Thermally Reversible Light Scattering Films Based on Droplets of a Liquid Crystal (*N*-4-Ethoxybenzylidene-4′-*n*-butylaniline)/Polystyrene Solution Dispersed in an Epoxy Matrix

C. E. Hoppe, M. J. Galante, P. A. Oyanguren, and R. J. J. Williams*

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), J. B. Justo 4302, 7600 Mar del Plata, Argentina

Received February 13, 2004; Revised Manuscript Received May 7, 2004

ABSTRACT: Thermally reversible light scattering (TRLS) films were synthesized by the reaction-induced phase separation of solutions of *N*-4-ethoxybenzylidene-4′-*n*-butylaniline (EBBA; 20−50 wt %) and polystyrene (PS; 1−5 wt %) in diglycidyl ether of bisphenol A (DGEBA), using benzyldimethylamine (BDMA) (0.06 mol with respect to epoxy groups), to initiate the polymerization. The material obtained after complete reaction consisted of a dispersion of EBBA/PS droplets in the epoxy network partially swollen by EBBA. The fractionation of EBBA between both phases was estimated using a simple thermodynamic model. Due to the matching of refractive indices of the three components, the multiphasic material was transparent above the nematic−isotropic transition temperature (T_{NI}) of the EBBA/PS droplets. Below T_{NI} the material exhibited a sharp transition to an opaque state due to the mismatching of refractive indices when EBBA was segregated as a nematic phase inside the droplets. The PS addition produced a significant decrease of the cloud-point conversion with respect to formulations devoid of PS. This led to relatively large domains that behave efficiently as light scattering centers in the PS-modified material, enabling high contrast ratios between transparent and opaque states to be obtained. The morphologies generated, and the corresponding optical properties of the TRLS films, did not change in the course of successive cooling/heating cycles.

Introduction

Films that can be thermally switched from opaque (translucent) to transparent states, called thermally reversible light scattering (TRLS) films, have potential uses in privacy windows, displays, thermal sensors, active elements in thermal memory all-optical devices, and other optical applications.[1−3] Materials developed for these purposes consist of two phases that exhibit a mismatch of refractive indices at a characteristic temperature, where one of the phases undergoes a disorder−order transition (i.e., a crystallization or an isotropic−nematic transition). A usual composition for TRLS films consists of domains of a relatively low molar mass compound (i.e., a fatty acid or a liquid crystal), dispersed in a polymer matrix. This compound exhibits a relatively high solubility in the polymer matrix that depends on temperature. This leads to a low activation energy for the variation of optical transmission with temperature, which is one of the main drawbacks for practical applications. Besides, changes in morphologies in the course of successive cooling/heating cycles lead to corresponding variations of optical properties.

In this paper it will be shown that the mentioned drawbacks may be eliminated by adding a small amount of a thermoplastic polymer to a solution of a liquid crystal in thermoset precursors. The thermoplastic polymer must have a refractive index matching that of the fully cured thermoset, and should exhibit a high compatibility with the liquid crystal and a low compatibility with the thermoset precursors. This would lead to phase separation of thermoplastic/liquid crystal solutions at low conversions in the polymerization reaction. This process has the following potential advantages: (a) a dispersion of droplets of adequate size for the scattering of visible light may be achieved at low thermoplastic concentrations, due to the fact that growth and coalescence processes are favored when phase separation occurs at low conversions, (b) the primary morphology should be stable at room temperature or in the course of successive cooling/heating cycles due to the high viscosity of droplets containing the thermoplastic polymer, (c) the residual concentration of the liquid crystal in the thermoset may be decreased, leading to an increase of its glass transition temperature. Although we will focus on generating an efficient TRLS film, these ideas can be applied as well to the development of new families of polymer-dispersed liquid crystal (PDLC) films.

A suitable thermoplastic/thermoset blend for optical applications is that composed of polystyrene (PS) and an epoxy network. We have recently shown[4] that the refractive indices of PS and an epoxy network produced by the homopolymerization of diglycidyl ether of bisphenol A (DGEBA), initiated by a tertiary amine, are very close. At the polymerization temperature (80 °C), PS is initially soluble in DGEBA but phase separates at low conversions in the polymerization reaction, leading to a transparent biphasic material at full conversion. Depending on the molar mass distribution of PS and its initial concentration in the solution with the monomer, the generated morphology may consist of a dispersion of PS-rich particles in the epoxy matrix, a dispersion of cross-linked epoxy particles in a PS matrix, or two bicontinuous PS and epoxy phases.[5] Using low concentrations of PS (typically less than 10 wt %) leads to a dispersion of PS-rich domains in the epoxy matrix.

