Thermal Characterization of Polymer-Dispersed Liquid Crystals by Differential Scanning Calorimetry

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The thermal behavior of polymer-dispersed liquid crystals prepared by polymerization-induced phase separation has been characterized using differential scanning calorimetry and polarized light microscopy. The thermally cured system studied, PolyBed 812/4-*n*-pentyl-4′-cyanobiphenyl (5CB), exhibited molecular mixing up to at least 30 wt % 5CB. The liquid-crystal solubility limit, *A*, in the polymer matrix was calculated to be 41.8. Above 60 wt % 5CB the mixtures exhibited macroscopic as well as microscopic phase separation, and this was detected as a splitting of the nematic–isotropic peak in the DSC thermograms. The nematic–isotropic transition temperature and associated enthalpy suggested that the phase-separated liquid crystal contained very small amounts of either prepolymer or partially cured polymer. A UV-cured system was investigated also, namely, Norland Optical Adhesive 65 (NOA65)/5CB. A very similar value of *A*, 42.1, was calculated for this system. For the NOA65/5CB mixtures macroscopic phase separation was not observed. The nematic droplets exhibited clearing temperatures equal to that of pure 5CB within experimental error, implying that essentially pure 5CB separates from the polymer matrix.

Introduction

Polymer-dispersed liquid crystals (PDLC) are a class of composite materials in which droplets having micron dimensions of a low molar mass liquid crystal are dispersed in a polymer matrix.[1] In the absence of an electric field the nematic droplets strongly scatter light, causing the film to appear opaque. On the application of an electric field, however, the directors of each droplet align parallel to the applied field, and if the refractive index of the liquid crystal is matched to that of the polymer, then the film becomes optically transparent.[1] This forms the basis of new types of display and projection devices,[1] which in turn has stimulated considerable interest in PDLCs. There are several methods by which to prepare PDLCs, although the most common is termed polymerization-induced phase separation.[1] In this method, the liquid crystal and a prepolymer are blended to yield a homogeneous mixture. The prepolymer is then either thermally[2] or photolytically cured.[3] As the molecular weight of the polymer increases, the solubility of the liquid crystal decreases and so separates, forming droplets. However, this process does not result in the complete separation of the two components, and inevitably a fraction of liquid crystal remains within the polymer matrix, while prepolymer or partially cured polymer is present to some degree in the liquid-crystal droplets.[3,4] This incomplete phase separation has several important consequences. The liquid crystal in the polymer acts as a plasticizer, reducing the glass transition temperature of the matrix.[3,5] Also, the liquid crystal dissolved in the polymer can cause a significant change in the carefully matched refractive index of the matrix and lead to a reduced on-state clarity for the device.[6,7] The prepolymer and/or partially cured polymer or, in the case of UV-cured systems, the initiator dissolved in the liquid-crystal droplets reduces their clearing temperature, which may have important implications for the operating temperature range for the device as well as reducing the photostability and resistivity of the PDLC.[8] It is also advantageous economically to minimize the amount of liquid crystal used in these devices. Smith and co-workers[9–11] have developed a calorimetric method (see later for details) for determining the solubility limit of the liquid crystal in the polymer matrix and, hence, a means of assessing the fraction of liquid crystal present in the droplets. Prior knowledge of these important material properties and their dependence on structure would allow for the

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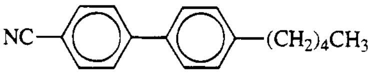
rationale formulation of new and improved mixtures for use in PDLC technologies. Our aim was, therefore, to use this method to quantitatively assess the degree of phase separation in both a UV- and a thermally cured PDLC system. In these studies we employed a single-component liquid crystal, 4-*n*-pentyl-4′-cyanobiphenyl, **1**,



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$$C \xrightarrow{24\ °C} N \xrightarrow{35\ °C} I$$

even though in prototype devices liquid-crystal mixtures are used; this has also been the approach adopted in other studies.[11,12] The reasons for this choice are first, that the components of a mixture have varying degrees of solubility in the polymer matrix,[6] so greatly complicating the interpretation of the data. Second, we expected that the melting endotherm would be sufficiently isolated from the other thermal transitions to extend the method described by Smith and co-workers[9-11] to an analysis of the melting transition. This has the distinct advantage of being a considerably stronger transition than the clearing transition, and hence its measurement is less subject to experimental error. The acronym used to refer to **1** is 5CB.

