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Polymer-dispersed liquid crystals based on epoxy networks: 1. Effects of the liquid crystal addition on the epoxy–amine reaction

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The kinetics of the epoxy–amine (diglycidylether of bisphenol A (DGEBA) and polypropylene oxide diamine D-400) reaction was studied with or without a liquid crystal additive (E7) using different concentrations. The neat system was found to obey the second-order kinetic model fairly well with a reactivity ratio n, i.e. the ratio of the rate constants for primary to secondary amines, equal to 1. The conversion at the gel point, x_{gel}, was found at the theoretical value 0.57 for such a system (diepoxide–aliphatic diamine). In contrast, the rate of the epoxy–amine reaction underwent a dramatic decrease upon addition of the liquid crystal. This retarding effect is not only due to the dilution effect. In addition, the gel point was always observed at a higher conversion than for the neat matrix ($x_{gel} \geq 0.60$), implying that the reactivity ratio n is strongly decreased. We suggest reasons accounting for such a retarding effect in view of the interactions of the liquid crystal with the epoxy–amine reaction mechanism or intramolecular reactions. After curing in a homogeneous phase (100°C), the polymer-dispersed liquid crystal systems were cooled down, which induced the phase separation of the liquid crystal-rich phase. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polymer-dispersed liquid crystals; epoxy–amine kinetics; liquid crystal addition)

INTRODUCTION

Polymer networks based on epoxy–amine monomers form a subject of great interest in polymer chemistry. Kinetic studies on these systems have been widely undertaken[1–5]. The role of the kinetics is of prime importance in understanding the reaction mechanism[6] and thus to master the desired reactions and the resulting material properties.

Previously these systems have also been studied with additives, e.g. rubber or thermoplastics, in order to improve their mechanical properties in view of their applications[7,8]. Epoxy–amine networks can also be used as electro-optical devices in the form of films with the inclusion of liquid crystals (LCs)[9–11]. One form of these systems is based upon the dispersion of LC droplets through the polymer matrix by a phase separation process induced by reaction; namely, polymer-dispersed liquid crystals (PDLCs). These films can be switched from a light-scattering to a transparent state by the application of voltage. Electro-optical devices based on PDLCs require no polarizers, operate at a low power level and have relatively rapid response times. Some of the potential applications include electronic displays, signs, windows for buildings or vehicles, automobile sunroofs, room dividers, light valves and temperature sensors/indicators[12].

A literature survey reveals that intensive research efforts have been devoted to these new systems to explore mainly their physical properties. PDLCs based on thermally cured epoxies have been studied by Smith and Vaz[11], who have investigated the influence of cure kinetics on the microdroplet size and the phase behaviour for epoxy-based PDLCs. They showed that the droplet size increases with increasing cure time constant τ_{max}, i.e. the time for maximum rate of heat release. However, this relation changed as the cure temperature varied. The LC acts as a plasticizer, depressing the glass transition temperature, T_g, of the PDLC sample slightly below that of the pure epoxy network. The temperature and the enthalpy of the nematic to isotropic transition of the LC in the droplets were both functions of cure temperature. Using the transition enthalpy values, Smith *et al.*[11] have estimated the fraction of LC contained in the droplets, which was found to decrease with increasing cure temperature. But, to the best of our knowledge, the role that the LC plays in the kinetic data of the cross-linking and on the structural changes occurring in the matrix for a system such as epoxy–amine–LC has not been studied. Chemical kinetics, however, is a key element for the control of the phase separation process, and the resulting morphology. So, this work was initiated to follow some kinetic events which occur when the pure epoxy–amine system is changed to a system with additional LC.

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This work comprises two parts, the first deals with the kinetics of the epoxy–amine (neat) system, and its kinetic modelling, whilst the second treats the epoxy–amine–LC system and gives some hypothesis to account for the differences observed.

To follow the extent of the reaction, i.e. epoxy conversion as a function of time, the basic analytical techniques employed are d.s.c. and size exclusion chromatography (s.e.c.).

EXPERIMENTAL

Materials

The formulae of monomers and the additive are given in *Figure 1*. The materials were used as received.

The diepoxide prepolymer used in this study is the diglycidyl ether of bisphenol A, DGEBA (DER 332 from Dow Chemicals), $\bar{n} = 0.03$ and $\overline{M_n} = 348.5\,\mathrm{g\,mol^{-1}}$ with an initial ratio of secondary hydroxyl to epoxy groups

