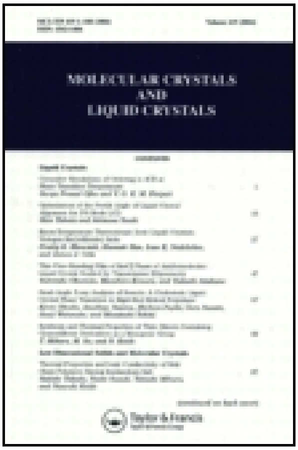

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A Calorimetric Study of Liquid Crystal/Polymer Mixtures: Cure Temperature Effects and Unusual Phase Behavior

George W. Smith [a]

[a] Physics Department, General Motors R&D Center, Warren, Michigan, 48090-9055

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A Calorimetric Study of Liquid Crystal/Polymer Mixtures: Cure Temperature Effects and Unusual Phase Behavior

GEORGE W. SMITH

Physics Department, General Motors R&D Center, Warren, Michigan 48090-9055

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Cure kinetics and energetics and phase behavior of a liquid crystal (LC)/matrix mixture have been investigated. This research complements a previous study of phase separation in mixtures of low molecular weight liquid crystals with an organic matrix. In the present case we used a LC with a molecular weight about twice that of the previous ones. For some samples we found evidence for phase separation and an anomalous phase transition (possibly a smectic induced by confinement of the LC in microvolumes). The effects of cure temperature, T_{cure}, on the cure kinetics and energetics were similar to those found for previously studied UV-cured systems. Plots of the heats of cure for the pure matrix and LC/matrix mixtures go through maxima at temperatures where the extent of matrix cure is greatest. The fact that the nematic-isotropic (NI) transition enthalpy is maximum in the same temperature range confirms previous conclusions that phase separation is greatest when the matrix is most fully cured. The time constants for the cure process exhibit minima at temperatures slightly above ambient (as observed previously for other systems). Phase behavior of mixtures was studied as a function of degree of cure, D_{cure}. Differential scanning calorimeter scans of two uncured or partially cured samples exhibited an abrupt decrease near 390 K. This transition may be a decrease in specific heat due to mixing. However, the step was an order of magnitude smaller than that for mixtures based on lighter LCs. In addition, its temperature remained fixed, rather than increasing with degree of cure, as was the case for previous systems. Although in one system this step co-existed with a NI transition for several values of D_{cure}, the possibility cannot be ruled out that the transition is in fact due to a NI phase change (perhaps in LC which is confined to micro-volumes other than droplets).

Keywords: phase separation, phase behavior, mixing, binary systems, liquid crystals, polymers, polymer-dispersed liquid crystals

INTRODUCTION

Understanding of phase separation in liquid crystal/matrix mixtures is becoming increasingly important, partially as a result of recent efforts to improve materials and fabrication methods for polymer-dispersed liquid crystal (PDLC) films.[1–4] These films, dispersions of micron-sized droplets of liquid crystal in a polymer matrix, are being evaluated for a number of applications, including displays, and privacy windows. PDLCs are formed by a two-step process: 1) a liquid crystal (LC) and a polymer precursor are initially mixed together to form a uniform solution; 2) the polymer matrix is hardened, during which process LC phase-separates from the polymer in the form of microdroplets.[1–4] The hardening can be carried out by several techniques: polymerization of the polymer precursor; cooling of a thermoplastic polymer/LC mixture; or evaporation of a common solvent in which both LC and thermoplastic are dissolved. Our research efforts have focussed primarily on polymerization by ultraviolet irradiation; this UV-curing technique produces a highly cross-linked matrix.[3,5,6]

Two aspects of phase separation are of particular importance to an understanding of the formation of a UV-cured PDLC: the solubility behavior of the uncured LC/precursor mixture and the "demixing" of the liquid crystal from the matrix which occurs as the curing reactions proceed. A calorimetric study of both aspects has been recently reported.[7] Two mixtures were investigated: 1) a multi-component liquid crystal added to a UV-curable polymer precursor and 2) a single component LC with the same polymer precursor. For system 1) both the solubility behavior of the uncured mixture and phase separation (demixing) during the cure process were examined. In order to eliminate the possibility of preferential dissolution of LC components in the matrix, the study of cure-induced demixing was repeated using system 2). The effect of degree of cure (D_{cure}) on phase separation behavior was similar for both systems. An important aspect of this work was the discovery of a step-wise decrease in the specific heat of uncured or partially cured systems which occurred upon heating through T_{mix}, the mixing temperature of the components. It was shown in Reference 7 that the decrease was attributable to the negative excess specific heat of mixing. The negative sign was expected for a LC/matrix mixture, which is characterized by a phase diagram with an upper critical solution temperature (UCST).

In the present paper we extend the previous work by examining the effect of degree of cure on phase behavior of a mixture based on a heavier liquid crystal molecule (molecular weight about twice that of the previous ones). Evidence for a mixing transition in some mixtures will be presented, together with an unexpected result: the discovery of an anomalous phase transition (possibly a smectic induced by confinement of the LC in micro-volumes) which appeared under certain circumstances during the cure process. In addition, we also studied the effect of cure temperature on the formation and phase behavior of this system.

In the next section we shall briefly review experimental aspects of the work.

EXPERIMENTAL ASPECTS

Materials and Sample Preparation

Liquid crystal. The LC employed in this study was a single component nematogen, *p*-pentylphenyl-2-chloro-4-(*p*-pentylbenzoyloxy)-benzoate (PCPB).[8] PCPB has a high molecular weight (~493) and melts at ~312 K to form a nematic phase which persists up to ~397 K. Samples of PCPB can form a glass upon rapid cooling from the nematic.

