

National Library of Canada Bibliothèque nationale du Canada

Direction des acquisitions et

des services bibliographiques

Acquisitions and Bibliographic Services Branch

395 Wellington Street Ottawa, Ontario K1A 0N4 395, rue Wellington Ottawa (Ontano) K1A 0N4

Your later - Sinteen enforcement

Our tae . Notice reference

#### NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments. La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

AVIS

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

Canadä

c

# The Crystallization of Poly(ethylene oxide) in Blends with Neat and Plasticized Poly(vinyl chloride)

Joanne M. Marentette Department of Chemistry McGill University, Montreal Canada

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

4

© Joanne M. Marentette June, 1995



National Library of Canada

du Canada Direction des acquisitions et

Acquisitions and Bibliographic Services Branch

395 Wellington Street Ottawa, Ontario K1A 0N4 des services bibliographiques 395, rue Wellington Ottawa (Ontario) K1A 0N4

Bibliothèque nationale

Your tile - Votre reference

Our Ne Notre reference

The author has granted an irrevocable non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of his/her thesis by any means and in any form or format, making this thesis available to interested persons. L'auteur a accordé une licence irrévocable et non exclusive à la Bibliothèque permettant nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de sa thèse de quelque manière et sous quelque forme que ce soit pour mettre des exemplaires de cette disposition thèse à la des personnes intéressées.

The author retains ownership of the copyright in his/her thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without his/her permission.

0

anada

L'auteur conserve la propriété du droit d'auteur qui protège sa thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

ISBN 0-612-08132-X

\$

Ð

#### Abstract

The crystallization of poly(ethylene oxide) (PEO) in blends with amorphous poly(vinyl chloride) (PVC), in a mixture with the PVC-selective plasticizer tricresyl phosphate (TCP), and in ternary mixtures with both PVC and TCP has been investigated at several structural levels using the techniques of: (i) theoretical surface interfacial tension calculations, (ii) thermal analysis, (iii) polarized light microscopy, and (iv) polarized infrared microspectroscopy.

The invariance of the glass transition temperature of the interlamellar, amorphous PEO suggests a relatively low degree of dispersion in PEO/PVC blends. A slight depression in the equilibrium melting temperature of PEO in blends of high PVC content was observed, and subsequent analysis of the data using the Flory-Huggins equation reveals that, at best, PEO and PVC exhibit limited miscibility in the melt. The melting temperature depression may be accentuated by the addition of TCP, but the depression observed in the ternary mixtures lies within the experimental uncertainty.

In general, the spherulites grown in the presence of additives are coarser and less birefringent than those grown in the pure melt, with the degree of coarseness increasing with increasing additive concentration. The interpretation of the crystallization kinetics of PEO using current nucleation theory clearly demonstrates that the crystallization of PEO in the temperature range of interest occurs within regime III. The slight kinetic discontinuity at ~ 51 °C that has been thought to arise from a regime II/III transition can be attributed to a transformation of the dominant crystal growth face from the (010) crystallographic face at lower temperatures to the (120) face at higher temperatures. The growth rates of PEO spherulites in PEO/PVC blends are not affected by the presence of PVC in the temperature range 49-55 °C, even at concentrations as high as 50% PVC. However, the growth rates of spherulites in mixtures containing TCP are significantly depressed. Dichroic infrared microspectroscopy was employed to investigate the variations in the crystalline structure at the sub-spherulitic level. The determination of the dichroic ratios and the selected peak ratios from the spectra of purely crystalline PEO (obtained by difference spectroscopy) reveals that PVC disturbs the orientation of the crystalline stems of PEO within the spherulites and causes an increase in the crystallization of PEO in the strained, planar zig-zag conformation. PEO, in turn, appears to induce a higher incidence of the planar zig-zag conformation in the PVC molecules. In the ternary mixtures, the plasticizing effect of TCP on PVC renders the PVC molecules more flexible and more mobile, thereby drastically reducing the shearing of the PEO and the resultant formation of the planar zig-zag conformation during crystallization. In effect, the crystallization kinetics and the basic crystalline structure of PEO can be controlled by selection of appropriate proportions of PVC and TCP, a result of major significance and practical importance to the field of polymer blends.

ii

#### Résumé

La cristallisation du poly(oxyéthylène) (POE) a été examiné dans les mélanges de POE et de poly(chlorure de vinyle) (PCV), dans les mélanges de POE et de tritolyle phosphate (TTP), et dans les mélanges ternaires de POE et de ces deux additifs. Les méthodes appliquées étaient: (i) le calcul théorique des tensions interfaciales, (ii) la calorimétrie différentielle à balayage, (iii) la microscopie polarisée, et (iv) la microspectroscopie infrarouge polarisée.

L'invariabilité de la température de transition vitreuse du POE amorphe et interlamellaire suggère un niveau de dispersion incomplet dans les mélanges POE/PCV. Une faible dépression de la température de fusion du POE a été observée dans les mélanges de POE/PCV d'une concentration de PCV élevée. Le traitement des données par la formule Flory-Huggins indique que, au mieux, le POE et le PCV sont miscibles en partie dans l'état fondu. Il est possible que la depression de la température de fusion soit accentuée par le TTP, mais la depression observée dans le cas des mélanges ternaires n'excède pas l'incertitude expérimentale.

En général, les sphérolites qui cristallisent en presence des additifs sont plus grossières et moins biréfringentes que celles qui cristallisent de l'état fondu pur. L'étendue de la grossièreté augmente avec l'augmentation de la concentration des additifs. L'interprétation des cinétiques de cristallisation de POE en employant la théorie courante montre que la cristallisation de POE est caractéristique du régime III entre les écarts de température de cette étude. La discontinuité faible qui a lieu à -51 °C, et qui a été attribuée auparavant à une transition de régime II/III, est en réalité le résultat d'une transformation du plan cristallographique principal (010) à basse température au plan (120) à haute température. La vitesse de croissance des sphérolites de POE dans les mélanges POE/PCV n'est pas influencée par le PCV de 49 à 55 °C, même à des

2

È ·

concentrations de PCV élevées; mais la vitesse de croissance des sphérolites en présence du TTP est notamment baissée.

La microspectroscopie infrarouge dichroïque a été appliquée à l'investigation de la variation de la structure cristalline au niveau sous-sphérolitique. La détermination de la proportion dichroïque et de la proportion de certaines absorbances des spectres du POE pur (par la soustraction des spectres des additifs) a révélé que le PCV dérange l'orientation des cristallites de POE dans les sphérolites et que le PCV provoque une augmentation de la conformation trans planaire de POE. Il est évident que le POE, pour sa part, provoque une augmentation de la fréquence de la conformation trans planaire des molécules de PCV. Dans les mélanges ternaires la plastification du PCV par le TTP rend les chaînes de PCV plus flexibles et plus mobiles, et diminue l'effet du PCV sur le POE et la formation de la conformation trans planaire de POE. En effet, les cinétiques de cristallisation et la structure cristalline de POE peuvent être contrôlées par la sélection des concentrations de ces deux additifs, un résultat de grande importance pour le domaine des mélanges polymères.

2.77

 $\mathbb{C}$ 

iv

### Acknowledgments

The author wishes to thank Prof. G. Ronald Brown for his patience and guidance throughout the course of this study.

The author also wishes to thank: Dr. S. Varshney, for his synthesis of the poly(ethylene oxide); Ms. Kathy Singfield, for providing a photomicrograph of poly(R-cpichlorohydrin); Mr. Ilie Saracovan, for plotting unit cell diagrams of poly(ethylene oxide), using the facilities at l'Institut des Recherches Cliniques de Montréal; and the Natural Sciences and Engineering Research Council (NSERC) of Canada and the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (FCAR) of Quebec, for awards of postgraduate research scholarships.

ē,

~

3

-

## **Table of Contents**

Abstract	i
Résumé	iii
Acknowledgements	v
List of Tables	xi
List of Figures	xiv
List of Symbols and Abbreviations	xxi

## **1** Introduction

4

2

÷

1.1 Polymer Blends	1
1.2 Polymer Miscibility	3
1.2.1 Determination of Miscibility	4
1.2.2 Semicrystalline-Amorphous Polymer Blends	5
1.3 Polymer Crystallization	7
1.3.1 Pure Semicrystalline Polymer	7
1.3.1.1 Spherulite Birefringence	8
1.3.1.2 Variations in Spherulite Birefringence and	
Morphology	15
1.3.2 Spherulites in Semicrystalline-Amorphous Polymer Blends	20
1.4 Crystallization of Poly(ethylene oxide) from the Melt	22
1.4.1 Pure Polymer	22
1.4.2 Blends Containing Poly(ethylene oxide)	<b>. 24</b>
1.5 This Study	27
1.6 References	28

\_

::'

## 2 Surface Interfacial Tension

2.1	Introduction	34
2.2	Calculation of Surface Interfacial Tension	38
	2.3.1 Surface Interfacial Tension at 100 °C	38
	2.3.2 Surface Interfacial Tension at Selected Crystallization	
	Temperatures	41
2.3	Summary	43
2.4	References	43

# 3 Thermal Analysis and Miscibility

2

. ÷

2 • ÷

÷

ε,

. : <sup>-</sup> :

3.1	Introduction	45
	3.1.1 The Glass Transition Temperature	45
	3.1.2 The Equilibrium Melting Temperature	47
	3.1.2.1 Polymer Blends	48
	3.1.2.2 Polymer-Diluent Mixtures	50
	3.1.2.3 Experimental Determination of the Equilibrium	
	Melting Temperature	51
3.2	Procedure	53
	3.2.1 Sample Preparation	53
	3.2.1.1 Poly(ethylene oxide)	53
	3.2.1.2 Poly(vinyl chloride)	54
	3.2.1.3 Tricresyl Phosphate	55
÷	3.2.1.4 Poly(ethylene oxide)/Poly(vinyl chloride) Blends	55
	3.2.1.5 Mixtures Containing Tricresyl Phosphate	56

:

:

3.3.2 Differential Scanning Calorimetry	57
3.2.2.1 Glass Transition Temperature	57
3.2.2.2 Melting Temperature	58
3.3 Results and Discussion	58
3.3.1 Glass Transition Temperature	58
3.3.1.1 Poly(ethylene oxide)	58
3.3.1.2 Poly(ethylene oxide)/Poly(vinyl chloride) Blends	
and Tricresyl Phosphate Mixtures	60
3.3.2 Equilibrium Melting Temperature	64
3.3.2.1 Poly(ethylene oxide)	64
3.3.2.2 Poly(ethylene oxide)/Poly(vinyl chloride) Blends	68
3.3.2.2.1 Evaluation of Literature Results	76
3.3.2.3 Tricresyl Phosphate Mixtures	79
3.4 Summary	85
3.5 References	86

# 4 Polarized Light Microscopy: Spherulite Morphology and Crystallization Kinetics

:

 $(\mathbf{j}_{1},\mathbf{j}_{2})$ 

C

:

4.1 Introduction		
4.1.1 Crystallization Kinetics of Pure Semicrystalline Polymers	90	
4.1.1.1 Regime Transitions	96	
4.1.2 Semicrystalline-Amorphous Polymer Blends	100	
4.2 Procedure		
4.2.1 Preparation of Thin Sections	104	
4.2.2 Sample Premelting Conditions	104	
4.2.3 Spherulite Nucleation	105	

C

1

Ň

4.2.4 Observation of Spherulite Morphology and Measurement	
of Radial Growth Rates	106
4.3 Results and Discussion	107
4.3.1 Morphology	107
4.3.1.1 Poly(ethylene oxide)	107
4.3.1.2 Poly(ethylene oxide)/Poly(vinyl chloride) Blends	111
4.3.1.3 Tricresyl Phosphate Mixtures	127
4.2.2 Crystallization Kinetics	137
4.3.2.1 Poly(ethylene oxide)	142
4.3.2.1.1 Comment on the Importance of the	
Equilibrium Melting Temperature	152
4.3.2.2 Poly(ethylene oxide)/Poly(vinyl chloride) Blends	154
4.3.2.3 Tricresyl Phosphate Mixtures	157
4.3.2.3.1 Comment Regarding the Discontinuity	
in the Growth Rate Curve	165
4.4 Summary	166
4.5 References	168
5 Polarized Infrared Microspectroscopy	
5.1 Introduction	171
5.2 Procedure	175
5.3 Results and Discussion	178
5.3.1 Infrared Dichroism of Spherulites of Poly(ethylene oxide)	179
5.3.1.1 Poly(ethylene oxide)	_179
5.3.1.2 Poly(ethylene oxide)/Poly(vinyl chloride) Blends	188
5.3.1.3 Tricresyl Phosphate Mixtures	197
2	

11.

:

c

÷

.

-

. .

5.3.2 Conformation of Poly(ethylene oxide)	202
5.3.2.1 Poly(ethylene oxide) and Poly(ethylene oxide)/	
Poly(vinyl chloride) Blends	202
5.3.2.2 Mixtures Containing Tricresyl Phosphate	208
5.3.3 Conformation of Poly(vinyl chloride)	210
5.4 Summary	213
5.5 References	215

## 6 Conclusion

6.1	General Summary	217
6.2	Contributions to Original Research	220
6.3	Suggestions for Further Research	223

c

1.

Appendix

2

.7

Data for Figures

2

224

2

Ĵ

2

.

÷ .

### Tables

Table 1.1Selected examples of recent literature studies of semicrystalline-amorphouspolymer blends.p 20

Table 1.2 Examples of literature studies of the crystallization of PEO in blends. (Thenotation c or a denotes the crystalline or amorphous nature of the second component,respectively.)25

Table 2.1 Surface tension and surface interfacial tension data for PEO, PVC and TCP at100 °C.40

Table 2.2Surface interfacial tension data for PEO, PVC and TCP at Tc. (The subscriptsa and c denote amorphous and crystalline PEO, respectively.)41

**Table 3.1** Isomer distribution range of commerical tricresyl phosphate.55

Table 3.2 Equilibrium melting temperature and heat of fusion data for PEO and thePEO/PVC blends.73

Table 3.3 Equilibrium melting temeprature and heat of fusion data for PEO and TCPplasticizer mixtures83

Table 4.1 The nucleation density of spherulites of PEO grown at 49 °C in pure PEO, thePEO/PVC blends, and the mixtures containing TCP.116

1

ς

Table 4.2 Regime dependence of Z and the substrate length L.149

Table 4.3 Surface interfacial free energies and work of chain folding of PEO and variousother polymers. (The weight average molecular weight of a given PEO sample is listed inbrackets.)151

Table 4.4 Nucleation constant, surface interfacial free energies, and work of chain foldingin PEO spherulites crystallized from PEO, PEO/TCP (67/33) and PEO/PVC/TCP(55/12/33). The results for PEO/PVC/TCP (44/23/33) are identical with the results forthe mixture with lower PVC content.161

Table 5.1Vibrational assignments and dichroism of crystalline region of spherulites ofPEO formed at 49 °C.183

Table 5.2 Dichroic ratio data for PEO at 49, 51, 53 and 55 °C.185

Table 5.3 Dichroic ratio data for PEO and the PEO/PVC blends at 49 °C.193

Table 5.4 The dichroic ratio at 1468, 1455 and 1344 cm<sup>-1</sup> for PEO and the PEO/PVCblends,  $T_c$  49 and 55 °C.196

Table 5.5 Dichroic ratio data for PEO and mixtures containing TCP.199

Table 5.6 Dichroic ratio data for the modes at 1468, 1455 and 1344 cm-1 for PEO andmixtures containing TCP, at  $\Delta T = -2$  °C and  $\Delta T = +4$  °C with respect to the reportedkinetic discontinuity.201

2

ŀ

**Table 5.7** Peak ratio data for the parallel spectra, that is  $r_{11}$ , of PEO and the PEO/PVCblends at 49 °C. Data for the perpendicular spectra are plotted in Figure 5.14. The ratioslisted are all in the form  $A_{planar}/A_{helical}$ .208

**Table 5.8** Peak ratio data for PEO and mixtures containing TCP,  $\Delta T = -2$  °C. The ratios of the perpendicular components of the absorbance,  $r_{\perp}$ , are given before the ratios of the parallel components,  $r_{\parallel}$ . The ratios listed are all in the form  $A_{\text{planar}}/A_{\text{helical}}$ . 209

Table 5.9 Dichroic ratio and peak ratio data for PVC-containing samples and a solution-cast PVC film. The film was cast from tetrahydrofuran at room temperature. The peakratios given correspond to the parallel spectra.211

7

### Figures

5

Figure 1.1 Photomicrograph, taken using a polarized light microscope, of a spherulite of poly(ethylene oxide) crystallized at 45 °C. p 9

Figure 1.2 (a) Diagram of a polymer spherulite with radially growing crystallite fibrils. (b) Enlarged oblique view of the tip of a spherulite fibril, growth direction G. The crystalline chain segments or "stems", shown as rectangular blocks, are laid down perpendicular to the fibril direction.

Figure 1.3 (a) The resolution of plane polarized light of amplitude A into two components along the principal refractive indices of a sample,  $n_1$  and  $n_2$ . (b) Resolution of the light transmitted by the sample by an analyzer that is positioned at a right angles with respect to the polarizer in (a). (After reference 28, p 89.) 12

Figure 1.4 Close-up of a negatively birefringent spherulite of PEO: (a) without any compensators; (b) with a sensitive tint plate; and (c) with a quarter-wave plate. The vibration directions of the slow and fast components of light in the compensators are indicated at the upper right.

Figure 1.5 Spherulites of  $poly(\beta-hydroxybutyrate)$  crystallized at 50 °C showing relatively regular extinction rings. 17

Figure 1.6 Spherulites of poly(*R*-epichlorohydrin) crystallized at 80 °C. 18

xiv

Figure 1.7Spherulites of isotactic polypropylene: (a) Types I (dark) and III (bright).crystallized at 122 °C; (b) "mixed" type, crystallized at 127 °C.19

Figure 3.1 (a) The glass transition of interlamellar, amorphous PEO. (b) The glass transition in (a) and the melting transition of mainly crystalline PEO. 61

Figure 3.2 Melting endotherms of PEO crystallized at 51, 55 and 59 °C. 66

Figure 3.3 Hoffman-Weeks plot for pure PEO. 67

Figure 3.4 Melting endotherms of PEO/PVC blends: (a) PEO/PVC (75/25),  $T_c$  51, 53 and 55 °C: (b) PEO/PVC (90/10), PEO/PVC (75/25) and PEO/PVC (50/50),  $T_c$  53 °C. 69

Figure 3.5 Hoffman-Weeks plots for various PEO/PVC blends: (a) PEO/PVC (90/10), PEO/PVC (82/18), (c) PEO/PVC (75/25), (d) PEO/PVC (65/35), and (e) PEO/PVC (50/50). (f) Equilibrium melting temperature,  $T_m^{\circ}$ , as a function of PVC content. 70

Figure 3.6 Flory-Huggins plot for PEO/PVC blends.75

 Figure 3.7 Melting endotherms of TCP mixtures: (a) PEO/TCP (67/33),  $T_c$  43, 45 and 47 °C; (b) PEO/PVC/TCP (44/23/33),  $T_c$  43, 45 and 47 °C.
 80

Figure 3.8 Hoffman-Weeks plots for (a) PEO/TCP (67/33), (b) PEO/PVC/TCP (55/12/33), and (c) PEO/PVC/TCP (44/23/33). 81

Figure 4.1 Schematic growth rate-temperature curve.

Figure 4.2 Secondary surface nucleation model showing stem deposition. 94

Figure 4.3 Ideal (a) logarithmic growth rate curve, and (b) Hoffman-Lauritzen plotshowing crystallization regimes I, II and III.97

Figure 4.4 PEO spherulite morphology at various  $T_c$ : (a) 45 °C, (b) 49 °C, and (c)  $T_n$ 40 °C (~ 120 µm) - $T_c$  55 °C.

 Figure 4.5
 PEO/PVC blends at 100 °C: (a) PEO/PVC (90/10), (b) PEO/PVC (82/18),

 (c) PEO/PVC (75/25), (d) PEO/PVC (65/35), and (e) PEO/PVC (50/50).
 112

Figure 4.6 Variation of spherulite morphology with PEO/PVC blend composition at  $T_c$ 49 °C: (a) PEO/PVC (90/10), (b) PEO/PVC (82/18), (c) PEO/PVC (75/25), (d) PEO/PVC (65/35), and (e) PEO/PVC (50/50). 113

Figure 4.7 Variation of nucleation density with PEO/PVC blend composition at  $T_c$ 49 °C: (a) PEO, (b) PEO/PVC (90/10), (c) PEO/PVC (82/18), (d) PEO/PVC (75/25), (e) PEO/PVC (65/35), and (f) PEO/PVC (50/50). 117

Figure 4.8 Nucleation density as a function of PVC content. 120

Figure 4.9 Variation of dispersion of PVC within the crystalline matrix as a function of PEO/PVC blend composition at  $T_c$  49 °C: (a) PEO, (b) PEO/PVC (90/10), (c) PEO/PVC (82/18), (d) PEO/PVC (75/25), (e) PEO/PVC (65/35), and (f) PEO/PVC (50/50).

Service - States - Service

Figure 4.11 Vein formation in the growth direction in PEO/PVC (50/50) at 49 °C.

128

Figure 4.12 Bloom formation in PEO/PVC (50/50), 49 °C, after annealing at 150 °C: (a) initial stage, and (b) completed bloom. 129

 Figure 4.13
 Mixtures containing TCP at 100 °C: (a) PEO/TCP (67/33), (b)

 PEO/PVC/TCP (55/12/33), and (c) PEO/PVC/TCP (44/23/33).
 130

Figure 4.14 Spherulite morphology in TCP mixtures at a constant undercooling of 2 °C from the kinetic transition in PEO at ~ 51 °C: (a) PEO/TCP (67/33),  $T_c$  40 °C, (b) PEO/PVC/TCP (55/12/33),  $T_c$  38 °C, and (c) PEO/PVC/TCP (44/23/33),  $T_c$  38 °C. 132

 Figure 4.15 Banding in spherulites in TCP mixtures at  $T_c$  35 °C: (a) PEO/TCP (67/33),

 (b) PEO/PVC/TCP (55/12/33), and (c) PEO/PVC/TCP (44/23/33).

 134

Figure 4.16 Nucleation density in TCP mixtures: (a) PEO/TCP (67/33),  $T_c$  40 °C, (b) PEO/PVC/TCP (55/12/33),  $T_c$  38 °C, and (c) PEO/PVC/TCP (44/23/33),  $T_c$  38 °C.

-

138

Figure 4.17 Dispersion of additives in TCP mixtures: (a) PEO/TCP (67/33),  $T_c$  40 °C, (b) PEO/PVC/TCP (55/12/33),  $T_c$  38 °C, and (c) PEO/PVC/TCP (44/23/33),  $T_c$  38 °C. 140

 Figure 4.18
 Spherulite radial growth rate of PEO as a function of crystallization temperature.
 143

 Figure 4.19
 Logarithmic growth rate plot for PEO.
 144

 Figure 4.20
 Fit of the growth rate data for PEO to the Hoffman-Lauritzen equation.
 146

 Figure 4.21
 Hoffman-Lauritzen plot for PEO using equilibrium melting temperatures of (a) 76 °C and (b) 62 °C.
 147

 Figure 4.22
 Spherulite radial growth rate as a function of PEO/PVC blend composition at various T<sub>c</sub>. (The average growth rate at each temperature is shown by a dotted line.)
 156

Figure 4.23 (a) Spherulite radial growth rate as a function of crystallization temperature in mixtures containing TCP. (b) Logarithmic growth rate plot. The corresponding plot for pure PEO is shown for reference. 158

Figure 4.24Hoffman-Lauritzen plots for spherulites grown in TCP mixtures. Thecorresponding plot for PEO is shown for reference.160

Figure 5.1 Schematic of the Perkin-Elmer Infrared Microscope (after reference 10).

Ţ

2

°177

Figure 5.2 Dichroic spectra of semicrystalline PEO,  $T_c$  49 °C: parallel spectrum (a) before and (b) after subtraction of the amorphous component of PEO. 180

Figure 5.3 Dichroic spectra of purely crystalline PEO,  $T_c$  49 °C: perpendicular spectrum (a) before and (b) after subtraction of the amorphous component of PEO. 181

Figure 5.5 Unit cell diagram of PEO showing (010) and (120) and radial directions.

Figure 5.6 Illustration of various CH<sub>2</sub> vibrational modes (after reference 12). 189

Figure 5.7 Spectrum of a solution-cast film of PVC. 190

Figure 5.8 Dichroic spectra of PEO/PVC (75/25),  $T_c$  49 °C (a) parallel spectrum before and after subtraction of the contributions from PVC and amorphous PEO, and (b) perpendicular spectrum before and after difference spectroscopy. 191

Figure 5.9 Dichroic ratio, R, as a function of PEO/PVC blend composition,  $T_c$  49 °C, at: (a) 1455 and 1344 cm<sup>-1</sup>, and (b) 1243 and 965 cm<sup>-1</sup>.

Figure 5.10 The Herman orientation function, F, at 1344 cm<sup>-1</sup> as a function of PVC content, T<sub>c</sub> 49 °C. 195

Figure 5.11 Original and difference spectra for (a) PEO/TCP (67/33),  $T_c$  40 °C, and (b) PEO/PVC/TCP (44/23/33),  $T_c$  38 °C. 198

;

Figure 5.12 (a) Distorted  $7_2$  helix and (b) planar zig-zag conformations of PEO. The upper view is along the crystallographic c axis, and the lower view is perpendicular to the c axis. (After reference 14.) 203

Figure 5.13 Difference spectra of PEO/PVC (50/50) (a) parallel spectrum before and after subtraction of pure PEO from the spectra of crystalline PEO obtained from the blend, and (b) perpendicular spectrum before and after difference spectroscopy. Note the residual peaks at 1344, 1243 and 965 cm<sup>-1</sup>. 206

Figure 5.14 Peak ratio,  $r_{\perp}$ , as a function of PEO/PVC blend composition for the following band pairs: (a) 1344/1360, (b) 1243/1281, (c) 965/1062 and (d) 965/843.

2

207

# Symbols and Abbreviations

Symbols

÷

a <sub>o</sub>	width of a crystallizing stem
A	amplitude
Α	absorbance
$A_{\parallel}, A_{\perp}$	absorbance with polarizer oriented parallel and perpendicular,
	respectively
b <sub>o</sub>	thickness of a crystallizing stem in the growth direction
С	concentration
C <sub>p</sub>	heat capacity
Ei	energy parameters (Bartczak-Galeski-Martuscelli equation)
ΔE <sub>d</sub>	activation free energy of transport
f	correction factor for heat of fusion (Hoffman-Lauritzen equation)
F	Herman orientation function
Δf	surface interfacial free energy difference (Bartczak-Galeski-Martuscelli
	equation)
$f_{1c2}$	surface interfacial free energy between component 2 and crystallizing
	front
<i>f</i> <sub>1a2</sub>	surface interfacial free energy between component 2 and molten
	component 1
g	rate of surface spreading
G	spherulite growth rate
Go	pre-exponential factor of Hoffman-Lauritzen growth rate equation
G <sub>I</sub> , G <sub>II</sub> , G <sub>III</sub>	growth rates in regime I II and III

$\Delta G$	change in Gibbs free energy	
$\Delta G_{\mathrm{m}}$	Gibbs free energy of mixing	
ΔΗ	change in enthalpy	
∆H <sub>bl</sub>	heat of fusion of blend	
$\Delta H_{f}$	heat of fusion	
∆H <sub>l</sub> °	equilibrium heat of fusion	
i	secondary surface nucleation rate	
j	regime constant (Hoffman-Lauritzen equation)	
k	Boltzmann's constant	
k	constant of Gordon-Taylor equation	
Kg	nucleation constant (Hoffman-Lauritzen equation)	
1	crystalline stem length	
L, L'	substrate length and effective substrate length, respectively	
Lcaic	calculated substrate length	
n	constant of Boon-Azcue equation nucleation term	
n <sub>s</sub> , n <sub>s</sub> '	number of surface nuclei	
<i>n</i> <sub>1</sub> , <i>n</i> <sub>2</sub>	principal refractive indices 1 and 2	
q	work of chain folding	
r	correlation coefficient	
r <sup>2</sup>	coefficient of determination	
I.	retardation	
r	peak ratio	
R	ideal gas constant	
R	dichroic ratio	
Ro	ideal dichroic ratio	: :
s <sup>2</sup>	variance	
ΔS	change in entropy	
		·

\_

ことないとうないであるという

**t** .

t	thickness
t	path length of absorption (Beer's law)
Т	temperature
T <sub>c</sub>	crystallization temperature
T <sub>cr</sub>	critical temperature
Т <sub>g</sub>	glass transition temperature
T <sub>g,bl</sub>	glass transition temperature of blend
T <sub>gi</sub>	glass transition temperature of component i
T <sub>m</sub>	melting temperature
Τ <sub>m</sub> °	equilibrium melting temperature
T <sub>m,bl</sub> °	equilibrium melting temperature of blend
T <sub>n</sub>	nucleation temperature
Τ <sub>Ιρ</sub>	rotating-frame spin-lattice relaxation time
T.	temperature of cessation of molecular motion
%T	percent transmittance
Ŭ*	activation energy for reptation in the melt
ν	specific volume
ν	wavenumber
Vi	molar volume of component i
w <sub>i</sub>	weight fraction of component i
x	nucleation parameter of Lauritzen Z-test
xp	polarity
2	Z parameter of Lauritzen Z-test
	:

Greek Symbols

×.

 $\alpha_{LH}$ 

.7

2

÷

Lauritzen-Hoffman parameter

2

÷

:

з.

ī

: 5

$\alpha_{g}, \alpha_{r}$	isobaric volumetric thermal expansion coefficient of glass and rubber,
	respectively
β	Macloed's exponent
γ	surface tension
γ <sub>o</sub>	empirical constant for temperature dependence of surface tension
γ <sub>12</sub>	surface interfacial tension
γP, γ <sup>d</sup>	polar and dispersive contributions to surface tension, respectively
Yc+ Ya	surface tensions of crystalline and amorphous phases, respectively
γ <sub>1c2</sub>	surface interfacial tension between component 2 and crystalline
	component 1
$\gamma_{1a2}$	surface interfacial tension between component 2 and amorphous
	component 1
3	molar absorptivity
κ	compressibility
η	lamellar thickening factor
θ	angle
ρ	density
ρ <sub>c</sub> , ρ <sub>a</sub>	crystalline and amorphous density, respectively
σ, σ <sub>c</sub>	lateral and fold surface interfacial free energy, respectively
υ <sub>i</sub>	volume fraction of component i
<b>•</b>	orientation angle between the draw direction and the molecular axis
ΔΦ	activation free energy for formation of a critical nucleus
Ψ	transition moment angle
X12	polymer-polymer interaction parameter

15

:

0

Ţ

xxiv

## Abbreviations

· \* •

DCE	1,2-dichloroethane
DES	dielectric spectroscopy
DMTA	dynamic mechanical thermal analysis
DSC	differential scanning calorimetry
EDS	electron dispersive spectroscopy
i	isotactic
IR	infrared spectroscopy
IRM	infrared microspectrscopy
NMR	nuclear magnetic resonance spectroscopy
ΡE	polyethylene
PECH	poly(epichlorohydrin)
PEO	poly(ethylene oxide)
PHB	poly(β-hydroxybutyrate)
PIRM	polarized infrared microspectroscpy
PLM	polarized light microscopy
PLLA	poly(L-lactic acid)
PMMA	poly(methyl methacrylate)
iPP	isotactic polypropylene
PVC	poly(vinyl chloride)
PVME	poly(vinyl methylether)
SANS	small angle neutron scattering
SAXS	small angle X-ray scattering
SEM	scanning electron microscopy
TCP	tricresyl phosphate
TEM	transmission electron microscopy

Ę

:

2

-

. =.

÷

:

## Introduction

#### **1.1 Polymer Blends**

The modification of polymers by copolymerization, filling, plasticization and, most recently, blending has produced materials with a wide variety of properties unparalleled by natural systems. A polymer blend is an intimate combination of two or more polymers that are constitutionally or configurationally different and are not bonded to one another (1). When two polymers are mixed the most common product is an almost completely phase-separated system due to the low entropy of mixing of large molecules which leads to a low driving force for miscibility. A miscible polymer blend, that is, a blend that is homogeneous at the molecular level, can result when the two constituent polymers exhibit a negative enthalpy of mixing which leads to a negative free energy of mixing. On the other hand, immiscible blends typically consist of polymers that exhibit a positive enthalpy of mixing. The term "compatible" is often used to describe blends that are visually homogeneous and that exhibit useful properties that are not attainable using either of the individual polymers; but this term does not imply miscibility or homogeneity at the molecular level (1).

The major incentive for the development of commercial blends is the economic advantage that is derived from the use of a second, inexpensive component that reduces the amount of a more expensive primary component that is required for a given end use (1). Another highly significant advantage of blending is that the careful selection of the blend components and the processing conditions permits the creation of high performance materials with properties that can be tailored to a specific application. Blending is also a

very important process in the recycling of plastics, mainly because of the prohibitive cost of extracting pure polymers from most of the materials that are received by recycling facilities.

There are several approaches to the preparation of polymer blends that include: (i) solution blending followed by film casting, freeze drying, or precipitation by a nonsolvent; (ii) mechanical mixing; and (iii) *in situ* polymerization of the components (1). Mechanical mixing, which may involve the mixing of fine powders or melt mixing, is frequently referred to as "dry blending", as opposed to the "wet" technique of solution blending. Dry blending techniques are predominant in industrial settings because these techniques are more economical for the processing of large quantities of materials. The dry blending techniques do not require the vast quantities of solvent that must be recycled. Additional compatibilizing agents can be added to dry blends to promote adhesion between the blend components, and thereby increase the degree of dispersion within the blend. Typical compatibilizers are either low molecular weight compounds that interact favorably with both of the polymers in a binary blend, or block or graft copolymers that may contain two different kinds of blocks that are designed to interact with each of the two polymers (1).

Binary polymer blends may consist of: (i) two amorphous polymers, (ii) two semicrystalline polymers, or (iii) a semicrystalline polymer and an amorphous polymer. Low molecular weight additives such as plasticizers can also be used to control the ultimate properties of a polymer or a polymer blend. Plasticizers are a class of additives that are commonly used to increase the flexibility of a polymer and thereby increase the number of possible applications, or to decrease the melt viscosity of a polymer, an important consideration in polymer processing (2). Obviously, the design of new materials demands a detailed knowledge of the interactions between the various pairs of components in a mixture as a function of the composition of the mixture under the relevant conditions for the processing and the application of the material. The most important consideration in the creation of polymer blends is the miscibility of the

1. 1. 1. 2. S. 2. A.

components. Miscibility is a governing factor in the morphology and the crystallization kinetics of semicrystalline polymers that are crystallized from the melt in blends with amorphous polymers. The following sections discuss aspects of polymer miscibility and crystallization that are relevant to the research presented in subsequent chapters.

#### **1.2 Polymer Miscibility**

As stated in the preceding section, the entropy of mixing of two polymers is very small; therefore the free energy of mixing is approximately equivalent to the enthalpy of mixing. The free energy of mixing of two polymers,  $\Delta G_m$ , can be described by the relation shown below, which was derived by Flory and Huggins,

$$\Delta G_{\rm m}/{\rm RTV} = \chi_{12}\upsilon_1\upsilon_2 \tag{1.1}$$

where R is the ideal gas constant, T is the temperature, V is the molar volume,  $\chi_{12}$  is the polymer-polymer interaction parameter, and  $\upsilon_i$  is the volume fraction of component i (3,4). The interaction parameter is a measure of polymer miscibility and is dependent on both temperature and composition. The value of  $\chi_{12}$  may also depend on molecular weight, the identity of end-groups in the case of short chains, and pressure (5).

For two polymers to be miscible the interaction parameter must be negative. The condition  $\chi_{12} < 0$  is met when two polymers exhibit favorable specific interactions such as hydrogen-bonding (see, for example references 6-10). It must be kept in mind that although the chemical miscibility of two polymers is a requirement for blend homogeneity at the molecular level, the degree of homogeneity achieved may depend on the processing conditions of a blend; that is, inadequate physical mixing may lead to an inhomogeneous mixture. On the other hand, the very thorough mixing of two immiscible polymers can

yield a blend with a very high, albeit not molecular, level of dispersion. Polymer miscibility will be discussed in more detail in Chapter 3.

#### 1.2.1 Determination of Miscibility

Among the wide variety of techniques that are available for the measurement of dispersion in polymer blends, there are several techniques that can be used to determine the miscibility of two polymers. For example, polarized light microscopy (PLM) permits a facile, visual inspection of samples for homogeneity at the micron level; while scanning and tunnelling electron microscopic techniques (SEM and TEM, respectively) have a spatial resolution that extends to the sub-nanometer scale (11). In addition, SEM in the electron dispersive spectroscopy (EDS) mode can be used to map local chemical variations in thin sections of samples (12). Infrared spectroscopy can provide valuable information about the nature and the degree of specific interactions in a blend (13), and can also be employed for chemical mapping, although only on the micron scale (14).

Thermal analysis is commonly used to estimate the value of the interaction parameter, although the use of this technique provides limited information in the case of blends that contain a crystallizing polymer. Diffraction techniques such as small angle neutron scattering (SANS) or wide and small angle X-ray scattering (WAXS and SAXS, respectively) are applicable on a sub-micron to nanometer scale, and provide an alternative route for the determination of the value of the interaction parameter (see, for example, references 15, 16). These and other methods are described in detail in reference 1.

Fluorescence and solid-state nuclear magnetic resonance spectroscopy (NMR) are two techniques that have been applied to the study of molecular level mixing in blends (1,5). The application of solid state NMR to the study of polymer miscibility will be discussed in Chapter 3. The most common type of fluorescence that is exploited for this purpose is excitation fluorescence (1). This type of fluorescence can be observed in polymers that contain aromatic functional groups which are capable of forming dimers or "excimers", where the aromatic groups are separated by a distance of approximately 5 Å (5). In a phase-separated blend that is composed of a fluorescent polymer, such as polystyrene, and a non-fluorescent polymer, such as poly(vinyl methylether) (17), the excimer fluorescence is expected to be close to the value measured for the pure fluorescent polymer. However, when molecular level mixing occurs, the formation of excimers is disrupted by the presence of the non-fluoresceng polymer, and the intensity of the excimer fluorescence can be reduced drastically, as in the case of blends of poly(vinyl naphthalene) and poly(vinyl acetate) (18). Alternatively, the two blended polymers may each possess complementary groups that form excimers when the molecules of the two different polymers are in close proximity (5). Another variation of the technique involves the addition of fluorescent labels to normally non-fluorescent polymers (19).

#### 1.2.2 Semicrystalline-Amorphous Polymer Blends

The crystallization of semicrystalline polymers in blends of semicrystalline and amorphous polymers is a topic of tremendous importance in the field of polymer science. Semicrystalline polymers, including polyethylene and polypropylene for example, account for the majority share of commercially produced polymers (1). Of this total production, more than half of the polymers are sold as blends.