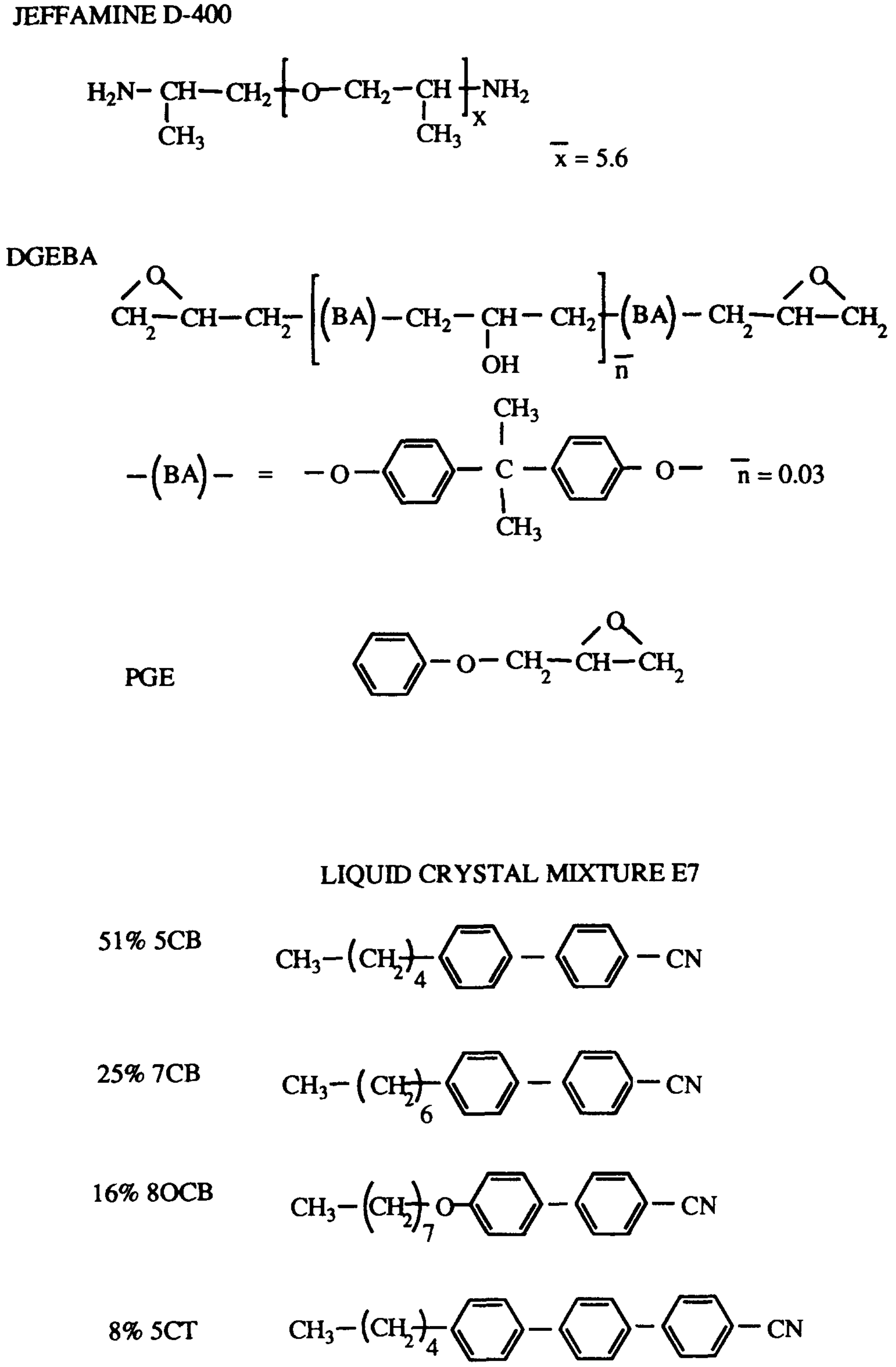

Figure 1 Chemical structures of the monomers and the LC mixture. For abbreviations, see the text

Table 1 ^{1}H n.m.r. assignment of Jeffamine D-400

δ (ppm)	Integration	Proton
3–3.8	99.49	CH, CH_2
1.1–1.2	71.03	CH_3 (in the chain)
0.9–1	25.67	CH_3 (chain ends)
1.3–1.6	17.15	NH_2

equal to 0.015. A polypropylene oxide diamine, Jeffamine D-400, $\bar{x} = 5.6$ and $\overline{M}_n = 400\,g\,mol^{-1}$, from Texaco Chemicals was used as the cross-linking agent. The choice of a Jeffamine is determined by the low T_g of the final network and later the possibility of choosing another amine of the same reactivity but with a different chain length and functionality.

The functionality of Jeffamine D-400 was calculated from ^{1}H n.m.r. From the integration of CH_3 at the chain ends (0.9–1 ppm, d, 6H) and the integration of CH_3 within the chain (1.1–1.2 ppm, d) we calculated an average polymerization degree of 5.55 (4.28 per proton). On the other hand, the integration of CH_2 and CH (3–3.8 ppm) gives a value of 4.40 per proton. The integration of the $_2H$N (1.3–1.6 ppm) gives a functionality of 3.95–4. *Table 1* gives the ^{1}H n.m.r. assignment of Jeffamine D-400.

A monoepoxide, phenylglycidyl ether, PGE (Aldrich) was used as a model reactant with Jeffamine D-400.

The additive chosen is the LC E7 (BL001, E-Merck), a nematic mixture of *p*-n-alkyl cyanobiphenyl (CB) and cyanoterphenyl (CT); *Figure 1* represents its composition as reported by Hasegawa *et al.*[13]. The nematic phase of this mixture is exhibited in between −20 and 61°C.

Kinetic experiments

Stoichiometric amounts of amino hydrogen to epoxy equal to 1 (molar proportion 2/1) were mixed and cured isothermally. Various mixtures using 0, 10, 30 and 50% by weight of the LC were prepared. D.s.c. aluminium pans were filled with the reactants and were kept at the desired temperature. These pans were then removed at various intervals of time, quenched in liquid nitrogen and were then analysed by d.s.c. or by s.e.c.

Differential scanning calorimetry

A Mettler TA 3000 calorimeter was used to measure the glass transition temperature, T_g, the specific heat capacity, ΔC_p, the nematic–isotropic transition, T_{N-I}, the enthalpy of the nematic–isotropic transition, ΔH_{N-I}, and the heat of the reaction, ΔH, throughout the reaction.

The glass transition temperature was considered as the temperature midpoint between the tangents of the two base lines above and below the transition region (inflection point). The nematic to isotropic transition temperature was taken as the maximum temperature of the endothermic peak. The rate of heat flow was kept at $10°C\,min^{-1}$ under argon atmosphere. Scans were recorded between −100 and 320°C.

