Effect of Thermal History on the Nematic State of a Thermotropic Liquid Crystal Polymer

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ABSTRACT: The effect of thermal history on the morphology and thermal behavior of a thermotropic liquid crystalline polyester based on alternating mesogenic and flexible units is studied by small-angle light scattering, optical microscopy, and thermal analysis. The average domain size corresponding to the nematic texture obtained following the transition from the isotropic to the nematic phase is found to be independent of the undercooling conditions. This is interpreted in terms of a proposed model for the formation of disclinations during the formation of the nematic phase. A kinetic study of the coarsening of the texture induced by isothermal aging in the nematic phase is presented. Thermal analysis results show that annealing can lead to an increase of up to 10 °C in the nematic to isotropic transition.

Introduction

Morphological studies of liquid crystal polymers (LCPs) have received much attention in recent years due to the ability of some of them to be processed into high mechanical performance materials. Recently, defects such as disclinations have been argued to be responsible for some of the unique rheological properties displayed by liquid crystal polymers.[1] The characterization of the often complex textures found in LCPs is a prerequisite in understanding the relationship between physical properties and molecular structures. One complication encountered in accomplishing this task is the fact that some physical[2] and rheological[3] properties are found to depend on thermal history.

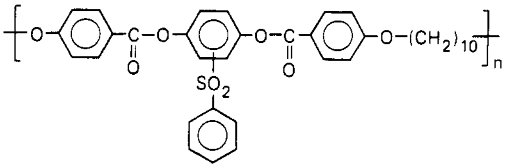
The aim of the present work is to study the effect of thermal history on the textures of thermotropic liquid crystals. We chose a semiflexible thermotropic liquid crystal that undergoes a nematic isotropic transition at temperatures below its decomposition to study the evolution of the nematic state by using the isotropic precursor as a reference state.

A common feature found in LCPs is the occurrence of large disclination densities that give rise to finer textures than those typically observed in low molecular weight liquid crystals. It has been observed that a spontaneous coarsening of fine schlieren textures can take place at temperatures within the nematic range. Shiwaku et al.[4] have shown that in a copolyester of poly(ethylene terephthalate) and *p*-oxybenzoate the coarsening of the texture occurs by the annihilation of disclinations of opposite sign.

The strong scattering of light by textured nematic liquid crystals is a consequence of the fluctuation in orientation corresponding to the director field imposed by the presence of disclinations. In fine schlieren textures, the orientation correlation length determined by the average disclination density can be characterized by small-angle light scattering (SALS).[5] Hereafter, the size parameter defining this correlation length will be referred to as a "domain size". In the present work, the SALS technique is used to quantitatively characterize the nematic textures, in terms of both an average domain size and a local order parameter. Furthermore, we present a calorimetric study of the effect of annealing on the nematic to isotropic (N-I) transition.

Experimental Section

The material studied was synthesized and cordially provided by Drs. Furakawa and Lenz of the University of Massachusetts; its synthesis and characterization are described elsewhere.[6] It consists of a thermotropic polyester based on a triad mesogenic unit containing an arylsulfonyl hydroquinone alternated with a decamethylene spacer. The structure of the polymer, referred to as PSHQ, is shown below.



The polymer was reported to have a glass transition temperature of 87 °C, a crystal to nematic transition at 100 °C, and a nematic to isotropic transition at 170 °C. The number-average molecular weight of PSHQ estimated by gel permeation chromatography using an Ultrastyragel column was M_n = 10 800 with a polydispersity index of 1.9.

