Inverse gas chromatography used to follow kinetics of epoxy–amine reactions in the molten state

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(Revised 17 March 1987; accepted 9 June 1987)

Polycondensation kinetics of epoxy–amine model systems were investigated with inverse gas chromatography. The results obtained were applied to the study of cross-linking kinetics of two epoxy prepolymers, tetraglycidyl diamino diphenyl methane and diglycidyl ether of bisphenol A, with diamino diphenyl sulphone. Data furnished by inverse gas chromatography showed zones of gelation and of vitrification. Based on kinetics established by isothermal microcalorimetry, it was possible to determine reaction advancement in these transition zones. The results show that advancement of both reaction systems to the transition points T_1 and T_2 is very sensitive to curing temperature and to the stoichiometry of the mixture. Finally, the vitreous transition temperatures of the cross-linked systems were determined and compared to those determined with differential scanning calorimetry.

(Keywords: inverse gas chromatography; polycondensation; kinetics; gelation; vitrification; microcalorimetry; epoxide; aromatic diamine)

INTRODUCTION

Following our prior work[1-4] on the polycondensation kinetics and mechanisms of heat hardened systems, we used inverse gas chromatography (i.g.c.) to study the reaction kinetics of two epoxy prepolymers, one bifunctional (diglycidyl ether of bisphenol A, DGEBA), the other tetrafunctional (tetraglycidyl diamino diphenyl methane, TGDDM) polycondensed with aromatic amines (diamino diphenyl sulphone, DDS) at different temperatures.

The results were compared with those obtained with Calvet microcalorimetry and various mechanical methods[5] and led to the definition not only of a 'gelation point', but also of a 'gelation zone' in both systems.

EXPERIMENTAL

Instrumentation

Inverse gas chromatography (i.g.c.). The reaction mixture (epoxide prepolymer and aromatic amine in stoichiometric and non-stoichiometric ratios depending on the system) was deposited on a silicaceous support comparable to porous glass beads. The 2–4 m long $\frac{1}{8}$ in (3.2 mm) diameter column was prepared by the usual methods. It was then rapidly brought to the temperature chosen for kinetic studies.

Different solute mixtures (alkanes, aromatic compounds and alcohols) were periodically added and the variations in retention volumes $(V_R)'$ were followed as a function of time.

Calvet microcalorimetry. Polycondensation kinetics of 2–3 g samples were followed by isothermal calorimetry in the temperature range 100–180°C with a high temperature model Calvet microcalorimeter. Calibration was by the electrical method. To relate thermograms to the advancement of the reaction, the total heat of reaction was used, established by differential scanning calorimetry on various epoxide prepolymer–aromatic amine systems[6].

Differential scanning calorimetry. A Perkin–Elmer DSC 4 differential scanning microcalorimeter was used. The scan rate was 5°C min^{-1} between −60 and +350°C.

Materials

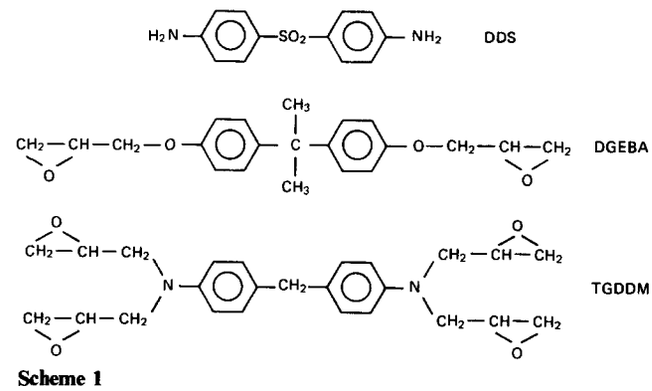
The formulae of reagents used in the study are shown in Scheme 1.

Two types of epoxide prepolymers were used: DER 332 ($n=0$) (Dow) and Lopox 3302 (CDF Chimie), on which a prior detailed analytical study had been carried out using h.p.l.c. and ^{13}C liquid nuclear magnetic resonance (n.m.r.)[7]. The stoichiometric ratio $r=e/a$ expresses the ratio of epoxide groups to amine functions.

ANALYSIS OF THE RESULTS

Principle of the method[8-11]

The retention volume of a solute in gas chromatography is related to the physical state of the



Scheme 1

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stationary phase. If it is a solid, retention volume is proportional to the specific surface area:

$$(V_R)'_A = K_A A_S \quad (1)$$

The partition coefficient K_A is related to the vapour pressure of the solute and to the adsorption properties of the stationary phase.