The epoxy conversion x was calculated by

$$x = 1 - \frac{\Delta H_t}{\Delta H_0}$$

where ΔH_0 is the heat of the reaction at the initial time, $t = 0$, and ΔH_t is the heat of the reaction at a time t.

Size exclusion chromatography

The epoxy conversion was also measured by s.e.c. A Waters device equipped with u.v. and refractive index detectors was used. Tetrahydrofuran is used as the eluant at a flow rate of $1.0\,ml\,min^{-1}$. Assuming the equireactivity of the DGEBA epoxy groups, epoxy group conversions were calculated using the following relationship[14];

$$x = 1 - (A_t/A_0)^{1/2}$$

where A_t is the peak area of DGEBA monomer at time t and A_0 is the peak area of DGEBA monomer at $t = 0$.

As the elution times of DGEBA and the LC peaks were in the same range for the LC-added system, the area of the DGEBA peak was calculated by subtracting the LC peak area, depending on the respective initial LC concentration (10, 30 or 50% by weight).

The appearance of an insoluble fraction in 1% THF solution of the reaction mixture was taken as the criterion used for detecting gelation. The value of conversion at gel, x_{gel}, was considered as the value between the appearance and non-appearance of the insoluble fraction. Several measurements from several experiments (2 or 3) were performed, leading to several values of x_{gel}. The value provided is given by

$$\frac{x_{gel\,max} + x_{gel\,min}}{2} \pm \frac{x_{gel\,max} - x_{gel\,min}}{2}$$

In the case of a model system based on a monoepoxy, phenyl glycidyl ether (PGE), the calculation is similar except that the epoxy conversion is equal to the epoxy monomer conversion:

$$x = 1 - A_t/A_0$$

RESULTS AND DISCUSSION

Neat system

The heat of the reaction was found to be 96.5 ± 2.5 kJ per equivalent of epoxy at a d.s.c. heating rate of $10°C\,min^{-1}$. However, changing the heating rate from 10 to $5°C\,min^{-1}$, a value of 103 kJ per equivalent of epoxy was obtained, which corresponds fairly well to the values reported in the literature[6]. The value of 96.5 ± 2.5 kJ per equivalent of epoxy was used to calculate the conversion because d.s.c. runs were recorded at $10°C\,min^{-1}$.

Depending upon the nature of the epoxy and amine components, these thermoset systems may undergo two types of structural changes during the thermal cure: gelation and vitrification. The first one is the appearance of a tridimensional macromolecular structure characterized by the presence of an insoluble gel fraction. For stoichiometric amounts of diepoxide (functionality $\bar{f} = 2$) and diamines (functionality $\bar{g} = 4$) equal to 1, and equireactivity of all the reactive groups, the reaction conversion at the gel point predicted theoretically is 0.577[2].

The second transformation is approached when T_g of the reactive system equals the curing temperature. In this state the polymer chains become frozen, i.e. the relaxation time tends towards infinity and the reaction becomes diffusion controlled. However, if the cure temperature is well above the glass transition temperature of the system, then the system never vitrifies during cure, and the reaction is always kinetically controlled.

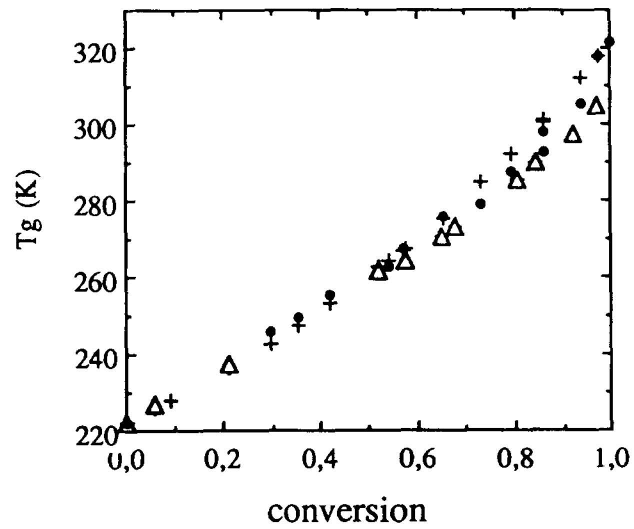

Figure 2 Evolution of glass transition temperature as a function of conversion. Experimental values (d.s.c. measurements) and calculated values according to Pascault and Williams[15]. Δ, experimental values cured at 30°C; ●, experimental values cured at 100°C; +, theoretical values

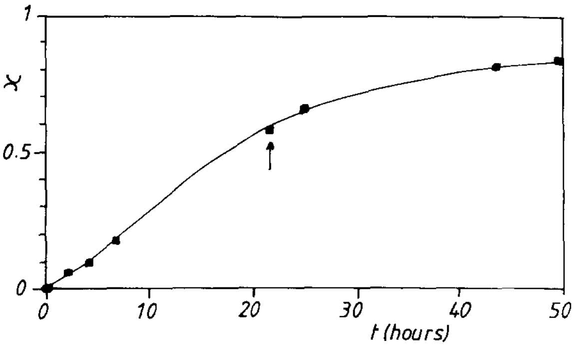

Figure 3 Epoxy group conversion as a function of time; system DGEBA–Jeffamine D-400 at 30°C. ■, experimental values (d.s.c. measurements); —, kinetic prediction. The arrow indicates the gel point