Experimental Section

A thermally cured system, PolyBed 812 (Polysciences Inc.), and a UV-curable optical adhesive, Norland 65 (NOA65), together with 5CB (Merck Ltd.) were used to prepare the PDLCs. Thus, appropriate amounts of the prepolymer and 5CB were mechanically mixed to give a homogeneous blend. These blends were prepared in incremental steps of either 5 or 10 wt % of 5CB. The mixtures were subsequently cured either in a DSC pan or as a thin film on a microscope slide. The blends containing PolyBed 812 were cured at 60 °C for 24 h, while for those containing NOA65, curing was achieved by exposure to UV radiation using a UVA Light Technology high-intensity lamp (≈500 mW cm^{-2}) for 20 min.

The cured systems were characterized by differential scanning calorimetry using a Polymer Laboratories PL-DSC equipped with an autocool accessory. The sample was heated from −50 to 150 °C, held at 150 °C for 3 min, cooled to −50 °C, held for a further 3 min at that temperature, and finally reheated to 150 °C. All heating and cooling rates were 10 °C min^{-1}. An additional set of experiments were performed using these samples in order to isolate the nematic−isotropic transition from the crystal−nematic transition. Thus the samples were cooled to 0 °C and heated to 60 °C. Again the heating/cooling rates were 10 °C min^{-1}. The glass transition temperatures were taken as the midpoint of the step in the baseline while peak maxima are quoted as the temperatures for first order transitions. The phase behavior of the PDLCs was investigated further by polarized light microscopy using an Olympus BH-2 microscope equipped with a Linkam THMS 600 heating stage and TMS91 control unit.

Results and Discussion

PolyBed 812/5CB Mixtures. The thermal behavior of pure 5CB was in excellent agreement with that reported by Smith et al.,[11] and aside from the melting and clearing transitions, a glass transition was observed at −63 °C. This value is also in agreement with that reported by Zeller[13] and Smith et al.[11] but opposes the view of Kirov et al.[14] that the 4-*n*-alkyl-4-cyanobiphenyls do not form glassy phases. Cured PolyBed 812 exhibited only a glass transition (T_g = 50 °C). Figure 1 shows the dependence of the transition temperatures on the weight percent of 5CB in the mixtures; for the sake of clarity crystal−crystal transitions have not been shown. A dramatic reduction in T_g on increasing the concentration of 5CB is evident, i.e., the addition of 5CB to the polymer has a clear plasticizing effect. This behavior is in marked contrast to that reported for Bostik/5CB mixtures for which the matrix T_g increases with increasing liquid-crystal content.[11] This may reflect the poorer solubility of 5CB in Bostik than in PolyBed 812 (see later). Indeed, complete miscibility between the PolyBed 812 matrix and 5CB was observed for the 10, 20, and 30 wt % 5CB mixtures; the DSC traces for these mixtures contained only a glass transition, while optically these compositions remained isotropic over the whole temperature range investigated. On increasing the weight percent of 5CB, phase separation occurs and crystal and nematic phases are observed. In contrast to the strong composition dependence exhibited by the glass transition temperatures, the melting points and clearing temperatures show only a very small dependence on composition, see Figure 1. In fact, the average change in the melting point of the mixtures on varying their composition is a reduction of just 0.3 °C, although for some mixtures a small increase in the melting point was observed; these changes lie within experimental error. Again this behavior is in contrast with that observed for Bostik/5CB mixtures in which crystallization was strongly suppressed.[11] The physical significance of this is unclear but may reflect differences in droplet size. By comparison to the behavior of the melting points, the clearing temperatures of the PolyBed 812/5CB mixtures were all lower than that of pure 5CB, the average reduction being 1.4 °C. The nematic−isotropic transition was evident as a shoulder to the much stronger melting transition in the DSC traces, preventing the analysis of the peak. To overcome this difficulty, the samples were cooled from above their clearing temperature to 0 °C and then reheated to 60 °C at 10 °C min^{-1}. This temperature profile avoided

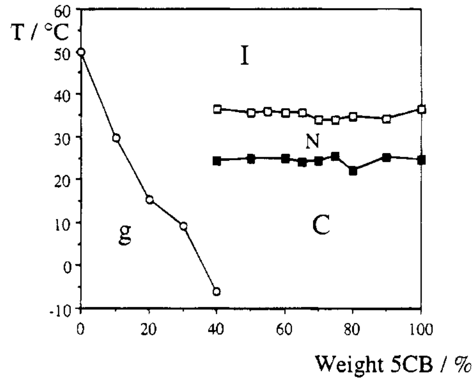

Figure 1. Dependence of the transition temperatures on the weight percent of 5CB for the PolyBed 812/5CB mixtures. Glass transition temperatures are denoted by □, ○ indicates the crystal−nematic transition, and ● the nematic−isotropic transition. Crystal−crystal transitions have not been shown.

