Cure kinetics and gravimetric analysis of a flexible aromatic dicyanate, cyanated phenylene sebacate oligomer

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Flexible cyanated phenylene sebacate oligomer (CPS) was prepared to characterize its cure kinetics and the gel point. A dynamic differential scanning calorimetry study revealed an apparent activation energy of 21.8 kcal mol^{-1} and first-order kinetics with rate expression $Af(\alpha)=7.8\times10^{6}(1-\alpha)s^{-1}$. Gravimetric analysis revealed a gel point at $\alpha_{gel}=51\%$, close to the theoretical value of 50%. The accessibility of cyanate groups during cure of CPS resulted in a lower gel point as compared with that of a rigid aromatic dicyanate such as 2,2-bis(4-cyanatophenyl)propane.

(Keywords: cure kinetics; gravimetric analysis; cyanated oligomer)

INTRODUCTION

Polycyclotrimerization of aromatic dicyanate has attracted increasing attention owing to theoretical interest and its practical applications in industry[1]. The reaction leading to the formation of the *sym*-triazine ring as an interconnecting crosslinking point can proceed thermally or be catalysed by transition-metal carboxylates or acetoacetonates[2-6] or by phenol[5-7]. The reaction kinetics, however, deserve further survey since conflicting results have been suggested from previous literature[4,7-10].

Polycyclotrimerization of 2,2-bis(cyanatophenyl)propane (BPADCy) has been studied by Bauer *et al.*[7,8]. Their results from differential scanning calorimetry (d.s.c.) indicated the characteristic autocatalytic behaviour in the early stage of reaction, but an apparent first-order kinetics could be used for the overall description. Based on experimental observations, a mechanistic scheme for the phenol-catalysed reaction was proposed. This pioneering work, however, is not consistent with the results from Gillham *et al.*[4,9]. In view of the catalytic effect of the *sym*-triazine ring, the experimental result for cure of a commercialized dicyanate derived from 4,4'-[1,3-phenylenebis(1-methylethylidine)]bisphenol can be fitted with an empirical rate expression of the form:

$$d\alpha/dt=k_1(1-\alpha)^2+k_2\alpha(1-\alpha)^2 \qquad (1)$$

where α is the fractional conversion and k_1 and k_2 are apparent rate constants. The second term on the right-hand side was due to the consideration of a competing (autocatalytic) reaction observed in dynamic d.s.c. thermograms as a second exothermic peak. The corresponding activation energies for k_1 and k_2 were 10.5 and 32.0 kcal mol^{-1}, respectively. Recently, Lin *et al.*[10] studied the cure kinetics of 4'-thiodiphenylcyanate of different impurity levels. Their result for uncatalysed reaction showed an autocatalysed first-order kinetics, $d\alpha/dt=k(h+\alpha)(1-\alpha)$, in which the parameter h is directly related to the amount of the phenolic impurity. With different catalyst loadings (n-nonylphenol, 1 to 15 phr), the kinetic features were quite different from those of the uncatalysed counterpart, and the cure reaction followed autocatalysed second-order kinetics. These observations can also be explained in terms of the mechanistic scheme proposed earlier by Bauer *et al.*[7].

In addition to the cure kinetics, the gel point is also of interest in considering the conflicting results reported previously[4,7,11-13]. Shimp *et al.*[11] found the gel point for cure of BPADCy to be between 60 and 65% conversion. Bauer *et al.*[7,12], however, reported that gelation occurred at 50% conversion. Other reported measurements as summarized by Gupta and Macosko[13] all revealed a gel point of over 60% conversion for several different aromatic dicyanates[13]. The gel point expected from existing statistical theories[14] or the recursion method[15] is 50%. Gupta and Macosko[13] suggested that the delayed gel point observed for cure of BPADCy is due to steric hindrance, which limits reactions to local domains. To exclude the possible steric hindrance, various amounts of monofunctional 2-(4-cyanatophenyl)-2-phenylpropane were intentionally added to the difunctional BPADCy to increase the amount of dead ends of the polymerizing chains and therefore resulted in a more open structure. In this way, a better agreement with statistical theories was achieved.