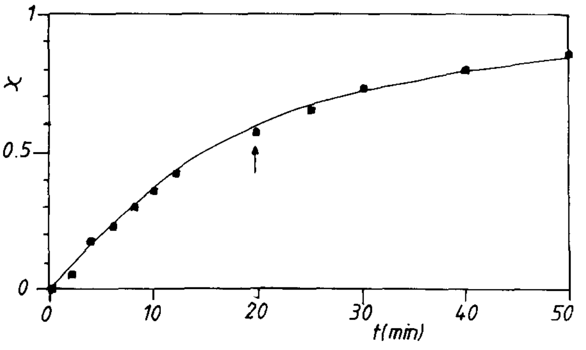

Figure 4 Epoxy group conversion as a function of time; system DGEBA–Jeffamine D-400 at 100°C. ■, experimental values (d.s.c. measurements); —, kinetic prediction. The arrow indicates the gel point

The initial T_g of the reacting mixture was found to be −51°C. The experimental evolution of T_g as a function of epoxy conversion (d.s.c. measurements) is given in *Figure 2*. With the help of the Di Benedetto's equation modified by Pascault and Williams[15], theoretical values of T_g as a function of conversion were calculated and are represented in the same figure. ($T_{g0}/T_{g\infty} = 0.69$ and $\Delta C_{p\infty}/\Delta C_{p0} = 0.62$). The experimentally measured values agree well with the predicted ones.

At 30°C the reaction attains a maximum conversion of 97% after approximately 7300 min with a T_g of 31°C equal to the cure temperature because of vitrification. For 100°C it reaches a full conversion after approximately 200 min, with a final $T_{g\infty}$ of 49°C (no vitrification).

The epoxy conversions with time as measured by d.s.c. for the neat system at 30 and 100°C are shown in *Figures 3* and *4*.

The kinetics of the epoxy–amine reactions, widely accepted in the literature[1–6], is found to follow a second-order rate law. It comprises of two reactions, a catalytic and a non-catalytic one[5]. This is valid subject to conditions that:

(i) Stoichiometric amounts of epoxy and amino hydrogen groups are used.
(ii) The reaction temperature does not exceed 100°C and thus the possibility of homopolymerization of the epoxy groups is overruled.

The kinetic scheme is represented as follows[5]:

(i) Autocatalytic reactions, when the reaction is catalysed by the hydroxyl groups already present in the initial mixture or formed during the epoxy–amine reaction:

$$e + a_1 + OH \xrightarrow{k_1} a_2 + 2OH \quad (1)$$

$$e + a_2 + OH \xrightarrow{k_2} a_3 + 2OH \quad (2)$$

(ii) Non-catalytic reactions:

$$e + a_1 \xrightarrow{k_1'} a_2 + OH \quad (3)$$

$$e + a_2 \xrightarrow{k_2'} a_3 + OH \quad (4)$$

Here, 'e' denotes epoxy and 'a' denotes amine, and the subscripts 1, 2 and 3 refer to primary, secondary and tertiary amines respectively. k_1, k_2 are rate constants of autocatalytic reactions for primary and secondary amines, and k_1', k_2' are rate constants of non-catalytic reactions for primary and secondary amines.

The reactivity ratio of secondary to primary amines, k_2/k_1 or k_2'/k_1', called the reactivity ratio n, is considered to be independent of the reaction temperature. This hypothesis has been verified elsewhere[16]. We have chosen the formalism where the ideal value of n without substitution effect is equal to 1. The literature shows that for aliphatic amines this ratio is often close to the ideal value 1 whereas for aromatic amines it is lowered[3,5,14,16].

If this ratio, n, differs from the ideal value, x_{gel} differs from the ideal value 0.577; two extreme cases can be distinguished[2],

$$n \to 0, \text{ then } x_{gel} \to 0.618$$

$$n \to \infty, \text{ then } x_{gel} \to 0.50$$

Following equations (1)–(4), the evolution of each species is given by the differential equations[5]

$$-\frac{de}{dt} = e(a_1 + na_2)\{k_1' + k_1(OH)\} \quad (5)$$

$$-\frac{da_1}{dt} = 2a_1e\{k_1' + k_1(OH)\} \quad (6)$$

$$\frac{\mathrm{da}_2}{\mathrm{d}t} = \mathrm{e}(\mathrm{a}_1 - n\mathrm{a}_2)\{k_1' + k_1(\mathrm{OH})\} \qquad (7)$$

$$\frac{\mathrm{d(OH)}}{\mathrm{d}t} = \mathrm{e}(\mathrm{a}_1 + n\mathrm{a}_2)\{k_1' + k_1(\mathrm{OH})\} \qquad (8)$$

Keeping

$$x = \frac{\mathrm{e}_0 - \mathrm{e}}{\mathrm{e}_0} \qquad \alpha = \frac{\mathrm{a}_1}{\mathrm{e}_0} \qquad \mathrm{a}_{10} = \mathrm{e}_0 \qquad n = \frac{k_2}{k_1} = \frac{k_2'}{k_1'}$$

where α is a reduced variable and x is the epoxy group conversion.

We define two modified rate constants:

$$K_1 = k_1 \mathrm{e}_0^2$$

$$K_0 = K_1(\mathrm{OH}_0/\mathrm{e}_0) + k_1'\mathrm{e}_0$$

We have derived equations for the degree of conversion:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{1-x}{2-n}(K_0 + K_1 x)[2\alpha(1-n) + n\alpha^{n/2}] \qquad (9)$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = -2\alpha(1-x)(K_0 + K_1 x) \qquad (10)$$

At 100°C, x_{gel} for the neat system was found to be 0.57 ± 0.015 (as determined by s.e.c., see *Table 3*). This value is the expected one when both the primary and the secondary amines have the same reactivities; for this reason a value of n equal to 1 can be assumed.

