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Studies on the gelation of photocatalysed dicyanate ester resins

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The gel point of a dicyanate ester resin (Arocy B-10 (4-4′-dicyanato-2,2′-diphenylpropane)) heated following irradiation in the presence of the catalyst tricarbonyl cyclopentadienyl manganese ($CpMn(CO)_3$) was studied using differential scanning calorimetry (d.s.c.) and dynamic rheological techniques over the temperature range 110–140°C. The gel times of another commercial cyanate ester (RTX366) were also studied using independent rheological techniques, and the results agreed within experimental error. Gel times decreased linearly with increasing catalyst level and with increasing temperature according to an Arrhenius relation with activation energy of $68 \pm 6\,\mathrm{kJ\,mol^{-1}}$. The gel conversion was calculated by correlation of the rheological gel data to d.s.c. data to be 0.57 ± 0.02, and differences between techniques, and between theoretical predictions, are discussed. Evidence is produced that the photocatalysed polymerization results in a greater rate of cyclotrimerization, less intramolecular cyclization and a more rigid network than the uncatalysed or metal salt-catalysed high-temperature polymerization. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Cyanate resin systems are of growing importance in the computer and composites industry due to their attractive mechanical and electric properties in comparison to conventional epoxy-based systems[1]. In particular, the cured network has a low dielectric constant and a high glass transition temperature (T_g). Typical applications thus include printed circuit board lamination and structural composite manufacturing. The understanding and control of such manufacturing operations require measurement of the kinetics and the gel point of the systems. There have been a number of reports[2–4] of the kinetics and network formation of the polymerization reaction of cyanate esters (*Figure 1*).

A feature of the network formation is the high temperature (>200°C) necessary in order to achieve cyclotrimerization of the cyanate ester in the uncatalysed system. The processing temperature may be reduced by up to 100°C by incorporating a catalyst such as a transition metal complex. The mechanism of polymerization in the presence of the catalyst has been controversial, particularly the role played by hydroxyl group-containing co-catalysts such as phenol. In an extension to these studies, the possibility of using photogenerated catalysts has been considered, as this would enable photodevelopment of the cross-linked network. The polymerization kinetics and properties of the network formed from a photogenerated transition metal catalyst have been studied in detail[5]. In this previous work[5], we have studied a bisphenol A cyanate ester (B-10) photocatalysed by an organometallic compound, cyclopentadienytricarbonyl manganese ($CpMn(CO)_3$). The polymerization involved two separate stages. In the first stage, the mixtures of B-10 and $CpMn(CO)_3$ were irradiated under u.v. light; and in the second stage the irradiated samples were cured at elevated temperatures. A mechanism was proposed as follows:

- *Initial stage.* Formation of active catalyst through u.v. irradiation:

$$\mathrm{CpMn(CO)_3} + x\mathrm{ROCN}$$
$$\xrightarrow{\text{u.v.}} \mathrm{CpMn(CO)_{3-x}(ROCN)_x}\,(x = 1\text{–}3) + x\mathrm{CO}$$

- *Curing stage.* Network formation:

$$\mathrm{CpMn(CO)_{3-x}(ROCN)_x} + (3 - x)\mathrm{ROCN}$$
$$\xrightarrow{\Delta} \mathrm{CpMn(CO)_{3-x}} + \text{triazine}$$
$$\mathrm{CpMn(CO)_{3-x}} + x\mathrm{ROCN} \longrightarrow \mathrm{CpMn(CO)_{3-x}(ROCN)_x}$$
$$\mathrm{CpMn(CO)_{3-x}(ROCN)_x} + (3 - x)\mathrm{ROCN}$$
$$\longrightarrow \mathrm{CpMn(CO)_{3-x}} + \text{cross-linking network}$$

This involved the photosubstitution of the carbonyls in the original catalyst by the cyanate functional groups during the irradiation stage and the formation of the active catalyst, CpMn or CpMn(CO), at the thermal curing stage. A model study with a premade catalyst

