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Characterization and Modeling of Rigid Branched Polycyanates[1]

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ABSTRACT: Synthesis and characterization of tightly branched, rigid, network polymers based on the cyanate functional group are reported. Monofunctional model compound 2-(4-cyanatophenyl)-2-phenylpropane (CPP) was reacted in bulk to establish the reaction chemistry. It is found that trimerization which forms the cyclic triazine ring is the dominant reaction occurring in excess of 90%. Polymers based on the bifunctional compound 2,2-bis(4-cyanatophenyl)propane (BCP) were synthesized thermally in bulk without a catalyst. Number-average molecular weight (from ^{13}C NMR and SEC) and weight-average molecular weight (from SEC) are reported as a function of cyanate group conversion (from ^{13}C NMR and IR). The gel conversion is found to be over 60%, significantly higher than the mean-field value of 50%. The source of this disagreement is discussed. Gel conversion of polymers based on the combinations of CPP and BCP is closer to the mean-field value with increasing CPP in the initial stoichiometry. One explanation which is consistent with all experimental results is that the growth of rigid polycyanate networks is controlled by the accessibility of functional groups. The experimental results point to the limitations of mean-field theory. The nature of these limitations is explored through Monte Carlo simulations.

Introduction

Experimental characterization of highly branched (network) polymers during polymerization is extremely difficult. Most experimental techniques are solution based and thus cannot be used after gelation. Before gelation the broad polydispersity of the molecules, in both size and shape, limits the use and interpretation of many methods. These experimental difficulties have necessitated the development of accurate models of polymerization. The Flory–Stockmayer theory,[2–6] which is a mean-field theory, has been successfully applied to many bulk stepwise chemistries.[7–13] However, the mean-field theory does not accurately predict the gel conversion for polycyanates. This paper is an attempt to understand the structure evolution of cyanate polymers.

From a practical viewpoint this work offers the understanding of polymerization of a useful commercial product. Cyanate resins are used as composites and in the electronic packaging industry, and their unique features are discussed in several publications.[14] Despite their increasing use, a fundamental study of the polymerization reaction has not yet been undertaken.

The reports in the literature on cyanate polymerization are conflicting. Shimp et al.[14] measured the gel point for the bifunctional monomer 2,2-bis(4-cyanatophenyl)propane (BCP) to be between 60% and 65% conversion. Bauer et al.[15,16] however report gelation at 50% conversion. Shimp and co-workers used DSC and IR to measure conversion; Bauer and co-workers used DSC, IR, and titration. Recently some other studies have also been reported on the measurement of gel conversion for different cyanate monomers.[17–21] The key results are summarized in Table I. Except for the results obtained by Bauer et al., the gel conversion is found by several different groups to be between 60% and 65%.[22,23] Results of this work are also included in Table I. Conversion was measured by ^{13}C NMR and IR. The motivation for this study is to establish and explain the reasons for the observed gel conversion.

Almost all studies in the cyanate literature consider trimerization to be the exclusive reaction (see Figure 1a and refs 14–21 and 24). However, there seems to be little published experimental evidence for or against it. Korshak[25] and Cercena[26] have hypothesized that cyanates can also undergo dimerization. In order to understand cyanate polymerization, it is necessary to first establish the basic linking chemistry. For this, the monofunctional model compound 2-(4-cyanatophenyl)-2-phenylpropane (CPP) was used (see Figure 1b). The oligomers of the model compound were synthesized under several conditions using different catalysts. The reaction products were then characterized by ^{13}C NMR and SEC. Commercially relevant bifunctional monomer 2,2-bis(4-cyanatophenyl)propane (BCP; see Figure 1a) was used to study the cross-linked polymer. Quenched samples were analyzed using ^{13}C NMR, IR, and SEC. The gel conversion was found to be higher than 60%. Samples with varying mole ratios of the bifunctional and monofunctional monomer were also synthesized and characterized in a similar fashion. Details of the synthesis and characterization are discussed below.

