Notes

Gelation and Development of Liquid Crystalline Order during Cure of a Rigid-Rod Epoxy

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Introduction

Recently, liquid crystalline thermosets (LCT's) have gained increasing interest as a new type of material combining the advantages of liquid crystalline polymers and highly cross-linked thermosets. One of the interesting questions that arises with LCT's is the extent to which the liquid crystalline structure and the cross-linked network affect each other. Various studies have examined the effects of ordered phases on reaction kinetics and the effect of the network on the stability of the liquid crystalline phases. In general it is found that reaction kinetics are enhanced in more ordered phases[1−6] and that the network formation tends to stabilize more ordered phases.[7−10] However, there are a few examples in which the network formation destabilizes the liquid crystalline phase.[11−13] In this study we are focused specifically on gelation and liquid crystalline phase development in a liquid crystalline epoxy, to show how these transformations depend on the degree of conversion.

Experimental Section

4,4′-Diglycidyloxy-α-methylstilbene (DOMS) was synthesized according to the method reported in the literature.[14] The epoxide equivalent weight (EEW) was measured using standard techniques.[15] To prepare samples for curing studies, DOMS was melted at 150 °C, and a stoichiometric amount of sulfanilamide (SAA, purchased from Acros) was dissolved in the melt. The mixture was poured into an aluminum boat and kept in a freezer to prevent further reaction. The liquid crystalline phases and transition times were determined by polarized optical microscopy, obtained by utilizing a Nikon Fluorophot microscope and a Linkham Scientific Instruments HFS 91 hot stage that was controlled by a TMS 91 temperature controller. The DOMS formulation was placed between two 12 mm round, glass microscope coverslips and isothermally cured at various temperature between 120 and 170 °C. Samples were observed between crossed polarizers. Gelation and vitrification times were determined by utilizing a Paar Physica UDS 200, TC 10 temperature controller and a modified TEK 600 with parallel plate geometry utilizing a 25 mm diameter top plate and a 50 mm diameter bottom plate. The sample chamber and plates were preheated to the curing temperature. After preheating, approximately 1 g of the DOMS formulation was loaded on the bottom plate, and the top plate was lowered to a set gap of 1 mm. Then oscillatory shear was applied with a 5% oscillating strain of 1 Hz frequency. The gel time was determined from the crossover point of the storage and loss moduli (tan $\delta = 1$), and the vitrification time was determined from the maximum point of the second peak of the tan δ curve. Conversion as a function of cure time at different temperatures was measured using differential scanning calorimetry (DSC). DSC was performed utilizing a Seiko Instruments SSC5200 DSC220C with an SDM5600H data station. A small quantity of the DOMS formulation (5−9 mg) was weighed into an aluminum, sealed pan and placed in an oven to be partially cured for various times. Then dynamic scans were performed within a temperature range of −30 to 330 °C at a heating rate of 10 °C/min in a nitrogen atmosphere. The residual enthalpy of the cure exotherm was measured and used in combination with the enthalpy of cure for an uncured sample to determine the degree of conversion.

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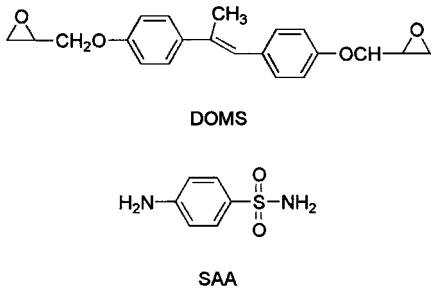

Figure 1. Molecular structures of diglycidyloxy-α-methylstilbene (DOMS) and sulfanilamide (SAA).

