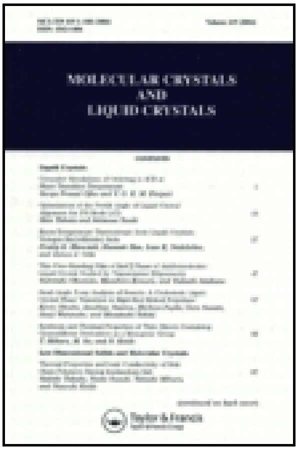

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Phase Properties of Poly(2-ethylhexylacrylate)/E7 Systems

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PHASE PROPERTIES OF POLY(2-ETHYLHEXYLACRYLATE)/E7 SYSTEMS

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This paper reports a comparative study of the phase properties of blends of Poly(2-ethylhexylacrylate) (PEHA) and the eutectic liquid cristalline mixture of cyanoparaphenylenes known as E7. These blends are prepared using different procedures. One is based on the process of Polymerization Induced Phase Separation (PIPS) under UV curing starting from a homogeneous solution of monomer (2-ethylhexylacrylate) and E7. The other method combines Solvent Induced Phase Separation (SIPS) and Thermally Induced Phase Separation (TIPS) processes starting from a polymer with a known molar mass i.e. $M_w = 48{,}000\, g/mol$*. These methods lead to systems with significant differences in terms of the miscibility between polymer and Liquid Crystal (LC). The polymer molar mass in the PIPS/UV method is determined in terms of the LC concentration by Gel Permeation Chromatography measurements.*

Keywords: monomer; nematic liquid crystal; phase properties; polymer

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INTRODUCTION

This paper deals with the phase properties of poly(2-ethylhexylacrylate) (PEHA) and the eutectic mixture of cyanoparaphenylenes E7 which exhibits a nematic to isotropic transition at 61°C. These composite materials are of the same type as Polymer Dispersed Liquid Crystals (PDLCs) and elaborated following different procedures [1–4]. The aim of this work is to see the influence of the method of preparation on their phase behaviour. Two methods of preparation are adopted. One is based on a combination of Solvent Induced Phase Separation (SIPS) and Thermally Induced Phase Separation (TIPS) using E7 and a commercial polymer PEHA with the molar mass $M_w = 48{,}000\,\text{g/mol}$ and the polydispersity $M_w/M_n = 3$. The other method consists of preparing films by a Polymerization Induced Phase Separation (PIPS) technique via UV-curing starting from a homogeneous solution of monomer (2-ethylhexylacrylate) (EHA), E7, and a photoinitiator. The experimental phase diagrams are established by Polarized Optical Microscopy (POM) and some of the data are analyzed with a theoretical model that combines standard mean field approximations [5–7]. By assessing the impact of the method of preparation on the phase behavior of these systems, one may be able to choose the proper conditions of preparation and design novel materials with a wide range of applications.

EXPERIMENTAL PART

Materials

The monomer 2-ethylhexylacrylate (2-EHA) and the polymer poly-2-EHA (PEHA) were supplied from Aldrich (France). PEHA was purified and characterized by Light Scattering (LS) and Gel Permeation Chromatography (GPC). LS measurements were performed for solutions in tetrahydrofuran (THF) at 20°C and $\lambda = 647.1\,\text{nm}$ yielding $M_w = 48{,}000\,\text{g/mol}$. The broadness of the molecular weight distribution was measured by GPC in THF giving $M_w/M_n = 3$. The eutectic mixture of LCs E7 was purchased from Merck Eurolab (Germany). It contains 51 weight percent (wt-%) of 4-cyano-4′-*n*-pentyl-biphenyl (5CB), 25 wt-% of 4-cyano-4′-*n*-heptyl-biphenyl (7CB), 16 wt-% of 4-cyano-4′-*n*-oxyoctyl-biphenyl (8OCB), and 8 wt-% of 4-cyano-4″-*n*-pentyl-p-terphenyl (5CT). It exhibits a nematic-isotropic transition temperature $T_{NI} = 61°C$ [8].

