

Morphological Studies of Bisphenol Series Thermotropic Liquid Crystalline Wholly Aromatic Copolyesters

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SYNOPSIS

A family of aromatic thermotropic liquid crystal (TLC) copolyesters are prepared based on terephthalic acid (TPA), isophthalic acid (IPA), *p*-hydroxybenzoic acid (HBA), and a family of bisphenols. The morphological behaviors of the copolyesters are studied by using polarized optical microscopy, small-angle light scattering (SALS), and depolarized light intensity (DLI) analysis. The copolyester melts exhibit nematic mesophase textures within wide temperature ranges without showing transitions to isotropic phases. The textures under different temperatures and deformation conditions are investigated. Scattering patterns of the mesophases change greatly during shear deformation and relaxation. The early formation of the mesophases is a one-dimension heterogeneous nucleation based on isothermal condition. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, morphological studies of thermotropic liquid crystal polymers (TLCPs) are receiving more and more attention in both academic and industrial fields.^{1,2} Textures and melt structures can be used not only as indicators of mesophase identity but also as key components in rheological control and physical property studies. Some of TLCPs derive their anisotropic melt morphologies and deformation-induced molecular orientation from rigid molecular chains and can be easily melt processed into intricate shapes with superior mechanical properties.³ A slight change in the molecular structure of the mesogenic units often results in a significant change in morphological behaviors. Meanwhile, many external factors such as temperature, pressure, shear, and so on, can also greatly influence the textures and organizations of melt mesophases. In complement to polarized optical microscopy, small-angle light scattering (SALS) is often used to obtain information on the morphological structures

of polymers in solid state. Since scattering with crossed polarizers (H_v) results from structural anisotropy, whereas scattering with parallel polarizers (V_v) results from both anisotropy and density fluctuation, H_v scattering characteristics are more useful for interpretation of the preferential molecular packing, aggregation, or crystallization and anisotropic contributions.^{4,5} Depolarization light intensity (DLI) analysis, on the other hand, provides a quantitative and effective approach for studies of the mesophase and anisotropic behaviors. It can be used to detect mesophase transition temperatures accurately based on the changes of depolarized light transmittance without the influence caused by the small enthalpy effect during DSC studies, especially for these high-molecular weight and low-crystal degree TLCPs.^{6,7} In a previous study, a family of melt-processable TLCPs were prepared⁷ based on terephthalic acid (TPA), isophthalic acid (IPA), *p*-hydroxybenzoic acid (HBA), and one of the following bisphenol monomers: 4,4'-dihydroxydiphenyl (BP), 4,4'-dihydroxydiphenyl methane (BPM), 4,4'-dihydroxydiphenyl propane (BPA), or 4,4'-dihydroxydiphenyl sulfone (SDP). The mole ratio of HBA/bisphenol/TPA/IPA was 60 : 20 : 14 : 6. The correspondent copolyesters were termed as *TIHBP*, *TIHBPM*, *TIHBPA*, and *TIHSDP*. Some basic

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morphological behaviors of copolyesters are discussed in this article.

EXPERIMENTAL

The optical microscopy studies were performed by using a Leitz–Wetzlar hot-stage polarization microscope. The sample powder was placed between two cover glasses to form a film sandwich and then heated under a nitrogen atmosphere to a molten state. The effects of temperature, shear, and pressure on the melt textures of the mesophases were surveyed and photographed.

For small-angle light-scattering studies, the sample film sandwich was prepared as above and then heated to a temperature of 30–40°C above its melting point. The melting points of the copolyesters were 331.0, 285.8, 310.0, and 291.9°C for TIHBP, TIHBPM, TIHBPA, and TIHSDP, respectively.⁷ After the sample melted completely, the sandwich was quickly put into an ice-water bath. In case of melt deformation, the melt sandwich was sheared by moving the two coverglasses under an applied force of 100 g and then quenched in the bath. The SALS characteristics of the sample was examined and photographed on an SALS-1 analyzer with a He–Ne (632.8-nm wavelength) laser at ambient temperature under crossed polarizers.