The mean-field prediction of gel conversion for the trimerization reaction of a bifunctional cyanate monomer is 50%.[27,28] This can be shown quite simply using the recursion method.[29] Let A represent a cyanate functional unit. Then 2,2-bis(4-cyanatophenyl)propane can be written as A_2. Figure 1a shows a branched cyanate trimer (see also the schematic in Figure 12a). If $E(W_A^{\text{out}})$ is the expected weight looking out of a randomly chosen cyanate functional unit and $E(W_A^{\text{in}})$ is the corresponding expected weight looking in,

$$E(W_A^{\text{out}}) = 2\alpha E(W_A^{\text{in}}) + (1 - \alpha)0 \tag{1a}$$

$$E(W_A^{\text{in}}) = M_{A_2} + E(W_A^{\text{out}}) \tag{1b}$$

α is the conversion of the cyanate functional groups, and M_{A_2} is the molecular mass of the A_2. The weight-average molecular weight is

$$M_w = M_{A_2} + 2E(W_A^{\text{out}}) = \frac{M_{A_2}(1 + 2\alpha)}{1 - 2\alpha} \tag{2}$$

Gel conversion, α_c, is the conversion where M_w diverges and therefore $\alpha_c = {}^1/_2$.

In the above derivation it has been assumed that trimerization is the only reaction; the monomers are purely

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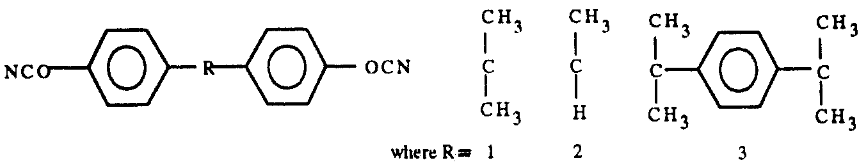
Table I. Summary of Gel Points for Bifunctional Cyanate Monomers from the Literature

					method for determination	
ref	R[a]	α_{gel}	T, °C	catalyst	convn	gel point
Shimp et al., 1989[14]	1	0.63	200	uncat.	DSC, IR	solubility
Bauer and Bauer, 1986, 1991[15,16]	1	0.50	200	uncat.	DSC, IR, titration	solubility
Osei-Owusu et al., 1992[17]	1	0.60–0.64	130	Zn^{2+}	IR	$G' = G''$
Galy et al., 1991[18]	2	0.60	120	Co^{2+}	DSC	η, solubility
Chen and Macosko, 1992[19]	2	0.64	140–160	Mn^{2+}	IR	η
Simon and Gillham, 1992[20]	3	0.64	105–190	Cu^{2+}	DSC	tan δ_{max}
Armistead and Snow, 1992[21]	2	0.58–0.64	200	Mn^{2+}	IR	solubility
Gupta and Macosko, 1993	1	0.58–0.62[b]	200	uncat.	^{13}C NMR, IR	solubility

[a] This column identifies the different monomers used.



[b] These are the lower limits of solubility.

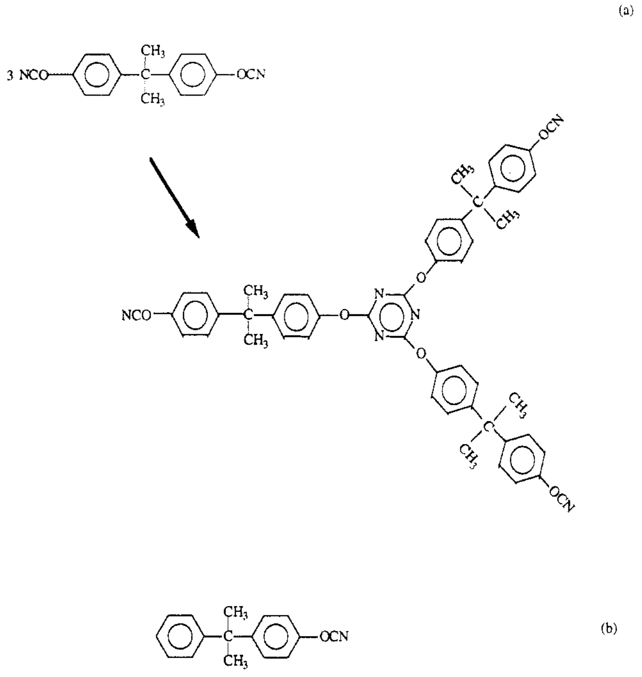


Figure 1. (a) Trimerization reaction of 2,2-bis(4-cyanatophenyl)propane; (b) 2-(4-cyanatophenyl)-2-phenylpropane.

