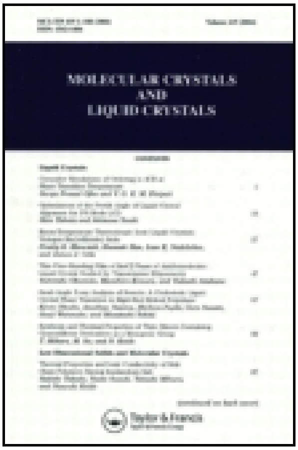

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A Calorimetric Study of Polymer-Dispersed Liquid Crystals: Cure Energetics and Kinetics

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A Calorimetric Study of Polymer-Dispersed Liquid Crystals: Cure Energetics and Kinetics

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Polymer-dispersed liquid crystal (PDLC) films are formed by the phase separation of liquid crystal (LC) microdroplets from a polymer matrix during cross-linking (cure) of the matrix. Thus, studies of the cure energetics and kinetics of PDLCs provide insights into the mechanisms of their formation. We have carried out such studies for PDLCs cured in two different ways. We have measured the heat released during cure (ΔQ_{cure}) and the time constant for the cure process (τ_{cure}) as a function of cure temperature (T_{cure}) for two thermally-cured and four UV-cured systems. The heat of cure for both types of systems exhibits similar behavior: ΔQ_{cure} goes through a broad maximum at a value of T_{cure} where the degree of matrix cure is greatest. On the other hand, the behavior of the cure time constant differs for the two systems: τ_{cure} for thermally-cured PDLCs decreases monotonically with temperature, whereas that for UV-cured PDLCs exhibits a minimum. Both quantities are of importance for optimization of PDLC electro-optic properties. ΔQ_{cure} is proportional to the degree of matrix cure and is therefore a measure of the extent of phase separation of LC from the matrix; τ_{cure} plays a role in determining liquid crystal microdroplet size.

Keywords: polymer-dispersed liquid crystals, cure kinetics, cure energetics, phase separation, liquid crystals, polymers

INTRODUCTION

Polymer-dispersed liquid crystals (PDLCs) are dispersions of micron-sized droplets of liquid crystal (LC) in a polymer matrix.[1–4] Understanding their formation is becoming increasingly important because of interest in optimizing PDLC films for a variety of applications (e.g., displays and privacy windows). They are most often formed by phase separation of LC microdroplets from a polymer matrix during cross-linking (cure) of the matrix.[1–9] Thus, investigations of the cure energetics and kinetics of PDLCs provide insights into their formation processes. This report will summarize studies of both thermally- and ultraviolet-cured PDLCs, comparing recent results with previously reported data.

We have used differential calorimetry to measure ΔQ_{cure}, the heat released during cure, and τ_{cure}, the time constant for the cure process, as functions of cure temperature. Both quantities are of importance for optimization of PDLC electro-optic properties: Since ΔQ_{cure} is proportional to the degree of matrix cure,[8,9] it is a measure of the extent of phase separation of LC from the matrix; τ_{cure} plays a role in determining liquid crystal microdroplet size.[5-8] Results for two thermally-cured and four ultraviolet-cured systems are reported. We found that the heats of cure for both types of systems exhibit similar behavior: ΔQ_{cure} goes through a broad maximum at a temperature where the degree of matrix cure is greatest. On the other hand, τ_{cure} for thermally-cured PDLCs decreases monotonically with temperature, whereas that for UV-cured systems exhibits a minimum.

Cure behavior studies of two thermally-cured[5,6] and two UV-cured PDLCs[8,10] have been reported previously. In this paper we shall compare the results of that research to recent measurements of ΔQ_{cure} and τ_{cure} for two additional UV-cured systems and draw some conclusions about PDLC formation. But first it is necessary to review the experimental aspects of these investigations.

EXPERIMENTAL ASPECTS

Materials and Sample Preparation

Liquid crystals. Five different liquid crystals were used in these studies. All but one were multi-component mixtures. Some relevant properties of the LCs are summarized in Table I.

