Effects of the structure of the aromatic curing agent on the cure kinetics of epoxy networks

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The curing of an epoxy prepolymer based on the diglycidyl ether of bisphenol A (DGEBA) with different aromatic diamines, i.e. 4,4′-diaminodiphenylmethane (DDM), 4,4′- and 3,3′-diaminodiphenylsulphone (DDS), bis[4,(4-aminophenoxy)phenyl]sulphone (BAPS) and 2,2′-bis[(4-aminophenoxy)phenyl]propane (BAPP), was analysed using size exclusion chromatography, viscosity measurements and differential scanning calorimetry as the main techniques. The diamines chosen have high melting temperatures. The diamines DDM, 4,4′-DDS, 3,3′-DDS and BAPP dissolve easily in DGEBA, but an unprocessable product results with BAPS. As determined by size exclusion chromatography and viscosity measurements, the reactivities of the diamines are in the order:

$$\text{4,4'-DDS} < \text{3,3'-DDS} < \text{BAPS} < \text{BAPP} < \text{DDM}$$

Using the fact that the molecules of aromatic diamines disappear more rapidly than the molecules of diepoxy, we have calculated a ratio of the reactivity of secondary to primary amine hydrogens (k_2/k_1) in the range 0.8–0.9 for DDS diamines. All of the results have been plotted on a time–temperature–transformation diagram. The adjustable parameter λ appearing in Di Benedetto's equation may be estimated from the ${}_{\mathrm{gel}}T_{\mathrm{g}}$ value or from ΔC_{p} measurements. This adjustable parameter is approximately 0.4 for DDM and 4,4′-DDS, and approximately 0.6 for 3,3′-DDS and BAPP.

(Keywords: polyepoxy; aromatic diamines; reactivity reaction; gelation; vitrification; phase diagram)

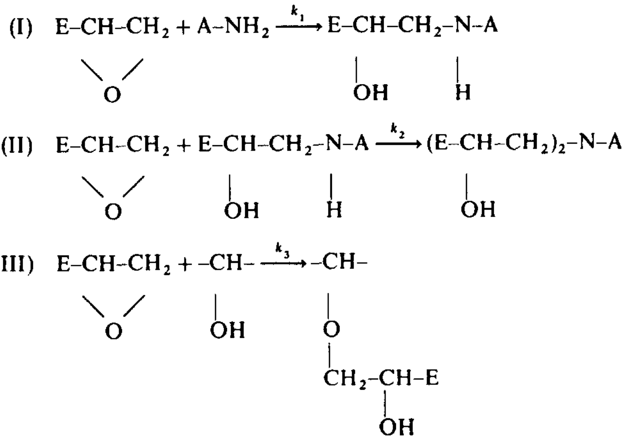
INTRODUCTION

Epoxy copolymers are widely used as adhesives and matrices for composite materials in aerospace and leisure industries. However, the main disadvantage of these materials is their brittleness, which is due to their highly crosslinked structures. Many studies have been conducted in order to improve their toughness. Generally, a reactive liquid rubber is incorporated in the epoxy network as a secondary phase[1–4]. But, depending on the kinetics of the reaction, phase segregation, which is a competitive mechanism, is not always complete. Therefore, part of the rubber is dissolved in the matrix, and unacceptable decreases in both modulus and glass transition temperature (T_g) are observed[4].

Another possible way of toughening epoxy networks is to alter the structure of the monomers[5,6]. Therefore, the aim of this work is to evaluate the effects of the structure of the curing agent on the kinetics of the reaction with pure diglycidyl ether of bisphenol A (DGEBA) prepolymer.

To maintain a high value of T_g, various aromatic diamines differing in their backbone stiffness are chosen. Some of them have been tested previously by Delvigs[6]. The mechanical properties of the epoxy networks will be presented in a later publication. In order to develop structure–property relations, it is essential to know how the networks link together. This requires characterization of the reactants, of the linking reaction and of the structural changes that occur during the cure of an epoxy oligomer with a diamine comonomer.

The mechanism and kinetics of the curing reaction have been analysed and reviewed by several investigators[7–15]. The reaction of a primary amine with an epoxide usually affords a secondary amine, which reacts with another epoxide resulting in a tertiary amine:



$$\text{(I)}\quad \mathrm{E{-}\underset{\diagdown\;O\;\diagup}{CH{-}CH_2}} + \mathrm{A{-}NH_2} \xrightarrow{k_1} \mathrm{E{-}\underset{OH}{CH}{-}CH_2{-}\underset{H}{N}{-}A}$$

$$\text{(II)}\quad \mathrm{E{-}\underset{\diagdown\;O\;\diagup}{CH{-}CH_2}} + \mathrm{E{-}\underset{OH}{CH}{-}CH_2{-}\underset{H}{N}{-}A} \xrightarrow{k_2} \mathrm{(E{-}\underset{OH}{CH}{-}CH_2)_2{-}N{-}A}$$

$$\text{(III)}\quad \mathrm{E{-}\underset{\diagdown\;O\;\diagup}{CH{-}CH_2}} + \mathrm{{-}\underset{OH}{CH}{-}} \xrightarrow{k_3} \mathrm{{-}\underset{\underset{\underset{\underset{OH}{|}}{CH_2{-}CH{-}E}}{|}}{\underset{O}{|}}}{CH}{-}}$$

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Other possible reactions, namely the homopolymerization of the epoxy groups or its reaction with hydroxyl functionalities, can be neglected under certain curing conditions: stoichiometric concentration and with no accelerator or catalyst[13].

Several researchers[8–10] have found that the reactivities of the epoxide groups in diglycidyl ether of bisphenol A (DGEBA) prepolymers are independent. Although experimental data are consistent with a single activation energy and heat of reaction for both steps (I) and (II), both reaction rates may be different owing to the different reactivities of the primary (rate constant k_1) and secondary (rate constant k_2) amino groups. The ratio $r = k_2/k_1$ is predicted to have a strong effect on the cure process, including parameters such as gel time, molecular weight and many other structural parameters of the growing network[8,9,14,15].

On the other hand, Horie *et al.*[7] and Riccardi *et al.*[11] have demonstrated that the reaction takes place via two competitive paths: one is catalysed by the hydroxyls initially present in DGEBA prepolymer and those generated during the reaction (k'_1, k'_2), and the other is a non-catalytic mechanism, (k_1, k_2) with higher activation energy. The non-catalytic reaction takes place over the entire temperature range. The catalytic mechanism is predominant at low temperatures ($T < 100°C$) and vanishes at high temperatures ($T > 100°C$) owing to the difficulty of forming the ternary transition complex[11].

The experimental results for the reaction kinetics and the structural changes for DGEBA reacted with four different aromatic diamines are presented and compared with the theoretical models for accurate control of the formation of the networks.