bifunctional and retain their functionality during the reaction. These conditions were found to be approximately true and are established in the following sections along with the nature of the deviations. In the above derivation it has also been assumed that there is no inherent or induced unequal reactivity (substitution effect[30]) of the cyanate functional groups. This is a reasonable assumption since the cyanate groups are symmetric and sufficiently separated from one another. Since the mean-field theory does not take into account intramolecular bonds, it may be argued that cyclization is responsible for the delay in gel conversion. Experimental evidence indicates that cyclization significantly effects the gel conversion in stepwise polymerization when they are dilute.[31,32] A survey of the literature shows that the vast majority of the observed gel conversions in bulk stepwise systems agree within 10% of the mean-field value.[7-13] It follows that the large discrepancy between the experimental gel conversion from bulk polymerization of BCP and mean-field prediction can partially be due to cycles. Thus bulk cyanate polymerizations which would appear to be nearly ideal from the perspective of the applicability of mean-field theory are clearly not so.

Experimental work reported in this paper was specifically tailored to obtain possible clues to the difference between the mean-field predicted value for α_c and the experimental observation. The results of the experiments are discussed in light of some recent Monte Carlo simulations.[33] These simulations help understand the rather surprising general success of mean-field theory. The simulations present a realistic basis for understanding the role of intramolecular reactions during polymerization. The simulations also offer one possible explanation for the observed results in cyanate polymerization.

Experimental Procedures

The model compound CPP was made available by Hi-Tek Polymers (Louisville, KY) and used as obtained. Its purity was greater than 98% based on size-exclusion chromatography (SEC). The compound was reacted in a three-necked flask (50 mL) with a magnetic stirbar immersed in an oil bath kept at the reaction temperature. The temperature was regulated by a thermocouple kept in the flask. Five different reaction conditions were used, one without a catalyst and four with different catalysts. The catalysts were supplied by Hi-Tek Polymers and used at typical commercial levels. The reaction temperature and catalyst concentrations are shown in Table II.

Samples were withdrawn with a pipette from the reaction flask at varying time intervals and quenched in ice as quickly as possible to freeze all reactions. These samples were then prepared for characterization. For SEC they were dissolved to about 0.1 w/v % in THF. Columns of pore size 50, 100, 500, 10^4, and 10^5 Å (Phenogel, from Phenomenex) of 5-μm particle size were used in series in a Waters 150C SEC (for low molecular weight products only the first three columns were used). The columns had an internal diameter of 7.8 mm and were filled with styrene–divinylbenzene particles. The choice of the columns was important in order to separate low molecular weight oligomers and identify the various reaction products. After filtering the samples twice through filters of average pore size 0.2 μm, 50 μL of sample was injected at a flow rate of 1 mL/min. Differential refractive index was used to measure weight concentration versus elution volume.

For NMR, quenched samples were dissolved to about 25% weight concentration in $CDCl_3$ (chloroform-*d*) solution. Previously, a $CDCl_3$ solution had been prepared by dissolving 0.5% weight percent chromium(III) acetylacetonate in $CDCl_3$. Chromium(III) acetylacetonate is a paramagnetic compound and is used to accelerate the relaxation times of the nuclei in the sample. A Bruker 300-MHz NMR facility was used to obtain the standard ^{13}C NMR spectra. A total of 400 scans with a relaxation time of 5 s between them was used. The relaxation time has previously been reported to be sufficient to ensure that all nuclei have relaxed between scans if the appropriate amounts of the paramagnetic compound chromium(III) acetylacetonate are used.[34]