In the course of the phase separation process induced by the epoxy polymerization, there is a fractionation of both polymers between the phases generated.[6,7] This

* To whom correspondence should be addressed. E-mail: williams@fi.mdp.edu.ar.

10.1021/ma0496955 CCC: $27.50
Published on Web 00/00/0000 PAGE EST: 5.9

may lead to a secondary phase separation consisting of the formation of cross-linked epoxy domains inside the PS-rich particles. As a consequence of this phenomenon, the volume fraction of dispersed-phase particles in the final material may be significantly higher than the volume fraction of PS in the initial formulation.

To generate a TRLS film, it was necessary to search for a particular liquid crystal (LC) with two main characteristics: (a) solubility with PS in all proportions at the temperature used to produce the polymerization-induced phase separation (80 °C), (b) a refractive index in the isotropic state similar to that of PS. *N*-4-Ethoxybenzylidene-4′-*n*-butylaniline (EBBA) fulfilled the required conditions and was selected for this study. Although Schiff-base liquid crystals are usually quite unstable,[8] no evidence of a reaction involving EBBA was found under the experimental conditions of this study.

Our aim in this paper is to show the feasibility of obtaining TRLS films by reaction-induced phase separation of a solution of EBBA and PS in DGEBA, including a small amount of a tertiary amine to initiate the homopolymerization. A simple thermodynamic model will be used to estimate the distribution of EBBA between the epoxy network and the segregated PS domains. Optical properties of these films will be compared with those of films consisting of an EBBA phase dispersed in the epoxy network (a typical PDLC). This will enable us to discuss the effect produced by the confinement of the liquid crystal in the dispersed domains containing the thermoplastic polymer.

Experimental Section

Synthesis of TRLS Films. The epoxy monomer was based on diglycidyl ether of bisphenol A (DGEBA; Der 332 Dow, 174 g/mol epoxy groups). The initiator of the homopolymerization was benzyldimethylamine (BDMA, Sigma), used in a molar ratio BDMA/epoxy groups = 0.06. A commercial polystyrene was used (PS; M_n = 39800 g/mol, M_w = 297000 g/mol). It was heated at 160 °C for 4 h before use to eliminate residual volatiles. The liquid crystal was *N*-4-ethoxybenzylidene-4′-*n*-butylaniline (EBBA; Aldrich), with a melting temperature of 38 °C and a nematic−isotropic transition temperature T_{NI} of 77.5 °C.

Selected amounts of DGEBA and PS were dissolved in tetrahydrofuran (THF) to give a homogeneous solution (about 0.6 g/mL). THF was removed by heating for 2 days at room temperature followed by 3 h at 90 °C. Then the blend was cooled to room temperature, the selected amount of EBBA was added, and the temperature was increased to about 50 °C with stirring, to obtain a homogeneous solution. After the solution was cooled to room temperature, the appropriate amount of BDMA was incorporated.

Films were obtained by casting solutions containing 1−5 wt % PS, 20−50 wt % EBBA, and DGEBA/initiator in the remaining percentage between glass covers separated by a spacer of desired thickness (in most cases a steel spacer of 0.5 mm thickness was used). The temperature was increased to 80 °C, and polymerization was allowed to proceed for 26 h. Under these conditions, full conversion of epoxy groups was attained as revealed by Fourier transform near-infrared spectroscopy (FTNIR).[9]

Characterization Techniques. Differential scanning calorimetry (DSC; Pyris 1, Perkin-Elmer) was used to determine the temperatures of various transitions occurring in both phases: the melting temperature (T_m) of EBBA, nematic−isotropic transition temperature (T_{NI}) of the EBBA-rich phase, and glass transition temperature (T_g) of the epoxy-rich phase. These temperatures were determined during a heating scan at 10 °C/min under nitrogen, following a cooling scan at the same rate. Both T_m and T_{NI} were measured at the end of the corresponding transition, and T_g was taken at the onset of the glass transition.

