A spectroscopic study of a stress-induced crystalline phase transition in poly(butylene terephthalate) and related copolymers/

Eva, Dobrovolny-Marand

University of Massachusetts Amherst

Follow this and additional works at: https://scholarworks.umass.edu/dissertations_1

Recommended Citation
https://doi.org/10.7275/nezd-ay42 https://scholarworks.umass.edu/dissertations_1/716

This Open Access Dissertation is brought to you for free and open access by ScholarWorks@UMass Amherst. It has been accepted for inclusion in Doctoral Dissertations 1896 - February 2014 by an authorized administrator of ScholarWorks@UMass Amherst. For more information, please contact scholarworks@library.umass.edu.
A SPECTROSCOPIC STUDY OF A STRESS-INDUCED CRYSTALLINE PHASE TRANSITION IN POLY(BUTYLENE TEREPTHALATE) AND RELATED COPOLYMERS

By

Eva Dobrovolny - Marand

Submitted to the Graduate School of the University of Massachusetts in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY

February 1987

Department of Polymer Science and Engineering
A SPECTROSCOPIC STUDY OF A STRESS-INDUCED CRystalline Phase Transition in Poly(butylene terephthalate) and Related Copolymers

By
Eva Dobrovolny - Marand

Approved as to style and content by:

Shaw Ling Hsu, Chairperson of Committee

Richard J. Farris, Co-chairman

Edwin L. Thomas, Member

Robert W. Lenz, Member

Edwin L. Thomas, Head

Department of Polymer Science and Engineering
ACKNOWLEDGMENTS

I would like to acknowledge Professor Shaw Ling Hsu for acting as my thesis advisor and for his helpful suggestions concerning my research work and research presentations. I also would like to thank Professor Richard Farris for acting as my thesis co-advisor and for his kind support and encouragement. I also thank Professors Robert Lenz and Edwin Thomas for serving on my dissertation committee and for their useful comments.

I extend special thanks to my friends and coworkers, Don Burchell, Jim Lasch, Steve Molis, Bruce Reinhold, Chih Chang, Ravi Saraf, Yachin Cohen, Jean-Marc Lefebre, Olimpia Federico and others for all their helpful discussions and teaching and especially for their good humor and kindness with which they treated me.

But the best of my thanks goes to my husband Hervé and my family for all their moral and financial support and many sacrifices which enabled me to complete this work.
ABSTRACT

A Spectroscopic Study of a Crystalline Phase Transition in Poly(butylene terephthalate) and related Copolymers.

(February, 1987)

Eva Dobrovolny - Marand, B.S. University of Illinois
M.S., University of Massachusetts
Ph.D., University of Massachusetts

Directed by: Professor Shaw Ling Hsu

The stress-induced α → γ crystalline phase transition is an important molecular mechanism which occurs during the deformation of poly(butylene terephthalate), PBT, and in the copolymers of PBT with poly(tetramethylene oxide). Using Fourier transform infrared spectroscopy coupled with mechanical measurements, we have studied the significant factors which control the character of this transformation process. It has been shown that temperature, crystalline size and perfection of the crystalline domains affect the sigmoidal transformation behavior and transformation-stress hysteresis between the loading and unloading portions of the deformation cycle. The experimental results of highly preoriented PBT and copolymer films were explained in terms of a cooperative model. This model considered both intramolecular and intermolecular interactions within the crystalline chains. The mean intramolecular energy was estimated to be 0.40 Kcal/mole, the extent of its contribution being determined by the length of the hard segment governing the thickness of the crystal lamellae. A force constant defined the strength of intermolecular interaction between neighboring terephthalate groups modeled as Hoo-
kean springs. This constant ranged between 140 kJ/mol·(nm)² and 150 kJ/mol·(nm)², depending on the crystalline dimensions and/or coherence of the crystalline structure. It has also been shown, that increasing the temperature, not only diminishes these molecular interactions, but also leads to certain conformational changes, most likely about the O-CH₂ bond in the terephthalate group. This raises the energy of the system resulting in a shift of the hysteresis center to lower stress values.

In order to compare the deformation behavior of unoriented and preoriented samples, we have also examined segmental orientation and transformation process in isotropic films subjected to very small strains. Using polarization modulation spectroscopy, we were able to measure certain orientation functions down to 1 x 10⁻⁵. Based on these results, it was concluded that the macroscopic deformation of the sample was primarily achieved by the orientation in the soft and amorphous hard segments.
# Table of Contents

ACKNOWLEDGEMENTS ........................................ iv
ABSTRACT ....................................................... v
LIST OF TABLES ................................................ ix
LIST OF FIGURES ................................................ x

Chapter

I. INTRODUCTION ............................................. 1

Thesis Objectives ........................................... 1
Survey of Dissertation ...................................... 3

II. POLYMER DEFORMATION ..................................... 8

Introduction ................................................... 8
Orientation Distribution Function
and Infrared Dichroism .................................... 11
Deformation Mechanism in Polyethylene ............... 21
Mechanical Properties of Poly(butylene terephthalate)
and its Copolymers with Poly(tetramethylene oxide) .... 28
Conclusion .................................................... 40

III. POLARIZATION MODULATION SPECTROSCOPY .............. 42

Introduction - objectives and Advantages of a Differential Measurement ................................... 42
Theory of Polarization Modulation and Calibration of Spectra .................................................... 46
Experimental ................................................... 58
Discussion of Results ........................................ 66
Conclusion .................................................... 78

IV. THE \( \phi \rightarrow \beta \) CRYSTALLINE PHASE TRANSITION .......... 80

Introduction ................................................... 80
Structure and Morphology .................................. 82
Experimental ................................................... 87
Discussion of Characterization Studies ................. 90
Spectroscopic Study of the \( \phi \rightarrow \beta \) Crystalline Transition ...................................................... 106
Discussion of Results ........................................ 107
Conclusion .................................................... 139
1. Summary of experimental samples and corresponding characterization parameters ........................................... 89

2. Normalized integrated intensities of selected deconvoluted absorption bands as a function of temperature ........... 134

3. Estimates of the number of repeat units traversing a tetramethylene terephthalate crystal for various hard segment compositions .............................................................. 169

4. Calculated energy difference, (e), between the ω and ρ conformational energies as a function of temperature .................. 175

5. Comparison between theoretically calculated and experimental plateau strains in the stress strain curve of poly-(butylene terephthalate) copolymers having various hard segment contents. ...................................................... 192
LIST OF FIGURES

figure

1. Geometric relationship between reference coordinates and molecular coordinates ........................................ 12
2. Geometric relationship between transition moment and the electric field vector ..................................... 15
3. Geometric relationship between fiber axis, chain axis, transition moment direction and electric field .......... 17
4. A relationship between the orientation function F and the dichroic ratio, R for $\alpha = 0^\circ$ ................................. 20
5. Simultaneous orientational, mechanical and microstructural responses to strain in low density polyethylene (Ref.60)
   a. Orientation functions of the a and b crystallographic axes as a function of strain .................................... 25
   b. Stress-strain curve ......................................................................................................................... 26
6. Stress-strain curves of preoriented PBT copolymers for different hard segment contents, 4GT (by weight)
   a. 4GT = 81% ................................................................................................................................. 30
   b. 4GT = 73% ................................................................................................................................. 31
   c. 4GT = 59% ................................................................................................................................. 32
   d. 4GT = 49% ................................................................................................................................. 33
7. Stress relaxation curve for a PBT film deformed to 30% strain in one second ......................................................... 36
9. Noise in infrared spectrum in the 1700 cm$^{-1}$ region as a function of the number of coadded scans, NSS, as measured by modulation spectroscopy and subtraction of parallel and perpendicular absorption ................................................................. 45
10. Interferogram corresponding to an AC signal ................................................................................................. 50
11. Interferogram corresponding to a DC signal ................................................................................................. 51
12. The arrangement of optical elements in the beam path of the spectrometer for a modulation experiment ........... 53
13. Wavenumber dependence of modulation efficiency for half-wave retardation when $\tilde{\nu}_r$ is set to 1.0 $\mu$m(a), 3.0 $\mu$m(b), 5.0 $\mu$m (c), and 7.0 $\mu$m(d),
14. Schematics of the modified signal detection and processing path for the modulation experiment

15. Absorption difference spectrum as obtained by
   a. Modulation
   b. Subtraction

16. Calibration spectra at $\nu = 700$ nm as
   a. Measured
   b. Calculated

17. Orientation function (based on CH$_2$ dichroism) as a function of strain for samples,
   a. H96
   b. H93

18. Orientation function (based on C=O dichroism) as a function of strain for samples,
   a. H96
   b. H93
   c. H88

19. Transformation behavior; $x_\alpha$ (in percent) as a function of strain for samples,
   a. H96
   b. H93
   c. H88

20. The chemical structure of a copolymer with tetramethylene terephthalate hard segment and poly(tetramethylene) soft segment

21. The crystalline structure and unit cell dimensions of (a) $\alpha$ form crystals and (b) $\beta$ form crystals (Ref. 27) in poly(butylene terephthalate)

22. DSC traces of PBT film
   a. Isotropic
   b. Coextruded at 40 $^\circ$C
   c. Coextruded at 80 $^\circ$C
   d. Coextruded at 120 $^\circ$C
   e. Coextruded at 160 $^\circ$C

23. DSC traces of poly(ether ester) films
   a. Isotropic H1
   b. Coextruded H1
   c. Isotropic H2
d. Coextruded H2 ........................................ 95
e. Isotropic H3 ........................................... 96
f. Coextruded H3 ........................................ 96

24. Two-dimensional morphological model illustrating the interconnectivity between lamellae before coextrusion ............... 98

25. Two-dimensional morphological model illustrating the oriented structure of coextruded films ............................ 99

26. Deformation of isotropic H2 copolymer at T=23 °C
   a. Stress-strain behavior .................................. 101
   b. Dichroic ratio of C=O band as a function of strain ........................................ 102

27. Deformation of isotropic H2 copolymer at T=90 °C
   a. Stress-strain behavior .................................. 103
   b. Dichroic ratio of C=O band as a function of strain ........................................ 104

28. Infrared spectrum of PBT in the methylene rocking region .. 108

29. Infrared spectrum of PBT in the methylene bending region .. 109

30. Difference spectrum obtained by subtracting a spectrum of an undeformed film from a spectrum of a deformed film (strained by 15%) ........................................ 110

31. Relationship between the intensity decrease of 917 cm⁻¹ band and intensity increase of 960 cm⁻¹ band, during a two cycle deformation to 30% strain (PBT film) ........................................ 112

32. Change in the integrated structural absorbance of the C-H stretching region (3200 to 2800 cm⁻¹) as a function of strain ....... 114

33. Change in the reduced structural absorbance (A/A₀) of the C-H stretching vibration as plotted against λ⁻¹/² ....... 115

34. Orientation function as a function of strain (sample H2) calculated from the dichroism of the
   a. 1716 cm⁻¹ band ........................................ 116
   b. 2940 cm⁻¹ band ........................................ 117

35. Fraction of β crystals, x₂ as a function of stress for two loading cycles of a PBT homopolymer ........................................ 119

36. Fraction of β crystals, x₂ as a function strain for two loading cycles of sample H1 ........................................ 120

37. Fraction of β crystals, x₂ as a function of stress for a series of
hard segment molar concentrations, .......................... 122
a. \( X_h = 100\% \)
b. \( X_h = 96\% \)
c. \( X_h = 93\% \)
d. \( X_h = 88\% \)

38. The \( \alpha \) fraction as a function of stress in PBT films coextruded at, .......................... 122
   a. 40 °C
   b. 80 °C
   c. 160 °C

39. X-ray diffraction patterns of a PBT film coextruded at ........ 123
   a. \( T = 40 °C \)
   b. \( T = 120 °C \)

40. The \( \beta \) fraction as a function of stress in PBT film, for a series of temperatures ......................... 126
   a. \( T = 22 °C \)
   b. \( T = 45 °C \)
   c. \( T = 80 °C \)
   d. \( T = 140 °C \)

41. Spectrum of a PBT film at room temperature in the methylene rocking region, (a) Original spectrum,
(b) Self-deconvoluted spectrum .......................... 129

42. Spectrum of a PBT film in the methylene rocking region with curve-fitted peaks
   a. \( T = 25 °C \) unannealed ............................. 130
   b. \( T = 25 °C \) annealed ............................. 131
   c. \( T = 200 °C \) .................................. 132

43. Integrated area of a deconvoluted peak as a function of temperature for the bands, 916.4 cm\(^{-1}\) and 929.0 cm\(^{-1}\) ..................... 135

44. Subtracted spectrum of an unstressed PBT film from a stressed PBT film collected at,
   a. 22 °C ............................................ 137
   b. 140 °C ......................................... 138

45. X-ray diffraction patterns of a PBT film collected at different temperatures ................................. 140

46. Energy contour map of a PBT repeat unit (Ref. 20) ............. 142

47. Free energy of the \( \alpha \) and \( \beta \) forms as a function of stress and corresponding theoretical stress curve for the first order transition model ................................. 147
48. A schematic representation of a crystalline chain where two tetramethylene segments in \( \alpha \) and \( \beta \) conformations share the same terephthalate group ........................................ 154

49. The \( \beta \) fraction as a function of stress as predicted by the modified mean field theory ........................................ 157
   a. \( T = 300 \, ^0\text{K}, \, Q = 0 \, \text{Kcal/mole} \)
   b. \( T = 300 \, ^0\text{K}, \, Q = 0.40 \, \text{Kcal/mole} \)
   c. \( T = 400 \, ^0\text{K}, \, Q = 0 \, \text{Kcal/mole} \)
   d. \( T = 400 \, ^0\text{K}, \, Q = 0.40 \, \text{Kcal/mole} \)

50. The hysteresis width estimated from the plots of \( \beta \) fraction vs. stress. The hysteresis width is plotted as a function of temperature for two mole fractions of hard segment; \( x_H = 100\% \) and \( x_H = 96\% \) and at one temperature for \( x_H = 93\% \) mole fraction of hard segment .................. 168

51. Predicted shift of the hysteresis center with temperature assuming a Boltzmann's distribution of the case where .................. 173
   a. \( T = 300 \, ^0\text{K} \)
   b. \( T = 350 \, ^0\text{K} \).
CHAPTER I
INTRODUCTION

Thesis Objectives

The goal of this dissertation is to gain a better understanding of the molecular mechanisms which take place when a polymeric film is deformed and how these processes, in turn, affect the mechanical response. Such knowledge may be especially useful in the attempt to improve the mechanical properties of polymeric materials or ultimately, to construct new materials possessing desired properties. One class of polymers with truly advantageous properties are thermoplastic elastomers (1-3). These elastomers exhibit thermal- or solvent- induced reversibility in their network structures, thus facilitating practical processing. At the same time, they can possess a combination of favorable properties, normally found in thermoset elastomers and engineering plastics, such as high strain capability, good elastic recovery, and mechanical strength. The unique properties of thermoplastic elastomers arise from the phase-separated morphologies in the bulk state. The long flexible chains of the rubbery network are held together by multifunctional junctions acting as physical, rather than covalent linkages. The fact that these domains are much larger than the typical tetra- or tri-functional chemical linkages of conventional elastomers, means that the domains also act as fillers. This filler effect has a favorable reinforcing influence on the mechanical properties. Depending on the polymer, the physical
linkages can be formed by dispersed glassy domains, regions of ionically attracted or strongly hydrogen bonded molecules, or regions of crystallinity. The latter is true for poly(butylene terephthalate), PBT, and the copolymers of PBT with poly(tetramethylene oxide), PTMO. The crystallization characteristics and morphology of these polymers have been studied extensively (4 - 17). Quenching from the melt, for example, induces the formation of a lamellar network formed by PBT hard segments with the amorphous PTMO soft segments and uncrystallized PBT chains in the surrounding matrix. The deformation of these polymers involves a complex response of the amorphous domains and the crystalline superstructure. One of the most interesting processes occurring in the crystalline domains upon the application of stress is a structural phase transition between two crystalline forms (18-34). It has been suggested that this transformation has a direct influence on the mechanical properties, being partly responsible for the high recoverability and drawing plateau region exhibited by these polymers (20,34). Understanding the nature of this transition and the significant factors which control it are the primary objectives in this study. Currently, only two techniques have been used to probe the structural chain characteristics and transformation behavior of the two crystalline forms; x-ray diffraction (25-28) and infrared spectroscopy (29-32). Generally, there are several inherent advantages associated with infrared spectroscopy. Fourier transform infrared spectroscopy (FT-IR) coupled with mechanical measurements can be used to follow vibrational bands characteristic of specific structural or chemical features which change when polymeric
films are deformed in a variety of mechanical experiments (35-39). Results of such studies are capable of describing the orientation behavior of different chemical or structural components, as well as concentration changes of particular molecular species. In addition, a combination of FT-IR with a recently developed technique, polarization modulation spectroscopy, allows one to observe very small orientation changes. Simultaneous recording of the mechanical response permits the correlation of changes occurring on a microscopic level with macroscopic properties. In our case, the infrared technique is especially suitable to study the crystalline phase transition found in PBT and in its copolymers.

Survey of Dissertation

In order to establish a basis on which to analyze the general deformation of PBT and the copolymers of PBT, a deformation mechanism known to exist in a less complex polymer, polyethylene, is examined. The deformation of polyethylene has been the subject of many publications (39-61). Generally, it is thought to involve the orientation of crystals and amorphous segments, crystal structure transformation (56-58) and irreversible deformation of the superstructure which includes lamellar slip, chain slip, and lamellar separation. The deformation usually occurs through several stages which also reflect the mechanical response of the sample (59-61).

Because the orientation of specific chains can be measured by infrared dichroism the theoretical and experimental aspects of the orient-
tation distribution function and infrared dichroism are presented. Next, the possible deformation mechanisms responsible for the observed mechanical response of PBT and poly(ether ester) copolymers are examined. Because several processes occurring simultaneously may give rise to the observed stress, experiments which minimize the number of such parameters are devised. The analysis is aimed at understanding the general behavior of these polymers as a function of crystalline content, sample preparation conditions and the type of deformation experiment.

As mentioned in the introduction, very small orientation changes can be measured with polarization modulation spectroscopy. Using this technique small differences between parallel and perpendicular absorptions or absorptions between left and right circularly polarized light are detected and in the former case, related to the orientation function. Several papers have been published describing the measurement of infrared circular dichroism by combining the polarization modulation with FT-IR spectroscopy (62-65). The spectra from such experiments were of high quality in both, signal to noise ratio and in spectral resolution. Dowrey and Marcot have compared subtraction and modulation measurements of linear dichroism and have also observed improved SNR in modulation as well as the elimination of certain artifacts associated with the subtracted spectra (66,67). Such sensitivity increase has been generally attributed to a reduced dynamic range in the modulation experiment (63,66-70). The modulation technique can also be combined with FT-IR spectroscopy to measure linear dichroism (66,71). The advantages of such experiments are discussed with respect to the conventional
dichroic measurements. The theoretical considerations necessary to understand the modulation experiments and results are reviewed. Next, this technique is applied to the orientation study of slightly strained isotropic poly(etherester) films. The molecular deformation processes prevailing at such small strains are expected to be quite different than those experienced by predrawn films at higher extensions, largely due to the unlike morphology. Explanations as to why the results of this study can be analyzed in terms of an ideal network model are proposed.

Finally, we examine the deformation behavior exhibited by highly preoriented PBT and poly(ether ester) samples, with special emphasis on the $\alpha \rightarrow \beta$ crystalline phase transition. The transformation of the $\alpha$ crystals into the $\beta$ form was shown to be dependent on the orientation of the $\alpha$ form c-axis with respect to the direction of stress (72). A hysteresis in the $\alpha$ and $\beta$ contents as a function of strain was believed to arise when the transformation of the $\alpha$ crystals took place faster than their rotation toward the stretching direction, but the transformation back was independent of the orientation during unloading. Unfortunately, this concept still did not explain the transformation hysteresis with stress, where the initial rates of transformation from largely $\alpha$ or largely $\beta$ crystals are very slow. Nor does it explain the hysteresis present in highly oriented systems. However, what one did learn, was that the orientation of crystals with respect to the stretch direction was indeed significant.

To begin with, a molecular model describing the chain orientation, structure and superstructure of PBT and its related copolymers needs to
be established. This can be achieved by putting together the knowledge from existing morphological and structural results and our own characterization experiments. Such a model will serve as a basis in the interpretation of the spectroscopic - mechanical data and helps to define the direction in which most of the polymer chains experience an applied stress. The behavior of the crystalline phase transition is examined as a function of hard segment content, perfection of the crystalline structure and temperature. These are considered to be the important variables which determine how the crystalline chains react to a particular stress level.

Finally, the results of these experiments are compared with selected thermodynamic and kinetic models which correlate the \( \alpha \rightarrow \beta \) transition with the mechanical response of the material (20,28,73-76). The models considered are; a first order transition model (20), a mean field model (28,76), and a nucleation-growth model (75). These models differ in their fundamental assumptions. For example, while in a first order transition, a change in state occurs discontinuously at some critical driving force, the mean field model assumes that the system starts reorganizing itself long before the culmination of a complete conversion. This means that the system must experience long-range interactions which influence the transformation ease of the subunits. A nucleation-growth model, however, limits the interaction only to a specific boundary. Thus transformation can occur only when several subunits form simultaneously a critical nucleus that has a boundary. However, none of these models are capable of fully predicting the observed behavior. Some
theoretical modification needs to be done in order to obtain a reasonable molecular model. Such a more complete model is obtained by considering the effect of crystalline size on the inter- and intramolecular interactions and the effect of temperature on the conformational energies of the individual crystalline units. This model is then used to explain the experimental results in terms of molecular changes and their influence on the mechanical history.
CHAPTER II.
POLYMER DEFORMATION

Introduction

The mechanical properties of semicrystalline polymers are determined by the structural changes which occur in the morphology during the deformation process. These changes may include orientation and reorganization of the crystalline superstructure, orientations of individual crystalline units and amorphous chains, as well as elastic lattice distortions, various types of molecular slip and crystal structure transformations (52). Such structural changes have been examined by a variety of techniques such as electron microscopy, small-angle neutron and x-ray scattering and a number of optical-mechanical techniques (29-61, 77-78). These techniques are capable of simultaneously measuring the stress-strain properties and an optical quantity such as birefringence, light scattering, IR absorption or x-ray diffraction as a function of time or frequency. Depending on the polymer structure of interest, the techniques may be used individually or in combination, to fully elucidate the microstructural deformation mechanism corresponding to the observed mechanical response.

