in work of this kind there is always a real difficulty in determining the supercooling which is critically dependent on an accurate measurement of the equilibrium dissolution temperature. A method has therefore been devised for the direct calorimetric measurement of the equilibrium dissolution temperature. This eliminates the ambiguity in the analysis of thermodynamic and kinetic data caused by the uncertainty in the value of this parameter.

- 55 -

The work is presented in three sections as follows:

Chapter II deals with the measurement of the equilibrium melting and dissolution temperature of the crystals as a function of molecular weight, and the variation of the lamellar thickness with crystallization temperture. The data are analyzed in order to estimate the basal surface free energies of the crystals.

Chapter III describes the measurement of the melting and dissolution temperatures and heats of fusion of crystals grown at various temperatures. From the data, equilibrium melting/dissolution temperatures and basal surface free energies of the crystals are estimated. The temperature variation of the heat of fusion of the crystals will be shown to provide evidence for a transition in the conformation of the molecules deposited on the growth faces.

Finally in Chapter IV the kinetics of isothermal growth of the crystals is described. The concentration, molecular weight and temperature dependence of the growth rates are discussed, and it will be shown that, as in the case of poly(ethylene oxide), the kinetic data provide evidence for a conformational transition in the molecules as the crystallization temperature is decreased.

٤.,

€.

REFERENCES

- E. Passaglia and H.I. Kevorkian, J. Appl. Polym. Sci., 7, 119 (1963).
- K.M. Hermann, O. Gerngross and W. Abitz, Z. Phys. Chem., <u>B10</u>, 371 (1930).
- 3. K.M. Hermann and O. Gerngross, Kautschuk, 8, 181 (1932).
- C.W. Bunn, in Fibres from Synthetic Polymers (R. Hill, ed.), Elsevier, New York (1953).
- 5. C.W. Bunn and T.C. Alcock, Trans. Faraday Soc., 41, 317 (1945).
- 6. W.M.D. Bryant, J. Polym. Sci., 2, 547 (1947).
- 7. K.H. Storkš, J. Am. Chem. Soc., 60, 1753 (1938).
- 8. R. Jaccodine, Nature, 176, 301 (1955).
- 9. P.H. Till, J. Polym. Sci., 24, 301 (1957).
- 10. A. Keller, Phil. Mag., 2, 1171 (1957).
- 11. E.W. Fischer, Z. Naturforsch., 12a, 753 (1957).
- 12. D.C. Bassett, F.C. Frank and A. Keller, Phil. Mag., <u>8</u>, 1739 (1963).
- 13. A. Keller and A. O'Connor, Polymer, 1, 163 (1960).
- R.A. Fava, Macromolecular Reviews, Vol. 5, Part D, J. Polym. Sci. (1971).
- 15. D.C. Bassett and A. Keller, Phil. Mag., 7, 1533 (1962).
- B.G. Ranby, F.F. Morehead and N.M. Walters, J. Polym. Sci., <u>44</u>, 349 (1960).
- 17. F.P. Price, J. Chem. Phys., 35, 1884 (1961).

18. B.G. Ranby and H. Brumberger, Polymer, 1, 399 (1960).

- A. Keller and A. O'Connor, Disc. Trans. Faraday Soc., <u>25</u>, 114 (1958).
- 20. E.W. Fischer and R. Lorenz, Kolloid-Z.Z. Polym., <u>189</u>, 97 (1963).
- 21. T. Kawai and A. Keller, Phil. Mag., 11, 114 (1965).

e

- 22. A. Nakajima, F. Hamada, S. Hayaski and T. Sumida, Kolloid-Z.Z. Polym., 222, 10 (1968).
- 23. A. Nakajima and F. Hamada, Pure Appl. Chem., 31, 1 (1972).
- 24. J.F. Jackson and L. Mandelkern, Macromolecules, 1, 546 (1968).
- R.K. Sharma, J.F. Jackson and L. Mandelkern, Polym. Prepr. Amer.
 Chem. Soc., Div. Polym. Chem., 10, 1327 (1969).
- 26. H.E. Bair and R. Salovey, Macromolecules, 3, 677 (1970).
- B. Wunderlich, P. Sullivan, T. Arakawa and T. Sumida, Kolloid Z.Z. Polym., 222, 124 (1968).
- B. Wunderlich, P. Sullivan, T. Arakawa, A.B. Dicyan and J.F.
 Flood, J. Polym. Sci., Part A, 1, 3581 (1963).
- 29. A. Peterlin and C. Reinhold, J. Polym. Sci., Part A, <u>3</u>, 2801 (1965).
- 30. H.E. Bair and R. Salovey, J. Macromol. Sci.-Phys., <u>B3</u>, 3 (1969).
- 31. T. Kawai, T. Hama and K. Ehara, Makromol. Chem., <u>113</u>, 282 (1968).
- 32. I.C. Sanchez and E.A. DiMarzio, Macromolecules, 4, 677 (1971).
- 33. P. Spegt, Makromol. Chem., 139, 139 (1970).
- 34. A.J. Kovacs and A. Gonthier, Kolloid-Z.Z. Polym., <u>250</u>, 530 (1972).

35. J.D. Hoffman and J.J. Weeks, J. Res. Bur. Std., <u>66A</u>, 13 (1962).

the management

「「「「「「「「「「「」」」」」」

- 36. J.W. Gibbs, Trans. Coun. Acad. III, 343 (1878); see also "The Scientific Work of J. Willard Gibbs", Vol. I, p. 219, Longmans, Green, New York (1906).
- 37. M. Volmer, Dresden:Steinkopff (1939).
- W. Kossel, Nachr. Ges. Wiss. Göttingen, Math.-Phys., <u>KI</u>, 135 (1927).
- 39. E.W. Fischer, Z. Naturforsch., A-14, 584 (1959).
- 40. A. Peterlin, J. Appl. Phys., 31, 1934 (1960).
- 41. A. Peterlin and E.W. Fischer, Z. Phys., 159, 272 (1960).
- 42. A. Peterlin, E.W. Fischer and C. Reinhold, J. Chem. Phys., <u>37</u>, 1403 (1962).
- 43. F.P. Price, J. Chem. Phys., <u>31</u>, 1679 (1959).
- 44. J.I. Lauritzen, Jr. and J.D. Hoffman, J. Chem. Phys., <u>31</u>, 1680 (1959).
- 45. J.I. Lauritzen, Jr. and J.D. Hoffman, J. Res. Nat. Bur. Stand., A64, 73 (1960).
- 46. F.P. Price, J. Polym. Sci., 42, 49 (1960).
- 47. J.D. Hoffman and J.I. Lauritzen, Jr., J. Res. Nat. Bur. Stand., _A65, 297 (1961).
- 48. F.C. Frank and M. Tosi, Proc. Roy. Soc., Ser. A, <u>263</u>, 323 (1961).
 49.** J.I. Lauritzen, Jr. and E. Passaglia, J. Res. Nat. Bur. Stand., A71, 261 (1967).
- 50. F. Gornick and J.D. Hoffman, Ind. Eng. Chem., 58, 41 (1966).
- 51. J.D. Hoffman, J.I. Lauritzen, Jr., E. Passaglia, G.S. Ross, L.J. Frolen and J.J. Weeks, Kolloid-Z.Z. Polym., <u>231</u>, 564 (1969).

- 52. I.C. Sanchez and E.A. DiMarzio, Bull. Amer. Phys. Soc., <u>15</u>, 377 (1970).
- 53. I.C. Sanchez and E.A. DiMarzio, J. Chem. Phys., <u>55</u>, 893 (1971).
 54. J.D. Hoffman, J. Chem. Phys., 28, 1192 (1958).
- 55. J.I. Lauritzen, Jr. and J.D. Hoffman, J. Appl. Phys., <u>44</u>, 4340 (1973).
- 56. J.D. Hoffman, L.J. Frolen, G.S. Ross and J.I. Lauritzen, Jr., J. Res. Nat. Bur. Stand., <u>79A</u>, 671 (1975).
- 57. I.C. Sanchez and E.Á. DiMarzio, J. Res. Nat. Bur. Stand., <u>76A</u>, 213 (1972).
 - 58. J.I. Lauritzen, Jr., J. Appl. Phys., 44, 4353 (1973).
 - 59. J.D. Hoffman, J.I. Lauritzen, Jr. and G.T. Davis in "Treatise on Solid State Chemistry", N.B. Hannay, Ed. (Plenum Press, New York, S Vol. 3, 1976).
 - 60. V.F. Holland and P.H. Lindenmeyer, J. Polym. Scil, <u>57</u>, 589 (1962).
 - 61. M. Cooper and R. St. John Manley, J. Polym. Sci., Polymer Letters Edition, 11, 363 (1973).
 - 62. A. Peterin, Makromol. Chem., 74, 107 (1964).
 - 63. M. Cooper and R. St. J. Manley, Macromolecules, 8, 219 (1975).
 - 64. C.P. Buckley and A.J. Kovacs, Kolloid-Z.Z. Polym., <u>254</u>, 695 (1976).
 - 65. A.J. Kovacs, A. Gonthier and C.J. Straupe, J. Polym. Sci. (C), 50, 283 (1975).
- 66. A.J. Kovacs, C. Straupe and A. Gonthier, J. Polym. Sci. (C), <u>59</u>, 31 (1977).

67.	J.J. Point and A.J. Kovacs, Macromolecules, 13, 399 (1980).
68	C.P. Buckley, Polymer, <u>21</u> , 444 (1980).
69.	P.J. Flory and A. Vrij, J. Am. Chem. Soc., <u>85</u> , 3548 (1963).
70.	F. Pierson, Thesis, Faculté des Sciences, Université de Stras
,	bourg, 1968.
71.	D.M. Sadler and A. Keller, Macromolecules, 10, 1128 (1977).
72.	A.J. Pennings, in "Characterization of Macromolecular Structure"

Washington, D.C. (1968).

Publication No. 1573 by the National Academy of Sciences,

- 61 -

Ċ

s

.**1**

SELECTED BIBLIOGRAPHY

D.A. Blackadder, "Ten Years of Polymer Single Crystals", J. Macromol. Sci., Cl, 297 (1967).

R.A. Fava, "Polyethylene Crystals", J. Polym., Sci., Part D, 5, 1 (1971).

P.H. Geil, "Polymer Single Crystals", Polymer Reviews, Vol. 5, Interscience-Wiley, New York, 1963.

- J.D. Hoffman, "Theoretical Aspects of Polymer Crystallization with Chain Folds: Bulk Polymers", SPE Trans., 4, 315 (1964).
- J.D. Hoffman, J.I. Lauritzen, Jr. and G.T. Davis, "The Rate of Crystallization of Linear Polymers with Chain Folding", pp. 497-614 in "Treatise on Solid State Chemistry", N.B. Hannay, Ed., Plenum Press, New York, Vol. 3 (1976).
- P. Ingram and A. Peterlin in "Encyclopedia of Polymer Science and Technology", H. Mark, N.G. Gaylord and N.M. Bikales, eds., Vol. 9, Wiley, New York, 1968.
- A. Keller, "Morphology of Crystalline Polymers", pp. 499-532 in Growth and Perfection of Crystals, R.H. Doremus, B.W. Roberts and D. Turnbull, eds., Wiley, New York, 1958.
- A. Keller, "Crystal Configurations and their Relevance to the Crystalline Texture and Crystallization Mechanism in Polymers", Kolloid-Z. Z. Polym., 197, 98 (1964).

A. Keller, "Polymer Crystals", Rept. Progr. Phys., 31, 623 (1968).

F. Khoury and E. Passaglia, "The Morphology of Crystalline Synthetic Polymers", pp. 335-496 in "Treatise on Solid State Chemistry", N.B. Hanney, ed., Plenum, Press, New York, Vol. 3 (1976).

- 62 -

- H.K. Livingstone, "Chemical Structure and Crystal Size in Polymer Single Crystals", Macromolecules, 2, 98 (1969).
- L. Mandelkern, "Crystallization in Polymers", McGraw-Hill, New York, 1964.
- L. Mandelkern, J. Macromol. Sci., <u>A15(6)</u>, 1211 (1981).
- A. Sharples, "Introduction to Polymer Crystallization", Arnold, London, 1966.

B. Wunderlich, "Macromolecular Physics" Vol. I, II and III, Academic

Press, New York, 1973.

「ないのないない」というないない。マイ

(à

CHAPTER II

ISOTHERMAL GROWTH OF LOW MOLECULAR WEIGHT POLYETHYLENE SINGLE CRYSTALS FROM SOLUTION. I. VARIATION OF EQUILIBRIUM DISSOLUTION FEMPERATURE WITH MOLECULAR WEIGHT AND LAMELLAR THICKNESS WITH CRYSTALLIZATION TEMPERATURE

 $\left(\right)$

ABSTRACT

- 65 -

The relation between the equilibrium melting/dissolution temperature $(T_m^{\circ}/T_d^{\circ})$, the molecular weight, the lamellar thickness and the crystallization temperature have been investigated for linear polyethylene fractions, with molecular weights ranging from 1000 to 11600, crystallized from dilute xylene solution. The values of T_{m}^{o}/T_{d}^{o} increase sharply with molecular weight and approach an asymptotic value above a molecular weight of about 5000. The measured values of T_° are found to be in excellent accord with the expected values calculated from the Flory-Vrij equation. On the other hand the observed values of T,° are always somewhat higher than estimates from either the Pennings equation or the Sanchez-DiMarzio equation. It is found that the lamellar thickness increases continuously with crystallization temperature. This is in contrast to the behavior of low molecular weight poly(ethylene oxide) fractions which show a step-wise variation with crystallization temperature. Analysis of the measurements of lamellar thickness as a function of supercooling yields values of the interfacial free energy σ_{a} ranging from 20 to 60 erg/cm². \neq These observed values of σ_{a} are low by comparison with the value of 93 erg/cm² expected for high The difference may be attributed to the molecular weight samples. effects of chain ends in the interfacial regions of the crystals.

INTRODUCTION

Flexible stereo regular polymers generally crystallize from solution as lamellar structures in which the chain molecules are folded (1,2). Although this phenomenon has been widely studied, it is still not completely understood. In this thesis, we propose to address the question of the origin of chain folding by studying the kinetics of crystal growth from solution, using low molecular weight fractions of polyethylene for which the transition from extended to folded chain growth should be observable. In this connection it is important to have accurate data on the variation of the lamellar thickness of the crystals with the temperature of crystallization and of the equilibrium dissolution temperature with molecular weight. This is the essential purpose of the present chapter. Comparison of the lamellar thickness with the overall chain length provides information on the structure of the crystals by indicating whether the chains are extended or folded in the crystal lattice and the number of folds per molecule. As will be seen later, these questions are important in attempting to analyze and interpret the results of the growth rate experiments.

The lamellar thickness of single crystals of linear crystalline polymers, notable polyethylene, is generally known to increase monotonically with the temperature of crystallization (T_c) (3-6). However, in the case of low molecular weight hydroxyl-terminated poly(ethylene oxide) (PEO) crystallized from the melt, the lamellar thickness increa-'ses in a step-wise manner with T_c (7). The question arises whether a

- 66 -

similar effect can be demonstrated in polyethylene by careful measurements on low molecular weight samples.

Previous studies of the variation of the lamellar thickness of solution-grown polyethylene crystals have been mainly concerned with samples of high molecular weight. Few attempts have been made so far to systematically explore these effects for well-defined low molecular weight material (8). In the present work we have measured the lamellar thickness of solution grown polyethylene crystals over a wide range of crystallization temperatures for fractions ranging from 1000 to 11600 in molecular weight. The data have been analyzed in terms of the kinetic theory of polymer crystal growth in order to derive values of the basal surface free energy.

In analyzing the experimental data a knowledge of the supercooling $(\Delta T = T_d^{\circ} - T_c)$ or the equilibrium dissolution temperature (T_d°) (where $T_{r_{i}}$ is the crystallization temperature) is critically important. T_d ° is defined as the temperature at which dilute polymer solution is in equilibrium with the equilibrium (i.e., extended chain) crystal and is dependent on the molecular weight of the polymer (10,11). A widely used procedure to determine T_{λ}^{*} is to measure the dissolution temperature of crystals of various lamellar thicknesses and extrapolate the data to infinite lamellar thickness using the Gibbs-Thompson equation (9). This procedure will be discussed in Chapter III. For polyethylene, an alternative approach is used to estimate T_d° using semi-empirical equations derived by Pennings (11) and by Sanchez and DiMarzio However, these equations do not give reliable results for low (10). molecular weight samples. For these reasons we have devised a method

- 67 -

for directly measuring the equilibrium dissolution temperature of crystals of the various fractions. The measurements were made by differential scanning calorimetry using suspensions of extended chain crystals in xylene. The results are compared with values estimated from Pennings equation (11) and the semi-empirical relation of Sanchez and DiMarzio (10).

