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X-ray structural analysis of the thermotropic copolyesters Xydar® and Vectra®

Cheng, Hsiao-Mo, Ph.D.

Case Western Reserve University, 1990
X-RAY STRUCTURAL ANALYSIS OF THE THERMOTROPIC COPOLYESTERS XYDAR® AND VECTRA®

by

HSIAO-MO CHENG

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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X-RAY STRUCTURAL ANALYSIS OF THE THERMOTROPIC COPOLYESTERS XYDAR® AND VECTRA®

Abstract

by

HSIAO-MO CHENG

X-ray diffraction has been used to investigate the solid-state structure of wholly aromatic main chain liquid crystalline copolyesters. In this thesis, attention is focussed on the copolyesters prepared from p-hydroxybenzoic acid (HBA), terephthalic acid (TPA), and biphenol (BP); and from HBA and 2-hydroxy-6-naphthoic acid (HNA). The chemical formulations of these copolymers are the bases for the Xydar® and Vectra® family of commercial resins, respectively.

X-ray fiber diagrams for four HBA/TPA/BP comonomer ratios show high orientation and the presence of three-dimensional order. The meridional region contains a series of aperiodic maxima that shift in position with the composition. These are reproduced in predictions of the scattering intensity for a nematic array of chains of completely random monomer sequence. The chains are modelled first as an array of points separated by the appropriate monomer lengths and subsequently via an atomic model, in which the monomer atomic coordinates are attached at each point residue. This leads to good agreement in terms of the position and intensity of the meridional intensity maxima, which is further improved
when the effect of chain nonlinearity is incorporated in the calculations, which leads to broadening of the predicted peak at \( d = 2.1 \) Å. Analysis of models with nonrandom sequence distributions shows that all but minimal blockiness can be ruled out by the x-ray data. The positions of the meridional maxima are unaffected by thermal annealing, and hence the heat treatment does not appear to affect the monomer sequence distribution.

The fiber diffraction patterns of copoly(HBA/HNA) change considerably as a result of annealing: notably a number of new Bragg reflections appear along the equator and layer lines. Two additional meridional reflections also appear on annealing, although the aperiodicity in this direction is maintained. We find that the meridional intensity at \( d \approx 3.33 \) Å is not generated in calculations for models consisting of registered array of chains of completely random monomer sequence. However, the observed meridionals are generated in calculations of the scattering for monomer sequence with a slight alternating tendency. Specifically, good agreement is obtained when the probability of HBA-HNA pairs is increased by approximately 10 % over the same probability in a completely random sequence. Calculation of the cylindrically averaged intensity transforms of single chains show very good agreement between the observed and calculated layer line positions for this degree of nonrandomness.
The Bragg equatorial reflections that develop for copoly(HBA/HNA) during annealing indicate a change in the chain packing. The structural changes between as-spun and annealed copoly(HBA/HNA) are similar to the polymorphic changes reported for homopoly(HBA). The annealed structure has a more tightly packed structure, in which the chain has a pseudo $2_1$ helical conformation. The DSC data correlate well with the observed structural changes due to thermal treatment.
Dedication

To my parents and my family for all they mean to me.

Also to my wife Bonita Lee and our forthcoming child.
Acknowledgements

The author would like to express his gratitude to Dr. J. Blackwell for his invaluable guidance and advice throughout the course of this endeavor.

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CHAPTER ONE

THERMOTROPIC LIQUID CRYSTALLINE COPOLYESTERS:
AN OVERVIEW

A. Introduction

In the last two decades, the liquid crystalline polymers (LCPs), a new group of polymeric materials, have been developed, and then have received a great deal of attention from both industry and academia. The liquid crystalline is a state of order between true crystal and isotropic liquid. LCPs are classified as lyotropic or thermotropic, depending on whether LC order occurs in solution or in the melt. This state is also referred to as a mesomorphic structure, this being a combined term adopted from the Greek "mesos" meaning "intermediate" and "morphe" meaning "form"; the term mesophase is also used. The main difference between these LC polymers and conventional liquid crystals used e.g. in electrical display devices is the molecular weight.

Liquid crystallinity in high molecular weight organic substances was first observed in solutions of biopolymers: examples are poly(r-benzyl-L-glutamate), hydroxypolyl cellulose and tobacco mosaic virus [1]. This property appears to have an important role in nature, in that the spatial organization of these macromolecules in the living organism give rise to specialized functions, such as the packaging of DNA in
chromosomes and the aggregation of microtubules to form the structural framework of the cell.

According to the Flory theory of concentrated polymeric solutions published in 1956 [2], polymers that exhibit liquid crystallinity typically consist of comparatively elongated, rigid-rod molecules, and a mesophase is formed when their concentration reaches a certain degree in a specific solvent. Since then, three historical milestones in the development of polymers were put in place by scientists at duPont, Eastman-Kodak, and Celanese companies. At duPont the Flory theory was verified qualitatively and it was discovered that certain aromatic polyamides give anisotropic solutions in alkylamide and alkylurea solutions. As a result, the ultra-high-modulus Kevlar aramid fiber (p-phenylene terephthalamide) was developed. The polymer made by the reaction of p-phenylene diamine and terephthloyl chloride at low temperature in an appropriate solvent [3-5]. Eastman-Kodak reported on and produced the first well characterized thermotropic aromatic-aliphatic copolyesters, the so-called X7G®, by the reaction of p-hydroxybenzoic acid (HBA) and poly(ethylene terephthalate) (PET) [6-10]; and Calundann at Celanese (now Hoechst-Celanese) developed various tractable, wholly aromatic thermotropic polyesters (under the Trademark Vectra® series) containing p-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid (HNA) [11]. The Kevlar fiber has very high modulus and tenacity. Similarly, the X7G® thermotropic copolyesters synthesized by Eastman-Kodak and the Hoechst-Celanese Vectra® series, also have exceptional
mechanical and thermal properties, etc. For example, the coefficient of thermal expansion of the polyesters are significantly lower than those of conventional isotropic polymers. As a result, the shrinkage of molded parts after molding is negligible. In addition, due to their low viscosities and high heat distortion temperatures, the molding cycles are much faster than that of conventional polymers. These impressive properties are due to the relatively rigid extended conformation of the polymer chains. The linear aromatic units show spontaneous anisotropy in solution or in the melt, leading to LC order, and hence are known as mesogens.

Today, Kevlar fiber has replaced steel, fiber-glass, asbestos, and graphite for a variety of applications, including radial tires, armorplate, brake linings, and composites. The Vectra® series of polymer has been molded for electronic parts and extruded as strength members. A similar product was announced in 1985 by Dartco Manufacturing (now Amoco), who introduced the first commercialized injection molding grades of LCPs under the Trademark Xydar® series [12]. Xydar® is produced from three monomers; HBA, terephthalic acid (TPA), and biphenol (BP) [13-15]. Products have also been announced by ICI, duPont, Bayer, Granmont, BASF, and Sumitomo companies.

The excellent mechanical properties of the above LCPs derive mainly from the flow characteristics in the melts or solutions. Other physical properties that determine the utility of these materials are the
chemical constitution and the manner in which the monomer units link and interact with each other. The excellent mechanical properties appear to correlate with the three-dimensional crystalline order which develops during processing and further thermal treatment. The objective of the work described in this thesis is to analyze the structures of copoly(HBA/TPA/BP) and copoly(HBA/HNA) using x-ray methods and molecular modelling techniques. This work is expected to contribute to a picture of the structures of Xydar® and Vectra®, which should lead to a better understanding of the structure-property relationships in these polymers.

B. Classification of Thermotropic LCPs

In general, there are two types of thermotropic polymers: the main-chain LCPs, in which the mesogenic groups form the backbone, and the side-chain liquid crystalline polymers, where the mesogenic units link to a polymer backbone as pendant side chains. These structures are illustrated as shown in Figure 1.1 [16]. The spacer between mesogenic groups in main chain LCPs or between the backbone and mesogenic units in side chain LCPs is sometimes necessary to form the LC phase. In most case, the mesogenic units are ellipsoidal, but flat and disk shapes units also occur in LCPs [16]. The mesogens usually consist of two or more linear substituted cyclic aromatic units that may or may not be linked by a short rigid central bridging group. The spacer may be either a
Figure 1.1  General structures of main chain and side chain liquid crystalline polymers [16].
combination of a functional unit (an ester or an ether) with a polyethylene, a polyethylene glycol, or something else. The multiple bond character in both the central linkage group and the spacer is of great importance in order to maintain polymer rigidity and linearity. The ester linkage unit owns some double bond character, and this is a relatively rigid structure. The backbone of the side chain LCPs are usually either flexible alkyl or an organosilicon polymer.

C. Basic Structure

Three basic structures have been identified for thermotropic LCPs: smectic, nematic, and cholesteric. Figure 1.2 illustrates their characteristics [17-18]. The term smectic describes a structure in which the mesogens are arranged side by side in layers. Depending on the degree of molecular orientation in each layer, there are at least nine or ten subclassifications of smectic structures [19-20]. In the nematic structure, the mesogens are aligned parallel to one another but there is random axial displacement. When viewed through a polarized microscope, one sees a thread-like pattern. The cholesteric structure is a special form of the nematic. Molecules are brought together in a nematic-like array in layers, but successive layers are rotated or twisted relative to its intermediate neighbor layers about an axis perpendicular to the layers; consequently, the overall structure is helical.
Figure 1.2  A schematic representation of the smectic, nematic, and cholesteric states of main chain liquid crystalline polymers [17].
LCPs generally exhibit a series of phase transitions. For example, polymeric crystals may form both smectic and nematic structures upon melting on a hot stage, but might become a completely nematic as the temperature is increased. Then at still higher temperatures, an isotropic melt is formed. However, in the case of the LC polyesters studied here, some or all of these phase transitions may not be seen before the polymers decompose at higher temperature. As a result, it is sometimes very difficult to determine the structure.

D. Synthesis of LC Polyesters

The usual synthetic routes used for the production of common aliphatic polyesters can also be utilized to obtain LC aromatic polyesters. The key to LC behavior lies in selecting appropriate monomers with mesogenic units. Some of the first thermotropic polyesters were made either by interfacial polymerization or by high temperature solution polymerization from diphenols and dicarboxylic acid chlorides [21]. These are typical polycondensation reactions. Transesterification reactions have also been used to prepare LCP starting with the phenyl esters of diacids and the aryl diols or with the acyl esters of the aryl diols. The most well known example is the acidolysis of PET with p-acetoxybenzoic acid [6]. Details of the synthesis of LCP existing in different phases can be found in the literature [22].
Most industrial aromatic LC polyesters are polymerized through a condensation reaction. The reaction equations for two well-known thermotropic copolyesters are illustrated in Figure 1.3. The first example describes the preparation of the two component polyester derived from the acetylated hydroxybenzoic and hydroxynaphthoic acids. In order to increase the efficiency of polymerization, the monomers are usually acetylated before polymerization using acetic anhydride in the presence of a suitable catalyst. In general, anhydrous sodium or potassium acetate is added in the reactor as a catalyst. Transesterification reactions start with the phenyl esters formed by the diacids reacting with the aryl diols, or with the acetylated aryl diols at relatively high temperatures. In order to reduce oxidation, the polymerization is conducted in a nitrogen atmosphere. Since in the late stage the condensation reaction is a diffusion controlled process, a stainless steel stirrer is desirable to improve the mixing and to accelerate the evolution of the reaction by-products, such as acetic acid. When a low melt viscosity pre-polymer is obtained, the melt becomes turbid, since the fluctuations of the mesogenic domain orientations are in the range of the wave length of visible light. A vacuum is then applied to the reactor in order to remove further acetic acid from the melt, as the molecular weight of the polymer is increased. Still higher molecular weights are obtained by solid-state polymerization of ground pellets under a reduced pressure or nitrogen environment. A multi-step change in the temperature profile is the key to facilitate the molecular weight enhancement: the final temperature is
Figure 1.3 Reaction equations for Vectra® and Xydar® polymers.
about 10 to 30 °C below the original melting point. Monomer purify and the reaction conditions play as very important determination of the overall properties and appearance of the final product. The second example in Figure 1.3 is for Xydar®: p-hydroxybenzoic acid, terephthalic acid, biphenol, and excess acetic anhydride are refluxed at 315 °C for 5 hours to assure acetylation, in situ, of the phenolic hydroxyl groups. The slurry temperature is gradually raised with simultaneous distillation to remove the acetic acid formed during acetylation as well as that formed during acidolysis polymerization reaction. Melt polymerization is continued until an oligomer is formed. The melt is then cooled to a solid which is ground to a powder, and solid-state polymerization is continued under a nitrogen sweep until high molecular weight is obtained.