A literature survey[10,13] indicates that most of the aromatic dicyanates previously used have a rigid structure of two cyanatophenyl units linked by central carbon or heteroatoms (such as sulfur and oxygen). Here, we proposed to study the cure behaviour of a flexible cyanated phenylene sebacate oligomer (CPS, *Figure 1*). This oligomer, with its inherently flexible aliphatic chains,

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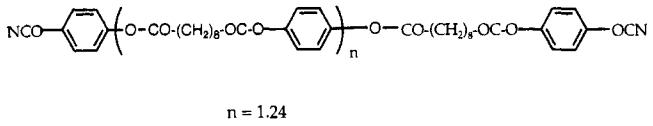


n = 1.24

Figure 1 Chemical structure of a flexible cyanated phenylene sebacate oligomer (CPS)

may have different kinetic features from the reported cases. Also, polycyclotrimerization of this flexible CPS should proceed with less steric hindrance than for most of the rigid aromatic dicyanates; a gel point close to theoretical prediction is therefore expected. Following this study, synthesis of CPS oligomer ('Experimental' section), kinetics study with d.s.c. and gel point evaluated from gravimetric analysis are reported.

EXPERIMENTAL

Materials and instrumentation

All solvent purifications were performed under a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from its mixture with sodium and benzophenone. Ethanol was purified by distillation after treatment with magnesium and iodine. Triethylamine was distilled after dehydration with barium oxide. Hydroquinone, sebacoyl chloride and cyanogen bromide were all purchased from TCI Chemicals and used without purification.

A DuPont DSC 910 cell connected to a DuPont 9900 data station were used in this study. Samples of approximately 5 mg were sealed in a hermetic aluminium pan and scanned in the calorimeter at a heating rate of 5, 10, 20 and 40°C min^{-1} in the temperature range of 30 to 400°C. Calibration of the calorimeter was conducted for each heating rate using an indium standard. ^1H and ^{13}C n.m.r. were studied with a VXR-300 *FT*-n.m.r. model. The infra-red spectrum was obtained from a Digilab FTS-40 *FT*-i.r. spectrometer.

Synthesis

Two-step synthesis procedures were performed. Hydroxyl-terminated phenylene sebacate oligomer was prepared first and then reacted with cyanogen bromide to yield the final product, cyanated phenylene sebacate oligomer.

Synthesis of hydroxyl-terminated phenylene sebacate oligomer (HPS). A mixture of triethylamine (0.3 mol) and hydroquinone (0.7 mol) in tetrahydrofuran (1000 ml) was stirred at ice-bath temperature for 1 h under a nitrogen atmosphere. Sebacoyl chloride (0.14 mol) was then added dropwise within a period of 30 min. Reaction was continued for another 1 h. The white salt was filtered and the residual solvent in the filtrate was removed by rotary evaporation. The final product was obtained by recrystallization of the crude product from ethanol. ^1H n.m.r. (300 MHz, acetone-d_6): $\delta = 7.14$, 6.90–6.94 and 6.79–6.84 (aromatic H); 2.49–2.62 (–OCO–CH_2–$(CH_2)_6$–CH_2–OCO–); and 1.41–1.73 ppm (–OCO–CH_2–$(CH_2)_6$–CH_2–OCO–).