The melt birefringence measurements and mesophase formation kinetics were performed with a DLI-2 analyzer, which was mainly composed of program temperature control sets, light sources, a pair of circular polarizers, a sample holder, a cooling water system, and a light transmittance recorder with a plotter. The sample sandwich with ca. 30 μm thickness had a good optical response. The sandwich was put into a sample carrier that had pinholes on both top and bottom through which light could enter, and the carrier was then put into sample holder for analysis. The system was calibrated with a hydroquinone standard and a quartz compensator of known birefringence for both temperature and birefringence accuracy. The samples were measured at a temperature of 35°C above their melting points.

RESULTS AND DISCUSSION

Polarized Optical Microscopy

When samples are heated to their melting points, the copolyesters exhibit scattering-point textures. Such scattering-point textures change into threaded

schlieren^{5,8} nematic mesophase textures when the temperatures are about 20°C above the melting points as in Figure 1.

Upon heating the samples further, the melts begin to flow with dislocations, and loops⁸ align along the flow direction [see Fig. 2(a)]. This fact indicates that molecular chains in the melt mesophase tend to orient easily in a flow field. Such an orientation structure is favorable for good mechanical properties and can be maintained if the melt deformation is quenched during processing of the material.

For all the four copolyesters, no isotropic transition is observed. When temperatures are high enough (about 70°C above the melting points), the nematic textures become brown in color and finally disappear. These temperatures were found consistent with the thermodegradation points as measured by DSC.⁷

When increasing the thickness of the sample sandwich, we note the mesophase texture becomes opaque. Meanwhile, boundary bands, which are caused by the spreading of the melt, appear around the melt as in Figure 3(a). For the thicker sample, when a small pressure is applied, the intensity of melt birefringence appears to be greatly enhanced, and some characteristics of the texture reoccur as in Figure 3(b); the original dark fields of view become bright. Since the melt spreads when under the pressure, it may be that flow is causing this chain reorientation. However, the reorientation phenomenon is also observed for a very thin sample, suggesting that the pressure alters the directions of the optical axes of the domains.

Upon shearing the melt, the molecular domains align along shear direction, and the regions in the direction become bright as shown in Figure 3(c). When the shear is stopped, some transverse bands^{9–17} appear in the texture [see Fig. 3(d)]. These pseudoperiodic bands of alternating molecular orientation are not known to occur in small-molecule liquid crystal systems. The banded texture is found to be thermal stable within a wide temperature range (ca. $\pm 30^\circ\text{C}$). Most of the results obtained from studies on the band formation process indicate that the specimens are first oriented in the shear direction, and banded texture is formed after shear cessation immediately or in a short period of time.^{13–17} The elastic energy stored during shearing gives the drive force for banded texture which occurs to relieve shear strain after shear cessation. The stability of the texture is also related to the thickness of the sample. The thicker the sample, the easier the orientation tends to relax if the melt temperature remains constant. The melt deformation and relaxa-

