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Study of delayed gelation of a rigid spiro aromatic dicyanate, 6,6′-dicyanato-3,3,3′,3′-tetramethyl-1,1′-spirobi-indane

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A rigid spiro aromatic dicyanate, 6,6′-dicyanato-3,3,3′,3′-tetramethyl-1,1′-spirobi-indane (DCSI), was synthesized and its polycyclotrimerization investigated. The critical gel point (α_{gel}) during polycyclotrimerization of DCSI was studied by gravimetric analysis. The resulting value of α_{gel} ($= 65 \pm 2\%$) deviates greatly from the theoretical value of 50%. To explore the possible reason for this high deviation, partially cured samples were analysed by fast atom bombardment mass spectrometry (FAB–MS). The predominant formation of trimer at a conversion $\leq 50\%$ is responsible for the delayed gelation. In addition to the small amounts of side products such as dimer and carbonate imine, the formation of products with internal cycles (i.e. tetramer and hexamer) is another reason for the high α_{gel}.

(Keywords: rigid aromatic dicyanate; gel point; FAB–MS)

INTRODUCTION

Aromatic dicyanates possess interesting features due to the capability of cyanate groups to undergo different chemical reactions with common nucleophilic groups (i.e. –OH, $-NH_2$ or –SH)[1]. The polycyclotrimerization of aromatic dicyanates[2] (*Figure 1*) brings three cyanate groups together to construct an *s*-triazine ring and therefore forms a network with this *s*-triazine ring as the interconnecting crossslinking point. This reaction, according to the result based on monofunctional 2-(2-cyanatophenyl)-2-phenylpropane[3], is fairly clean and yields mainly the trimerized product (>90–95%) in addition to small amounts of dimeric and oligomeric products. Several research projects have been undertaken in the past few years to investigate this unique feature of polycyclotrimerization. Among them, the argument about the gel point deserves further exploration.

The earliest report on gel conversion (α_{gel}) is from Bauer *et al.*[4,5]. The resulting α_{gel} for cure of bisphenol A dicyanate (BPADCy) is 50%, coincident with the theoretical prediction from either a statistical approach[6] or the recursion method[7]. Nevertheless, a later report from Shimp *et al.*[8] concluded higher values of α_{gel}, ranging from 60 to 65%. Other experimental results, as summarized by Gupta and Macosko[3], all revealed gel points >50% for several aromatic dicyanates at various curing conditions. Gupta and Macosko 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 potential 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, resulting therefore in a more open structure. In this way, a better agreement with the theoretical prediction was achieved. Recently, Lu and Hong[9] studied the gel point (α_{gel}) of a flexible oligomer, cyanated phenylene sebacate (CPS). The flexible moiety in CPS reduces the limitation of steric hindrance, as mentioned above. The resulting value of $\alpha_{gel} = 52\%$ is close to the theoretical value, which suggests that the accessibility of the cyanate terminals plays an important role in gel formation. In addition to the reports cited above, several other investigations[10,11] had been performed previously, and all resulted in the deviation of the gel point.

A literature survey[3,12] indicates that most of the aromatic dicyanates previously studied have a chemical structure of two terminal cyanatophenylene moieties linked by a central carbon atom or heteratoms (X = $-(CH_3)_2C-$, –S– etc. in *Figure 1*). It is perceivable that the accessibility of cyanate groups in the initially formed oligomer would be influenced by the ease of rotation of bonds connecting phenylene rings and X. This would consequently affect the steric bulkiness in the branched oligomers formed initially and therefore the resulting gel point, according to the conclusion of Gupta and Macosko[3]. In this manner, the use of rigid X as the central linkage on an aromatic dicyanate is expected to have a dramatic effect on its corresponding α_{gel}. Accordingly, we report here the first synthesis of a rigid dicyanate, 6,6′-dicyanato-3,3,3′,3′-tetramethyl-1.1′-spirobi-indane (DCSI, see *Scheme 1*), and its characterization as regards gelation behaviour. As indicated by the chemical structure of DCSI, the central spiro structure would completely freeze the rotation of the terminal phenylene rings, and a dicyanate with a more rigid structure than those previously reported has been synthesized. The rigid structure would restrict the motion of cyanate groups in the partially cured branched oligomers and affect the gel behaviour. Therefore, we would like to report our preliminary study, especially on the aspect of gel point, on this new type of rigid dicyanate, DCSI.

