Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Cure Parameters and Phase Behavior of An Ultraviolet-Cured Polymer-Dispersed Liquid Crystal

George W. Smith [a]
[a] Physics Department, General Motors Research Laboratories, Warren, Michigan, 48090-9055
Version of record first published: 24 Sep 2006.

To cite this article: George W. Smith (1991): Cure Parameters and Phase Behavior of An Ultraviolet-Cured Polymer-Dispersed Liquid Crystal, Molecular Crystals and Liquid Crystals, 196:1, 89-102

To link to this article: http://dx.doi.org/10.1080/00268949108029689

Mol. Cryst. Liq. Cryst., 1991, Vol. 196, pp. 89–102
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Cure Parameters and Phase Behavior of An Ultraviolet-Cured Polymer-Dispersed Liquid Crystal

GEORGE W. SMITH

Physics Department, General Motors Research Laboratories, Warren, Michigan 48090-9055

(Received August 5, 1990; in final form September 20, 1990)

Using calorimetry and scanning electron microscopy we have investigated the formation energetics and kinetics as well as the phase behavior of an ultraviolet-cured polymer-dispersed liquid crystal (PDLC) system. The purpose of this work was to determine those cure conditions which lead to liquid crystal microdroplet formation. We have found that a range of cure temperatures exists in which the degree of polymer cure is highest. In this range phase separation of liquid crystal from the polymer is maximized, and the best droplet microstructure occurs. Samples cured in the optimum temperature range also have the highest nematic-isotropic transition temperature. Results of calorimetric and electron microscopic studies are presented.

Keywords: Polymer-dispersed liquid crystals; liquid crystals; phase behavior; calorimetry; PDLC formation

INTRODUCTION

Polymer-dispersed liquid crystal (PDLC) films, dispersions of micron-sized droplets of liquid crystal (LC) in a polymer matrix, have considerable potential for electro-optic applications, including information displays and privacy windows. It has been shown[1–3] that the electro-optic properties of PDLC films depend strongly on the size of the LC droplets. Furthermore, droplet size is determined by the rate of droplet formation,[4,5] i.e., by the cure (polymerization) rate of the polymer matrix.

For a PDLC film formed from an ultraviolet (UV) curable polymer precursor, the matrix cure rate is determined by the UV intensity,[6–12] with cure temperature generally playing a less important role.[5] In addition, the cure temperature affects the mutual solubility of the LC and the polymer precursor as well as the solubility of the LC in the final polymer matrix.[13] For the most efficient use of liquid crystal, we want to maximize the fraction of LC contained in the microdroplets; thus the fraction retained in the matrix should be minimized. In order to extend our knowledge of the factors which control droplet size, we have studied the influence of cure temperature and ultraviolet intensity on cure kinetics and energetics as well as on droplet morphology for a UV-curable PDLC system.

Cure parameters were determined by isothermal calorimetry (IC), and phase behavior by differential scanning calorimetry (DSC). These techniques help us to determine values of cure parameters for which electro-optic properties should be optimum and for which LC is used most efficiently. By means of IC we can measure the kinetics and energetics of the cure process. The temperature range and the amount of liquid crystal in the microdroplets can then be determined by DSC. Droplet morphology was examined using scanning electron microscopy (SEM).

This paper describes how we used these procedures to optimize cure parameters for a specific UV-curable polymer/liquid crystal system. We will see that, for a given LC concentration and cure temperature, increased UV intensity produces shorter cure times, leading to decreased droplet size.[5,14] A change in cure temperature leads to changes in LC solubility as well as cure rate, both of which can affect the resulting droplet morphology. For very low cure temperatures UV-cure rate is slow due to decreased molecular mobility; at high temperatures the cure rate is also low due to reduced radical lifetime. Consequently, there is an intermediate temperature range over which UV-cure rate is a maximum. Sufficiently high cure temperatures can result in the occurrence of undesirable thermally-induced reactions.

In addition to affecting cure kinetics, cure temperature can also greatly influence the extent to which the cross-linking reaction is completed (i.e., the degree of cure). As we shall see, the degree of cure can greatly affect the properties of a PDLC; our calorimetric technique provides a simple and direct method for determining this parameter. We shall show that the maximum degree of cure occurs in the same temperature range where the rate of cure is fastest.

In the next sections we shall describe our experimental methods and present results of our studies of cure parameters and phase behavior of a pure thiol-ene polymer precursor as well as for a PDLC based on that precursor.

EXPERIMENTAL ASPECTS

Materials

The principal polymer matrix used in this study was Norland UV-curable optical adhesive 65 (abbreviated NOA65)[15] use of which has been previously discussed.[2,16] The four primary constituents of this thiol-ene photomer are trimethylolpropane diallyl ether, trimethylolpropane tris thiol, isophorone diisocyanate ester, and benzophenone photoinitiator.[17]

The liquid crystal (LC) was a mixture containing five cyano-compounds: two biphenyls, a terphenyl, a cyclohexylphenyl, and a cyclohexylbiphenyl. We found that the mixture has a nematic-isotropic transition temperature of about 350 K (77°C) and a transition enthalpy of 1.05 ± 0.1 cal/g. Since it is a multicomponent system, it does not easily freeze, usually forming a glass below about 209 K (−64°C). In the present investigation we examined cure and phase behavior of pure NOA65 and of a PDLC composed of a 1:1 mixture (by volume) of LC and NOA65.