The question of miscibility in this type of blend is much more complex than in the case of a blend consisting of two amorphous polymers. Two amorphous polymers may be miscible, immiscible, or partially miscible, where partial miscibility implies miscibility under specific conditions of molecular weight, temperature, and concentration. In blends containing a semicrystalline polymer and an amorphous polymer, the miscibility of the amorphous phase of the semicrystalline component with the amorphous second component must be considered separately from the miscibility of the crystalline phase of

the semicrystalline polymer with the second component. In each instance, the two polymers may be miscible, immiscible, or partially miscible, although the miscibility of the amorphous second component with the crystalline phase of the semicrystalline polymer is rare (1).

In a completely immiscible blend, the crystallization of the semicrystalline polymer is generally unperturbed by the presence of the second component. However, in some systems of this type the crystalline morphology and the crystallization kinetics may be affected due to the interfacial interactions between the two polymers. It must be kept in mind that in spite of the absence of miscibility, the two polymers may still be highly dispersed. Furthermore, they may also exhibit a significant degree of adhesion, in particular between the amorphous phases of the semicrystalline polymer and the second component. As a result, the two components may interact in such a way as to alter the crystalline structure of the crystallizing component.

Semicrystalline-amorphous polymer blends that are miscible in the amorphous phase are considered to be "miscible" blends (1). The amorphous component is observed to be miscible with the melt of the crystallizing polymer. In such systems, the crystallization of the semicrystalline polymer occurs from a one-phase melt. Because the amorphous component acts as a diluent in the melt, a melting temperature depression is frequently observed (20). During the crystallization process, portions of the amorphous component can be included within the crystalline matrix in amorphous regions that are located between the crystalline lamellae or between other crystalline structures. Obviously, this inclusion of the amorphous component can have drastic morphological and kinetic ramifications (see, for example, references 21-26), some of which will be examined in the appropriate sections of the thesis.

#### **1.3 Polymer Crystallization**

#### 1.3.1 Pure Semicrystalline Polymer

The apparently simple process of the crystallization of polymers from the melt is, in fact, a complex process that results in the ordering of long, randomly coiled polymer chains into specific three-dimensional chain-folded arrangements in the crystalline state. The ordering process involves a decrease in entropy, the magnitude of which depends largely on the degree of ordering in the melt; hence, according to the definition of Gibbs' free energy,

$$\Delta G = \Delta H - T \Delta S \tag{1.2}$$

this entropy decrease must be compensated by a negative change in enthalpy in order to cause a favorable change in the free energy. As the temperature of a polymer sample is decreased from above its melting temperature to its melting temperature, the volume available to the macromolecules decreases, restricting their rotational and translational freedom. This restriction of movement, which is favored by the presence of substituent groups that promote intramolecular attraction or rigid close-packing of chain segments, allows neighboring segments to align in an ordered fashion in close-packed arrays known as crystallites. Variations in the density of the melt created by chain ordering (homogeneous nucleation) or an impurity (heterogeneous nucleation) can act as a nucleus from which a spherulite can form (27).

A wide variety of substances, ranging from naturally occurring minerals to stereochemically regular synthetic polymers crystallize in the form of spherulites. Differences in chemical composition among these materials lead to significant differences in crystal packing, and therefore spherulite birefringence, morphology, and growth rate.
The growth of polymer spherulites from the melt, when viewed with a polarized light microscope, is a phenomenon that is truly striking in its beauty and apparent simplicity. Spherulites are regular birefringent structures with spherical symmetry in three dimensions and circular symmetry in thin section. An example of a thin section of a spherulite of poly(ethylene oxide) is shown in Figure 1.1. Spherulites are composed of crystallite fibrils that grow radially outward from the nucleus as shown schematically in Figure 1.2a (28). Low-angle branching occurs along the fibrils due to the presence of defects in fibril structure, or material, usually residual amorphous polymer or foreign particles, that have not been incorporated into the spherulite. This branching is responsible for the space-filling geometry of spherulites. Within a fibril, polymer chain segments or "stems" are laid down on the growth surface in an analogous manner to bricklaying (see Figure 1.2b) (29). It is important to note that the stems are oriented perpendicular to the spherulite radius. The stem length, that is the fibril thickness, is typically  $\sim 0.1 \,\mu\text{m}$  and is a characteristic specific to a given polymer and set of crystallization conditions. In general, macromolecules possess an end-to-end distance in the crystalline conformation that is greater than the stem length and consequently must fold to accommodate the fibril thickness (29). Depending on the relative lengths of the stems and the chains, a given chain may fold numerous times before crystallization is complete. Re-entry into the fibril after folding may be adjacent or nonadjacent. The noncrystalline chain folds and loose chain ends constitute part of the amorphous material found within the crystalline matrix. A straightforward, detailed examination of spherulite structure is given in the text by Sharples (30).

1.3.1.1 Spherulite Birefringence

=:

Spherulites are birefringent structures that can range in size from approximately  $1 \mu m$  to 1 mm in diameter, depending on the nucleation density. They are generally not



Figure 1.1 Photomicrograph, taken using a polarized light microscope, of a spherulite of poly(ethylene oxide) crystallized at 45 °C.

~



stem

à,

Figure 1.2 (a) Diagram of a polymer spherulite with radially growing crystallite fibrils. (b) Enlarged oblique view of the tip of a spherulite fibril, growth direction G. The crystalline chain segments or "stems", shown as rectangular blocks, are laid down perpendicular to the fibril direction. visible in ordinary light but can be seen readily in thin section between crossed polars using a polarized light microscope. A polymer melt is amorphous and therefore optically isotropic, and no light is viewed through the analyzer when the polars are crossed. On the other hand, polarized light of amplitude A that is incident upon optically anisotropic, doubly refracting regions such as spherulites is resolved into a fast component and a slow component vibrating in the directions of the mutually perpendicular principal refractive indices of the crystalline structure,  $n_1$  and  $n_2$  (see Figure 1.3a) (31). In spherulites, the principal refractive indices are radial and tangential. Due to the difference between  $n_1$ and  $n_2$ , the two components of light travel through the sample at different velocities and therefore exit the sample with a path difference or retardation. If  $n_1 > n_2$ , then the amplitude of the slow component is given by  $A \cos\theta$ , and the amplitude of the fast component is given by A sin $\theta$  (see Figure 1.3a); if  $n_1 < n_2$ , then the opposite is true. When the refractive index parallel to the radial direction of the spherulite is greater than that perpendicular to the radial direction, the spherulite is said to be "positive". When the converse is true, the spherulite is "negative". Most polymer spherulites are negatively birefringent.

In the analyser, which is set perpendicular to the polarizer, the two components are recombined to yield a single component vibrating in the direction of the analyzer, with an amplitude of (A sin $\theta \cos \theta$  + A  $\cos \theta \sin \theta$ ) (see Figure 1.3b). The path difference causes constructive and destructive interference of specific wavelengths of white light. The resultant wavelengths yield interference colors of the sample, which vary in accordance with Newton's series (32). The Maltese cross extinction pattern characteristic of regularly birefringent spherulites, that is, the black cross clearly visible on the spherulite in Figure 1.1, is observed due to the coincidence of the mutually perpendicular optic axes of the spherulite with the respective orientations of the polarizer and the analyzer. The regions of the sample that have optic axes parallel to the vibration direction of the polarizer will transmit the light from the polarizer, but this light will not be observed



Figure 1.3 (a) The resolution of plane polarized light of amplitude A into two components along the principal refractive indices of a sample,  $n_1$  and  $n_2$ . (b) Resolution of the light transmitted by the sample by an analyzer that is positioned at a right angles with respect to the polarizer in (a). (After reference 31, p 89.)

2

2

12

Ċ,

through the analyzer when the latter is perpendicular to the polarizer. The regions of the sample with optic axes perpendicular to the vibration direction of the polarizer will not transmit any light, so that in this case also, no light will be transmitted through the analyzer. The regions of the sample that have optic axes that are not perpendicular to either the polarizer or the analyzer transmit light through the analyzer and are seen as the bright areas of the spherulite in Figure 1.1.

The sign and the magnitude of the birefringence of a spherulite can provide information about the relative orientation of crystalline substructures within the spherulite, providing the unit cell of the polymer is known. Generally, a polarized light microscope is equipped with accessories that can be inserted between the objective and the analyzer to obtain fixed or variable retardation, thereby permitting the determination of the retardation of a wide range of samples. The sign of the birefringence of a sample can be determined using a first-order red (or sensitive tint) plate or a quarter-wave plate. The direction of vibration of the slower component is usually marked by the manufacturer on these plates. When the slow component of light transmitted by the sample is parallel to that of the sensitive tint plate, that is, the sample is positively birefringent, then retardation is added to the sample, which changes the interference color to a shade of blue. If the slow component is perpendicular to that of the sample, that is, the sample is negatively birefringent, then retardation is subtracted from the sample, which changes the interference color to a shade of yellow. In the case of a quarter-wave plate, when the slow components of the plate and the sample are parallel, the sample appears bright white or yellow; when the two components are perpendicular, the sample appears dark gray or black (33). Figure 1.4 is a series of photomicrographs of a typical spherulite of poly(ethylene oxide) viewed through crossed polars, without a compensator (Figure 1.4a), and with sensitive tint and quarter-wave plates (Figures 1.4b and 1.4c, respectively). Comparison of the vibration direction of the slower component of light of the compensators with the colors observed using these plates indicates that the given



Figure 1.4 Close-up of a negatively birefringent spherulite of PEO: (a) without any compensators; (b) with a sensitive tint plate; and (c) with a quarter-wave plate. The vibration directions of the slow and fast components of light in the compensators are indicated at the lower right.

spherulite is negatively birefringent. A positively birefringent spherulite would exhibit similar colors, but the pattern would be rotated by 90°.

Knowledge of the interference colors and the thickness of a sample permit calculation of the birefringence from the relation

$$\mathbf{r} = \mathbf{t}(n_1 - n_2) \tag{1.3}$$

where r is the retardation or the interference color (in units of nm), t is the thickness (nm), and  $(n_1 - n_2)$  is the difference between the two principal refractive indices, that is, the birefringence (32). This relation permits a very accurate determination of birefringence, providing that the measurement of the sample thickness is accurate. Sample thickness can be measured with a micrometer screw gauge or the fine focusing micrometer on most microscopes. In the latter method, the microscope is focused on the top surface of the coverslip and then on the slide surface. The sample thickness is the difference between these two readings less the coverslip thickness. It is important to take the average of a number of measurements of a given sample to allow for local variations in the thicknesses of the sample and the glass. The details of the procedure for the accurate determination of the interference colors of different classes of samples, using a quartz wedge and the Michel-Lévy interference color chart, which provides a graphical relation among the three parameters in equation 1.3, are given in many polarized light microscope instruction manuals and numerous texts (see, for example, references 31-35).

### 1.3.1.2 Variations in Spherulite Birefringence and Morphology

Although the basic structure of most spherulites resembles the schematic diagram presented in Figure 1.2, the observation of the growth of spherulites of different polymers at a variety of crystallization temperatures reveals that spherulite birefringence and

morphology vary with chemical identity, unit cell, and crystallization temperature and pressure. Certain polymers, such as linear poly(ethylene) (36) and poly( $\beta$ -hydroxybutyrate) (37) (Figure 1.5) exhibit regularly spaced extinction rings or bands in addition to radial extinction. Stereoregular poly(epichlorohydrin) (Figure 1.6) is an outstanding example of a polymer that forms banded spherulites (38). In general, concentric rings are attributed to the cooperative twisting of radial fibrils along the axes of growing crystallite fibrils. These patterns range from the rough, herringbone bands to regular rings depending on the polymer and the crystallization conditions.

Isotactic polypropylene (iPP) is a particularly interesting example of the rich morphological diversity of semicrystalline polymers because over a 20-degree temperature range, it crystallizes in five different types of spherulitic morphologies, classified according to crystal structure, birefringence, banding, and crystallization temperature (39). The polymer crystallizes in a monoclinic unit cell in Types I, II and a "mixed" type, and in a hexagonal unit cell in Types III and IV. The appearance of Types I and II resembles the spherulite of PEO shown in Figure 1.1, also the result of a monoclinic unit cell, and they are visually indistinguishable; but Type I (the dark spherulites in Figure 1.7a) is positively birefringent and crystallizes below ~ 134 °C; whereas Type II is negatively birefringent and crystallizes above ~ 134 °C. The mixed type (Figure 1.7b) is positively and negatively birefringent in different regions of the spherulite and crystallizes below ~ 140 °C. Types III (<127 °C) (the bright spherulite in Figure 1.7a) and IV (127-132 °C) appear much brighter than the monoclinic types, and they are both negatively birefringent. These last two types of spherulites also exhibit longer induction times, higher radial growth rates, and lower melting temperatures than the monoclinic types. Jagged concentric banding distinguishes Type IV from Type III. It is important to note that, as has been observed in the case of iPP, spherulites that crystallize in different morphologies at a given temperature also have different radial growth rates.

d .



Figure 1.5 Spherulites of  $poly(\beta-hydroxybutyrate)$  crystallized at 50 °C showing relatively regular extinction rings.



Figure 1.6 Spherulites of poly(*R*-epichlorohydrin) crystallized at 80 °C.



**(b)** 

(a)

## 1.3.2 Spherulites in Semicrystalline-Amorphous Polymer Blends

The addition of a second, amorphous polymer or a low molecular weight compound to a semicrystalline polymer can influence the observed spherulite morphology (see, for example, reference 21). Some recent examples of studies of semicrystallineamorphous polymer blends are listed in Table 1.1.

 Table 1.1
 Selected examples of recent literature studies of semicrystalline-amorphous

 polymer blends.

Semicrystalline Component	Amorphous Component	Reference
<i>i</i> -poly(β-hydroxybutyrate)	a-poly(β-hydroxybutyrate)	40,41
<i>i</i> -polypropylene	ethylene-propylene rubber	42
i-poly(β-hydroxybutyrate)	poly(methyl methacrylate)	43
poly(vinylidene fluoride)	poly(ethyl acrylate)	44
poly(E-caprolactone)	polystyrene	45
cis-1,4-polyisoprene	poly(vinyl ethylene)	46
i-poly(1-butene)	hydrogenated oligo-	
	cyclopentadiene	47

All of the blends listed are miscible or partially miscible in the melt, except the iPP/ethylene-propylene rubber blend (42). In general, the presence of the second, miscible, amorphous component has a disruptive effect on the crystalline morphology. The extent to which the crystalline morphology is affected depends mainly on the degree to which the additive is incorporated within the spherulite. The degree of incorporation

depends, in turn, on the degree of adhesion or miscibility between the two components and the molecular size and the mobility of the additive. If the additive is an amorphous polymer that exhibits some miscibility with the melt of the semicrystalline polymer, then portions of the additive chains may be incorporated within the amorphous fold surfaces of the crystallites. The molecular size and the amorphous, entangled nature of the polymer would generally preclude its incorporation within the unit cell. If the additive is present in excess, then the bulk of it may be excluded to interfibrillar or interspherulitic regions of the sample. In the case of an immiscible blend, all of the additive is expected to be found in these latter two locations. Any structural changes that evolve as the result of the inclusion or the exclusion of additives by the spherulites are reflected by variations in the spherulite morphology, such as a reduction in the birefringence due to the disordering of the anisotropic spherulite structure, or an increase in the spacing between adjacent spherulite fibrils that results from the accumulation of foreign species in these zones.

Unlike the case of a polymeric additive, a low molecular weight substance can be included within the crystalline structure at the level of the unit cell under the necessary conditions of miscibility or very rapid crystallization kinetics. On the other hand, immiscible, small molecules can be excluded more easily from the crystalline matrix than entangled, long-chain polymeric additives. In this respect, a low molecular weight material may have a more profound effect on the crystalline structure.

Changes in spherulite morphology should also be considered in the context of the growth rate of the spherulites examined. The growth rate of spherulites grown from miscible blends is usually significantly depressed relative to that of spherulites grown from the pure melt (see, for example, reference 40). Spherulites grown from immiscible blends generally grow at the same rate as those grown from the pure melt; however, in some cases a depression in the growth rate can arise due to the energy expended by the growing spherulites in the rejection, engulfment and deformation of the second component (26). The occurrence of a composition-dependent crystallization rate is an important

consideration in the processing of blends. The crystallization kinetics of blends and mixtures will be discussed in further detail in Chapter 4.

## 1.4 The Crystallization of Poly(ethylene Oxide) from the Melt

### 1.4.1 Pure Polymer

The crystal structure, crystallization kinetics and morphology, and thermal properties of poly(ethylene oxide) (PEO) have commanded a tremendous amount of attention during the past three decades. Among the reasons behind this interest are the ready availability of the polymer and its broad spectrum of applications. The rapid crystallization, high degree of crystallinity, slight polarity, and extensive solubility of PEO are properties that have led to its application as a thickening agent in foods, as a dispersant in paints and coatings, as a matrix in drug delivery devices, and as a solid polyelectrolyte, to name a few examples.

PEO is also a highly attractive subject for the study of fundamental aspects of polymer crystallization. A significant portion of the crystallization temperature range of PEO is experimentally accessible, and crystallization from the melt yields large, distinct spherulites (that is, > 100  $\mu$ m in diameter) at low to intermediate supercoolings that are easily observed in thin section via PLM. The unit cell of PEO has been well-characterized and, under most conditions, is monoclinic with four distorted 7<sub>2</sub> helices passing through the cell (48). Modified unit cells have been observed in strained samples (49) and in complexes of PEO with low molecular weight materials such as aromatic compounds (50-53), sodium thiocyanate (54), mercuric choride (55,56), and urea (57).

Early crystallization studies of PEO employed industrially available polydisperse samples (see, for example, reference 58). As a result, a number of these studies focused on the effect of the broad molecular weight distribution in the crystallization process (2I).

The preferential rejection of the low molecular weight material by the growing spherulites was found to be a determining factor in the development of spherulite morphology and occasionally in the spherulite radial growth rate (18), as noted in later, analogous studies of semicrystalline-amorphous polymer blends. Towards the end of the crystallization process, that is, just prior to the impingement of the spherulites, the growth rate was observed to be slightly retarded due to the accumulation of the rejected low molecular weight material in the interspherulitic regions. Subsequent developments in fractionation techniques (59) permitted the examination and the measurement of the crystallization kinetics of narrow molecular weight fractions (see, for example, references 60-62). In addition, the fractional crystallization of PEO from mixtures containing selected molecular weight fractions has been investigated (63-67). Within the past decade, such experiments have been facilitated by the commercial availability of anionically polymerized, monodisperse fractions of PEO. The crystallization of PEO has generally been examined at atmospheric pressure and under static conditions; however, high-pressure (68) and dynamic, shearing experiments (69,70) have been published. The crystallization of PEO from solution has been explored as well (71).

A recent study of low molecular weight fractions of PEO described the observation of integrally and nonintegrally folded chain crystals, and confirmed that the crystallization process involves a balance between kinetics and thermodynamics (72-74). In the literature study, initially nonintegrally-folded chain crystals were annealed to eventually form more perfect, integrally-folded chain crystals. Another recent, important development in the investigation of the crystallization of PEO has been the report of the occurrence of three regimes of crystallization, or two regime transitions, in intermediate molecular weight PEO by Cheng and coworkers (75). However, a subsequent study by Point and others (76) has questioned the occurrence of one of the reported regime transitions. This conflict will be addressed in Chapters 4 and 5.

5

### **1.4.2** Blends Containing Poly(ethylene oxide)

The crystallinity, the flexibility and the polarity of PEO are features that govern its interactions with other materials. The presence of the polar carbon-oxygen bond in the repeat unit provides the opportunity for dipolar interaction with other polar moieties, such as carbon-halogen bonds, of other polymers. The flexibility of PEO allows for the accommodation of foreign species within the crystalline structure and possibly even inside the unit cell, as in the case of the complexes mentioned in the preceding section; and a high degree of crystallinity permits crystallization in the presence of these foreign molecules. Because the crystallization of individual spherulites is facile to observe, PEO is an ideal candidate for the study of the effect of a second component on the crystallization of a semicrystalline polymer. In fact, numerous studies of the crystallization of PEO in blends have been presented in the literature, examples of which are listed in Table 1.2.

All of the amorphous second components that are listed in Table 1.2 are miscible or partially miscible in the melt with PEO (23,78-81,86-92), except poly(N-vinyl carbazole) (82). The morphology of the spherulites grown from all of the miscible blends was disturbed by the presence of the second component; the spherulite structure generally became coarser with increasing concentration of the amorphous polymer (23,78-81,86-92). A depression in the crystallization kinetics occurred in all of the miscible blends (23,78-81,86-90) except the blend containing poly(vinyl chloride) (PVC) (91).

As is evident from Table 2.1, the crystallization of PEO in blends with poly(methyl methacrylate) (PMMA) has been studied extensively. PEO and PMMA are miscible in the melt; that is, PMMA forms a homogeneous mixture with the amorphous phase of PEO. SAXS and SANS experiments (93,94) have confirmed the molecular-level mixing proposed based on the melting temperature depression observed by thermal analysis (23), and have demonstrated that PMMA is present in the amorphous, interlamellar regions of crystallized PEO.

Table 1.2 Examples of literature studies of the crystallization of PEO in blends. (The notation c or a denotes the crystalline or amorphous nature of the second component, respectively.)

Second Component	c or a	Reference
poly(β-hydroxybutyrate)	с	77
poly(vinyl alcohol)	8	78
poly(vinyl acetate)	a	79
poly(ethylene-co-vinyl acetate)	c/a	80
poly(bisphenol-A hydroxy ether)	a	81
poly(N-vinyl carbazole)	a	82
poly(vinylidene fluoride)	С	83
poly(L-lactic acid)	с	84,85
poly(methyl methacrylate)	a	23,86-88
i-poly(methyl methacrylate)	c	86
poly(ethyl methacrylate)	a	89
poly(butyl methacrylate) (1)	a	90
poly(vinyl chloride)	a	91,92

(1) modified with poly(dimethyl siloxane)

The morphology of PEO spherulites is influenced substantially by PMMA (86-88). An increase in the coarseness of the spherulite texture is observed with increasing PMMA content. In addition, the spherulite growth rate at a given temperature decreases substantially with increasing PMMA content (86-88).

 $\sim$ 

Blends of PEO and PVC have been characterized to a lesser extent, even though PVC would constitute one of the simplest possible polymeric additives. PVC is a mainly amorphous, linear polymer that possesses weakly acidic  $\alpha$ -protons which can be expected to interact with the proton-accepting PEO. Most of the existing literature concerned with blends of PEO or other polyethers with chlorinated polymers has focused on the application of polyethers as additives to systems containing chlorinated polymers, as evidenced by the large number of patent applications pertaining to this type of mixture. Polyethers have been shown to improve the impact strength and the thermal stability, and to decrease the melt viscosity of such systems (95).

PEO/PVC blends have been described as being partially miscible in the melt at high concentrations of PVC (91,92,96). This description is contradictory in that it implies that low concentrations of PVC are immiscible with molten PEO, a situation that is highly improbable. The condition of miscibility when large amounts of the PVC are mixed with the amorphous PEO phase dictates that a finite proportion of the PVC must be miscible when small amounts of the amorphous polymer are mixed with PEO. Furthermore, PEO/PVC blends are the only reported, partially miscible blends of PEO and an amorphous polymer that do not exhibit any depression in the spherulite growth kinetics of PEO (91), crystallization behavior that is characteristic of an immiscible blend (26). However, changes in spherulite morphology that resemble the types of changes observed in other miscible blends have been reported (91). The questions that arise form the available information are: 1. Are PEO and PVC partially miscible or immiscible? What is the nature of the morphological changes observed in these blends? 3. Is complete, molecular-level miscibility a requirement for the occurrence of the morphological or structural changes that are generally induced in semicrystalline-amorphous polymer blends? Clearly, blends of PEO and PVC bear further investigation.

2

In spite of the tremendous potential of plasticizers as additional tools for the control of the crystallization of semicrystalline polymers from the melt in semicrystallineamorphous polymer blends, no study published to date has compared the crystallization behavior of a binary semicrystalline-amorphous polymer blend with that of a ternary mixture also containing a low molecular weight plasticizer that acts specifically on the amorphous polymer. The specific plasticization and the resultant modification of the physical properties of the amorphous polymer that can be expected to occur in this type of ternary mixture would alter the nature of the interaction between the two polymeric components and therefore modify the crystallization process of the semicrystalline component relative to that observed in the binary blend. Thus, the use of specific plasticization could potentially broaden the spectrum of applications of a given semicrystalline polymer.

Although PVC consists of a relatively simple structure, the bulky chlorine atoms that are attached to the backbone lead to a material that is rigid and that requires the addition of plasticizers to improve its flexibility and processability (2). Tricresyl phophate is a plasticizer that is frequently used in combination with PVC, and that fulfills another important role as a flame-retardant (2). Although TCP has the potential to exhibit some affinity for PEO, the use of an excess of the plasticizer relative to the PVC content in ternary mixtures with PEO and PVC ensures its overwhelming influence on the physical properties of PVC.

The research presented in this thesis examines the crystallization of a semicrystalline polymer, PEO, (i) from the pure melt, (ii) from binary blends with a partially miscible, amorphous polymer, PVC, (iii) from a binary mixture with a low molecular weight plasticizer, tricresyl phosphate (TCP), that is a specific plasticizer for PVC, and (iv) from ternary mixtures that contain the two polymers and the plasticizer.

Several techniques have been employed to gain an understanding of the macroscale and microscale properties of PEO, PEO/PVC blends, and PEO/TCP and PEO/PVC/TCP mixtures. The first approach is a theoretical computation of the surface interfacial tension between the various pairs of components in these mixtures that aids in the prediction of the adhesion between the pairs. The three subsequent experimental approaches adopted for the purpose of this study focus on the crystallization of PEO in increasingly fine detail: 1. Thermal analysis is employed to observe the bulk thermodynamic properties of the samples and to evaluate the miscibility of PEO and PVC. 2. Then polarized light microscopy is used to observe the morphology and the crystallization kinetics of the spherulites that are formed in all of the samples. 3. Finally, the novel technique of polarized infrared microspectroscopy, as applied to the examination of local spherulite structure, reveals valuable information about the orientation and the conformation of individual polymer chains of both PEO and PVC.

## **1.6 References**

- 1. Utracki, L. A. Polymer Alloys and Blends; Hanser: New York, 1989.
- Sears, J. K.; Darby, J. R. The Technology of Plasticizers; Wiley-Interscience: New York, 1982.
- 3. Huggins, M. L. J. Chem. Phys. 1941, 9, 440.
- 4. Flory, P. J. J. Chem. Phys. 1941, 9, 660.
- 5. Krause, S. Chemtracts Macromol. Chem. 1991, 2, 367-383.
- 6. Djordjevic, M. B.; Porter, R. S. Polym. Eng. Sci. 1983, 23, 650.
- 7. Garcia, D. In Current Topics in Polymer Science; Ottenbrite, R. M., Utracki, L. A., Inoue, S., Eds.; Hanser: Munich, 1987.
- 8. Riedl, B.; Prud'homme, R. E. J. Polym. Sci., Polym. Phys. Ed. 1986, B24, 2565.
- 9. Garton, A. Polym. Eng. Sci. 1984, 24, 112.

- Paul, D. R.; Barlow, J. W. J. Macromol. Sci., Rev. Macromol. Chem. 1980, C18, 109.
- 11. Gabriel, B. L. Scanning Electron Microscopy: A User's Manual for Materials Science; American Society for Metals: Metals Park, Ohio, USA, 1985.
- 12. Blahovici, T.; Brown, G. R. Polym. Eng. Sci. 1988, 28, 1381-1391.
- Koenig, J. L. Spectroscopy of Polymers; American Chemical Society: Washington, DC, USA, 1991.
- 14. Messerschmidt, R. G.; Harthcock, M. A., Eds. Infrared Microspectroscopy: Theory and Applications; Practical Spectroscopy Series, Vol. 6; 1988.
- 15. Bates, F. S.; Wignall, G. D. Macromolecules 1986, 19, 932.
- 16. Wendorff, J. H. Polymer 1982, 23, 543.
- 17. Gelles, R.; Frank, C. W. Macromolecules 1983, 16, 1448.
- 18. Frank, C. W. Plastics Comp. 1981, Jan/Feb, pp 67-74.
- Albert, B.; Teyssié, J.; Selb, J. J. Polym. Sci., Polym. Phys. Ed. 1986, 24, 537, 551 and 2577.
- 20. Nishi, L.; Wang, T. T. Macromolecules 1975, 8, 909.
- 21. Keith, H. D.; Padden, Jr., F. J. J. Appl. Phys. 1964, 35, 1270-1285 and 1286-1296.
- 22. Boon, J.; Azcue, J. M. J. Polym. Sci., Part A-2 1968, 6, 885-894.
- 23. Alfonso, G. C.; Russell, T. P. Russell Macromolecules 1986, 19, 1143-1152.
- 24. Saito, H.; Okada, T.; Hamane, T.; Inoue, T. Macromolecules 1991, 24, 4446-4449.
- 25. Bartczak, Z.; Galeski, A.; Martescelli, E. Polym. Eng. Sci. 1984, 24, 1155-1165.
- 26. Martuscelli, E. Polym. Eng. Sci. 1984, 24, 563-586.

- 27. Mandelkern, L. Crystallization of Polymers; McGraw-Hill:New York, 1964.
- 28. Marentette, J. M.; Brown, G. R. J. Chem. Ed. 1993, 6, 435-439.
- 29. Hoffman, J. D.; Davis, G. T.; Lauritzen, Jr., J. I. In Treatise on Solid State Chemistry; Hannay, N. B., Ed.; Vol. 3; Plenum: New York, 1976; ch. 7.

- 30. Sharples, A. Introduction to Polymer Crystallization; Edward-Arnold: New York, 1966.
- 31. Saville, B. P. In Applied Polymer Microscopy; Hemsley, D. A. Ed.; Elsevier: New York, 1989.
- 32. Delly, J. G. Industr. Res. 1973, 10, 44-50.
- 33. Hartshorne, N. H.; Stuart, A. Crystals and the Polarizing Microscope; 4th ed.; Elsevier: New York, 1970.
- Mason, C. W. Handbook of Chemical Microscopy; 4th ed.; Wiley: New York, 1983; pp 189-199.
- 35. Rochow, T. G.; Rochow, E. G. An Introduction to Microscopy by Means of Light, Electrons, X-Rays, or Ultrasound; Plenum:New York, 1978.
- 36. Chiu, G.; Alamo, R. G.; Mandelkern, L. J. Polym. Sci., Polym. Phys. Ed. 1990, 28, 1207-1221.
- Barham, P. J.; Keller, A. Otun, E. L. Holmes, P. A. J. Mater. Sci. 1984, 19, 2781-2794.
- 38. Singfield, K. L.; Brown, G. R. Macromolecules 1995, 28, 1290-1297.
- 39. Padden, Jr., F. J.; Keith, H. D. J. Appl. Phys. 1959, 30, 1479-1484.
- 40. Pearce, R.; Brown, G. R.; Marchessault, R. H. Polymer 1994, 35, 3985-3989.
- 41. Hideki, A.; Doi, Y.; Satkowski, M. M.; Noda, I. Macromolecules 1994, 27, 50-54.
- 42. D'Orazio, L.; Mancarella, C.; Martuscelli, E.; Sticotti, G.; Ghisselini, R. J. Appl. Polym. Sci. 1994, 53, 387-404.
- 43. Lotti, N.; Pizzoli, M.; Ceccorulli, G.; Scandola, M. Polymer 1993, 34, 4935-4940.
- 44. Briber, R. M.; Khoury, F. J. Polym. Sci., Polym. Phys. Ed. 1993, 31, 1253-1272.
- 45. Li, Y.; Jungnickel, B. J. Polymer 1993, 34, 9-15.

46. Zemel, L.S.; Roland, C. M. Polymer 1992, 33, 3427-3432.

2.1

47. Bonfatti, A. M.; Canetti, M.; Sadocco, P.; Seves, A.; Martuscelli, E. Polymer 1993, 34, 990.

- 48. Takahashi, Y.; Tadokoro, H. Macromolecules 1973, 6, 672-675.
- 49. Takahashi, Y.; Sumita, I.; Tadokoro, H. J. Polym. Sci. 1973, 11, 2113-2122.
- 50. Damman, P.; Point, J. J. Macromolecules 1995, 28, 2050-2053.
- 51. Damman, P.; Point, J. J. Macromolecules 1994, 27, 3919-3925.
- Delaite, E.; Point, J. J.; Damman, P.; Dosière, M. Macromolecules 1992, 25, 4768-4778.
- 53. Point, J. J.; Damman, P. Macromolecules 1991, 24, 2019-2023.
- 54. Chatani, Y.; Fujii, Y.; Takayanagi, T.; Honma, A. Polymer 1990, 31, 2238-2244.
- 55. Yokoyama, M.; Ishihara, H.; Iwamoto, R.; Tadokoro, H. Macromolecules 1969, 2, 184-192.
- 56. Iwamoto, R.; Saito, Y.; Ishihara, H.; Tadokoro, H. J. Polym. Sci., Part A-2 1968, 6, 1509-1525.
- 57. Tadokoro, H.; Yoshihara, T.; Chatani, Y.; Murahashi, S. Polym. Lett. 1964, 2, 363-368.
- 58. Barnes, W. J.; Luetzel, W. G.; Price, F. P. J. Phys. Chem. 1961, 65, 1742-1748.
- 59. Booth, C.; Price, C. Polymer 1966, 7, 85-90.
- 60. Maclaine, J. Q. G.; Booth, C. Polymer 1975, 16, 191-195.
- 61. Price, C.; Evans, K. A.; Booth, C. Polymer 1975, 16, 196-200.
- 62. Maclaine, J. Q. G.; Booth, C. Polymer 1975, 16, 6880-684.
- 63. Prud'homme, R. E. J. Polym. Sci., Polym. Phys. Ed. 1982, 20, 307-317.
- 64. Cheng, S. Z. D.; Wunderlich, B. J. Polym. Sci., Polym. Phys. Ed. 1986, 24, 577-594.
- 65. Cheng, S. Z. D.; Wunderlich, B. J. Polym. Sci., Polym. Phys. Ed. 1986, 24, 595-617.
- 66. Cheng, S. Z. D.; Bu, H. S.; Wunderlich, B. J. Polym. Sci., Polym. Phys. Ed. 1988, 26, 1947-1964.
- 67. Cheng, S. Z. D.; Noid, D. W.; Wunderlich, B. J. Polym. Sci., Polym. Phys. Ed. 1989, 27, 1149-1160.

1.1.1

68. Li, W.; Radosz, M. Macromolecules 1993, 26, 1417-1433.

- 69. Fritzsche, A. K.; Price, F. P. Polym. Eng. Sci. 1974, 14, 401-412.
- 70. Buerger, D. E.; Engberg, K.; Jansson, J.-F.; Gedde, U. W. Polymer Bull. 1989, 22, 593-598.
- 71. Ding, N.; Amis, E. J. Macromolecules 1991, 24, 3906-3914 and 6464-6469.
- Cheng, S. Z. D.; Chen, J.; Barley, J. S.; Zhang, A.; Habenschuss, A.; Zschack, P. R. Macromolecules 1992, 25, 1453-1460.
- 73. Cheng, S. Z. D.; Chen, J.; Zhang, A.; Barley, J. S.; Habenschuss, A.; Zschack, P. R. Polymer 1992, 3, 1140-1149.
- 74. Cheng, S. Z. D.; Barley, J. S.; Chen, J.; Habenschuss, A.; Zschack, P. R. Macromolecules 1991, 24, 3937-3944.
- 75. Cheng, S. Z. D.; Chen, J.; Janimak, J. J. Polymer 1990, 31, 1018-1024.
- 76. Point, J. J.; Damman, P.; Janimak, J. J. Polymer 1993, 34, 3771-3773.
- 77. Avella, M.; Martuscelli, E.; Greco, P. Polymer 1991, 32, 1647-1653.
- Quintana, J. R.; Cesteros, L. C.; Peleteiro, M. C.; Katime, I. Polymer 1991, 32, 2793-2798.
- 79. Martuscelli, E.; Silvestre, C.; Gismondi, C. Makromol. Chem. 1985, 186, 2161-2176.
- 80. Martuscelli, E. E.; Saviano, M.; Silvestre, C. Polymer 1991, 32, 1461-1467.
- 81. Iriarte, M.; Iribarren, J. I.; Exteberria, A.; Iruin, J. J. Polymer 1989, 30, 1160-1165.
- Cesteros, L. C.; Quintana, J. R.; Rodriguez Caneiro, M.; Katime, I. Brit. Polym. J. 1989, 21, 487-490.
- 83. Privalko, V. P.; Petrenko, K. D.; Lipatove, Yu. S. Polymer 1990, 31, 1277-1282.
- 84. Younes, H.; Cohn, D. Eur. Polym. J. 1988, 24, 765-773.
- 85. Nakafuku, C.; Sakoda, M. Polym. J. 1993, 25, 909-917.
- 86. Cimmino, S.; Martuscelli, E.; Silvestre, C. J. Polym. Sci., Polym. Phys. Ed. 1989, 27, 1781-1794.
  - 57. Martuscelli, E.; Pracella, M.; Yue, W. P. Polymer 1984, 25, 1097-1106.
  - 88. Calahorra, E.; Cortazar, M.; Guzman Polymer 1982, 23, 1322-1324.

- Cimmino, S.; Martuscelli, E.; Silvestre, C. Makromol. Chem., Macromol. Symp. 1988, 16, 147-159.
- Chu, E. Y.; Pearce, E. M.; Kwei, T. K.; Yeh, T. F.; Okamoto, Y. Makromol. Chem., Rapid Commun. 1991, 12, 1-4.
- 91. Iragorri, J. L; Cesteros, L. C.; Katime, L. C. Polym. Int. 1991, 25, 225-228.
- Margaritis, A. G.; Kalfoglou, N. K. J. Polym. Sci., Polym. Phys. Ed. 1988, 26, 1595-1612.
- 93. Ito, H.; Russell, T. P.; Wignall, G. D. Macromolecules 1987, 20, 2213-2220.
- 94. Russell, T. P.; Ito, H.; Wignall, G. D. Macromolecules 1988, 21, 1703-1709.
- 95. Dreyfuss, P.; Dreyfuss, M. P.; Tucker, A. In Polymerization Kinetics and Technology; Platzer, N. A. J., Ed.; Adv. in Chem. Ser. No. 128; American Chemical Society: Washington, DC, USA, 1973; p 125.
- 96. Marco, C.; Gomez, M. A.; Fatou, J. G.; Exteberria, A.; Elorza, M. M.; Iruin, J. J. Eur. Polym. J. 1993, 11, 1477-1481.