The orientation of crystals is very important to the mechanics of deformation because it helps to distribute the applied stress over the entire structure. If this did not happen, all of the strain would be borne by the disordered or amorphous regions resulting in a high locali-
zation of stress. Furthermore, the extent of this redistribution can determine the modulus of the material (58-61, 79-81). The orientation of tie molecules responsible for interlamellar connectivity and the plasticizing action of other interlamellar material are also critical. The former appears to account for the mechanical strength and toughness of the polymeric material. The latter has a direct bearing on the rate of crystal orientation, as well as the extent of elongation. Crystal structure transformations, on the other hand, may absorb applied energy which would otherwise be used to irreversibly disrupt the superstructure (25,26,34,55-57).

As mentioned, there are several techniques capable of measuring the orientation of molecular chains and structures. For example, light scattering characterizes changes in the crystalline superstructure, birefringence describes the total orientation of crystalline and amorphous regions, and x-ray diffraction defines the orientation of the crystalline structure (52). A desirable characteristic of infrared dichroism is that it is able to follow different components such as crystalline, amorphous or phase separated regions simultaneously. This is because infrared data can distinguish between chemically distinct chains, different conformations, hydrogen bonded molecules and various types of crystalline chain packing (82-86).

The purpose of orientation measurements is to specify the location of molecular structures with respect to the external frame of reference (85-91). Because these structures are not uniformly oriented, but rather assume a range of orientations, information about their overall ori-
Orientation distribution is instead desirable. Such distribution can be characterized by a complete set of weighted moments. The theoretical considerations summarized in this chapter show how the average orientation of the polymer structure can be related directly to these moments. In addition, it is demonstrated how one particular moment can be measured by infrared dichroism.

In order to define the deformation mechanism in terms of orientation and changes in the molecular structure and to see how it affects the mechanical properties, it is always easier to first understand a simple, well characterized system. For this reason, the deformation processes believed to exist in low density and high density polyethylene are discussed. In addition, we point out several models used to partially explain the mechanical response in terms of the drawing behavior on a molecular level. With this information in mind, the mechanical properties of poly(butylene terephthalate) PBT and its related copolymers are examined. The copolymers are convenient on several counts. First; the percent crystallinity can be controlled by the ratio of hard to soft segments, and second; the facile processing of these polymers makes it convenient to prepare morphologically well-defined films. This chapter describes the results of stress relaxation and force temperature studies which are necessary in interpretation of data presented in subsequent chapters.
Orientation Distribution Function

A summary of theoretical considerations dealing with the orientation distribution is formulated here by following the work of several authors (85-91).

While the location of a polymeric body can be characterized by a set of Cartesian coordinates ($x, y, z$), the position of a molecular subunit within the body can be described by the Cartesian coordinates ($a, b, c$). The two coordinate systems can be related by means of Eulerian angles ($\theta, \phi, \psi$) as illustrated in figure 1. The orientation distribution of the subunits, $\rho(\theta, \phi, \psi)$ in the polymeric body in terms of the Eulerian angles is,

$$\int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{0}^{2\pi} \rho(\theta, \phi, \psi) \sin \theta \, d\theta \, d\phi \, d\psi = 1$$  \hspace{1cm} (2.1)

where the integral is normalized over all orientations. The evaluation of this equation is considered in the case of uniaxial extension. As an example, when the chain axis coincides with the $c$-axis and has fiber symmetry, i.e. no preferred orientation exists in the planes perpendicular to the draw direction, the orientation distribution $\rho(\theta)$ is just a function of $\theta$, the angle between the chain axis of one unit and the draw direction.

$$\int_{0}^{\pi} \rho(\theta) \sin \theta \, d\theta = 1$$  \hspace{1cm} (2.2)

The distribution function $\rho(\theta)$ can be expressed in terms of an orthogonal set of spherical harmonics (86), the Legendre functions:
Figure 1. Geometric relationship between reference coordinates and molecular coordinates.
\[
\overline{P_n(\cos \theta)} = \rho(\theta)P_n(\cos \theta)\sin \theta \, d\theta
\]  
(2.3a)

where

\[
\rho(\theta) = \sum_{m=0}^{\infty} [(2m+1)/2]P_m(\cos \theta)P_n(\cos \theta)
\]  
(2.3b)

or

\[
\rho(\theta) = A_0P_0(\cos \theta) + A_1P_1(\cos \theta) + A_2P_2(\cos \theta) + \ldots
\]  
(2.3c)

where

\[
A_n = [(2n+1)/2]P_n(\cos \theta)
\]  
(2.3d)

When \(\rho(\theta)\) is an even function (as in the case of uniaxial orientation), then

\[
P_0(\cos \theta) = 1
\]  
(2.4a)

\[
P_2(\cos \theta) = 1/2 (3\cos^2 \theta - 1)
\]  
(2.4b)

\[
P_4(\cos \theta) = 1/8 (35\cos^4 \theta - 30\cos \theta + 3)
\]  
(2.4c)

The second moment of the orientation distribution can be determined from birefringence and polarized infrared measurements. Raman scattering, polarization fluorescence and broad line NMR studies can give second and fourth moments, while x-ray diffraction is the only technique which, in principle, can characterize the complete crystallite orientation distribution (86).

Infrared Dichroism and Orientation

The absorption of infrared radiation by a polymeric material is defined as follows

\[
A = A_0 (\mathbf{M} \cdot \mathbf{E})^2
\]  
(2.5)
where $\mathbf{M}$ is the transition moment vector of the normal mode, and $\mathbf{E}$ is the electric field vector of the incident beam. For unoriented polymeric materials, gases and liquids, the absorbance is independent of the polarization of the incident beam because the orientation of the transition moment vector assumes a random distribution, namely $(\mathbf{M} \cdot \mathbf{E})^2$ equals one. In this case, the absorbance can be expressed as the product of the extinction coefficient, the path length and the concentration of the absorbing species, as shown in equation 2.6a.

However, for uniaxially oriented polymers, the situation is different. The electric field vector, whose propagation direction is normal to the sample plane, can be linearly polarized in two mutually perpendicular directions. The absorbance resulting when the electric field vector is either parallel or perpendicular to the preferred sample orientation is expressed by the following equations,

$$A_0 = \mathbf{e} \cdot \mathbf{b} \cdot \mathbf{c} \quad (2.6a)$$
$$A = A_0 \cos^2 \theta_z \quad (2.6b)$$
$$A = A_0 \sin^2 \theta_z \cos^2 \psi \quad (2.6c)$$

Here $\theta_z$ is the angle between the $M_z$ component and $\mathbf{E}$ in the plane normal to the propagation direction of the incident radiation and $\psi$ is the angle of the transition moment with respect to the propagation direction as illustrated in figure 2. The perpendicular absorption component $A_\perp$ in plane of the sample is the same as the absorption component perpendicular to the plane of the sample when uniaxial symmetry is assumed, namely,

$$A_0 \sin^2 \theta_z \cos^2 \psi = A_0 \sin^2 \theta_z \sin^2 \psi \quad (2.7)$$

or
Figure 2. Geometric relationship between transition moment and the electric field vector.
\[ \text{A}_0 = \text{A}_n + 2\text{A}_\perp \]  

(2.8)

Infrared orientation measurements begin by determining the dichroic ratio, \( R \), where

\[ R = \frac{\text{A}_n}{\text{A}_\perp} \]  

(2.9)

The value of \( R \) can range from zero to infinity depending on the chain orientation and the particular vibrational mode. For an isotropic sample, \( R \) just equals one.

The dichroic ratio has been related to macromolecular orientation through several models (90-92, 94-95). Marinnan (92) followed the reasoning of Kuhn and Grun who derived the optical properties of a long-chain amorphous polymer by representing the molecular structure by an idealized chain of identical, completely independent links (93). The absorption for the whole chain was then calculated using a function describing the distribution of links within a particular angular range and integrating over all space. Fraser's model, on the other hand is not concerned with the length of the chain or the overall organization of the chains, but only the position of absorbing species with respect to the chain and fiber axis (90,91). Because of its simplicity, we shall limit our discussion to this particular model.

Given the geometry in figure 3, the dichroic ratio is given by equation 2.10, where \( \alpha \) is the angle between the transition moment and the chain axis, \( \Theta \) is the angle between the chain axis and the \( z \) preferred axis. In axially oriented polymers all orientations of \( M \) around the chain axis are equally probable and all values of \( \phi \) are equally probable.
Figure 3. Geometric relationship between fiber axis, chain axis, transition moment direction and electric field.
The trigonometric relations depict the projected contributions of the transition moment to either of \( \mathbf{r} \) and \( \mathbf{r} \) directions. The function \( \rho(\theta) \) describes the distribution of chain axes in the range of \( 0 \leq \theta \leq 1/2 \). In case of perfect alignment, namely, \( \theta = 0 \), the value of \( R \) is given by \( R_0 = 2\cot^2 \alpha \) and equation 2.10 can be written as

\[
R = \frac{\int_0^{\pi/2} \left[ \cos^2 \alpha \cos^2 \theta + 1/2 \sin^2 \alpha \sin^2 \theta \right] \rho(\theta) \, d\theta}{\int_0^{\pi/2} \left[ 1/2 \cos^2 \alpha \sin^2 \theta + 1/4 \sin^2 \alpha (1 + \cos^2 \theta) \right] \rho(\theta) \, d\theta}
\] (2.10)

\[R = \frac{\int_0^{\pi/2} \left[ 1 + (R_0 - 1) \cos^2 \theta \right] \rho(\theta) \, d\theta}{\int_0^{\pi/2} \left[ 1 + 1/2(R_0 - 1) \sin^2 \theta \right] \rho(\theta) \, d\theta}
\] (2.11)

Since \( \int_0^{\pi/2} \rho(\theta) \, d\theta = 1 \) (2.12)

then \( R = \frac{1 + (R_0 - 1) I}{1 + 1/2(R_0 - 1)(1 - I)} \) (2.13)

Letting \( I = 1/3(1 + 2F) \) (2.14)

where \( I = \int_0^{\pi/2} \rho(\theta) \cos^2 \theta \, d\theta \) (2.15)

equation (2.15) can be rearranged to give

\[
F = \int_0^{\pi/2} \rho(\theta) \left[ (3 \cos^2 \theta - 1)/2 \right] \, d\theta
\] (2.16)

From previous orientation considerations, we know that \( F \) is just the average of the second moment of the orientation distribution function.
More commonly, it is known as the Hermann's orientation function (96). Rearranging equation (2.13), one can show that this orientation function can be calculated from the dichroic ratio.

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

(2.17)

The value of $F$ varies from +1 to zero to -1/2 for orientations that are respectively parallel, random and perpendicular to the uniaxial direction.

Several practical aspects concerning orientation measurements need to be mentioned. One major problem is the determination of the transition moment angle, $\alpha$, with respect to the chain axis. Generally, it is assumed that the transition moment direction is the same as the chemical bond direction whose relationship to the chain axis is known. This is true for highly localized vibrations such as C-H, S-H, N-H stretching. However, the direction of the transition moment in other vibrations such as symmetric CH$_2$ stretching or bending is displaced from the bond direction (85,90). In these cases the transition moment is actually perpendicular to the chain axis. Depending on the polymer, the transition moment of the C=O stretching vibration of an amide group can be displaced between 5° to 20° from the C=O direction (85,90). Methods used to determine $R_0$ from infrared and x-ray diffraction measurements are discussed in the literature (87,88).

The sensitivity of Hermanns' orientation function to the actual orientation of the molecular chains depends largely on the choice of the
Figure 4. A relationship between the orientation function $F$ and the dichroic ratio, $R$ for $\alpha = 0^\circ$. 
absorbing species. When $\alpha = 54.74^\circ$, the ratio $(R_0 + 2)/(R_0 - 1)$ is infinite and $F$ remains constant for all real orientations. The greatest change in the Hermann's function with increasing orientation can be detected in cases where $\alpha = 0^\circ$ or $90^\circ$, in the former the chain orientation is measured directly (85). A plot of $F$ vs. $R$ for this example is shown in figure 4. This particular curve also illustrates the fact that although the dichroic ratio may still rise dramatically when highly pre-oriented samples are strained, further increase in the chain orientation is actually quite minimal. Therefore reporting dichroic measurements by themselves is not sufficient.

The deformation mechanism in polyethylene

The relative orientation of crystalline and amorphous components is particularly important in semicrystalline polymers. Due to its structural simplicity, the most widely studied polymer has been low density and high density polyethylene. The deformation process experienced by polyethylene serves as a model and basis in interpreting the deformation mechanisms of other, more structurally complex polymer systems. In simple terms, the deformation in polyethylene is thought to involve a coupled response of crystalline and amorphous regions. The response of the crystal lamellae depends largely upon their orientation, thickness, and perfection. In an isotropic sample, where the lamellae are distributed with equal probability at all angles to the applied force, the mechanism of transmission of force from one lamellae to the
next will vary depending on their orientation (58-61). For example, for lamellae lying parallel to the force, the crystalline and amorphous regions effectively act in parallel to each other. If the crystalline chains traverse the lamellae, lamellae having long axes perpendicular to the stretching direction respond in series with the amorphous regions. The forces between lamellae are primarily transmitted through the intervening amorphous regions. Lamellae with long axes tilted to the strain direction experience a torque which may shear lamellae past each other. The extent of this shear is determined by interlamellar ties and the viscosity of interlamellar material (52). Since during deformation the superstructure is continuously changing, the kinds of mechanisms occurring will largely be determined by the particular strain state. In general this deformation occurs through several stages. The first stage, corresponding to the elastic part of the stress strain curve is thought to involve an elastic deformation of the lamellar superstructure as a whole. For example, spherulites change into ellipsoidal entities and rodlike structures align in the stretching direction (46-48, 52-54). The spherulitic deformation as studied by light scattering and electron microscopy, generally consists of twisting and shearing of lamellae. This type of orientation is facilitated by the surrounding amorphous regions which, at this stage, are primarily responsible for the observed macroscopic elongation (52). Infrared orientation studies of low density polyethylene have examined the orientation changes experienced by the crystalline blocks (60,61) forming the lamellae. As shown in figure 5a, at low strains the crystalline a-axis orients perpendicular to the draw
direction (decrease in $F_a$) the longer $b$-axis orients parallel to the draw direction (increase in $F_b$), thus reflecting the orientation of the crystalline block as a whole. This process is illustrated in figure 5b. Because this orientation is reversible and it does not destroy the coherence of the crystalline block, it is consistent with the corresponding elastic mechanical response.

The exact nature of the deformation process in the second stage, however, is still highly debatable (41,45,51,77,78). Orientation studies (60,61) suggest that at the yield point, the superstructure is broken into smaller crystalline blocks which orient with little force in the direction of stretching, as is evident in a large decrease of the $F_a$ and an increase of $F_b$ orientation functions, seen in figure 5a. Several models have been introduced which describe the detailed "breaking" of the superstructure. Pope and Keller (51) proposed a model which consists of stacks of lamellae that have axes along the original draw direction and which deform by lamellar slip, chain slip, and lamellar separation. The order and extent of these processes depends on the temperature of deformation and the molecular structure (51). High density polyethylene, for example, exhibits larger void formation and lower lamellar separation because the lamellae are laterally more extended than in LDPE. HDPE also experiences a greater amount of irreversible chain slip due to lower content of amorphous material which acts as a source of elastic restoring forces in LDPE. These molecular processes are thought to be largely instrumental in achieving the final drawn material. According to Peterlin (41,42,55), the drawn material is made up of microfibrils which
are strings of small chain-folded blocks. These microfibrils are formed by unfolding and breaking off blocks of folded chains primarily by gradual chain tilt and chain slip in the lamellae. The results of the infrared studies also support this mode because the orientation of the crystalline b-axis begins to decrease and the rate of decrease in $F_a$ becomes lower, as seen in figure 5a. Such behavior implies chain unfolding, illustrated in figure 5b, which, as the rise in the corresponding modulus shows, also requires a larger force.

Other models suggest that the drawing involves unfolding and bending of chain segments of all molecules in the deformation region, as opposed to breaking off blocks of folded chains (45). The subsequent incorporation of chain folds into the drawn structure is then thermally activated. Still other models insist that the plastic deformation does not proceed via a structural mechanism, but involves melting and subsequent recrystallization into the drawn structure (77). Their argument is that although the energy input during the deformation is insufficient to raise the temperature of the drawn crystals above their melting point, there still may be partial (local) melting during the lamellae to fibril transformation process. Similar mode has been suggested by Liu, Juska and Harrison (78), based on their heat of fusion measurements of polypropylene films drawn at different temperatures. The higher heat of fusion associated with higher draw temperature was explained by a stress-activated phase transition model. This model assumes that randomization or melting of chains is induced by local strain energy and that recrystallization proceeds within the strained melt (occurring very
Figure 5a. Orientation functions of the a and b crystallographic axes and stress as a function of strain in low density polyethylene (Ref. 60)
Figure 5b. Microstructural response to strain in low density polyethylene (Ref. 60).
fast). The crystallinity in drawn PP is therefore a function of the draw temperature. However, there is no reason why this increased crystallinity cannot be attributed to the annealing of imperfect crystalline regions.

Although the elongation of the crystalline regions is crucial to the strength of polyethylene, the deformation of the amorphous regions can be just as equally important. Some of the amorphous chains, such as the trans sequences, most likely crystallize as indicated by the decrease in the infrared structural absorbance of amorphous chains and an increase in the structural absorbance characteristic of the crystalline structure (39). The higher crystallinity increases the modulus of the material (97).

The final stage of elongation, as suggested by Peterlin (41) is believed to be a plastic deformation of the fibre structure, involving sliding of the microfibrils past each other and stretching the interfibrillar tie molecules. Furthermore, additional unfolding may occur in chain sections by which the tie molecules are anchored.

In addition, polyethylene single crystals have been shown to undergo crystalline transformation under stress (55-57). Preoriented either by rolling or by coextrusion, polyethylene single crystals transform from orthorhombic to monoclinic phase when stretched along the b-axis direction (55-57). Such phase transition can account only for few percent of the plastic deformation, the larger deformations being primarily produced by chain tilt (55). Interestingly enough, the transition can be reversed when the stress is removed.
Our study of poly(butylene terephthalate) focuses on a similar aspect of molecular organization. This process is the crystalline phase transition, which, just as the PE orthorhombic to monoclinic transition, is largely reversible (25,26). However, in PE the transformation back to the orthorhombic cell supposedly takes place without reverse stress, while in PBT the number of transformed crystals is intimately related to the overall macroscopic stress. The stress-strain behavior thus indirectly reflects the crystal-crystal transformation process. It is therefore important that in studying the transition, one is aware of the other deformation processes, such as those described earlier in the case of PE, and is able to separate them from the crystalline transition itself.

Mechanical properties

The stress-strain curves of preoriented PBT homopolymer as well as of its copolymers of various compositions are shown in figures 6a-d. The films have been preoriented by a solid state extrusion technique (98) to a draw ratio of 3.5. The percent hard segment by weight is designated by %4GT. The crystallinity as measured by DSC for each sample is 81% 4GT: 34.4%, 73% 4GT: 32.7%, 59% 4GT: 24.9% and 49% 4GT: 20.7%. All data have been obtained at room temperature. As is evident from the results, the plateau region becomes more apparent and the stress hysteresis increases with more hard segment content. Furthermore, the hysteresis
Figure 6. Stress-strain curves of preoriented PBT copolymers for different hard segment contents, 4GT (by weight).

a. 4GT = 81%
b. 4GT = 73%
c. 4GT = 59%
d. 4GT = 49%
Figure 6a.
Figure 6b.
Figure 6d.
between the unloading and reloading curve also increases with hard segment content.

A number of investigators have been tempted to explain the plateau in terms of the \( \alpha = \varphi \) crystalline phase transition \((20,34)\). They have postulated that the increase in strain at constant stress is a result of the increase in length of the crystal unit cell. However, even when assuming perfect crystalline orientation (c-axis parallel to the strain direction), the strain length of the plateau region for a given % crystallinity cannot be accounted for simply by an elongated crystalline unit cell (see appendix A.). Other contributions such as plastic deformation; lamellar slip, crystal twinning and amorphous deformation are also important. As seen in figures 6a through 6d, increasing the percent hard segment (or % crystallinity), results in a wider strain distance between the initial loading and all subsequent cycles at zero stress. This means that the plastic (irrecoverable) deformation occurs largely in the crystalline regions. Further loading and unloading follows the same path as long as the strain stays below the maximum imposed strain.

In general, materials which show similar mechanical behavior to PBT and its copolymers, such as filled elastomers, SBR and certain polyurethanes, also exhibit a substantial stress softening. In certain cases, however, there is no apparent hysteresis loop between the unloading and reloading cycles, suggesting an irreversibility of the microstructural breakdown \((99,100)\). On the other hand, an appearance of a hysteresis between these two curves implies the presence of a time-dependent or a strain dependent restructuring mechanism \((100)\). In the
case of PBT, it was proposed, that the reason for a hysteretic recovery is the cooperative behavior of the $\alpha \rightarrow \gamma$ transition.