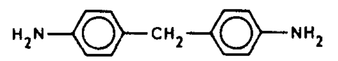
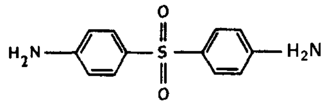
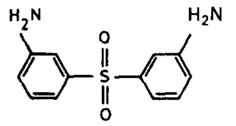
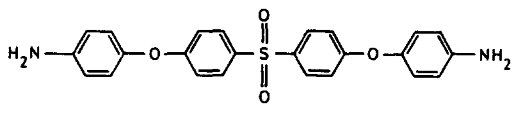
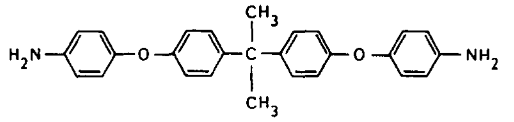
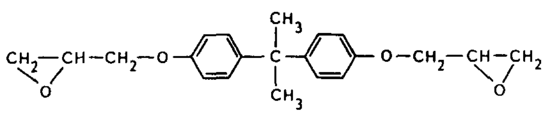
EXPERIMENTAL

Materials

The formulations used in this study were based on diglycidyl ether of bisphenol A (DGEBA) prepolymer, DOW DER 332, cured with various aromatic diamines as comonomers: 4,4′-diaminodiphenylmethane (DDM), 4,4′-diaminodiphenylsulphone (4,4′-DDS), 3,3′-diaminodiphenylsulphone (3,3′-DDS), bis[4-(4-aminophenoxy)-phenyl]sulphone (BAPS) and 2,2′-bis[(4-aminophenoxy)-phenyl]propane (BAPP). The formulae, suppliers, molecular weights and melting temperatures of the materials are listed in *Table 1*. The various products were used as received. The curing agents were not soluble in the epoxy prepolymer at room temperature, and therefore the stoichiometric mixture of 2 mol DGEBA plus 1 mol diamine was heated to 135°C until a clear solution was obtained. In all cases, the reaction between epoxy functions and amino hydrogen groups had begun. The extent of this pre-cure schedule depends on the nature of the curing agent and its ability to dissolve in DGEBA.

For the kinetic study, the well mixed samples were prepared in small PTFE moulds ($\phi = 4$ cm, $e = 2$ mm) and placed on a stainless-steel plate (to ensure good thermal contact) in a regulated oven ($T = 100$ or 120°C). After selected time intervals, the samples were removed and

Table 1 Characteristics of the different monomers used

Monomers	Formulae	Supplier	Molecular weight (g mol^{-1})	Melting temperature (°C)
4,4′-Diaminodiphenylmethane (DDM)		Fluka	198	88
4,4′-Diaminodiphenylsulphone (4,4′-DDS)		Fluka	248	175
3,3′-Diaminodiphenylsulphone (3,3′-DDS)		BASF	248	164
Bis[4-(4-aminophenoxy)phenyl] sulphone (BAPS)		Mallinkrodt	432	193
2,2′-Bis[(4-aminophenoxy)phenyl] propane (BAPP)		Mallinkrodt	410	126
Diglycidyl ether of bisphenol A (DGEBA)		Dow Chemicals	340	47

studied by differential scanning calorimetry (d.s.c.) and size exclusion chromatography (s.e.c.).

Differential scanning calorimetry measurements

D.s.c. analyses were run in a Mettler TA 3000 apparatus under an argon atmosphere at a heating rate of 10°C min^{-1}. The first scan, on a reactive mixture, leads to the value of the enthalpy of reaction, ΔH (J g^{-1} or kJ per epoxy equivalent (ee)), and to the values of the initial, maximum and final temperatures of the exothermic peak, T_1, T_p and T_2. A second scan gives the value of the glass transition temperature, T_g, taken at the inflection point on the d.s.c. curve.

The T_g and heat capacity change, ΔC_p, at T_g for cured samples are obtained directly during the first scan. The determination of ΔC_p has been described previously. Ten d.s.c. runs were made for each product[16].

Size exclusion chromatography

The analyses of the soluble products were made on a Waters chromatograph equipped with a 6000 A pump, U6K injector, double detection (u.v. at $\lambda = 254$ nm and differential refractometer R401). The eluant used was tetrahydrofuran (THF), and the separation was carried out on four μ-Styragel columns (10^3 Å + 500 Å + 100 Å + 100 Å) with an elution rate of 1.5 ml min^{-1}. The approximate average molecular weight ($\bar{M}_n$, $\bar{M}_w$) was calculated using a polystyrene calibration.

Viscosimetry

The change in the viscosity was followed on a Contraves viscosimeter (Rheomat 30, coaxial cylinders type, Searl) between 100 and 160°C. The time when the viscosity approaches infinity due to gelation or vitrification was approximated to be the time required to reach a viscosity of 10 000 Pa s.

RESULTS

Extent of reaction during the dissolution of the hardener at 135°C

Since the diamines used have high melting temperatures (*Table 1*), there are some difficulties in mixing the two comonomers at low temperatures without causing any reaction. So two types of experiments were conducted:

(i) First, the stoichiometric mixtures of epoxy prepolymer and diamine powder are analysed by d.s.c., without previous dissolution of the diamine, in order to obtain the complete reaction in the d.s.c. chamber. The results for the four systems are reported in *Table 2*. The enthalpy of reaction, ΔH_0, ranges between 93 and 113 kJ/ee depending on the structure of the diamine. The reported values in the literature for epoxy–amine systems are generally around 110 ± 10 kJ/ee[7,11,12]. However, the glass transition temperatures obtained during the second scan are low compared to the expected values[6,14]. This suggests that the reactions are not complete in this case, though no residual exothermic peak appears during the second scan. The values of ΔH_0 obtained during the first scan are considered to be representative of the main reactions between epoxy and amino hydrogen groups. For the system DGEBA–4,4′-DDS the lower values obtained can be due to passing through the melting temperature during the reaction.

Table 2 D.s.c. results just after mixing the two monomers and before any dissolution of the diamine powder has occurred

Comonomers		4,4′-DDS	3,3′-DDS	BAPP	BAPS
Temp. (°C)	T_1	130	125	95	140
of the peak	T_p	225	204	185	193
of reaction	T_2	320	305	285	285
ΔH_0 (J g^{-1})		402	428	413	361
ΔH_0 (kJ/ee)		93.5	99.1	112.9	99.7
T_g (°C) 2nd scan		177	147	130	142

Table 3 D.s.c. results after mixing the two monomers and after dissolution of the diamine has occurred

Comonomers	4,4′-DDS	3,3′-DDS	BAPP	BAPS
Time (min) of dissolution	15	13	9	30
T_g (°C) after dissolution	−2	−5	−2	40
ΔH (J g^{-1})	386	406	349	178
x (%)[a]	4	5	15.5	50.6
T_g (°C), 2nd scan	193	154	161	174

[a] $x = 1 - (\Delta H/\Delta H_0)$ with ΔH_0 from *Table 2*

(ii) Secondly, the same experiments were conducted on homogeneous mixtures, after dissolution of the diamine at 135°C. The data are reported in *Table 3*. Compared to ΔH_0, ΔH decreases in each case and the extent of reaction after dissolution can be evaluated by $x = 1 - \Delta H/\Delta H_0$. The values of x are also listed in *Table 3*, where it is seen that x is very high for the BAPS curing agent: half of the reaction occurred during the mixing at 135°C, just under the theoretical gel point. A high T_g (40°C) of this mixture after dissolution is also noticed. For these reasons, this formulation is difficult to process compared to the three others, and obtaining kinetic measurements was not possible in this case. The values of T_g after mixing are below 0°C for the three other systems, and they remain processable. The smallest extent of reaction ($\simeq 4\%$) is observed for 4,4′-DDS.

