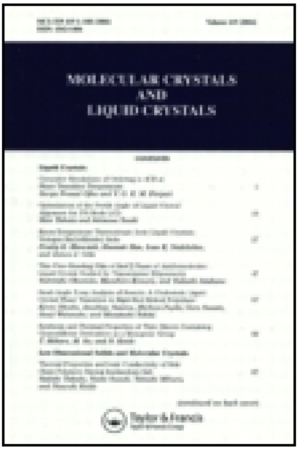

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F. Roussel [a], U. Maschke [b], X. Coqueret [b] & J. M. Buisine [a]

[a] Laboratoire de Dynamique et Structure des Matériaux Moléculaires, Equipe de Thermophysique de la Matiére Condensée, CNRS (URA N^0 801). Université du Littoral, MREID, 59140, Dunkerque, France

[b] Laboratoire de Chimie Macromoléculaire, CNRS (URA N^0 351), Bǎtiment C6, Université des Sciences et Technologies de Lille, 59655, Villeneuve d' Ascq, France

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Phase Behavior of Poly(Ethylhexylacrylate)/E7 Mixtures

F. ROUSSEL[a], U. MASCHKE[b], X. COQUERET[b] and J.-M. BUISINE[a]

[a]*Laboratoire de Dynamique et Structure des Matériaux Moléculaires, Equipe de Thermophysique de la Matière Condensée, CNRS (URA N° 801), Université du Littoral, MREID, 59140 Dunkerque, France and* [b]*Laboratoire de Chimie Macromoléculaire, CNRS (URA N° 351), Bâtiment C6, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France*

Reactive blends of monofunctional 2-ethylhexyl acrylate monomer and the low molecular weight liquid crystal (LC) mixture E7 have been efficiently polymerized by a polymerization induced phase separation (PIPS) mechanism using UV radiation. An experimental phase diagram of the obtained Poly(ethylhexylacrylate)/E7 blends has been investigated as a function of temperature and composition of the initial reactive mixtures. Polarized optical microscopy and DSC techniques were employed to determine the phase behavior. The observed temperature/composition phase diagram shows qualitatively an Upper Critical Solution Temperature (UCST) behavior. At LC concentrations below 50 wt%, a direct transition from the (nematic + isotropic)(N+I) to the isotropic (I) phase is detected. From 50 to 90 wt% LC, there is clear evidence of the existence of an (I+I) phase located between the (N+I) and the I phases. Above 90 wt% LC, the (I+I) phase is also expected but has not been observed experimentally.

Keywords: Phase diagram; ultraviolet radiation; phase separation; nematic liquid crystals; polymer dispersed liquid crystals

INTRODUCTION

In recent years, mixtures of nematic liquid crystals (LCs) and polymers have received considerable attention. In particular, Polymer Dispersed Liquid

Crystals (PDLCs) are important materials for optical applications[1-7]. PDLC films consist commonly of low molecular weight LC dispersed as micron-sized droplets within a solid polymer matrix. The morphology including the size, shape, spatial distribution and number density of LC droplets is particularly influencing the electro-optical properties of these films. The above mentioned parameters are controlled by the phase behavior and the phase separation process. To understand the phase properties of LC/polymer mixtures, studies on theoretical equilibrium phase diagrams for various hypothetical LC/polymer systems were reported[8-12]. Less attention has been given to experimental determinations of phase diagrams. Kyu et al. investigated the phase behavior of Poly(benzylmethacrylate)/E7[8], Poly(styrene)/E7[9], Poly(methylmethacrylate) (PMMA)/E7[10], and functionalized PMMA/E7[11], whereas Carpaneto et al.[13] studied the Poly(n-butylmethacrylate)/E7 and the PMMA/E7 system. Generally, only the cloud point curve observed by polarized optical microscopy (POM) and light scattering (LS) was reported by these authors. A more detailed investigation of the phase diagrams of PMMA/7CB and PS/7CB has been performed by Ahn et al.[14] using POM, LS and differential scanning calorimetry (DSC) techniques. These authors have found nematic, nematic–isotropic (N+I), isotropic-isotropic (I+I) and isotropic (I) phases.

