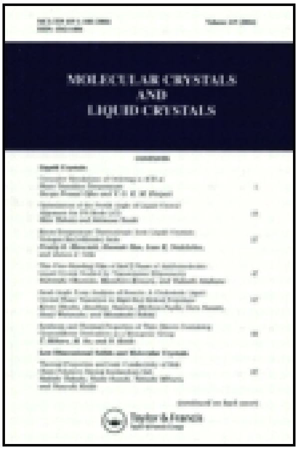

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PHYSICAL PROPERTIES OF ELECTRON BEAM-CURED TRIPROPYLENEGLYCOLDIACRYLATE AND LIQUID CRYSTAL SYSTEMS

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Some salient features of physical properties of Tripropyleneglycol diacrylate (TPGDA) and the low molecular weight nematic liquid crystal E7 are discussed. A variety of experimental techniques giving complementary information of monomer and Electron Beam (EB) cured systems are employed to illustrate the effect of curing. A detailed thermophysical analysis is made first to assess the conditions of miscibility, determine the order-disorder transition and the glass transition temperature. DSC spectra yield the energy change at the transitions from which important parameters are readily extracted such as solubility limits and amount of liquid crystal dissolved in the polymer. Polarized Optical Microscopy enables us to follow phase transitions and morphology changes in different regions of the phase diagram. Consistent data are obtained from mechanical measurements in particular with regards to the variation of the glass transition temperature with liquid crystal concentration and the related plasticizing effect.

Keywords: electron beam curing; glass transition; mechanical moduli; phase diagram; polymer dispersed liquid crystal

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INTRODUCTION

Electron Beam (EB) curing is a powerful technique for thin film preparation, suface coatings, adhesive applications, paintings etc. [1–3]. It has a major advantage over curing by UV light exposure for at least one reason since it does not require the presence of an initiator and yields generally high conversion ratios. The film performance when expressed in terms of the electro-optical response is found to be superior in the case of EB cured films compared to their counterparts made by UV radiation [4,5]. This technique is widely used in our laboratory in a variety of applications and in particular for curing PDLC (Polymer Dispersed Liquid Crystals) [6–9] films. In recent years we reported a systematic investigation of the physical properties of EB-cured PDLC films using a variety of techniques. In the present communication, we focus on the particular system made of Tripropyleneglycoldiacrylate (TPGDA) and the nematic liquid crystal (LC) E7. The latter is an eutectic mixture of cyanoparaphenylenes showing a single nematic to isotropic transition temperature. These films consist of micron-sized droplets filled with LC molecules and dispersed in the polymer matrix. Their importance stems from the variety of potential applications, mainly in smart windows, display devices and communication technologies. Assessment of their performance in most applications is intimately related to the quality of electro-optical responses, parameter values related to thermophysical properties, nature of morphologies emerging under various conditions of temperature and concentration, textures of coexisting phases, mechanical moduli and stability criteria for long term handling under severe conditions. This is the reason why it is necessary to investigate each of those aspects and establish correlations between them to reach the optimal conditions for a high performance in practical applications. This paper is a contribution along these lines and attempts to elucidate the relationship between thermophysical,morphology and mechanical properties of such promising materials. For this purpose, at least four experimental techniques are used to characterize the physical properties of the TPGDA/E7 system yielding consistent results.

EXPERIMENTAL PART

Materials

The Low Molecular Weight Liquid Crystal (LMWLC) E7 was purchased from Merck Eurolab (Darmstadt, Germany). It is an eutectic mixture containing 51 weight percent (wt%) of 4-cyano-4′-*n*-pentyl-biphenyl (5CB), 25 wt% of 4-cyano-4′-*n*-heptyl-biphenyl (7CB), 16 wt%

of4-cyano-4′-*n*-octyloxy-biphenyl (8OCB), and 8 wt% of 4-cyano-4″-*n*-pentyl-p-terphenyl (5CT). It admits a nematic to isotropic transition at $T_{NI} = 60°C$ [10].

The monomer Tripropyleneglycoldiacrylate (TPGDA) is a donation from Cray Valley (France).