Sample Preparation

SIPS/TIPS Samples

Blends of PEHA and E7 were dissolved in a common organic solvent (THF) at a concentration of 50 wt-% and room temperature (20°C). The resulting mixtures were stirred mechanically overnight. A small quantity of such a blend was cast on a clean glass slide, and dried for two days. After complete evaporation of THF, another glass slide was put on top of it. Samples with pure components were prepared using the same procedure as the polymer/E7 blends.

Several duplicate samples at each composition were prepared independently to check the reliability of the results.

PIPS/UV-cured Samples

The precursor mixtures 2-EHA/E7 were exposed to the UV radiation under nitrogen atmosphere at $T = 22°\mathrm{C}$. The UV lamp has a wavelength $\lambda = 365\,\mathrm{nm}$ and its intensity was fixed at $17.5\,\mathrm{mW/cm^2}$ while the exposure time was 3 min. Polymerization was induced by the photoinitiator (Darocur 1173 from CIBA, Rueil Malmaison, France) at a concentration of 0.8 wt% with respect of the amount of monomer used. Molecular weights of the obtained polymers were determined by Gel Permeation Chromatography (GPC) in THF at room temperature and the measurements were calibrated with polystyrene standards.

POM Measurements

The thermo-optical studies were performed on a POM Jenapol, equipped with a heating/cooling stage Linkam THMS 600 and a Linkam TMS 92 temperature control unit. All samples underwent the same treatment. They were submitted to a heating ramp of 5°C/min from room temperature to 15 degrees above the transition temperature (first ramp up) and left for 5 min in the isotropic state. Afterwards, they were cooled to temperatures far below room temperature at a rate of −5°C/min (first ramp down). This procedure was followed after 5 min by a second heating ramp at a rate of 1°C/min (second ramp up) and left for 5 min in the isotropic state. Subsequently, the samples were cooled at a rate of −1°C/min (second ramp down). The second heating/cooling cycle was repeated (third ramp up and down). The difference between maximum and minimum temperatures was at least 50°C in order to cover the whole phase diagram. Transition temperatures were recorded during the three successive heating and cooling ramps.

RESULTS AND DISCUSSION

Monomer System

Figure 1 exhibits the phase diagram of the monomer system (2-EHA/E7) to show the extend of miscibility prior to UV curing. The absence of a

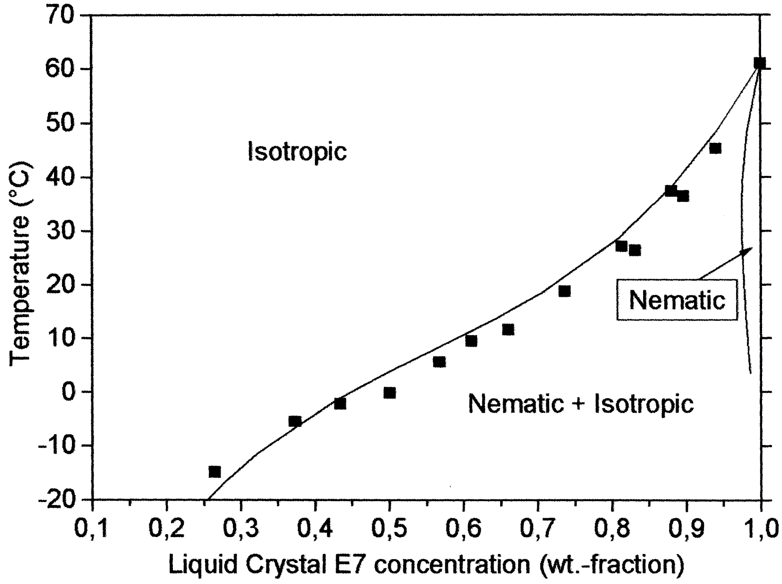

FIGURE 1 Phase diagram of the monomer system 2-EHA/E7 as obtained by POM. The solid curve represents the calculated binodal according to the theory described in references 9 and 10. The numbers of repeat units is 1 for the LC and 2 for the monomer and the Flory-Huggins interaction parameter $\chi = -0.4 + 400/T$ and $T_{\mathrm{NI}} = 61°\mathrm{C}$.