Table II. Composition and Catalysts Used for Synthesis and Characterization Based on 2-(4-Cyanatophenyl)-2-phenylpropane and Number Fraction of Reaction Products for Different Synthesis Conditions (SEC)

catalyst (g)[a]	T (°C)	time (min)	monomer	trimer	dimer	higher M_w[b]	convn
	200 ± 5	440	0.09	0.84	0.01	0.06	0.91
Zn^{2+} (0.25)	150 ± 5	90	0.08	0.87	0.01	0.04	0.92
Cu^{2+} (0.42)	130 ± 10	164	0.06	0.90	0.03	0.01	0.94
Mn^{2+} (0.42)	155 ± 10	62	0.01	0.90	0.03	0.06	0.99
Sn^{2+} (0.024)	140 ± 10	177	0.04	0.84	0.01	0.11	0.96

[a] The catalyst is reported as grams mixed per 100 g of monomer and 2 g of nonylphenol. The latter provides active hydrogens and a medium for dispersing the catalyst (ref 14). The napthenates of zinc, copper, and manganese were used, while stannous octoate provided the Sn^{2+} ions. [b] These are peaks due to higher molecular weight products, possibly four- and five-membered structures (see text and Figure 2a).

Cyanate polymers based on the bifunctional monomer BCP were synthesized in a 50-mL three-necked flask with a magnetic stirbar immersed in an oil bath kept at the reaction temperature. The monomer was supplied by Hi-Tek Polymers and had a reported purity of greater than 99.5%. The reaction temperature was 200 ± 5 °C. Samples were withdrawn periodically and quenched in ice. The samples were prepared as described above for ^{13}C NMR and SEC. An IBM IR-44 FTIR facility was used to obtain the infrared (IR) spectra of the reaction samples. The three different modes used for characterization were diffuse reflectance, film, and solution IR. For diffuse reflectance, the samples were crushed to a homogeneous particle size and mixed in even proportions with crushed KBr. For film casting, methyl ethyl ketone (MEK) was used as a solvent for the samples which were then cast as a thin film on NaCl crystals. For solution IR, three different solvents were tested: tetrahydrofuran (THF), MEK, and trichloromethane (TCM). Of these TCM was most suitable because of its low volatility and because it does not interfere with any of the cyanate absorbance frequencies. Results from diffuse reflectance and film IR were within 15% of the conversion values from NMR. Results from solution IR were reproducible within 10% of the NMR values. IR results reported here are exclusively those obtained from the solution technique with TCM as the solvent.

A Perkin-Elmer 7 series DSC was used to obtain the thermal traces of the monomer. A total of 5 ± 2 mg of BCP (which is a fine crystalline powder at ambient temperatures) was sealed in aluminum pans. Isothermal scans and several dynamics scans at 20 °C/min were performed. The DSC traces were irreproducible, possibly due to the high volatility of the sample which results in varying weight loss. The heat evolved varied between 700 ± 100 J/g. Therefore, only results based on SEC, IR, and NMR are discussed below.

Samples with mixed compositions of monofunctional monomer CPP and bifunctional monomer BCP were synthesized in a similar apparatus uncatalyzed at 200 ± 5 °C. Three compositions were prepared in the mole ratio ρ (moles of BCP/moles of CPP) = 2, 1, and $^1/_2$. The characterization methodology using ^{13}C NMR, IR, and SEC is the same as that described above.