Sample Preparation

Samples for the UV cure studies were prepared using methods discussed briefly in Reference 5. We shall describe the technique to prepare a sample containing both liquid crystal and polymer. Small quantities (typically enough to produce a total volume of 100 μl) of NOA65 and LC 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). A small amount (about 5 μl) of the mixture was then pipetted into a custom made gold-plated copper DSC pan and then covered with an ultrathin (0.1–0.2 mm) quartz disc.[18] The disc rested on a shoulder around the pan bottom so as to give a sample of uniform thickness (typically on the order of 100 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. The procedure for pure NOA65 was simpler since mixing was not involved.

Calorimetric Techniques

The differential scanning calorimeter used in these studies was a Perkin-Elmer DSC2 instrument described previously.[1–3,19,20] Operated isothermally, it permits measurements of the rate of heat evolution, dQ/dt, during the PDLC cure process. From the time dependence of the heat evolution, τ_{cure}, the time constant of the cure process can be determined.

Isothermal Calorimetry. We have modified the DSC system to allow ultraviolet radiation to be introduced into the sample chamber so that kinetics of either a UV-induced or a thermally-induced PDLC cure can be followed. The UV irradiation was provided by a 100 watt high pressure mercury lamp mounted in an ITI Model 15060 UV source[21] and was introduced into the calorimeter by a fiber optic ultraviolet light guide.[22] A satellite light guide branching off the main guide made it possible to monitor and adjust the UV intensity during an experiment. Intensity calibrations were performed using an International Light Model IL700A Research Radiometer and Model A309 sensor.[23] The sensor's range of response was 257 to 390 nm, which coincided with the wavelength range of the filter used with the ITI source. Intensities during a run were monitored by means of an Ultraviolet Products Model UVX Digital Radiometer.[24]

The output end of the UV light guide was situated above and between the DSC sample and reference pans so that a "cone" of irradiation illuminated both pans. Since the UV intensity at the pans was some 10 to 50% lower than at the center of the irradiation cone (where the intensity was calibrated), our UV values were only nominal. Furthermore, a UV gradient (estimated to be less than 50%) probably existed over the sample area. As will be seen, cure energetics and phase behavior are insensitive to UV intensity, I_{UV}, so that this non-uniformity did not affect those results. However, since the time constant for the cure process varies[6] as $(I_{UV})^{-1/2}$, the observed kinetics were probably affected to a small extent. The spread in the measured values of τ_{cure} should not exceed 25%, even for a UV gradient as large

as 50% (an overestimate) across the sample area. Thus, UV non-uniformity should have a minor effect on our results.

A typical heat release curve for a UV-cured PDLC is shown in Figure 1, where exothermic power associated with the cure process is plotted versus time. The baseline is flat during the initial period when no UV irradiation occurs. As soon as sample irradiation begins, an abrupt increase in exothermic power occurs, followed by an almost exponential decay. The time constant for the cure process can be determined from a fit to the decay portion of the curve. In Figure 1 it is clear that the baseline during irradiation (as extrapolated to long times) is offset with respect to that prior to irradiation. This offset, which is due to a difference in absorbance of UV by the sample and reference pans of the calorimeter, is of no consequence for the determination of the kinetics or energetics of the cure process as long as the final (UV on) baseline is used for analysis.

The time constant for the cure process was determined from the isothermal heat release curves using an IBM AT personal computer and a program, DSC_RATE.[25] DSC_RATE is capable of fitting one or two exponentials to isothermal data previously extracted from the calorimeter's thermal analysis data station[20] and transferred to the PC using two additional programs.[25]

The total heat released during the cure process, ΔQ_{cure}, was determined by integration of isothermal exothermic power curves like that of Figure 1, using software provided by the calorimeter manufacturer. Values of ΔQ_{cure} obtained using this software were in excellent agreement with results obtained from our program DSC_RATE. As pointed out by Hoyle, *et al.*,[8] ΔQ_{cure} is a direct measure of the degree (extent) of cure.

Scanning Calorimetry. The DSC technique for determining PDLC phase behavior has also been previously described.[4] For these studies the calorimeter was operated in its temperature scanning mode, in which the sample temperature was programmed linearly (at 20 K/min) over the range of interest while changes in the sample's heat absorption rate were recorded.