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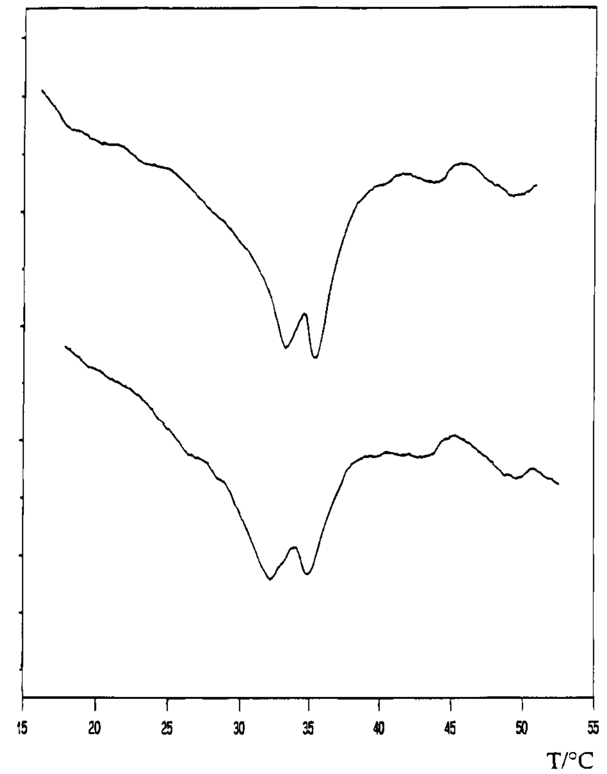

Figure 2. Normalized DSC traces for two independently prepared and cured mixtures containing 65 wt % 5CB in PolyBed 812.

the crystallization of the liquid crystal component and revealed that the peak associated with the nematic-isotropic transition exhibited by mixtures containing 60, 65, and 70 wt % 5CB, was clearly split. To confirm this unexpected result a fresh sample containing 65 wt % 5CB was prepared. Figure 2 shows a comparison of the DSC traces obtained for the two mixtures and reveals the splitting of the nematic–isotropic peak to be reproducible; the small difference between the nematic–isotropic transition temperature for these mixtures reflects a slight difference in their compositions. Closer inspection of the thermograms for all the mixtures revealed that those containing less than 60 wt % 5CB exhibit the higher temperature peak observed for the 60, 65, and 70% 5CB mixtures, while for the remaining mixtures the lower temperature peak dominates; in constructing Figure 1 the higher T_{NI} has been used. Optical microscopy showed that macroscopic, as well as microscopic, phase separation occurred in the mixtures containing ≥60 wt % 5CB. This separation resulted in the formation of macroscopic liquid-crystal drops on the surface of the cured polymer. Thus the higher temperature transition in the thermograms of the 60–70 wt % 5CB mixtures corresponds to the clearing temperature of the microscopic droplets, while the lower temperature transition is the nematic–isotropic transition of the macroscopic drops. For the mixtures containing more than 70 wt % 5CB, the peak associated with the clearing transition of the macroscopic drops obscures that of the microscopic droplets. The higher clearing temperature of the microscopic droplets implies that the level of contamination by the prepolymer or partially cured polymer in the droplets is lower than that in the macroscopic drops. Indeed, the average reduction in T_{NI} for the droplets was just 0.5 °C. For the macroscopic drops the maximum reduction was 2.5 °C. The larger reduction in T_{NI} for the macroscopic drops is evident as a shallow dip in the clearing temperature curve between 55 and 100 wt % 5CB; see Figure 1. It should be stressed, however, that both these reductions are very small and for the microscopic droplets within experimental error. This implies that the prepolymer or partially cured polymer was present in very small quantities in the phase-separated liquid crystal.