Films of PSHQ for optical microscopy and light scattering measurements were prepared by slow casting from a 0.8 wt % tetrahydrofuran (THF) solution on microscope cover glasses. The thicknesses of the solvent-cast films were in the range 0.8–1.0 μm. The quantitative scattered intensities were measured by an OMAIII optical multichannel analyzer (EG&G Princeton Applied Research) detector system included in a SALS setup previously described.[7] The source consisted of a 2-mW He–Ne laser with a wavelength of 632.8 nm. The absolute values of the scattered intensities were determined by calibration with a Lambertian diffuser. The intensities were corrected for multiple scattering by dividing by the transmittance. This procedure suffices if the multiple scattering is not too high and only corrects for the loss in intensity due to this effect, and not for the intensity gain arising from the rescattering of light into the detector. A more correct procedure taking this into account has been described by Prud'homme et al.[8] However, the method requires the a priori knowledge of the scattering function. The polarized light optical micrographs were obtained with a Zeiss microscope incorporating a Mettler FP-2 hot-stage unit. The thermal analysis was performed on a Perkin-Elmer DSC-2 differential scanning calorimeter calibrated with indium and lead. The N–I transition temperatures were taken as the onset of the endotherm peak measured at a heating rate of 20 °C/min.

Results

The evolution of the nematic texture upon quenching from the isotropic precursor was studied by optical

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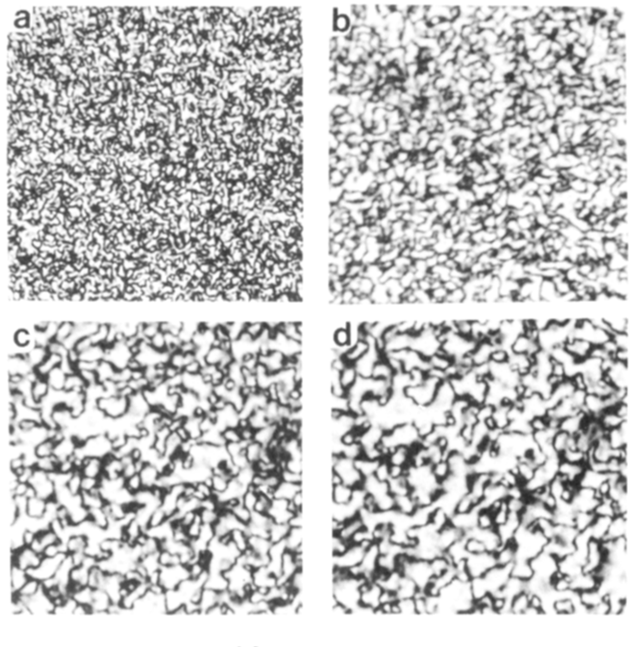

Figure 1. Polarized micrographs of PSHQ as a function of annealing time at 150 °C: (a) 1 h; (b) 3 h; (c) 9 h; (d) 20 h.

microscopy and SALS. As-cast isotropic films were initially treated in the isotropic phase at 210 °C for 10 min, cooled to 180 °C until the temperature was stabilized, and then rapidly transferred to a hot stage preset at a constant temperature in the range 130–160 °C. The quenching of the films induced the formation of a fine schlieren texture. A continuous birefringent texture extending over the entire field of view of the optical microscope could be observed ca. 5 s after the quenching step.

Figure 1 shows the polarized optical micrographs recorded during annealing at 150 °C, where the annealing time is measured from the point at which the sample was quenched from the isotropic state. Annealing results in a relatively slow coarsening of the fine schlieren texture, indicated by a decrease in the density of the extinction lines. No significant changes in the texture could be detected for annealing times longer than 24 h, up to a total of 4 days.

The large concentration of defects present in the observed textures (as indicated by the proximity of adjacent extinction lines) did not allow for a definite identification of the type of defects. The resemblance of these textures to those observed in other systems,[4] however, suggests the textures are composed of disclinations lines, which are the lowest energy type of defects in quiescent nematic textures.

The texture coarsening, which can be referred to as a "domain growth" process, greatly affects the SALS patterns, as shown in Figure 2. The H_v scattered intensity moves to smaller angles, indicating an increase in the orientation correlation length. The time dependence of the H_v intensity was used to study the kinetics of the domain growth. The SALS technique was found to be more sensitive than optical microscopy to the coarsening occurring in the initial three hours.