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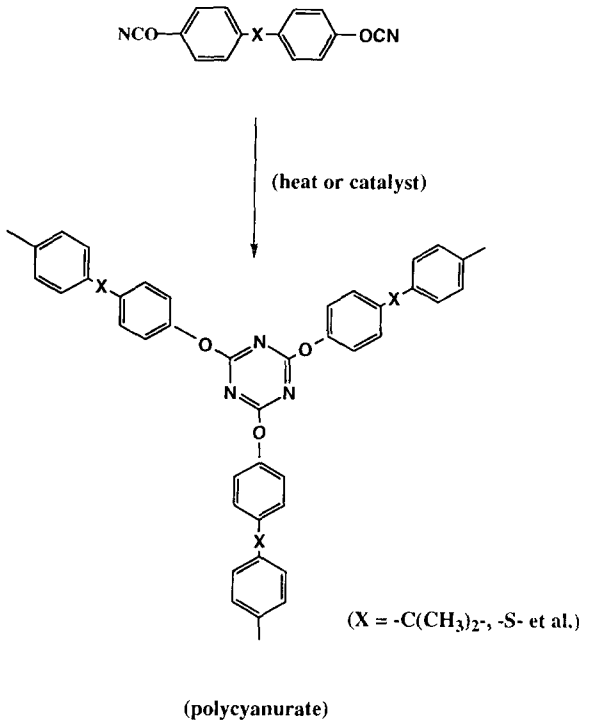
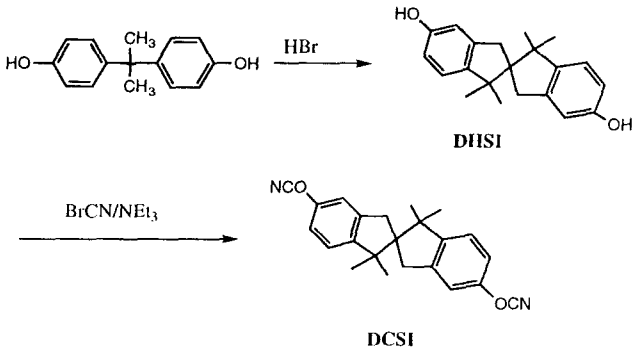


Figure 1 Polycyclotrimerization of different aromatic dicyanates



Scheme 1 Synthesis of DCSI by a two-step process

EXPERIMENTAL

Materials and instrumentation

^{1}H and ^{13}C n.m.r. spectra were recorded with a VXR-300 MHz *FT*-n.m.r. model. A Perkin-Elmer DSC-7 differential scanning calorimeter connected to the thermal analysis data station was used in this study. Samples of approximately 3.5 mg were sealed in a hermetic aluminium pan and scanned in the calorimeter at heating rates of 10, 20, 30 and 40°C min^{-1} over a temperature range of 40 to 400°C. The calorimeter was calibrated for each heating rate using indium and lead standards. A VG Quattro-5022 model equipped with a standard FAB source was used to obtain mass spectra. The instrument was scanned from $m/z = 4000$ to $m/z = 40$, with a scan rate of 10 s per decade. The accelerating voltage was 10 kV. Glycerol was used for calibration. DCSI samples were heated at 270°C for different periods and then quenched by liquid N_2. These partially cured samples were then dissolved in tetrahydrofuran, placed on the target of the direct insertion probe, and mixed with 3-nitrobenzyl alcohol. For one particular case, pure trimer, obtained by thin layer chromatography with ethyl acetate/hexane (1:4 v/v) as eluent, was analysed.

Synthesis

Two-step synthesis procedures according to *Scheme 1* were carried out. Hydroxyl-terminated spiro compound, DHSI, was prepared first and then reacted with cyanogen bromide to yield the final product. The detailed synthesis procedures are given below.