Smith and co-workers[9-11] have shown that the liquid-crystal solubility limit, A, in the polymer matrix may be related to the ratio of the nematic isotropic enthalpy of the mixture, $\Delta H_{NI}(X)$, to that of the pure liquid crystal, $\Delta H_{NI}(LC)$, using

$$\frac{\Delta H_{NI}(X)}{\Delta H_{NI}(LC)} = \frac{X - A}{100 - A} \tag{1}$$

where X is the weight percent liquid crystal in the sample and $X \geq A$. The fraction α of liquid crystal contained within the droplets is given by

$$\alpha = \frac{100}{X}\frac{\Delta H_{NI}(X)}{\Delta H_{NI}(LC)} \tag{2}$$

Combining eqs 1 and 2 gives

$$\alpha = \frac{100}{X}\frac{X - A}{100 - A} \tag{3}$$

Physically if $X < A$, then α must be zero. Two assumptions are made in the derivation of these equations: (i) the liquid crystal dissolved in the polymer matrix does not contribute to the nematic–isotropic enthalpy and the phase-separated liquid crystal is contained wholly within droplets; (ii) the amount of liquid crystal a given mass of the polymer matrix can dissolve is constant for $X \geq A$.[9-11] A third assumption is also inherent in this approach, namely, that the presence of either prepolymer or partially cured polymer in the liquid-crystal droplets does not affect ΔH_{NI}. For the PolyBed/5CB system the clearing temperatures show only a weak dependence on composition, implying that the phase-separated liquid crystal is essentially pure and hence ΔH_{NI} may be treated as a constant. However, for systems in which the clearing temperature shows a strong dependence on composition and in particular, ones in which liquid-crystal mixtures are used for which preferential solvation of certain components may occur, this assumption should be examined more closely.[12]

ΔH_{NI} exhibits a linear dependence on the weight percent of 5CB in the PolyBed 812-based mixtures (see Figure 3), validating the mathematical approach of Smith et al.[9-11] Using these data, α was calculated in two ways: (i) A was determined using a linear fit to the data shown in Figure 3 and subsequently used to calculate α using eq 3 or (ii) α was calculated for each composition using eq 2. The value of A determined from the data shown in Figure 3 was 41.8. To our knowledge this is the highest value of A measured for a thermally cured system;[12] typically values range from ≈10 to 20.[10,11] Figure 4 shows the dependence of α on composition, and a comparable degree of scatter was observed between analogous sets of data by Smith et al.[11] These differences between the values of α may be accounted for in terms of the relatively large experimental error

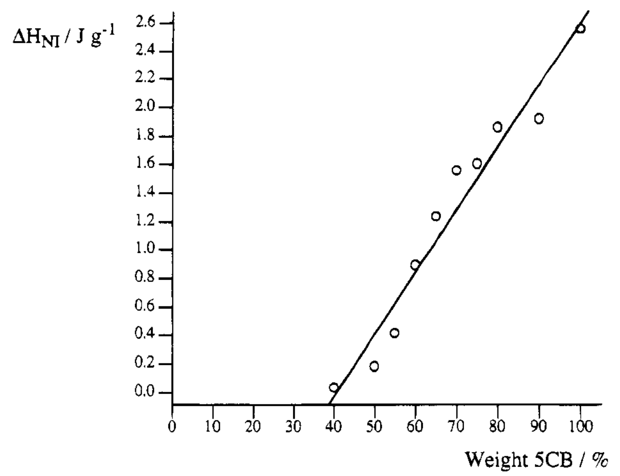

Figure 3. Dependence of the nematic–isotropic enthalpy on the weight percent 5CB in the PolyBed 812-based mixtures.

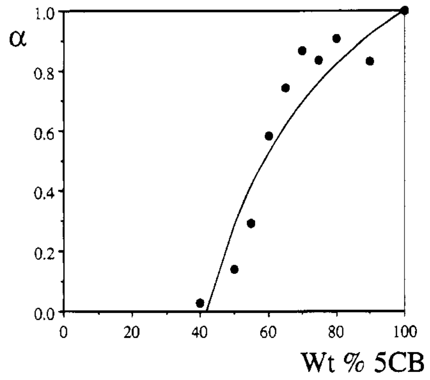

Figure 4. Dependence of the fraction of liquid crystal, α, separated from the polymer matrix in the PolyBed 812-based mixtures: the solid line has been calculated using a value of *A* calculated using Figure 3, while the circles represent the values of α calculated using individual values of the enthalpy.