Since the transition does account for a certain percentage of the strain, the recovery of this component of strain will be dependent on the relative content of $\alpha$ and $\gamma$ units at any particular time. This concept will be examined further in the subsequent chapters. Another explanation for the observed loop may be a time-dependent restructuring of the superstructure, as aided by the relaxing amorphous chains. In other words, the mechanical hysteresis may be related to a viscoelastic hysteresis. Polybutylene homopolymer at room temperature is near its glass transition. Therefore during the deformation, the material may be slow to respond and a hysteresis may result. As more PTMO plasticizer is incorporated into the matrix, the Tg is lowered (6,7) and the material behaves more rubbery and retracts rather easily, allowing the loop to narrow. For this reason, deformation experiments need to be conducted at sufficiently slow speeds to allow the material to reach its relaxed stress at any strain.

Figure 7 shows the stress relaxation curve for a PBT film deformed at room temperature to 30% strain, (rate of elongation was 30% per second). Assuming that the relaxation modulus is given by the equation,

$$E(t) = E \ e^{-t/\tau} + E_0$$ (2.18)

where $E_0$ is the elastic modulus of the crystalline units and $E$ of the viscoelastic amorphous chains. Then the stress as a function of the applied constant strain and time is given as

$$\sigma(\epsilon, t) = \dot{\epsilon}(t)[E \ exp(-t/\tau) + E_0]$$ (2.19a)
Figure 7. Stress relaxation curve for a PBT film deformed to 30% strain in one second.
From the stress relaxation curve we can obtain all the necessary constants. Assuming at very large times the stress reaches a value of approximately $4 \times 10^7$ N/m$^2$, then

$$\tau = 190 \text{ sec}$$

$$E_0 = 1.33 \times 10^8 \text{ N/m}^2 \quad \text{and}$$

$$E = 1.87 \times 10^8 \text{ N/m}^2.$$ 

In the actual stress-strain experiments the deformation proceeds at a much slower rate, namely 1.8% strain a minute. In this case the stress can be expressed as

$$\sigma(t) = \dot{\varepsilon} t E_0 + \int_0^t E \exp \left[ -\frac{(t - \dot{\varepsilon})}{\tau} \right] \left( \frac{d\varepsilon}{d\gamma} \right) \cdot d\gamma \quad (2.19b)$$

If the strain rate is constant, $d\varepsilon / d\gamma = \dot{\varepsilon}$, and

$$\sigma(t) = \dot{\varepsilon} t E_0 + \dot{\varepsilon} \tau E \left( 1 - \exp \left( -\frac{t}{\tau} \right) \right) \quad (2.19c)$$

Since the applied strain as a function of time is triangular, in the second half of the deformation cycle, $\dot{\varepsilon}$ is negative. Calculation of the relaxed stress at 15% strain during the loading and unloading portions of the cycle yielded 35.1 MPa and 34.6 MPa, respectively. Because 0.50 MPa is the order of magnitude associated with the error of the stress measurement, at this rate of deformation a stress hysteresis cannot result from a viscoelastic effect. Since the relaxation times are even faster for the softer copolymers or at elevated temperatures, we feel that any viscoelastic contributions to the stress hysteresis are also negligible. Therefore, the hysteresis between the loading and unloading curves must be entirely due to the cooperative nature of the transition.
A similar conclusion has been reached by graphical subtraction of a calculated stress-strain diagram based on a viscoelastic model from an experimentally obtained stress-strain diagram (73). The new diagram represented a mechanical hysteresis related to the relative amount of $\alpha$ and $\beta$ crystal phases.

Furthermore, a force temperature study conducted at a strain point in the unloading curve suggests that the amorphous domains behave more like elastic rubber than viscoelastic material. These results are shown in figure 8. Instead of decreasing with temperature, as would be the case when a viscoelastic material softens and becomes more viscous, the stress actually rises with temperature. According to rubber elasticity, the restoring force of an ideal elastomer having no internal energy contributions is directly proportional to the absolute temperature (101,102), namely

$$f = -T \left( \frac{\partial S}{\partial L} \right)_{T,P}$$

(2.20)

The elastic response is governed by the decrease in entropy, $S$, experienced upon extension. If this was true for PBT, extrapolation of the force-temperature curve down to $0^\circ$ K should yield $f = 0$. This obviously is not the case, because at $T = 0^\circ$ K the restoring force, $f$, is approximately -30 MPA. This means that other processes associated with a change in enthalpy must occur during the deformation. Although the data shows a slight hysteresis as a result of nonequilibrium conditions, for simplicity, we assume that the temperature - stress behavior is reversible. In addition, we assume that the strain is reversible. Hence an expres-
Figure 8. Force-temperature response of PBT film (The film was first strained by 30%, then down to 15% and allowed to relax before the temperature was varied).
sion for the restoring force is given by,

\[ f = -T \left( \frac{\partial S}{\partial L} \right)_{T,P} + \left( \frac{\partial H}{\partial L} \right)_{T,P} \]  (2.21)

where

\[ \left( \frac{\partial H}{\partial L} \right)_{T,P} = \left( \frac{\partial H}{\partial L} \right)_{T,V} + T \frac{1}{\xi} \left( \frac{\partial V}{\partial L} \right)_{T,P} \]  (2.22)

Here \( \gamma \) and \( \varsigma \) are the coefficients of thermal expansion and isothermal compressibility respectively. It has been pointed out that the coefficient \( (\partial V/\partial L) \) is very small for most crosslinked elastomers (101). On the other hand, a small volume change in the crystalline regions is possible when \( \alpha \) units transform to \( \beta \) units. An eight percent increase in the volume is calculated based on the different dimensions of the two unit cells. The negative contribution to the \( (\partial H/\partial L) \) term may also originate from the change in internal energy. The energies of the individual chains are not constant as a function of their conformations, nor are the chains completely free in space and unaffected by other chains. It would not be surprising, if this negative change in internal energy upon deformation was due to the alteration of inter- and intra-molecular interactions upon the \( \alpha \leftrightarrow \beta \) transformation. This idea was already considered in a deformation calorimetry study (103). However, no definite conclusions could be drawn.

**Conclusion**

The relationship between measurable dichroism and average orienta-
tion of chemical groups or structure has been clearly defined. Crystalline lamellae and amorphous orientation, as well as structural transformation have been discussed with respect to observed mechanical behavior. The stress-strain behavior of poly(butylene terephthalate), PBT, and its related copolymers was explained in terms of plastic deformation of the crystalline superstructure, as well as the α-β crystalline phase transition. It was demonstrated that, in the case of PBT homopolymer, the observed mechanical hysteresis cannot arise from a viscoelastic effect if the rate of deformation is less than two percent strain a minute. This also applies to all copolymers whose relaxation rates are even faster. In addition, a force temperature study has suggested that the amorphous domains behave more like an elastic rubber rather than a viscoelastic material. The retractive force is most likely governed by the chain entropy and internal energy changes due to the α-β transformation process.
Chapter III
POLARIZATION MODULATION SPECTROSCOPY

Introduction

As discussed in the previous chapter the mechanical properties of polymers are strongly influenced not only by the chemical structure of the material, but also by its mechanism of molecular orientation. Generally, in its final usage the material is subjected to very small deformations. It may be, therefore, enlightening to relate the immediate properties, such as strength, durability or dimensional stability to the orientation of polymeric chains at small levels of strain.

Most commonly, orientation obtained in infrared-mechanical experiments is determined by individually measuring the absorbance of IR radiation polarized parallel and perpendicular to the stretching direction of the material, and then taking the ratio or difference of these two values. In this type of measurement, the absolute signal requires a large dynamic range. The deficiency of this technique consequently arises when at small strains, the changes in the absorbed radiation are on the order of the noise in the measurement. The noise itself primarily originates in the (MCT) detector, its level being independent of the light level falling on the detector (70).

As an example consider the case where $A_\perp$ is 1.00000, $A_\parallel$ is 1.00011, that is $\Delta A = 1.1 \times 10^{-4}$. An upper limit of the interferogram dynamic range (ratio of largest to smallest signal), has been estimated to be
\(n^{1/2}\) times the spectral dynamic range, where \(N\) is the number of resolution elements (70). In the case of a spectrum from 400 to 4000 \(\text{cm}^{-1}\) collected at 4 \(\text{cm}^{-1}\) resolution, the \(n^{1/2}\) is about 30. Hence the requirement for 10:1 dynamic range in \(\Delta A\) is that the interferogram dynamic range be \(3 \times 10^6\) to 1. Normally, a 15 bit A/D converter has a dynamic range only of \(3.2 \times 10^4\) to 1 (72) and therefore is not sufficient to measure such small signal changes.

On the other hand, a direct differential measurement would require an interferogram dynamic range of 300 to 1. This can be easily achieved. A method capable of such a measurement is polarization modulation spectroscopy. In this method, two differently polarized infrared beams are alternately passed through a sample. The detected signal is processed by a phase sensitive amplifier. The reference frequency of the lock-in amplifier is synchronized with the frequency of the polarization changes. The final output signal then represents the intensity difference between the two polarizations. The primary advantages of the technique are the improved signal to noise (SNR) and the convenience and time resolution associated with a direct measurement. In addition, spectral artifacts caused by uneven sampling when polarizers have to be rotated in the beam path, are eliminated in the modulation experiment (65,66).

Comparison of absorbance differences obtained by polarization modulation and by direct subtraction have been discussed in view of the noise associated with each measurement (71,72). When using a highly oriented sample, it was shown that subtraction produced better results for any given number of scans (71,72). However, at the time of these
measurements, the optimization conditions have not been well understood and therefore the S/N was not as large as it could have been. New results obtained under improved conditions indicate that for a highly oriented sample, the signal to noise ratio in the modulation technique is on the same order of magnitude, if not better than direct subtraction technique. This can be clearly seen in figure 9. In addition, the differential signal corresponding to a highly oriented film is very large, forcing it to be strongly attenuated before being processed by the lock-in amplifier. This attenuation further degrades the S/N. Therefore noise studies comparing the subtraction and modulation techniques should primarily utilize slightly oriented films. The true advantage of the modulation technique should be particularly apparent in lowly dichroic films.

Using the modulation technique, we have examined the orientation of a series of PBT copolymer films at small strains. These samples differ in the mole fraction hard segment and percent crystallinity. When melt pressed and quenched from the melt, a certain fraction of the hard segments form an interpenetrating lamellar morphology with the soft segments and uncrystallized hard segments excluded in the surrounding matrix. Due to the elastic nature of the mechanical response at low strains (34), one would expect that the primary deformation would occur in the amorphous regions combined with small orientation of the crystalline domains. With the crystalline hard segments acting as junction points, this problem could be analyzed using an ideal network model. However, it should be also kept in mind that the percent crystallinity
Figure 9. The ratio of noise to signal in an infrared spectrum in the 1700 cm$^{-1}$ region as a function of the number of coadded scans, NSS$^{1/2}$, as measured by Modulation spectroscopy ($\bullet$) and subtraction of parallel and perpendicular spectra ($\cdot$).
in the film ranges between 20 to 40 percent. Generally, systems which are described by this network model are crosslinked amorphous polymers, elastomers and rubber with no or very low percent crystallinity (97,101,102). However, as long as it can be shown that the crystalline regions in the PBT copolymers do not participate in the initial deformation, the assumption of a network model should be reasonable.

An ideal network model shows how the orientation function varies with strain depending on the number of random links, N, between adjacent crosslink points. If the films are subjected to less than 15% strain, for N = 10 to 100, the orientation function can range from $9 \times 10^{-4}$ to $9 \times 10^{-3}$. This means that the dichroic ratio of an absorbing group vibrating $90^\circ$ to the chain axis will increase from 1.000 to 1.0014 or to 1.014. Since these represent maximum achievable values, obtaining the orientation changes with sufficient signal to noise ratio, throughout the extension cycle, by conventional dichroic measurement would be very difficult. For reasons already discussed in the beginning of this chapter, polarization modulation spectroscopy would be particularly suitable in studying this problem.

Theory of Polarization Modulation

The theory of polarization modulation and its application to FT-IR has been discussed in detail by Nafie and Vidrine (62). Presented here is a summary of the important considerations necessary to understand polarization modulation.
Given the correct optical arrangement, the light passing through a sample can be defined in terms of two polarized components, \( I_\parallel(\tilde{\nu}) \) and \( I_\perp(\tilde{\nu}) \). Here \( \tilde{\nu} \) is the frequency of the infrared radiation and \( I_\parallel \) and \( I_\perp \) are the parallel and perpendicular intensities. The total intensity which reaches the detector varies with time and wavenumbers a result of a sinusoidal modulation between these two intensities at a frequency \( \omega_d \). The total intensity is given by

\[
I(\tilde{\nu},t) = I_{DC}(\tilde{\nu}) + I_{AC}(\tilde{\nu})\sin(2\pi\omega_d t) \tag{3.1}
\]

The average single beam intensity, \( I_{DC} \), and the difference single beam intensities are given by

\[
I_{DC} = 0.50 \left[ I_\parallel(\tilde{\nu}) + I_\perp(\tilde{\nu}) \right] \tag{3.2a}
\]
\[
I_{AC} = 0.50 \left[ I_\parallel(\tilde{\nu}) - I_\perp(\tilde{\nu}) \right] \tag{3.2b}
\]

These, in turn, can be expressed in terms of the dacadic absorbance \( A \), which is a quantity more practical in the interpretation of molecular properties. In other words,

\[
I_{DC}(\tilde{\nu}) = 0.50 I_0(\tilde{\nu}) \left[ 10^{-A_\parallel(\tilde{\nu})} + 10^{-A_\perp(\tilde{\nu})} \right] \tag{3.3a}
\]
\[
I_{AC}(\tilde{\nu}) = 0.50 I_0(\tilde{\nu}) \left[ 10^{-A_\parallel(\tilde{\nu})} - 10^{-A_\perp(\tilde{\nu})} \right] \tag{3.3b}
\]

where \( I_0(\tilde{\nu}) \) is the single beam throughput without a sample. Taking the ratio of \( I_{AC}/I_{DC} \):

\[
I_{AC}/I_{DC} = \frac{\left[ 10^{-A_\parallel(\tilde{\nu})} - 10^{-A_\perp(\tilde{\nu})} \right]}{\left[ 10^{-A_\parallel(\tilde{\nu})} + 10^{-A_\perp(\tilde{\nu})} \right]} \tag{3.4a}
\]

or

\[
I_{AC}/I_{DC} = \tanh [0.50(\ln 10)\Delta A] \tag{3.4b}
\]

where \( \Delta A(\tilde{\nu}) \) is \( A_\parallel - A_\perp \). For small values of \( \Delta A \), the hyperbolic tangent can be approximated by its argument. Thus the single beam ratio is directly proportional to the absorbance difference spectrum, namely
\[
\begin{align*}
I_{AC}/I_{DC} &= 1.1513 \Delta A(\tilde{v}) \tag{3.5}
\end{align*}
\]

When using a Fourier transform spectrometer for the measurement, a new corresponding set of equations needs to be developed. The radiant intensity \( I(\tilde{v}) \) in watts is converted to an electronic signal \( B(\tilde{v}) \) in volts, in accordance with the response function of the detector \( R(\tilde{v}) \) in volts per watt (70). This relationship is simply,

\[
B(\tilde{v}) = R(\tilde{v}) \cdot I(\tilde{v}) \tag{3.6}
\]

The interferogram \( V \) from an FT spectrometer is related to the transmission signal \( B(\tilde{v}) \) by (70),

\[
V(\xi) = \int_{0}^{\infty} B(\tilde{v}) \cos[2\pi\xi\tilde{v} - \Theta(\tilde{v})] d\tilde{v} \tag{3.7}
\]

where \( \xi \) is the retardation caused by the moving mirror and \( \Theta(\tilde{v}) \) is a function describing the phase of the individual wavenumber frequencies. If the transmission signal is modulated, the expression for the total interferogram becomes

\[
V(\xi) = \int_{0}^{\infty} [B_{DC}(\tilde{v}) + B_{AC}(\tilde{v}) \sin 2\pi \omega_{d} t \cos[2\pi\xi\tilde{v} - \Theta(\tilde{v})] d\tilde{v} \tag{3.8}
\]

The modulation frequency, \( \omega_{d} \) can be between 50 to 200 kHz, while the Fourier frequencies range from 160 Hz to 1.6 kHz when spectral limits are between 400 cm\(^{-1}\) and 4000 cm\(^{-1}\). When the detector signal is sent through a low-pass electronic filter, the higher frequency components are removed, yielding a DC interferogram corresponding to the average transmission

\[
V_{DC}(\xi) = \int_{0}^{\infty} B_{DC}(\tilde{v}) \cos[2\pi\xi\tilde{v} - \Theta_{DC}(\tilde{v})] d\tilde{v} \tag{3.9}
\]
where $\Theta_{DC}(\nu)$, includes the electrical phase shifts added by the filters. The AC interferogram is obtained by first passing the detector signal through a band-pass filter centered at $\omega_d$ and then to a lock-in amplifier with a reference frequency equal to $\omega_d$. The expression for the demodulated interferogram is

$$V_{AC}(\nu) = \int B_{AC}(\nu) \exp[-(2V\nu)\tau] \cos[2\pi\nu - \Theta_{AC}(\nu)]d\nu$$

(3.10)

where $\Theta_{AC}(\nu)$ incorporates all phase shifts added by the lock-in amplifier and the electronic filters. The factor $\exp[-(2V\nu)\tau]$ approximates the attenuation of Fourier frequencies by the time-constant circuitry, where $\tau$ is the time constant.

Examples of AC and DC interferograms are illustrated in figures 10 and 11. It is interesting to note that the AC interferogram contains much more information on the side lobes relative to the point of zero retardation. Beats are more common in the $I_{AC}$ interferograms because absorption peaks in the DC spectrum may have a positive and a negative component in the AC spectrum. If one has a maximum at $\nu_1$ cm$^{-1}$ and the other at $\nu_2$ cm$^{-1}$, the waves will be in phase after a retardation of $1/(\nu_2 - \nu_1)$ cm. Because the separation of the peaks ($\nu_2 - \nu_1$) is much greater than the spectral resolution (2 cm$^{-1}$), the waves come in phase fairly often within the maximum retardation of the interferometer. Ideally, if the sum of all negative peak intensities and the sum of all positive intensities were equivalent, the center burst in the interferogram would equal zero.

The Fourier transformed interferograms decribed by equations (3.9)
Figure 10. Interferogram corresponding to an AC signal in polarization modulation experiment.
Figure 11. Interferogram corresponding to a DC signal in polarization modulation experiment.
and (3.10) can be ratioed, as in equation (3.4), yielding

\[
\frac{\text{FT}[V_{AC}(\omega)\Delta]}{\text{FT}[V_{DC}(\omega)\Delta]} = \exp[-(2V\hat{\omega})T](1.1513)\Delta A
\]  

(3.11)

This equation shows the direct proportionality of the absorption difference to the ratio of AC and DC spectra. A way to obtain this measurement experimentally is described below.

The arrangement of optical elements in the beam path is illustrated in figure 12. The photoelastic modulator is capable of a sine-wave modulation of the polarization at 74 kHz. A linearly polarized light incident on the modulator will emerge elliptically polarized. Circularly polarized light and linearly polarized light are actually two extreme cases of elliptically polarized light, which can be isolated by tuning the lock-in frequency to \(2\omega_d\) or \(\omega_d\). It can be shown that when the plane polarization of an incoming radiation is placed at forty-five degrees to the principal axes of the modulator, the amplitude of the circularly polarized output is given by \(\sin\alpha_e\) and the linear component by \(\cos\alpha_e\) (see appendix B). Here \(\alpha_e\) is the retardance introduced by the birefringent plate and is equivalent to

\[
\alpha_e = \frac{2\pi d}{\lambda}(n_x - n_y)
\]  

(3.12)

Because the photoelastic crystal is subjected to a sinusoidal strain,

\[
e = e_0 \sin \omega dt
\]  

(3.13)

the true retardance as a function of time is

\[
\alpha = \alpha_e \sin \omega dt
\]  

(3.14)

In case of modulation of linearly polarized light, the parallel and
Figure 12. The arrangement of optical elements in the beam path of the spectrometer in polarization modulation experiment.
perpendicular polarized beams are alternately passed to the detector. For a modulator driven at frequency $w_d$, the signal reaching the detector is therefore given by

$$I(t) = I_{DC} + I_{AC} \cos[\alpha \cdot \sin w_d t]$$  \hspace{1cm} (3.15)

where $I_{AC}$ and $I_{DC}$ are given by equations 3.3a and 3.3b. The cosine term can be expanded in terms of the even order spherical Bessel functions:

$$\cos[\alpha \cdot \sin w_d t] = J_0(\alpha) + \sum_{n=1}^\infty 2J_n(\alpha) \cos(2n \omega_d t)$$  \hspace{1cm} (3.16)

The zeroth order term, $J_0$, contributes to the DC component. The lowest frequency component is $2w_d$ when $n = 1$, and can be isolated by tuning the mixer to $2w_d$. The factor of two signifies that the polarization alternates between parallel and perpendicular states twice each modulation cycle, since $+180^\circ$ and $-180^\circ$ are equivalent. Hence after passing through the lock-in amplifier, the signal is

$$I(\tilde{\nu}, t) = I_{DC}(\tilde{\nu}) + I_{AC}(\tilde{\nu}) 2J_2[\alpha(\tilde{\nu})] \cos 2\pi w_d t$$  \hspace{1cm} (3.17)

The measured ratio of the Fourier transformed AC and DC interferograms is equal to

$$\frac{\text{FT}[V_{AC}(\tilde{\nu})]}{\text{FT}[V_{DC}(\tilde{\nu})]} = 2J_2[\alpha(\tilde{\nu})] \exp[-(2\tilde{\nu})^\tau] 1.1513 \Delta A(\tilde{\nu})$$  \hspace{1cm} (3.18)

where $\Delta A(\tilde{\nu})$ is $A_\perp(\tilde{\nu}) - A_\parallel(\tilde{\nu})$. Therefore, in order to determine the absolute value of $\Delta A(\tilde{\nu})$, the ratio first has to be divided by $2J_2[\alpha(\tilde{\nu})] \exp[-(2\tilde{\nu})^\tau] 1.1513$. This quantity can be estimated from calibration spectra.
Calibration

Because the birefringence of the modulator is chromatic, only one wavenumber has the retardance which varies from $+180^\circ$ to $-180^\circ$. The amplitude of oscillating retardance, $\alpha_0$, at other wavenumbers is given by equation 3.12. The experimental modulation efficiency, $n$, is given by

$$n_{\text{exp}} = 2J_2[\alpha_0(\tilde{\nu})]$$

(3.19)

Its wavenumber dependence can be measured by placing the modulator between crossed polarizers. This efficiency is equal to the ratio of $I_{AC}$ to $I_{DC}$ where the AC component of the single beam spectrum is given by

$$I_{AC}^* = I_p J_2[\alpha_0(\tilde{\nu})]$$

(3.20)

and the DC component of the single beam spectrum is given by

$$I_{DC}^* = I_{DC}(\tilde{\nu}) - J_0[\alpha_0(\tilde{\nu})] I_{AC}(\tilde{\nu})$$

(3.21a)

$$I_{DC}^* = 0.50 I_p(\tilde{\nu})[1 - J_0[\alpha_0(\tilde{\nu})]]$$

(3.21b)

(see appendix C for derivation)

The theoretical efficiency hence equals

$$n_{\text{cal}} = \frac{2J_2[\alpha_0(\tilde{\nu})]}{1 - J_0[\alpha_0(\tilde{\nu})]}$$

(3.22)

The calculated and experimentally obtained efficiencies are shown in figures 13a and 13b. For each curve, the retardation at wavenumber $\tilde{\nu}$ is calculated by $\alpha(\tilde{\nu}) = \pi \tilde{\nu} / \tilde{\nu}_\pi$. Here $\tilde{\nu}_\pi$ corresponds to the wavenumber at which the modulation has been set to (half-wave). As has been previously pointed out (71,72), there is a good agreement between these curves for the case where $J_2$ is large and the term $1/(1 - J_0)$ is small, namely at low retardation values. The factor $(1 - J_0)$ modifies the time-independent function of light passing through the crossed polarizers,
Figure 13a. Experimental results of wavenumber dependence of modulation efficiency for half-wave retardation when $\tilde{R}$ is set to 1.0 $\mu$m(a), 3.0 $\mu$m(b), 5.0 $\mu$m(c), and 7.0 $\mu$m(d).
Figure 13b. Theoretical results of wavenumber dependence of modulation efficiency for half-wave retardation when $\nu_\pi$ is set to 1.0 $\mu$m(a), 3.0 $\mu$m(b), 5.0 $\mu$m(c), and 7.0 $\mu$m(d).
At large retardation values, the factor $(1 - J_0)$ is small and therefore other sources contributing to $I_{DC}$ will dominate this term. The primary source is the additional light passing through the crossed polarizers because their polarization efficiency is less than 100%. Therefore at large retardation values, the experimental efficiency, $n_{exp}$, is lower than the calculated efficiency, $n_{calc}$. As can be seen in equation 3.21a, for samples with very small dichroism, $I_{AC} \ll I_{DC}$ and the $J_0(\tilde{v})$ term does not become important. Hence $I_{DC}$ can be approximated by setting both polarizers mutually parallel and turning off the modulator.

