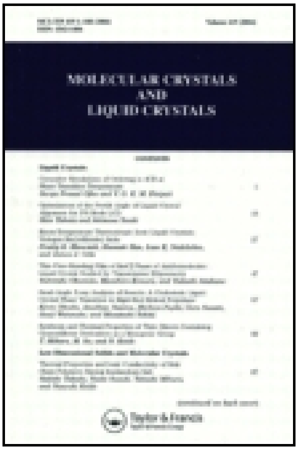

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Thermophysical Properties in Phenyletheracrylate / Liquid Crystal Mixtures: Effects of Photoinitiator Concentration

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Thermophysical Properties in Phenyletheracrylate / Liquid Crystal Mixtures: Effects of Photoinitiator Concentration

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The influence of the amount of photoinitiator (Darocur 1173) on the phase behavior of Phenyletheracrylate/Liquid Crystal (E7) mixtures prepared by a PIPS-UV process are investigated. The phase diagrams of polymer/LC systems prepared with various photoinitiator contents are established by polarized optical microscopy. The miscibility between the polymer and the liquid crystal increases when the photoinitiator content increases. The polymer glass transition temperatures are strongly affected by the presence of LC. These phenomena can be explained by a lower extent of the degree of polymerization when the photoinitiator concentration increases.

Keywords: polymer dispersed liquid crystals; photoinitiator; phase diagram; glass transition; conversion

INTRODUCTION

Polymer-Dispersed Liquid Crystals (PDLC) have received particular attention due to potential electro-optical applications such as flexible information displays and light shutter devices [1]. These materials consist commonly of low molar mass liquid crystals dispersed as micrometer-sized droplets in a solid polymer matrix. PDLC are usually prepared via Polymerization Induced Phase Separation (PIPS) which occurs when a homogeneous mixture of polymer precursors and Liquid Crystals (LC) is polymerized. A good understanding of the PIPS mechanism is of main interest because the morphology and the electro-optical properties of the PDLC films are closely linked to the phase separation process [2, 3].

In this work UV-radiation is used to initiate the polymerization of mixtures including a monofunctional monomer and a nematic liquid crystal. A particular attention is given to the influence of the quantity of photoinitiator on the PIPS-UV mechanism The phase behavior of PDLC samples prepared with various photoinitiator concentrations were investigated as a function of LC contents by Polarized Optical Microscopy (POM) and Differential Scanning Calorimetry (DSC). The glass transition temperature of the polymer and the Nematic-Isotropic transition temperature of the LC are presented. The phase diagrams of three systems formed with different photoinitiator contents are also established. The thermodynamic results are discussed with regard to the extent of cure determined by Isothermal Photocalorimetry (IP) and Fourier Transform InfraRed spectroscopy (FTIR).

EXPERIMENTAL

Materials and Sample Preparation

The monofunctional monomer PhenylEtherAcrylate (PEA) was supplied from Aldrich (France). The LC E7 was purchased from Merck-Clevenot (France). It exhibits a single Nematic-Isotropic transition temperature at T_{NI}=62°C. The photopolymerization process was induced by including 0.25 to 5.2 weight-percent (wt-%) of Darocur 1173 (Ciba, France) in the reactive initial mixtures, with respect to the amount of monomer used. x wt-% of LC ($10<x<90$) and (100-x) wt-% of the monomer were mixed together at room temperature for several hours. Samples for calorimetric measurements were prepared by introducing approximately 3mg of the initial mixture into aluminium DSC pans. Samples for microscopy observations were prepared by placing one drop of the reactive blend between standart glass plates. The UV-polymerization was performed at room temperature under nitrogen atmosphere using a Seiko UV-1 Unit. The UV wavelength was set at λ=365nm with a beam intensity of 17.5mW/cm^2. The UV irradiation was applied for 4 minutes.

Characterization methods

The Differential Scanning Calorimetry measurements (DSC) were performed on a Seiko DSC 220C calorimeter equipped with a liquid nitrogen system allowing cooling experiments. The DSC cell was purged with 50ml/min of nitrogen. Rates of 10°C/min (heating) and 30°C/min (cooling) were used in the temperature range –100 to +100°C. The program consists first in cooling the sample followed by several heating and cooling cycles. Data analysis have been carried out on the second heating ramp.

