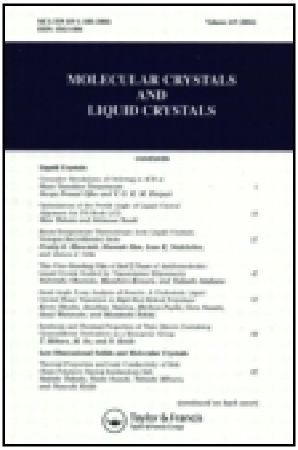

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Polymer/Liquid Crystal Composites: Phase Separation and Morphology of Blends of PBMA or PMMA and E7

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POLYMER/LIQUID CRYSTAL COMPOSITES: PHASE SEPARATION AND MORPHOLOGY OF BLENDS OF PBMA OR PMMA AND E7

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Abstract Phase separation behaviour has been investigated for composite films made of the nematic mixture E7 embedded in a thermoplastic matrix of PBMA or PMMA. Different approaches, based on optical and calorimetric analyses, have been applied to PDLC films, prepared by solvent coating techniques followed by thermal treatments, in order to determine the solubility limit of E7 in the matrices and the fraction of LC contained within the segregated domains. The two systems exhibit distinct mechanisms of phase separation: nucleation and growth occurs in PBMA/E7, whereas PMMA/E7 separates through spinodal decomposition. PBMA/E7 composites, because of the low Tg of the polymer and the high solubility of the LC in the matrix at room temperature, seem to be unsuitable for PDLC application; a higher degree of phase separation characterizes the PMMA-based films. Preliminary electro-optic properties have been investigated on the latter system.

INTRODUCTION

Composite films made of a low molecular weight nematic liquid crystal (LC) embedded in a polymer matrix (PDLC) exhibit reversible light scattering - light transmission switching under the imposition of an electric field. Due to their unique characteristics of self-supported LC films these materials appear to be extremely promising for various applications in the field of optoelectronics. Anisotropic electric and optical properties of the LC component are fundamental in determining the performance of the PDLC; other key factors are the matching between the ordinary refractive index of the LC (n_o) and the refractive index of the polymer matrix (n_p), the size and shape of the LC domains (which are generally spherical because of the difference in surface tension between the LC and the matrix), the nematic director configuration of the droplets, the resistive and dielectric properties of the LC and polymer components and the solubility of the LC in the matrix.[1-3] Most of these factors depend on the nature of the component materials and on the technique of the PDLC preparation, that can be polymerization induced, if the LC is homogeneously mixed with polymer precursors and segregation takes place during polymerization, or achieved by controlled solvent evaporation from a solution of the LC and the polymer (method SIPS) or by cooling a homogeneous mixture of the LC and a thermoplastic matrix (method TIPS). In all cases the phase separation mechanism and kinetics determine the properties of the final product; therefore a full understanding of this process is fundamental to improve the performance of the composites.

This paper considers phase separation and morphology of blends of thermoplastic poly(n-butyl methacrylate) (PBMA) or poly(methyl methacrylate) (PMMA) containing the nematic mixture E7 as dispersed LC. Solvent evaporation has been used in conjunction with thermal processing for sample preparation. Different approaches have been applied to determine the solubility limit of E7 in the matrices and, consequently, the fraction of LC contained within the droplets. The two polymers, characterized by a substantially different Tg (33 and 105°C, respectively)[4] are both optically isotropic and transparent and are reported to give blends with E7 that, after thermal quenching, exhibit distinct mechanisms of phase separation.[3] Electro-optical properties of PMMA/LC heterogeneous films have been tested by several authors.[5-8]