Transmission optical microscopy (TOM) was used to determine cloud-point temperatures (T_{cp}), cloud-point times (t_{cp}), and T_{NI} values, as well as to obtain micrographs of final morphologies. A Leica DMLB microscope, provided with a video camera (Leica DC 100) and a hot stage (Linkam THMS 600), was used for these purposes. T_{cp} values of initial formulations were determined by TOM, in the course of cooling scans at 1 °C/min; t_{cp} values were measured during isothermal polymerizations at 80 °C. T_{NI} values were determined using crossed polarizers (polarized optical microscopy, POM), during heating scans at 1 °C/min. The transition temperature was defined as the maximum temperature at which nematic domains were still observed. Optical transmittance measurements in the wavelength of visible light were made using a photodetector incorporated into the optical path of the microscope, at a heating/cooling rate of 2 °C/min.

Near-infrared spectroscopy (NIR) was used to determine the polymerization kinetics of different formulations. An FTIR instrument (Genesis II, Mattson), provided with a heated transmission cell (HT-32, Spectra Tech) with quartz windows (32 mm diameter) and a programmable temperature controller (Omega, Spectra Tech, $\Delta T = \pm 1$ °C), was employed. The sample was placed between quartz windows using a spacer of 0.5 mm. The reaction was carried out at 80 °C, following the height of the absorption band at 4530 cm^{-1} with respect to the height of a reference band at 4621 cm^{-1}.[9]

Times to gel, t_{gel}, were determined from solubility tests in THF. A set of test tubes containing the initial formulation were placed in an oven at 80 °C. Each one of them was extracted from the oven at different times, and the solubility of the partially reacted material in THF was observed. The presence of a gel was evidenced when a fraction of the initial sample remained in a swollen state.

Results and Discussion

Phase Diagram of Initial Formulations. For the development of TRLS films we are interested in formulations containing small amounts of PS in a DGEBA/EBBA solution. To illustrate the different phase separation processes that can take place in this range of compositions, formulations containing 5 wt % PS were selected. Figure 1 shows the phase diagram of these formulations (the *x*-axis represents the mass fraction of EBBA in the binary mixture with DGEBA; the amount of EBBA + DGEBA constitutes 95% of the total mass).

The curve at low EBBA concentrations is a cloud-point curve. Above this curve a single isotropic phase is present. Below this curve the system phase-separates, generating two isotropic phases with different compositions (one rich in PS and the other rich in DGEBA). The cloud-point temperature of the binary formulation containing 5 wt % PS and 95 wt % DGEBA, read at EBBA = 0, is close to 77 °C. The addition of EBBA produces a

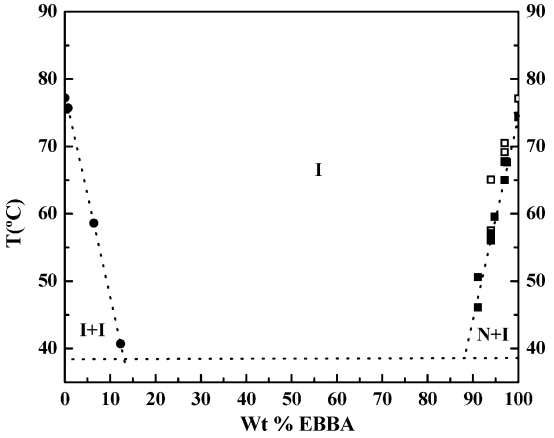

Figure 1. Phase diagram for ternary formulations (PS−EBBA−DGEBA), containing 5 wt % PS (the *x*-axis represents the mass percent of EBBA with respect to the amount of EBBA + DGEBA). Nematic−isotropic transition temperatures were determined using POM (filled squares) and DSC (open squares).

significant increase in the solubility of PS. When the mass fraction of EBBA (in the mixture with DGEBA) is 12%, the cloud-point temperature is 38 °C. Below this temperature crystallization of EBBA may take place (the melting temperature of pure EBBA is 38 °C). Therefore, EBBA is a very good solvent of PS.

The curve at high EBBA concentrations shows the nematic−isotropic transition. Below this curve, EBBA is segregated as a nematic phase. The nematic−isotropic transition for a formulation containing 5 wt % PS and 95 wt % EBBA, read at EBBA = 100, is close to 77 °C. This value is very close to the T_{NI} of pure EBBA, indicating that diluted solutions of PS in EBBA produced only a slight decrease of T_{NI}, as was previously shown.[10] However, small additions of DGEBA to the PS/EBBA solution lead to a sharp decrease of T_{NI}. This means that, in the TRLS film composed of dispersed droplets of a PS/EBBA solution in the epoxy matrix, the presence of a small fraction of residual monomer in the droplets (or any other low molar mass species as the initiator) will provoke a sharp decrease of the T_{NI} value.