The previously mentioned studies were conducted by a solvent induced phase separation mechanism followed by a thermally induced phase separation process. To our knowledge, phase diagrams of linear homopolymer/LC blends obtained by a PIPS process have not been mentioned in literature. Only phase diagrams of NOA65 (Norland Optical Adhesive, commercial product from Norland Products)-E7[15] and 2-ethylhexyl acrylate (2-EHA)-E8[16], both in the uncured state before undergoing a PIPS process, have been reported.

In the present paper, an experimental phase diagram for mixtures of Poly(2-EHA) (PEHA) and E7 is presented. Blends covering the whole concentration range have been prepared by a photoinitiated PIPS process. The phase behavior has been entirely explored by DSC and POM, and the results of these complementary techniques are compared.

EXPERIMENTAL

Materials

The monomer 2-EHA was purchased from Aldrich (Saint Quentin Fallavier, France) and used without further purification. The eutectic LC mixture E7 (Merck Ltd, Poole, GB) has been employed during this work exhibiting a nematic phase in a wide temperature range from -10°C up to 58°C. The nematic-isotropic transition of E7 occurs at T_{NI}=61°C[17]. The UV polymerization was induced by 0.8 wt% of Darocur 1173 (CIBA, Rueil Malmaison, France) with respect to the amount of monomer used.

Preparation of PEHA/E7 blends

2-EHA and E7 with various LC compositions were mixed together at room temperature for several hours. Samples for calorimetric measurements were prepared by introducing 2.9±0.1 mg of the initial mixture into aluminium DSC pans, which have been sealed after UV exposure to avoid evaporation effects during the temperature treatment. Samples for optical microscopy observations were prepared between standard glass slides resulting in a film thickness of approximately 3 μm.

UV radiation was carried out in the DSC furnace under isothermal conditions (T=22°C) and nitrogen atmosphere. The wavelength of the UV lamp was fixed at λ=365 nm with a beam intensity of 17.5 mW/cm^2. The UV exposure time was set at three minutes.

In this way, four monomer samples were polymerized between standard glass slides under identical conditions in the absence of E7. The molecular weights and molecular weight distributions of the obtained PEHA samples were determined by gel permeation chromatography (GPC), calibrated with PS standards. GPC measurements were performed in tetrahydrofuran at room temperature yielding $\overline{M}_w$=108000±5000 g/mol and $\overline{M}_w/\overline{M}_n$=2.1±0.2. These results represent averages from one GPC measurement performed on each of the four PEHA samples.

Characterization methods

The DSC measurements were performed on a Seiko DSC 220C. A liquid nitrogen system allows cooling experiments. The DSC cell was purged with 50 ml/min of nitrogen. Rates of 10°C/min (heating) and 30°C/min (cooling) were used in the temperature range from −120 to 100°C. The program consists first in cooling the sample followed by several heating and cooling cycles. Data analysis has been carried out on the second heating ramp.

The thermo-microscopy studies were performed on an optical polarizing microscope Leica DMRXP, equipped with a heating/cooling stage Chaixmeca. Samples were first heated with a rate of 5°C/min from room temperature to a temperature located 15 degrees above the isotropic phase limit. Secondly, applying a rate of −1°C/min, the samples were cooled down to a temperature situated 15 degrees below the (N+I)/I or (I+I)/I transition temperature. Another heating cycle with a rate of 1°C/min up to the isotropic state was carried out. Transition temperatures have been deduced from the second heating ramp. Two independently prepared samples of the same composition have been analyzed. Optical micrographs were taken at different given temperatures with magnifications from 200 to 320.