If the stationary phase is a liquid, retention is proportional to the volume of stationary phase added to the column:

$$(V_R)'_S = K_{S^\circ} V_L \quad (2)$$

The value of the coefficient K is

$$K = \frac{RT}{\gamma^\circ P^\circ} \frac{\rho}{M_L} \quad (3)$$

where T is temperature, ρ the density of the stationary phase, M_L the molecular mass of the stationary phase, P° the vapour pressure of the solute and γ° the activity coefficient of the solute.

The following is obtained by combining (2) and (3):

$$(V_R)'_S = \frac{RT\omega}{\gamma^\circ P^\circ M_L} \quad (4)$$

with $\omega = V_L$ (weight of the stationary phase in the column).

The present report describes two types of experiment on reaction kinetics in the molten state. At the beginning of the reaction, we are dealing with a liquid mixture whose polycondensate becomes increasingly insoluble as the reaction progresses. When changes in state are determined, however, a solid state is transformed into a more or less molten state as the temperature increases, depending on the complexity of the systems examined.

At any given moment, solute retention can be described by:

$$(V_R)' = (V_R)'_S + (V_R)'_A \quad (5)$$

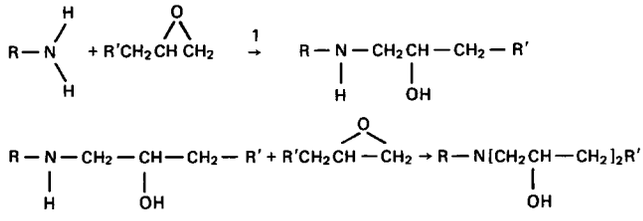
or

$$(V_R)' = K_A A_S + K_{S^\circ} V_L$$

and generally $K_A \ll K_S$, enabling changes in state to be observed.

In the liquid state, the retention of probe molecules is determined only by the solubilization term. The retention volume of a solute is sensitive to the molecular mass of the stationary phase, which increases as the reaction advances, and to the variations of the activity coefficient, related to chemical modifications of the stationary phase.

In epoxide–amine systems, the normal reactions expected in these systems are shown in Scheme 2.



Scheme 2

To determine the role of different functions appearing (hydroxyl, secondary or tertiary amine) or disappearing (epoxide, primary and secondary amines) in the course of cross-linking reactions of polycondensed systems, we first investigated model molecules similar to the prepolymers studied in this work.

I.g.c. study of model compounds

By changing the stoichiometric epoxide/amine ratios, model molecules were synthesized, characteristic of the different functional groups expected when the cross-linking kinetics of epoxide prepolymers are studied[14].

We were thus able to obtain intermediate and final reaction products with a satisfactory degree of purity. Using these model compounds (*Figure 1*), chromatography columns were prepared. Various probe molecules were chromatographed in the temperature range 40–160°C. Quantities injected were optimized in order to obtain the most symmetrical peaks possible so that the systems would be in the linear portion of the adsorption or solubilization isotherm[8–11].

A typical plot of ln V'_R against $f(1/T)$ for the four model compounds is shown in *Figure 2*.

Three zones can be distinguished:

Zone 1. At temperatures lower than T_1, the stationary phase is solid. Adsorption of solute compounds injected (*Figure 1*) is the major contribution to the value of V'_R. Chromatographic equilibrium is obtained and the slope of this linear portion is proportional to the heat of adsorption (solid gas chromatography).

Zone 2. This is the zone of fusion of the model compounds. Mobility of the chains enables the solute to diffuse. Surface retention mechanisms are now accompanied by the mechanism of sorption in the molten mass, which is shown by a progressive increase of the retention volume with increasing temperature until all the new sites rendered accessible are reached.

Zone 3. At high temperatures all the new sites of sorption rendered accessible are effectively reached, conditions of chromatographic equilibrium are re-established and ln V'_R against $f(1/T)$ again obeys a decreasing law and the slope of the line is proportional to the heat of dissolution in the model compound (liquid gas chromatography).

The activity coefficients calculated in Zone 3 (*Table 1*) show that for the alcohols (perfectly soluble since $\gamma^\circ < 1$) these values are independent of the nature of the stationary phase. For this family of solutes, retention volume is thus sensitive only to the molecular mass of the stationary phase, and equation (4) can be written

$$(V_R)'_S = \frac{cte}{M_L} \quad (6)$$

In the case of slightly polar or non-polar solutes, e.g. alkanes and aromatic derivatives, the activity coefficient decreases slightly as the molecular mass of the stationary phase increases. These results, in agreement with the theory of athermal solutions[8], enable γ° to be calculated on the basis of the ratio R of the molecular volumes of solvent and solute:

$$\gamma^\circ = \frac{\alpha R}{(R+\beta)^2} \quad (7)$$

with α and β numerical constants.