Polymerization-Induced Phase Separation. Initial formulations containing 1−5 wt % PS, 20−50 wt % EBBA, and DGEBA in the remaining percentage were polymerized at 80 °C with the addition of BDMA as initiator. At this temperature the initial solutions were homogeneous. However, at a particular conversion in the epoxy homopolymerization, phase separation took place, leading to a PS/EBBA-rich phase and an epoxy/EBBA-rich phase. At this temperature, PS and EBBA are soluble in all the composition range,[10] and as EBBA is a better solvent of PS than the epoxy (monomer or polymer), it may be inferred that EBBA must be largely fractionated with PS. However, as the initial amount of PS is low, a large fraction of EBBA will also remain dissolved in the epoxy. At full epoxy conversion, the two isotropic phases (at 80 °C) will consist of an epoxy network partially swollen with EBBA and a PS/EBBA solution (a phase consisting of pure EBBA cannot exist in equilibrium due to the complete solubility of PS in EBBA at this temperature).

Figure 2 shows the conversion of epoxy groups determined by FTNIR as a function of time, at 80 °C, for the neat DGEBA and for solutions containing 5 wt % PS, 50 wt % EBBA, and both 5 wt % PS and 50 wt % EBBA. The polymerization rate decreased slightly with the addition of 5 wt % PS, but the decrease was significant in the presence of 50 wt % EBBA.

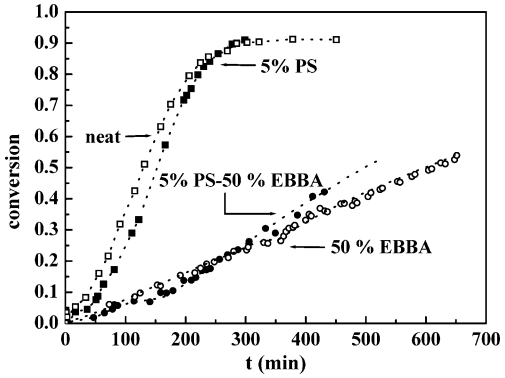

Figure 2. Conversion of epoxy groups as a function of time at 80 °C, determined by FTNIR, for neat DGEBA and solutions containing 5 wt % PS, 50 wt % EBBA, and both 5 wt % PS and 50 wt % EBBA.

Cloud-point times, determined by TOM, were close to 20 min for the solution containing 5 wt % PS, 160 min for the solution containing 5 wt % PS and 50 wt % EBBA, and 375 min for the solution containing 50 wt % EBBA. Using the kinetic curves plotted in Figure 2, this leads to cloud-point conversions less than $x_{cp} = 0.1$ for the solutions containing PS and $x_{cp} = 0.3$ for the solution containing only EBBA. Due to the lack of compatibility of PS and the epoxy, phase separation occurred at a significantly lower conversion when a small amount of PS was present in the initial formulation.

From experimental values of gel times, the gel conversion was close to 0.35 for every one of the formulations.

Morphologies and Thermal Transitions of Fully Cured Films. Thin films (about 20 μm thickness) were obtained for different formulations by polymerizing at 80 °C for 26 h, to complete the reaction. Examples of morphologies generated are shown in the transmission optical micrographs of Figure 3, obtained at room temperature.

In every case, a dispersion of particles in a continuous matrix was observed. Increasing the amount of PS in the initial formulation produced a significant increase in the average size of the dispersed domains. In the absence of PS, final morphologies consisted of two cocontinuous phases, with a much lower characteristic size.[9] The relatively large domains generated in the presence of PS may be associated with the fact that phase separation took place at much lower conversions, increasing the rates of growth and coalescence.

These primary morphologies remained invariant during successive heating/cooling cycles between 20 and 80 °C. However, a reversible phase separation process inside dispersed domains was observed as is shown in Figure 4. The new phase segregated on cooling below a particular temperature that depended on the initial composition was a nematic phase, as assessed with the use of crossed polarizers. Nematic domains were dissolved again on heating above this particular temperature.