The four leaf clover shape H_v patterns are characterized by a maximum intensity at a scattering angle $\theta = \theta_{\max}$ occurring at azimuthal angles $\mu_{\max}$,$\mu_{\max}$ being integer multiples of 90°. At the present time, no model can be found in the literature describing the complex orientation fluctuations occurring in textured nematics which could be used for the analysis of the scattering. A semiquantitative model proposed by Hashimoto et al.[5] describing the orientation fluctuations imposed by groups of disclinations predicts H_v SALS patterns with intensity maxima at scattering angles $\theta_{\max}$ as the case in the experimentally observed patterns. In analogy with the treatment of the scattering from anisotropic spheres, it is found that the system can be described in terms of the dimensionless constant $U_{\max}$, defined as

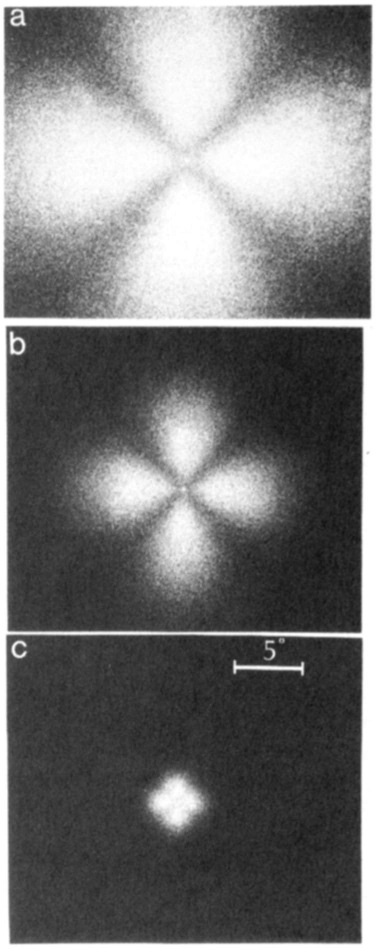

Figure 2. H_v SALS patterns from PSHQ films quenched from the nematic phase after various annealing periods (incident polarization is vertical): (a) 1 min; (b) 30 min; (c) 5 h.

$$U_{\max} = \frac{4\pi}{\lambda} a \sin \frac{\theta_{\max}}{2} = a q_{\max} \tag{1}$$

where λ is the wavelength, q is the magnitude of the scattering vector, and a is a characteristic size of the scattering entity. While the value of the constant $U_{\max}$ is not known for the system presently discussed, the orientation fluctuations in the fine schlieren textures can be characterized by the quantity $1/q_{\max}$, differing from the actual value of a in eq 1 by a proportionality constant. Figure 3 shows a series of scattering curves, represented in terms of $Iq_{\max}^2$ versus the scattering vector q, corresponding to increasing annealing times at 150 °C. The factor $q_{\max}^2$ is a normalization factor to account for the increase in the scattering intensity due to the change in the correlation length. The correlation length dependence of the intensity is discussed in the following paragraph. The kinetics of the coarsening can be represented in terms of growth curves, obtained by plotting the values of $1/q_{\max}$ extracted from the curves in Figure 3, as a function of annealing time. Figure 4 shows the growth curves obtained for annealing temperatures in the range 130–160 °C. One important observation is that the growth curves obtained

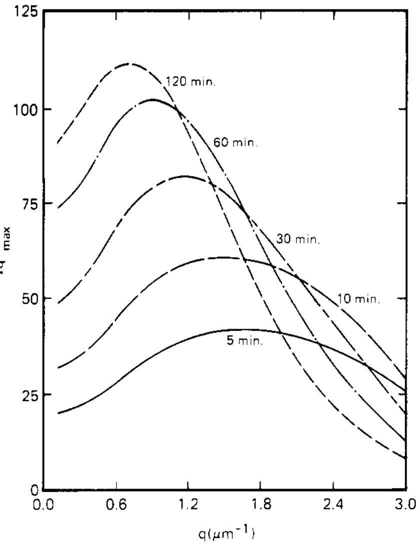

Figure 3. H_v intensity distribution at μ = 0° measured at increasing annealing time at 150 °C.