The advancement of the reaction after dissolution can also be determined by s.e.c. analysis of the mixture by measuring the peaks of the monomers (see next section), and similar results are obtained.

Gelation and kinetics

The gel point is defined as the conversion at which the weight-average molecular weight $\bar{M}_w$ diverges and an infinite network begins to form, which is insoluble in any solvent. Therefore, s.e.c. is a suitable method to determine the gel time and the extent of reaction at the gel point during the same experiment. After a given time at an isothermal curing temperature T_i, 0.1 g samples are dissolved in 10 ml THF. The solution is filtered on a Millipore membrane (0.2 μm), gelation occurs when the filter becomes plugged. The solution is analysed by s.e.c. to obtain $\bar{M}_w$ and $\bar{M}_n$ before gelation and the conversion as a function of time.

Examples of the chromatograms obtained for DGEBA–3,3′-DDS at $T_i = 100$°C at different curing times are shown on *Figure 1*. At $t = 0$ (in fact, $t = 0$ in this case means just after solubilization of the curing agent at 135°C – *Table 2*) four peaks are noticed: (i) two peaks are attributed to dimers and trimers and are due to the reaction occurring during mixing ($t_e = 17.9$ and $t_e = 18.7$ min); (ii) a peak at $t_e = 20.2$ min attributed to 3,3′-DDS; and (iii) a peak at $t_e = 20.6$ min attributed to

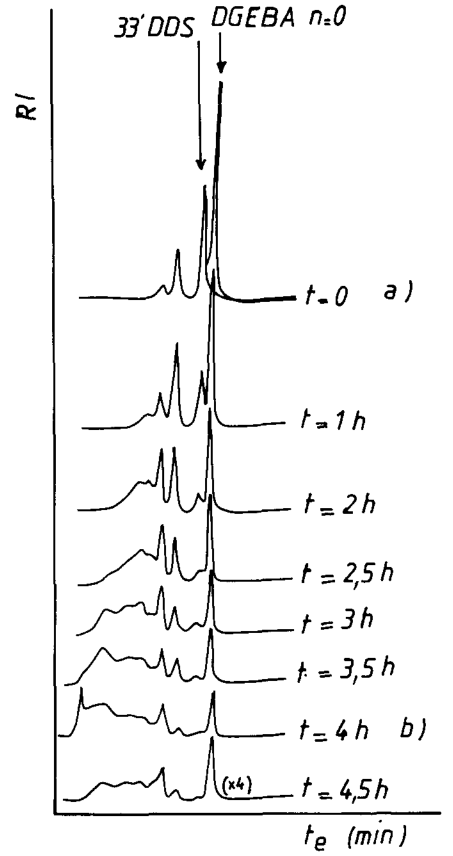


Figure 1 S.e.c. chromatograms at different reaction times for the DGEBA + 3,3'-DDS system in stoichiometric proportion: (a) $t=0$ plus 13 min at 135°C for the dissolution of DDS; (b) insoluble fraction, gelation occurs between $t=4$ h and $t=4.5$ h

the DGEBA monomer. As time increases, the intensity of these last two peaks decreases while products of higher molecular weight are produced. In this case insoluble fractions are produced after 4 h at $T_i = 100°C$.

Figure 2 represents the kinetic scheme of curing of diepoxide with a diamine. By a calibration curve previously developed, the disappearance of the two monomers $X_e = 1 - [E_{ee}]_t/[E_{ee}]_0$ and $X_a = 1 - [A_{tt}]_t/[A_{tt}]_0$ can be followed, while the polystyrene calibration leads to the approximate values for $\bar{M}_w$ and $\bar{M}_n$. $[E_{ee}]$ and $[A_{tt}]$ are respectively DGEBA and diamine concentrations proportional to the heights of the peak, h, (h_0 is the height of the peak before dissolution).

The change of $\bar{M}_w$ vs. time at $T_i = 100°C$ is plotted in *Figure 3* for DGEBA–4,4'-DDS, DGEBA–3,3'-DDS and DGEBA–BAPP and in *Figure 4* for DGEBA–BAPS studied at 100 and 120°C but without previous solubilization of BAPS. In *Figures 3* and *4* arrows indicate the times at which insoluble fractions in THF were first detected. As expected by the theory, $\bar{M}_w$ diverges at the gel point.

The conversions of DGEBA monomer X_e and curing agent X_a as a function of time are shown in *Figures 5* and *6*. We observed that for every system the molecules of diamine disappeared more rapidly than the molecules of DGEBA. Since s.e.c. allows the separation of molecules, this representation does not exhibit the disappearance of epoxy or amine groups.

However, as both epoxides have equal reactivities and there are no substitution effects[8–10], the fraction of unreacted DGEBA at a certain epoxy conversion x_e is given by the simultaneous probability that both epoxy

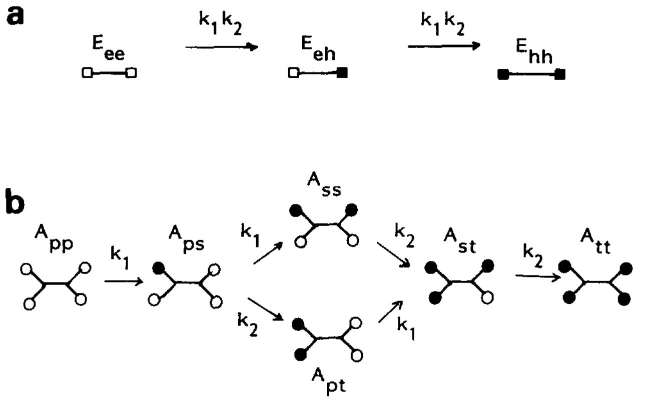


Figure 2 Kinetic scheme of the curing of a diepoxide (a) with a diamine (b) for fractions of monomer units with different numbers of reacted functionalities

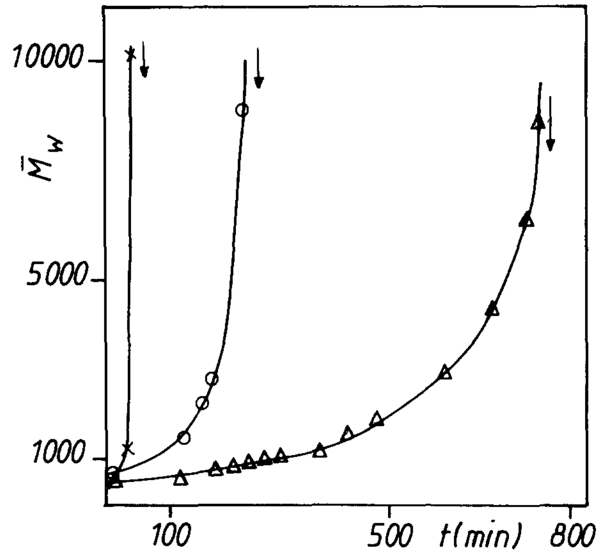


Figure 3 Change in approximate weight-average molecular weight $\bar{M}_w$ as a function of reaction time at $T_i = 100°C$ for different comonomers dissolved at 135°C: (△) 4,4'-DDS; (○) 3,3'-DDS; (×) BAPP