Results

Monofunctional Monomer. The SEC traces of oligomers based on a CPP uncatalyzed reaction (see Table II) at three different stages of conversion are shown in Figure 2a. The monomer peak appears at elution volumes of 27.8–30 mL. This peak defines the resolution available in these columns. The trimer elutes at between 23.6 and 24.8 mL. At higher conversions, additional peaks are also discernible. A small peak, possibly from a dimer product, appears at between 25.4 and 26 mL. Double peaks appear at the high molecular-weight end between elution volumes 22 and 24 mL. These might be due to the formation of four- and five-membered oligomeric species. The appearance of a small shoulder on the monomer peak at the high molecular-weight end is not explained at this stage. Assuming that the refractive index of the trimer is not significantly different from that of the monomer, conversion can be calculated as the ratio of the areas under the peaks (Table II). Figure 2b shows the conversion plot for the uncatalyzed samples. Results from two different syntheses under "identical" conditions are shown. A simple nth-order kinetic expression cannot describe one set of the data (set A, Figure 2b), which suggests that the reaction is autocatalytic. However, the second set of data (set B, Figure 2b) approximately fits a simple 2nd-order kinetic reaction. This suggests that the reaction is sensitive to small external impurities which do not affect the reaction products and hence are primarily catalytic in action. The SEC, IR, and NMR spectra of the two sets are identical. The agreement of conversion between these techniques is established in Figure 2b. On the basis of these spectra, we conclude that trimerization is the dominant reaction (~90%). Of the alternate structures, dimers are likely, and also higher-membered species.

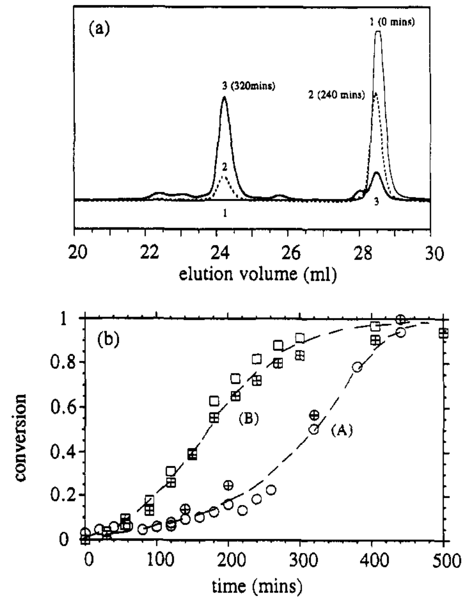


Figure 2. (a) SEC traces of uncatalyzed formation of oligomers of 2-(4-cyanatophenyl)-2-phenylpropane. Looking in from the largest to the smallest monomer peak (28–29 mL), the times of reaction are 0, 240, and 320 min. The units on y axis are arbitrary but proportional to concentration. See Table II for reaction conditions. (b) Kinetic results of uncatalyzed oligomers of 2-(4-cyanatophenyl)-2-phenylpropane for two different syntheses are shown: (□ and ○) from SEC; (⊕) from NMR; (⊞) from IR.

The SEC traces for the catalyzed samples of CPP are qualitatively similar. The elution peaks and consequently the reaction products from samples using different catalysts are identical to each other and to the uncatalyzed case. Again trimerization is the dominant reaction (see Table II). The side products are dimers and higher-membered oligomers (~10%). The amount of each of the side products varies with the catalyst (see Table II) and can be significant. No further studies were performed to investigate the side reactions. The reaction was qualitatively second order when external catalysts were used.

^{13}C NMR and IR was used to verify the conversion results for the uncatalyzed samples. In NMR only one reaction peak was discernible under all conditions corresponding to the triazine ring carbon atoms. For NMR conversion was followed by monitoring the area under the cyanate peak at 108.8 ppm, using the quaternary carbon peak at 42.7 ppm as the internal reference. Values of conversion obtained from NMR and SEC compare favorably and are shown in Figure 2b. IR conversion values were monitored by ratioing the peak area for the cyanate doublet at 2640 cm^{-1} against the internal reference at 2690 cm^{-1} which corresponds to the symmetric CH_3 stretch.

The side products are most likely to be straight chains as opposed to cyclic structures, like the triazine ring. This follows for two reasons. First, two-membered rings with bond angles of 90° are highly strained and improbable. Second, it is unlikely that the higher oligomers are cycles, due to the statistical improbability of four or more cyanate groups reacting synchronously to form a closed loop. Therefore, it is speculated that other than the stepwise addition mode of the trimerization reaction there is an alternate chemistry that produces straight oligomeric species, most likely a chainwise polymerization.[35]