Synthesis of cyanated phenylene sebacate oligomer. A mixture of triethylamine (0.07 mol) and HPS (13 g) in tetrahydrofuran (300 ml) was stirred at ice-bath temperature for 30 min under a nitrogen atmosphere. A solution of cyanogen bromide (0.07 mol) in tetrahydrofuran (20 ml) was slowly added dropwise to the reaction mixture. Reaction was continued for 4 h. The white salt was filtered and the filtrate was precipitated with the ice–water. The solid precipitate was filtered and recrystallized from ethanol. The first portion of the precipitated sample during recrystallization in a refrigerator was discarded. The second portion was collected and further recrystallized from ethanol to obtain the final product. ^1H n.m.r. (300 MHz; $CDCl_3$): $\delta = 7.30$–7.33, 7.16–7.19, 7.08 (aromatic H); 2.53–2.59 (–OCO–CH_2–$(CH_2)_6$–CH_2–OCO–); and 1.39–1.75 ppm (–OCO–CH_2–$(CH_2)_6$–CH_2–OCO–). ^{13}C n.m.r. (300 MHz, $CDCl_3$): $\delta = 108.59$ (–OCN); and 172.06, 171.83 ppm (–OCO–). *FT*-i.r. (KBr pellet): 2274, 2232 (–OCN), and 1756 cm^{-1} (–COO–).

Characterization of the cyanated phenylene sebacate oligomer (CPS)

The number-average molecular weight of cyanated phenylene sebacate oligomer (CPS) can be determined from ^1H n.m.r. The number-average molecular weight evaluated from the intensity ratio between peaks at $\delta = 7.08$ to $\delta = 2.53$–2.59 is 798 g mol^{-1}.

Gravimetric analysis

CPS (~50 mg) in an aluminium pan was isothermally cured (at 180 or 200°C) for a period of 10 to 50 min. The partially cured sample was withdrawn from the heating oven and directly quenched in liquid nitrogen. A portion (~5 mg) of the cured sample was scanned in d.s.c. to determine its conversion. The remaining sample was continually extracted with methylene chloride overnight. The insoluble portion was vacuum dried and subsequently weighed to obtain the gel fraction.

RESULTS

Dynamic d.s.c. scans of cyanated phenylene sebacate oligomer (CPS) were performed at heating rates of 5, 10, 20 and 40°C min^{-1} (*Figure 2*). All thermograms showed an endothermic melting transition followed by an exothermic curing peak. The exotherms, representing the occurrence of polycyclotrimerization, move progressively with increasing heating rates. Cure kinetics can be evaluated by analysing the cure exotherm.

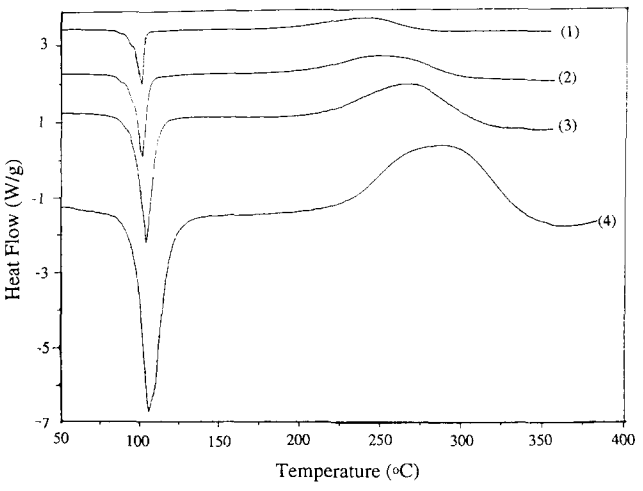


Figure 2 Dynamic d.s.c. scans of CPS at heating rates of: (1) 5; (2) 10; (3) 20; and (4) 40°C min^{-1}

Table 1 Specific heat of reaction (ΔH_{rxn}), peak temperature (T_p) and conversion at peak temperature (α_p) at different heating rates (Φ)

Heating rate (°C min^{-1})	ΔH (cal g^{-1})	T_p[a] (°C)	α_p[b]
5	52.1	238	56.7
10	53.3	252	55.2
20	50.4	267	58.1
40	53.8	290	57.4

[a] Peak temperature, temperature at maximum rate of reaction
[b] Peak conversion, conversion at peak temperature