E. Effect of Molecular Architecture on Melting Temperatures

Although highly rigid LCPs have attractive properties, the high melting points present serious problems for plastics processing. For example, commercial Xydar® LCP has a melting point of 420 - 435 °C. So that injection molders have to install high-temperature ceramic heaters to their extruder barrels and also heat molds to between 360 and 400 °C in order to process the resin. This disadvantage may offset the unique properties which this LCP has to offer.
Strategies for lowering \( T_m \) in rigid chain LCPs can be evaluated from a thermodynamic viewpoint [23]. At the melting point,

\[
\Delta H_f \\
T_m = \frac{\Delta H_f}{\Delta S_f}
\]  

(1.1)

where \( \Delta H_f \) is the enthalpy and \( \Delta S_f \) is the entropy of fusion. \( \Delta H_f \) is directly related to the degree of crystallinity or order in the system. It is also sensitive to molecular cohesion and chain irregularities. \( \Delta S_f \) defines the increase in the disorder in the system during its transition from the solid to the molten state. In order to reduce \( T_m \), one must either lower \( \Delta H_f \), increase \( \Delta S_f \), or do both. In thermotropic LCPs, \( \Delta S_f \) is low due to the inherent order which does not undergo appreciable change on melting, e.g. passing through the solid state to nematic transition. Decreasing chain stiffness will lead to higher \( \Delta S_f \) values. On the other hand \( \Delta H_f \) can be decreased by introducing defects or irregularities into linear chain segments and by diminishing inter- chain bonding. Each of these distinct possibilities can be incorporated separately into the polymer structure in order to obtain optimum melting points. For example, Vectra®, the copolymer of HBA and HNA, can be processed at 280 - 340 °C, i.e., at temperatures comparable to that used for PET.
The general methods used for lowering $T_m$ in main chain LCPs are illustrated in Table 1.1. The first obvious choice is to introduce a comonomer. Copolymerization with collinear rigid units to form random copolymers, as in Xydar®, does result in the reduction of $T_m$. For example, homopoly(HBA) and poly(TPA-BP) have estimated melting points of ~600 °C, and copolymerization can reduce the melting point to 420 - 435 °C. However, this temperature is still too high to allow for fiber extrusion and further disruption of the main chain order is required. This can be achieved by incorporating “crankshaft” comonomers which have parallel but offset chain-continuing bonds, which leads to a substantial further decrease of $T_m$. Figure 1.4 shows plots of $T_m$ vs molar % composition for two different copolyesters with and without crankshaft moieties [24]. Melt processing is most easy around the minimum of $T_m$, which occurs at intermediate mole ratios. Bent and kinked units lead to an even greater deviation in chain straightness, resulting in further reduction in $T_m$. However, introduction of large proportion of such units can lead to a loss of liquid crystallinity [21], resulting in a polymer that is much more difficult to process because of the higher shear viscosity. It has been found that bent comonomers are more effective in lowering $T_m$ than the introduction of substituent groups such as phenyls. So far we have considered rigid structures only. The use of swivel bonds like -O- or -S- and flexible aliphatic spacers increase $\Delta S_f$, thereby reducing $T_m$. The best known example for the latter category is the X7G® copolyester (HBA/PET) [6]. Figure 1.5 summarizes the several strategies to reduce
Copolymerization

Parallel Offset
"Crank Shaft"

Bent Rigid

Ring Substituted

Swivel

Aliphatic

Table 1.1 Strategies for lowering \( T_m \) in LCPs.
Figure 1.4 Variation of $T_m$ with composition for two copolymers with and without a crankshaft moiety (HNA) [24].
Copolymer

\[
\begin{align*}
&\text{Melting Temp.} \\
&{^\circ}C \\
&> 600
\end{align*}
\]

Crank-Shaft Unit

\[
\text{\(= 400\)}
\]

Crank-Shaft & Bent Unit

\[
\text{\(= 350\)}
\]

Small Substituent

\[
\text{\(> 400\)}
\]

Large Substituent

\[
\text{\(= 340\)}
\]

Aliphatic Unit

\[
\text{\(= 210\)}
\]

Figure 1.5 Strategies to reduce \(T_m\) for LC copolyesters.
Tm and Table 1.2 lists some LCP developed by the industry based on the above principles.

F. Physical Properties of LC Copolyesters

Polymers that exhibit liquid crystalline order in solution or in the melt can potentially produce materials with a high degree of molecular orientation and excellent mechanical properties. Several successful technologies based on these characteristics of rodlike polymers have been developed, and of these the aramid fibers spun from anisotropic solutions have attracted a great deal of attention. Comprehensive reviews of the chemistry and physics of lyotropic systems have appeared in the literature [25,26]. The technology for thermotropic polymers, on the other hand, is still in the early phase of development. At present, most of the developments have been in the areas of fibers and plastics.

F-1 High-Modulus, High-Strength Fiber

Compared to other conventional fibers, the properties of melt spun LCPs stand up very well. Figure 1.6 illustrates this statement by showing the stress-strain curves for several types of fibers [27]. As in the case of the lyotropic nematic polymers, thermotropic copolyesters orient easily in
<table>
<thead>
<tr>
<th>Company</th>
<th>Structural units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Du Pont</td>
<td><img src="image1" alt="Structural unit" /></td>
</tr>
<tr>
<td>Du Pont</td>
<td><img src="image2" alt="Structural unit" /></td>
</tr>
<tr>
<td>Eastman Kodak</td>
<td><img src="image3" alt="Structural unit" /></td>
</tr>
<tr>
<td>Celanese</td>
<td><img src="image4" alt="Structural unit" /></td>
</tr>
<tr>
<td>Celanese</td>
<td><img src="image5" alt="Structural unit" /></td>
</tr>
<tr>
<td>Celanese</td>
<td><img src="image6" alt="Structural unit" /></td>
</tr>
<tr>
<td>Carborundum</td>
<td><img src="image7" alt="Structural unit" /></td>
</tr>
<tr>
<td>Carborundum</td>
<td><img src="image8" alt="Structural unit" /></td>
</tr>
</tbody>
</table>

Table 1.2   LCPs developed by the industry, as examples of the strategies to control $T_m$.  

Figure 1.6 Comparison of typical stress-strain curves of liquid crystalline polymers and other high performance materials [27].
an extensional flow field, producing highly oriented uniaxial structures with moduli as high as 140 GPa in melt spinning. Drawdown is the critical extrusion variable and low drawdowns are sufficient to achieve almost perfect molecular orientation (Figure 1.7). The extrusion processes employed are identical to those used for conventional thermoplastics, with the exception that full molecular orientation is achieved during the spinning process and no further orientation through drawing in the solid state is possible. Typical fiber properties for thermotropic copolymesters are a tensile modulus of 65 - 124 GPa at a strength of about 3 GPa. The broad modulus range reflects differences in molecular architecture within the known thermotropic copolymesters.

As-spun LCP fibers are not drawable in the conventional sense, but properties can be enhanced by heat treatment or annealing. Figure 1.8 summarizes the fiber-property changes as a function of annealing near \( T_m \) for a typical thermotropic copolyester [11]. Typically, annealing is done at zero tension in a flowing dry air or inert gas environment for a couple of hours at temperatures 10 to 30 °C below the melting point of the as-spun fiber. Figure 1.9 shows that the heat treated fiber retains its superior properties over a wide range of temperature better than the as-spun fiber or the conventional fiber [28]. The heat treatment is thought to result in solid-state polymerization and removal of critical flaws in the system, thereby improving mechanical as well as thermal properties and chemical stability. The melting point rises and there is an increase in
Figure 1.7  Development of fiber properties of copoly(HBA/HNA) with drawdown ratio [11].
Figure 1.8  Fiber-property changes as a function of annealing near $T_m$ for a typical thermotropic copolyester [11].
Figure 1.9  Variation of fiber tensile strength with temperature for as spun and heat treated LC copolyester fiber compared to a conventional fiber (PET) [28].
three dimensional order, which is substantiated by x-ray diffraction patterns before and after heat treatment [11]. As a result, the tensile strength is sometimes increased by a factor of six to eight. The modulus, on the other hand, is much less affected by this treatment, but may still increase by a factor to two [28]. This increase in modulus suggests that the heat treatment leads not only to an increase in molecular weight, but must also result in an improvement in the order and the lateral packing of the molecules in the fibers.

In process of fiber forming from the melt, the melt viscosity and its shear-rate dependence are the parameters of greatest importance. If the melt viscosity is plotted as a function of composition over a range in which the polymer exhibits a transition from the isotropic to an anisotropic melt, the onset of liquid crystallinity is reflected by a sharp decrease in the melt viscosity; this phenomenon is illustrated in Figure 1.10 for the case of PET modified with HBA [6]. At low HBA content the melt viscosity increase with increasing content of HBA. This trend is reversed at about 30 % HBA content, which marks the onset of liquid crystallinity. The decrease in viscosity amounts to one to two orders of magnitude, depending on the shear rate. The low melt viscosities can be attributed to the existence of domains -- possibly because these domains can flow more or less as a whole, in contrast to amorphous melts in which flow occurs by movement of individual, entangled polymeric molecules. The viscosity reaches a minimum at a HBA content of about 65 %, when a sudden increase is
Figure 1.10 Effect of composition on melt viscosity at different shear rates for the copoly(HBA/PET) [6].
observed. It is possible that at this point increasing oxybenzoyl blockiness, causing incomplete polymer fusion at 275 °C (the measurement temperature), would explain the rapid increase in melt viscosity for polymers of greater than 70 mole % HBA content. Although the melts are highly elastic, LCPs exhibit negligible die swell after extrusion from a capillary [29].

F-2 Molded Plastic

The mechanical properties of molded articles and films not only depend on composition and molecular weight but also on fabrication conditions. Figure 1.11 illustrates how the tensile strength of injection-molded bars change as a function of composition [6]. Due to anisotropic nature of these polymers, one would expect different properties in the transverse and flow directions, and hence molded LCPs are sometimes referred to as self-reinforcing composites. In addition, they exhibit good impact strength, superior chemical resistance, high heat deflection temperature, and low thermal expansion coefficients, which are desirable properties for industrial moldings. At present, the possibilities for blending LCPs with commercial thermoplastics are being looked into [30,31].
Figure 1.11  Effect of composition on the tensile strength of injection-molded bars of copoy(HBA/PET) [6].
In 1985, both the Dartco of Kraft Inc. and the Celanese Corporation announced decisions to proceed toward commercialization of their thermotropic copolyester compositions: Xydar® and Vectra® respectively. Table 1.3 compares their reported properties and illustrates their processibility compared to e.g. glass-filled PET. Vectra® can be processed using standard injection-molding equipment; Xydar® requires some modification because of a higher melting point. Both products have 100% reground capability with more cycles possible for Vectra® because of lower processing temperature. The transparency to microwave and high heat-deflection temperature make Xydar® highly suitable for microwave ovenware, a large captive market. Because of low creep, low linear coefficient of thermal expansion, and low mold shrinkage, intricate parts as thin as 0.4 mm are possible. In addition, good electrical insulating properties make LC polymers suitable for electrical and electronics applications. The excellent chemical resistance makes these polymers suitable for use in molded chemical distillation tower packing: a single Vectra® molding replaces several expensive metal parts. Deficiencies include weak weld lines, poor compressive strength, and poor transverse properties caused by anisotropy. Fillers such as talc (upto 50%), glass fibers, and metal powder reduce and can even eliminate the anisotropy of the moldings, eliminating these deficiencies.
Table 1.3  Properties of Xydar® and Vectra®.

<table>
<thead>
<tr>
<th>Property</th>
<th>Xydar®(SRT-500)*</th>
<th>Vectra®**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength, Mpa</td>
<td>126</td>
<td>138-241</td>
</tr>
<tr>
<td>Tensile modulus, GPa</td>
<td>8.3</td>
<td>9.6-38</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>5</td>
<td>1.2-5.5</td>
</tr>
<tr>
<td>Flexural strength, Mpa</td>
<td>131</td>
<td>151-296</td>
</tr>
<tr>
<td>Flexural modulus, GPa</td>
<td>13.1</td>
<td>8.9-34.4</td>
</tr>
<tr>
<td>Tm or Vicat softening point, °C</td>
<td>358</td>
<td>275-330</td>
</tr>
<tr>
<td>Heat-deflection temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 1.8 MPa, °C</td>
<td>337</td>
<td>180-240</td>
</tr>
<tr>
<td>Coefficient thermal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>expansion, ppm, °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>flow</td>
<td>0-27</td>
<td></td>
</tr>
<tr>
<td>transverse</td>
<td>27-54</td>
<td></td>
</tr>
<tr>
<td>Mold shrinkage</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>Flammability (UL 94)</td>
<td>V-0</td>
<td>V-0</td>
</tr>
<tr>
<td>Limiting oxygen index, %</td>
<td>42</td>
<td>35-50</td>
</tr>
<tr>
<td>Dielectric strength, V/um,</td>
<td>31</td>
<td>31-43</td>
</tr>
</tbody>
</table>

* Ref. 12.
** Ref. 32.
G. Structural Investigations

There are two basic approaches that are used to determine if the structure of a synthetic polymer is liquid crystalline: optical microscopy and x-ray diffraction. Other techniques have been used to detect the alignment in e.g. nematic structures notably by proton and deuterium NMR.

G-1 Microscopy

A hot-stage and a polarizing microscope are required for the microscopic examination of a thin LC polymeric film so as to watch for structural changes as the temperature is varied. Hartshorne [19] and Demus and Richter [33] have described the test methods and summarized the means of identification. A classification of LC polymers in terms of their optical textures, as seen in the polarizing microscope, has been given by Noel [34]. In short, nematics show threaded Schlieren and silk-like textures; cholesterics exhibits some sort of oily streaks and striated texture; and, to a great extent, smectic structures has a focal-conic or fan-shaped appearance. Since LC phases are optically anisotropic, this technique represents an easy method to study the onset and the disappearance of liquid crystallinity in melts and solutions as a
function of temperature and other parameters. However, due to
differences in viscosity, slow relaxation response, low light transmission,
and low thermal stability, identification of structure type for an LCP is more
difficult than for a low-molecular weight LC sample.

G-2 X-ray Diffraction

Wendorff [35] and Azaroff [36] have given some comprehensive
reviews on the study of x-ray scattering of both main chain and side chain
LCPs. Blackwell and coworker [37-39], Windle et al. [40], Stamatoff [41],
Noel et al. [42], and Liebert et al. [43] employing x-ray diffraction
techniques to characterize the orientation and molecular structure of main
chain LCPs. Similarly, Lipatov [44], Konstantinov [45], and Finkelmann
et al. [46] have investigated side chain LCPs. Summarizing these
analyses, the nematic state gives rise to two diffuse halos: A weak inner
halo derives from the length of a repeating unit along the chain axis for
main chain LCPs, or from the length of the side group in side chain LCPs.
A strong outer halo is due to the lateral packing and has a Bragg d spacing related to the distance between adjacent mesogens. The
diffraction pattern of the cholesteric state is similar to that of a nematic
phase. However, for smectic structures, the mesogens are mutually
parallel and arranged in layers, and several sharp diffraction rings are
frequently seen which are orders of the layer spacing. There is generally
also a diffuse outer halo due to the relatively disordered packing of the mesogen in the layers.

G-3 NMR Spectroscopy

The use of NMR spectroscopy to characterize thermotropic LCPs was initiated by McFarlane et al. [7] at Eastman. Solution studies using $^1$H NMR and $^{13}$C NMR revealed that the HBA/PET copolymers are nearly random with a slight preference for HBA units to be adjacent to each other: they set a preference factor of 1.3 as the upper limit for the data [7]. Recently, the sequence distribution in copoly(HBA/HNA) has been inferred to be random on the basis of diad sequence distribution based on $^{13}$C NMR results for the copolymer dissolved in pentafluorophenol [47]. However, NMR studies on aromatic LC copolyesters have generally run into difficulty due to low solubility and insufficient resolution to obtain further information on the sequence distribution. Measurements of the nematic order parameter S and the fraction of nematic phase ($F_N$) as a function of temperature for LCPs were first conducted by Blumstein and his coworkers [48] and by Samulski [49] using proton and deuterium NMR. The order parameter was calculated from the dipolar or quadrupolar splittings of the NMR spectrum that develop while cooling from the isotropic stage. The fraction of the mesogenic alignment was deduced from the NMR free-induction-decay (FID) curve. Mitchell and Ishii [50] applied NMR to investigate the chain
orientation and molecular motions in two well-characterized copolyesters: copoly(HBA/HNA) and HBA-modified PET. From a polymer processing viewpoint, if the relationship among S, $F_N$, and temperature is identified, and if the rigid rod-like domains in the LCP melt behave like the short fiber-reinforcing elements in a polymeric matrix, one may be able to manipulate the degree of orientation as well as the mechanical properties of fabricated parts by following the existing theories for short fiber composites.