Bifunctional Monomer. The ^{13}C NMR spectrum of BCP is shown in Figure 3a. The spectrum for the typical polymer is shown in Figure 3b. The inset structures depict the relevant peak identifications. These were used as reported by Fang[34] and verified where possible by a DEPT (*D*istortionless *E*nhanced *P*olarization *T*ransfer) experiment. Conversion was monitored by the same procedure as that for the monofunctional CPP samples. The symmetrical structure of the polymer and excellent distinguishability of backbone carbons from end-group carbons can be used to calculate the number-average degree of polymerization $(DP)_n$. Figure 3c is the upfield NMR spectrum that depicts the four different aromatic carbon environments. The four peaks correspond to the following: the cyanate functional group on the same aromatic ring has reacted while the other cyanate group on the same monomer has not (5a); the other way around (5b); both cyanates have reacted (5c); and neither group has reacted (5). These were used to calculate $(DP)_n$ as:

$$(DP)_n = 3\frac{R + R' + 2}{3R - R' + 2} \qquad (3)$$

Here, R is the ratio of the peak areas 5 and 5a and R' is the ratio of the peak areas 5c and 5a. For the derivation and basis of this formula, see Fang.[34]

The number-average molecular weight (M_n) versus conversion (α) results are shown in Figure 4. All samples in Figure 4 (and in Figure 6) were completely soluble; therefore, gelation is after 60% conversion. Since postgelation conversions were not measured accurately, the precise gel conversion is unknown at this time. However, on the basis of solubility tests, the polymer was found to gel soon after 60% conversion. Thus, these results agree with those of Shimp et al.[14] and others[17-21] and are in conflict with those of Bauer et al.[15,16] (see Table I). The typical accuracy of ^{13}C NMR is 10%.

The weight-average molecular weight (M_w) of the BCP polymer is shown in Figure 6a. This was obtained through SEC. A typical SEC chromatograph of reaction products is reproduced in Figure 5a. Use of monodisperse low pore size columns allows clear distinguishability of oligomers up to monomer size 13. Spectra of polymers derived at approximately 30% conversion from two different syntheses are shown in Figure 5a. It is noted that for one of these sets a dimer peak was seen which was missing in the other case. Since the reaction conditions were identical in the two cases, the reasons for this difference are not clear. There was no notable difference in the NMR and IR spectra for these two different sets. On the basis of the absolute assignment of the mass to size-excluded peaks in the SEC spectra, a calibration curve can be generated to determine the molecular weight distribution of the polymer. This is shown in Figure 5b. It is assumed that the linearity observed in this range holds at higher molecular weights as well. On this basis M_w was calculated as shown