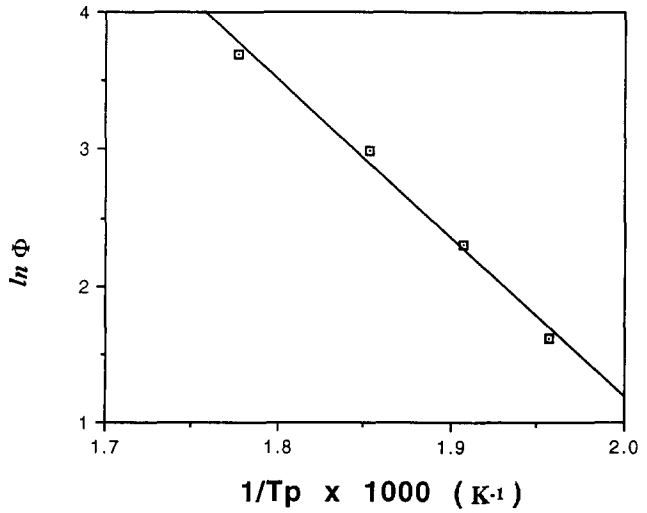


Figure 3 Linear relationship between ln(heating rate) ($\ln\Phi$) and reciprocal peak temperature ($1/T_p$) for cure of CPS

The specific heat of the cure reaction (ΔH_{rxn}, cal g^{-1}) corresponds to the total area under the peak divided by the heating rate (*Table 1*). The fractional conversion (α) is the ratio between the heat evolved up to a given moment and the total specific heat (ΔH_{rxn}). The peak conversion (α_p) refers to the conversion at the peak temperature. It had been observed that peak conversion is constant and independent of heating rate for many thermosetting systems[16–19]. Under the premise of constant peak conversion with different heating rate, Prime[16] suggested that apparent activation energy can be evaluated from:

$$E_a = -0.951R[\mathrm{d}\ln\Phi/\mathrm{d}(1/T_p)] \quad (1)$$

where R is gas constant, Φ is the heating rate and T_p is the peak temperature. The plot of $\ln\Phi$ *versus* reciprocal peak temperature ($1/T_p$) is given in *Figure 3*. The apparent activation energy can be obtained by multiplying the slope of the resulting straight line by -0.951 according to equation (1). The resulting value of 21.8 kcal mol^{-1} is close to the published value of 22.1 kcal mol^{-1} for 4,4'-thiophenylcyanate[10].

In view of the complex nature of the cure reaction, all the rate expressions should be considered empirical. The general way to express the rate of reaction is to start with:

$$\mathrm{d}\alpha/\mathrm{d}t = kf(\alpha) = Af(\alpha)\exp(-E_a/RT) \quad (2)$$

where $\mathrm{d}\alpha/\mathrm{d}t$ (rate of reaction) corresponds to the height (with respect to the baseline) of the thermogram at a given temperature, $k = A\exp(-E_a/RT)$ is the apparent rate constant, A is the pre-exponential factor and $f(\alpha)$ is an empirical function representing the conversion-dependent part of the rate expression. Another approach to survey activation energy throughout the entire conversion range can be obtained by using Friedman's method[20]. When the apparent activation energy is taken as constant, equation (2) can be rewritten as:

$$\ln(\mathrm{d}\alpha/\mathrm{d}t) = \ln[Af(\alpha)] - E_a/RT \quad (3)$$

According to equation (3), a plot of $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ against reciprocal temperature at a selected conversion should yield a straight line with a slope equal to $-E_a/R$ (*Figure 4*). A relationship between activation energy and conversion can thus be obtained (*Figure 5*). The average value of 21.9 kcal mol^{-1} is close to that obtained from Prime's method and can be used for further investigation of the kinetic expression. Nevertheless, fluctuation of E_a values with conversion would result in unacceptable $\ln[Af(\alpha)]$ if Friedman's original method was adopted. Therefore, an average value of 21.9 kcal mol^{-1} was used throughout

