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Curing kinetics of liquid-crystalline epoxy resins

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By endcapping mesogenic rigid rod molecules with reactive epoxy groups a novel class of liquid-crystalline thermoset has been obtained. In fact it has been shown that the nematic molecular arrangement is sustained over the crosslinking reaction of liquid-crystalline epoxy resins when the curing reaction is carried out in the thermal stability range of the liquid-crystalline phase. Calorimetric analysis was used in characterizing the isothermal cure. An unsophisticated model is proposed for evaluating the activation energies of the crosslinking reaction. For liquid-crystalline epoxy resins lower activation energies result with respect to the cure reactions for non liquid-crystalline epoxy resins.

1. Introduction

Liquid-crystalline thermosetting elastomers have been extensively studied by Finkelmann *et al.* [1]. More recently Hoyt *et al.* [2] have found that, by endcapping rigid rod molecules with maleimide groups, it is possible to crosslink the polymer as a stable mesophase by heating the monomers in the molten state. In recent years intense scientific and patent activity has been concentrated on the synthesis of new liquid-crystalline epoxy resins [3-7]. These resins can offer a new rewarding challenge in the field of high performance materials. In fact they can combine potentially the performances of epoxies with the outstanding properties of liquid-crystalline polymers. Therefore a mesogenic epoxy resin can unveil higher mechanical properties, better chemical and heat resistance, lower viscosity during the processing. In particular, the Achilles' heel of commercial epoxy resins, their brittleness, can be strongly reduced in the case of an ordered crosslinked material [8].

Curing of epoxy resins has been studied extensively [9-12]. In particular large efforts have been directed towards finding the relationship between the cure kinetics and the physical properties of the crosslinked polymers. The conditions of ideality, identified by Flory for an infinite network, no longer hold true as the molecular weight increases during the curing process [13]. An ideal network has been defined by Dusek and Prins as 'a collection of gaussian chains between f -functional junction points (crosslinks) under the condition that all functionalities of the junction points have reacted with the ends of all and different chains' [14]. The non-ideality of the real network can be caused by structural imperfections which may be an actual feature of the system prior to crosslinking or may form as a result of crosslinking. Among these

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imperfections, Dusek and Prins include the presence of a pre-existing order, that could be natural, involving the presence of crystallites, or imposed by external means, such as shear or liquid convection flows. In the case of liquid-crystalline epoxy resins the non-ideality of the network could be caused by the rigid rod nature of the reactive monomers which affects the order of the growing thermoset. This effect could be relevant in the first step of the reaction, modifying the reactivity of the reagents before gelation of the network. Moreover, since the formation of a nematic mesophase usually causes a strong reduction of the viscosity for thermotropic polymers, it is expected that during the second step of crosslinking, in which the reactivity of the molecules is diffusion controlled, the degree of cure can also be influenced by order of the material.

Here we present and discuss the cure kinetics of two mesogenic liquid-crystalline epoxy resins, cured with a diamine, and compare them with the curing kinetics of epoxy resins that give an isotropic network upon crosslinking. Due to the complexity of the phenomenon, the experimental procedure and the kinetic equation selected to explain the mechanism of cure are very simple, but appear to be suitable to explain the differences between the two classes of compounds. We are aware of the huge amount of literature regarding the mechanism of cure of epoxies, in particular those cured with amine, for which different theories have been developed to explain the different reactivity of primary and secondary amine hydrogen atoms. However a complete theory of the curing of liquid-crystalline epoxy resins is beyond the scope of this paper.

2. Experimental

4,4'-Dihydroxy- α -methylstilbene was synthesized according to the procedure described in the literature [15]. In a typical preparation chloroacetone (5.5 g) and phenol (107 g) were placed in a 500 ml, four-neck flask equipped with a stirrer, temperature probe, N₂ sweep and addition funnel. While stirring, it was cooled to 8°C; H₂SO₄ (96 per cent, 59 g) was added dropwise maintaining the temperature at 5°C. After one hour, 90 per cent of the H₂SO₄ had been added, the temperature increased to 43°C. 100 ml of isopropyl alcohol were added. At the end of the addition of acid the mixture was added to 1 l of cold water. The water was decanted off and more [11] added. The product was recrystallized from a water-ethanol mixture. $T_m = 182^\circ\text{C}$ (lit. 182°C [15]).

4-Methyl-*m*-phenylen-diamin, hydroquinone and dihydroxydiphenyl were purchased from Aldrich Chemical Company and used without any further purification. 2,6-Diamino-3,5-diethyltoluene (Shell Oil) was used as received. Figure 1 reports the molecular structures of the compounds selected for this study.

Functionalization of the hydroxy terminated compounds with glycidyl groups was readily achieved by using epichlorohydrin in the presence of sodium hydroxide according to the procedure described in the literature [16]. In the case of 4,4'-diglycidyl- α -methylstilbene (DOMS) a white solid (yield 96 per cent) was obtained with a WPE (epoxy equivalent) 185 (theoretical 169) and a T_m of 130°C. The elemental analysis gave the following results: carbon 74.32 per cent; hydrogen 6.51 per cent (theoretical values: C 74.54 per cent; H 6.55 per cent). In the case of 4,4'-diglycidyl-diphenyl (DIF) the yield was 65 per cent, WPE 166 (theoretical 149) and T_m of 153°C. The elemental analysis gave the following results: carbon 72.44 per cent; hydrogen 5.99 per cent (theoretical values: C 72.47 per cent; H 6.08 per cent). 4,4'-Diglycidylbenzene (HQ) (yield 30 per cent) was characterized by a WPE of 120 (theoretical value 111) and a T_m of 115°C. The elemental analysis gave: carbon 64.59 per cent; hydrogen 6.28 per cent (theoretical values: C 64.85 per cent; H 6.35 per cent).