The formation of a nematic phase inside droplets proceeded through a nucleation−growth−coalescence mechanism. Phase separation occurred earlier inside the smallest droplets, a phenomenon that will be explained in another section. TOM micrographs taken at lower

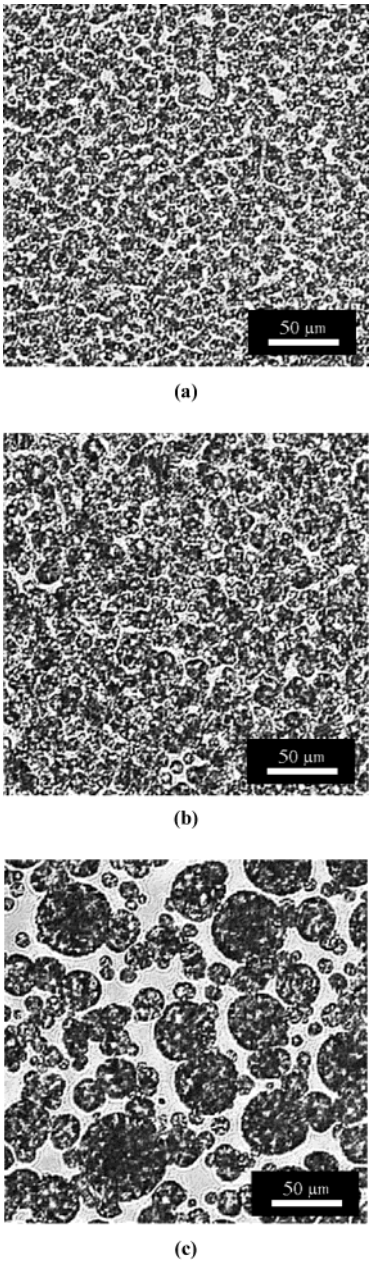

Figure 3. TOM micrographs obtained at room temperature for films containing 50 wt % EBBA and (a) 1 wt % PS, (b) 3 wt % PS, and (c) 5 wt % PS.

temperatures showed a significant coalescence of the nematic domains generated inside the droplets.

On the basis of these observations, it may be concluded that droplets were constituted by a PS/EBBA blend and that the continuous matrix was the epoxy network partially swollen with EBBA.

Thermal transitions observed during a DSC heating scan of a film containing 1 wt % PS and 40 wt % EBBA, previously cooled to 5 °C, are shown in Figure 5. The cooling to this low temperature produced crystallization of EBBA inside the droplets. The subsequent heating revealed the glass transition temperature of the matrix at about 23 °C (onset value), the melting of EBBA crystals at 38 °C (end value), regenerating nematic domains inside the droplets, and the nematic−isotropic transition at 73 °C (end value).

Below T_{NI} EBBA was segregated from its solution in PS, forming a nematic phase inside the droplets. This phase is characterized by two different refractive indices that are, in turn, different from the isotropic one. A mismatching of refractive indices is produced, and the film becomes translucent when cooled below T_{NI}. Above T_{NI} EBBA is completely soluble in PS. This reestablishes the matching between refractive indices and the film becomes transparent above T_{NI}. What is actually important is the fact that this process was confined to the interior of the droplets, which are in fact acting as the light scattering centers below T_{NI}.

Estimation of the Composition of Phases at Full Conversion. A simple thermodynamic model was developed to estimate the fractionation of EBBA between the swollen epoxy network and the PS solution, after completion of the polymerization at 80 °C. The analysis was performed using the Flory−Huggins equation, including an elastic contribution for the epoxy network, described by the affine deformation model (details of similar calculations may be found in the literature).[11,12]

Model parameters were estimated as follows. The concentration of elastic chains was obtained by applying a simple mean-field model derived for initiated polymerizations.[13] The fractional probability of chain propagation was estimated as $q = 0.588$, on the basis of the experimental value of the gel conversion ($x_{gel} = 0.35$). Elastic chains including at least one DGEBA unit were counted. At complete conversion, their concentration per mole of DGEBA was equal to 0.213. Both interaction parameters were defined, taking the molar volume of the constitutional repeating unit of PS as the reference volume. For the couple PS−EBBA, the corresponding value was already reported in the literature,[10] $\chi_{PS-EBBA} = 0.169$ at 80 °C. For the couple EBBA−epoxy, the interaction parameter was estimated from the maximum solubility of EBBA in the epoxy network at 80 °C, which was about 30 wt % EBBA.[9] This led to $\chi_{EBBA-epoxy} = 0.285$. From these values it may be inferred that the concentration of EBBA in the PS solution will be higher than in the swollen network (this arises from the relative values of interaction parameters and the presence of an elastic free energy contribution in the epoxy network).

