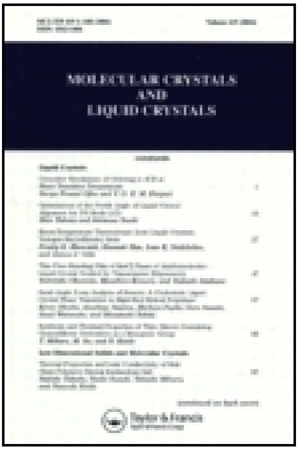

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Curing Reaction Kinetics of Liquid Crystalline Resin Based on 6,6′-Bis (2,3-Epoxypropoxy)-2,2′ Binaphthyl

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To cite this article: Eugenio Amendola, Cosimo Carfagna, Marta Giamberini, Nicola Fuccia & Giovanni Micco (1999): Curing Reaction Kinetics of Liquid Crystalline Resin Based on 6,6′-Bis (2,3-Epoxypropoxy)-2,2′ Binaphthyl, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 336:1, 183-198

To link to this article: http://dx.doi.org/10.1080/10587259908026031

Mol. Cryst. and Liq. Cryst., 1999, Vol. 336, pp. 183-198
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Curing Reaction Kinetics of Liquid Crystalline Resin Based on 6,6'-Bis (2,3-Epoxypropoxy)-2,2' Binaphthyl

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The curing kinetics of an epoxy stoichiometrically equivalent mixture of 6,6'-bis (2,3-epoxypropoxy)-2,2' binaphthyl (EPBN) and 4,4'-diaminodiphenyl sulfone (DDS) has been determined experimentally. A liquid crystalline phase forms during the curing reaction. A phenomenological model of the curing process has been developed, with parameter values extracted from the data by fitting of separate parts of the DSC curves. If the conventional reaction scheme proposed for the addition reaction of amines to epoxy groups holds true, then the overall reaction can be modeled, and the contribution of the phase transition occurring during the hardening reaction can be evaluated and modeled.

Keywords: epoxy resins; liquid crystalline thermosets; curing kinetics

INTRODUCTION

Scientific literature in the field of liquid crystalline polymers has kept growing in the last years, and this has increased interest in the field of thermosetting liquid crystalline systems, due to their unique properties and promising applications in different fields. Thermosetting liquid crystalline polymers (TLCP's) have been considered since the early 1970 (1-8), and several main classifications are recognized today. The distinctive feature of polymeric networks is the presence of inter-chain links preventing the viscous shearing and flow of molecules even at temperatures higher than Tg.

However, in TLCP's the molecular arrangement is far from the random coil conformation, and molecular ordering is still reminiscent of the liquid crystalline structure developed before the crosslinking of the network..

The structural characteristics leading to the formation of liquid crystalline phases in the TLCP are analogous to the features of low molecular weight or thermoplastic liquid crystalline polymers. We will restrict our discussion to phases originated by rigid and elongated mesogenic moieties, included in the primary chemical structure forming the network. Once the final network is formed, only micro-brownian motions and small-scale molecular movements are permitted. Depending on the crosslinking density and on the chemical structure (i.e. the side-group or main-chain network) the clearing point of the mesophase can be observed or not. In the case of main chain TLCP, the clearing point can be observed only if the crosslinking extent is rather low. On the other hand, in the case of high crosslinking extent, it has been reported that the liquid crystalline phase is stable up to very high temperatures.

It has been reported that the overall curing reaction kinetics is strongly affected by the presence of a liquid crystalline phase (9-11). On the other hand, the reaction mechanism has not been investigated directly. If the conventional reaction scheme proposed for the addition reaction of organic amines to epoxy groups holds true, then the overall reaction can be modeled, and the contribution of the phase transition occurring during the hardening reaction can be evaluated and modeled according to an Avrami like equation (12-14). The literature concerned with the modeling of reactive systems suitable to form liquid crystalline phases is quite recent (9-11).