Matrix. The matrix material was Norland ultraviolet-curable optical adhesive 65 (abbreviated NOA65).[9] This thiol-ene mixture of monomers, oligomers, and a photoinitiator has been used in several of our previous studies of PDLC formation.[2,5–7,10]

Mixture formation. Mixtures of liquid crystal and uncured NOA65 were prepared using previously described techniques.[6,7] Small quantities (typically enough to produce a total volume of 100 μl) of NOA65 and PCPB were measured into a watch glass using precision micropipettes. The components were then vigorously stirred until a uniform mixture was obtained (generally 30 to 60 s was sufficient time). Because the LC is a solid at room temperature, it was necessary to carry out the mixing process at a temperature high enough to keep the mixture fluid. About 5 μl of sample were then transferred to a custom-made gold-plated copper DSC pan and covered with an ultrathin (0.1–0.2 mm) quartz disc.[6] The disc rested on a shoulder around the pan bottom to maintain uniform sample thickness (on the order of 100 to 200 μm). Thickness uniformity was necessary to produce uniform cure rates throughout the sample upon exposure to UV radiation. The pan's gold coating insured that the sample would not react with the container material.

Measurement Techniques

Calorimetry. The differential scanning calorimeter used in these studies was a Perkin-Elmer DSC2 instrument.[11] The calorimetric methods have been described in detail in previous prublications[6,7]; only a few aspects will be discussed here.

The DSC system was modified to allow introduction of ultraviolet radiation into the sample chamber so that kinetics and energetics of a UV-induced cure process could be determined.[6,7] The output of the calorimeter, when operated isothermally, is a plot of the time dependence of dQ/dt, the rate of heat evolution during the cure process.[6,7] A typical heat release curve for UV cure of a PDLC is shown in Figure 1. The baseline is flat during the initial period when no UV irradiation occurs. With the initiation of UV irradiation an abrupt increase of exothermic power occurs, followed by an almost exponential decay. Integration of dQ/dt yields ΔQ_{cure}, the total heat released during the cure process,[6,7] which is important since it is a direct measure of degree of cure.[12] Exponential fits to the decay portion of the dQ/dt curve make it possible to determine τ_{cure}, the time constant for the cure process.[6] The effect of cure temperature on ΔQ_{cure} and τ_{cure} has been reported for a related PDLC system[6]; the present paper extends that study to PCPB/NOA65.

The effects of degree of cure were also investigated using the incremental cure

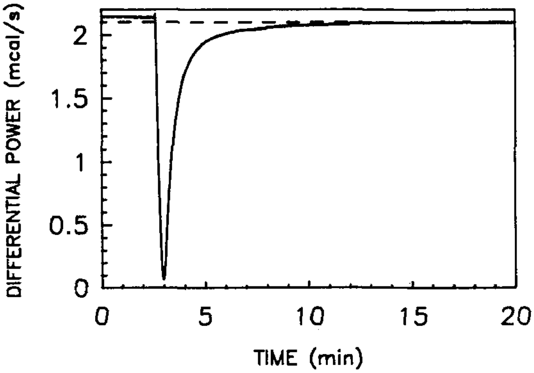

FIGURE 1 Plot of dQ/dt versus time for UV cure of a liquid crystal/NOA65 mixture. Such curves make it possible to determine ΔQ_{cure}, the total heat released during cure, and τ_{cure}, the time constant for the cure process. By convention, exotherms are taken as downward-going.

procedure of Reference 7. In this technique a sample was exposed to UV for times as short as 20–30 s to achieve a partial cure. A sequence of these cure steps was repeated until final cure was as complete as possible. Phase behavior of a sample in states of increasing degree of cure was determined by scanning calorimetry (see next paragraph) prior to the initial UV exposure and following each subsequent incremental cure step. Measurement of the heat release, ΔQ, during each cure step made it possible to calculate the cumulative degree of cure (in percent) by summing the ΔQ values:

$$D_{\text{cure}} = 100(\Sigma\, \Delta Q)/\Delta Q_{\text{cure}}, \tag{1}$$

where the sum is over all incremental cure steps prior to a given DSC phase behavior determination, and ΔQ_{cure} is the sum of the ΔQ values for all the cure steps.

In the scanning mode, the calorimeter output is a plot of dQ/dt versus temperature. From such a plot we obtain temperatures and enthalpies of first order phase transitions as well as specific heat changes associated with glass transitions (or, in some cases, mixing transitions).[6,7,13] Figure 2 shows a DSC temperature scan for pure PCPB. The four thermal events are: glass transition; crystallization exotherm; crystal-nematic (KN) endotherm; and nematic-isotropic (NI) transition peak. DSC methods for obtaining values of the specific heat increment, ΔC_g, at the glass transition and magnitudes of the NI transition enthalpy, ΔH_{NI}, have been previously described.[6,7,13]

In the Results section we shall examine thermal spectra of cured PDLCs and also of PCPB/NOA65 mixtures in various states of cure.

Scanning electron microscopy. Because PCPB/NOA65 mixtures at times exhibited unusual phase behavior (see below), we examined morphologies of several cured samples of this system using scanning electron microscopy. The essential steps of our SEM procedure[14] were: (1) the quartz disc was removed from the custom DSC pan and a cross-sectional slice taken from the cured sample; (2) the slice was mounted vertically on an aluminum SEM stud so that the cross-sectional face would be normal to the electron beam; (3) the stud was placed in a sputtering unit which was then evacuated to approximately 20 mtorr of Hg overnight to remove liquid; (4) the sample was coated with thin Au-Pd coating to provide the conductive surface required for the SEM; (5) the stud/sample combination was then placed in

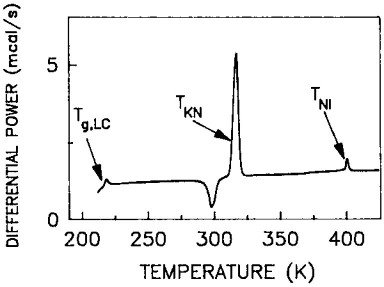

FIGURE 2 DSC thermal spectrum for the liquid crystal PCPB. The specific transitions are discussed in the text. Endotherms are upward-going.

the SEM and examined at magnifications up to 8000×, using an acceleration potential of 15 kV.