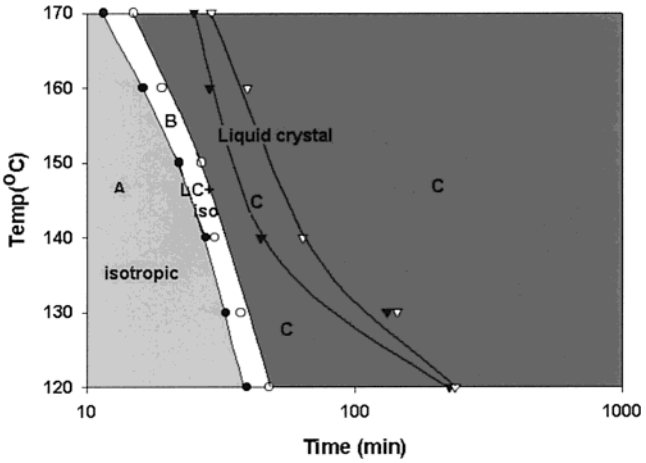

Figure 2. LCPTTT diagram for the DOMS−SAA system: ●, onset of liquid crystalline phase formation; ○, completion of liquid crystalline phase formation; ▼, gelation; ▽, vitrification.

Results and Discussion

Figure 2 shows the liquid crystalline phase time−temperature transformation (LCPTTT) diagram for the DOMS/SAA system. This diagram shows the well-known transition from isotropic to liquid crystalline phase during cure for DOMS/SAA.[16] This diagram is similar to other transformation diagrams for LCT's,[8,9,17,18]

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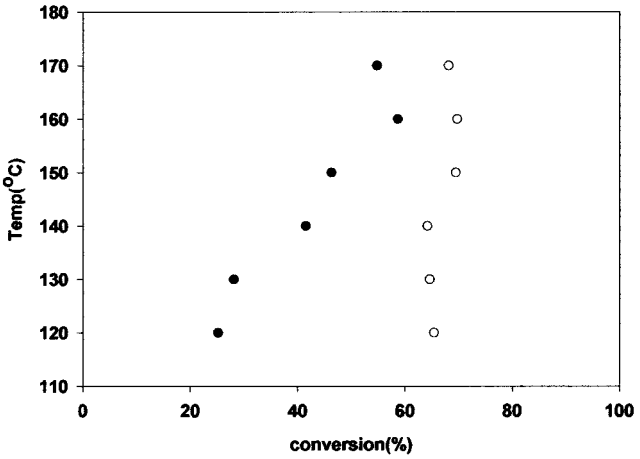

Figure 3. Temperature vs conversion for phase transition (●) and gelation (○).

Table 1. Times of Liquid Crystalline Phase Appearance (t_{lc}), Gel Point (t_{gel}), and Conversion at Phase Transition (α_{lc}) and at Gel Point (α_{gel})

T (°C)	t_{lc} (min)	t_{gel} (min)	α_{lc} (%)	α_{gel} (%)
120	48.03	222.50	25.17	70.16
130	37.52	131.50	28.10	64.56
140	30.05	44.50	41.49	64.14
150	26.70	37.00	46.27	69.44
160	19.00	28.50	58.63	69.71
170	14.93	22.00	54.73	68.15

although in our case we include the gelation and vitrification times, which are usually not included on such diagrams.

Figure 3 shows the conversion at the gel point as a function of cure temperature. Most notably, Figure 3 shows that the isoconversion theory of gelation holds for this system, as has been previously shown for isotropic epoxies.[19−21] This is true even though DOMS/SAA experiences different amounts of cure in liquid crystalline phases at different cure temperature. For example, at the cure temperature of 120 °C, cure in the isotropic phase occurs up to a conversion of 25%, while at 160 °C cure in the isotropic phase occurs up to a conversion of 59% (see Table 1). At both temperatures gelation occurs at 70% conversion, so at 120 °C considerably more of the reaction prior to gelation occurs in the liquid crystalline phase. Even though the amount of reaction that occurs in the liquid crystalline phase is different at these different cure temperatures, the isoconversion theory of gelation fits quite well. Thus, gelation is independent of liquid crystalline phase as well as cure temperature.