Equating the chemical potentials of EBBA in both solutions and numerically solving the resulting equations led to the equilibrium mass fractions shown in Table 1 for different initial formulations.

The model predicts that the concentration of EBBA in the droplets increases by increasing the initial EBBA amount or decreasing the PS content. In every case, the residual EBBA amount in the epoxy network is less than the saturation value at 80 °C (29.2 wt %).

For the range of initial formulations selected for the present study, droplets contain an EBBA amount ranging from 35 to 97 wt % (or equivalently, a PS amount in the range of 3−65 wt %), while the epoxy matrix contains an amount of EBBA that is lower than the saturation value at 80 °C. Figure 6 shows the region of interest of the binary PS/EBBA phase diagram, previously reported.[10] Some experimental T_{NI} values for TRLS films are indicated in Figure 6, at the concentrations in the droplets predicted by the thermodynamic model. The experimental trend is reasonably predicted by the model (the contamination of droplets by the rest of the initiator or small amounts of unreacted monomer may be the cause of a decrease in the experimental values of T_{NI} as shown in Figure 1).

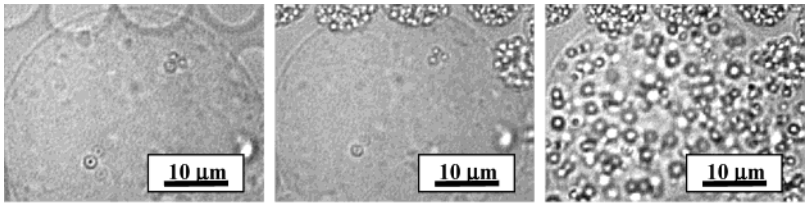

Figure 4. TOM micrographs showing the segregation of nematic domains inside droplets for a film obtained using 50 wt % EBBA and 5 wt % PS with cooling at 1 °C/min from 80 °C: (a) at 80 °C, (b) at 69.5 °C, (c) at 69 °C.

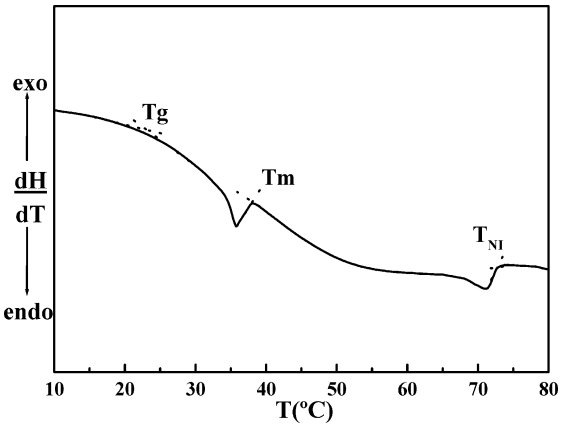

Figure 5. Thermal transition observed in a DSC heating scan of a fully cured film containing 1 wt % PS and 40 wt % EBBA, previously cooled to − 18 °C.

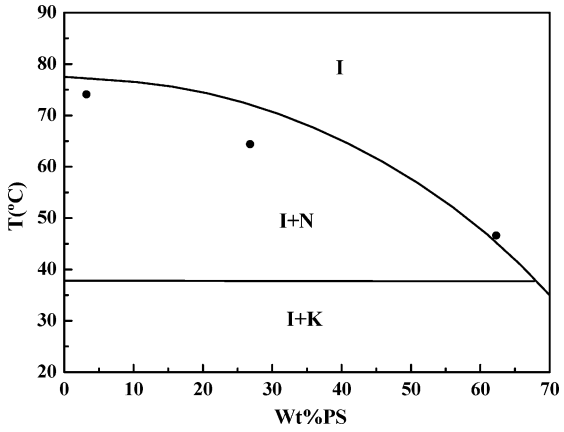

Figure 6. Binary phase diagram of PS/EBBA solutions (I = isotropic, N = nematic, K = crystal). Points indicate experimental values of T_{NI} represented at concentrations predicted by the thermodynamic model.