Synthesis of 6,6'-dihydroxy-3,3,3',3'-tetramethyl-1,1'-spirobi-indane (DHSI). 6,6'-Dihydroxy-3,3,3',3'-tetramethyl-1.1'-spirobi-indane (DHSI) was prepared according to the procedures described by Curtis[13]. ^{1}H n.m.r. (300 MHz, acetone-d_6): δ 7.95 (s, 2 H, –OH), 7.02–7.05 (d, 2 H, $J = 8.4$ Hz, aromatic H), 6.69–6.72 (dd, 2 H, $J =$ 8.1, 2.4 Hz, aromatic H), 6.21–6.22 (d, 2 H, $J = 2.7$ Hz, aromatic H), 2.18–2.35 (q, 4 H, $-CH_2-$), 1.30–1.36 (d, 12 H, $-CH_3$). ^{13}C n.m.r. (300 MHz, acetone-d_6): δ 157.7, 152.8, 143.9, 123.2, 115.3, 111.2, 60.5, 58.2, 43.3, 32.2, 30.8. m.p.: 181–182°C.

Synthesis of 6,6'-dicyanato-3,3,3',3'-tetramethyl-1,1'-spirobi-indane (DCSI). Cyanation of DCSI was accomplished by a similar procedure to that described by Grigat and Putter[14]. To a nitrogen-blanketed mixture of DHSI (5 g) and triethylamine (6.7 ml) in THF (80 ml), a solution of BrCN (5 g) in THF (5.6 ml) was slowly added dropwise at ice-bath temperature. The reaction was continued for 6 h. The white salt was filtered and 500 ml of ice water was added to precipitate the crude product. The precipitate was allowed to stay in the ice water for 3 h to decompose the unreacted BrCN. The solid precipitate was then collected and dried in a vacuum oven. The crude solid was then recrystallized from CCl_4 to obtain the final product. ^{1}H n.m.r. (300 MHz, acetone-d_6): δ 7.45–7.48 (d, 2H, $J =$ 8.1 Hz, aromatic H), 7.29–7.33 (dd, 2 H, $J = 8.4$, 2.4 Hz, aromatic H), 6.82–6.83 (d, 2H, $J = 2.4$ Hz, aromatic H), 2.33–2.54 (q, 4 H, $-CH_2-$), 1.39–1.46 (d, 12 H, $-CH_3$). ^{13}C n.m.r. (300 MHz, $CDCl_3$): δ 152.6, 152.1, 151.0, 124.0, 114.9, 110.7, 108.9, 59.1, 57.7, 43.4, 31.6, 30.0.

Gravimetric analysis

DCSI (~50 mg) in an aluminium pan was isothermally cured (at 250 or 270°C) under a nitrogen atmosphere. The partially cured sample was then withdrawn from the heating oven and directly quenched in liquid nitrogen. A portion (~3.5 mg) of the cured sample was scanned in d.s.c. to determine its conversion. The remaining sample was continuously extracted with THF for 6 h. The insoluble portion was vacuum dried and subsequently weighed to obtain the gel yield.

RESULTS AND DISCUSSION

DCSI was scanned dynamically in d.s.c. at heating rates of 10, 20, 30 and 40°C min^{-1} (*Figure 2*). All thermograms showed melting of DCSI at around 132°C and then the curing exotherms ranged from 250 to 390°C, dependent on the heating rates. Curing exotherms were further analysed in order to evaluate the curing kinetics. The specific heat of the curing reaction (ΔH_{rxn}, kJ mol^{-1} –OCN) corresponds to the total area under the peak divided by the heating rate. The resulting ΔH_{rxn} from dynamic and isothermal heatings at 270°C are summarized in *Table 1*.