Equations (9) and (10) along with the experimental values of x *versus* time (d.s.c. measurements) are used in a Runge–Kutta-type mathematical method of solving the differential equations[5] so as to obtain the values of n, K_1, K_0 and theoretical values of x *versus* curing time.

The Runge–Kutta resolution is frequently used for determining K_0 and K_1 values from a known n value. But in this case we have also tried to determine the value of n. The criterion for choosing a value of n depends upon the square error values between the experimental and calculated values. The value of n for which this error is minimum is taken. These calculations confirmed a value of n close to 1 both for 30 and 100°C, proving again that this value is independent of the temperature and in good agreement with $x_{\mathrm{gel}} = 0.57$.

The experimental and calculated values of x *versus* time are plotted in *Figure 3* ($T_{\mathrm{i}} = 30$°C) and *Figure 4* ($T_{\mathrm{i}} = 100$°C), and show good agreement, thus justifying the selected second-order kinetic model.

The values of the rate constants k_1, k_1', k_2 and k_2' derived for $n = 1$, and energies of activation, are given in *Table 2*. Comparing these values one can say that:

(a) at 30°C, $k_1 \geq k_1'$, and so the autocatalytic reaction dominates;
(b) at 100°C, $k_1' \geq k_1$, and the non-catalytic reaction dominates.

The comparatively low activation energy E_{a} for the autocatalytic reaction of $51 \pm 2\,\mathrm{kJ\,mol^{-1}}$ and the slightly higher activation energy value of $61.5 \pm 2\,\mathrm{kJ\,mol^{-1}}$ for the non-catalytic reaction support the above comparison of the reaction rate constants. In the literature, the value of E_{a} for the non-catalytic reaction ranges from 57 to $62\,\mathrm{kJ\,mol^{-1}}$ [1,11], but there are exceptions[17]. As we have derived this value from only two temperatures, there is an uncertainty in its exactness. However, it can be improved by working at more than two temperatures, but this was not the principle aim of this work.

The reactivity ratio calculated here close to unity is comparable to the reactivity ratios of other aliphatic amines (butylamine, BA[3]; hexylamine, HA[1]; ethylenediamine, EDA[4]; trimethylenediamine, TMDA[1]; and hexamethylenediamine, HMDA[1]).

The rate constants of several aliphatic amines simulated at the same temperature (100°C)[18] were compared with the present polyether diamine, and the following

Table 2 Kinetic rate constants of the different systems

	DGEBA–Jeffamine D-400	DGEBA–Jeffamine D-400	DGEBA–Jeffamine D-400–10% E7	DGEBA–Jeffamine D-400–30% E7	DGEBA–Jeffamine D-400–50% E7
Temperature (°C)	30	100	100	100	100
n	1 ± 0.05	1 ± 0.02	0.87 ± 0.1	0.6 ± 0.1	0.45 ± 0.1
K_1 ($\mathrm{min^{-1}}$)	2.63×10^{-3}	1.14×10^{-1}	8.5×10^{-2} ± 0.005	5.25×10^{-2} ± 0.0075	2×10^{-2} ± 0.0015
K_0 ($\mathrm{min^{-1}}$)	3.18 ± 10^{-4}	3.57×10^{-2}	1.8×10^{-2} ± 0.002	2×10^{-2} ± 0.005	1.6×10^{-2} ± 0.002
k_1 ($\mathrm{mol^{-2}\,l^2\,s^{-1}}$)	0.33×10^{-5}	1.43×10^{-4}	1.32×10^{-4}	1.34×10^{-4}	1×10^{-4}
k_1' ($\mathrm{mol^{-1}\,l\,s^{-1}}$)	0.127×10^{-5}	1.55×10^{-4}	8.51×10^{-5}	1.26×10^{-4}	1.43×10^{-4}
k_2 ($\mathrm{mol^{-2}\,l^2\,s^{-1}}$)	0.315×10^{-5}	1.40×10^{-4}	1.15×10^{-4}	8.04×10^{-5}	4.5×10^{-5}
k_2' ($\mathrm{mol^{-1}\,l\,s^{-1}}$)	0.121×10^{-5}	1.52×10^{-4}	7.4×10^{-5}	7.5×10^{-5}	6.46×10^{-5}

n, reactivity ratio; K_1, K_0, apparent rate constants including e_0, OH_0
k_1, k_2, absolute rate constants for autocatalytic reactions
k_1', k_2', absolute rate constants for non-catalytic reactions
1,2, denote primary and secondary amines, respectively

order of reactivity is obtained:

$$\text{TMDA} > \text{HMDA} \sim \text{BA} \sim \text{EDA} > \text{HA} > \text{D-400}$$

Systems with an LC additive and cured at an isothermal temperature $T_i = 100°C$ *higher than the nematic–isotropic transition,* T_{N-I}, *of the additive*

Three systems were studied containing, in addition to epoxy–amine monomers, 10, 30 or 50% by weight of the LC. The reactions were first carried out at 100°C, a temperature higher than the T_{N-I} value. At this temperature the LC is totally dissolved in the reactive system, and the initial mixture is homogeneous. During the reaction at 100°C, the systems remained homogeneous, and no phase separation occurs. At 100°C the LC is quite miscible with the polymer network even in the rubbery state.

The measured heat of the reaction is approximately the same as the neat system (98.8 ± 1.1 kJ per equivalent of epoxy at a rate of $10°\mathrm{C\,min^{-1}}$).