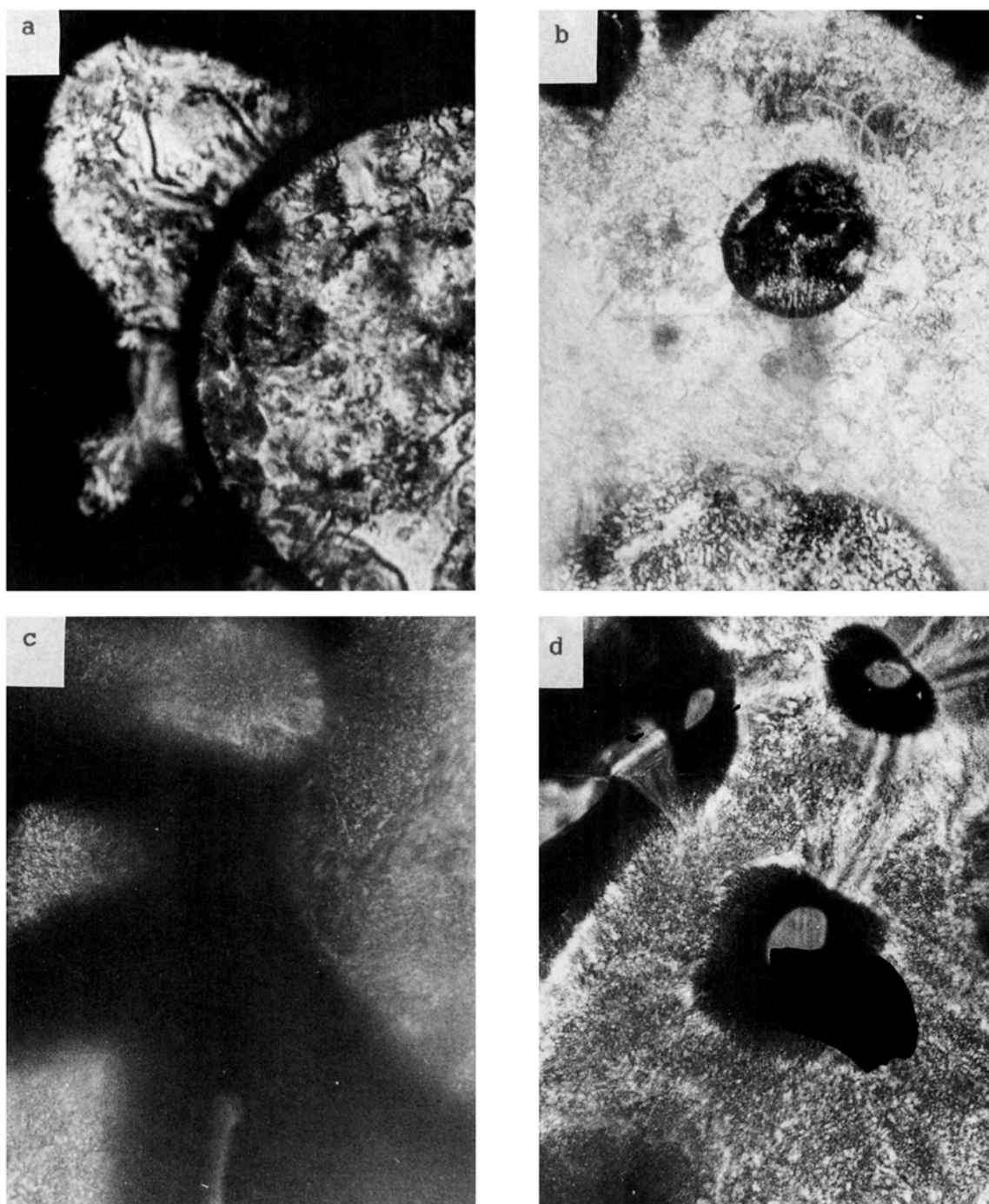


Figure 1 Polarized optical micrographs of the bisphenol family copolyesters: (a) TIHBP, (b) TIHBPM, (c) TIHBPA, (d) TIHSDP; 500 \times magnification.

tion are also found by the small-angle light-scattering studies as presented later.

Small-Angle Light Scattering

The H_v SALS patterns of the copolyesters are circularly symmetric and azimuthally independent as

shown in Figure 4. Although spherulites, lamellae, or rod-like elements can all lead to the same scattering patterns under certain conditions, the nature of the scattering is quite different.^{6,18-21} For most polymer systems, a four-leaf pattern is typical for spherulites, whereas a circularly symmetric and azi-

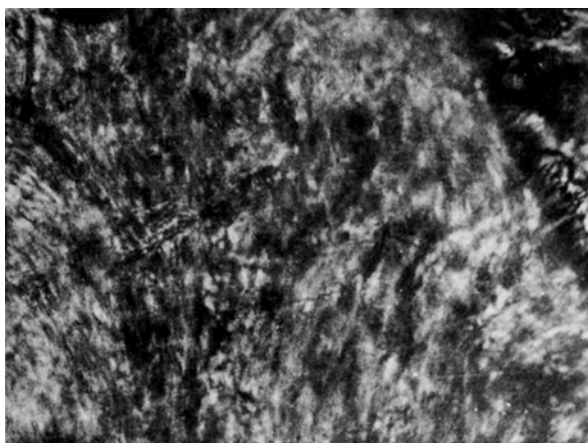


Figure 2 Flow texture of the nematic melt at 380°C, TIHBP sample, 500× magnification.