EXPERIMENTAL RESULTS AND ANALYSIS

Cure Temperature Effects

The influence of temperature on the cure process and on phase behavior of PDLCs has been reported previously for both thermally-cured[14,15] and UV-cured[6] systems. We shall present results of a similar study of PCPB/NOA65 mixtures with LC concentrations of 0, 33, and 50 volume percent.

The dependences of ΔQ_{cure} on cure temperature, T_{cure}, for the three systems are plotted in Figure 3. The curves exhibit maxima at temperatures where the degree of matrix cure is greatest; this result is consistent with previous work[6] which showed that D_{cure} of a UV-cured system is low for *both* low and high cure temperatures. Both the magnitude of heat of cure and the temperature of its maximum decrease with increasing LC concentration, in agreement with previous studies.[6,15]

Cure time constants for a UV intensity of 1.5 mW/cm^2 are plotted versus T_{cure} in Figure 4. [The τ_{cure} values for the 50% sample were measured using a UV intensity of 2.8 mW/cm^2 and were therefore corrected by a factor $(2.8/1.5)^{0.5}$.] The curves exhibit minima like those found for other UV-cured systems.[6] The increase in τ_{cure} with addition of LC has also been previously observed for thermally cured systems.[15]

DSC thermal scans for cured 33% and 50% mixtures are shown in Figures 5 and 6. In both figures the liquid crystal KN transition peaks for $T_{cure} \geq 380$ K are considerably more prominent than for lower cure temperatures. (In addition, the 50% samples exhibit an apparent crystal-crystal (KK) transition near 300 K.) A strong KN peak seems to indicate that some LC is phase-separated from the matrix at the melting temperature. However, the NI peak of the 33% samples cured at or above 380 K is small, suggesting that most of the liquid crystal subsequently dissolves in the matrix during warmup from T_{KN} to T_{NI}. On the other hand, the

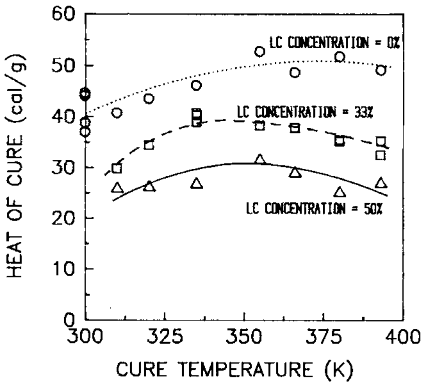

FIGURE 3 Dependence of ΔQ_{cure} on cure temperature for PCPB/NOA65 mixtures.

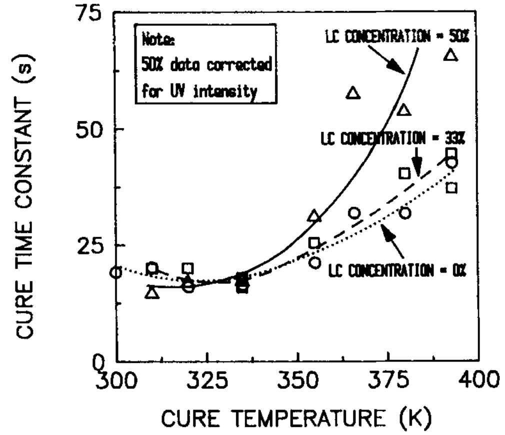

FIGURE 4 Dependence of τ_{cure} on cure temperature for PCPB/NOA65 mixtures. The values are for a UV intensity of 1.5 mW/cm^2 (see text).

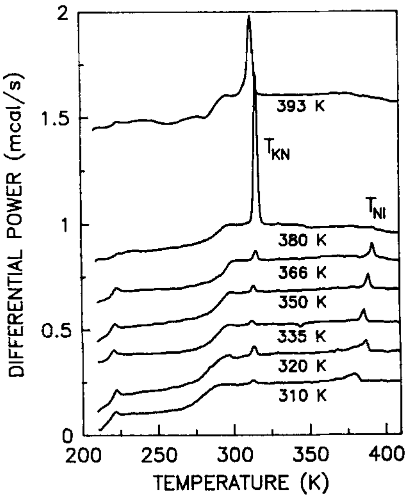

FIGURE 5 DSC thermal spectra for 33% PCPB/NOA65 mixtures cured at temperatures from 310 K to 393 K.

NI peak of the 50% samples is only slightly reduced by high temperature cure; this result may be due to a greater extent of phase separation for higher LC content.[13,15] For $T_{\text{cure}} \leq 320$ K, the NI peaks of both sets of samples are somewhat broadened, perhaps due to greater impurity levels or to differences in LC behavior near droplet interfaces. In Figure 7 KN transition enthalpies are plotted versus T_{cure}. ΔH_{KN} is greatest for samples cured at high temperatures; as discussed below, uncured mixtures also have a large KN enthalpy (see Figures 11, 13, 18, and 19). Thus, surprisingly, the enhanced value of ΔH_{KN} for high T_{cure} may be associated with a lower degree of matrix cure.