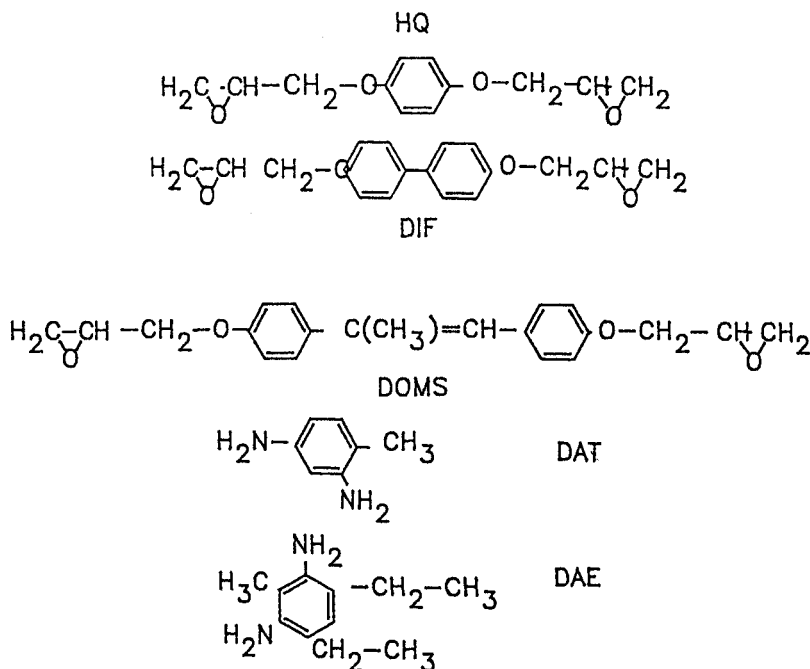


Figure 1. Molecular structures of the compounds used in this study.

Curing of the networks was carried out by mechanically mixing a 2:1 stoichiometric ratio of the glycidyl terminated molecules to the diamine compounds and then heating the mixture directly in the DSC pan to the desired temperature. The calorimetric analysis was performed with a Du Pont DSC (mod. 2940) at a heating rate of $10^\circ\text{C min}^{-1}$ for dynamic scans. N_2 was used as the purge gas. The textures of the liquid-crystalline phases were observed by means of an optical microscope (Reichert-Jung, mod. Polyvar) under crossed polarizers equipped with an hot stage (Linkam, mod. TH 600). FTIR spectra were recorded at room temperature with a Nicolet model 5PC spectrophotometer with 5 cm^{-1} resolution. Films were prepared by curing the polymer between two steel plates at 135°C for 10 min for DOMS-DAT, and for 60 min for DOMS-DAE.

3. Results and discussion

DOMS and DIF exhibit monotropic mesomorphism on cooling from the isotropic phase. In the case of DOMS the analysis of the textures by optical microscopy (see figure 2) indicates that the liquid-crystalline phase is nematic in the temperature range between 115 and 68°C , with a transition enthalpy of 0.94 kJ mol^{-1} centred at 115°C , revealed by DSC analysis. The small value of the transitional enthalpy is also indicative of a nematic phase. In the case of DIF the nature of the monotropic phase is intriguing. The small supercooling from the isotropic state likely suggests the development of a liquid-crystalline phase. The analysis of the textures (see figure 3) and the high viscosity of the liquid could indicate a high level of order for the mesophase. The observation of low supercooling, mosaic textures and plastic behaviour in similar compounds, suggests the presence of a stable and highly ordered smectic mesophase [17, 18]. No

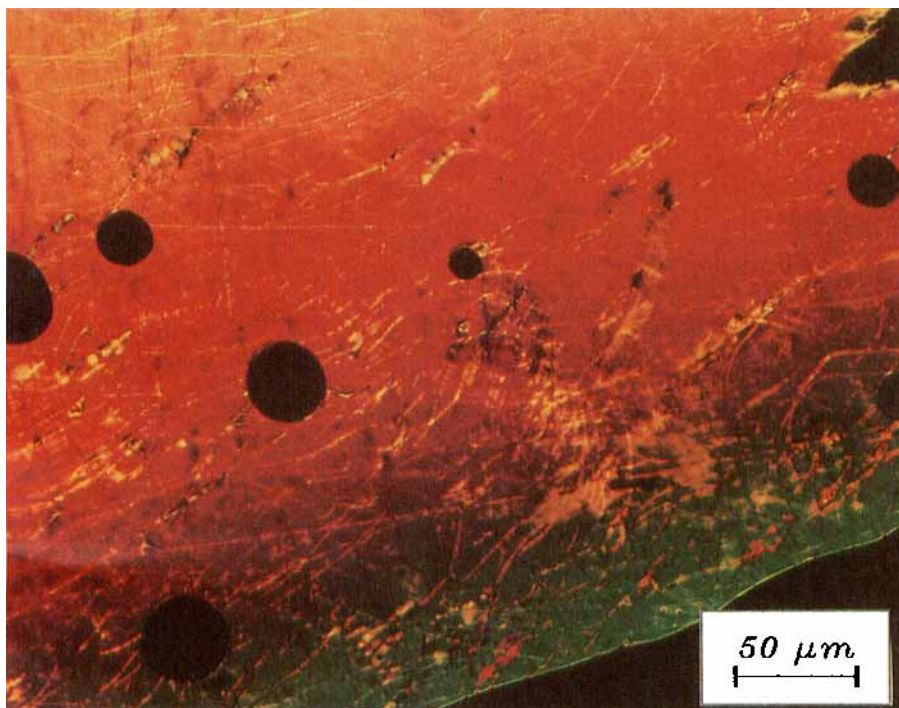


Figure 2. Monotropic phase of DOMS, crossed polarizers, at 98°C.