Experimental

The photoelastic modulator, Hinds International series II, is made with a ZnSe photoelastic crystal. This element can produce half wave retardance between 20,000 to 1200 (cm$^{-1}$) wavenumbers. The transmittance range of the crystal is from 20,000 to 505 cm$^{-1}$. Although the octagonal optical element has a 45 mm diameter between opposing edges, the actual useful aperture has a diameter of 30 mm (104). In addition the samples used generally have dimensions of 4.0 cm x 1.0 cm. A mask was therefore used to isolate a 150 mm x 100 mm area to insure a uniform retardance of the infrared beam. The oscillating frequency of the modulator is 74 kHz.

A control unit attached to the photoelastic crystal allows the modulation amplitude (wavelength of half-wave retardation) to be set to the desired value. The practical working range is from 0 to 740 nm. The control unit also provides the output for a reference signal either at $w_d$ or $2w_d$. 
As shown in figure 12, the optical axes of the photoelastic crystal form a 45° angle with the reference coordinate axes. In general, a quad diamond polarizer set at 45° to the reference axes was used to insure that equal intensities of parallel and perpendicular polarizations reach the modulator. However, the beam can also be balanced with a KBr plate by removing the sample and adjusting the angle of the KBr plate until the AC signal is minimized (66,67). This procedure not only diminishes the intensity losses, but also allows the gain on the lock-in amplifier to be increased, thus reducing the dynamic range. In this way the experiment is not digitization-noise limited. In a case where a polarizer was required after the modulator, a Perkin-Elmer wire grid polarizer was directly mounted on the modulator head.

The lock-in amplifier used was a Princeton Applied Research model 124A, which has a specified frequency response up to 200 kHz. A model 116 preamplifier was used in the direct input mode and the input high pass filter was set to 50 kHz. In a case of a strong signal, it was necessary to place a 1/20 attenuator in front of the amplifier which has a 1.6 Volt clipping level. The reference phase was adjusted by turning it initially to 90° by adjusting the fine tuning knob until the signal was zeroed. Subsequently, the phase was flipped back to 0 or 180° thus obtaining the maximum possible signal.

Figure 14 shows the schematics of the signal processing. The signal from the detector can be either sampled at port labeled detector 1, corresponding to I_{DC}, or detector 2, corresponding to I_{AC}. In the latter case the detector signal is fed into the lock-in input from
Figure 14. Schematics of the modified signal detection and processing path in the modulation experiment.
Figure 15a. Absorption difference spectrum of PBT as obtained by the modulation technique.
Figure 15b. Absorption difference spectrum of PBT as obtained by the subtraction of parallel and perpendicularly polarized spectra.
detector 1 and the lock-in output is fed into the detector 2 input on the beam-path control board. The signals of both $I_{AC}$ and $I_{DC}$ are subjected to the band pass filters of the FT-IR.

The $I_{AC}$ interferogram is Fourier transformed and processed in the same manner as a regular interferogram, with the exception that the phase correction is done with respect to a chosen peak position (PEK). This is because the signal at the point of zero retardation need not be necessarily a maximum and therefore, has to be found by inspection. In addition it is always desirable to have a slight positive offset in the difference spectrum, otherwise negative intensities associated with the spectrum of the sample occur. When these peaks are phase corrected, they will be incorrectly inverted, because normal phase correction routines assume that there are no negative intensities (63,66). The effect of the baseline shift, log(x), on the differential measurement can be described as (71),

$$I_{AC}/I_{DC} = \tanh \left[ 0.50 \ln 10 \left( (A_\parallel - A_\perp) + \log(x) \right) \right]$$

(3.23)

Therefore as long as $(A_\parallel - A_\perp) \leq \log(x)$, the peaks will be properly phase corrected.

Difference spectra for a highly oriented PBT film obtained by modulation and by direct subtraction are shown in figures 15a and 15b, respectively. While the position and relative intensities of the peaks match upon comparison of the two spectra, the polarity of the peaks is inverted in the lower frequency half of the spectra and near 3000 wave-numbers. The reason for this, is that the value $\text{FT}(I_{AC})/\text{FT}(I_{DC})$ includes the efficiency factor which falls negative in these particular frequency
Figure 16a. Measured calibration spectra at $\tilde{\nu}_r = 700$ nm in modulation experiment.
Figure 16b. Calculated calibration spectrum at $\tilde{\nu}_m = 700$ nm in a modulation experiment.
regions when $\tilde{\nu}_r = 700$ nm. This can be seen upon the comparison of the calculated and measured efficiencies shown in figures 16a and 16b.

Results and Discussion

Using polarization modulation, we have examined the orientation behavior of isotropic poly(butylene terephthalate) (PBT) copolymer films strained by 15 to 18 percent. The rate of deformation was 1% strain a minute and the half-wave retardation wavelength was set to 500 nm. The copolymers have a poly(tetramethylene oxide) soft segment and a PBT hard segment, whose molar fraction is used to code the particular sample, i.e. H88, H93, and H96. A summary of the copolymer characteristics used in these experiments is in Table I. A more detailed description of this material can be found in Chapter 3.

The integrated 2940 cm$^{-1}$ band of the C-H stretching vibration was used to follow the orientation of the soft segments, while the 1716 cm$^{-1}$ band of the C=O vibration was used to monitor the hard segment orientation. The orientation function was capable of being measured down to 1.0 x 10$^{-5}$. The results are presented in figures 17 through 18.

As can be seen by the behavior of the carbonyl group, the hard segments orient slowly in the beginning, especially in the case of a sample with higher hard segment content. The orientation is also quite reversible. It is difficult to assess the actual orientation of the crystalline chains based on the behavior of $F_{C=O}$, due to the low content of C=O units in the crystalline phase. However, the orientation of the
Figure 17a. Orientation function (based on CH₂ dichroism) as a function of strain for sample H96.
Figure 17b. Orientation function (based on CH$_2$ dichroism) as a function of strain for sample H93.
Figure 18a. Orientation function (based on C=O dichroism) as a function of strain for sample H96.
Figure 18b. Orientation function (based on C=O dichroism) as a function of strain for sample H93.
Figure 18c. Orientation function (based on C=O dicroism) as a function of strain for sample H88.
amorphous chains, represented by the CH$_2$ groups is quite clear. As shown in figure 17, the magnitude of the amorphous chain orientation increases as the percent crystallinity increases. The higher amorphous chain orientation may reflect the decrease in the average length of the amorphous segments between entanglement points or crystalline junctions. In addition, one can assume that no appreciable deformation of the crystalline junctions occurs, because the transformation of α-form to β-form crystalline units is below 5%. This phenomenon, more detailed in subsequent chapters, reflects the structural elongation of the crystalline chains. The transformation behavior of all three isotropic films deformed to 15% strain as a function of stress is shown in figure 19. Hence, it is reasonable to assume that at small strains, the isotropic film deforms mainly as a result of the orientation and elongation of the amorphous chains. If this is indeed true, then it should be possible to consider this deformation as a network.

The orientation function of a Gaussian amorphous chain having N number of statistical segments is given in terms of the draw ratio, λ, as

$$ F = \frac{1}{5N} (\lambda^2 - \lambda^{-1}) $$

(3.24)

This is an equation for crosslinked network, derived assuming a Gaussian distribution of N freely jointed statistical segments between successive crosslink points (95). On deformation the end-to-end vectors of the segments undergo an affine transformation. However, in real networks, the chains are neither freely jointed, nor do they transform affinely. Deviations of measurements of segmented orientation from predictions of
Figure 19a. Transformation behavior; $x_\alpha$ (in percent) as a function of strain for sample H96.
Figure 19b. Transformation behavior; \( x_\alpha \) (in percent) as a function of strain for sample H93.
Figure 19c. Transformation behavior; $x_\alpha$ (in percent) as a function of strain for sample H88.
equation 3.24 are significant, especially at higher draw ratios (93,97,102,105-109). Theoretical improvements of this relationship have been formulated in two ways. One way was to consider non-Gaussian chains (93,102,105,107,110) which introduced higher order terms of N into the relationship, namely,

\[ F = \langle P_2(\cos \phi) \rangle = \frac{1}{5N}(\lambda^2 - 1/\lambda) + \frac{36}{875N^2} \times (\lambda^4 + \lambda^3 - 4/3\lambda^2) \]

\[ + \frac{108}{6125N^2} \times (\lambda^6 + 3\lambda^3/5 - 8/5\lambda^3) \]

(3.25)

For long chains, however, the higher order terms are insignificant and the equation reduces back to (3.24). In case of separated rodlike crystals or micelles surrounded by an amorphous medium, Kratky (111) developed an ideal model for an axially symmetric deformation. As discussed elsewhere (85), deviations from this model are expected if the amorphous domains are viscoelastic or too soft to support the orientation. Still another case considered local intermolecular orientational correlation of segments (106,112,113). These interactions have been shown to be significant experimentally; large decrease of orientation (114) and birefringence (113) in networks has been observed upon dilation with isotropic solvents. Since we are only concerned with very small strains, for simplicity sake, our results are analyzed in terms of the ideal network model.

The orientation function of the CH\textsubscript{2} group was analyzed in terms of equation 3.24. As expected, the number of statistical segments between crosslinks increased with percent crystallinity. Using a least square fit, the value of N was found to be 50 and 150 for the H96 and H93
copolymers respectively. The amorphous orientation function of the H88 copolymer was not detected, suggesting that the value of N was indeed very large. This seems reasonable in view of the fact that H88 copolymer has the lowest percent crystallinity. The fact that the N values were large is consistent with the assumption of an ideal network. It is difficult to estimate N theoretically because at the moment there are no theories available which could relate this value to the chemical structure of the chain, or even the morphology. Hence, only comparison with other experimental results is possible.

The number of equivalent random links, N, was determined experimentally in the case of poly(ethylene terephthalate) (115) drawn from \( \lambda = 1 \) to 6. The second and fourth moments of the orientation distribution, obtained by Raman and fluorescence methods, were compared with theoretical predictions of Roe and Krigbaum (110) and Nobbs and Bower (107). The calculated N value was between 5 to 6 random links. It seems reasonable that the calculated N values for the copolymer films are larger than those predicted for PET. The terephthalate groups in the PET chain render it much more stiffer than the CH₂ repeat units in the soft segment of the copolymer. Hence, the chain in the poly(tetramethylene oxide) soft segment is capable of a greater number of conformations per particular length. It would be interesting to actually compare the development of orientation of the individual conformations along the lines proposed by Flory and Abe (94) in the PET and PTMO polymers.

Similar orientation experiments on the copolymer series were attempted with the usual dichroic measurements, however, no changes in
the dichroic ratio were detected. This suggests, that the modulation technique is indeed superior to the common dichroic measurement, especially when measuring very small orientations.

Conclusions

Difference spectra obtained by separate measurements of parallel and perpendicular polarizations passing through a sample have been compared with a direct differential measurement using polarization modulation spectroscopy. This comparison suggested that the noise in modulated spectra is on the same order of magnitude, if not lower, than the noise found in regular subtracted spectra in the case of highly oriented films. On the other hand, small orientation changes measured in slightly deformed isotropic films by the modulation technique could not be detected by simple subtraction or ratio of parallel and perpendicular polarized spectra. These changes in the orientation function were measured with $1 \times 10^{-5}$ precision. Further advantages of the modulation technique include the convenience and precision of a direct measurement, rather than two separate measurements. In the case of continuously deforming materials there is also the advantage of increased time resolution.

The modulation technique was applied to the orientation study of strained copolymer films having a poly(butylene terephthalate) hard segment and a poly(tetramethylene oxide) soft segment. Results indicated that the average length of the amorphous segments decreased as the mole fraction of the hard segments increased. Based on the analysis of CH$_2$
and C=O orientations, as well as the transformation behavior of the crystalline phase, it was concluded that the deformation of the copolymer structure at small strains could be modeled as that of an ideal network. This means that the macroscopic elongation of the sample was primarily achieved by the orientation change in the soft and amorphous hard segments.
CHAPTER IV.
THE PBT α ↔ β CRYSTALLINE PHASE TRANSITION

Introduction

The stress-strain behavior of poly(butylene terephthalate) is a result of a combined response of crystalline and amorphous regions. For example, the observed stress hysteresis is believed to arise from two different deformation modes. One mode is due to viscoelastic response of the amorphous segments and the other mode is the time-independent stress-induced crystalline phase transition. This time-independency is assumed because, the transformation of crystals follows an applied strain function accurately with a time resolution of 125 msec (33). A similar mechanism controls the deformation in the copolymers of PBT and poly(-tetramethylene oxide). The reversible nature of the phase transition and its ability to absorb stress is partly responsible for the desired properties, such as resilience, dimensional stability and toughness exhibited both by the PBT homopolymer and its copolymers. The significant factors which control the character of the transition are therefore of practical as well as of fundamental interest. The size of the crystalline domains, for example, or the perfection of the crystalline structure may influence the character of the transformation. This would be especially true if intra- and intermolecular interactions control the microscopic mechanism of the crystalline transition. In order to examine these variables, a means of achieving a well characterized crystalline structure
and variable crystalline size is necessary. A way to obtain these conditions will be discussed. Therefore, included in this section is a brief review of the morphological studies conducted on the PBT homopolymer and its copolymer with poly(tetramethylene oxide) when processed or crystallized under different conditions.

Due to the difference in unit cell dimensions of the two crystalline forms, wide angle x-ray reflections characteristic of either crystalline structure have been assigned (18-27). In fact, changing x-ray data have been used to assess the degree of transformation as function of the applied stress (25,26,28). Since the x-ray technique is only sensitive to long range order or disorder, isolated crystalline forms cannot be detected. In addition, the long exposure time necessary to obtain a diffraction pattern make it inconvenient to conduct experiments where many data points are required. Simultaneous spectroscopic and mechanical measurements, on the other hand, offer an alternative means to correlate microstructural changes with macroscopic stress-train results directly. Infrared spectroscopy can selectively identify conformational differences such as those characteristic of the two crystalline forms (29-33). The high sensitivity of this technique permits the detection of isolated and conformationally different units at all levels of applied stress.

Besides observing the effects of crystalline size and coherence on the transformation process, it is desirable to compare its behavior with theoretical predictions (to be discussed in Chapter V). For this reason, deformation experiments need to be conducted as a function of temperature, which is an important independent variable in the theoretical
relationships. Hence, the influence of the temperature on the infrared spectra must be decoupled from the effect temperature has on the transformation behavior. The results of infrared-temperature studies, combined with wide angle x-ray temperature data and theoretical energy calculations show how this can be achieved.

Structure and Morphology

The structure and morphology of poly(butylene terephthalate) has been the subject of several investigations (4,5,18-27). Crystalline domains are believed to exist in the lamellar form where the short dimension coincides with the chain direction. The important parameters which determine the morphology are the degree of supercooling and whether the crystallization is carried out isothermally or by quenching, subsequent annealing or under shear-flow conditions. Spherulitic structure can generally be achieved by crystallizing isothermally at low degrees of supercooling, the size of the spherulite being dependent upon the temperature of crystallization. Quenching from the melt state does not produce an optically detectable superstructure, indicating a high concentration of nuclei (4). In addition, annealing the quenched samples (or prolonged times at room temperature) gives high crystallinities comparable to those obtained by direct crystallization from the melt. Despite the increased crystallinity, however, the films still remain transparent because the superstructure is so small, it cannot be detected by small-angle light scattering or polarizing microscopy (4).
Figure 20. The chemical structure of a copolymer with tetramethylene terephthalate hard segment and poly(tetramethylene) soft segment.
The same crystalline structure has been shown to exist in the copolymers of butylene terephthalate and poly(tetramethylene ether glycol) (6-15). These random copolyesters are made by melt-transesterification of terephthalic acid, 1,4-butanediol chain extender and α-hydroxy-hydroxy poly(oxytetramethylene), a low molecular weight polymer with MW = 1100. The chemical formula and the definition of soft and hard segment sequences are shown in figure 20. The lengths of the hard sequences follow a geometric distribution, with the average being determined by the molar composition of the sample, namely \( L = 1/(1 - x_h) \). This relationship has been derived from the copolymerization equation assuming equal reactivity ratios of the reactants (116,117). Currently, only NMR studies have provided an experimental verification for this model (118). The line widths of the \(^{13}\text{C}\) NMR, scalar-decoupled 29-ppm and the 73 ppm shifts depend linearly on the average hard block length. This observation has been interpreted in terms of restriction of the angular range over which the internal butylene units in the hard domains can reorient (118).

The early work on the structure, morphology and properties of these polyether-polyesters has been conducted by Cella (6). The morphological model he presented applies mainly to samples quenched from the melt and consists of interpenetrating crystalline domains which are lamellar in nature. The overall arrangement of the lamellar aggregates (i.e. spherulitic, dendritic, sheaf-like or shish-kebab-like) depends on the crystallization conditions (12) just as in the homopolymer. The crystalline phase is formed by a certain fraction of the hard ester sequences, and the amorphous matrix is constructed from the remaining ester segments.
which have mixed with the soft ether segments. This has been established by electron diffraction and WAXD studies which recognized that the crystalline regions were made up of pure 4GT segments, same as in the PBT homopolymer (6,8,16). Dynamic mechanical, SAXS and DSC results also confirm the two phase model (12,14,15). The copolymers have a single glass transition temperature, \(T_g\) which depends strongly on the composition and the sample history. The \(T_g\) has been shown to vary with the weight fraction of the non-crystalline hard segments in accordance with the Gordon-Taylor equation (15). The melting of the hard segment domains is observed near that of the hard segment homopolymer, but the temperature is depressed with increasing fraction of the soft segments. This indicates that the crystal size also decreases with decreasing hard segment fraction. In fact, a study of the crystallization behavior has shown that the lateral dimensions of the crystal are controlled by the number of 4GT sequences long enough to traverse the crystal (16,17). Since the lengths of these hard sequences are determined by the molar composition of the sample, the dimensions of the crystal are also controlled by the hard segment fraction.

Wide-angle x-ray diffraction studies have shown that PBT crystals have a triclinic unit cell, whose dimensions change with the application of uniaxial stress along the fiber axis. This stress-induced crystalline phase transformation is nearly reversible (25,26). Recently, various crystalline structures have been reported for PBT in both the relaxed and strained forms (18-24). In the case of the relaxed \(\alpha\)-form, the unit cell parameters reported do not differ significantly, however, there is some
Figure 21. The crystalline structure and unit cell dimensions of α form and β form crystals in poly(butylene terephthalate) (Ref. 27).
discrepancy in the unit cell parameters of the strained $\beta$-form. A critical discussion of the experimental and computational procedures leading to different results has been published (19). However, for our purposes, these discrepancies are not significant and we adapt the structure suggested by Desborough and Hall (19). The main differences between the crystalline $\alpha$ and $\beta$ forms lie in the conformations of the middle tetramethylene segment. In the $\alpha$-form, this conformation is (GTG') with bond rotation angles ($-92.5, -76, 180, 76, 92.5^\circ$) and for the $\beta$-form the methylenes are all-trans (TTT) with angles ($-155.2, 154.7, 180, -154.7, 155.2^\circ$) (19). The conformations of the two structures are illustrated in figure 21. Furthermore, the placement of the terephthalate residues differs in the $\alpha$ and $\beta$ unit cells. In the $\alpha$-form, the plane of the benzene rings is inclined approximately $19^\circ$ to the c-axis of the unit cell, whereas in the $\beta$-form, the plane of the benzene rings is nearly parallel to the c-axis. The placement of the terephthalate groups may indeed be instrumental in the reversibility of the transformation (22). While the stress serves as the driving force to overcome the potential barrier going from $\alpha$ to $\beta$ energy state, the favorable placement of the terephthalate groups in the $\alpha$-form is the driving force when going from $\beta$ to $\alpha$ state. The packing of the terephthalate groups in the $\alpha$-form serves to reduce the ester-ester interactions.

