Effects of the Method of Preparation on the Molar Mass of Polymer and Phase Diagrams of Poly(2-ethylhexylacrylate)/5CB Systems

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1. Introduction

Polymers and liquid crystals (LCs) form heterogeneous composite materials consisting of micrometer-sized LC droplets dispersed in a solid polymer matrix. These materials exhibit remarkable properties from the fundamental point of view and find applications in various domains of modern technology such as display devices and privacy windows.[1,2] Most applications are related to the specific electrooptical behavior of these materials under the effect of an external field, which in turn depends on various thermophysical parameters and phase properties of the compounds at given temperatures and compositions.[3−6] In the present work, we focus on the case of poly(2-ethylhexyl acrylate) in short PEHA and the single component LC 4-cyano-4′-*n*-pentylbiphenyl (5CB) and study the correlation between the method of preparation, on one hand, and the binary phase diagram, on the other hand. Two series of systems elaborated under different scenarios are considered. The first series consists of photopolymerized samples which undergo phase separation as the polymerization reaction proceeds and the molar mass of polymer increases. An important outcome of this investigation is to calculate the drop in the molar mass of polymer with the LC concentration. This evaluation is made using gel permeation chromatography (GPC). The present scenario is commonly known as a polymerization-induced phase separation (PIPS) mechanism under UV curing.[1,2] The precursor mixture consists of a monofunctional monomer (2-EHA), 5CB, and a small amount of photoinitiator (Darocur 1173) added to initiate the photopolymerization process (i.e., 2 wt %). The concentration of monomer in the monomer/LC mixture was varied from 100 wt % (pure monomer) to 5 wt % to cover nearly the whole range of composition and to construct the complete phase diagram. The second series of samples is prepared using a commercial homopolymer PEHA with a molar mass of $M_w = 48\,000$ g/mol and a polydispersity $M_w/M_n = 3$. Mixtures of this polymer and 5CB are prepared according to a combination of solvent-induced phase separation (SIPS) and thermally induced phase separation (TIPS).[1,2] Since this molar mass is quite high, the polymer miscibility with the LC reaches a saturation limit at a relatively low concentration. For instance, at room temperature this limit is slightly above 40 wt % LC and in order to obtain a single phase homogeneous solution, it is necessary to add a common solvent to the polymer/LC mixture. Letting the solvent to evaporate induces a phase separation according to the SIPS mechanism. On the other hand, the TIPS process takes place when the system is brought from the single phase region to the biphasic region by a sudden drop of temperature. More details on these various phase separation processes are given in the literature[1−6] and summarized below.

2. Experimental Section

Materials. The monomer 2-ethylhexyl acrylate (EHA) and the polymer poly(2-ethylhexyl acrylate) (PEHA) were supplied by Aldrich. PEHA was purified and characterized by light scattering and gel permeation chromatography (GPC). The light scattering measurement was made in a tetrahydrofuran (THF) solution at 20 °C ($\lambda = 647.1$ nm) yielding $M_w = 48\,000$ g/mol. The broadness of the molecular weight distribution was obtained by GPC in THF giving an index of polydispersity $M_w/M_n = 3$. These measurements were calibrated using narrow distributed polystyrene standards. The LC 4-cyano-4′-*n*-pentylbiphenyl (5CB) was purchased from Merck Eurolab GmbH and is characterized by the transition temperatures $T_{CN} = 23$°C (crystalline−nematic) and $T_{NI} = 35.3$°C (nematic−isotropic).

Sample Preparation. (a) SIPS/TIPS Samples. Blends of PEHA and 5CB were dissolved in a common organic solvent (THF) at a concentration of 50 wt % and different PEHA/5CB compositions. These systems were prepared at room temperature and stirred mechanically overnight. A small amount of the resulting solution was cast on a clean glass slide and dried at room temperature for 2 days. After complete evaporation of THF, another glass slide was put on top of it. The preparation of samples without THF was also made according to the same procedure.

(b) PIPS/UV Samples. Mixtures of EHA and 5CB were prepared with different LC concentrations and stirred mechanically until they became homogeneous. A drop of the reactive mixture was placed between standard glass slides and exposed to the UV beam. The UV-curing was performed using a Seiko-UV 1 Unit at the wavelength $\lambda = 365$ nm, a beam intensity of 17.5 mW/cm^2 and an exposure time of 3 min. The polymerization process was induced by a photoinitiator (Darocur 1173 from Ciba, Rueil Malmaison, France) at a concentration of 2 wt % with respect to the amount of monomer.