# **Chapter Two**

## Surface Interfacial Tension

## 2.1 Introduction

Surface tension depends on the chemical composition of a surface and is defined as the amount of energy required for the formation of a unit of surface area at constant temperature, pressure and composition (1). The surface interfacial tension is the surface tension that results from the formation of a boundary or an interface between two substances. The determination of the latter quantity provides information about the degree to which one substance will spread on another, or the degree of adhesion between two materials. A surface interfacial tension of zero implies that two materials will spread on each other, while a small, positive value implies that the two materials may still exhibit very good adhesion. A negative surface interfacial tension implies a cohesive system. In the case where one component is dispersed within a matrix of the other, the surface interfacial tension can provide information about the nature and the level of dispersion.

There are two contributing factors to surface tension,  $\gamma$ , that also influence the surface interfacial tension. Thus,

 $\gamma = \gamma^p + \gamma^d$ 

(2.1)

where the superscripts p and d denote the polar and nonpolar contributions, respectively(2). The temperature independent polarity, xP, of a material is defined as

$$x^{p} = \frac{\gamma^{p}}{\gamma}$$
(2.2)

In general, more polar polymers possess larger surface tensions. The surface tension is temperature dependent, as shown by the following empirical relationship

$$\gamma = \gamma_{o} \cdot \left(1 - \frac{T}{T_{cr}}\right)^{11/9}$$
(2.3)

where  $\gamma_0$  is a parameter that is characteristic of a given substance, and  $T_{cr}$  is the critical temperature (2). Thus, in the temperature range of interest the temperature coefficient of the surface tension of polymers

$$\frac{d\gamma}{dT} = \frac{11}{9} \cdot \left(\frac{\gamma_0}{T_{cr}}\right) \left(1 - \frac{T}{T_{cr}}\right)^{2/9}$$
(2.4)

is approximately constant because the application temperature is invariably much less than the critical temperature of a polymer (~1000 K) (2).

At the glass transition temperature, surface tension is continuous, but the temperature coefficient is discontinuous (2), that is

$$\left(\frac{\mathrm{d}\gamma}{\mathrm{d}T}\right)_{\mathrm{g}} = \left(\frac{\alpha_{\mathrm{g}}}{\alpha_{\mathrm{r}}}\right) \left(\frac{\mathrm{d}\gamma}{\mathrm{d}T}\right)_{\mathrm{r}}$$
(2.5)

where the subscripts g and r denote the glass and the rubber, respectively, and  $\alpha$  is the isobaric volumetric thermal expansion coefficient. Typically  $\alpha_r$  is greater than  $\alpha_g$ , so that

surface tension varies less with temperature in the glassy region than in the rubbery region. Because the temperature derivative of surface tension is usually small, the effect of the glass transition can be neglected when the temperature range of interest is small.

In contrast, a crystalline surface possesses a much greater surface tension than an amorphous surface of the same material (2), as shown by the following empirical equation

$$\gamma_{\rm c} = \gamma_{\rm a} \cdot \left(\frac{\rho_{\rm c}}{\rho_{\rm a}}\right)^{\beta} \tag{2.6}$$

where  $\beta$  is known as Macleod's exponent, which assumes values between 3.0 and 4.5 for most polymers. In the case of a mixture of a semicrystalline polymer with an amorphous additive, the increase in the surface tension that results from the formation of the crystallizing phase causes an increase in the surface interfacial tension between the two components. This increase can drive phase separation, even in a system that shows evidence of miscibility when the crystalline component is in the molten state.

The surface interfacial tension between two liquids can be measured experimentally using a technique such as the pendent drop method. In this technique, the equilibrium deformation of a pendent drop of one liquid in a medium of a second liquid is used to calculate the surface interfacial tension through the use of tables of data that correlate drop dimensions with surface interfacial tension (2). Recently, these data tables have been supplanted by computer programs which facilitate the procedure (3). Unfortunately, such a method is difficult, if not impracticable, to implement in the case where the two substances of interest are polymers because of the high melting temperature, high melt viscosity, and low degradation temperature characteristic of many organic polymers. Because of the high melt viscosities involved, the pendent drop can require days to attain

.

its equilibrium shape. The high temperature and long time needed for the experiment can result in substantial degradation of one or both of the polymers.

An alternative route to the estimation of the surface interfacial tension,  $\gamma_{12}$ , between two polymers is provided by an empirical relation referred to as the harmonicmean equation

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p}$$
(2.7)

where the subscripts 1 and 2 denote substances 1 and 2 respectively (4,5). If the surface tensions and the polarities of the individual polymers are known from separate experiments, then the above equation can be used to estimate the surface interfacial tension. This technique is applied to estimate the surface interfacial tension between PEO and PVC, between PEO and TCP, and between PVC and TCP, and to help predict the degree of adhesion between the various components.

Two polymers that are partially miscible or immiscible may still exhibit significant adhesion. If adhesion occurs between the amorphous polymer and the amorphous component of the semicrystalline polymer at interfaces such as lamellar fold surfaces or at the external boundaries of fibrils, then the nature of the interface will be altered. The physical interlocking between the two polymers at the interface has the potential to induce specific conformational changes in both polymers at the interface. If the incidence of such interlocking is significant, it may even be sufficient to induce changes within the crystalline structure. Such changes can be expected to be observed on the spherulitic scale. Thus, the question of interfacial interactions or adhesion in crystalline-amorphous polymer blends must be considered in addition to the question of miscibility.

2:2

## 2.2 Calculation of Surface Interfacial Tension

#### 2.2.1 Surface Interfacial Tension at 100 °C

A knowledge of the surface interfacial tensions in PEO/PVC blends and PEO/TCP and PEO/PVC/TCP mixtures at the experimental melting temperature and at selected crystallization temperatures provides insight into the potential mixing behavior of these systems in the melt and within the crystalline matrix. Estimates of the surface interfacial tension between PEO and PVC, PEO and TCP, and PVC and TCP at 100 °C can be computed using reported surface tension data for the individual species and the harmonicmean equation (equation 2.7). The surface tension of neat PEO has been measured over the temperature range 80-200 °C by the pendent drop method, so that the value at 100 °C could be obtained directly from literature results (5). The polymer used in the above study was a Union Carbide Carbowax 6000 (MW 6000) purified by extraction with diethyl ether.

Surface tension data for PVC are available in the temperature range 20-60 °C (3,11). In one case, the PVC was free of any additives (4), while in the second case an organotin stabilizer and a lubricant were present at levels of ~ 2% each (6). The reported surface tension data obtained in the latter experiments are slightly lower than the corresponding data for the pure material; however, the presence of the additives is not expected to affect the value of the temperature coefficient significantly due to the similar temperature-dependence of the surface tension of the additives (6). The average value of (dy/dT) for the additive-containing samples and the independent surface tension measurement of a pure PVC sample were combined with the following equation to calculate the parameter  $\gamma^{*}$ ,

$$\gamma = \left(\frac{d\gamma}{dT}\right) \cdot T + \gamma^*$$
 (2.8)

which in turn permitted the estimation of the surface tension of pure PVC at 100 °C. Because the temperature of interest is close to the glass transition temperature of PVC (~80 °C) (7), the effect of the glass transition on the temperature coefficient of the surface tension was neglected.

The surface tension of TCP has been recorded as 40.9 mN/m at 20 °C (2), which is almost identical to the surface tension of pure PVC at the same temperature, 40.5 mN/m. The surface tension coefficient of TCP has not been reported, but examination of the temperature coefficients of other plasticizers (8) indicates that it can be expected to fall within the range of -0.0648 to -0.100 mN/m. The surface tension of TCP at 100 °C was estimated based on this assumed range for the temperature coefficient.

The results of computations of the surface interfacial tensions at 100 °C are listed in Table 2.1. These data reveal that the surface interfacial tensions of PEO/PVC and PVC/TCP pairs are comparable at this temperature. The surface interfacial tension between PEO and TCP is substantially larger than the values obtained for the other two pairs. The uncertainty given for mixtures containing TCP arises from the range of possible values for the temperature coefficient of TCP; while the uncertainty for the remaining results is estimated to be approximately 5%. The low interfacial tension of the PEO/PVC pair suggests that the PVC may adhere slightly to the molten PEO at this temperature. In contrast, the PEO/TCP pair possesses a much higher interfacial tension that does not favor the adhesion between these two phases. In a ternary mixture, the PVC may exhibit a tendency to adhere to both the PEO and the TCP, but the TCP will exhibit a marked preference for adhesion to PVC.

÷.,

 Table 2.1
 Surface tension and surface interfacial tension data for PEO, PVC and TCP at 100 °C.

Polymer	γ (mN/m)	γ <sup>ρ</sup> (mN/m)	γ <sup>d</sup> (mN/m)	Contact Pair	γ <sub>12</sub> (mN/m)
<b>PEO</b> (1)	36.8	10.3	26.5	PEO/PVC	1.8
PVC (2)	36.7	5.5	31.2	PEO/TCP	8.7 ± 0.4
TCP (3)	35 ± 2	0.94 ± 0.05	$34 \pm 2$	PVC/TCP	2±2
PMMA <sup>(4)</sup>	35.0	9.80	25.2	PEO/PMMA	0.040

<sup>(1)</sup>  $(d\gamma/dT) = -0.076 \text{ mN/m} \cdot \text{K}, x^{\text{p}} = 0.28$ 

 $^{(2)}(d\gamma/dT) = -0.0648 \text{ mN/m} \cdot \text{K}, x^{p} = 0.15$ 

<sup>(3)</sup>  $(d\gamma/dT) = -0.082 \pm 0.018 \text{ mN/m} \cdot \text{K}, \text{ xP} = 0.027$ 

<sup>(4)</sup>  $(d\gamma/dT) = -0.076 \text{ mN/m} \cdot \text{K}, \text{ xP} = 0.28$ 

.5

-

The surface interfacial tension between PEO and PMMA, two miscible polymers, was calculated for the purpose of comparison. The relevant surface tension data for PMMA were obtained from the literature (9). It is important to note that not only do PEO and PMMA possess similar surface tensions, they also possess identical polarities. In effect, the polarity of a material reflects its chemical composition; therefore the miscibility of these two polymers is not surprising. The computed surface interfacial tension is close to zero and significantly less than the value obtained for PEO and PVC. This result indicates that PEO/PVC blends are characterized by a degree of adhesion that is less than that observed in PEO/PMMA blends.

### 2.2.2 Surface Interfacial Tension at Selected Crystallization Temperatures

The crystallization of PEO introduces a surface of high surface tension into the blends and the mixtures. The density of perfectly crystalline PEO is  $1.23 \text{ g/cm}^3$  (10). The temperature dependence of the specific volume, v, of molten PEO is given by the expression

$$\mathbf{v} = 0.862 + (7.3 \cdot 10^{-4}) \mathrm{T} \tag{2.9}$$

where T is in units of °C, which yields densities of 1.11 g/cm<sup>3</sup> and 1.12 g/cm<sup>3</sup> at 50 and 40 °C, respectively (10). The surface tension of crystalline PEO was estimated using equation 2.6 with values of 3.0 and 1.11 g/cm<sup>3</sup> for  $\beta$  and  $\rho_a$ , respectively. The surface interfacial tension data at typical crystallization temperatures of 40 and 50 °C are listed in Table 2.2.

Table 2.2 Surface interfacial tension data for PEO, PVC and TCP at  $T_c$ . (The subscripts a and c denote amorphous and crystalline PEO, respectively.)

	T <sub>c</sub> (°C)	Contact Pair	γ <sub>1c2</sub> (mN/m)	γ <sub>1a2</sub> (mN/m)
- -	50.0	PEO/PVC	4.5	2.0
• •	40.0	PEO/PVC	4.4	2.1
	<u>n</u> 1	PEO/TCP	12 <sup></sup>	10
		PVC/TCP	n/a	4
- -		PEO/PMMA	-2.5	0.037

At 40 °C, the surface tension of TCP was assumed to be equivalent to the value for PVC. The results listed in Table 2.2 have an estimated accuracy of  $\pm 5\%$ .

While the surface interfacial tension between various amorphous pairs is similar to the computed results at 100 °C, the interfacial tension between the crystalline PEO and the additives is significantly larger, thereby reducing the probability of mixing between PEO and the additives upon crystallization. The surface interfacial tension between PVC and the amorphous PEO indicates the possibility of adhesion between these two phases, but the degree of adhesion is expected to be less than that between PMMA and amorphous PEO. Once again, the surface interfacial tension between the miscible PMMA and the amorphous phase of PEO is very close to zero, indicating a high probability of adhesion between the two phases. In fact, small angle neutron and X-ray scattering studies of a series of PEO/PMMA blends have demonstrated the presence of PMMA in the amorphous, interlamellar regions of PEO (11).

Although the computed surface interfacial tension between PVC and TCP is a small, positive value, the chemical interaction between the PVC and the liquid plasticizer must be considered. TCP is in fact a solvent for PVC (11). A mixture of PVC and TCP that contains about 15% PVC is essentially a gel that exhibits the same vapor pressure as that of pure TCP (12). Thus, the TCP is expected to dissolve a significant portion of the PVC present in the ternary mixtures. Under these circumstances, the surface interfacial tension between the TCP and the PEO is of greater importance than that between the PVC and the PEO. If a sufficient amount of the PVC and the PEO. As a result, the influence of the PVC on the morphology of PEO can be expected to be diminished by the presence of the plasticizer.

Ś

## 2.3 Summary

The estimation of the surface interfacial tension of PEO/PVC, PEO/TCP and PVC/TCP pairs at 100 °C, using the harmonic-mean equation, indicates that the PVC is expected to adhere slightly to the molten PEO, while the TCP is not expected to exhibit any significant adhesion to the PEO. The solvation of PVC by TCP is expected to interfere with any possible adhesion between PVC and PEO in the ternary mixtures.

The increase in the density, and therefore the surface tension, of PEO that occurs upon crystallization leads to an increase in the interfacial tension between PEO and the additives. As a result, the adhesion between the additives and the crystalline PEO is expected to be significantly less than that observed between the additives and the molten PEO. The surface interfacial tension between two miscible polymers, PMMA and PEO, is close to zero and less than that computed for the other systems. Therefore, the degree of adhesion between PVC and PEO is anticipated to be less than that observed between PMMA and PEO. The level of dispersion of PVC in PEO/PVC blends, and the miscibility of these two polymers are examined in the following chapter.

### 2.4 References

- Shaw, D. J. Introduction to Colloid and Surface Chemistry, 3rd ed.; Butterworths: London, 1980.
- 2. Wu, S. Polymer Interface and Adhesion; Marcel-Dekker: New York, 1982.
- 3. Demarquette, N. R., Ph.D. Thesis, McGill University, Montreal, Quebec, Canada, 1993.
- 4. Wu, S. J. Polym. Sci., Part C 1971, 34, 19-30.
- 5. Wu, S. J. Adhesion 1973, 5, 39-55.
- 6. J. Piglowski Angew. Makromol. Chem. 1985, 136, 129-134.
- 7. Roy, S. K.; Brown, G. R.; St. Pierre, L. E. Intern. J. Polymeric Mater. 1983, 10, 13-20.
- 8. Wu, S. In *The Polymer Handbook*, 3rd ed.; Brandrup, J. and Immergut, E. H., Eds., Wiley-Interscience: New York, 1989; pp VI411-434.
- 9. Wu, S. J. Phys. Chem. 1970, 74, 632.

- ...

- 10. Roe, R.-J. J. Phys. Chem. 1968, 72, 2013-2017.
- 11. Russell, T. P; Ito, H.; Wignall, G. D. Macromolecules 1988, 21, 1703-1709.
- 11. Sears, J. K.; Darby, J. R. The Technology of Plasticizers; Wiley-Interscience: New York, 1982.

5

 $\vec{\sigma}$ 

12. Verhoek, F. H.; Marshall, A. L. JACS 1939, 61, 2737-2742.

# Chapter 3

# **Thermal Analysis and Miscibility**

# 3.1 Introduction

Thermal analysis, in particular differential scanning calorimetry, is a standard technique employed for the evaluation of the level of dispersion and the miscibility of polymer blends (1). In addition, knowledge of the glass transition temperature  $(T_g)$ , the equilibrium melting temperature  $(T_m^{\circ})$ , and the heat of fusion  $(\Delta H_f^{\circ})$  of a semicrystalline polymer, values of which can be determined by thermal analysis, is essential to the understanding of the crystallization process of a given polymer. Accurate values of these three thermodynamic properties are required for the interpretation of crystallization kinetics using current nucleation theory, as will be discussed in Chapter 4.

# 3.1.1 The Glass Transition Temperature

There is an ongoing discussion in the literature concerning the precise definition of the glass transition (2). The glass transition can be described as a pseudo-second order phase transition. At the glass transition termperature, the polymer heat capacity,  $C_p$ , the compressibility,  $\kappa$ , and the thermal expansion coefficient,  $\alpha$ , are discontinuous with temperature, as is expected from a second order phase transition. However, the measured value of the glass transition temperature is dependent on the experimental method applied and the time scale of the experiment; that is, the glass transition is also a kinetic process. As a consequence, different techniques such as NMR, dynamic mechanical thermal analysis (DMTA), or differential scanning calorimetry (DSC) can yield different values of the glass transition temperature for a given sample.

Many polymers, in particular long-chain, linear polyolefins, undergo multiple relaxation processes as they settle into the glassy state (3). The true glass transition temperature is generally taken as the temperature at which large-scale molecular motion ceases. The glass transition temperature has also been described as the temperature at which the onset of cooperative molecular motion involving approximately 50 to 100 adjacent atoms on the polymer backbone occurs (3). At temperatures below this temperature, a polymer is ideally a clear, glass-like solid that possesses a mobility that is restricted to the local motion of groups of 3 to 5 atoms; at a temperature approximately 30 K below that of the glass transition, molecular motion ceases altogether. At temperatures above this transition, a non-crystalline polymer is a relatively flexible, rubberlike material that may still be relatively clear.

The glass transition temperature is also the lower boundary of the temperature range within which the crystallization of semicrystalline polymers can occur, with the upper boundary being the equilibrium melting temperature. The observation of the rubbery state of semicrystalline polymers requires the use of rapid melt quenching techniques due to the driving force for crystallization at temperatures above the glass transition temperature. In instances where quenching is not sufficiently rapid to outpace nucleation, the glass transition that is observed arises from amorphous polymer that has been trapped within the crystalline structure during crystallization.

The glass transition behavior observed in a polymer blend has frequently been used as a gauge of polymer miscibility, although it is more appropriately used as a gauge of dispersion (1). Depending on the miscibility and the degree of dispersion of the two polymers, the formation of a polymer blend can alter the glass transition temperatures of both polymers. Because the degree of dispersion depends on the method of sample preparation, the observed transition temperature is also dependent on the method of

sample preparation. An immiscible blend can be expected to exhibit two distinct glass transition temperatures that correspond to the glass transition temperatures of the pure components. However, a miscible blend may exhibit a single glass transition temperature,  $T_{g,bl}$ , that can be described by the Gordon-Taylor equation (4) which was adapted by Wood (5)

$$w_1(T_{g,1} - T_{g,bl}) + kw_2(T_{g,2} - T_{g,bl}) = 0$$
(3.1)

where  $w_i$  represents the weight fraction of polymer i, and the subscripts 1 and 2 refer to the semicrystalline and the amorphous components, respectively. The empirical parameter k is a measure of the miscibility of the two polymers. A similar equation derived by Kwei and others includes an additional, polymer-polymer interaction term (6,7).

In fact, the incidence of a single glass transition temperature indicates that the size of the domains in the blend is less than 2-15 nm, but is not evidence of molecular miscibility (1). In some cases, two polymers that form a blend with a sufficiently high degree of mixing to exhibit a single glass transition temperature, but that do not mix at the molecular level, are said to be "compatible". The presence of a miscible, low molecular weight diluent can influence the glass transition temperature in an analogous manner. Due to the frequent occurrence of complex miscibility, for example composition-dependent miscibility, many polymer blends exhibit intermediate behavior that cannot be described by a straightforward mathematical relationship such as the above equation (1).

#### 3.1.2 The Equilibrium Melting Temperature

÷.,

The equilibrium melting temperature of a polymer is the melting temperature of perfect crystals of a polymer of infinite molecular weight (8). The heat of fusion,  $\Delta H_f^{\circ}$ , of a polymer is the heat of fusion that corresponds to this phase transition. The estimation of

the equilibrium melting temperature of polymers is particularly complicated because polymers do not possess a sharp, well-defined melting point as do low molecular weight species ( $\delta$ ). Although polymers crystallize within well-defined unit cells, the length of the chains does not normally permit the formation of uniform crystal structures; that is, a certain number of defect sites or structural irregularities are present in all of the crystals formed from the melt. Polymers also differ from low molecular weight species in that typical polymer samples consist of chains of varying lengths and molecular weights. The ultimate structure that is adapted by a semicrystallize polymer at a specific crystallization temperature is also strongly influenced by the crystallization kinetics that correspond to that temperature (9). In some instances, one set of crystallization conditions will yield more than one unit cell, each crystal structure possessing different melting behavior, as in the case of isotactic polypropylene, for example (10). In addition, during the heating process, a single crystal population may recrystallize to a refined crystal form with melting characteristics different from those of the original form.

# 3.1.2.1 Polymer Blends

As in the case of the glass transition temperature, the equilibrium melting temperature can be influenced by the addition of a miscible polymer or a low molecular weight diluent. The melting temperature depression in blends of semicrystalline and amorphous polymers has been described by the Flory-Huggins equation

$$\frac{1}{T_{m bl}^{o}} - \frac{1}{T_{m}^{o}} = \frac{-RV_{2}}{(\Delta H_{f}^{o})V_{1}} \chi_{12} (1 - \upsilon_{2})^{2}$$
(3.2)

where R is the ideal gus constant,  $V_i$  is the molar volume of a repeat unit,  $v_i$  is the volume fraction of a polymer in the blend, and  $\chi_{12}$  is the thermodynamic interaction parameter that describes the nature and the degree of the interaction between the two components (11-13). The subscripts 1 and 2 denote the amorphous polymer and the crystalline polymer, respectively. Nishi and Wang demonstrated that equation 3.2 can be used to relate the melting temperature of the pure semicrystalline polymer to that of the crystalline component crystallized from a blend that is miscible in the melt (14). The Flory-Huggins equation (equation 3.2) also provides a means of estimating the heat of fusion of a perfectly crystalline polymer. A large, negative value of  $\chi_{12}$  is characteristic of a miscible blend; whereas a large, positive value is characteristic of an immiscible blend. Values that are small and close to zero are commonly derived for blends that exhibit partial or limited miscibility under specific conditions. In general, caution must be exercised in the interpretation of the value of the interaction parameter because the sign and magnitude depend on molecular weight, the identity of the end groups in the case of low molecular weight polymers, temperature, pressure, and relative blend composition (15).

Ċ

It is important to bear in mind that several assumptions are made in the use of experimentally observed melting temperature depressions and the Flory-Huggins equation to determine the interaction parameter of a miscible blend (1). In particular, the crystals should be at equilibrium, a condition which requires crystallization at temperatures close to the actual melting temperature. The melting should be carried out under conditions that are as close to equilibrium as possible; that is, slow heating rates should be employed. On the other hand, recrystallization processes are more important under slow heating. Also, the unit cell dimensions and the lamellar thickness of the semicrystalline polymer should not be altered in the blend. Any phase transitions of the amorphous component should not occur at temperatures that are close to the melting transition of the semicrystalline component.

0

5

# 3.1.2.2 Polymer-Diluent Mixtures

Plasticizers, typically low molecular weight species, are frequently added to polymers to improve the mechanical properties of the product and to facilitate processing. In some cases, a plasticizer can act as a diluent and thereby influence the equilibrium melting temperature of the polymer. The melting temperature depression in polymer-plasticizer mixtures has been described by a relation that resembles equation 3.2

$$\frac{1}{T_{m}} - \frac{1}{T_{m}^{o}} = \frac{RV_{2}}{(\Delta H_{f}^{o})V_{1}} [(1 - \upsilon_{2}) - \chi_{12}(1 - \upsilon_{2})^{2}] \quad (3.3)$$

where the subscripts 1 and 2 correspond to the diluent and the polymer, respectively; the remaining parameters are as defined in the previous equation (11-13). A plasticizer that is a good solvent for the polymer, that is, one associated with a small value of the interaction parameter, will cause a substantial melting temperature depression. On the other hand, a poor solvent will cause a small melting temperature depression at low concentrations. The magnitude of the depression in the latter case continues to increase slightly with further addition of plasticizer until a critical concentration is reached; above this concentration, the melting temperature depression will remain constant. The use of a poor solvent results in a material with complex melting behavior. At the equilibrium melting temperature, at least three phases are present simultaneously: the crystalline polymer, the molten polymer, and the liquid plasticizer.

# 3.1.2.3 Experimental Determination of the Equilibrium Melting Temperature

Differential scanning calorimetry is a technique that is commonly used in the determination of the thermodynamic properties of polymers. This technique permits the observation of transitions such as glass or melting transitions that occur during the heating or cooling of a sample. In the case of a glass transition, a change in the heat capacity of the sample is observed; while in the case of a melting transition, an endothermic transition is observed. While the glass transition temperature can be estimated directly by this technique, an estimate of the equilibrium melting temperature can only be obtained by an extrapolative procedure because the melting of perfect crystals of a polymer of infinite molecular weight cannot be observed in practice. One such extrapolative method developed by Hoffman and Weeks employs the following relation

$$T_{\rm m} = \frac{1}{\eta} T_{\rm c} + T_{\rm m}^{\rm o} \left( 1 - \frac{1}{\eta} \right)$$
 (3.4)

where  $\eta$  is referred to as the lamellar thickening factor (16). The equilibrium melting temperature can be determined from a plot of the experimentally observed melting temperature,  $T_m$ , as a function of the crystallization temperature,  $T_c$ .

The values obtained for  $T_m$  should correspond to the melting temperatures of the most perfect crystals that can be formed at the chosen crystallization temperatures. For this requirement to be upheld, the experimental conditions must be selected so as to obtain individual, extended chain crystals. While it may be possible to obtain extended chain crystals of some low molecular weight polymers at early crystallization times and low degrees of crystallinity (17), it is not possible to obtain extended chain crystals with most polymer samples due to the length of the chains, or due to the crystallization kinetics. The most perfect crystals that can be obtained in practice are those that are formed at early

crystallization times and low degrees of crystallinity (18). However, a further requirement of the Hoffman-Weeks technique is that no annealing of the original crystal structure occurs during scanning. In some instances where crystallization is particularly rapid, this requirement can only be satisfied by allowing samples to crystallize to completion at temperatures close to their melting temperature, preferably in a temperature range where the lamellar thickening factor is small and constant. The experiment must also employ a heating rate that is sufficiently slow to minimize thermal lag yet rapid enough to minimize lamellar thickening during the scan.

The same extrapolative procedure that is applied to pure polymers can be applied to the study of polymer blends and polymer-diluent mixtures. The addition of a second polymer or a low molecular weight diluent can depress the melting temperature and alter the shape of the observed melting transition (9). A lesser effect is expected in the case of a polymer blend due to the relatively small number of polymer molecules as compared with the number of low molecular weight diluent molecules for a given percent composition. The addition of foreign material to the crystallizing polymer may also have an effect on the basic crystalline structure; this type of interaction can be expected to lead to irregularities in the plot of the Flory-Huggins equation (equation 3.2), in particular if the induced structural changes vary with blend composition.

As is the case with the equilibrium melting temperature, the heat of fusion of a perfectly crystalline polymer cannot be measured by direct experiment. The value of the heat of fusion for an ideal crystal can be determined indirectly through the use of a low molecular weight diluent and melting temperature depression measurements (8). Comparison of a measured value of the heat of fusion with the corresponding ideal value for that polymer provides an estimate of the degree of crystallinity of a sample, a parameter of particular importance in the consideration of polymer blends and polymer-diluent systems.

Extensive glass transition temperature (19-25) and equilibrium melting temperature (26-33) data for pure PEO are available in the literature, in addition to data for PEO/PVC blends (34-36). In this chapter, in the case of the glass transition temperature, a brief review of the literature results is presented along with the results of selected experiments that were conducted to verify the literature data. The equilibrium melting temperatures of all of the samples were determined by the Hoffman-Weeks method. The results of the thermal analysis are discussed in terms of the dispersion and the miscibility of the various blends and mixtures.

# 3.2 Procedure

#### **3.2.1 Sample Preparation**

# 3.2.1.1 Poly(ethylene oxide)

The selection of sample molecular weight and polydispersity is extremely important to the study of the crystallization of semicrystalline polymers, in particular with regard to crystallization kinetics. A broad molecular weight distribution can lead to fractional crystallization, that is, segregation of different molecular weight fractions during crystallization (37-40). The use of a monodisperse sample minimizes the incidence of fractional crystallization. High molecular weight polymers typically crystallize more slowly than their lower molecular weight counterparts. Therefore, the use of a high molecular weight sample greatly facilitates the observation of individual spherulites and fine morphological details, and the measurement of spherulite radial growth rates.

Monodisperse PEO, having the formula  $(-CH_2-CH_2-O_n)_n$ , was synthesized and characterized by S. Varshney for this study. The anionic polymerization method employed diphenylmethylpotassium as the catalyst and tetrahydrofuran as the solvent. The sample

was dissolved in toluene (1% weight/volume) at room temperature and precipitated by slow addition of an excess of hexanes to remove low molecular weight contaminants. The resultant white powder was then dried under vacuum at room temperature for four weeks prior to initial crystallization measurements. Due to the adverse effect of water or other solvents on the crystallization kinetics measurements, all of the samples were stored under vacuum when not in use. Spherulite radial growth rates that were measured using solvent-contaminated samples were significantly depressed and characterized by a very large experimental uncertainty relative to the growth rates measured using the dry material.

The molecular weight distribution was determined by gel permeation chromatography using polystyrene standards. The instrument used was a Varian DS-600, equipped with Waters Ultrastyragel columns running on a tetrahydrofuran mobile phase, and interfaced with a Varian RI-4 refractive index detector. The Q-factor correction (41) was applied to the results, yielding a weight average molecular weight,  $M_w$ , of  $1.8 \cdot 10^5$ and a polydispersity,  $M_w/M_n$ , of 1.4.

# 3.2.1.2 Poly(vinyl chloride)

 $\mathcal{L}$ 

22

The resin PVC Esso 366 was supplied by Esso Petroleum Ltd. The PVC, with molecular formula  $(-CH_2-CHCl-)_n$ , was selected from commercially available samples and reprecipitated to remove the low molecular weight fraction from the industrial sample and to obtain a material having a weight average molecular weight slightly less than that of the PEO sample. The material was dissolved in tetrahydrofuran (2% weight/volume) at room temperature, precipitated by slow addition of an excess of methanol, washed with methanol, and dried under vacuum at room temperature. The weight average molecular weight average molecular weight average molecular weight average molecular (2% weight/volume) at room temperature, precipitated by slow addition of an excess of methanol, washed with methanol, and dried under vacuum at room temperature. The weight average molecular weight and the polydispersity were determined as  $1.1 \cdot 10^5$  and 1.8, respectively, by gel permeation chromatography using polystyrene standards and the Q-factor method.

Tricresyl phosphate was purchased from Anachemia as tritolyl phosphate, 90%. It is a viscous liquid at room temperature and has a melting point of -33 °C. The industrial plasticizer consists predominantly of *meta* and *para* tricresyl isomers (90%). The remainder of the liquid consists of various side-products, as shown in Table 3.1. The liquid was used as received.

Isomer	Weight Percent		
triphenyl phosphate	0.0-0.3		
phenyl, di(m-cresyl) phosphate	1.0-2.5		
phenyl, di(p-cresyl) phosphate	1.0-2.5		
tri(m-cresyl) phosphate	29.0-35.0		
di(m-cresyl), p-cresyl phosphate	39.0-45.0		
m-cresyl, di(p-cresyl) phosphate	17.0-22.0		
tri(p-cresyl) phosphate	2.5-5.0		
xylenyl phosphates	0.5-2.0		

 Table 3.1 Isomer distribution range of commercial tricresyl phosphate.

# 3.2.1.4 Poly(ethylene oxide)/Poly(vinyl chloride) Blends

PEO can be expected to crystallize in recognizable spherulitic form in blends of PVC composed of as much as 50% PVC (35). Since the crystallization of PEO is the primary focus of this study, PEO/PVC blends of concentrations 10, 18, 25, 35 and 50%

PVC were prepared by solution blending in 1,2-dichloroethane (DCE), followed by precipitation in chilled hexanes. Abbreviations of the form PEO/PVC (weight percent PEO / weight percent PVC) will be used in the following text to denote the different blends. PVC (10-50 mg, depending on the desired blend composition) was added to 125 mL of DCE and stirred under nitrogen, at room temperature for 24 h, then at ~ 45 °C for 1 h to ensure complete dissolution. The PEO (90-50 mg) was then added to the solution and stirred for an additional 24 h. The blend solution was poured rapidly into a five-fold excess of hexanes chilled to 2 °C by addition of dry ice. Vigorous stirring was maintained during pouring and for another 30 min. The precipitate was collected on a polypropylene filter, washed with hexanes, and dried under vacuum at room temperature for four weeks prior to crystallization experiments.

# 3.2.1.5 Mixtures Containing Tricresyl Phosphate

Due to the low melting temperature of TCP and the differing solubilities of the liquid plasticizer and the polymers, solution blending followed by precipitation is not an appropriate preparative technique for the polymer-plasticizer mixtures. Solution casting from DCE provides a viable alternative. Industrial polymer-plasticizer mixtures commonly consist of 50 phr plasticizer, that is, 50 parts of plasticizer for one hundred parts of resin. This amount of plasticizer was added to appropriate amounts of PEO, PEO/PVC (82/18), and PEO/PVC (65/35). Abbreviations of the form PEO/PVC/TCP (weight percent PEO / weight percent PCC) will be used to denote the various mixtures.

TCP (100 mg) was added to an Erlenmeyer flask, followed by DCE (25 mL), and then resin (200 mg). The solutions were stirred at room temperature under ambient atmosphere for 24 h before being poured into glass crystallizing dishes. The dishes were partially covered to allow for room temperature evaporation of the solvent over a period of three days. The resultant thin films were peeled from the dishes using a metal spatula.

>

They were then placed under vacuum at room temperature to dry for four weeks prior to crystallization measurements.

#### 3.2.2 Differential Scanning Calorimetry

TCP were studied using a Perkin-Elmer DSC-7.

#### 3.2.2.1 Glass Transition Temperature

2

The observation of glass transitions required subambient operation of the instrument, with liquid nitrogen cooling; a two-point temperature calibration was carried out with cyclohexane and indium standards. The glass transition of PEO was observed using samples quenched from the melt: (a) in a dry ice/acetone bath, or (b) in the DSC itself. In both cases, the sample size was 10 mg, the hold time at the quench temperature was 1 h, and the heating rate for the scan was 20 °/min. A relatively high sample weight was required due to the low intensity of the glass transition that is typically observed for PEO. In case (a), an aluminum sample pan containing the PEO was heated for 15 min on a hot plate set at 100 °C. The sample pan was then immersed in a dry ice/acetone bath (-78 °C) for 5 min before rapid transfer to the DSC sample holder with a preset temperature of -120 to -100 °C. In case (b), a sample of PEO was heated at 100 °C. The glass transition of PEO was examined following procedures (a) and (b), and the glass transitions of the PEO/PVC blends were examined following procedure (b).

The melting transitions of all of the samples were observed with the instrument operating in ambient mode, with rapid cooling provided by a Perkin-Elmer Intracooler. A two-point temperature calibration was performed using octadecane and indium standards, with indium as the reference for area calibration. Because the results can be affected slightly by the sample geometry, the geometry within a given sample and from sample to sample was maintained as uniform as possible. All samples were cut in the shape of thin, square slabs, each weighing  $5.0 \pm 0.2$  mg. Each sample was held in the melt at 100 °C for 15 min in the DSC, then quenched at a nominal rate of 200 °/min to a crystallization temperature between 48 and 60 °C in the case of pure PEO and the PEO/PVC blends, or between 40 and 48 °C in the case of the plasticizer mixtures. The sample was maintained at the crystallization temperature for 24 h or, in the instance of very low supercooling, a length of time sufficient to ensure complete crystallization, then heated at 10 °/min to 100 °C.

# 3.3 Results and Discussion

### **3.3.1 Glass Transition Temperature**

3.3.1.1 Poly(ethylene oxide)

The glass transition of PEO has been examined using a variety of techniques, including dynamic mechanical analysis (DMA), DMTA, dielectric spectroscopy (DES), NMR, electron spin resonance (ESR) and DSC (19-25). All of these methods indicate the existence of multiple relaxations below the melting temperature. There are three distinct transitions associated with amorphous PEO, located at  $-130 \pm 5$ ,  $-78 \pm 5$  and  $-38 \pm 5$  °C.

2

The lowest temperature transition of amorphous PEO, sometimes referred to as the " $\gamma$  transition", has been attributed to the motion of very short (that is, 3 to 5 CH<sub>2</sub> or equivalent units) chain segments. This motion is thought to consist of the local twisting of the polymer backbone in ordinary, amorphous regions as well as in possible crystal defect zones (25). The two transitions that are observed at -78 ± 5 and -38 ± 5 °C are referred to as the  $\beta$  and  $\alpha$  transitions, respectively. An alternative designation has been used by Boyer, where the terms  $T_g(L)$  and  $T_g(U)$  refer to the low and high temperature transitions, respectively (2). Both of these types of transitions are common to semicrystalline polymers. The transition at -78 ± 5 occurs within the purely amorphous material and is the result of long-range coordinated motion that can involve up to 50 consecutive backbone atoms; therefore it corresponds to the true glass transition temperature of PEO (3).

The transition that occurs at the higher temperature corresponds to the glass transition of amorphous material that is constrained within the crystalline matrix, mainly within interlamellar regions. The temperature and the intensity of this transition are dependent on the degree and the nature of the crystallinity of a sample. This transition occurs at approximately -53 °C in high molecular weight samples that possess a high degree of crystallinity (25). This transition is of particular interest in the case of polymer blends due to its potential sensitivity to the presence of the second component in the interlamellar regions.

The selection of one of the two techniques described above should permit the observation of either the glass transition of amorphous PEO or that of the amorphous PEO constrained within the crystalline network. As would be expected, the procedure that involves rapid quenching of molten PEO in dry ice/acetone yields a thermogram characteristic of mainly amorphous PEO; however, the overall thermogram shape is irregular, with a drastic positive slope that arises due to the exothermicity of the crystallization of the polymer during heating. Unfortunately, the presence of residual

carbon dioxide and acetone on the sample pans prevented the observation of the true glass transition. The thermograms contained endotherms due to the melting of acetone (-94 °C) and the sublimation of carbon dioxide (-78 °C); these features interfered with the observation of any low intensity transitions between -100 and -70 °C.

Alternatively, when a sample was melted and quenched in the DSC, the resulting thermogram was characteristic of highly crystalline PEO, with a low-intensity, reproducible transition that occurs at  $-53 \pm 2$  °C, as shown in Figure 3.1a. The given value is the average of value for three samples. The low intensity of this transition relative to that of the melting endotherm is illustrated by Figure 3.1b.