Experimental

Poly(butylene terephthalate), trade name Valox@ 310, with Mn 20,000 was obtained from the Plastics Division of General Electric Company. The
copolymers of poly(butylene terephthalate) with poly (tetramethylene oxide), were kindly supplied by Dr. Shih of the DuPont Company. Copolymers having hard segment molar fraction of 0.96, 0.93, 0.88 and 0.83 with an average molecular weight of the polyol of Mn•1100 were used in this study.

Samples were melt-pressed between two aluminum sheets coated with Teflon, then quenched in ice-water. Resulting films were oriented (draw ratio 3.5) by coextrusion using the split-billet technique (98). The temperature during coextrusion was set 130 degrees above the particular glass transition, Tg, of the sample. All films prepared this way were highly oriented and had a thickness of 20 µm - 50 µm. Strips of 0.5 cm x 2.5 cm were used in the deformation experiments. Percent crystallinity was determined by Differential Scanning Calorimetry (DSC) taking Hf = 28.7 kJ/mol (13). The hard segment molar fraction, xH, coextrusion temperature, Tco, glass transition Tg, melting temperature, Tm, calculated average hard segment length, L, and percent crystallinity, xC, and final orientation function as measured by the dichroism of the carbonyl group for each sample are summarized in Table I.

Wide angle x-ray diffraction patterns were obtained on a Statton camera with nickel filtered Cu Kα radiation. Film thickness of 1 mm was achieved by stacking several films oriented in the same direction. A PBT film (sample P4) was studied at 22, 50, 100, 150 and 200 °C. The film exposure time for all films in the temperature study was 3.5 hours, and all films were developed simultaneously.

Simultaneous infrared spectra and stress-strain measurements were
### TABLE I
Summary of Experimental Samples and Corresponding Parameters

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>( X_h )</th>
<th>L</th>
<th>( X_c(%) )</th>
<th>( T_{co}^* )</th>
<th>( T_g )</th>
<th>( T_m )</th>
<th>( F(C=0) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1</td>
<td></td>
<td></td>
<td>39.3</td>
<td>40</td>
<td>50</td>
<td>222</td>
<td>0.62</td>
</tr>
<tr>
<td>P2</td>
<td></td>
<td></td>
<td>39.2</td>
<td>80</td>
<td>50</td>
<td>222</td>
<td>0.60</td>
</tr>
<tr>
<td>P3</td>
<td></td>
<td></td>
<td>39.5</td>
<td>120</td>
<td>50</td>
<td>222</td>
<td>0.55</td>
</tr>
<tr>
<td>P4</td>
<td></td>
<td></td>
<td>40.2</td>
<td>160</td>
<td>50</td>
<td>222</td>
<td>0.49</td>
</tr>
<tr>
<td>COPOLYMER</td>
<td>0.96</td>
<td>23</td>
<td>34.4</td>
<td>120</td>
<td>-10</td>
<td>216</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.93</td>
<td>15</td>
<td>32.7</td>
<td>100</td>
<td>-30</td>
<td>211</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.88</td>
<td>8</td>
<td>24.9</td>
<td>75</td>
<td>-54</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.83</td>
<td>6</td>
<td>20.7</td>
<td>-</td>
<td>-60</td>
<td>194</td>
<td></td>
</tr>
</tbody>
</table>

* All temperatures are in °C
obtained on a Nicolet 7199 Fourier Transform Infrared Spectrometer employing a Nicolet model 7000 optical bench, all coupled with a hydraulic stretcher. The details of this particular equipment and its operation are described briefly in Appendix D. Deformation experiments were carried out at 1.5% strain per minute to a maximum strain of 30%, over two complete loading cycles. All spectra were collected at 4 cm\(^{-1}\) resolution.

Infrared spectra as a function of temperature were obtained with IBM model 32 Fourier transform infrared spectrometer. The film was placed in a heating cell built in our laboratory and spectra were obtained at temperatures ranging from 20 to 200 °C. All spectra were taken at a 2 cm\(^{-1}\) spectral resolution. Generally, 100 scans were signal averaged to obtain a high signal to noise ratio. The rocking region between 1000 and 900 wavenumbers was selected to follow any temperature-induced conformation changes. The multicomponent band contour was first self-deconvoluted in order to identify possible peaks and their positions which were later fitted by a least-squares routine. These techniques are described in Appendix E.

Discussion of Characterization Studies

In our goal to characterize this crystalline phase transition, we wish to define the microscopic mechanism whereby the crystalline structure experiences the applied force. Because the stress felt by an isotropic sample is multi-directional, an effort was made to orient all films, such that the molecular chains were parallel to the applied force. This
Figure 22a. DCS trace of a isotropic PBT film.
Figure 22b. DSC trace of a PBT film coextruded at 40 °C.

Figure 22c. DSC trace of a PBT film coextruded at 80 °C.
Figure 22d. DSC trace of a PBT film coextruded at 120 °C.
Figure 22e. DSC trace of a PBT film coextruded at 160 °C.
Figure 23a. DSC trace of an isotropic H1 poly(ether ester) film.

Figure 23b. DSC trace of a coextruded H1 poly(ether ester) film.
Figure 23c. DSC trace of an isotropic H2 poly(ether ester) film.

Figure 23d. DSC trace of a coextruded H2 poly(ether ester) film.
Figure 23e. DSC trace of an isotropic H3 poly(ether ester) film.

Figure 23f. DSC trace of a coextruded H3 poly(ether ester) film.
can be achieved by extruding the polymeric film through a die having a
diameter smaller than the width of the film. The high pressures and shear
near the die orient and partially shear the lamellae. A comparison of
the thermal properties of extruded and isotropic films has been made
using differential scanning calorimetry (DSC). These results are shown in
figures 22-23. In the case of PBT homopolymer, although the maximum
melting peak is not affected by coextrusion, the endotherm does become
appreciably more narrow. Apparently, this narrowness is independent of
the coextrusion temperature, which means that it is caused by the mecha-
nical processing rather than annealing. An interesting observation is
that a shoulder appearing at a temperature higher than the melting maxi-
mum in the isotropic sample disappears completely upon extrusion, as
shown in figure 22a-b. A similar effect is observed in the copolymer
series where the DSC traces contain several melting peaks, seen in figure
23a-f. The highest melting endotherm always diminishes, although it does
not disappear completely, after the sample has been coextruded. Because
the temperature of an endotherm is generally considered to be dependent
on the lamellar thickness (119), we postulate that the bimodal nature of
the endotherms is dependent on the crystalline superstructure. In parti-
cular, the higher temperature peak corresponds to regions where two
lamellae are intimately connected by tie molecules as illustrated in
figure 24. During extrusion the tie molecule bridges are broken by lamel-
lar shear at the entrance zone of the die, giving rise to single lamellae
with the lower narrower endotherm. This picture is consistent with one
deduced from SAXS studies of solid state extruded PBT copolymers
Figure 24  Two-dimensional morphological model illustrating the interconnectivity between lamellae before coextrusion.
Figure 25. Two-dimensional morphological model illustrating the oriented structure of coextruded poly(ester ether) films (Ref. 120).
(120,121) and is illustrated in figure 25. The structural features pointed out in the SAXS studies include: axial symmetry and long range structural periodicity along the extrusion direction, finite dimensions and random arrangement of domains in the direction normal to the extrusion. This model also takes into account the chain orientation in the crystalline domains, the direction, which also agrees with our infra-red dichroic results discussed below.

Orientation measurements were conducted on a copolymer of tetramethylene terephthalate and poly(tetramethylene oxide) with a hard segment molar fraction $x_h = 0.93$. In this particular case, the hard segment orientation has been followed by the dichroism of the $C=O$ absorbance (1716 cm$^{-1}$ band) and the amorphous orientation was estimated by the dichroism of $C-H$ absorbance (2940 cm$^{-1}$ band). The results were analyzed in terms of the uniaxial orientation function by using a transition momentum direction of $90^\circ$ for the $C-H$ vibration and $79^\circ$ for the $C=O$ vibration (90). Because the $C-H$ and $C=O$ functional groups are present in amorphous as well as crystalline domains, their relative concentration in both environments needs to be determined. These calculations are based on the known molar fraction of hard segment and the percent crystallinity of the sample film ($x_c = 32.7\%$). For the H2 copolymer, the percent of CH$_2$ groups in the amorphous phase was estimated at 85% and percent of $C=O$ groups in the hard segments at 93%. Only 30% of $C=O$ groups are present in the crystalline phase. The orientation of the hard segments was examined at two different temperatures. This behavior along with the mechanical response is depicted in figures 26 and 27. Starting from an isotropic
Figure 26a. Stress-strain behavior during the deformation of isotropic H₂ copolymer at T=22 °C.
Figure 26b. Dichroic ratio as a function of strain during the deformation of isotropic H2 copolymer at $T = 22^\circ C$. 
Figure 27a. Stress-strain behavior during the deformation of isotropic H2 copolymer at $T = 90 \, ^{\circ}\text{C}$. 
Figure 27b. Dichroic ratio as a function of strain during the deformation of isotropic H2 copolymer at $T = 90 \, ^\circ\text{C}$. 
film at room temperature, a rapid increase in the orientation is observed at the yield point. This steep slope persists up to approximately 180% strain, above which no further drastic rise in the orientation is observed. Uniaxial deformation of the copolymer at elevated temperature (T=90 °C) avoids the yield point in the mechanical stress-strain curve. Correspondingly, the orientation increases gradually with no apparent discontinuity up to 280% strain where it begins to level off.

The purpose of this study is to assess the degree and character of orientation under which the isotropic films are processed. Although in principle, uniaxial elongation obtained by drawing and by extrusion from a die are not the same, the degree of orientation at a particular extension ratio obtained by either technique is similar. For example, \( F=0.5 \) for a sample drawn at 90 °C to a draw ratio of 2.8 and \( F=0.43 \) for a coextruded sample to a draw ratio of 2.8. Since extrusion of the sample film was conducted at 100 °C, one would expect the molecular orientation to be homogeneous, similar to the one depicted in figure 27b. Had the orientation been more discontinuous, as the one shown in figure 26b, the crystalline regions would not have oriented simultaneously and some inhomogeneities could have occurred. Such inhomogeneities can be the source of stress localization when the sample is subsequently restrained. Preorientation at elevated temperatures, on the other hand, mobilizes the amorphous matrix which, in turn, facilitates even rotation of the crystals (52). The assumption of homogeneous stress distribution will be critical point in the theoretical interpretation of the experimental results concerning the crystalline phase transition.
In general, PBT homopolymer films which have been coextruded at lower temperatures possess a greater degree of orientation than those coextruded at higher temperatures. This observation is based on the measured orientation function calculated from the dichroic ratio of the carbonyl group, summarized in Table I. However, measurements of the orientation function of the crystals from wide angle x-ray diffraction data indicate that, on the contrary, films coextruded at higher temperatures contain more oriented crystalline domains (121). Because these films are of the homopolymer, the orientation function measured by infrared dichroism reflects the combined orientation of segments in different environments. Since over 60 percent of the carbonyl groups are in the amorphous regions, the decreasing orientation function with increasing coextrusion temperature probably results from the greater mobility and faster relaxation of the amorphous segments at elevated temperatures.

Spectroscopic study of the \( \alpha \rightarrow \beta \) crystalline phase transition

Introduction

In this study we shall examine the effect of crystalline size, perfection of the crystalline structure and temperature on the stress-induced \( \alpha \rightarrow \beta \) transformation. A quantitative analysis can be carried out only if the spectral changes are directly associated with the phase transition. It is therefore important, that the origins of the spectral peaks be well understood and that a direct relationship between the change in the number of \( \alpha \) units and the number of \( \beta \) units be established.
The infrared spectrum of a polymeric film may undergo several changes as the temperature is varied. For example, shifts in peak position to lower frequencies are observed when vibrational force constants are reduced due to the population of higher vibrational states in the case of lattice vibrations (122,123). Furthermore, peaks broaden and their integrated intensity may fall with increasing temperature as a result of anharmonic interactions between intramolecular and weak intermolecular vibrations (124). Increasing the temperature may also change the population distribution of vibrational modes associated with probable rotational isomers (125). Thus the intensity of low energy conformational modes will decrease, while those of higher energy conformations will increase. In certain cases, where temperature driven crystal-crystal phase transitions occur, conformational changes may accompany the appearance or disappearance of characteristic lattice modes. In the case of poly(butylene terephthalate) it is imperative that any temperature-induced structural changes be recognized and their contribution to the stress-induced transition be known.

Discussion of Results

The infrared spectra are well established for PBT (126-132). The $\alpha$ and $\beta$ crystalline phases differ in the conformation of the central tetramethylene group. The methylene rocking region (1000-900 cm$^{-1}$), shown in figure 28, as well as the methylene bending region (1495-1440 cm$^{-1}$), shown in figure 29, contain infrared bands associated with the vibra-
Figure 28. Infrared spectrum of PBT in the methylene rocking region.
Figure 29. Infrared spectrum of PBT in the methylene bending region.
Figure 30. Difference spectrum of PBT obtained by subtracting a spectrum of an undeformed film from a spectrum of a deformed film (strained by 15%).
tional modes observed only in the $\alpha$ or $\rho$ conformations. The methylene rocking region is particularly sensitive due to its coupling with skeletal vibrations. An infrared band found at 917 cm$^{-1}$ is characteristic of the GTG' conformation of the tetramethylene group present only in the PBT crystalline regions, as this absorbance band is absent from the spectrum of the melt (128). A 960 cm$^{-1}$ band is known to have contributions from the TTT conformation of the tetramethylene group found in the crystalline as well as amorphous regions of the PBT hard segment. The 917 cm$^{-1}$ and 960 cm$^{-1}$ bands arise primarily from a torsional mode about the C-O-C-C bond in either conformation (130, 132). Another absorption is found at 935 cm$^{-1}$ to 938 cm$^{-1}$ which has been associated with the CH$_2$ rocking vibration of the amorphous hard segments (127). In the copolymer, these uncrystallized hard segments are rejected to the crystal fold surface and the surrounding matrix. Consequently, they do not participate in the transformation process and as expected, the amorphous band (935-938 cm$^{-1}$) cancels during the subtraction of the spectra.

In our study the quantitative measurements of the relative changes in the $\alpha$ and $\rho$ contents were obtained by subtracting the first spectrum of the undeformed film from all the consecutive spectra obtained during the deformation. Figure 30 shows the resulting difference for one case of PBT at 15% strain. The areas above the baseline represent the increase of the chains in $\rho$ conformation, $\Delta \rho$, and below the line, the decrease of chains in the $\alpha$ conformation, $\Delta \alpha$. These integral areas are plotted against each other in figure 31. The plot of $\Delta \alpha$ and $\Delta \rho$ shows a linear relationship, suggesting that there is an equivalent conversion of one crystalline form
Figure 31. Relationship between the intensity decrease of 917 cm\(^{-1}\) band and intensity increase of 960 cm\(^{-1}\) band, during a two cycle deformation to 30% strain (PBT film). Values represent the integrated peak areas in (absorbance wavenumber) units.
into the other, with no possibility left for a third component. The results of x-ray diffraction experiments also support the idea of an equivalent conversion (25,26,28). Stress-induced crystallization can therefore be ruled out. The same conclusion has been reached by other investigators based on factor analysis of spectra collected during several deformation cycles (30).

Before subtraction, all spectral intensities have been scaled to the same thickness using an internal reference band. We have used the integrated structural absorbance of the C-H stretching region which decreased linearly with strain as shown in figure 32. The deformation was nearly uniaxial as suggested by the plot of A/A₀ vs. λ⁻¹/₂ in figure 33, where is the draw ratio. In order to facilitate comparison of α and β stress-induced changes between samples with different percent crystallinity, all Δα and Δβ values were reduced. This was accomplished by dividing by the highest expected change in α or β, namely Δα_max or Δβ_max. The value of Δα_max was obtained by integrating the resolved 917 cm⁻¹ band in the original undeformed spectrum. The value of Δβ_max was then extrapolated from the curve in figure 31. For the sake of clarity, the relative changes of α and β contents will be represented by the change in the β content only, as one is the negative of the other, i.e. x_α + x_β = x_c and -Δα = Δβ.

The hard segment orientation has been followed by the dichroism of the C=O absorbance (1716 cm⁻¹ band) and the amorphous orientation was estimated by the dichroism of the C-H absorbance (2940 cm⁻¹ band). Only the orientation behavior of the copolymer sample (H2) was examined. The
Figure 32. Change in the integrated structural absorbance of the C-H stretching region (3200 to 2800 cm\(^{-1}\)) as a function of strain.
Figure 33. Change in the reduced structural absorbance ($A/A_0$) of the C-H stretching vibration as plotted against $\lambda^{-1/2}$. ($A_0$ is the absorbance of an undeformed film).
Figure 34a. Orientation function as a function of strain (sample H2) calculated from the dichroism of 1716 cm⁻¹ band.
Figure 34b. Orientation function as a function of strain (sample H2) calculated from the dichroism of the 2940 cm\(^{-1}\) band.
percent of CH\textsubscript{2} groups in the amorphous phase was estimated at 85% with 53% of the CH\textsubscript{2} groups in the soft segments themselves. The percent of C=O groups in the hard segments was 93% with 30% of the C=O groups being actually in the crystalline phase.

Results shown in figure 34a-b, suggest that the hard segments do not orient further during the deformation to 30% strain. The amorphous chains, however, do improve their orientation to some extent. In addition, we observed that neither component shows hysteresis in segmental orientation as a function of strain. These results are important to the analysis of the $\alpha \rightarrow \beta$ transition, because they exclude the possibility of orientational effects on the transformation behavior. A more detailed discussion of the final assumptions is presented in Chapter V.

A typical response of the crystalline conversion over two deformation cycles is shown in figure 35. The transition is not completely recoverable in the first cycle since some residual crystals are present even at zero stress. However, the following cycles repeat the pattern outlined by the unloading and reloading curves. The same phenomenon is observed in the relationship between the $\beta$ fraction and strain shown in figure 36. A plastic deformation of the crystalline superstructure must cause an incomplete recoverability of the strain even when the $\beta$ fraction during unloading is extrapolated to zero. It is therefore important to separate the hysteresis caused by the plastic deformation from the hysteresis due to the $\alpha \rightarrow \beta$ crystalline transition. Since greater part of the plastic deformation takes place during the initial extension (34,129), all hysteresis measurements will be limited to the maximum
Figure 35. Fraction of \( \beta \) crystals \( (x_\beta) \) as a function of stress for two loading cycles of a PBT homopolymer film.
Figure 36. Fraction of $\rho$ crystals ($x_\rho$) as a function of strain for two loading cycles of sample H1.
stress width between the unloading and reloading curves. Figures 37a-d show the \( \beta \) fraction as a function of the applied stress for a series of molar concentrations of the hard segment \( (x_h) \) in the copolymer. Comparison of \( \beta \) fractions during initial deformation conditions indicates that the rate of crystalline transformation with stress is slower as the average crystallizable hard segment length increases. This suggests that \( \alpha \) crystallites with greater dimensions are initially more restricted to transform into \( \beta \) form, and do so only at higher stress values. However, once this transformation does begin, the rate of transformation becomes greater for larger crystals. Furthermore, the hysteresis between the unloading and the reloading curves decreases with decreasing \( x_h \), being nearly zero when \( x_h = 88\% \).

This decrease in hysteresis width is also found in a series of PBT samples coextruded at different temperatures, as shown in figure 38a-c. The x-ray diffraction patterns corresponding to these films indicate a variation in the perfection of the crystalline structure as shown in figure 39a-b. Samples coextruded at 160 °C have a well defined crystal structure, whereas those subjected to the same process at a lower temperature, 40 °C, possess some crystalline disorder and defects as indicated by the presence of several diffuse reflections and complete absence of other higher order reflections.

The width of the hysteresis cycle is quite sensitive to temperature. A series of deformation runs is shown in figure 40a-d. The characteristic values of the hysteresis loop widths at higher temperatures [32 MPA (295 °K), 21 MPA (320 °K), 14 MPA (335 °K)] are in good agreement with
Figure 37. Fraction of \( \beta \) crystals \((X_\beta)\) as a function of stress (second loading cycle shown only) for a series of hard segment molar concentrations,

a. \( X_h = 100\% \)
b. \( X_h = 96\% \)
c. \( X_h = 93\% \)
d. \( X_h = 88\% \)
Figure 38. The \( \beta \) fraction as a function of stress during the second loading cycle of PBT films coextruded at 40 \(^\circ\)C (■), 80 \(^\circ\)C (▲) and 160 \(^\circ\)C (●).
Figure 39. X-ray diffraction patterns of a PBT film coextruded at two different temperatures,

a. $T = 40 \, ^\circ\text{C}$
b. $T = 120 \, ^\circ\text{C}$
The $\beta$ fraction as a function of stress during two consecutive loading cycles of PBT film, for a series of temperatures,

a. $T = 22 \, ^\circ\text{C}$
b. $T = 45 \, ^\circ\text{C}$
c. $T = 80 \, ^\circ\text{C}$
d. $T = 140 \, ^\circ\text{C}$
similar data obtained by Brereton (28) from wide-angle x-ray diffraction, [37 MPA (300 °K), 24 MPA (330 °K)]. However at higher temperatures, although the trend is similar, some discrepancy between the spectroscopic and X-ray results is evident. Infrared measurements indicate a slower decrease of hysteresis values with temperature, [11.5 MPA (353 °K), 10 MPA (415 °K)], than do corresponding x-ray results [9 MPA (373 °K), 3 MPA (427 °K)]. The larger hysteresis values obtained from infrared measurements become especially apparent when one realizes that they have been measured between the unloading and reloading curves, whereas the x-ray hysteresis values have been measured between the first loading and unloading cycle. Because of the shorter measurement time needed, we obtained a much more complete set of data with our spectroscopic studies than the earlier x-ray results. Therefore we have a greater confidence in the present study.

