

EFFECT OF ANNEALING ON MORPHOLOGY OF THERMOTROPIC LIQUID CRYSTALLINE POLYESTERS

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ABSTRACT

Liquid crystal polymers with semiflexible polymer backbone exhibit crystalline order despite of some defects in crystal packing. Isothermal heat treatment of the polymers below and above their liquid crystalline temperatures is expected to provide the necessary energy and time for the molecular chains to overcome the defects in crystal packing and to be arranged in a more perfect crystal lattice. A number of liquid crystalline polyesters, possessing both rigid mesogenic groups and flexible aliphatic spacers in the polymer backbone, have been considered for this experiment and were annealed at different temperatures. An improvement in molecular and crystal structure of the polyesters has been observed and the results of such experiment using FTIR spectroscopy, optical microscopy and wide angle X-ray diffraction of the sample before and after annealing are presented here.

Key words: *Annealing; mesogen; semiflexible.*

1. INTRODUCTION

Annealing of polymers can be defined as a secondary process wherein the polymer is brought to a certain temperature, kept there for a time and then cooled to room temperature. The annealing of the semicrystalline polymers may change the crystal structure, the degree of crystallinity, the perfection of the crystals, the orientation of both crystalline and amorphous phase, their contiguous structural morphology and the number of tie chains between the crystallites as stated in the Encyclopedia of Polymer Science and Engineering. Direct morphological changes are also observed on annealing bulk crystallized samples below their equilibrium temperature. Polymorphism may result due to annealing crystalline polymers as its one crystalline form transforms into another.

Annealing process is time and temperature dependent. Annealing of liquid crystalline polymers between the glass transition temperature and the melting temperature leads to increased level of crystallinity and increased crystalline perfection analogous to the behavior of conventional semicrystalline polymers. Annealing at or above the melting point also leads to enhanced crystallinity and crystalline perfection. The effect of annealing at different temperature region on liquid crystal polymers have been reported by various authors. The effect of annealing on the structure of liquid crystalline copolyesters has been studied by Kaito et al. (1990). In the course of annealing, not only is the lateral order of the random copolyester improved but also the random sequences crystallize into ordered crystals with higher melting temperatures. Jin & Chang (1989) worked with a series of sequentially ordered copolyesters prepared from terephthalic acid and isomeric naphthalenediyl bis (4-hydroxybenzoates). According to their findings, molecular weights, melting temperature and degree of crystallinity have been increased by annealing the polymers at high temperature. Economy (1979) have annealed a sample of HBA/HNA (50/50) copolymer at 210°C for 24 hours and examined the annealed sample by DSC. DSC thermogram showed an approximate 4 times increase in transition enthalpy indicating an increased crystallinity. It was reported by Carpentio et al. (1992) that on increasing the annealing temperature, recrystallization of the mesogenic polyester in a more perfect form was observed and the melting temperature increased until it superimposed onto the clearing temperature

Isothermal heat treatment or annealing of the liquid crystal polyesters below and above their liquid crystallization temperature will provide the necessary energy and time for the molecular chains to overcome the defects in crystal packing and to be arranged in a more perfect crystal lattice. Sequentially ordered thermotropic liquid crystal polyesters have been annealed at different temperature above and below their liquid crystallization temperature. FTIR spectroscopy has been used to analyze the molecular interactions among the polymer chains before and after annealing. The effect of annealing on the morphology of the polymers has been studied by optical microscopy. The improvement of crystal structure of the polyester was supported by X-ray diffraction studies.

2. EXPERIMENTAL METHODS

2.1. Annealing Studies:

Annealing of the polymers have been done on a Mettler FP 84 hot stage. The sample was taken on a glass slide and heated above its melting temperature. It was kept at that temperature for 5 minutes to destroy prior thermal history before cooling it down to room temperature. After crystallization it was then heated to the predetermined annealing temperature and annealed for 1 hour. Annealing temperatures were chosen below and above the melting temperatures of the polymers (ranging from 160⁰ – 195⁰ C). It was then brought to room temperature by natural cooling.