# 3.3.1.2 Poly(ethylene oxide)/Poly(vinyl chloride) Blends and Tricresyl Phosphate Mixtures

The situation becomes more complex with the addition of another material to the crystallizing polymer. The addition of an amorphous polymer or a low molecular weight diluent frequently enhances the nucleation of the crystallizing polymer, as in the case of additive-containing PEO, thereby rendering quenching to a temperature below the glass transition temperature prior to nucleation impossible. The glass transition of pure PVC occurs at approximately 80 °C (42). In the DSC experiment, the glass transition of PVC can be obscured by the melting endotherm of PEO due to the proximity of the two transitions, in particular if the glass transition temperature of PVC renders this transition difficult to observe when PVC is the minor component of a blend. As a result, only the transition that corresponds to the glass transition of amorphous material constrained within the crystalline matrix is experimentally accessible in the PEO/PVC blends.

Several PEO/PVC blends of compositions 10, 25 and 50% PVC were quenched according to procedure (b) described above. Similar experiments were not carried out



(b)

0

-120.0

I

-80.0

Sand and the second second second

Figure 3.1 (a) The glass transition of interlamellar, amorphous PEO. (b) The glass transition in (a) and the melting transition of mainly crystalline PEO.

0.0

. مرد

:

T (°C)

ł

-40,0

Ĩ

Ξ

 $\hat{\phantom{a}}$ 

80.0

40.0

with the TCP mixtures due to the relatively high melting temperature of TCP (-33 °C), and to the glass transition of this compound which occurs at approximately -57 °C (43), that is, in the immediate vicinity of the transition of pure PEO.

62

 $\mathbb{C}$ 

The very low intensity of the transition in the PEO/PVC blends precluded an exact determination of the midpoint of the transition, but a slight transition was observed at approximately -53 °C in all of the blends examined, as in the case of the pure polymer. Similar results were reported by Margaritis and Kalfoglou, who reported DMTA data for blends of PEO and PVC of compositions similar to those employed in this study (34). The samples in the literature study were prepared by solution-blending in dichloromethane, followed by the removal of the solvent by rotary evaporation (34). The literature samples may have been compression-molded into films at 160-200 °C for 1 min, then quenched at 0 °C; however, the description of the procedure in reference 34 does not state clearly whether or not the samples examined by thermal analysis were compression-molded.

The use of DMTA permitted the observation of the glass transition of PVC as well as that of the entrapped, amorphous PEO. The literature results confirm that the temperature of the relaxation of the entrapped PEO is invariant, although at  $-44 \pm 2$  °C, with increasing PVC content in the composition range 0-80% PVC (34). The difference between the literature value and the value obtained in this study may be due to the method of sample preparation or to the experimental technique employed for the measurement. However, the glass transition temperature of PVC does decrease from a value of (*sic*) ~92 °C for pure PVC to a value of ~ 84 °C for the PEO/PVC (25/75) blend, and then to a value of ~ 62 °C for the PEO/PVC (50/50) blend (34). Based on other literature data relating to the glass transition of pure PVC (42), it seems likely that the aforementioned value for pure PVC was reported incorrectly. Furthermore, values of ~ 80 °C were reported for the PEO/PVC (95/5) and the PEO/PVC (90/10) blends in the same study (34). The decrease in the glass transition temperature of PVC from the value noted for the PEO/PVC (75/25) blend to that noted for the PEO/PVC (50/50) blend suggests that the PVC becomes dispersed to a significant degree within the amorphous phase of PEO at a PVC concentration between 25 and 50% PVC.

It is significant to compare the glass transition data for the PEO/PVC blends with literature results for miscible blends of PEO with PMMA. Data compiled by Alfonso and Russell (44) from experiments by the authors and additional literature data (45,46) demonstrate that the sole glass transition temperature observed in blends containing  $\leq 30\%$  PMMA is invariant with blend composition, at approximately -38 °C (44). However, at higher concentrations of PMMA the glass transition temperature increases monotonically with increasing PMMA content to -5 °C for PEO/PMMA (50/50), 35 °C for PEO/PMMA (25/75), and eventually to ~105 °C for pure PMMA. A separate glass transition is not observed for PMMA in these blends; however, a separate, depressed glass transition that corresponds to PMMA that is not highly dispersed could be obscured by the melting transition of PEO, as noted by the authors (44). Subsequent experiments with the PEO/PMMA blends that employed neutron and X-ray scattering revealed that some of the PMMA in the PEO/PMMA blends is actually included in the amorphous interlamellar regions of PEO (47).

The glass transition behavior of the PEO/PMMA blends is in sharp contrast with that of the PEO/PVC blends. This comparison strongly suggests that the level of dispersion of PVC in blends with PEO is significantly less than the level of dispersion of PMMA in its blends with PEO. Therefore, PEO and PVC may be immiscible or exhibit limited misciblity in the melt.

<u>\_\_\_</u>

# 3.3.2 Equilibrium Melting Temperature

## 3.3.2.1 Poly(ethylene oxide)

Buckley and Kovacs (26) analyzed data for low molecular weight fractions of PEO based on a technique developed for molecular crystals by Flory and Vrij (27), and calculated a frequently quoted value of the equilibrium melting temperature of PEO, 69 °C. However, Mandelkern has examined the determination of the equilibrium melting temperature of polymers in general and specifically the case of PEO (28). Mandelkern distinguishes between techniques that can be applied to: (i) oligomers that form molecular crystals, and (ii) real polymer chains of finite length that cannot form molecular crystals. He points out that the approach of Buckley and Kovacs was not applicable to the samples examined because the fractions studied did not consist of molecules of the same length; that is, these molecules could not form molecular crystals. In addition, it is evident from experimental data that samples exhibiting endotherms that continue beyond 69 °C must have an equilibrium melting temperature significantly higher than 69 °C. Beech and Booth (29), and Afifi-Effat and Hay (30) obtained more accurate estimates of the equilibrium melting temperature of PEO of 76 °C and 75  $\pm$  3 °C, respectively, using monodisperse, high molecular weight fractions that were crystallized to a low degree of crystallinity (~ 10-15%) prior to melting in very slow dilatometry measurements.

Measurements of imperfectly crystalline samples of PEO have yielded values of the equilibrium heat of fusion as high as ~ 180 J/g, thus climinating reports of values in this vicinity or lower from consideration (31,32). Afifi-Effat and Hay obtained a value of  $216 \pm 2$  J/g, using a series of low molecular weight fractions of PEO (30); and Braun and others obtained a value of 218 J/g via adiabatic calorimetry and density measurements (28). Therefore, it appears that  $216 \pm 2$  J/g is a reasonable estimate of this parameter.

To minimize the possibility of annealing the crystalline structure during sample heating, in particular in the case of the blends, all of the samples were crystallized to completion prior to scanning. Lamellar thickening at long crystallization times can influence the results of a Hoffman-Weeks plot and a Flory-Huggins analysis, as stated previously; however, it is unannealed, completely crystallized samples that are of primary interest in this study. Any deviation from the Flory-Huggins theory that arises from such a procedure is of interest as a potential source of structural information.

Figure 3.2 shows melting endotherms of PEO as a function of crystallization temperature. Each endotherm exhibits a well-defined, principal peak that is accompanied by a slight, low temperature shoulder which migrates to higher temperature with increasing crystallization temperature. The shoulder indicates the presence of a relatively small population of crystals that are annealed as the temperature is increased during the scan. The melting temperature was taken as the endotherm maximum. The peak of the endotherm is well-defined and represents the average melting temperature of the more perfect crystalline material, whereas the low temperature shoulder may include contributions from the melting of metastable material.

The Hoffman-Weeks plot shown in Figure 3.3 was constructed using melting data of pure PEO crystallized in the range 48-59 °C, a range close to the sample melting temperature and characterized by a small, constant lamellar thickening factor. A line where  $T_m$  is equal to  $T_c$  is also shown in Figure 3.3 for reference. The resultant equilibrium melting temperature determined from the intersection between the two plots is  $76 \pm 2$  °C, where the uncertainty is the uncertainty in the intercept of the Hoffman-Weeks plot as determined by linear least squares analysis. The result obtained in this study is in excellent agreement with the aforementioned literature data (29,30) obtained for samples crystallized to low degrees of crystallinity. The average heat of fusion is  $168 \pm 11$  J/g, which corresponds to a degree of crystallinity of  $78 \pm 5\%$ .

2

65

C



Figure 3.2 Melting endotherms of PEO crystallized at 51, 55 and 59 °C.

-

-

:

2

S





đ

đ

.

:

A previous study demonstrated that the extrapolation of the melting temperature data for samples crystallized in the temperature range 37-45 °C yielded an equilibrium melting temperature of 61 °C (48), a value that is unrealistically low given the observed crystallization of PEO at 61 °C. Although this temperature is clearly an underestimate for the equilibrium melting temperature of PEO, it is possible that this temperature corresponds to the melting temperature of imperfect crystals that do not participate in the actual equilibrium melting process that occurs at 76 °C.

#### 3.3.2.2 Poly(ethylene oxide)/Poly(vinyl chloride) Blends

PEO/PVC blends ranging in composition from 10 to 50% PVC were crystallized under conditions similar to those of the experiments with pure PEO, and the melting endotherms were recorded. As in the case of pure PEO, the endotherms exhibit a large main peak and a slight shoulder, shown for example, by the 25% PVC blend in Figure 3.4, although the endotherms are, in general, narrower than the corresponding endotherms obtained for pure PEO. As the crystallization temperature is increased, the low temperature shoulder merges with the main peak.

The Hoffman-Weeks plots constructed for the blends are shown in Figures 3.5a-e. The extrapolated equilibrium melting temperature data listed in Table 3.2 demonstrate that the equilibrium melting temperature decreases very slightly in the PEO/PVC blends. The melting temperature depression lies within the experimental uncertainty for the 10-35% PVC blends, and only a slight reduction is observed in the case of the 50% blend, as is evident from Figure 3.5f. Visual inspection of the Hoffman-Weeks plot for the PEO/PVC (75/25) blend suggests that the uncertainty given in Table 3.2 for the melting temperature of this blend is an overestimate; it is likely that a more realistic value of the uncertainty lies in the range 2-4  $^{\circ}$ C, as in the case of the other blends.



Figure 3.4 Melting endotherms of PEO/PVC blends: (a) PEO/PVC (75/25),  $T_c$  51, 53 and 55 °C: (b) PEO/PVC (90/10), PEO/PVC (75/25) and PEO/PVC (50/50),  $T_c$  53 °C.

------

· .



(a)

c

Figure 3.5 Hoffman-Weeks plots for various PEO/PVC blends: (a) PEO/PVC (90/10), PEO/PVC (82/18), (c) PEO/PVC (75/25), (d) PEO/PVC (65/35), and (e) PEO/PVC (50/50). (f) Equilibrium melting temperature,  $T_m^{\circ}$ , as a function of PVC content. (Cont'd)



T<sub>c</sub> (°C)



5

(c)

(d)



1



. - -

:

ę.

1

% PVC	T <sub>m</sub> ° (°C)	∆H <sub>hl</sub> (J/g blend)	ΔH <sub>r</sub> (J/g PEO)	% crystallinity	η
	-4 -				
0	$76 \pm 2$	$168 \pm 11$	$168 \pm 11$	$78 \pm 5$	$3.36 \pm 0.03$
10	$73 \pm 4$	$156 \pm 4$	$173 \pm 4$	$80 \pm 2$	$3.13 \pm 0.05$
18	$72 \pm 3$	$140 \pm 3$	$171 \pm 4$	$79 \pm 2$	$3.25 \pm 0.04$
25	$72 \pm 7$	$130 \pm 3$	$173 \pm 4$	$80 \pm 2$	$3.38 \pm 0.10$
35	$72 \pm 4$	$108 \pm 1$	$166 \pm 2$	<b>77</b> ± 1	$3.07 \pm 0.05$
50	$71 \pm 2$	82 ± 2	$164 \pm 4$	$76 \pm 2$	3.61 ± 0.03

**Table 3.2** Equilibrium melting temperature and heat of fusion data for PEO and the PEO/PVC blends. The lamellar thickening factor is given by  $\eta$ .

The lamellar thickening factor,  $\eta$ , is also listed in Table 3.2, and decreases slightly in the 10-35% PVC blends relative to the value obtained for pure PEO. However, the factor determined in the case of the 50% blend is significantly larger than that of pure PEO. These results suggest that in the 10-35% blends, the PVC inhibits the lamellar thickening process of PEO; but in the 50% blend, where a slight melting temperature depression has been noted, the amorphous second component appears to promote the thickening process.

The data show good agreement with the literature data for PEO/PVC blends of similar composition (34). A discrepancy of 2-3 °C between the above data and the results of Margaritis and Kalfoglou (34), which are also plotted in Figure 3.5f, can be attributed to the use of the endotherm onset temperature in the literature calculations instead of the peak temperature. The very small melting temperature depression suggests that at best,

0.1622.

PEO and PVC are only slightly miscible and more likely completely immiscible in the melt. Martuscelli has noted the occurrence of a small melting temperature depression in blends that are immiscible in the melt, for example isotactic polypropylene blended with low density polyethylene (49). He attributes this depression to unspecified kinetic and morphological factors associated with the presence of isolated domains of the noncrystallizing component in the melt.

Given the variation in the lamellar thickening factor with blend composition, it is probable that the melting temperature depression in these blends arises due to the interference of PVC with the crystalline structure of PEO. The surface interfacial tension calculations in Chapter 2 predict the potential for some adhesion at the interface between the two amorphous phases of these polymers. It is reasonable to expect this adhesion to disrupt the lamellar thickening process, in particular if the adhesion occurs at the amorphous lamellar fold surfaces.

To further investigate the question of miscibility, the data were analyzed according to the Flory-Huggins equation. If the assumptions of the theory are valid for the system under investigation, then a plot of  $[(1/T_m^{\circ}_{,bl} - 1/T_m^{\circ})]/\upsilon_1$  as a function of  $\upsilon_1$  will yield a straight line with a slope of  $-RV_2\chi_{12}/(\Delta H_1^{\circ})V_1$ . The molar volumes of PEO and PVC at 100 °C were calculated from specific volume or density data available in the literature (50-53) as 41.2 and 45.9 cm<sup>3</sup>/mol, respectively. The volume fraction of PVC at 100 °C was also calculated. Weight fractions of 10, 18, 25, 35 and 50% PVC are equivalent to volume fractions of 8, 15, 21, 30 and 44%, respectively.

The resultant Flory-Huggins plot, shown in Figure 3.6, is distinctly curved. The determination of the slope of the two linear segments yields values of  $\chi_{12}$  of 1.5 and 0.15 for the segments at low and high PVC content, respectively. These values are presented for the purpose of discussion only and are not intended as estimates of the interaction parameter. This curvature definitely does not indicate limited miscibility at PVC concentrations of  $\geq$  35%, as proposed in the literature (34,35,36). In fact, the significantly

0

.





.

large, positive value of the interaction parameter obtained at low concentrations of PVC suggests that the two polymers are immiscible. However, if PEO and PVC exhibit limited misciblity, then the values taken for the volume fraction do not reflect the actual volume fraction of the miscible blend. Therefore, the volume fraction of PVC would be less than the given values.

The most probable source of the curvature in the plot is the failure of at least one of the assumptions of the theory. It is evident from the preceding discussion that the assumption of the non-interference of the second component with the lamellar thickening process of the semicrystalline polymer is not valid in this case. It is highly probable that the primary explanation for the melting temperature depression is the disruption of the crystalline morphology of PEO by the PVC.

The addition of PVC to PEO exerts a small effect on the degree of crystallinity of PEO, as demonstrated by the results listed in Table 3.2. The degree of crystallinity of PEO may be slightly elevated in the blends of intermediate composition, that is, the 18-25% PVC blends; whereas the 10, 35 and 50% PVC blends yield values that are identical with the data obtained for pure PEO, although these changes are within the experimental uncertainty. It is interesting to note that the possible elevation in the crystallinity of PEO disappears at a concentration where the change in the slope of the Flory-Huggins plot occurs, a result that provides additional support for changes in the crystallization process of PEO with increasing PVC content.

### 3.3.2.2.1 Evaluation of Literature Results

بسيب ا

Various attempts have been made to characterize the miscibility of PEO and PVC by thermal analysis (34,35) as well as solid state NMR (36). The molecular weights of the polymers used in the thermal analysis study of Margaritis and Kalfoglou are similar to those in this thesis (PEO:  $M_n 3 \cdot 10^5$ , PVC:  $M_n 2.7 \cdot 10^4$ ) (34). The authors also obtained

a curved plot using the Flory-Huggins equation; a slightly lower value of the equilibrium melting temperature of PEO, 72 °C, was used as well. A value of 0.05 was determined for  $\chi_{12}$  by the determination of the slope of a linear segment of the plot at intermediate to high PVC content (34). A plot constructed for a blend of high molecular weight PEO (M<sub>n</sub> 4.0 · 10<sup>6</sup>) with PVC (M<sub>n</sub> 2.7 · 10<sup>4</sup>) was also curved, and a value of -0.03 was calculated for  $\chi_{12}$  from the slope of a linear segment at high PVC content. The authors conclude from this procedure that PEO and PVC exhibit "limited miscibility in the melt at high PVC contents" (34). Margaritis and Kalfoglou failed to note that the determination of  $\chi_{12}$  from plots that exhibit such distinct curvature is invalid. Furthermore, if PVC exhibits limited miscibility with the PEO melt at high concentrations of PVC, then PVC and PEO may also exhibit limited miscibility at low concentrations of PVC, a result that is clearly not reflected by the available data.

An additional study by Katime and others has examined the melting behavior of PEO/PVC blends by DSC (35). The molecular weights of PEO and PVC in one series of blends were  $3.5 \cdot 10^4$  and  $1.0 \cdot 10^5$ , respectively (unspecified molecular weight type). A second series of blends containing lower molecular weight polymers was also studied. The blends were prepared by solution-blending in chloroform, followed by film-casting at room temperature and drying under vacuum. The authors obtained a linear Flory-Huggins plot for PVC concentrations  $\geq 30\%$ ; values of approximately -0.30 and -0.10 were computed for  $\chi_{12}$  using the linear data obtained for the high and low molecular weight blends, respectively (35). Again, the melting behavior of the blends of low PVC content has been neglected. In addition, unreasonably low values of the equilibrium melting temperatures of the samples were determined and used in further calculations. For example, the value reported for PEO was 66 °C. Other sources of experimental error include the sample premelting temperature. The premelting temperature for the samples, 80 °C, not only was substantially less than the appropriate value for PEO of 100 °C, but

was also in the vicinity of the glass transition temperature of pure PVC. As a result, this study also arrived at erroneous conclusions about the interactions in these blends.

A third study by Marco and others employed solid state <sup>13</sup>C-NMR relaxation experiments to probe the miscibility of PEO  $(M_y 2.0 \cdot 10^4)$  and PVC  $(M_y 4.3 \cdot 10^4)$  (36). The blends were prepared by solution-blending in dichloromethane, followed by the removal of the solvent by rotary evaporation and vacuum-drying at room temperature (36). The spin-lattice proton relaxation time in the rotating frame,  $T_{10}(H)$ , can be used as an indication of the distance between individual molecules of the two components of a binary blend (54). In an immiscible system that contains separate domains of the two components, two values of  $T_{10}(H)$  that correspond to the values of the individual components will be observed. However, in a miscible system, where molecules of the two components are separated by a distance of less than 2 nm, only one, intermediate value of  $T_{10}(H)$  will be observed. In the literature study, the relaxation time of the PEO/PVC (80/20) blend at "ambient" temperature was the same as that measured for pure PVC (9.1 ms); but the relaxation time measured for the PEO/PVC (70/30) blend was slightly longer (10 ms), and the times measured for blends  $\geq 40\%$  PVC were "very different" (12 ms) from that of pure PVC (36). Once again, the proposal that the two polymers are slightly miscible solely at high PVC content was offered to explain the results.

Marco and others interpret this increase in the relaxation time of PVC as evidence of miscibility in blends containing  $\geq 40\%$  PVC (36). Unfortunately, the authors do not report relaxation time data for PEO, citing the complexity of the corresponding relaxation process. An independent study of the relaxation of the crystalline and amorphous components of PEO suggests that  $T_{1\rho}(H)$  for the amorphous component of PEO is approximately 10 ms at 25 °C (55). Without a knowledge of the relaxation time of PEO in the blends, no definitive conclusions regarding miscibility can be drawn from this NMR study, although the existence of limited miscibility is still possible.

1

÷

All of these literature results confirm the possibility of limited miscibility between PVC and amorphous PEO; however, this limited miscibility should apply throughout the blend concentration range, and not only at high concentrations of PVC, as suggested by the various authors. It is evident that the degree of miscibility is very low, and therefore does not play a significant role in the observed melting temperature depression. Instead, it is the influence of PVC on the crystalline structure of PEO and the possible adhesion between PVC and the amorphous fold surfaces of PEO that are the determining features of these blends.

## 3.3.2.3 Tricresyl Phosphate Mixtures

Preliminary crystallizations of the plasticizer mixtures showed that the TCP exerts a strong influence on the crystallization kinetics of PEO. As a result of the substantial depression of the crystallization rate of PEO in all of the plasticizer mixtures, as noted in the experimental section of this chapter, the crystallization temperature range used for these samples was 41-47 °C, instead of 49-59 °C as in the case of PEO and the PEO/PVC blends. The endotherms of PEO/TCP (67/33) shown in Figure 3.7a, are of approximately the same width as the corresponding endotherms for the PEO/PVC blends, but with a lowtemperature shoulder that represents a larger portion of the total endotherm area than in the case of the blends. The position of this shoulder shifts dramatically to higher temperature with increasing crystallization temperature. The endotherms obtained in the case of PEO/PVC/TCP (55/12/33) were identical in shape with those obtained for PEO/TCP (67/33). The third blend, PEO/PVC/TCP (44/23/33), exhibits endotherms with smooth low-temperature shoulders as illustrated in Figure 3.7b, implying a broader distribution of low-melting material.

The Hoffman-Weeks plots for the mixtures containing TCP are shown in Figure 3.8. The equilibrium melting temperature data, which are listed in Table 3.3, reveal that in


Figure 3.7 Melting endotherms of TCP mixtures: (a) PEO/TCP (67/33),  $T_c$  43, 45 and 47 °C; (b) PEO/PVC/TCP (44/23/33),  $T_c$  43, 45 and 47 °C.



(a)

(b)

:

1011

Figure 3.8 Hoffman-Weeks plots for TCP mixtures: (a) PEO/TCP (67/33), (b) PEO/PVC/TCP (55/12/33), and (c) PEO/PVC/TCP (44/23/33). (Continued)

81



Figure 3.8 (cont'd)

Ţ

ње 1. – Се

spite of the drastic reduction in the crystallization rate, there is no apparent melting temperature depression in the PEO/TCP mixture. This result suggests that PEO and TCP are immiscible or exhibit only limited miscibility in the melt. In addition, the equilibrium melting temperature of PEO in the ternary mixtures cannot be distinguished from the values estimated for the pure polymer or the blends due to the large experimental uncertainty.

 Table 3.3 Equilibrium melting temperature and heat of fusion data for PEO and TCP
 plasticizer mixtures.

% PVC	% TCP	T <sub>m</sub> ° (°C)	∆H <sub>r</sub> (J/g)	ΔH <sub>r</sub> (J/g PEO)	% crystallinity	η
0	0	$76 \pm 2$	168 ± 11	$168 \pm 11$	78 ± 5	3.36 ± 0.03
0	33	74 ± 1	$105 \pm 3$	$158 \pm 4$	73 ± 2	$1.88 \pm 0.01$
12	33	76±9	87 ± 3	$159 \pm 6$	74±3	1.73 ± 0.08
23	33	66 ± 11	70 ± 5	161 ± 11	75±5	$2.62 \pm 0.16$

Again, visual inspection of the plots for the two ternary mixtures suggest that the uncertainty listed in the above table is unrealistically large. In addition, the extrapolated value obtained for the equilibrium melting temperature of the PEO/PVC/TCP (44/23/33) mixture appears to be an underestimate, with the actual value lying closer to 70 °C. It is possible that a melting temperature depression occurs in the PEO/PVC/TCP (44/23/33) mixture, but the magnitude of this depression is expected to be approximately the same as in the case of the original binary blend. The large experimental uncertainties of the melting

÷

temperature results for the ternary mixtures are due to the substantial scatter in the data; they do not arise due to any curvature that can occur due to a temperature dependence of the lamellar thickening factor of equation 3.4. The scatter in these Hoffman-Weeks plots reflects a major problem that is encountered in the thermal analysis of mixtures that contain a low molecular weight liquid: the maintenance of uniform geometry within a given sample and among different samples.

The values of the lamellar thickening factor listed in Table 3.3 decrease substantially on addition of TCP to PEO. The value obtained for the PEO/PVC/TCP (55/12/33) mixture is similar to that obtained for the PEO/TCP mixture; but the value obtained for the PEO/PVC/TCP (44/23/33) mixture is closer to the value obtained for pure PEO. Again, it is possible that the regression in Figure 3.8c yields an underestimate of the slope and therefore an overestimate of the lamellar thickening factor. A more realistic, larger slope would yield a lower value for  $\eta$  that would be similar to the values obtained for the other TCP mixtures.

It is evident that the plasticizer is responsible for the suppression of lamellar thickening in the ternary mixtures. Based on the surface interfacial tension calculations in Chapter 2, the suppression of the lamellar thickening of PEO by TCP cannot be attributed to any significant adhesion between the TCP and the amorphous phase of PEO, although it is possible that TCP is slightly miscible with the amorphous phase of PEO. It is likely that the rejection of the small plasticizer molecules by the crystalline PEO leads to an accumulation of these small molecules in interlamellar, interfibrillar and interspherulitic regions. The resultant interaction between the amorphous fold surfaces of PEO and the rejected TCP molecules appears to severely impede the thickening process. It is possible that the solubilization of the amorphous PEO in the fold surfaces by TCP could facilitate the process of chain folding.

...:

The degree of crystallinity of PEO, also listed in Table 3.3, may be reduced slightly by the addition of plasticizer. The plasticizer appears to be responsible for this reduction in crystallinity, possibly through the entrapment of small molecules of TCP or portions of plasticized PVC chains within the crystalline matrix of PEO. In contrast with the PEO/PVC blends, where PVC is not plasticized, no increase in the degree of crystallinity of PEO is observed in these samples.

# 3.4 Summary

Measurements conducted in the composition range 0-50% PVC, in addition to an evaluation of literature data at other compositions, indicate that the glass transition temperature of interlamellar, amorphous PEO is invariant with the PEO/PVC blend composition. This behavior is in contrast with that of miscible PEO/PMMA blends (44-46), thereby suggesting that the level of dispersion of PVC in PEO/PVC blends is less than the level of dispersion of PMMA in PEO/PMMA blends.

The equilibrium melting temperature data obtained for PEO/PVC blends indicate the possibility of a slight melting temperature depression. However, the analysis of the data using the Flory-Huggins equation reveals that the two polymers exhibit limited miscibility or are immiscible in the melt. This equation cannot be applied to determine an accurate value of the interaction parameter due to the distinct curvature of the plot. This curvature suggests that PVC exerts an influence on the crystalline structure of PEO, which may include interference in the lamellar thickening process of PEO. The adhesion between the PVC and the lamellar fold surfaces of PEO, which influences the crystalline morphology of PEO, plays a more significant role in the observed melting temperature depression than the slight, limited miscibility of the two polymers. While the degree of crystallinity of PEO is only slightly elevated in PEO/PVC blends of intermediate concentration, the endotherm shape suggests that the degree of crystal perfection may be influenced significantly by subtle changes introduced into the crystalline structure of PEO by PVC.

No melting temperature depression can be detected outside of the experimental uncertainty for the mixtures containing TCP, although a depression may occur in the case of the PEO/PVC/TCP (44/23/33) mixture. TCP does not cause any elevation in the degree of crystallinity of PEO, but instead may cause a slight depression in this quantity. The substantial decrease in the lamellar thickening factor that occurs upon addition of TCP to PEO can be attributed to the facile rejection of the small plasticizer molecules into interlamellar and other intercrystalline regions, and not to any significant adhesion between TCP and PEO. The resultant accumulation of these small molecules at the fold surfaces then impedes the lamellar thickening process. Limited miscibility of TCP with the amorphous phase of PEO could possibly enhance or facilitate chain folding, thereby leading to thinner lamellae than in the case of pure PEO. The analysis of the relevant endotherms demonstrates the occurrence of more drastic structural adjustments on the part of the crystalline PEO to compensate for the presence of the low molecular weight material and the plasticized PVC than in the case of the PEO/PVC blends. Because the DSC experiment does not provide any information regarding the nature of the changes that occur within the crystalline structure of PEO as a result of the addition of PVC or TCP, recourse must be taken to other experimental techniques such as polarized light microscopy and infrared microspectroscopy, as will be discussed in Chapters 4 and 5, respectively.

# **3.5 References**

- 1. Utracki, L. A. Polymer Alloys and Blends; Hanser: New York, 1989.
- 2. Eisenberg, A. In *Physical Properties of Polymers*; Mark, J. E., Ed.; 2nd Ed.; American Chemical Society: Washington, DC, USA, 1993; pp 61-95.
- Boyer, R. F. In The Encyclopedia of Polymer Science and Technology; Bikales, N. M. Ed.; Suppl., Vol. 2; Interscience: New York, 1977; p 745.

- 4. Gordon, M.; Taylor, J. S. J. Appl. Chem. 1952, 2, 493.
- 5. Wood, L. A. J. Polym. Sci. 1958, 28, 318.
- 6. Kwei, T. K. J. Polym. Sci., Lett. Ed. 1984, 22, 307.
- Kwei, T. K.; Pearce, E. M.; Pennacchia, J. R.; Charton, M. Macromolecules 1987, 20, 1174.
- 8. Mandelkern, L. Crystallization of Polymers; McGraw-Hill: New York, 1964.
- 9. Wunderlich, B. Macromolecular Physics; Vol. III; Academic: New York, 1980.
- 10. Padden, Jr., F. J.; Keith, H. D. J. Appl. Phys. 1959, 30, 1470-1484.
- 11. Scott, R. L. J. Chem. Phys. 1949, 17, 279.
- 12. Flory, P. J. J. Chem. Phys. 1941, 9, 660.
- 13. Huggins, M. L. J. Chem. Phys. 1941, 9, 440.
- 14. Nishi, I.; Wang, T. T. Macromolecules 1975, 8, 909.
- 15. Krause, S. Chemtracts Macromol. Chem. 1991, 2, 367-383.
- 16. Hoffman, J. D.; Weeks, J. J. J. Research Natl. Bur. Standards 1962, 66A, 13.
- 17. Hoffman, J. D. Polymer 1991, 32, 2828-2841.
- 18. Alamo, R. G.; Viers, B. D.; Mandelkern, L. Macromolecules 1995, 28, 3205-3213.
- 19. Faucher, J. A.; Koleske, J. V.; Santee, Jr., E. R.; Stratta, J. J.; Wilson, III, C. W. J. Appl. Phys. 1966, 37, 3962-3964.
- 20. Miller, G. W.; Saunders, J. H. J. Appl. Polym. Sci. 1969, 13, 1277-1288.
- 21. Ishida, Y.; Matsuo, M.; Takayanagi, M. Polym. Lett. 1965, 3, 321-324.
- 22. Törmälä, P. Eur. Polym. J. 1977, 10, 519-521.
- 23. Privalko, V. P.; Lobodina, A. P. Eur. Polym. J. 1974, 10, 1033-1037.
- 24. Lal, J.; Trick, G. S. J. Polym. Sci.: Part A-1 1970, 8, 2339-2350.
- 25. Lang, M. C.; Noel, C.; Legrand, A. P. J. Polym. Sci., Polym. Phys. Ed. 1977, 15, 1319-1327 and 1329-1338.
- 26. Buckley, C. P.; Kovacs, A. J. Progr. Colloid and Polym. Sci. 1976, 254, 695-715.
- 27. Flory, P. J.; Vrij. A. JACS 1963, 85, 3548.

- 28. Mandelkern, L.; Stack, G. M. Macromolecules 1984, 17, 871-878.
- 29. Becch, D. R.; Booth, C. Polym. Lett. 1970, 8, 731-734.
- 30. Afifi-Effat, A. M.; Hay, J. N. J. Chem. Soc., Faraday Trans. II 1972, 68, 656-661.
- 31. Booth, C.; Devoy, C. J.; Gee, G. Polymer 1971, 12, 327-334.
- 32. Mandelkern, L. J. Appl. Phys. 1955, 26, 443-451.
- 33. Braun, W.; Hellwege, K.-H.; Knappe, W. Coll. Polym. Sci. 1967, 215, 10-15.
- Margaritis, A. G.; Kalfoglou, N. K. J. Polym. Sci., Polym. Phys. Ed. 1988, 26, 1595-1612.
- Katime, I. A.; Anasagasti, M. S.; Peleteiro, M. C.; Valenciano, R. Eur. Polym. J. 1987, 23, 907-911.
- Marco, C.; Gomez, M. A.; Fatou, J. G.; Exteberria, A.; Elorza, M. M.; Iruin, J. J. Eur. Polym. J. 1993, 11, 1477-1481.
- 37. Prud'homme, R. E. J. Polym. Sci., Polym. Phys. Ed. 1982, 20, 307-317.
- 38. Cheng, S. Z. D.; Wunderlich, B. J. Polym. Sci., Polym. Phys. Ed. 1986, 24, 577-594 and 595-617.
- Cheng, S. Z. D.; Bu, H. S.; Wunderlich, B. J. Polym. Sci., Polym. Phys. Ed. 1988, 26, 1947-1964.
- 40. Cheng, S. Z. D.; Noid, D. W.; Wunderlich, B. J. Polym. Sci., Polym. Phys. Ed. 1989, 27, 1149-1160.
- 41. Stevens, M. P. Polymer Chemistry: An Introduction; Oxford: New York, 1990: pp 61-63.
- 42. Roy, S. K.; Brown, G. R.; St. Pierre, L. E. Intern. J. Polymeric Mater. 1983, 10, 13-20.
- 43. Ceccorulli, G.; Pizzoli, M.; Scandola, M. Polymer 1987, 28, 2077-2080.
- 44. Alfonso, G. C.; Russell, T. P. Macromolecules 1986, 19, 1143-1152.
- Hoffman, D. M., Ph.D. Thesis, University of Massachusetts, Amherst, Massachusetts, USA, 1979.

- 46. Martuscelli, E.; Pracella, M.; Yue, W. P. Polymer 1984, 25, 1097-1106.
- 47. Russell, T. P.; Ito, H.; Wignall, G. D. Macromolecules 1988, 21, 1703-1709.
- 48. Marentette, J. B.Sc. Honors Thesis, McGill University, Montreal, Quebec, Canada, 1990.
- 49. Martuscelli, E. Polym. Eng. Sci. 1984, 24, 563-586.
- 50. Roe, R.-J. J. Phys. Chem. 1968, 72, 2013-2017.

Conversion of the second

- 51. The Polymer Handbook; Brandrup, J. and Immergut, E. H. Eds.; Wiley: New York, 1989; p V62.
- 52. Malac, J. Sb. Prednasek, Macrotest, Celostatni Konf., 4th 1976, 2, 345.
- 53. Hellwege, K. H.; Knappe, W.; Lehman, P. Kolloid-Z. 1962, 183, 110.
- 54. Koenig, J. L. Spectroscopy of Polymers; American Chemical Society: Washington, DC, USA, 1992.
- 55. Johansson, A.; Tegenfeldt, J. Macromolecules 1992, 25, 4712-4715.

# Chapter 4

# Polarized Light Microscopy: Spherulite Morphology and Crystallization Kinetics

# 4.1 Introduction

The examination of the microscale aspects of the crystallization of semicrystalline polymers, such as spherulite morphology, nucleation density and growth rate, is crucial to the comprehension of macroscale material properties As stated in the introductory chapter of this thesis, many semicrystalline polymers crystallize in the form of spherulites or related structures that are readily observed using polarized light microscopy (PLM). Some of the possible variations in spherulite morphology were also discussed in the Introduction.

# 4.1.1 Crystallization Kinetics of Pure Semicrystalline Polymers

The radial growth rate of a spherulite grown in thin section can be measured using a polarized light microscope equipped with a hot stage for regulation of sample temperature, by either time-lapse photomicroscopy or videomicroscopy (1). The crystallization temperature influences the manner in which the macromolecular segments fold and pack together. Changes in packing lead to significant variation in the radial growth rate of spherulites as well as changes in morphology. As the crystallization temperature is decreased below the melting temperature, the rate of crystallization is nucleation-controlled and increases due to an increase in the driving force for crystallization. After attaining a maximum value about midway between  $(T_m - 10 \text{ K})$  and  $(T_g + 30 \text{ K})$ , the growth rate decreases with decreasing temperature due to a continuing decrease in molecular motion; that is, the growth rate becomes diffusion-controlled.

In general, the isothermal radial growth rate of a spherulite grown from a pure polymer melt is linear until spherulite impingement occurs. The growth rate of polymer spherulites, G (in units of cm/s), was originally described by the classical Turnbull-Fisher equation

$$G = G_{o} exp\left(\frac{-\Delta E_{d}}{kT}\right) exp\left(\frac{-\Delta \Phi}{kT}\right)$$
(4.1)

a Gaussian-like function shown schematically in Figure 4.1. In equation 4.1,  $G_0$  is a preexponential factor,  $\Delta E_d$  is the activation free energy of transport of a crystallizing segment across the melt-crystal interface,  $\Delta \Phi$  is the activation free energy required to form a nucleus of critical size, and k is Boltzmann's constant (2). Thus, the first exponential term is often referred to as the "transport" term while the second exponential is the "nucleation" term.

Current nucleation theory, as developed by Hoffman, Davis, Lauritzen and Miller, describes the growth rate of spherulites by an expression having a form similar to that of equation 4.1, as shown below

$$G = G_{o} exp\left[\frac{-U^{*}}{R(T_{c} - T_{\infty})}\right] exp\left[\frac{-K_{g}}{T_{c}(\Delta T)f}\right]$$
(4.2)

where  $G_0$  is again a preexponential factor (cm/s), U\* is the activation energy for reptation in the melt, R is the ideal gas constant (8.314 J/mol-K), T<sub>c</sub> is the crystallization temperature (K), T<sub>∞</sub> is the temperature of cessation of molecular motion (often taken as





÷

2

-

.

 $T_g$  - 30 K), and  $\Delta T$  is the supercooling ( $T_m^\circ - T_c$ ),  $T_m^\circ$  being the equilibrium melting temperature (3-5). The dimensionless correction factor, f,

$$f = \frac{2 \cdot T_c}{T_m^0 + T_c}$$
(4.3)

in equation 4.2 is intended to compensate for the decreasing heat of fusion with decreasing temperature.

