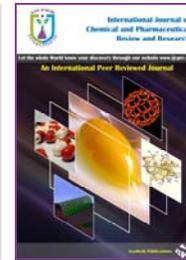




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## Thermo-optical Behavior of Liquid Crystalline Polyesters

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### ABSTRACT

Liquid crystals are highly anisotropic fluids that exist between the boundaries of solid and conventional isotropic liquid phase. Within certain ranges of temperature, in melts or in solutions, some organic substances are solid in terms of flow; the other fluid aspects to their physical states still exist. This dualism of physical properties of liquid crystal polymers results in an unusual combination of mechanical, thermal and chemical properties. Polarizing microscope is widely used for studying the morphology of liquid crystals during their phase transitions. The measurement of transmission of polarized light through a sample of polymer by a polarizing microscope fitted with a hot-stage is known to be a useful technique for investigating the microstructure and crystalline behavior of semicrystalline polymers.

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### 1. Introduction

Biphasic behavior of liquid crystal polymers implies the presence of two or more distinct phases between the melting and clearing transitions. These phases are typically liquid crystalline phase or mesophase and isotropic melt. The use of light transmission technique for liquid crystalline polymers to study phase transitions had been reported by several investigators<sup>1-3</sup>. Wunder and coworkers studied the change in intensity of the transmitted light as a function of temperature for three liquid crystalline copolyesters which formed nematic mesophase<sup>4</sup>. The work reported by Bhattacharya and Lenz<sup>5</sup> involved the measurement of the total transmitted intensity for an LC-copolyester and a blend of an LC with a non LC polymer, both as a function of temperature. The transition temperatures observed by light transmission studies closely matched those obtained from DSC and optical microscope studies.

Within the temperature range, in which an LC phase existed, it was observed that the transmission intensity increased almost linearly until complete isotropization occurred. For some slowly crystallizable liquid crystalline polymers, the DSC thermograms of the cooling cycle generally give little information about the formation of liquid crystalline or crystalline phases.

Thermal transitions of liquid crystalline polymers are normally studied by a combination of DSC and visual observation on a hot-stage polarizing microscope. While the actual transitions are determined from the DSC studies, an analysis by microscopy is generally based on subjective evaluations and descriptions of the observations. A characteristic threaded texture of nematic mesophase was observed by M. Kawbe and coworkers in the optical micrographs of molten liquid crystalline poly (ester-co- carbonate)<sup>6</sup>. Liquid crystalline phase can be observed during both the heating and cooling cycles of the material. Barbera et.al<sup>7</sup> have synthesized five main chain polymers and studied their phase behavior by optical microscopy and DSC. The polymers above their melting points threaded optical texture for nematic melt. A series of thermotropic liquid crystalline polymers have been

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reported by Sung et.al<sup>8</sup>. DSC thermograms clearly indicated the transition from smectic E to smectic B phase and from smectic B to isotropic phase. For a series of polymers based on cyclo-octyl units with varying length of methylene units, only smectic phase could be detected<sup>9</sup>. Wang and coworkers<sup>10</sup> studied the morphology of two thermotropic polyesters with mesogenic units and flexible spacers during the isotropic and liquid crystallization transition by using polarizing microscope.

Four thermotropic liquid crystalline polyesters with suitable mesogens and flexible spacers have been synthesized<sup>11</sup> and textural analysis and thermal transitions of their liquid crystalline phases have been optically investigated using DSC and a hot-stage polarizing microscope.

## 2. Experimental

Combined optical and thermal analysis: Phase transition processes taking place during the thermal operation of the polymers were visualized by a combination of optical microscopy and DSC. For this purpose, a polarizing microscope (Leitz Laborux<sup>12</sup> pol S) fitted with a Wild leitz MPS 46/52 photoautomat and a Mettler FP 84 HT hot stage was used.

5-10 mg sample was taken in sapphire crucible and was kept on the hot stage which itself was mounted on the platform of the microscope. Scanning rate has been fixed at 10°C/min through the heating and cooling cycles. Liquid crystalline textures and phase transitions taking place have been established by the photomicrographs.

## 3. Results and Discussion

The structures of the polyesters under study have been presented in Fig. 1.

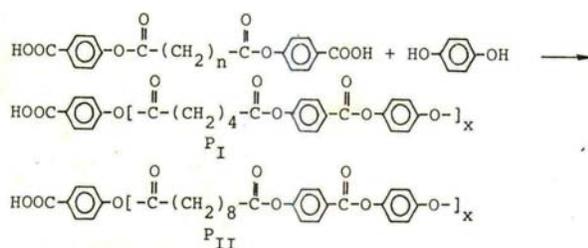


Fig. 1. Structures of polyester P<sub>I</sub> and P<sub>II</sub>

The textures of liquid crystalline polymers characterize their mesophases. As several phase transition processes take place during thermal analysis of the thermotropic polymers, textural changes are also expected with varying temperature.