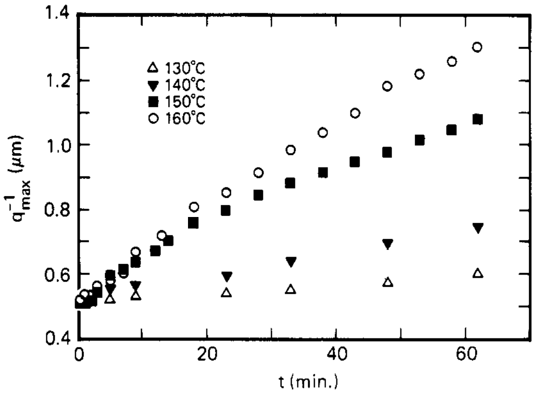

Figure 4. Growth curves of PSHQ at various temperatures.

at different temperatures (Figure 4) have a common intercept at $t = 0$ ($1/q_{max} = 0.52 \pm 0.01$ μm), suggesting that for the range of temperatures studied, the initial disclination density is independent of the degree of undercooling. As the rate of the phase transition is comparable to the estimated cooling rates used, it could not be unambiguously established whether the nematic phase formation occurred at isothermal conditions. The temperature independence of the initial disclination density, however, is supported by the observation that the same initial value of $1/q_{max}$ was obtained for as-cast, isotropic films that were subject to temperature jumps from room temperature to the respective temperatures in the nematic range (cold liquid crystallization).

As already indicated by Figure 3, the domain growth is accompanied by a significant increase in the scattering intensity. During the first 8 h of annealing at 150 °C, the scattered intensity at q_{max} increases by 2 orders of magnitude, from an initial Rayleigh ratio of 30 cm^{-1} up to 4000 cm^{-1}. In addition to the analysis of its angular distribution, the scattering can be used for obtaining information regarding the local anisotropy. In the Rayleigh–Gans–Debye approximation, the scattered intensity depends both on the size of the structural unit giving rise to it and on the scattering efficiency of the system.[9] For systems in which the scattering arises from orientation fluctuations, the latter is related to the anisotropy of polarizability. The dependence of the H_v intensity on the various parameters can be generalized as

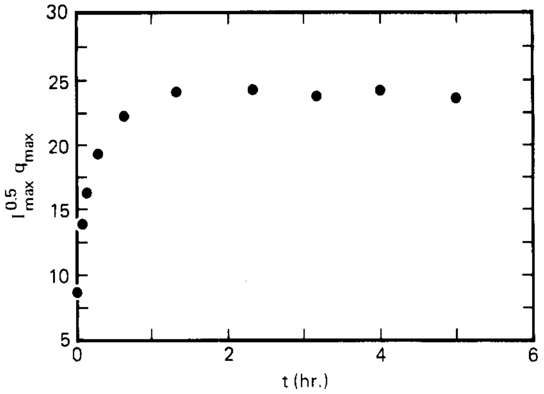

Figure 5. Local order parameter (in arbitrary units) of PSHQ as a function of annealing time at 150 °C.

$$I_{H_v}(q) = KP(q)\delta_{loc}{}^2 a^n \qquad (2)$$

where K is a constant, $P(q)$ is the normalized intensity distribution function, and $\delta_{loc}{}^2$ is the local anisotropy of polarizability, which is related to the molecular anisotropy of polarizability δ_{mol} by

$$\delta_{loc} = p\delta_{mol} \qquad (3)$$

p being a local order parameter defined as

$$p = {}^1/_2[3\cos^2\theta - 1] \qquad (4)$$

where θ is the angle between the molecular axis and the optic axis of the volume element and the square brackets represent a local average.