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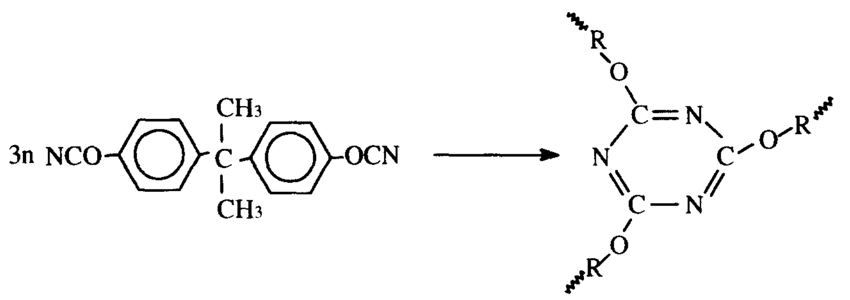
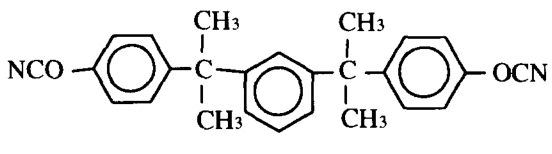


(I)

Figure 1 Polymerization reaction of a dicyanate ester (R is the bisphenol moiety)

Table 1 A comparison of experimental T_g data of B-10 + premade (photoirradiated) catalyst system with that predicted from a DiBenedetto relation[5,6]

Premade catalyst concentration (10^4 mol Mn (mol OCN)$^{-1}$)	Conversion (α)	T_g (°C) (experimental)	T_g (°C) (DiBenedetto)
0	0.84	153	152
0	0.91	202	205
4.1	0.65	96	64
4.1	0.70	107	80
4.1	0.74	116	98
8.1	0.66	99	66
8.1	0.71	111	84
8.1	0.75	122	101
12.4	0.60	80	48
12.4	0.62	82	53
12.4	0.71	101	83



(II) RTX366

Scheme 1

consisting of $CpMn(CO)_3$ irradiated in the presence of B-10 to form the solid $CpMn(CO)_{3-x}(ROCN)_x$ ($x = 1-3$) was also performed, as this model system was supposed to react by a similar mechanism. In this previous work, it was found that glass transition temperatures for all the photocatalysed systems at a certain conversion were higher than those obtained from a modified DiBenedetto equation[5,6] while the uncatalysed system showed close agreement as given in *Table 1*.

This indicates the network formed in the photocatalysed systems could be different from that formed by higher-temperature uncatalysed cyclotrimerization, and the thermal transition metal catalysed reaction. The gel point is a very important parameter for a cross-linking network. The gel conversion values for the cyanate esters have been frequently reported[2,7] between 0.58 to 0.64, which are higher than the mean-field predicted value, 0.5. This work aims to investigate the network formation of the photocatalysed system by measuring the gel conversion using dynamic rheological techniques. In addition to the bisphenol A cyanate ester B-10 (**I**), a liquid, higher molecular weight cyanate ester RTX366 (**II**) has been studied, principally to establish the rheological properties.

MATERIALS AND METHODS

Materials

The RTX366 cyanate resin (Ciba-Geigy) was kindly supplied by Printed Circuits Queensland. Bisphenol A cyanate ester was synthesized by a modified method of Fyfe[8]. The product was needle-like crystals with a melting point of 80°C. The tricarbonyl cyclopentadienyl manganese $CpMn(CO)_3$ was purchased from Aldrich and used as obtained (elemental analysis results: C 47%; H 2.5%; O 21%).

Sample preparation

RTX366 + 1% $CpMn(CO)_3$ samples were prepared by mixing 20.162 g of RTX366 and 10.72 mg of $CpMn(CO)_3$. The mixture was irradiated for 30 min. The irradiation source was broad-band u.v.-visible radiation from a 150 W high-pressure mercury lamp. The lamp intensity was measured to be approximately $0.15\,\mathrm{mW\,cm^{-2}}$ using an Oriel pyroelectric detector.