The relation of equation 4.2 to experimental data requires further definition of the parameter  $K_g$ . If spherulite growth is assumed to proceed via two-dimensional secondary surface nucleation, that is, new crystalline material is deposited on the surface of the growing spherulite, then the nucleation constant, is given by

$$K_{g} = \frac{2jb_{o}\sigma\sigma_{c}T_{m}^{o}}{k(\Delta H_{f}^{o})}$$
(4.4)

where  $b_0$  is the crystalline molecular thickness in the growth direction (cm) (shown schematically in Figure 4.2),  $\sigma$  is the lateral surface interfacial free energy (erg/cm<sup>2</sup>),  $\sigma_e$  is the fold surface interfacial free energy (erg/cm<sup>2</sup>), and  $\Delta H_f^{\circ}$  is the heat of fusion per unit volume of monomer units (erg/cm<sup>3</sup>) (3-5). The parameter j depends on the so-called "regime" of crystallization.

If the values of the parameters  $b_0$  and  $\Delta H_f^\circ$  in equation 4.4 are known from X-ray diffraction measurements and calorimetry, respectively, determination of the slope of a plot of  $\ln (G) + [U^*/R(T_c - T_{\infty})]$  as a function of  $1/T_c(\Delta T)f$ , which is equivalent to  $2jb_0\sigma\sigma_c T_m^\circ/k(\Delta H_f^\circ)$ , permits calculation of the product of the surface interfacial free



Figure 4.2 Secondary surface nucleation model showing stem deposition.

:

..

energies,  $\sigma\sigma_e$ , for a given polymer and regime. Furthermore, the empirical relation given below

$$\alpha_{\rm LH} = \frac{\sigma}{(\Delta H_{\rm f}^{\rm o})(a_{\rm o}b_{\rm o})^{1/2}} \tag{4.5}$$

where  $a_0b_0$  is the cross-sectional area of the polymer (in units of cm<sup>2</sup>), as shown in Figure 4.2, permits estimation of the lateral surface interfacial free energy (5). The parameter  $\alpha_{LH}$  is an empirical parameter that has been estimated to be equal to 0.1 for most linear polyolefins (5). A value of  $0.25 \pm 0.03$  for  $\alpha_{LH}$  has been found to apply to various highmelting polyesters, such as poly(pivalolactone) (6). The calculated lateral surface interfacial free energy from the product of the two surface interfacial free energies.

Recently, Hoffman and others proposed a relationship between the lateral surface interfacial free energy and the characteristic ratio of polymer chain dimensions,  $C_{\infty}$  (6). The derivation of the relationship between these two parameters assumes that the entropy change associated with  $\sigma$  during the localization of a polymer chain prior to surface nucleation can be approximated by the total entropy change of stem addition scaled by  $1/C_{\infty}$ . Therefore, the lateral surface interfacial free energy was predicted to be proportional to  $C_{\infty}$  multiplied by a constant. The theory was found to show good agreement with experimental data for polyethylene, isotactic polystyrene and poly(L-lactic acid) (6). However, subsequently Tonelli demonstrated that "the conformational entropy of a flexible polymer chain is not correlated with its conformationally-averaged dimensions ( $C_{\infty}$ )" (7). The conformational entropies and the dimensions of a varied assortment of over 24 polymers were examined, and no relationship was found between these two parameters (7). As a result, the scaling relationship suggested by Hoffman and others (6) does not appear to be applicable.

. . . . . . . .

More careful examination of the plot of the growth rate as a function of the crystallization temperature indicates that for a number of polymers, discontinuities occur at temperatures between the equilibrium melting temperature and the temperature of the maximum growth rate. To account for this behavior Hoffman has identified three regimes of crystallization kinetics that occupy different regions of the growth rate-temperature curve, as shown by the logarithmic growth rate-temperature curve in Figure 4.3a (3). In regimes I and III, the parameter j is equal to 2, and in regime II, j is equal to 1, so that a plot of  $\ln (G) + U^*/[R(T_c - T_{\infty})]$  as a function of  $1/T_c(\Delta T)$ f should resemble the plot in Figure 4.3b in the ideal case, where the ratio of the equivalent slopes in regimes I and III to the slope in regime II is 2:1. If  $b_0$  and  $\Delta H_f^{\circ}$  can be determined, then calculation of the slopes of the linear segments permits determination of the product of the surface interfacial free energies for a specific polymer and regime.

The fundamental difference among the regimes is the rate at which portions of polymer chains are deposited on the crystal surface. Within the highest temperature regime, that is, regime I, after deposition of the first crystalline stem on an exposed surface, other stems from the same or other macromolecules are deposited adjacent to the surface nucleus until the new layer completely covers the available surface area. The growth rate in this regime is described by the expression

$$G_{\rm I} = a_0 b_0 n_{\rm S} i \tag{4.6}$$

where  $n_s$  is the number of stems of width  $a_0$ , and i is the secondary surface nucleation rate (in units of nuclei/cm  $\cdot$  s) (3). As the crystallization temperature is decreased, that is, as the supercooling is increased, the rate of surface nucleation becomes greater than the rate



Figure 4.3 Ideal (a) logarithmic growth rate curve, and (b) Hoffman-Lauritzen plot showing crystallization regimes I, II and III.

Ļ

of crystallization of each molecule, resulting in the development of multiple surface nuclei. Crystallization characteristic of regime II is described by the following equation

$$G_{II} = b_0 (2ig)^2 \tag{4.7}$$

where g is the substrate completion rate (3). Regime III crystallization arises when the distance referred to as the niche separation on a given lamella, that is, the distance between neighboring nucleation sites, in regime II approaches the width of a crystalline stem. The elementary growth rate equation in this regime takes on the same form that in regime I, as shown by the following expression

$$G_{III} = b_0 i' L' = a_0 b_0 n_s i'$$
(4.8)

where i' is the surface nucleation rate,  $n_s'$  is the average number of stems laid down in the niche adjacent to the initial stem, and L' is defined as the effective substrate length (3). Regime III is strictly defined to apply only to temperatures in the range above the temperature corresponding to the temperature of the maximum growth rate. For certain polymers, a reversion from regime I to regime II at very low supercoolings has been proposed (8,9).

Thus, nucleation theory demonstrates that the growth rate curve of a variety of polymers does not follow the simple Gaussian-like shape that it appears to exhibit on initial inspection. In practice, growth rate data can be analyzed for the possible incidence of regime transitions by plotting ln (G) as a function of crystallization temperature, as shown in Figure 4.3a. A discontinuity in the slope of such a plot is the first indication of the occurrence of a regime transition. A plot of the logarithmic form of equation 4.2,  $[\ln (G) + U^*/R(T_c - T_{oo})]$  as a function of  $1/T_c(\Delta T)f$ , as shown in Figure 4.3b, provides a more rigorous test of the existence of regime transitions. However, difficulties arise in the

interpretation of these plots. For example, a systematic error in growth rate measurements can lead to a slope ratio that is not equal to 2:1 for an actual regime transition in the latter plot. On the other hand, a slope ratio of  $\sim$  2:1 is not irrefutable evidence of a regime transition. A change in slope can result from the incorrect estimate of one or more of the relevant parameters in equation 4.2. In addition, it is possible for a change in the slope ratio to arise due to a transformation in the crystal habit of the polymer that leads to different growth rate behavior.

An extremely important assumption of the preceding theory is that the secondary surface nucleation in each regime occurs on the same crystal growth face. That is, the general crystallographic orientation of the unit cell with respect to the spherulite radial and tangential directions must remain constant. Discontinuities observed in the growth rate curve that are coincident with changes in the dominant crystal growth face cannot be described as regime transitions.

Both regime I/II and regime II/III transitions have been reported to occur in PEO (8). However, an additional study of single crystals of PEO has proposed that the kinetic discontinuity that has been designated as a regime II/III transition coincides with a change in the dominant crystal growth face of PEO (10). Should this growth face transformation actually occur in spherulites, then the designation of this discontinuity as a regime transition would be invalid.

The examination of spherulite morphology in the light of current nucleation theory reveals a complex picture. The relationship between regimes and morphology is the subject of much debate in the literature (8,9,11-13). Regime transitions have been observed in selected polymers, and in some cases they have been associated with morphological transitions. Studies involving isotactic polypropylene (iPP) (11) and poly(phenylene sulfide) (12) have yielded no evidence for such a relationship in the samples examined. However, a morphological transition from axialitic structures in regime I to regular spherulites in regime II has been described in polyethylene (PE) (13).

A study of samples of *cis*-polyisoprene (9) has suggested a similar direct relationship, although the morphological transition is not as well-defined as in the case of PE. A morphological transition has been associated with the proposed regim II/III transition in PEO (8), but the occurrence of this regime transition is questionable and will be examined in this chapter.

#### 4.1.2 Semicrystalline-Amorphous Polymer Blends

The crystallization kinetics of spherulites in polymer blends can be independent of the presence of the second component, as in many immiscible blends, or can be depressed or accelerated, depending on the miscibility of the two polymers. For example, the growth rate of spherulites of PEO was found to be depressed in miscible blends with poly(methyl methacrylate) (PMMA), where the depression in the growth rate at a given crystallization temperature increased with increasing PMMA content (14). However, the growth rate of spherulites of isotactic polystyrene (iPS) in blends with poly(vinyl methyl ether) (PVME) (15) or in mixtures with benzophenone (16) was accelerated, a result that in both cases was attributed to the plasticization of iPS by the partially miscible additive.

Several attempts have been made to devise equations that describe the crystallization of semicrystalline polymers in blends, all of which have employed the Turnbull-Fisher equation (equation 4.1) or the Hoffman-Lauritzen equation (equation 4.2) as a starting point (16-20). Crystallization from a miscible, one-phase melt in systems such as the iPS/benzophenone mixture mentioned previously has been treated by Boon and Azcue (16), who modified the Turnbull-Fisher equation to take into account the proportionality between the rate of nucleation and the concentration of crystallizable units to yield the following relation

$$G = G_{o}' exp\left[\frac{-U^{*}}{R(T_{c} - T_{\infty})}\right] exp\left[\frac{-K_{g}'}{T_{c}(\Delta T)}\right]$$
(4.9)

where  $G_0'$  is  $\upsilon_2 G_0$ , with  $\upsilon_2$  as the volume fraction of the semicrystalline polymer, and  $K_g'$  is defined as (16)

$$K_{g'} = \frac{nb_{o}\sigma\sigma}{k(\Delta H_{c}^{o})} - \frac{2\sigma T_{c}T_{m}^{o}[\ln(\upsilon_{2})]}{b_{o}(\Delta H_{c}^{o})}$$
(4.10)

The parameter n was defined as 4 by Boon and Azcue; however, comparison of equation 4.10 with the later equation developed by Hoffman and Lauritzen (equation 4.2) indicates that n in equation 10 should be replaced by 2j. In addition, the correction factor f of equation 4.2 should be incorporated into the nucleation term of equation 4.9. The equation of Boon and Azcue has been applied successfully to a number of miscible blends, a recent example being the case of semicrystalline poly(butylene terephthalate) blended with a polyarylate (21).

Alfonso and Russell developed an alternative equation, based on the Turnbull-Fisher equation, for miscible blends that incorporates the cooperative diffusion coefficient of the blend and the Flory-Huggins interaction parameter, as well as the crystalline lamellar thickness (17). The authors then applied the complex equation to the analysis of crystallization kinetics data for miscible blends of PEO and PMMA. Subsequent to its development, this equation has not been applied to other blends, mainly due to the lack of availability of accurate values of the required parameters. Inoue and others also pursued an approach that considers diffusion in the melt, although they employed the Hoffman-Lauritzen equation (equation 4.2) as a starting point (18). In the latter case, the additional

parameters of the equation described a two-step diffusion mechanism consisting of the mutual diffusion that occurs during secondary nucleation and the self-diffusion that occurs during the surface-spreading of the semicrystalline polymer (18).

In spite of the prevalence of immiscible semicrystalline-amorphous polymer blends, the crystallization kinetics in such blends have received the least attention. The primary reason for the lack of theoretical interest in this area is that the radial growth rates of spherulites are frequently unperturbed relative to the those measured for the pure crystallizing polymer (20). Based on the observation of immiscible blends containing semicrystalline iPP and amorphous PE-based rubbers, Bartczak, Galeski and Martuscelli proposed that the growth rate depression observed in some immiscible blends arises mainly due to the energy expended by the crystallizing polymer in the process of the engulfment, rejection, and deformation of the immiscible second component (19,20).

If a two-phase blend is allowed to crystallize, the non-crystallizing component is thought to become ordered within the structure of the crystallizing component. The ordering that takes place in immiscible blends via the rejection, engulfment or deformation of the non-crystallizing component is of interest due to its macroscopic significance. The effect of the energy barriers of these processes on the growth rate of spherulites was described by Bartczak, Galeski and Martuscelli using a modified form of the Turnbull-Fisher equation, as shown below

$$G = G_{0} \exp\left(\frac{-\Delta E_{d}}{kT}\right) \exp\left(\frac{-\Delta \Phi}{kT}\right)$$
$$\cdot \exp\left[\frac{-(E_{1} + E_{2} + E_{3} + E_{4} + E_{5})}{kT}\right] \quad (4.11)$$

where  $E_1$  is the energy expended by the spherulite in the rejection of the second component into interlamellar regions,  $E_2$  is the energy expended by the crystallizing front

in the rejection of drop-like domains in the melt,  $E_3$  is the kinetic energy required to overcome the inertia of the drops,  $E_4$  is the energy required to create new interfaces between the spherulite and the drop when engulfment occurs, and  $E_5$  is the energy dissipated when the engulfed drops are deformed by the crystallizing front (19,20). These energy terms are discussed in more detail in the original references (19,20).

The driving force behind this rejection, engulfment or deformation is the difference between the interfacial free energies given below

$$\Delta f = f_{1c2} - f_{1a2} \tag{4.12}$$

where  $f_{1c2}$  is the interfacial free energy between the crystallizing polymer and the second component, and  $f_{1a2}$  is the interfacial free energy between the melt and the second component (19,20). If  $\Delta f$  is positive for a given domain of noncrystallizing material, at low rates of crystallization the domain will be pushed by the crystallizing front; while at high rates, the domain will be engulfed. At intermediate rates the domain may be transported by the crystallizing front, then engulfed once the opposing viscous drag is great enough to overcome the forces of repulsion. Domain size influences the outcome over the entire range of growth rates. This theory has since been applied to other immiscible blends of iPP with terpolymers derived from ethylene and methacrylic acid (22,23).

The addition of a low molecular weight plasticizer that is specific to the amorphous component of a semicrystalline-amorphous polymer blend is a novel approach to increasing the degree of incorporation of the amorphous polymer within the crystalline matrix. The plasticized polymer can be more readily deformed by the crystallizing front; thereby increasing the facility of rejection of this component, but also increasing the possibility of the inclusion of portions of the plasticized, long chains in mixed, crystalamorphous interfacial regions throughout the material. In this chapter, the morphology and the crystallization kinetics of PEO will be analyzed in the pure polymer and in PEO/PVC blends, PEO/TCP mixtures, and PEO/PVC/TCP mixtures.

# 4.2 Procedure

#### **4.2.1** Preparation of Thin Sections

The preparation of the blends and mixtures was described in detail in Chapter 2. Thin sections of pure PEO, PEO/PVC blends, and PEO/TCP and PEO/PVC/TCP mixtures approximately 20  $\mu$ m in thickness and several mm in width were prepared by placing a small amount (~ 1 mg) of sample on a circular, glass coverslip (0.1 mm thickness, 13 mm diameter) and melting the sample at 100 °C. Aluminum spacer shims (~ 15  $\mu$ m thickness) were positioned on either side of the sample before a top coverslip was placed on the molten material. Light pressure was applied to the molten sample to ensure uniform sample spreading. Samples were cooled at room temperature for a minimum of 30 min before use.

## 4.2.2 Sample Premelting Conditions

To observe the isothermal crystallization of a sample, the thin section was placed inside a Linkam 600 series hotstage (THMS-600) mounted on the sample stage of a Nikon Optiphot-Pol polarized light microscope. The temperature of the hot stage heating block was regulated by a Linkam TMS-91 temperature controller and a CS-196 cooling unit that provided a temperature control of  $\pm$  0.1 degree and permitted temperature changes at rates up to and including 130 °/min.

The effect of sample premelting conditions on the growth rate of PEO spherulites was examined at various crystallization temperatures. In the case of pure PEO, a premelting time of 2 min and a premelting temperature of 100 °C were the minimum conditions required to erase the thermal history of a sample and to reduce the nucleation density at the crystallization temperature to a level where individual spherulites could be observed. The blends required a longer premelting time of 5 min to reduce the nucleation density at the crystallization temperature.

## 4.2.3 Spherulite Nucleation

The crystallization temperature range of PEO lies between -53 and 76 °C, with only the high temperature, that is, low supercooling, region being experimentally accessible due to the very rapid nucleation and crystallization rates at temperatures approaching the maximum growth rate. The induction times for the crystallization of PEO (intermediate to high molecular weight) are significantly beyond reasonable experiment times. The use of a nucleating agent such as silica is obviously undesirable due to the possible effects of the nucleating agent on the crystalline morphology and the crystallization kinetics that have been described in the literature (24). The self-seeding procedure developed by Kovacs (25) has been used in other studies (see, for example, reference  $\vartheta$ ). However, the self-seeding procedure involves an annealing step that can influence spherulite structure during subsequent crystallization.

Low-temperature nucleation followed by isothermal crystallization at the temperature of interest provides a viable alternative. In this method, a single "nucleation" temperature,  $T_n$ , is selected for a given polymer or blend based on the induction times and the nucleation densities of the polymer over a range of temperatures. At  $T_n$ , a few spherulites must start to grow within a reasonable induction time (several minutes), but the growth rate must be sufficiently low to allow adequate time for the equilibration and the crystallization of the sample at the selected crystallization temperature. Experiments were conducted that varied  $T_n$  and  $T_c$  and confirmed that the value of  $T_n$  does not influence the

crystallization kinetics at  $T_c$ . If the transition from  $T_n$  to  $T_c$  is conducted rapidly, then the growth at  $T_n$  has a negligible effect on the morphology at  $T_c$ .

The molten sample was cooled from 100 °C at 130 °/min to the selected crystallization temperature in the range 45-56 °C in the case of pure PEO and the PEO/PVC blends, or 35-48 °C in the case of the mixtures containing TCP. The observation of spherulite growth in pure PEO at temperatures greater than 45 °C required nucleation at 45 °C followed by equilibration at the crystallization temperature. Low temperature nucleation was also carried out for PEO spherulites grown from the blends and the mixtures.

# 4.2.4 Observation of Spherulite Morphology and Measurement of Radial Growth Rates

The morphologies and the radial growth rates of PEO spherulites grown in thin section from supercooled melts were recorded using a Nikon Optiphot-Pol polarized light microscope equipped with a black-and-white Cohu video camera, a Mitsubishi U-80 video cassette recorder and an Electrohome RGB monitor interfaced with a personal computer equipped with a Jandel image analysis system (PC Vision framegrabber board with Java software). An additional image analysis system consisting of a Sony video cassette recorder, an Electrohome monitor and a personal computer equipped with a second Jandel package (Targa framegrabber board with Mocha software) was used to make spherulite growth rate measurements. Still photographs were obtained using a Nikon F-401 camera attached to the microscope trinocular tube. The same magnification was used for all of the photomicrographs presented in this chapter. The scale has been provided for reference on the first photomicrograph in each series.

For a given sample and crystallization temperature, the radial growth rates of at least two spherulites from each of a minimum of three different thin sections were measured to obtain an average growth rate. Typical spherulite size ranged from 100 to

/

1000  $\mu$ m; and the crystallization time ranged from 20 s to 3 h. A minimum of 8 radius measurements were recorded for each spherulite at a given time to obtain an average value of the radius at that time. Each growth rate was calculated by applying a first order linear regression to a plot of spherulite radius as a function of time that consisted of measurements at a minimum of five different times. The growth rate of PEO spherulites is significantly faster than that of the spherulites of many other crystallizing polymers. In general, the radial growth rate of PEO spherulites is more conveniently reported in units of  $\mu$ m/min; however, the growth rate of PEO spherulites is more conveniently reported in units of  $\mu$ m/s. Thin sections of pure PEO were melted and recrystallized up to six times with no effect on the growth rate; but thin sections of the blends and the mixtures were crystallized only once due to the possibility of additive degradation that can result from repeated melting.

# 4.3 **Results and Discussion**

## 4.3.1 Morphology

## 4.3.1.1 Poly(ethylene oxide)

Spherulite morphology depends strongly on the identity of the crystalline polymer and on the crystallization temperature, as well as on the presence or absence of impurities. The birefringence and morphology of PEO spherulites have been discussed in detail in the literature (25-27). PEO crystallizes from the pure melt to form large (that is, > 100  $\mu$ m diameter), well-defined spherulites at temperatures in the selected range. Figure 4.4 illustrates the variation in PEO spherulite morphology within the temperature range of this study. As stated in the experimental section, the same magnification was used for all of the photomicrographs presented in this chapter. At intermediate supercooling, that is, at



Figure 4.4 PEO spherulite morphology at various  $T_c$ : (a) 45 °C, (b) 49 °C, and (c)  $T_n$  40 °C (~ 120  $\mu$ m) -T<sub>c</sub> 55 °C. (Continued next page.)



(c)

Figure 4.4 (cont'd)

÷

2

-

temperatures between 40 and 51 °C, PEO crystallizes as negatively birefringent spherulites that exhibit a distinct Maltese cross extinction pattern, as shown by the spherulite crystallized at 45 °C in Figure 4.4a. As the supercooling is decreased to temperatures in the vicinity of the supposed regime II/III transition (8) at  $\sim$  51 °C, the spherulite structure becomes coarser, or looser, and the birefringence becomes more step-like, as shown by the spherulite crystallized at 49 °C in Figure 4.4b; however, the sign of the birefringence is conserved.

Figure 4.4c illustrates the change in spherulite structure that results from an increase in temperature from 40 to 55 °C. The spherulites shown in this photomicrograph were nucleated at 40 °C and allowed to grow for ~ 120  $\mu$ m (radius) before the sample temperature was rapidly increased to 55 °C, where the sample was allowed to crystallize isothermally for an additional 50  $\mu$ m. The center of the spherulite exhibits the typical, well-defined birefringence pattern of the lower crystallization temperature, but the regions of the spherulites farthest from the center exhibit a very diffuse, mixed morphology. There is a definite evolution of spherulite structure with the variation in supercooling, with a transformation from a tight, closed structure with a well-defined Maltese cross at temperatures below ~ 51 °C to an open, mixed structure at temperatures above 51 °C.

This morphological transformation has been attributed to a regime II/III transition by Cheng, Chen and Janimak (8). However, a later X-ray diffraction study by Point, Damman and Janimak determined that at a crystallization temperature of  $\sim 50$  °C, the dominant growth face of PEO single crystals changes from the (010) crystallographic plane at lower temperatures to the (120) plane at temperatures between  $\sim 50$  and 58 °C (10). As stated previously, one of the important criteria for the classification of a kinetic discontinuity as a regime transition is the conservation of the identity of the dominant crystal growth face from one regime to the next (4). Therefore, this morphological transition appears to occur independently of any regime transition. The kinetic aspects of

this issue will be discussed in the section that deals with the crystallization kinetics of PEO.

# 4.3.1.2 Poly(ethylene oxide)/Poly(vinyl chloride) Blends

The presence of additives can exert a significant influence on spherulite structure as well as on melt morphology and nucleation density. The melt of pure PEO is featureless, as expected, while the PEO/PVC blends clearly contain a second amorphous phase that differs in refractive index from molten PEO. Figure 4.5 reveals the variation of melt features with PVC content at 100 °C, as seen with parallel microscope polars. The melt of pure PEO is featureless; while the slight texture of the 10% blend gradually evolves into large aggregates (~ 10-50  $\mu$ m long) in the 25% blend, and finally into the interconnected network and still larger domains of the 50% blend. Consideration of the DSC results (Chapter 3) that demonstrate that the degree of crystallinity of PEO is only slightly affected by the existence of such complex aggregation of the second component strongly suggests that the PEO spherulite structure itself must be altered significantly to permit complete crystallization.

The variation of spherulite morphology with blend composition at a crystallization temperature of 49 °C is shown in Figure 4.6. It is interesting to note that the comparison of spherulites of PEO grown from melts of pure PEO (Figure 4.4b) and PEO/PVC (90/10) reveals a tightening of the crystalline structure, or a higher incidence of space-filling branching upon addition of 10% PVC. The other blends generally exhibit a gradual coarsening in structure, implying an increase in the interfibrillar spacing, along with blurring of the Maltese cross extinction pattern and diminishing luminescence. The loss of the distinct Maltese cross and the reduction in the luminescence of the spherulites result from a substantial decrease in the anisotropy of the crystalline structure at the level of the fibrils. This change in morphology may also reflect a disruption of the crystalline structure



Figure 4.5 PEO/PVC blends at 100 °C: (a) PEO/PVC (90/10), (b) PEO/PVC (82/18), (c) PEO/PVC (75/25), (d) PEO/PVC (65/35), and (e) PEO/PVC (50/50).





Figure 4.6 Variation of spherulite morphology with PEO/PVC blend composition at  $T_c$  49 °C: (a) PEO/PVC (90/10), (b) PEO/PVC (82/18), (c) PEO/PVC (75/25), (d) PEO/PVC (65/35), and (e) PEO/PVC (50/50). (Continued)

(b)

113



(d)







Figure 4.6 (cont'd)

(e)

115

ź
at the level of the individual chains. This issue is addressed in more detail in a study using polarized infrared microspectroscopy presented in Chapter 5.

A further effect of PVC on the crystallization of PEO is seen in the nucleation densities of samples nucleated and crystallized at 49 °C. The photographs shown in Figure 4.7 are representative images of central areas of samples. The nucleation densities of spherulites grown from PEO and the PEO/PVC blends are listed in Table 4.1.

**Table 4.1** The nucleation density of spherulites of PEO grown at 49 °C in pure PEO, the PEO/PVC blends, and the mixtures containing TCP.

Sample	Nucleation Density (spherulites/cm <sup>2</sup> )		
PEO	3 · 10 <sup>2</sup>		
PEO/PVC (90/10)	1 · 10 <sup>3</sup>		
PEO/PVC (82/18)	2 · 10 <sup>3</sup>		
PEO/PVC (75/25)	5 · 10 <sup>3</sup>		
PEO/PVC (65/35)	7 · 10 <sup>3</sup>		
PEO/PVC (50/50)	$> 7 \cdot 10^{3}$		
PEO/TCP (65/35)	1 - 10 <sup>3</sup>		
PEO/PVC/TCP (55/12/33)	$7 \cdot 10^2$		
PEO/PVC/TCP (44/23/33)	2 - 10 <sup>3</sup>		

Spherulites grown from the 50% blend are very diffuse in appearance, thereby rendering discernment of spherulite borders rather difficult; however, based on the large number of spherulites visible in Figure 4.6e, it can be inferred that the nucleation density in this blend is very high. The data are plotted in Figure 4.8. The nucleation density increases with

(a)



Figure 4.7 Variation of nucleation density with PEO/PVC blend composition at  $T_c$ . 49 °C: (a) PEO, (b) PEO/PVC (90/10), (c) PEO/PVC (82/18), (d) PEO/PVC (75/25), (e) PEO/PVC (65/35), and (f) PEO/PVC (50/50). (Continued)





(c)

(d)

(e)

(f)







Figure 4.8 Nucleation density as a function of PVC content.

:

increasing PVC content in the composition range studied. A similar trend is observed at other crystallization temperatures.

In spite of the substantial incorporation of PVC into the spherulite structure, though, it is apparent that not all of the PVC is trapped in interfibrillar regions. Blends of PVC content 25% or greater display a tendency for primary nucleation to occur in two stages. The first stage occurs as several isolated spherulites nucleate. During the second stage, clusters of spherulites nucleate primarily near the growth front (i.e. within 100  $\mu$ m of the growth front) of the first few of spherulites, leading to rapid filling of the sample area. This behavior is most obvious with spherulites of the 50% blend, as shown in Figure 4.6e. It is possible that some of the PEO chains that are in the process of diffusing towards the crystallizing front are adsorbed onto glass-like domains of PVC in the melt, thereby causing the heterogeneous nucleation of spherulites in close proximity to the growth front. It is expected that the local concentration of PVC will be slightly elevated at the spherulite centers as well as in the interfibrillar regions.

Examination of the regions shown in Figure 4.7 with parallel microscope polars, in Figure 4.9, supports the hypothesis that a portion of the second component is relegated to interspherulitic regions during crystallization. As the concentration of PVC is increased from 25% to 35 and 50% (Figure 4.9d-f), small, dark regions and then veins appear in interspherulitic spaces. Thus, at a PVC content between 18 and 25%, the amount of the second component is more than can be accommodated during crystallization of the PEO. As a result, the second component is found at more than one level of inclusion within the crystalline matrix: in interfibrillar and interspherulitic regions. Figure 4.10 is an example of vein formation initiated at the edge of a sample of PEO/PVC (50/50) where, in some instances, vein spreading appears to precede spherulite growth. Due to the possibility of limited miscibility between molten PEO and PVC at high PVC content, it is likely that the excluded phase contains some molten PEO, thereby enhancing the mobility of this material. In the extreme case of the 50% blend, veins also appear in groups in the interior



Figure 4.9 Variation of dispersion of PVC within the crystalline matrix as a function of PEO/PVC blend composition at  $T_c$  49 °C: (a) PEO, (b) PEO/PVC (90/10), (c) PEO/PVC (82/18), (d) PEO/PVC (75/25), (e) PEO/PVC (65/35), and (f) PEO/PVC (50/50). (Cont'd)

Э



Figure 4.9 (cont'd)





.

---

-

.

:

.



Figure 4.10 Vein formation in PEO/PVC (50/50) initiated at the sample edge at 49 °C. (Continued)



.

Figure 4.10 (cont'd)

of spherulites, in which case they exhibit preferential orientation in the growth direction, as shown in Figure 4.11.

High temperature annealing of the 25 and 50% blends at 150 °C, at which temperature PVC is molten, followed by rapid recrystallization results in the initiation of diffuse "blooms" in interspherulitic regions that eventually spread above and below the outer regions of existing spherulites, presumably due to the more facile rejection of the softened PVC. The term "bloom" was chosen to describe these features because they appear to spread partially on the surface of spherulites, that is, between the spherulite thin section and the glass coverslip. One example of this phenomenon is shown in Figure 4.12, which illustrates the final stages of spherulite growth in a sample of PEO/PVC (50/50) that has been annealed at 150 °C. PVC appears to have a definite effect on the crystalline morphology of PEO, as inferred from DSC studies.

## 4.3.1.3 Tricresyl Phosphate Mixtures

As in the case of PVC, DSC results demonstrated that the presence of TCP in mixtures with PEO or PEO/PVC blends has only a small effect on the crystallinity of PEO in the composition range examined. The comparison of the morphological characteristics of the TCP mixtures with those of the blends must be made bearing in mind that although all of the mixtures are 33% TCP, the addition of 50 phr TCP to the 18 and 35% PVC blends results in mixtures that contain 45 and 56% noncrystallizing components, respectively. While the examination of the PEO/TCP (67/33) mixture at 100 °C using parallel polars, shown in Figure 4.13a, reveals a more highly dispersed system than PEO/PVC (65/35) (Figure 4.5d), the melt features of PEO/PVC/TCP (55/12/33) (Figure 4.13b) resemble those PEO/PVC (50/50) (Figure 4.5e). The melt texture of PEO/PVC/TCP (44/23/33) (Figure 4.13c) appears to be more dense and more textured than that of PEO/PVC (50/50).



Figure 4.11 Vein formation in the growth direction in PEO/PVC (50/50) at 49 °C.

 $\sum_{i=1}^{n}$ 

÷

÷

.



(a)



Figure 4.12 Bloom formation in PEO/PVC (50/50), 49 °C, after annealing at 150 °C: (a) initial stage, and (b) completed bloom.

;





Although the aromatic TCP can be expected to mix slightly with the PEO phase, based on the solubility of PEO in common aromatic solvents, the ternary mixtures appear to contain approximately the same amount of featureless molten PEO as PEO/PVC blends containing the same weight percent of PVC alone. That is, the TCP appears to associate preferentially with the PVC phase instead of the amorphous PEO phase. The diluent effect of TCP on the glass transition temperature of PVC is expected to be substantial. A literature study has reported a measurement of approximately -22 °C for the glass transition temperature of PVC and TCP (28). Therefore, the PVC in the ternary mixtures is undoubtedly rubber-like and significantly flexible.

For consistency, the spherulites shown in Figure 4.14 were photographed at temperatures where nucleation occurred readily and where the spherulite growth rate is similar to that of pure PEO and PEO in the the PEO/PVC blends. The selected crystallization temperatures were 40 and 38 °C for PEO/TCP and the ternary mixtures, respectively. The morphology of individual spherulites grown from the TCP mixtures is similar to that of spherulites grown from PEO/PVC blends of similar weight percent of noncrystallizing material, with the exception of some evidence of irregular tangential extinction marks. In fact, crystallization at temperatures a few degrees below the selected temperatures reveals the incidence of broad tangential banding, as shown in Figure 4.15a, a feature that is not seen in spherulites grown from either pure PEO or the PEO/PVC blends at equivalent or more rapid growth rates, in the temperature range studied. This extinction pattern appears predominantly in two diagonal quadrants of the spherulites and is most evident in spherulites grown from PEO/TCP, where the band spacing is approximately 50 µm. The bands become more irregular and diffuse with the addition of 12% PVC (Figure 4.15b), and at 23% PVC (Figure 4.15c) they have all but disappeared, implying that the introduction of PVC into the system disrupts or diffuses the effect of TCP.

2



Figure 4.14 Spherulite morphology in TCP mixtures at a constant undercooling of 2 °C from the kinetic transition in PEO at ~ 51 °C: (a) PEO/TCP (67/33),  $T_c$  40 °C, (b) PEO/PVC/TCP (55/12/33),  $T_{\rm c}$  38 °C, and (c) PEO/PVC/TCP (44/23/33),  $T_{\rm c}$  38 °C. (Cont'd)





**(a)** 



Figure 4.15 Banding in spherulites in TCP mixtures at T<sub>c</sub> 35 °C: (a) PEO/TCP (67/33), (b) PEO/PVC/TCP (55/12/33), and (c) PEO/PVC/TCP (44/23/33). (Continued)

**(b)** 





Such extinction patterns are generally attributed to the radial twisting of fibrils (27). Although very diffuse banding in spherulites of PEO grown from the pure melt has been noted previously in the literature (29), distinct, tangential extinction patterns have only been reported in instances where PEO crystallized in the form of a stoichiometric complex with low molecular weight materials such as resorcinol (30) or *p*-nitrophenol (31). These complexes (30,31) also exhibited melting and crystallization kinetic behavior that differed drastically from that of pure PEO.

Keith, Padden and Russell have observed the appearance of distinct bands in spherulites of poly(E-caprolactone) (PCL) grown from the melt in miscible blends with PVC, in a temperature range where PCL does not normally exhibit banding (26). The same phenomenon was noted for blends of poly(vinyl butyral) or poly(vinyl formal) with PCL (26). The morphological changes were also accompanied by a reduction in the nucleation density of PCL. The authors of the literature study attribute these effects to the accumulation of the diluent in interlamellar regions of the spherulites in concentrations that are elevated with respect to that in the melt, and to the resultant adsorption of diluent molecules both on the growth faces and on the fold surfaces of the crystals (26,32). In this study, it is highly likely that some of the TCP molecules are incorporated between the radially stacking lamellae during spherulite growth. Given that the TCP is a specific plasticizer of PVC, it is probable that most of the TCP remains dispersed in the PVC phase, in interfibrillar or interspherulitic regions, during crystallization. Likewise, it is also possible that the plasticization of PVC permits portions of the amorphous chains to be trapped in interlamellar regions along with TCP in a manner that interferes with the fibrillar twisting that leads to the appearance of tangential extinction patterns. Support for the latter hypothesis can be drawn from the distinct lack of features such as veins or blooms in these samples, even in the sample containing the largest proportion of noncrystallizing material.

c

2

<u>\_</u>

The examination of the nucleation density and the degree of dispersion of the additives in the TCP mixtures provides further evidence that the TCP present within the crystalline matrix is relegated to predominantly interlamellar regions. The nucleation densities of representative areas of PEO/TCP, PEO/PVC/TCP (55/12/33) and PEO/PVC/TCP (44/23/33) shown in Figure 4.16 and listed in Table 4.1, are significantly lower than in the PEO/PVC blends. The data are also plotted in Figure 4.8 for the purpose of comparison. Furthermore, the plasticization of PVC by TCP leads to the suppression of the influence of PVC on the primary nucleation of PEO, by the promotion of the more facile incorporation or expulsion of plasticized PVC.

The appearance of the above spherulites when viewed with parallel polars, shown in Figure 4.17, is similar to the appearance of corresponding samples of the PEO/PVC blends, with the existence of some pockets that resemble "blooms", but with the absence of any veins or other such concentrated features.

In summary, it can be inferred from this scrutiny of sample morphology that both of these additives exert a significant influence on the crystalline structure formed by PEO. Each substance is capable of exerting an influence at a different minimum structural level: that is, both PVC and TCP appear to be incorporated within interspherulitic and interfibrillar regions, while TCP also appears to be incorporated within interlamellar regions. When the two additives are present in combination, TCP appears to plasticize the PVC molecules, an interaction that allows for easier inclusion or exclusion of PVC chains within the spherulite structure in general and may permit the incorporation of portion, of PVC molecules within interlamellar regions as well.

## 4.3.2 Crystallization Kinetics

The radial growth rates of spherulites of PEO grown from the melt of pure PEO, PEO/PVC blends, and PEO/TCP and PEO/PVC/TCP mixtures were measured and

137



Figure 4.16 Nucleation density in TCP mixtures: (a) PEO/TCP (67/33),  $T_c$  40 °C, (b) PEO/PVC/TCP (55/12/33),  $T_c$  38 °C, and (c) PEO/PVC/TCP (44/23/33),  $T_c$  38 °C. (Continued)

**(b)** 

138

(a)





 $\sim$ 



Figure 4.17 Dispersion of additives in TCP mixtures: (a) PEO/TCP (67/33),  $T_c$  40 °C, (b) PEO/PVC/TCP (55/12/33),  $T_c$  38 °C, and (c) PEO/PVC/TCP (44/23/33),  $T_c$  38 °C. (Continued)

17-

(a)

(b)



Figure 4.17 (cont'd)

analyzed according to current nucleation theory. In all instances, plots of radius as a function of time were linear until the spherulite approached within  $\sim 100 \,\mu\text{m}$  of another spherulite, or until the spherulite impinged upon a so-called "vein", at which point the growth rate decreased slightly. The decrease in the growth rate just prior to spherulite impingement has been noted previously (32), and has been attributed to the depletion of crystallizable material in the region between approaching spherulites. The veins, which are expected to be composed primarily of PVC, also represent depleted zones; furthermore, the predominantly glass-like nature of the PVC presents a physical barrier to spherulite growth. The features referred to as "blooms" did not appear to influence the spherulite growth rate significantly. These latter features, which contain PVC that has been melted prior to quenching to the crystallization temperature, do not present a barrier to spherulite growth, but instead represent material that is readily rejected to the surface of the thin section.