Polymer matrices. Our studies have focused on three different polymer matrices, two thermally-cured and one UV-cured. The thermally-cured systems were a 3-part epoxy[5] and a polyurethane.[6] The sole UV-cured matrix was NOA65, an optical adhesive used in previous studies.[2,7-10] In their initial (precursor) states, the matrices were liquid mixtures of low molecular weight components. Thermally- or UV-induced cross-linking reactions led to an increase in molecular weight and consequent hardening of the matrix. Information concerning the matrices is given in Table II.

Mixture formation. Since PDLCs are formed by phase separation of the liquid crystal during matrix cure, it was first necessary to mix the LC and matrix precursor to form a solution. Small quantities (typically enough to produce a total volume of 100 μl) of LC and precursor were measured into a watch glass using precision micropipettes. The components were vigorously stirred until a uniform mixture was obtained (generally 30 to 60 s was sufficient time). About 5 to 10 μl of sample were then transferred to a calorimeter sample pan.

For UV-cure studies the pan was a custom-made gold-plated copper pan with a shoulder around the pan bottom. An ultrathin (0.1–0.2 mm) quartz disc rested on the shoulder to maintain a constant sample thickness (100 to 200 μm) to ensure 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 copper pan.

In the case of thermal cure, the sample was placed in an aluminum pan and covered with a lid which was cold-welded in place to produce a hermetic seal. Samples were then transferred to the calorimeter where matrix cure was monitored (see below).

TABLE I

Liquid crystals used in present studies

LC	Mixture	T_{KN} (K)	T_{NI} (K)	Source
E7	4 components [biphenyls, terphenyls]	glass*	333	a
ROTN-404	6 components [biphenyls, terphenyls, phenylpyrimidines]	glass*	384	b
E63M	5 components [biphenyls, terphenyl, cyclohexylphenyl, cyclohexylbiphenyl]	glass*	350	c
PCPB	1 component [p-pentylphenyl-2-chloro-4-(p-pentylbenzoyloxy)-benzoate]	312	397	d
BL009	7 components [biphenyls, terphenyls, ester]	glass*	386	a

*multi-component LCs usually form glasses rather than crystallise

a. E. Merck Ltd., Poole, England

b. F. Hoffman-LaRoche, Nutley, NJ.

c. See reference 8.

d. Eastman Organic Chemicals, Rochester, NY.

Calorimetric Techniques

The differential scanning calorimeter used in these studies was a Perkin-Elmer DSC2 instrument.[11] The DSC was operated isothermally to determine cure energetics and kinetics of both the pure matrix and the LC/matrix mixtures. The calorimetric methods have been described in detail in previous publications[5,6,8]; a few aspects will be discussed here.

Thermally-cured systems. The output of the calorimeter, when operated isothermally, is a plot of dQ/dt, the rate of heat evolution during the cure process[5,6,8] as a function of time, t. Typical heat release curves for thermal cure of an epoxy matrix and an epoxy-based PDLC are shown below in Figures 1 and 2. Integration of dQ/dt yields ΔQ_{cure}, the total heat released during the cure process, which is important since it is a direct measure of D_{cure}, the degree of cure.[12]

The method used for determining the cure time constant depended on the shape

TABLE II

Polymer matrices

Matrix	Components	Cure Method	Reference
3 part epoxy	Devcon 5A, Epon 812, Capcure 3-800 (1:1:2)	Thermal	5
Polyurethane	Desmodur W, Polyol TP440, Polyol TP410 (2:2:3) + trace catalyst	Thermal	6
Norland Optical Adhesive 65	4 components	Ultraviolet	a

a. Norland Products, Inc., North Brunswick, NJ (see also reference 8).