The B-10 sample was prepared by mixing B-10 with different amounts of premade catalyst. The premade catalyst was a coordination compound of $CpMn(CO)_3$ with cyanate ester which was synthesized by irradiating a mixture of B-10 and $CpMn(CO)_3$ with a molar ratio of OCN/Mn of 2 in a benzene solution. The premade catalyst concentrations were 4.1×10^{-4}, 8.1×10^{-4} and 1.24×10^{-3} mol Mn (mol OCN)$^{-1}$, respectively, as determined by i.c.p. (inductively coupled plasma atomic emission spectroscopy). The system was calibrated using standard $MnCl_2$ in 2% HNO_3 solutions.

Rheological measurements

A Rheometrics dynamic spectrometer (RDS II, Rheometrics Scientific) was used to determine the gel point of the resin–catalyst mixtures. The rheometer was used in parallel plate configuration (diameter (D) = 25 mm, gap (H) = 0.5 mm) and at temperatures of 100–140°C.

Rheological methods have been used to determine the gel point of network forming materials, and have been summarized in a recent paper[9]. The methods used were:

(1) the independence of loss tangent ($\tan\delta$) on frequency (ω) method using multiwave time tests;
(2) the infinite steady shear viscosity (η) method using steady time tests;

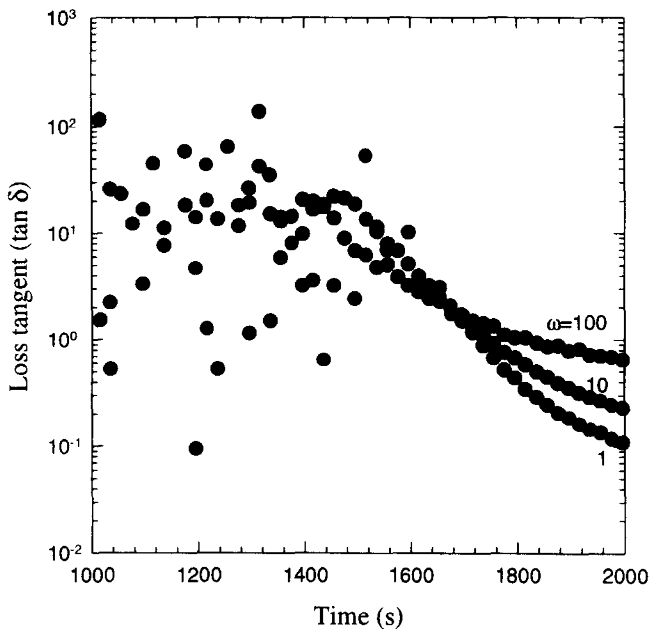


Figure 2 Loss tangent as a function of time for RTX366 cyanate ester resin at $\omega = 1$, 10 and 100 rad s^{-1}, $\gamma = 10\%$, and $T = 160°\mathrm{C}$

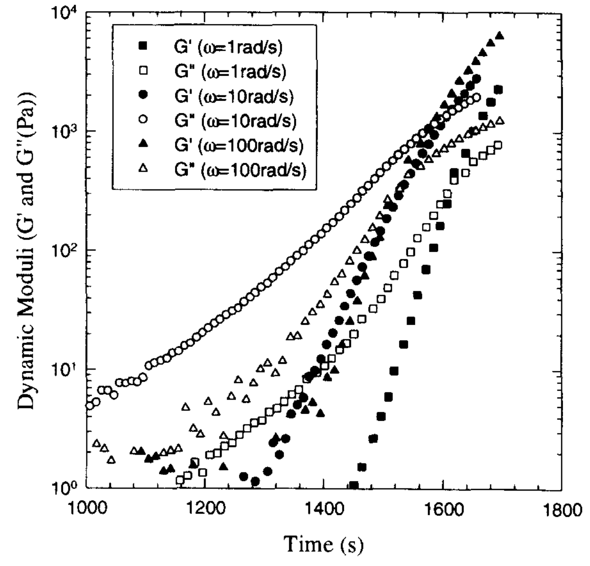


Figure 3 Dynamic moduli as a function of time for RTX366 cyanate ester resin from independent frequency tests at $\omega = 1$, 10 and 100 rad s^{-1}, $\gamma = 10\%$, and $T = 160°\mathrm{C}$

(3) the infinite first normal stress difference (N_1) method using steady time tests;

(4) the cross-over of the storage (G') and loss (G'') moduli method using dynamic time tests.