EXPERIMENTAL

Samples of PBMA (M_w=320000, M_w/M_n=4.35, d=1.053g/cm^3, n_p=1.483) and PMMA (M_w=93300, M_w/M_n=2.02, d=1.188g/cm^3, n_p=1.492) have been used as matrix polymers and the nematic mixture of cyanobiphenyl derivatives E7 ($\Delta\varepsilon$=13.8 at 20°C, d=1.0095g/cm^3, n_o=1.5211, n_e=1.7464, Tg=-60°C, T_{SN}=-30°C, T_{NI}=58°C) as LC component. The polymer/LC composite films have been prepared at room temperature on suitable substrates by standard film coating methods from chloroform solutions of concentration 10-30 weight percent; the final thickness of the samples ranged between 10 and 50 μm and the LC weight fraction from 0 to 80%. The solvent-induced phase separation technique was applied in conjunction with the thermally-induced method; to this aim samples, after removing solvent by evaporation, have been maintained in a single phase regime (85°C) for 60 min and then quenched or cooled with controlled rates to room temperature.

The aggregation structure of the films has been investigated by using a Reichert-Jung Polyvar Pol polarizing microscope equipped with a Mettler FP 82 HT hot stage connected to a FP 90 central processor. Glass transition temperatures Tg and the related increases in specific heat ΔCp have been measured with a Mettler TA 3000 DSC system and its dedicated software. Preliminary electro-optic studies have been carried out on PMMA/E7 samples sandwiched between two indium-tin oxide (ITO) coated glass plates, by using a He-Ne laser beam (wavelength 632.8 nm) incident normal to the film surface; the transmitted light intensity through the films has been measured under the modulation of an a.c. electric field with a photodiode.

RESULTS AND DISCUSSION

Blends of PBMA/E7

Blends containing various E7 weight percentages, after being maintained 60 min at 85°C in the hot stage in order to get complete miscibility, have been cooled down to room temperature at different rates to detect optically the upper critical solution temperature UCST[9] of the mixtures, as a function of the scan rate and the composition. The results are given in Table I.

TABLE I UCST of blends PBMA/E7 under different cooling rates.

E7, w%	5°C	2°C	1°C	0.2°C
30	25.0	24.8	24.7	24.2
40	31.2	32.0	32.3	33.2
60	36.2	36.8	37.1	38.0
80	41.8	42.1	43.4	43.8

The temperature/composition phase diagram of Figure 1 has been drawn by using the values of Table I referring to the slowest cooling rate. Data suggest a solubility limit of the LC in the polymeric matrix at room temperature approaching 30%.

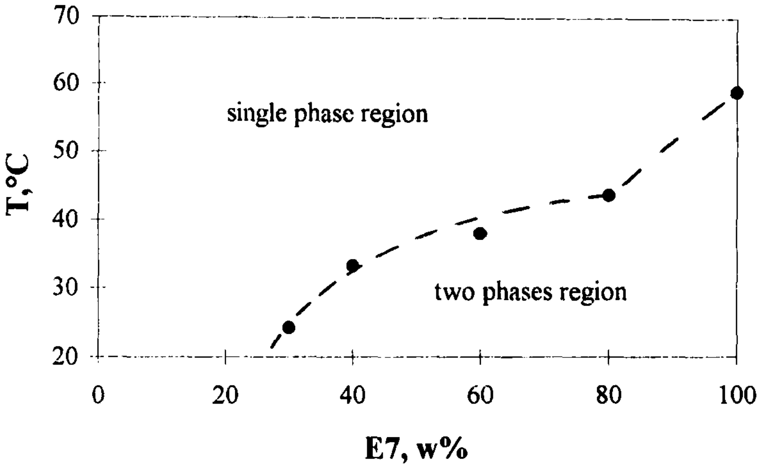

FIGURE 1 Phase diagram for blends of PBMA/E7.

TABLE II Tg values of blends PBMA/E7.