EXPERIMENTAL

Materials

The materials used cover the molecular weight range from the paraffin-dotriacontane (MW' = 450) to 11600. Dotriacontane was obtained from the Eastman Kodak Company. PE1000 and PE2000 were obtained from Polysciences Inc. and characterized by Springborn Laboratories, Inc., Enfield, Conn. The number average molecular weights were determined by vapour pressure osmometry. The polydispersity $(M_{\rm w}/M_{\rm p})$ is not known exactly, but analytical gel permeation chromatograms 'showed only a single narrow peak suggesting a fairly sharp distribution. The rest of the fractions were prepared and characterized at the Research Center of SNPA at Lacq, France. The technique of fractionation by preparative gel permeation chromatography (GPC) has been described by Peyrouset et al (12,13)[°]. The weight average molecular weights (M_{μ}) were determined by analytical GPC previously calibrated by light scattering. Number average molecular weights (M_n) were determined by vapour pressure osmo-The molecular parameters of the various samples are given in metry. Table 2.1.

- 68 -

	Characteristics of	the Polyethylene	Fractions Studied	
Fractions	s <u>M</u> w	M _n	\bar{M}_{w}/\bar{M}_{n}	
PE11600	11,600	11,100	1.11	
PE6750	6,750	6,100	1.10	
PE4050	4,050	3,900	1.04	
PE3100	3,100	2,900	1.07	i
PE2000	4. 	1,791	- , , ,	
PE1000	-	980	-	

TABLE 2.1

Measurement of the Equilibrium Dissolution Temperature (T_{1}°)

By definition the equilibrium dissolution temperature is the melting point of a perfect extended chain crystal in equilibrium with an infinite amount of solvent. Accordingly the procedure used to determine T_d° rests upon the following premise. The melting point of pure extended chain crystals corresponds to the thermodynamic melting point T_m° which is depressed in the presence of a solvent. Thus the dissolution temperature of the extended chain crystals was measured at various crystal/solvent weight fractions and the data extrapolated to infinite dilution to give T_d° .

The samples were retained in glass tubes (5 mm in internal diameter) which were evacuated and sealed in order to minimize oxidative degradation. The sealed tubes were placed in a silicone oil bath

maintained at 150° C for about 20 minutes in order to ensure complete melting of the sample. The melted sample was then quickly transferred to another thermostat set at a predetermined crystallization temperature and controlled to better than 0.05° C. After allowing the sample to crystallize for the desired length of time, the temperature of the thermostat was slowly lowered (at about 8°/hour) to room temperature. The crystals were then removed from the glass tubes and their lamellar thickness was determined by small angle x-ray scattering in order to determine the degree of chain extension.

Thermal measurements on the crystals were made on a Perkin-Elmer differential scanning calorimeter, DSC-2C. The temperature scale was calibrated with naphthalene, benzoic acid and indium standards over the temperature range. The crystals were placed in a pre-weighed sample pan and weighed on a Cahn microbalance. p-xylene was delivered by a microsyringe and the sample pan was then hermetically sealed. The pan was weighed again to determine the amount of solvent. At least 5 samples were prepared for each fraction in the concentration range 4% to 100% (w/w). Each sample pan was weighed again after the thermal measurement to check for leakage. The procedure for the thermal measurements was as follows. The sample was heated at 10° C/min up to a preselected temperature which was about 10° C below the estimated dissolution temperature. The calorimeter was allowed to remain at this temperature for 20 to 30 min to permit the solvent to penetrate the crystal lattice. The heating was then resumed at 0.625 or 1.25 deg C/min. These low heating rates were used in order to allow annealing to

- 70 -

لغر

produce more perfect crystals. The peak temperature was used to define the dissolution temperature and melting point of the polymer. Standard corrections were made for changes in apparent melting point and thermal resistance as a function of heating rate (14).

n,

Preparation of Crystals and Measurement of Lamellar Thickness

The crystallizations were carried out isothermally in p-xylene as solvent at temperatures (T_c) spanning the range of 65 to 90° C. At higher crystallization temperatures self-seeding (15,16) was used in order to minimize the time necessary to obtain complete crystallization.

More precisely, the procedure was as follows. A suspension of the polymer was heated in an oil bath at 100° C for 20 mins in order to ensure complete dissolution. An aliquot of the solution was then transferred to a thermostat held at the crystallization temperature T and allowed to equilibrate. An appropriate amount of pure solvent, previously equilibrated at the crystallization temperature, was poured into the polymer solution. The time required to establish thermal equilibrium was thus minimized. The final concentration at which the crystals grew was in the range 0.02 - 0.57 (w/w) depending on the supercooling. The precipitate was filtered at the crystallization temperature; the resulting mats were washed with acetone and dried in vacuo at room temperature. The mats thus obtained were examined by small angle x-ray scattering (SAXS) in order to determine the lamellar thickness of the crystals. The SAXS patterns were recorded photographically with pin hole collimation using nickel filtered CuK_a radiation.

- 71 -

In all cases clearly defined low angle reflections were observed in several orders, sometimes as high as four. Long spacings were derived from measurements on microdensitometer tracings of the SAXS patterns. The Lorentz correction (12) was estimated to be negligible and was not applied.

For all the fractions, electron diffraction patterns of the single crystals showed only (hk0) spots; this indicates that the chain molecules are oriented normal, or nearly so, to the lamellar surfaces.

RESULTS AND DISCUSSION

Equilibrium Melting and Dissolution Temperatures

The crystallization conditions and lamellar thickness of the crystals used for the measurement of the equilibrium melting and dissolution temperatures are listed in Table 2.2. Comparison of the extended chain length with the lamellar thickness reveals that crystals of PE1000, PE2000, PE3100 and PE4050 are composed of extended chains; sample PE6750 consists of defect extended chain crystals and PE1600 has chains that are approximately once folded.

Selected thermograms are shown in Figures 2.1 and 2.2. Figure 2.1 shows the melting behavior of the pure PE11600 and PE4050 fractions. For PE11600 there is a major peak at 409.17 K and a small peak at 412.7 K. It is interesting to note that the temperature of the small peak agrees very well with the theoretically expected equilibrium melting temperature T_m° calculated from the Flory-Vrij equation (17).

TABLE 2.2

Crystallization Conditions and Lamellar Thickness of Low <u>Molecular Weight Polyethylene Single Crystals</u> *Fractions* Chain Crystallization Lamellar L/2

3	Length (L)	Condition 1	Chickness (1)	
PE11600	991	l week at 125°C	407	2,43
PE6750	544	l week at 125°C	356	1.53
PE4050	348	1 week at 120° C	299	1.16
PE3100	259	l week at 115°C	242	1.07
PE2000	176*	3 days at 110° C	167	1.02
PE1000	117*	3 days at 105° C	110	1.06

Estimated from the asymptotic values of lamellar thickness of the single crystals (see Figs. 2.5 and 2.6).

Ļ

A tentative explanation of the thermograms for this fraction may therefore be given as follows. During the crystallization at 125° C, only a small fraction of the polymer crystallized as extended chain crystals. The amount is not detectable by SAXS but is revealed by the small endotherm peak at 412.7 K. When the temperature was slowly decreased as described in the experimental section, the polymer crystallized more rapidly at a temperature somewhere below 125° C and the once folded chain crystals were formed. Accordingly the major endotherm peak can be assigned to the melting of the once folded chain crystals and the

- 73 -

smaller endotherm peak to the melting of the extended chain crystals.

74

For fraction PE4050 the thermogram shows a sharp endotherm peak with two shoulders at temperatures lower than the main peak. The temperature of the main peak corresponds closely with the expected equilibrium melting temperature for extended chain crystals of this fraction as, calculated from the Flory-Vrij equation (17). In general, for all the pure fractions, the highest melting peak in the thermogram could be identified as corresponding to the melting of the extended chain crystals. Values of the equilibrium melting temperature T_m° observed for the various fractions are listed in Table 2.3 and compared with the theoretically expected values calculated from the Flory-Vrij equation.

Figure 2.2 shows typical endotherms for dissolution of the polyethylene fractions in xylene. In general the endotherm peaks are broader when the polymer is in contact with solvent. It should be noted that sample PE11600 is mainly composed of once folded chains and the observed endotherm peak corresponds to the dissolution of such crystals. Consequently T_d° could not be measured directly for this sample.

Plots of the dissolution temperatures as a function of concentration are shown in Figure 2.3. The equilibrium dissolution temperature (T_d°) was obtained by extrapolation of the data to zero concentration. The values thus obtained are listed in Table 2.3. It is of interest to compare these results with theoretical estimates of T_d° calculated from equations given by various authors.



Typical DSC fusion thermograms for samples PE11600 and PE4050 at a heating rate of 0.625 deg C/min. The temperature scale is adjusted for standard temperature corrections.

- 75 -

10



DSC dissolution thermograms of single crystals of PE4050 in the presence of xylene at various concentrations. The heating rate is 0.625 deg C/min. The temperature scale is adjusted for standard corrections. The concentration is expressed as weight percent of crystals suspended in xylene.

- 76 -

, zu



€

Plots of dissolution temperature in the presence of xylene as a function of concentration for the various fractions of polyethylene. The concentration is expressed as weight percent of crystals.

TABLE 2.3

List of the Calculated and Experimental T_m° and T_d° Values for Various Low Molecular Weight

	·	Polyethy	lene Samples	—	۲r	
Fraction	T°(K) from	T [°] (K) from	T _d °(K) from	Τ _d °(K) from	T _d °(K) from	
	Flory-Vrij eq.	This Work	Pennings eq.	S-D eq.	This Work	
Dotriacontane	341.8	341.2	244.7	· 278.8	302.0	
PE1000	386.4	386.0	325.2	3,38.7	352.0	
PE2000	396.3	e 396.2	334.1	350.7	364.1	
PE3100	403.5	403,7	349.2	361.9	367.4	
PE4050	406.7	406.8	356.2	• 366.9	371.5	
PE6750	. 411.0	410.1	366.4	374.2	376.8	e
PE11600	413.8	412.7	373.8	379.3	382.0*	-

Extrapolated value

A STATISTICS

۰ ,

Ł

From fundamental thermodynamic considerations it can be shown (10) that the equilibrium dissolution temperature of a lamellar polymer crystal can be estimated by one of the following equations depending on the assumptions made in deriving an expression for the free energy difference between liquid polymer and crystal:

- 79 -

$$T_{d}^{\circ} = T_{m}^{\circ} [1/(1 - \gamma)]$$
, (2.

1)

 $T_{d}^{\circ} = T_{m}^{\circ} [\gamma + (1 + \gamma^{2})^{1/2}]$ (2.2) $T_{d}^{\circ} = T_{m}^{\circ} (1 + \gamma)$ (2.3)

where ${\rm T_m}^\circ$ is the equilibrium melting temperature and

 $\gamma = RT^{\circ}_{m} \ln a_{u}(T^{\circ}_{d}) / \Delta H_{u}(T^{\circ}_{m})$

where a is the activity which is a measure of the polymer/solvent interaction and AH is the heat of fusion per mole of monomer.

These equations show that T_d° depends on two variables, T_m° and a, which are molecular weight dependent. The molecular weight dependence of T_m° has been estimated (17-19).

Pennings (11) has given a method for determining a_u . For dilute, solutions his equation is

 $\ln a_{u} = \frac{V_{u}}{V_{1}} \left[\frac{\ln v_{2}^{+1}}{x} - \left(\frac{1}{2} + \frac{V_{1}A_{2}}{v_{2}^{-2}} \right) \right]$ (2.4)

where A_2 is the second virial coefficient, \bar{v}_2 is the partial specific volume of the polymer, v_2 is the volume fraction of the polymer, V_1 is the molar volume of the solvent, V_u the molar volume of the monomer unit, and x is the ratio of the molar volumes of the polymer and solvent. Pennings (11) and Krigbaum and Trementozzi (18) have estimated A_2 from osmotic pressure measurements of polyethylene in xylene as a function of molecular weight. The Pennings relation between A_2 and molecular weight (M) is

$$A_2 = 1.45 \times 10^{-3} + 0.29 \text{ M}^{-0.5}$$
 (2.5)

Sanchez and DiMarzio (10) have shown that the dependence of T_d° on the approximate form of Equations 2.1 - 2.3 is weak. We have calculated values of T_d° from Equation 2.2 and the Pennings relations, Equations 2.4 and 2.5, using the following input data: $\Delta H_u = 980 \text{ cal/mol}^*$, $v_1/v_2^2 = 87.0 \text{ g}^2/(\text{ml mol})$, $v_1/v_u = 7.73$ and $v_2 = 10^{-4}$. Values of T_m°

In accordance with normal practice in work of this kind we have used the following units in this thesis: crystallization temperature T_c in degree Celcius (° C), lamellar thickness ℓ in Angstrom unit, Å, the heat of fusion in erg cm⁻³ or cal g⁻¹, surface free energies σ and σ_e in units of erg cm⁻², gas constant R = 1.987 cal mol⁻¹ K⁻¹. The conversion factors to SI units are 0° C = 273.16 K, 1 Å = 10⁻¹ nm = 10⁻¹⁰ m, 1 erg cm⁻³ = 0.1 J m⁻³, 1 cal g⁻¹ = 4.12 x 10⁶ J m⁻³, 1 erg cm⁻² = 1 mJ m⁻², 1 cal mol⁻¹ = 4.184 J mol⁻¹ and R = 8.314 J mol⁻¹ K⁻¹.

80 -

were calculated from the Flory-Vrij equation (17). The results are tabulated in Table 2.3.

Sanchez and DiMarzio (10) have proposed the following semi-empirical relation for T_d° for polyethylene in xylene:

$$T_{d}^{\circ} = [T_{m}^{\circ} - 29 + \tau_{d}^{\circ}]/2$$
 (2.6)

÷.

where T_m° and τ_d° are, respectively, the Flory-Vrij estimates for the equilibrium melting temperature and the Pennings estimates for the equilibrium dissolution temperature. Values of T,° calculated from Equation, 2.6 are also listed in Table 2.3. In Figure 2.4 the measured values of T_d° and T_m° are shown as a function of molecular weight and compared with estimates from the Pennings, Sanchez-DiMarzio and Flory-Vrij equations, respectively. It is seen that the measured values of T_m° obtained in the present work are in good agreement with the values given by the Flory-Vrij equation. At low molecular weights the difference is insignificant. At molecular weights of 6750 and 11600 the observed value of T is about 1 K lower than the theoretical value. This difference is probably due to experimental difficulties in obtaining perfect extended chain crystals for these samples. On the other hand, the measured values of T_d° are considerably higher than those estimated from either the Pennings or Sanchez-DiMarzio equation. The lower the molecular weight the greater is the difference. The discrepancy is not surprising since Pennings (11) has already noted that the expression for the second virial coefficient, A_2 , breaks down for low



(

Comparison of the molecular weight dependence of T_m° and T_d° , as measured in the present work, with the relationship estimated from the Flory-Vrij equation, the Pennings equation and the Sanchez-DiMarzio equation. For the T_m° /molecular weight relation the data points are the observed values while the curve is calculated from the Flory-Vrij equation.

- 82 -

molecular weights, probably because of the neglect of the temperature dependence of A₂.

Variation of Lamellar Thickness with T

Figures 2.5 and 2.6 show the dependence of the long spacing on the crystallization temperature for the various molecular weight fractions studied. The experimental data are listed in Table 2.4. For the four fractions with molecular weights from 3100 to 11600 the principal trend is the apparently continuous increase of the long spacing with crystallization temperature. For these fractions all the curves seem to show a limiting long spacing at lower crystallization temperatures while at higher temperatures the curves are displaced from each other in such a manner that the crystallization temperature required to produce crystals with a given long spacing increases with molecular weight. This behavior is consistent with the known fact that for a given chain length the long spacing depends on the reciprocal supercooling ($\Delta T = T_d^{\circ} - T_c$) and shorter chains are expected to have a lower equilibrium dissolution temperature.

Considering now the fractions with molecular weights of PE1000 and PE2000, the long spacing tends progressively towards a limiting value near the length of the extended chain. It is interesting to note that for sample PE1000 significant departures from the classical ΔT relation is observed (see Figure 2.7). This behavior has already been predicted by Mandelkern et al (20) using nucleation theory pertinent to Δr

- 83 -



Lamellar thickness as a function of crystallization temperature for various low molecular weight polyethylene single crystals.