Multiwave tests were primarily used in this study to determine the rheological gel point of the system, where the gel time is defined as the time where $\tan\delta$ becomes independent of frequency. Superimposed signals of 1, 10 and 100 rad s^{-1} with a strain of 10% at each frequency were used. For comparison, dynamic time tests and steady time tests were also used. Dynamic time tests measure the gel point as the time where G' and G'' cross over, at a constant frequency, ω. These tests were made at a frequency of 1, 10 and 100 rad s^{-1} and at 10% strain.

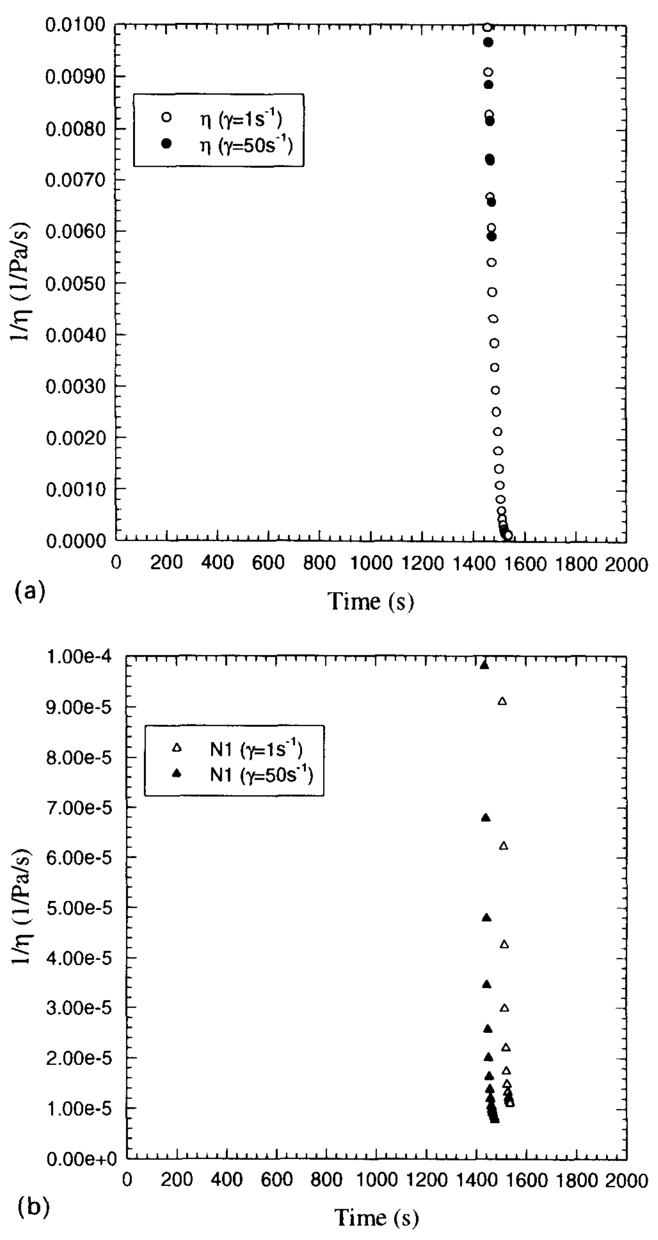


Figure 4 Reciprocal of (a) viscosity and (b) first normal stress difference as a function of time for RTX366 cyanate ester resin at $\gamma = 1$ and 50 s^{-1} and $T = 160°\mathrm{C}$

Steady time tests determine the gel point by the time at which the viscosity and the first normal stress difference become infinite. These tests were conducted at shear rates of 1 and 50 s^{-1}.

All tests were conducted under a nitrogen atmosphere. The temperature of the sample was monitored by a K-type thermocouple which was inserted through the centre of the bottom shaft, with its tip 1 mm from the shear surface of the bottom plate. The temperature reached the set point 3 min after sample insertion, through adjustable temperature control parameters following an oven warm-up time of 60 min prior to the sample being placed in the rheometer. The steady state temperature was kept to within 0.5°C of the set point.