Curves of ΔH_{NI} (Figure 8) exhibit maxima near the cure temperature for which ΔQ_{cure} (and hence D_{cure}) are greatest (see Figure 3). Such maxima have been

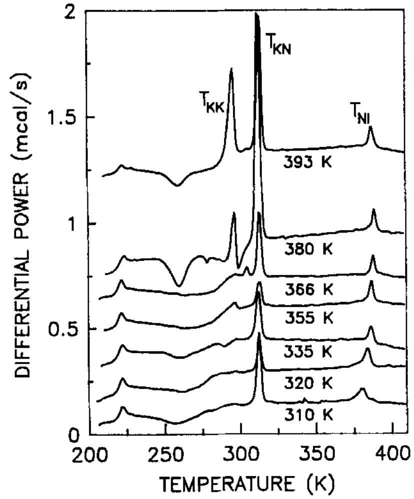

FIGURE 6 DSC thermal spectra for 50% PCPB/NOA65 mixtures cured at temperatures from 310 K to 393 K.

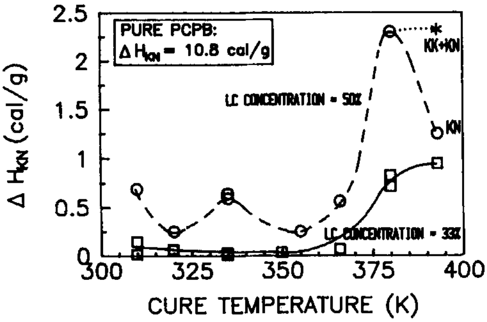

FIGURE 7 Crystal-nematic transition enthalpy for 33% and 50% PCPB/NOA65 mixtures cured at various temperatures.

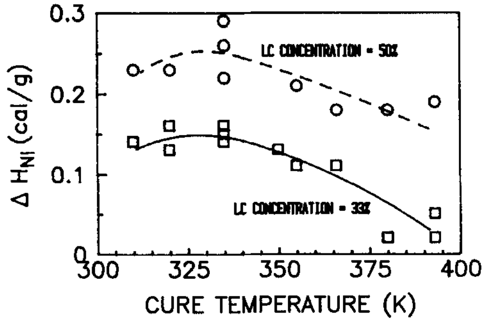

FIGURE 8 Nematic-isotropic transition enthalpy for 33% and 50% PCPB/NOA65 mixtures cured at various temperatures.

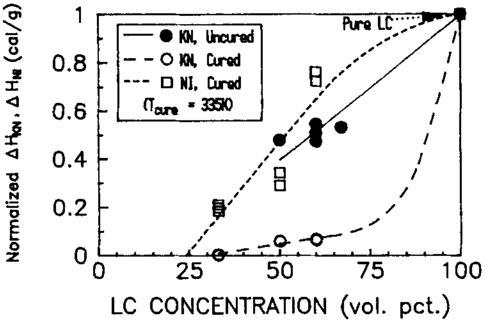

FIGURE 9 Normalized values of ΔH_{KN} and ΔH_{NI} for 11650/NOA65 systems. KN ratios for both cured and uncured systems are shown; NI transitions were observable only for cured samples.

observed for other UV-cured systems.[6] It has been shown[6,13–15] that ΔH_{NI} is proportional to α, the fraction of LC which is phase separated from the matrix at T_{NI}. Thus, Figure 8 indicates that phase separation is greatest when degree of cure is maximized. This result is seemingly contradicted by the ΔH_{KN} results of the previous paragraph: If we assume that ΔH_{KN} is also a measure of α, it appears that phase separation at T_{KN} is enhanced at high T_{cure} when the degree of cure is low. The explanation for this apparent contradiction may lie in the microdroplet morphology of a fully cured sample. Comparison of the KN and NI enthalpies for uncured and cured samples is helpful in elucidating this point. In Figure 9 are plotted the dependences on LC concentration of normalized values of ΔH_{KN} and ΔH_{NI}, defined as their ratio to the corresponding quantities for the pure liquid crystal. (No ΔH_{NI} values are given for uncured samples since they do not exhibit a nematic-isotropic transition.) A single cure temperature (335 K) was used. For all LC concentrations investigated, ΔH_{KN} for the cured samples is appreciably smaller than that for uncured ones. We interpret this result to mean that, in a cured sample, the LC is likely to form a glass; i.e., crystallization is suppressed by confinement in microdroplets. (Scanning electron microscopy verified the formation of microdroplets for both 33% and 50% samples, with droplet diameters on the order of 0.5 μm and 4 μm respectively. Droplet size decreased for the highest cure temperatures.)

The view that crystallization is suppressed in the cured samples is supported by the nematic-isotropic enthalpy results in Figure 9. The high values of the normalized ΔH_{NI} ratio for the cured sample clearly indicate that an appreciable fraction of the LC is phase-separated from the matrix. Since LC solubility should decrease at low temperatures, low ΔH_{KN} ratios for the cured system are most likely due to suppression of crystallization. The LC solubility limit[13] in the cured matrix at T_{NI} is ~25%, the concentration for which the extrapolated value of the NI ratio is zero (Figure 9). The absence of a NI peak for uncured samples supports the view that LC and matrix usually form a single phase somewhere between T_{KN} and T_{NI}.

Curves of the NI transition temperature versus T_{cure} exhibit a broad maximum (Figure 10) with very little effect due to a change in the LC concentration. A similar maximum in T_{NI} has been observed for at least one other system.[6]

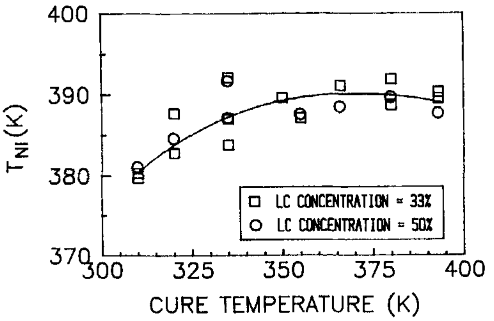

FIGURE 10 Nematic-isotropic transition temperatures for 33% and 50% PCPB/NOA65 mixtures cured at various temperatures.