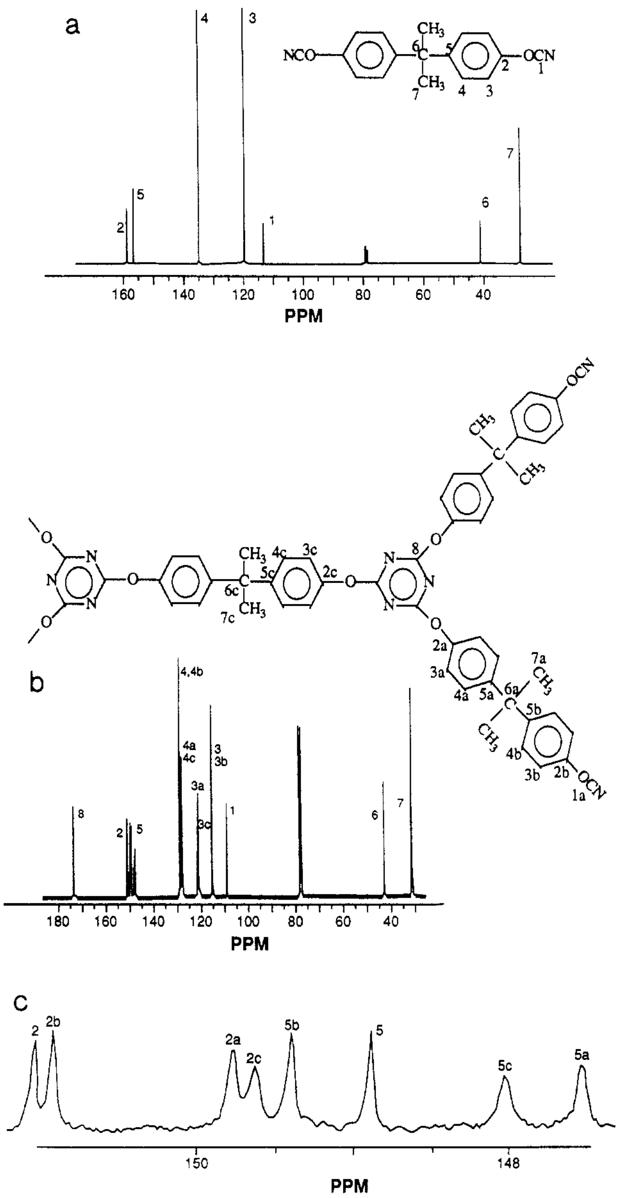


Figure 3. (a) ^{13}C NMR spectra of 2,2-bis(4-cyanatophenyl)propane. The inset structure shows the peak identifications. (b) ^{13}C NMR spectra of polymers of 2,2-bis(4-cyanatophenyl)propane. The inset structure shows the peak identifications. (c) ^{13}C NMR spectra in the upfield region.

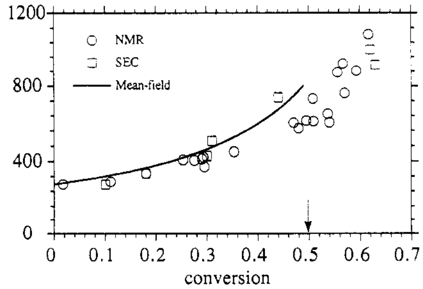


Figure 4. Number-average molecular weight for polymers of 2,2-bis(4-cyanatophenyl)propane. The solid line is the mean-field result. The arrow points to the mean-field gel conversion, $\alpha_c = {}^1/_2$.

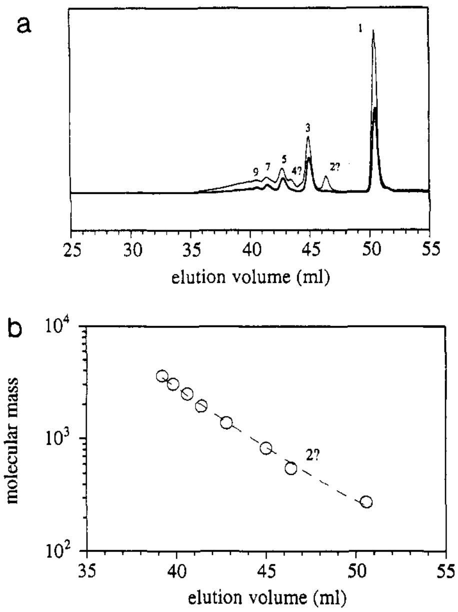


Figure 5. (a) SEC trace of reaction products of 2,2-bis(4-cyanatophenyl)propane uncatalyzed. Oligomer size in monomer units as marked. The conversion of both samples is about 30%. One of them shows the peak corresponding to a dimer (and tetramer). (b) The calibration curve on the basis of the peak identification in Figure 5a, except 11 and 13 which were taken from other SEC results (for example, Figure 8).

in Figure 6a. The conversion values are those obtained from IR. The accuracy of SEC is expected to be about 10%. From the solubility of the polymer in THF it follows that gelation occurs after 60% conversion.

Using IR conversion was monitored by ratioing the peak area for the cyanate doublet at 2640 cm^{-1} against the internal reference of the symmetric CH$_3$ stretch at 2690 cm^{-1}. On the basis of the solubility of the sample in TCM, the gel conversion was found to be beyond 60%. The conversion values obtained from IR and NMR compare favorably and are plotted in Figure 7. Recently other work on conversion measurements using DSC and ^{15}N NMR has also been reported.[36] These techniques for measuring conversion also show good agreement. ^{15}N NMR also shows only one reaction peak corresponding to the formation of the triazine ring.[36]