Table 1. Equilibrium Concentrations (wt %) of EBBA in PS and in the Epoxy Network, Predicted by the Thermodynamic Model

starting composition (wt %)		equilibrium concentrations (wt %)	
PS	EBBA	EBBA in PS	EBBA in epoxy
1	50	96.8	29.1
3	50	91.1	29.0
5	50	86.4	28.9
1	40	94.0	29.1
3	40	84.9	28.9
5	40	78.2	28.6
1	30	73.8	28.3
3	30	63.5	27.0
5	30	58.5	26.1
1	20	37.7	19.7
3	20	36.4	19.2
5	20	35.3	18.7

The experimental observation that the segregation of nematic domains occurred earlier in the smallest droplets on cooling from 80 °C (Figure 4) implies that the PS concentration in these droplets is lower than in the large droplets. Large droplets are those that were born earlier during the phase separation process and could therefore attain larger sizes by growth and coalescence. This means that the composition of the segregated PS/EBBA phase was richer in PS at the beginning of the phase separation process, a fact that is consistent with the low compatibility between PS and the epoxy monomer. However, the appearance of nematic domains in the largest droplets was retarded by less than 1 °C with respect to the smallest droplets. For the use of these materials as TRLS films, these temperature variations are completely negligible.

By selecting the amounts of EBBA and PS in the initial formulation, the composition of dispersed droplets in the epoxy network could be varied along the nematic−isotropic transition curve. For a TRLS film it is desirable to produce a sharp change from a transparent to an opaque state by a small decrease of temperature below T_{NI}. Observing the shape of the nematic−isotropic transition curve, the best range of droplet compositions for a TRLS film is that with the highest EBBA concentrations (close to 0 wt % PS). Application of the lever rule indicates that a small decrease of temperature in this range produces a large fraction of nematic phase. From the composition values shown in Table 1 it is concluded that adequate formulations for the synthesis of a TRLS film should contain 1 wt % PS and 40−50 wt % EBBA. Lower EBBA mass fractions lead to TRLS films with T_{NI} values significantly lower than that of the pure liquid crystal. However, the low mass fraction of the nematic phase segregated on cooling would give rise to a TRLS material with a low contrast ratio between opaque and transparent states. The final selected composition was that with 1 wt % PS and 50 wt % EBBA.

As observed in the phase diagram, at temperatures lower than 38 °C the stable phase is the crystalline one. The nematic to crystal transition was found to be extremely slow at room temperature, but it took place at a fast rate at −18 °C.

Optical Properties of TRLS Films. Figure 7 illustrates the effect of the addition of 1 wt % PS on the optical properties of TRLS films.

Curve a shows the fraction of visible light transmitted by a TRLS film composed of EBBA (50 wt %) and epoxy as a function of temperature. These films exhibit cocontinuous structures as previously reported.[9] Above the nematic−isotropic transition temperature of EBBA, the material was transparent due to the matching of refractive indices of both phases. Below T_{NI} the material became translucent due to the mismatching of refractive

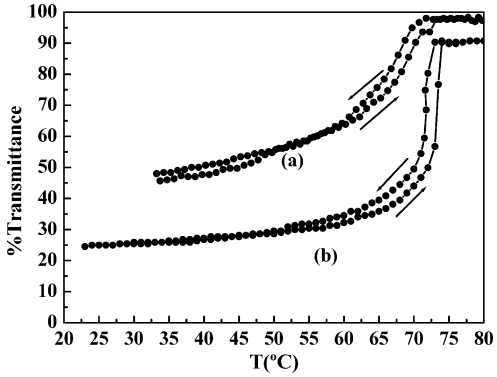

Figure 7. Fraction of visible light transmitted by TRLS films during cooling and heating cycles: (a) film of 1295 μm thickness synthesized from a formulation containing 50 wt % EBBA and no PS; (b) film of 270 μm thickness synthesized from a formulation containing 50 wt % EBBA and 1 wt % PS.

indices when EBBA was present as a nematic phase. However, the decrease in transmittance at T_{NI} was not very high despite the large thickness of the film (1295 μm). A continuous variation of transmittance with temperature was the result of the continuous phase separation of EBBA from its solution in the epoxy network.

The situation changed dramatically when 1 wt % PS was added to the initial formulation, keeping the same amount of EBBA and polymerization conditions. As shown by curve b, the TRLS film exhibited a sharp opaque−transparent transition at T_{NI} and a good contrast ratio between both states, even when using a much smaller film thickness (almost 5 times less). Reasons for this behavior are the significant change in the morphologies generated (droplets of a PS/EBBA solution dispersed in an epoxy network instead of two cocontinuous phases, together with an increase in the characteristic size of the dispersed domains), and the fact that a small decrease of temperature below T_{NI} produced a large segregation of the nematic phase, enabling droplets to behave as efficient light scattering centers. As the primary morphology of droplets dispersed in the epoxy network remained invariant during successive cooling/heating cycles, so did the transmittance behavior of TRLS films synthesized in the presence of PS.