X-ray analyses of main chain LC copolyesters form the subject of this thesis and the relevant literatures will be reviewed in more detail in the following two chapters. In general, the x-ray fiber patterns exhibit a few meridional maxima, broad diffuse non-Bragg scatter on the equator, plus some Bragg maxima on and close to the equator, indicating the presence of some three-dimensional order. The meridional maxima for copoly(HBA/HNA) were found to be aperiodic and shift in their positions depending on the monomer ratio [51]. Viney, Windle and coworkers [40] have studied the orientation and chain conformation of a few copolyesters, such as the copolymer of HBA and HNA, by electron and optical microscopy along with x-ray data, and have proposed a biaxially nematic structure arising out of the formation of non-periodic lattice crystals which consist of short identical copolymer sequence.
Work in this laboratory [37,38] has concentrated on developing a model for the LCP chain, i.e., its structure and conformation. A list of the systems under study is given in Table 1.4. Treating the copolymer chain as an aperiodic lattice, the position and relative intensities of the meridional maxima were found to be consistent with totally random sequences. The effect of non-random, i.e. blocky, microstructures on the meridional maxima has been analyzed and it has been concluded that all but minimal blockiness can be ruled out by x-ray data. In the present work the one-dimensional modelling scheme for x-ray diffraction data has been applied to the copoly(HBA/TPA/BP) system, which contains three monomer units where not all monomer pairs are chemically feasible.

A particularly intriguing observation in the x-ray data for thermotropic wholly aromatic copolysterethers is the evidence of substantial three-dimensional crystallinity, despite the fact that the aperiodic meridional data indicate a random monomer sequence. Extension of the modelling from the one-dimensional case to consider all three dimensions has been performed for the copoly(HBA/HNA) system [52]. By introducing limited axial register between adjacent chains it has been possible to generate the off-equatorial Bragg maxima. Furthermore, after considering the several models for the conformation and packing of the chains, the data indicated a preference for a chain conformation in which successive aromatic planes along the chain are mutually inclined at
Copolyesters under study

Celanese  | HBA/HNA  | (Vectra)  
          |        |         
Eastman Kodak | HBA/PET | (X7G)   
          |        |         
Amoco     | HBA/BP/TPA | (Xydar) 
          |        |         
Granmont   | P-HQ/TPA/PE-HQ | (Granlar) 
          |        |         
Celanese   | HBA/DHN/TPA |         
          |        |         

Copolyamide under study

Teijin     | PDA/TPA/DPE | (HM-50) 
          |        |         

Copoly(ester carbonate) under study

Bayer      | HBA/HQ/Carbonate |         
          |        |         

Table 1.4   A list of liquid crystalline copolymer under study.
about 60°, the packing is analogous to that in poly(p-phenyleneterephthalamide). The conformation correlations of the dimers along adjacent chains are relatively limited. Thermal annealing of these copolymers generally results in a sharpening of reflections corresponding to an increase in crystalline size. The annealing may also lead to generation of additional Bragg maxima. We have seen particularly interest in the development of two additional meridional maxima, and whether these indicate changes in the monomer sequence during the thermal treatment.
CHAPTER TWO

X-RAY ANALYSIS OF THERMOTROPIC COPOLYESTER
XYDAR®

A. Introduction

This chapter describes x-ray analysis of the structure of the wholly aromatic thermotropic copolyesters prepared from p-hydroxybenzoic acid (HBA), terephthalic acid (TPA), and biphenol (BP). This formulation is the basis for the Xydar® family of high-temperature, high performance resins: the properties of these copolymers are described elsewhere [12,53]. The structural analysis follows on from our work on other wholly aromatic copolyester and copolyamide systems [51,54-56], notably the copolymer of HBA and 2-hydroxy-6-naphthoic acid (HNA). As was the case for the latter copolymers, x-ray fiber diffraction patterns of copoly(HBA/TPA/BP) exhibit a series of aperiodic meridional maxima (along the fiber axis direction); i.e., these maxima do not occur at orders of a simple repeat. The positions (Bragg d-spacings) of these maxima also shift in systematic manner with the comonomer mole ratio. Such features are inconsistent with extensive block copolymer character. The analogous copolyesters examined previously also give rise to aperiodic meridional data [51,57], which we have shown point to a completely random comonomer sequence. In this chapter we have investigated the meridional data for copoly(HBA/TPA/BP) in terms of the sequence distribution. We have also
compared data for as-spun and annealed fibers to investigate possible changes in microstructures as a result of heat treatment.

B. Experimental Section

B-1 X-ray Diffraction

Specimens of copoly(HBA/TPA/BP) were supplied by Dartco Manufacturing Inc., Augusta, GA, in the form of melt spun fibers for four different HBA/TPA/BP mole ratios: 33/33/33, 50/25/25, 60/20/20, and 72/14/14. The fibers were examined in the as-drawn state and after annealing at 345 °C for 1 hour. Specimens for x-ray analysis were prepared as parallel bundles of about 50 fibers. X-ray fiber diagrams were recorded on Kodak no-screen film using Ni-filtered CuKα radiation and a Searle toroidal focusing camera. The d-spacings were calibrated with calcium fluoride.

X-ray data were also recorded for an oriented molded specimen of the 50/25/25 copolymer, also supplied by Dartco. This specimen was part of a 6 in. x 6 in. x 1/8 in. plaque processed by injection molding (full edge gate) at 400 °C. A piece 1/2 in. x 1 in. was cut from the center of the plaque and ground to approximately one-third of the original thickness by removal of the top and bottom surface layers. The specimen showed high orientation of the chain axes perpendicular to the fill direction in the mold. X-ray patterns were recorded on film, with the chain axis direction
perpendicular to the beam, and then tilted at the appropriate angle (θ) for successive meridional maxima. These patterns were scanned by using an Optronics densitometer to record the meridional intensity profiles. Meridional data were also recorded as a θ / 2θ diffractometer scan, using a Phillips PN 3550/10 diffractometer in the transmission mode.

B-2 Model Building

Atomic models for the monomer residues were derived by using standard bond lengths and angles, and the planar aromatic and ester group are inclined at 30°. Atomic models for the residues are shown in Figure 2.1; the lengths of the residues (ester oxygen to ester oxygen) are 6.35 Å for HBA, 7.15 Å for TPA, and 9.86 Å for BP. A model of a short chain segment with a typical random comonomer sequence is shown in Figure 2.2 (a). The chain can be seen to have an extended conformation, such that the axial advance per monomer is approximately equal to the residue lengths.

The intensity on the meridian, I(Z), depends on the projection of the structure on the fiber axis. If we approximate each monomer in the chain in Figure 2.2 (a) to a point, positioned at the ester oxygen, then the axial projection of the chain is represented by a linear array of points separated by the corresponding monomer lengths, as in Figure 2.2 (b). This can then be converted to an atomic model for the chain, by adding the projection of the atomic structure of the appropriate monomer at each
Figure 2.1  Projection of the monomer residue structures based on standard bond lengths and angles. Hydroxybenzoic acid, terephthalic acid, and biphenol are abbreviated to HBA, TPA, BP, respectively.
Figure 2.2  
(a) Projection of a model of a typical random sequence of copoly(HBA/TPA/BP). (b) Point residue approximation of the chain in (a). (c) Atomic model for the above sequence.
ester oxygen, as in Figure 2.2 (c). For the actual chain in three dimensions, the conformation depends on the torsion angles that define the mutual orientation of adjacent monomers. However, the projection of the extended chain onto the fiber axis will be approximately independent of torsion angles, due to the fact that the aromatic-ester bonds are approximately parallel to the chain axis.

B-3 Prediction of Meridional Intensity, $I(Z)$

If the structure is modeled as a nematic array of parallel copolymer chains, then the meridional intensity is derived from the scattering of a single "average chain". We have shown [58,59] that the extended infinite copolymer chain can be modeled as a one-dimensional paracrystal. The meridional intensity, $I(Z)$, for a chain of point monomers is derived as the Fourier transform of the autocorrelation function, $Q(z)$, that defines the neighbor probability of the point monomers. $Q(z)$ is zero except at $z = z_m$, i.e., at allowed combinations of the monomer lengths. $I(Z)$ is give by

$$I(Z) = \Im [Q(z)] = \sum_{m} Q(z_m) \exp(2\pi i z_m) \quad (2.1)$$

For an infinite chain, the summation in equation (2.1) has the following closed form:
\[ I(Z) = 1 + 2 \text{Re} \frac{H_1(Z)}{1 - H_1(Z)} \]  

(2.2)

where \( \text{Re} \) designated the real component and \( H_1(Z) \) is the Fourier transform of the first nearest-neighbor probability function. \( H_1(Z) \) can be written as

\[ H_1(Z) = \sum_A \sum_B H_{AB}(Z) \]  

(2.3)

where the \( H_{AB}(Z) \) terms are the components for the AB nearest-neighbor pairs. Each \( H_{AB}(Z) \) is a product of composition and phase terms which depend on the monomer proportions \( (p_A, p_B, \ldots) \), the allowed chemical combinations, and the monomer axial lengths. In the case of copoly(HBA/TPA/BP), the HBA monomer has a sense, unlike TPA and BP which have symmetrical structures, and thus in effect there are four monomers: up-HBA, down-HBA, TPA, and BP. These are further approximated to B, D, T, and P, respectively. The proportions of up- and down- HBA are taken as half the total HBA content.

Out of 16 possible monomer pairs, only eight are chemically feasible: for example, TPA can react only with BP or the hydroxyl end of HBA. \( H_1(Z) \) can be conveniently written in matrix form:
$H_1(Z) = \begin{bmatrix}
H_{BB}(Z) & H_{BT}(Z) & 0 & 0 \\
0 & 0 & H_{TP}(Z) & H_{TD}(Z) \\
H_{PB}(Z) & H_{PT}(Z) & 0 & 0 \\
0 & 0 & H_{DP}(Z) & H_{DD}(Z)
\end{bmatrix}$  \hspace{1cm} (2.4)

The nonallowed pairs are denoted by the zeros. This matrix can be written as the product of three components:

$H_1(Z) = P.M.X(Z)$ \hspace{1cm} (2.5)

where

$P = \begin{bmatrix}
P_B & 0 & 0 & 0 \\
0 & P_T & 0 & 0 \\
0 & 0 & P_P & 0 \\
0 & 0 & 0 & P_D
\end{bmatrix}$

$M = \begin{bmatrix}
M_{BB} & M_{BT} & 0 & 0 \\
0 & 0 & M_{TP} & M_{TD} \\
M_{PB} & M_{PT} & 0 & 0 \\
0 & 0 & M_{DP} & M_{DD}
\end{bmatrix}$

$X = \begin{bmatrix}
X_{B}(Z) & 0 & 0 & 0 \\
0 & X_{T}(Z) & 0 & 0 \\
0 & 0 & X_{P}(Z) & 0 \\
0 & 0 & 0 & X_{D}(Z)
\end{bmatrix}$

$X_B(Z) = \exp(2\pi i z_B)$, where $z_B$ is the length of monomer B. $M_{BB}$ is the combination probability for the BB monomer pair and is defined as $M_{BB}$
= 2 \, P_B \, r_{BB}. \text{ In a completely random copolymer, } r_{BB} = 1 \text{ and } MBB = 2 \, P_B. \, r_{BB} \text{ can be varied from unity to simulate nonrandom sequence distributions as will be discussed later in this chapter. } I(Z) \text{ can now be written}

\[ I(Z) = 1 + \sum_A \sum_B 2 P_B \text{ Re } [T_{AB}(Z)] \quad (2.6) \]

where \( T_{AB}(Z) \) is an element of the matrix \( T(Z) \) corresponding to the pair \( AB \), and \( T(Z) \) is defined as

\[ T(Z) = \frac{M_X(Z)}{I - M_X(Z)} \quad (2.7) \]

and \( I \) is the unity matrix.

When we consider an atomic model, the effects of intrarresidue interference are included by multiplying the element \( T_{AB}(Z) \) in matrix \( T(Z) \) by \( F_{AB}(Z) \), the Fourier transform of the cross-convolution of monomer \( A \) and \( B \). Equation (2.5) becomes

\[ I(Z) = \sum_A P_A F_{AA}(Z) + \sum_A \sum_B 2 P_A \text{ Re } [F_{AB}(Z) \, T_{AB}(Z)] \quad (2.8) \]

where
\[ F_{AB}(Z) = \sum_J \sum_k f_{A,j} f_{B,k} \exp[2\pi i Z(z_{B,k} - z_{A,j})] \] (2.9)

The subscript pairs \( A,j \) and \( B,k \) designate the \( j \)th atom in residue \( A \) and the \( k \)th atom in residue \( B \) when both residues have the same origin: \( f \) is the atomic scattering factor and \( z \) is the axial atomic coordinate.

In the model defined above it is assumed that the axial projections of the residues are constant for each monomer type. In any real chain there will be significant nonlinearity, as can be seen in Figure 2.2 (a), and hence the residue projections will not be identical for each monomer type, only approximately so. The distributions of axial lengths for the three monomers are estimated by setting up a large number of random chains by computer and then obtaining histograms of the actual axial lengths. Three distributions are then incorporated into the calculations of \( I(Z) \) by replacing the terms in the \( X(Z) \) matrix by the summations \( X_A(Z) = \sum P_{i,A} \exp(2\pi i Z z_{i,A}) \), where \( P_{i,A} \) is the fraction of the total content of monomer \( A \), which has axial length \( z_{i,A} \). When we move to an atomic model, in principle separate \( F_{AB}(Z) \) terms need to be computed for each set of residue lengths for monomer \( A \) and \( B \). However, the \( F_{AB}(Z) \) functions vary only slowly with \( Z \) and use of \( F_{AB}(Z) \) terms calculated for a single combination of residue lengths is an adequate approximation. Introduction of this distribution leads to a more realistic model for the chain and allows for calculation of a correlation length for the extended conformation, based on the width of certain invariant peaks in \( I(Z) \).
C. Results and Discussion

C-1 X-ray Fiber Diagrams

The x-ray fiber diagrams for as-drawn and annealed fiber preparations of the 33/33/33, 50/25/25, 60/20/20, 72/14/14 copolymers are shown in Figure 2.3 (a)-(d) and 2.4 (a)-(d). The fiber axis is vertical for all diffraction patterns. Figure 2.5 shows the x-ray patterns of the core of the molded plaque, taken with the chain axis perpendicular to the beam and then inclined at 21.5° to that direction.