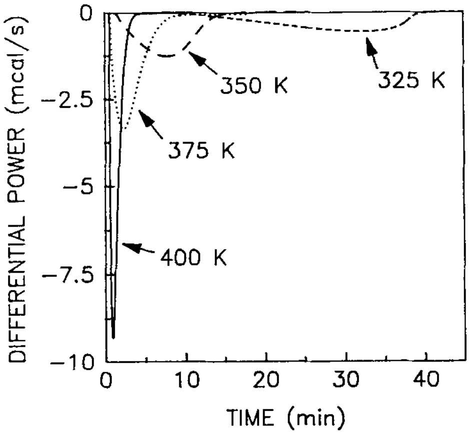

FIGURE 1 Heat release curves (plots of dQ/dt versus time) for thermal cure of 3-part epoxy cured at four different temperatures. For the lower cure temperatures the curves depart appreciably from ideal behavior. By convention, exotherms are downward-going.

of the heat release curve. For a more-or-less "ideal" shape (i.e., a rapid rise followed by a smooth decay), τ_{cure} was obtained by fitting exponentials to the decay portion of the curve.[6] For "non-ideal" shapes (e.g., Figures 1 and 2), the best measure of τ_{cure} was the time at which dQ/dt attained its maximum value.[5]

UV-cured systems. The DSC system was modified to allow introduction of ultraviolet radiation into the sample chamber so that energetics and kinetics of a UV-induced cure process could be determined.[8,10] A typical heat release curve for UV-cure (Figure 7) shows ideal behavior: the baseline is flat during the initial period when no UV irradiation occurs. With the initiation of UV irradiation an

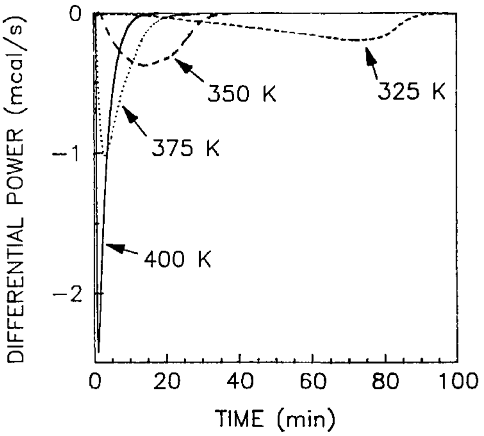

FIGURE 2 Heat release curves for 33% E7/epoxy PDLCs cured at four temperatures. Curve shapes are similar to those of Figure 1, but time and differential power scales are appreciably different.

abrupt increase of exothermic power occurs, followed by an almost exponential decay. In Figure 7 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 energetics or kinetics of the cure process as long as the final (UV on) baseline is used for analysis. As for thermal cure, ΔQ_{cure} is determined by integration of the heat release curve. Exponential fits to the decay portion of the dQ/dt curve yield values of τ_{cure}.[8]

We shall discuss the heat release curves in greater detail in the next section where we present results for each of six PDLC systems: E7/epoxy, ROTN-404/polyurethane, E63M/NOA65, PCPB/NOA65, BL009/NOA65, and ROTN-404/NOA65.

EXPERIMENTAL RESULTS AND ANALYSIS

Thermally-cured PDLCs

E7/epoxy. In Figure 1 are presented isothermal heat release curves for the 3-part epoxy (Table II) cured at four different temperatures, T_{cure}.[5] It is apparent that the curves are far from ideal for the three lowest values of T_{cure}. This complex behavior is apparently associated with competition between two cure reaction processes.[5] Figure 2 gives the corresponding curves for cure of an E7/epoxy mixture containing 33 volume percent of the liquid crystal. Although the shapes of the curves in Figures 1 and 2 are quite similar, two striking changes are produced by the addition of the LC: 1) the magnitude of the maximum dQ/dt values for the E7/epoxy systems is about four times smaller than for the pure epoxy; 2) the time scale for cure of the LC/epoxy mixture is almost 3 times larger than that for the epoxy. Thus, there is an appreciable dilution effect due to the addition of the liquid crystal.