S

C

Ø



三日のあっ

FIGURE 2.6

Lamellar thickness as a function of crystallization temperature for single crystals of PE1000 and PE2000

TAE	LE	2.	4	

- 86 -

Lamellar Thickness of Low Molecular Weight Polyethylene Single

٠.	·····				•
Sample	T _C (° C)	£ (Å)	Sample	™ _€ (°C)	r (Å)
PE1000	36.6	101	PE2000	36.6	95
	51.2	105	<i>P</i> .	51.2	101
	56.2	114	,	56.2	106
	58.9	115		60.5	109
	64.6	117		65.0	125
	, ⁷		د	69.7	140
				72.0	145
1	ب	~	٥	75.1	155
PE3100	40.2	104	PF4050	50.0	103
r 03100	49.9	105	1 04050	55.0	105
	54.9	106		64.5	113
	60.4	116	•	68.4	120
	64.5	119		73.8	129
	66.8	121		75.1 *	137
-	71.0	131		77.4	138
,	74.0	137		80.2	144
	75.0	144		82.2	153
	82.2	174		85.2	165
· · · · · · · ·		<u> </u>			
PE6750	60.1	103	PE11600 *	64.0	103
~3	67.0	105		69.0	111
	74.0	115		75.1	113
	80.9	126		,81.0	128
	84.5	136	₩.	82.9	133
•	90 ₂ .0 ,-	1/0		85.7	140
• ور			•	87.3	149
			· · · · · · · · · · · · · · · · · · ·		

C

Crystals at Various Crystallization Temperatures



Ne.

Lamellar thickness as a function of supercooling ($\Delta T = T_d^{\circ} - T_c$), for polyethylene single crystals of various molecular weights. The data for Marlex 6000 is taken from the literature (see reference 9).

\$

- 87 -

The temperature variation of the long spacing for fractions PE1000 and PE2000 suggests a model in which the terminal portions of the chains are excluded from the crystal interior leading to cilia dangling from the basal surfaces of the lamella. This model is consistent with the findings of Keller and Priest (21), that about 90% of the chain ends are localized on the fold surfaces of solution grown polyethylene crystals. For the present low molecular weight samples the asymptotic approach of the long spacing to full chain extension indicates that the degree of surface disorder in these crystals decrea-\$\$ ses with increasing crystallization temperature.

For the low molecular weight polyethylene samples the apparently continuous increase of the long spacing with crystallization temperature is at variance with the behavior of low molecular weight hydroxyl terminated poly(ethylene oxide) fractions crystallized from the melt. For this case it has been reported that the long spacing increases discontinuously with T_c (7). The long spacings of such crystals show that the chains are either fully extended or folded a small, integral number of times. The chain ends are thus localized in the surface layers of the lamella. The lamellar thickness is therefore an integral submultiple of the overall chain length. It has been suggested that this behavior is due to strong attractive forces (hydrogen bonds) between the hydroxyl end groups resulting in end group pairing. Thus a step-wise or discontinuous increase in lamellar thickness with T would not be expected in polymers such as polyethylene where there can be no Nevertheless, it is interesting to association of the end groups.

- 88 -

consider whether a step-wise change in lamellar thickness could have remained undetected by the SAXS measurements. Taking into consideration the chain length of the various fractions used in the present work, the number of stem lengths per molecule can be readily estimated for the crystals over the accessible range of crystallization tempera-For this purpose we have taken the length of the -CH₂- unit in tures. the planar 'zig-zag conformation as 0.125 nm and the molecular mass of the -CH₂- unit as 14. The mean extended chain length is therefore (M_/14) x 1.25 Å. For example, for PE3100 the extended chain length is 259 Å and over the temperature range investigated the lamellar thickness changes from 104 to 174 A'which, assuming rejection of fractional stems from the crystal lattice (21), corresponds to a change from one to two stems per molecule. Thus if the chain ends were localized on the lamellar surfaces and the change from one to two stems per molecule occurred in a step-wise manner, the change in long spacing would have been 130 Å which is sufficiently large to be easily, detected by SAXS. A similar conclusion can be drawn for sample PE 4050 but for samples PE6070 and PE11600 -a discontinuous change in the lamellar thickness could not be easily detected by SAXS because of the small incremental Accordingly, taking the favourable case of the change in each step. fractions PE3100 and PE4050 it seems reasonable to conclude that the observed apparent continuous increase of the lamellar thickness with T is substantially correct. As will be seen later these considerations are important in attempting to interpret the growth rate data to be presented in Part III.

- 89 -

The Basal Surface Free Energy (σ_{p})

いっしい とうちょう あいまん

According to the kinetic theory of polymer crystal growth from solution, the initial thickness (\mathfrak{l}^*) of a chain folded lamella is of the form

$$\ell_g^* = 2\sigma_e^T d^{\circ}/\Delta h_f(\Delta T) + \delta \ell \qquad (2.7)$$

where σ_e is the fold surface free energy, i.e., the work involved in the formation of a unit area of folded surface; T_d° is the equilibrium dissolution temperature; $\Delta T = T_d^{\circ} - T_c$ is the degree of supercooling corresponding to the crystallization temperature T_c ; Δh_f is the bulk enthalpy of fusion per unit volume, and δt is an approximately constant term whose explicit form is different in various theories. According to Equation 2.7 a plot of t_g^* against $T_d^{\circ}/\Delta T$ should be linear and have a positive intercept of δt on the t_g^* axis and a slope of $2\sigma_e/\Delta h_f$. Thus if Δh_f is known σ_e can be determined.

It may be noted that polymer crystals are thermodynamically metastable and slowly increase in thickness spontaneously at the crystallization temperature. It is assumed that this process, which is often encountered on crystallization from a cooled melt, is virtually absent at the temperatures involved in crystallization from dilute solution. Indeed evidence in support of this assumption has been reported (22). Consequently the measured lamellar thickness can be identified with the initial fold length as predicted by the theories.

Figure 2.8 shows the results that are obtained when the long
spacing data for the various fractions are plotted according to Equation 2.7. For samples PE3000 to PE11600 Equation 2.7 is obeyed within the experimental error, giving an intercept of δl of 60 - 75 Å. This may be compared with the value of 43 - 55 Å obtained with higher molecular weight polyethylene samples crystallized from xylene (23). Taking $\Delta h = 2.80 \times 10^9 \text{ erg/cm}^3$ the values of σ_e obtained as shown in Table 2.5 are in the range 50 to 60 erg/cm². These values are somewhat lower than the 93 erg/cm² that is considered to be the upper limit of this parameter (23). In this connection it is pertinent to emphasize that σ_e is known to depend on chain length for low molecular weights and reaches the asymptotic value of 93 erg/cm² at high molecular weight (24,25). The observed values of σ_e are therefore well within the anticipated range.

For samples PE1000 and PE2000 the plots of l_g^* versus $1/\Delta T$ show deviations from linearity at low supercooling ΔT . This is certainly related to the fact that l_g^* reaches an asymptotic value at low supercooling where the lamellar thickness and the chain length became equal. From the slope of the linear portion of these curves at higher supercooling we calculate a value of $\sigma_e = 20 \text{ erg/cm}^2$ for sample PE1000 and $\sigma_e = 40 \text{ erg/cm}^2$ for PE2000. The crystals of sample PE1000 are essentially extended chain crystals and hence the low value of σ_e for this sample undoubtedly reflects the exclusive contribution of the chain ends. The value of $\sigma_e = 40^\circ \text{ erg/cm}^2$ for PE2000 suggests that this sample contains some folds in spite of its short chain length.

V



FIGURE 2.8

Plots of lamellar thickness versus reciprocal supercooling for single crystals of various low molecular weight polyethylene fractions.

- 92 -

TAB	LE	2	5	5

	Obtained from the Plots of 2 vs 1/2	ΔT
Sample	$\sigma_{e} (erg cm^{-2})$	δ£ (Å)
PE1000	20.4	
PE2000	42.1	81.5
PE3100	48.9	75.2
PE4050	48.5	75.2
PE6750	51.7	·71 . 1
PE11600	60.1	61.5

Values of the Basal Surface Free Energy σ and the Intercept

CONCLUSIONS

The equilibrium melting $(T_m^{\circ})/dissolution (T_d^{\circ})$ temperature of molecular weight polyethylene fractions have been determined low directly by calorimetric measurements on macroscopic extended chain crystals. The measured values of T_m° are in good agreement with the theoretically expected values calculated from the Flory-Vrij equation. For T_d° the calorimetrically measured values are somewhat higher than those predcited by the relations of Pennings and Sanchez-DiMarzio but, as will be shown in Chapter III, they are in good accord with values obtained from thermodynamic measurements.

When the same low molecular weight fractions are crystallized

from dilute solution the long spacing or lamellar thickness increases continuously with crystallization temperature. The chains thus undergo a gradual unfolding as the supercooling decreases. This implies that the chain ends must either be located outside the lamellae where they dangle as cilia of variable length, or are incorporated into the crystal lattice. The former interpretation would be consistent with the finding of Keller and Priest that in polyethylene single crystals 90% of the chain ends are localized on the basal surfaces.

The observed behavior of these low molecular weight polyethylenes stands in sharp contrast to that of low molecular weight poly(ethylene oxide) single crystals grown from the melt where the chain ends are preferentially rejected onto the lamellar surfaces so that the folding occurs in a quantized manner.

Analysis of the observed temperature variation of the lamellar thickness for these low molecular weight polyethylene fractions, using the kinetic theory of polymer crystal growth, yields values of the basal surface free energy of 20 to 60 erg/cm². These values are well within the anticipated range.

0

- 94 -

	REFERENCES
1.	A. Keller, Phil. Mag., <u>2</u> , 1171 (1957).
2.	E.W. Fischer, Z. Naturforsch., <u>12A</u> , 753 (1957).
3.	A. Keller and A. O'Connor, Discuss. Faraday Soc., 25, 114 (1958).
4.	A. Nakajima, F. Hamada, S. Hayashi and T. Sumida, Kolloid-Z.u.Z.
	Polymere, <u>222</u> , 10 (1968).
5.	A. Nakajima, S. Hayashi, T. Korenaga and T. Sumida, Kolloid-
	Z.u.Z. Polymere, <u>222</u> , 124 (1968).
6.	T. Kawai and A. Keller, Phil. Mag., <u>11</u> , 1165 (1965).
7.	J.P. Arlie, P. Spegt and A. Skoulios, Makromol. Chem., <u>104</u> , 212
	(1967).
8.	A. Keller and Y. Udagawa, J. Polymer Sci., A2, <u>10</u> , 221 (1972).
9.	T.W. Huseby and H.E. Bair, J. Appl. Phys., <u>39</u> , 4969 (1968).
10.	I.C. Sanchez and E.A. DiMarzio, Macromolecules, 4, 677 (1971).
11.	A.J. Pennings, in "Characteization of Macromolecular Structure",
	Publication No. 1573 by the National Academy of Science, Washing-
	ton, D.C., 1968, p. 214.
12.	A. Peyrouset and R. Panaris, J. Appl. Polym. Sci., 16, 315
	(1972).
13.	A. Peyrouset, R. Prechner, R. Panaris and H. Benoit, J. Appl.
	Polym. Sci., <u>19</u> , 1363 (1975).
14.	Perkin-Elmer, Instruction Manual for the Model DSC-2C Differen-
	tial Scanning Calorimeter.
15.	D.J. Blundell, A. Keller and A.J. Kovacs, J. Polym. Sci., <u>B4</u> , 481
	(1966).

Ō

95 -

X

Ņ

>

(

D.J. Blundell and A. Keller, J. Macromol. Sci., <u>B2</u>, 301 (1968).
 P.J. Flory and W. Vrij, J. Amer. Chem. Soc., 85, 3548 (1963).

こ、ここをしたいとういい。

- W.R. Krigbaum and Q.A. Tremontozzi, J. Polymer Sci., <u>28</u>, 295 (1958).
- 19. M.G. Broadhurst, J. Res. Nat. Bur. Stand., Sect. A, <u>70</u>, 481 (1966).
- 20. L. Mandelkern, J.G. Fatou and C. Howard, J. Physical Chem., <u>68</u>, 3386 (1964).
- 21. A. Keller and J.D. Priest, J. Macromol. Sci.-Phys., <u>B2</u>, 479 (1968).
- 22. J.F. Jackson and L. Mandelkern, J. Polymer Sci., Part B, <u>5</u>, 557 (1967).
- 23. J.D. Hoffman, G.T. Davis and J.L. Lauritzen, Jr., in "Treatise on Solid State Chemistry", Vol. 3, N.B. Hannay.
- J.D. Hoffman, L.J. Frolen, G.S. Ross and J.I. Lauritzen, Jr., J.
 Res. Nat. Bureau. Stds.-A, Physics and Chemistry, <u>79A</u>, 671 (1975).
- 25. L. Mandelkern, A.L. Allou, Jr. and M. Gopalan, J. Phys. Chem., 72, 309 (1968).

- 96 -



C,

ISOTHERMAL GROWTH OF LOW MOLECULAR WEIGHT POLYETHYLENE SINGLE CRYSTALS FROM SOLUTION. II. MELTING AND DISSOLUTION BEHAVIOR.

ABSTRACT

- 98 -

Melting and dissolution temperatures (T_m and T_d) and enthalpies of fusion (ΔH) have been measured as a function of crystallization temperature (T_c) for solution grown crystals of polyethylene fractions covering the molecular weights range 1000 to 11600. Analysis of the data yields values of the basal surface free energies σ_e which increase with molecular weight and lie in the range 40 - 60 erg/cm² for the molecular weights from 3000 to 11600. Values of the equilibrium melting/dissolution temperatures obtained from the intercept of T_m (T_d) plots versus the reciprocal lamellar thickness are in good agreement with those obtained from direct measurements on extended chain crystals of large lateral dimensions and thickness.

The enthalpies of fusion of the crystals of the various fractions generally increase monotonically with T_c in parallel with their thickness. 'However, for samples with molecular weights of 3100 and 4050 sigmoidal curves are obtained when the enthalpies of fusion are plotted against crystallization temperature. This is interpreted to mean that in this molecular weight range there is a transition from extended to folded chain crystallization as T_c decreases.

ø

INTRODUCTION

The problem of chain folding in polymers has attracted much interest since Keller's discovery (1) of the phenomenon some twenty-five years ago. Despite the considerable advances that have been achieved a complete understanding of the mechanism remains a challenge. As stated in Part I, the basic aim of the present work is to study the growth kinetics and physical properties of solution grown crystals of low molecular weight polyethylene fractions for which the transition from extended chain to folded chain growth can be observed. The first phase of the investigation, described in Part I, involved the measurement of the variation of the lamellar thickness of the crystals with the temperature of crystallization and of the equilibrium dissolution temperature of the samples with molecular weight. It was found that the lamellar thickness increases monotonically with crystallization temperature which Madicates that the chains undergo a gradual unfolding as the supercooling decreases. This behavior may be contrasted with that of low molecular weight poly(ethylene oxide) single crystals grown from the melt for which the lamellar thickness increases in a step-wise manner with T_{c} (2,3).

The immediate purpose of the present paper is to further characterize the low molecular weight polyethylene crystals by examining their thermal behavior using differential scanning calorimetry. The pattern of the paper is as follows. First we consider the effect of the heating rate on the melting/dissolution temperature of crystals grown from solution at various temperatures. By analysis of the ther-

- 99 -

mograms the melting and dissolution temperatures of the crystals are obtained. The next stage in the paper involves the analysis of melting point $(T_m)/dissolution$ temperature (T_d) and crystal thickness (ℓ) measurements in order to estimate values of the basal surface free energies and the equilibrium melting/dissolution temperatures. The validity of carrying out this analysis by the classical method, which assumes a unique linear relation between T_m or T_d and $1/\ell$ is discussed.

Finally, measurements are presented of the enthalpy of fusion of the low molecular weight polyethylene crystals grown at various temperatures. From these data information on the structure of the basal crystal surfaces is derived. The principal finding of these studies was that crystals in the molecular weight range of 3000 to 4000 exhibit a transition from extended to folded chain growth as the crystallization temperature is decreased.

- 100 -

EXPERIMENTAL

- 101 -

The samples used were linear polyethylenes covering the molecular weight range from 1000 to 11600. Details of the origin and characterization of the samples have been given in Table 2.1 in Chapter II. The solvent used was commercial p-xylene distilled before use.