In this paper the epoxy stoichiometrically equivalent mixture composed by 6,6'-bis (2,3-epoxypropoxy)-2,2' binaphthyl (EPBN) and 4,4'-diaminodiphenyl sulfone (DDS) is analyzed. A kinetic model is proposed, taking into account the phase transition occurring during the crosslinking reaction. The high reactivity of the epoxy group makes it an excellent candidate for the preparation of crosslinking resins. The reaction proceeds through completion with high yields using a variety of crosslinking agents. The most frequently used are amines, carboxylic acids, anhydrides, thiols etc. In particular, the addition of aromatic and aliphatic amines to the epoxy group has been studied extensively (15-17). The reaction proceeds through a nucleophilic attack of the amine onto the epoxy ring, and is very sensitive to the presence of traces of water, alcohol or protons that strongly catalyzes the reaction. The hydroxyl produced from the opening of the epoxy rings also behaves as catalyst, determining the autocatalytic features of the reaction. Primary amines are generally used in the formulation of crosslinking resins, because each of the two hydrogen atoms reacts with the epoxy group, determining the formation of a crosslink. After the formation of the secondary amines, a competition establishes between the addition of the primary amines still present in the reacting mixture and secondary amines previously formed. It has been reported that the addition of the primary amines is favored with respect to the addition of the secondary ones, because of reduced steric hindrance (15,18). Nevertheless, it cannot be assumed that the addition of the secondary amines to the epoxy groups starts only after the exhaustion of the primary ones. The aliphatic or aromatic nature of the organic amines also strongly affects the overall reaction kinetics, being the aromatic amines more reactive than the aliphatic ones.

Despite the complexity of the reaction mechanism involved in the reaction of epoxy resins with amines, the overall reaction rate can be expressed by means of relatively simple and phenomenological kinetic equations(15-17).

EXPERIMENTAL

Materials

The chemical structure of EPBN and DDS used in the formulation of the mixture is illustrated in Figure 1. The synthesis of the epoxy compound has already been reported in the literature by our group (19).

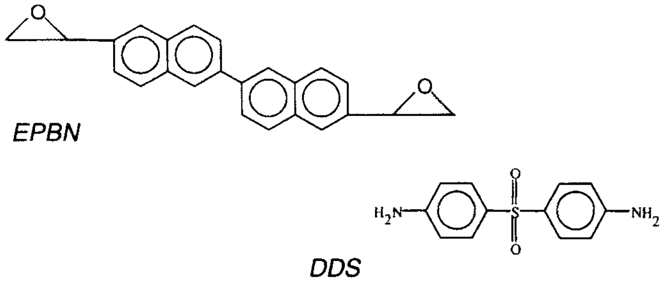

FIGURE 1, Chemical structures of 6,6'-bis (2,3-epoxypropoxy)-2,2' binaphthyl (EPBN), and 4,4'-diaminodiphenyl sulfone (DDS)

The epoxy terminated compound and the tetrafunctional amine were mixed in the molar stoichiometric ratio of 2/1. The mixture was prepared by dissolving the epoxy compound and the amine in chloroform at room temperature. The solvent was subsequently evaporated and the solid residue finely ground. The sample was then desiccated under vacuum. Care has been taken to perform the previously described procedure at room temperature and as fast as possible in order to prevent the crosslinking reaction during the mixture formulation.

Differential Scanning Calorimetry (DSC)

Thermal characterization was performed with a TAI differential scanning calorimeter (DSC) mod. 2910. Both isothermal and dynamic scans at 10°C/min were run using nitrogen as purge gas.

Optical Microscopy (OM)

The liquid crystalline texture formed during the curing reaction was observed with a Reichert-Jung optical microscope (OM) mod. Polyvar under crossed polarizers using a magnification of 100X. The curing temperature was controlled by means of a hot stage Linkam mod. TH 600. DSC and OM were performed on two separate samples, taking care that initial and operating conditions were as close as possible in the two samples. Formation of the liquid crystalline phase during isothermal observations was recorded on videotape and the images subsequently captured for further evaluation. The analysis of time based sequences of pictures were performed on a Macintosh computer using the public domain NIH Image program (developed at the U.S. National Institutes of Health and available on the Internet at http://rsb.info.nih.gov/nih-image/)". The extent of phase transformation was evaluated by measuring the birefringent fractional area, ranging from 0 to 1. The plots of birefringent fractional area vs. time are used to correlate the extent of reaction and the phase transition during isothermal experiments.