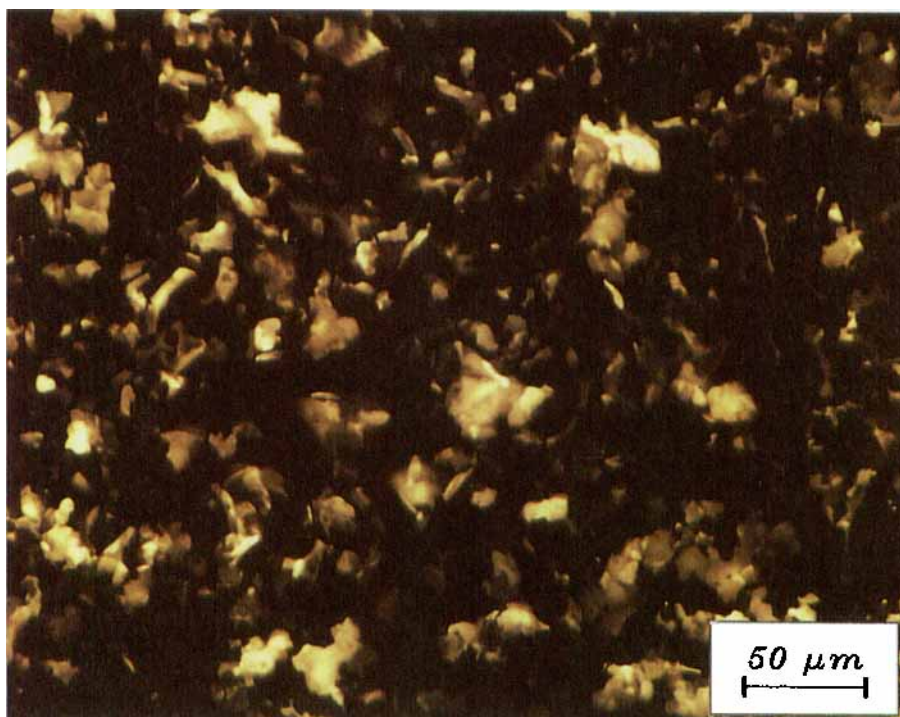


Figure 3. Monotropic phase of DIF, crossed polarizers, at 144°C.