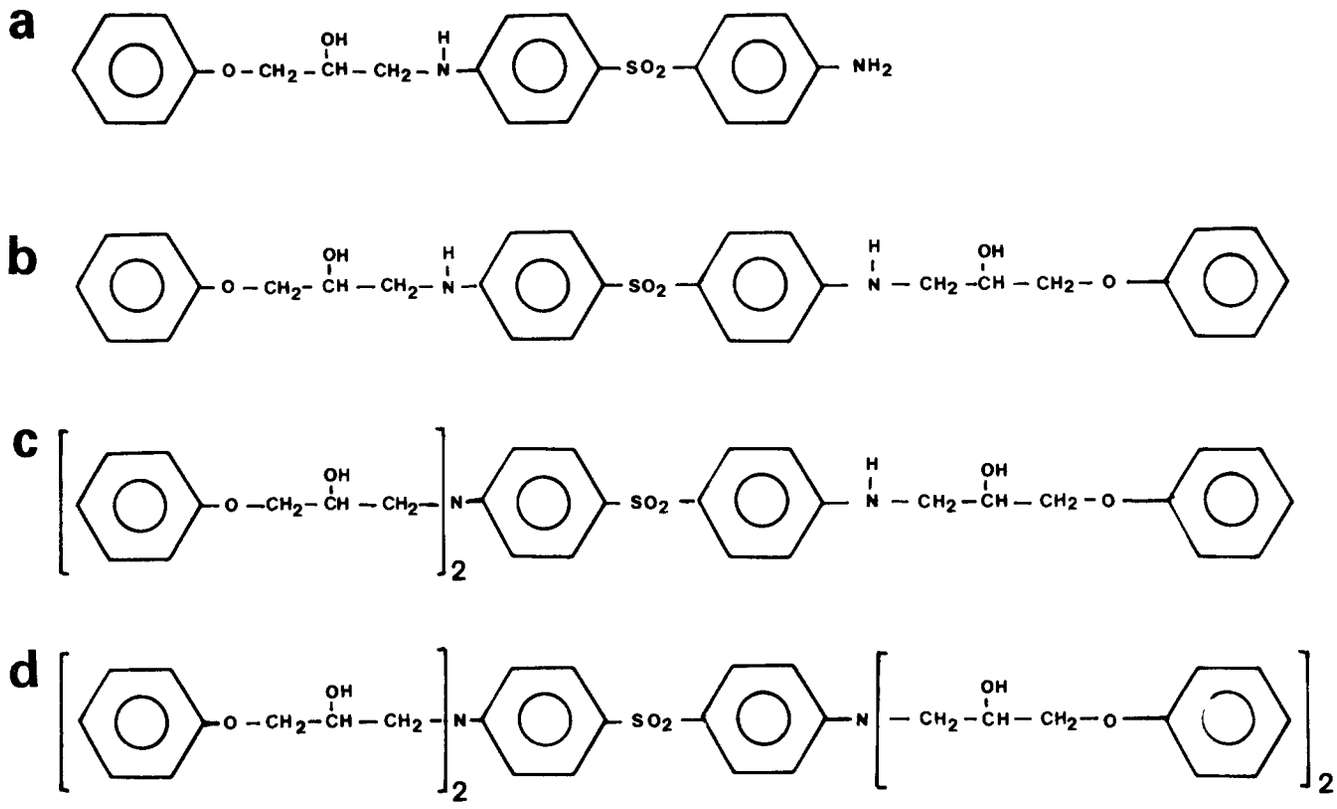


Figure 1 Model compounds studied

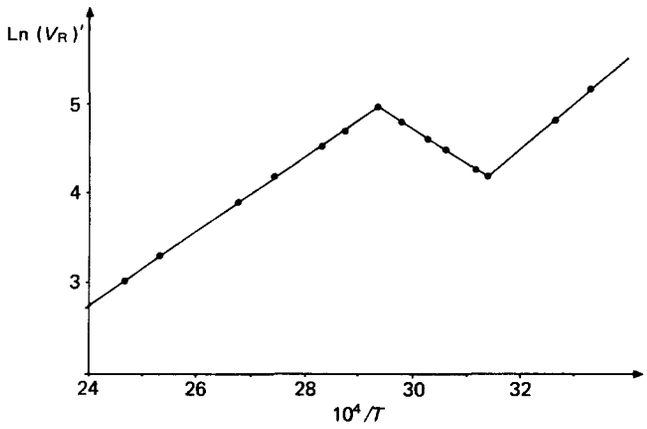


Figure 2 Typical variation in retention volume as a function of temperature for model compounds. I.g.c.; probe molecule, propyl benzene

If molar volume and molecular mass are taken to have the same value, we have the following expression for the retention volume

$$(V_R)'_S = K\frac{(M_L + K_1)^2}{M_L^2} \quad (8)$$

where K and K_1 are constants which depend on the solute.