mutually independent pattern is typical for rod-like elements. This is also true for liquid crystalline polymers. When the scattering units are spherulites, the nematic mesophase shows a four-leaf pattern

with maxima along the 0 and 90° angles.^{5,22} The circularly symmetric and azimuthally independent patterns in Figure 4 indicate that the scattering elements are rod like. It seems that well-developed spherulites are not easy to form in the mesophase for this series of copolyesters. In a nematic mesophase the laser beam “sees” a multitude of oriented regions, each of which has its optical axis oriented along a different direction, the texture is thus composed of randomly oriented anisotropic domains that lead to the above patterns. Since it is known that H_v scattering with crossed polarizers is due to structural anisotropy, the intensity of scattering light represents the anisotropic behavior in the mesophase. The scattering-light intensities of TIHBP and TIHBPM copolyesters are much stronger than those of TIHSDP and TIHBPA copolyesters because of the more linear structures of the bridge groups in BP and BPM. The different sizes of the scattering patterns implicate the different sizes of the scattering elements in the mesophases. The bigger the pattern, the smaller the scattering elements.

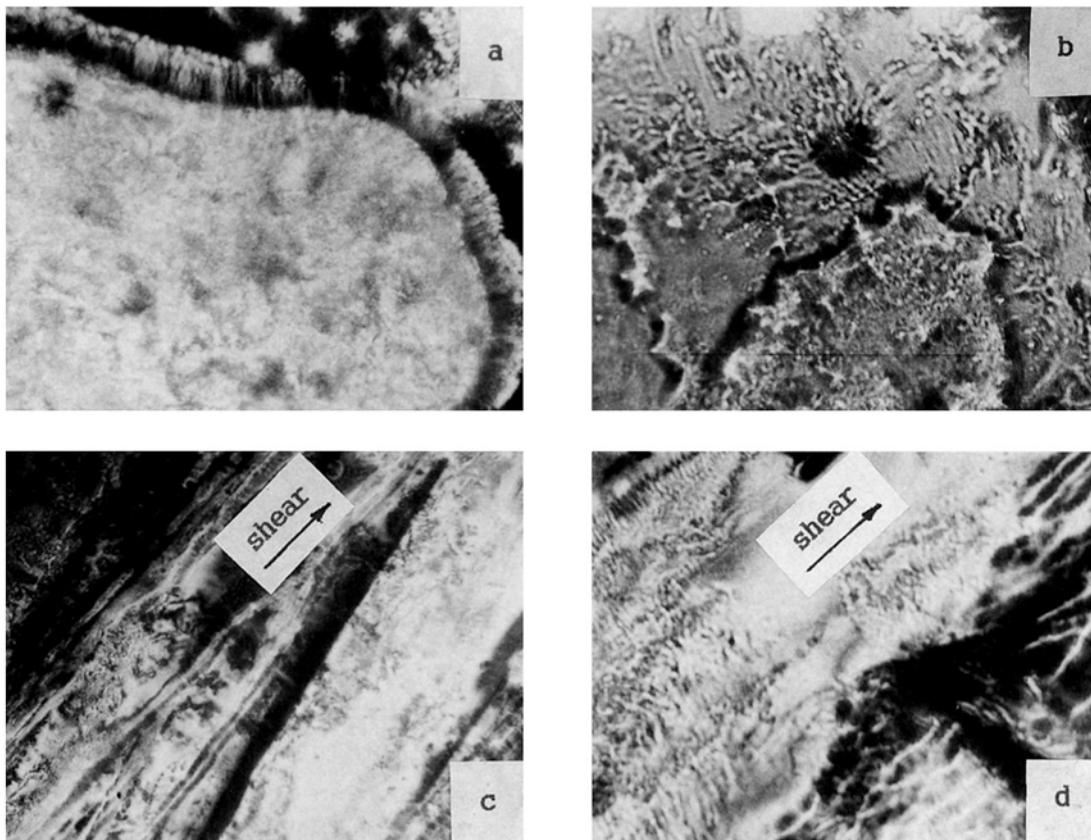


Figure 3 Textures of the nematic melt at 370°C under the condition: (a) thicker sample; (b) after a small pressure is applied; (c) when a shear is applied; and (d) when the shear is stopped for 1 min; TIHBP sample, 500× magnification.