The x-ray data consist of a series of intensity maxima that appear as relatively short arcs, indicating a high degree of orientation parallel to the fiber axis. A number of sharp Bragg reflections, both on and off the equator, point to the presence of three-dimensional order. These reflections are more numerous in the case of annealed specimens. These data indicate that polymorphic structures can occur for these copolymers; one form is present for the as-drawn state, whereas the annealed fibers appear to contain two forms. This has been discussed elsewhere [60,61] and will also be the subject of chapter 3.

Our aim in the present work is to derive a model for the polymer chains, which depends on the scattering along the meridian. Table 2.1 has been shows the d-spacings of the meridional maxima for all four copolymer compositions, both as-drawn and annealed. Four maxima are
Figure 2.3 X-ray fiber diagrams of as drawn copoly(HBA/TPA/BP) in the following monomer ratios: (a) 33/33/33; (b) 50/25/25; (c) 60/20/20; (d) 72/14/14.
Figure 2.4  X-ray fiber patterns of annealed copoly(HBA/TPA/BP) in the following monomer ratios: (a) 33/33/33; (b) 50/25/25; (c) 60/20/20; (d) 72/14/14.
Figure 2.5  X-ray diffraction patterns of the core of a molded plaque: (a) the chain axis is perpendicular to the x-ray beam; (b) the chain axis is inclined at 21.5° from the plane perpendicular to the beam.
Table 2.1  d-spacings of observed and calculated meridional intensity maxima for copoly(HBA/TPA/BP).

<table>
<thead>
<tr>
<th>Monomer Mole ratio</th>
<th>Expd. d-spacings Å</th>
<th>Calcd. d-spacings Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-drawn</td>
<td>Annealed</td>
</tr>
<tr>
<td>HBA/TPA/BP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33/33/33</td>
<td>7.7 ± 0.2</td>
<td>7.8 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>7.94</td>
<td>7.88</td>
</tr>
<tr>
<td></td>
<td>5.77 ± 0.05</td>
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seen in the fiber diagrams of the specimens when approximately perpendicular to the beam. A fifth meridional at $d \approx 2.9$ Å is resolved on tilting three of the specimens (ratios 33/33/33, 50/25/25, and 60/20/20): this fifth meridional at $d = 2.92$ Å can be seen in Figure 2.5 for the 50/25/25 composition. In the case of the 72/14/14 composition, a shoulder at lower d-spacing is seen on the maximum at $d = 3.1$ Å.

Examination of the data in Table 2.1 shows that the meridional maxima are both aperiodic and different for all four compositions. The differences between compositions are most apparent from the d-spacing of the first maximum, which shifts from 7.7 to 6.6 Å as the content of HBA increases from 33 to 72 %. The second and third maxima are more intense and hence can be measured more accurately. These shift from 5.77 to 5.93 Å and from 3.27 to 3.11 Å, respectively, over the same composition range. The very strong peak at $2.08 \pm 0.03$ Å remains constant throughout. The figures quoted are for the as-spun specimens. The data for the annealed specimens are within experimental error of those for as-spun in all cases. The aperiodicity of the maxima suggests a random sequence distribution, which will be tested below.

C-2 Intensity Calculation

Figure 2.6 and 2.7 show the computed meridional intensity for infinite chains of point and atomic monomers for the four HBA/TPA/BP compositions. These data utilized a model for the chain with fixed residue
Figure 2.6  Point model calculations of the meridional intensity distribution for four different monomer ratios of copoly(HBA/TPA/BP): (a) 33/33/33; (b) 50/25/25; (c) 60/20/20; (d) 72/14/14.
Figure 2.7 Calculated meridional intensity distribution for four copoly(HBA/TPA/BP) ratios using the atomic model: (a) 33/33/33; (b) 50/25/25; (c) 60/20/20; (d) 72/14/14.
lengths equal to their maximum values, i.e., the ester oxygen - ester oxygen distances. The d-spacings of the calculated peaks are compared with the experimental data in Table 2.1.

It can be seen that there is good agreement between the observed and calculated d-spacings in all cases: for most maxima the agreement is within experimental error. The shifts in the positions with composition are also predicted in the same systematic manner as is observed. Looking at the data in more detail, certain aspects merit comment. First, the calculated d-spacings are all slightly higher than those observed. This reflects the fact that we have assumed maximum lengths for the monomer residues, which will not be the case when there is any nonlinearity, as must occur in an actual chain. Secondly, the calculated peak at $2\theta = 43^\circ$ ($d = 2.12 \text{ Å}$) is very sharp and invariant. This maximum is the third-order of the HBA length (6.35 Å) and the eighth-order of the TPA-BP dimer length (17.01 Å) and hence is seen for all monomer ratios. This calculated half width is much less than that observed but is increased by consideration of chains with a distribution of monomer axial lengths, as will be discussed below.

When we convert from point to atomic monomers, it can be seen that the meridional peaks are predicted in essentially the same positions. Indeed, the agreement is improved in that we now resolve a peak in the 2.9 Å region. (No such peak is resolved for the point model, although the peak at $d = 3.2 \text{ Å}$ is asymmetric, suggesting a weak component at lower d
Visual inspection of the fiber diagrams shows that the intensity agreement is also reasonable, in that the first and second peaks are very weak compared to those at $d \approx 3.2$ and 2.1 Å. Note that in Figure 2.7, the peak at $d \approx 2.1$ Å has been truncated so that only ~ 6% of the peak height is shown. Furthermore, the first peak in the calculated data has a much broader profile than the second, as is observed.

The observed and calculated intensities are compared by study of the diffractometer data and the densitometer scan of the film data. Curve c in Figure 2.8 shows a $\theta / 2\theta$ diffractometer scan in the meridional direction for the 50/25/25 composition; the specimen used was the core of the molded plaque. Curve a shows the calculated data for this composition. It can be seen that the relative intensities in the 3 Å region match reasonably well. In the 6 Å region, the first peak is not resolved in the diffractometer scan, and the second peak is clearly more intense than that calculated. From our work on copoly(HBA/TPA/DHN) we know that the intensities in the 6 Å region are very sensitive to the molecular model chosen for the monomers. These intensities are weak because the $F_{AB}(Z)$ terms in equation (2.8) have minima in this region. Modification of the molecular model, e.g. by tilting the average monomers relative to the fiber axis to take account of nonlinearity of the chain, shifts these minima and can increase the intensity of the second peak relative to that of the first. However, we believe that the observed intensity discrepancy is more likely to be due to the development of three-dimensional order. The present one-dimensional calculations assume a nematic structure,
Figure 2.8  Observed and calculated meridional intensity data for 50/25/25 copoly(HBA/TPA/BP): (a) calculated data for an atomic model with constant residue lengths; (b) calculated data for an atomic model using a distribution of residue lengths shown in Figure 2.10; (c) observed data from a θ / 2θ diffractometer scan of a molded plaque along the meridional direction.
whereas the x-ray data indicates that the chains are packed in some type of register, at least in parts of the specimen. Our analyses of the three-dimensional structure in copoly(HBA/HNA) as described elsewhere [62] predict effects comparable to the observed intensification of certain meridional maxima.

The other obvious discrepancy between curves a and c in Figure 2.8 is in the width of the peak at \( d \approx 2.1 \AA \). The calculated peak is sharp due to the fact that it is an invariant Bragg peak. The finite half width of \( 0.006^\circ \) (26) is due to the fact that the ratio of lengths of the HBA residue and the TPA-BP dimer is only approximately (i.e., not exactly) integral (\( \sim 3:8 \)). The calculated peak has been truncated, and the actual integrated intensity is closer to that observed than it appears at first glance.

In the diffractometer data, some of the width of the 2.1 Å peak is due to instrumental effects. A truer representation of the meridional intensity is obtained by taking densitometer scans of the film data recorded with the specimen tilted for each successive meridional maximum. (Even then, some of the peak width is due to molecular disorientation.) Figure 2.9, curve a, shows these densitometer scans for the 6, 3, and 2 Å regions, taken from film data for the molded plaque interior tilted at the approximate Bragg angle. The three separate scans have been placed on approximately the same scale, based on the exposure time. It can be seen that the 2.1 Å peak is much narrower in the densitometer data. The width at half height is 1.4 °, which would yield a
Figure 2.9  
(a) Intensity profiles of meridional maxima at the 6, 3, and 2 Å regions for the molded 50/25/25 copoly(HBA/TPA/BP) plaque obtained by densitometer scans of the x-ray film data with the specimen tilted at the approximate Bragg angles.  
(b) Observed meridional intensity from a θ / 2θ diffractometer scan of the molded plaque.
crystallite size of 70 Å using the Scherrer equation. As has been discussed previously [55], the invariant peak can be treated as a Bragg reflection from a limited lattice. The 70 Å "crystallite size" is a measure of the correlation length for the extended chain conformation.

The discrepancy in peak width arisen (at least in part) from the fact that the model used for the chain is idealized in a fully extended conformation. Figure 2.10 shows a histogram of actual residue lengths derived from a survey of 50 chains of 16 monomers for the 50/25/25 copolymer set up using random monomer sequences. Construction of such a series of chains requires assumptions to be made with regard to the conformation: we assumed that the phenyl-ester torsion angles would be ± 30 ° or ± 150 ° (0 ° and 180 ° correspond to all planar conformations). The torsion angles were selected at random, but we required that there be approximately equal numbers (±2) of 130 °I and 1150 °I angles. This led to relatively extended conformations, but we also required that all the atoms of an individual chain should lie within a cylinder of diameter of 12 Å. This is somewhat arbitrary, but without such a restriction, a random monomer sequence can become appreciably nonlinear after 10 monomers, whereas the results so far indicate that the chain must be almost, if not complete, extended. It seems likely that the forces leading to liquid crystallinity also force the adoption of an extended conformation, just as the converse is true. The distribution of residue lengths in Figure 2.10 is broadest for TPA and narrowest for BP, with HBA intermediate. This arises largely for the way the monomers are defined,
Figure 2.10 Histogram of axially projected lengths of the comonomers in chain of 50/25/25 copoly(HBA/TPA/BP). This distribution was generated by considering 50 chains of 16 comonomers each.
i.e., for ester oxygen to ester oxygen. If the monomers were defined from the center of the C-O (ester) bond, then the distributions for the three residues would be more similar. (This would ultimately lead to generation of the same chain and hence the same intensities.)

When the residue distribution is incorporated into the calculations of \( l(Z) \), the results for an atomic model of the 50/25/25 copolymer are shown in Figure 2.8 (b). It is immediately apparent that incorporation of the distribution of residue lengths has broadened the peak at 2.1 Å, without having any major effects on the peaks at higher \( d \) (lower 2θ). Table 2.1 shows the \( d \) spacings of the predicted peaks. The changes are minor and in fact are all in the right direction. Previously the calculated \( d \) spacings were slightly higher than those observed: use of the length in distribution leads inevitably to shorter average residue lengths, and this results in a shift of all the peaks to slightly higher angles. The agreement now is well within experimental error. Table 2.1 also shows the equivalent data for other compositions. These were derived by using the length distributions for the 50/25/25 copolymer, which is not entirely justified but is probably an adequate approximation. It can be seen that the agreement for the \( d \)-spacings is also improved for each composition.

The use of monomer length distributions has improved our ability to predict the intensity distribution. In particular, the width of the peak at \( d = 2.1 \) Å is increased from 0.006° (2θ) for fixed lengths to 0.09°. At the same time, the peak height declined by a factor of 15, such that the
integrated peak intensity remains approximately the same. However, it is clear that further refinement of the model is necessary in order to increase the calculated width, which is still an order of magnitude less than the observed value of 1.4 °. (Note however, that some of this observed width is due to molecular disorientation, which results in smearing of the layer line streak.) We conclude that the polymer chains are more nonlinear than those considered so far and that the constraints on the torsion angles and overall chain diameter need to be relaxed further, so as to broaden the length distributions for the monomers. We are modifying the atomic coordinates consistent with nonlinearity of the chain to see if we can improve the match in the 2 Å region. In addition, we are extending our analyses to the three-dimensional structure, where the effects of chain packing are included.

C-3 Sensitivity of the X-ray Data to Nonrandomness

It is clear at this point that the nematic random copolymer model gives very good agreement with the observed diffraction data. Such defects as remain are only minor details. No independent information is available on the actual sequence distribution: NMR methods cannot be used due to insolvency of the polymer. Thus it is necessary to address the sensitivity of the data to nonrandomness. This can be done by modifying the monomer sequence statistics, via alteration of the $f_{BB}$ terms in the $M$ matrix.
We have considered a simple model in which the B-B, D-D, T-P, and P-T reactions that produce homopoly(HBA) and the alternating copoly(TPA/BP) are more likely than the four cross-reaction B-T, T-D, D-P, and P-B, which are all assumed to have the same probabilities, i.e.

\[
\begin{align*}
    r_{BB} &= r_{DD} \\
    r_{TP} &= r_{PT} \\
    r_{BT} &= r_{TD} = r_{DP} = r_{PB}
\end{align*}
\]

These \( r_{AB} \) terms are normalized such that \( \sum_B r_{AB} p_B = 1.0 \), and the homopolymer terms are related through

\[
r_{TP} = \frac{p_T - p_B - r_{BB} p_B^2}{p_T^2}
\]  \( (2.10) \)

We then define a ratio \( r_H / r_C \) as a measure of blockiness, where

\[
r_H / r_C = r_{BB} / r_{BT}
\]  \( (2.11) \)

It is of course debatable whether these probabilities will be equal or whether the first nearest-neighbor probabilities will be independent of the second and third nearest neighbors, but the present model is a good starting point for consideration of the effects of blockiness.
Figure 2.11 shows plots of \( I(Z) \) for the 50/25/25 composition calculated for the random copolymer (\( r_H / r_C = 1.0 \)) and for nine blocky compositions up to \( r_H / r_C = 100 \). It can be seen that blocky composition leads to shifts in the peaks that are predicted for the random structure and to the development of new peaks. The peak position for a wider range of \( r_H / r_C \) ratios are listed in Table 2.2. When \( r_H / r_C = 100 \), the structure is extremely blocky, and maxima are predicted at orders of 6.35 and 17.01 Å, which correspond to the repeats for the blocks of poly(HBA) and poly(TPA/BP). Essentially the same peaks are seen at \( r_H / r_C = 10 \) and 5: the peak widths increase with decreasing \( r_H / r_C \), reflecting the fact that the homopolymer blocks get shorter as cross-reaction becomes more likely. As \( r_H / r_C \) is decreased to 3 and 2, the peak positions begin to change, but the calculated data are easily distinguished for those observed. Figure 2.11 shows equivalent data between \( r_H / r_C = 2.0 \) and 1.0, where the changes become less obvious. The peaks at 5.92, 3.30, and 2.12 Å remain constant. There is a small shift in the peak at 2.95 Å (to 2.88 Å) and a larger shift in the peak at 7.47 Å (to 8.00 Å). These data were obtained by using constant residue lengths, but the same sort of effects would be expected if we incorporated the length distribution function.