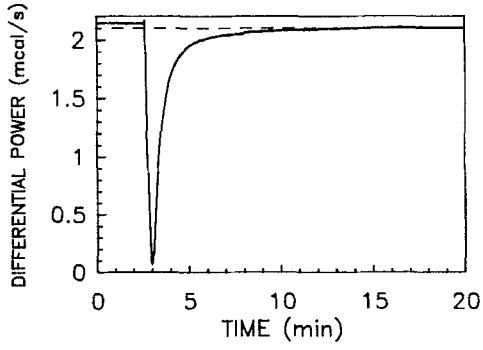

FIGURE 1 Isothermal heat release cure for UV cure of a PDLC precursor mixture (1:1 by volume) at 300 K. Nominal UV intensity = 6 mW/cm^2. By convention, exotherms are plotted as downward-going. The exothermic heat of reaction, obtained by integration of the curve, is 24.65 cal/g.

In Figure 2a is a DSC temperature scan for a sample of NOA65 cured at 300 K (27°C) using a nominal UV radiation intensity of 6 mW/cm^2. Only one feature is observed, a baseline shift associated with a heat capacity change due to the polymer glass transition at a temperature T_g = 273 K (0°C).

Figure 2b shows a thermal scan for a PDLC sample cured under the same conditions. This thermal spectrum exhibits three transitions: baseline shifts at about 209 K (−64°C) and 262 K (−11°C) and an endothermic peak at approximately 348 K (75°C). The baseline shift at 209 K is due to the glass transition of the liquid crystal.[19] (As mentioned above, the LC is a multicomponent mixture and cannot easily be frozen in bulk or in the PDLC microdroplets; instead it usually forms a glass upon cooling). The baseline shift at 262 K is associated with the glass transition of the PDLC matrix; its T_g is about 11 K lower than that of the pure NOA65 due to the plasticizing effect of the liquid crystal.[4,19] The endothermic peak occurs at the nematic-isotropic transition temperature, T_{NI}, of the liquid crystal in the microdroplets[4] and for this sample is about 2 K lower than T_{NI} of the pure LC (350 K). This shift is due to two causes: polymer precursor material remaining in solution in the LC and preferential dissolution of lighter LC components in the cured matrix. The first effect tends to decrease T_{NI}; the second increases it. The area under the endotherm is proportional to the NI transition enthalpy, ΔH_{NI}, which is, in turn, a measure of the fraction of LC contained within the droplets.[4] Liquid crystal dissolved in the matrix does not contribute to the peak. (However,

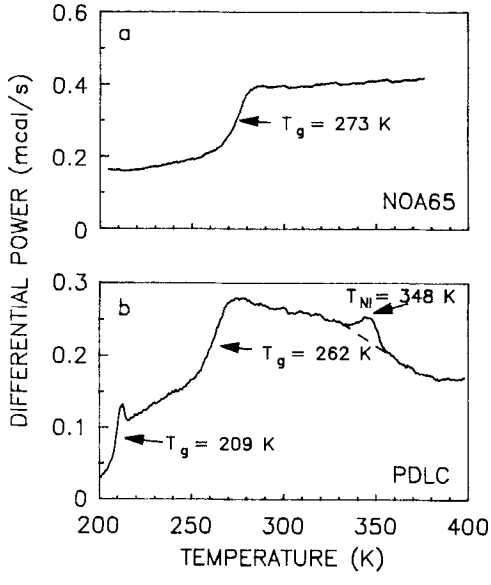

FIGURE 2 a) DSC thermal scan of a NOA65 sample cured at 300 K, using a UV intensity of 6 mW/cm^2. The baseline shift at about 273 K is due to the glass transition of the cured polymer. b) DSC scan of the PDLC sample whose isothermal heat release curve is shown in Figure 1. The baseline changes at about 209 K and 262 K are associated with the glass transitions of the liquid crystal in the microdroplets and of the matrix respectively. The peak at about 348 K is due to nematic-isotropic transition of the LC in the droplets.

if the liquid crystal content in a PDLC mixture is so large that some LC is expelled from the matrix as "pools" or "puddles," ΔH_{NI} will include contributions from this free LC and thus will no longer be proportional to the amount of LC contained in the microdroplets.)

The scanning mode was also used to determine the temperature at which thermally-induced reactions (e.g., decomposition or thermally-induced cure) occurred. Such reactions could interfere with UV cure. These experiments were carried out in the absence of UV irradiation by programming the temperature of an uncured sample upward until the onset of a reaction exotherm was observed. For pure NOA65 thermally-induced reactions occurred above about 440 K; for the uncured PDLC mixture the onset temperature for thermal reactions was reduced to about 380 K.

Scanning Electron Microscopy

PDLC droplet morphologies were examined using scanning electron micrographs (SEMs) of samples cured in the calorimeter. Thus, for these samples cure temperatures and formation kinetics were well characterized, and their influence on PDLC microstructure and droplet number density could be assessed. Our SEM procedure has been previously described.[4]

EXPERIMENTAL RESULTS AND DISCUSSION

Cure Energetics and Kinetics

Pure NOA65. As mentioned above, ΔQ_{cure}, the total heat evolved during the UV cure process, is determined by integration of heat release curves like that of Figure 1. The dependence of ΔQ_{cure} for pure NOA65 on cure temperature is shown in the upper curve of Figure 3. Very little UV-induced cross-linking occurs at low temperatures (i.e., near T_g of the uncured polymer precursor below which the molecular mobility is low); this finding agrees with the results of a study of the cure of a multifunctional acrylate.[12] Likewise, at high temperatures, just below the range where thermal reactions commence, UV-induced cure is incomplete; as previously mentioned, in this temperature range the lifetime of the free radicals responsible for the polymerization reaction is short.