2.2. FTIR Studies:

IR spectra of the samples were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer. 16 scans at a resolution of 4 cm⁻¹ were signal averaged. The sample was used in pelletized form with KBr.

2.3. Optical Microscopy

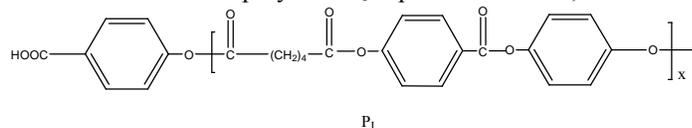
A polarizing microscope (Leitz Laborlux 12 Pol S) fitted with a Wild Leitz MPS 46/52 photoautomat was used for observing the liquid crystalline texture of the polymers.

2.4. WAXD

X-ray diffraction pattern was obtained from a Phillips X-ray diffraction unit. CuK_α target and Ni filter were used and scattering angles (2θ) were chosen between 0⁰ to 33⁰. The corresponding d values and degree of crystallinity were calculated by equation 1 and 2 respectively.

3. RESULTS AND DISCUSSION

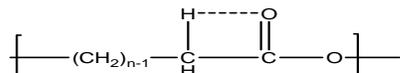
Four sequentially ordered copolyesters, with both rigid mesogenic groups and flexible aliphatic spacers in the polymer backbone, have been synthesized by Talukdar & Achary [2010]. Though the effect of annealing on crystallization behavior of all four polyesters was studied, the result of annealing study on polyester P₁ is presented here. The structure of polyester P₁ is presented below,



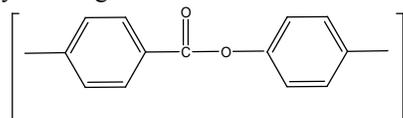
Molecular and crystal structure of the polymer was studied by FTIR spectroscopy, optical microscopy and wide angle X-ray diffraction.

3.1. FTIR Spectroscopy

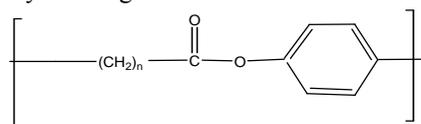
The polyester was subjected to FTIR spectroscopy and splitting of carbonyl stretching region into three distinct bands were observed. The lowest frequency band at 1686 cm⁻¹ has been assigned to carbonyls involved in ordered hydrogen bonds



Other two higher frequency components at 1734 cm⁻¹ and 1750 cm⁻¹ were assigned to carbonyls in different environments. Absorption at higher frequency level, i.e., at 1750 cm⁻¹, was assigned to carbonyl group attached to the phenylene ring on either side



The frequency component at 1734 cm⁻¹ ascribed to ester carbonyls attached to a methylene group on one side and a phenylene ring on the other side.



The orderliness of the samples generally increases by annealing. The intensity of the bands in the carbonyl region increases for the annealed samples. On annealing, the parallel molecular chains become more arranged in space and come closer to each other. This would result in increased hydrogen bonding. This is illustrated by the associating

frequency change in hydrogen bonded carbonyl region. Carbonyl bands of polyester P_1 , after annealing for 1 hour at 160° , 170° , 180° and 195°C are shown in Figure 1,