The actual value of the conversion at the gel point averaged across all temperatures is 0.677. This experimental value is slightly higher than the calculated theoretical value of 0.577, and the difference is due to the failure of the assumptions of this theory. In reality, there is a reactivity difference between the two amine groups of SAA and intramolecular connections are possible. Therefore, to reach the critical point, the reaction must go further since some linkages are wasted for intramolecular ring formation.[22]

Under kinetically controlled conditions, the reaction rate can expressed by an Arrhenius rate expression.[19,23] Table 1 shows the times and conversions at the phase transition and gel point. From an Arrhenius plot of these data we obtain an activation energy of 68.4 kJ mol^{-1}. This is a comparable value to that for the diglycidyl ether of bisphenol A cured with different amines.[23,24] Laza et al.[24] calculated the activation energy from the gel time method as 53−71 kJ mol^{-1}, and Cadenato et al. [23] calculated it as 47.2−52.9 kJ mol^{-1}. The similarity of the activation energy for DOMS/SAA with non-liquid crystalline epoxies further confirms that gelation is unaffected by the liquid crystalline phase.

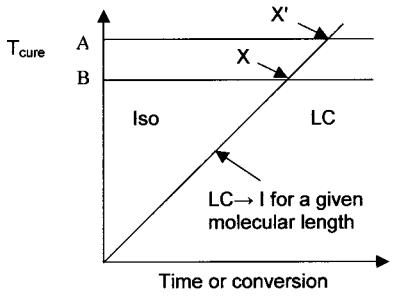

Figure 4. Idealized plot for cure temperature vs time or conversion.

Our results can be compared to previous studies on gelation in LCT's. Jahromi et al. have shown that gelation occurs at the same conversion as expected for a non-liquid crystalline epoxy, although measurements were made at only a single cure temperature.[25] A similar result has been found by Shiota et al. for a dicyanate LCT.[26] However, Mormann and Zimmermann found that a dicyanate LCT did not follow the isoconversion theory for gelation.[27] They found that the gel point conversion increases with increasing temperature and explain this as being caused by some type of molecular association. It is not clear why their results differ from ours, but it may be related to differences in the monomer structure or differences in the nature of the curing reaction between epoxies and cyanates.

Figure 3 also shows the plot of phase transition temperature vs conversion. In contrast to gelation, the phase transitions do not show isoconversion behavior. Instead, the conversion at the point where the isotropic phase changes to a liquid crystalline phase tends to increase with temperature. This is due to the fact that the critical length of the molecules needed for liquid crystallinity increases with temperature. Figure 4 is an idealized plot that explains this phenomenon. The straight line shows the increase of isotropization temperature with increasing cure time or molecular length (i.e., conversion). We note that Fukuda et al. have modeled this increase in isotropization temperature with chain length for thermotropic semiflexible polymers,[28] and it has been observed experimentally for DOMS/SAA by Lin et al.[7] and in a dicyanate LCT by Mormann and Zimmerman.[29] If DOMS is cured at temperature A, it will start to show liquid crystallinity at point X, where the straight line and the cure temperature line cross. If the cure temperature increases to B, DOMS needs more time to show liquid crystallinity (X′). Therefore, the molecular length needs to be longer; i.e., the conversion needs to be higher. Our result showing the increase in transformation time as the cure temperature increases for the DOMS−SAA system (isotropic-to-smectic transition) has also been reported for epoxies exhibiting an isotropic-to-nematic transition,[30] suggesting that this is a general phenomenon related to the mechanism of epoxy cure and is not dependent on the type of liquid crystalline phase that forms. However, a dicyanate LCT was found to show isoconversion behavior for the isotropic-to-nematic tran-

sition.[26] In this case the authors attribute the formation of the nematic phase to oligomers with a very high glass transition. Thus, the difference between the dicyanate and epoxy systems may be attributed to the mesogenic potential of the monomers and/or oligomers that form early in the reaction.

In summary, by curing the liquid crystalline epoxy, 4,4′-diglycidyloxy-α-methylstilbene, with the curing agent, sulfanilamide, the isoconversion theory of gelation was confirmed; i.e., the conversion at gelation was uniform regardless of the liquid crystalline phase as well as cure temperature. This result indicates that the actual network formed by these molecules is unaffected by any long-range order that may be present and is only controlled by the functionality of the individual molecules. We note that this study does not address the issue of whether the reaction actually occurs at a faster rate in the liquid crystalline phase, but rather that gelation occurs in the same manner as non-liquid crystalline epoxies with respect to the conversion dependence and the structure of the resulting network.

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