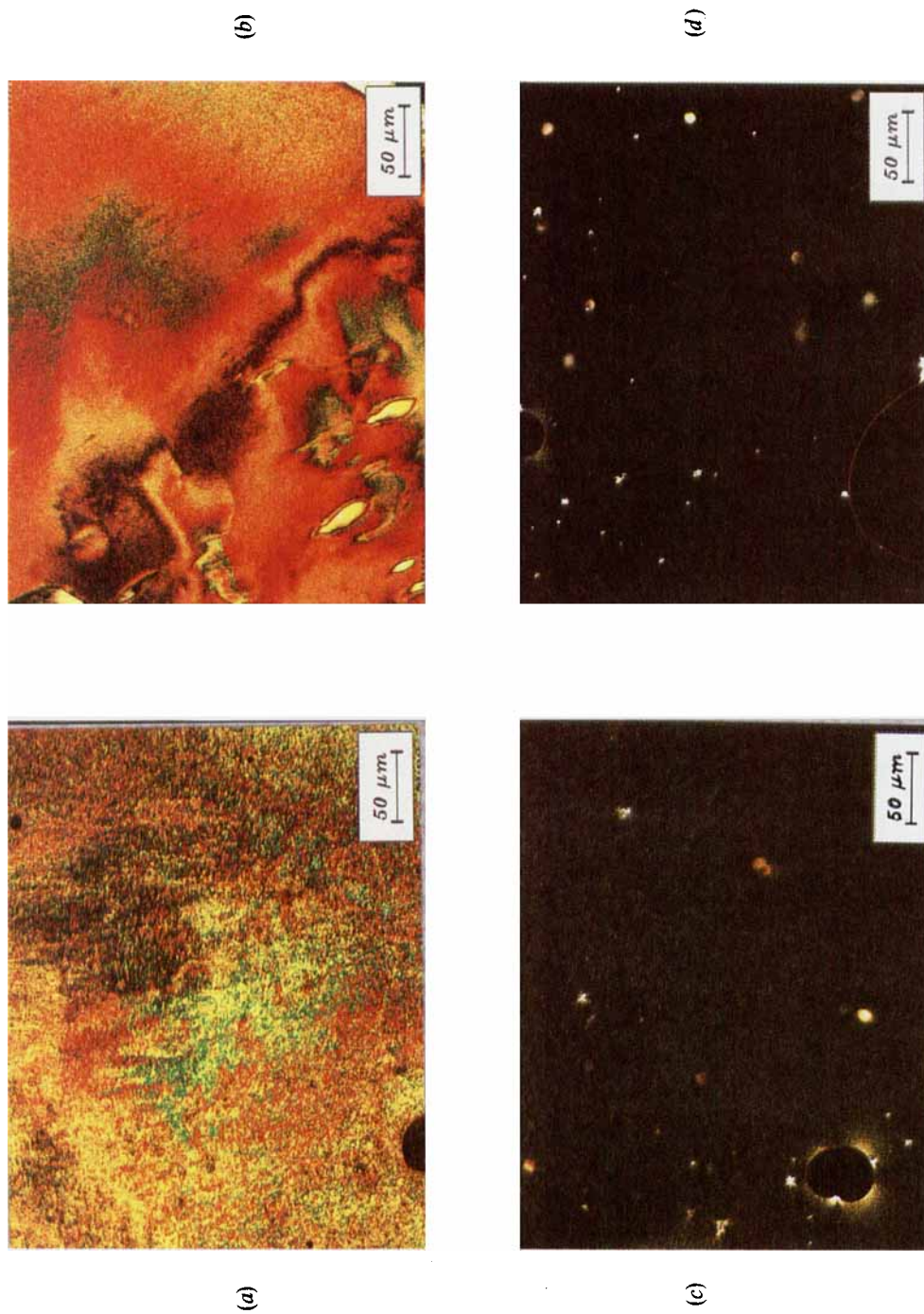


Figure 6. Optical micrography, under crossed polarizers, of the DOMS-DAT system, cured at: (a) 115°C; (b) 130°C; (c) 160°C; (d) 180°C.

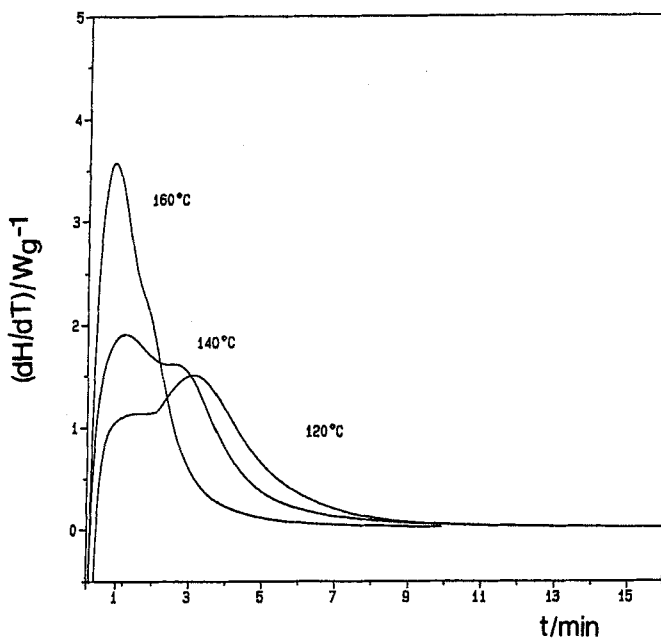


Figure 4. DSC curves for the isothermal cure of the system DOMS-DAT.

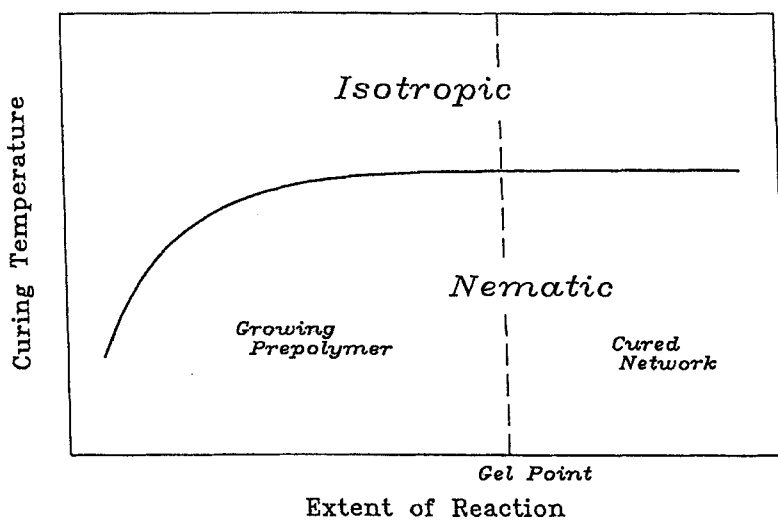
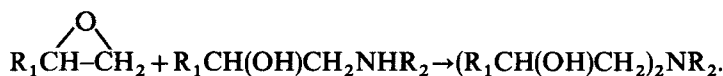
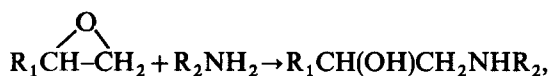


Figure 5. Schematic diagram of the development of the liquid-crystalline phase during the cure reaction.

liquid-crystalline behaviour can be detected for HQ, since the molecular aspect ratio is close to unity.