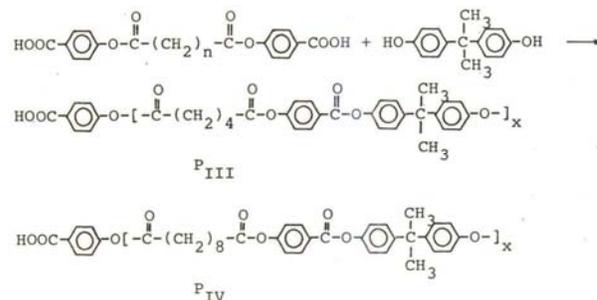


Fig. 2. Structures of polyester P<sub>III</sub> and P<sub>IV</sub>

Optical micrographs for polyesters, shown in a number of panels in Fig. 3-6, are quite suggestive about their phase transition processes upon heating from room temperature up to 300 °C and on cooling to the starting temperature.

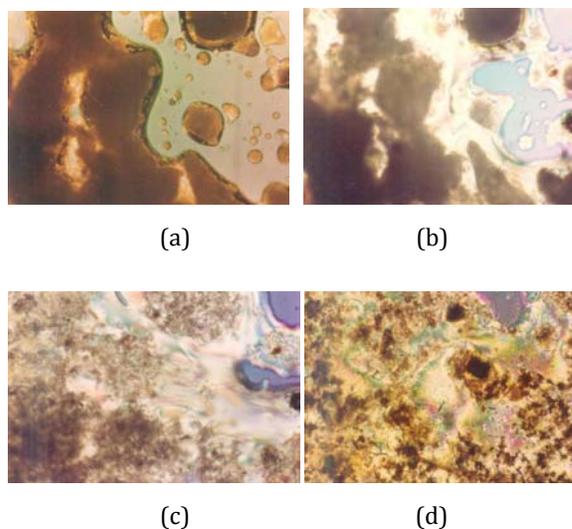
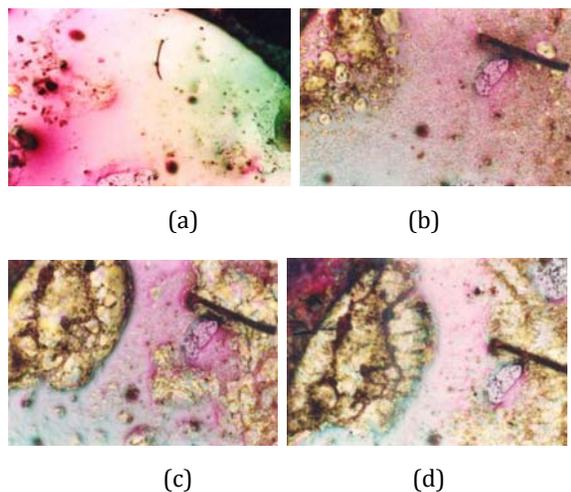


Fig. 3. Textural changes of polyester P<sub>I</sub> upon heating and cooling cycles

- Onset of melting of polyester P<sub>I</sub>
- Intensity of flow increased
- Flow of nematic phase started
- Regeneration of smectic layers upon cooling

Micrographs of polyester P<sub>I</sub> shows the onset of melting with the formation of smectic mesophase. Nematic black threads were seen in the flowing birefringent smectic mass. The flow was intense at higher temperature. At 237°C, nematic threads also started flowing along with the smectic one and were being identified more prominently as they uncoiled themselves in the flowing mass. At this temperature, the smectic layers completely passed into an ordinary fluid state within a couple of minutes. The smectic layers reappeared upon cooling from the isotropic state at around 200°C. Darkening of a part of the total mass

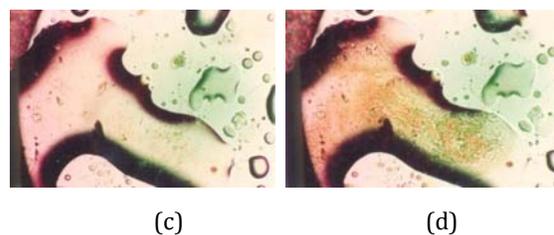
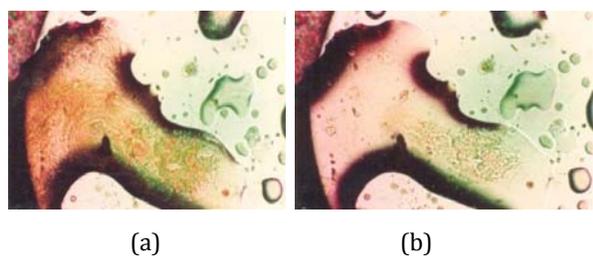
was due to the decomposition of the nematic threads which did not undergo isotropization up to 300°C.