The final glass transition temperature for the 10% LC system was found to be 23°C, for the 30% LC system 2.6°C, while for the 50% LC system it was measured at 5.0°C. For the two-phase systems, the T_g values are those of the polymer-rich phase. Thus, LC addition affects the final transition temperature of the matrix and acts as a plasticizer, like many other additives.

Kinetic measurements were taken. The epoxy conversions with time can be seen in *Figure 5* (d.s.c. measurements). The reaction rate slows down with the added concentration of the LC, and it requires a longer time to reach a conversion above 90% (more than 400 min) in the case of 30 and 50% by weight of the LC.

To check whether it is only a dilution effect of epoxy and amino hydrogen groups due to the presence of the LC which decreases the rate of the reaction, the values of K_1 and K_0 were recalculated using the concentration of the epoxy used in the respective LC-modified system, but keeping constant the values of n and the rate constants of the neat system. In this way, we could simulate the dilution effect only, using the same differential equations, equations (9) and (10), provided that the system in the presence of the LC remains homogeneous. The simulated curves are also shown in *Figure 5*, and can be compared with the experimental values. It is apparent from the figure that the simulated values lie well above the experimental ones, the difference becoming higher as we increase the LC concentration, suggesting that there might be some factors other than dilution which are operative in the presence of the LC and tend to slow down the reaction rates.

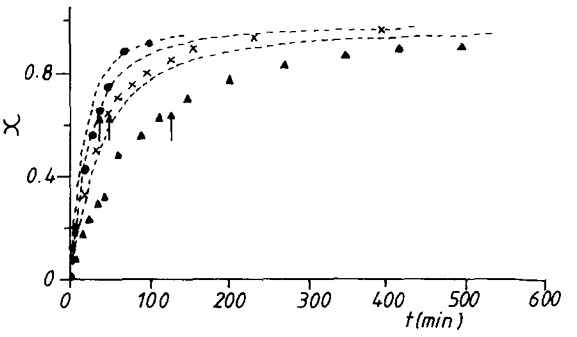

Figure 5 Experimental (d.s.c. measurements) and simulated values of conversion *versus* time for systems with LC. ●, 10% LC; ×, 30% LC; ▲, 50% LC; - - -, kinetic prediction

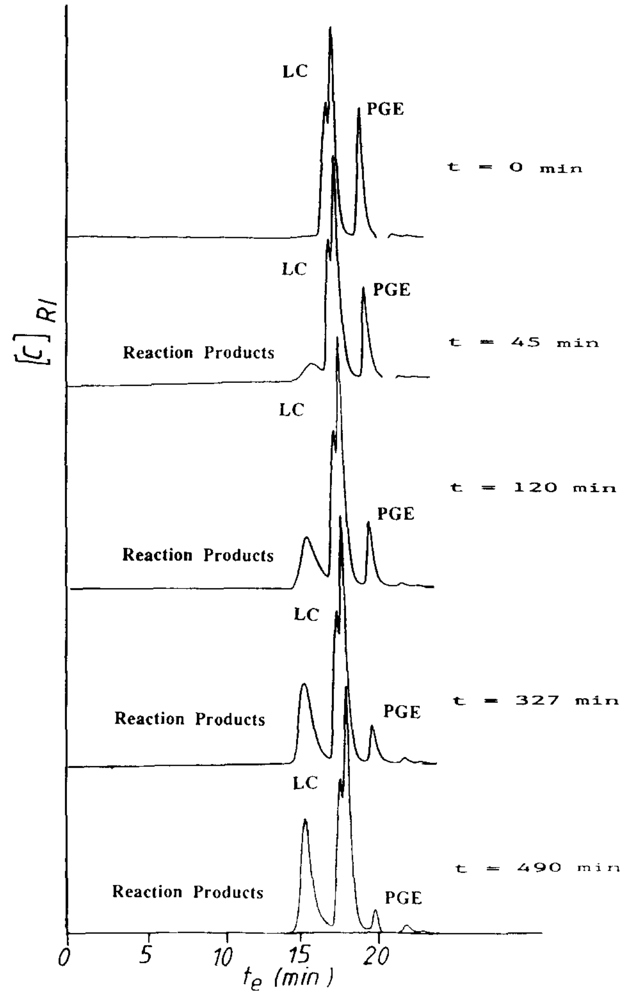

Figure 6 S.e.c. chromatograms for PGE–Jeffamine D-400, 50% by weight of LC

To rule out the hypothesis of a reaction of the LC with any other species (epoxy or amine), PGE was employed as a model reactant with Jeffamine D-400 in the presence and absence of the LC. As it is a monoepoxide, only soluble species can be formed. The reaction was followed by s.e.c. *Figure 6* shows some chromatograms for the system with 50% of the LC. It was found that the area of the LC peak remained constant throughout the reaction, while that of the PGE peak decreased, indicating that the LC does not react with any species. The reaction occurs only between PGE and Jeffamine D-400, giving rise to a new product whose peak area increases with time. (It should be noted that the reaction products—mono-, di-, tri- and tetrasubstituted amino species, are not quantifiable due to the polymolecularity of Jeffamine D-400 and the fact that the differently substituted amino products are eluted at almost the same time, thus giving a single accumulative broad peak, and, unfortunately, no kinetic measurement such as n values could be done.)