As an example, the retention volumes of propyl benzene are listed in *Table 2*. They are verified by taking $K = 19$ and $K_1 = 144$.

In conclusion, the results obtained with the model compounds bearing the different chemical functions of epoxy–amine heat hardening systems show that the retention volume of the solutes is related to (1) the molar mass of the chromatographic solvent, in the case of systems changing towards reaction advancement; and (2) to the change in state. The appearance of molecules in the solid state is shown by a drop in the value of retention volumes, since the partition coefficients in adsorption are much lower than those of solubilization.

Epoxide prepolymer–aromatic diamine systems

The reactions involved in systems of bi- or tetrafunctional epoxide prepolymers of the type DGEBA and TGDDM with the aromatic amine DDS are theoretically identical to those described above. For the TGDDM–DDS system, however, we have shown that 'secondary' reactions other than epoxide–primary or – secondary amine can occur during the polycondensation process. Also, the resin-hardener systems are bi- or tetrafunctional, and so the reaction medium itself is cross-linked.

Isothermal reaction kinetics – $(V_R)'$ against $f(t)$. Figures 3 and *4* are examples of $(V_R)'$ against time curves obtained with non-polar solutes (alkanes, aromatics) and polar solutes (alcohol) for the TGDDM–DDS system. Similar curves for the systems studied exhibit different points of discontinuity. The first part (the beginning of the reaction) agrees with our kinetic model[2–4] based on an autocatalytic reaction mechanism:

$$\frac{dx}{dt} = k(R-x)(D-x) + k_1 x(R-x)(D-x)$$

where R and D are the number of resin and hardener molecules, respectively, at $t = 0$, and x is the number of molecules formed.

Table 1 Activity coefficients of two model compounds

Stationary phase	M_L	Probe molecules: Propyl benzene $T=140°C$	Propyl benzene $T=150°C$	1-butanol $T=140°C$	1-butanol $T=150°C$
Monosubstituted[a]	398	1.48	1.53	0.44	0.35
Disubstituted[b]	548	1.35	1.24	0.42	0.41
Trisubstituted[c]	698	1.16	1.04	0.42	0.38
Tetrasubstituted[d]	848	1.05	0.98	0.35	0.33

[a] *Figure 1(a)*
[b] *Figure 1(b)*
[c] *Figure 1(c)*
[d] *Figure 1(d)*

Table 2 Model compounds – calculated and experimental retention volumes; propyl benzene probe molecule

Stationary phase	M_L	$(V_R)'$ calc.[e]	$(V_R)'$ exp.
Monosubstituted[a]	398	35.2	35.2
Disubstituted[b]	548	30.3	30.5
Trisubstituted[c]	698	27.6	28.6
Tetrasubstituted[d]	848	26.0	26.0

[a] *Figure 1(a)*
[b] *Figure 1(b)*
[c] *Figure 1(c)*
[d] *Figure 1(d)*
[e] Equation (8) with $K=19$ and $K_1=144$

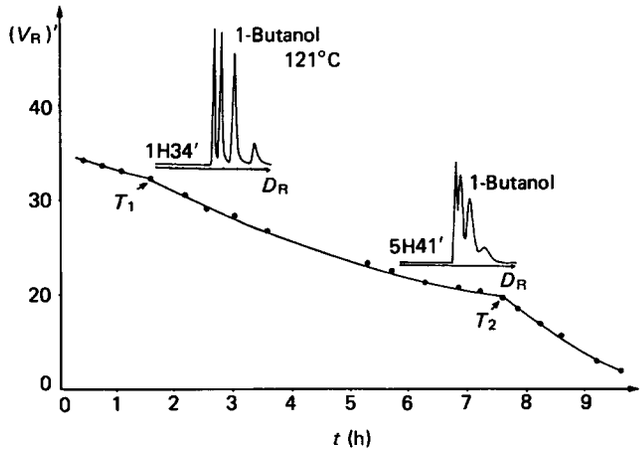


Figure 3 Retention volume $(V_R)'$ as a function of time for TGDDM–DDS ($r=2$). I.g.c.; probe molecule, 1-butanol; $T=121°C$

This part of the curve thus corresponds to the elongation of chains, involving primarily primary amines of the hardener (the retention volume decreases as a function of the increase in molecular mass). The first discontinuity would thus be due to the appearance of the first insoluble components. In this hypothesis, the zone observed between points T_1 and T_2 would be associated with gelation.