As the value of δ_{mol} is not known for the system presently studied, it is not possible to obtain absolute values for the local order parameter. Nevertheless, the relative value of the order parameter can be evaluated by the quantity $(I_{max})^{1/n}q_{max}$.

The value of the exponent n in eq 2 depends on whether the scattering arises from particles dispersed in a continuous matrix or from continuous fluctuations in a one-phase system. Examples for continuous fluctuations include systems that can be described by exponential correlation functions[10,11] and systems consisting of volume-filling particles, such as anisotropic spheres.[12] In such systems the value of n is equal to the dimensionality of the system. Assuming that the orientation of the director is not a function of the z coordinate representing the plane normal (planar textures), the corresponding exponent is 2 and the local order parameter is given by $I_{max}{}^{0.5}q_{max}$. Figure 5 shows a plot of the local order parameter as a function of annealing time at 150 °C. A significant increase in the local order parameter occurs during the initial annealing period, reaching a constant value after ca. 2 h. This indicates that the nematic phase obtained following the fast transition from the isotropic phase does not immediately reach its maximum, stable degree of order.

The total H_v scattered intensity of PSHQ has been studied by Goldman,[13] who observed that the scattered intensity increases significantly during the early annealing times, followed by a slower increase that continues for several hours. These observations are the result of the combined effect of the time dependence of the local order parameter and the coarsening process.

The most significant evidence for the nonequilibrium state of the initial nematic phase comes from the thermal analysis studies. Isothermal annealing at temperatures in the nematic range was found to affect the nematic to isotropic (N–I) transition, as shown in Figure 6. The DSC thermograms show that annealing induces an increase in

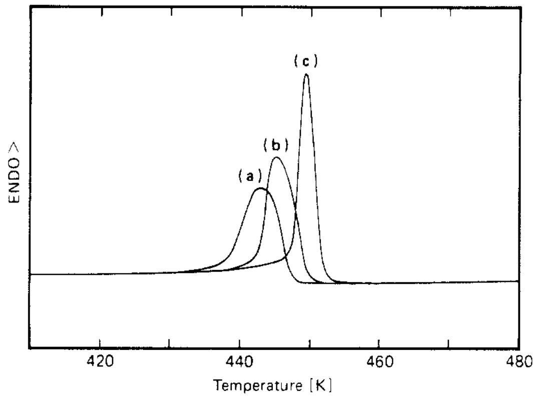

Figure 6. Effect of annealing at 150 °C on the DSC endotherms of the N–I transition: (a) unannealed; (b) 3 h; (c) 12 h.

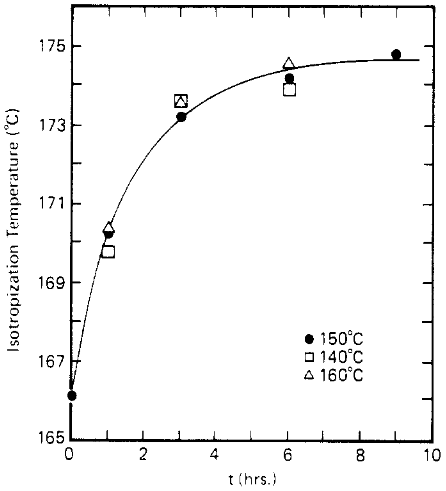

Figure 7. Nematic to isotropic transition temperature as a function of annealing time.

the N–I transition temperature along with a sharpening of the endotherm peak. The enthalpy of the transition given by the area under the endotherm was found to be independent of annealing time and annealing temperature within the experimental error ($\Delta H = 1.20 \pm 0.10$ cal/g). Figure 7 shows the N–I transition temperature as a function of annealing time for various annealing temperatures. The points corresponding to the different annealing temperatures fall on a single curve, suggesting that within experimental error, the effect of annealing on the N–I transition is independent of annealing temperature. The shift in the isotropization temperature was found to be reversible in the sense that the effect of annealing could be erased by heat treating the samples in the isotropic state. This is an indication that the changes induced by annealing cannot be attributed to changes in the chemical structure (e.g., transesterification, postpolymerization). GPC results showed no significant changes in the average molecular weight after annealing for 12 h at 150 °C.