The addition of 1 wt % PS produced an increase in the contrast ratio, using a thickness that was 5 times less than that of the film devoid of PS. This proves that the idea explored in this study works in an efficient way. Obviously, the development of a commercial formulation would need to decrease the light transmitted at low temperatures to reduce the film thickness. Crystallization of EBBA at low temperatures produced a further decrease of the transmittance of TRLS films. Heating above the melting temperature (38 °C) restablished the previous transmittance level. The influence of different variables on the resulting optical properties of these new TRLS films will be discussed in another paper.

Conclusions

The addition of a small amount of PS to a DGEBA/EBBA solution produced a significant change in the morphologies generated in the course of the polymerization-induced phase separation. Cocontinuous structures obtained in the absence of PS were transformed into a dispersion of droplets of a PS/EBBA blend in a continuous epoxy matrix partially swollen by EBBA. By adjusting the initial composition, it was possible to control the average size and the composition of the droplets. When the droplets contained high EBBA concentrations, a small decrease in temperature below T_{NI} led to phase separation of a large amount of a nematic phase. The droplets were thus transformed into very effective light scattering centers, leading to a high contrast ratio between opaque and transparent states, an effect generated in a small temperature range. As primary morphologies were not sensitive to temperature variations, optical properties were not affected by successive cooling/heating cycles. Therefore, these materials may be efficiently used as TRLS films, a possibility that could not be achieved for formulations that did not include PS.

The idea of adding small amounts of a thermoplastic polymer exhibiting the characteristics described in this study may also be explored to generate new families of PDLCs.

Acknowledgment. We thank the following institutions for financial support: University of Mar del Plata, National Research Council (CONICET), National Agency for the Promotion of Science and Technology (ANPCyT), and Fundación Antorchas.

References and Notes

(1) Hotta, Y.; Yamaoka, T.; Morohoshi, K.; Amano, T.; Tsutsui, K. *Chem. Mater.* **1995**, *7*, 1793.
(2) Mormile, P.; Petti, L.; Abbate, M.; Musto, P.; Ragosta, G.; Villano, P. *Opt. Commun.* **1998**, *147*, 269.
(3) Mucha, M. *Prog. Polym. Sci.* **2003**, *28*, 837.
(4) Hoppe, C. E.; Galante, M. J.; Oyanguren, P. A.; Williams, R. J. J.; Girard-Reydet, E.; Pascault, J. P. *Polym. Eng. Sci.* **2002**, *42*, 2361.
(5) Pascault, J. P.; Williams, R. J. J. In *Polymer Blends Vol. 1: Formulation*; Paul, D. R., Bucknall, C. B., Eds.; Wiley: New York, 2000; pp 379−415.
(6) Riccardi, C. C.; Borrajo, J.; Williams, R. J. J. *Polymer* **1994**, *35*, 5541.
(7) Williams, R. J. J.; Rozenberg, B. A.; Pascault, J. P. *Adv. Polym. Sci.* **1997**, *128*, 95.
(8) Khoo, I. C. *Liquid Crystals. Physical Properties and Nonlinear Optical Phenomena*; Wiley: New York, 1995.
(9) Hoppe, C. E.; Galante, M. J.; Oyanguren, P. A.; Williams, R. J. J. *Macromolecules* **2002**, *35*, 6324.
(10) Hoppe, C. E.; Galante, M. J.; Oyanguren, P. A.; Williams, R. J. J. *Macromol. Chem. Phys.* **2003**, *204*, 928.
(11) Borrajo, J.; Riccardi, C. C.; Williams, R. J. J.; Masood Siddiqi, H.; Dumon, M.; Pascault, J. P. *Polymer* **1998**, *39*, 845.
(12) Riccardi, C. C.; Borrajo, J.; Williams, R. J. J.; Masood Siddiqi, H.; Dumon, M.; Pascault, J. P. *Macromolecules* **1998**, *31*, 1124.
(13) Williams, R. J. J.; Vallo, C. I. *Macromolecules* **1988**, *21*, 2571.

MA0496955