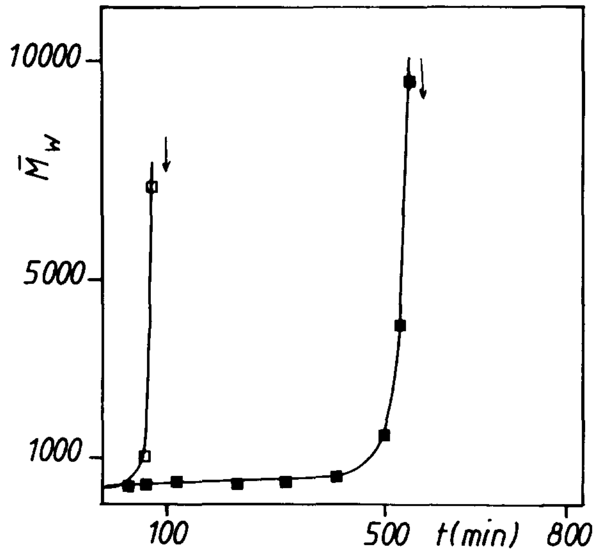


Figure 4 Change in approximate weight-average molecular weight $\bar{M}_w$ as a function of time at different isothermal curing temperatures T_i and for the BAPS comonomer dispersed as a powder in the DGEBA prepolymer: (■) $T_i = 100°C$; (□) $T_i = 120°C$

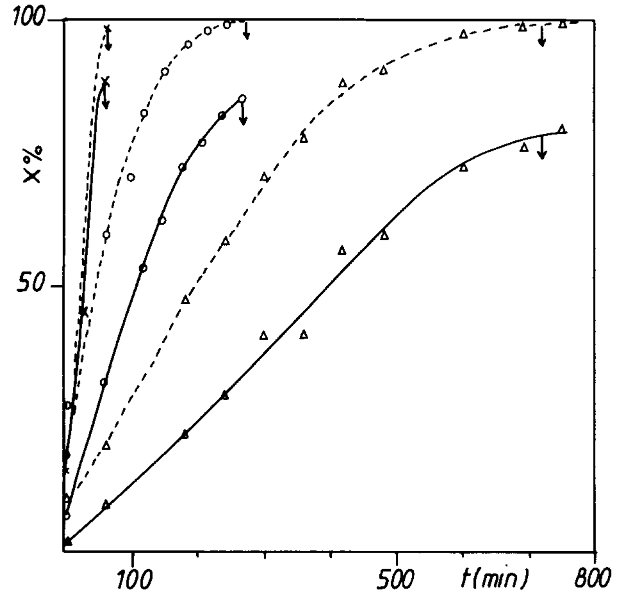


Figure 5 Monomer conversion vs. reaction time at $T_i = 100°C$ for DGEBA and different diamines dissolved at 135°C: (△) 4,4′-DDS; (○) 3,3′-DDS; (×) BAPP; full curves, X_e; broken curves, X_a

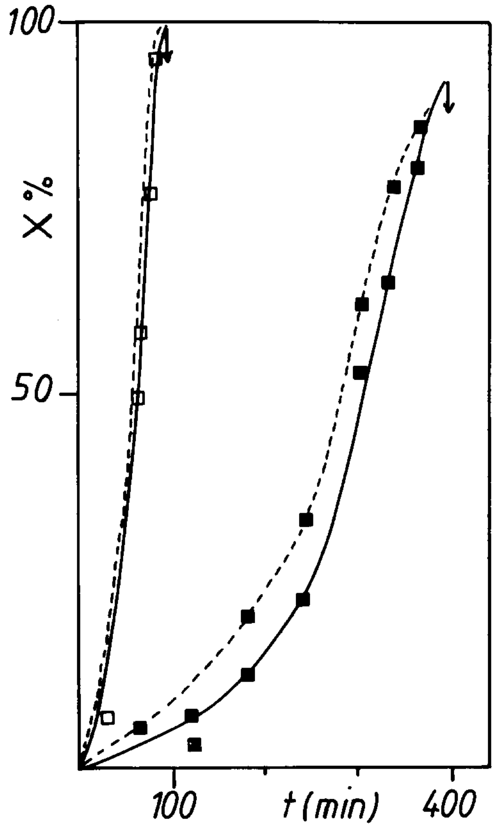


Figure 6 Monomer conversion vs. reaction time at different isothermal temperatures for DGEBA and BAPS powder: (■) 100°C; (□) 120°C; full curves, X_e; broken curves, X_a

groups remain unreacted[17]. Thus:

$$[E_{ee}]_t/[E_{ee}]_0 = 1 - X_e = (1 - x_e)^2 \qquad (1)$$

and if $[E_{ee}]_t/[E_{ee}]_0$ is equal to $(h_t/h_0)_e$, the ratio of the actual height of the peak with respect to the initial one (before the dissolution of the diamine), then equation (1) leads to:

$$x_e = 1 - (h_t/h_0)_e^{1/2} \qquad (2)$$

Figure 7 shows the change in epoxy conversion with time at $T_i = 100°C$ for three diamines previously dissolved at 135°C. Gelation, defined by the time at which the presence of an insoluble fraction in THF was first detected, takes place at a conversion x_e close to 0.62 ($X_e = 0.85$).

Since we have determined the epoxy conversion, it is now possible to plot the experimental values of the weight-average molecular weight $\bar{M}_w$ as a function of epoxy conversion x_e (*Figure 8*). This representation is independent of time (and also of temperature T_i, not presented here); a single curve is obtained for the three diamines. With a cycloaliphatic diamine, Verchère *et al.*[17] have shown that there is an excellent agreement between $\bar{M}_w$ calibrated with polystyrene standards and theoretical predictions.

With diepoxide and diamine systems, gelation takes place when $x_{gel} = 0.577$ for the reactivity ratio $r = k_2/k_1 = 1$, and increases to 0.618 when k_2/k_1 tends to zero[8,9]. Our value at $x_{gel} = 0.62$ agrees with the theoretical prediction for the case when $k_1 \gg k_2$.