Another explanation of the decrease of the reaction rates might be given in the light of some interactions between the epoxy, the amine and the LC. Rozenberg has studied in detail the mechanism of epoxy–amine reactions[6]. The trimolecular transition state usually

Table 3 Conversions at gel point and glass transition temperatures of the neat and modified systems

LC (wt%)	0	10	30	50
LC (mol%)	–	13.9	37.9	58.7
x_{gel}	0.57 ± 0.015	0.61 ± 0.015	0.63 ± 0.02	0.61 ± 0.015
T_g (°C)	49	23	2.6	5.0
ΔC_p ($J\,g^{-1}\,K^{-1}$)	0.41	0.49	0.47	0.33

involved in epoxy–amine-catalysed reaction is formed in two steps. The first step consists of the formation of a donor–acceptor complex between the epoxy ring and a hydroxyl group. The second step is the nucleophilic attack of the complex by an amine group. This nucleophilic attack needs electrophilic assistance, i.e. the formation of the donor–acceptance complex.

In the presence of LC molecules, the first step can be slowed down because the LC is itself a donor–acceptor molecule and interacts strongly both with the diamine and with the first donor–acceptor complex between the epoxy and hydroxyl groups. Such an interaction between two donor–acceptor systems can weaken the electrophilic assistance necessary for the nucleophilic attack of the amino group, and therefore slows down the opening of the epoxy ring. This explanation is coherent with that of Smith[19], who concluded that the reaction rates for the cross-linking of the epoxide monomers with amines were retarded in the presence of acetophenone and nitrobenzene. These molecules, being polar and hydrogen bond acceptors, interfere with the transition state. In our case the LC molecule can be regarded as having a similar polar and hydrogen bond acceptor behaviour, and thus exhibits the similar effects.

Also, this dipole–dipole interaction requires the close proximity of the epoxy group to an LC molecule, and is therefore an important source of steric hindrance to nucleophilic attack by the amine.

But even if these phenomena play a role in slowing down the reaction rate, we have also to take into account the fact that the decrease of reactivity is accompanied by an increase in conversion at x_{gel}. As soon as the LC content reaches 10%, $x_{gel} = 0.62 \pm 0.015$ (*Table 3*, as measured by s.e.c.). Thus, even 10% of the LC increased the gel conversion by approximately the same extent. According to the statistics of diepoxide–diamine network formation, if the gel point tends to 0.618, the value of n approaches 0.

However, in our case, possible intramolecular reactions are favoured by the dilution with LC, a gel conversion higher than the ideal value 0.577 is indicative of epoxy–amine intramolecular reactions[20]. Dusêk and co-workers[20] studied Jeffamine D-400, reacted with PGE, in the presence of polyethylene glycol $\overline{M_n} = 200$ (PEO 200) or n-butanol (BuOH), and showed a subsequent substitution effect. They calculated a ratio of $n = 0.4$ ($\rho = 0.2$ in the other formalism) in the case of Jeffamine D-400–PGE–PEO 200 (1/1/5) and a ratio of $n = 0.6$ in the case of Jeffamine D-400–PGE–BuOH (1/1/5). They have correlated these differences with hydrogen bonding (within the polyoxypropylene chain and between the oxypropylene and oxymethylene chains of PEO) and with cyclization reactions. Such reactions are possible because of the flexibility of the Jeffamine chains. Indeed, the presence of OH groups and ether bridges in PEO 200 and BuOH probably changes the hydrogen bonding states of the systems and therefore changes the values of the reactivity ratios for the same epoxy–amine reaction. In fact, it seems that the more hydrogen bonding occurs, the weaker the value of n (or ρ). These facts (hydrogen bonding and cyclization) can be well applied to our system (PEO plays the role of the LC).

The experimental values of the degree of conversion x as a function of time were treated as for the neat system to estimate the values of n, K_1 and K_0. Values of $n = 0.87$, 0.6 ± 0.1 and 0.45 ± 0.1 for 10, 30, and 50% LC systems, respectively, were found to satisfy the experimental and calculated values.

The values for the rate constants of the autocatalytic and non-catalytic reactions thus calculated are reported in *Table 2*. A comparison between all the systems reveals the fact that at 100°C the values of k_1 and k_1' remain in the same order of magnitude for 0, 30 and 50% LC concentrations (with the exception of the k_1' value for the 10% LC system) whereas the values of k_2 and k_2' are lowered compared to the neat system. From these values we can conclude that the secondary amine reaction with epoxy is much more hindered in the presence of the LC than for the primary amine. The value of $n < 1$ is confirmed by our experimental gel point conversions according to the statistics of curing of diepoxide with diamine by Dusêk[2], i.e. if the gel point conversion tends to 0.618, the value of n approaches to 0.

But even if the values of n calculated here show a decrease, they are still too large to explain the values of x_{gel} obtained experimentally. Other secondary reactions such as intramolecular reactions are certainly also probable, as we mentioned previously.

Upon cooling to room temperature, only the 50% LC system exhibits a phase separation phenomenon. Therefore, we have studied the curing of this system at 30°C.