The spherulite radial growth rate data presented in the following sections are data obtained from spherulites or sectors of spherulites that did not impinge on other spherulites or on veins during the time span of the measurement. Correlation coefficients of better than 0.9990 were obtained in the case of spherulites crystallized from all of the samples except those crystallized from PEO/PVC (50/50), PEO/PVC/TCP (55/12/33) and PEO/PVC/TCP (44/23/33), where irregular, diffuse spherulite boundaries resulted in correlation coefficients with a minimum value of 0.990.

## 4.3.2.1 Poly(ethylene oxide)

The radial growth rate of PEO is plotted as a function of crystallization temperature in Figure 4.18. The corresponding logarithmic plot is shown in Figure 4.19. Both plots are restricted to temperatures where the nucleation term predominates. The latter plot exhibits an apparent discontinuity in the vicinity of 51 °C, as described in the





c



Figure 4.19 Logarithmic growth rate plot for PEO.

1.1

Ċ

. C

literature (8). The growth rate data were evaluated using the Hoffman-Lauritzen equation (equation 4.2), with values of -78 and 76 °C for the glass transition and equilibrium melting temperatures, respectively. The determination of these two constants was discussed in Chapter 3. The parameter  $T_{\infty}$  was taken as ( $T_g$  - 30 K) or -108 °C.

Hoffman has proposed that a "universai" value of 6.28 kJ/mol for U\* can be applied to most linear polyolefins (4). However, previous studies (see, for example, references 8,17,33) have noted that this value appears to be an underestimate for some polymers. For example, a value of 16.5 kJ/mol was obtained by fitting the growth rate data for poly( $\beta$ -hydroxybutyrate) to the Hoffman-Lauritzen equation (33). A larger value of 23.9 kJ/mol has been proposed for the activation energy, U\*, of PEO (34). Cheng and others reported that a value of 29.3 kJ/mol appeared to fit the growth rate data for PEO well; whereas the "universal" value "obscured" the regime transitions observed in that study (8). Alfonso and Russell employed a different value of 12.0 kJ/mol, and also reported an excellent fit to the growth rate data for PEO (17). The values of T<sub>ex</sub> used in the latter two literature studies were -97 °C (8) and -140 °C (17), respectively.

A fit of the growth rate data obtained in this study according to equation 4.2 with  $T_g$  and  $T_m^\circ$  as constants, and  $G_o$ , U\* and  $K_g$  as variable parameters yielded an excellent fit (r = 0.9991), shown in Figure 4.20, and a value of U\* of 29.1 kJ/mol. Therefore the literature value of 29.3 kJ/mol (34) was accepted for further calculations.

The Hoffman-Lauritzen plot shown in Figure 4.21a is in fact a straight line (correlation coefficient r = 0.9996) that gives no evidence of a change in slope near the temperature of the discontinuity seen in Figure 4.19 at 51 °C, thereby indicating that the data fall within a *single* regime. As stated previously, the supposed discontinuity was originally attributed to the occurrence of a regime II/III transition by Cheng and others (8). However, Alfonso and Russell also obtained a linear plot using growth rate data for PEO of a similar molecular weight in the temperature range 40-60 °C; that is, they found no evidence of a regime transition (17). Previous studies have demonstrated that the

C



Figure 4.20 Fit of the growth rate data for PEO to the Hoffman-Lauritzen equation.

Ċ

1



Figure 4.21 Hoffman-Lauritzen plot for PEO using equilibrium melting temperatures of (a) 76 °C and (b) 62 °C.

(a)

**(b)** 

ratios of the nucleation constants, that is,  $K_g(III)/K_g(II)$  and  $K_g(I)/K_g(II)$ , are very sensitive to the value of the equilibrium melting temperature (see for example references 3,9,35). The values of the parameters in the transport term of equation 4.2 influence the value of the preexponential factor G<sub>0</sub>, but exert a negligible influence on the ratios of the nucleation constants (3). The study by Cheng and others (8) employed an unrealistically low value of the equilibrium melting temperature of PEO, 69 °C; whereas the study by Alfonso and Russell employed a value of 76 °C, as in this chapter. The evaluation of the crystallization kinetic data according to nucleation theory, using a more accurate value of the equilibrium melting temperature of PEO than was used in the study by Cheng and coworkers (8) confirms the absence of a regime transition in pure PEO in the temperature range explored.

Recently, the proposed transition (8) was found to coincide with a change in the dominant crystal growth face of PEO (10). X-ray diffraction experiments demonstrated that the dominant growth face of PEO single crystals grown at temperatures lower than  $\sim 50$  °C corresponds to the (010) crystallographic plane, while the dominant growth face of crystals grown at temperatures between  $\sim 50$  and 58 °C corresponds to the (120) plane. If such a transformation also occurs in spherulites of PEO, then the discontinuity observed in the logarithmic growth rate-temperature curve (Figure 4.19), which does not appear in the corresponding Hoffman-Lauritzen plot (Figure 4.21a), does not arise due to a regime II/III transition. Evidence for the occurrence of this growth face transition in spherulites will be presented in Chapter 5.

The nucleation constant,  $K_g$ , for the crystallization of PEO was calculated form the slope of the Hoffman-Lauritzen plot as  $(1.22 \pm 0.01) \cdot 10^5 \text{ K}^2$ , where the uncertainty assigned to  $K_g$  is the uncertainty in the slope that results from a first order linear regression using 95% confidence intervals. The identity of this single regime can be estimated using a procedure known as the "Lauritzen Z-test", where the Z parameter is defined as (3,5,36)

$$Z = 1.2 \cdot 10^{3} \left(\frac{L}{a_{o}}\right)^{2} exp\left(\frac{2\sigma_{c}a_{o}b_{o}}{kT}\right) exp\left(\frac{-X}{T_{c}(\Delta T)}\right) \quad (4.13)$$

Because the first exponential term in equation 4.13 is approximately equal to unity, the equation can be simplified as shown by equation 4.14

$$Z = 10^{3} \cdot \left(\frac{L}{a_{o}}\right)^{2} exp\left(\frac{-X}{T_{c}(\Delta T)}\right)$$
(4.14)

The variable X is equivalent to  $K_g$  in regimes I and III, and to  $2K_g$  in regime II. The regime dependence of the parameter Z and the substrate length L are given in Table 4.2.

Table 4.2 Regin	me dependence	of Z and the	substrate length L.
-----------------	---------------	--------------	---------------------

Regime	Z	L	L <sub>culc</sub> (Å)
I	≤ 0.1	l µm	$2 \cdot 10^1 - 3 \cdot 10^2$
п	≥ 1	10 <sup>1</sup> - 10 <sup>3</sup> Å	$4 \cdot 10^4 - 8 \cdot 10^6$
III	≤ 0.1	10 Å	$2\cdot 10^1 - 3\cdot 10^2$

The application of the Z-test to the data for PEO using various crystallization temperatures in the range 45-55 °C, trial values of Z, and a value of 4.62 Å for  $a_0$  (37) leads to the values of the substrate length,  $L_{calc}$ , that are listed in in Table 4.2. The calculated value of the substrate length in each regime ( $L_{calc}$  in Table 4.2) and the known

magnitude of this parameter (L in Table 4.2) (36) are expected to correspond in only one regime. The substrate length that is calculated for regime I is much less than the predicted value for this regime. On the other nand,  $L_{calc}$  in regime II is much greater than the predicted value. Only  $L_{calc}$  in regime III shows reasonable agreement with the predicted value. This leads to the conclusion that the temperature range of this study lies within regime III. This conclusion is reasonable given that the rapid growth rates in this temperature range are the result of a very high rate of secondary surface nucleation that is characteristic of regime III.

The product of the surface interfacial free energies,  $\sigma\sigma_c$ , was calculated using equation 4.4 with j equal to 2,  $b_0$  equal to  $4.62 \cdot 10^{-8}$  cm (37), and  $\Delta H_f^{\circ}$  equal to  $2.66 \cdot 10^9 \text{ erg/cm}^3$  (216 ± 2 J/g) (38,39). An estimate of the lateral surface interfacial free energy,  $\sigma$ , of 12.3 erg/cm<sup>2</sup> was obtained from equation 4.5; and this result was in turn used to estimate the fold surface interfacial free energy,  $\sigma_c$ . A value of 0.1 was adopted for  $\alpha_{LH}$ , as in the case of vinyl polymers such as PE and iPP. As stated in the introduction to this chapter, a value of 0.25 has been determined empirically for high-melting polyesters such as poly( $\beta$ -hydroxybutyrate) (PHB) and poly(L-lactic acid) (PLLA) (6). The results of the calculations are given in Table 4.3, along with literature data for other polymers for comparison. An additional quantity of interest, the work of chain folding q

 $q = 2a_0 b_0 \sigma_c \tag{4.15}$ 

can be computed from the fold surface interfacial free energy as shown above (4), and is also listed in Table 4.3. The uncertainties in the parameters derived for PEO in Table 4.3 were estimated by taking into account the relative uncertainty in  $K_g(III)$  and its components. In the case of literature data, estimates of experimental uncertainty are not available from some sources, but the relative uncertainty can be considered to be approximately the same as that of PEO.

 Table 4.3 Surface interfacial free energies and work of chain folding of PEO and various

 other polymers. (The weight average molecular weight of a given PEO sample is listed in

 brackets.)

Polymer (MW)	Regime	σσ <sub>e</sub> (erg <sup>2</sup> /cm <sup>4</sup> )	σ <sub>e</sub> (erg/cm²)	q (kJ/mol)	T <sub>m</sub> ° (°C)	Ref.	
PEO (1.8 · 10 <sup>5</sup> )	111	697 ± 70	57 ± 6	15 ± 2	76±2		
(1.45 · 10 <sup>5</sup> )	n/a	496	40 (1)	10(1)	76	17	
(5.94 · 10 <sup>5</sup> )	n/a	627	51 (1)	13 (1)	76	17	
(1.10 · 10 <sup>5</sup> )	ш	274	27	7.1	69	8	
PE	I, II, III	$1182 \pm 141$	94	23	145	3	
iPP	II, III	777 ± 29	68 ± 3	28	185	3	
R- or S-PECH (2)	111	494	55 (3)	14 (3)	138	40	
РНВ	II, III	1334	46	21	203	33	
PLLA	I, II	733	61	23	207	41	
iPS	II	267	35	30	242	5	

<sup>(1)</sup>  $\sigma_{e}$ , q not reported, but calculated as in this chapter

<sup>(2)</sup> *R*- or *S*-poly(epichlorohydrin)

. IN

<sup>(3)</sup> calculated from literature data using  $\alpha_{LH} = 0.1$ 

The results obtained in this study are similar to the results obtained by Alfonso and Russell (17) that are also listed in Table 4.3. The product of the interfacial free energies reported by Cheng and others (8), which is based on the assumption of a much lower equilibrium melting temperature, is substantially less than the other values listed for PEO,
iPP and PLLA. However, Cheng and coworkers do note that the re-analysis of their data using an equilibrium melting temperature of 80 °C alters the values of  $K_g$  and  $G_o$ , and yields a value of ~ 660 erg<sup>2</sup>/cm<sup>4</sup> for the product of the surface interfacial free energies (8), a value that correlates well with the results obtained in this study and that of Alfonso and Russell (17). Cheng and others assert that "the regime phenomena in those PEO fractions can still be observed" using an equilibrium melting temperature of 80 °C (8), but no supporting evidence is presented.

The interfacial free energy product of PEO is similar to that of iPP and PLLA, as expected for a linear polymer that resembles PE. The higher flexibility of the linear PEO as compared with the other, higher melting polymers is visible in the smaller amount of work required for chain folding in PEO. The work of chain folding of PEO is very similar to that of another polyether, optically pure poly(epichlorohydrin) (40), but less than that of the less flexible polyester, PHB (33). The low value of the product of the surface interfacial free energies of polystyrene is due to the low surface entropy that results from the relatively rigid chain folds of this aromatic polymer; likewise, the work of chain folding of polystyrene is greater than that of the more flexible polymers listed in Table 4.3.

#### 4.3.2.1.1 Comment on The Importance of the Equilibrium Melting Temperature

As stated in the preceding discussion, the equilibrium melting temperature is the most important parameter required for the treatment of crystallization kinetics data by current nucleation theory. A recent study by Huang, Prasad and Marand (35) presented a technique that can be used to obtain the value of the equilibrium melting temperature from kinetics data where the circumstances render the accurate experimental determination of this parameter difficult. In the aforementioned study, the variance  $(s^2)$  of the fit of the data for a given regime was minimized with respect to the equilibrium melting temperature; that is, the growth rate data were fitted to the Hoffman-Lauritzen equation

using  $T_m^{\circ}$  as a variable parameter. In the case where two regimes were present, the variances corresponding to both regimes were minimized. The values of the equilibrium melting temperature obtained by this technique agreed well with values obtained by thermal analysis using the Hoffman-Weeks method for the same samples.

The authors of the above study specify that this technique should only be applied to data that exhibit kinetic discontinuities that arise due to regime transitions and not those that can arise due to changes in the dominant crystal growth face. No reason is given as to why the procedure is inapplicable to polymers that exhibit a change in the crystal growth face. The general approach used in the literature study was used to further analyse the growth rate data of PEO in this chapter. A series of Hoffman-Lauritzen plots were prepared as a function of the equilibrium melting temperature, with U\* = 29.3 kJ/mol and  $T_{\infty} = -108$  °C. The coefficient of determination, that is, r<sup>2</sup>, was maximized with respect to the value of the equilibrium melting temperature of PEO for the data in the crystallization temperature range below the growth face transition, and for the data in the temperature range above the transition. The best fits obtained for the data in the former and the latter segments of the plot were obtained for values of the melting temperature of 62 and 76 °C, respectively.

The significance of utilizing an accurate estimate of the equilibrium thelting temperature is illustrated by the plots of the logarithmic form of equation 4.2 using the realistic equilibrium melting temperature of 76 °C determined by the Hoffman-Weeks method, and the hypothetical value of 62 °C, as shown in Figures 4.21a and 4.21b, respectively. An equilibrium melting temperature of 62 °C yields a plot consisting of two linear segments with satisfactory correlation coefficients of 0.9996 and 0.988 for the assumed regimes III and II, respectively, and a slope ratio of 2.0, a highly misleading result; although visual inspection of the high-temperature segment reveals the fit to these data is rather poor. Not only is a value of 62 °C for the equilibrium melting temperature of PEO, but

the calculation of the product of the interfacial surface free energies corresponding to regimes II and III yields values of ~  $174 \text{ erg}^2/\text{cm}^4$  for both regimes, which are unrealistically less than the values calculated for other crystalline polymers (3).

Interestingly, an estimate of approximately 61 °C is obtained for the equilibrium melting temperature of PEO by the Hoffman-Weeks method (42) if the extrapolation described in Chapter 3 is carried out using samples that were crystallized in the temperature range 37-45 °C, as noted in the preceding chapter. This temperature range includes that of the lower temperature segment in Figure 4.21b. As noted in Chapter 3, although 62 °C is clearly an underestimate for the equilibrium melting temperature of PEO, it is possible that this temperature corresponds to the melting temperature of imperfect crystals of PEO that do not participate in the equilibrium melting that occurs at 76 °C. This hypothesis suggests that crystals possessing a dominant growth face that corresponds to the (010) plane are not present at the equilibrium melting temperature of PEO; that is, only crystals with a (120) growth face undergo equilibrium melting at 76 °C. In fact, there may be two distinct equilibrium melting temperatures that correspond to the melting of crystals with the two different growth faces.

Clearly, this issue must be addressed by further experiments with other semicrystalline polymers that exhibit the same type of kinetic discontinuity in the logarithmic growth rate-temperature curve as exhibited by PEO. In addition, it is possible that the Hoffman-Lauritzen model of polymer crystallization is incomplete, and that the various parameters involved in the mathematical description of the model, in particular those related to crystal melting, require refinement or modification.

4.3.2.2 Poly(ethylene oxide)/Poly(vinyl chloride) Blends

÷

The radial growth rate of spherulites as a function of blend composition is plotted in Figure 4.22. The growth rate data were recorded at various crystallization

temperatures that span the temperature range of interest. In spite of the morphological changes undergone by spherulites of PEO upon addition of PVC, the radial growth rates of the spherulites grown in the blends at 49, 51, 53 and 55 °C are identical within the experimental uncertainty to the growth rates of the spherulites grown in the pure polymer. Spherulite radial growth rate data obtained at 53, 55 and 58 °C by Katime and others also showed no variation in the radial growth rate for 0-50% PVC blends (43). If PEO and PVC exhibit limited miscibility in the melt, as suggested in Chapter 3, this miscibility does not have a significant effect on the crystallization kinetics of PEO.

The lack of variation in the growth rate, even at high concentrations of PVC, is a result that would be expected for an immiscible blend. If PEO and PVC are essentially immiscible, then the growth rate data can be analyzed in terms of equation 4.11. Because the growth rate data of the PEO spherulites in the PEO/PVC blends essentially do not differ from the results obtained in the case of pure PEO, then it appears that in the case of PEO/PVC blends the values of the parameters  $E_1$ - $E_5$  in equation 4.11 are negligible. Based on the theoretical surface interfacial tension calculations in Chapter 2, the surface interfacial free energy,  $\Delta f$ , of equation 4.12, is expected to be greater than zero for PEO/PVC blends. The combination of the positive surface interfacial free energy between PEO and PVC and the rapid growth rates of PEO spherulites lead to spherulite gr<sub>4</sub>, wth rates that are unperturbed by the presence of the second component.

The occurrence of aligned features such as veins implies that PVC is pushed and distorted during crystallization. However, it is possible that some of these features are formed during the initial preparation of the samples. During subsequent melting and crystallization the samples conserve the initial blend morphology. This hypothesis is supported by the photomicrographs of the melt morphologies (Figure 4.5). Therefore, the variations in the supermolecular morphology of PEO noted earlier in this chapter, which





Figure 4.22 Spherulite radial growth rate as a function of PEO/PVC blend composition at various  $T_c$ . (The average growth rate at each temperature is shown by a dotted line.)

are also inferred from calorimetric studies (Chapter 3), can be expected to arise due to structural variations that occur predominantly at interfaces between PEO and PVC, for example between the crystalline fibrils and the interfibrillar material, and not throughout the crystalline structure. The nature of the structural variations that occur at the interface between PEO and PVC will be examined in detail in Chapter 5.

Due to the enhanced nucleation density of PEO spherulites in the PEO/PVC blends, growth rate data could not be obtained at temperatures below 49 °C. As a result, the possibility of the presence of a discontinuity in the growth rate-temperature curve could not be confirmed definitively.

### 4.3.2.3 Tricresyl Phosphate Mixtures

In contrast with the crystallization kinetics of spherulites in the PEO/PVC blends, spherulites grown from mixtures containing TCP grow at rates substantially lower than those observed in the pure polymer. The accessible portions of the growth rate curves of spherulites grown in PEO/TCP (67/33) and PEO/PVC/TCP (55/12/33), shown in Figure 4.23a, overlap at low supercoolings and are substantially displaced to lower temperatures with respect to the curve for pure PEO. The growth rate data for the ternary mixtures are very similar to the data for the PEO/TCP mixture. The data for spherulites grown from PEO/PVC/TCP (44/23/33) are coincident with the corresponding data for the ternary mixture with lower PVC content. In the mixtures containing both PVC and TCP, the growth rate depression can be attributed mainly to the low molecular weight material; however, the plasticization of PVC appears to be responsible for a small portion of the depression. In addition to exhibiting a depression in crystallization kinetics at a given temperature, the plasticizer mixtures exhibit a slightly different curve shape than that of PEO. The logarithmic growth rate plots in Figure 4.23b reveal that the kinetic







<u>/</u>.

discontinuity visible at ~ 51 °C in PEO, and at ~ 42 and 40 °C in PEO/TCP and PEO/PVC/TCP (55/12/33), respectively, appears to be accentuated on addition of TCP.

Because PEO and TCP exhibit, at best, limited miscibility in the melt, as demonstrated by melting temperature measurements in Chapter 3, the modified Turnbull-Fisher equation (equation 4.9) that was devised for the analysis of the crystallization from a one-phase melt is not applicable to the PEO/TCP mixture. The equation developed for immiscible polymer blends (equation 4.11) is not applicable to mixtures containing a semicrystalline polymer and a low molecular weight compound that does not form dropor particle-like domains for the spherulites to engulf, reject, or deform. In addition, none of the available equations can be applied to ternary mixtures such as those examined in this study. Therefore, the growth rate data for PEO/TCP and PEO/PVC/TCP (55/12/33) are plotted using the original Hoffman-Lauritzen equation (equation 4.2) in Figure 4.24.

The values of the equilibrium melting temperature that were employed are those obtained by Hoffman-Weeks analysis in Chapter 3, that is,  $74 \pm 1$  and  $76 \pm 9$  °C for PEO/TCP and PEO/PVC/TCP (55/12/33), respectively. The values of T<sub>∞</sub> and U\* were those used for PEO. As stated in Chapter 3, the effect of additives on the true glass transition temperature of PEO could not be determined by the available methods due to the nucleation of PEO by the additives during quenching. The growth rate data cannot be fitted to equation 4.2 with both T<sub>∞</sub> and U\* as variable parameters, and without any available data on the transport-controlled side of the growth rate-temperature curve. If both the numerator and the denominator of the transport term are varied, in addition to G<sub>0</sub> and K<sub>g</sub>, the fit does not converge. Any uncertainties in the estimates chosen for T<sub>∞</sub> and U\* are expected to influence the resultant values of G<sub>0</sub>, but are not expected to have a significant effect on the nucleation term.

The plots for PEO/TCP and PEO/PVC/TCP (55/12/33) in Figure 4.24 are linear with correlation coefficients of 0.9957 and 0.9960, respectively. The Lauritzen Z-test indicates that these data all lie within regime III, as is the case of pure PEO. Equations



Figure 4.24 Hoffman-Lauritzen plots for spherulites grown in TCP mixtures. The corresponding plot for PEO is shown for reference.

:-----

4.4, 4.5 and 4.15 were used to estimate the product of the surface interfacial free energies, the fold surface interfacial free energy and the work of chain folding in the mixtures. The values of the  $a_0$ ,  $b_0$ ,  $\Delta H_1^{\circ}$ ,  $\alpha_{LH}$ , and  $\sigma$  were those used in the previous calculations for pure PEO. The values of the equilibrium melting temperatures were those obtained by the Hoffman-Weeks method, as stated above. The data listed in Table 4.4 show that, other parameters remaining constant, the decrease in the radial growth rate reflects an increase in the product of the surface interfacial free energies.

Table 4.4 Nucleation constant, surface interfacial free energies, and work of chain folding in PEO spherulites crystallized from PEO, PEO/TCP (67/33) and PEO/PVC/TCP (55/12/33). The results for PEO/PVC/TCP (44/23/33) are identical with the results for the mixture with lower PVC content.

Sample	К <sub>2</sub> (К <sup>2</sup> )	σσ <sub>e</sub> (erg <sup>2</sup> /cm <sup>4</sup> )	σ <sub>e</sub> (erg/cm <sup>2</sup> )	q (kJ/mol)
PEO	$1.22 \pm 0.01 \cdot 10^5$	697 ± 70	57 ± 6	15 ± 2
PEO/TCP	$1.81 \pm 0.05 \cdot 10^{5}$	$1038 \pm 104$	84 ± 8	22 ± 3
PEO/TCP <sup>(1)</sup>	$1.88 \pm 0.05 \cdot 10^{5}$	1077 ± 108	88 ± 9	23 ± 3
PEO/PVC/TCP	$2.05 \pm 0.06 \cdot 10^{5}$	1170 ± 117	95 ± 10	25±3

(1) results calculated using equation 4.9

The fold surface interfacial free energy shows a concomitant increase, which indicates an unfavorable alteration of this surface. The fold surfaces within the crystalline matrix are more accessible to the smaller TCP molecules than to the polymeric PVC. However, the values listed in the preceding table assume that the lateral surface interfacial free energy

remains constant. It is likely that both the fold and the lateral surface interfacial free energies are affected by the presence of the TCP.

Also listed in Table 4.4 are the results obtained when the data for PEO/TCP are analyzed in terms of the equation of Boon and Azcue (equation 4.9) (16) for miscible systems. The correction factor f of equation 4.3 was included in the denominator of the terms on the right-hand side of equation 4.9, and n was taken as 4. The volume fraction of the crystallizing component was calculated as 0.68, using densities of 1.17 g/cm<sup>3</sup> (44) and 1.12 g/cm<sup>3</sup> (45) for TCP and amorphous PEO, respectively. A plot of the left-hand side of the following equation

$$\ln (G) + \frac{U *}{R(T_c - T_{\infty})} - \frac{2\sigma T_m^o [\ln (\upsilon_2)]}{b_o (\Delta H_f^o) (\Delta T) f}$$
$$= \frac{K_g'}{T_c (\Delta T) f}$$
(4.16)

as a function of  $1/T_c(\Delta T)$ f yielded a straight line with a correlation coefficient of 0.9960. The results obtained using this equation do not differ from the results obtained using the Hoffman-Lauritzen equation; therefore the effect of the correction term of equation 4.9 is negligible in this case.

Recent studies have demonstrated the tendency of PEO to include other aromatic compounds such as resorcinol (30), p-nitrophenol (31,46) and various dihalogenobenzene compounds (47) within the unit cell in stoichiometric ratios when these compounds are present is excess relative to PEO. The decrease in the secondary nucleation rate in the TCP mixtures could arise from the occupation of some potential surface nucleation sites by TCP molecules. The unfavorable interactions due to the creation of a  $PEO_c/TCP$ 

C

interface as opposed to a  $PEO_c/PEO_c$  or a  $PEO_c/PEO_a$  interface, where the subscripts c and a denote the crystalline and amorphous phases, respectively, could be responsible for the significant increase in the surface interfacial free energies of the crystalline PEO.

However, it is difficult to account for the increase in the work of chain folding that appears to occur upon the addition of the plasticizer. Furthermore, the inclusion of TCP molecules on the fold and lateral surfaces is expected to cause an increase in the entropy of these surfaces. This entropy increase is expected to overwhelm any positive enthalpic contribution that could arise due to the presence of the TCP molecules. Therefore, the product of the surface interfacial free energies should remain the same as in the case of pure PEO, or even decrease slightly. In general, this product has been observed to remain constant or to decrease with increasing amount of the noncrystallizing component in miscible blends (see, for example, references 48,49). In only one instance has the product been noted to increase relative to the value for the pure polymer (50). The increase was reported in a study of the crystallization of miscible mixtures of iPP and dotriacontane  $(C_{32}H_{66})$ , in the composition range 10-100% iPP (50). However, no measurements of the melting temperatures of these mixtures were reported in the literature study; and the value of the equilibrium melting temperature that was employed in the analysis of the spherulite radial growth rate data of the blends by the Hoffman-Lauritzen equation was the value for pure iPP (50).

The unexpected increase in the product of the surface interfacial free energies observed in this study, combined with the depression in the spherulite growth rates and the analysis of the available literature data, strongly suggests that the estimates of the equilibrium melting temperatures of PEO/TCP and PEO/PVC/TCP that were obtained by DSC in the preceding chapter are, in fact, overestimates of the actual values. It is possible that the noted interference of TCP in the lamellar thickening process of PEO precludes an accurate determination of the equilibrium melting temperatures of the plasticizer mixtures by the Hoffman-Weeks method. If the products of the surface interfacial free energies of

- -

τî.

these mixtures are assumed to be unchanged relative to that of PEO, then the equilibrium melting temperatures of these mixtures should be lower than the reported values. In the case of PEO/TCP, an equilibrium melting temperature of ~ 69 °C yields a value of  $\sigma\sigma_e$  of ~ 697 erg<sup>2</sup>/cm<sup>4</sup>; in the case of PEO/PVC/TCP (55/12/33), the equilibrium melting temperature will be slightly lower. The literature data for iPP and dotriacontane (*S0*) would benefit from a similar analysis.

In contrast with PVC, TCP does exert an influence on the crystallization kinetics of PEO, thereby suggesting that the inclusion or exclusion mechanism active in the case of TCP differs from the corresponding mechanism for PVC. The difference in the molecular weight of the two additives alone provides adequate support for this hypothesis. TCP, as a relatively small, mobile species, offers less resistance to an advancing crystalline front than the cumbersome, long-chain PVC, a characteristic which could lead to widespread expulsion of TCP molecules by the growth front. On the other hand, the small size of the TCP molecules could facilitate incorporation of some of these molecules in interlamellar regions, a structural level generally inaccessible to the large, entangled PVC molecules.

Furthermore, the plasticizating effect on PVC by the excess amount of plasticizer present in the ternary mixtures will increase the mobility of the PVC molecules, which may also be expelled or incorporated by the crystallizing front more easily than is the case in the blends containing unplasticized PVC. As a result, the growth rates observed in the ternary mixtures are not as depressed as would be expected given the growth rate depression in the PEO/TCP mixture, and the increased proportion of TCP relative to that of PEO in the ternary mixtures. The effect of TCP on the crystallization kinetics of PEO may also be diminished in the ternary mixtures by the preferential mixing of the TCP with the PVC phase such that the amount of plasticizer that is available to mix with the molten PEO phase is reduced.

### 4.3.2.3.1 Comment Regarding the Discontinuity in the Growth Rate Curve

The fits to the data for the ternary mixtures in Figure 4.24 indicate a small degree of curvature in the data. A slight discontinuity is visible in each of the plots in Figure 4.23b, at 42 and 40 °C for PEO/TCP and PEO/PVC/TCP (55/12/33), respectively. The discontinuity is more pronounced in the case of the ternary mixture. The ratio of the slope of the low-temperature segment (35-42 °C) to that of the high-temperature segment (43-48 °C) for PEO/TCP is 0.72. The value of this ratio is similar for the ternary mixture. If a lower value of the equilibrium melting temperature of PEO/TCP, such as 69 °C, is employed for the Hoffman-Lauritzen plot, then the corresponding slope ratio is 0.78. Again, the plot is characterized by a slight degree of curvature, but the presence of a regime transition is not indicated by any of these results.

A possible explanation for the deviation of the data from linearity would be the temperature-dependence of the product of the surface interfacial free energies. That is, as more TCP molecules are entrapped in interlamellar regions with decreasing temperature, the entropy of the fold surface will increase and  $\sigma\sigma_e$  will decrease, thereby causing a decrease in K<sub>g</sub>. In fact, a decrease in K<sub>g</sub> at lower temperatures is the trend that has been observed for these samples.

The growth rate data of the PEO/TCP mixture were examined in further detail following the same procedure as that used for the data obtained for pure PEO. That is, a series of Hoffman-Lauritzen plots were constructed as a function of the equilibrium melting temperature. Then the coefficient of determination was maximized with respect to the value of the equilibrium melting temperature for the data in the temperature range above the discontinuity, and for the data in the temperature range below the discontinuity. Again, the values of  $T_{\infty}$  and U\* were held constant. As in the case of pure PEO, the fits to the two segments yielded different values of the equilibrium melting temperature: 54 °C

- 5



for the low-temperature segment, and 75 °C for the high-temperature segment. The correlation coefficients were 0.9991 and 0.9980, respectively.

A value of 54 °C is a significant underestimate of the equilibrium melting temperature because crystallization can be observed at this temperature. A value of 75 °C agrees with that obtained by the Hoffman-Weeks method in Chapter 3; however, this value has been questioned on the basis of the growth rate depression and other factors that were discussed in the preceding section. The agreement between the latter value and the Hoffman-Weeks result more probably confirms that the suppression of the lamellar thickening of PEO that was observed in the bulk samples also occurs in the thin sections. If the (010)-(120) growth face transition also occurs in mixtures containing TCP, then it is possible that the determination of two distinct values for the equilibrium melting temperature by this method reflects the two different melting temperatures characteristic of (010) and (120) growth, as in the case of pure PEO.

### 4.4 Summary

The observation of the morphology and the crystallization kinetics of PEO spherulites grown from pure PEO, PEO/PVC blends, and PEO/TCP and PEO/PVC/TCP mixtures by polarized light microscopy has shown that the crystallization of PEO is influenced at different structural levels by the two additives. Neither additive appears to mix substantially with the PEO melt to a significant degree at 100 °C or at any given crystallization temperature. The supermolecular morphology of PEO becomes coarser with increasing crystallization temperature and increasing additive content, although both additives cause a disordering of spherulite structure not seen in spherulites of pure PEO. The incidence of tangential extinction patterns visible in spherulites grown from mixtures containing TCP indicates that the low molecular weight additive is incorporated in

interlamellar as well as interfibrillar and interspherulitic regions; whereas the polymeric PVC appears to be confined to interfibrillar and interspherulitic regions.

The proposed existence of a regime II/III transition in PEO has been disproved by the interpretation of the growth rate data using a more accurate value of the equilibrium melting temperature of PEO than that employed by literature (8) calculations. It is highly probable that the discontinuity observed in the growth rate-temperature curve of PEO arises due to the transformation of the dominant crystal growth face from the (010) crystallographic plane to the (120) plane, as suggested by literature data (10) obtained from X-ray diffraction of single crystals. This hypothesis will be explored further in the following chapter. Furthermore, it is postulated that there are two distinct equilibrium melting temperatures that correspond to crystallization with the (010) or the (120) growth face as the dominant growth face. The (120) growth face leads to the formation of material with an equilibrium melting temperature of  $76 \pm 2$  °C; whereas the (010) face exhibits a lower equilibrium melting temperature of approximately 62 °C.

As in the case of pure PEO, crystallization in the blends and the mixtures occurs within regime III. The presence of PVC does not affect the crystallization kinetics of PEO, even at a blend composition of 50%, in the accessible temperature range. The presence of a discontinuity in the growth rate data of the PEO/PVC blends could not be verified definitively due to the limitation of the accessible temperature range by the enhanced nucleation density of the PEO spherulites in the blends. By contrast, the presence of TCP reduces the spherulite growth rate significantly. The plasticization of PVC by TCP in the ternary mixtures causes a slight, additional depression in the growth rate that may arise due to the incorporation of portions of the plasticized PVC molecules within the fold surfaces of PEO.

The increase in the product of the fold and lateral surface interfacial free energies in the TCP-containing mixtures may reflect the unfavorable interfacial area created by the inclusion of TCP molecules in the fold surfaces and possibly within the lamellae

themselves. However, the depression in the growth rate data, the anomalous increase in the product of the surface interfacial free energies, and the observed trends in literature data suggest that it is more likely that the estimates of the equilibrium melting temperatures of the plasticizer mixtures obtained by the Hoffman-Weeks method are overestimates of the actual values. As in the case of PEO, it is possible that the crystallization of PEO in mixtures containing TCP occurs with the (010) and the (120) growth faces as the dominant growth faces at lower and higher temperatures, respectively. Again, these two different growth faces may lead to material with two distinct equilibrium melting temperatures.

The influence of the additives on the orientation and the conformation of the individual polymer chains will be investigated using infrared microspectroscopy in Chapter 5.

## 4.5 References

- 1. Marentette, J. M.; Brown, G. R. J. Chem. Ed. 1993, 7, 539-542.
- 2. Turnbull, D.; Fisher, J. C. J. Chem. Phys. 1945, 17, 71-73.
- 3. Clark, E. J.; Hoffman, J. D. Macromolecules 1984, 17, 878-885.
- 4. Hoffman, J. D. Polymer 1983, 24, 3-26.
- 5. Lauritzen, Jr., J. I.; Hoffman, J. D. J. Appl. Phys. 1973, 44, 4340-4352.
- Hoffman, J. D.; Miller, R. L.; Marand, H.; Roitman, D. B. Macromolecules 1992, 25, 2221-2229.
- 7. Tonelli, A. E. Macromolecules 1992, 25, 7199-7203.
- 8. Cheng, S. Z. D.; Chen, J.; Janimak, J. J. Polymer 1990, 31, 1018-1024.
- 9. Phillips, P. J.; Vatansever, N. Macromolecules 1987, 20, 2138-2146.
- 10. Point, J. J.; Damman, P.; Janimak, J. J. Polymer 1993, 34, 3771-3773.
- 11. Cheng, S. Z. D.; Janimak, J. J.; Zhang, A. Macromolecules 1990, 23, 298-302.

- 12. Lovinger, A. J.; Davies, D. D.; Padden, Jr., F. P. Polymer 1985, 26, 1595-1604.
- Hoffman, J. D.; Ross, G. S.; Frolen, L.; Lauritzen, Jr., J. I. J. Res. Natl. Bur. Stand., Sect. A 1975, 79A, 671.
- 14. Martuscelli, E.; Pracella, M.; Ping Yue, Polymer 1984, 25, 1097-1106.
- 15. Martuscelli, E.; Sellitti, C.; Silvestre, C. Makromol. Chem., Rapid Commun. 1985, 6, 125.
- 16. Boon, J.; Azcue, J. M. J. Polym. Sci.: Part A-2 1968, 6, 885-894.
- 17. Alfonso, G. C.; Russell, T. P. Macromolecules 1986, 19, 1143-1152.
- 18. Saito, H.; Okada, T.; Hamane, T.; Inoue, T. Macromolecules 1991, 24, 4446-4449.
- 19. Bartczak, Z.; Galeski, A.; Martescelli, E. Polym. Eng. Sci. 1984, 24, 1155-1165.
- 20. Martuscelli, E. Polym. Sci. Eng. 1984, 24, 563-586.
- Runt, J.; Miley, D. M.; Zhang, X.; Gallagher, K. P.; McFeaters, K.; Fishburn, J. Macromolecules 1992, 25, 1929-1934.
- 22. St-Jean, G; Barreto, M. C.; Brown, G. R. Polym. Eng. Sci. 1990, 30, 1098-1105.
- 23. Caldas, V.; Brown, G. R.; Willis, J. M. Macromolecules 1990, 23, 338-345.
- Kennedy, M. A.; Turturro, G.; Brown, G. R.; St-Pierre, L. E. J. Polym. Sci.: Polym. Phys. Ed. 1983, 21, 1403-1413.
- 25. Vidotto, G.; Levy, D.; Kovacs, A. J. Coll. Polym. Sci. 1969, 230, 289-305.
- 26. Keith, H. D.; Padden, Jr., F. J.; Russell, T. P. Macromolecules 1989, 22, 666-675.
- 27. Padden, Jr., F. P.; Keith, H. D. J. Appl. Phys. 1959, 30, 1479-1484.
- 28. Czekaj, T.; Kapko, J. Eur. Polym. J. 1981, 17, 1227-1229.
- 29. Balta Calleja, F. J.; Hay, I. L.; Keller, A. Koll. Z.-Z. Polym. 1966, 209, 128-135.
- 30. Delaite, E.; Point, J.-J.; Damman, P.; Dosière, M. Macromolecules 1992, 25, 4768-4778.
- 31. Damman, P.; Point, J. J. Macromolecules 1995, 28, 2050-2053.
- 32. Keith, H. D.; Padden, Jr., F. J. J. Appl. Phys. 1964, 35, 1286-1296.
- 33. Pearce, R.; Brown, G. R.; Marchessault, R. H. Polymer 1994, 35, 3984-3989.