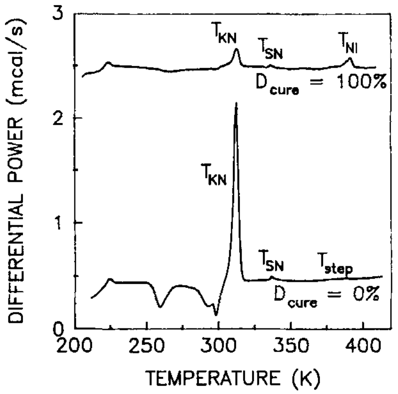

FIGURE 11 DSC thermal spectra for 50% PCPB/NOA65 mixture in uncured (0%) and fully cured (100%) states. The cure temperature was 335 K. The melting peak is identified as a crystal-nematic (KN) transition since it was felt that only part of the PCPB melted to form an "induced smectic," with the remainder melting to a nematic phase.

Effect of Degree of Cure

Let us now examine the effect of degree of cure upon phase behavior of PCPB/NOA65 samples. Mixing and cure were generally carried out at temperatures above the PCPB melting point; however, in some cases T_{cure} may have been low enough to allow partial phase-separation of the LC and matrix prior to cure. Under certain circumstances an anomalous phase transition (possibly a smectic induced by confinement of the LC in micro-volumes) was observed. However, this anomaly was not consistently seen; rather, it depended on a number of factors: LC concentration and degree of cure, and perhaps mixing and curing temperatures. In the next sections we shall discuss phase behavior for PCPB/NOA65 mixtures having three different LC concentrations: 50, 60, and 67 volume percent.

50% PCPB. Figure 11 shows thermal spectra for this sample in two cure states: D_{cure} = 0% and 100%. The low temperature glass transition and the LC melting peak are visible in both scans, as are transitions at ~337 K and slightly above 390 K. The melting peak for the cured sample is much smaller than that for the uncured one. As discussed above, confinement of LC to small volumes during matrix cure apparently resulted in glass formation, with concomitant diminishment of the melting peak. Small transitions observable at higher temperatures are discussed in the next paragraph.

The high temperature transitions are seen more clearly in the expanded scale of Figure 12. We suggest that the 337 K peak for both the uncured and cured samples is due to a smectic-nematic transition which (as seen in Figure 2) does not exist in the pure LC. (Further evidence regarding this "SN" transition will be presented below.) The peak at 392 K for D_{cure} = 100% is clearly due to the nematic-isotropic phase change. Both the "SN" and NI peaks for the cured sample were repeatable and observed on both heating and cooling. It could be argued that the small negative step at 390 K for D_{cure} = 0% is also a NI transition, one associated with LC microcrystals co-existing with LC microdroplets (see discussion of SEM results, below). (The fact that the temperature of the step is close to T_{NI} for the LC does not necessarily mean that it is actually a NI transition. We recall that the increase in solubility above the T_{NI}[16] can lead to phase separation and coincidence of mixing and NI transitions (see Figures 15 and 19 of Reference 7)). Another possibility is that the step is due to mixing which must occur at a temperature above the "SN" peak (since the existence of both KN and "SN" peaks indicates that LC is phase-separated from the NOA65 at lower temperatures). In this scenario the NI peak would be impurity-broadened and perhaps undetectable. The step-like shape of the peak at 390 K seems to be more consistent with a specific heat change due to mixing than with a weak NI transition which should be broad and bell-shaped. In the next section, we will see that the co-existence of both a NI peak and a step transition in a partially cured 60% mixture can also be interpreted in terms of either of these two points of view.

60% PCPB. A sequence of incremental partial cures was carried out for this sample. DSC thermal spectra for five different degrees of cure are shown in Figure 13. The low temperature glass transition appears at ~220 K and the LC melting peak at ~313 K. As for the 50% sample, the melting peak is tall and sharp for

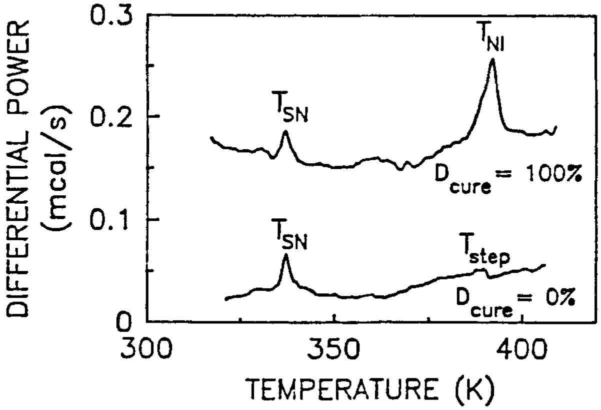

FIGURE 12 DSC thermal spectra of Figure 11 plotted on an expanded scale. The transitions at ~337 K are felt to be due to an "induced smectic" phase (see text).

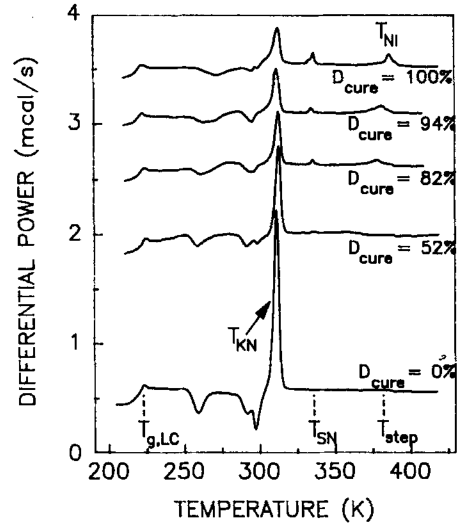

FIGURE 13 DSC thermal spectra of 60% PCPB/NOA65 mixture with five degrees of cure (0% to 100%). Cure temperature was 335 K. See caption of Figure 11 regarding the KN transition.