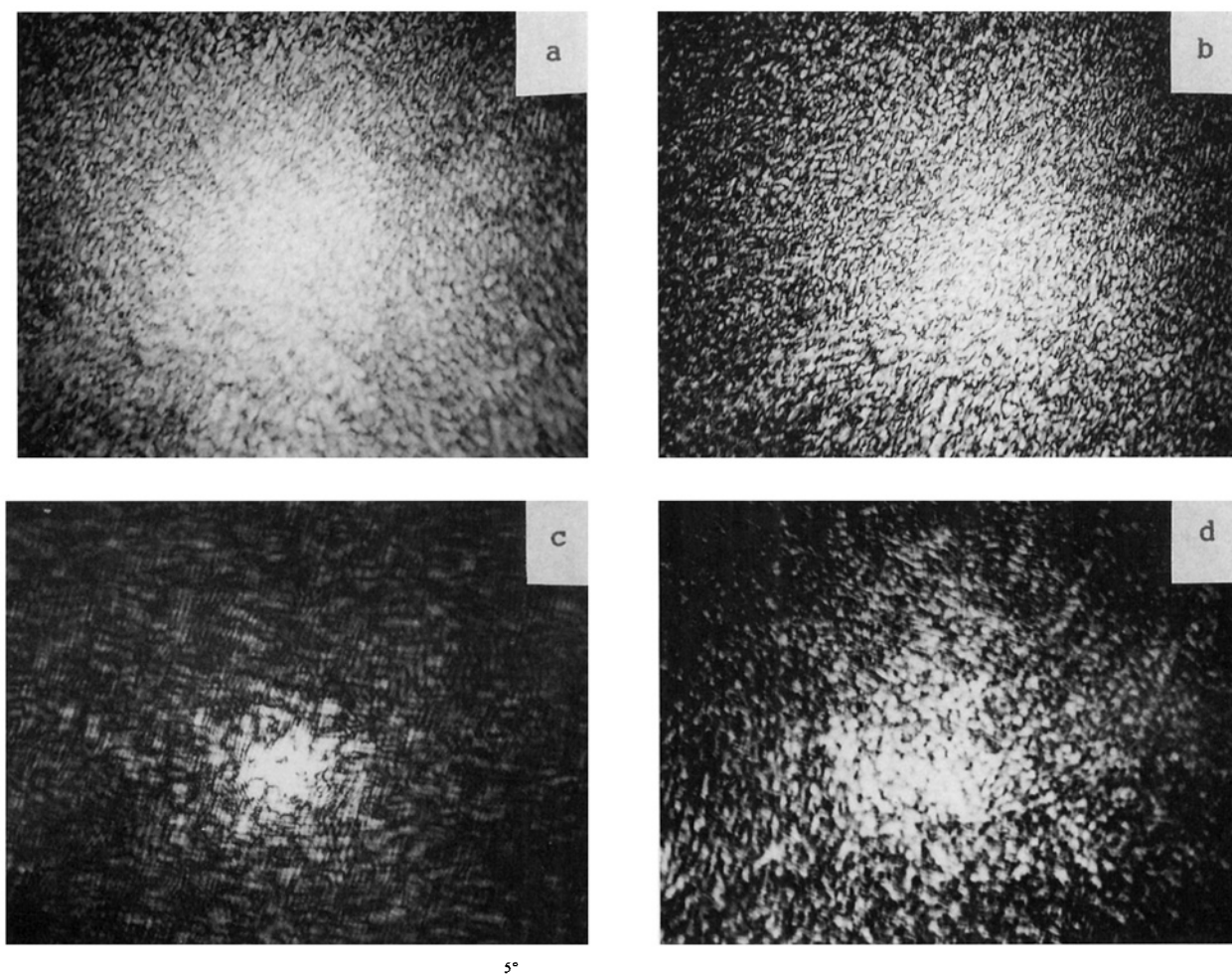


Figure 4 SALS (H_v) patterns \leftarrow of the quenched specimens from the nematic mesophases: (a) TIHBP; (b) TIHBPM; (c) TIHBPA; and (d) TIHSDP.

Therefore, it can be inferred from the photographs that the sizes of scattering elements of TIHBPA and TIHSDP copolyesters are larger than those of TIHBP and TIHBPM copolyesters.

The circular patterns change greatly when the mesophases are sheared. The patterns seem to contract along shear direction and elongate in the perpendicular direction as in Figure 5. Such scattering pattern changes produce to relieve the shear strain, internal stress, and excess free energy produced during the melt deformation.^{21,22} However, only part of the deformation can relax because of the rigid molecular chains of the copolyesters.