Crystallization from dilute xylene solutions was carried out isothermally over attemperature range 35 to 65° C for PE1000 and 65 to 90° C for the other fractions. The procedure used was similar to that described by Holland and Lindenmeyer (4). A solution of the polymer in xylene was prepared at 110° C. A suitable aliquot of this solution was added with gentle stirring to an appropriate amount of pure xylene which had previously been brought to the crystallization temperature. In this way the time required to establish thermal equilibrium was minimized and the stirring was discontinued. The final concentration at which the crystals grew was in the range 0.02 - 0.5% (w/w) depending on the supercooling. The suspension of crystals was filtered at the crystallization temperature, washed first with aliquots of fresh xylene and then with acetone and dried in vacuo at room temerature.

Thermal measurements of the different fractions were performed in a Perkin-Elmer Differential Scanning Calorimeter, model DSC-2C. For the measurement of melting and dissolution temperatures, approximately 0.1 mg of the dry sample was weighed into sealable sample pans using a Cahn electrobalance. When dissolution temperatures were to be measured an aliquot of xylene was delivered to the sample pan by microsyringe, the sample pan was then hermetically sealed and weighed to determine

z

0

the amount of solvent. The concentrations were in the range 0.4 - 0.5% (w/w). It has been demonstrated in Chapter II that the dissolution temperature measured by DSC is essentially independent of concentration within this concentration range.

The apparent melting/dissolution temperature was determined from the peak temperature of the endotherms. It is well known that polymer crystals tend to thicken during heating and rapid heating rates have often been used to minimize this effect (5). In the present work the samples were heated at different rates up to 160° C/min; the apparent melting/dissolution temperatures were plotted against heating rate and extrapolated to zero heating rate to obtain the true melting/dissolution temperature.

The temperature scale of the calorimeter was calibrated with naphthalene (T_m = 80.2° C), benzoic acid (T_m = 122.4° C) and indium (T_m = 156° C). Standard corrections were made for changes in melting temperature and thermal resistance as a function of heating rate (6).

The heats of fusion of the dry crystals were determined from the area under the melting endotherm. For these measurements the sample sizes were in the range of 0.2 - 0.3 mg. The DSC baseline was stored in the calorimeter computer and was subtracted from subsequent runs. The value of the heat of fusion was calibrated with indium heated under the same running conditions. Heating rates of 5 to 20 deg C/min were found to have no effect on the value of the heat of fusion. At least four runs were made for each sample and averaged to obtain the heat of fusion. The precision of the results from these repeated experiments was $\pm 1 \text{ cal/g}$.

- 102 -

RESULTS AND DISCUSSION

Melting and Dissolution Behavior

When simple substances such as benzoic acid are heated in the DSC only a single melting peak is observed. Moreover the melting peak . temperature T_p increases monotonically with heating rate, s. This is illustrated in Figure 3.1 for benzoic and adipic acid. The continuous increase in T_p with heating rate has been explained as due to the thermal inertia of the sample (7) and possibly the finite melting rate of the crystals (8,9). The true melting temperature T_m can be obtained by extrapolating the curve to zero heating rate.

When the melting peak temperature of the dry polyethylene single crystals is plotted against heating rate, the results are quite diffe-'rent from those of simple substances. As shown in Figure 3.2 for the single crystals of the fractions PE11600 and PE6750 the fusion curves usually show two melting peaks at low heating rates (i.e., below s = 20). At higher heating rates the two peaks broaden and merge to a single peak. For the first (low temperature) peak T remains in the same position as s increases. On the other hand, for the second (high temperature) peak T first decreases with heating rate, then after passing through a minimum it increases monotonically with heating rate (Figure 3.3). These results can be interpreted in terms of partial melting followed by recrystallization. Thus the peak at the lower temperature represents the partial melting of the initially present crystals, while the upper peak corresponds to the complete melting of recrystallized or reorganized material. Accordingly, for these samples

- 103 -



ł,

2

ATT. March

ſ

Melting peak temperatures T_p as a function of heating rate s for adipic and benzoic acid.

1

\$

ŧ



FIGURE 3.2

۰ ۸

兵戦

Melting endotherms obtained at different heating rates s (in deg C/min) for fraction PE6750 crystal aggregates grown at 84.5° C from xylene solution.

1



(

Melting peak temperatures T_P versus heating rate s for sample PE6750 crystallized from xylene at 74° C.

I

\$

the true melting temperature can be obtained by extrapolating the apparent melting point of the first peak to zero heating rate. As mentioned above, for the second peak T_p passes through a minimum and then increases with s in the manner characteristic of simple substances. Experimental results show that the extrapolated value of the second melting peak T_p at s = 0 is within the experimental error equal to T_m of the first peak. This suggests that at sufficiently high heating rates the origin of the second peak changes. No longer does it represent the melting of recrystallized material; rather, since the crystals are unable to reorganize in the time scale of the experiment, it corresponds to zero entropy production melting (10) of the original material at the particular heating rate. Accordingly it may be assumed that extrapolation of T_p of the second peak from higher s values to s = 0 gives the true melting point of these fractions. Due to the long extrapolation the error in estimating T_m in this way is about $\pm 1^\circ$ C.

Let us now consider the fractions PE3100 and PE4050. As an example, Figure 3.4 shows typical endotherms for PE3100 crystallized at temperatures in the range of 60 to 75° C. At the lower heating rates of 0.25 - 10 deg C/min, only a single endotherm peak is observed and this is assigned to the melting of reorganized or recrystallized material. This may be compared with the behavior of the higher molecular weight fractions for which two peaks appear even at heating rates as low as 0.625 deg C/min. Clearly reorganization in these samples is much more rapid than in the previous examples. This is not surprising since PE3100 and PE4050 are composed only of extended, once or twice folded chains depending on the crystallization temperature. As the

heating rate increases two peaks appear corresponding to partial melting of the original crystals (lower peak) and complete melting of recrystallized material (upper peak). Finally, at the highest heating rates (s > 80 deg C/min) a single endotherm peak is again observed because sufficient time is not available for reorganization. This single high temperature peak thus represents zero entropy production melting of the original crystals. By plotting T_p of the high temperature peak against s, the extrapolation procedure described above was used to obtain the true melting point of these samples (Figure 3.5).

Finally, for the fractions PE1000 and PE2000 the thermograms show only one endotherm peak at all heating rates. This is consistent with the fact that these crystals are essentially extended chain structures and therefore less susceptible to reorganization than the higher molecular weight samples. As shown in Figure 3.6, the melting peak temperatures are almost independent of s at the lowest heating rates, but at higher heating rates T_p increases with s as for simple substances. Thus the true melting point could be obtained by the extrapolation procedure described before.

Figure 3.7 shows an example of the thermograms obtained when the crystals of the various fractions were heated in the presence of solvent. In all cases only a single endotherm peak is observed. The principal effect of the solvent is to cause a lowering of the melting temperature. As illustrated in Figure 3.8, the endotherm peak temperature increases continuously with s. This indicates that there is little or no rearrangement or annealing in the crystals before dissolution.

- 108 -



)

đ

Melting endotherms obtained at various heating rates s (deg C/min) for PE3100 crystals grown from xylene at 74.5° C.



Heating rate, °C/min

FIGURE 3.5

Melting peak temperature T_p as a function of heating rate s for crystals of PE4050 grown from xylene at two different temperatures.



FIGURE 3.6

いないことない

Melting peak temperature T_p as a function of heating rate s for crystals of PE2000 grown in xylene at 65° C.

- 110 -



[·

いいないないたの間であ

~ # 4 + + + + - - - - = + = - here

Melting endotherms obtained at various heating rates s (deg C/min) for PE4050 crystals ($T_c = 78.2^{\circ}$ C) in the presence of xylene.

- 111 -



1

Melting peak temperatures T_p in the presence of xylene versus heating rate s for crystals of PE2000 and PE4050.

ł

This observation is in agreement with the results obtained by Blackadder and Schleinitz (11) which show that heating rates of $1 - 2^{\circ}$ C/min are high enough to suppress the annealing of crystals in the presence of solvent. Extrapolation of the curve to s = 0 gives the true dissolution temperature.

The various values of T_m and T_d obtained from the fusion and dissolution studies are summarized in Table 3.1. As expected, the values of T_m and T_d increase with T_c in parallel with the thickness of the crystals.

Surface Free Energies and Equilibrium Melting/Dissolution Temperatures

A widely used method for determing the basal surface free energy σ_e and the equilibrium melting temperature T_m° of polymer crystals is based upon the following equation derived by Hoffman and Weeks (12)

$$\mathbf{T}_{\mathbf{m}} = \mathbf{T}_{\mathbf{m}}^{\circ} \left[1 - \frac{2\sigma}{\Delta h_{f}} \frac{1}{k} \right]$$
(3.1)

where Δh_f is the heat of fusion per unit volume of the crystal, T_m is the observed melting point of the crystal, and \pounds is the crystal thickness. Accordingly a plot of T_m against $1/\pounds$ should be linear with a slope of $2\sigma_e T_m^{\circ}/\Delta h_f$ and an intercept of T_m° . Thus if Δh_f is known, σ_e can be determined. In the case of dissolution experiments T_m in Equation 3.1 is replaced by T_d° , the equilibrium dissolution temperature. For high molecular weight polyethylene samples (13,14) Equation 3.1 is obeyed within the experimental error and a value of $\sigma_e^{=93 \pm 8 \text{ erg/cm}^2}$

	<u>т</u> , к	T _m , K	<u>т_d, к</u>	$\frac{1/2 \times 10^3}{1/2}$	-1
PE11600	341.46	397.7	369.2	9.372	
	347.16	398.4	369.4	8.850	٠.
•	354.06	400.9	372.1	7.937	
	358.06	401.3	372.5	7.246	
	365, 76	405.7	375.6	5.000	
PE6750	333.26	391.7	364.5	9.804	
	341.46	391.9	365.6	9.372	
	347.16	393.4	366.1	8.850	
	354.06	394.4	366.6	7.968	
	357.66	395.5	366.7	7.353	
	363.06	396.5	369.8	6.061	
PE4050	333.26	388.5	360.2	9.259	
	341.16	389.9	361.5	8.547	
¢	347.16	390.1	361.8	7.752	
	351.41	391.6	363.1	7.246	
•	353.36	392.4	363.4	6.579	
	358.36	393.4	364.1	6.042	
PE3100	333.26	386.8	355.4	8.968	
	341.16	387.6	356.9	8.032	
	347.66	388.5	357.3	7.090	•
	353.16	390.4	359.2	6.211	
	357.46	391.0	359.5	5.236	·
PE2000	333.66	382.6	351.0	9.079	
	338.16	383.5	352.0	8.130	
	342.86	384.0	354.1	7.246	
	348.16	386.1	354.4	6.494	
	353.36	386.5	359.6	6.154	
PE1000	309.46	380.4	339.8	10.152	
	324.36	381.3	341.1	9,390	
	332.06	383.1	342.9	8.696	
	337.76	383.4	345.9		

Melting/Dissolution Temperature and the Reciprocal of the Lamellar Thickness* of Polyethylene Single Crystals Grown at Various Temperatures T.

* Lamellar thickness data have already been presented in Chapter II.

(),

- 114 -

TABLE 3.1

' is obtained for both dried single crystals and single crystals in xylene suspensions. The value of T_m° is about 146° C for dried single crystals and the equilibrium dissolution temperature T_d° is 114° C (xylene). Bair and Salovey (15) have shown that σ_e is approximately independent of molecular weight in the moderate to high range. However it is known that for low molecular weight samples, σ_e depends upon the chain length and increases to the asymptotic value of 93 erg/cm² at high molecular weights (16,17).

For the various fractions studied in the present work the data compiled in Table 3.1 were plotted in accordance with Equation 3.1. Examples are shown in Figures 3.9 and 3.10. Linear relations were obtained for all but the two lowest fractions. Adopting $\Delta h_f = 2.8 \text{ x}$ 10⁹ erg/cm³, values of σ_e , T_m° and T_d° obtained from the plots are collected in Table 3.2. Also included in the Table are values of o obtained from the analysis of measurements of lamellar thickness as a function of supercooling as described in Chapter II. It is seen that within the experimental error the values of σ_{a} obtained by the two methods are in good agreement but they are somewhat lower than the accepted value of 93 erg/cm² obtained for high molecular weight sam-The difference is undoubtedly caused by the inclusion of chain ples. end effects in the effective value of σ_{p} due to the finite chain length of the samples. It may also be noted that σ increases with molecular weight over the range encompassed. This behavior is expected for these low molecular weight samples since chain end effects will diminish with increasing molecular weight; furthermore, it implies that as the

- 115 -



•

Melting T_m and dissolution T_d temperatures as a function of reciprocal lamellar thickness for PE11600 crystals.

7



C

Melting T_m and dissolution T_d temperatures as a function of reciprocal lamellar thickness for crystals of PE1000.

ı.

TABLE 3.2

Basal	Surface	Free	Energy	σ	and	the	Equilibrium	Melting	/Dissolution	Temeprature	(T_	°/T	,°)	Obtained	from	a	Plót
-------	---------	------	--------	---	-----	-----	-------------	---------	--------------	-------------	-----	-----	-----	----------	------	---	------

of T_m (or T_d) vs. 1/2

•		o, erg ci	m_−2 ౕ		T _m °,	T _d °,	deg K	$T_m^{\circ}(\infty), T_d^{\circ}(\infty)$ deg K deg K		
- [°] Fraction	From melting temp.data	From dissolution temp. data	Average	From Chapter II*	From Eq. 3.1	From Chapter II**	From Eq. 3.	From Chapter II	* From Eq.3.2	Fтоm Eq.3.2
PE11600	62.8	60.7	61.7	60.1	415.0	412.7	384.8	382.0	417.9	387.0
PE6750	49.1	48.7	48.9	51.7	406.8	410.1	377.7	376.8	411.3	381.7
PE4050	45.3	45.6	45.5	48.5	401.8	406.8	372.0	371.5	408.6	378.1
PE3100	42.2	40.7	41.5	48.9	398.2	403.7	365.7	367.4	406.6	373.3

From the analysis of lamellar thickness as a function of supercooling.

3

**

From the direct calorimetric measurements on macroscopic extended chain crystals.

molecular weight increases there are significant differences in the structure of the surface layers of the lamellae.

Turning now to the results for the equilibrium melting and dissolution temperatures, it can be seen from Table 3.2 that the values derived from Equation 3.1, are in reasonably good accord with the directly measured values using extended chain crystals of each fraction as described in Chapter II. It should be emphasized that in the present work the values of the equilibrium melting and dissolution temperatures obtained from Equation 3.1 relate to extended chain crystals of large lateral dimensions and thickness corresponding to n chain units. It is therefore not surprising that the values are lower than the equilibrium melting/dissolution temperatures of polyethylene chains of infinite length ($T_m^{\circ} = 419$ K; $T_d^{\circ} = 387$ K) as cited above. Buckley and Kovacs (18) have discussed the applicability of Equation 3.1 to crystals of low molecular weight poly(ethylene oxide) fractions and have shown that when the effect of finite chain length is taken into consideration, the following relation is valid as a first approximation:

$$T_{m} = T_{m}^{\circ} \left[1 - \frac{2\sigma_{e}}{\Delta H_{f}} \cdot \frac{1}{2} \right] - \frac{R(T_{m}^{\circ})^{2}}{\Delta H_{f}} \frac{\ln p}{p} \quad (3.2)$$

In this equation, T_m° refers to the equilibrium melting temperature for infinite molecular weight polymers and p is the number of monomer units per molecule. According to Equation 3.2 a plot of T_m (or T_d) versus 1/2 will give the same value of σ_e as Equation 3.1. However, the ordinate intercept at 1/2 = 0 will be less than the true value of T_m° (T_d°)

- 119 -

for a chain of infinite length by the amount of the $(\ln p)/p$ term. Furthermore, the discrepancy in T_m° (T_d°) is predicted to increase with decreasing p as observed. It can be seen from Table 3.2, however, that the correct values of T_m° (T_d°) are not obtained when the ordinate intercept is corrected by adding the $(\ln p)/p$ term. To resolve the problem a more exact analysis of the melting/dissolution behavior of these low molecular weight polyethylene fractions is required, but this is beyond the scope of the present investigation.

Enthalpies of Fusion

£.