Thus we predict a shift of 0.5 Å for the first peak for the 50/25/25 copolymer as blockiness is increased from random to \( r_H / r_C = 2.0 \). Unfortunately this peak is weak and diffuse and difficult to measure to an accuracy better than \( \pm 0.2 \) Å using the film data. Hence we can rule out
Figure 2.11  Calculated meridional intensities of an atomic model of 50/25/25 copoly(HBA/TPA/BP) chain at different degrees of blockiness defined by the ratio $r_H/r_C$. The random copolymer corresponds to $r_H/r_C = 1$. 
Table 2.2  Effect of nonrandomness of the peak positions of meridional maxima for 50/25/25 copoly(HBA/TPA/BP).

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Obsd.

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nonrandomness for \( r_H / r_C \geq 1.6 \), based on the peak positions. In comparison, the first peak for copoly(HBA/HNA) is predicted to shift by 0.7 Å over the same range and is sharper and more intense, and we can rule out \( r_H / r_C \geq 1.4 \). However, for the present polymer we predict a peak at 4.17 Å for \( r_H / r_C = 1.4 \) which is not detected in the observed data, and hence we can extend the limits to the latter figure. Note that, at \( r_H / r_C = 1.4 \), there is still significant nonrandomness: for example, the possibility of \((\text{HBA})_4\) units is 1.59 times greater than in the random copolymer. Nevertheless, the proportion of homopolymer blocks is still very low, and the high crystallinity observed cannot be due to just these sequences; rather it must involve crystallization of random sequences.

Hence we are able to use x-ray methods to rule out blocky structures, at least within the limits defined above, with \( r_H / r_C \geq 1.4 \). This is a significant observation, since we are currently unable to investigate sequence distribution by NMR methods. The conclusion that the polymer is at least close to having a completely random structure is interesting in view of the fact that the monomers probably have different reactivities and that TPA is insoluble in the initial synthesis mixture. It seems likely that transesterification will randomize the copolymer at a relatively early stage of the synthesis, perhaps after the formation of oligomers.
CHAPTER THREE

X-RAY ANALYSIS OF ANNEALED STRUCTURE OF COPOLY(p-HYDROXYBENZOIC ACID / 2-HYDROXY-6-NAPHTHOIC ACID)

A. Introduction

The x-ray diffraction patterns of as-spun copolymers of p-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) show a high degree of axial orientation and the presence of three-dimensional order. The meridional maxima are aperiodic and imply a random comonomer sequence [63,57]. The d-spacings of the equatorial maxima indicate hexagonal packing of the chains [62]. Nevertheless, there has been extensive debate as to whether this structure is retained in the annealed specimens, especially as regards the random chain sequence. Polymorphism in the analogous liquid crystalline polyester based on HBA, terephthalic acid, and 4,4'-biphenol has been reported to occur as a result of annealing [64,61]. The wide angle x-ray diffraction data indicated that three different crystalline packings can exist: a quenched hexagonal form, Bq, an orthorhombic form, B, and a low-temperature orthorhombic form, A, which can only be reconverted to the B form. Recently, the structural changes of another copolymer of HBA and HNA during thermal treatment were studied by thermal analysis [65]. The DSC data indicated that two transition processes for the thermotropic
copolymesters: a fast process which occurs during quenching from their nematic melts and forming quenching form crystals with hexagonal packings, and a slow process which develops gradually with increasing annealing time as annealed form crystals with orthorhombic packings. In this chapter, we describe x-ray analyses of the structures that develop on annealing in oriented specimens of copoly(HBA/HNA), as regards the monomer sequence distribution and the chain conformation and packing.

As will be seen below, the fiber diffraction data of 75/25 copoly(HBA/HNA) change considerably as a result of annealing: notably a number of new Bragg reflections appear, such that a series of layer lines and row lines become clearly visible in the x-ray pattern. The appearance of two additional meridional reflections and small changes in d-spacings for some of the others mean that we must consider the possibility that the monomer sequence is modified via transesterification during annealing. The effect of non-randomness on the meridional maxima and layer line positions will be addressed by calculating intensity transforms of single chains, arranged over all possible sequences defined by the monomer combination statistics. In addition, the Bragg reflections that develop during thermal treatment indicate a change in the chain packing. In the as-spun state, three equatorial maxima are seen at \( d = 4.6, 2.6, \) and 2.3 Å, plus an off-equatorial at \( d \approx 3.3 \) Å, and these can be indexed by a two-chain pseudohexagonal unit cell with dimension \( a = 5.3 \) Å and \( b = 9.18 \) Å [62]. In the case of annealed fibers, seven Bragg equatorial maxima are observed, and these are indexed for a two chain
orthorhombic unit cell with dimension \( a = 7.6 \) Å and \( b = 5.7 \) Å. The dimensional changes between the as-spun and annealed states may result from the differences in the chain conformation. Models for the chain packing in the solid state have been constructed and the calculated equatorial intensities has been compared with the observed data in order to refine the structure.

A-1 Cylindrically Averaged Intensity Transforms

The intensity from a three-dimensional arrangement of \( N \) atoms in space is given by

\[
I(X,Y,Z) = F(X,Y,Z) F^* (X,Y,Z) \tag{3.1}
\]

where

\[
F(X,Y,Z) = \sum_{j=1}^{N} f_j \exp[2\pi i (Xx_j + Yy_j + Zz_j)] \tag{3.2}
\]

and \( * \) denotes the complex conjugate. \( f_j \) is the atomic scattering factor of the \( j \)th atom having coordinates \( x_j, y_j, z_j \), and \( X, Y, Z \) are the reciprocal space coordinates. In the case of fiber symmetry, it is convenient to express \( F(X,Y,Z) \) in cylindrical polar coordinates, whereupon equation (3.2) can be rewritten
\[ F(R,\Phi,Z) = \sum_{j=1}^{N} f_j \exp[2\pi i (n_R \cos(\Phi - \phi_j) + Z z_j)] \] (3.3)

where \( r_j, \phi_j, z_j \) and \( R, \Phi, Z \) are the real space atomic coordinates and reciprocal space coordinates, respectively. The intensity, \( I(R,\Phi,Z) \), is proportional to \( |F(R,\Phi,Z)|^2 \). For fiber symmetry, there will be cylindrical averaging of \( I(R,\Phi,Z) \), and the fiber diagram is a representation of the two-dimensional intensity, \( I(R,Z) \).

A model of a short segment of a chain of copoly(HBA/HNA) with a typical random sequence is shown in Figure 3.1. The planar aromatic and ester groups along with the 1,4 and 2,6 aromatic linkages lead to a relatively straight chain. Consequently, the axial advance per residue is approximately independent of the torsion angles between the aromatic and ester groups. The theoretical meridional intensity, \( I(0,Z) \), is derived by considering the projection of the structure on the chain axis, and is thus approximately independent of the chain conformation. However, when we consider the entire diffraction pattern, i.e., \( I(R,Z) \), then the actual chain conformation becomes important. Chivers and Blackwell [66] have derived equations for the diffracted intensity from copolymer chains at two extremes of the possible conformation:

1. An extended random conformation for which there is a completely random set of torsion angles between the planar aromatic and ester groups in the chain. This corresponds approximately to cylindrically
Figure 3.1 A model of a short segment of a chain of copoly[HBA/MNA] with a typical random sequence [54].
averaging each monomer residue independently in real space, as is shown schematically in Figure 3.2 (a). The resulting chain would have a cylindrical cross section with no rotational correlation between adjacent monomers and would be expected to pack in an hexagonal array, consistent with the equatorial data for the as-spun fibers. The intensity distribution for such a chain is given by

\[
I(R,Z) = \sum_{A} \sum_{B} \sum_{l} Q_{AB}(z_l) [A_{AB}(R,Z) \cos(2\pi Z z_l) + B_{AB}(R,Z) \sin(2\pi Z z_l)]
\]

(3.4)

where

\[
A_{AB}(R,Z) = \sum_{j} \sum_{k} f_{A,j} f_{B,k} J_0(2\pi R r_{A,j}) J_0(2\pi R r_{B,k}) \cos[2\pi Z(z_{B,k} - z_{A,j})]
\]

(3.5)

and \(B_{AB}(R,Z)\) is the equivalent sine term. \(Q_{AB}(z_l)\) defines the probability of a comonomer sequence of length \(z_l\) starting with monomer A and ending with monomer B. The subscripts \(A,j\) and \(B,k\) denote the jth atom of monomer A and the kth atom of monomer B. \(J_0\) is the zeroth-order Bessel function for the argument specified.

(2) An extended rigid chain with specific torsion angles repeated along the chain. In the example shown in Figure 3.2 (b), the aromatic-ester and ester-aromatic torsion angles were set at +30° and -30°, respectively
Figure 3.2  (a) Schematic representation of cylindrical averaging of monomers for an extended random conformation model of the copolymer chain. (b) Schematic representation of cylindrical averaging of the entire chain leading to the extended rigid conformation model [54].
leading to a ribbon-like chain conformation in which the planes of the aromatic groups are all parallel to one another. In this case, \( I(R, Z) \) is derived by cylindrical averaging of the full three-dimensional intensity transform \( I(R, \Phi, Z) \); i.e., the cylindrical averaging is done in reciprocal space. \( I(R, Z) \) has the same form as equation (3.4) except that \( A_{AB}(R, Z) \) and \( B_{AB}(R, Z) \) are defined as sums over nth-order Bessel functions of the first kind

\[
A_{AB}(R, Z) = \sum_{n} \sum_{j} \sum_{k} f_{A,j} f_{B,k} J_n(2\pi R r_{A,j}) J_n(2\pi R r_{B,k}) 
\cos[n(\phi_{A,j} - \phi_{B,k}) + 2\pi Z(z_{A,j} - z_{B,k})]
\] (3.6)

and \( B_{AB}(R, Z) \) is the equivalent sine term.

The above calculations can be simplified by modelling the chain as a one-dimensional paracrystalline lattice with random coordination statistics for the constituent polyatomic monomers [59]. Following our previous treatment of the one-dimensional case in chapter 2, the meridional intensity distribution for an infinite chain is written as

\[
I(Z) = \sum_{A} P_{A} F_{AA}(Z) + 2 \operatorname{Re} \sum_{A} \sum_{B} F_{AB}(Z) T_{AB}(Z)
\] (3.7)

where \( T_{AB}(Z) \) represents an element of the matrix \( T \), defined as

\[
T = P \frac{M \cdot X(Z)}{1 - M \cdot X(Z)}
\] (3.8)
\( P = \begin{bmatrix} P_B & 0 \\ 0 & P_N \end{bmatrix} \quad M = \begin{bmatrix} M_{BB} & M_{BN} \\ M_{NB} & M_{NN} \end{bmatrix} \quad X = \begin{bmatrix} X_B & 0 \\ 0 & X_N \end{bmatrix} \)

where the subscripts B and N are further abbreviations of HBA and HNA, respectively. For example, \( P_B \) is the molar composition of monomer B, and \( X_B \) is the phase term for monomer B (equal to \( \exp(2\pi Z_{zB}) \)). \( M_{BB} \) is the combination probability for the BB monomer pair and is defined as \( M_{BB} = r_{BB} P_B \). In a completely random copolymer, \( r_{BB} = 1 \) and \( M_{BB} = P_B \). \( r_{BB} \) can be varied from unity to simulate non-random sequence distributions.

Since the total probability of each neighbor must equal unity, the following relationships are obtained:

\[
M_{BB} + M_{BN} = r_{BB} P_B + r_{BN} P_N = 1.0 \quad (3.9)
\]

\[
M_{NB} + M_{NN} = r_{NB} P_B + r_{NN} P_N = 1.0 \quad (3.10)
\]

\[
r_{BN} - r_{NB} = 0 \quad (3.11)
\]
We then define \( r_H \) and \( r_C \) represent tendencies for forming homopolymer blocks (\( B_N \) or \( N_N \)) and alternating copolymer blocks (\( B_N \)), respectively. The deviations from randomness are defined by the ratio \( r_H / r_C \). For this ratio we will use \( R_{HC} = r_{BB} / r_{BN} \). This is related to the alternative \( r_{NN} / r_{NB} \), but is not the same except for the 50/50 composition or for the random monomer sequence. \( r_{BB}, r_{BN}, r_{NB}, \) and \( r_{NN} \) terms are related through

\[
\begin{align*}
  r_{BB} &= \frac{r_{BB}/r_{BN}}{(r_{BB}/r_{BN})P_B + P_N} = \frac{R_{HC}}{R_{HC}P_B + P_N} \\
  r_{BN} &= r_{NB} = \frac{1}{R_{HC}P_B + P_N} \\
  r_{NN} &= \frac{R_{HC}P_B + P_N - P_B}{P_N(R_{HC}P_B + P_N)}
\end{align*}
\]  

(3.12) (3.13) (3.14)

It will be seen that in order to generate the intense layer line that occurs between the equator and the first meridional maximum, a physical dimer repeat must be assumed [67]. In this case the interference effects originate from the spatial correlations of the four dimers BB, BN, NB, and NN, and the matrices \( P, M, \) and \( X \) are defined as
\[ P = \begin{bmatrix} P_{BB} & 0 & 0 & 0 \\ 0 & P_{BN} & 0 & 0 \\ 0 & 0 & P_{NB} & 0 \\ 0 & 0 & 0 & P_{NN} \end{bmatrix} \]

\[ M = \begin{bmatrix} M_{BBBB} & M_{BBBN} & M_{BBNB} & M_{BBNN} \\ M_{BBNB} & M_{BBNN} & M_{BBNN} & M_{BBNN} \\ M_{NNBB} & M_{NNBN} & M_{NNNB} & M_{NNNN} \\ M_{NNNB} & M_{NNBN} & M_{NNNB} & M_{NNNN} \end{bmatrix} \]

\[ X = \begin{bmatrix} X_{BB} & 0 & 0 & 0 \\ 0 & X_{BN} & 0 & 0 \\ 0 & 0 & X_{NB} & 0 \\ 0 & 0 & 0 & X_{NN} \end{bmatrix} \]

The dimer composition term is defined as, for example, \( P_{BN} = r_{BN} P_{BN} \). \( M_{BNBN} \) is the combination probability for the BN dimer pair and is defined as \( M_{BNBN} = r_{NB} P_{BN} \). The phase term for dimer BN, \( X_{BN} \), is equal to \( \exp(2\pi i z_{BN}) \), where \( z_{BN} \) is the length of dimer BN.