RESULTS AND DISCUSSION

The overall heat for complete reaction evolved during isothermal experiment can be affected by the occurrence of gelation. If the curing reaction is performed at temperatures higher than Tg of the cured network, the ΔH is insensitive to the curing reaction. On the other hand, if the reaction is performed at temperatures lower than Tg, at some value of $\alpha < 1$ (where α is the fractional conversion of the crosslinking reaction) the sample gets into the glassy state. The slow diffusion through the glassy polymer greatly reduces the reaction speed, eventually stopping the crosslinking before the complete exhaustion of reagents. In this case, the enthalpy of reaction is proportional to the curing temperature (20-22). Fractional conversion α can be expressed by equation 1.

$$\alpha_{(t)} = \frac{\int_0^t dHdt}{\int_0^\infty dHdt} \qquad (1)$$

where *dH* is the DSC heat flow.

We have performed the DSC analysis in the temperature range between 225 and 260°C. The glass transition of the cured resin is around 140°C, and therefore the reaction enthalpy is expected to be constant. However, the DSC baseline at the beginning of the reaction is disturbed by the introduction of the sample in the cell. Therefore, the use of a straight horizontal baseline underestimates the reaction enthalpy. A second run on the completely reacted sample can be used as baseline to properly evaluate the total heat evolved during the reaction (23). The results of this analysis are reported in Table 1.

TABLE 1. Reaction enthalpy at different curing temperatures.

Temp (°C)	ΔH measured (J/g)	ΔH corrected (J/g)	correction %
225	248.7	275.1	10.6
230	252.6	283.2	12.1
235	250.1	278.4	11.3
240	245.6	280.1	14.1
250	229.3	269.0	17.3
260	238.9	277.8	16.3

Typical DSC curves are shown in Fig.2. Increasing the temperature results in increased reaction speed. The distinguishing features of double peaks and shoulders can be observed in the temperature range at which the curing was performed. Similar behavior was previously reported for liquid crystalline thermosets, but was never detected for conventional epoxy resins.

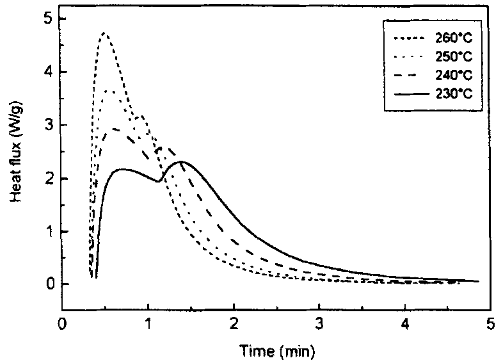

FIGURE 2, DSC spectra of EPBN/DDS mixtures recorded in isothermal mode at 225, 230, 235, 240, 250, and 260°C. N_2 flow was used as purge gas.

Double peaks have been related to the formation of a liquid crystalline phase by means of optical microscopy. In fact, an isotropic phase results after melting of the reactants at the beginning of the reaction. During the first stages of the reaction, statistical and thermodynamic arguments strongly induce the formation of dimers and trimers with respect to the development of branching and crosslinking, and this leads to an increase in concentration and average molecular weight of the linear oligomers. The liquid crystalline phase appears at some intermediate fractional conversion as a consequence of increased geometric constraints between the semi-rigid molecules and the insurgence of hydrogen bonds. The primary role of hydrogen bonds in stabilizing the liquid crystal phase is inferred by the formation of liquid crystalline phase also in the case of very short rigid groups(24), whose geometric aspect ratio is close to unity. Formation of the liquid crystalline phase can be monitored by optical microscopy, measuring the fraction of birefringence in the sample, as shown in Fig.3.