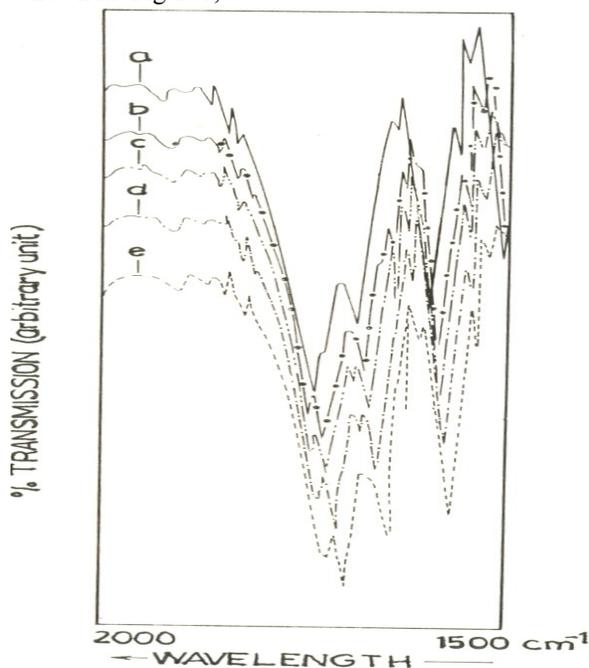


Figure 1. FTIR spectra for polyester P_1 , (a) unannealed sample, (b) annealed at 160°C , (c) annealed at 170°C , (d) annealed at 180°C , (e) annealed at 195°C .

The annealing temperatures were chosen between the glass transition temperature (T_g) and mesophase formation temperature of the polymer. Annealing at a temperature below T_g did not provide any noticeable improvement in crystal structure due to lack of mobility of the molecular chains. As the melting temperature was approached, mobility of the chains provided an efficient chain packing. Above the mesophase formation temperature at 195°C , flow of the chains and recrystallization due to annealing took place simultaneously and a more perfect chain packing resulted. A progressive increase in the intensity of the hydrogen bonded component with respect to the free carbonyls, with annealing temperature was observed. Relative increment of the bonded carbonyl frequency with respect to the annealing temperature is presented in Figure 2.

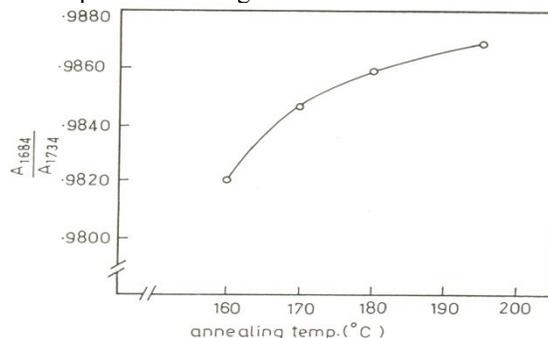


Figure 2. Relative increment of the bonded carbonyl frequency with respect to the annealing temperature.

3.2. Optical Microscopy

Annealing above the flow temperature of the polymer resulted in a highly improved molecular structure. This fact, as explained in terms of chain aggregation, has been demonstrated by the frequency enhancement of the hydrogen bond through the FTIR spectroscopy of the annealed polyester sample. The microscopic study of the unannealed polyester sample indicated separate domains where parallel smectic layers and nematic black threads were identified in Figure 3.

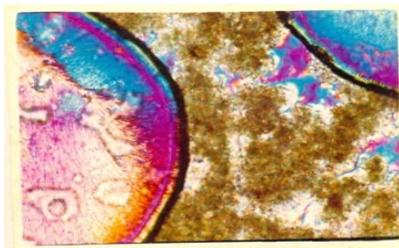


Figure 3. Optical texture exhibited by thin film of polyester P_1 .

In the present case of the annealed sample, attention has been focused on the nematic region in order to study the effect of annealing on improvement of chain aggregation. The optical micrographs, taken after heating the sample isothermally for 1 hour at 160°C , 170°C , 180°C and 195°C are also in consistency with the results obtained from the spectroscopic study. The photomicrographs are shown in Figure 4 (a) – (d).