When we extend from a one- to a two-dimensional calculation in order to predict \( I(R, Z) \), equation (3.4) is written in the form of equation (3.7) as

\[
I(R, Z) = \sum_{A} P_{A} F_{AA}(R, Z) + 2 \text{Re} \sum_{A} \sum_{B} F_{AB}(R, Z) T_{AB}(Z)
\]  \hspace{1cm} (3.15)

For the extended random conformation, \( F_{AB}(R, Z) \) is given by
\[ F_{AB}(R, Z) = \sum_{j} \sum_{k} f_{A,j} f_{B,k} J_0(2\pi R r_{A,j}) J_0(2\pi R r_{B,k}) \]
\[ \exp[2\pi iZ(z_{B,k} - z_{A,j})] \quad (3.16) \]

and for the extended rigid conformation, the corresponding \( F_{AB}(R, Z) \) is given by

\[ F_{AB}(R, Z) = \sum_{n} \sum_{j} \sum_{k} f_{A,j} f_{B,k} J_n(2\pi R r_{A,j}) J_n(2\pi R r_{B,k}) \]
\[ \exp[2\pi i [(n/2\pi)(\phi_{A,j} - \phi_{B,k}) + Z(z_{A,j} - z_{B,k})]] \]
\[ = \sum_{j} \sum_{k} f_{A,j} f_{B,k} J_0(2\pi R r_{A,j}, B,k) \exp[2\pi iZ(z_{B,k} - z_{A,j})] \quad (3.17) \]

\( r_{A,j}, B,k \) represents the interatomic distance between the jth atom of dimer A and the kth atom of dimer B. The paracrystalline lattice defined by \( T_{AB}(Z) \) remains the same while the Fourier transforms of the monomer pair convolutions, \( F_{AB}(R, Z) \), change with conformation.

**A-2 Diffraction by Ordered Regions in Fibers**

Streaks along layer lines are common occurrences in x-ray fiber patterns. They indicate that although the chains are oriented and have a regular conformation, the crystalline order in directions perpendicular to the fiber axis is poor developed. Biswas and Blackwell [62] have demonstrated that sampling on all the non-periodic layer lines for random
copoly(HBA/HNA) occurs when (finite) random sequences have their origins in a register plane perpendicular to the chain axes. This chain register along the lateral direction can be reduced by incorporating a normal distribution of the origin monomers about the register plane. Sampling on higher layer lines is reduced as \( \sigma \), the standard deviation of the normal distribution, is increased, corresponding to a reduced preference for registration.

Biswa and Blackwell [68] also showed that the total interference function for a parallel bundle of \( M \) finite chains can be separated into intra- and interchain interference components, that is

\[
I(R,Z) = I_1(Z) + I_2(R,Z) \tag{3.18}
\]

where

\[
I_1(Z) = M I_a(Z)
\]

and \( I_a(Z) \) is the intrachain interference between \( N \) dimers, given by

\[
I_a(Z) = N \text{Re} \left[ \frac{1 + H(Z)}{1 - H(Z)} - \frac{2 H(Z) (1 - H^N(Z))}{N (1 - H(Z))^2} \right] \tag{3.19}
\]

\( H(Z) \) is the product of matrices \( M \) and \( X \), defined previously. Two extreme cases are considered for the total interchain interference, \( I_2(R,Z) \):
(1) When there are no rotational correlations between dimers on adjacent chains:

\[ I_2(R,Z) = A(Z) I_B(R,Z) I_C(R) \]  \hspace{1cm} (3.20)

where \( I_B(R,Z) \) and \( I_C(R) \) are the interchain interference and the interference function on the basal plane attributed to the packing arrangement, respectively. \( A(Z) \) is the distribution function describing axial register.

\[ A(Z) = \exp(-2\pi^2 Z^2 \sigma^2) \]  \hspace{1cm} (3.21)

and \( I_B(R,Z) \) and \( I_C(R) \) can be expressed as

\[ I_B(R,Z) = \text{Re} \sum_A \sum_B F_{AB}(R,Z) [U_{AB}(Z) + 2V_{AB}(Z)] \]  \hspace{1cm} (3.22)

\[ I_C(R) = \sum_m \sum_{m'} J_0(2\pi R r_{mm'}) ; \quad m \neq m' \]  \hspace{1cm} (3.23)

where

\[ F_{AB}(R,Z) = \sum_j \sum_k f_{A,j} f_{B,k} J_0(2\pi R r_{A,j}) J_0(2\pi R r_{B,k}) \exp[2\pi i Z(z_{B,k} - z_{A,j})] \]  \hspace{1cm} (3.24)

Here, \( F_{AB}(R,Z) \) is the Fourier transform of the cross convolution of dimer \( A \) with dimer \( B \) after each has been cylindrically averaged in real space.
\( r_{mm} \) represents the interchain vector. \( U_{AB}(Z) \) and \( V_{AB}(Z) \) are elements of \( U(Z) \) and \( V(Z) \) matrices of interference terms arising from interactions between corresponding and noncorresponding residues on different chains, respectively. \( U(Z) \) and \( V(Z) \) are defined as [62]

\[
U(Z) = C_{0} + C(Z) \left[ \frac{I - S^{N-1}(Z)}{I - S(Z)} \right]
\]

\[
V(Z) = C_{0} H(Z) \left( \frac{I - H^{N-1}(Z)}{I - H(Z)} \right) + \frac{C(Z) H(Z)}{S(Z) - H(Z)} \left[ \frac{I - S^{N-1}(Z)}{I - S(Z)} \right] - \frac{I - H^{N-1}(Z)}{I - H(Z)}
\]

where

\[
C_{0} = P.M
\]

\[
S = \begin{bmatrix} K(Z) & 0 \\ 0 & K(Z) \end{bmatrix}
\]

\[
K(Z) = H(Z) H^{*}(Z)
\]

\[
C = \begin{bmatrix} C_{BBBB} & C_{BBBN} & C_{BBNB} & C_{BBNN} \\ C_{BBNB} & C_{BBNN} & C_{BBNB} & C_{BBNN} \\ C_{NBBB} & C_{NBBN} & C_{NBNB} & C_{NBNN} \\ C_{NNBB} & C_{NNBN} & C_{NNNB} & C_{NNNN} \end{bmatrix}
\]

and
\[ C_{BBB} = P_{BB}^r P_{BB} P_{BB} \]
\[ C_{BBBN} = P_{BB}^r P_{BB} P_{BN} \exp[2\pi i Z(z_{BN} - z_{BB})] \]

etc.

(2) When definite correlations between residues of different chains in the crystallite are imposed, the separation of the \( I_B(R,Z) \) and \( I_C(R) \) terms in the total interchain interference is not allowed. Biswas and Blackwell [68] have derived equations for rigid correlations between all dimers on all chains, where \( F_{AB}(R,Z) \) has to be replaced by \( F'_{AB}(R,Z) \) which incorporates \( I_C(R) \). Then

\[ I_2(R,Z) = A(Z) \text{Re} \sum_{A} \sum_{B} F'_{AB}(R,Z) [U_{AB}(Z) + 2V_{AB}(Z)] \quad (3.27) \]

where

\[ F'_{AB}(R,Z) = 2 \sum_{n=0}^{\infty} [R_n(R) A_{n,AB}(R,Z) + S_n(R) B_{n,AB}(R,Z)] \quad (3.28) \]

The prime in the summation over \( n \) indicates that only half weight is given to \( n = 0 \). For a \( M_1 \times M_2 \) array of chains separated by \( a \) along the x-axis and \( b \) along the y-axis in an orthorhombic lattice, \( R_n(R) \) and \( A_{n,AB}(R,Z) \) can be further expressed as follows:
\[
R_n(R) = 4 \sum_{p=0}^{M_1-1} \sum_{q=0}^{M_2-1} (M_1-p) (M_2-q) J_n[2\pi R(p^2 a^2 + q^2 b^2)^{1/2}] \cos(n\phi_{11}) \\
+ 4 \sum_{p=0}^{M_1-1} \sum_{q=0}^{M_2-1} [M_1-(p+1/2)] [M_2-(q+1/2)] J_n[2\pi R((p+1/2)^2 a^2 + (q + 1/2)^2 b^2)] \cos(n\phi_{12})
\]

where

\[
\phi_{11} = \tan^{-1}(qb / qa) \\
\phi_{12} = \tan^{-1}[(q+1/2)b / (p+1/2)a]
\]

\[
A_{n,AB}(R,Z) = \sum_j \sum_k f_{A,j} f_{B,k} J_n(2\pi R r_{A,j} B_k) \exp[2\pi i Z(z_{B,k} - z_{A,j})] \cos(n\phi_{A,j} B_k)
\]

where $\phi_{A,j} B_k$ is the angle between the jth atom of dimer A and kth atom of dimer B. $S_n(R)$ and $B_{n,AB}(R,Z)$ are the corresponding sine components.

The layer line intensity can be partially simulated by calculation of the cylindrically averaged transforms of single chains. The two extremes of chain conformations (random and rigid) were used for these calculations. Therefore, the entire diffraction pattern was predicted using equation (3.15) with consideration of the two cases of correlations between dimers. The effects of dimer conformation on the equatorial intensity, $I(R,0)$, will be discussed further.
B. Experimental Section

Sample Preparation Specimens of the copolymer containing 75 % HBA and 25 % HNA were supplied by Hoechst-Celanese Corp., Summit, NJ, in form of pellets. Specimens for x-ray analysis were bundles of parallel fibers drawn by hand from the melt. The fibers were examined in the as-drawn state and after annealing for different lengths of time at 270° C, which is about 20° C below the melting point. The fibers were heat treated inside a glass tube, which had been purged several times with nitrogen gas and then sealed. For the DSC scans, the pelletized samples were sliced into small pieces, which were sealed in glass tubes and annealed for different times at 270° C.

X-ray Diffraction X-ray fiber diagrams were recorded on Kodak no-screen film using Ni-filtered CuKα radiation and a Searle toroidal focusing camera. The d-spacings were calibrated with calcium fluoride. Equatorial data were recorded as a θ / 2θ scan, using a Nicolet X-200 area detector at E. I. du Pont de Nemours, Wilmington, DE. The intensity profile of first layer line in the R,Z map was obtained by scanning the film pattern using an Optronics P1000 densitometer.

Thermal Analysis The thermal properties of the material were investigated with a Perkin-Elmer DSC 7. The heating rate was 20° C/min. Samples weights for DSC scan were controlled in a range of 10-15 mg. All thermal analyses were run under dry nitrogen.
C. Results and Discussion

C-1 X-ray Fiber Diagrams

The x-ray fiber diffraction patterns of 75/25 copoly(HBA/HNA) are shown in Figure 3.3 (a) for the as-drawn state and (b) for the same specimen annealed for 30 days. The fiber axis is vertical for these and all subsequent diffraction diagrams, except where specified. Figure 3.4 shows the x-ray patterns of annealed specimen, taken with the chain axis inclined at 14° to the x-ray beam, in the vertical plane. The x-ray data consist of a series of intensity maxima that appear as relatively short arcs, indicating a high degree of orientation parallel to the fiber axis. It can be seen that off-equatorial and off-meridional maxima, which point to the presence of three-dimensional order, increase in sharpness as we go from the as-drawn (Figure 3.3 (a)) to annealed (Figure 3.3 (b)). It is interesting that, for the annealed specimen, sampling occurs on the higher layer lines, which are only continuous streaks for the as-drawn specimen, i.e. axial register is improved as a result of the heat treatment.

The monomer sequence will be analyzed based on the meridional maxima and layer line positions. Table 3.1 shows the d-spacings of the meridional maxima for the as-drawn and annealed specimens. For most semicrystalline polymers, there is a repeat along the chain, which is defined by the physical arrangement of identical units. The reflections along the meridian have to be orders of this repeat. However, in the x-ray
Figure 3.3  Fiber diffraction patterns from (a) melt-drawn and (b) annealed samples of 75/25 copoly(HBA/HNA). The annealing time was 30 days. The fiber axis is vertical.
Figure 3.4  X-ray diffraction pattern from annealed fiber of 75/25 copoly(HBA/HNA). The chain axis is inclined at 14° from the plane perpendicular to the beam.
Table 3.1  d-spacings of observed meridional intensity maxima for the as-spun and the annealed specimens of 75/25 copolymer. The annealed sample was subjected to 30 days annealing.

<table>
<thead>
<tr>
<th>d spacings (Å)</th>
<th>As-spun</th>
<th>Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>13.5 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>6.71 ± 0.05</td>
<td></td>
<td>6.82 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>3.33 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>3.03 ± 0.02</td>
<td></td>
<td>3.02 ± 0.02</td>
</tr>
<tr>
<td>2.05 ± 0.03</td>
<td></td>
<td>2.06 ± 0.03</td>
</tr>
</tbody>
</table>


diagram of 75/25 copoly(HBA/HNA) in the as-drawn state, we observe three non-periodic maxima. This aperiodicity implies a random monomer sequence [69]. Five maxima are observed in the fiber diagrams of the annealed sample. The d-spacing of the first meridional reflection, $13.5 \pm 0.2$ Å, is about within experimental error of the length of the average dimer: for 75/25 copolymer this is about $13.7$ Å. A meridional at $d \approx 3.33$ Å is resolved on tilting of the specimen (Figure 3.4). The other three maxima are similar to those for the as-spun state, although there is a small variation in d-spacings for one of these: the d-spacing of the first meridional reflection for as-drawn, $6.71 \pm 0.05$ Å, is changed to $6.82 \pm 0.05$ Å on annealing; the other two reflections at $3.03$ and $2.05$ Å stay as unchanged within experimental error. This would suggest that, if there are changes in the monomer sequence as a result of annealing, these are only small deviations from a fully random structure.