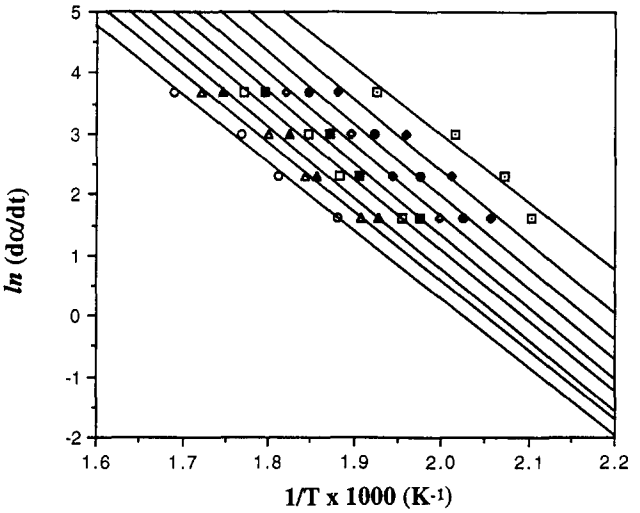


Figure 4 Friedman plots for cure of CPS; lines are corresponding least-squares fits: (⊡) $\alpha=0.1$; (◆) $\alpha=0.2$; (●) $\alpha=0.3$; (◇) $\alpha=0.4$; (■) $\alpha=0.5$; (□) $\alpha=0.6$; (▲) $\alpha=0.7$; (△) $\alpha=0.8$; and (○) $\alpha=0.9$

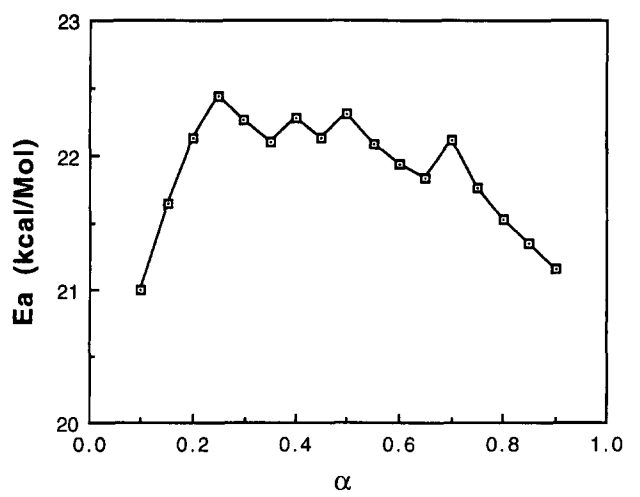


Figure 5 Variation of activation energy (E_a) with conversion (α) for cure of CPS

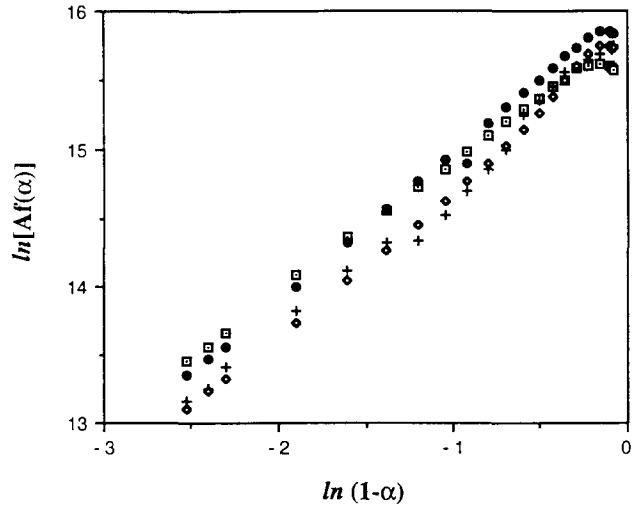


Figure 6 Relationship between $\ln[Af(\alpha)]$ and $\ln(1-\alpha)$ for cure of CPS. Data points are extracted from d.s.c. dynamic scans at heating rates of: (⊡) 5; (+) 10; (●) 20; and (◇) 40°C min^{-1}