Depolarized Light Intensity Analysis

It is very commonly observed that thermotropic mesophases nucleate from the isotropic liquid in various shapes that subsequently grow into the

larger structures that produce the typical microscopic textures.^{23,24} Since there are no nematic-isotropic transitions for this group copolyesters, it is impossible for us to study the mesophase transformations by cooling the melts from isotropic states. Instead, the copolyesters are isothermally investigated at a temperature of 35°C above their melting points starting from a solid state. The samples melt within seconds and the mesophase transformations then begin. In Figure 6, the anisotropic light intensities under crossed polarizers increase with time and eventually reach a plateau where the solid-nematic transitions are considered complete. This event corresponds to the impingement of the growing nematic regions. The time for the copolyesters to reach the plateau follows the sequence $T_{\text{TIHBP}} < T_{\text{TIHBPM}} < T_{\text{TIHSDP}} < T_{\text{TIHBPA}}$. This order is the reverse of the order of plateau light intensity even though the light intensity scale has been enlarged

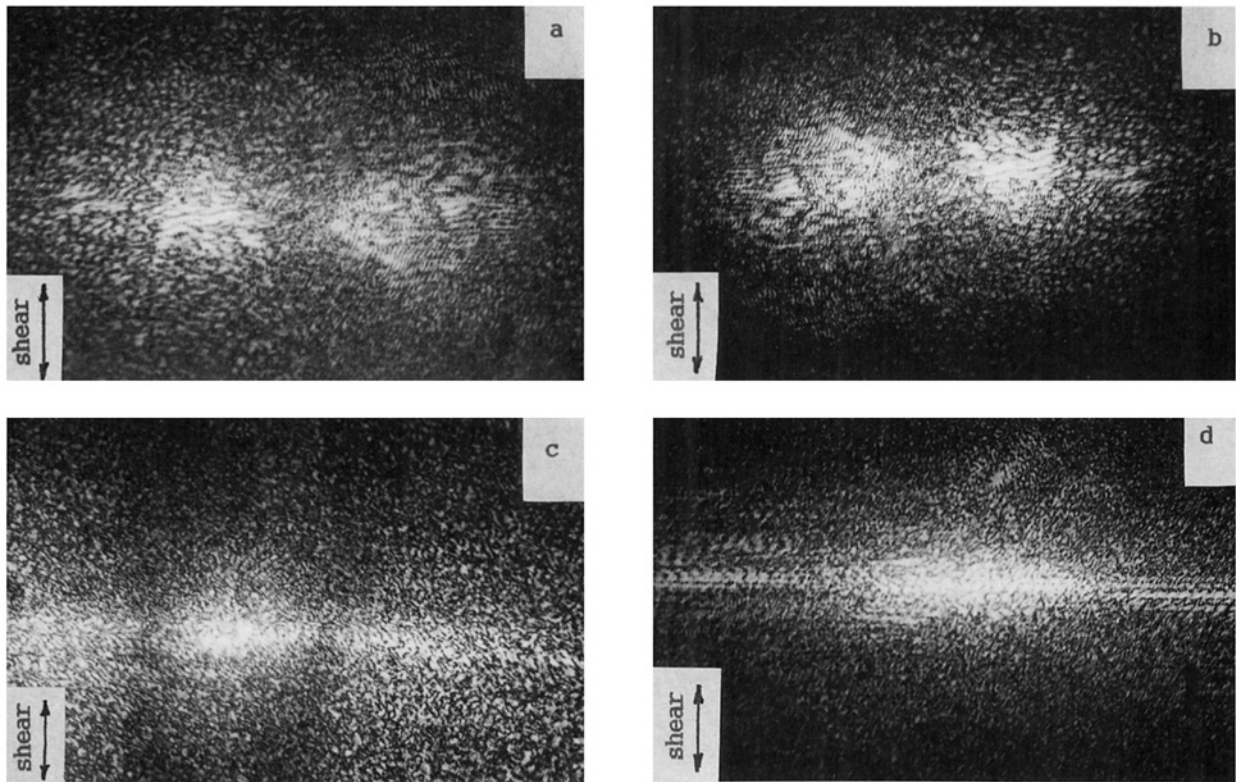


Figure 5 SALS (H_v) patterns 5° of the quenched specimens from the sheared nematic mesophases: (a) TIHBP; (b) TIHBPM; (c) TIHBPA; and (d) TIHSDP.