Gravimetric analyses were carried out for the partially cured products obtained at two isothermal temperatures, 250 and 270°C. The resulting gel yield *versus* sample conversion is shown in *Figure 3*. Conversion can be evaluated from the

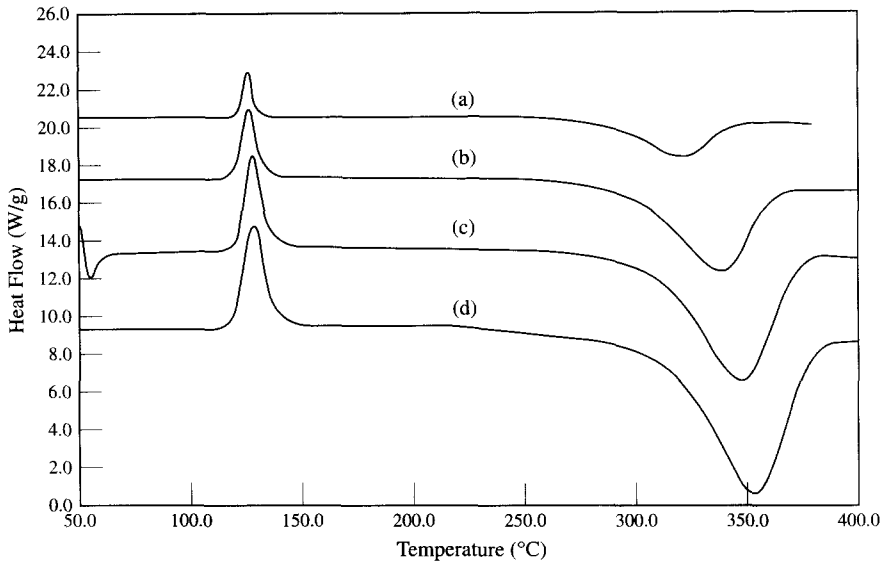


Figure 2 Dynamic d.s.c. scans at heating rates of (a) 10, (b) 20, (c) 30 and (d) 40°C min^{-1}

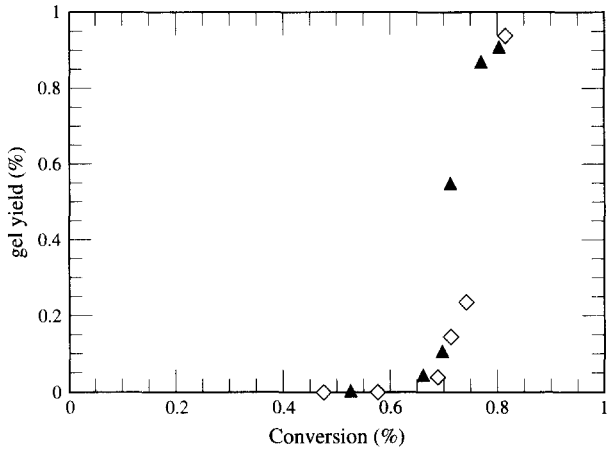


Figure 3 Gel yield *versus* conversion for a partially cured DCSI obtained from isothermal heating at (◇) 250 and (▲) 270°C

residual heat obtained from the dynamic d.s.c. scans of the corresponding cured sample. Gel points determined from heatings at 250 and 270°C are well correlated. The gel point thus obtained is approximately at $\alpha_{gel} = 65 \pm 2\%$, a value much higher than the theoretical prediction. The partially cured samples at conversion $\leq 60\%$ were further analysed by FAB–MS. The general features of mass spectra from samples of conversions less than 50% are basically similar; therefore, only the sample of 50% (*Figure 4a*) conversion was selected for comparison with the sample of 55% conversion (*Figure 4b*). The common feature of all spectra below 50% conversion is that the trimer peak at 1075 is the most intense peak. Increasing the conversion from 50 to 56% resulted in a significant decrease of trimer (cf. *Figure 4a* and *4b*). Both spectra showed several peaks at $m/z = 359$, 717, 1075, 1434 and 1792, corresponding to molecular weights of monomer, dimer, trimer, tetramer and pentamer, respectively. In addition, peaks of $m/z = 318$, 692, 742 and 1008 were detected; their structural assignments are depicted in *Figure 5*. In order to confirm the source of the dimer, a small quantity of pure trimer was isolated from the partially cured sample by thin layer chromatography. The