The mesogenic character of the epoxy compounds is critical for the attainment of a liquid-crystalline thermoset, as will be demonstrated in the following. As indicated in the experimental section, the glycidyl terminated molecules were cured with two different curing agents. The DSC traces, reported in figure 4, refer to isothermal cures performed at different temperatures for the DOMS-DAT system. Several considerations can be drawn from their analysis. The maximum of the peak in the heat flow versus time curve occurs for shorter times as the temperature is increased. This is an obvious consequence of the thermally activated nature of the curing process. It is worth making some further considerations on the shape of the exothermic peaks. In fact, two separate peaks can be resolved for the lowest temperatures, while at higher temperatures the two exothermic effects overlap more closely, resulting eventually in a single peak.

In general the amine-epoxy resin curing reactions show complex kinetics typified by an initial acceleration due to autocatalysis, while the later post-gelation stages may exhibit retardation as the mechanism becomes diffusion controlled [19]. The following aspects of the reaction are well-established in the literature: both hydrogen atoms of the amino group take part successively in the addition reaction [12]:



The initial reaction of the epoxy group with a primary amine produces a secondary amine and a secondary alcohol, located on the carbon atom adjacent to the carbon atom containing the amine. The resulting secondary amine, which is now more sterically hindered than the original primary amine, will react with another epoxy group, but more slowly to form a tertiary amine with two secondary alcohol groups [20]. In this hypothesis, the curing reaction of epoxy-amine systems can be realistically described by an autocatalytic model and easily represented by means of a naive equation of the form

$$dC/dt = kC^m(1-C)^n, \quad (1)$$

where C is the concentration of reactant, k is the kinetic rate constant and m and n are kinetic exponents. The reaction kinetics for this epoxy-amine system can be accurately described by means of a second order kinetic expression, irrespective of temperature. Therefore, assuming that the overall reaction order for the epoxy-amine system is of second order, yields: $m+n=2$. Equation (1) can be rewritten in terms of the degree of conversion $\alpha = \Delta H_t / \Delta H_0$ (ratio of the heat evolved up to a time t over total reaction heat)

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

Table 1 reports the kinetic parameters obtained with this approximation. The last column of table 1 shows the time, t_{LC} , required for the appearance of the liquid-crystalline phase, as revealed by birefringence under the optical microscope. This time is always found between $t_{\max I}$ and $t_{\max II}$, which are the times required for the first and

Table 1. The kinetic parameters for the DOMS-DAT system.

T/K	$\Delta H/kJ\ mol^{-1}$	t_{max1}/min	t_{max2}/min	m	n	k/min^{-1}	t_{LC}/min
393	0.98	1.38	3.08	0.239	1.76	0.323	2.67
404	1.03	1.55	3.17	0.285	1.72	0.425	2.08
413	1.16	1.21	2.48	0.322	1.68	0.617	1.88
426	1.12	1.06	2.08	0.324	1.68	0.822	1.60
433	1.11	0.92	1.82	0.436	1.56	1.41	1.22

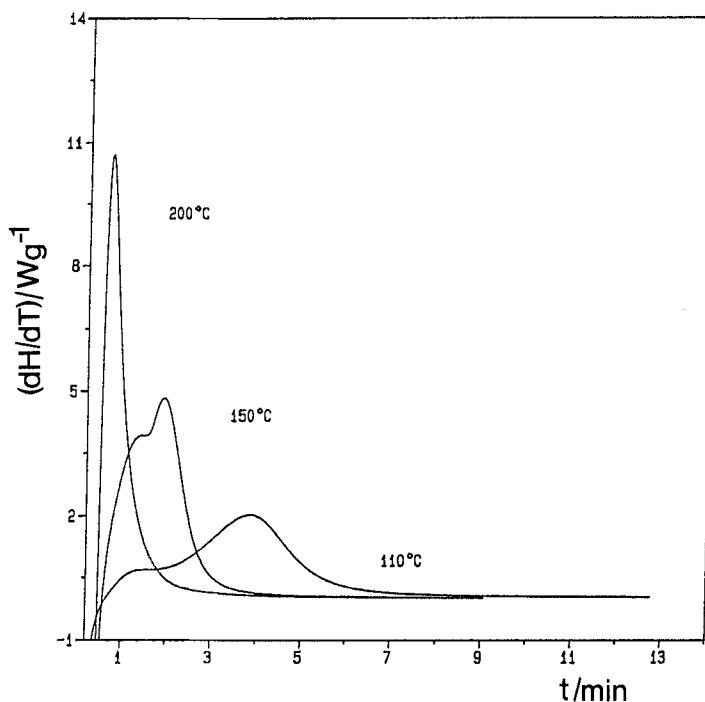


Figure 7. DSC curves for the isothermal cure of the DIF-DAT system.

the second maximum in the heat release versus time curve respectively, and follows the same trend with temperature.

On the basis of the analysis of t_{LC} the following considerations can be noted. At a certain temperature, higher than the melting temperature of either of the two components, the mixture of epoxy resin and curing agent is in its isotropic state. Upon reaction of the primary reactive groups a linear prepolymer forms, whose molecular weight increases with time. At this point the system is not yet crosslinked but only a linear prepolymer has formed. The range of stability of the liquid-crystalline phase of the growing oligomer increases with time and is larger than that of the epoxy monomer. It is well known that the range of stability of the liquid-crystalline phase for a polymer is much broader than for low molecular weight compounds, while the transition temperatures increase with increasing molecular weight of the polymer [21]. Continuing the curing process in the nematic state results in the development of covalent

Table 2. The kinetic parameters for the DIF-DAT system.