Sample Preparation

The monomer TPGDA is used without further purification. The TPGDA/E7 mixtures were stirred at room temperature until they became homogeneous. The blends were applied uniformly on glass plates and submitted to EB-curing.

The EB generator was an Electrocurtain Model CB 150 (Energy Sciences Inc.) delivering a high voltage of 175 kV. The samples were placed on a tray moving under the radiation source on a conveyor belt in a nitrogen atmosphere. They were exposed to a dose of 105 kGy by using a beam current of 7 mA and a conveyor speed of 0.19 m/s. For the monomer and for the blends, at least four duplicate samples were prepared to check the validity of the results.

Polarized Optical Microscopy (POM) Measurements

The samples prepared as mentioned earlier were submitted to a heating rate of 5°C/min from room temperature to at least 15 degrees above the transition temperature leading to the isotropic phase. Then samples were left approximately 5 min in the isotropic state before they were cooled to temperautres below room temperature at a rate of −5°C/min. After 5 min this cycle was repeated twice by heating/cooling ramps at a rate of 1°C/min. Transition temperatures were recorded during the second heating ramp.

Differential Scanning Calorimetry (DSC)

DSC measurements were performed on a Mettler 30 calorimeter equipped with a liquid nitrogen system allowing cooling experiments. A rate of 2°C/min (heating and cooling) was used in the temperature range –100 to +100°C. The program consists first in cooling the sample followed by two heating and cooling cycles. Data analysis was carried out on the first heating ramp. In each case, at least two duplicate samples having the same composition and prepared independently were used to check the reproducibility of results.

Light Scattering (LS)

LS experiments were conducted by using a He–Ne laser ($\lambda = 0{,}6328\,\mu$m, power 10 mW), a set of polarizers, and a Hamamatsu C3077 CDD video camera. The scattered intensities were investigated as a function of temperature using a heating-cooling stage (Linkam THMS 600) and a temperature control unit (Linkam 90). The laser was polarized perpendicular to the scattering plane. The HV mode was considered which means that the analyzer axis is perpendicular to the polarization direction of the incident beam. The signal was digitized and analyzed with the help of a Small Angle X-Ray Scattering software (Bruker Analytical X-Ray System, Wisconsin, USA).

Mechanical Measurements

Mechanical measurements were made on a mechanical testing machine Instron 6022 (static) and a Rheometrics RMS 800 mechanical spectrometer (dynamic). Rectangular samples of dimensions $15 \times 4 \times 0.1\,\text{mm}^3$ were cut from the film. Young moduli were determined from the slope of the stress/draw ratio curves at zero strain. Dynamic results yield the storage shear modulus at a constant deformation frequency of 10 rad/s and a heating rate of 2°C/min starting from $T = -100$°C up to a temperature where the rubbery state plateau modulus was detected.

RESULTS AND DISCUSSION

Figure 1 shows the phase diagram in the temperature, composition frame for the EB-cured TPGDA/E7 system. This diagram was obtained for 3 ramps and different techniques such as POM, DSC, and LS. Several remarks are in order here. Some data dispersion is found under certain conditions but nevertheless, similar qualitative tendencies are shown regardless of the methods used. The results show a significant drop of the nematic to isotropic transition temperature on the right hand side of the figure when the polymer concentration is low. Above 10 wt% 35 wt%, the transition temperature drops suddenly and the observation of the N→I transition if it exists becomes more difficult. This behavior is somewhat different with the case of uncured TPGDA/E7 systems where T_{NI} drops by more than 100°C when one goes from the bulk LC to 30 wt-% TPGDA. For the polymer, this temperature varies only slightly with composition (i.e., roughly between 40 and 60°C).