These results agree with the data obtained with ^{13}C liquid n.m.r., where we showed that insoluble products appeared between points T_1 and T_2, most often due to epoxy–secondary amine cross-linking reactions[8].

In the system TGDDM–DDS (non-stoichiometric), at $T>135°C$, we observed a third transition point T_3, after which the V_R' of the probe molecules remained constant, since the chromatography was on a solid surface which did not change with time.

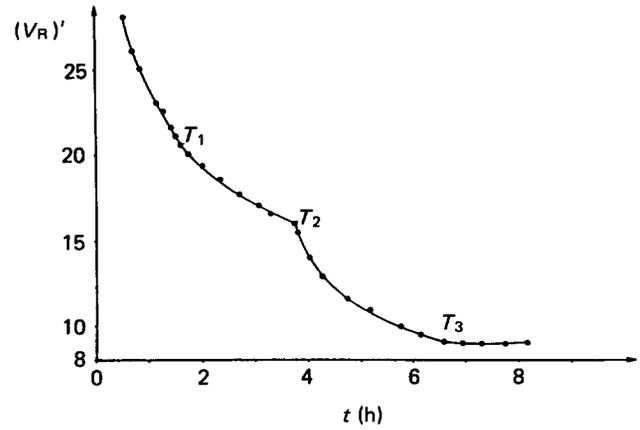


Figure 4 Retention volume $(V_R)'$ as a function of time for TGDDM–DDS ($r=2$). I.g.c.; probe molecule, 1-butanol; $T=140°C$

To compare these results with those determined by more conventional viscometry-type methods, *Figures 5–7* show Arrhenius plots of $\ln t(h)$ against temperature. *Table 3* gives the values of coefficients A and B after processing the curves from the equation $\ln t=(A/T)+B$ for the three pure systems studied and compares the results with published data[12].

The results found for the systems DGEBA–DDS and TGDDM–DDS ($r\,(e/a)=1$) (*Figures 5* and *6*) indicate that the gel time determined by the viscometric method is close to transition T_2 observed in i.g.c. On the other hand, there is a substantial divergence in the TGDDM–DDS system ($r\,(e/a)=2$), where the viscometric curve is close to transition point T_1 at low temperature and to transition point T_2 at temperatures greater than 140°C.

These results do not appear to be contradictory when we consider that in the DGEBA–DDS or TGDDM–DDS systems ($r=1$) the reactions involved are normal inter- or intramolecular epoxy–amine type reactions. In the TGDDM–DDS ($r=2$) systems, however, we have shown[6] that the secondary intra- or intermolecular hydroxyl–epoxy or epoxide–epoxide reactions occurred before all the primary amines were consumed, subsequently becoming predominant and causing considerable structural defects in the cross-linked network formed (ether chains, morpholine ring, etc.). These defects have a very large effect in i.g.c. on the retention volumes of probe molecules and may explain the dispersion of values compared with those obtained with viscometric methods. This is because the latter are less sensitive to the chemical functions in the network.

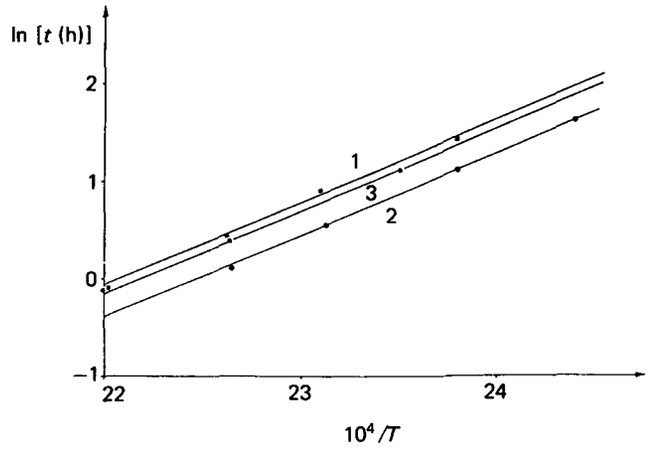


Figure 5 Ln t against $f(1/T)$ for DGEBA–DDS at: (1) T_2 (i.g.c.); (2) T_1 (i.g.c.); (3) T (viscometry)