Table 3.3 lists the results for the measurement of the enthalpy of fusion of the various fractions crystallized isothermally from solution at different temperatures and filtered at the crystallization temperature. In Figure 3.11 the enthalpies of fusion are plotted against crystallization temperature. For PE11600 and PE6750 (Figure 3.11a) the results fall on a common curve that increases monotonically with temperature in the range investigated. Similar behavior is observed for PE1000 and PE2000 although two separate curves are obtained. In striking contrast for PE3100 and PE4050 the data fall on sigmoidal curves as shown in Figure 3.11b. Thus for these fractions ΔH increases with T_c slowly at first, then at an accelerating rate and finally at higher crystallization temperatures AH reaches a level where it increases more slowly with temperature. Since AH is proportional to the degree of crystallinity which is very sensitive to morphological detail, it can reasonably be supposed that the sigmoidal curves

١

- 120 -

Fraction	™ _c , °C	ΔH , cal/g	Fraction	™ _c , °C	ΔH , cal/
PE11600	68.3	52.8	PE6750	68.3	53.6
	74.0	53.5		74.0	56.0
نظویہ رو	80.9	56.7		80.9	57.0
	84.9	58.0		84.5	58.1
	92.6	60.4		89.9	59.9
PE4050	60.1	54.8	PE3100	60.1	54.3
	68.0	55.4		68.0	55.5
	70.0	56.4		69.8	56.6
	74.0	55.9	·	74.0	58.5
	78.2	59.1		83.2	64.7
à c c a	82.2	63.7	- ,	86.9	65.7
- P	85.2	64.7	,		
PE2000	60.5	63.5	PE1000	36.3	63.0
	65.0	64.4		51.2	64.2
	70.4	64.9		58.9	64.7
	75.0	65.4		64.6	64.9
	80.2	65.7			

- 121 -

3

0

 \tilde{r}_1

(a) Plots of the enthalpy of fusion ΔH versus crystallization temperature T_C for fractions PE6750 and PE11600 crystallized from xylene solution.

(b) Plots of the enthalpy of fusion AH versus crystallization temperature T_C for fractions PE1000, PE2000, PE3100 and PE4050 crystallized from xylene solution.



C

ø



. .



Ľ

ĺ

Plots of enthalpy of fusion ΔH as a function of reciprocal lamellar thickness for various polyethylene fractions crystallized from xylene. The slopes of the straight lines for PE1000 and PE2000 are so close to each other that, within the experimental error, a common line can be drawn (broken line).

reflect changes in the structure of interfacial regions of the crystals as the crystallization temperature increases.

The enthalpy of fusion data can be further examined in terms of the molecular nature of the crystals. The measured enthalpy of fusion ΔH is related to the surface enthalpy of the crystals q_e by the following expression which can be derived from thermodynamic principles (19,20)

$$\Delta H = \mathbf{\mathcal{I}}_{u} - 2q_{\rho}/\xi \qquad (3.3)$$

where ΔH_{u} is the heat of fusion per segment for extended chain crystals of infinite molecular weight, and ξ is the average number of segments in a section of the polymer chain running between the two lamellar surfaces and is equal to 1/a, where 1 is the lamellar thickness and a = 1.25 Å is the projected length of the polyethylene monomer unit on the crystal c-axis. Thus a plot of ΔH against 1/1 should be linear with an intercerpt equal to ΔH_{u} and a slope equal to $2aq_{e}$. Plots of the data according to Equation 3.3 are shown in Figure 3.12 for the various fractions. It is seen that good linear relations are obtained for the fractions PE1000, PE2000, PE6750 and PE11600; the points for PE6750 and PE11600 fall on a single line, while PE1000 and PE2000 give a line with a different slope. On the other hand for PE3100 and PE4050 the data points corresponding to higher values of 1/2 coincide with the line for the two highest fractions, while the points corresponding to the lowest values of 1/2 follow a different linear relationship with a slope intermediate between that of the highest and lowest fractions. For all the lines the intercept corresponding to 1/1 = 0 is 69.6 cal/g which agrees well with the value of 68.6 cal/g expected for ΔH_u for polyethylene (21). From the slopes of the plots, the values of the surface enthalpies q_e were calculated. Then combining these values with the known surface free energies σ_e , the values of the surface entropies s_e were calculated at T = 400 K in accordance with the well known relation $\sigma_e = q_e - Ts_e$. The results are given in Table 3.4. It is interesting to compare the magnitudes of the observed surface enthalpies and entropies with values obtained by other investigators. For example, for solution grown single crystals of a high molecular weight polyethylene (Marlex 6000 Type 50) Roe and Bair found $q_e = 22.1 \pm 2.0$ kcal/mol of folds and $s_e = 39 \pm 5$ eu/mol of folds at T = 400 K. The experimental values found for the present low molecular weight fractions are thus abnormally low, most probably because of chain end effects.

In order to interpret these results in terms of the molecular nature of the crystals we must consider how the number of stems per molecule v (i.e., the ratio of extended chain length to lamellar thickness) varies with the temperature of crystallization for the various fractions. The relevant data are derived from measurements described in Chapter II. For crystals of PE2000, v varies from about 1.6 to 1.0 over the accessible temperature range. Thus the crystals of this fraction are essentially extended chain structures. The surface free enthalpy of these crystals thus represents the enthalpy of a surface with only chain ends and cilia. Larger q_e values would suggest the existence of folds, chain ends and possibly surface roughness.

1
- 127 -

4

1

9

(

The second of the second

Ì

TABLE 3.4

	Surface Enthalpy	Surface Entropy
Fraction -	q _e , K cal/mol of folds	S _e , eu/mol of segment
PE11600	9.4	15.7
PE6750	. 9.4	16.8
PE4050 (high supercooling	9.4	17.3
PE3100 (high supercooling	9.4	17.3
PE4050 (low supercooling)	4.8	6.0
PE3100 (low supercooling)	4.8	6.5
PE2000	3.9	4.3
PE1000	. 3.4	5.7

Surface Enthalpy and Entropy of the Polyethylene Single Crystals

Crystals of PE3100 and PE4050 grown in the high supercooling range (i.e., with larger values of 1/1) have the same surface enthalpy as crystals of PE6750 and PE11600, which are at least twice folded over the range of crystallization temperatures studied. Lamellar thickness data for PE3100 and PE4050 crystals grown in this temperature range also indicate that the polymer chains are at least once folded. From these it must be concluded that the structure of the interfacial expressions of these crystals must be similar. The picture that emerges is that these crystals are composed principally of folded chains but because of the low values of σ_e and q_e they must also have a substantial amount of chain ends in ther interfacial regions.

For PE3100 and PE4050 the crystals grown at lower supercoolings (i.e., with lower values of 1/2) have a surface enthalpy that is larger than that of extended chain crystals but considerably lower than that of folded chain crystals. This is consistent with the fact that the corresponding average values of v (the average stem length per molecule) are about 1.5 for PE3100 and 2.3 for PE4050. The data thus suggest that the interfacial regions of these crystals contain both chain ends and folds, the former being in higher proportion. From these considerations it may be inferred that for the fractions PE3100 and PE4050 the sigmoidal shape of the ΔH versus T_c plots indicates a transition from folded chain to extended chain crystals as T_c increases. As will be seen in Chapter IV, evidence for such a transition is also obtained from growth data.

- 128 -

CONCLUSIONS

The magnitude of the surface free energy $\sigma_{\rm e}$ of polymer single crystals is an important indicator of the structure of the interfacial regions. The present work has shown that for low molecular weight solution grown polyethylene single crystals the value of $\sigma_{\rm e}$, obtained from plots of melting/dissolution temperatures against the reciprocal of the lamellar thickness, are in good agreement with those previously derived from an analysis of measurements of lamellar thickness as a function of undercooling. The values obtained increase with molecular weight and lie in the range of 40 - 60 erg/cm² for the molecular weights from 3100 to 11600. By comparison with the value of 93 erg/cm² expected for high molecular weight samples, which are essentially free of chain end effects, the observed low values may be attributed to the presence of chain ends in the interfacial regions of the crystals.

Values of the equilibrium melting/dissolution temperatures obtained from the intercept of the T_m or T_d versus 1/2 plots are in good agreement with those obtained from direct measurements on macroscopic extended chain crystals of each fraction. These equilibrium " melting/dissolution temperatures correspond to the values for polymer chains of finite length and will be used subsequently in Chapter IV as the temperatures from which to measure the supercooling when analyzing kinetic data.

The enthalpies of fusion increase monotonically with crystallization temperature. This is to be expected from the previously observed

- 129 -

increase of lamellar thickness with crystallization temperature for the same samples. Surprisingly, however, for the samples with molecular weights in the range of 3000 to 4000, the increase in the enthalpy of fusion follows a sigmoidal pattern. From this observation it is suggested that in this molecular weight range there is a transition in the structure of the interfacial regions of the crystals as the crystallization temperature increases. It is proposed that this change in¹/_v interfacial structure involves a transition from extended to folded chain growth as T_c decreases. If this interpretation is correct it is anticipated that evidence for such a transition should also be found in growth rate data. This will be discussed in Chapter IV.