Table 1 Enthapies (ΔH_{rxn}) evolved during cure of DCSI in d.s.c. scans

D.s.c. mode	ΔH_{rxn} (kJ mol^{-1} of OCN)
(a) Dynamic scans:	
Heating rate (Φ, °C min^{-1})	
10	99.96
20	99.09
30	99.44
40	101.42
	Avg. = 99.99
(b) Isothermal heating at 270°C	
	95.10

corresponding mass spectrum (*Figure 4c*) did not show the presence of a dimer peak at $m/z = 717$, which suggests that the dimer is truly a reaction byproduct instead of a fragmentation species from the trimer. The same rationale can be applied to species corresponding to $m/z = 692$ and 742.

At first glance, the high value of α_{gel} ($= 65 \pm 2\%$) for DCSI may be attributed to its rigid structure. In analogy with the proposition from Gupta and Macosko[3], the rigid structure of DCSI would make the reactions of neighbouring cyanate groups difficult because of the hindered rotation of the spiro moiety, and this should leave a high percentage of unreactive cyanates hidden in the growing branched oligomers before gelation, resulting in the deviation of the gel point from its theoretical prediction. Dynamic d.s.c. scans of DCSI (cf. *Table 1*) revealed an average curing enthalpy of 99.99 kJ mol^{-1} of OCN, a value close to cure of BPADCy (104 kJ mol^{-1} OCN). Also, isothermal heatings at 270°C (close to the low-temperature end of the curing exotherm in the dynamic d.s.c. scans) resulted in a value of similar magnitude, 95.10 kJ mol^{-1} OCN. This is unexpected since the rigid moiety in DCSI was originally thought to affect the accessibility of the cyanate group and to reduce the corresponding ΔH_{rxn} considerably. Therefore, the argument that the delayed gel point is due to the presence of lots of unreactive cyanates hidden in the growing branched oligomers needs to be justified. It is perceivable that a high percentage of hidden cyanates before gelation is required in order to correlate the high deviation of the gel point from $\alpha_{gel} = 50$ to $65 \pm 2\%$. These unreacted