RESULTS AND DISCUSSIONS

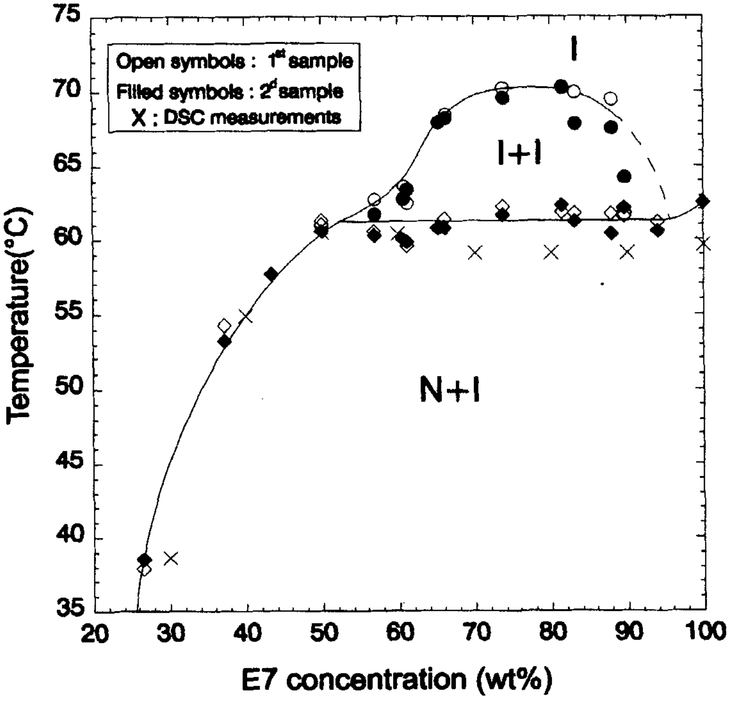

FIGURE 1 Phase diagram of PEHA/E7 obtained from DSC and POM techniques. The continuous lines and the dashed line are guidelines for the eyes.

Figure 1 shows the phase diagram of the PEHA/E7 system. For a given composition, two identically but independently prepared samples were investigated both in the heating and cooling mode. The results for POM given in Figure 1 are the heating measurements. The open symbols represent the first sample whereas the filled symbols correspond to the results obtained from the second samples. Circles indicate the (I+I)/I transition temperature whereas the diamond shaped symboles represent the (N+I)/(I+I) or (N+I)/I transition. These results were obtained from POM measurements. The x-symbols are DSC data obtained from the nematic-isotropic transition temperature. The continuous lines and the dashed line represent guidelines for the eyes. Theoretical investigations are underway to confirm with a thermodynamic model the position of these lines. The T_g's of the mixtures are not included in the phase diagram. Their range is located far below the scaling of Figure 1. Furthermore, due to the low value of T_g of the polymer, the phase behavior can also be explored in the experimentally accessible temperature range for LC concentrations lower than 30 wt%. A small amount of LC remains dissolved in the polymer for LC concentrations below 30 wt%. This well-known phenomenon leads to a decrease of T_g (polymer) and can be explained by the

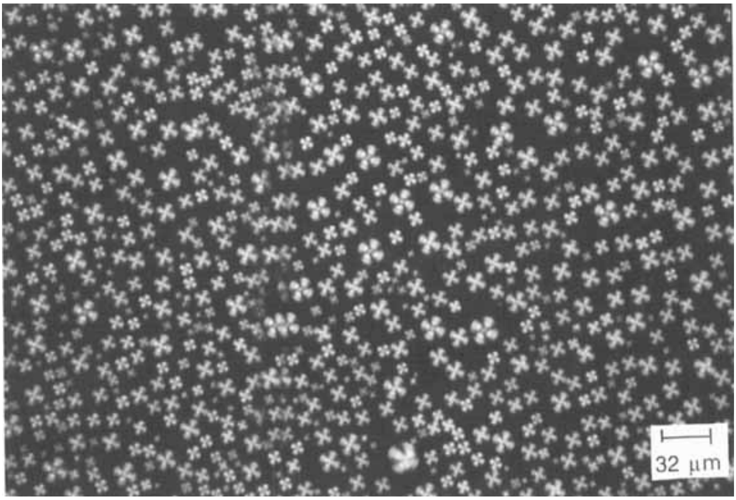

FIGURE 2 Optical micrograph showing the morphology of a E7/EHA (50:50) UV polymerized blend (cross-polarized transmission mode); T=21°C, 1cm≈50μm.
(See Color Plate VIII at the back of this issue)