Figure 3.5 shows a schematic representation of the flat plate x-ray diffraction fiber diagram for the annealed specimen. Annealing leads to the sampling of the layer lines, which are indicated by the dashed lines in Figure 3.5. The reciprocal space Z coordinates and meridian d-spacings for the observed layer lines are given in Table 3.2. The first, second, third, and fifth layer lines at $d = 13.5, 6.82, 4.52,$ and $3.33$ Å could be the first, second, third, and fourth orders of $13.5$ Å. But the d-spacing of the seventh layer line, $2.51$ Å, is neither the fifth nor the sixth order of $13.5$ Å ($= 2.7$ Å or $2.25$ Å); similarly, the layer lines at $d = 3.98, 3.02,$ and $2.06$ Å
Figure 3.5  Schematic representation showing numbers of the layer lines of the flat plate x-ray diffraction fiber diagram for the annealed specimen. The layer lines are indicated by the dashed lines.
Table 3.2  Observed layer line positions for a specimen of 75/25 copoly(HBA/HNA) that had been annealed for 30 days.

<table>
<thead>
<tr>
<th>Layer Line #</th>
<th>Z (Å(^{-1}))</th>
<th>Meridian d-spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.074</td>
<td>13.5 ± 0.2</td>
</tr>
<tr>
<td>2</td>
<td>0.146</td>
<td>6.82 ± 0.05</td>
</tr>
<tr>
<td>3</td>
<td>0.221</td>
<td>4.52 ± 0.03</td>
</tr>
<tr>
<td>4</td>
<td>0.251</td>
<td>3.98 ± 0.03</td>
</tr>
<tr>
<td>5</td>
<td>0.300</td>
<td>3.33 ± 0.03</td>
</tr>
<tr>
<td>6</td>
<td>0.331</td>
<td>3.02 ± 0.02</td>
</tr>
<tr>
<td>7</td>
<td>0.398</td>
<td>2.51 ± 0.02</td>
</tr>
<tr>
<td>8</td>
<td>0.485</td>
<td>2.06 ± 0.03</td>
</tr>
</tbody>
</table>
are not order of 13.5 Å. Thus, the layer line positions indicate that the annealed specimen retains a non-periodic structure.

In this thesis we will also investigate the changes in chain conformation and packing, based on the equatorial and off-equatorial maxima. Three equatorial maxima at \( d = 4.55, 2.63, \) and \( 2.29 \) Å observed for the as-drawn sample indicate a hexagonal base plane unit cell with dimensions \( a = 5.2 \) Å. However, in order to index the first layer line reflection at \( d = 3.3 \) Å, it is necessary to use a two chain pseudohexagonal unit cell with dimensions \( a = 9.18 \) Å and \( b = 5.30 \) Å [62]. For the annealed specimen seven equatorial maxima are observed, with d-spacings listed in Table 3.3. Least square refinement yields an orthorhombic unit cell with dimensions \( a = 7.6 \) Å and \( b = 5.7 \) Å. The hkl indices for the reflections are also given in Table 3.3. The differences between the observed and calculated d-spacings are within experimental error. Note that the equatorial d-spacings for the as-drawn specimen are very close to the d-spacings of the 110, 120, and 220/310 reflections for the annealed fiber. It seems that two forms of unit cell may co-exist in the annealed fiber, and this is further confirmed by the DSC data, which will be discussed later. Significantly, the base plane of unit cell for the as-drawn specimen is approximately 12 % larger than that for the annealed specimen. This is a large decrease in density, greater than that expected due to a polymorphic change without a major change in chain conformation.
Table 3.3  Comparsion of the observed and calculated equatorial d-spacings of the annealed 75/25 copoly(HBA/HNA).

<table>
<thead>
<tr>
<th>hkl</th>
<th>$d_{\text{obs}}$ (Å)</th>
<th>$d_{\text{calc}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>7.6 ± 0.1</td>
<td>7.60</td>
</tr>
<tr>
<td>010</td>
<td>5.7 ± 0.1</td>
<td>5.70</td>
</tr>
<tr>
<td>110</td>
<td>4.57 ± 0.03</td>
<td>4.56</td>
</tr>
<tr>
<td>200</td>
<td>3.83 ± 0.05</td>
<td>3.80</td>
</tr>
<tr>
<td>210</td>
<td>3.13 ± 0.04</td>
<td>3.16</td>
</tr>
<tr>
<td>120</td>
<td>2.69 ± 0.04</td>
<td>2.67</td>
</tr>
<tr>
<td>220/310</td>
<td>2.33 ± 0.05</td>
<td>2.32</td>
</tr>
</tbody>
</table>
Similar changes of base plane dimensions have been reported to occur for the homopolymer poly(HBA) [70-72], based on x-ray and electron diffraction data. At least three crystalline modifications were reported [71]: at room temperature, the lattice parameters \(a = 7.52\), \(b = 5.70\), and \(c = 12.49\) Å were for polymer crystals of phase I. For oligomer crystals, a designated phase II was observed, with dimensions \(a = 3.77\), \(b = 11.06\), and \(c = 12.89\) Å. At about 360° C, the lattice parameters for the polymer changed to \(a = 9.2\), \(b = 5.3\), and \(c = 12.4\) Å, and this structure was designated phase III. By application of heating and cooling cycles to an oligomer crystal of phase II, it was found that modification I appears with increasing temperature, but it coexists with phase II. During further heating phase II disappears first at approximately 260° C. After further heating to 360° C, phase III appears at the expense of phase I. Cooling of the crystal from this stage, however, leads back to the phases I and II. It is very significant that the lattice parameters for 75/25 copoly(HBA/HNA), as described above, are very similar to those of poly(HBA) single crystals. Specifically, the lattice parameters \(a\) and \(b\) of the as-spun sample are close to those of phase III. For the annealed sample, the \(a\) and \(b\) parameters are like those of phase I. Thus, it seems appropriate to adopt phase I of poly(HBA) as a model for the structure of the annealed copolymer and the structural analysis will be addressed below.
C-2 Effects of Non-randomness on Intensity Transform

We have assumed a pseudo \(2_1\) conformation for four dimers in the copolymer, analogous to the proposed structure of poly(HBA) [73]. Atomic coordinates for the dimer residues were derived by using standard bond lengths and angles and the torsion angle between the planar aromatic and ester groups was set 38.4°, which was proposed by Sun and Blackwell [74] for the structure of poly(HBA). Figure 3.6 shows the conformation of the HBA dimer with parallel aromatic planes. The phenyl-ester torsion angles, \(\phi_1\) and \(\phi_2\), were set alternately at 38.4°, 141.6°, leading to a \(2_1\) helix; \(\phi_1 = 0^\circ\) when \(C_1=O_2\) (carbonyl) is cis to \(C_2-C_4\), \(\phi_2 = 0^\circ\) when \(C_1'=O_2'\) is cis to \(C_2'-C_4'\). \(I(R,Z)\) was calculated on a 201 X 201 grid along the positive R and Z axes, respectively, but limited to scattering angles of \(2\theta \leq 50^\circ\) \((\theta = \sin^{-1} \left[ \lambda/2(R^2 + Z^2)^{1/2} \right])\). The data were displayed on the monitor of an AED 512 color terminal. All four R,Z quadrants were plotted for comparison with the observed diffraction pattern.

Figure 3.7 shows a series of diffraction patterns calculated using equation (3.18) for chains with a random dimer conformation, i.e., there was no rotational correlation between successive dimers. 200 chains of 75/25 copoly(HBA/HNA) were arranged in a pseudo hexagonal lattice with \(a = 7.6\ \text{Å}\) and \(b = 5.7\ \text{Å}\). The monomer sequence was assumed to be completely random, i.e., \(R_{HC} = r_{BB} / r_{BN} = 1.0\). Random axial stagger was simulated by setting \(\sigma = 2.0, 1.0, 0.5,\) and \(0.0\ \text{Å}\) in equation (3.21). Biswas and Blackwell [62] found that for as-spun copoly(HBA/HNA) there
Figure 3.6 Conformation of the HBA dimer with parallel aromatic planes and a $2_1$ screw axis relating the two monomers [54].
Figure 3.7 Calculated diffraction patterns of 75/25 copoly(HBA/HNA) for 200 chains of random conformation and random monomer sequence with (a) $\sigma = 2.0 \text{ Å}$, (b) $\sigma = 1.0 \text{ Å}$, (c) $\sigma = 0.5 \text{ Å}$, and (d) $\sigma = 0.0 \text{ Å}$.
is a normal distribution of chain origins about the register plane, with $\sigma \approx 2.0$ Å. Sampling by the interchain interference function is responsible for the sharpening (in the R direction) of the meridional maxima. As we go from Figure 3.7 (a) to (d), it can be seen that sampling occurs on progressively higher layer lines as $\sigma$ is decreased, corresponding to progressively narrower distributions of the chain origins about the register plane. Also the intensification of meridional maxima at small values of R can be seen as $\sigma$ is reduced from 2.0 to 0.0 Å. The point to note here is that although the sharpening of the calculated meridional at $d \approx 3.08$ Å (i.e., the third meridional maximum in the calculated data) develops as $\sigma$ decreases, no additional meridional maximum is predicted near this d-spacing region. Thus, the observed meridional reflection at $d \approx 3.33$ Å does not arise as a result of the change in conformation or the increased lateral registration. There remains the possibility that the changes on the meridional may result from development of a non-random sequence, which will be tested below.

Figure 3.8 shows the meridional intensity for sequence distribution on either side of the random case. The intensity distribution along the meridian was calculated by setting $R = 0$ in equation (3.15), in which case, the term $F_{AB}(0,Z)$ has the same form for both random and rigid conformations. When $R\text{HC} = 100$, the structure is extremely blocky, and maxima are predicted at orders of 12.7 and 16.5 Å, which correspond to the repeats for the blocks of HBA and HNA dimers. Essentially the same peaks are seen at $R\text{HC} = 5.0$: the peak widths increase with decreasing
Figure 3.8  Meridional intensity distribution for 75/25 copoly(HBA/HNA) with varying degrees of nonrandomness on either side of the random copolymer. The random copolymer corresponds to $R_{HC} = 1$. 
$R_{HC}$, reflecting the fact that the homopolymer blocks get shorter as cross-reaction becomes more likely. At $R_{HC} = 2.0$, the peak positions are changed, but the calculated data are easily distinguished for those observed. When $R_{HC}$ is reduced to 1.0 (random sequence), the d-spacings of the meridional maxima are close to those observed. The d-spacings ($1/Z$) of calculated meridional maxima for random and alternating sequences are listed in Table 3.4. However, the observed reflection at $3.33 \pm 0.03$ Å is not predicted for the completely random structure. When $R_{HC}$ is less than unity, formation of the alternating copolymer is favored. It can be seen that a shoulder develops on the peak at 3.06 Å ($2\theta \approx 29.2^\circ$), if $R_{HC}$ is progressively decreased from unity. At $R_{HC} = 0.8$, the d-spacing of this shoulder maximum is at 3.36 Å, and the d-spacings of the other meridional maxima are in good agreement with the observed data. If $R_{HC}$ is further reduced to 0.7, the shoulder shifts to higher d-spacing of 3.42 Å, which does not fit well with the observed. From these one-dimensional intensity distribution (Figure 3.8), we can find that if the tendency for forming alternating copolymer is favored, a shoulder at $d \approx 3.36$ Å can be generated.

At this point, it should be noted that the numerator in equation (3.14), $(R_{HC} \cdot P_B + P_N - P_B)$, should not be less than zero. This results in a limiting value for $R_{HC}$, i.e., $R_{HC} \geq (P_B - P_N) / P_B$. For 50/50 copoly(HBA/HNA), the lowest limit of $R_{HC}$ is 0.0, which corresponds a completely alternating structure. However, for the 75/25 copolymer, $(R_{HC})_{\min} = 0.667$ and indicates that only limited extension of alternating
Table 3.4  Calculated layer line positions for 75/25 copoly(HBA/HNA) with varying degrees of alternating tendency. The random copolymer corresponds to $R_{HC} = 1.0$.

<table>
<thead>
<tr>
<th>$1/2Z (\text{Å})^\dagger$</th>
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<tbody>
<tr>
<td>$R_{HC} = 1.0$</td>
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<tr>
<td>$R_{HC} = 0.9$</td>
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<tr>
<td>$R_{HC} = 0.8$</td>
</tr>
<tr>
<td>$R_{HC} = 0.7$</td>
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<td>Obs.</td>
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$^\dagger$ The meridional d-spacings are indicated by star sign (*).
tendency is possible if the structure is to remain homogeneous. If \( R_{HC} \) is reduced below this minimum barrier, phase separation will occur, with the formation of N-rich and N-poor regions. A structure of this sort can be modelled by a Monte Carlo approach, in which chains are built up from a finite supply of monomer units. The probability of adding a monomer unit to the propagating end depends on the unreacted monomer concentration and the reactivity ratio for this propagating end. This results in a concentration gradient along the chain, ultimately reaching a point where one monomer is completely depleted, whereupon the other monomer form a homopolymer block. The meridional intensity for the sequence generated can be obtained by calculating the axial transform of chains [69]. Averaging over a large number of sequences is then necessary to model the scattering by an array. A program was written to perform these calculations, but in the end it was found that the observed effects was predicted for lesser degrees of non-randomness, with \( R_{HC} > 0.667 \).

So far, the calculated meridional intensity shows that the sequence distribution for the annealed fibers slightly favors the alternating tendency. The effects of alternating structure on the two-dimensional intensity, more specifically on layer line positions, will now be discussed. The layer line intensity was modelled by the cylindrically averaged intensity transforms of a single chain, as defined in equation (3.15). \( I(R,Z) \) was calculated for an infinite chain of four possible dimers. A line of constant intensity was
assigned to the equator \((Z = 0)\) because the equation predicts infinite intensity.