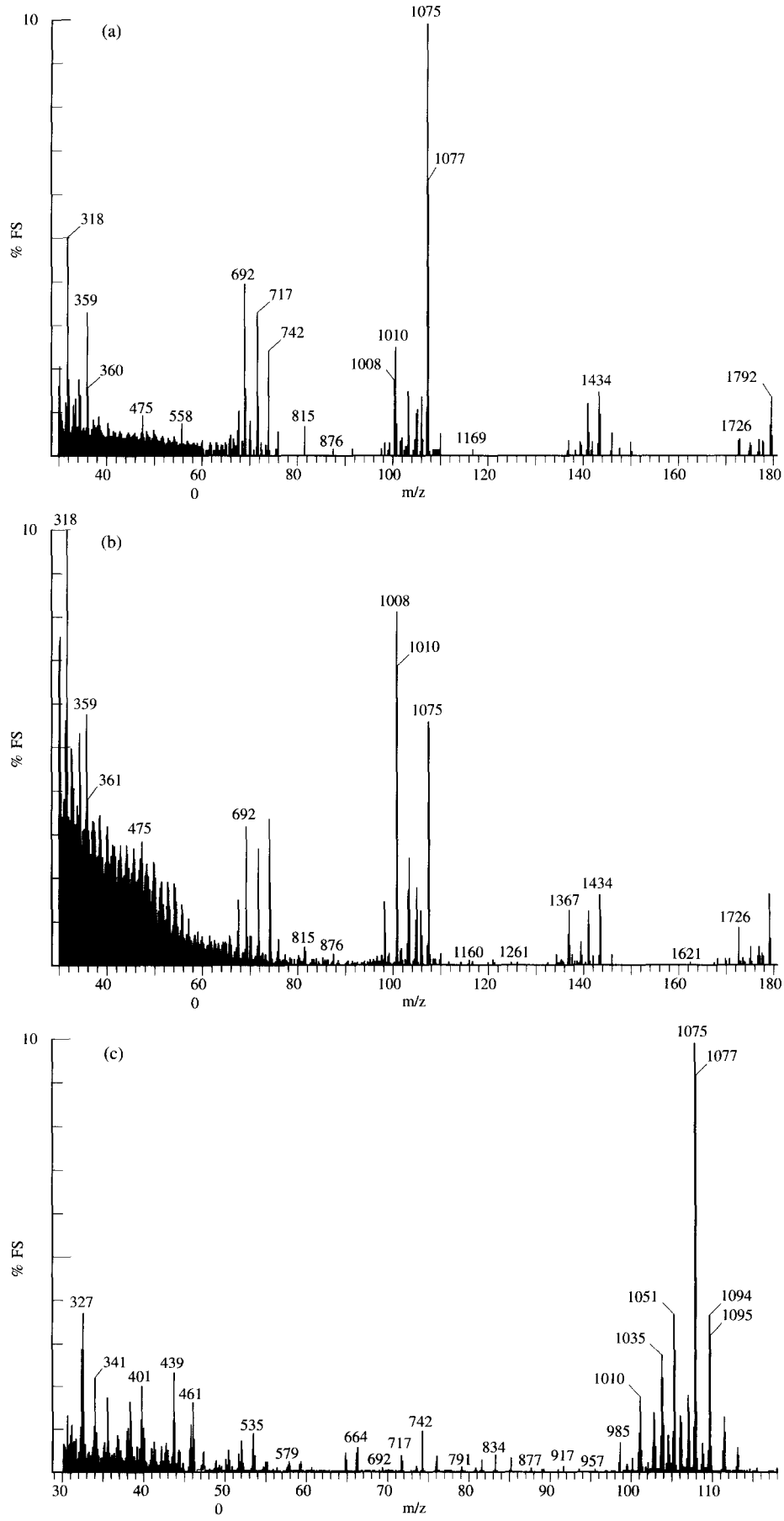
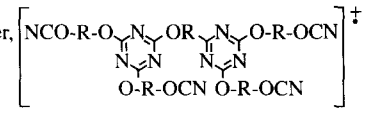
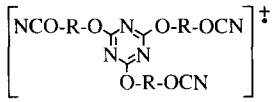
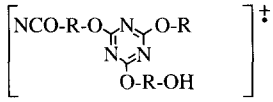
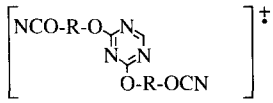
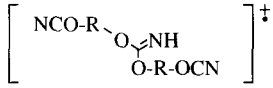
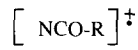


Figure 4 Mass spectra of (a) 50%-, (b) 55%-cured samples and (c) pure trimer obtained from TLC

m/z	Assigned chemical structure[a]
1,792	Pentamer, 
1,434	Tetramer,
1,075	Trimer, 
1,008	
742	
692	
359	Monomer,
318	

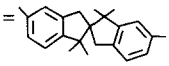
[a] R = 

Figure 5 Structural assignments for the major peaks in the mass spectra

cyanates would be less labile after gelation since reaction should be restricted by the network as compared with the ungelled, branched oligomers before gelation. This deduction is especially true when vitrification takes place. Therefore, if rigidity were the major reason for the delayed gelation, we would expect a major reduction of the ΔH_{rxn} value from those for aromatic dicyanates.

Mass spectroscopy provides valuable information. First, we should realize that possible molecular fragmentations during atomic bombardment may obscure the interpretation of the mass peak and, consequently, prohibit a strict quantitative analysis. The selected mass spectra in *Figure 4a* and *b* indicate the presence of monomer, dimer, trimer, tetramer and pentamer, along with other species. For samples of less than 50% conversion, the highest peak of all corresponds to the trimer species ($m/z = 717$). The spectrum of the pure, isolated trimer suggests that the monomer and dimer peaks in *Figure 4a* and *b* were not generated from fragmentation of the trimer. That the dimer is a side product can therefore be assured.