Examination of the infrared spectra at various temperatures required the use of deconvolution and fitting techniques to analyze spectral changes. A self-deconvoluted spectrum obtained at room temperature along with the original spectrum is shown in figure 41. From these results, it is quite evident, that the amorphous band at 935 cm\(^{-1}\) really has two components. Other peaks on the higher frequency side of the spectrum become also apparent. Figure 42a-c shows the fitted band contour at room temperature and 200 °C. The intensities of six assigned bands have been calculated and normalized to the total intensity of the multicomponent contour. Tabulated results as a function of temperature are found in Table II. These results indicate that while certain modes increase in
Figure 41. Spectrum of a PBT film at room temperature in the methylene rocking region (a) Original spectrum (b) Self-deconvoluted spectrum.
Figure 42a. Spectrum of a PBT film with curve fitted peaks at $T = 25 \, ^\circ\text{C}$, unannealed.
Figure 42b. Spectrum of a PBT film with curve fitted peaks at $T = 25^\circ$C, annealed.
Figure 42c. Spectrum of a PBT film with curve fitted peaks at $T = 200 \, ^\circ\text{C}$. 
intensity, others tend to decrease. Since increasing the temperature of the polymer increases the number of internal degrees of freedom of the chain segment, it is possible that bands sensitive to other conformations appear. As an example, we point to the linear intensity decrease of the 916.4 cm\(^{-1}\) band associated with the \(\alpha\) conformation and a corresponding intensity increase of the 929 cm\(^{-1}\) band with rising temperature. These relative changes are plotted in figure 43. It is interesting to note that a calculated frequency of 923 cm\(^{-1}\) from normal coordinate analysis (130,132) falls between the two observed frequencies. Due to the proximity to the calculated band we postulated that both observed bands have the same gauche-trans-gauche conformation of the tetramethylene segment, but differ in the rotation about the O-C-C internal angle. Similar observation has been made in the case of bands sensitive to the \(\phi\) conformation. Calculated frequency, 963 cm\(^{-1}\) falls between the observed frequencies 955.7 cm\(^{-1}\) and 972.8 cm\(^{-1}\). In this case the 955.7 cm\(^{-1}\) band increases linearly with temperature, while the 972.8 cm\(^{-1}\) band intensity decreases. Again, if the difference arises from the higher rotation about the O-C-C angle, it is not surprising that the higher temperature bands lie closer to the amorphous peak. This would also explain the annealing behavior. Annealing the PBT film at 190 °C for 10 hours under vacuum, then cooling back to room temperature causes the intensity of the 916.4 cm\(^{-1}\) to increase and that of the 929 cm\(^{-1}\) band to decrease as shown in figure 42b. This suggests that the 929 cm\(^{-1}\) band corresponds to a less stable conformation. However, another evidence in support of a crystalline component in the 929 cm\(^{-1}\) band are the subtracted spectra of stressed and unstres-
## TABLE II.

Normalized Intensities of Deconvoluted Absorption Bands

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Normalized Intensities (in percent)</th>
<th>Infrared Absorption Band (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>916.4 929 938.5 955.7 963.5 972.8</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>19.7  6.2 33.3 13.4  7.3  9.0</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>19.5  6.9 33.1 13.5  7.3  8.9</td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>19.0  7.4 33.4 13.6  7.3  8.8</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>18.8  7.5 33.8 13.9  7.7  7.6</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>18.1  7.8 34.4 14.2  7.6  7.4</td>
<td></td>
</tr>
<tr>
<td>82</td>
<td>17.3  8.3 34.2 14.3  7.6  6.8</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>16.5  8.5 34.1 14.5  7.7  6.6</td>
<td></td>
</tr>
<tr>
<td>132</td>
<td>14.8  9.8 32.9 14.7  7.8  6.0</td>
<td></td>
</tr>
<tr>
<td>148</td>
<td>14.3 10.0 33.6 14.9  7.9  5.9</td>
<td></td>
</tr>
<tr>
<td>162</td>
<td>13.6 10.2 33.3 15.1  8.2  5.6</td>
<td></td>
</tr>
<tr>
<td>174</td>
<td>12.7 10.4 33.0 15.7  8.1  5.4</td>
<td></td>
</tr>
<tr>
<td>190</td>
<td>12.4 10.5 33.4 16.0  8.2  5.3</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>11.8 10.8 33.2 16.3  8.0  5.2</td>
<td></td>
</tr>
<tr>
<td>210</td>
<td>11.3 11.0 33.6 16.9  8.0  5.1</td>
<td></td>
</tr>
</tbody>
</table>
Figure 43. Integrated area of a deconvoluted peak as a function of temperature for the bands, (a) 916.4 cm$^{-1}$ and (b) 929.0 cm$^{-1}$.
sed films at 22 °C and 140 °C shown in figure 44. The net change below the zero line includes a much greater contribution from the 929 cm⁻¹ band at the higher temperature. This means that this particular conformation also participates in the stress-induced crystalline transition. The absorption difference located at 872 cm⁻¹ is due to the C-H out of plane vibration of the ring and is used as a reference in the comparison of the two spectra. (The 872 cm⁻¹ band is slightly shifted to higher frequency under stress). Furthermore, there is clearly no apparent change with temperature in the intensity of the amorphous 938.5 cm⁻¹ band.

The X-ray diffraction patterns at several different temperatures are depicted in figure 45. Although the overall intensity of the reflections drops at higher temperatures due to the change in the temperature factors, no other changes such as shifts in reflection position or appearance of new reflections are observed. This suggests, that the conformational transformation seen in the infrared data is not accompanied by strong alterations in the lattice dimensions. Rather, it is possible that the higher temperatures induce greater mobility of atoms about their equilibrium positions. The aspects of mobility have been investigated in solid state ²H and ¹³C NMR studies, conducted on a range of PBT copolymers and model compounds which have been selectively deuterated (118,133 − 135). Based on relaxation data and chemical shift anisotropy considerations, Jelinsky et.al. have concluded that the most favored motions are concentrated in the central methylene groups with no large scale reorientation of the O-CH₂ carbons, the motion of the terephthalate group being even slower in comparison. These measurements were conducted from
Figure 44a. Subtracted spectrum of an unstressed PBT film from a stressed PBT film collected at 22 °C.
Figure 44b. Subtracted spectrum of an unstressed PBT film from a stressed PBT film collected at 140 °C.
-89 °C to 22 °C. Because the ω and ρ characteristic conformation bands begin to show strong intensity changes especially above room temperature, one can postulate that the crankshaft-like motions of the central carbons (133-135) can stimulate an angular rotation about the O-CH₂ bond. This seems reasonable in view of the fact, that the 917 cm⁻¹ and 960 cm⁻¹ bands arise primarily from a torsional mode about the C-O-C-C bond in either conformation. However, not all segments need to be affected equally by temperature. The relative number of conformations with high and low energies is usually determined by the temperature according to Boltzmann's distribution. The idea that repeat segments whose tetramethylenes have a GTG' or TTT conformation can be in more than one energy state is plausible. One evidence is the presence of three energy minima for one GTG' conformation and three minima for one TTT conformation as seen on energy contour maps (27) reproduced in figure 46. These minima only differ in the choice of the internal rotational angle, \( \gamma_2 \), defined as the angle about the O-CH₂ bond.

Conclusion

Solid state extrusion of quenched PBT and copolymer films has produced well oriented, uniform samples with finite lamellar dimensions. This precedence was necessary to insure homogeneous stress distribution within the sample, and crystalline chains primarily parallel to the component of stress in the draw direction. Hard segment orientation results of so prepared films indicated little or no improvement in the
Figure 45. X-ray diffraction patterns of a PBT film collected at

a. $T = 22 \, ^\circ\text{C}$
b. $T = 50 \, ^\circ\text{C}$
c. $T = 100 \, ^\circ\text{C}$
d. $T = 150 \, ^\circ\text{C}$
e. $T = 200 \, ^\circ\text{C}$
Figure 46. Energy contour map of a PBT repeat unit (Ref. 20).
orientation upon further deformation, although some additional orientation of the soft segments became apparent.

The deformation behavior with stress is sigmoidal in shape and exhibits a hysteresis between the loading and unloading cycles. The width of this hysteresis can be reduced by increasing the temperature or by decreasing the perfection of the crystalline structure. Hysteresis widths obtained at various temperatures using infrared spectroscopy were compared with those measured by x-ray diffraction. The data are in good agreement except at higher temperatures, where, although the trend is the same, the infrared measurements indicate a slower decrease of the hysteresis values with temperature. This has been attributed to the sensitivity of infrared spectroscopy to isolated crystalline units and shorter measurement time between data points defining the hysteresis.

The rate of the transition is also affected by the size of the crystal. The crystallites with greater dimensions are initially more restricted to transform into the other form, only to give later a rise to a much steeper conversion slope.

Examination of spectra as a function of temperature indicates a presence of a conformational change, most likely an increased rotation about the O-CH₂ bond, which tends to raise the energy of the whole crystalline chain. In addition, x-ray results suggest that this conformational change is not accompanied by detectable alterations in the lattice dimensions. The particular intensity variations with temperature of bands believed to represent the high energy and low energy conformations imply a Boltzmann's relationship over a certain temperature range.
CHAPTER V.
THEORETICAL MODELS OF THE PBT PHASE TRANSITION

Introduction

In striving to explain the crystal-crystal phase transition in poly(butylene terephthalate), several theoretical models have been proposed \((20,28,73-76)\). The assumptions made in each case are critical in the final prediction of the transformation properties and will be discussed accordingly. In general, transitions can be characterized based on the behavior of the chemical potential with the thermodynamic driving force, such as temperature or stress. Familiar phase transitions, like melting and boiling are accompanied by changes of enthalpy and volume. The definition of these changes in terms of the gradient of the chemical potential is,

\[
\Delta V_m = \left( \frac{\partial \Delta \mu}{\partial P} \right)_T = \left[ \left( \frac{\partial \mu(p)}{\partial P} \right)_T - \left( \frac{\partial \mu(\alpha)}{\partial P} \right)_T \right] \tag{5.1}
\]

\[
\Delta H_m = T \Delta S_m \tag{5.2}
\]

\[
\Delta H_m = -T \left( \frac{\partial \Delta \mu}{\partial T} \right)_P = -T \left[ \left( \frac{\partial \mu(p)}{\partial T} \right)_P - \left( \frac{\partial \mu(\alpha)}{\partial T} \right)_P \right] \tag{5.3}
\]

Since the derivatives of \(\mu(p)\) and \(\mu(\alpha)\) differ, the changes are finite. The discontinuity in the chemical potential and infinity of its second derivative are the requirements of a first order phase transition. The physical explanation is that the heat (or stress) added to the system is used in driving the transition rather than raising the temperature (or
stress) of the system. Another type of transition, which is not first order, but whose second order derivative of the chemical potential approaches infinity is a cooperative transition. This transformation is typical of order-disorder transitions in alloys, the onset of ferromagnetism, the fluid-superfluid transitions in helium (136) and helix-coil transformation in polypeptides (137,138). Although the second derivative has a singularity at the transition point, it differs from a first order transition because instead of changing abruptly, the singularity is attained slowly. Thermodynamically, a cooperative transition is characterized by a continuous gradient of $\mu$, which means that there is no enthalpy or volume change at the transition point. In physical terms, this means that the system is already reorganizing itself long before the actual transition point. Using our experimental results, we shall compare the applicability of first order and cooperative transitions in their ability to predict the observed crystal-crystal transition in poly(butylene terephthalate). In addition, we shall discuss the nucleation-growth model which has been just recently proposed (75).

First Order Transition

The discussion of this model is based on the work of Tashiro et.al. (20). The primary assumption of a first-order transition is that the $\alpha \rightarrow \beta$ crystalline transformation is induced by tension and occurs at constant stress, $f^*$. On the macroscopic stress-strain curve, this would
correspond to the constant stress plateau observed in the strain range of about 4-15%. Furthermore, the actual elongation in this region is believed to arise from the increase of the unit cell dimensions in the c-axis direction. At the critical stress, $f^*$, the free energy of the $\alpha$ form, $G_\alpha$, becomes equal to $G_\beta$, as illustrated in figure 47. At this point the two crystalline forms coexist and the relative amount of $\alpha$ and $\beta$ depends linearly on strain. When $f$ increases beyond $f^*$, $G_\alpha$ becomes higher than $G_\beta$, so only the $\beta$ form exists. (It should also be clarified that Tashiro's free energy graph should indicate a general increase in the free energy with stress. This is because the thermodynamic relationship $dG = VdP - SdT + FdL$ holds in this case. Generally, in temperature driven transformations, the free energy decreases with temperature, however, for stress driven transformations, the opposite is true.) The amorphous phase supposedly deforms only below and above this constant stress region. Based on these assumptions, the relationship between the critical stress, temperature and entropy, enthalpy change caused by the transition are derived (20).

$$\frac{\Delta H}{A_\alpha \Delta L} = \frac{(f^*/T)}{(1/T)} p$$  \hspace{1cm} (5.4)

and

$$S = \frac{H - F^* \Delta L}{T}$$  \hspace{1cm} (5.5a)

where

$$F^* = f^* A_\alpha$$  \hspace{1cm} (5.5b)

From the temperature dependence of the critical stress, $f^*$, the values of $\Delta H$ and $\Delta S$ have been obtained, 5.10 kJ/(moles monomer unit) and 12.6 J/(K moles monomer unit) respectively. From these values, the free
Figure 47. Free energy of the $\alpha$ and $\beta$ forms as a function of stress and corresponding theoretical stress curve for the first order transition model (Ref. 20).
energy difference between the two forms was estimated at 0.32 kcal/(moles of monomer unit). Results based on conformational energy calculations, taking both intra and intermolecular interactions into consideration, estimate this free energy at 5.87 Kcal/(moles monomer unit) (27).

The first order transition model has several inconsistencies with the observed experimental data. Firstly, as it stands, equation (5.4) predicts that the $\alpha \leftrightarrow \rho$ transition should occur under free tension at a temperature of 150 °C. Based on the results of Tashiro (20) this is the extrapolated point of the $f^*/T$ vs. $1/T$ line to $f^*/T=0$, assuming that the $\Delta H$ and $\Delta S$ values remain constant over the entire temperature range. Clearly, this does not happen, as the structural changes have been monitored via x-ray diffraction and infrared spectroscopy up to the PBT melting point (220 °C), and no increase in the $\rho$ form has been observed. Furthermore, the assumption that the transition occurs only at some constant stress, $f^*$, is unsubstantiated. The shape of the deformation curve depends critically on the sample history, i.e., the crystallization conditions, processing, and annealing treatments. In fact, the plateau region can be made slanted or virtually removed with the proper coextrusion conditions (120,121), and the $\alpha \leftrightarrow \rho$ transformation can still be detected. Also, changes in the crystal structure have been observed throughout the deformation cycle of oriented specimens below and above 30% strain. Although one can argue that this observation may originate from the inhomogeneous stress distribution (when some regions in the polymer are highly stretched and some others are only weakly stretched), it is still very unlikely that highly preoriented films with long range
structural periodicities (120) would entertain such a wide distribution of stress values. Furthermore, as it stands, this model cannot account for the hysteresis seen in the \( \beta \) content with stress curves, (see figure 37). Based on these considerations, it must be concluded that the first-order transition model is not suitable to represent the behavior of the \( \alpha \rightarrow \beta \) crystalline transformation in PBT.

**Mean Field model**

Recognizing that the sigmoidal behavior of the \( \beta \) content fraction with applied stress is a characteristic of a cooperative transition gives a new perspective to the problem. The idea of cooperative behavior is an old concept in physics. It was first proposed in 1907 by Pierre Weiss to describe the paramagnetic-ferromagnetic phase transition (139). This theory assumes that the alignment of electron spins in a lattice lowers their energy, creating a "mean field" at each individual molecule. At low temperatures this mean field is sufficient to maintain order, but as the temperature is increased, the molecules having higher kinetic energy get more and more out of alignment. As the system becomes disordered, the average ordering field is diminished, and it becomes even easier for the system to become more disordered. The major assumption of this theory, is that the interaction between molecules is spacially independent, hence it does not lend itself well to systems with short range, local interactions. On the other hand, the Ising Model (140) assumes nearest-neighbor interactions only and in certain cases it has sufficiently described the
cooperative transitions in hydrogen bonded macromolecules (141). These are linear systems, existing in the \( \alpha \)-helix structure which is stabilized by intramolecular hydrogen bonds up to a certain critical temperature. Beyond this temperature, the molecule melts abruptly into a random coil structure. This phase transition phenomenon is possible only if the free energy change during the hydrogen bond formation in a given molecule depends strongly on the presence or absence of hydrogen bonds in the preceding monomers. The cohesion and finite compressibility of molecular crystals, on the other hand, is due to intermolecular attractive and repulsive forces, respectively, acting in three dimensions (142). The molecules in the crystal, therefore, assume equilibrium positions at which the attractive van der Waals forces are balanced by the repulsive forces.

In poly(butylene terephthalate), the transformation from the \( \alpha \)-phase to the \( \beta \)-phase proceeds with a net change in the unit cell dimensions, causing a disruption of the equilibrium molecular positions. Therefore, the long-range intermolecular forces are perturbed to a degree which depends on the relative content of \( \alpha \) and \( \beta \) crystalline units. Because of the three-dimensional nature of the interaction and long-range crystalline order, the mean field model is probably more applicable to this problem than the Ising model. (The three dimensional Ising model has not been solved so far (143).) The implicit assumptions of the mean-field theory, however, is that the tension is equal in all the chain segments of a crystallite (143). A simple version of this model was presented by Brereton et al. (28). The approach adopted the idea of a
local stress, $T_L$ which was dependent on the applied tensile stress and
the order parameter, $m$. In other words, the stress, defined as the force
acting on the cross-sectional area of the unit cell is defined as

$$T_L = T + \kappa m$$  \hspace{1cm} (5.6)

where

$$m = \left( \frac{x_\beta - x_\alpha}{x_\beta - x_\alpha} \right)$$  \hspace{1cm} (5.7)

and $\kappa$ is an adjustable parameter which describes the strength of the
cooperative interactions. The $x_\alpha, x_\beta$ is the mole fraction of the sample
in the crumpled or extended crystalline form, respectively. Based on
these considerations, the free energies of the two forms were derived
and substituted in the Boltzmann's equation to obtain the ratio of $\alpha$ and
$\beta$ forms in the crystalline domains. The final equation describing the
relationship between the order parameter and the applied stress is

$$m = \tanh \left[ \frac{(mkV - G^0 + V \mu)}{kT} \right]$$  \hspace{1cm} (5.8)

where $V = \left( V_\alpha + V_\beta \right)/2$, and $V_\alpha, V_\beta$ are parameters with the dimensions of volume. Also $G^0 = \left( G^0_\alpha - G^0_\beta \right)/2$, and $G_\alpha, G_\beta$ are the $\alpha, \beta$ free
energies (per monomer unit) at zero stress. The "$k_B$" is the Boltzmann's
constant. Although the relationship derived in equation 5.8 can predict
the existence of the hysteresis as well as its trend with the tempera-
ture, the presence of adjustable parameters with no physical meaning
lend the theory more or less empirical. Based on a fit with wide-angle x-
ray diffraction results, the value of $G^0$ was found to vary from 0.46
Kcal/mole at -24 °C to 0.078 Kcal/mole at 154 °C. Not only are these
values an order of magnitude lower than predicted by the energy calcu-
lations (27), but the fact that $G_0$ varies with temperature is incon-
sistent with the definition of Boltzmann's distribution. According to this definition (136), the ratio of the number of conformations in the states with energies $E_i$ and $E_j$ at a temperature $T$ is given by

$$\frac{N_i}{N_j} = \exp[-(E_i - E_j)/RT]$$

(5.9)

Here $E_i$ and $E_j$ are discrete energy levels independent of temperature. Likewise, in the case of PBT crystalline forms, $E_\kappa$ and $E_\beta$ should correspond to the two different conformational states that are only structure dependent. (The free energies may change with temperature, but then they cannot be substituted into a Boltzmann's relationship.)

A more realistic approach was taken by Datye and Taylor (76) who have applied the mean field approximation to a model specifically considering the internal forces which propagate order from one unit to another. This model assumes that significant intermolecular interactions occur only between the terephthalate residues belonging to neighboring chains. These Van der Waals interactions which constrain the benzene rings to remain in registry are modeled as Hookean springs. Thus dimensional changes in the lattice, prompted by the crystalline transition will be hindered, especially when the transformation occurs from species present in large concentrations to those present in very low concentrations. However, as presented, Taylor's model does not take into consideration the influence of crystalline size, which our experimental results show to be significant. In particular, the effect of the hard segment length needs to be incorporated into the model, because the intramolecular interactions along the chain should be of considerable importance. These arise from the different placement of the terephthalate residues in the $\kappa$ and $\beta$
crystalline unit cells. In the α form, the plane of the benzene rings is inclined approximately 19° to the c-axis of the unit cell, whereas in the ρ form, the plane of the benzene rings is nearly parallel to the c-axis. When unlike tetramethylene conformations share the same benzene ring, their energies will be perturbed owing to the undefined nature of the benzene ring placement. A schematic representation of this concept is depicted in figure 48, where a unit having an all-trans conformation of the tetramethyles connects to terephthalate groups having two different inclinations of the benzene planes.