1

- 130 -

REFERENCES

1.	A. Keller, Phil. Mag., <u>2</u> , 1171 (1957).
2.	J.P. Arlie, P. Spegt and A. Skoulios, Makromol. Chem., <u>99</u> , 160
	(1966); ibid <u>104</u> , 212 (1967).
3.	P. Spegt, Makromol. Chem., <u>139</u> , 1 39 (1970); ibid <u>140</u> , 167 (1970).
4.	V.F. Holland and P.H. Lindenmeyer, J. Polymer Sci., 57, 589.
	(1962).
5.	F. Hamada, B. Wunderlich, T. Sumida, S. Hayashi and A. Nakajima,
0	J. Phys. Chem., <u>72</u> , 178 (1968).
6.	Manual for DSC-2C, Perkin Elmer Corp., Norwalk, Conn., U.S.A.
7.	M.J. O'Neill, Analytical Chem., <u>36</u> , 1238 (1964).
8.	E. Melnuth and B. Wunderlich, J. Appl. Phys., <u>36</u> , 3039 (1965).
9.	A.J. Kovacs, A. Gonthier and C. Straupe, J. Polymer Sci., Part C,
	<u>50,</u> 283 (1975).
10.	B. Wunderlich, Thermochim. Acta, 4, 175 (1972).
11.	D.A. BLackadder and H.M. Schleinitz, Polymer, 7, 603 (1966).
12.	J.D. Hoffman and J.J. Weeks, J. Res. Nat. Bur. Std., <u>66A</u> , 13
	(1962).
13.	T.W. Huseby and H.E. Bair, J. Appl. Phys., <u>39</u> , 4969 (1968).
.14.	H.E. Bair, T.W. Huseby and R. Salovey, ACS Polymer Prepaints, 9,
	795 (1968).
15.	H.E. Bair and R. Salovey, J. Macromol. SciPhys., <u>B3</u> ; 3 (1969).
16.	J.D. Hoffman, L.J. Frolen, G.S. Ross and J.I. Lauritzen, Jr., J.
	Research Nat. Bureau StdsA, Physics and Chemistry, 79A, 671
	(1975).
	````

Name 1

· .

# - 131 -

>

4

t

C

C

- L. Mandelkern, J.M. Price, M. Gopalan and J.G. Fatou, J. Polymer Sci., A2, <u>4</u>, 385 (1966).
- C.P. Buckley and A.J. Kovacs, Colloid and Polymer Science, <u>254</u>, 695 (1976).
- 19. L. Mandelkern, A.L. Allou, Jr. and M. Gopalan, J. Phys. Chem., 72, 309 (1968).
- 20. Ryong-Joon Roe and J.E. Bair, Macromolecules, 3, 454 (1970).
- 21. L. Mandelkern, Rubber Chem. Technol., <u>32</u>, 1392 (1959).

7 N

- 132 -

## CHAPTER IV

ISOTHERMAL GROWTH OF LOW MOLECUALR WEIGHT POLYETHYLENE SINGLE CRYSTALS FROM SOLUTION. III. KINETIC STUDIES

、 法政府与政府

Y

Z

## ABSTRACT

Single crystals of four polyethylene fractions ranging in molecular weight from 3100 to 11600 were grown isothermally from solution using the self-seeding technique. Growth rates of the crystals were measured as a function of solution concentration, molecular weight, and temperature of crystallization. The growth rates were found to be proportional to the concentration raised to a power less than unity. The variation of the concentration exponent with crystallization temperature and molecular weight is discussed qualitatively in terms of a dilute solution theory of polymer crystal growth, proposed by Sanchez and DiMarzio, in which it is considered that the secondary nucleation required for continued growth may involve cilia as well as solution molecules.

The most interesting results concern the temperature variation of the growth rates. For the higher molecular weight fractions the growth rate decreases monotonically with the crystallization temperature. In contrast for fractions in the molecular weight range of 3000 to 4000 the growth curves show a notched appearance in which two branches can be distinguished. These branches intersect at a transition temperature where the temperature coefficient of the growth rates changes discontinuously. This behavior is interpreted to mean that the transition temperatures correspond to changes in the conformation of the chains deposited on the growth faces. Thus above and below the transition, the crystals are composed of n-times and (n + 1)-times folded chains, respectively. This interpretation of the growth transitions is

- 134 -

四日 そうく

rationalized with the observed continuous variation of the lamellar thickness by assuming a model of the growth process in which the chain ends are preferentially rejected to the exterior of the lamellae.

In accordance with the kinetic theory of polymer crystal growth based on coherent surface nucleation, the growth rate data for the four fractions were analyzed by plotting log G versus  $1/T\Delta T$ , where G is the growth rate, T is the crystallization temperature and  $\Delta T$  is the supercooling. Values of the basal surface free energies obtained from the analysis are discussed in relation to the molecular structure of the crystals.

#### INTRODUCTION

Flexible macromolecules with a sufficiently regular structure characteristically crystallize from dilute supersaturated solutions or from the melt in the form of thin lamellae. Since the chains are normal to the plane of the lamellae and the chain length greatly exceeds the lamellar thickness it has been proposed that the chains must fold on themselves many times (1).

For most polymers it has been observed that the lamellar thickness generally increases monotonically with the temperature of crystallization  $T_c$  so that the mean number of folds per chain decreases as  $T_c$ increases (2). This observation forms the basis for most theoretical analyses of the chain folding problem. Several kinetic theories have been advanced to account for the chain folding phenomenon (3-12). These theories are usually based on a modification of coherent nucleation theory and predict the rate of growth and lamellar thickness as a function of the supercooling  $\Delta T$ . The theories generally imply sharp molecular folds with adjacent re-entry; it is assumed that the fold length and hence the crystal thickness is equal to the critical nucleus size and is therefore determined by the interfacial energies and the bulk free energy of crystallization. The theories have been remarkably successful and provide an excellent fit of the experimental data (11,13).

These conclusions are valid for polymers of sufficiently high molecular weight that the chain length greatly exceeds the lamellar thickness. They are, however, only partially applicable to chains

- 136 -

whose length is of the same order of magnitude as the lamellar thickness. A particularly interesting case in point is the behavior of low molecular weight fractions of hydroxyl terminated poly(ethylene oxide). For these fractions the increase of lamellar thickness with  $T_c$  occurs in a discontinuous or step-wise manner and the lamellar thickness assumes discrete values which are whole number multiples of the length of the chain (14-16). This step-wise variation of the lamellar thickness is due to the localization of the chain ends in the lamellar surface as a result of hydrogen bonding between the end groups.

Kovacs and Gonthier (17) have measured the isothermal growth rates of hydroxyl terminated poly(ethylene oxide) single crystals from the melt using low molecular weight fractions. Their results show abrupt variations in the temperature coefficient of the growth rate corresponding to sudden changes in the number of folds per molecule and therefore of the lamellar thickness. Application of kinetic theories to the ogrowth rates and lamellar thickness of these low molecular weight poly(ethylene oxide) fractions has revealed a series of fundamental inconsistencies contradicting the model of coherent surface nucleation resulting in a sequential deposition of chain segments of fixed length (18). In particular it was found that the lateral surface free energy ( $\sigma$ ) appears to vary as the inverse of the lamellar thickness instead of remaining invariant as required by the theoretical model.

The work of Kovacs et al invites the question whether the observed phenomena are general or arise from end group pairing in the

- 137 -

special case of hydroxyl terminated poly(ethylene oxide). It therefore seems of obvious interest to extend the observations to a polymer such as polyethylene where strong attractive forces do not exist between the end groups. Accordingly the purpose of the present work is to further probe the origins of the chain folding phenomenon by studying the growth rates of polyethylene single crystals from solution as a function of molecular weight, crystallization temperature and solution Sharp molecular fractions have been used covering the concentration. range from 3000 to 11000. In this range the transition from extended to folded chain crystallization should be observable. Solution growth has permitted a wider range of supercoolings to be encompassed than would be possible in crystallization from the melt. The results have been analyzed in combination with data on the equilibrium dissolution temperature of the fractions and the temperature variation of the lamellar thickness as presented in Chapters II and III.

Finally it may be noted that several authors have previously studied the growth rates of single crystals from solution. Holland and Lindenmeyer (18) found that the growth rate of single crystals of polyethylene crystallized from xylene decreases with decreasing molecular weight and with decreasing temperature; Keller et al (20,21) and Cooper and Manley (22) found that the growth rates of polyethylene single crystals from xylene is proportional to the concentration raised to a power less than unity, and Johnson and Lehmann (23) found a similar concentration exponent for poly-3,3-bis(chloromethyl)-oxet ane (PENTON) crystallized from m-xylene. In all of these cases the molecu-

· San Starta

- 138 -

lar weights of the samples were in excess of 10000. As indicated above, the present work covers a lower range of molecular weights.

## EXPERIMENTAL

The samples were the same low molecular weight linear polyethylene fractions used in the previous work (Chapters II and III). The molecular weights, polydispersities and equilibrium dissolution temperatures  $T_d^{\circ}$  are listed in Table 4.1. The solvent was commercial pxylene distilled before use.

#### Table 4.1

Fractions	^M w	M _n	^៷ _w / ^៳ n	T _d °, deg K	T _s , deg K
PE11600	11600	11600	1.11	382.0	369.7
PE6750	6750	6100	1.10	376.8	368.4
PE4050	4050	3900	1.04	371.5	367.6
PE3100	3100	2900	1.07	367.4	365 <b>.9</b>

#### Characteristics of the Polyethylene Fractions

Solutions of the desired concentration (usually about 0.1%;  $\dot{w}/w$ ) were prepared by mixing carefully weighed amounts of polymer and solvent and refluxing under nitrogen for 15 minutes. The solutions were

Γ.

- 139 -

สั

\$P [™]

crystallized at 75° C and then cooled to room temperature. These crystal suspensions were used as stock samples in the crystallization kinetics experiments.

The self-seeding method (24,25) was used to initiate crystal growth at the desired temperature and concentration. Approximately 5 mL of the crystal suspension, contained in a test tube equipped with a ground glass stopper, was immersed in an oil bath at 75° C. The temperature was increased to some value T at a rate of 8 deg C/min and held at this temperature for 30 min. T is the temperature at which only the crystal nuclei remain in suspension. The sample tube containing the nuclei was transferred to a thermostat at the desired crystallization temperature T and a suitable amount of pure solvent, previously equilibrated at  $T_{\mu}$ , was immediately added with gentle stirring. In this way thermal equilibrium as rapidly attained and growth immediately commenced on the nuclei. The growth rate of the crystals was then uniform throughout any one preparation so that at any time all the crystals had reached the same size. Measurement of about a dozen crystals at each sampling time during the growth indicated that the individual measurements were within 1% of the average. As found previously by Holland and Lindenmeyer (19) and Blundell and Keller (26) the growth of the crystals was initially linear and then falls off as the polymer becomes depleted. The measurement of the initial growth rate is of particular interest since it is related to the initial concentration. The T value has a direct influence on the duration of the linear growth phase.

At a low  $T_g$  more nuclei will exist and the polymer molecules in solution will be consumed more rapidly during the crystallization process. Thus the duration of the linear growth phase will be shorter. Ideally, a low density of nuclei should be used so that constant growth rate can be maintained over a long period. However, a compromise was sought in order to obtain a suitable number of crystals on sampling the preparation for electron microscopy. Values of  $T_g$  were chosen such that the growth rate was linear during the initial 1000 nm of growth as measured from the center of a crystal to any {110} face. The  $T_g$  values used for each fraction in the present work are listed in Table 4.1.

The crystal population was sampled at any required stage of growth using the method described by Blundell and Keller (26). Using a pre-heated micropipette, a few drops were transferred from the crystallizing solution to a test tube containing pure solvent at a lower temperature  $T_{c2}$ . At this stage, the solutions contained self-seeded crystals grown to a certain size and the remaining uncrystallized polymer. On quenching into pure solvent at a lower temperature  $T_{c2}$ , the crystals continued to grow at a lower rate and with a thickness appropriate to crystallization at the lower temperature. Thus a discontinuous downward step on the crystal surface was formed and this defined the size of the crystals at the time of sampling. The actual observation of the growth rates were made from measurements in the electron microscope after depositing drops of the crystal suspension on specimen grids and shadowing with platinum. The linear crystal dimensions, as measured from the center of a crystal up to the step on a  $\{110\}$ -growth face,

- 141 -

were plotted against the crystallization time. Linear growth with time, during the initial stages of growth, was observed in most cases. For , very rapid crystallization rates, where the linear phase of growth was short, the initial slope of the curve was used for the measurements. The slope of a plot of crystal size versus time gave the growth rate which was studied as a function of crystallization temperature, solution concentration and molecular weight.

The quench temperature  $T_{c2}$  was mainly determined by the molecular weight of the sample. Ideally, the lowest practical quench temperature should be used since the larger the difference of the lamellar thickness characteristic of the two temperatures  $\hat{T}_c$  and  $T_{c2}$ , the more clear and easily observed the step will be. Too low values of  $T_{c2}$  give rise to the formation of undesirable multilayer crystals. For the fractions PE11600 and PE6750, it was found that simple monolayer growth occurred when 60° C <  $T_{c2}$  < 70° C. For the fractions PE4050 and PE3100,  $T_{c2}$  was conveniently set at 50° C for monolayer growth.

The measurement of the size of a given crystal could be made within 2% from calibrated electron micrographs. On considering other possible sources of error, such as fluctuations in the temperature of the oil baths used for crystallization and the precision of the timing of the crystal sampling, it is estimated that the uncertainty in the growth rates is about  $\pm$  3%. 17

- 142 -

Ì

#### RESULTS AND DISCUSSION

#### Concentration and Molecular Weight Dependence of the Growth Rate

Growth rate data for the four fractions studied are shown in Tables 4.2 to 4.5 as a function of solution concentration and crystallization temperature. It has previously been shown (21,22) that the concentration dependence of the growth rate may be described by the relation

where G is the growth rate, C is the concentration and  $\alpha$  is a constant, hereafter referred to as the concentration exponent. In the present work a pronounced concentration dependence was observed in all cases. As seen in Figure 4.1 for the higher molecular weight fractions (PE11600 and PE6750), logarithmic plots of growth rate against concentration show a good linear relationship over the entire concentration Thus for these cases a reliable value of  $\alpha$  can range investigated. readily be derived. On the other hand for the lower molecular weight fractions (PE4050 and PE3100), the plots are curved indicating that the concentration exponent is not a constant if the whole concentration range is considered (Figure 4.2). Nevertheless, if we choose to ignore the point at the highest concentration a straight line can readily be drawn through the remaining points. Values of the concentration exponent thus obtained are listed in Table 4.6 together with the values for the two higher fractions. It is seen that under the conditions

- 143 -

-	1	4	4	-
---	---	---	---	---

# TABLE 4.2

Growth Rate Data for the [110] Faces of Polyethylene Single Crystals

	<u> </u>	from	Xylene Solu	tion. Frac	tion PE3100	)		
Concn:	0.05 wt%	Concn:	0.01 wt%	Concn:	0.005 wt%	Concn:	0.001 wt%	
Tc	G	Tc	G	т _с	G	Tc	G	-
± 0.01° C	(nm/sec)	± 0.01° C	(nm/sec)	± 0.01° C	(nm/sec)	± 0.01° C	(nm/sec)	
70.45	7.67	68.90	5.77	68.90	3.93	70.45	1.06	
72.93	6.53	70.45	5.11	<b>69.9</b> 0	3.57	71.20	1.01	
74.05 .	5.27	72.10	4.83	71.20	2.88	72.93	0.89	
76.10	4.41	72.93	3.98	73.06	2.42	74.05	0.69	
77.00	4.40	74.05	2.39	74.05	1.68	74.95	0.64	
78.25	2.93	74.95	2.24	74.95	1.27	76.10	0.56	
7 <b>9.8</b> 0	° 1.16	76.10	2.09	76.10	1.20	, 77.00	0.48	
81.00	1.25	77.00	2.03	77.00	1.11	78.25	0.47	
83.00	0.72	77.70	1.51	78.40	0.96	79.80	0.32	
84.00	0.60	79.80	0.88	79.80	0.73	81.00	0.20	
85.00	0.36	81.00	0.71	80.30	0.54	83.00	0.17	•
86.25	0.18	82.40	0.54 ″	83.20	0.34	85.00	0.10	
		84.00	0.35	84.00	0.21	86.40	0.05	
		85.00	0.25	86.25	0.10			
		86.25	0.13	87.70	0.03			
		87.70	0.06					

ेह ्र

( i

- State State

TABLE 4.3

- 145 -

Growth Rate Data for the {110} Faces of Polyethylene Single Crystals

from Xy	7lene	Solution.	Fraction	PE4050
---------	-------	-----------	----------	--------

Concn:	0.05 wt%	Concn:	0.01 wt%	Conca:	0.005 wt%	Concn:	0.001 wt%
Tc	G	Tc	G	Т _с	G	Tc	G.
± 0.01° C	(nm/sec)	± 0.01° C	(nm/sec)	± 0.01° C	(nm/sec)	± 0.01° C	(nm/sec)
70.85	9.93	68.90	6.04	68.90	4,43	<b>69.</b> 10	1.21
73.40	6.67	69.90	5.80	69.10	4.29	71.00	1.16
74.85	5.41	70.85	4.62	70.85	3.63	73.40	0,82
77.00	3.21	72.10	4.80	<b>73</b> ≈ 06	2.71	75.00	0.58
77.50	2.91	74.00 .	3.01	75.00	1.52	77.00	0.30
78.05	2.18	74.85	2.57	76.00	1.17	77.60	0.30
78 <b>.9</b> 0	1.93	77.00	1.42	77.00	1.13	<b>.78.9</b> 0	0.22
80.00	1.88	77.70	1.28	78.40	0.70	80,00	0.21
81.60	1.26	78.05	0.97	<b>78.9</b> 0	0.67	81.60	0.16
82.00	1.22	78.90	0.86	80.30	0.57	82.00	0.13
83.00	0.72	80.00	0.79	81.60	0.41	82.95	0.12
84.10	0.52	80.50	0.71	82.00	0.38	85.00	0.05
85.00	0.30	81.60	0.63	83.20	. 0.28	. <b>86.7</b> 0	0.03
86.10	0.24	82.40	0.59	84.10	0.17	web. D	- •
88.00	0.07	85.00	0.26	85.00	0.13	o	
		86.70	0.12	86.70	0.06		
		87.70	0.05	87.70	0.03		ĩ

ų

-	146	-

TABLE 4.4
-----------

Growth Rate Data for the {110} Faces of Polyethylene Single Crystals

from Xylene Solution. Fraction PE6750

		Concn: 0.05 wtZ	Concn: 0.01 wt%	Concn: 0.001 wt%
T _c .	- , <u>, , , , , , , , , , , , , , , , , ,</u>	G	G	G
± 0.01° C	•	(nm/sec)	(nm/sec)	(nm/sec)
75.50		21.60	11.25	3.40
77.80		13.10	5.55	1.50
78.95		11.33	3.79	0.96
81.60	4	3.33	1.09	0.35
83.60		1.08	0.36	0.13
86.00		0.25	0.13	0.05
88.10		0.07	0.04	0.02
•				

TABLE 4.	5
----------	---

- 147 -

Growth Rate Data for the  $\{110\}$  Faces of Polyethylene Single Crystals

> ÷ ĭ

- Come and the second of the second

**(**)

from Xylene Solution. Fraction PE11600

	Concn: 0.05 wt%	Concn: 0.01 wt%	Concn: 0.001 wt%
T _c	G	G	G
± 0.01° C	(nm/sec)	(nm/sec)	(nm/sec)
76.00	26.67	14.56	6.79
78.00	16.33	8.49	3.20
80.00	10.83	4.96	" 1 <b>.71</b>
81.40	7.17	2.83	1.19
83.00	4.01	1.82	0.61
86.00	0.99	0.42	0.17
87.40	0.38	-	· –
88.00	0.24	0.10	0.04
<b>89.1</b> 0	0.07	·  0.03	0.01

# TABLE 4.6

## Values of the Concentration Exponent $\alpha$ as a Function of

Crystallization Temperature T				
T _c ,°C	α for fraction			
	PE3100	PE4050	PE6750	PE11600
70	0.652	0.673		
72	0.634	0.673	-	-
74	0.612	0.669	-	-
76	0.571	0.650	0.503	0.348
78	0.552	0.625	0.554	0.417
80	0.522	0.621	0.602	0.471
82	0.506	0.611	0.605	0.474
84	0.457	0.604	0.575	0.452
86	0.413	0.544	0.493	0.443

•

「「「「「「「」」

2 . 1. 1. 1. 1. 1. 2. . there a she are a so a

t

C



Street Property of

Typical logarithmic plots of the linear growth rate, G, of the [110] faces as a function of concentration for fraction PE11600 at different temperature.

()



## FIGURE 4.2

([†]

Typical logarithmic plots of the linear growth rate, G, of the  $\{110\}$  faces as a function of concentration for fraction PE4050 at different temperature.