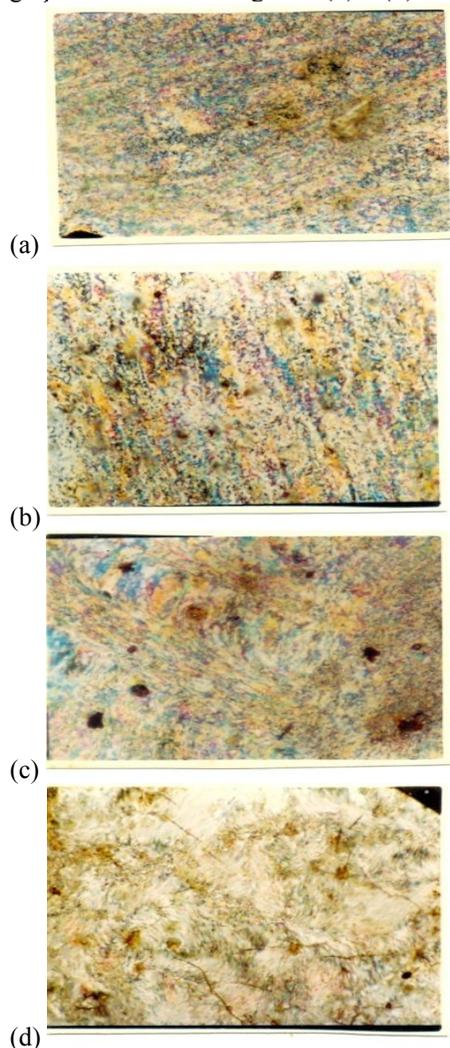


Figure 4. Textural changes for polyester P_1 annealed at (a) 160°C , (b) 170°C , (c) 180°C and (d) 195°C .

The sample, annealed at 160°C exhibited a lot of discontinuous nematic threads which were not very different from the original sample. At 170°C , the threads were becoming arranged in space, though they still represented a nematic phase. As the onset of melting to a mesophase is approached, i.e. at 180°C , reorganization of the chains was favored by the mobility of the molecules which has been induced as a result of annealing. There was a clear demonstration of transformation of the nematic threads to a bunch of smectic layers in the micrographs taken for the sample annealed at 180°C . A complete transformation to smectic layers were found to take place on annealing above the

flow temperature of the sample, i.e., at 195°C. Flow of the molecular chains favored the recrystallization process and the molecular chains appeared in a more arranged packing, representative of a smectic mesophase. Thus, in order to improve the molecular structure, transformation of the less ordered nematic arrangement to a stable smectic mesophase was achieved by annealing the sample above its flow temperature.

3.3. Wide Angle X-ray Diffraction

From the Polymer Hand Book, it was found that the polyester crystals are orthorhombic in nature and was oriented in different directions along the axes of the orthorhombic plane. The d spacing corresponding to different planes have been calculated from the well known Bragg equation,

$$2d \sin \theta = n\lambda \quad (1)$$

θ being the scattering angle known as Bragg angle. With the help of the d value at different scattering angles, one can identify three dimensional orientations of the crystals following the equation,

$$d = (h^2/a^2 + k^2/b^2 + l^2/c^2)^{-1/2} \quad (2)$$

where h, k, l are Miller indices and a, b, c are constants for the particular crystal plane. X-ray pattern of the polyester sample showed a number of strong reflections which provided information about the crystal orientations in three dimensional arrays. Powder pattern of P₁ showed strong reflection at $2\theta = 18^\circ$, 21.8° and 22.8° which correspond to the crystal orientation along 011, 111 and 200 planes in orthorhombic form.

X-ray diffractograms of the annealed polyester sample at different temperature, shown in Figure 5, have indicated the improvement of the molecular structure of the polymer on annealing.