E7, w%	Tg phase 1, °C	Tg phase 2, °C	ΔCp phase 2, J/gK
0	33.0	-	-
10	-15.0	-	-
20	-20.2	-	-
30	-27.5	-56.5	0.03
40	-28.0	-58.0	0.07
50	-32.0	-59.3	0.12
60	-32.9	-59.3	0.15
100	-	-59.0	0.51

In order to verify this result by means of a proper approach glass transition temperatures of films of various compositions have been determined. Indeed the most unambiguous criterion of compatibility is the detection of a single Tg, intermediate between those of the pure components; segregation into distinct phases can be revealed by glass transition identical in temperature and width to those of the unblended constituents.[10] The obtained results are collected in Table II; they indicate a plasticizing effect of E7 on the PBMA matrix and a substantial exclusion of the polymeric component from the segregate LC domains revealed, at high enough E7 concentration, by the independence of the LC (phase 2) glass transition of the blend composition.

The observed dependence of Tg of the polymer-rich phase 1 on the composition cannot be approximated by the simple Fox equation,[11] that relates Tg of a compatible blend only to the mass fractions w_1, w_2 and the glass transitions temperatures Tg_1, Tg_2 of the respective components

$$1/Tg = w_1/Tg_1 + w_2/Tg_2 \qquad (1)$$

A more detailed approach is the one offered by the Gordon-Taylor equation[12]

$$Tg = (w_1Tg_1 + kw_2Tg_2) / (w_1 + kw_2) \qquad (2)$$

where k is a constant dependent on the system under consideration. Mixtures of various compositions have been submitted within the DSC to thermal treatments aimed at the maintenance of homogeneous solutions at low temperature: after 60 min at 85°C and a rapid quench to -100°C, DSC analysis has been performed between -100 and 100°C at 20K/min. In such conditions a single phase appeared up to 40% E7; these data have been used to draw the Tg/composition curve of Figure 2, based on a k value derived from the best fit of the linearized form of the Gordon-Taylor equation

$$Tg = Tg_1 + k\,(w_2/w_1)\,(Tg_2 - Tg) \qquad (3)$$

Phase 1 Tg values of Table II are superimposed on this curve; they underline a solubility limit of the LC in the matrix just below 30%.

Since the phase 2 glass transition is due solely to the LC contained within the microdroplets, the magnitude of the increase in specific heat ΔCp measures the amount of segregated E7. According to Smith et al.[13] ΔCp should increase linearly with LC concentration above an intercept which represents the solubility limit of the LC in the matrix. Such dependence is shown in Figure 3; the intercept indicates a value of about 25% E7.

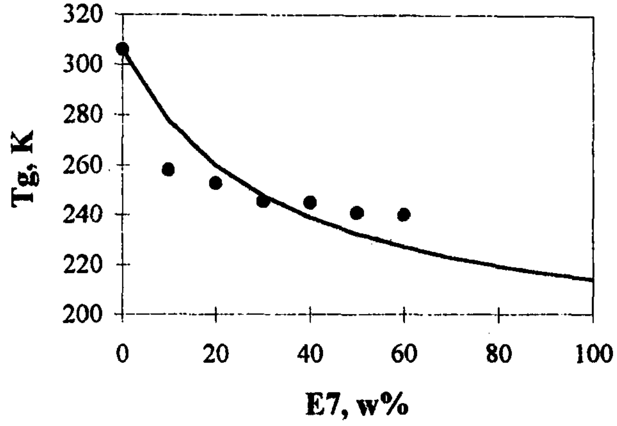

FIGURE 2 Gordon-Taylor curve for homogeneous mixtures PBMA/E7 (black points indicate the experimental values of Table II).

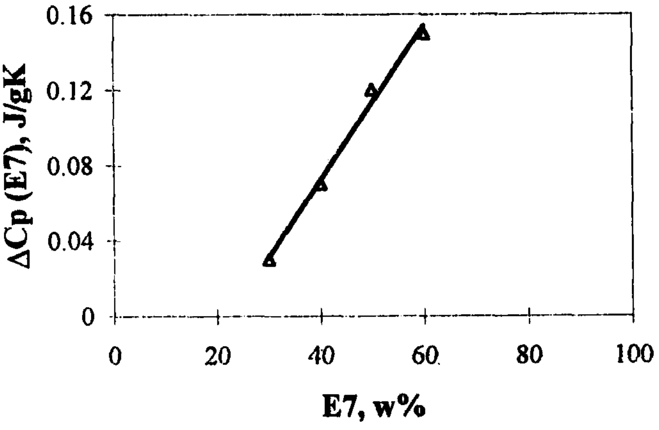

FIGURE 3 Specific heat increment at Tg for E7 in the microdroplets.