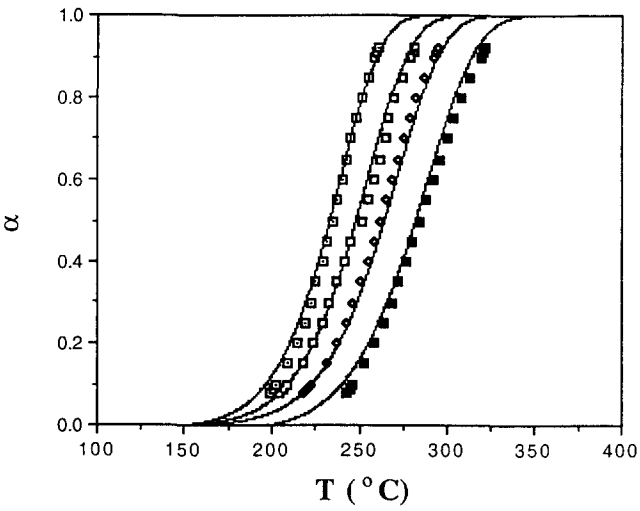


Figure 7 Comparison between experimental and calculated conversion for cure of CPS at different heating rates: (⊡) 5; (□) 10; (◇) 20; and (■) 40°C min^{-1}

this study. For further formulation, equation (3) can be rewritten as:

$$\ln[Af(\alpha)] = \ln(d\alpha/dt) + E_a/RT \quad (4)$$

The $\ln[Af(\alpha)]$ values can be calculated from experimentally determined $d\alpha/dt$ and E_a/RT. For simple nth-order reactions, the relationship $\ln[Af(\alpha)] = \ln A + n\ln(1-\alpha)$ should hold and a plot of $\ln[Af(\alpha)]$ *versus* $\ln(1-\alpha)$ should yield a straight line with slope equal to n. The resulting $\ln[Af(\alpha)]$ and $\ln(1-\alpha)$ are linearly related (*Figure 6*). Kinetics for cure of CPS can be illustrated with a first-order equation of form:

$$Af(\alpha) = 7.8 \times 10^6(1-\alpha)\,s^{-1} \quad (5)$$

Calculated curves are compared to experimental results in *Figure 7*. Use of equation (5) results in a conversion–temperature curve correlated well with experimental data.

Gel point was evaluated from gravimetric analysis of CPS samples subjected to different degrees of isothermal

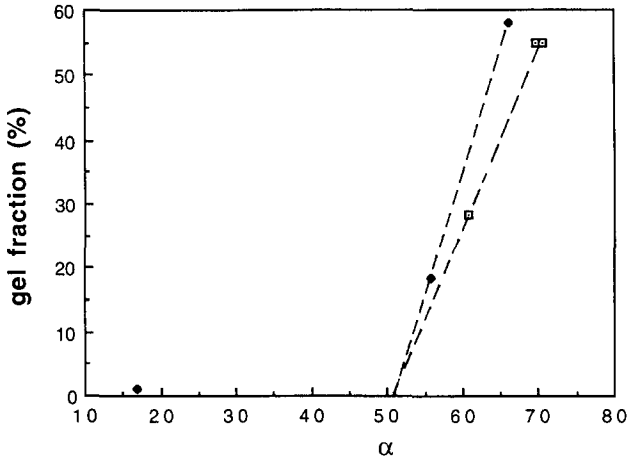


Figure 8 Relationship between gel fraction and conversion. Data are extracted from isothermal cure of CPS at: (⊡) 180; and (◆) 200°C

cure at 180 or 200°C, respectively (*Figure 8*). Conversion of the partially cured sample can be evaluated from:

$$\alpha = \Delta H_{rxn} - \Delta H_{res}/\Delta H_{rxn} \quad (6)$$

where ΔH_{rxn} is the total specific heat of the cure reaction and ΔH_{res} is the residual heat obtained from dynamic d.s.c. scans of the partially cured samples. Gel points determined from cure at 180 or 200°C are well correlated. The gel point thus obtained is approximately at $\alpha_{gel} = 51\%$.