Considering only the repeat units along one chain, one can write the conformational energy of a chain, n units long, as the sum of the energies of the separate units and the energy of interaction between these units, i.e.,

\[
E(\text{chain}) = \sum_{k=1}^{n} E(k) + E(1,2,...n) \quad (5.10)
\]

where

\[
E(1,2,...n) = \frac{1}{2!} \sum_{x \neq y} E(x,y) \quad (5.11)
\]

This term is incorporated into the Hamiltonian for the total system having N as the total number of units in the lattice, where m is the number of chains in a cross-sectional area, and n is the number of units in the chain defining the crystal thickness. The value K is the inter-chain interaction force constant and F is the force along the chain. One obtains
Figure 48. A schematic representation of a crystalline chain where two tetramethylene segments in α and β conformations share the same terephthalate group.
\[ H = -Kb^2 \sum_{ijk}^N \left[ (\mathbf{v}_{ijk} \mathbf{v}_{i+1,jk}) + (\mathbf{v}_{ijk} \mathbf{v}_{i,j+1,k}) \right] \]

\[ + \ e \sum_{ijk}^N \mathbf{v}_{ijk} \]

\[ + \sum_{ij}^m \frac{1}{2!} q \sum_{x=1}^n \sum_{y=1}^n 1 - \left( \mathbf{v}_{kx} + \mathbf{v}_{ky} \right)/2 - Fb \sum_{ijk}^N \mathbf{v}_{ijk} \]

\[ + \text{constant} \]  \hspace{1cm} (5.12)

where \( b = 1/2 \ (r_\rho - r_\alpha) \), the \( r_\rho \) or \( r_\alpha \) being the lengths of the tetramethylene in either of the two conformations with corresponding energies \( E_\rho \) and \( E_\alpha \) and \( e = 1/2(E_\rho - E_\alpha) \). Furthermore, \( E(k_x, k_y) = q \) if \( r_{kx} \neq r_{ky} \) and 0 if \( r_{kx} = r_{ky} \). Here \( q \) is the intramolecular interaction energy per repeat unit. The value \( \mathbf{v}_{ijk} \) will be 1 or -1 according to whether the repeat unit at position \( ijk \) assumes a \( \rho \) or an \( \alpha \) conformation, respectively. The absolute sign in the third term is necessary because the energy of the chain is the lowest at either conversion extreme, i.e. all \( \alpha \) or all \( \rho \) units. With mean-field approximation, the Hamiltonian in equation 5.12 becomes

\[ H_{MF} = -2NKB^2 <\mathbf{v}>^2 + Ne<\mathbf{v}> - \left[ N(n-1)^2/2(n+1)n \right] Q <\mathbf{v}> \]

\[ - NbF <\mathbf{v}> + \text{constant} \]  \hspace{1cm} (5.13)

where \( Q \) is the mean value of \( q \). The entropy of the system is given by (97),

\[ S = -Nk_b[p \ln p + (1-p)\ln(1-p)] \]

\[ \hspace{3cm} (5.14) \]

where \( p = ( <\mathbf{v}> + 1)/2 \). Minimization of the free energy (\( H_{MF} - TS \)) with respect to \( p \) and rearranging, yields an explicit solution for the applied
force;

for $<\sigma> > 0$ \[ F = \frac{1}{b}[k_b T \tanh(<\sigma>) - 4Kb^2<\sigma>] + \frac{e}{b} - \left[\frac{(n-1)^2}{n(n+1)}\right]Q/2b \] (5.15)

for $<\sigma> < 0$ \[ F = \frac{1}{b}[k_b T \tanh(<\sigma>) - 4Kb^2<\sigma>] + \frac{e}{b} + \left[\frac{(n-1)^2}{n(n+1)}\right]Q/2b \] (5.16)

The existence of multiple solutions for $F$ as a function of $<\sigma>$ indicates the presence of metastable states and leads to a hysteresis in the stress vs. $<\sigma>$ behavior. In particular, in the case of three $<\sigma>$ solutions for one value of $F$, the two extreme $<\sigma>$ values define the hysteresis while the central $<\sigma>$ value defines an unstable state corresponding to the free energy maximum separating the two free energy minima. The width of the hysteresis therefore varies as

\[ F = \frac{1}{b}[8Kb^2<\sigma> - 2k_b T \tanh(<\sigma>) + \left[\frac{(n-1)^2}{n(n+1)}\right]Q] \] (5.17)

Figure 49 shows the effect temperature and the incorporation of $Q$ have on the width of the hysteresis, $\Delta F$. As is evident from the equations, the sensitivity of $\Delta F$ to $Q$ will increase as the crystallizable chain length, $n$, increases. In addition, as long as $Q$ has some value, the hysteresis will be present regardless of the temperature.

Nucleation Growth model

Finally, a recently proposed nucleation growth model (75) will be critiqued in its application to the $\alpha \rightleftharpoons \gamma$ crystalline transition. The
Figure 49. The \( \phi \) fraction as a function of stress as predicted by the modified mean field theory.

a. \( T = 300 \, ^\circ K, Q = 0 \) Kcal/mole  
b. \( T = 300 \, ^\circ K, Q = 0.40 \) Kcal/mole  
c. \( T = 400 \, ^\circ K, Q = 0 \) Kcal/mole  
d. \( T = 400 \, ^\circ K, Q = 0.40 \) Kcal/mole
Figure 49a.
Figure 49b.
Figure 49d.
primary motivation for its introduction consisted of several observations which the original Taylor model could not predict, and which can be indeed explained, as we shall show, by the modified version of Taylor's model. These observations include the fact that the critical stress for the onset of the transition varies with temperature and that all hysteresis does not vanish sharply at some critical temperature $T_c$.

The principal assumption of the nucleation theory is that a nucleus of the $\beta$ phase is formed when the stress applied to the $\alpha$ phase reaches a certain value. Complimentarily, a nucleus of the $\alpha$ phase is formed when the stress experienced by the $\beta$ phase is reduced to some value. If this nucleus succeeds in reaching a critical size, it will continue to grow freely afterwards. Although the 'growth' part of the theory cannot be adequately addressed, it can be shown that the "nucleation" concept can alone explain the observed hysteresis. By maximizing the free energy due to formation of the $\beta$ phase nucleus,

$$F = (-SA \Delta l + \Delta V)xy/A + 2 \Omega 1(x+y)$$

one can derive the critical stress for $\alpha$ to $\beta$ transition.

$$S_{\beta}^* = \frac{\Delta V}{A_{\beta} \Delta l} + \frac{4T^2l^2}{F^* T \Delta l}$$

(5.19)

Similarly, the critical stress for $\beta$ to $\alpha$ transition is

$$S_{\alpha}^* = \frac{\Delta V}{A_{\alpha} \Delta l} - \frac{4T^2l^2}{F^* T \Delta l}$$

(5.20)

Here the nucleus was assumed to be a rectangular parallopiped whose height equals the lamellar width, $l$, and the nucleus width is $x$ and $y$ in
the a and b directions, respectively. Furthermore, \( \Delta l \) is the increase in chain length due to \( \alpha \rightarrow \beta \) transformation, \( \Delta V = V_\beta - V_\alpha \), with \( V_\alpha \) and \( V_\beta \) being the average energy of a chain in either conformation and \( v \) is the surface energy density of the wall separating the two phases. The hysteresis width is defined as, \( \Delta S = S^*_{\beta} - S^*_{\alpha} \), and equals

\[
S = \frac{\Delta V}{\Delta l} \left[ \frac{1}{A_\beta} - \frac{1}{A_\alpha} \right] + \frac{2 v T}{\Delta F^* T \Delta l}
\]

Since the difference between \( A_\alpha \) and \( A_\beta \) is small, only the second term is significant. The surface energy density, \( v \), depends on the interchain interaction which is assumed to be temperature dependent. The interchain coupling is radically reduced at the surface between the \( \alpha \) and \( \beta \) phases. Basically, this concept is no different from the mean field model which also considers the perturbation of the interchain coupling energy between neighboring molecules with unlike conformations. The only difference is that in the "nucleation" model, this coupling interaction is limited to the interface on the nucleus, whereas in the mean field model, the coupling interaction is present wherever one individual \( \beta \) conformation is introduced in an \( \alpha \) form domain (or vice versa). Physically, the mean field model is more realistic, because more than one "originating site" is possible in a polymeric crystal having defects and crystalline-amorphous edges. The parameter \( v \), in the "nucleation" model is equivalent to the term \( 1/2 K [\Delta x^2 + \Delta y^2] \) in the mean field theory, as both represent the strength of the intermolecular interactions. The temperature dependence of the \( v \) parameter is introduced via the temperature dependence of the interatomic interaction energy. In other words, the mean deviations
from the atomic equilibrium positions, $<\vec{\mu}_i^2>^{1/2}$, become greater as the temperature increases. The dependence was shown to be linear, since $<\vec{\mu}_i^2>^2 = k_bT$ (144) and consequently $\mathbf{v}(T) = C_1 - C_2(T)$, where $C_1$ and $C_2$ are adjustable parameters. (The interatomic interaction energy between atoms $i$ and $j$ is defined as $V(R_i - R_j) = V(R_{i0} - R_{j0}) + k/2(<\vec{\mu}_i - \vec{\mu}_j)^2> + ... (144)$, where $R_i$ is the vector position of atom $i$). Physically, this means that the interchain coupling energy, $V(R_i - R_j)$, which is reduced at the interface, tends to increase again as the temperature is raised. Since $\mathbf{v}$ is proportional to $-V(R_i - R_j)$, it, in turn, will decrease. From equation (5.21), the temperature dependence of the hysteresis width in the PBT transformation becomes

$$\Delta S = (a - bT)^2$$

where $a$ and $b$ are constants related to $C_1$ and $C_2$. By choosing the proper values for the constants, one can fit the observed hysteresis trend with temperature.

Using the same argument, there is no reason why this temperature dependence cannot be introduced into the the mean-field model. In other words, the atomic deviations from equilibrium position can contain two summable terms, one the thermal position fluctuations and second the displacement due to conformational changes. The displacement of atoms due to a conformational change, i.e., $\alpha = \beta$ transformation, would depend on the atom in the structure. However, since the c-axis dimension changes by 1.4 Å, one would expect the position of the terephthalate group to change along the same order of magnitude. The root-mean-square amplitude of
vibration of atoms in an organic molecule at room temperature is approximately 0.10 Å and 0.30 Å at 120 °C (145). However, because the $1/2K (\Delta X)^2$ term (in the mean field model) requires the measurement of a net displacement caused by the transformation from a high energy conformation to another high energy conformation, the $\rho$, the term $\Delta X$ will not be significantly affected. Instead, what may change, is the value of $K$. Since at higher temperatures the atoms forming the chains fluctuate farther apart, the strength of the intermolecular interactions would be lower and consequently $K$ will decrease. The net effect will be a lower value of $F$ at any particular conversion value, $\chi_p$, and a lower hysteresis width $\Delta F$. What will not change, however, is the position of the hysteresis center along the $x$-axis. This is contrary to the shift predicted by the nucleation growth theory, which forces this behavior by letting $\nabla(T) = C_1 - C_2T$. In fact, as will be shown later, this shift can be explained by the unlike temperature dependence of the conformational energies characteristic of the $\alpha$ or $\beta$ crystalline structures.

Application of the mean field model to data interpretation

Based on the conclusions of the previous discussion, the modified mean field model is most suitable and convenient to explain the results of our transformation studies. Based on the orientational behavior examined in our study, a quantitative analysis requires two important assumptions. They are: 1) Since the hard segment orientation stays nearly constant throughout the 30% strain, the sigmoidal shape of the transfor-
mation curves cannot arise from the stress or strain dependent orientation of the crystalline domains; 2) the hysteresis cycle observed in the \( \alpha \leftrightarrow \beta \) transition does not result from any type of hard segment orientation relaxation.

Our spectroscopic data, shown in figures 37, suggest that the phase transition depends on the crystalline dimensions. As the average hard segment length decreases, the transformation of \( \beta \) fraction with stress becomes less sigmoidal in shape and the width of the stress hysteresis also decreases. Such behavior implies the decrease in cooperative strength. The cooperativity between the hard segments originates from the interchain retractive forces which hold the lattice together. Cooperativity along the hard segments arises from trying to prevent intramolecular interactions which occur between units with unlike conformations. The larger the crystal the greater is the coherence in both types of interactions. Once these barriers are overcome, the transformation becomes increasingly easier up to the near depletion of the crumpled \( \alpha \)-form.

Theoretical predictions are in agreement with this picture. According to the mean field model proposed, the hysteresis width should be partly determined by the value of \( Q \), the average intramolecular interactions, whose relative contribution is controlled by \( n \), the crystalline chain length and \( K \) whose value reflects the strength of the intermolecular interactions. This can be deduced from equation 5.17.

If \( Q \) equaled zero, the change of \((\Delta F)^{2/3}\) with temperature should yield a linear line according to

\[
(\Delta F)^{2/3} = (16Kb/3)^{2/3} [ 1 - T/T_C ] 
\]

(5.23)
This clearly is not the case due to the presence of an offset in $\Delta F$, that prevents $\Delta F$ from reaching zero at $T_c = 415 \text{ K}$ (76) as seen in figure 50. According to the modified mean field theory, this offset should arise from the contribution of $(n-1)Q/n(n+1)$.

Although the exact relationship between the average hard segment length, $L$, and the corresponding crystal thickness, $n$, is not known, the value of $n$ can, nevertheless, be estimated as follows. Lamellae thickness was observed on the order of 75 - 100 Å for the PBT copolymer having a 0.79 mole fraction hard segment (9,12). Since the length of the repeat unit is approximately 12 Å, it seems reasonable to assume that there are between 6-8 units in this copolymer. Also its melting point is at 186 °C. The higher melting temperature of the samples we have used suggests that their lamellar thicknesses must be greater than 75-100 Å.

Using the relationship $T_m = T_m^0 - c/L$ (119) with $T_m^0 = 509 \text{ K}$ (13), we estimate the number of units defining the homopolymer crystal thickness between 22 to 29. Based on the melting points of the other copolymers, the number of repeat units traversing their crystals can also be estimated. These values are listed in Table III. It should be stressed that these values are only estimates. More exact values can only be determined by diffraction methods.

We can get an idea of the magnitude of $Q$ by considering the case where a terephthalate group is shared by a tetramethylene segment in an $\alpha$ and a $\beta$ conformation on either side. If the benzene ring has the same placement and tilt as it would had it been in a perfect $\alpha$-crystal, the carbonyl group on the $\beta$ conformation side has to rotate 20 degrees about
Figure 50. The hysteresis width estimated from the plots of $\rho$ fraction vs. stress. The hysteresis width is plotted as a function of temperature for two mole fractions of the hard segment; $X_h = 100\%$ and $X_h = 96\%$ and at one temperature for $X_h = 93\%$ mole fraction of hard segment.
<table>
<thead>
<tr>
<th>Sample</th>
<th>$x_h$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBT</td>
<td>1.00</td>
<td>22-29</td>
</tr>
<tr>
<td>H1</td>
<td>0.96</td>
<td>15-20</td>
</tr>
<tr>
<td>H2</td>
<td>0.93</td>
<td>12-16</td>
</tr>
<tr>
<td>H3</td>
<td>0.88</td>
<td>8-11</td>
</tr>
<tr>
<td>H4</td>
<td>0.83</td>
<td>7-9</td>
</tr>
</tbody>
</table>
the $\phi$-C=O bond in order to accommodate the extended tetramethylene conformation in the crystal. The resistance to this rotation can be estimated from the sum of nonbonded interactions of the ester group and an intrinsic twofold torsional potential resulting from the delocalization of $\pi$-electrons over the entire terephthalate residue. Rotational barrier of 0.4 Kcal/mole (1.67 kJoules/mole) was estimated from a potential energy - rotational angle plots (146).

Since the width of the stress hysteresis, $\Delta F$, for pure PBT at 293 $^\circ$K is 32 MPA or 1.7 Kcal/mole, (multiplying by the cross-sectional area of the unit cell and the length of the repeat unit) the contribution of the calculated intramolecular potential to this value is significant. The offset measured in the hysteresis of the PBT homopolymer is equivalent to $0.30 \pm 0.05$ Kcal/mole. Since this offset is just $Q(n-1)/(n+1)n$, then considering a chain length of 22-29 repeat units, this value must equal between 0.35 Kcal/mole and 0.36 Kcal/mole. The measured offset for the H1 copolymer is $0.20 \pm 0.05$ Kcal/mole. Assuming that $n$ is between 15 and 20 repeat units, the calculated offset should be 0.32 to 0.34 Kcal/mole.

However, subtraction of these estimated offset values from the measured $F$ values and calculation of $(\Delta F)^{2/3}$ still does not lend a linear line. This means that the intramolecular interactions must also decrease with temperature. Hence, one would expect the stress hysteresis to drop to zero near the melting point, where the structural coherence is lost. Unfortunately, due to the softening of the films and inability to generate sufficient stress for complete transformation, deformation expe-
riements at temperatures higher than 160 °C are difficult.

The values of $r_{\alpha}$, $r_{\beta}$, and $E_{\alpha}$, $E_{\beta}$ have been obtained from literature (27) and are 1.16 nm, 1.30 nm and -6.60 KJ/mole, -1.21 KJ/mole, respectively. Since the force constant $K$ represents the strength of cohesion between terephthalate groups in the crystalline matrix, disruption of order in the crystalline lattice by the introduction of defects or partial separation of lateral faces by shearing will decrease the value of $K$. The fact that the width of the hysteresis, as measured from the infrared data, decreases with decreasing perfection of the crystal structure seems to support this concept. However, there may be another possible explanation for this observation. As already mentioned, the crystalline size affects the coherence of the intermolecular interactions. When the crystallites become too small, the mean field approximation may not be valid, because the interactions are no longer uniform. Interactions at the crystalline-amorphous interface, for example, may perturb the crystalline retractive forces, when the surface to volume ratio of the crystallite becomes too large. This may indeed be the situation in the samples with lower perfection of the crystal structure as well as in those with lower hard segment content, where the crystals are small. In fact, a morphological study using electron microscopy has shown that the lateral dimensions of the single crystal lamellae vary between 10 $\mu$m x 25 $\mu$m to less than 5 $\mu$m x 10 $\mu$m from 93% to 83% mole fraction hard segment (17). Using the lamellar thicknesses estimated previously (Table III), the surface to volume ratios for the two samples have been derived. These are 1.2x10^{-2} $\AA^{-1}$ and 2.1x10^{-2} $\AA^{-1}$ for 93% to 83% mole
fraction hard segment. Since the hysteresis practically vanishes in samples having less than 93% mole fraction hard segment, cooperativity between chains must diminish when the surface to volume ratio of the crystals increases above $1.2 \times 10^{-2} \text{Å}^{-1}$.

The value of $K$ was estimated from the hysteresis width obtained by subtracting the estimated offset value from the measured hysteresis width at room temperature. So calculated values are 153 and 147 kJ/mol (nm)$^2$ for the PBT homopolymer and the copolymer with 0.96% mole fraction hard segment, respectively. For copolymers with (0.93) and (0.88) mole fractions, $K < 140$ kJ/mol (nm)$^2$. The decrease in the $K$ constant reflects the higher concentration of lattice imperfections and greater surface to volume ratio of crystals present in samples with lower mole fraction hard segment.

The shift of the hysteresis center to lower values with increasing temperature of deformation (seen in figure 40) can also be explained by the mean field model. The term which causes this shift is "e", defined as the difference between the and conformational energies. As pointed out in the temperature study of the PBT spectrum, there may be two or more energy states associated with the $\alpha$ or $\beta$ crystalline segments. These states are characterized by the 929 cm$^{-1}$ and 916 cm$^{-1}$ absorption bands and by 972.8 cm$^{-1}$ and 955.7 cm$^{-1}$ absorption bands, respectively. Their simultaneous intensity growth and reduction suggests an equivalent conversion according to Boltzmann's distribution. Consequently, the energy difference term "e" is perturbed at higher temperatures and it can be therefore modified to include the relative population of each conforma-
Figure 51. Predicted shift of the hysteresis center with temperature assuming a Boltzmann's distribution of the case where (a) $T = 300 \, ^\circ \text{K}$ and (b) $T = 350 \, ^\circ \text{K}$.
tion.

\[ e = \left[ (E'_\alpha y'_\alpha + E''_\alpha y''_\alpha) - (E'_\beta y'_\beta + E''_\beta y''_\beta) \right] \]

where \( y'_\alpha + y''_\alpha = 1 \) \hspace{1cm} (5.25a)
\( y'_\beta + y''_\beta = 1 \) \hspace{1cm} (5.25b)

and \( E'_\alpha, \ E'_\beta \) and \( E''_\alpha, \ E''_\beta \) are the low and high energy conformations respectively. The quantity "e" should decrease with increasing temperature if the conformational energy of the \( \beta \) units increases more than that of the \( \alpha \) units with increasing temperature. This seems plausible in view of the energy calculations conducted for the \( \alpha \) and \( \beta \) molecular models (27). Comparison of the calculated minima \( I_\alpha \) and \( I_\beta \) indicates that the conformational energy of \( I_\beta \) is located within a broad energy contour map as compared to the \( I_\alpha \) conformational energy located in a deep well. Furthermore, the energy calculation also predict the existence of two more minima for both the \( \alpha \) and \( \beta \) forms. The energy difference between the two lowest energy minima is 3.9 Kcal/mole (\( \Delta E_\alpha \)) in the \( \alpha \)-conformation and 2.3 Kcal/mole (\( \Delta E_\beta \)) in the \( \beta \)-conformation. Therefore there is a possibility of a conformational change in the 0-C-C bond in either crystalline form without appreciable change in the lattice spacings. Consequent decrease in "e" would then causes the observed hysteresis shift to lower stress values as shown in Figure 51. The values of e at different temperatures have been calculated as follows. Using Boltzmann's relationship,

\[ y''_\beta = \frac{\exp - \frac{E''_\beta}{kT}}{1 + \exp - \frac{E''_\beta}{kT}} \] \hspace{1cm} (5.26a)
and
\[ y_\beta' = \frac{1}{1 + \exp -\frac{E'}{kT}} \] (5.26b)

Similarly for \( y_\alpha'' \) and \( y_\alpha' \), and substituting in equation 5.24, one obtains,
\[ e = (E_\beta' - E_\alpha') + [(\Delta E_\beta/(1 + \exp -\Delta E_\beta/kT)) - \Delta E_\alpha/(1 + \exp -\Delta E_\alpha/kT)] \] (5.27)

Values of "e" at several temperatures as obtained from the experimental results are listed in Table IV. The maximum expected "e" is 5.87 Kcal/mole (27).