The aggregation structure of the films has been investigated by optical microscopy on cooling them at different rates from single phase temperature conditions. A multiple droplet morphology, characteristic of a typical nucleation and growth phase separation mechanism[3] can be discerned. The pattern formations on films about 10 µm thick are shown in Figures 4 and 5 for PBMA/E7 60/40 and 40/60 w/w compositions.

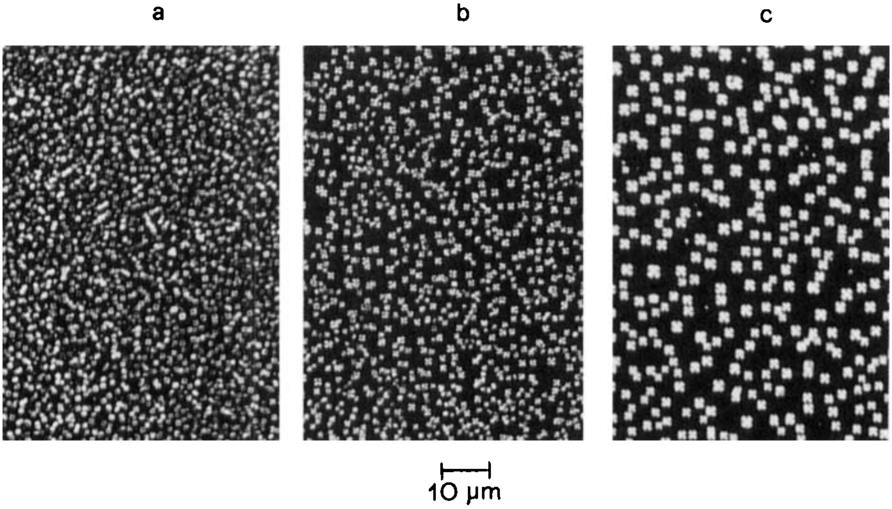

FIGURE 4 Room temperature droplet structure of PBMA/E7 60/40 cooled from 85°C at different rates [5 (a), 0.2 (b) and 0.1 (c) K/min].

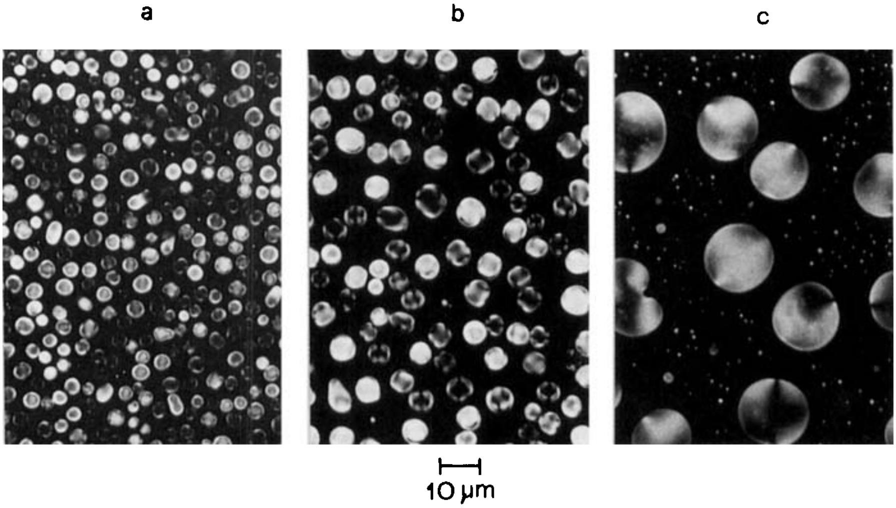

FIGURE 5 Room temperature droplet structure of PBMA/E7 40/60 cooled from 85°C at different rates [5 (a), 1 (b), and 0.1 (c) K/min].