Integration of the curves of Figures 1 and 2 (and others like them) yields values of the heat of cure (Figure 3). It appears that there is a broad maximum in ΔQ_{cure} for both the pure epoxy and the 33% mixture, with the PDLC values reduced by about 1/3 relative to those for the pure epoxy. Since ΔQ_{cure} is a measure of the degree of cure,[12] it appears that D_{cure} is greatest near 375 K for both the pure epoxy and the PDLC.

The dilution effect of the liquid crystal, in addition to reducing ΔQ_{cure}, greatly lengthens the cure time constant, as seen in Figure 4. However, the dominant effect is due to T_{cure}: τ_{cure} is reduced by about two orders of magnitude when the cure temperature is increased from 325 K to 425 K. As shown in Reference 5, the temperature dependence of τ_{cure} is well described by an Arrhenius expression. The activation energy for the LC/epoxy system (16.2 kcal/mole) is slightly larger than that for the pure epoxy (14.0 kcal/mole).

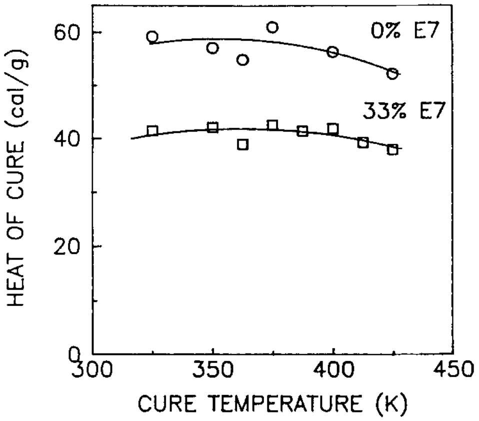

FIGURE 3 Plots of ΔQ_{cure} versus T_{cure} for 3-part epoxy and for 33% E7/epoxy PDLC.

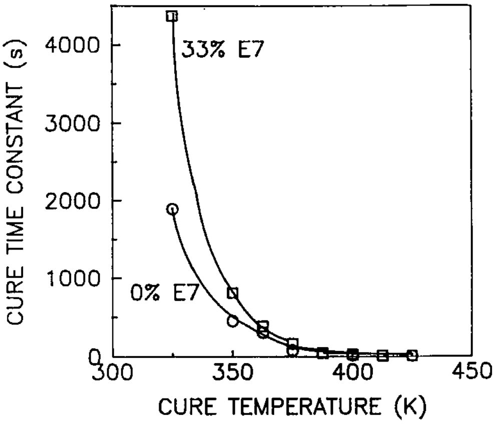

FIGURE 4 Plots of τ_{cure} versus T_{cure} for 3-part epoxy and for 33% E7/epoxy PDLC.

ROTN-404/polyurethane. The heat release curves for cure of ROTN-404/polyurethane samples are nearly ideal[6] (like the 400 K curve in Figure 2). Plots of ΔQ_{cure} versus T_{cure} for four different LC concentrations are given in Figure 5. Despite the scatter, there is evidence for broad maxima near 375 K. The reduction in ΔQ_{cure} due to dilution is apparent.

Temperature and LC concentration affect τ_{cure} in a manner similar to that for the E7/epoxy system (see Figure 6). As for the epoxy-based system, the temperature dependence follows an Arrhenius expression[6] with the activation energy increasing only slightly with LC content (13.5, 14.6, and 14.8 kcal/mole for LC concentrations of 0, 31.4 and 53.3 volume percent). It is clear from Figure 6 that temperature has a much more significant effect on τ_{cure} than does liquid crystal concentration.