- 34. Buckley, C. P.; Kovacs, A. J. Coll. Polym. Sci. 1976, 254, 695-715.
- 35. Huang, J.; Prasad, A.; Marand, H. Polymer 1994, 35, 1896-1908.
- 36. Hoffman, J. D. Polymer 1985, 26, 803-810.
- 37. Takahashi, Y.; Tadokoro, H. Macromolecules 1973, 6, 672-675.
- 38. Afifi-Effat, A. M.; Hay, J. N. J. Chem. Soc., Faraday Trans. 11 1972, 68, 656-661.
- 39. Braun, W.; Hellwege, K.-H.; Knappe, W. Coll. Polym. Sci. 1967, 215, 10-15.
- 40. Singfield, K. L.; Brown, G. R. Macromolecules 1995, 28, 1290-1297.
- 41. Vasanthakumari, R.; Pennings, A. J. Polymer 1983, 24, 175-178.
- 42. Marentette, J. M., B.Sc. Honors Thesis, McGill University, Montreal, QC, Canada, 1990.
- 43. Iragorri, J. I.; Ceswteros, L. C.; Katime, I. Polym. Int. 1991, 25, 225-228.
- 44. Toensmeir, P. A., Ed., Modern Plastics Encyclopedia 1994, 71, p C-105.
- 45. Roe, R.-J. J. Phys. Chem. 1968, 72, 2013-2017.
- 46. Damman, P.; Point, J. J. Macromolecules 1993, 26, 1722-1728.
- 47. Point, J. J.; Damman, P. Macromolecules 1991, 24, 2019-2023.
- 48. Martuscelli, E.; Silvestre, C.; Gismondi, C. Makromol. Chem. 1985, 186, 2161-2176.
- 49. Cimmino, S.; Martuscelli, E.; Silvestre, C. Makromol. Chem., Macromol. Symp. 1988, 16, 147-159.
- 50. Wang, Y. F.; Lloyd, D. R. Polymer 1993, 34, 2324-2329.

-

# Chapter 5

## **Polarized Infrared Microspectroscopy**

### **5.1 Introduction**

The ability to obtain polarized spectra of small, selected areas of thin samples makes polarized infrared microspectroscopy (PIRM) ideally suited to the analysis of crystallite orientation and polymer chain conformation within spherulites, an application that has not been reported to date in the literature. When combined with difference spectroscopy, PIRM is of particular use where spherulites have grown in the presence of additives. Although the technology employed by infrared microscopes has been available for several decades, it is only recently that this technique has seen significant application in materials analysis (1-3). Like regular infrared spectroscopy (IR), infrared microspectroscopy (IRM) provides information about molecular structure and conformation; however, unlike IR, IRM can be used to obtain this information from welldefined areas as small as ~ 30 µm x 30 µm in thin sections only 10-20 µm thick. An infrared microscope is composed of a visible light microscope and an infrared microscope that share the same optical path, thereby permitting visual inspection of a sample at a specific magnification and selection of a region of interest from which to acquire a spectrum, with the area of interest defined by an aperture of specific size and geometry. Furthermore, the use of an infrared polarizer permits dichroism experiments that reveal information about orientation in nonisotropic samples (3).

Examination of the spectrum of one component of a multicomponent system is possible through the technique of difference spectroscopy or spectral subtraction. Difference spectroscopy involves the removal of individual components from the spectrum of a mixture based on a knowledge of the spectra of the pure components. Although infrared measurements are commonly recorded in terms of percent transmittance, %T, spectral arithmetic is carried out using absorbance, A,

$$A = 2 - \log(\%T) \tag{5.1}$$

a linear and not a logarithmic quantity. Absorbance is described by Beer's law

$$A = \varepsilon C t \tag{5.2}$$

where  $\varepsilon$  is the absorptivity coefficient, C is the concentration (which equals unity in the case of single-component, solid samples), and t is the path length or sample thickness (2). In some cases the spectra of the individual components are perturbed in the mixture, and this result in itself can provide valuable information about the interactions within the mixture (2). On the other hand, in an immiscible polymer blend or mixture containing a semicrystalline polymer the spectra of the additives should not deviate from the corresponding neat spectra. As a result, any microstructural variations in the semicrystalline polymer become evident in the difference spectrum once the spectrum of the additive has been removed.

Due to the sensitivity of infrared vibrations to the local environment of groups of atoms, distinct spectra are observed for specific molecular conformations (2). Difference spectroscopy can be applied to reduce the spectrum of a semicrystalline polymer, containing contributions from a distribution of chain conformations in both the crystalline and the amorphous states, to a spectrum representative of the crystalline material alone. A spectrum of the amorphous melt of the polymer of interest is used to remove the contribution of the amorphous component present within the matrix of the semicrystalline polymer. Spectra of the purely crystalline phase have been obtained for several crystalline polymers by this method, including polyethylene (4), polypropylene (5), poly(ethylene terephthalate) (6), polystyrene (7) and poly(vinylidene fluoride) (8). Because most polymers can adopt a variety of conformations in the crystalline state, these so-called "crystalline" spectra can be composed of contributions from more than one conformation; however, subtraction of a particular conformer requires knowledge of the spectrum that corresponds entirely to that conformer. In general, normal mode analysis permits determination of the frequencies characteristic of a given conformation, but conformation-specific spectra cannot be obtained due to the impossibility of preparing a sample composed of a single conformer (2). In practice, variations in the conformer population distribution resulting from changes in crystallization conditions can be followed by comparison of the values of the absolute absorbance or absorbance ratios at relevant frequencies. The presence of additives can influence crystalline polymer chain orientation as well as conformation.

Comparison of polarized spectra obtained with the polarizer oriented at 0 and 90° with respect to a defined direction in oriented samples reveals information about the orientation of the vibrations within the sample. The dichroic ratio, R, defined as

$$R = \frac{A_{\rm II}}{A_{\perp}} \tag{5.3}$$

where the subscripts II and  $\perp$  denote parallel and perpendicular orientation relative to the reference direction, respectively, is used to describe the degree of sample orientation. Typically, the parallel direction of drawn samples is the draw direction or the direction of the polymer chain axes, and the perpendicular direction lies perpendicular to the chain axes (2). In polymer spherulites, the polymer chain axes are typically perpendicular to the spherulite radius; therefore the radial direction is designated as the "perpendicular" direction. Throughout

نېر<u>ين</u>

3

**:** 

the following discussion, a spectrum acquired where the infrared polarizer is oriented parallel to the spherulite radius will be referred to as a "perpendicular spectrum"; while a spectrum acquired where the polarizer is oriented along the tangential direction of the spherulite will be referred to as a "parallel spectrum". Because the parallel direction does not coincide with the length of the chain axes, the magnitude of the dichroism observed in spherulitic thin sections is tess than that observed in oriented samples, such as drawn fibers, composed of the same material. However, spherulitic dichroic ratio measurements provide a measure of the degree and nature of the orientation found in sub-spherulitic structure.

The Herman orientation function, defined below

=

$$F = \frac{3 < \cos^2 \phi > -1}{2}$$
(5.4)

where  $\phi$  is the orientation angle between the designated "parallel" direction (the draw direction in the case of oriented samples or the tangential direction in the case of spherulites) and the local molecular chain axis, is an alternative measure of sample orientation (2). This function is equal to -0.5 when the chain axes are all oriented perpendicular to the draw direction, and 0 when the sample has random orientation. Dichroic ratio data can be used to calculate F using the following relation

$$F = \frac{(R-1)(R_0+2)}{(R+2)(R_0-1)}$$
(5.5)

where  $R_o$  is the dichroic ratio in the case of perfect orientation. The parameter  $R_o$  can be determined from a knowledge of the transition moment angle,  $\psi$ , of a given vibration with respect to the local chain axis, as shown below

2

Ð

$$R_o = 2 \cot^2 \psi \tag{5.6}$$

The transition moment angle is dependent on the vibration of interest and the molecular conformation. A method such as rotational isomeric states modelling has been used to determine an average transition moment angle for a particular vibrational mode of PEO (9); however, in crystalline samples an average angle of 0 or 90° is more realistic.

The morphological variations in spherulites crystallized from the melt of pure PEO. PEO/PVC blends, and PEO/TCP and PEO/PVC/TCP mixtures that are discussed in the preceding chapter indicate the occurrence of microstructural variations as well. While the preceding chapter examined spherulitic structure at the level of spherulites and crystalline fibrils, this chapter uses PIRM to probe the changes in crystalline stem orientation and polymer chain conformation that give rise to the observed macrostructure. Difference spectroscopy, along with dichroism and peak ratio measurements, is applied to the task of determining the influence of PVC and TCP on the crystalline structure of PEO at the level of the individual crystalline chains. In addition, the effect of PEO on chain conformation in PVC is examined.

## 5.2 Procedure

The technique employed for the preparation of thin sections in the previous chapter was modified for infrared experiments to minimize the potential of introducing strain or damaging the spherulites during the removal of the samples from their substrates. For these experiments, a thin section was prepared by placing a small amount of sample (< 1 mg) on a Teflon sheet on a standard glass microscope slide. The slide was placed on a hotplate set at 110 °C and the sample was allowed to melt before the addition of a second Teflon sheet and glass slide on top of the sample. This ensemble was covered with a metal weight to provide sufficient pressure to ensure that the sample would spread to the

desired thickness (~ 20  $\mu$ m) between the Tetlon sheets. After a total melt time of 5 min, the glass slide sandwich was transferred to a digital hotplate set at the appropriate crystallization temperature and covered with another metal weight preheated to the same temperature. Samples were prepared at temperatures corresponding to an undercooling of 2 °C with respect to the growth rate discontinuity described in the preceding chapter, that is, at 49 °C in the case of PEO and the PEO/PVC blends, 40 °C in the case of PEO/TCP, and 38 °C in the case of the PEO/PVC/TCP mixtures. Additional experiments were carried out using higher crystallization temperatures as well. Crystallization times were chosen to permit complete crystallization at the selected temperatures. The samples were allowed to cool to room temperature, removed from between the Tetlon sheets, and stored in a dessicator containing fresh dessicant for no longer than 24 h prior to acquisition of spectra.

Spectra were acquired using a Perkin-Elmer Infrared Microscope equipped with a fixed 100  $\mu$ m diameter aperture and a mercury-cadmium-telluride (MCT), and interfaced with a Perkin-Elmer 16PC Infrared Spectrometer and a personal computer. A schematic drawing showing the general design of the microscope is given in Figure 5.1. A thin section was placed between potassium bromide plates (13 mm diameter, 1 mm thick) to ensure that the sample remained flat during the experiment. The sample was viewed between crossed, visible light polaroid sheets to locate areas suitable for data acquisition. The selected areas of 100  $\mu$ m diameter were all ~ 200  $\mu$ m from the spherulite center so that fibril orientation was relatively uniform. To acquire a statistically significant set of data, two to three areas were selected in each of a minimum of three thin sections for every sample. "Parallel" and "perpendicular" spectra were recorded with the infrared polarizer oriented tangentially and radially, respectively, at each location. A background spectrum of 16 scans at a resolution of 2 cm<sup>-1</sup> was acquired prior to each sample spectrum, and a total of 32 scans were accumulated for each spectrum. In addition,

0

č,





:

.

2

2

A construction

· . ·

nonpolarized spectra were acquired for a thin. solution-cast film of PVC and the neat liquid TCP.

To obtain a spectrum of amorphous PEO at 100 °C, the infrared microscope stage was modified to enable attachment of a Mettler FP52 microscope hotstage interfaced with an FP5 Temperature Controller. A thin section of PEO mounted between potassium bromide plates was heated at a rate of 1 °/min to 100 °C and allowed to equilibrate for 2 min. A background spectrum of 32 scans was acquired at 100 °C prior to acquisition of a sample spectrum of 128 scans.

### 5.3 Results and Discussion

The dichroic ratios for the well-defined peaks at 1468, 1455, 1360, 1344, 1281, 1243, 1062, 965, 947 and 843 cm<sup>-1</sup> were determined for each set of parallel and perpendicular spectra. The values of the absorbances used in the ratios were less than 1.0, with the exception of some values obtained for high-intensity vibrations, where  $1.0 \le A \le 1.5$ . In addition, the absorbance ratio was determined for the following pairs of vibrations: 1344 and 1360 cm<sup>-1</sup>, 1243 and 1281 cm<sup>-1</sup>, 965 and 843 cm<sup>-1</sup>, and 965 and 1062 cm<sup>-1</sup>. The average dichroic ratio at each frequency and the average of each of the peak ratios was calculated for a given sample and crystallization temperature. The spectral pair exhibiting results closest to the average results for a given sample and crystallization temperature was then used as the starting spectral pair for difference spectroscopy. The contributions arising from amorphous PEO, PVC and TCP were removed, where applicable, from the starting pairs of spectra to reveal spectra of purely crystalline PEO. Subsequently, the dichroic ratio at the above frequencies and the peak ratio for the above peak pairs were determined for purely crystalline PEO.

t Š

### 5.3.1 Infrared Dichroism of Spherulites of Poly(ethylene oxide)

### 5.3.1.1 Poly(ethylene oxide)

2

Infrared dichroic spectra reflect the orientation of crystalline stems within the spherulite. To examine the spectra of the purely crystalline component of PEO, hereafter referred to as "crystalling spectra", the contribution of the amorphous component must be removed from the spectra. Parallel and perpendicular spectra of PEO crystallized at 49 °C, shown in Figures 5.2a and 5.3a, can be refined to yield the purely crystalline spectra in Figures 5.2b and 5.3b by subtraction of the melt spectrum of PEO, shown in Figure 5.4, using the appropriate scaling factor. To subtract the amorphous component of the PEO spectrum, the baselines of all three spectra were aligned, by adding a constant to each of the original PEO spectra so that the absorbance at 1500 cm<sup>-1</sup> in the semicrystalline spectra was equal to the corresponding value in the amorphous spectrum. Because the amorphous component of PEO accounts for 22% of a fully crystallized sample, as stated in Chapter 3, this portion of the area under the curve in the semicrystalline spectra can be attributed to the amorphous component. Therefore, the area under a representative part of the curve between 1400 and 1215 cm<sup>-1</sup> in all of the spectra was measured using a baseline drawn between the two limiting wavenumbers. Then the amorphous spectrum was scaled by the factor required to give a corresponding area in the amorphous spectrum that constituted 22% of the area determined for the semicrystalline spectra, before subtracting the amorphous spectrum from each of the semicrystalline spectra. Comparison of the dichroism of the vibrations of spherulitic PEO, listed in Table 5.1, with the dichroism of the vibrations of oriented, fibrous PEO reported in the literature (11) confirms the perpendicular orientation of the chain axes with respect to the spherulite radius.



Figure 5.2 Dichroic spectra of semicrystalline PEO,  $T_c$  49 °C: parallel spectrum (a) before and (b) after subtraction of the amorphous component of PEO.

÷.

?

مرد سرد

the second states and the se

an an an tra ta S



Figure 5.3 Dichroic spectra of purely crystalline PEO,  $T_c$  49 °C: perpendicular spectrum (a) before and (b) after subtraction of the amorphous component of PEO.



Figure 5.4 Melt spectrum of PEO, 100 °C.

Ţ,

:

:

<u>الماريني</u>

2

v (cm <sup>-1</sup> )	Vibrational mode <sup>(1)</sup>	Dichroism	
1468	$bd(CH_2)_a - bd(CH_2)_s$	Ţ	
1455	$bd(CH_2)_a$	11	
1360	$wg(CH_2)_s + str(CC)$	Ť	
1344	wg(CH <sub>2</sub> )a	H	
1281	$tw(CH_2)_a + tw(CH_2)_s$	Ť	
1243	tw(CH <sub>2</sub> ) <sub>a</sub>	11	
1062	str(COC)a - rk(CH <sub>2</sub> )s	Ť	
965	rk(CH <sub>2</sub> )	u	
947	rk(CH <sub>2</sub> ) - str(COC) <sub>a</sub>	11	
843	rk(CH <sub>2</sub> )a	T	

Table 5.1Vibrational assignments and dichroism of crystalline region of spherulites ofPEO formed at 49 °C.

<sup>(1)</sup> The abbreviations bd, wg, str, tw and rk denote bending, wagging, stretching, twisting and rocking modes, respectively.

The vibrations at 1468, 1360, 1281, 1062 and 843 cm<sup>-1</sup> are perpendicular to the chain axis, while the vibrations at 1455, 1344, 1243, 965 and 947 cm<sup>-1</sup> are parallel to the chain axis, as indicated by dichroic ratios less than and greater than unity, respectively. According to the literature vibrational assignments (11), the parallel bands generally correspond to unique vibrations, whereas the perpendicular bands correspond to two different vibrations in combination.

To illustrate the significance of these vibrations in terms of the basic crystalline structure of PEO, the orientation of the unit cell of PEO with respect to the spherulite radius is shown in Figure 5.5. Figures 5.5a and 5.5b illustrate the possible orientations of the unit cell in samples crystallized at temperatures above and below the growth face transition that is thought to occur at ~ 51 °C, as stated in Chapter 4. It is important to note that lower temperature crystallization with the (010) face as the growth front, that is, with the crystallographic b axis as the radial direction, results in chain axes that are perpendicular to the plane of the spherulite. However, higher temperature crystallization with the (120) face as the growth front also leads to chain axes that are perpendicular to the spherulite, but in this case the helices are rotated ~ 45 ° about the c axis with respect to the spherulite radius.

Comparison of dichroic ratio data for PEO crystallized at 49, 51, 53 and 55 °C, which are listed in Table 5.2, reveals that the data obtained at 55 °C deviate significantly from the data obtained at the other three temperatures. While the dichroic ratios of all of the corresponding bands recorded for the samples crystallized at 49-53 °C are identical within the experimental uncertainty, with the exception of slight deviations at 1243 and 965 cm<sup>-1</sup>, the dichroic ratios of most of the relevant bands recorded for the samples crystallized at 55 °C differ in terms of their absolute value and orientation. More specifically, the dichroic ratios of the perpendicular vibrations at 1468, 1360, 1281, 1062 and 843 cm<sup>-1</sup> in samples crystallized at 49-53 °C are all close to unity in the samples crystallized at 55 °C. The dichroic ratios at 1468 and 843 cm<sup>-1</sup> show a slight parallel orientation. The parallel vibration at 1455 cm<sup>-1</sup> changes orientation, and the dichroic ratios of the parallel vibrations at 1344, 1243 and 965 cm<sup>-1</sup> decrease at 55 °C. Only the vibration at 947 cm<sup>-1</sup> appears to be relatively insensitive to the crystallization temperature.

This uniform change in the dichroic ratios of the perpendicular bands that is accompanied by smaller adjustments in the orientation of the parallel bands is consistent with the growth face transformation and concomitant change in the orientation of the crystalline chain axes described previously and illustrated in Figure 5.5.

v (cm <sup>-1</sup> )	49 °C	51 °C	53 °C	55 °C
1468	0.92	0.91	0.94	1.08
1455	1.50	1.30	1.22	0.93
1360	0.82	0.82	0.92	1.02
1344	1.64	1.70	1.65	1.37
1281	0.91	0.89	0.95	1.01
1243	2.17	1.74	1.80	1.46
1062	0.91	0.86	0.95	1.00
965	1.90	1.69	1.53	1.29
947	1.23	1.16	1.20	1.21
843	0.89	0.81	0.97	1.05

Table 5.2 Dichroic ratio data for PEO at 49, 51, 53 and 55 °C.

The perpendicular vibrations that are oriented radially when the (010) face is the dominant growth face acquire a significant parallel component when the (120) face becomes the dominant growth face. Because the shift in the radial direction is 45°, vibrations that are predominantly radial in the case of a (010) growth face acquire an orientation that is intermediate between the radial and tangential orientations in the case of a (120) growth face. Therefore, the dichroic ratios of these vibrations are expected to be intermediate between parallel and perpendicular orientation; that is, the ratios should be close to unity.

The parallel vibrations are not influenced by the growth face transformation to the same extent as the perpendicular vibrations because these vibrational modes are oriented



10 Å

2

2

. •

Figure 5.5 Unit cell diagram of PEO showing (010) and (120) and radial directions. (Continued)






mainly along the chain axes, which are perpendicular to the plane of the spherulite. The parallel component of these modes decreases in the case of a (120) growth face, but only the independent  $CH_2$  bending mode at 1455 cm<sup>-1</sup> undergoes a change in orientation. The bending mode at 1455 cm<sup>-1</sup> and the rocking mode at 965 cm<sup>-1</sup> exhibit the most pronounced changes, as expected for modes involving motions perpendicular to the chain axes (illustrated by the diagram in Figure 5.6), or in the plane of the spherulite. The independent modes at 1243 and 965 cm<sup>-1</sup> also exhibit significant changes. Although some of the changes noted in Table 5.2 lie close to or within the given experimental uncertainty (e.g. 1468 cm<sup>-1</sup>), the results obtained for half of the normal modes examined lie distinctly outside of the experimental uncertainty. The overall trends observed provide strong support for the occurrence of the (010)-(120) growth face transformation.

#### 5.3.1.2 Poly(ethylene oxide)/Poly(vinyl chloride) Blends

Photomicrographs in the preceding chapter illustrate the disordering effect of additives on the morphology of the PEO spherulites. Examination of the crystalline spectra of PEO in the PEO/PVC blends requires spectral subtraction of the PVC prior to subtraction of the spectrum of the amorphous PEO. The first step in the subtraction process was to adjust the baselines of the blend spectra so that the absorbance at  $1500 \text{ cm}^{-1}$  was equivalent to the value for the PVC spectrum shown in Figure 5.7. In this case, the difference in absorbance between two peaks characteristic of PVC at 1427 and 1400 cm<sup>-1</sup> and the known blend composition were used to determine the scaling factor for subtraction of the PVC spectrum. Then the procedure described in the preceding section for removal of the amorphous component of PEO was carried out. As an example, the spectra of PEO/PVC (75/25) crystallized at 49 °C before and after difference spectroscopy are shown in Figure 5.8.





C-H stretch (symmetric)





CH<sub>2</sub> twist



 $CH_2$  wag





C-H stretch (antisymmetric)

:

2

 $CH_2$  rock





Figure 5.7 Spectrum of a solution-cast film of PVC.

ſ





Figure 5.8 Dichroic spectra of PEO/PVC (75/25),  $T_c 49 \,^{\circ}C$  (a) parallel spectrum before and after subtraction of the contributions from PVC and amorphous PEO, and (b) perpendicular spectrum before and after difference spectroscopy.



Figure 5.9 Dichroic ratio, R, as a function of PEO/PVC blend composition,  $T_c$  49 °C, at: (a) 1455 and 1344 cm<sup>-1</sup>, and (b) 1243 and 965 cm<sup>-1</sup>.

t

:

(a)

**(b)** 

n an an airte Marson a chro

The presence of PVC has a significant effect on the dichroic ratio of several PEO crystalline vibrations. As the PVC content in the blends increases, the dichroic ratios of the parallel vibrations at 1455, 1344, 1243 and 965 cm<sup>-1</sup> decrease towards unity and remain close to unity, as shown in Figure 5.9; these vibrations do not change orientation to become perpendicular vibrations. At a PVC content of 50%, the dichroic ratio for all of the vibrations is ~ 1, as shown by the data in Table 5.3.

	% PVC	-				
ν (cm <sup>-1</sup> )	0	10	18	25	35	50
1468	0.92	0.82	0.86	0.93	0.96	0.89
1455	1.50	n/a	1.43	1.28	1.20	1.27
1360	0.82	n/a	n/a	0.91	0.95	0.84
1344	1.64	1.54	1.50	1.37	1.25	1.02
1281	0.91	0.84	0.88	0.94	0.95	0.87
1243	2.17	2.24	1.69	1.63	1.36	1.25
1062	0.91	0.83	0.80	0.96	0.99	0.84
965	1.90	1.85	1.60	1.50	1.31	1.11
947	1.23	1.04	1.00	1.09	1.06	0.95
843	0.89	0.85	0.82	0.94	0.98	0.80

Table 5.3 Dichroic ratio data for PEO and the PEO/PVC blends at 49 °C.

On the other hand, the dichroic ratios of the perpendicular vibrations, already close to unity, remain unchanged within an experimental error of  $\pm 10\%$ . The vibrations that exhibit the largest changes with changing blend composition are those having the highest degree of orientation, that is, the vibrations at 1243 and 965 cm<sup>-1</sup>, while the slightly less

,

oriented vibrations at 1455 and 1344 cm<sup>-1</sup> also approach unity but exhibit smaller relative changes, as shown in Figure 5.9. Because a dichroic ratio of 1 implies an isotropic sample in the plane of the polarizer it is clear that as the PVC content increases, the arrangement of the crystalline stems within the PEO spherulites becomes disordered relative to the case of pure PEO, a result that is not surprising given the disordered morphologies observed by polarized light microscopy.

The independent  $CH_2$  vibrational modes are expected to be the most sensitive to any structural changes, and reference to Table 5.1 indicates that the modes at 1455, 1344, 1243 and 965 cm<sup>-1</sup> are indeed independent methylene vibrational modes. The high sensitivity of the  $CH_2$  wagging mode at 1344 cm<sup>-1</sup> strongly suggests that the structural changes in PEO involve modifications to the shape of the backbone, that is, to the polymer conformation, because the wagging mode involves the cooperative motion of the methylene carbon atom along the polymer backbone, as illustrated by the diagram in Figure 5.6. The  $CH_2$  twisting and rocking modes at 1243 and 965 cm<sup>-1</sup>, respectively, are also more dependent on polymer conformation than the bending mode at 1455 cm<sup>-1</sup>.

The Herman orientation function, F, was calculated using the dichroic ratio data at 1344 cm<sup>-1</sup> to further explore the disordering effect of PVC on the crystalline structure of PEO. This particular vibrational mode was selected due to its evidently high sensitivity to structural changes. The average transition moment angle was taken as 90°; that is, the factor  $(R_0 + 2)/(R_0 - 1)$  is equal to -2.0.

The orientation function is plotted as a function of PEO/PVC blend content in Figure 5.10. Clearly, as the PVC content in the blends increases, the sample proceeds from a state where the crystalline chains are oriented perpendicular to the spherulite radius, as indicated by a value of F of -0.35 for pure PEO, to a highly disordered state that approaches random orientation, as indicated by a value close to zero for the 50% blend. As the spherulite growth front encounters immobile PVC that cannot be



ner se

2

Land Martin Course

Figure 5.10 The Herman orientation function, F, at 1344 cm<sup>-1</sup> as a function of PVC content,  $T_c 49$  °C or  $\Delta T = -2$  °C.

195

incorporated within the crystalline structure at a level lower than that of interfibrillar regions, the PEO is forced to grow around the foreign bodies in order to proceed. An overall radial growth direction demands that the orientation of the crystallizing blocks change as the structure accommodates the inclusions (13), thereby leading to a randomized orientation of the crystallites.

For the purpose of comparison, the dichroic ratios of the modes at 1468, 1455 and 1344 cm<sup>-1</sup> of PEO and the PEO/PVC blends at 49 and 55 °C are listed in Table 5.4.

**Table 5.4** The dichroic ratio at 1468, 1455 and 1344 cm<sup>-1</sup> for PEO and the PEO/PVC blends,  $T_c$  49 and 55 °C.

	<b>R</b> 14	468	R	455		344
% PVC	49 °C	55 °C	49 °C	55 °C	<b>49 °C</b>	55 °C
-						
0	0.92	1.08	1.50	0.93	1.64	1.37
10	0.82	0.90	n/a	1.31	1.54	1.62
18	0.86	0 <del>9</del> 3	1.43	1.13	1.50	1.63
25	0.93	0.95	1.28	1.35	1.37	1.12
35	0.96	0.99	1.20	1.07	1.25	1.16
50	0.89	0.91	1.27	1.25	1.02	1.08

The dichroic ratio of the representative perpendicular mode at 1468 cm<sup>-1</sup> appears to increase slightly towards unity from 49 to 55 °C, as in the case of PEO. However, the dichroic ratios of the two parallel modes at 1455 and 1344 cm<sup>-1</sup> do not show the substantial decrease that was observed for pure PEO. The increase in R of the perpendicular mode is consistent with a change in the growth face from the (010) to the

(120) face. The absence of a significant change in the orientation of the parallel bands does not indicate the absence of a growth face transition, as it was noted that these modes are expected to be less sensitive to such a transformation. Instead, it is apparent that the presence of the PVC perturbs the crystalline structure of PEO at the level of the crystalline stems sufficiently to diminish the observed effect of a change in the growth face. The nature of this perturbation will be examined in detail later in this chapter.

### 5.3.1.3 Tricresyl Phosphate Mixtures

The contribution of TCP to the mixture spectra was removed using the absorbance at 1550 cm<sup>-1</sup> as a baseline reference and the area between 1625 and 1565 cm<sup>-1</sup> as the area for determination of the scaling factor. The contributions arising from PVC and amorphous PEO were then subtracted according to the procedures described in the preceding two sections. Sample original and difference spectra are given in Figure 5.11. The dichroic ratio data for spherulites crystallized from PEO/TCP at 40 °C, that is, at an undercooling of 2 °C with respect to the kinetic discontinuity that may represent the (010)-(120) growth face transition that occurs in pure PEO, as discussed in Chapter 4, are given in Table 5.5. The results for PEO/TCP are very similar with the corresponding data for spherulites crystallized from pure PEO for all of the vibrations except those at 1243 and 965 cm<sup>-1</sup>, within an experimental uncertainty of  $\pm 10\%$ . It should be noted that the vibration at 965 cm<sup>-1</sup> lies in a region of the spectrum where a larger uncertainty was introduced by the subtraction of a strongly absorbing peak of TCP. In cases where the high intensity TCP peak between 950 and 1000 cm<sup>-1</sup> was slightly off-scale, as in Figure 5.11b, the subtraction of this peak led to a negative peak in the resultant difference spectrum. In contrast with the results obtained for the PVC blends, the dichroic ratio data for the PEO/TCP mixture indicate that TCP alone does not exert a significant effect on the orientation of the crystalline stems.



Figure 5.11 Original and difference spectra for (a) PEO/TCP (67/33),  $T_c$  40 °C, and (b) PEO/PVC/TCP (44/23/33),  $T_c$  38 °C.

	PEO	PEO/TCP	PEO/PVC/TCP	PEO/PVC/TCP
v (cm <sup>-1</sup> )		(67/33)	(55/12/33)	(44/23/33)
1468	0.92	0.93	0.85	0.91
1455	1.50	1.41	1.25	0.99
1360	0.82	0.87	0.83	0.94
1344	1.64	1.52	1.62	1.19
1281	0.91	0.84	0.82	0.97
1243	2.17	1.71	2.05	1.73
1062	0.91	0.85	0.88	1.00
965	1.90	1.20	1.26	1.17
947	1.23	1.12	1.20	1.24
843	0.89	0.83	0.82	1.00

 Table 5.5 Dichroic ratio data for PEO and mixtures containing TCP.

The dichroic ratio data for PEO/PVC/TCP (55/12/33) (Table 5.5) are also identical, within the experimental uncertainty, to the data obtained for pure PEO, with the exception of the CH<sub>2</sub> bending mode at 1455 cm<sup>-1</sup>, which exhibits a significant decrease in R. The change in the dichroic ratio of this mode is more pronounced in the case of PEO/PVC/TCP (44/12/33) (Table 5.5), which contains a larger proportion of PVC relative to the amount of plasticizer. The parallel modes at 1344, 1243 and 843 cm<sup>-1</sup> also show a significant decrease in the second ternary mixture. In fact, the results for PEO/PVC/TCP (44/23/33) are very similar to the data obtained for the original PEO/PVC (65/35) blend (listed in Table 5.3). In the ternary mixture with the lower relative amount

of PVC, the effect of the plasticizer appears to predominate; but in the ternary mixture with the higher relative PVC content, the effect of PVC predominates. Not only does TCP not affect the orientation of the crystalline stems, but it drastically reduces the disruptive effect of PVC. It is likely that TCP plasticizes PVC to a sufficient extent that the amorphous polymer no longer presents an immobile obstacle to the crystallizing front. As a result, the spherulitic structure is less severely deformed than it is by PVC alone.

These results strongly suggest that the small, mobile TCP can be included in interspherulitic, interfibrillar and interlamellar regions as proposed in the preceding chapter, but that it is unlikely that it is to be found trapped among the crystalline stems or in the unit cell. Therefore the possible change that was noted in the product of the surface interfacial free energies could be attributed entirely to the change in the fold surface interfacial free energy.

The values of the Herman orientation function at 1344 cm<sup>-1</sup> for the TCP mixtures are also plotted in Figure 5.10. The values obtained for PEO/TCP and PEO/PVC/TCP (55/12/33) are close to the value obtained for pure PEO, but the value obtained for the third mixture is much closer to that expected for a sample that possesses a low degree of orientation. Again, in the ternary mixture of lower PVC content the plasticizing effect of TCP overcomes the disruptive effect of PVC on the crystalline structure of PEO, but in the ternary mixture of higher PVC content the influence of PVC predominates.

The dichroic ratio data at 1468, 1455 and 1344 cm<sup>-1</sup> for samples crystallized at temperatures 2 °C lower than and 4 °C higher than the temperature of the kinetic discontinuity noted in Chapter 4 are listed in Table 5.6. There is no significant change in the dichroic ratios at 1468 and 1344 cm<sup>-1</sup> with increasing temperature in the case of PEO/TCP, although the ratio of the bending mode at 1455 cm<sup>-1</sup> decreases as in the case of PEO. On the other hand, the dichroic ratio data for PEO/PVC/TCP (55/12/33) behave in a very similar manner to the data for pure PEO. It is evident that a well-defined (010)-(120) growth face transition occurs in the ternary mixture, but the incidence of the

transition in the PEO/TCP mixture is not as certain. When PVC is present in addition to PEO and TCP, the TCP is expected to segregate into the PVC phase and to be incorporated to a lesser degree within the crystalline matrix.

**Table 5.6** Dichroic ratio data for the modes at 1468, 1455 and 1344 cm<sup>-1</sup> for PEO and mixtures containing TCP, at  $\Delta T = -2$  °C and  $\Delta T = +4$  °C with respect to the reported kinetic discontinuity.

	R <sub>1468</sub>		R1455		R <sub>1344</sub>	
PVC/TCP	(-2 °C)	(+4 °C)	(-2 °C)	(+4 °C)	(-2 °C)	(+4 °C)
0/0	0.92	1.08	1.50	0.93	1.64	1.37
0/33	0.93	0.89	1.41	1.11	1.52	1.56
12/33	0.85	0.95	1.25	0.74	1.62	0.84
23/33	0.91	0.84	0.99	1.41	1.19	1.60

The different behavior of these two samples in the vicinity of the proposed transition was noted in the corresponding logarithmic growth rate-temperature plots (Figure 4.23b) in the preceding chapter. The kinetic discontinuity was much more obvious in the relevant plot for the ternary mixture than in the plot for the PEO/TCP mixture. It appears that the plasticizer diminishes the tendency for the growth face of PEO to shift, most probably by the inclusion of plasticizer molecules in the amorphous fold surfaces of the crystalline lamellae and the resultant suppression of lamellar thickening.

.

The dichroic ratio data obtained for the PEO/PVC/TCP (44/23/33) mixture contrasts markedly with the data obtained for the other samples. While the dichroic ratio at 1468 cm<sup>-1</sup> decreases slightly with increasing temperature, the dichroic ratios at 1455

÷

and 1344 cm<sup>-1</sup> increase substantially. This behavior is in sharp contrast with that of PEO and the other ternary mixture. Apparently a structural transformation does occur with increasing temperature in this ternary mixture; however, the nature of this transformation differs from that in PEO. It actually appears as though the growth face in PEO/PVC/TCP (44/23/33) changes from the (120) growth face at the lower temperature to the (010) growth face at the higher temperature. This reversal of behavior is a distinct possibility, although it is remarkable given that the (120) growth face is assumed to represent the more stable growth face due to its occurrence at high temperature in the case of PEO.

### **5.3.2 Conformation of Poly(ethylene oxide)**

### 5.3.2.1 Poly(ethylene oxide) and Poly(ethylene oxide)/Poly(vinyl chloride) Blends

PEO generally crystallizes in the form of a distorted  $7_2$  helix in a monoclinic unit cell, but a chain-extended planar zig-zag conformation in a triclinic unit cell has also been observed in stretched or wet samples (14) and in miscible blends with PMMA (15,16). Because the former, more stable *ttg* and the latter *ttt* conformation, shown in Figure 5.12, provide significantly different local environments for the atoms on a given chain, the two conformations give rise to different infrared vibrational modes.

A literature study of the infrared spectra of miscible PEO/PMMA blends found evidence for the simplification of the spectrum of the PEO component in the presence of amorphous PMMA (16). Such spectral simplification strongly suggests an overall simplification of the conformation of the crystalline chains from the complex, distorted  $7_2$ helical structure to a more symmetrical conformation, such as the planar zig-zag form. The authors conducted group theory analysis of the planar zig-zag conformation of PEO to predict the allowed infrared vibrational modes of this conformation, resulting in the assignment of CH<sub>2</sub> vibrational modes at ~1358, 1280, 1060 and 844 cm<sup>-1</sup> to the helical





Figure 5.12 (a) Distorted  $7_2$  helix and (b) planar zig-zag conformations of PEO. The upper view is along the crystallographic c axis, and the lower view is perpendicular to the c axis. (After reference 14).

Ċ

SECONDENSION STATES

conformation, and modes at ~1341, 1241 and 962 cm<sup>-1</sup> to the planar zig-zag conformation (16). The examination of the orientation of the vibrations listed in Table 5.1 reveals that the helical modes are all perpendicular, or radial, in terms of spherulite geometry, while the planar zig-zag modes are all parallel or tangential, so that any changes in the population distribution of these two conformations definitely influence the dichroism of PEO.

A recent literature study (17) has reported that no significant changes in the conformation of PEO in PEO/PMMA blends were observed by IR. Straka and others asserted that "the presence of relatively high concentrations of *ttt* conformational structures based on the increase of the absorbance ratio  $A_{1343}/A_{1362}$  is not well-founded" (17). The evidence presented for this assertion was the observation of the preferential orientation of the PEO chains that was observed to occur in films that were solution-cast onto KBr plates. No such orientation was observed either in powder samples of PEO or in KBr pellets prepared from PEO (17). The authors claimed that this preferential orientation precludes any conclusions about the PEO chain conformation in these blends from being drawn (17).