At each composition, several samples were prepared independently to check the reproducibility of the results.

Polarized Optical Microscopy (POM) and Experimental Procedure. The thermooptical 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 thermal treatment. They were submitted to a heating ramp of 5 °C/min from room temperature to 15 deg above the transition temperature (first ramp up) and left for 5 min in the isotropic state. Afterward, they were cooled 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

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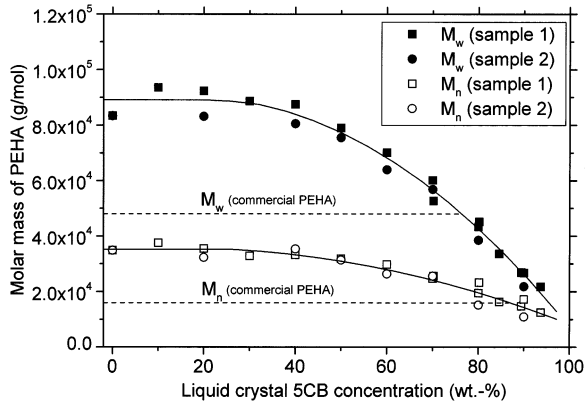

Figure 1. Variation of the molar mass of PEHA as a function of 5CB concentration for the system elaborated by PIPS mechanism under UV curing. The symbols represent GPC data of systems prepared independently under similar conditions. Upper (filled symbols) and lower curves (open symbols) correspond to M_w and M_n, respectively. Dashed horizontal lines indicate the molar masses of the commercial PEHA sample (M_w = 48 000 g/mol, M_n = 16 000 g/mol). Solid lines are guides for the eye.

(third ramp up and third ramp down). Differences between maxima and minima of temperature exceeded 50 °C in order to cover a large domain of the phase diagram. Transition temperatures were recorded during the three successive heating and cooling ramps.

Gel Permeation Chromatography. The measurement of the molar masses by gel permeation chromatography (GPC) was performed at T = 25 °C using a Waters apparatus including a Waters 515 pump, a Waters 717 plus autosampler, a differential refractometer Waters 410, and Stryragel columns HR3 and HR 3E (5 μm particles). Each experiment elapsed nearly 1 h. The solvent used was THF with a flow rate of 1 mL/min.

3. Results and Discussion

The experimental phase diagrams of a series of systems were established by POM to demonstrate the strong impact of the method of preparation on the miscibility of PEHA and 5CB. More importantly, the variation of the polymer molar mass with the LC concentration in the precursor mixture prior to radiation curing is reported for the first time using GPC.

Variation of the Polymer Molar Mass vs LC Concentration in PIPS/UV Systems. A series of samples with a monomer concentration ranging from 100 (no LC) to 5 wt % (95 wt % LC in the monomer/LC mixture) were exposed to the UV light. The obtained polymer-dispersed liquid crystal (PDLC) films were analyzed, and the results were compared with those of analogous films prepared according to a combination of the SIPS and TIPS processes. We were able to measure the variation of the polymer molar mass in terms of the LC concentration using GPC as shown in Figure 1. Weight- and number-averaged molar masses M_w and M_n exhibit a sharp drop when the LC concentration increases. This result means that as the precursor system is more dilute, the polymerization stops at a smaller mass of the polymer which is expected since the probability of contact between two reacting species decreases. The dashed horizontal lines in Figure 1 refer to M_w and M_n of the commercial PEHA. These values coincide with those of the polymer in the PIPS/UV systems in the vicinity of 80 wt % LC. Below this concentration, the PIPS/UV samples have higher molar masses compared to those of the commercial polymer