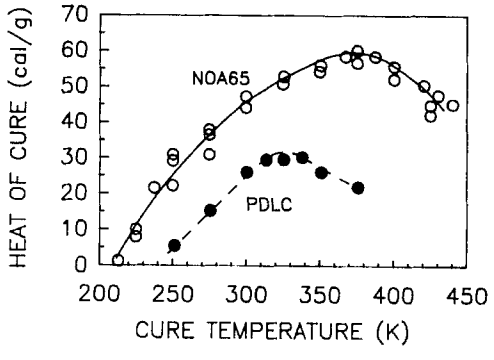

FIGURE 3 Heat of cure for pure NOA65 (upper curve) and for the 1:1 PDLC (lower curve) as a function of cure temperature.

A pronounced maximum in the heat of cure occurs for cure temperatures in the vicinity of 380 K. As already pointed out, ΔQ_{cure} is directly proportional to D_{cure}, the relative degree of cure. We assign D_{cure} a value of 100% at the maximum of ΔQ_{cure} for NOA65. The cure temperature for greatest D_{cure} (380 ± 20 K) is higher than the maximum glass transition temperature for the cured polymer (290 K, see Figure 5 below) in agreement with results for a cured acrylate.[12] For cure temperatures below the maximum T_g, the degree of cure is reduced, also in accord with the findings of Reference 12. Not surprisingly, we found that the heat (and therefore the degree) of cure is independent of UV intensity. Thus, non-uniformity of UV intensity across the sample has essentially no effect on the measured energetics of the cure process.

The cure time constant, τ_{cure}, is, as discussed, sensitive to cure temperature. As anticipated, τ_{cure} for pure NOA65 (lower curve of Figure 4) goes through a minimum at intermediate temperatures. Fast cure rate occurs at a cure temperature of about 330 K, some 50 K lower than the temperature for maximum ΔQ_{cure}; this result is in good agreement with the work of Hoyle, *et al.*,[8] for a different thiolene polymer precursor. At temperatures where thermal reactions occur (>440 K) the cure kinetics become complicated; therefore values of τ_{cure} are not plotted for this range. It is possible that thermally-induced reactions may also affect the cure process at temperatures below 440 K. The cure time constant, unlike ΔQ_{cure}, is affected by the UV intensity. We found that, as expected,[6] τ_{cure} decreases as $(I_{UV})^{-1/2}$.

PDLC. In the lower curve of Figure 3 is plotted the dependence of ΔQ_{cure} on T_{cure} for UV cure of a PDLC system formed from a 1:1 (by volume) mixture of LC and NOA65. As was the case for the pure polymer precursor, the heat of cure exhibits a maximum at a temperature (325 K ± 20) higher than the maximum glass transition temperature (270 K, see Figure 5) of the cured system. Two other important aspects are apparent: dilution effects have reduced the maximum ΔQ_{cure} for the PDLC mixture relative to that of the pure polymer; and the temperature of the maximum is roughly 55 K lower than that for NOA65. If the inclusion of the LC did not affect the extent of cross-linking of the mixture matrix, we would expect the maximum degree of cure for the matrix to be 100% (i.e., the same as

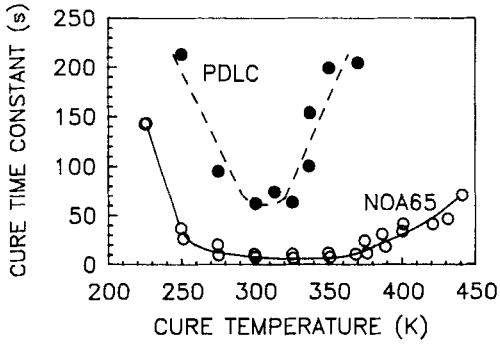

FIGURE 4 Cure time constant of pure NOA65 and of the PDLC mixture as a function of cure temperature. Nominal UV intensity = 3 mW/cm².

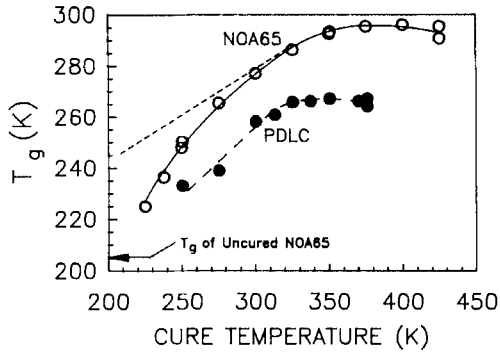

FIGURE 5 Cure-temperature dependence of matrix T_g for cured PDLC sample (lower curve) compared to that for pure cured NOA65 (upper curves). The two curves for NOA65 are discussed in the text.