It is interesting to note that no mention of the spherulitic crystallization of PEO appears in this reference (17). The authors failed to note that the preferential orientation of the PEO chains in solution-cast films is the result of the spherulitic crystallization of PEO. Obviously the use of powdered or ground samples would eliminate any information about the conformation of the PEO chains within the spherulites. If the purpose of a study is the comparison of the conformation of PEO in a series of melt- or solution-crystallized blends, then both the thermal history and the crystallization conditions of the samples must be controlled rigorously. Contrary to the conclusion of Straka and coworkers, the use of spherulitic films is, in fact, a *requirement* for any study of the influence of additives on the conformation of the PEO chains. In addition, such a study must also include an investigation of the orientation of the crystalline chains, as in this chapter.

As noted earlier in this discussion, the dichroic ratios of the vibrations at 1344, 1243 and 965 cm<sup>-1</sup> were affected to the greatest extent by the addition of PVC. In fact, if an additional spectral subtraction that results in the subtraction of pure PEO from the spectra of crystalline PEO in PEO/PVC (50/50) is carried out using 1400 and 1413 cm<sup>-1</sup> as the baseline and absorbance references, respectively, the remaining spectrum does not approximate a flat line as would be expected if the structure of PEO in the blend were identical to the structure of PEO crystallized from the pure melt. Instead, the resulting spectrum consists predominantly of three peaks at 1344, 1243 and 965 cm<sup>-1</sup>, as shown in Figure 5.13, that is, the peaks that have been proposed as characteristic of the planar zig-zag conformation.

Because spectra of the individual conformations of PEO are not available, peak ratios where the numerator and the denominator are the absorbance values of representative parallel (planar zig-zag) modes and perpendicular (helical) modes, respectively, are used to compare the relative amounts of the two conformations in PEO and the other samples. Plots of the peak ratios  $A_{1344}/A_{1360}$ ,  $A_{965}/A_{1062}$ ,  $A_{1243}/A_{1281}$  and  $A_{965}/A_{843}$  as a function of PEO/PVC blend composition in Figure 5.14 for the perpendicular spectra demonstrate that these peak ratios, and therefore the relative proportion of planar zig-zag conformers, increases with increasing PVC content, within an experimental uncertainty of  $\pm$  15%. The data for the parallel spectra that are given in Table 5.7 show that the given peak ratios do not change significantly over the entire range of blend composition. More perfectly crystalline samples prepared at higher temperatures exhibit a significantly lower proportion of planar zig-zag character and similar peak ratio trends.

The observed increase in the proportion of the planar zig-zag conformer with increasing PVC content is consistent with the concomitant decrease in the dichroism of PEO. The parallel components of the spectra show a negligible change relative to each other with changing composition.

:





:

- Second Street



Figure 5.14 Peak ratio,  $r_{\perp}$ , as a function of PEO/PVC blend composition for the following band pairs: (a)  $A_{1344}/A_{1360}$  and  $A_{965}/A_{1062}$ , (b)  $A_{1243}/A_{1281}$  and  $A_{965}/A_{843}$ ,  $T_c$  49 °C.

**Table 5.7** Peak ratio data for the parallel spectra, that is  $r_{\rm ll}$ , of PEO and the PVC blends at T<sub>c</sub> 49 °C. Data for the perpendicular spectra are plotted in Figure 5.14. The ratios listed are all of the form  $A_{\rm planar}/A_{\rm helical}$ .

% PVC	A <sub>1344</sub> /A <sub>1360</sub>	A <sub>1243</sub> /A <sub>1281</sub>	A965/A1062	A965/A843	
0	1.73	0.57	1.03	0.81	
10	n/a	0.67	1.24	1.00	
18	n/a	0.57	1.22	0.99	
25	1.81	0.49	1.10	0.84	
35	2.09	0.58	1.24	0.97	
50	1.89	0.67	1.41	1.06	

However, the perpendicular components increase with respect to the parallel components, thereby causing a decrease in the dichroic ratio of the predominantly parallel modes. In the process, the overall crystalline order of the spherulite is disturbed as well. It is likely that the introduction of planar zig-zag segments into the unit cell of PEO is responsible for the diminished effect of the expected (010)-(120) growth face transition on the dichroic ratios determined for the spherulites grown in the PEO/PVC blends.

### 5.3.2.2 Mixtures Containing Tricresyl Phosphate

1

As in the case of the dichroic ratio measurements, peak ratio data for mixtures containing TCP demonstrate that TCP has a very different effect on the crystalline structure of PEO than does PVC. Peak ratios for the perpendicular and parallel spectra at  $\Delta T = -2$  °C listed in Table 5.8 are generally similar to the corresponding data for PEO.

**Table 5.8** Peak ratio data for PEO and mixtures containing TCP,  $\Delta T = -2$  °C. The ratios of the perpendicular components of the absorbance,  $r_{\perp}$ , are given before the ratios of the parallel components,  $r_{\parallel}$ . The ratios listed are all in the form  $A_{\text{planar}}/A_{\text{helical}}$ .

	PEO	PEO/TCP (67/33)	PEO/PVC/TCP (55/12/33)	PEO/PVC/TCP (44/23/33)
$r_{\perp}$				
A1344/A1360	0.87	1.21	1.26	1.37
A1243/A1281	0.24	0.23	0.21	0.19
A965/A1062	0.49	0.80	0.54	0.41
A965/A843	0.38	0.57	0.40	0.31
ות				
A1344/A1360	1.73	2.13	2.45	1.73
A1243/A1281	0.57	0.48	0.53	0.34
A965/A1062	1.03	1.14	0.78	0.48
A965/A843	0.81	0.82	0.62	0.36

Only one absorbance ratio, the perpendicular  $A_{1344}/A_{1360}$  ratio, exhibits a consistent increase for the three plasticizer mixtures relative to the value obtained for PEO. The PEO/TCP mixture exhibits a slight increase in the absorbance ratio of two of the other perpendicular absorbance ratios relative to PEO, indicating perturbation of the crystalline structure by the plasticizer. In contrast, the parallel ratios  $A_{965}/A_{1062}$  and  $A_{965}/A_{843}$ decrease in the PEO/PVC/TCP (44/23/33) mixture relative to PEO. The decrease in the proportion of the planar zig-zag conformation in the second ternary mixture could account for the observation of the more stable (120) growth face at lower temperatures in this sample.

These results illustrate the plasticizing effect of TCP on PVC, which, in turn, reduces the effects of PVC on the crystalline structure of PEO. The presence of TCP in the PVC phase leads to a reduction in the shear deformation of PEO caused by PVC during spherulite growth, which in turn leads to a reduction in the incidence of the strained planar zig-zag conformation.

### 5.3.3 Conformation of Poly(vinyl chloride)

いたいないまであるのであるのであるとうないのであった。

Because the interaction between PEO and PVC results in induced conformational changes in PEO, the question arises as to whether or not the conformation of PVC is affected in the process as well. The dependence of the vibrational spectrum of PVC, where the spectrum of a solution-cast film of PVC is shown in Figure 5.7, on the zdistribution of different conformations of PVC has been characterized in detail (18-23). The carbon-chlorine (C-Cl) region of the spectrum, which falls between 600 and 700 cm<sup>-1</sup>, is of particular interest because the various C-Cl vibrational modes have been associated with specific conformations of PVC. For example, the modes at 615, 638 and 695 cm<sup>-1</sup> arise due to C-Cl vibrations associated with short ttt sequences in syndiotactic segments, longer-tttt sequences in syndiotactic segments, and tgtg sequences in isotactic segments, respectively (18). The former two modes are thought to arise from sequences of PVC molecules that are partly crystalline, although caution must be exercised in the interpretation of such data because vibrational spectroscopic data alone cannot be used to determine the existence of crystallinity in PVC (23). Such modes can be used to ascertain the segmental orientation of PVC in oriented samples, as was the case in a recent study of the segmental orientation in PVC/poly( $\alpha$ -methyl- $\alpha$ -*n*-propyl- $\beta$ -propiolactone) blends (24).

The possibility of orientation of the PVC molecules in the PEO/PVC blends and the PEO/PVC/TCP mixtures was explored by examination of the dichroic ratios of the C-Cl vibrations at 615, 638 and 695 cm<sup>-1</sup>. The dichroic ratios of these bands in all of the samples containing PVC and in a reference, solution-cast film are listed in Table 5.9.

Table 5.9 Dichroic ratio and peak ratio data for PVC-containing samples and a solutioncast PVC film. The film was cast from tetrahydrofuran at room temperature. The peak ratios given correspond to the parallel spectra.

	R <sub>615</sub> (tttt)	R <sub>638</sub> (tttt)	R <sub>695</sub> (tgtg)	A <sub>615</sub> /A <sub>695</sub> (tttt/tgtg)	A638/A695 (tttt/tgtg)
PEO/PVC					
82/18	0.20	0.29	0.48	0.47	0.71
75/25	1.62	1.56	1.08	1.52	1.44
65/35	1.12	1.12	0.89	1.84	1.70
50/50	0.90	0.91	1.07	1.17	1.21
PEO/PVC/TCP					
55/12/33	2.17	14.2	0.18	8.87	10.5
44/23/33	13.7	3.19	1.85	1.04	1.47
PVC film	1.11	1.10	1.00	1.44	1.39
.*					

The experimental uncertainties in the dichroic ratio data and peak ratio data for the PEO/PVC blends and the PVC film are  $\pm 10\%$  and  $\pm 15\%$ , respectively, as in the case of previous analyses. However, the uncertainties associated with the data for the TCP

mixtures are greater due to the spectral subtraction of a high intensity TCP peak in the . C-Cl vibration region.

The solution-cast film exhibits a slight degree of orientation, shown by the dichroic ratios which are close to unity, as expected from the casting procedure (20). Relative to the vibrations in the solution-cast film, the vibrations in the PEO/PVC blends exhibit significant orientation; that is, the dichroic ratios are significantly greater than or less than unity. The vibrations in the TCP mixtures appear to be highly oriented, as shown by dichroic ratios that are substantially greater than unity in all cases except in the case of  $R_{695}$  for the PEO/PVC/TCP (55/12/33) mixture (R = 0.18). As the PVC content in the PEO/PVC blends increases, the direction of the orientation of the C-Cl bonds associated with *tttt* sequences changes from an initial, predominantly radial orientation (i.e. R < 1) in the PEO/PVC (82/18) blend to a tangential orientation (i.e. R > 1), then resumes a slightly radial orientation in the PEO/PVC (50/50) blend. At a PEO/PVC blend composition of 50/50, the effect of PEO on PVC is diminished by the lower relative concentration of PEO. The behavior of the C-Cl bonds associated with *tgtg* sequences follows a similar, but mildly irregular pattern.

This change in the orientation of the C-Cl vibrations reflects the evolution in the nature of the physical interaction between the crystallizing PEO and the amorphous PVC. At low PVC concentration, the PVC is simply compressed between the PEO fibrils, thereby forcing the bulky C-Cl bonds into a preferred radial orientation. As the PVC concentration increases and the larger aggregates of PVC molecules start to induce the occurrence of the planar zig-zag conformation in PEO, the C-Cl bonds show a change in orientation. The peak ratios listed in Table 5.9 also demonstrate an increase in the proportion of *ttt* sequences relative to *tgtg* sequences. These ratios increase dramatically from the 82/18 blend to the 65/35 blend, then decrease in the 50/50 blend. It is likely that as the PVC molecules come into contact with the advancing, crystallizing front, the rigid

nature of the effectively planar growth front promotes the formation of the oriented, planar *tttt* conformation in the strained, amorphous chains.

In fact, the concomitant tendency towards an increased formation of the planar zig-zag conformation in both PEO and PVC may be a cooperative effect. That is, when both polymers are strained at an interface, their respective conformations are deformed in a manner that readily accommodates both species at the interface. In addition, such adaptation on the part of the PVC molecules need not necessarily be confined to syndiotactic sequences. Molecular modelling studies have demonstrated the potential for isotactic sequences to emulate the shape of the *tttt* conformation (25). The occurrence of this type of epitaxial effect, which involves mainly interfibrillar PVC, strongly suggests the incidence of cooperative crystallization between the spherulite fibrils, or, at the very least, highly specific orientation between the fibrils.

In the plasticizer mixtures, the C-Cl vibrations are, overall, highly oriented in the tangential direction (i.e. R > 1) of the spherulite. The ratio of *tttt* sequences to *tgtg* sequences is very high in the PEO/PVC/TCP (55/12/33) mixture relative that in to the PEO/PVC/TCP (44/23/33) mixture. Because the plasticization of PVC by TCP increases the flexibility of the PVC molecules, it is expected that the influence of the crystallizing PEO on the conformation of PVC will be much greater than the opposite interaction. In effect, the conformation of PEO is only perturbed to a small degree by the additives in these mixtures, as discussed earlier; however, the relatively rigid, planar crystallizing front has a substantial impact on the plasticized PVC molecules that it confronts.

## 5.4 Summary

The technique of infrared microspectroscopy has confirmed the incidence of the (010)-(120) growth face transition in spherulites of PEO. The occurrence of this transition has been observed in the PEO/PVC blends and in the TCP mixtures; however, the

influence of the PVC on the crystalline structure of PEO diminishes the effects of this transformation on the orientation of the relevant vibrational modes, in particular in the PEO/PVC blends. The dichroic ratio data obtained for the PEO/PVC/TCP (44/23/33) mixture suggest that the dominant, low-temperature growth face of this sample is the more stable (120) face, and not the (010) face as in the case of PEO. This anomalous behavior can be attributed to a reduction in the proportion of the less stable, planar zig-zag conformation of the PEO molecules that was observed in this sample.

This technique has also elucidated the complementary influence of PVC and TCP on the crystalline structure of PEO. Dichroism measurements confirm the disordering effect of PVC on PEO spherulite structure visible using polarized light microscopy, and demonstrate that this disorder arises from the disruptive effect of the PVC on the arrangement of the crystalline stems during crystallization. The substantial curvature of the Flory-Huggins plot in Chapter 3 was also proposed as evidence of the perturbational effect of the PVC on the crystalline structure of PEO. The crystallization of PEO in the presence of the relatively immobile PVC not only disturbs the orientation of the crystalline stems, but also induces the crystallization of the PEO in the strained, planar zig-zag conformation. The PEO, in turn, promotes the formation of the planar zig-zag conformation in the amorphous PVC molecules. The coincident formation of planar zigzag structures in both the crystallizing polymer and the additive may be an epitaxial effect that involves the cooperative crystallization between spherulite fibrils or the specific orientation of the fibrils.

The lack of influence of TCP on the conformation of PEO indicates that the plasticizer is not included within the unit cell of PEO, and that the possible difference in the product of the surface interfacial free energies determined by crystallization kinetics studies (Chapter 4) arises solely from the change in the fold surface free energy. In contrast with the PVC, the low molecular weight TCP does not perturb the PEO chain orientation or conformation significantly. The addition of the TCP to the PEO/PVC

blends results in the plasticization of the PVC that, in turn, increases the mobility of the PVC molecules. Thus, the shearing between the crystallizing front and the amorphous PVC is reduced, and likewise, the effect of the PVC on the conformation of PEO is diminished.

# **5.5 References**

- 1. Infrared Microspectroscopy: Theory and Applications; Messerschmidt, R. G. and Harthcock, M. A., Eds.; Practical Spectroscopy Series; Vol. 6; Publ/: Pl/, 1988.
- Koenig, J. L. Spectroscopy of Polymers; American Chemical Society: Washington, DC, USA, 1992.
- 3. Katon, J. E.; Sommer, A. J. Anal. Chem. 1992, 64, 931A-940A.
- 4. Painter, P. C.; Koenig, J. L. J. Polym. Sci., Polym. Phys. Ed. 1977, 15, 1223 and 1235.
- 5. Painter, P. C.; Watzek, M.; Koenig, J. L. Polymer 1977, 18, 1169.
- 6. D'Esposito, L.; Koenig, J. L. J. Polym. Sci., Polym. Phys. Ed. 1976, 14, 1731.
- 7. Painter, P. C.; Koenig, J. L. J. Polym. Sci., Polym. Phys. Ed. 1977, 15, 1885.
- 8. Bachman, M. A.; Gorden, M.; Koenig, J. L. J. Appl. Phys. 1979, 50, 6106.
- 9. Myers, C. W.; Cooper, S. L. Appl. Spectroscopy 1994, 48, 72-78.
- Users Manual: FT-IR Microscope; Perkin-Elmer: Norwalk, Connecticut, USA, 1990; pp 1-8 and 1-11.
- 11. Yoshihara, T.; Tadokoro, H.; Murahashi, S. J. Chem. Phys. 1964, 41, 2902-2911.
- 12. Lambert, J. B.; Shurvell, H. F.; Lightner, D.; Cooks, R. G. Introduction to Organic Spectroscopy; Macmillan:New York, 1987; p 162.
- 13. Schulze, G. E. W.; Bierman, M. J. Mat. Sci. Lett. 1993, 12, 11-13.
- 14. Takahashi, Y.; Sumita, I.; Tadokoro, H. J. Polym. Sci. 1973, 11, 2113-2122.
- 15. Marcos, J. I.; Orlandi, E.; Zerbi, G. Polymer 1990, 31, 1899-1903.

- Ramana Rao, G.; Castiglioni, C.; Gussoni, M.; Zerbi, G.; Martuscelli, E. Polymer 1985, 26, 811-820.
- Straka, J.; Schmidt, P.; Dybal, J.; Schneider, B.; Spevacek, J. Polymer 1995, 36, 1147-1155.
- 18. Compton, D. A. C.; Maddams, W. F. Appl. Spectroscopy 1986, 40, 239-245.
- 19. Theodorou, M.; Jasse, B. J. Polym. Sci.: Polym. Phys. Ed. 1983, 21, 2263-2274.
- Chartoff, R. P.; Lo, T. S. K.; Harrell, Jr., E. R.; Roe, R. J. J. Macromol. Sci., Phys. 1981, B20, 287-303.
- 21. Koenig, J. L.; Antoon, M. K. J. Polym. Sci.: Polym. Phys. Ed. 1977, 15, 1379-1395.
- Krimm, S.; Folt, V. L.; Shipman, J. J.; Berens, A. R. J. Polym. Sci.: Part A 1963, 1, 2621-2650.
- 23. Gilbert, M. J. Macromol. Sci., Rev. Macromol. Chem. Phys. 1994, C34, 77-135.
- Chabot, P.; Prud'homme, R. E.; Pézolet, M. J. Polym. Sci.: Polym. Phys. Ed. 1990, 28, 1283-1296.
- 25. Hobson, R. J.; Windle, A. H. Polymer 1993, 34, 3582-3596.

# Conclusion

## 6.1 General Summary

The modification of materials properties through the creation of polymer blends permits the design of materials with properties that are tailored to a specific application. The crystallization of semicrystalline polymers in semicrystalline-amorphous polymer blends is an extremely important topic in the field of polymer science. In spite of the tremendous potential of plasticizers as additional tools for the control of the crystallization of semicrystalline polymers from the melt, this thesis is the first reported study that compares the behavior of a binary, semicrystalline-amorphous polymer blend with that of a ternary mixture also containing a low molecular weight plasticizer that acts specifically on the amorphous polymer.

The crystallization of PEO in blends with amorphous PVC, and in a mixture with the PVC-selective plasticizer TCP, and in ternary mixtures with both PVC and TCP was investigated at several structural levels using the techniques of: (i) theoretical surface interfacial tension calculations, (ii) thermal analysis, (iii) polarized light microscopy, and (iv) polarized infrared microspectroscopy. The theoretical surface interfacial tension calculations predict the potential for a low degree of adhesion between the amorphous phase of PEO and PVC, and the preferential adhesion of the low molecular weight TCP to the PVC phase in the ternary mixtures.

The invariance of the glass transition temperature of the interlamellar, amorphous PEO suggests a relatively low degree of dispersion in PEO/PVC blends. A slight depression in the equilibrium melting temperature of PEO in blends of high PVC content

was observed, and subsequent analysis of the data using the Flory-Huggins equation reveals that, at best, PEO and PVC exhibit limited miscibility in the melt. The polymer-polymer interaction parameter between PEO and PVC cannot be determined by melting temperature depression experiments and the Flory-Huggins treatment due to the deviation of this plot from linearity. The notable curvature in the plot indicates that PVC influences the crystalline morphology of PEO, most probably through the interference in the lamellar thickening process of PEO.

The melting temperature depression may be accentuated by the addition of TCP, but the depression observed in the ternary mixtures lies within the experimental uncertainty. The plasticizer suppresses the lamellar thickening of PEO substantially, through the inclusion of the small plasticizer molecules in the amorphous fold surfaces of the PEO lamellae. This marked interference of TCP in the lamellar thickening of PEO may prevent the determination of accurate values of the equilibrium melting temperatures of mixtures containing plasticizer. Although the variations in the shape of the melting endotherm of PEO indicate variations within the crystalline structure, the degree of crystallinity of PEO is only slightly influenced by the presence of the additives.

The morphology and the crystallization kinetics of thin sections of individual spherulites crystallized from the melt were studied using temperature-controlled polarized light microscopy. The examination of the dispersion of the additives in the PEO melt provides evidence of the preferential partitioning of TCP into the PVC phase. The morphology of the spherulites crystallized from PEO/PVC blends, and PEO/TCP and PEO/PVC/TCP mixtures deviates from that of spherulites crystallized from pure PEO. In general, the spherulites grown in the presence of additives are coarser and less birefringent than those grown in the pure melt, with the degree of coarseness increasing with increasing additive concentration.

Both additives appear to be incorporated within the crystalline matrix, but at different structural levels. The incidence of banding in spherulites grown in mixtures

k...

Sand The State

Š.

containing TCP indicates that the small TCP molecules are included in interlamellar as well as interfibrillar and interspherulitic regions; while the much larger, entangled PVC molecules are included predominantly in the latter two regions.

The interpretation of the crystallization kinetics of PEO using current nucleation theory clearly demonstrates that the crystallization of PEO in the temperature range of interest occurs within regime III, and that the regime II/III transition proposed in the literature does not occur. The slight kinetic discontinuity at  $\sim 51$  °C that has been thought to arise from a regime II/III transition can be attributed to a transformation of the dominant crystal growth face from the (010) face at lower temperatures to the (120) face at higher temperatures. Furthermore, this discontinuity is not apparent when the kinetic data are analyzed using the more accurate equilibrium melting temperature of 76 °C for PEO.

The measurement of the radial growth rates of the spherulites of PEO demonstrates that the growth rates are not affected by the presence of PVC in the temperature range 49-55 °C, even at concentrations as high as 50% PVC. However, the growth rate is severely depressed by the presence of TCP. The anomalous increase in the product of the lateral and fold surface free energies of PEO that is caused by TCP can be attributed to an increase in the fold surface interfacial free energy due to the energetically unfavorable entrapment of some of the TCP molecules within the fold surfaces of the PEO lamellae. However, it is much more probable that the equilibrium melting temperature data obtained for the TCP mixtures by the Hoffman-Weeks method are significant overestimates of the actual values, and that the interfacial surface free energy product remains constant or even decreases slightly.

Dichroic infrared microspectroscopy was employed to investigate the variations in the crystalline structure at the sub-spherulitic level. The determination of the dichroic ratios and the selected peak ratios from the spectra of purely crystalline PEO (obtained by difference spectroscopy) reveals that the PVC disturbs the orientation of the crystalline

stems of PEO within the spherulites and causes an increase in the crystallization of PEO in the strained, planar zig-zag conformation. PEO, in turn, appears to induce a higher incidence of the planar zig-zag conformation in the PVC molecules, undoubtedly due to an epitaxial interaction in interfacial zones between the two polymers. This behavior strongly suggests the occurrence of cooperative crystallization between the spherulite fibrils or the very specific orientation of the fibrils. The occurrence of a (010)-(120) growth face transformation at  $\sim 51$  °C is highly probable in the PEO/PVC blends, but the effects of PVC on the crystalline microstructure of PEO diminish the observed effects of the growth face transformation on the dichroic ratio data.

In contrast, TCP does not appear to exert a significant influence on the arrangement of the crystalline stems; nor does it have a significant effect on the chain conformation of PEO. In the ternary mixtures, the plasticizing effect of TCP on PVC renders the PVC molecules more flexible and more mobile, thereby drastically reducing the shearing of the PEO and the resultant formation of the planar zig-zag conformation during crystallization. A (010)-(120) growth face transformation was observed at a temperature in the vicinity of the observed discontinuities in the spherulite growth rate-temperature plots in each of these samples.

In effect, the crystallization kinetics and the basic crystalline structure of PEO can be controlled by the selection of appropriate proportions of PVC and TCP, a result of major significance and practical importance in the field of polymer blends.

6.2 Contributions to Original Research

 This study is the first comparative study of the crystallization of a semicrystalline polymer in binary blends with an amorphous polymer and in ternary mixtures containing

 the amorphous polymer and (ii) a specific plasticizer for the amorphous polymer. The amorphous polymer, PVC, did not influence the spherulite growth rates of the

 semicrystalline polymer, PEO, in the accessible temperature range; however the low molecular weight plasticizer, TCP, caused a substantial depression in the growth rate of the PEO spherulites. Both additives appeared to cause the spherulite structure to become coarser and less birefringent. Unusual radial extinction bands were observed in spherulites crystallized from mixtures containing TCP. Such extinction bands were not observed in spherulites grown in the PEO/PVC blends. These patterns indicate that some of the TCP molecules are incorporated within the amorphous fold surfaces of the spherulites.

The effects of the two additives on the crystalline microstructure of PEO are of particular importance and will be noted in subsequent sections.

2. It has been proven that the widely accepted regime II/III transition in PEO does not occur. Instead, the observed kinetic discontinuity arises due to a transformation of the dominant crystal growth face of PEO from the (010) face at temperatures below  $\sim 51 \,^{\circ}$ C to the (120) face at temperatures above  $\sim 51 \,^{\circ}$ C. The significance of the use of an accurate value of the equilibrium melting temperature in the analysis of crystallization kinetics data using the Hoffman-Lauritzen theory has been confirmed.

يتبيني في

The occurrence of this discontinuity in the growth rate-temperature curve of the PEO/PVC blends is highly probable, but could not be confirmed definitively due to the limited accessible crystallization temperature range of these samples. However, the discontinuity was observed in the relevant plots for mixtures containing TCP.

3. Infrared microspectroscopy has been applied for the first time to the microstructural analysis of local spherulite areas in thin section. This technique, coupled with dichroic and difference spectroscopy, has been shown to be applicable to the analysis of the orientation and the conformation of the crystalline chains within polymer spherulites. The technique can also be employed for the examination of the orientation of amorphous, polymeric additives within the crystalline matrix.

This novel technique permitted the confirmation of the occurrence of a transformation in the dominant crystal growth face of PEO at ~ 51 °C. In addition, the PEO/PVC blends and mixtures containing TCP were examined for evidence of this growth face transformation. The effects of PVC on the crystalline microstructure of PEO diminish the observed effects on the dichroic ratio data for the PEO/PVC blends. However, the dichroic ratio data for the mixtures containing TCP confirmed the occurrence of a growth face transformation in these samples.

The use of polarized infrared microspectroscopy demonstrated that PVC has a substantial disordering effect on the basic crystalline structure of PEO. The presence of PVC in the PEO/PVC blends causes a disordering of the orientation of the crystalline stems of PEO within the spherulites. and induces a higher incidence of the trans planar zig-zag conformation of the PEO chains. In contrast, the plasticizer has a minimal effect of the orientation and the conformation of the individual chain: of PEO. In ternary mixtures containing PEO, PVC and TCP, the plasticization of PVC by TCP drastically reduces the effects of PVC on the crystalline structure of PEO.

4. It has been shown that PEO and PVC, at best, exhibit limited miscibility in the melt. The polymer-polymer interaction parameter for this polymer pair cannot be determined by melting temperature depression experiments and subsequent data analysis using the Flory-Huggins relation. The influence of PVC on the crystalline structure of PEO is the determining factor in the melting temperature depression observed in PEO/PVC, and not the slight degree of miscibility between PVC and the PEO melt

5. It has been demonstrated that the specific plasticization of PVC in a series of blends with PEO can lead to a depression of the crystallization kinetics of PEO, mainly due to the presence of TCP. However, the plasticizer effectively masks the disruptive influence of the amorphous polymer on the microstructure of the crystallizing polymer. The highly the amorphous polymer on the microstructure of the crystallizing polymer. The highly significant implication of this result is that the crystallization kinetics, the orientation, and the conformation of PEO can be controlled by the careful selection of the relative proportions of PVC and TCP.

This study demonstrates that it is possible to control the microstructure and the crystallization kinetics of semicrystalline polymers in semicrystalline-amorphous polymer blends by the selection of appropriate concentrations of the amorphous polymer and the plasticizer that acts specifically on the amorphous polymer. This result is of profound importance to the field of polymer blends and can aid in the development of new materials with properties tailored to specific applications.

### **6.3 Suggestions for Further Research**

1. X-ray analysis should be applied to confirm the conformational changes in PEO that were observed by infrared microspectroscopy.

2. SEM in the energy dispersive mode or X-ray photoelectron spectroscopy should be used to determine the dispersion of PVC in the blends and to examine the samples for evidence of the surface segregation of PVC or TCP.

3. The microstructure of the samples used in this study should be explored further by scanning electron microscopy (SEM).

4. Similar studies should be conducted using different blend and mixture components to determine the prevalence of the effects observed in this study. In particular, polarized infrared microspectroscopy should be employed to examine polymer chain orientation and conformation in other pure polymer and polymer-additive systems.
## Appendix

# Data for Figures

## Figure 3.3

T <sub>c</sub> (°C)	T <sub>m</sub> (°C)
47.0	67.74
51.0	68.70
53.0	68.81
54.0	69.31
55.0	70.10
56.0	70.40
57.0	70.42
59.0	71.22

#### Figure 3.5

data for PEO cf. Figure 3.3

(a) PEO/PVC (90/10)		(b) PEO/PVC (82/18)				
T <sub>c</sub> (°C) T <sub>m</sub> (°C)		T <sub>c</sub> (°C)	T <sub>m</sub> (°C)			
49.0	64.94	51.0	65.37			
51.0	66.33	52.0	65.63			
53.0	66.40	53.0	65.56			
55.0	67.25	55.0	66.52			
57.0	67.68	56.0	66.79			

(c) PEO/PVC (75/25)

(d) PEO/PVC (65/35)

T <sub>c</sub> (°C)	T <sub>m</sub> (°C)	T <sub>c</sub> (°C)	T <sub>m</sub> (°C)
49.0	64.57	49.0	64.35
51.0	65.72	51.0	65.14
52.0	65.84	52.0	65.48
53.0	66.63	53.0	66.07
55.0	66.24	55.0	66.21

4

2

 $\{ i_{i}, i_{i}\}$ 

#### Figure 3.5 (cont'd)

(e) PEO/PVC (50/50)

T <sub>c</sub> (°C)	T <sub>m</sub> (°C)
47.0	64.57
49.0	65.45
51.0	65.60
53.0	66.31
55.0	66.91

11	• •
٠.	

% PVC	T <sub>m</sub> ° (°C)	Uncertainty in T <sub>m</sub> °	$T_m^{\circ} (\circ C) (1)$
		(°C)	

0	76	2	73
10	73	4	71
18	72	3	n/a
25	72	3	71
35	. 72	4	n/a
50	71	2	. 70

2

t

÷

(1) reference 34, Ch. 3

3

### Figure 3.6

υI	(1/T <sub>m,bl</sub> ° - 1/T <sub>m</sub> °)/v <sub>1</sub> (K <sup>-1</sup> )
0.080	3.11 · 10-4
0.15	2.21 · 10 <sup>-4</sup>
0.21	1.58 · 10-4
0.30	1.11 - 10-4
0.44	9.47 · 10 <sup>-5</sup>

### Figure 3.8

'EO data cf. Figure 3.3

(a) PEO/TCP (67/33)		(b) PEO/PVC/TCP (55/12/33					
T <sub>c</sub> (°C)	T <sub>m</sub> (°C)	T <sub>c</sub> (°C)	T <sub>m</sub> (°C)				
43.0	57.57	41.0	56.14				
44.0	58.09	44.0	57.41				
45.0	58.66	45.0	58.65				
46.0	59.21	46.0	58.54				
47.0	59.67	47.0	59.74				

:

;

(c) PEO/PVC/TCP (44/23/33)

T <sub>c</sub> (°C)	T <sub>m</sub> (°C)	
42.0	56.94	
43.0	58.09	
43.0	56.21	
44.0	57.84	
45.0	57.39	
46.0	58.87	
47.0	58.63	
	_	1

:

-

#### PEO/PVC Blends

% PVC	Nucleation Density
	(spherulites/cm <sup>2</sup> )
0	$3 \cdot 10^2$
10	1 · 10 <sup>3</sup>
18	2 · 10 <sup>3</sup>
25	5 · 10 <sup>3</sup>
35	7 · 10 <sup>3</sup>

#### TCP Mixtures

% PVC	Nucleation Density				
·	(spherulites/cm <sup>2</sup> )				
)) ))					
0	1 · 10 <sup>3</sup>				
12	7 · 10 <sup>2</sup>				
23	2 · 10 <sup>3</sup>				·
- 					
,					2

1

÷.,

T <sub>c</sub> (°C)	G (µm/s)	Uncertainty in G (µm/s)
45.20	13.83	1.5
46.15	11.93	0.96
47.20	8.86	0.50
48.25	7.03	0.51
49.20	4.82	0.41
50.20	3.13	0.33
51.15	2.30	0.17
52.15	1.47	0.055
53.20	0.958	0.082
54.10	0.469	0.052
55.15	0.247	0.028
56.15	0.126	0.015

÷

T <sub>c</sub> (°C)	ln (G) (G in μm/s)
45.20	2.63
46.15	2.48
47.20	2.18
48.25	1.95
49.20	1.57
50.20	1.14
51.15	0.833
52.15	0.387
53.20	-0.0433
54.10	-0.757
55.15	-1.40
56.15	-2.07

(a)

(b) y axis as in (a)

$10^4 \cdot 1/T_c(\Delta T)f$	$\ln (G) + U^*/[R(T_c - T_\infty)]$	10 <sup>4</sup> · 1/Τ <sub>ι</sub> (ΔΤ)f
(K <sup>-2</sup> )	(G in cm/s)	(K- <sup>2</sup> )
1.074	16.40	1.924
1.104	16.11	2.030
1.138	15.66	2.164
1.176	15.27	2.318
1.212	14.76	2.479
1.254	14.19	2.678
1.296	13.75	2.900
1.347	13.15	3.196
1.400	12.59	3.545
1.452	11.75	3.934
1.518	10.97	4.519
1.588	10.17	5.373

. : :

-

;

	G (μm/s)			
% PVC	49 °C	51 °C	53 °C	55 °C
0	4.82	2.30	0.958	0.247
10	5.28	2.39	0.962	0.314
18	5.06	2.28	1.04	0.363
25	5.12	2.50	1.10	0.288
35	5.35	2.31	1.05	0.297
50	n/a	2.09	0.738	0.212

#### Uncertainty in G (µm/s)

% PVC	49 °C	51 °C	53 °C	55 °C
0	0.41	0.17	0.082	0.028
10	0.31	0.14	0.063	0.022
18	0.42	0.29	0.11	0.032
25	0.22	0.19	0.048	0.027
35	0.44	0.16	0.093	0.021
50	n/a	0.46	0.12	0.070
				-

-

-

C

PEO data cf. Fig. 4.18

(a)

	PEO/TCP		PEO/PVC/TC	P
T <sub>c</sub> (°C)	G (μm/s)	sd <sup>(1)</sup> of G (µm/s)	G (μm/s)	sd of G (µm/s)
35.3	14.98	2.0	12.88	0.77
36.3	14.59	1.3	11.77	0.61
37.3	11.83	0.51	10.16	0.55
38.3	11.11	0.45	9.26	0.92
39.3	8.90	0.31	6.60	0.22
40.3	7.61	0.24	4.89	0.44
41.3	5.42	<b></b>	4.67	0.34
42.3	3.68	0.39	3.17	0.40
43.3	3.06	0.26	1.85	0.43
44.3	2.12	0.31	1.39	0.086
45.3	1.01	0.19	0.641	0.14
46.3	0.594	0.041	0.495	0.071
47.3	0.248	0.045	0.203	0.034
48.3	0.143	0.006	n/a	n/a

-

-

- 2

2

1

t

(1) uncertainty

;

(b)

PEO/TCP		PEO/PVC/TCP	
	T <sub>c</sub> (°C)	ln (G) (G in µm/s)	ln (G)
	35.3	2.71	2.56
	36.3	2.68	2.47
	37.3	2.47	2.32
	38.3	2.41	2.23
	39.3	2.19	1.89
	40.3	2.03	1.59
	41.3	1.69	1.54
	42.3	1.30	1.15
	43.3	1.12	0.613
	44.3	0.752	0.329
	45.3	0.0050	-0.444
	46.3	-0.520	-0.703
	47:3	1 <b>.39</b>	-1.60
	48.3	-1.95	n/a

Ξ

÷

data for PEO cf. Figure 4.21

PEO/TCP		PEO/PVC/TCP	
$10^4 \cdot 1/T_c(\Delta T) f(K^{-2})$	y axis <sup>(1)</sup>	$10^4 \cdot 1/T_c(\Delta T) f(K^{-2})$	y axis (1)
0.8935	18.06	0.8521	17.91
0.9128	17.87	0.8693	17.65
0.9332	17.49	0.8875	17.34
0.9547	17.26	0.9066	17.04
0.9776	16.88	0.9269	16.58
1.002	16 <b>.56</b>	0.9483	16.12
1.028	1 <b>6.06</b>	0.9710	15.91
1.055	15.52	0.9951	15.37
1.084	15.18	1.021	14.89
1.116	14.66	1.048	14.24
1.149	13.76	1.077	13.31
1.185	13.09	1.108	· 12.90
1.224	12.07	1.142	11.86
1.266	11.37	n/a	n/a

Ń

 $\mathbb{C}$ 

# (1) $\ln (G) + U^{*}/[R(T_c - T_{\infty})]$ (G in cm/s)

### Figure 5.9

(a)		(b)		
	R	R		
% PVC	1455 cm <sup>-1</sup>	1344 cm <sup>-1</sup>	1243 cm <sup>-1</sup>	965 cm <sup>-1</sup>
0	1.50	1.64	2.17	1.90
10	1.78	1.54	2.24	1.85
18	1.43	1.50	1.69	1.60
25	1.28	1.37	1.63	1.50
35	1.20	1.25	1.36	1.31
50	1.27	1.02	1.25	1.11

1

્

#### Figure 5.10

PEO/PVC Blends

% PVC	F
0	-0.35
10	-0.31
18	-0.29
25	-0.22
35	-0.15
50	-0.013

TCP Mixtures

% PVC	F
0	-0.30
12	-0.34
23	-0.12

ē

ζ

### Figure 5.14

(a)		(b)		
	r⊥		<b>r</b> _	
% PVC	A 1344/A 1360	A965/A1062	A1243/A1281	A965/A843
0	0.87	0.49	0.24	0.38
10	1.16	0.56	0.25	0.43
18	1.26	0.61	0.30	0.51
25	1.20	0.70	0.28	0.53
35	1.58	0.94	0.40	0.72
50	1.55	1.07	0.46	0.77

·

· :

.

.