Discussion

It has been previously demonstrated by Shiwaku et al.[4] that the mechanism of the texture coarsening in typical fine schlieren textures characteristic of polymeric liquid crystals involves the annihilation of disclination defects. The spontaneous coarsening observed during annealing at constant temperature following the nematic phase formation suggests that the initial disclination density is larger than the density determined by the substrate. Thus, the domain growth can be interpreted as a relaxation process driven by the excess elastic free energy of deformation related to the initial texture.

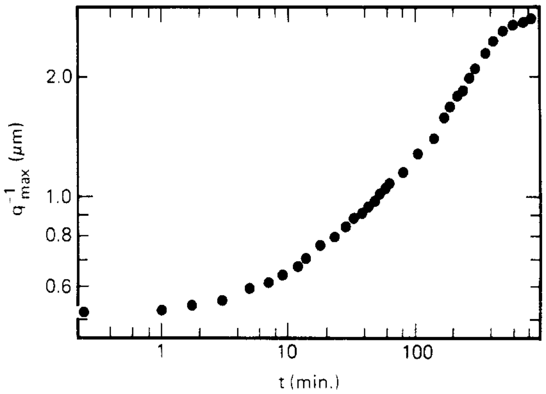

Figure 8. Logarithmic plot of the growth curve of PSHQ at 150 °C.

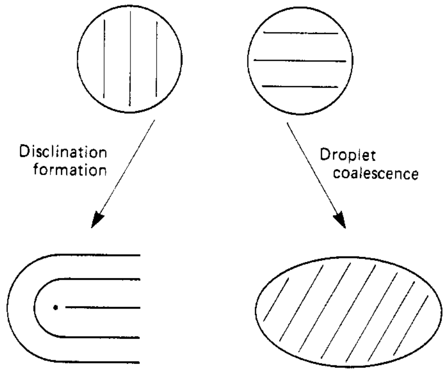

Figure 9. Schematic representation of a model for the formation of disclinations during the formation of the nematic phase.

In a previous study of a *p*-methyl-substituted PSHQ polymer,[14] the domain size was found to follow a power-law behavior with a scaling exponent of 0.37. A power-law behavior was also reported by Shiwaku et al.[4] for the time dependence of the average distance between neighboring disclinations, with a scaling exponent of 0.35. In the unsubstituted PSHQ studied in the present work we were able to measure the domain growth over a larger size scale. Figure 8 shows a logarithmic plot of the growth curve measured during annealing of PSHQ at 150 °C for a period of 15 h, covering $1/q_{max}$ values from 0.5 to 2.8 μm. The present data, however, cannot be described by a single scaling parameter.

Concerning the temperature dependence of the domain growth, Figure 4 shows an increase in growth rate, given by the initial slope of the growth curves, with increasing temperature. This observation indicates that in the temperature range studied, the temperature dependence of the annihilation of disclinations is controlled by the viscosity of the system.

We shall now discuss the observation that the initial disclination density was found invariant to the degree of undercooling. One possible explanation for this is based on a model for the formation of disclinations which we shall presently describe.