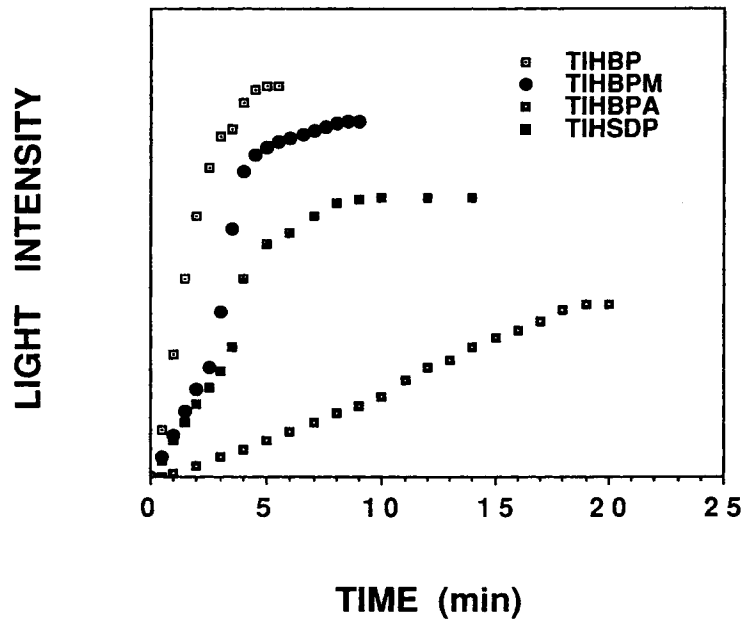


Figure 6 Isothermal mesophase transformations measured by depolarized light intensity analyzer.