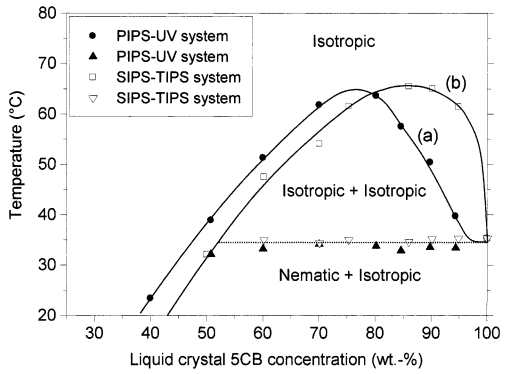

Figure 2. Comparison of the phase diagrams of PEHA/5CB mixtures prepared under different conditions: (a) system prepared by the PIPS mechanism using UV-curing (filled symbols); (b) system prepared by the SIPS/TIPS mechanism (open symbols, M_w(PEHA) = 48 000 g/mol). The symbols are averaged values of POM data, while solid and dotted lines are guides for the eye.

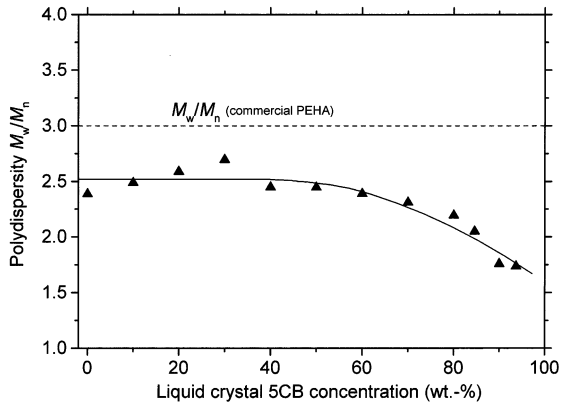

Figure 3. Variation of the polydispersity M_w/M_n vs 5CB concentration for the PEHA/5CB samples prepared according to the PIPS/UV mechanism. The horizontal dashed line corresponds to M_w/M_n of the commercial sample. The solid line is a guide for the eye.

while above it, the concentration of reacting monomers is low and the polymerization time is reduced, hence the chains are shorter. The symbols are averaged values of two or three measurements made on samples prepared independently under similar conditions for the same composition and temperature.

The Phase Diagrams. Part a of Figure 2 (filled symbols) gives the phase diagram of the PEHA/5CB system obtained by the PIPS method with UV curing while part b (open symbols) shows the corresponding plot for the systems elaborated under the SIPS and TIPS mechanisms using a commercial polymer with a fixed molecular weight. These diagrams cross each other in the vicinity of 80 wt % LC. Beyond this concentration, the SIPS/TIPS diagram is above exhibiting a lower miscibility while below it, the tendencies are reversed and it is the PIPS/UV diagram that shows a reduced miscibility.

Several arguments could be invoked to explain these observations. One could invoke the relatively high polydispersity in the molar mass distribution of both systems. The commercial PEHA has a fixed polydispersity (M_w/M_n = 3) while that of the UV-cured systems varies with the LC concentration. This variation is illustrated in Figure 3 exhibiting a trend somewhat similar to those of the molar mass curves. The polydispersity drops remarkably in the upper range of the LC

concentration as a direct consequence of the fact that the M_w and M_n curves come close to each other in this region. The polydispersity may induce some scattering in the data of the phase diagrams but it cannot explain the qualitative trends revealed by Figure 2. On the other hand, it is not ruled out that defects in the chemical structure of PEHA in the case of UV-cured systems emerge after radiation exposure, but such defects are unlikely to explain the observed trends in a consistent way. A sound explanation resides in the variation of the polymer molar mass with the LC concentration in the PIPS/UV system and the plots of Figure 1 confirm this view. The fact that the crossing point of the diagrams of Figure 2 falls in the vicinity of the concentration at which the molar mass of polymer in the PIPS/UV system decreases below that of the commercial sample (namely near 80 wt % LC) favors this interpretation.

4. Conclusion

The molar mass of polymer in PDLC systems prepared according to the PIPS/UV methods is found to decrease with the LC concentration. This result is used to analyze the phase diagram in the temperature vs composition frame. A comparison is made with the diagram of analogous systems prepared according to the SIPS and TIPS methods based on polymers with fixed molar masses. These two diagrams are found to cross each other in the vicinity of the LC concentration where the polymer molar mass of the PIPS/UV sample decreases below that of the commercial sample. Further investigations are under progress to corroborate those findings and check whether they can be generalized to other polymer and LC systems.

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