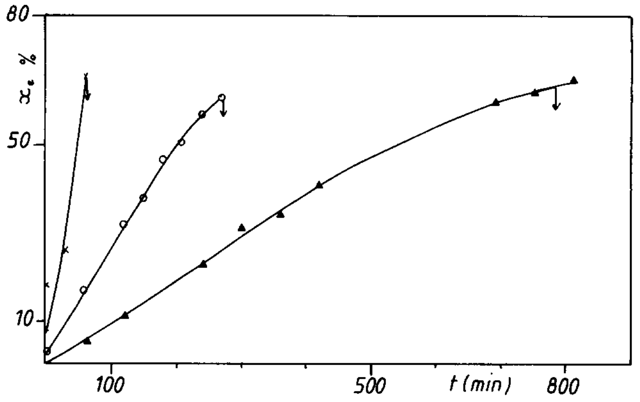


Figure 7 Epoxy conversion as determined by s.e.c. vs. reaction time at 100°C for different comonomers dissolved at 135°C (see *Table 3*): (▲) 4,4′-DDS; (○) 3,3′-DDS; (×) BAPP. Arrows (↓) indicate gelation time (insoluble fraction)

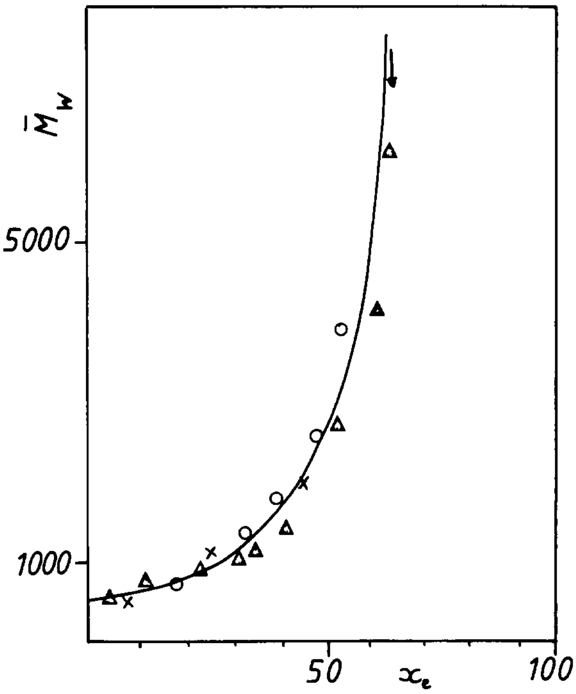


Figure 8 Change in approximate weight-average molecular weight as a function of epoxy conversion for different diamines at $T_i = 100°C$: (△) 4,4′-DDS; (○) 3,3′-DDS; (×) BAPP

In the literature, the existing results concerning the r values are somewhat controversial. For aliphatic diamines the majority of the reported r values are close to unity[9,10], the ideal value without substitution effects. The situation is quite different for aromatic diamines. Some authors[10,14] have also proposed r values close to unity, while others reported values for 4,4′-DDS or DDM ranging from 0.2 to 0.6[9,15]. More recently Verchère *et al.*[17] found $r = 0.4$ for a cycloaliphatic diamine with steric hindrance: 3,3′-dimethyl-4,4′-diaminodicyclohexylmethane (3DCM).

There are generally two types of experimental methods for determining the r values: determination of the critical stoichiometric ratio[9,15,18], or comparison between the theoretical and experimental distribution curves of the i-mers[10,14,15,17]. We have chosen to use the second method.

If we consider the ideal situation, $k_2 = k_1$, the fraction of unreacted diamine at a certain amino hydrogen conversion x_a is given by the simultaneous probability that four aminohydrogen groups remain unreacted. Thus:

$$1 - X_a = (1 - x_a)^4 \tag{3}$$

At the time of reaction $x_a = x_e$. Taking this into account in equation (1) results in:

$$1 - X_a = (1 - X_e)^2 \tag{4}$$

and

$$X_a = X_e(2 - X_e) \tag{5}$$

In *Figure 9*, we have plotted X_a vs. $X_e(2 - X_e)$ for 3,3′- and 4,4′-DDS. All of the experimental points are above the ideal situation, which is depicted by the bisecting line. Thus the hypothesis that the reactivities of the four amino hydrogen groups are equal is not correct. The secondary amine groups formed are less reactive than the primary ones. Therefore, the diamine monomer disappears faster than DGEBA:

$$X_a > X_e(2 - X_e)$$

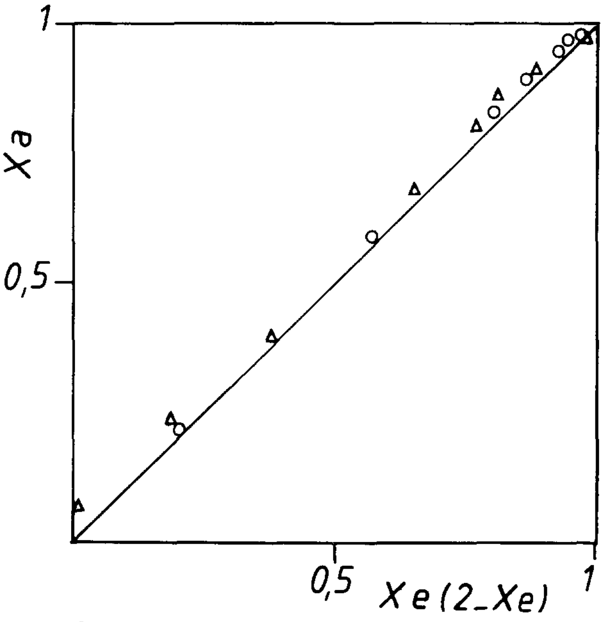


Figure 9 Comparison between the two monomer conversions X_a and X_e as determined by s.e.c. at $T_i = 100°C$ for different comonomers dissolved at 135°C: (△) 4,4′-DDS; (○) 3,3′-DDS; full line, ideal ratio $k_2/k_1 = 1$

As we have demonstrated that $r < 1$, we can now calculate its value. On the basis of *Figure 1*, and assuming that:

(i) the reactivities of the epoxide group are independent,

(ii) the ratio of rate constants k_2/k_1 does not depend on conversion,

(iii) no etherification occurs, and

(iv) the predominant reaction mechanism is the non-catalytic reaction ($T_i > 100°C$), one can write a series of differential equations as described by Dusek *et al.*[8]:

$$-d[A_{pp}]/dt = 4k_1[A_{pp}][b] \tag{6}$$

$$-d[A_{ps}]/dt = \{2k_1[A_{ps}] + k_2[A_{ps}] - 4k_1[A_{ps}]\}[b] \tag{7}$$

$$-d[A_{ss}]/dt = \{2k_2[A_{ss}] - 2k_1[A_{ps}]\}[b] \tag{8}$$

$$-d[A_{pt}]/dt = \{2k_1[A_{pt}] - k_2[A_{ps}]\}[b] \tag{9}$$

$$-d[A_{st}]/dt = \{k_2[A_{st}] - 2k_2[A_{ss}] - 2k_1[A_{pt}]\}[b] \tag{10}$$

$$-d[A_{tt}]/dt = -k_2[A_{st}][b] \tag{11}$$

where [b] is the concentration of unreacted epoxy groups, A_{pp} is the fraction of unreacted diamine and A_{ps}, A_{ss}, A_{pt}, A_{st}, A_{tt} correspond to the fractional amounts of cure products as defined in *Figure 2*.