The model relates the formation of disclinations to the mechanism of the phase transition from the isotropic to the nematic phase. It is assumed that the nematic phase is formed by a nucleation and growth mechanism. The molecules within a nucleus are assumed to be homogeneously aligned, as schematically shown in Figure 9. For simplicity, the nuclei are represented as circular nematic droplets; however, the results of the qualitative model will not be affected if the nematic nuclei would be of different geometry. The director within a droplet can take any possible orientation, independent of the orientation of neighboring droplets. As the nematic droplets grow, neighboring droplets impinge on each other. The angle α defined by the direction of the directors of impinging domains is a random variable. The impingement of two nematic droplets can result in either of two competing processes. One process is defined as a "droplet coalescence", resulting in the formation of a larger nematic droplet in which the director orientation varies only gradually, without defects. This process involves a molecular reorientation, its extent determined by the value of α. A second possible result of the impingement is the formation of a defect such as a disclination. As the formation of a disclination allows for abrupt changes in orientation, this process can take place without involving a significant reorientation of molecules. Figure 9 illustrates how the creation of a $S = {}^1/_2$ disclination can nearly preserve the overall orientation of impinging droplets with $\alpha = 90^\circ$. According to this model, the disclination density of the texture formed at the isotropic to nematic transition is kinetically determined by the orientational viscosity of the system, leading to the prediction of an increase in the initial disclination density with increasing molecular weight. This would account for the observation of fine textures in polymeric systems as compared to the coarser textures typical of low molecular weight liquid crystals.

The kinetic model for the formation of disclinations predicts the initial disclination density being proportional to the nucleation density of the nematic phase. Thus, the temperature dependence of the initial disclination density is given by the temperature dependence of the nucleation rate of the nematic phase. In this context, the experimentally observed temperature independence of the initial disclination density could be accounted for by this model, assuming that the effective nucleation rate is temperature independent. While it would be tempting to suggest a mechanism for the formation of the nematic phase involving heterogeneous nucleation as a way to account for the temperature independence of the nucleation rate, it should be pointed out that the formation of the nematic phase bears some significant differences with the crystallization process, and there are other factors that could lead to an effective nucleation rate being independent of temperature.

The picture of a monodomain droplet depicted in Figure 9, in which the molecular orientation is not affected by the presence of the interphase, is an oversimplification. Due to the anisotropy of the interfacial energy, it is expected that the interphase will induce a specific local orientation, introducing a distortion of the director field. As such, the free energy of a nematic nucleus should include a term representing the excess free energy due to the distortion of the director field, its value being proportional to an effective elastic constant k_{eff}. Since the excess energy due to the elastic deformation depends both on the nucleus size and on temperature, it is possible that more than one parameter could be responsible for an apparent temperature-independent nucleation rate.

The DSC results concerning the effect of annealing on the N–I transition indicate that the nematic state obtained immediately following the formation of the nematic phase is not an equilibrium state. The reversible increase in the transition temperature and the sharpening of the N–I endotherm peak can be interpreted as in increase in the microscopic degree of order. While at the present time the precise mechanism responsible for this process is not clear, the fact that the kinetics of this process are independent of annealing temperature is a clear indication that the N–I transition temperature is not related to the disclination density. The time scale for the shift in the N–I transition temperature, however, correlates well with the increase in the local parameter calculated based on the SALS data.

Conclusions

The present study shows that in the system studied, while the nematic phase formation is a fast process (on the order of seconds), it takes much longer for the system to reach its stable ordered state. The effect of annealing can be described by the occurrence of two independent relaxation processes.

The first process is the coarsening of the initially fine schlieren texture, the so-named domain growth process. The domain growth is a consequence of the fact that the concentration of disclinations determined during the formation of the nematic phase is higher than the stable concentration, the latter believed to be determined by the nature of the substrate. The domain growth involves the annihilation of disclinations, and the increasing growth rate observed at higher temperatures indicates that in the temperature range studied, the temperature dependence of the texture coarsening is determined by the viscosity of the system. On the other hand, the second ordering process responsible for the increase in the N–I transition temperature is independent of the annealing temperature.

In conclusion, it has been shown that the nematic phase of polymer systems, in spite of being a liquid state, is not necessarily an equilibrium state. Future morphological studies aimed at elucidating the mechanisms of the various ordering processes occurring in thermotropic LCPs should provide further insight on the nonequilibrium nature of such systems.

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