employed fractional order growth kinetics is observed, the values of a

being in the range 0.3 to 0.7.

As illustrated in Figure 4.3 the variation of  $\alpha$  with crystallization temperature depends upon the molecular weight of the sample. For molecular weights of 3100 and 4050,  $\alpha$  decreases monotonically with increasing crystallization temperature. On the other hand for the samples with molecular weights of 6750 and 11600,  $\alpha$  first increases with crystallization temperature, then it passes through a maximum and decreases. These observations may be compared with earlier work (22) using polyethylene samples with molecular weights in the range 15700 to 450000 where the value of  $\alpha$  was found to increase with crystallization temperature for all but the sample of highest molecular weight for which  $\alpha$  remained essentially constant.

When considering the values obtained for  $\alpha$  with the different fractions at fixed crystallization temperature it was seen that  $\alpha$  first increases and passes through a maximum as the molecular weight increases (Figure 4.4). By contrast, it has previously been shown experimentally that for high molecular weight samples  $\alpha$  decreases with increasing molecular weight (22).

The various trends in the concentration dependence of the growth rate as described above can be qualitatively discussed in relation to a dilute solution theory of polymer crystal growth proposed by Sanchez and DiMarzio (12). The theory predicts the effects of molecular weight, solution concentration, and crystallization temperature on the growth rate of single crystals from solution. It is considered that

( ;



## FIGURE 4.3

C

The variation of the concentration exponent  $\alpha$  with the temperature of crystallization T_C for the different molecular weight fractions.



# FIGURE 4.4

Examples of the variation of the concentration exponent  $\alpha$  with molecular weight for four crystallization temperatures  $T_{C}$ .

京

ų

the secondary nucleation required for continued growth of a crystal may involve cilia as well as solution molecules.

Cilia are the dangling ends of molecules that are partially incorporated into the crystal lattice. They are generated in the course of crystal growth in the following manner. When the first segments are attached to a growing strip at some arbitrary position along the chain, the two ends of the molecule are left dangling in solution. If now the longer chain portion is incorporated into the lattice by chain folding, the shorter portion will be left dangling in solution as a permanent cilium. Sanchez and DiMarzio proposed that these cilia can participate in nucleating a new growth strip (fold plane) on the crystal surface by a kind of "self nucleation" mechanism.

The theory makes the following predictions. For high molecular weights, if cilia nucleation is the only means of propagating the growth of the crystal the concentration exponent  $\alpha = 0$  and the nucleation rate S^c is independent of concentration. For low molecular weights S^c is proportional to concentration raised to a power less than unity. On the other hand, when nucleation by solution molecules is the sole mechanism, the nucleation rate S⁵ is proportional to the concentration raised to the first power, except at very low molecular weight when the concentration exponent tends to exceed unity. Usually the secondary nucleation is a mixed process involving both cilia and solution molecule nucleation, hence  $\alpha$  will be between unity and zero. The theory further predicts that for cilia nucleation  $\alpha$  should increase with increasing T_c at fixed molecular weight or decrease with molecular weight at fixed T.

- 154 -

÷

The observed trends in  $\alpha$  are more complex than the theoretical predictions and detailed analysis and explanation is not possible because the theory, although derived for finite molecular weights, breaks down when applied to the very low molecular weight samples used in the present work. For samples PE6750 and PE11600 the observed initial increase of  $\frac{1}{2}$  with T as shown in Figure 4.3 is in harmony with the theoretical prediction for cilia nucleation. As discussed by Sanchez and DiMarzio (12) the reason why the concentration dependence of  $S^{C}$  tends to increase with  $T_{c}$  can be understood on physical grounds as follows. With increasing T the lamellar thickness increases and this is accompanied by a decrease in the length of the primary cilia in a growth strip. When the cilia become sufficiently short they are no longer able to stabilize themselves by chain folding and molecules from solution are required to stabilize the nucleus. Since the availability of solution molecules for stabilization depends on the concentration of the polymer solution, the concentration dependence tends to increase.

Proceeding further with the discussion of the data in Figure 4.3 it is reasonable to interpret the maximum in the  $\alpha$  versus  $T_c$  plots for samples PE6750 and PE11600 as indicating that some other mechanism of propagation opposes cilia nucleation and eventually supervenes. It is tempting to suggest that the opposing mechanism is nucleation by polymer molecules in solution but this cannot be the correct explanation since in that case the value of  $\alpha$  should remain close to unity. For fractions PE3100 and PE4050, for which  $\alpha$  decreases monotonically with  $T_c$ , it seems quite safe to conclude that the crystallization process

- 155 -

should be entirely different from a cilia nucleation mechanism. In fact, whatever the detailed mechanism may be, the behavior of these fractions seems to be similar to that of fractions PE6750 and PE11600 at temperatures above the maximum.

Finally, the variation of  $\alpha$  with molecular weight (Figure 4.4) seems to show very clearly that the mechanism of crystal growth changes with molecular weight. The behavior at high molecular weights, where  $\alpha$ decreases with molecular weight, is predicted by the theory of Sanchez and DiMarzio for a cilia nucleation mechanism. At low molecular weights the observed increase in  $\alpha$  with molecular weight strongly suggests the operation of a different mechanism in that range.

The variation of growth rate with molecular weight is shown in Figure 4.5 for various crystallization temperatures and concentrations. The characteristic feature of these isotherms is that as the molecular weight increases the growth rate passes through a minimum and then increases sharply. The increase in growth rate with molecular weight at higher molecular weights is in agreement with the observations of Jackson and Mandelkern (28) and Blundell and Keller (6) who found that higher molecular weight fractions crystallize faster than low molecular weight fractions. This effect can readily be explained in terms of the increase in supercooling ( $\Delta T = T_d^{\circ} - T_c$ ) with molecular weight, since the growth rate is proportional to  $\exp(-K_g/\Delta T)$ , where K is the nucleation parameter (10), and the equilibrium dissolution temperature  $T_d^{\circ}$ increases with molecular weight.

The existence of a minimum in the growth rate/molecular weight

- 156 -

がいろういろちょうを



# FIGURE 4.5

C

۲₎

Growth rate as a function of molecular weight at various crystallization temperature and solution concentration. 6

- 157 -

isotherms has not previously been reported, presumably because measurements were not made at sufficiently low molecular weights. A detailed interpretation of this phenomenon is not possible at present, but the general shape of the isotherms seems to be consistent with the suggestion made above that the mechanism of crystal growth changes at the molecular weight corresponding to the minimum in the isotherms.

### Temperature Variation of the Growth Rates

Figures 4.6 and 4.7 show growth rate data as a function of crystallization temperature for the fractions PE4050 and PE11600. For PE11600 the growth rate decreases monotonically with the temperature of crystallization  $T_c$ . This behavior is typical of high molecular weight melt crystallized polyethylene samples (10). Similar results were obtained with PE6750. In contrast, for fractions PE3100 and PE4050 the growth curves show a notched appearance in which two branches can be distinguished. These branches appear to intersect at a definite temperature  $T^*$  (78° C for PE4050 and 74° C for PE3100) where the temperature coefficient of the growth rate d(log G)/dT changes discontinuously with  $T_c$ . For a fixed molecular weight the transition temperature  $T^*$  is seems to be independent of the concentration of the polymer solution.

The results obtained with the lower molecular weight fractions are strikingly similar to the behavior exhibited by low molecular weight melt crystallized fractions of poly(ethylene oxide) as studied by Kovacs et al (17). In that case the transition temperatures were considered to correspond to changes in the conformation of the chains

- 158 -



## FIGURE 4.6

Temperature dependence of the growth rate for fraction PE4050 at various concentrations. The upper abscissa scale shows the number of stems per molecule ( $\nu$ ) corresponding to the temperature scale. For fraction PE3100, because of the difficulty of accurately measuring the growth rates at the highest supercoolings, the low temperature branch of the growth curve has fewer data points and the notched apperance is not as pronounced as for PE4050. æ

· ,

Ô



deposited on the growing faces. Thus above the transition temperature growth proceeds by deposition of n-times folded chains, whereas below the transition temperature, growth consists of the deposition of (n + 1)-times folded chains. This interpretation followed logically from the observation that the lamellar thickness shows a quantized change at the transition temperature.

In the case of the polyethylene samples studied in the present work the interpretation of the apparent transition temperatures is not as straightforward as for poly(ethylene oxide) because the lamellar thickness apparently increases continuously with  $T_c$  as demonstrated in Chapter II. Nevertheless, there are two lines of evidence suggesting that, as in the case of poly(ethylene oxide), the transition temperatures correspond to changes in the conformation of the molecules deposited on the growth faces.

First, as described in Chapter III, the temperature variation of the heat of fusion follows a sigmoidal pattern for samples with molecular weights in the range of 3000 to 4000. This has been interpreted to mean that there is a change in the structure of the interfacial regions of the crystals as  $T_c$  decreases, corresponding to a transition from extended to folded chain growth. The second line of evidence in support of the proposed interpretation of the apparent growth transitions comes from an examination of the morphology of crystals of PE3100 grown at various temperatures, and filtered and washed with pure solvent at the crystallization temperature. As illustrated in Figure 4.8 the crystals grown at high supercooling below the transition temperature exhibit sectorization which is an inherent consequence of chain folding. On the other hand, crystals grown at low supercooling above transition temperature are not sectorized, indicating that they are principally composed of extended chains. Clearly there must be a temperature at which there is a transformation from one form of growth to the other.

Having presented evidence in support of the interpretation that the growth transitions correspond to changes in the conformation of the molecules deposited on the growth faces, we now consider the molecular nature of the transitions.

From the measurements of the temperature variation of the lamellar thickness (£) described in Chapter II together with the known extended chain length (L) the number of stems per molecule can be readily estimated as v = L/2. It turns out that the number of stems per molecule increases as  $T_c$  decreases and the transition temperatures observed in the growth cutwes for PE3100 and PE4050 correspond respectively to 1.9 and 2.5 stems per molecule (see Figure 4.6). Accordingly, assuming that the incorporation of v stems into the crystal results in the formation of v = 1 chain folds, the growth transitions can, to a fair approximation, be interpreted as corresponding to a change from once folded to extended chain growth for PE3100 and from twice folded to once folded chain growth for PE405Q. It is, however, important to emphasize that the validity of this interpretation depends on what happens to the chain ends during crystal growth. Three models of the crystallization process can be envisaged, viz:- (a) chain ends

- 162 -
FIGURE 4.8

Bright field (left) and dark field (right) electron micrographs of single crystals of PE3100 grown from dilute xylene solution and filtered from solution at the crystallization temperature which is  $81^{\circ}$  C in (a) and 55° C in (b). The crystals in (a) are typical of those grown above the growth transition temperature (74° C) and are not sectorized, indicating they are composed of extended chains. The crystals in (b) are typical of those grown below the growth transition temperature and exhibit the characteristic sectorization which is an inherent consequence of chain folding. The dark field micrographs were taken using a {110} reflection. Bar lines represent 1  $\mu m$ .

た

- 163 -



P





localized on the surface of the lamellae, (b) chain ends rejected to the exterior of the lamellae as cilia and (c) chain ends incorporated within the crystal lattice. According to the proposed interpretation of the growth transitions, model (a) would require a step-wise change in lamellar thickness as T_increases in contrast to the observed continuous increase. For model (c) as pointed out by Sanchez and DiMarzio (12) the surface energy product  $\sigma\sigma_{a}$  would tend to increase with decreasing molecular weight which is the opposite of what is observed. According to model (b) it can be assumed that fractional stems are rejected from the crystal lattice as cilia. In this case it is evident that as T decreases the pendant cilia would become longer and following Hoffman et al (10) it can be postulated that when the length of the cilium becomes equal to the lamellar thickness a fold will appear. In this process the temperature variation of the lamellar thickness would be expected to be continuous. Thus according to this model a quantized change in the conformation of the molecules deposited on the growth faces can occur even though the lamellar thickness changes continuously with temperature.

In concluding this section it may be of interest to note that growth transitions of the type described above have not previously been observed in studies of the growth kinetics of low molecular weight polyethylene samples. Hoffman et al (10) and Labaig (27) have measured the growth rates of polyethylene fractions crystallized from the melt covering the molecular weight range from 3600 to 17000. The results show that log G decreases monotonically with temperature over the range of  $T_c$  explored. The failure to observe the growth transitions in these experiments is presumably related to the relatively low supercoolings accessible in melt crystallization as compared to crystallization from solution. In the work of Hoffman et al for the fraction with a molecular weight of 3600 the maximum supercooling was 15.4° C, whereas in our experiments with the fraction of molecular weight 3100 the transition temperature occurs at a supercooling of about 20° C.

¥ 166 -

.

ななないですれた

### Basal Surface Free Energies

We now wish to analyze the growth rate data in order to estimate basal surface free energies for the crystals of the various fractions. The kinetic theory of nucleation controlled growth of polymer crystals with infinitely long folded chains leads to the following expression for the growth rate G (10).

$$G = G_{o} \exp(-\Delta F^{*}/kT) \exp[-K_{g}/T(\Delta T)f] \qquad (4.1)$$

where  $\Delta H^*$  is the activation energy for transport of chain segments to the crystal-solution interface,  $G_0$  contains factors not strongly dependent on temperature, T is the crystallization temperature,  $\Delta T$  is the supercooling  $T_d^\circ - T$ , f which is given by  $2T/(T_d^\circ + T)$  is a factor near unity that accounts for the slight diminution of the heat of fusion  $\Delta h_f$ as the temperature falls below the equilibrium temperature  $T_d^\circ$  and k is the Boltzmann constant. The nucleation parameter K has the general  $\overset{\circ}{\underset{g}{}}$  form

$$K_{g} = \frac{1}{\kappa} b \sigma \sigma_{ed}^{T} (\Delta h_{f}) k \qquad (4.2)$$

where b is the thickness of the depositing growth layer;  $T_d^{\circ}$  is the equilibrium dissolution temperature which is molecular weight dependent;  $\sigma$  and  $\sigma_e$  are respectively the lateral and basal surface free energies; and  $\Delta h_f$  is the heat of fusion. The value of x depends on the nucleation regime. In regime I growth where the formation of a surface nucleus is followed, by rapid completion of the entire substrate, x has a value of 4. For regime II growth where numerous nuclei form on the substrate and spread slowly, x has a value of 2.

By plotting log G against  $1/T(\Delta T)f$  a linear relationship should be obtained if Equation 4.1 is obeyed and the numerical value of K can be derived from the slope. Hence the important parameter  $\sigma_e$  can be estimated, if the lateral surface free energy is known.

In carrying out the analysis a precise knowledge of the equilibrium dissolution temperature  ${}^{\#}T_{d}^{\circ}$  is required since  $K_{g}$  and the supercooling  $\Delta T$  are very sensitive to it. In the present work, which involves chains of finite length with n chain units,  $T_{d}^{\circ}(n)$  has been determined experimentally by measuring the dissolution tmeperature of large extended chain crystals corresponding to n, as described in Chapter II. For the four fractions studied, the values of  $T_{d}^{\circ}(n)$  used throughout the data analysis are listed in Table 4.1.

Figures 4.9 and 4.10 show plots of log^G versus  $1/T(\Delta T)f$  for fractions PE11600 and PE4050 at various concentrations. For PE11600 and PE6750 linear relationships are obtained over the entire range of supercoolings investigated. On the other hand, for the two lowest molecular weight fractions, PE3100 and PE4050, one can distinguish two ranges of supercooling in which the slopes of the plots have substantially different values. According to Equations 4.1 and 4.2 the change. in slope of these log G curves must be due to a change in  $\sigma_e$  since all the other parameters,  $\Delta H^*$ , b,  $\sigma$  and  $\Delta h_f$ , are independent of chain length and conformation. For the various fractions, values of nucleation constant K derived from the slopes of the log G versus  $1/T(\Delta T)f$  ' plots are collected in Table 4.7. Differences in the value of K for growth at the various concentrations do not appear to be significant; consequently it was assumed that  $K_{\rho}$  is independent of concentration and the average value was used in the calculations to follow. In order to estimate whether the observed values of  $K_{g}$  for a given fraction corres  $^{(i)}$  pond to regime I or regime II kinetics, we have used the so-called Zcriteria proposed by Lauritzen (29). According to this proposal the parameter governing the distinction between regime I and II is the dímensionless quantity

 $Z = iL^2/4g$  (4.3)

where i is the surface nucleation rate, g is the spreading rate and L is the substrate length. If  $Z \leq 0.1$ , regime I behavior holds, while

an all the state



169

後になるが

Ċ

# FIGURE 4.9

()

Plots of the logarithm of the linear growth rate G against  $1/T(\Delta T)$ f for fraction PE11600 at various concentrations. Fraction PE6750 shows similar behavior.



# FIGURE 4.10

C

Plots of logarithm of the linear growth rate G against  $1/T(\Delta T)$ f for fraction PE4050 at various concentrations. Fraction PE3100 shows aimilar behavior.

<u>بة.</u> 1

273***** 5227