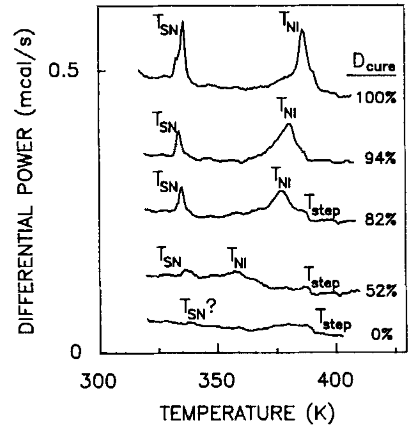

FIGURE 14 DSC thermal spectra of Figure 13 plotted on an expanded scale. The transitions at ~337 K are felt to be due to an "induced smectic" phase (see text).

D_{cure} = 0%, becoming progressively weaker and broader with increasing degree of cure.

Several small transitions at higher temperatures are more clear in Figure 14, where the scale is expanded. For the uncured sample indications of the "SN" peak (at ~339 K) and step (at $T_{step} \simeq 390$ K) are slight, but both were repeatable on a subsequent DSC scan. For D_{cure} = 52% the "SN" peak (at ~335 K) and also a broad NI peak (near 357 K) are evident. The 40 K temperature downshift of T_{NI} from the value for pure PCPB (~397 K) is undoubtedly due to a large amount of matrix material dissolved in the LC. In addition to the two peaks, the step transition is again seen at ~390 K. The "SN", NI, and step transitions were all reproducible.

For $D_{cure} > 52\%$, the temperature of the "SN" peak decreases slightly (to ~335 K at $D_{cure} = 100\%$) while the NI peak narrows and shifts to higher temperatures. The step is clearly visible for $D_{cure} = 82\%$ but appears only as a shoulder on the NI peak for $D_{cure} = 94\%$ and 100%.

The dependences of the various transition temperatures on degree of cure are plotted in Figure 15. The dependence of T_{NI} upon degree of cure for this sample is, to some extent, similar to that for a previously studied E7/NOA65 mixture (see Figure 15 of Reference 7). In both cases the NI peak was observed for values of D_{cure} well below 100% (52% for the PCPB/NOA65 sample, 76% for the E7/NOA65 system).

In Figure 16 ΔC_{step}, the specific heat decrease associated with the step transition, is plotted versus D_{cure}. ΔC_{step} for this mixture is almost an order of magnitude smaller than ΔC_{mix} for the E7/NOA65 and 5CB/NOA65 systems of Reference 7, but is comparable to calculated and experimental values of the excess specific heat of mixing for a polymer blend.[17] If the step transition is, in fact, due to mixing, its small value could be due to the large molecular weight of PCPB. It should be borne in mind, however, that the step could also be a weak nematic-isotropic transition for LC in the microcrystals to be discussed below (section on SEM). If the step is a weak NI transition, the associated enthalpy is ≤ 0.02 cal/g.

The dependences of the transition enthalpies for the "SN" and NI peaks of Figure 14 are plotted versus D_{cure} in Figure 17. Both ΔH_{SN} and ΔH_{NI} increase with

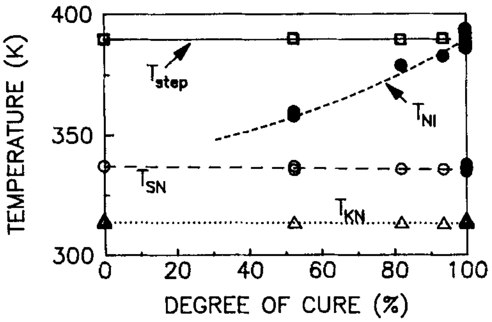

FIGURE 15 Dependence of transition temperatures on degree of cure for a 60% PCPB/NOA65 mixture (T_{cure} = 335 K).

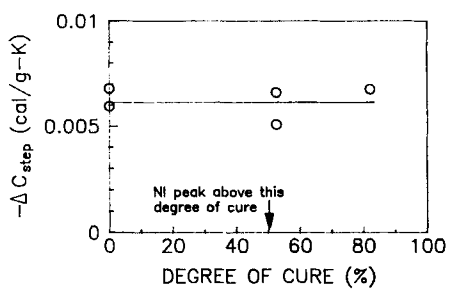

FIGURE 16 Dependence of magnitude of (negative) ΔC_{step} on degree of cure for a 60% PCPB/NOA65 mixture (T_{cure} = 335 K).

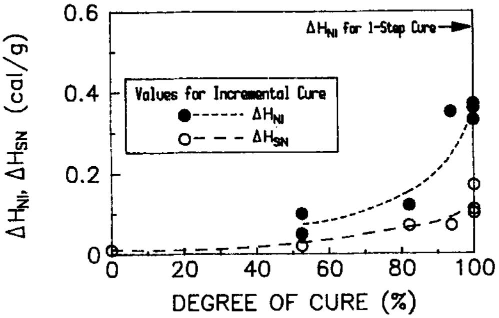

FIGURE 17 Dependence of "smectic-nematic" and nematic-isotropic transition enthalpies on degree of cure for 60% PCPB/NOA65 mixture (T_{cure} = 335 K).