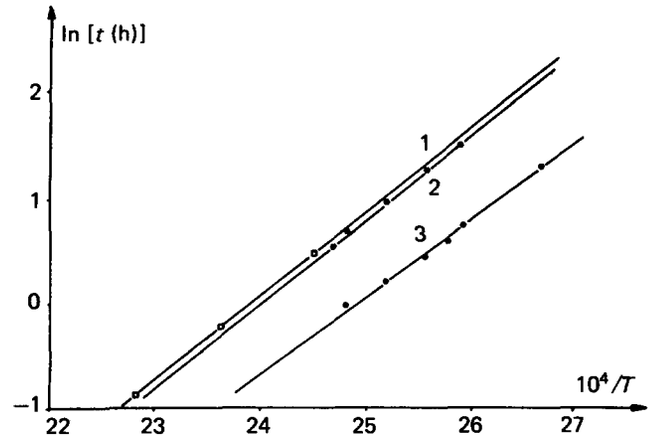


Figure 6 Ln t against $f(1/T)$ for TGDDM–DDS ($r=1$) at: (1) T (viscometry); (2) T_2 (i.g.c.); (3) T_1 (i.g.c.)

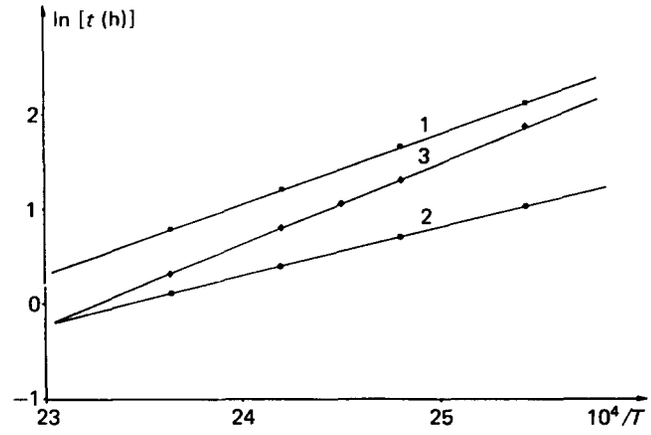


Figure 7 Ln t against $f(1/T)$ for TGDDM–DDS at: (1) T_2 (i.g.c.); (2) T (viscometry); (3) T_1 (i.g.c.)

Isothermal reaction kinetics – ln $(V_R)'$ *against* (f(*advancement rate*)). In parallel to this work, we examined the reaction kinetics of the DGEBA–DDS and TGDDM–DDS systems with Calvet microcalorimetry. Reaction kinetics obeyed the law proposed above. For example, *Figure 8* gives the thermograms obtained at 140°C for the two stoichiometries examined in the TGDDM–DDS system and the kinetic law obtained.

We thus determined for the two systems a kinetic law in the temperature range 100–180°C. The linearization of the curves enabled us to determine the advancement of the reaction at any temperature in isothermal mode.

Table 4 lists the values of the kinetic coefficients and activation energies. For the two stoichiometries studied for the TGDDM–DDS system, E (initiation energy) has the same slope (about 57 kJ mol^{-1}), while the autocatalysis term E_1 differs slightly, but both values for the three systems agree with published data[14].

Figures 9 and *10* show examples of plots of V_R' (i.g.c.) against the degree of advancement (α), determined by microcalorimetry.

The points of discontinuity observed in *Figures 3* and *4* are more pronounced. Point T_1 is more clearly observable as the temperature is lower. In the first part of the curve, retention volume decreases in proportion to the advancement of the reaction. The formation of the first insoluble components leads to the appearance of the adsorption term, which, added to the solubilization term, reduces the slope of the curve.

The system is totally rigid after point T_2. The chromatography is now on a surface which appears to decrease substantially as a function of the final reactions.

Table 3 Values of coefficients A and B in the equation $\ln t = A/T + B$ between 100 and 180°C, determined at times T_1, T_2, T_3 (i.g.c.) and T (gel viscometry)

System		A	B
DGEBA–DDS ($r=1$)	T	9000	−20.68
	T_2	8450	−19.47
	T_1	8400	−19.70
TGDDM–DDS ($r=1$)	T	8220	−19.60
	T_2	7400	−17.57
	T_1	7000	−17.37
TGDDM–DDS ($r=0.5$)	T	8980	−20.87
	T_3	5666	−11.84
	T_2	7230	−16.31
	T_1	5046	−11.83