The second peaks in DSC plots observed in the temperature range between 225 and 260°C are due to an increase of reaction speed and to the exothermic contribution of phase transition from isotropic to nematic. Nevertheless, the enthalpy transition of similar compounds is about 4-5 J/g, and therefore can be neglected with respect to the reaction enthalpy, reported in Table 1. The DSC plots have been converted to reaction rate vs. fractional conversion plots in Fig. 4. The shift of the curves is due to the initial offset calculated in Table 1. The decreasing contribution of the second peaks as the temperature increases (see Fig.2 and 4) is due to the destabilization of the liquid

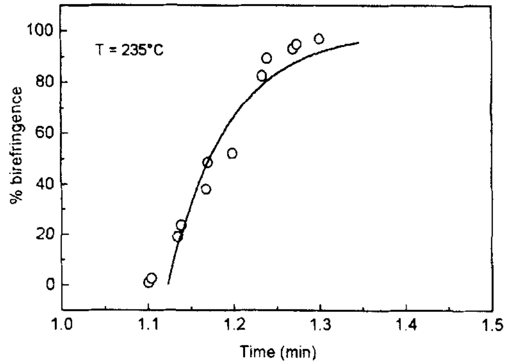

FIGURE 3, Percentage of birefringente sample area vs. total sample area measured by optical microscopy during curing performed at 235°C. Open circle: experimental values; solid line: drawn to assist reading.

crystalline phase at higher temperatures. In fact, the formation of the liquid crystalline phase is not observed if the curing temperature exceeds the transition temperature to the isotropic phase of the growing polymer. Moreover, the critical fractional conversion for the formation of the liquid crystalline phase progressively shifts towards higher values, as the temperature increases, because longer molecules with increased overall aspect ratio are needed to induce the liquid crystalline phase transition as the temperatures goes up.

We wish to develop a phenomenological model capable of describing all the essential features of the experimentally observed curing behavior. We do not intend to infer any specific chemical meaning to the parameters appearing into the model itself. The first experimental observation to be taken into account is that the birefringence, which is regarded as the indication of the existence of the liquid crystalline phase, appears only at a critical value of fractional conversion greater than zero. Let W be the fractional volume of the liquid crystalline phase in the sample. The plot in Fig. 3 can infer the trend of

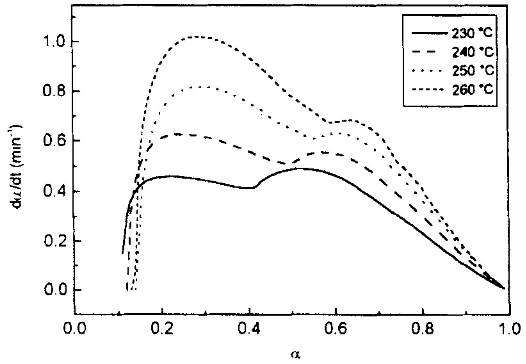

FIGURE 4. Reaction rate plots vs. fractional conversion at 225, 230, 235, 240, 250, and 260°C.

W during the curing reaction. Even if the real behavior is rather complicated, and many factors are responsible for the formation of the liquid crystalline phase during the crosslinking reaction, we split the fractional conversion range into three regions, namely the

isotropic kinetic range;	$0<\alpha<\alpha_i$;	W=0
transition kinetic range;	$\alpha_i<\alpha<\alpha_e$;	0<W<1
liquid crystalline kinetic range;	$\alpha_e<\alpha<1$;	W=1

Isotropic range kinetics.

The isotropic kinetics is certainly autocatalytic(15-17), since the hydroxyl produced from the opening of the epoxy rings behaves as catalyst, as shown by the fact that $d\alpha/dt$ initially grows. The fitting of data in the range $0<\alpha<\alpha_i$ by equation 2 results in the data summarized in Tab. 2.

$$\phi = d\alpha/dt = k\alpha^m (1-\alpha)^n \qquad (2)$$

Linear fitting of the Arrhenius plot for k gives the values of E_a = *107 kJ/mol* and $\ln k_0$ = *26*. An Arrhenius like equation can also predict the values for m and n, the reaction orders. The use of variable reaction orders is an indication that the reaction mechanism is rather complex, nevertheless the overall reaction order range between 2 and 3, as described in the literature (15-17).