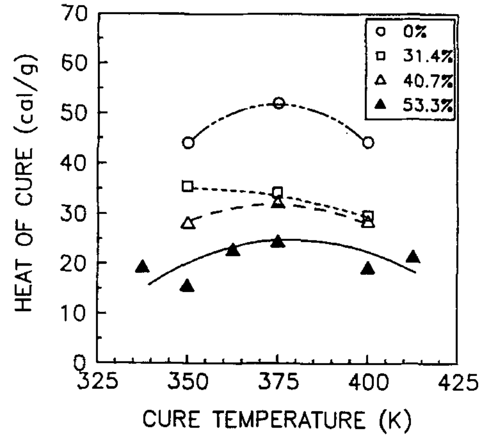

FIGURE 5 Plots of ΔQ_{cure} versus T_{cure} for ROTN-404/polyurethane systems with LC concentrations ranging from 0 to 53.3%.

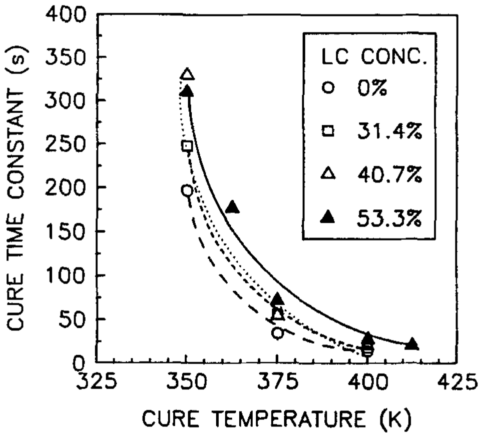

FIGURE 6 Plots of τ_{cure} versus T_{cure} for ROTN-404/polyurethane systems with LC concentrations ranging from 0 to 53.3%.

UV-Cured PDLCs

E63M/NOA65. As is the case for most ultraviolet-cured PDLCs, the shapes of the heat release curves (*dQ/dt* vs. time) for E63M/NOA65 mixtures are nearly ideal (Figure 7).[8] The dependence of ΔQ_{cure} on T_{cure} for this system and also for pure NOA65 are shown in Figure 8. Inasmuch as the temperature range is considerably greater than for the thermally-cured systems, the maxima in the curves are quite prominent. The small values of ΔQ_{cure} at low cure temperatures are due to reduced mobility of the reacting species; at high T_{cure} the reduction results from a shorter lifetime of the radicals.[8] The reduction in ΔQ_{cure} due to the diluting effect of the liquid crystal is also apparent in Figure 8. Of greater interest, however, is the fact that the temperature for maximum cure is considerably down-shifted by the addition of LC. Thus, while pure NOA65 achieves its greatest degree of cure

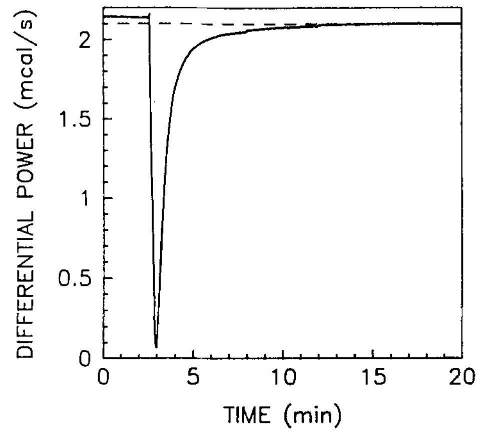

FIGURE 7 Heat release curve for 50% E63M/NOA65 PDLC UV-cured at 300 K (UV intensity = 6 mW/cm^2). Shape is essentially ideal.

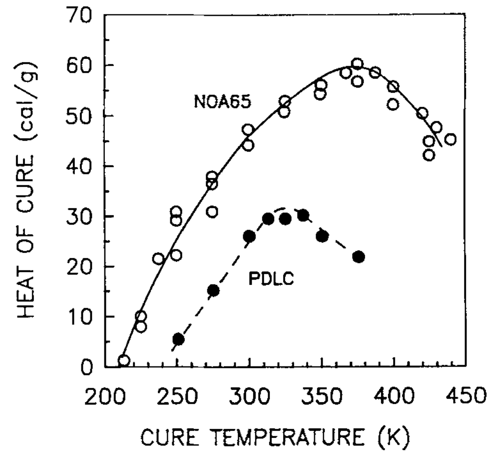

FIGURE 8 Plots of ΔQ_{cure} versus T_{cure} for UV-cured NOA65 and 50% E63M/NOA65 systems.