plasticizing effect of the LC. Above 30 wt% of LC, the T_g of the polymer does not further change, indicating the limited solubility of the LC in the polymer. In the range from 25 up to 50 wt% of LC, only the direct transition from the (N+I) to the I phase is observed by POM. Above 50 wt% and below 90 wt% of LC, two different transitions have been detected by means of POM : The first corresponding to approximately 61 °C indicates the transition from (N+I) to (I+I) whereas the second corresponding to higher temperatures represents the (I+I) to I transition. DSC data, obtained from the (N+I) transition temperature, are in reasonable agreement with the POM measurements. However, it can be observed that DSC results give slightly lower transition temperatures than those obtained from POM. In the pure LC state, POM measurements give T_{NI}=62.5°C whereas DSC data yield T_{NI}=59.6°C. Approximately the same difference can also be detected for PEHA/E7 blends in the range from 60 to 100 wt% of LC. This discrepancy is probably due to the different analyzing methods and calibration techniques. Furthermore, one can easily see that the (N+I)/(I+I) transition temperature remains nearly constant above 50 wt% of LC and represents roughly the same value as that of pure LC. These observations indicate that the phase separated LC is essentially pure and not contaminated by remaining monomer.

Figure 2 represents an optical micrograph of the blend 50 wt% LC/50 wt% PEHA at T=21°C using the cross-polarized mode. An optical micrograph of the blend 65 wt% LC/35 wt% PEHA at T=62.3°C is given in Figure 3, where polarizer and analyzer were oriented parallel to each other. Microscopy observations in the cross-polarized mode could not prove the existence of the (I+I) phase. The (N+I) phase is presented in Figure 2 whereas Figure 3 shows unambigously the (I+I) morphology. The phase diagram suggests that there is no (I+I) region above 90 wt% of LC. This behavior has already been discussed in literature[14,18] and attributed to the difficulty to distinguish experimentally the transitions between the (N+I)/I and the (N+I)/(I+I) boundary. Dubault et al.[18] has shown that the phase separation process for polymer/LC mixtures

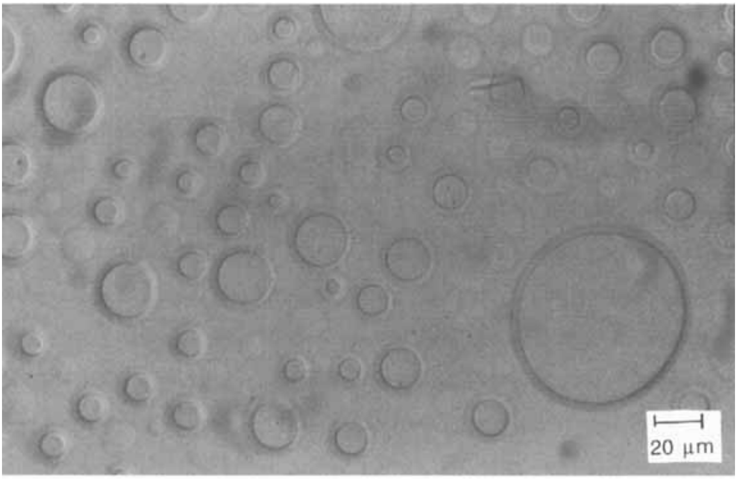

FIGURE 3 Optical micrograph showing the morphology of a E7/EHA (65:35) UV polymerized blend (transmission mode, polarizer and analyzer were parallel); T=62.3°C, 1cm≈30μm.
(See Color Plate IX at the back of this issue)

with low polymer concentrations may require several days, which is beyond the timescale used for our experiments. The (I+I)/I transition cannot be observed by DSC measurements since this transition is only accompagnied by a small enthalpy change.