The theoretical approach from either Flory–Stockmeyer[15] or the recursion method[16] is based on the mean-field assumption. The observation that the cured mixture contains mainly the trimer product at $\alpha < 50\%$ obviously violates the mean-field assumption. It is interesting, at this point, to search for the origin of this predominant trimer formation (in other words, the origin of unequal reactivity). Since no previous study on the reactivity ratios of aromatic dicyanates is available, we therefore turned our attention to the isomeric isocyanate system, i.e. 4,4′-methylenediphenyl diisocyanate (MDI). The triethylamine-catalysed reaction of *n*-butanol and MDI 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. We may also press our doubt on aromatic dicyanates. A mechanism for polycyclotrimerization of aromatic cyanate was previously proposed[17,18]. Basically, the reaction was initiated by the nucleophilic addition of active-hydrogen species (presumably water or phenol residues) to the cyanate group. The cyanate group, as a strong e-withdrawing group, would inductively enhance the nucleophilic addition of the active-hydrogen species to the cyanate on the other side of the same molecule. As long as one of the cyanates in aromatic dicyanate has transformed into a less e-withdrawing *s*-triazine ring, the reactivity of the cyanate group on the other side will be reduced and remains intact until most of the monomer has been consumed. This effect may be especially true for DCSI because the space-oriented inductive effect would be significant for the cynate terminals in the rigid DCSI; but once one of its cyanates has reacted, the remaining cyanate should have much reduced reactivity compared to its originally unreacted state. This basically explaines the fact that trimer is the predominant species at low conversion.

In the case of polycyclotrimerization, the critical condition of gel formation can be described by the equation[19]

$$\alpha_{gel} = 1/[(f-1)(j-1)]$$

where f is the number of functional groups of the monomer and j is the number of functional groups involved in the formation of the junction between the molecules. If it is supposed that all reactions leading to higher oligomers can proceed only after the complete transformation of all monomers into trimers, a highest value of $\alpha_{gel} = 62.5\%$ ($= 50\% + [1/(3-1)(3-1)] \times 50\%$) can be achieved according to the above equation. Therefore, other factors in addition to the nonequal reactivity mentioned above should also contribute to this delayed gelation. A few possible factors are given below. First, global diffusion of the partially cured oligomer should affect the reaction of its inherent cyanate groups and, therefore, the gel point. However, this effect had been previously excluded by Macosko et al.[3] in their study of BPADCy. *Figure 3* shows that gel points evaluated from either 250 or 270°C are approximately the same, indicating that global diffusion is not the major factor in this case. Secondly, the accessibility of functional groups would also deviate α_{gel} from the theoretical approach. This argument has been excluded by the discussion presented in the first paragraph of this section. Thirdly, the presence of side products generally changes the gel conversion to a higher value than the theoretical prediction. Gupta and Macosko[3] concluded, on the basis of their study of the model 2-(2-cyanatophenyl)-2-phenylpropane, that small amounts of dimer were detected in addition to the main trimerized product (> 90% yield). A side product with a carbonate imine bond was also certified by ^{13}C and ^{15}N n.m.r. of a solution-cured BPADCy[20]. In this study, side products such as dimer and tetramer are present, as judged from their corresponding mass spectra. The side product, like the carbonate imine with an m/z value of 692 (cf. *Figure 4a* and *b*), should result in an increase of the linear structure in the cured branched oligomers, contributing to the increase of α_{gel}. In any event, all these products are