In order to explore a wider range of temperature, Figure 2 exhibits the glass transition temperature of the polymer matrix and of the LC versus

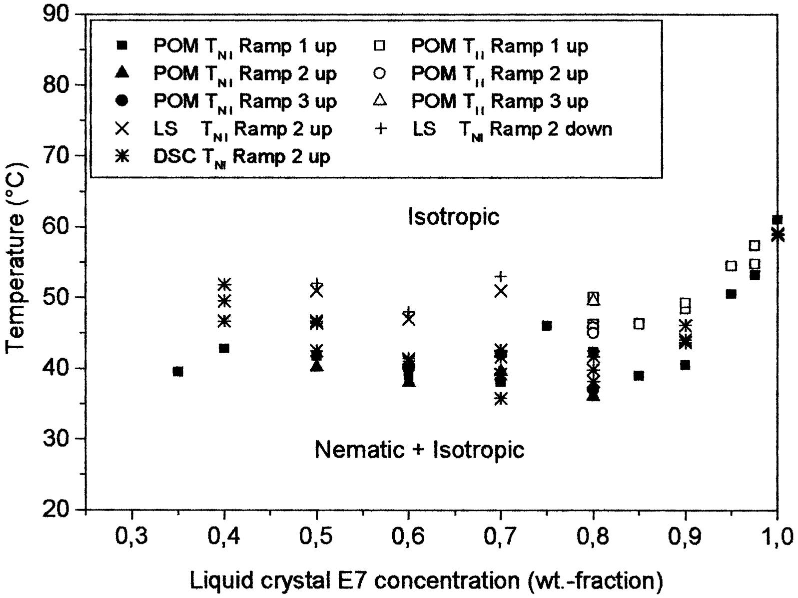

FIGURE 1 Experimental phase diagram for the EB-cured TPGDA/E7 system (dose 105 kGy). Different measurements obtained by POM, DSC, and LS are shown using different symbols.

concentration. While T_{gLC} of the LC remains practically unchanged, T_{gP} of the polymer undergoes a sharp drop indicating a severe plasticising effect. Similar data for the uncured system show that T_{gm} of the monomer remains essentially constant. Figure 3 shows the enthalpy change ΔH_{NI} (filled squares) at the nematic→isotropic transition temperature versus LC concentration. This figure exhibits also the variation of the heat capacity ΔC_P (open circles) with the LC concentration. ΔH_{NI} is a direct measure of the energy change at the nematic-isotropic transition whereas the heat capacity ΔC_P is related to the glass transition of polymer. The solubility limits are obtained by linear regression of these data (ΔC_P: 17 wt.-%, ΔH_{NI}: 28 wt.-%) as shown in Figure 3. Extrapolation of the lines shows a discrepancy between the 2 estimates which is expected since one is dealing with data exploring the phase behavior of different environments. On the other hand, we find consistent results between thermal and mechanical data. The plateau modulus and the tan δ of the loss angle decrease sharply with the LC concentration as a direct consequence of the plasticizing effects [11]. An illustration of these results is given in Figure 4 where E' and tan δ are shown in terms of the concentration. These quantities are directly related to T_g and their decrease is reminiscent of a strong plasticising effect.

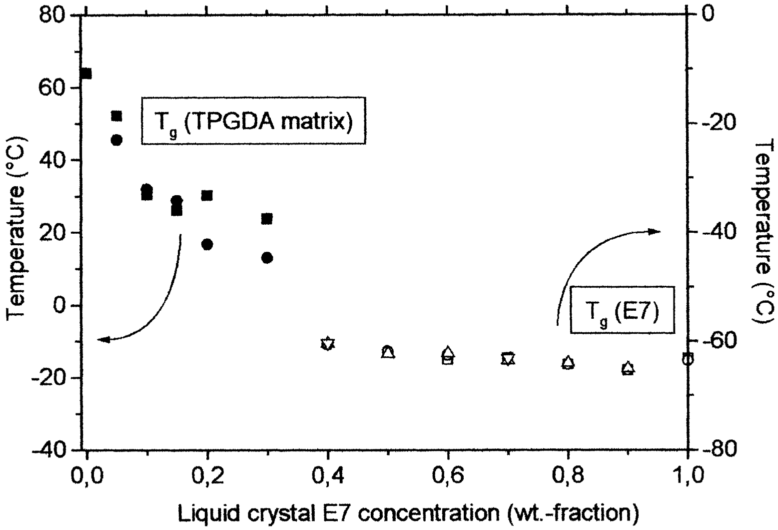

FIGURE 2 Glass transition temperatures of the polymer matrix and E7 as a function of LC weight fraction.