DISCUSSION

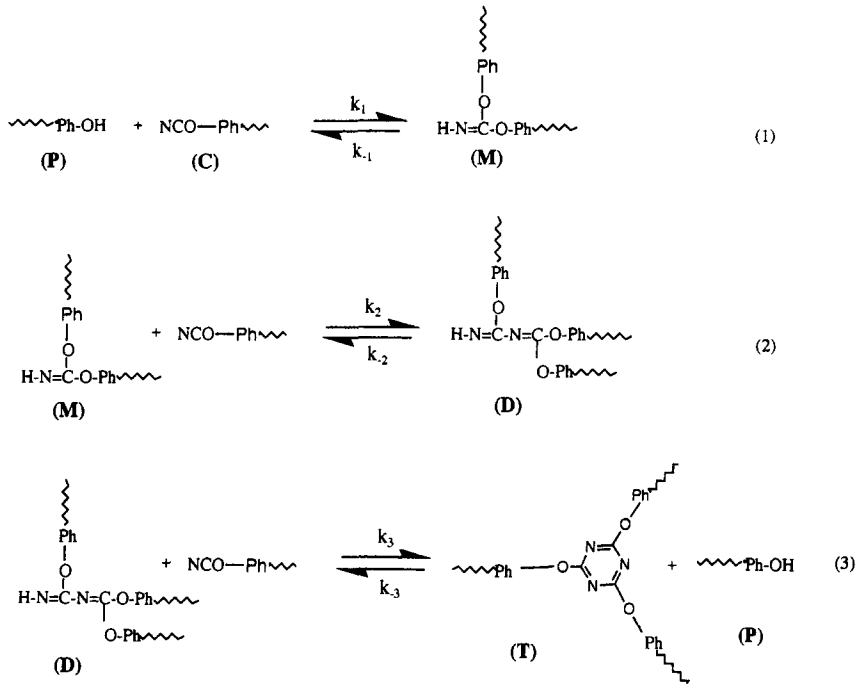
The mechanism for cyclotrimerization of cyanate group previously proposed by Bauer[7] is shown in *Scheme 1*, in which C, P, M, D and T represent the cyanate group, the phenol group, the monomeric intermediate, the dimeric intermediate and the *sym*-triazine ring, respectively. Under the assumptions of pseudo-steady state ($d[M]/dt = d[D]/dt = d[P]/dt = 0$), $k_{-2} = 0$ and $k_{-3} = 0$, a second-order kinetic expression can be deduced with the form:

$$d\alpha/dt = k_1k_2[H][C]^2/(k_{-1} + k_2[C]) \quad (7)$$

where k_1, k_{-1}, k_2, k_{-2}, k_3 and k_{-3} are rate constants of the respective forward and backward reactions of steps 1, 2 and 3 in *Scheme 1*. In the case of CPS, the concentration of impure phenol is presumably low; the formation of monomeric intermediate (M) should be the rate-determining step. Taking $k_2[C] \gg k_{-1}$, equation (7) can be further reduced as:

$$d\alpha/dt = k_1[H][C] \quad (8)$$

This first-order rate expression coincides with our experimental results (as in equation (5)). Nevertheless, the above deduction considers no autocatalytic effect of the resulting *sym*-triazine ring, which was generally introduced in either Gillham's[4] or Lin's[10] results. The absence of autocatalytic effect may be attributed to the inherent ester bond in CPS. The ester bond can coordinate to the impure phenol, as the key component for the initiation of polycyclotrimerization, via a hydrogen bond and facilitate the initial nucleophilic addition of hydroxyl group to cyanate (step 1 in *Scheme 1*). The catalysis due to the ester bond should be dominant over the autocatalytic reaction, considering the higher concentration



Scheme 1 Proposed mechanistic steps for cyclotrimerization of aromatic cyanate

and more flexible nature of the ester unit as compared to the *sym*-triazine ring.