T/K	$\Delta H/kJ\ mol^{-1}$	t_{maxI}/min	t_{maxII}/min	m	n	k/min^{-1}
383	1.12	1.45	3.86	0.288	1.71	0.225
395	0.81	1.61	3.19	0.357	1.64	0.360
405	1.40	1.54	2.68	0.355	1.64	0.515
423	1.40	1.21	1.75	0.451	1.55	1.23
473	1.64	0.51	—	0.475	1.52	4.03
497	1.17	0.37	—	0.479	1.52	5.91
516	0.93	0.35	—	0.444	1.56	5.85

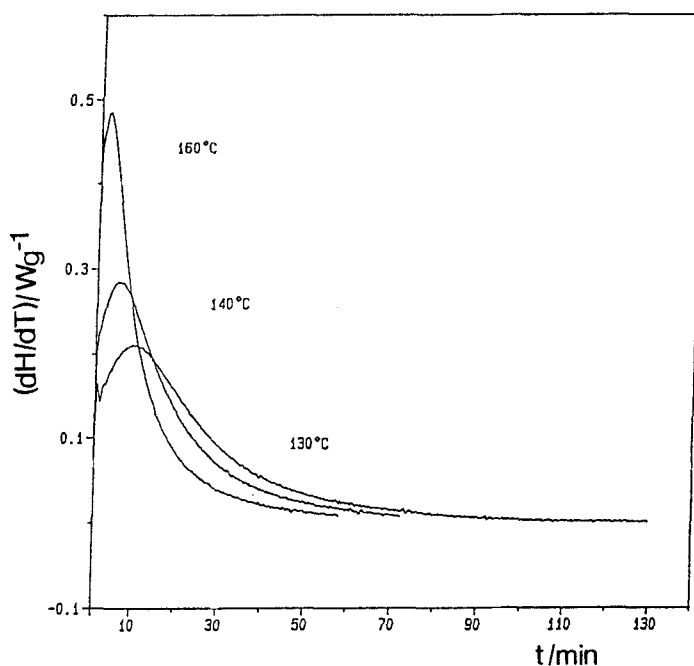


Figure 8. DSC curves for the isothermal cure of the DOMS-DAE system.

linkages due to the reaction of secondary reactive groups which stabilize the nematic state further to the point that it cannot be destroyed by heating (see figure 5).

When systems are cured at temperatures higher than a temperature T_{NI} , the nematic-isotropic temperature of the linear prepolymer, crosslinking locks the network in the isotropic state. In fact, as revealed by figure 6, an increase in curing temperature causes a reduction of the birefringent regions leading to a two-phase material, in which the isotropic parts are progressively larger. A nematic multi-domain morphology, in which the ordered parts are surrounded by disordered regions, can be supposed also for the thermoset crosslinked at the lower temperatures, with the difference that the isotropic regions are much less extended.

Figure 7 reports the isothermal cure kinetics for the DIF-DAT system. In this case too, a first exotherm is followed by a second peak, which transforms into a shoulder with increasing temperature. The kinetic data are contained in table 2, and show a similar trend to the previous system.

Table 3. The kinetic parameters for the DOMS-DAE system.

T/K	$\Delta H/kJ\ mol^{-1}$	t_{max}/min	m	n	k/min^{-1}
403	1.17	10.43	0.305	1.70	0.0688
413	0.95	5.83	0.281	1.72	0.0882
425	1.04	4.35	0.343	1.66	0.170
433	0.99	3.17	0.287	1.71	0.182

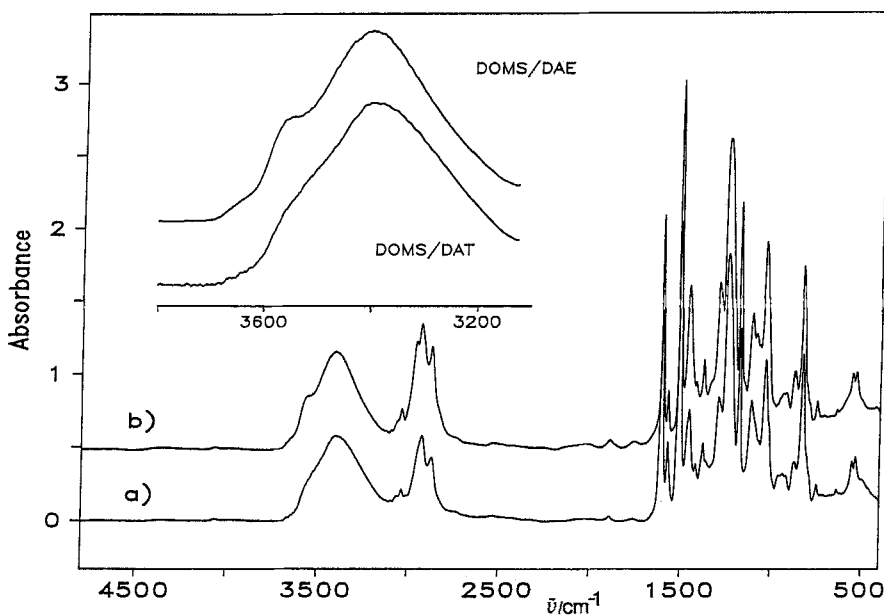


Figure 9. Room temperature FTIR spectra of: (a) DOMS-DAT; (b) DOMS-DAE. The region of the hydroxyl stretching vibration ($3581\text{--}3430\text{ cm}^{-1}$) is highlighted.