If the reaction takes place by two competitive paths, we also have an autocatalytic mechanism by OH groups and we must introduce a second similar set of differential equations with two other rate constants k'_1 and k'_2 and introduce the hydroxyl concentration [OH] as a factor[15,17]. But if it is assumed that the ratio of uncatalysed primary to secondary amine reactions, k_2/k_1, is the same as the ratio for the catalysed reaction, k'_2/k'_1 (ref. 9), the two sets of equations have the same analytic solution.

The set of differential equations (6) to (11) may be solved by dividing all the equations by the first one, thus eliminating the dependence on time. The following solution is obtained[8], where the fraction of each cure species is expressed as a function of the reactivity ratio k_2/k_1 and the fraction of unreacted diamine $[A_{pp}]$:

$$[A_{ps}]/[A_{pp}]_0 = 2p\{[A_{pp}]^q - [A_{pp}]\} \tag{12}$$

$$[A_{ss}]/[A_{pp}]_0 = p^2\{-2[A_{pp}]^q + [A_{pp}] + [A_{pp}]^{r/2}\} \tag{13}$$

$$[A_{pt}]/[A_{pp}]_0 = -2p[A_{pp}]^q + rp[A_{pp}] + 2[A_{pp}]^{1/2} \tag{14}$$

$$\begin{aligned}[A_{st}]/[A_{pp}]_0 = p^2\{(r+2)[A_{pp}]^q - r[A_{pp}] - (2-r)[A_{pp}]^{1/2} \\ - 2[A_{pp}]^{r/2} + (2-r)[A_{pp}]^{r/4}\}\end{aligned} \tag{15}$$

$$\begin{aligned}[A_{tt}]/[A_{pp}]_0 = p^2\{-r[A_{pp}]^q + (r^2/4)[A_{pp}] + (r/p)[A_{pp}]^{1/2} \\ + [A_{pp}]^{r/2} - (2-r)[A_{pp}]^{r/4} + (r/2-1)^2\}\end{aligned} \tag{16}$$

where $[A_{pp}]_0$ is the initial concentration of the diamine, $r = k_2/k_1$, $p = 1/(1 - r/2)$ and $q = (1 + r/2)/2$.

Then the overall extent of reaction x_a:

$$x_a = \frac{[A_{ps}] + 2[A_{ss}] + 2[A_{pt}] + 3[A_{st}] + 4[A_{tt}]}{4[A_{pp}]_0} \tag{17}$$

can now be written in terms of $[A_{pp}]$ and r only, as follows:

$$x_a = 1 - \frac{1}{2-r}\{(1-r)[A_{pp}]^{1/2} + [A_{pp}]^{r/4}\} \tag{18}$$

At different curing times, x_a and $[A_{pp}]$ can be determined experimentally utilizing the following expressions:

$$x_a = x_e = 1 - (h_t/h_0)_e^{1/2}$$

$$[A_{pp}] = (h_t/h_0)a$$

We determined the r values that best fit the experimental data; r was determined to be 0.9 for the DGEBA–4,4′-DDS system and to be 0.8 for the DGEBA–3,3′-DDS system.

These values just lower than 1 agree well with the experimental data in *Figure 9*, but are larger than the ones expected after the x_{gel} determination. Indeed, at the stoichiometric balance when $r = 0.2$, the predicted gel conversion is 0.61, while the gel conversion is 0.59 when $r = 0.6$ (note that the gel conversion is most sensitive to variations in r in systems containing excess amine[8]). This discrepancy could be explained by the reaction of epoxy groups with hydroxyl functionalities. But we verified that we have no ether linkages ($\rangle$*CH–O–CH$_2$ band at 76.5 ppm[13]) using the ^{13}C n.m.r. high-resolution spectra (62.89 MHz) in the solid state. Therefore we were unable to explain this discrepancy except by an experimental error range.

For this reason, and also because we are not sure that we only have an uncatalysed reaction, we think that it is difficult to calculate precisely the rate constants. However we can integrate equation (6) and evaluate an average k_1 value. We found k_1 values of $5 \times 10^{-4}\,\mathrm{min}^{-1}$ for 4,4′-DDS and $2 \times 10^{-3}\,\mathrm{min}^{-1}$ for 3,3′-DDS at 100°C, which are in the same order of magnitude as found by Paik Sung *et al.*[14] (these authors use $r = 1$ for an uncatalysed reaction).

Finally, the gel time, which was taken to be the time when insoluble fractions were first detected in THF, was determined at different temperatures in the range of 50–140°C. The results are reported in *Table 4*.

Comparison of the reactivities of aromatic diamines

The change of viscosity was determined at different isothermal temperatures for homogeneous mixtures based on DGEBA ($n = 0.03$) and 4,4′-DDS, 3,3′-DDS and BAPP. For different systems and for certain reaction times, η tends to infinity, which signifies either gelation or vitrification.

Assuming Arrhenius kinetics, the time required to reach a high viscosity of 10 000 Pa s, t_η (equal to a given degree of conversion x at the gel point, which is assumed to be temperature-independent), can be written:

$$t_\eta = t_0 \exp(E_a/RT) \tag{19}$$

Experimental results are also reported in *Table 4* and are in the same range of values as t_{gel} determined previously. With this type of measurement it is easy to compare rapidly the reactivities of the diamines. An Arrhenius plot is shown in *Figure 10* for each system at T_i higher than 60°C. The apparent activation energy determined from the slope of the curve is 53 kJ mol^{-1} for the three formulations but also for the DGEBA–DDM system used for comparison. In the range of temperatures studied (60–140°C), if the reactivity of 4,4′-DDS is 1, the others can be estimated to be 3–4 for 3,3′-DDS, 12 for BAPP and 16 for DDM.

The SO$_2$ group has a delaying action on the reactivity of the amine functions because it is a high-electron-attracting group which decreases the basicity of the diamine. This effect is emphasized for *para* substitution because the electron transfer from NH$_2$ to SO$_2$ is the easiest. The group –CH$_2$– is an electron donor, and therefore DDM is more reactive than DDS.

BAPS is also expected to be less reactive than BAPP. This is verified by s.e.c. measurements (*Figures 3* and *4*). But it is satisfactory to find BAPP (and also BAPS) more reactive than DDS and less reactive than DDM due to the action of the –O– group.