associated in determining ΔH_{NI} for the dilute liquid-crystal mixtures. The maximum value of α, i.e., the fraction of 5CB contained within the microscopic droplets, for the PolyBed/5CB system is 0.41 (calculated using *A*) and is observed for the 55 wt % 5CB mixture. At higher concentrations macroscopic phase separation occurs, and so α is no longer the fraction of liquid crystal in the microscopic droplets but instead represents the total fraction of liquid crystal in the microscopic droplets and macroscopic drops. This is a particularly low value of α maximum, and more typical values lie in the range 0.7–0.9.[5,9,10]

It had been expected that the crystal–nematic enthalpy, ΔH_{CN}, could be used to determine more reliable estimates of *A* and α. This expectation was not realized, however, because even though all the mixtures that exhibited phase separation also crystallized, the melting endotherm was not sufficiently isolated from other endotherms associated with crystal–crystal transitions or exotherms associated with cold crystallization to allow ΔH_{CN} to be determined accurately.

NOA65/5CB Mixtures. We now turn our attention to the thermal behavior of 5CB dispersed in NOA65. The fully cured optical adhesive exhibited a glass transition temperature at 12 °C, in good agreement with that reported by Smith.[15] This was reduced to 4 °C by the addition of 10 wt % 5CB to the prepolymer, to −4 °C for 20 wt % 5CB, and to −13 °C for 30 wt % 5CB. No other phase transitions were observed for these mixtures, and when viewed through the polarizing microscope, they appeared optically isotropic. As with the PolyBed 812 mixtures, the 40 wt % 5CB composition was the first to exhibit phase separation and all the mixtures containing ≥ 40 wt % 5CB exhibit complex crystallization and melting behavior; this again prevented the quantification of phase separation using ΔH_{CN}. The clearing transition was, to varying degrees, masked by the much larger melting transition. Thus to overcome this difficulty, the temperature profile described earlier was used to isolate the nematic–isotropic transition for each sample. Macroscopic phase separation was not observed on curing the NOA65-based mixtures.

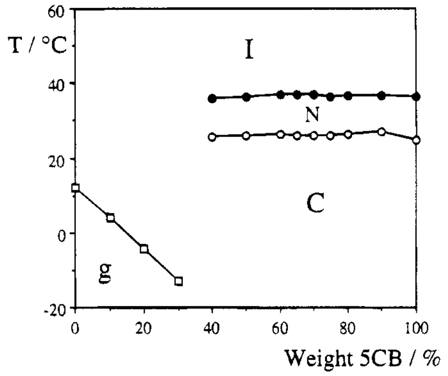

Figure 5. Dependence of the transition temperatures on the weight percent of 5CB for the NOA65/5CB mixtures. Glass transition temperatures are denoted by □ , ○ indicates the crystal-nematic transition, and ● the nematic–isotropic transition. Crystal–crystal transitions have not been shown.

Figure 5 shows the dependence of the glass transition temperature, melting point, and nematic–isotropic transition temperature on the composition of the mixture for the NOA65-based systems. As with the PolyBed 812-based mixtures, the plasticizing effect of 5CB was evident as a dramatic reduction in the glass transition temperature of the polymer matrix as the concentration of 5CB was increased. This reduction of T_g may, in part, also be accounted for by a reduction in the degree of cure.[15] All the melting points of these mixtures were slightly higher than that of pure 5CB; the average increase was 1.5 °C. By contrast, the nematic–isotropic transition temperatures exhibited by the NOA65 mixtures were scattered about that of 5CB, with the average difference being an increase of just 0.1 °C. These changes were well within experimental error and suggested that the phase-separated liquid crystal was essentially pure and not contaminated by either prepolymer or partially cured polymer.

Figure 6 shows the dependence of ΔH_{NI} on composition for the NOA65/5CB mixtures, and a linear relationship is evident. The value of *A* calculated using these data is 42.1 and this is comparable for that determined for PDLCs comprising of NOA65 and liquid-crystal mixtures.[12] The dependence of α, calculated as described earlier, on composition is shown in Figure 7, and there is reasonable agreement between the values of α obtained using *A* together with eq 3 and those obtained directly using eq 2. The high value of *A* results in low