In order to compare curing kinetics of liquid-crystalline epoxy resins with those of non liquid-crystalline epoxies, we decided to study the isothermal cure of two epoxy systems that give isotropic networks upon curing. Figure 8 reports the isothermal kinetics for DOMS-DAE. The exotherms show only one peak; the data is contained in table 3. As expected the optical microscopy analysis reveals that the thermoset is completely isotropic. The fact that the same mesogenic epoxy resin can be cured in an isotropic state, if crosslinked in the same range of temperatures, with two different curing agents, is worth further discussion. DAE is a very slow curing agent, much more than DAT. Its slowness in curing can be attributed to the presence of some hindered groups close to the reactive hydrogens on the nitrogen atoms. These groups could oppose the arrangements of the prepolymer chains in a liquid crystalline state. This hypothesis is supported by the infrared analysis. In fact, as reported in figure 9, the spectra of cured DOMS-DAT and DOMS-DAE are quite similar but not in the region of hydroxyl stretching vibration ($3581\text{--}3430\text{ cm}^{-1}$) [22, 23]. For DOMS-DAE a small shoulder near 3550 cm^{-1} is well evident. This shoulder has been attributed to intramolecular hydrogen bonding [24]. In epoxy resins hydrogen bonding may occur

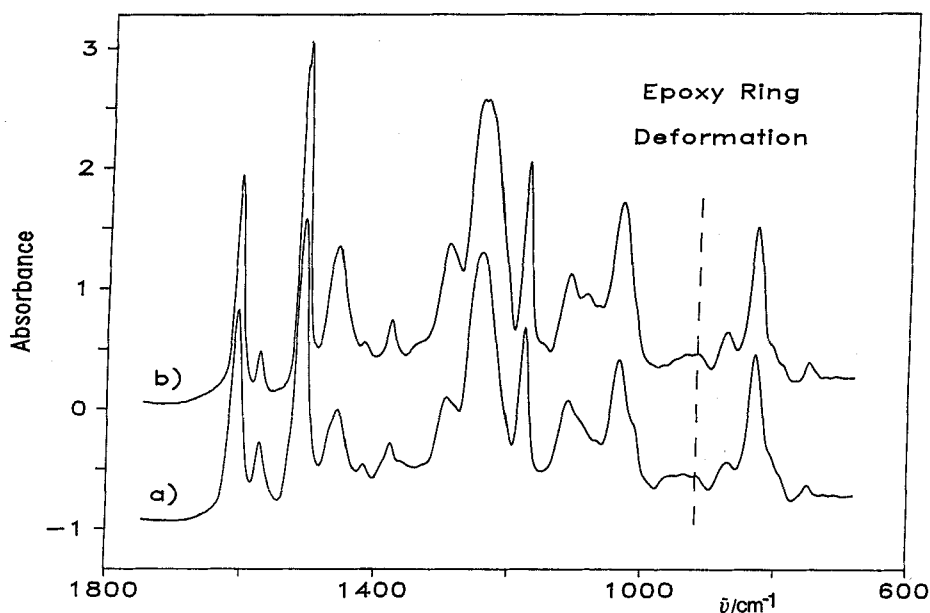


Figure 10. Room temperature FTIR spectra in the range $600\text{--}1800\text{ cm}^{-1}$ of: (a) DOMS-DAT; (b) DOMS-DAE.

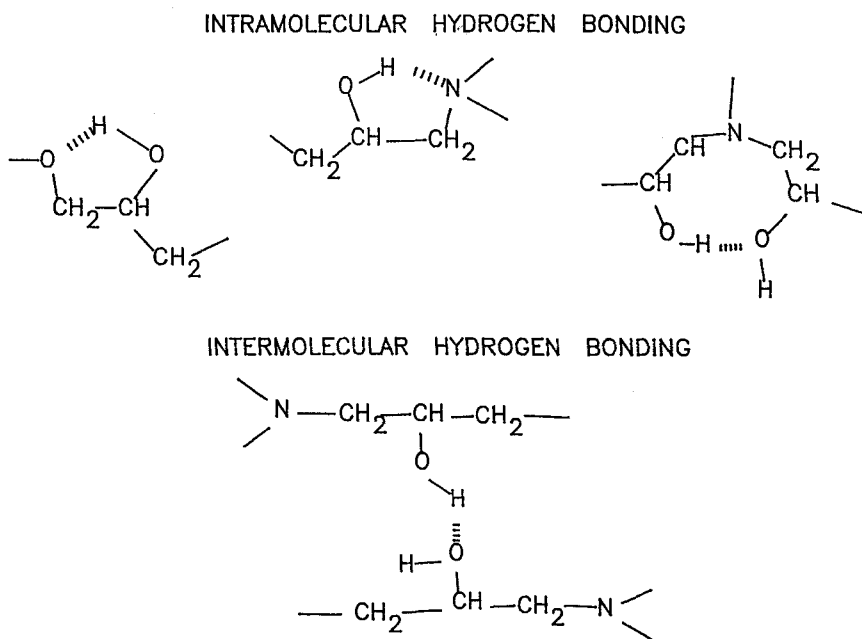


Figure 11. Molecular arrangements of the prepolymer chains in the presence of intramolecular or intermolecular hydrogen bonding.

both intramolecularly and intermolecularly, but comparative studies of model compounds show that intermolecular bonds largely predominate. The equilibrium between various hydrogen-bonded species can be easily shifted by a change of temperature or by the amine nucleophilicity [25].