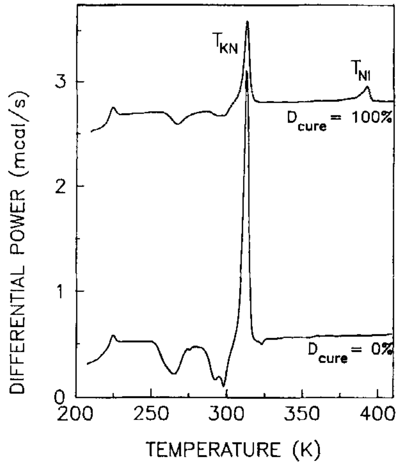

FIGURE 18 DSC thermal spectra for a 60% PCPB/NOA65 mixture in uncured (0%) and fully cured (100%) states (T_{cure} = 335 K). No evidence for an "induced smectic" is seen.

degree of cure. However, only the "SN" peak was detectable for the uncured sample. As suggested above, for D_{cure} = 0% impurities may have rendered the NI peak too broad to be observed, or else the LC was completely dissolved at T_{NI}. Also shown in the figure is the ΔH_{NI} value for a sample fully cured in a single step. This value, 0.56 ± 0.01 cal/g, is about 60% larger than that for the incrementally cured sample, suggesting that the step-wise cure process allowed a sizable fraction of LC to remain dissolved in the polymer matrix.

Samples which did not form "induced smectic." Not all PCPB/NOA65 samples formed an "induced smectic" phase. Indeed, some sort of thermal processing of a sample seemed necessary in order to obtain a "SN" peak. This processing involved either carrying out one or more DSC scans (from ~200 K to ~420 K) prior to cure or performing a sequence of incremental cures. However, thermal processing did not guarantee formation of an "induced smectic." Although the 50% and 60% samples discussed in the two preceding sections unambiguously exhibited "SN" peaks, others did not. For example, in Figures 18 and 19 are DSC scans of two

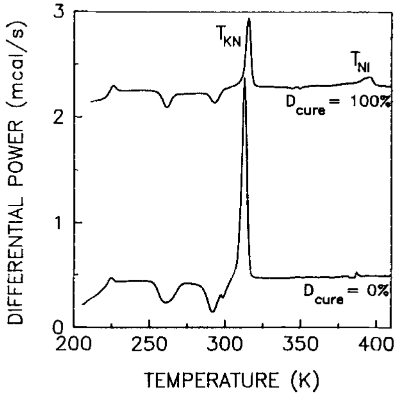

FIGURE 19 DSC thermal spectra for a 67% PCPB/NOA65 mixture in uncured and fully cured states (T_{cure} = 335 K). No evidence for an "induced smectic" is seen.

mixtures (LC concentrations of 60% and 67%) which did not exhibit the "SN" peak, even though their thermal treatment was similar to that for the 50% sample. Furthermore, in one-step cure studies carried out at temperatures ranging from 310 K to 393 K (see previous discussion of cure temperature effects), no samples with LC/matrix ratios of 50% or 33% yielded a verifiable "SN" peak. Thus, apparently a subtle combination of thermal treatment and concentration played a role in producing the unusual "SN" peak; it appears that incremental cure was most effective.

SEM evidence relevant to formation of "induced smectic." We tried to identify morphological features associated with the "SN" peak by examining some cured samples using scanning electron microscopy. Figure 20 shows three electron micrographs, as follows: Figure 20a: the 50% sample whose DSC scans are given in Figures 11 and 12; Figure 20b: the incrementally cured 60% sample (DSC scans in Figures 13 and 14); and Figure 20c: a 60% sample, cured in a single step at 335 K, which did not exhibit an "SN" peak. All three SEMs reveal microdroplets characteristic of PDLCs; the diameters of the droplets in Figure 20b are much smaller (~1 μm) than those in either 20a (5 μm) or 20c (4 μm). The fact that the droplets of Figure 20b are smaller than those of Figure 20c is consistent with the reduced intensity of the KN peak of Figure 13 (for D_{cure} = 100%) relative to that of Figure 18 (for D_{cure} = 100%). We would expect crystallization of the LC to be more greatly suppressed in smaller droplets.

In addition, a few needle-like structures are visible in Figure 20a and a great many in Figure 20b; none are seen in Figure 20c. These needles are felt to be crystals with thicknesses ≤1 μm. We speculate that the step-wise cure process was responsible for both major features of Figure 20b: the initial incremental cure pulse was sufficiently short that the hardening of the matrix allowed only small droplets to form. Some excess liquid crystal, which phase separated from the matrix in the early stages of cure, found only a restricted space available for crystallization at ambient temperatures. The resulting small crystallite dimensions may have permitted the formation of an "induced smectic," with the LC in microdroplets forming