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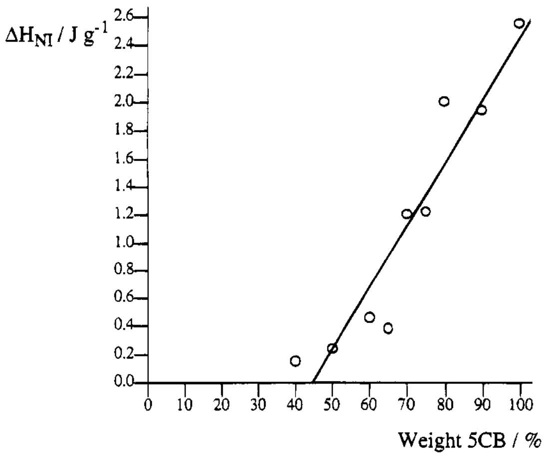

Figure 6. Dependence of the nematic–isotropic enthalpy on the weight percent 5CB in the NOA65-based mixtures.

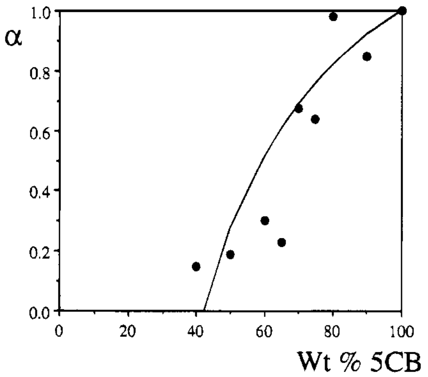

Figure 7. Dependence of the fraction of liquid crystal, α, separated from the polymer matrix in the NOA65-based mixtures: the solid line has been calculated using a value of A calculated using Figure 3, while the circles represent the values of α calculated using individual values of the enthalpy.

values of α; for example, for the 50 wt % 5CB mixture, α is 0.27 (calculated using A) and this is comparable to data reported by Smith.[15] Quite different behavior was reported by Nolan et al.[6] for a cured mixture containing NOA65 and E7, a liquid-crystal mixture containing 5CB, in a 2:3 mass ratio. Analysis of the phase-separated material revealed that 5CB dissolved preferentially in the matrix while some 10% impurity was found in the droplets, depressing the clearing temperature by 10 °C. The authors estimated that 12 wt % liquid crystal remained in the cured polymer. For a second mixture, BLO38, 18 wt % of the liquid crystal remained molecularly mixed. For both these mixtures, the level of molecular mixing is considerably lower than that reported here, while the level of impurities in the liquid crystal phase is higher. Similar behavior was reported by Vaz et al.[3] for a UV-curable/7CB system, i.e., for a 50 vol % 7CB composition some 15 vol % remains dissolved in the cured matrix while the T_{NI} is reduced by 9 °C.

It is interesting to note that the phase behavior of the two systems described here is remarkably similar to that reported by Ahn et al.[16] for mixtures of 7CB and poly(methyl methacrylate) and also for 7CB and polystyrene. For the former system the two components exhibited molecular mixing up to 45 wt % 7CB, while for the latter system phase separation occurred for mixtures containing more than 30 wt % 7CB. For both systems the melting transitions and clearing temperatures were essentially independent of composition. These similarities strongly suggest that the factors responsible for phase separation in blends of low molar mass liquid crystals and conventional thermoplastics are similar to those for polymerization-induced phase-separated liquid crystals. The molecular significance of this is unclear, and speculation must await the results for a wider range of PDLCs currently in progress.

Conclusions

The main objective of this study was to quantify the degree of phase separation in two quite different PDLC systems using the melting and clearing enthalpies associated with the liquid-crystal component. Unfortunately, the melting enthalpy was not suited to this task because complex sequences of solid transitions prevented its accurate determination. Using the clearing enthalpy, particularly high values of the liquid-crystal solubility limit, A, were determined in a thermally cured and a UV-cured matrix, i.e., 41.8 and 42.1, respectively. Thus a considerable fraction of the liquid crystal remains molecularly mixed with the cured polymer. By contrast, the phase-separated liquid-crystal droplets consisted of essentially pure 5CB. This behavior is consistent with a thermodynamic model for phases separation proposed by Smith.[17] There are surprisingly few studies in the literature concerning the degree of phase separation in PDLCs, especially considering the importance of this question to the application of these materials in electrooptic devices. The degree of phase separation reported here for both systems differs from that described for other systems and underlines the need now for further investigations in order to understand the phase behavior of PDLCs. Such studies will underpin the rational formulation of new systems for application in electrooptic devices.

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