the maximum value for pure NOA65). Calculation of D_{cure}, the degree of cure of the PDLC matrix relative to that for the pure polymer, is fairly straightforward. Assuming (as above) that D_{cure} is proportional to ΔQ_{cure}, we need only to take account of the LC concentration and the difference in the polymer and LC densities. For the 1:1 mixture,

$$D_{cure} = \frac{\Delta Q_{cure}^{mix} \times m_{mix}}{\Delta Q_{cure}^{NOA65} \times m_{NOA65}} = \frac{\Delta Q_{cure}^{mix} \times (\rho_{NOA65} + \rho_{LC})}{\Delta Q_{cure}^{NOA65} \times \rho_{NOA65}} \quad (1)$$

where the ΔQ's are the heats of cure (in cal/g), the m's are the masses, and the ρ's are the densities of the samples (PDLC mixture, LC, or pure NOA65 as appropriate). Since $\rho_{NOA65} = 1.12$ and $\rho_{LC} = 1.02$, equation 1 becomes

$$D_{cure} = 1.911 \times \frac{\Delta Q_{cure}^{mix}}{\Delta Q_{cure}^{NOA65}}. \quad (2)$$

The calculated maximum degree of cure of the PDLC matrix is about 93% of the maximum value for pure NOA65. Evidently the diluting effect of the liquid crystal tends to interfere with the cross-linking reaction. As for the pure polymer precursor, the heat and degree of cure for the PDLC are independent of UV intensity.

In the upper curve of Figure 4 is plotted the cure time constant for the PDLC mixture. As for pure NOA65, τ_{cure} exhibits a minimum at a temperature somewhat lower than that for the maximum in ΔQ_{cure}. However, the minimum is narrower, and the magnitudes of the time constant are everywhere larger than for NOA65. The slower kinetics are undoubtedly due to the diluting effect of the liquid crystal; radicals must diffuse further before they can find a partner with which to react. The cure time constant for the PDLC, like that for the pure polymer, exhibits an inverse dependence on the square root of the UV intensity.

Phase Behavior

As has been shown previously[4,19] the phase behavior of thermally cured PDLC films is sensitive to both liquid crystal content and cure temperature. As we shall see, the glass transition temperature of both cured NOA65 and the matrix of the PDLC film are sensitive to cure temperature, as is the nematic-isotropic (NI) transition temperature and enthalpy of the cured mixture. However, both transitions are essentially unaffected by UV intensity. None of these conclusions is very surprising.

Possibly the most important result of our phase behavior study is the conclusion (based on NI transition enthalpy measurements) that the greatest degree of phase separation of the liquid crystal from the matrix occurs in the temperature range where cure is most complete. The SEM studies will show that best droplet formation also occurs in this same temperature range.

Pure NOA65. Figure 5 (upper curves) plots T_g for pure NOA65 cured at various temperatures. The glass transition temperature increases with increasing T_{cure} until about 400 K, above which it decreases slightly due to the lower degree of cure at higher temperatures. It should be pointed out that samples cured at low temperatures initially have rather low T_g values (solid curve) due to incomplete cure. The initial measurement of T_g is performed by cooling to 200 K immediately following cure and then carrying out a DSC thermal scan. During the initial DSC scan additional curing occurs (due in part to increased mobility of previously frozen free radicals). Consequently glass transition temperatures measured later are somewhat higher (short dashed curve). Values of T_g are unaffected by UV intensity.

PDLC. In Figure 5 (lower curve) is plotted the dependence of the matrix T_g on T_{cure} for the PDLC. A slight downward trend is discernible for cure temperatures above about 340 K. Thus, T_g values for both pure NOA65 and the PDLC are maximized for a cure temperature giving the greatest degree of cure. The fact that glass transition temperatures for the PDLC are lower than for the pure polymer is ascribable to the plasticizing effect of residual liquid crystal in the matrix. As we shall see, a large fraction of LC is apparently retained in the matrix for this system. As for the pure NOA65, the glass transition temperature is unaffected by UV intensity.

The nematic-isotropic transition temperature of the PDLC increases with cure temperature (Figure 6). This is not surprising since less polymer precursor material should be dissolved in the liquid crystal when the matrix is more fully cured. The maximum value of T_{NI} for the highest cure temperature actually exceeds the value for the pure liquid crystal, probably as a result of lighter LC components (with lower T_{NI} values) being preferentially retained in the matrix. Thermally-induced reactions at high cure temperature may also play a role. T_{NI} is independent of UV intensity, which is consistent with the fact that irradiation intensity does not affect degree of cure.

The most dramatic result of the phase behavior studies is the dependence of nematic-isotropic transition enthalpy on cure temperature (Figure 7). The maximum of T_{NI} coincides with the maximum of ΔQ_{cure} (Figure 3). In Figure 8 the data of Figure 7 are replotted versus degree of cure of the PDLC matrix (as determined

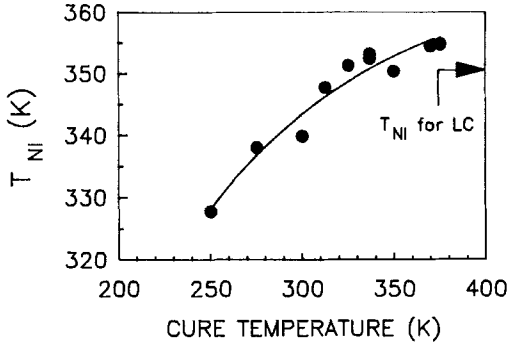

FIGURE 6 Nematic-isotropic transition temperature of cured PDLC sample versus cure temperature.