Figure 3.9 shows the calculated intensity transforms for random conformations of chains defined by \(R_{HC} = 1.0, 0.9, 0.8, \) and \(0.7\). The \(Z\) coordinates of calculated layer lines for different \(R_{HC}\) values are listed in Table 3.4. At \(R_{HC} = 1.0\) (Figure 3.9 (a)), a series of continuous layer lines are predicted. The layer line at \(Z = 1/2.1 \text{ Å}^{-1}\) is the most intense, and high intensity is maintained in the \(R\) direction, which is consistent with the observed diffraction data. The sharpness of this layer line in the \(Z\) direction is due to the assumption of an infinite straight chain, and it can be broadened by use of a finite chain length or by modeling the nonlinearity of an actual chain conformation [75]. Examining this calculated diffraction pattern, we find that only one layer broad line is predicted at the region of \(Z = 1/4.2 \text{ Å}^{-1}\). The calculated pattern for \(R_{HC} = 0.9\), as shown in Figure 3.9 (b), is similar to that for \(R_{HC} = 1.0\), except that the layer line at \(Z = 1/4.0 \text{ Å}^{-1}\) becomes broader and a diffuse region can be seen below the layer line at \(Z = 1/3.07 \text{ Å}^{-1}\). The 4.0 Å layer line increases in width as \(R_{HC}\) is decreased and splits into two when \(R_{HC} = 0.8\), as seen in Figure 3.9 (c). A further separation between these two layer lines occurs when \(R_{HC}\) is decreased to 0.7 (Figure 3.9 (d)). Another interesting point to note is that at \(R_{HC} = 0.8\), a new layer line streak can be seen at \(Z = 1/3.36 \text{ Å}^{-1}\) in Figure 3.9 (c), which does not occur at \(R_{HC} = 1.0\) or 0.9. This layer line shifts to lower \(Z\) when \(R_{HC}\) is reduced to 0.7.
Figure 3.9  Calculated fiber patterns for infinite chains of 75/25 copoly(HBA/HNA) for a random dimer model with (a) RHc = 1.0, (b) RHc = 0.9, (c) RHc = 0.8, and (d) RHc = 0.7.
Inspection of the data in Table 3.4 shows that a small variation of $R_{HC}$ value leads to the shift of layer line positions. Figure 3.10 shows the intensity distribution along the row line at R coordinate = 1/3.21 Å$^{-1}$ ($2\theta = 27.8^\circ$ on the equator) for $R_{HC} = 0.7, 0.8, 0.9, \text{ and } 1.0$ and the maxima of peaks correspond to the layer line positions. Two layer line streaks at $Z = 1/4.61$ Å$^{-1}$ and 1/3.91 Å$^{-1}$ are predicted for $R_{HC} = 0.7$, but the differences between calculated and observed (1/(4.52±0.03) Å$^{-1}$ and 1/(3.98±0.03) Å$^{-1}$) are outside experimental error. As $R_{HC}$ increases to 0.8, these two layer lines (at 1/4.50 Å$^{-1}$ and 1/3.95 Å$^{-1}$) move closer to each other and the agreement in $Z$ position is improved. However, further increase in $R_{HC}$ leads to merging of these two layer line streaks. Thus, $R_{HC} = 0.8$ shows the best match of these two layer line positions. In addition, the d-spacings of the other layer lines are in good agreement with the observed, as shown in Table 3.4.

The other extreme case, in which the chain has a pseudo 21 rigid conformation, gives the similar results. For example, Figure 3.11 shows the calculated intensity transforms for random and rigid dimer models with $R_{HC} = 0.8$. The rigid model leads to the prediction of more intense layer line intensity along the R direction, but the layer line positions are not changed. Thus, it is concluded that, at $R_{HC} = 0.8$, the best agreement between calculated and observed data can be obtained.

Note that, at $R_{HC} = 0.8$, the structure has an small alternating tendency, but the sequence is still highly random: for example, the
Figure 3.10  Intensity distribution of row line at R coordinate $= 1/3.21 \, \text{Å}^{-1}$ for 75/25 copoly(HBA/HNA) with varying degrees of alternating tendency; $R_{HC} = 1.0, 0.9, 0.8,$ and 0.7.
Figure 3.11 Calculated fiber patterns of 75/25 copoly(HBA/HNA) for (a) a random dimer model and (b) a rigid dimer model. Both pattern are calculated at $R_{HC} = 0.8$. 
possibility of (HBA)$_4$ units in the random copolymer is only 1.2 times greater than that when $R_{HC} = 0.8$. The possibility of (HNA)$_2$ units for the random case is only about 2.1 times greater than that when $R_{HC} = 0.8$. However, for (HNA)$_4$ units this factor is dramatically increased to 72. The possibility for alternating dimers, e.g. (HBA-HNA)$_2$, is 1.6 times greater than that in the random copolymer. Thus, the development of (HBA-HNA) blocks is more favored than that of homopolymer blocks, with a striking decrease in the occurrence of (HNA)$_n$ blocks. Solid state transesterification is believed to occur on annealing leading to an increase in the molecular weight, and it has been proposed by Lenz and Feichtinger [76] that there may be some changes in sequence distribution. The non-randomness proposed here is only very slight, and may arise in order to separate HNA units, thereby minimizing the kinks in the chain and leading to better alignment.

C-3 Chain Packing

The changes that occur in the unit cell dimensions for the 75/25 copoly(HBA/HNA) are analogous to those seen for homopoly(HBA). Form I of poly(HBA) has an extended $2_1$ helical conformation, with two monomers in the repeat [70,71,73]. The two chains in the unit cell have opposite sense related by space group $P2_12_12_1$ [71]. We have assumed a pseudo $2_1$ conformation for the four dimers in the copolymer. The $2_1$ axis was placed on the center position of ab projection of atom C$_1$ and atom C$_1'$, as designated in Figure 3.6, which are the carbons of the
carbonyl groups. The atomic coordinates used for intensity calculation are the same as those used in previous section where each dimer has parallel aromatic planes. Two hundred chains were arranged as shown in Figure 3.12, where we have depicted thirty poly(HBA) chains as an example. The lattice dimensions are a = 7.6 Å and b = 5.7 Å. The dimers at the center and corner units in the unit cell are related by a pseudo P2₁2₁2₁. The orientation of corner chain was set as proposed for poly(HBA) by Sun and Blackwell [74], as shown in Figure 3.12, which is based on the refinement against the equatorial intensity data. The center chain orientation was obtained by rotating the corner chain about a 2₁ axis parallel to b axis. The equivalent positions are x, y, z and 0.5+x, 0.5-y, 1.0-z. Each chain had 7 dimer units, and the probabilities for dimer combinations were set by using R_{HC} = 0.8. Orders of Bessel functions from 0 to 5 were included in equation (3.27): inclusion of higher orders did not lead to significantly different results.

Figure 3.13 compares the calculated and observed intensity on the equator. Since we used a 10 X 10 finite lattice in the calculation, a series of subsidiary maxima at low 2θ angles are generated. Curve a in Figure 3.13 is obtained for a structure in which there are no rotational correlations between successive rigid dimers. Four major peaks are predicted, and these are indexed 110, 200, 020, and 220/310, all of which are for h+k = even. Curve b shows the result for a structure made up of rigid chains, in which the correlations between adjacent chains are imposed by the pseudo P2₁2₁2₁ symmetry. For this structure, more
Figure 3.12  Projection of portion of a layer of packed HBA dimers.
Figure 3.13  Observed and calculated equatorial intensity data for 75/25 copoly(HBA/HNA): (a) calculated data with no correlations between any dimers; (b) calculated data with rigid correlations between all dimers; and (c) observed data from a 0/20 area detector scan of fiber specimen along the equatorial direction.
peaks are predicted, including the reflections of $h+k = \text{odd}$. Curve c shows a $\theta/2\theta$ diffractometer scan in the equatorial direction.

In the random conformation case, each chain has the same cylindrical cross section and there is no any correlation between neighboring chains. Thus, the projection of structure reduced to a one chain unit cell, so that for the present two chain indexing, only $h+k = \text{even}$ reflections are predicted. When we use a rigid chain and the space group is pseudo $P2_12_12_1$, other $hk0$ reflections of $h+k = \text{odd}$ reflections are able to occur, such as the 210 and 120 reflections shown in Figure 3.13 curve (b). Weak 100 and 010 reflections are also predicted: these would be absent if the space group was a perfect $P2_12_12_1$, but we only has pseudo symmetry due to the non-repeating sequence and asymmetry structure of HBA-HNA dimer. Compared with the observed data (curve c), the calculated equatorial intensity matches the trend of relative intensity. The observed 100, 010, 120, and 310/220 reflections are all very weak, but are clearly visible in the film data.

The calculated intensity distribution along the first layer line ($Z = 1/13.5 \ \text{Å}^{-1}$), which contains the most intense off-equatorial maxima, is shown in Figure 3.14 (a). Curve b in Figure 3.14 shows the intensity profile of the first layer line. For convenience, we will refer to the reflections along this layer line as the $hk1$ reflections since they occur on the first aperiodic layer line. The three observed reflections on the first layer line can be indexed as 011, 111, and 211; note that the 011
Figure 3.14  (a) Calculated first layer line intensity data for 75/25 copoly(HBA/HNA) with rigid correlations between all dimers; (b) Intensity profile of R,Z map along the first layer line for the annealed 75/25 copoly(HBA/HNA).
reflection is very weak and is not resolved in curve b, although it is visible in the original film data. No reflections are seen in the higher 2θ regions, probably due to disorder. The 011, 111, and 211 reflections are predicted in the calculated data and their intensities are in relatively good agreement with those observed. Further refinement of dimer conformation may well improve the agreement in intensity distribution. At the present stage, we have used the same torsion angles for all four dimer residues. However, the existence of naphthalene ring could easily distort the chain linearity, since it is difficult to pack the naphthalene ring without any loss of regularity. Thus, variations of successive torsion angles are to be expected. Nevertheless, the present results are a good starting point for further refinement.

At this point, the analysis based on the reflections along equator and first layer line suggests that the chains in the annealed fiber have a rigid pseudo $2\overline{1}$ chain conformation, and that there are extensive lateral correlations between residues of different chains. Adjacent chains have different stagger and sense, and are related by a pseudo $P2_12_12_1$ space group. This structure shows a large changes from that in the as-spun fiber. Biswas and Blackwell [68] have reported that, in the as-spun fiber, the chain conformation has successive aromatic planes inclined by approximately 60°, and that the conformational correlations of the dimers along adjacent chains are relatively limited. In fact, this polymorphism in copoly(HBA/HNA) is very similar to that observed for poly(HBA) single crystals. Besides the similar changes in lattice dimensions, as mentioned
previously, the phase III structure of poly(HBA) appears to have extensive torsional disorder along the polymer chain at high temperature [71]. The average cross section of the chains becomes more or less circular, and the packing in the ab plane becomes pseudohexagonal and less dense. Thus, the lateral correlations between adjacent chains becomes more limited. These results are further confirmed by the DSC data, which are presented below.

C-4 Thermal Analysis

Figure 3.15 shows a series of DSC heating scans for different pellet samples of 75/25 copoly(HBA/HNA), which were annealed at 270° C for different lengths of time. Curve a in Figure 3.15 is the scan for the as-received sample, for which one transition temperature is observed at about 275° C. After annealing for 2 days, this transition peak moves upwards to 300° C, as shown in curve b. For the specimen subjected to 5 days annealing time, there are no major changes in the heating scan (curve c), except that the peak at 300° C becomes broader. However, a second transition peak is observed in curve d, when the specimen had been annealed for 6 days. Curve e shows the heating trace for the sample after 8 days annealing, and the separation between the first and second peaks becomes more clear. The second peak shifts higher temperatures in both curve f and g, for which the specimens were annealed for 15 and 30 days, respectively.
Figure 3.15  Set of DSC heating scans for an as-received (curve a) and a series of the annealed specimens, which were annealed at 270° C for (b) 2 days, (c) 5 days, (d) 6 days, (e) 8 days, (f) 15 days, and (g) 30 days.
The DSC data show that there is an additional transition peak develops as the specimen was annealed for 6 days (curve d). The formation of this peak indicates some sort of structural changes after thermal treatment. This suggests the development of a second polymorphic form, as indicated by the x-ray data. As annealing time is increased, the new phase of structure becomes more ordered, and the transition peak moves to higher temperatures. Thus, the DSC data imply that the structural changes occur during thermal treatment, and the new structure becomes more ordered as the annealing time is prolonged. Consequently, the DSC results are consistent with those obtained from x-ray analysis.

D. Conclusions

In this chapter we have studied the monomer sequence, chain conformation, and chain packing of the annealed structure of 75/25 copoly(HBA/HNA). The sequence distribution has been investigated as regards the meridional maxima and the layer line positions. The appearance of two additional meridional reflections in x-ray fiber pattern for the annealed specimen indicates the possibility of changes of monomer sequence occurred during thermal treatment. The meridional intensity at \( d \approx 3.33 \text{ \AA} \) does not result from lateral aggregation of a array of copolymer chains with random sequence \( (R_{HC} = 1) \). The predicted effects of non-randomness, favoring the formation of homopolymer blocks \( (R_{HC} > 1) \) and alternating copolymer blocks \( (R_{HC} < 1) \), on the meridional
maxima show that the monomer sequence of the annealed fiber slightly favors the alternating sequence distribution. When the cylindrically averaged intensity transforms were calculated for single chains in which we have manipulated the degree of non-randomness, we successfully predicted the layer line positions of x-ray pattern of the annealed specimen. At $R_{HC} = 0.8$, very good agreement in layer line positions was obtained. As $R_{HC}$ declines from 1.0, HNA-HNA dimers become less and less common, until at 0.67, all the HNAs are separated by available number of HBAs. $R_{HC} = 0.8$ corresponds to a structure in which the probability of HBA-HNA pairs is increased by approximately 10 % over this probability in a completely random sequence. The alternating structure is favored, but not by very much, and sequences with these statistics still appear very random.

The changes in lattice dimensions between as-drawn and annealed copoly(HBA/HNA) are similar to those that occur when homopoly(HBA) changes from phase III to phase I. A pseudo $2_1$ conformation for the copolymer with rigid rotational correlations between successive dimers gives good agreement with the observed intensity distribution on equator and first layer line, although some intensity discrepancies still exist, implying that further refinement is needed. The structural changes of copoly(HBA/HNA) after thermal treatment indicated by the x-ray data are consistent with the DSC analysis.
References


74. Z. Sun, Ph.D. thesis, Case Western Reserve University, Cleveland, Ohio (1990).