The cooling rate affects the resulting droplet morphology; Figure 6 is a plot of the average droplet diameter as a function of the scanning rate; slower cooling results in larger droplets, allowing longer time for phase separation and droplet growth and coalescence.

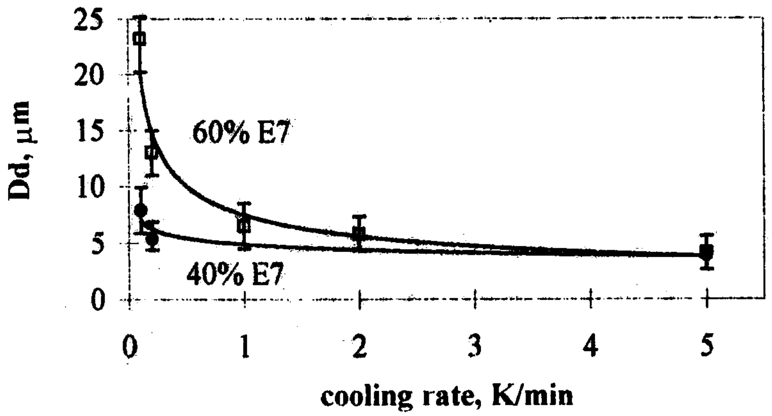

FIGURE 6 Droplet diameter vs. cooling rate for blends PBMA/E7.

The LC solubility limit in the matrix has been also evaluated from the volumetric droplet number density n_v. Micrographs of Figures 4 and 5 allow the determination of the average number of droplets per unitary area n_a, which can be converted into n_v assuming that this number be the same on normal planes. Data are given in Tables III and IV for mixtures PBMA/E7 60/40 and 40/60 w/w cooled to room temperature at different rates: D_d is the average droplet diameter (see Figure 6), V_d the volume of a droplet, assumed of spherical shape, and n_vV_d the total volume of E7 per unitary volume of PDLC. When D_d exceeds the film thickness droplets can no longer be considered spherical and the assumption of a cylindrical shape seems to be more adequate; data of Table IV for cooling rate of 0.2 and 0.1 K/min have been derived according to this hypothesis.

TABLE III PBMA/E7 60/40: total volume of E7 per unitary volume of PDLC n_vV_d of films cooled at different rates.

rate (K/min)	D_d (μm)	V_d 10^{11} (cm^3)	n_v 10^{-8} (cm^{-3})	nvVd 10^2 (cm^{3}E7/cm^{3}PDLC)
5	3.9	3.2	17.8 (42.9)	5.7 (13.7)
0.2	5.4	8.1	7.8 (16.9)	6.3 (13.7)
0.1	7.9	25.4	3.2 (5.4)	8.2 (13.7)

TABLE IV PBMA/E7 40/60: total volume of E7 per unitary volume of PDLC n_vV_d of films cooled at different rates.

rate (K/min)	D_d (μm)	V_d 10^{10} (cm^3)	n_v 10^{-8} (cm^{-3})	nvVd 10^1 (cm^3E7/cm^3PDLC)
5	4.1	0.4	60.6 (80.9)	2.2 (2.9)
2	5.8	1.0	17.8 (28.6)	1.8 (2.9)
1	6.5	1.4	14.5 (20.5)	2.1 (2.9)
0.2	13.0	13.3	1.8	2.4
0.1	23.2	42.4	0.7	2.8