RESULTS AND DISCUSSION

Effects of rheological test method on gel time

A comparison of the gel point of the RTX366 system, measured by a multiwave test, dynamic time tests and

Table 2 Gel times for a range of rheological techniques for RTX366 cyanate ester resin at 160°C

Test	Conditions	t_{gel} (s)
Multiwave	$\omega = 1;\ 1,\ 10,\ 100\ \mathrm{rad\,s^{-1}}$	1660 ± 50
Dynamic time	$\omega = 1\ \mathrm{rad\,s^{-1}}$	1610 ± 50
	$\omega = 10\ \mathrm{rad\,s^{-1}}$	1610 ± 50
	$\omega = 100\ \mathrm{rad\,s^{-1}}$	1525 ± 50
Steady time—infinite viscosity	$\gamma = 1\ \mathrm{s^{-1}}$	1560 ± 100
	$\gamma = 50\ \mathrm{s^{-1}}$	1520 ± 100
Steady time—infinite normal stress difference	$\gamma = 1\ \mathrm{s^{-1}}$	1560 ± 100
	$\gamma = 50\ \mathrm{s^{-1}}$	1520 ± 100

Table 3 Gel times and gel conversion levels for the B-10 cyanate ester resin as a function of temperature and catalyst level

Catalyst concentration (10^4 mol Mn (mol OCN)$^{-1}$)	Temperature (°C)	Gel time (s)	Gel conversion
4.1	120	3315	0.57
4.1	130	1900	0.57
4.1	130	1886	0.57
4.1	140	1210	0.58
4.1	140	1144	0.57
8.1	120	2360	0.55
8.1	120	2365	0.55
8.1	130	1301	0.55
8.1	140	953	0.60
8.1	140	950	0.60
12.4	105	3646	0.55
12.4	110	2662	0.53
12.4	110	2652	0.53
12.4	120	1496	0.59
12.4	120	1466	0.59

steady time tests is shown in *Figures 2–4* and *Table 2*. Experimental conditions are noted below each figure.

In the multiwave test, the torque is initially below the resolution of the transducer, hence the loss tangent is indeterminable. Near the gel point, however, the torque becomes measurable, and the gel point may be estimated from the position at which $\tan\delta$ becomes independent of frequency at 1660 s (refer to *Figure 2*). This result is reproducible to within 50 s (3% accuracy).

In the dynamic time tests, gel point (defined by the cross-over point) has been measured as a function of frequency (refer to *Figure 3* and *Table 2*). It is clear that the cross-over points are independent of frequency within experimental error and in agreement with the results from the loss tangent method. This is in agreement with data obtained for a glycidylamine epoxy resin (TGDDM) cured with diaminodiphenyl sulfone (DDS)[9].

Steady time tests determine the gel time as the time where either the viscosity or the first normal stress difference become infinite. The gel time can thus be estimated from a plot of $1/\eta$ or $1/N_1$ *versus* time as shown in *Figures 4a* and *4b*. Here the effect of shear rate on gel times is also measured. Clearly there is no effect of shear rate on the gel times. This is in agreement with earlier work on a TGDDM/DDS epoxy[9], but is in direct contrast to the recent study of a polyester/styrene system[10]. In that study the polyester/styrene system showed a marked increase of the gel time with shear rate. This increase was postulated[11] to have been due to the inhibition of macrogelation in network formation. However, in the system studied here, network formation follows a cyclotrimerization process[5], and this would be less sensitive to shear than a macrogelation-type process. There is also good agreement of the steady shear test gel times with the earlier gel times measured from multiwave and dynamic time tests. Thus, these results indicate that for the RTX366 system examined, all four gel time methods provide consistent values for the gel time. This is in conflict with the results of another liquid cyanate ester, 4,4′-dicyanato-1,1′-diphenylethane, where gel times measured by steady shear test were longer than those obtained from dynamic measurement[7]. One possible explanation offered was the molecular structure breakup caused by the large deformation of constant shear operation.