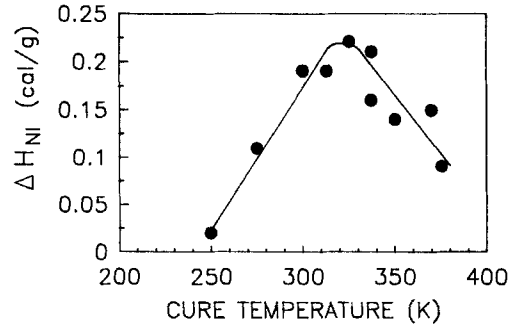

FIGURE 7 Dependence of nematic-isotropic transition enthalpy of cured PDLC sample on cure temperature.

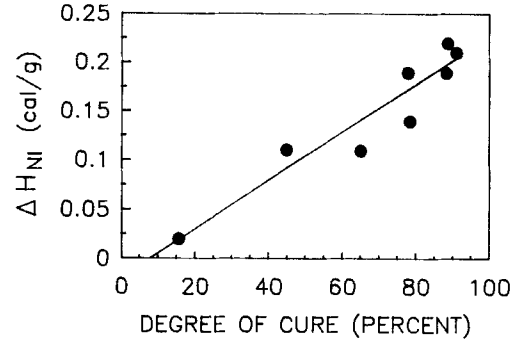

FIGURE 8 Data of Figure 7 replotted versus degree of cure of the PDLC matrix.

from Equation 2); it is apparent that ΔH_{NI} depends more or less linearly on D_{cure}. Although the straight line fit of Figure 8 does not pass through the origin, the scatter in the data is sufficiently large that we cannot rule out a direct proportionality ($\Delta H_{NI} = \text{const} \times D_{cure}$). Like T_{NI}, ΔH_{NI} is essentially independent of UV intensity.

It is known[4] that α, the (volume or mass) fraction of liquid crystal contained in the microdroplets after cure, is given by

$$\alpha = (1 + F)\Delta H_{NI}/\Delta H_{NI}(LC) \tag{3}$$

where $\Delta H_{NI}(LC)$ is the transition enthalpy for the pure liquid crystal. F, the mass ratio of polymer to LC in the sample, is given by

$$F = \rho_{NOA65}V_{NOA65}/(\rho_{LC}V_{LC}), \tag{4}$$

where the ρ's are densities and the V's are the volumes of polymer precursor and liquid crystal in the sample. For the present system the volumes are equal, $\rho_{NOA65} = 1.12$, $\rho_{LC} = 1.02$, and $\Delta H_{NI}(LC) = 1.05 \pm 0.1$ cal/g. Thus, Equation 3 becomes

$$\alpha = 2.0 \times \Delta H_{NI}. \tag{5}$$

The maximum value of α calculated from Equation 5 is slightly less than 0.5. Thus, for the present polymer/liquid crystal combination, less than half of the liquid crystal is contained in the microdroplets; the remainder is therefore retained in the polymer matrix. This low value of α contrasts with results for other PDLCs in which 70 to 90% of the liquid crystal has been incorporated into the droplets.[1,4,19]

ELECTRON MICROGRAPHS

Scanning electron micrographs of LC/NOA65 samples cured at various temperatures are shown in Figure 9. It is apparent that cure temperature has an important influence on microdroplet formation. Specifically, it can be seen that best droplet formation has occurred in the range 300–325 K, where the greatest degree of cure was observed. The present study did not focus on the influence of UV on droplet morphology. However, it has been shown that greater UV intensity shortens the cure time constant[5] which, in turn, leads to smaller droplets.[5,14] Since degree of cure is not affected by UV intensity, this UV control of droplet size can be achieved apparently without affecting the fraction of liquid crystal in the droplets.

SUMMARY

The present study has yielded a number of useful results. The value of coupled calorimetric and electron-microscopic techniques for optimizing PDLC film cure and microstructure has been demonstrated. For instance, the cure time constant and the heat of cure (which is a useful measure of the degree to which the polymer matrix is cured) have been shown to be sensitive to the cure temperature. Furthermore, degree of cure affects both the glass and nematic-isotropic transition temperatures, the amount of liquid crystal in the microdroplets, and the droplet morphology of the film. Although UV intensity is extremely important in determining the size of the microdroplets in a fully cured film,[5,14] it evidently does not strongly influence the amount of liquid crystal contained in the droplets.