TABLE IV.

Calculated Energy Difference between the \( \alpha \) and \( \beta \) Conformational Energies for various Temperatures

<table>
<thead>
<tr>
<th>( T (^0K) )</th>
<th>e</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>4.22 Kcal/mole</td>
</tr>
<tr>
<td>318</td>
<td>2.44 Kcal/mole</td>
</tr>
<tr>
<td>353</td>
<td>1.59 Kcal/mole</td>
</tr>
<tr>
<td>413</td>
<td>1.10 Kcal/mole</td>
</tr>
</tbody>
</table>

Conclusion

Experimental results describing the crystalline phase transition in poly(butylene terephthalate) and in its related copolymers have been compared with several theoretical models. A mean field model which considered intramolecular as well as intermolecular interactions was particu-
larly suitable in explaining the observed behavior. The mean intramolecular energy was estimated to be 0.40 Kcal/mole and the weight of its contribution is determined by the length of the hard segment incorporated into the crystal. The intermolecular interactions vary with the perfection and size of the crystallites. The retractive forces arising from these interactions are primarily responsible for the hysteresis and sigmoidal behavior of the crystal transformation with stress.

It has also been shown, that increasing the temperature leads to certain conformational changes which raise the energy of the system. Incorporation of these results into the mean field model adds an additional temperature-dependent term to the expression for the free energy of the system. Consequently, shifts of the hysteresis center to lower stress values with increasing temperature can be predicted.
CHAPTER VI.
SUMMARY AND FUTURE WORK

This chapter presents the conclusions regarding the crystalline phase transition in poly(butylene terephthalate) and in its copolymers with poly(tetramethylene oxide) as studied by vibrational spectroscopy coupled with mechanical measurements. Some suggestions for future efforts in this area are also mentioned. In addition new applications for polarization modulation spectroscopy are presented.

The stress-strain behavior of PBT and the poly(ether esters) has been explained in terms of a plastic deformation of the crystalline superstructure and the $\alpha \leftrightarrow \beta$ crystalline phase transition. A morphological model of solid state extruded films was verified, establishing an oriented crystalline structure with finite dimensions. Deformation of so processed films resulted in a minimal improvement of the hard segment orientation and small increase in the soft segment orientation. The crystalline phase transition was shown to be primarily responsible for a stress hysteresis between the loading and unloading portions of the cycle. The width of the hysteresis decreased with increasing temperature and lower perfection of the crystalline structure. Comparison of hysteresis widths at various temperatures obtained by infrared spectroscopy and by x-ray diffraction showed good agreement, especially at lower temperatures. The transformation behavior and the hysteresis width were also affected by the crystallite size. Crystallites with
greater dimensions transformed more slowly initially, giving rise to a strongly sigmoidal transformation curve.

These experimental results were compared with the predictions of first order transition, mean field and nucleation-growth models. The mean field model was particularly suitable in explaining the changes and shifts of the hysteresis width in terms of average molecular interactions. Intermolecular interactions, here modeled as Hookean springs between the terephthalate groups of neighboring chains, were shown to vary with the perfection and size of the crystallites. The mean intramolecular energy was estimated to be 0.40 Kcal/mole and the strength of its contribution was determined by the length of the hard segment governing the thickness of the crystal lamellae. It has also been shown, that increasing the temperature leads to certain conformational changes, most likely about the O-CH bond in the terephthalate group, raising the energy of the system. X-ray results suggested that the conformational change was not accompanied by alterations in the lattice dimensions. The assumption of a Boltzmann's distribution of conformational energies, added an additional temperature dependent term to the expression for the free energy of the system. Consequently, shifts of the hysteresis center to lower stress values with increasing temperature could also be predicted.

Polarization modulation spectroscopy has proven to be a very practical technique for studying orientation changes associated with very small deformations. Besides being able to measure the orientation function down to $1 \times 10^{-5}$, modulation spectroscopy has the advantage of
increased time resolution, and the convenience and precision of a direct measurement which cannot be achieved in a conventional dichroism experiment. The modulation technique was used to study the orientation changes of weakly strained poly(ether ester) films. Analysis of the orientation of the CH$_2$ and C=O functional groups as well as the transformation behavior of the crystalline phase, suggested that the deformation at small strains could be modeled as that of an ideal network. When judged in terms of this model, the experimental results indicated that the average length of the amorphous segments decreased as the mole fraction of the hard segments increased. Thus it was concluded that the macroscopic deformation of the sample was primarily achieved by the orientation change in the soft and amorphous segments. This is different from the deformation mode of pre-oriented films which, as already mentioned, elongate as a result of a crystalline transformation, a plastic deformation of the superstructure and additional small orientation of the amorphous segments.

A parameter which still has not been truly isolated in its effect on the deformation mechanism is percent crystallinity. One would expect that the distribution of stress within the film would be particularly influenced by the crystalline content. In this case, the $\alpha \Rightarrow \beta$ phase transition could serve as an molecular probe describing the percentage of stressed crystalline units. In this experiment, one could keep the hard segment content the same and vary the percent crystallinity by selective crystallization conditions; for example quenching and slow crystallization at various temperatures or by casting from solution.
Such conditions change the overall organization of the crystalline units in the superstructure and hence the deformation mechanisms will differ. The orientation of crystals towards the direction of strain would be determined by the mobility and interconnectivity with the surrounding matrix. For example, PBT films crystallized at low degrees of undercooling are very brittle and break almost immediately when stressed. Thus, although the crystals are present to absorb the stress, the lack of amorphous chains prevents the stress from being distributed uniformly throughout the sample. In this case, one would not expect to observe a transformation of the crystals, even at high stress values. In addition it would be particularly interesting to observe the effect of stress on a single crystal and study how the $\alpha \Leftrightarrow \beta$ transition propagates.

The physical basis for one of the parameters representing inter-chain interaction between neighbouring terephthalate groups has never been established. Because the interaction is modeled as a simple Hookean spring, it is very difficult to compare it with the more complex interactions which truly occur between neighboring atoms. However, it may be possible to calculate a mean potential energy between two terephthalate groups, based on the sum of all the possible interactions of one terephthalate group in a lattice. Then knowing the average separation of the benzene rings from the x-ray data, the mean force constant $K$ can be estimated. Comparison of so calculated force constant with experimental values can lend some additional insight into the true applicability of the mean field model.

In the homopolymer and copolymer films the orientation of the
crystal axes with respect to the stress direction is critical to the transformation process. The crystalline orientation itself is most likely coupled to the orientation of the soft segments and hard uncry stallized segments in the amorphous matrix. Hence, one would expect that the relative orientation changes of crystalline hard segments, amorphous hard segments and soft segments would be dependent on the hard segment concentration in the copolymer. Generally, the hard segment and soft segment orientations have been estimated by measuring the dichroism of the C=O and CH2 absorption bands. However, depending on the copolymer composition, 74 to 96 percent of the carbonyl groups are present in the hard segments and 43 to 86 percent of the CH2 groups are actually in the soft segments. Hence, measured orientation changes are biased, making relative quantitative comparison difficult. Copolymerization of selectively deuterated hard or soft segments forming the poly(ether ester) may solve this problem. Frequency shift in the CD2 or CDH absorption band will be induced owing to the mass dependence of the vibrational frequency, thus resolving the hard CH2 and soft CH2 groups. The dichroic behavior of these bands may lend some additional insight into the true orientational response of each component.

The deuteration of soft segments would be especially useful when using modulation spectroscopy to study the deformation at small strains which, as we have shown, occurs primarily in the amorphous regions. The resolution of particular absorbance bands may not only be used for dichroic measurements but also to get an idea of the most probable conformations in the soft segments. The modulation technique itself may
be exploited in a variety of deformation or static experiments. In particular, a combination of polarization modulation and dynamic deformation (time resolved) could give information as to the relative orientation rates of individual components in semi-crystalline polymers. However, these experiments would have to be limited to isotropic and highly elastic materials (which actually may not be a problem at small strains). The reason is that the films have to be deformed over several cycles before enough scans are collected for a sufficient signal to noise ratio. One disadvantage of polarization modulation is that it cannot be used to measure orientation changes in already dichroic samples, unless some way is found to null the initial differential signal.

Analysis of PBT crystal structure using results of x-ray diffraction and computational techniques has been limited to room temperature study. Although the scattering intensities obviously decrease with rising temperature as a result of the change in the temperature factor, it is possible that they may also reflect the conformational change in the ester group as suggested by the infrared experiments. The scattering intensity at any reflection depends on both, the atomic scattering factor and the temperature factor of all atoms in the unit cell. Hence, one way to alter this intensity is by changing the position of atoms in the unit cell. If this action does not perturb the dimensions or symmetry of the unit cell, then the positions of the reflections will remain the same, but the scattering intensity will be redistributed. However, if the temperature varies at the same time, the intensity change caused by the atomic rearrangement will be masked by the change in the tempera-
ture factor. One way to check whether the decrease in scattering intensity induced by the higher temperature has a contribution from a conformational change, is to assume an appropriate temperature factor (145) and carry out a structure analysis using PBT diffraction patterns at several selected temperatures.
REFERENCES


42. A. Peterlin, Polymer Eng. & Sci. 19(2), 118 (1979)

186
75. Radi Al Jishi and P.L. Taylor (Case Western Reserve University), Private communication.


111. O. Kratky, Kolloid-Zeitschrift 64(2), 213 (1933).


125. A. Anton, J. Appl. Polymer Sci. 12, 2117 (1968).


153. Moog Inc., Industrial Division, East Aurora, New York, 14052.
APPENDIX A

Theoretical Calculation of a Plateau Region in the Stress-Strain Curve

Assuming that all crystalline chains are oriented with their c-axis in the strain direction, a relationship between the initial long period, \( L_0 \) and the crystalline length, \( L_C \) can be written as,

\[
L_C = X_L L_0
\]  

(A.1)

The factor \( X_L \) can be related to the bulk crystallinity \( X_C \) of the sample (20). The estimated values of \( X_L \) from the experimental results of Tashiro et.al. (20) are summarized Table V.

<table>
<thead>
<tr>
<th>%4GT</th>
<th>( X_C(%) )</th>
<th>( X_L(%) )</th>
<th>( \Delta\varepsilon_{\text{obs}} )</th>
<th>( \Delta\varepsilon_{\text{calc}}(%) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>81</td>
<td>34.4</td>
<td>80</td>
<td>20</td>
<td>9.3</td>
</tr>
<tr>
<td>73</td>
<td>32.7</td>
<td>75</td>
<td>15</td>
<td>8.7</td>
</tr>
<tr>
<td>59</td>
<td>24.9</td>
<td>60</td>
<td>3</td>
<td>7.0</td>
</tr>
<tr>
<td>49</td>
<td>20.7</td>
<td>50</td>
<td>0</td>
<td>5.8</td>
</tr>
</tbody>
</table>

The length of the plateau region, \( \Delta\varepsilon_{\text{obs}} \) is estimated from the stress-strain curve by drawing a horizontal line between the two inflection points. These measurements are summarized above. Since the unit cell elongates from 1.165 nm to 1.30 nm upon transformation from \( \alpha \) to \( \beta \) form, the new crystallite length is given by

\[
L_C = X_L L_0 (1 + 0.116)
\]  

(A.2)

Hence, \( \Delta\varepsilon_{\text{calc}} \) is just \( X_L \times (0.116) \times 100\% \). These calculated values are also summarized above. Comparison of \( \Delta\varepsilon_{\text{obs}} \) with \( \Delta\varepsilon_{\text{calc}} \) indicates poor
agreement between these values. Therefore, in the case of samples with higher 4GT content, other forms of processes must contribute to the elongation to account for the total length of the plateau region. For samples with low 4GT content, the plateau region is masked by other elongation mechanisms.
APPENDIX B

Derivation of Intensity Components in Elliptically Polarized Light

Assuming that the first polarizer is set along the y-axis shown in figure 12, the electric field vector along the x' and y' axes of the modulator is given by (152),

\[ E(\hat{x}') = E_y \cos \theta \]  \hspace{1cm} (A.3a)
\[ E(\hat{y}') = E_y \cos \theta \]  \hspace{1cm} (A.3b)

where \( \theta = 45^\circ \).

After passing through the modulator, the electric field becomes elliptically polarized,

\[ E_m = E_y [e^{i\alpha(t)} \cos \theta \hat{x}' + \sin \theta \hat{y}'] \]  \hspace{1cm} (A.4)

where \( \alpha(t) \) is the periodic retardance introduced by the modulator.

If a dichroic sample is present after the modulator, its configuration is given by

\[ S = f_\parallel (\hat{x}' - \hat{y}') \cos \theta + f_\perp (\hat{x}' + \hat{y}') \cos \theta \]  \hspace{1cm} (A.5a)
\[ S = (f_n + f_\perp) \cos \theta \hat{x}' + (f_\perp - f_n) \cos \theta \hat{y}' \]  \hspace{1cm} (A.5b)

where \( f_n \) and \( f_\perp \) are the factors which attenuate the amplitude of the electric field vector, due to the absorption in parallel and perpendicular directions. In the case of an isotropic sample, \( f_\perp = f_n \).

The electric field reaching the detector is

\[ E = E_m \cdot S \]  \hspace{1cm} (A.6)
\[ E = E_y/2 [(f_n + f_\perp) e^{i\alpha(t)} - (f_\perp - f_n)] \]  \hspace{1cm} (A.7)
Since the intensity is \( I = E \times E \)

\[
I = E_y^2/4[(f_\perp + f_\parallel)^2 + (f_\perp - f_\parallel)^2 \\
+ 2\cos \alpha(t)(f_\perp - f_\parallel)(f_\perp + f_\parallel)]
\]  
(A.8a)

\[
I = E_y^2/2[f_\perp^2 + f_\parallel^2 + \cos \alpha(t)(f_\perp^2 - f_\parallel^2)]
\]  
(A.8b)

Assuming that \((E_yf_\parallel)^2 = I_\parallel\) and \((E_yf_\perp)^2 = I_\perp\),

\[
I = (I_\parallel + I_\perp)/2 + \cos \alpha(t)(I_\perp - I_\parallel)/2
\]  
(A.9)

Here the first part of the term corresponds to the DC intensity and the second part to the AC intensity.

A circularly polarized light would result if a 90° retardation was introduced to the linear polarization. In other words,

\[
I = (I_R + I_L)/2 + \cos[\alpha(t) + \delta](I_R - I_L)/2
\]  
(A.10)

where \( \delta = 90° \)

Since

\[
\cos[\alpha(t) + \delta] = \cos \alpha(t)\cos \delta - \sin \alpha(t)\sin \delta
\]  
(A.11)

\[
I = (I_R + I_L)/2 - \sin \alpha(t)(I_R - I_L)/2
\]  
(A.12)

because \( \cos \delta = 0 \). Here again, the first term is the DC component and the second term is the AC component.
APPENDIX C

Derivation of Modulation Efficiency

Consider the same arrangement of elements as in the previous derivation (Appendix B), except the sample is substituted by a polarizer, such that the modulator rests between two crossed polarizers. In this case the configuration of the second polarizer is given by

\[ S = (\hat{x}' - \hat{y}')/2 \]  \hspace{1cm} (A.13)

and the electric field reaching the detector is

\[ E = E_y/2[e^{i\phi(t)} - 1] \]  \hspace{1cm} (A.14)

Hence, the intensity is

\[ I = I_0/2[1 - \cos \alpha(t)] \]  \hspace{1cm} (A.15)

Since \( \alpha(t) = \alpha_0 \sin w_d t \),

\[ \cos \alpha(t) = \cos(\alpha_0 \sin w_d t) \]  \hspace{1cm} (A.17)

Expansion of equation (A.17) in Fourier series using Bessel functions yields

\[ \cos \alpha(t) = J_0(\alpha_0) + 2 \sum_{n=1}^{\infty} J_{2n}(\alpha_0) \cos(2nw_d t) \]  \hspace{1cm} (A.18)

Substituting equation A.18 into equation A.15, gives

\[ I = I_0/2[1 - J_0(\alpha_0) - 2 \sum_{n=1}^{\infty} 2J_{2n}(\alpha_0) \cos 2nw_d t] \]  \hspace{1cm} (A.19a)

where \( I_{DC} = I_0/2[1 - J_0(\alpha_0)] \) \hspace{1cm} (A.19b)

\[ I_{AC} = I_0 J_2(\alpha_0) \]  \hspace{1cm} (A.19c)

Here only the \( J_2(\alpha_0) \) term has been considered since the lock-in reference frequency is \( 2w_d \).

Then

\[ \frac{I_{AC}}{I_{DC}} = \frac{2J_2(\alpha_0)}{J_0(\alpha_0)-1} \]  \hspace{1cm} (A.20)
APPENDIX D

Equipment and Operations

A Nicolet 7199 Fourier Transform Infrared Spectrometer employing a Nicolet model 7000 optical bench with an MCT detector and a Nicolet 1180 minicomputer is used for all our experiments. Data storage is achieved on a 10 Megabyte Diablo 44B Disk and a 9800 Kennedy magnetic tape system. An optional 20 bit parallel input/output interface board (Nicolet 308) is used for controlling the stretcher, function generator and to access stress and strain information from an external AD converter. All the I/O lines can be addressed from the 1180 computer by programs written in assembly language (35). These programs are callable by higher level languages such as Basic of Fortran. The entire stretcher and mounting platform fit into the sampling area of the optical bench, such that the radiation is normally incident to film samples stretched between the sample mounts. These mounts are directly coupled to a piston driven by a hydraulic power supply, thus ensuring fast response and accuracy. The hydraulic flow is controlled by a MOOG, model 30, servovalve rated at 1 gallon per minute flow rate (153). A maximum piston velocity of 5 inch/sec and a maximum stroke of 2 inch are achievable. The servovalve is controlled by a MOOG model 82-300 dc servocontroller which accepts a load or position feedback signal. The load value is measured by Data Instruments JP10 load cell (rated at 10 pounds) attached directly to the fixed sample jaw by two stabilization rods to eliminate rotation. The strain is
measured by a Trans-Tek linear variable differential transformer (LVDT). The analog outputs from the load cell and the LVDT are digitized by an AD572 analog to digital converter. The stress and strain data can be stored in main memory and/or in the file status block, available on each FT-IR file. The values can then be recalled later for analysis. Experiments can be conducted within a temperature of -50 to 200 °C. High temperatures are obtained via electric cartridge heating elements attached to a removable cover that encloses the sampling area. Lower temperatures are achieved by immersing heat generating resistors in liquid nitrogen and guiding the N₂ boil-off into the sample compartment. The rate of heating and cooling, i.e. voltage supplied to the electric heating elements as well as the immersed resistors is controlled by a Variac. Temperatures are measured to the nearest degree by an Omega thermocouple.
Self-deconvolution consists of multiplying the interferogram by an exponential function \( \exp(2\pi l|x|) \) followed by a box-car apodization and then Fourier transforming the modified interferogram. The exponential function is the inverse Fourier transform of the line shape function \( (154) \), here assumed to be Lorentzian in nature. The experimental spectrum can be expressed as a convolution of a lineshape function \( G(\tilde{\nu}) \) and the true spectrum \( E'(\tilde{\nu}) \), namely,

\[
E(\tilde{\nu}) = G(\tilde{\nu}) \times E'(\tilde{\nu}) \quad \text{(A.21)}
\]

The experimental interferogram is given by

\[
I(x) = \mathcal{F}^{-1}\{G(\tilde{\nu})\} \cdot I'(x) \quad \text{(A.22)}
\]

Hence, the true spectrum can be obtained by Fourier transforming the true interferogram or

\[
E'(\tilde{\nu}) = \mathcal{F}\{I'(x)\} \quad \text{(A.23)}
\]

\[
E'(\tilde{\nu}) = \mathcal{F}\{I(x)/\mathcal{F}^{-1}\{G(\tilde{\nu})\}\} \quad \text{(A.24)}
\]

where \( \mathcal{F}^{-1}\{G(\tilde{\nu})\} = \exp(2\pi l|x|) \).

The factor \( 2\pi \) is the width at half-height and has to be properly chosen in order to avoid over- or under- deconvolution, the first characterized by large negative side-lobes. Both self-deconvolution and band fitting was conducted on an IBM 9000 computer associated with an IBM 32 Fourier Transform Infrared Spectrometer. Curve fitting involved approximating the observed band by a sum of Lorentzian and Gaussian function.
\[f_1(x) = \exp[-(\ln 2)(2(x-x_0/\Delta x))^2]\]  
\[f_2(x) = \frac{x^2/4}{(x-x_0)^2 + \Delta x^2/4}\]  
(A.25)  
(A.26)

where \(f(x) = A[g f_1(x) + (1-g)f_2(x)]\). Here \(x\) is the wavelength frequency along the abscissa, \(\Delta x\) is the band width, \(x_0\) is the position of the peak maximum, \(g\) is the relative contribution of the Gaussian function, and \(A\) is the amplitude. The last four parameters are integrated using pre-designated increments until a sufficiently close fit with the observed data is obtained. In general, this means that the residual variance is reduced by less than 0.1% of the previously iterated value.