The Polarized Optical Microscopy studies (POM) were performed on a Leica DMLSP microscope equipped with a heating/cooling stage Linkam THMSE 600. The phase diagrams were obtained by using the following temperature treatment. Samples were first heated from room temperature to a temperature located 15°C above the isotropic phase limit then cooled to 20°C. Subsequently another cycle up to the isotropic state was carried out. The whole procedure was repeated twice. Cycles with rates of 2, 5 and 10°C/min were used. Two independent samples of the same composition were analyzed.

Isothermal Photocalorimetry (Seiko DSC 220C + UV1 Unit) was used to measure the heat of polymerization ΔQ. The acrylate double bond conversion during cure was deduced from ΔQ [3,4]. Infra-Red spectroscopy measurements were carried out in the transmission mode with a Perkin Elmer FTIR2000. The spectra of thin films were recorded at room temperature before and after the polymerization.

RESULTS AND DISCUSSION

Figure 1 collects the phase diagrams of PEA/E7 mixtures prepared with 0.25, 2 and 4 wt-% of Darocur 1173, respectively. The three diagrams exhibit a Upper Critical Solution Temperature (UCST) and three distinct regions : Nematic+Isotropic (N+I), Isotropic+Isotropic (I+I) and Isotropic (I). At T=30°C the phase separation occurs at low LC contents (~20 wt-%). The critical temperature is observed for mixtures including 75 to 85 wt-% LC. These experimental results clearly indicate the relatively high incompatibility between E7 and PEA. However one can see that increasing the amount of Darocur 1173 leads to a shift of the phase diagrams at lower temperature showing an improved miscibility between PEA and E7 when the Darcocur 1173 concentration goes from 0.25 to 4 wt-%. Indeed, it can be assumed that an increasing photoinitiator content will provoke a decrease of the average polymer chain length [5]. As a consequence the polymer/LC miscibility increases thus explaining the shift of the observed phase diagrams.

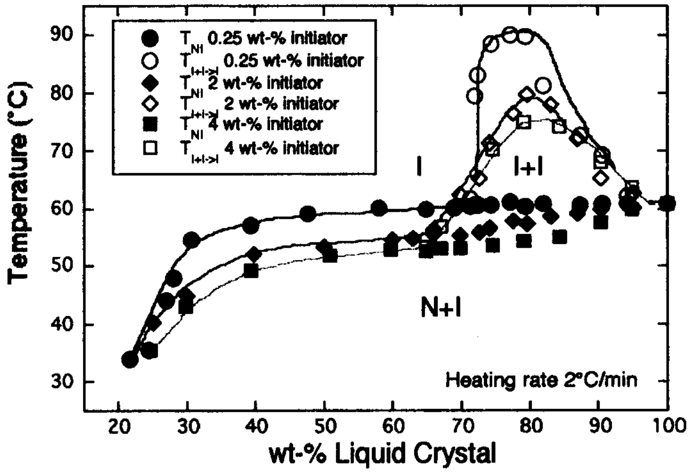

FIGURE 1 Experimental Phase diagrams of PEA/E7 mixtures prepared with 0.25, 2 and 4 wt-% of Darocur 1173. The open and filled symbols are average values of POM measurements and the lines are guides for the eye.

This behavior is clearly displayed in Fig. 2 where the Nematic-Isotropic transition temperature T_{NI} measured for PEA/E7(50 :50) samples is plotted versus the photinitiator concentration. T_{NI} decreases roughly linearly when the amount of Darocur 1173 increases from 0.25 to 5.2 wt-%. The miscibility between the two compounds is then increased, that is less favorable for potential electro-optical applications.

The effects of the photoinitiator concentration on the glass transition temperature Tg of the polymer matrix are presented in Fig. 3. The filled symbols represent Tg of the pure polymer matrix whereas the open symbols represent Tg of the polymer matrix measured for PEA/E7 (50 :50) samples. In the case of pure PEA, Tg_{PEA} remains almost constant below 1 wt-% of Darocur 1173 then decreases linearly for higher contents.