at about 380 K, D_{cure} for the PDLC matrix is largest at about 325 K. Values of ΔQ_{cure} have been shown to be insensitive to UV intensity.[8]

The dependences of the cure time constants (for a UV intensity of 3 mW/cm^2) on T_{cure} for NOA65 and the PDLC are shown in Figure 9. The behavior is dissimilar to that for thermally cured systems which show monotonic decreases rather than minima. The increase in τ_{cure} of a UV-cured system at low and high T_{cure} is undoubtedly associated with the mobility and lifetime effects discussed in the previous paragraph. Measurements carried out at higher temperatures suggest that thermal decomposition of the matrix commences above 450 K. As for thermally-cured systems, the addition of LC increases the cure time constant. It is known[13] that τ_{cure} for UV-cured systems should scale inversely with the square root of the UV intensity; the E63M/NOA65 system has been shown to obey that relation.[8]

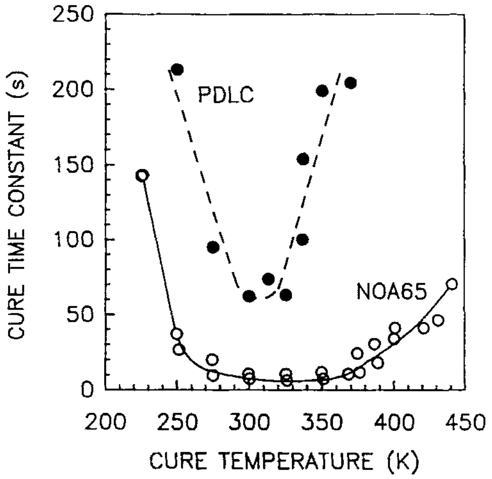

FIGURE 9 Plots of τ_{cure} versus T_{cure} for UV-cured NOA65 and 50% E63M/NOA65 PDLC (UV intensity = 3 mW/cm^2).

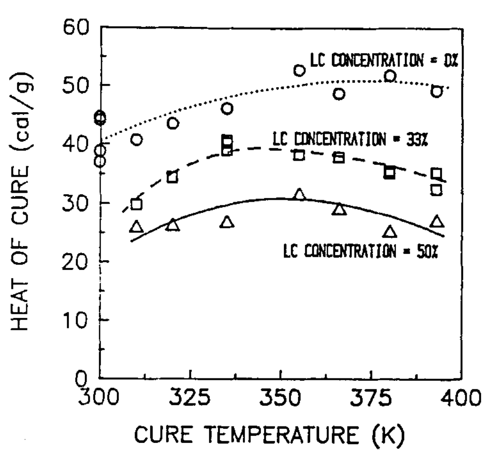

FIGURE 10 Dependence of ΔQ_{cure} on cure temperature for PCPB/NOA65 mixtures.

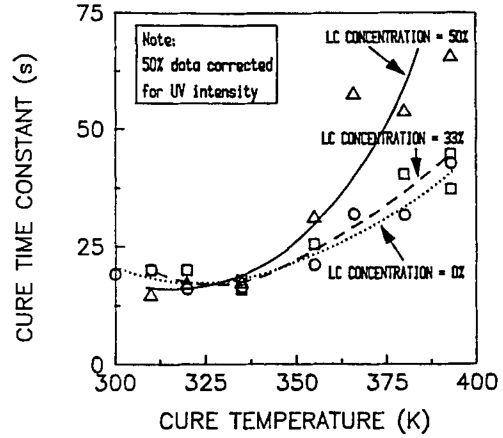

FIGURE 11 Dependence of τ_{cure} on cure temperature for PCPB/NOA65 mixtures. The values are for a UV intensity of 1.5 mW/cm^2 (see text).