TABLE 2, Isotropic kinetics parameters.

Temp (°C)	k	m	n
225	1.17	0.42	1.66
230	1.46	0.50	1.68
235	1.89	0.53	1.84
240	2.43	0.61	1.80
250	3.94	0.75	1.87
260	6.20	0.87	2.13

Consider now the case at $\alpha>\alpha_i$, where W>0. We make the following assumptions:

a) The kinetics of crosslinking is different in the isotropic and in the liquid crystalline phase.

b) Although there is now a volumetric fraction of the sample W which is liquid crystalline, and a fraction 1-W which is still isotropic, the value of α is the same through the sample. This is a rather strong assumption, but necessary assumption. Detailed studies of diffusion mechanism through the domain boundary should be performed to postulate a more refined model.

If the phase transition kinetics is much faster than the reaction kinetics, which indeed is the case, the second assumption can be considered quite reasonable. In fact, W very soon reaches a value close to unity, and the fractional conversion range where the assumption b) has to be considered is very limited indeed.

Liquid crystalline range kinetics.

The reaction kinetics in the range $\alpha_e<\alpha<1$ is also autocatalytic, and fitting results of experimental data by Equation 3 are reported in Table 3.

$$\Phi = d\alpha/dt = K\alpha^M (1-\alpha)^N \qquad (3)$$

Linear fitting of the Arrhenius plot for K gives the values of E_a = *81 kJ/mol* and $\ln k_0$ = *20*. The reaction order is still variable with the temperature, the overall reaction order ranging again between 2 and 3.

TABLE 3. Liquid crystalline kinetics parameters.

Temp (°C)	K	M	N
225	1.97	0.73	1.37
230	2.52	0.85	1.35
235	3.04	0.97	1.38
240	3.76	1.13	1.38
250	5.36	1.36	1.46
260	7.05	1.62	1.57

Phase transition range kinetics

The increased reaction rate in the liquid crystalline phase is responsible for the formation of peaks in the DSC curve. The mechanism of transition from isotropic to liquid crystalline phase can be investigated by optical microscopy. Nevertheless, the microscopic data are invariably biased by the sensitivity of the technique, which is not suitable to detect the formation of liquid crystalline domains. The overall reaction kinetics can be expressed by Equation 4.

$$\frac{d\alpha}{dt} = (1-W)k\alpha^{m}(1-\alpha)^{n} + WK\alpha^{M}(1-\alpha)^{N} \qquad (4)$$

After having extracted the parameters for the isotropic and liquid crystalline kinetics it is possible to calculate the values of W which better describe the phase transition and the formation of peaks in the reaction rate plots. W is considered as an adjustable parameter in the phase transition range.

TABLE 4, Avrami-like parameters.

Temp (°C)	α_i	θ	v
225	0.31	267	3
230	0.33	267	3
235	0.34	267	3
240	0.38	267	3
250	0.41	267	3
260	0.46	267	3

The values obtained are then fitted with an Avrami like equation (12). The Avrami equation was originally developed to describe the formation and growth of oxide particles onto metallic surfaces. Since then it has been applied in the polymer science to model the crystallization phenomenon. The Avrami equation is simply phenomenological, and we have slightly modified the original form of the equation resulting in the following:

$$W = 1 - \exp(-\theta\alpha^{v}) \qquad (5)$$

The parameters used to model the Avrami-like equation are summarized in Table 4. The values of α_i are assigned to give the best fitting of the overall reaction rate plots, and to test the validity of the model they have been compared with the microscopy observation. In fact the appearance of birefringence was investigated by OM, and the corresponding α_i values calculated are in very good agreement with data of Table 4. They can be modeled by an Arrhenius equation, with activation energy $E_a = 25\ kJ/mol$ and pre-exponential factor $ln\ k_0 = 5$.