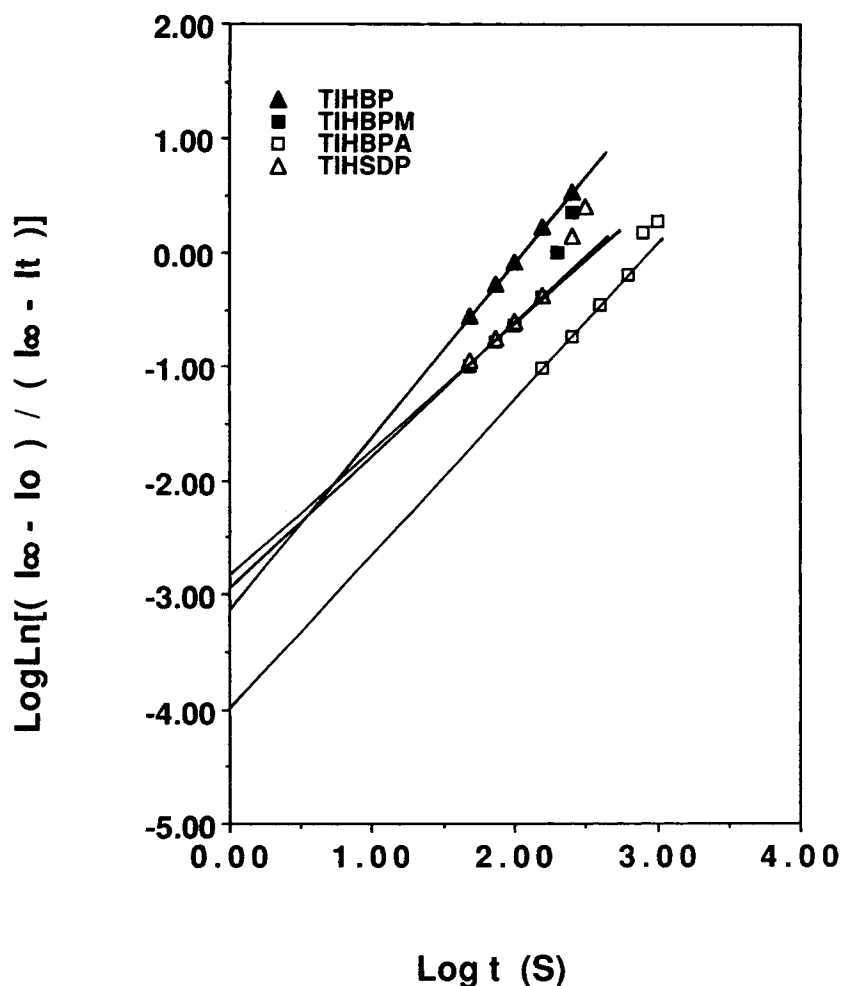


Figure 7 $\text{LogLn} [(I_{\infty} - I_0)/(I_{\infty} - I_t)]$ versus $\text{log } t$ curves of the bisphenol family copolyesters.

for samples TIHSDP and TIHBPA in the plot. The results indicate that the more linear the structure of the bisphenol bridge group, the easier the formation of the mesophase and the stronger the plateau light intensity. Quantitative comparison of the anisotropic behaviors of these copolyesters by using DLI has been studied.²⁵

Although some limitations exist on the validity and applicability of the Avrami equation,^{26,27} it has been used to describe a variety of mesophase transitions.²⁸⁻³⁰ The solid-nematic transitions of this group of copolyesters are also analyzed in terms of the Avrami equation which will allow us to do some qualitative studies.

By measuring the depolarized light intensities at different time, the Avrami equation can be used to describe isothermal transformations of the mesophases.

$$(I_{\infty} - I_t)/(I_{\infty} - I_0) = \exp(-kt^n) \quad (1)$$

$$\log \ln [(I_{\infty} - I_0)/(I_{\infty} - I_t)] = \log k + n \log t \quad (2)$$

where I_0 , I_t , and I_{∞} represent light intensities at initial, time t , and terminal moments, respectively; n is Avrami exponent dependent on the mode of nucleation and growth; k is the rate constant which is a combination of the nucleation density and growth rate.

Linear relationships are found between $\log \ln [(I_{\infty} - I_t)/(I_{\infty} - I_0)]$ and $\log t$ in the primary stage of the solid-nematic transitions as in Figure 7. The Avrami exponent, n , and rate constant, k , can be, therefore obtained and are listed in Table I. The Avrami equation exponents indicate that the primary stage of the formation of the mesophases is a one-dimensional and heterogeneous nucleation, and

Table I Avrami Equation Parameters of the Bisphenol Family Copolyesters

Sample	k	n
TIHBP	6.99×10^{-4}	1.54
TIHBPM	1.17×10^{-3}	1.15
TIHBPA	1.00×10^{-4}	1.36
TIHSDP	1.43×10^{-3}	1.12

the liquid crystal nuclei grow along one direction. This is why a well-developed supermolecular structure such as spherulites cannot form in the mesophase for these copolyesters. In fact, only rod-like supermolecular structures were observed in SALS patterns. The nematic-phase nucleates in droplets then coalesce into bigger nematic domains, which produce the typical threaded schlieren textures.²³ Such a growth process is supported by the polarized optical microscopy observation, where the scattering-point textures were found growing into nematic textures.

With the increase of nucleation density and the formation of nematic domains, the dependence of $\log \ln [(I_\infty - I_t)/(I_\infty - I_0)]$ on $\log t$ deviates from the linear portion in the primary stage. No direct relationship is found to characterize the later-stage mesophase transformations.

CONCLUSION

When the copolyesters are heated to temperatures above their melting points, the samples show nematic textures. Furthermore, increasing temperature causes the melts to flow and the mesophase textures to align along the flow direction. When temperatures are above the sample's thermodegradation points, the textures disappear. Increasing sample thickness causes an opaque texture, whereas a small pressure can increase the melt birefringence in the thicker sample. When a shear force is applied, the molecular domains in the mesophase align along the shear direction, which tend to partially relax when the shear is stopped. The texture change during the melt deformation and relaxation is consistent with the result displayed by small-angle light-scattering studies. The H_v SALS patterns of the copolyesters are circularly symmetric and azimuthally independent,

which change into a two-leaf or a belt shape after the mesophases are sheared. Such pattern changes occur to relieve the internal stress and excess free energy produced during the melt deformation. The depolarized light intensity analysis indicates that the early formation of the mesophases is a one-dimensional heterogeneous nucleation.

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