Gel conversion

The effect of catalyst level and temperature on the gel time of the Arocy B-10 cyanate ester system was measured by multiwave tests, and the results are summarized in *Table 3*. It can be seen that, as expected, gel times decrease with increasing catalyst level and temperature. Also shown in *Table 3* is the extent of conversion at the gel point as determined by d.s.c. isothermal tests.

The average value of the gel conversion is 0.566 with a standard deviation of 0.023. Catalyst concentration and curing temperature have no significant effect on the gel conversion.

As mentioned in the Introduction, the gel conversion values reported in the literature[2,7] are between 0.58 and 0.64 for the cyanate ester system catalysed by Co^{2+}, Zn^{2+}, Mn^{2+} or Cu^{2+} compounds. The deviation has been discussed in a number of papers[2–4]. Since the mean-field theory assumes equal reactivity of all participating functional groups, all systems are expected to have deviation to some extent, and the mean-field value of gel conversion of 0.5 is said to be the lowest bound for homogeneous polymerization. Gupta and Macosko[2] suggested that the steric hindrances of functional sites are the main reason for the gelation delay. However, the functional sites which were hampered were not completely screened, because no kinetic slow down was observed[2], and these sites do react, albeit in local domains. The force field calculation results[3], which found that no steric repulsion between the end-groups had been observed for calculations up to 20 monomer units, also favour the preference for intramolecular cyclization relative to the intermolecular counterpart. Korshak[4] found that for the polymerization of cyanate ester in nitrobenzene solution, gel conversion increased as the monomer concentration decreased. This was considered as evidence of the intramolecular cyclization effect.

If the above argument is true, then intramolecular cyclization in our system is less serious, because the gel conversion values are lower than other reported data and are much closer to the mean-field value.

It also has been argued that other factors which contribute to the delay of the gel point include non-network-forming side-reactions. These side-reactions could be formation of cage compounds[3] such as triazine bicyclophane or carbamate by addition of water to the cyanate[8]. Pascault's[6] gel conversion results for B-10 under argon ranged from 0.50 to 0.53, and from 0.58 to 0.67 under air. This suggests that the ambient water vapour can play an important role in the delay of gelation[6,12].

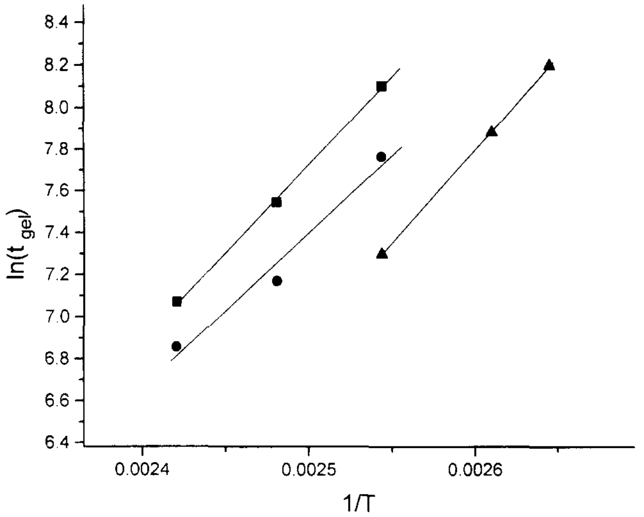


Figure 5 Arrhenius plot of gel times for the different photocatalysed B-10 systems (■, B-10 + 4.1 × 10^{-4} mol Mn (mol OCN)$^{-1}$; ●, B-10 + 8.1 × 10^{-4} mol Mn (mol OCN)$^{-1}$); ▲, B-10 + 1.24 × 10^{-3} mol Mn (mol OCN)$^{-1}$)

Table 4 A comparison of activation energy values obtained from the rheology and d.s.c. tests for the different photocatalysed B-10 systems

Catalyst concentration (10^4 mol Mn (mol OCN)$^{-1}$)	Activation energy—rheology (kJ mol^{-1})	Activation energy—d.s.c. (kJ mol^{-1})
4.1	72 ± 1	67 ± 2
8.1	61 ± 10	64 ± 4
12.1	70 ± 2	70 ± 5