Both DOMS–DAT and DOMS–DAE were completely cured, as can be inferred by the absence of the band at 915 cm^{-1} due to the epoxide ring deformation (see figure 10). However in the case of DOMS–DAE crosslinking locks the segments in such a way that intramolecular hydrogen bonds are more favoured. This molecular organization can oppose the formation of a liquid-crystalline phase: in fact, as can be observed in figure 11, in the case of intramolecular hydrogen bonding the chains of the growing prepolymer would fold, opposing the nematic order of the rigid parts. This order could be reached more easily in the cured resin in which intermolecular hydrogen bonds occur.

Another reason for the different behaviour of the two systems could be found in the reaction of an epoxy group with the secondary alcohol formed in the first step of curing. Even if this reaction is negligible for most epoxies, it could become competitive when the reactivity of the secondary hydrogen on the nitrogen atom is reduced due to steric hindrance [26]. In this case the reaction of homopolymerization of the epoxide would decrease the sum of hydroxyl and epoxy groups. Also in the case of the HQ–DAT system, for which the liquid-crystalline phase would be practically impossible, the isothermal peaks show a single maximum (see figure 12) and no nematic textures can be observed under crossed polarizers. The data are reported in table 4.

At this point a useful comparison can be made among the apparent activation energies calculated for the four different systems by means of Arrhenius plots. Table 5

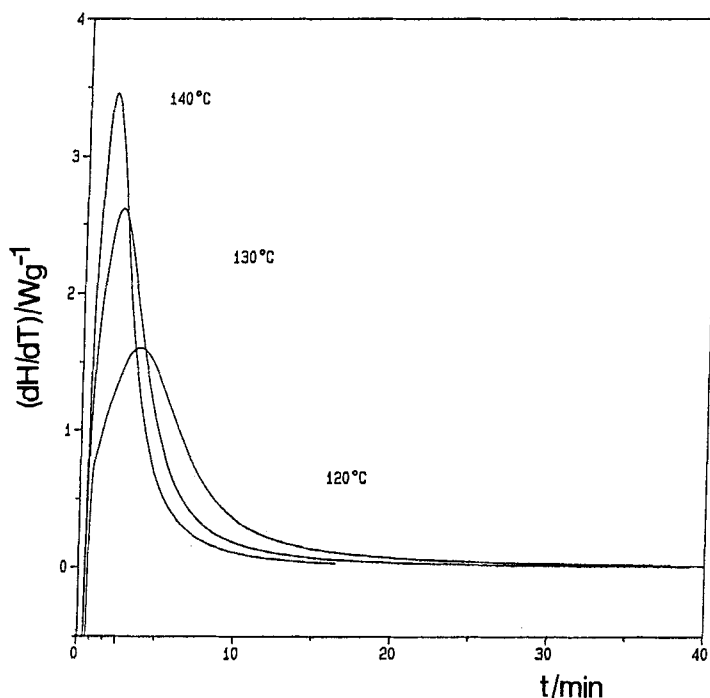


Figure 12. DSC curves for the isothermal cure of the HQ–DAT system.

Table 4. The kinetic parameters for the HQ-DAT system.

T/K	$\Delta H/\text{kJ mol}^{-1}$	$t_{\text{max}}/\text{min}$	m	n	k/min^{-1}
384	2.61	5.50	0.382	1.62	0.179
393	2.61	3.66	0.375	1.62	0.267
403	2.77	2.34	0.389	1.61	0.466
413	2.71	1.73	0.407	1.59	0.651

Table 5. The activation energies as calculated from Arrhenius plots.

System	$\Delta E_{\text{att}}/\text{kJ mol}^{-1}$
DOMS-DAT	49
DOMS-DAE	58
DIF-DAT	42
HQ-DAT	58

reports the values of the activation energies. The two liquid-crystalline epoxy resins exhibit lower activation energies. This means that the cure process is made easier if the thermoset is crosslinked in a liquid-crystalline state. The lower activation energy values can be due to higher reactivity of the groups during the curing process. Perhaps a more realistic reason may be found in the lower viscosity of the nematic phase. In fact it is well-known that in the case of thermoplastic polymers the nematic phase has a lower viscosity with respect to the isotropic state [27]. When sheared, the rods line up nearly parallel, thereby reducing the resistance to flow. Since the second step in the curing of epoxy resins is under diffusive control, the translational motion of the chains of the prepolymer is easier if the rods are arranged in a liquid-crystalline phase.

4. Conclusions

New epoxy resins can be cured in a liquid-crystalline phase. By glycidyl terminating mesogenic compounds it is possible to obtain a reactive substance that can be subsequently cured in a nematic state. The liquid-crystalline phase develops during the first step of prepolymerization and is maintained during gelation and post curing. The curing kinetics can be easily described by means of an autocatalytic mechanism with a single kinetic constant. A double peak exotherm indicates that the thermoset is crosslinked in a liquid-crystalline phase. The second maximum in heat release progressively decreases with increasing cure temperature. Also, the extent of ordered regions is reduced as the curing temperature is increased. The calculated activation energies are reduced if the polymer is crosslinked in the nematic phase. The lower values observed have been explained on the basis of the easier mechanism of gelation and post cure of the nematic epoxy. The nature of the curing agent is also important to obtain an epoxy resin cured in a liquid-crystalline phase.

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