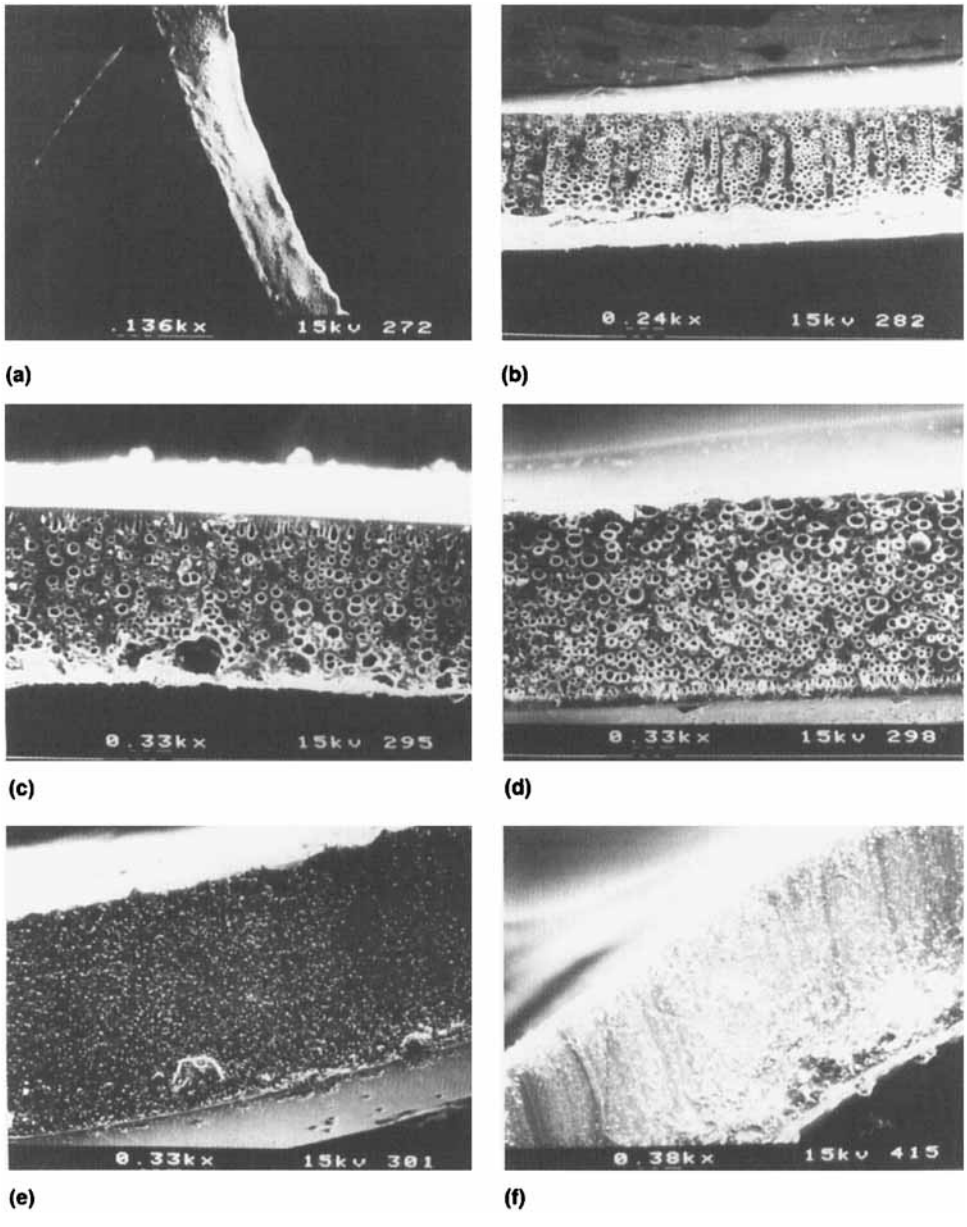

FIGURE 9 Scanning electron micrographs of PDLC samples cured (nominal UV intensity = 3 mW/cm^2) at different temperatures: a) 275 K, b) 300 K, c) 313 K, d) 325 K, e) 337 K, and f) 350 K. The best microdroplet formation occurs in the range of cure temperatures where maximum degree of cure is attained (300 K to 325 K).

In the following paragraphs we shall summarize results specific to the present system.

Pure NOA65. The heat of cure for the pure polymer (and consequently the degree of cure) exhibits a maximum at temperatures in the range 380 ± 20 K,

appreciably above the maximum glass transition temperature of the cured polymer. ΔQ_{cure} is reduced at low temperatures due to low molecular mobility; at high temperatures short radical lifetime is presumably responsible for the reduction. These factors also affect the time constant for the cure process, which goes through a minimum at intermediate temperatures. UV intensity does not influence heat or degree of cure, but does, of course, affect τ_{cure} (which goes as the inverse square root of UV intensity).

The glass transition temperature of the cured polymer increases monotonically with cure temperature up to almost 400 K at which point it decreases slightly due to lower degree of cure. T_g is unaffected by the intensity of the ultraviolet cure radiation.