The values obtained for the activation energy for the two measurements t_η and t_{gel} (insoluble fraction) are of the same order :53 ± 3 kJ mol^{-1}. Our value for DGEBA–4,4′-DDS is smaller than the value obtained by Paik Sung

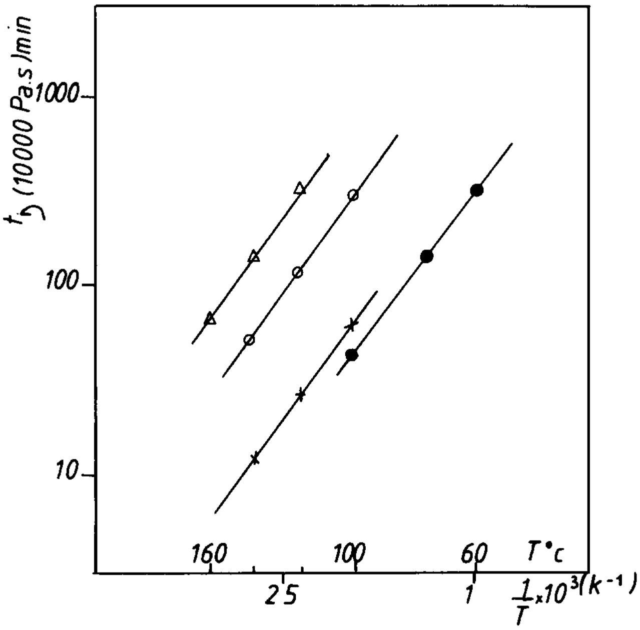


Figure 10 Variations in the time required to reach 10 000 Pa s *versus* 1/*T* for the various systems: (△) 4,4′-DDS; (○) 3,3′-DDS; (×) BAPP; (●) DDM

Table 4 Gelation time, t_{gel} (min), and vitrification time, t_{vit} (min), at different isothermal temperatures, T_i, compared with the time when the viscosity tends to infinity, t_η ($\eta = 10\,000$ Pa s)

	4,4′-DDS			3,3′-DDS			BAPP		
T_i (°C)	t_η	t_{gel}	t_{vit}	t_η	t_{gel}	t_{vit}	t_η	t_{gel}	t_{vit}
50	–	∞	16 800	–	∞	4680	–	–	–
60	–	–	–	–	–	–	–	480	390
80	–	–	–	–	690	810	–	150	155
100	–	810	1 170	305	270	420	60	60	85
120	318	365	580	119	135	270	26	–	–
140	141	165	380	51	–	–	11	–	–

et al.^{14} using kinetic measurements (60 kJ mol^{-1}) and by Harran *et al.*^{19} (63 kJ mol^{-1}) for the same system followed by viscoelasticimetry. The differences observed can be mainly related to the experimental preparation of the samples (times and temperature of dissolution).

Vitrification and TTT diagrams

Vitrification occurs when the glass transition temperature $T_g(t)$ of the reactive system reaches the isothermal curing temperature T_i. Vitrification marks the transformation from a rubber to a gelled glass if gelation has occurred, or from a liquid to an ungelled glass if gelation has not occurred.

D.s.c. is used to follow the evolution of $T_g(t)$ *versus* time at various T_i for the three homogeneous systems under study. An example of the curves obtained at 100°C is shown in *Figure 11*. For these three systems, at this temperature, vitrification follows gelation. After reaching the reaction temperature, T_g increases much slower and practically stops—at least in a time-scale for days—at a $(T_g - T_i)$ close to 35°C. The beginning of vitrification, as defined by t_{vit}, does not freeze the chemical reaction, but the reactions begin to be diffusion-controlled. The times required to reach vitrification obtained at various temperatures are also reported in *Table 4*.

The concept of a time–temperature–transformation (TTT) cure diagram has been developed by Gillham^{20} for polymer systems and represents the time required to reach gelation and vitrification during an isothermal cure.

Figure 12 shows gelation and vitrification curves in a TTT diagram for the three systems studied. T_{g0} represents the glass transition temperature of the initial reactive mixture before any reaction has taken place. As the systems are not initially homogeneous, T_{g0} is obtained by extrapolation to $x = 0$ of the curve x vs. T_g in the range between x after dissolution (*Table 3*) and $x = 0.15$. $T_{g\infty}$ represents the glass transition temperature of the fully cured networks determined on plates. The curing cycles will be described with the mechanical properties in a later publication^{21}.

T_{g0} and $T_{g\infty}$ values are given in *Table 5*. The highest T_g (218°C) is obtained for the system based on 4,4′-DDS; networks based on 3,3′-DDS and BAPP have the same $T_{g\infty} \simeq 170$°C. For the DGEBA–BAPS system, $T_{g\infty} = 183$°C but the TTT diagram has not been plotted, owing to experimental problems previously noted. For comparison $T_{g\infty}$ is equal to 178°C for the DGEBA–DDM system.

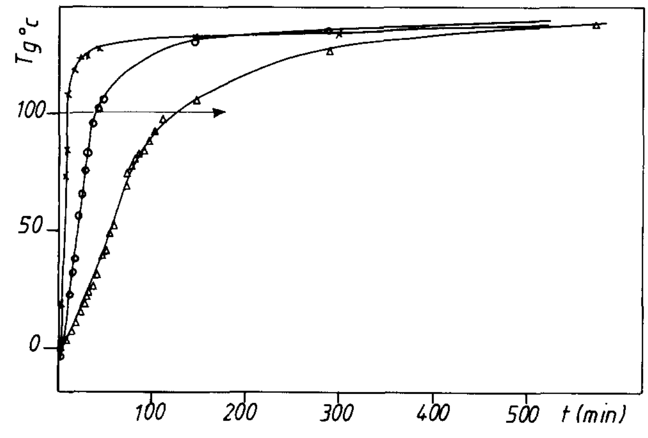


Figure 11 Increase in the glass transition temperature as a function of curing time at $T_i = 100$°C for DGEBA ($\bar{n} = 0.03$) with: (△) 4,4′-DDS; (○) 3,3′-DDS; (×) BAPP

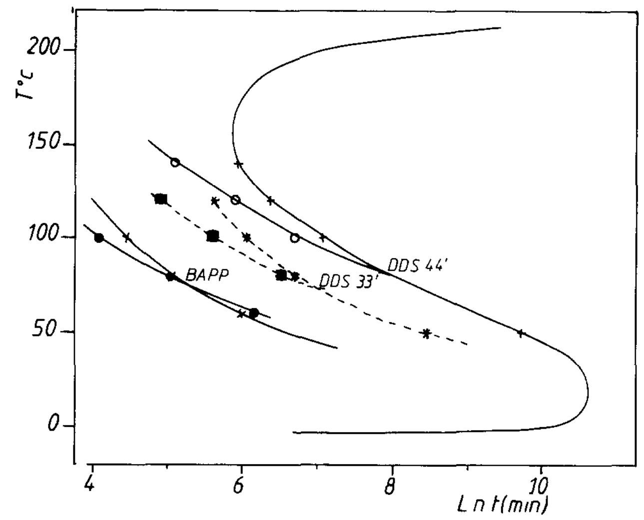


Figure 12 Time–temperature–transformation (TTT) diagram for DGEBA ($\bar{n} = 0.03$) and different aromatic diamines. BAPP: (●) gelation; (×) vitrification. 3,3′-DDS: (■) gelation, (✱) vitrification. 4,4′-DDS: (○) gelation; (+) vitrification

The temperature at which gelation and vitrification take place simultaneously is defined as ${}_{gel}T_g$. The values of ${}_{gel}T_g$ are estimated to be 81°C for DGEBA–4,4′-DDS, 74°C for DGEBA–3,3′-DDS and 75°C for DGEBA–BAPP. At $T_i > {}_{gel}T_g$ gelation takes place before vitrification and the opposite occurs at $T_i < {}_{gel}T_g$. It is interesting to note that for the 4,4′-DDS curing agent, gelation is not observed at 50°C even after three months.