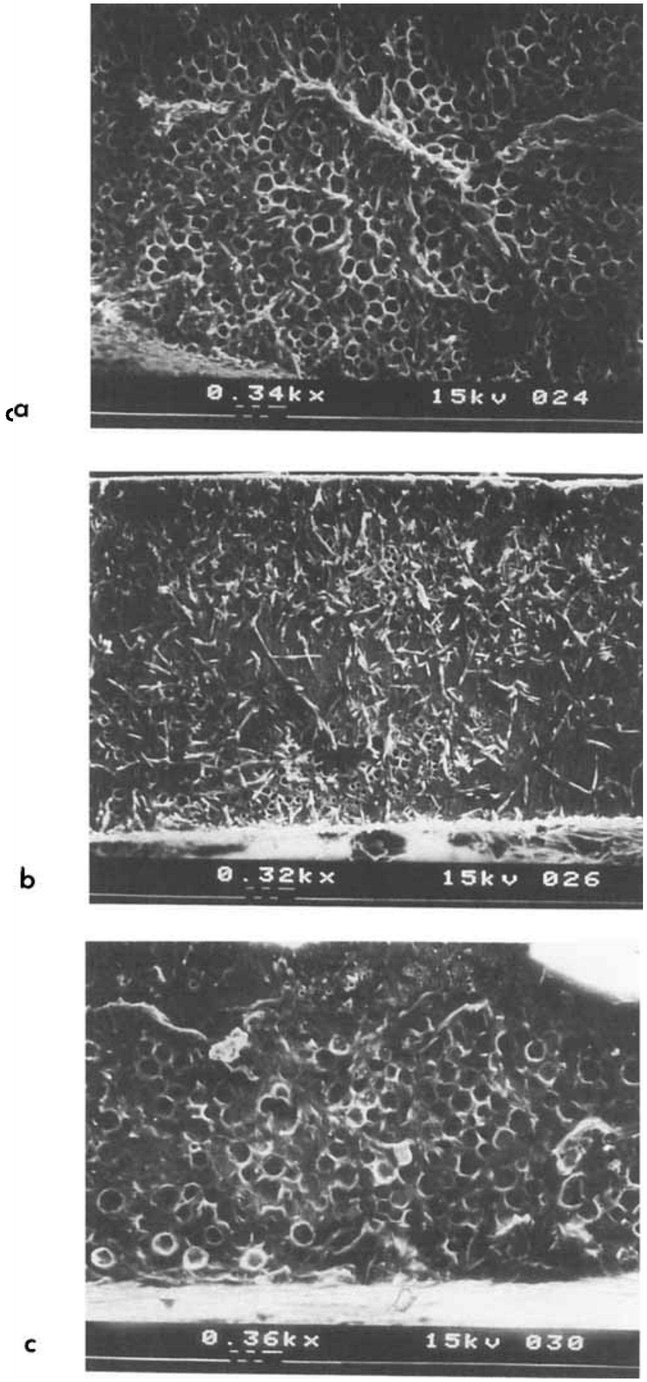

FIGURE 20 Scanning electron micrographs of cured PCPB/NOA65 mixtures. In each case, right-hand of three small bars is a 10 μm scale marker. Figure b is SEM for 60% sample which exhibited prominent "SN" peak.

a nematic phase. This supposition must, however, be viewed with caution since a few needle-like structures were seen in some samples which did not show a "SN" peak. Based on the present work, we were not able to identify conclusively the apparent induced phase as a smectic or to determine the mechanism for its formation.

CONCLUSIONS

This research complements a previous study of phase separation in mixtures of low molecular weight liquid crystals with an organic matrix.[7] In the present case we used a LC with a molecular weight about twice that of the previous ones. The effect of cure temperature on the cure process and phase behavior was investigated. For some samples evidence for phase separation and an anomalous phase transition (possibly an "induced smectic") was observed.

Effect of cure temperature. The effects of cure temperature on the cure kinetics and energetics were similar to those found for previously studied UV-cured systems.[6] Plots of the heats of cure for the pure matrix and LC/matrix mixtures go through maxima at temperatures between 330 K and 375 K where the degree of matrix cure is greatest. The fact that the nematic-isotropic transition enthalpy is maximum in the same temperature range confirms previous conclusions[6] that phase separation is greatest when the matrix is most fully cured. The magnitudes of ΔQ_{cure} decrease with increasing LC content. The time constants for the cure process exhibit well-known minima[6] at temperatures slightly above ambient.

The dependence of the melting enthalpy of cured samples on T_{cure} was somewhat unusual, with the largest values of ΔH_{KN} occurring at the highest cure temperatures, where degree of cure is apparently low. This unexpected behavior is in accord with the observation that uncured samples have larger KN enthalpies than fully cured ones. The explanation perhaps lies in the fact that confinement of the LC to microdroplets in cured samples can suppress crystallization, whereas LC crystallites may form as phase separation takes place during cooling of an uncured system.

Effect of degree of cure. Phase behavior of PCPB/NOA65 mixtures was studied as a function of D_{cure}, which was varied by incremental UV-cure of the polymer matrix. DSC scans of two uncured or partially cured samples (LC concentrations of 50% and 60%) exhibited an abrupt decrease near 390 K. This transition may be a decrease due to a negative excess specific heat of mixing, ΔC_{mix}.[7] However, the step was an order of magnitude smaller than that for mixtures based on lighter LCs.[7] In addition, its temperature remained fixed, rather than increasing with degree of cure, as was the case for previous systems.[7] Although this step co-existed with a nematic-isotropic transition for several values of D_{cure} in the 60% system, the possibility cannot be ruled out that the transition is actually due to a NI phase change, perhaps in small crystallites observed in the SEM. The simultaneous presence of both microdroplets and microcrystals may also explain the "induced smectic" discussed in the next paragraph. A number of PCPB/NOA65 mixtures cured in a single step did not exhibit either the "mixing" step or the "induced smectic."

"Induced Smectic" in several PCPB/NOA65 mixtures. The identification of the DSC thermal spectra peak at ~337 K (Figures 11–14) as a smectic-nematic transition is inferred from the fact that the only phase expected between crystal and nematic states is a smectic. The suggested mechanism whereby such a phase is induced is based on a single piece of evidence: the abundance of microcrystals found in the SEM (Figure 20b) of the 60% system which has the most pronounced "SN" peak. It may be that the phase behavior of the LC in the microcrystals is different from that of LC in the co-existing microdroplets. Since microdroplets (without co-existing crystallites) are found in the majority of cured samples which exhibit no "SN" peak, it may be that the supposed smectic phase is induced by the small dimensions of the microcrystals. In addition, the "mixing" step in the DSC thermal spectra of Figures 12 and 14 may actually be a NI transition of LC in the microcrystals. If these suggestions are correct, the phase sequence for the LC in the microdroplets would be crystal (or glass)-nematic-isotropic; in the microcrystals the sequence would be crystal-smectic-nematic-isotropic.

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