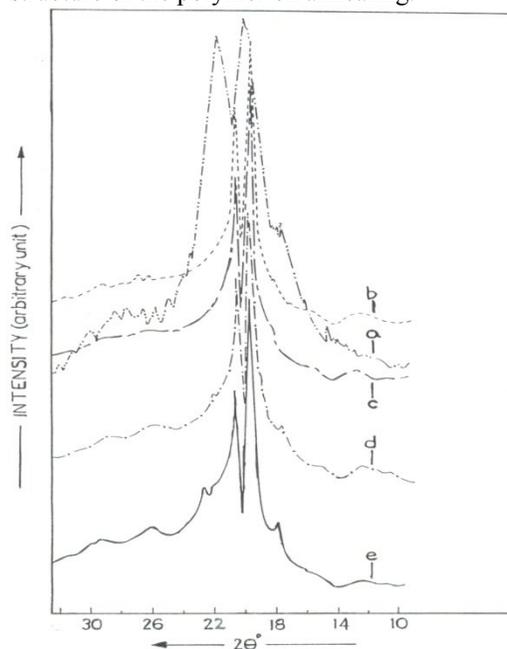


Figure 5. WAXD patterns for polyester P₁, (a) before annealing, (b) annealed at 160°C, (c) annealed at 170°C, (d) annealed at 180°C and (e) annealed at 195°C.

As the polymer was annealed at 160°C for 1 hour a pseudo-hexagonal phase was generated due to a measure of conformational disorder. It is characterized by a strong interchain peak at an almost identical angle ($\theta = 20.3^\circ$) to the 110 plane of the orthorhombic phase. As the annealing temperature increased to 170°C, still much lower than the melting temperature to a mesophase, the X-ray diagram was almost identical to the former one except the mild hint of another interchain peak at $2\theta = 23^\circ$. Upon further increasing the annealing temperature, i.e., at 180°C, an important observation is that the interchain peak, indexed as 200, appeared prominently. Along with this peak, a second interchain peak developed at $2\theta = 18^\circ$, indexed as 011. The result shows that the lateral packing of the molecular chains was changed by annealing at higher temperature. The two newly generated peaks appeared more prominently on annealing the sample at 195°C, which was quite above its mesophase formation temperature. In this state, the aromatic planes might be freely distributed along the chain axis. Molecular chains with disordered conformation can pack in a hexagonal lattice. On annealing the disordered conformation tends to be transformed into the energetically stable form. Molecular chains with an ordered conformation can no longer stay in the hexagonal array which induces the structural transition to the orthorhombic packing. The fact that the pseudo-hexagonal phase transformed into orthorhombic one on annealing, indicated that it was a metastable state.

The intermediate structures are metastable with respect to the final equilibrium phase but are stable as small entities on account of their lower interface energy – a significant factor when they are very small. The crystallites of the stable orthorhombic phase are not able to form initially as the density difference between them and the molten mesophase is significant. On the other hand, the pseudohexagonal structure which has lower density, quite smaller to that of the melt, will have a much smaller surface energy. The transformation to orthorhombic on annealing, could be associated either with an increase in crystal thickness, thus reducing the area to volume ratio or a reduction in the interface energy itself, probably as a result of diffusion of the chain ends to the interface so as to compensate for the density difference. The observation that there was neither a significant increase in crystallinity, nor an initial transformation from pseudohexagonal to orthorhombic phase would suggest that the model involving the diffusion of chain ends is appropriate. The possible arrangement in an annealed crystallite is shown schematically in Figure 9.

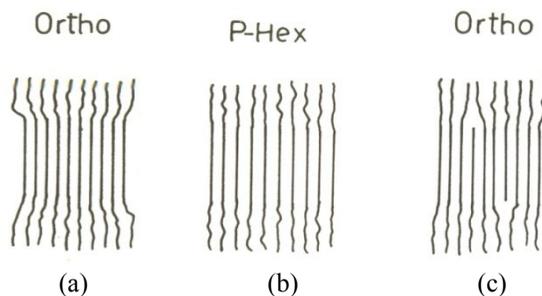


Figure 6. Schematic diagrams showing (a) the strain energy between the orthorhombic crystals and the surrounding nematic phase, (b) between the pseudohexagonal crystals and the nematic phase and (c) incorporation of some chain ends in the interface which reduces the strain energy and stabilizes the equilibrium orthorhombic phase.

4. CONCLUSION

Annealing of the polyesters in their mesophase region results in an enhanced structural arrangement. The process of annealing was expected to favour the crystal packing which in turn enhanced the degree of crystallinity. A transition from a hexagonal lattice structure to an orthorhombic one has also been observed on annealing the sample above its mesophase transition temperature.

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