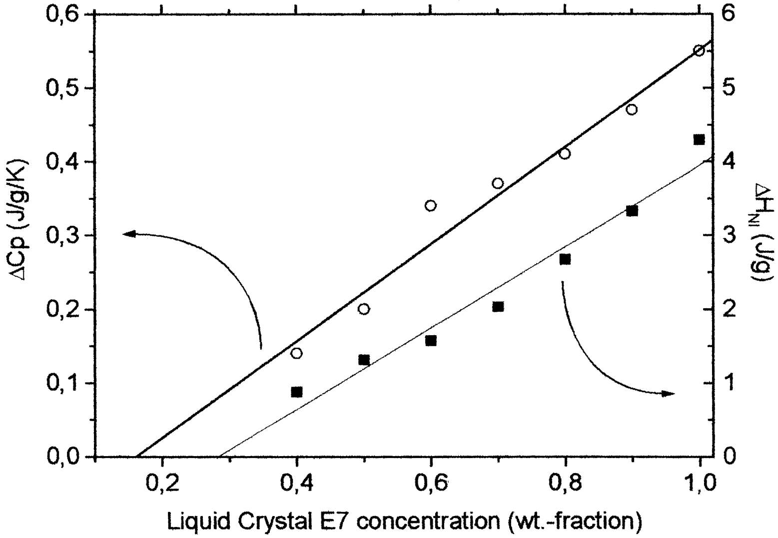

FIGURE 3 Enthalpy change ΔH_{NI} and heat capacity change ΔC_P vs LC concentration of the EB-cured TPGDA/E7 system.

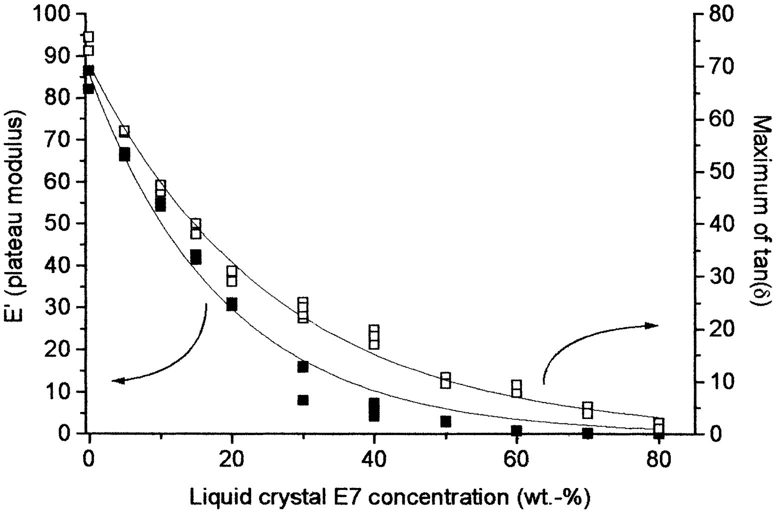

FIGURE 4 Plateau modulus E' and tan δ versus LC weight fraction where δ is the loss angle for the EB-cured TPGDA/E7 system.

CONCLUSIONS

Thermophysical properties, phase behaviour and mechanical responses are investigated for TPGDA/E7 mixtures prepared under EB exposure. The transition temperature from (N + I) to (I) in the case of cured samples varies a little with the LC concentration as compared to the uncured systems where this variation is much larger. The glass transition drops by more than 50°C when adding 50 wt.-% LC to the polymer indicating a strong plasticizing effect. In the precurseor mixture, T_g is practically independent of composition. The miscibility limit is not the same whether deduced from enthalpy changes or from the heat capacity. In the absence of LC, mechanical data of cured systems show a rubbery plateau with a high modulus indicating a high cross-linking density. LC molecules dissolved in the polymer matrix lead to a lower modulus and a drop in the glass transition temperature reminiscent of the plastisizing effect. A complete consistency is found between the thermal data and mechanical measurements.

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