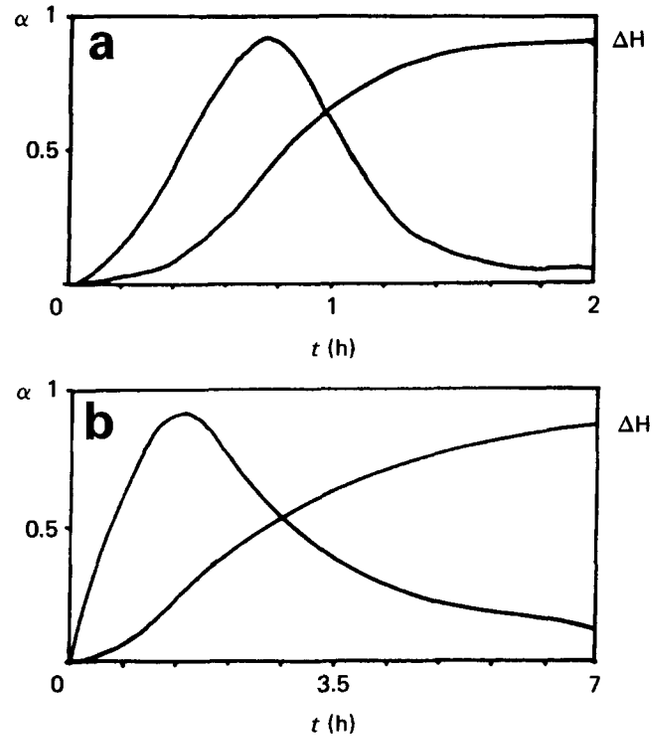


Figure 8 Examples of Calvert microcalorimetry thermograms at 140°C and kinetic curves: (a) TGDDM–DDS ($r=1$); (b) TGDDM–DDS ($r=2$)

Table 4 Rate constants and activation energies determined by Calvert microcalorimetry in the two systems

System	T (°C)	$r(e/a)$	K	K_1	E (kJ mol^{-1})	E_1
DGEBA–DDS	120	1	0.0596	0.551		
	135	1	0.0977	0.598	44.0	94.3
	150	1	0.155	4.302		
	180	1	0.355	25.50		
TGDDM–DDS	100	1	0.0204	0.308		
	135	1	0.100	0.104	57.4	87.7
	150	1	0.183	18.88		
	180	1	0.542	144.30		
TGDDM–DDS	100	2	0.0118	0.840		
	135	2	0.0579	0.960	57.4	107
	150	2	0.106	2.410		
	180	2	0.312	12.650		

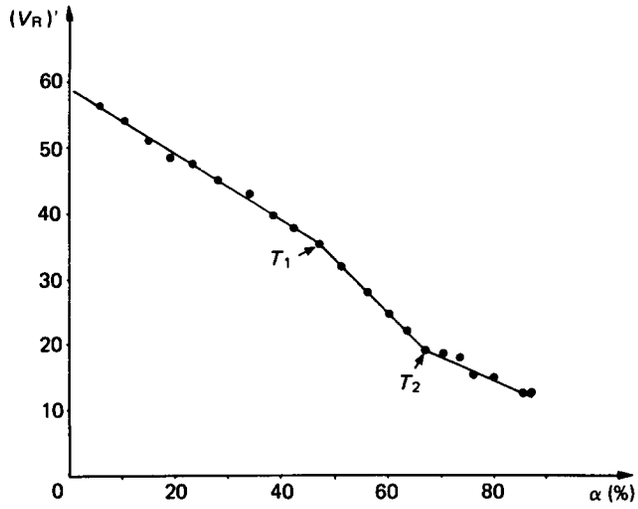


Figure 9 Retention volume $(V_R)'$ against advancement of the reaction (α) for DGEBA–DDS. I.g.c.; $T = 120$°C

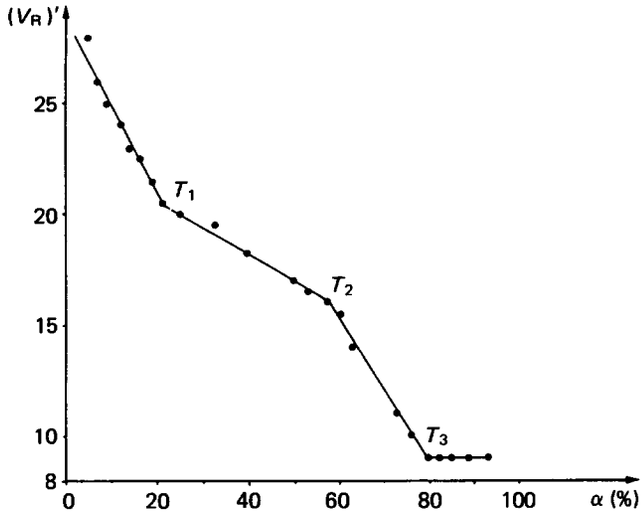


Figure 10 Retention volume $(V_R)'$ against advancement of the reaction (α) for TGDDM–DDS. I.g.c.; $T = 140$°C

In the DGEBA–DDS system (*Table 5*), advancement of the reaction at points T_1 and T_2 increases slightly with temperature. Point T_1 is located at about 50% advancement of the reaction, i.e. when the primary amines are almost totally consumed. Point T_2 occurs when the advancement is between 64 and 70%, a value in agreement with high resolution ^{13}C n.m.r. assays in solids (cross polarization and magic angle rotation) and liquids carried out with samples whose curing was stopped at the gel time determined by rheology[13].