Compositions of PBMA/E7 60/40 and 40/60 w/w correspond to 0.414 and 0.616 gE7/cm^3 PDLC, respectively; assuming as equilibrium values the ones derived under the lowest cooling rate the results of n_vV_d indicate segregation of 0.083 and 0.282 gE7/cm^3 PDLC and solubility of 0.331 and 0.334 gE7/cm^3 PDLC (about 31 w% E7); this latter result appears to be slightly overestimated if compared with the limit determined with the other approaches. From an analysis of calorimetric data and an estimate of D_d from SEM micrographs for two different PDLC systems, Smith[14] found a relation between the volumetric droplet number density n_v and the droplet diameter D_d (n_v=const x D_d^{-3}); in a successive paper this author[13] derived a relationship between the calorimetric quantity ΔCp and the droplet diameter D_d to compute n_v

$$n_v \approx 6\,P\;/\;\pi\,D_d^3 \qquad (4)$$

where $P = \Delta Cp / \Delta Cp^{*}$[14] is the ratio of the specific heat increment for a sample containing a certain weight percent LC to that for the pure LC. Data of ΔCp and D_d from Tables II, III and IV allow the evaluation of n_v and n_vV_d according to equation (4); the results, given in brackets in Tables III and IV, appear to agree quite well with the ones derived from micrograph analysis. We can conclude that the solubility of E7 in PBMA should be between 25 and 30%; occurrence of phase separation in PBMA/E7 70/30 has been recently shown by Challa et al.[15] through FT-IR microspectroscopy.

The basic expression for the calculation from ΔCp of the fraction of LC contained within the microdroplets, α, was given by Smith and Vaz[16]

$$\alpha = (1 + F)\,P \tag{5}$$

where $F = m_p/m_{LC}$ is the ratio of polymer LC mass in the sample. Equation (5) can be rewritten[13] as

$$\alpha = (100 / X)\,P \tag{6}$$

for a sample containing X weight percent LC. Using for P the Smith expression[14]

$$P = (X - A) / (100 - A) \tag{7}$$

where A is the LC solubility limit in the matrix, and combining equations (6) and (7) give[13]

$$\alpha = 0 \qquad (X \leq A)$$

$$\alpha = (100 / X)(X - A) / (100 - A) \qquad (X > A) \tag{8}$$

For PBMA/E7, assuming A ranging between 25 and 30%, α grows from 0.11±0.11 to 0.43±0.07, 0.62±0.05 and 0.74±0.04 on increasing the E7 content X from 30 to 40, 50 and 60 w%.

Blends of PMMA/E7

Figure 7 shows the phase diagram for blends of PMMA/E7, derived on the basis of optical observations and DSC analysis. Films containing E7 weight percentages of 30, 40, 60 and 80 have been maintained 60 min at 85°C in the hot stage to get complete miscibility and then cooled down at 0.1K/min. Black points in the Figure indicate the occurrence of phase separation detected by optical analysis; between 60 and 80% E7 separation occurs being the LC phase still isotropic. Whereas polymeric chains seem to be completely excluded from the nematic domains, as revealed by the unvarying Tg value of the separated LC with the composition, the polymer-rich phase contains some dissolved E7 molecules. Indeed, the matrix glass transitions of films bearing 40 and 60 wt% of E7 decrease to about 38°C from the value of 75°C, measured on a film of pure PMMA obtained under the same conditions. It must be pointed out that the reduction of Tg observed on the unblended sample, respect to the literature value of 105°C,[4] arises from the plasticizing effect of chloroform used for film preparation, which remains entrapped into the glassy polymer, even if the treatment temperature is raised up to 110°C, because of the higher Tg of PMMA, as compared with the one of PBMA. From the simple Fox equation[11] a critical solubility of about 18w% of the LC in the matrix can be supposed.