**Fig. 4.** Textural changes of polyester P<sub>II</sub> during cooling from the isotropic melt

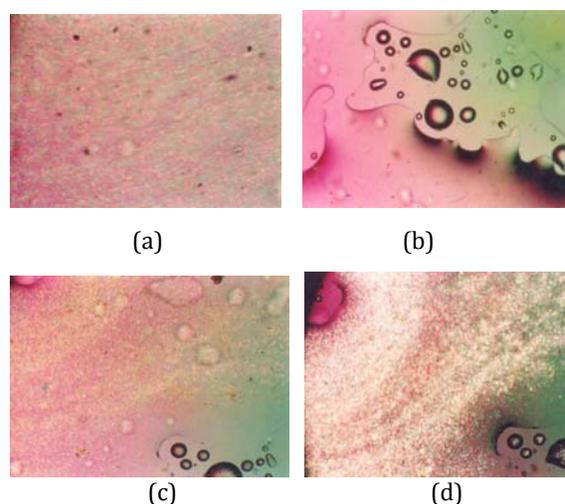
- (a) Isotropic melt of polyester P<sub>II</sub>
- (b) Grains of nematic phase appeared in the melt
- (c) Transformation of nematic grains to fan like texture of smectic phase
- (d) Transformation to smectic phase completed.

The transition processes of P<sub>II</sub> during the cooling cycle from its isotropic melt were represented in Fig. 4. When the isotropic melt was cooled, birefringent mass appeared with featureless grainy texture and were identified as nematic phase. The transformation of these grains to smectic fans started at 130°C and completed within 2 minutes. Generally, the polymers containing very large spacers (approximately eight or more atoms) will enhance the occurrence of smectic phase<sup>12</sup>. While comparing the transition processes of the two presently discussed polyesters P<sub>I</sub> and P<sub>II</sub>, co-existence of smectic and nematic phases for polyesters P<sub>I</sub> was evident. For polyester P<sub>II</sub>, a transition from nematic to smectic phase was likely to take place during the cooling cycle. Because of the presence of longer spacers, P<sub>II</sub> completely passed in to an isotropic melt without any decomposition whereas more rigid polyester P<sub>I</sub> partly decomposed before completion of isotropization.



**Fig. 5.** Textural changes of polyester P<sub>III</sub> during heating and cooling cycles

- (a) Mesophase formation
- (b) Onset of isotropization
- (c) Isotropic melt
- (d) Appearance of crystallites upon cooling.



**Fig. 6.** Textural changes of polyester P<sub>IV</sub> during heating and cooling cycle

- (a) Onset of mesophase formation
- (b) Completely disordered isotropic melt
- (c) Appearance of grains on cooling the isotropic melt
- (d) Development of grain like structure completed

Polyester P<sub>III</sub> was found to exhibit a smectic C mesophase which was characterized by the birefringent grain like texture in its flowing mass. At 140°C the grains started flowing and it became more intense as the temperature increased. The ordered structure started disappearing at around 160°C above which the mass transformed into an entirely disordered fluid state. On cooling, featureless grain like structure began to develop in the melt at 135°C. On further cooling, the grains were observed more prominently and within a few minutes covered the whole volume.

The transition processes were visually investigated and presented in Fig. 6. The transition processes for polyester P<sub>IV</sub> were similar to that of P<sub>III</sub>. Birefringent smectic grains were recognized in the molten mass at 135°C and flow with intense birefringence was found to exist till 160°C. Above that temperature the mass started transforming into an isotropic melt. At 166°C the melt was completely disordered. On cooling, the liquid crystalline phases reappeared at 122°C. Within a few minutes the whole volume was covered with intensely birefringent smectic grains. The micrographs, presented in Fig. 6 were evident for the transition processes.

Unlike polyesters P<sub>I</sub> and P<sub>II</sub>, polyesters P<sub>III</sub> and P<sub>IV</sub> with 4, 4'-isopropylidene diphenylene groups as mesogens possessed only smectic mesophases. They neither showed smectic- nematic co-existence like P<sub>I</sub> nor exhibited smectic- nematic transition like P<sub>II</sub>. It is probably due to the sterical hindrance of the isopropylidene groups present in the mesogens and sterical interlocking of the chains favoured the molecules to be packed in an efficient crystal packing in order to possess a smectic mesophase

#### 4. Conclusion

A combined thermal and optical study of the thermotropic liquid crystalline polyesters demonstrated the phase transition processes during the thermal analysis of the polymers. They exhibited more than one phase transitions on approaching their isotropization temperatures. The entire mesophase regions can be utilized during processing of the four polyesters because the clearing of the mesophases attended at temperatures much below the onset of their decomposition.

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