In the TGDDM–DDS system (*Table 5*), variations of α for T_1 and T_2 were very sensitive to temperature and to the stoichiometry of the mixture. T_1 occurred at between 10 and 30% of reaction advancement and T_2 between 45 and 68% in the DGEBA–DDS system.

In the non-stoichiometric (TGDDM–DDS) system, there was a third transition point T_3 between 66 and 87% of reaction advancement. Considering that $(V_R)'$ values no longer change, this corresponds to chromatography on an unchanging solid, which can be compared to the vitrification of the reaction mixture.

Determination of vitreous transition temperatures with i.g.c. Once kinetics were terminated, the chromatography column was placed at 180°C for several hours to ensure completion of the reaction.

Next, the retention of different solutes was followed in the temperature range 100–240°C. A typical curve of $\ln (V_R)'$ against $1/T$ is shown in *Figure 11*. All the curves have the general shape shown in *Figure 6*. At low temperatures the curve is a straight line, but it subsequently exhibits a V-shaped break at temperature T_g. After T_g the curve is linear and the slope is the same as

Table 5 Advancement (%) of reactions at transition points T_1, T_2 and T_3 (i.g.c.)

System	T (°C)	T_1 t (h)	T_1 α (%)	T_2 t (h)	T_2 α (%)	T_3 t (h)	T_3 α (%)
DGEBA–DDS							
($r=1$)	120	5.29	47	7.56	64		
	130	3.11	49	4.44	65		
	140	1.88	51	2.67	67		
	150	1.16	53	1.65	69.5		
TGDDM–DDS							
($r=1$)	120	1.47		3.26			
	130	0.95		2.05			
	140	0.62		1.32			
	150	0.42		0.86			
TGDDM–DDS							
($r=2$)	120	2.73	10	8.11	46	13.03	66
	130	1.95	16	5.14	52	9.11	75
	140	1.46	22	3.33	58	6.49	82
	150	1.10	28	2.13	67	4.69	87

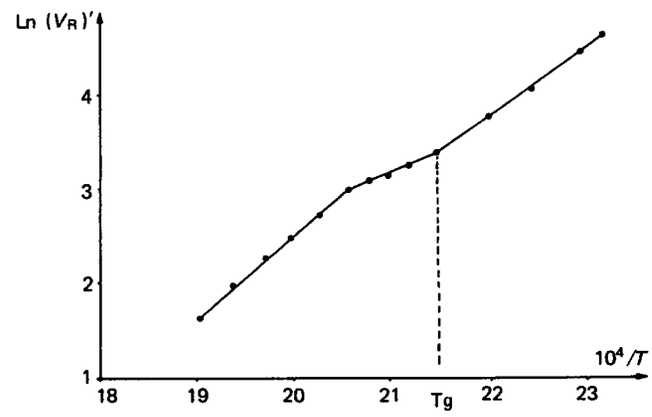


Figure 11 Determination of vitreous transition temperatures by inverse gas chromatography for TGDDM–DDS ($r=2$)

Table 6 Vitrous transition temperatures determined by i.g.c. and d.s.c. (curing temperature 135°C)

System	T_g	
	I.g.c.	D.s.c.
DGEBA–DDS	180	175
TGDDM–DDS ($r=1$)	170	188
TGDDM–DDS ($r=2$)	190	192

that of the first part. The discontinuity at T_g is the vitreous transition temperature of the polymer. We compared these values to those determined by d.s.c. for the same curing cycles (*Table 6*). The results are comparable and confirm that the networks obtained are perfectly cross-linked.

CONCLUSION

Inverse gas chromatography was used to follow the kinetics of molten epoxy–amine reactions occurring in heat hardening systems. The method was developed using model compounds with the different expected chemical functions and the results were applied to the kinetic (isothermal) study of the cross-linking of the prepolymers TGDDM and DGEBA polycondensed with DDS. The data gathered by this method led to the demonstration of zones of gelation and vitrification. Based on the kinetics established with isothermal microcalorimetry, we could determine the progress reactions in these transition zones. The results show that the advancement to transition points T_1 and T_2 is very sensitive to curing temperature and to the stoichiometry of the mixture.

Using this technique we were able to show that vitreous transition temperatures could be determined and that the values obtained are very close to those obtained with d.s.c., confirming the good cross-linking of the system in the chromatographic column.

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