Deviation of the gel point from statistical theories may be attributed to a few possible factors. First, the assumption of equal reactivity may not apply to real situations. The previous investigation on the triethylamine-catalysed reaction of n-butanol and 4,4′-methylenediphenyl diisocyanate[21], an isomer of aromatic dicyanate, at 40°C revealed a reactivity difference of approximately three times between the first and second isocyanate groups. Although this difference may be negligible at higher temperatures, one is still sceptical that the principle of equal reactivity should hold for the isomeric aromatic dicyanate. In our opinion, the reactivity of the cyanate group would be inductively reduced if the cyanate group, a strong electron-withdrawing group, connected at the other end of the same molecule reacted intermolecularly to form a *sym*-triazine ring of less electron-pulling power. This inductive effect may be more prevalent in a smaller molecule like 2,2-bis(4-cyanatophenyl)propane (BPADCy) than in a larger molecule like CPS. The reduced reactivity of cyanate group should result in gelation at higher conversion. Secondly, the presence of side reaction causes deviation as well. Gupta and Macosko[13] concluded, based on the study of the model 2-(2-cyanatophenyl)-2-phenylpropane, that the main trimerization reaction occurred in excess of 90% yield. The side reaction produces more highly branched polymers and should cause gelation at even earlier conversions. Therefore, presence of side reaction cannot explain the high gel point for BPADCy. The final possible source of deviation concerns the applicability of statistical theories, which assume all functional sites are equally accessible to each other. For cure of BPADCy, reactions are only occurring in a local neighbourhood on account of the rigid aromatic ring and the *sym*-triazine ring. Therefore, if some sites are completely screened, the average branch functionality is reduced and the gel conversion is delayed. This is suggested to be the main source of deviation by Gupta and Makosko[13]. In our opinion, this description is correlated with the concept of 'microgel' and 'macrogel' involved in the solution cure of BPADCy as suggested by Korshak *et al.*[22]. The formation of gel proceeds with the primary generation of polymer molecule (microgel) and then the inter-reaction of a small number of 'external' functional groups in the individual microgel to form a network structure (macrogel), an effective gel form obtained experimentally. It is assumed that polymer molecules with rigid structures and therefore limited mobility may grow to high conversion as individual microgel structures without being linked together to form a common network (macrogel).

The assumption of equal reactivity should hold for CPS since the terminal cyanates are separated by long aliphatic chains and are irrelevant to each other (a situation that cannot be met for BPADCy or other rigid aromatic dicyanates). At the present time, we still cannot comment on the possible presence of side reactions during polycyclotrimerization of CPS. The oligomeric nature of CPS inhibited an unambiguous evaluation of side reaction using size exclusion chromatography as conducted by Gupta and Macosko[13]. We may speculate the presence of cyclic products for polycyclotrimerization of flexible CPS. Nevertheless, the most important factor should be the inherent chemical structures of the corresponding aromatic dicyanates. As described above, the formation of macrogel requires inter-reaction of the branched cyanates in the individual microgels. During cure of rigid aromatic dicyanates, small molecules of microgels are easily formed but the inter-reactions of microgels to form macrogels are relatively inhibited due to the inherently rigid structures. In contrast, the cyanate groups in CPS are all attached to long aliphatic chains, yielding flexible branches in the microgel stage. Intermolecular reactions between these long, flexible branched cyanates are not so difficult as in rigid aromatic dicyanates. The ease of macrogel formation resulted in a gel point close to the theoretical prediction.

CONCLUSIONS

Cyanated phenylene sebacate oligomer (CPS) of molecular weight 798 g mol^{-1} was prepared to characterize its cure kinetics and gel point. Dynamic d.s.c. study revealed first-order kinetics with rate expression $Af(\alpha) = 7.8 \times 10^6(1-\alpha)\,s^{-1}$. The absence of autocatalytic effect in the final rate expression may be due to the catalytic effect of the inherent ester bonds.

Gravimetric study revealed a gel point at approximately $\alpha_{gel} = 51\%$, close to the theoretical value of 50%. The accessibility of cyanate group during cure of CPS resulted in the lower gel point as compared with a rigid aromatic dicyanate such as BPADCy.

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