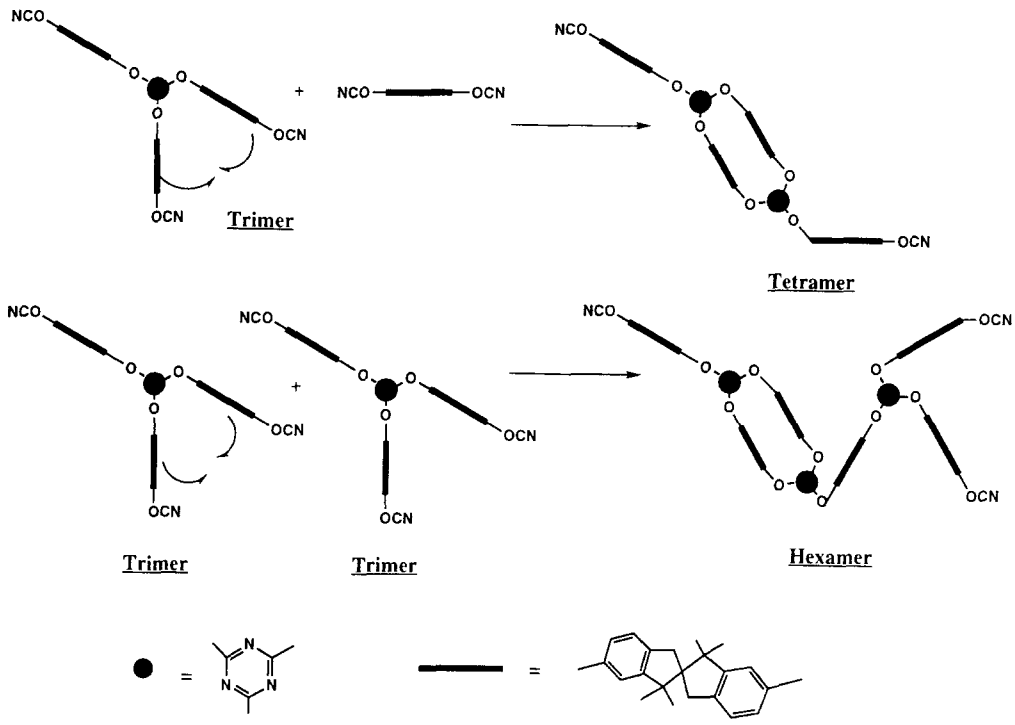


Figure 6 Formation of tetramer (or hexamer) by polycyclotrimerization of trimer and monomer (or trimer)

supposed to be minor and should not contribute much to the high deviation of α_{gel}. Finally, formation of internal cycles during cure would eventually increase α_{gel}. It is expected that the inherent rigid nature of DCSI would increase the possibility of formation of cyclic products. Unfortunately, this proposal is hard to verify. Previously, Wertz and Prevorsek[2] measured the tensile properties of an SIPN material made by curing a 50:50 mixture of BPADCy and dibutylphthalate. Despite the expected high crosslinking density, the resulting high elongation-to-break (70%) indicates the possible formation of large amounts of internal cycles besides the 'normal' crosslinking points. Likewise, cyclic formation is a reasonable cause for the deviation of α_{gel} for DCSI, considering its rigid nature. The formation of tetramer (or hexamer) is therefore possible by reactions between trimer and monomer (or trimer), as shown in *Figure 6*. The formation of internal cycles needs the rotation of the spiro moieties to a nearby position to have the cyanate terminals close enough to react (as indicated by the arrow in *Figure 6*). In other words, a sterically unfavourable trimer conformation is required for the formation of internal cycles, and this may be the reason for the minor quantities of tetramer and hexamer. In addition, the formation of an internal cycle can efficiently reduce the amounts of hidden cyanates, resulting, therefore, in an unexpectedly high ΔH_{rxn} for polycyclotrimerization of DCSI.

CONCLUSIONS

Pure rigid aromatic dicyanate, DCSI, can be prepared and studied. The abnormal high gel point at $\alpha_{gel} = 65 \pm 2\%$ can be attributed to a few possible factors as listed below:

(1) The predominant formation of trimer before gelation is one major reason for the delayed gelation. The cause of trimer formation is the unequal reactivity of the two cyanates on DCSI originating from the intensified inductive effect.

(2) Several side products, e.g. dimer and carbonate imine, are also responsible for the high gel point. Nevertheless, this should not contribute much, considering the low intensities of these side products in mass spectra.

(3) Internal cyclization is a potential cause for deviation of α_{gel}, and this leads to the formation of tetramer and hexamer.

In addition, the high ΔH_{rxn} from either dynamic or isothermal d.s.c. scans suggests that hidden cyanates in the growing branched oligomers are mostly consumed during cure. This high value of ΔH_{rxn} is possibly related to the formation of internal cycles.

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