miscibility gap of the type (I + I) where I refers to the isotropic phase, confirms the relative low interaction parameter of the monomer 2-EHA and the LC E7. Note that the critical point and spinodal lie outside the range of temperature and composition shown in Figure 1. The symbols in this figure represent data obtained by POM while the solid line is the calculated binodal using a combination of Flory-Huggins [5] theory of isotropic mixing and Maier-Saupe [6,7] theory of nematic order. For a lack of space, we cannot reproduce details of the calculations and simply refer the reader to references [9,10] where these details can be found. In the calculations, the number of repeat units is 1 for the LC and 2 for the monomer. The interaction parameter $\chi(T)$ is obtained by the best fit to data.

Polymer Systems

In order to establish the phase diagram of PEHA/E7, samples covering the whole composition range were prepared using a combination of PIPS process and UV curing. The experimental phase diagram is given in Figure 2. The diagram obtained with the commercial polymer having a known

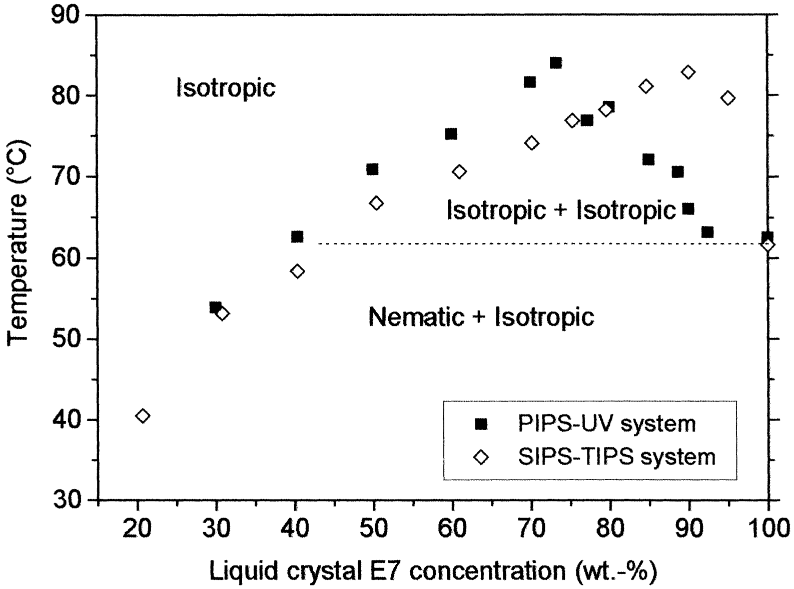

FIGURE 2 Experimental phase diagrams involving the commercial PEHA with $M_w = 48{,}000$ g/mol and the system prepared according to the PIPS/UV-curing technique. The symbols are POM data.

molecular weight $M_w = 48{,}000$ g/mol is also included in this figure. The preparation of the samples is made according to the SIPS/TIPS methods but the transition temperatures are obtained with the POM technique following the same procedure as the systems elaborated by PIPS/UV curing. Interestingly, the two diagrams cross each other at a certain concentration. To our knowledge, such a behavior has not been reported before. A possible explanation of this phenomenon can be found in a concentration dependence of the polymer molecular weight obtained by the PIPS-UV procedure. Indeed, the molar mass of the polymer formed during UV-polymerization might vary due to changes in the dilution conditions of the monomer in the precursor blends. In order to check this hypothesis Gel Permeation Chromatography (GPC) measurements of the molecular weight of the polymer obtained by the PIPS-UV process have been performed depending on the initial LC concentration. Figure 3 exhibits the weight (M_w) and the number average (M_n) of the polymer molecular weight obtained by GPC analysis. At low LC concentrations i.e. below 30 wt.-% constant values for both M_w and M_n were found. If the LC content exceeds 30 wt.-%, the polymer molecular weight starts to decrease. This behavior is more pronounced at high LC concentrations. For instance at 80 wt.-% LC a value of $M_w = 40{,}000$ g/mol was observed which means that