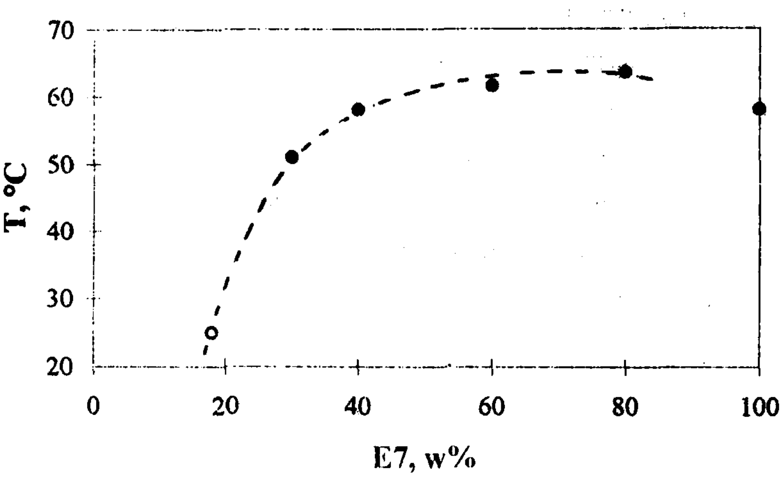

FIGURE 7 Phase diagram for blends PMMA/E7 (blank point from Fox equation).

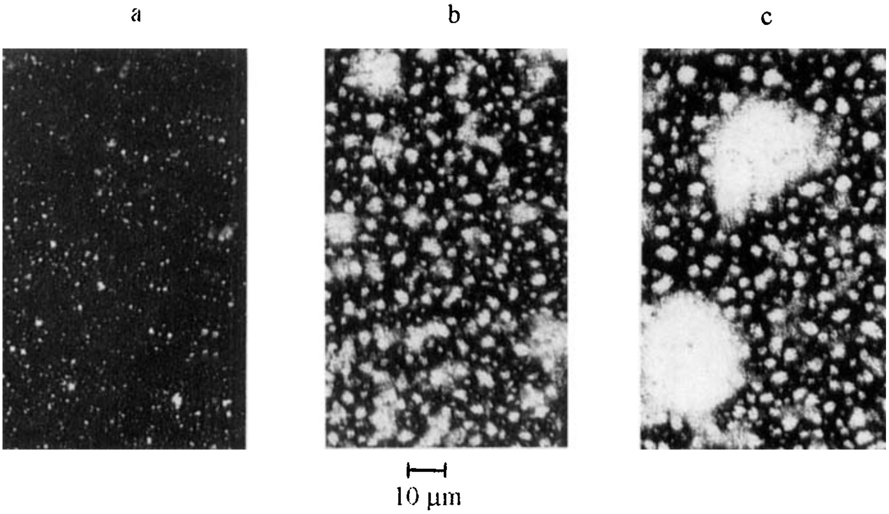

FIGURE 8 Time evolution at room temperature of the spinodal decomposition after quenching: PMMA/E7 60/40 [1 (a), 17 (b), 22 (c) h].

These data appear to agree well with the experimental points of Shen and with their comparison with the theoretical diagram calculated on the basis of the combined Flory-Huggins and Maier-Saupe free energies for a liquid-liquid phase equilibrium overlapped with the nematic-isotropic transition of the LC.[3,17,18] If A is ≈ 18%, for compositions of 40, 60 and 80% E7 the fraction of LC in the droplets, α, results 0.67, 0.85 and 0.95 respectively.

Morphological investigations of a film 60/40 after thermal quenching from 85°C to a two-phase regime (room temperature) reveal the interconnected two-phase structure illustrated in Figure 8, that resembles the characteristics of phase separation by spinodal decomposition.[19] Although texture analysis provides just an indication of the kinetic mechanism, since a definite proof comes only from the study of the growth rate of the different domains, our observations qualitatively agree with the analysis of pattern formation given by Kyu et al. for the same system.[3,20]