Relations between the glass transition temperature T_g and the conversion x

In his analysis of crosslinking effect on physical properties of polymers, Nielsen^{22} reported unpublished results by Di Benedetto leading to an equation relating the shift in the glass transition temperature to the reaction extent x:

$$\frac{T_g - T_{g0}}{T_{g0}} = \frac{(\varepsilon_x/\varepsilon_m - F_x/F_m)x}{1 - (1 - F_x/F_m)x} \tag{20}$$

where F_x/F_m is the ratio of segmental mobilities for a certain extent x, with respect to the mixture of monomers ($x = 0$); $\varepsilon_x/\varepsilon_m$ is the corresponding ratio of lattice energies.

Enns and Gillham^{23} showed that a very good fit of several experimental T_g vs. x relationships could be obtained when both $\varepsilon_x/\varepsilon_m$ and F_x/F_m were taken as adjustable parameters. Moreover from equation (20) when $x = 1$ the ratio of both parameters is given by:

$$\frac{\varepsilon_x/\varepsilon_m}{F_x/F_m} = \frac{T_{g\infty}}{T_{g0}} \tag{21}$$

Introducing equation (21) into equation (20) and setting $F_x/F_m = \lambda$, we get:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda x}{1 - (1 - \lambda)x} \tag{22}$$

where λ must be considered as an adjustable parameter lying between 0 and 1.

On the other hand, experimental determination of TTT diagrams leads to the location of ${}_{gel}T_g$ (*Figure 12* and *Table 5*). Accepting the validity of equation (22) and taking into account the rough approximation that for $x = 0.6$, $T = {}_{gel}T_g$ (for our system we have measured

Table 5 Comparison of λ and $\Delta C_{p\infty}/\Delta C_{p0}$ values for different diepoxy (DGEBA, $\bar{n}=0.03$) – aromatic diamine systems

Diamine comonomer	T_{g0} (K)[a]	$T_{g\infty}$ (K)	${}_{gel}T_g$ (K) (± 2 K)	λ (± 0.02)	ΔC_{p0}[b] ($J g^{-1} K^{-1}$) (± 0.02)	$\Delta C_{p\infty}/\Delta C_{p0}$ (± 0.04)	$T_{g0}/T_{g\infty}$
4,4′-DDM	257	451	–	–	0.64	0.39	0.57
4,4′-DDS	268	491	354	0.42	0.51	0.38	0.55
3,3′-DDS	266	444	347	0.56	0.52	0.60	0.60
BAPP	265	442	348	0.59	0.53	0.56	0.60

[a] T_{g0}, see text

[b] ΔC_{p0} measured just after the dissolution of the diamine has occurred

$x=0.62$), the adjustable parameter λ is given by:

$$\lambda=\frac{2({}_{gel}T_g-T_{g0})}{3(T_{g\infty}-{}_{gel}T_g)}$$

This equation has been used recently by Pascault and Williams for different DGEBA ($\bar{n}=0.03$)–cycloaliphatic diamine systems[24].

Considering the thermosetting polymer as an equivalent random solution of monomers ($T_g=T_{g0}$) and a fully crosslinked network ($T_g=T_{g\infty}$) and applying Couchman's approach[25] for the expression of the compositional variation of T_g, these authors have also shown that the adjustable parameter λ may be estimated by the experimental value $\Delta C_{p\infty}/\Delta C_{p0}$ (ΔC_{pi} are the heat capacity changes at respectively $T_{g\infty}$ and T_{g0}). They have also noted that $\varepsilon_x/\varepsilon_m \simeq 1$ means $\Delta C_{p0}T_{g0}=\Delta C_{p\infty}T_{g\infty}$.

Our results with the same DGEBA prepolymer ($\bar{n}=0.03$) and different aromatic diamine comonomers are given in *Table 5*. We have a good correlation between λ and $\Delta C_{p\infty}/\Delta C_{p0}$. This result confirms that the Di Benedetto equation may be regarded as based on entropy considerations.

The values for λ and $\Delta C_{p\infty}/\Delta C_{p0}$ are around 0.4 for the two rigid comonomers, 4,4′-DDM and 4,4′-DDS, and around 0.6 for 3,3′-DDS and BAPP. The *meta* position on DDS compared to the *para* position has a similar effect as an increase in the length of the molecule in the case of BAPP compared to 4,4′-DDM. These values will be discussed in relation to the mechanical properties in a later publication[21].

To visualize the relative increase of T_g vs. x we have plotted in *Figure 13* the shape of the curves for $\lambda=0.4$ and $\lambda=0.6$. The relative increase of T_g is larger at higher reaction extents and this effect is more pronounced for $\lambda=0.4$.

The comparison between $\Delta C_{p\infty}/\Delta C_{p0}$ and $T_{g0}/T_{g\infty}$ indicates that the assumption $\Delta C_pT_g=$ constant (or $\varepsilon_x/\varepsilon_m=1$) is a good approximation only for the more flexible networks: DGEBA–3,3′-DDS and DGEBA–BAPP.

It is also interesting to compare the results of aromatic and cycloaliphatic diamines. For bis(p-aminocyclohexyl) methane and 4,4′-diamino-3,3′-dimethylcyclohexylmethane, λ and $\Delta C_{p\infty}/\Delta C_{p0}$ have been found in the range 0.44–0.50[24] with $\Delta C_{p\infty}/\Delta C_{p0} \neq T_{g0}/T_{g\infty}$.

CONCLUSIONS

Characterization of the mixing of reactants, the rate of reaction and the structural changes that occur during the cure have been done on model systems based on pure DGEBA and aromatic diamines differing in their backbone stiffness. We are now able to control the network formation and to develop structure–property relations.

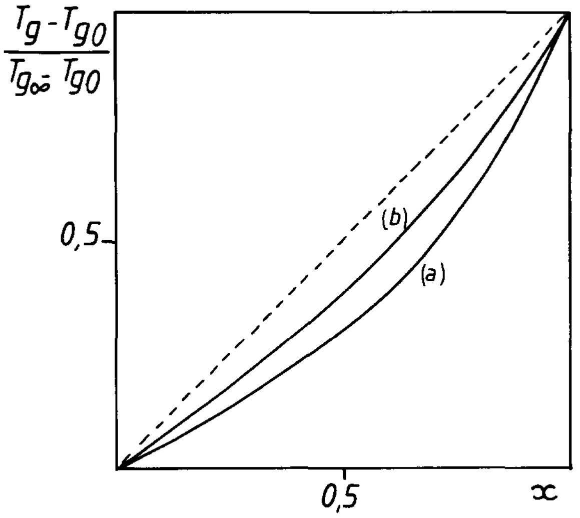


Figure 13 Relative increase of the glass transition temperature as a function of the thermoset conversion x for: (a) $\lambda=0.4$, case of 4,4′-DDM and 4,4′-DDS; (b) $\lambda=0.6$, case of 3,3′-DDS and BAPP

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