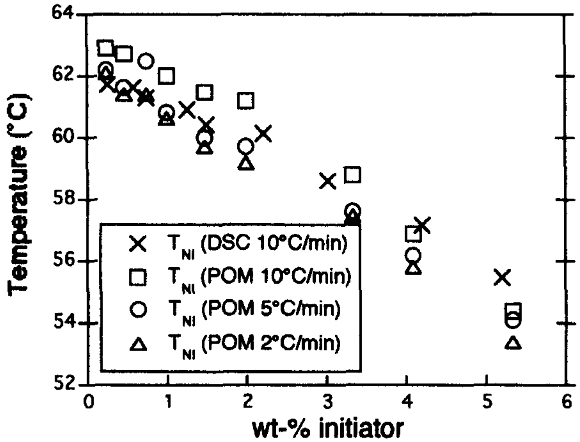

FIGURE 2 Influence of the amount of photoinitiator on the Nematic-Isotropic transition temperature T_{NI} in PEA/E7 (50 :50) samples.

This behavior has already been discussed in the literature and has been attributed to the dependence of Tg on the average macromolecular weights. In the case of PEA/E7 (50 :50) mixtures, the polymer glass transition temperature $Tg_{PEA/E7}$ is shifted by 10°C showing a plasticizing effect of PEA by LC molecules [6]. As for pure PEA, increasing the amount of photoinitiator leads to a decrease of Tg indicating a decrease of the polymer chain length. However the plateau obtained for pure PEA at low Darocur contents is not observed which can be explained by a higher influence of the LC molecules on Tg than short polymer chains.

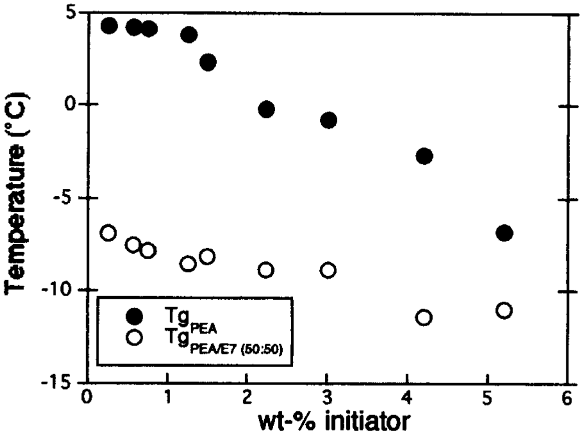

FIGURE 3 Influence of the amount of photoinitiator on the polymer glass transition in PEA and PEA/E7 (50 :50) samples.

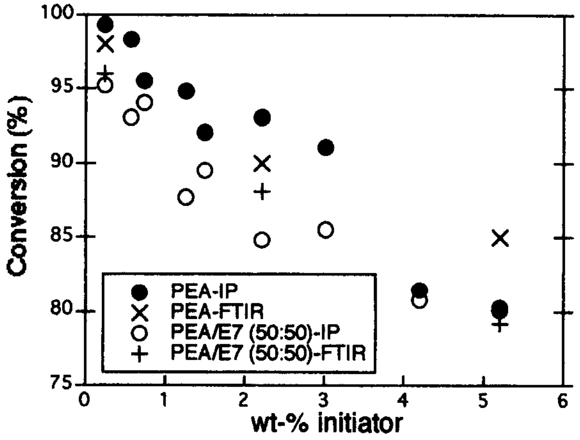

FIGURE 4 Acrylate double bond conversion vs photoinitiator content.

In order to understand these results, the conversion of the carbon-carbon double bond of the acrylate groups was monitored by Isothermal Photocalorimetry [3] and InfraRed spectroscopy. Figure 4 shows the conversion versus the amount of photoinitiator. One can see that for both systems (PEA and PEA/E7 (50 :50) the conversion decreases with increasing Darocur 1173 content which clearly indicates a lower extent of the degree of polymerization and therefore lower average polymer chain lengths [7]. This behavior explains the decrease of the polymer glass transition temperatures and the improved miscibility between PEA and E7 when the photoinitiator content increases.

CONCLUSION

The effects of the amount of photoinitiator (Darocur 1173) on the thermophysiscal properties in Phenyletheracrylate/Liquid Crystal (E7) mixtures formed by a PIPS-UV process are investigated. Three phase diagrams of PDLC samples prepared with various photoinitiator contents are established exhibiting a UCST shape. The Nematic+Isotropic, Isotropic+Isotropic and Isotropic regions have been clearly observed for all the systems. By increasing the Darocur 1173 content, the miscibility between PEA and E7 increases whereas the polymer glass transition temperature decreases due to plasticizing effects. These phenomena result from a lower extent of the degree of polymerization when the photoinitiator concentration increases.

Acknowledgement

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