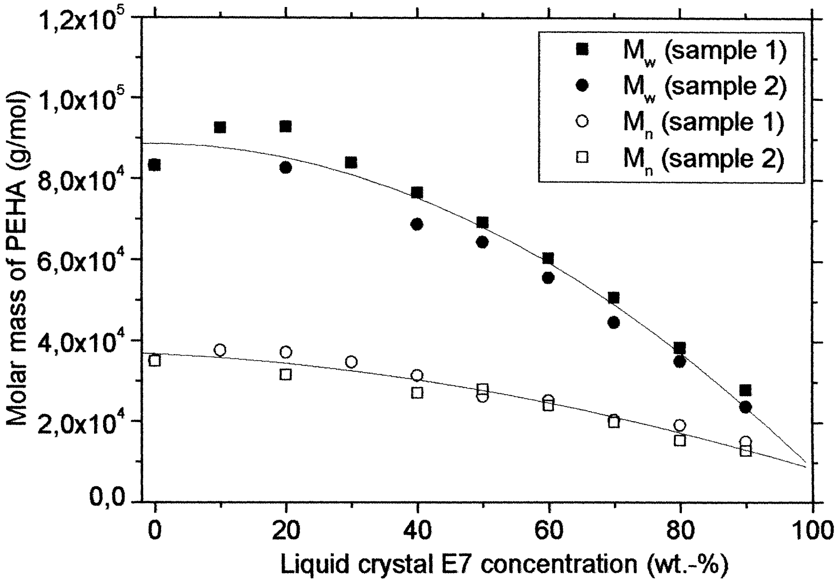

FIGURE 3 M_w and M_n versus LC concentration for PEHA/E7 obtained by PIPS/UV-curing methods. Data are obtained by GPC measurements. The solid lines are guides for the eye.

the molecular weight was reduced by more than a factor 2. The fact that the above mentioned cross-over takes place approximately at the LC concentration where the polymer molecular weight drops below $M_w = 48000$ g/mol (namely, that of the commercial polymer) is not surprising. Below this LC concentration, the polymer obtained by PIPS/UV process has a higher molar mass than the commercial polymer, hence its miscibility with E7 is low. This behaviour is inverted when the LC concentration goes beyond this limit. In this case the molar mass of the polymer in the PIPS/UV system is below $M_w = 48000$ g/mol and its miscibility with E7 higher than the commercial polymer.

Since the molar mass of the polymer varies with the composition, the theoretical model appropriate to this system is not available yet. We hope to be able to rationalize these data in terms of a simple theory in the near future.

CONCLUSIONS

PEHA/E7 systems prepared by a combination of SIPS/TIPS methods with a polymer of known molecular weight exhibit remarkable differences with analogous systems elaborated by a combination of the PIPS and UV curing techniques.

In the latter case, the molar mass of the polymer is determined by GPC and found to decrease with the LC concentration. The phase diagrams of these systems cross each other at the concentration where the polymer mass of the PIPS/UV system is below that of the commercial polymer.

The polymer/LC mixtures investigated in this paper represent model systems to analyse the influence of the method of preparation on their phase behaviour. It might be interesting to compare the electro-optical properties of the SIPS and PIPS systems considered here but the corresponding films scatter light only weakly [10] due to droplet diameters between 10 and 20 μm in the range of composition 40–60 wt.%LC.

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