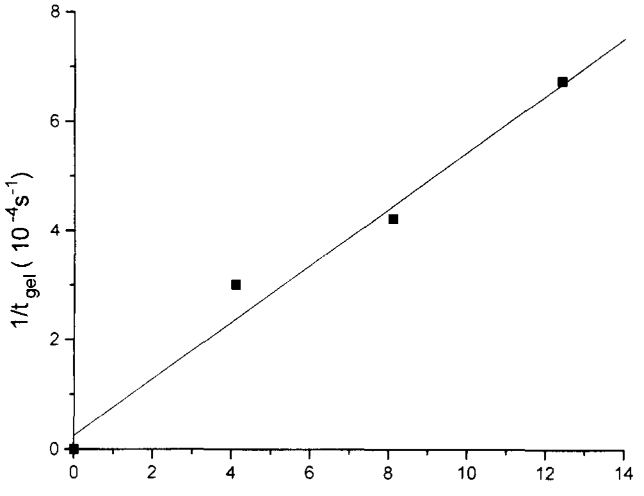


Figure 6 Dependence of average reaction rate ($1/t_{gel}$) on premade catalyst concentration for B-10 resin

To further investigate the difference of our study of the photoinitiated catalyst compared to the thermal catalyst (transition metal salt), a comparison of the efficiency of this catalyst is made. The pseudo first order reaction rate coefficients at 130°C are 4.7 × 10^{-4} s^{-1} for the manganese octoate (100 ppm Mn) catalysed B-10 system in the presence of a cocatalyst (4 phr nonylphenol)[12] and 7.0 × 10^{-4} s^{-1} for the photocatalysed (100 ppm Mn) system without any added cocatalysts[5], respectively. The above values clearly show that the photoinitiated catalyst is more efficient than the manganese octoate. This efficiency would result in a greater yield of trimer ring formation and faster network development.

Although we have no kinetic data for the non-network-forming side-reaction, if it is assumed that these reaction rates are independent of catalyst type in B-10 systems, then the photocatalysed trimerization would be more competitive. Thus the effects of side-reactions on the network formation would be minimized and the gel conversion would be decreased. The low gel conversion of 0.57 ± 0.04 compared to values of up to 0.64 for the thermally catalysed systems implies that a more rigid network has formed. This is consistent with the higher T_g values at the same conversions measured before (*Table 1*).

Activation energy

It can also be shown that the gel times at each catalyst level follow an Arrhenius relationship with temperature (*Figure 5*), and the activation energies are summarized in *Table 4*, along with activation energies obtained from chemical kinetic analysis by isothermal d.s.c. Clearly the activation energies obtained from each technique agree well within experimental error, indicating the chemorheological control of network formation.

Effect of catalyst concentration on gel time

As expected, the gel time decreases with increasing catalyst concentration, as the rate of the polymerization reaction increased with catalyst concentration. Because the gel conversion values are almost constant for different catalyst systems, the average reaction rates are proportional to the reciprocal of gel time (t_{gel}), and these values for the cure temperature of 120°C are plotted against catalyst concentrations (*Figure 6*). A straight line through the origin was obtained. This indicates a first-order dependence of reaction rate on catalyst concentration, which is in agreement with the d.s.c. results and the mechanism previously proposed[5].

CONCLUSIONS

Various rheological techniques have been used to measure isothermal gel times in two cyanate ester resin systems, and gave consistent results. Gelation data for the Arocy B-10 cyanate ester resin containing premade catalyst systems [$(CpMn(CO)_{3-x}(ROCN)_x$] were measured using the multiwave technique and isothermal d.s.c. It was found that the average gel conversion value was 0.57 ± 0.02 for the systems studied, and catalyst concentration and cure temperature did not affect the gel conversion significantly. The gel time for the different catalyst concentrations followed an Arrhenius relationship, and the activation energy values calculated from rheological data are in good agreement with those obtained from d.s.c. data.

The gel conversion values for these photocatalysed systems are higher than predicted from mean-field theory but lower than those reported using other thermal catalysts. It is assumed then that the intramolecular cyclization reactions in these photocatalysed systems are less significant and that a more rigid network was formed during cure. This explanation is in agreement with the higher T_g measured in the previous work[5].

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