System with an LC additive and cured at an isothermal temperature, T_i, lower than the nematic–isotropic transition, T_{N-I}, of the additive

The system with 50% of the LC was investigated at 30°C and was followed by d.s.c. and s.e.c. techniques. The reaction proceeded very slowly (*Figure 7*). Furthermore, a phase separation phenomenon was observed at 30°C; therefore, after the phase separation the kinetics is carried out in an heterogeneous medium. Gelation was observed after the occurrence of the phase separation. The conversion at gel point was observed to be decreased from 0.57 to 0.48 (as determined by s.e.c.). This trend has

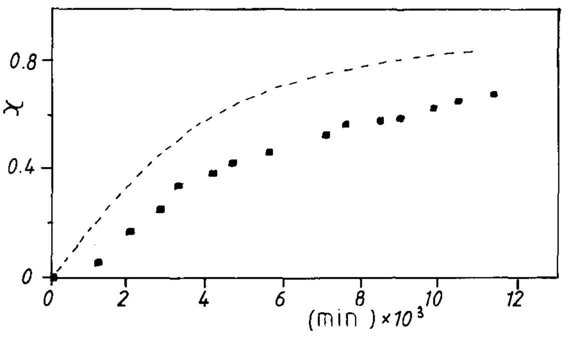

Figure 7 Experimental and simulated values of conversion *versus* time for the system with 50% by weight of LC cured at 30°C. ■, experimental values; - - -, kinetic prediction

also been observed by Girard-Reydet *et al.*[16], who explained it in terms of fractionation phenomena which occur during the phase transition process. Epoxy–amine monomers, or low molar mass species, with the lower functionalities being thermodynamically more miscible with the LC-rich phase, are extracted from the epoxy–amine rich phase, leading to an increase in the second moment of the functionality distribution $\overline{f_w}$, in the epoxy-rich phase.

We have simulated the effect of dilution on the kinetic results. In fact, this type of simulation is true only for a homogeneous medium, so it should be considered only before the phase separation occurs. Again, we can observe the difference between the experimental and simulated values (*Figure 7*).

CONCLUSION

This kinetic study on epoxy–amine–LC systems has led us to draw the following conclusions:

(i) The epoxy amine reaction performed with DGEBA–Jeffamine D-400 showed the classical kinetic behaviour obeying a second-order model of the reaction.

(ii) The reactivity ratio n for the neat system was found to be close to 1, the ideal value for the aliphatic amines, and is independent of the reaction temperature.

(iii) At 100°C all the systems remained homogeneous. The rate of the reaction slowed down drastically upon the addition of the LC. The gel point values for the systems with the LC are higher, implying that the value of n decreased. Several reasons can account for such a retarding effect. We have discussed here the possibility of (a) epoxy–amine intramolecular reactions, (b) strong hydrogen bonding in the polypropylene oxide diamine chains, and, finally, (c) an influence of the donor–acceptor LC molecules on the first transition state of the epoxy–amine involved in the reaction mechanism.

The LC showed an important influence on the final T_g values, thus acting as a strong plasticizer. A large quantity of the LC is dissolved in the matrix.

(iv) After the curing at 100°C, only for the experiment with 50% by weight of the LC can phase separation be induced by a thermal quench.

(v) At 30°C, the 50% LC system undergoes a real phase separation during cure.

We are now studying the phase separation phenomenon. With these kinetic results, it is now possible to determine the overall phase diagrams of such LC-modified epoxy systems.

REFERENCES

1 Horie, K., Hiura, H., Sawada, M., Mita, I. and Kambe, H. *J. Polym. Sci. (A)* 1970, **8**, 1357

2 Dusêk, K., Ilavsky, M. and Lunak, S. *J. Polym. Sci.: Symp.* 1975, **53**, 29

3 Dusêk, K. and Bleha, M. *J. Polym. Sci., Polym. Chem. Ed.* 1977, **15**, 2393

4 Riccardi, C. C., Adabbo, H. E. and Williams, R. J. J. *J. Appl. Polym. Sci.* 1984, **29**, 2481

5 Titier, C., Pascault, J. P., Taha, M. and Rozenberg, B. A. *J. Polym. Sci.* 1994, **33**, 175

6 Rozenberg, B. A. *Adv. Polym. Sci.* 1986, **75**, 115

7 Verchères, D., Sautereau, H., Pascault, J. P., Moschiar, S. M., Riccardi, C. C. and Williams, R. J. J. *Polymer* 1989, **30**, 107

8 Chen, D., Pascault, J. P. and Sautereau, H. *Polym. Int.* 1993, **326**, 361

9 West, J. L. *Mol. Cryst. Liq. Cryst.* 1988, **157**, 427

10 Vaz, N. A., Smith, G. W. and Montgomery, G. P., Jr *Mol. Cryst. Liq. Cryst.* 1987, **146**, 1

11 Smith, G. W., and Vaz, N. A. *Liq. Cryst.* 1988, **3**, 543

12 Montgomery, G. P., Jr, Smith, G. W. and Vaz, N. A. in 'Liquid Crystalline and Mesomorphic Polymers', Springer-Verlag, Berlin, 1994

13 Hasegawa, R., Sakamoto, M. and Sasaki, H. *Appl. Spectrosc.* 1993, **47**, 1386

14 Verchères, D., Sautereau, H., Pascault, J. P., Riccardi, C. C., Moschiar, S. M. and Williams, R. J. J. *Macromolecules* 1990, **23**, 725

15 Pascault, J. P. and Williams, R. J. J. *J. Polym. Sci., Polym. Phys. Ed.* 1990, **28**, 85

16 Girard-Reydet, E., Sautereau, H., Pascault, J. P. and Riccardi, C. C. *Macromolecules* 1995, **28**, 7599

17 Serier, A., Pascault, J. P. and Lam, T. M. *J. Polym. Sci., Polym. Chem. Ed.* 1991, **29**, 209

18 Titier, C. Ph.D. Thesis, Institut National des Sciences Appliquées de Lyon, 1994

19 Smith, I. T. *Polymer* 1961, **2**, 95

20 Dusêk, K., Ilavsky, M., Stokrova, S., Matejka, L. and Lunak, S. in 'Crosslinked Epoxies', Walter de Guyter, Berlin, 1987