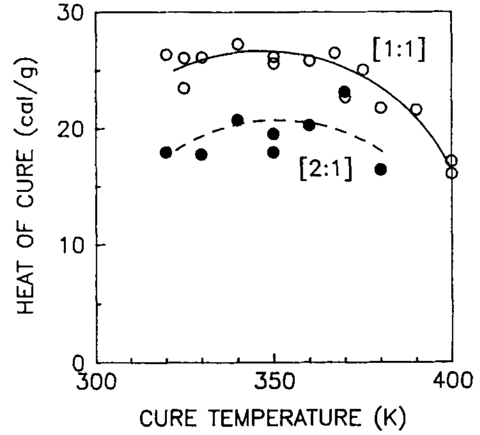

FIGURE 12 Plots of ΔQ_{cure} versus T_{cure} for UV-cured BL009/NOA65 systems with LC concentrations of 50% [1:1] and 67% [2:1].

PCPB/NOA65. The heat release curves for this system are also nearly ideal. Plots of ΔQ_{cure} versus cure temperature are given in Figure 10 for the pure matrix and PDLCs with two different LC concentrations. Maxima like those for E63M/NOA65 are evident.

The cure time constants (for a UV intensity of 1.5 mW/cm^2) are given in Figure 11. Since the data for the 50% samples were taken using a UV intensity of 2.8 mW/cm^2, τ_{cure} values were corrected by a factor (2.8/1.5)$^{0.5}$ The curves exhibit minima like those of other UV-cured systems.[8] As for thermally cured systems,[6] τ_{cure} increases with addition of LC.

BL009/NOA65. The DSC isothermal *dQ/dt* curves for this system are, as for the other UV-cured mixtures, nearly ideal. In Figure 12 are plotted the temperature dependences of ΔQ_{cure} for PDLCs containing 50% and 67% LC ([1:1] and [2:1]

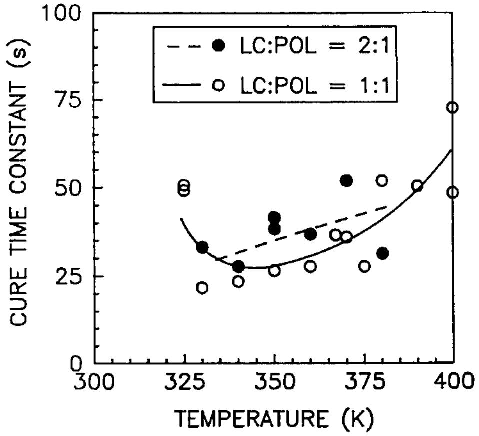

FIGURE 13 Plots of τ_{cure} versus T_{cure} for UV-cured BL009/NOA65 systems with LC concentrations of 50% [1:1] and 67% [2:1] (UV intensity = 3.8 mW/cm^2).

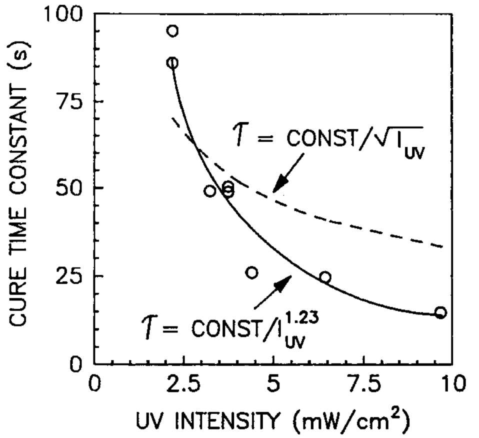

FIGURE 14 Dependency of τ_{cure} on UV intensity for UV-cured 50% BL009/NOA65 PDLC for T_{cure} = 325 K. Clearly the theoretical inverse square root dependence is not obeyed.

mixtures respectively). Again the characteristic broad maxima are seen. As expected, the decrease in the maxima is greater for large LC concentration. No data are shown for $T_{cure} < 320$ K since at lower temperatures demixing of LC and matrix occurs prior to cure. Although the behavior for 50% BL009/NOA65 is similar to that for the 50% mixtures of E63M with NOA65, the maximum for the E63M system is narrower, indicating a greater sensitivity to the choice of cure temperature.