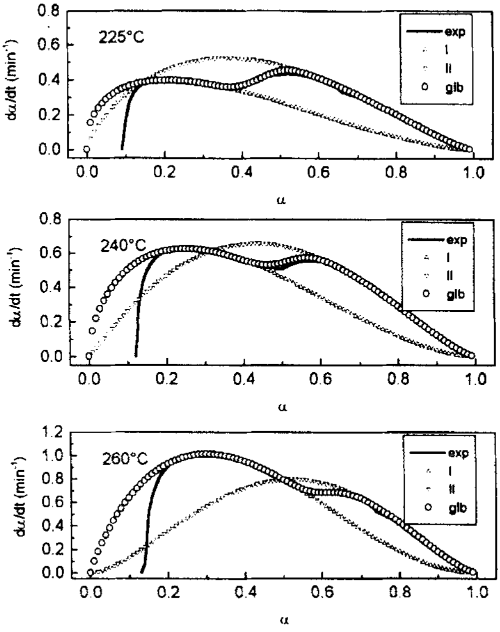

FIGURE 5. Fitting results: reaction rate plots vs. fractional conversion at 225, 240, and 260°C. Solid line: experimental; upright triangle: isotropic kinetics; upside-down triangle: liquid crystalline kinetics; circle: overall kinetics.

CONCLUSIONS

The observation of unusual curing kinetics of liquid crystalline resins led to the conclusion that the formation of liquid crystalline phase during curing reaction is responsible for the unique curing pattern. The appearance of double peaks and shoulders in the DSC plots is invariably associated to formation of the liquid crystalline phase during the curing reaction, and has never been reported for the curing reaction of conventional epoxy resins. We present a kinetic model that takes into account different reaction rates for the isotropic and liquid crystalline phase, and the phase transition as well. We

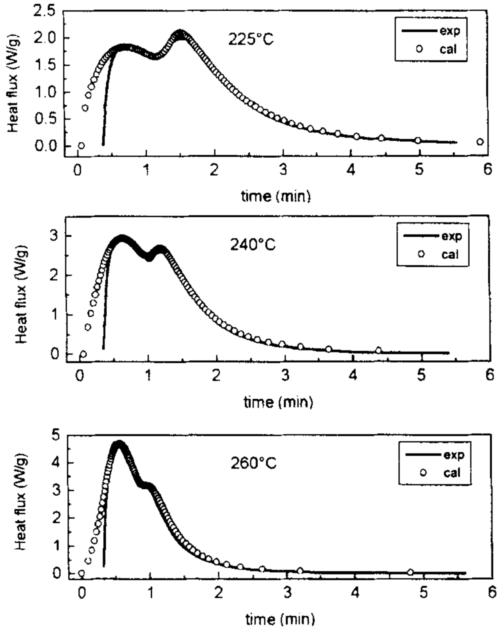

FIGURE 6. Fitting results: heat flux vs. time at 225, 240, and 260°C. Solid line: experimental; upright triangle: isotropic kinetics; upside-down triangle: liquid crystalline kinetics; circle: overall kinetics.

have tested the model for different epoxy systems, and the agreement between the experimental data and the calculated reaction rate values has been very good, despite the quite strong approximations we have adopted. All the parameters in the model have been extracted by fitting of different regions of reaction rate plots and by OM observation. Therefore they are not the result of a multiparameter non-linear regression.

The results of the fitting are shown in Fig.5 (reaction rate vs. fractional conversion) and in Fig.6 (heat flux vs. time). The agreement between the experimental data and the calculated values is good enough to support the reliability of the proposed model. We plan to check the model reliability for different classes of reaction leading to the formation of a liquid crystalline phase during the formation of a network.

Acknowledgments

The financial support of MURST (Research Programme of National Relevance 1997) is gratefully acknowledged.

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