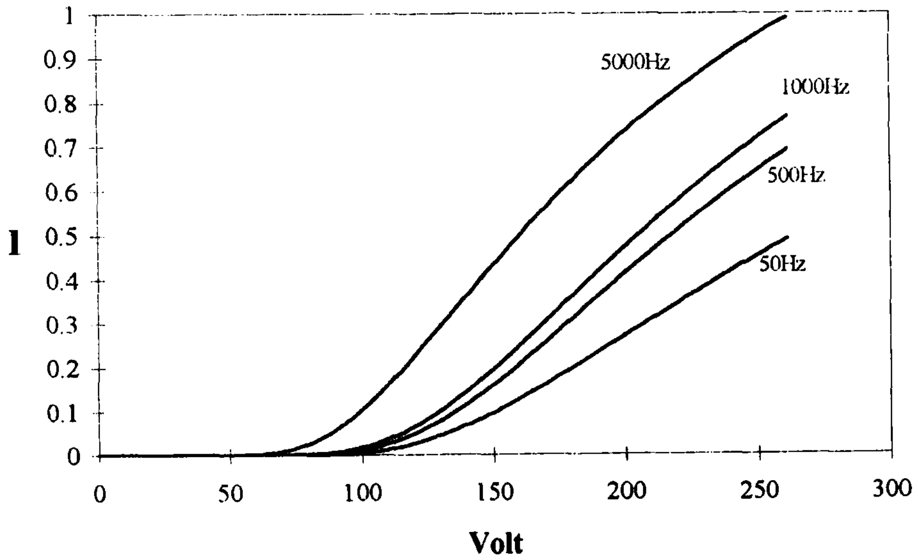

FIGURE 9 Transmittance vs. applied voltage (rate 2V/s): film of PMMA/E7 40/60 10 μm thick, a.c. field frequencies 50-5000 Hz.

Electro-optic transmission characteristics of PMMA/E7 films of different thickness, using a fixed weight proportion of 40/60, have been preliminary investigated in terms of variation with the applied voltage V of the transmitted intensity I expressed as

$$I = I_{measured} / I_{max} \tag{9}$$

where I_{max} has been evaluated under the same conditions on a film of pure PMMA. Figure 9 shows a set of transmittance versus applied field curves for a film 10 μm thick tested at different frequencies: higher frequencies increase the ON-state transmission and lower the threshold voltage, according to the results of Miyamoto et al.[5] on PMMA/nematic mixture E44 composites. As expected, an increase of the cell thickness to 25 μm arises the threshold voltage; therefore the threshold field can be evaluated to be of the order of 6-7 V/μm, in a quite good agreement with the results obtained by Jain et al.[7] on blends of PMMA/E8.

CONCLUSIONS

As generally observed for composite films prepared by methods SIPS or TIPS from thermoplastic matrices,[21-23] the added LC has the principal effect of acting as a plasticizer, lowering the polymer glass transition temperatures. Such an effect, on one hand enhances the blend mouldability and processability, but on the other hand reduces the amount of segregated LC, giving rise to systems of poor technological interest when the amount of molecularly dispersed LC exceeds a reasonable value. This is the case of PBMA/E7 composites that, because of the low Tg of the polymer and the high solubility of the LC in the matrix, at room temperature, seem to be unsuitable for PDLC application. Compatibility of any two components of a blend can be predicted on the basis of solubility parameters, that can be found listed in tables for many polymers or calculated with the group contribution method.[24] For PBMA and PMMA the reported values[25] are 18.9 and 17.9 $MPa^{1/2}$; for the LC component, taking into account the composition of the nematic mixture E7 and the Hoy and Van Krevelen[24] data for all the chemical groups of the constituent molecules, we calculated 23 $MPa^{1/2}$. These values indicate poor compatibility of E7 with both PBMA and PMMA and appear to be inadequate to justify the different behaviour of the two matrices. The considerable disparity between the glass transition temperature of the two polymers and, eventually, the occurrence of specific interactions between alkyl side groups of both LC molecules and PBMA chains could account for the higher solubility of E7 in this matrix.

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