The T_{cure}-dependences of τ_{cure} (UV intensity = 3.8 mW/cm^2) for the two BL009 PDLCs are given in Figure 13. The curve for the 50% mixture shows the expected minimum. The scatter in the data for the 67% system may be due to non-uniformities in cure due to demixing prior to cure (frequently observed for high LC concentrations). In Figure 14 is plotted the dependence of τ_{cure} on UV intensity. The behavior is unlike that reported for the E63M/NOA65 system[8] in that the inverse

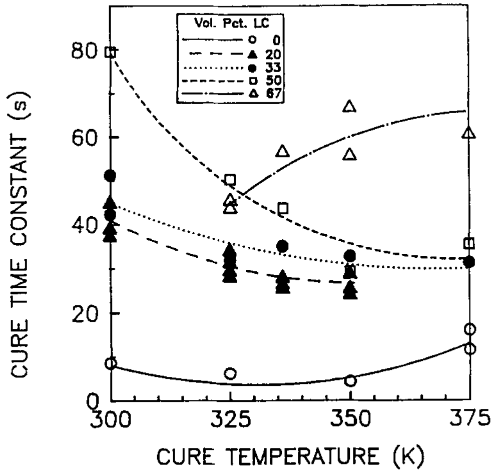

FIGURE 15 Plots of τ_{cure} versus T_{cure} for UV-cured ROTN-404/NOA65 systems with LC concentrations ranging from 0 to 67 volume percent (UV intensity = 10 mW/cm^2).

square-root behavior is not observed. At present we have no explanation for this departure from the norm.

ROTN-404/NOA65. Heat release curves for this PDLC are again nearly ideal. Plots of ΔQ_{cure} for four LC concentrations exhibit considerable experimental scatter. However, there is some evidence for the broad maxima seen for the other UV-cured systems, with the greatest values occurring somewhat above ambient. An increase in LC concentration produces an expected reduction in ΔQ_{cure}.

Plots of τ_{cure} versus T_{cure} are shown in Figure 15 (UV intensity = 10 mW/cm^2). The minima observed for other UV-cured systems are not as pronounced. The behavior for the 67% ROTN-404/NOA65 PDLC is clearly anomalous, perhaps due to demixing effects expected for large LC concentrations. As for the other UV-cured PDLCs, addition of LC increases the cure time constant.

SUMMARY

Since this paper focuses narrowly on cure energetics and kinetics, the conclusions are accordingly brief.

The dependences of the heat of cure of thermally-cured and UV-cured PDLCs on cure temperature are, for the most part, similar. ΔQ_{cure} values exhibit broad maxima at temperatures ranging from 325 K to 400 K for all systems studied. Addition of liquid crystal dilutes the matrix so that the heat of cure decreases monotonically with increasing LC concentration. For all systems ΔQ_{cure} is a measure of the degree of cross-linking (cure) of the matrix.[6,8] For a large degree of cure, phase separation of liquid crystal from the matrix is enhanced, thus increasing the efficiency of LC use.

Cure time constants for the two types of PDLC exhibit differing dependences on T_{cure}. For thermal cure, τ_{cure} decreases monotonically with temperature, obeying an Arrhenius relation. For UV cure, the cure time constant generally exhibits a minimum at cure temperatures somewhat above ambient. An increase in UV intensity reduces τ_{cure}. For both thermal and UV cure, addition of LC increases the cure time constant. As discussed elsewhere,[5-8] τ_{cure} plays a role in determining PDLC microdroplet size, with longer values leading to larger droplets.

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