CONCLUSIONS

Reactive blends of EHA and E7 have been efficiently polymerized by a photoinitiated PIPS process. An experimental phase diagram of the PEHA/E7 system obtained by DSC and POM techniques is presented and discussed. The dependence of the highest transition temperatures, leading to the isotropic phase, on the LC content is qualitatively similar to a phase diagram characterized by an UCST. DSC measurements allowed to obtain the glass transition temperatures of the mixtures as well as the (N+I)/I and the (N+I)/(I+I) transition temperatures. (N+I), (I+I) and (I) phases have been found by POM measurements. Further analysis is in progress to compare the experimental findings with theoretical results obtained from the calculations of the free energy involving the Flory-Huggins and Maier-Saupe approaches.

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References

[1] J.W. Doane, in *Liquid Crystals – Applications and Uses,* edited by B. Bahadur (World Scientific, Singapore, 1990).

[2] P.S. Drzaic, *Liquid Crystal Dispersions* (World Scientific, Singapore, 1995).

[3] *Liquid Crystals in Complex Geometries,* edited by G.P. Crawford and S. Zumer (Taylor&Francis, London, 1996).

[4] U. Maschke, X. Coqueret, and C. Loucheux, *J. Appl. Polym. Sci.,* **56,** 1547 (1995).

[5] U. Maschke, J.-M. Gloaguen, J.-D. Turgis, and X. Coqueret, *Mol. Cryst. Liq. Cryst.,* **282,** 407 (1996).

[6] U. Maschke, A. Traisnel, J.-D. Turgis, and X. Coqueret, *Mol. Cryst. Liq. Cryst.,* **299,** 371 (1997).

[7] F. Roussel, J.-M. Buisine, U. Maschke, and X. Coqueret, *Mol. Cryst. Liq. Cryst.,* **299,** 321 (1997).

[8] C. Shen, and T. Kyu, *J. Chem. Phys.,* **102,** 556 (1995).

[9] W.-K. Kim, and T. Kyu, *Mol. Cryst. Liq. Cryst.,* **250,** 131 (1994).

[10] T. Kyu, C. Shen, and H.-W. Chiu, *Mol. Cryst. Liq. Cryst.,* **287,** 27 (1996).

[11] T. Kyu, I. Ilies, C. Shen, and Z.L. Zhou, Chapter 13 in *Liquid-Crystalline Polymer Systems – Technological Advances,* edited by A.I. Isayev, T. Kyu and S.Z.D. Cheng (ACS Symposium Series 632, Washington DC, 1996).

[12] F. Benmouna, L. Bedjaoui, U. Maschke, X. Coqueret, and M. Benmouna, *Macromol. Theory Simul.,* **7,** 599 (1998).

[13] L. Carpaneto, A. Ristagno, P. Stagnaro, and B. Valenti, *Mol. Cryst. Liq. Cryst.,* **290,** 213 (1996).

[14] W. Ahn, C.Y. Kim, H. Kim, and S.C. Kim, *Macromolecules,* **25,** 5002 (1992).

[15] G.W. Smith, *Phys. Rev. Lett.,* **70,** 198 (1993).

[16] Y. Hirai, S. Niiyama, H. Kumai, and T. Gunjima, *Proceedings of SPIE,* **1257,** 2 (1990).

[17] Value given by Merck Ltd, Merck House, Poole, Great Britain.

[18] A. Dubault, C. Casagrande, and M. Veyssie, *Mol. Cryst. Liq. Cryst. Lett.,* **72,** 189 (1982).