	Values of K	Calculated	i from Plo	ts of log (	G vs 1/T(A1	r)f
		K (	(K ² ) at com	ncn. (% w/v	v) (	Average
	Temperature					•
Fraction	range, °C	0.05	0.01	0.005	<u>0.001</u> ,	
PE3100	70-74	27000	25000	26000	<b>232</b> 00	25300
	74-86	<b>~1690</b> 0	17000	16300	1,5200	<b>"16300</b>
	•			*		ą
ре4050	69-78	45300	45300	44800	41300	44200
`	78-86	27600	26700	26700	23300	26100
,				•		*
PE6750	75-88	80000	77000	- *	74200	77200
	1	,		•		
PE11600	76-89	90900	88600		87300	88900
				*		_

í

1.1

• • • •

≯

44528 2

# TABLE 4.7

- 171 -

 $\mathbf{O}$ 

E

for regime II behavior, Z > 1. From the experimental value of K the Z parameter can be estimated from the approximate expression

$$Z = \frac{1L}{4g} \cong z(L/2a)^2 \exp[-X/T\Delta T] \exp[2ab\sigma_e/kT] (4.4)$$

where z is the number of  $-CH_2$ - units corresponding to the lamellar thickness, a and b are the molecular width and layer thickness respectively, k is the Boltzmann constant and where  $X = K_g$  when Z < 0.1(regime I) and  $X = 2K_g$  when Z > 1 (regime II).

From Equation 4.4 it is possible to estimate the range of L values that are consistent with regime I or regime II behavior. Usually the correct choice of regime can be made by considering whether the value of L is reasonable or unrealistic. The value of L must be consistent with morphological information: for example, L cannot exceed the known lateral dimensions of the single crystals and it should be at least several times larger than the molecular width.

The following input data were used in the calculations: molecular width  $a = 4.55 \times 10^{-8}$  cm; layer thickness  $b = 4.15 \times 10^{-8}$  cm;  $T_d^*$ values as listed in Table 4.1, z was estimated from the lamellar thickmess at a given crystallization temperature divided by the projected length of the -CH₂- unit which is 1.25 A; values of the basal surface free energies as estimated in Chapters II and III.

To illustrate the results of the calculations we consider two examples. First for fraction PEI1600 assuming that the observed value of  $K_{c}$  refers to regime I kinetics we calculate using  $\Delta T = 21.8^{\circ}$  C, T =

85° C and Z < 0.1 that L < 8A. This value is too small to be realistic since it is of the same order of magnitude as the molecular width. A recalculation assuming regime II kinetics gives L > 750 nm which is considered to be too large in comparison with the observed dimensions of crystals grown at the chosen temperature. We are thus led to the conclusion that for these crystals the growth kinetics is intermediate between regime I and regime II so that  $K_g = 3b\sigma\sigma_e T_d^{\circ}/(\Delta h_f)k$  must apply; this implies mixed regime I and regime II behavior. A Similar conclusion is reached for fraction PE6750.

Considering now the calculation for fraction PE4050 in the low temperature range, a test for regime I behavior at  $T_c = 75^\circ$  C and  $\Delta T = 23.3^\circ$  C gives L < 0.73 A which is clearly absurd. For the test of regime II behavior we obtain L > 12.4 A which is considered to be a reasonable substrate length. For the high temperature range at T =  $83^\circ$  C and  $\Delta T = 15.3^\circ$  C, L < 0.5 A for regime I behavior and L > 17 A for regime II behavior. It is thus concluded that for this fraction the growth follows regime II kinetics, so that  $K_g = 2\sigma_c T_d^{\circ}/(\Delta h_f)k$ . The calculations for fraction PE3100 lead to conclusions similar to those for fraction PE4050.

Table 4.8 summarizes the conclusions concerning the assigned growth regimes and lists the corresponding values of the product  $\sigma_e$ for each fraction. In order to extract the kinetic value of  $\sigma_e$  from the product  $\sigma\sigma_e$  we need to know the value of the lateral surface energy  $\sigma$ . For polyethylene, studies of both bulk and dilute solution crystallization rates yield a  $\sigma\sigma_e$  value of about 1300 erg/cm² corresponding to

- 173 -

$\sim$		•	° ¢	· · · · ·		, ''	·
	۔ ۲			- 174 -	,	, ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	
		· ·	rface energy	TABLE 4.8	hagal surfac	e energies.	<b>4</b>
	· •		, race energy	,	σ _e , er	g cm ⁻²	$\sigma_{\rm e}^{\rm , erg \ cm^{-2}}$
Fraction	Temperature range, °C	Growth	Average σσ _e erg ² cm ⁻⁴	σ _e , erg cm ⁻² - (kinetics)	(Ærçm ደ plo	vs 1/ΔT ts)	.(from T _d (or T _m ) vs
PE3100	70-74	 II 71	320	22.9	41	.5	48.9
	-74 00		~ ·	-	* • •	•	
PE4050	69-78 ·78-86	II ·	555 327	39.6 · 23.3	, 45 •	•5 •	48.5
		× 47	• ``,	· · · ·			1
PE6750	75-88	mixed I & II	~~636 `	45.4	. 48	.9	51.7
PE11600	76-89	mixed J & II	727 -	51.9	<b>*</b> 61	.7	60.1
-			•	, <b>*</b>	•	*	· · · · · · · · · · · · · · · · · · ·
			, ,	,	<i>i</i>	~~ -	• •

Particular 1

the limiting value at high molecular weights. Also for high molecular weight polyethylene samples a value of  $\sigma_e = 93 \text{ erg/cm}^2$  has been determined independently by thermodynamic means (30). This gives a value of  $\sigma = 14 \text{ erg/cm}^2$  which is implicitly assumed to be independent of chain length. For the four fractions studied, values of  $\sigma_e$ , calculated by dividing  $\sigma_e$  by 14, are given in Table 4.8. For purposes of comparison the table also includes values of  $\sigma_e$  derived by the two independent methods described in Chapters II and III.

On considering these results several points of interest emerge. First, it is seen that the kinetic values of  $\sigma_e$  are generally somewhat lower than the values derived from plots of lamellar thickness versus reciprocal supercooling and dissolution temperature versus reciprocal lamellar thickness. The significance of this deviation is not immediately apparent. Nevertheless, for the two highest fractions and for PE4050 in the low temperature range the three sets of values agree within about 15% which considering the errors and approximations is satisfactory. This inspires confidence in the assignment of the growth regimes that was made on the basis of the Z-criterion. From Equation 4.2 it is obvious that no other assignment would have given acceptable values for  $\sigma_e$ .

It is also interesting to note that for fraction PE4050 the value of  $\sigma_e$  for the high temperature branch is essentially equal to the value of  $\sigma_e$  derived from the low temperature branch of fraction PE3100. This indicates that the structure of the interfacial regions of the crystals of these fractions is similar in the temperature ranges in question.

í – 175 <del>–</del>

This is consistent with the interpretation discussed above, that the high temperature branch of fraction PE4050 and the low temperature branch of PE3400 correspond to the growth of crystals that are once folded.

For fraction PE3100 the value of  $\sigma_e$  obtained from the slope of the high temperature growth branch is 14.9 erg/cm² which is essentially equal to the accepted value of the lateral surface free energy of polyethylene crystals (14 erg/cm²) and must be the same as the basal surface free energy in the absence of chain folding. This is in excellent accord with the interpretation that for this fraction the high temperature branch corresponds to the growth of extended chain crystals.

The foregoing analysis has demonstrated that the data yield linear plots of log G versus  $1/T(\Delta T)f$  and reasonable values of the basal surface free energies are obtained. In this sense the data are evidently consistent with the theory of polymer crystal growth involving coherent surface nucleation. Nevertheless, it should be noted that the theory was derived for infinite chains and questions have been raised about its applicability to short chains. The problems that thus arise have been discussed by Kovacs et al (31).



The main conclusion of the present work is that for solution grown polyethylene single crystals, with molecular weights in the range of 3000 to 4000, the temperature coefficient of the growth rate undergoes a sharp transition. This is interpreted to mean that at the transition temperature there is an abrupt change in the conformation of the molecules deposited on the growth faces. For a fraction with a molecular weight of 3100 the change is from extended to once folded chains, while for a molecular weight of 4050 the transition temperature corresponds to a change from once folded to twice folded chains.

At first sight the proposed interpretation of the growth transitions would appear to be inconsistent with the observed continuous variation of the lamellar thickness with temperature. However, this objection is only valid if the chain ends are considered to be preferentially localized on the lamellar surfaces as in the case of poly-(ethylene oxide). The apparent paradox can be resolved if a model of the growth process is invoked in which the chain ends are rejected to the exterior of the lamellae as pendant cilia. Thus as the crystallization temperature decreases a pendant cilium will increase in length and form a fold when it becomes equal to the lamellar thickness. In this process the change in lamellar thickness with temperature would be expected to occur in a continuous manner.

The present experiments confirm and generalize the results of Kovacs et al on low molecular weight hydroxyl terminated poly(ethylene oxide) fractions crystallized from the melt. Since the same basic phenomenon (i.e., the existence of growth transitions) is observed not only in polyethylene, but also in solution crystallization it, is evident that the behavior of poly(ethylene oxide) is not special after all. It has been assumed that in poly(ethylene oxide) the growth transitions are attributable to the quantized increase of the lamellar thickness with crystallization temperature. It is now apparent, however, that this is not a necessary condition for the observation of the growth transitions.

The origin of the observed transition between growth modes with different number of folds per molecule remains unexplained. The approach to this question requires the development of an appropriate theory of the growth process, but this is beyond the scope of the present investigation.

- 178 -

•	
	REFERENCES
1.	A. Keller, Phil. Mag., <u>2</u> , 1171 (1957).
2.	A. Keller and A. O'Connor, Disc. Faraday Soc., 25, 114 (1958).
3.	J.I. Lauritzen, Jr. and J.D. Hoffman, J. Res. Nat. Bur. Stand.,
۲	<u>64A</u> , 73 (1960°).
4.	F.P. Price, J. Polymer Sci., <u>42</u> , 49 (1960).
5.	F.C. Frank and M. Tosi, Broc. Roy. Soc., <u>A</u> 263, 323 (1961).
6.	J.D. Hoffman and J.J. Weeks, J. Chem. Phys., <u>37</u> , 1723 (1962).
7.	J.D. Hoffman, S.P.E. Trans., <u>4</u> , 315 (1964).
8.	J.I. Lauritžen, Jr. and E. Passaglia, J. Res. Nat. Bur. Stand.,
	<u>71A, 261 (1967).</u>
<b>.</b>	J.I. Lauritzen, Jr. and J.D. Hoffman, J. Appl. Phys., 44, 4340
	(1973).
10.	J.D. Hoffman, L.J. Frolen, G.S. Ross and J.I. Lauritzen, Jr., J.
	Res. Nat. Bur. Stand., <u>79A</u> , 671 (1975).
11.	J.D. Hoffman, G.T. Davis and J.I. Lauritzen, Jr., Treatise on
8	Solid State Chemistry, ed. N.B. Hannay (Plenum Press, New York,
	1976), vol. 3, chap. 7.
12.	I.C. Sanchez and E.A. DiMarzio, Macromolecules, 4, 677 (1971).
13.	R.L. Miller, "Status of the Analysis of Crystallization Kinetic
	Data", in "Flow-Induced Crystallization" (Gordon and Breach,
	N.Y., 1979).
14.	J.P. Arlie, P.A. Spegt and A. Skoulios, Makromol. Chem., 99, 160
د	(1966).
15.	J.P. Arlie, P.A. Spegt and A. Skoulios, Makromol/. Chem., <u>104</u> , 212
	(1967).

9,;

(

# - 179 -

ŧ

16.	P.A. Spegt, J. Terrisse, B. Gilg and A. Skoulios, Makromol.
١	Chem., <u>107</u> , 29 (1967).
17.	A.J. Kovacs and A. Gonthier, Kolloid Z.u.Z. Polymere, 250, 530
~	(1972).
18.	J.J. Point and A.J. Kovacs, Macromolecules, <u>13</u> , 399 (1980).
19.	V.F. Holland and P.H. Lindenmeyer, J. Polymer Sci., 57, 589
	(1962).
20.	D.J. Blundell and A. Keller, J. Polym. Sci., <u>B6</u> , 433 (1968).
21.	A. Keller and E. Pedemonte, J. Crystal Growth, <u>18</u> , 111 (1973).
22.	M. Cooper and R. St. John Manley, Macromolecules, <u>8</u> , 219 (1975).
23.	V. Johnson and J. Lehmann, Kolloid Z.u.Z. Polymere, 230, 317
<i>p</i> t	(1969).
24.	D.J. Blundell, A. Keller and A.J. Kovacs, J. Polymer Sci., <u>B4</u> ,
	481 (1966).
25.	D.J. Blundell and A. Keller, J. Macromol. Sci., <u>B2</u> , 301 (1968).
26.	D.J. Blundell and A. Keller, J. Polym. Sci., <u>B6</u> , 443 (1968).
27.	J.J. Labaig, Thesis, Univ. L. Pasteur, Strasbourg (1978).
28.	J.F. Jackson and L. Mandelkern, Macromolecules, <u>1</u> , 548 (1968).
29.	J.I. Lauritzen, Jr., J. Appl. Phys., <u>44</u> , 4353 (1973).
30.	J.W. Huseby and H.E. Bair, J. Appl. Phys., <u>39</u> , 4969 (1968).
31.	A.J. Kovacs, C. Straupe and A. Gonthier, J. Polym. Sci., Polymer
	Symposia, <u>59</u> , 31 (1977).

2

ち していというかいかい

- 180 -

## CLAIMS TO ORIGINAL RESEARCH

The following points are considered to be the original and significant findings of this work.

#### Chapter II

(1) A method was devised to directly determine the equilibrium melting/dissolution temperatures  $(T_m^{\circ}/T_d^{\circ})$  of low molecular weight polyethylene single crystals. The measured  $T_m^{\circ}$  values were compared with the values calculated from the Flory-Vrij equation while the/measured values of  $T_d^{\circ}$  in xylene were compared with the Pennings and Sanchez-DMMarzio equations.

(2) The variation of lamellar thickness of single crystals of low molecular weight polyethylene fractions with crystallization temperature was measured. The result is in sharp contrast with the behavior of low molecular weight poly(ethylene oxide) fractions. The significance of this finding was discussed.

(3) Basal surface free energy  $(\sigma_e)$  of crystals of low molecular weight polyethylene fractions were estimated by the analysis of measurements of lamellar thickness as a function of supercooling. The variation of the  $\sigma_e$  values with molecular weight was discussed in terms of chain-end effects.

181, -

### Chapter III

(4) Melting and dissolution temperatures of low molecular weight polyethylene crystals grown at different temperatures were measured and the validity of the linear relation between  $T_m$  or  $T_d$  and 1/1 was tested.

- 182 -

(5) The enthalpies of fusion of low molecular weight polyethylene single crystals were measured as a function of crystallization temperature. An abrupt change of enthalpy of fusion and surface enthalpy was detected in the fractions of  $\overline{M}_{w} = 3100$  and  $\overline{M}_{s} = 4050$ . This behavior was interpreted in terms of a transition in the conformation of the molecules deposited on the growth faces of the crystals.

#### Chapter IV

(6) The growth rate G of the [110] faces of low molecular weight polyethylene single crystals crystallized from xylene solution were measured as a function of molecular weight, solution-concentration and crystallization temperature. The experimental trends for the variation of growth rate with molecular weight and the variation of concentration exponent with crystallization temperature and molecular weight are quite different from what has been previously observed in high molecular weight polyethylene and cannot be explained by the existing theories.

(7) Distinct branches of the growth rate-temperature curves, similar to the low molecular weight poly(ethylene oxide) system, were observed in two low molecular weight polyethylene fractions. This is the first time that this behavior has been observed in polyethylene. The significance of this finding was discussed.

(8) For low molecular weight polyethylene fractions, growth rate data were analysed with the current kinetic theories of polymer crystallization. It was found that the linear relation of log G against  $1/T(\Delta T)$ , was obeyed. The growth regime was estimated for each fraction and values of  $\sigma_e$  were extracted from the analysis. The results were discussed in terms of the molecular structure of the crystals.

- 183 –

#### SUGGESTIONS FOR FURTHER RESEARCH

## F. Solvent Effects

In the present work all measurements were made on crystals grown from dilute xylene solutions. It is known that the conformation of a polymer molecule in solution is partially dependent upon the properties of the solvent, and there is evidence to suggest that the variation of the growth rate with concentration and temperature is affected by the solvent (1). Thus Keller and Pedemonte (1) found that the concentration dependence of the crystal growth rate was generally more marked when using octane as the polymer solvent than was found when using xylene as the solvent. Accordingly, as an extension of the present work it might be of interest to investigate the effect of 'solvents other than xylene on the rates of crystal growth. Octane and decalin could be chimen as 'representative' of solvents respectively poorer and better than xylene.

## 2. Growth Rates of Poly(ethylene oxide) Single Crytals from Solution

As indicated elsewhere in this thesis, low molecular weight fractions of hydroxyl terminated poly(ethylene oxide) show a discontinuous change of the lamellar thickness with crystallization temperature when crystallized from the melt. On the other hand it has recently been reported (2) that when crystallized from solution, the same polymer shows a continuous change of the lamellar thickness with crystallization temperature. The explanation for this difference, in behavior is provided by infrared analysis which shows that almost all of the mole-

5

cular chain ends are associated in the molten state, whereas a large part of the ends are free in dilute solution (2). For these reasons it would be of considerable interest to carry out a study similar to that described in the present thesis using solution grown crystals of low molecular weight hydroxyl termintaed poly(ethylene oxide).

Such a study would provide a further test as to whether a quantized increase in lamellar thickness with temperature is a necessary condition for the observation of distinct branches in the growth rate curves.

# 3. Development of a Theory of Polymer Crystal Growth Applicable to Solution Crystallization of Low Molecular Weight Polyethylene.

An important question which has not been answered in the present thesis is the origin of the observed transition between growth modes with different numbers of folds per molecules. A definitive answer to this question would probably solve the problem of chain folding in polymers. The approach to this problem requires the development of a model of the crystallization process. Sanchez and DiMarzio (3) have proposed a kinetic theory for crystallization from dilute solution allowing for finite molecular weight, but this theory is not sufficiently detailed to resolve the problem. Therefore as a problem for further research, it is suggested that attempts should be made to develop a theory that would allow prediction of the growth rate versus temperature curves for low molecular weight polyethylene fractions and account for the transition from extended to folded-chain crystal growth with increasing supercooling. Growth Kinetics of Crystals of n-Paraffins

In the present work growth rate measurements were made with samples covering the molecular weight range of 3000 to 11600. It would be of interest to extend these measurements to lower molecular weights into the range of n-paraffins. In this range problems of chain folding would not arise since we would be dealing essentially with extended chain crystals. It would be of particular interest to know whether the concept of coherent surface nucleation applies to these very low molecular weight polymers. Furthermore by the application of the reduction rule of Kovacs (4) it should be possible to determine the lateral surface energy  $\sigma$  involved in the crystallographic attachment of a new chain segment onto the growth face. According to Kovacs' analysis of growth rate data for low molecular weight poly(ethylene oxide) samples,  $\sigma$  varies with chain length in contradiction to the theoretical predic-The proposed experiments would provide a test of these contions. clusions.

#### References

A. Keller and E. Pedemonte, J. Crystal Growth, <u>18</u>, 11 (1973).
T. Shimada, N. Okui, and T. Kawai, Makromol. Chem., <u>181</u>, 2643 (1980).

3. I.C. Sanchez and E.A. DiMarzio, Macromolecules, 4, 677 (1971).

4. J.J. Point and A.J. Kovacs, Macromolecules, 13, 399 (1980).

- 186 -