PDLC (1:1 by volume). As for the pure polymer, the heat (and degree) of cure of the PDLC mixture goes through a maximum at a T_{cure} greater than the maximum T_g of the cured system. However, the cure temperature for the maximum (at about 325 ± 20 K) is roughly 55 K lower than for the pure polymer. For the PDLC system the degree of cure of the matrix (as derived from ΔQ_{cure}) is some 7% lower than that for the matrix material without liquid crystal. As for pure NOA65 the heat (and degree) of cure are unaffected by UV intensity. Cure time constant for the PDLC is always greater than that for NOA65, and the minimum in τ_{cure} is shifted to about 310 ± 20 K, lower than for the pure polymer. The cure time constant decreases with increasing UV intensity.

Both the glass and nematic-isotropic transition temperatures of the cured mixture (i.e., the PDLC film) increase with T_{cure} and degree of cure; neither is affected by UV intensity. The maximum value of T_{NI} is actually higher than the magnitude for the pure liquid crystal, probably due to preferential retention of light LC components in the matrix.

Usually only liquid crystal in the microdroplets contributes to the calorimetrically measured nematic-isotropic transition enthalpy. Thus, ΔH_{NI} can be used to determine the fraction of LC in the droplets. ΔH_{NI} exhibits a maximum (UV-independent) in the same temperature range (325 ± 20 K) for which degree of cure is a maximum. The important (but not surprising) conclusion is reached that phase separation is greatest for the greatest degree of cure. This calorimetric result is supported by electron microscopic evidence which clearly shows that best microdroplet formation occurs in the temperature range (300 to 325 K) where cure is most complete. For the present system, less than half the liquid crystal is incorporated into the droplets, compared to values as high as 70 to 90% for other systems.

Acknowledgments

The author thanks Nuno A. Vaz for providing the liquid crystal, Dr. Vaz, and G. Paul Montgomery, Jr., for useful suggestions and discussions, Daniel B. Hayden for developing the computer codes and for performing the scanning electron microscopy, Thomas H. VanSteenkiste for his contributions to the calorimetric experiment, and Wilson D. Marion for assistance with several computer-related problems. Useful interactions with J. William Doane, John L. West, J. David Margerum, Anna D. Lackner, Leroy J. Miller, and Fred G. Yamagishi are also gratefully acknowledged.

REFERENCES

1. N. A. Vaz, G. W. Smith and G. P. Montgomery, *Mol. Cryst. Liq. Cryst.*, **146**, 17 (1987).
2. N. A. Vaz, G. W. Smith and G. P. Montgomery, *Mol. Cryst. Liq. Cryst.*, **146**, 1 (1987).
3. G. P. Montgomery, J. L. West and W. Tamura-Lis, submitted for publication.
4. G. W. Smith and N. A. Vaz, *Liq. Cryst.*, **3**, 543 (1988).
5. G. P. Montgomery, N. A. Vaz and G. W. Smith, *Proc. SPIE*, **958**, 104 (1988).
6. G. Pasternack, "Fundamental Aspects of Ultraviolet Light and Electron Beam Curing," Radiation Curing Workshop, A.F.P. of SME, Chicago, IL, 15 September 1981.
7. G. R. Tryson and A. R. Shultz, *J. Polymer Sci.*, **17**, 2059 (1979).
8. C. E. Hoyle, R. D. Hensel and M. B. Grubb, *J. Polymer Sci.*, **22**, 1865 (1984).
9. D. D. Le, "A Method for Optimizing UV-Curing Conditions," in *Radcure '84 Conference Proceedings*, Atlanta, GA, 10–13 September, 1984, p. 8–33.
10. G. Oster and N. Yang, *Chem. Revs.*, **68**, 125 (1968).
11. J. E. Moore, "Calorimetric Analysis of UV Curable Systems," in *UV Curing, Science and Technology*, S. P. Pappas, Ed., Technology Marketing Corp., Norwalk CT, 1978, p.134.
12. B. K. Appelt and M. J. M. Abadie, "Calorimetry of Photosensitive Materials," North American Thermal Analysis Society, San Francisco, CA, September 1985; ibid, Polymer Composites **25**, 931 (1985).
13. G. W. Smith, N. A. Vaz and T. H. VanSteenkiste, *Mol. Cryst. Liq. Cryst.*, **174**, 49 (1989).
14. A. M. Lackner, J. D. Margerum, E. Ramos and K. C. Lim, *Proc. SPIE*, **1080**, 53 (1989).
15. Norland Products, Inc., P. O. Box 145, North Brunswick, NJ 08902.
16. N. A Vaz and G. W. Smith, U.S. Patent 4,728,547, 1 March 1988.
17. M. E. Myers, C. A. Drumm and K. L. Olson, private communication.
18. Quartz Scientific, Inc., Fairport, OH.
19. G. W. Smith, *Mol. Cryst. Liq. Cryst.*, **180B**, 201 (1990).
20. Perkin-Elmer Corp., Norwalk, CT.
21. Instrument Technology, Inc., Westfield, MA.
22. Highlight Fiber Optics, Caldwell, ID.
23. International Light, Newburyport, MA.
24. Ultraviolet Products, Inc., San Gabriel, CA.
25. The programs for data transfer and analysis were written by D. B. Hayden.