Mixed (BCP + CCP) Synthesis. The bifunctional and monofunctional monomers were mixed for synthesis in three mole ratios ρ (moles of BCP/moles of CCP) = 2, 1, and $^1/_2$. The typical SEC spectrum of such a system ($\rho = {^1/_2}$) is shown in Figure 8. The trimer can have four possible structures based on the number of bifunctional monomers and monofunctional monomers on it. These are $3*0$, $2*1$, $1*2$, and $0*3$. Here $a*b$ means a bifunctional monomers and b monofunctional monomers. All four peaks are distinguishable in the SEC spectra (though only the last three are seen in Figure 8). A similar sensitivity in separation of higher oligomers is not seen in these SEC columns. The average molecular weight of the higher oligomers was assigned to their elution peaks in order to determine the calibration curve. The calibration curve for all three syntheses (different ρ) was the same. The M_w and M_n values of these samples were determined on this basis. The conversion values were determined from IR, and some of these were verified through NMR (Figure 7). These results are shown in parts b–d of Figure 6.

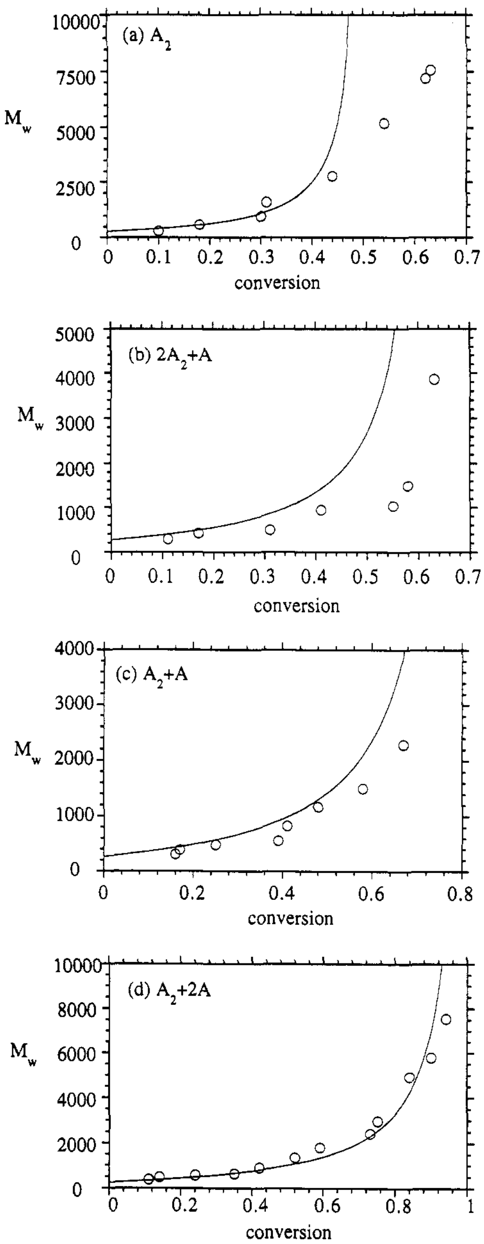


Figure 6. Weight-average molecular weight (SEC) and conversion (IR) for mixtures of A$_2$ (2,2-bis(4-cyanatophenyl)propane) and A (2-(4-cyanatophenyl)-2-phenylpropane). The inset identifies the stoichiometry. From the top the figures are referred to as a–d in the text. The solid line is the mean-field result.

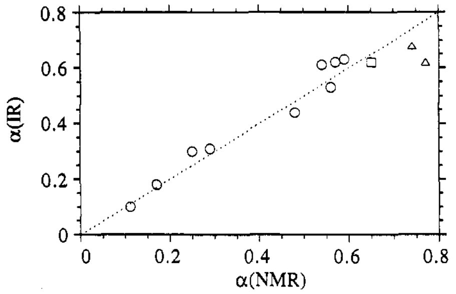


Figure 7. Comparison of conversion values from IR and ^{13}C NMR. Different symbols are used for different sets of synthesis: (○) for A$_2$; (□) for 2A$_2$ + A; (△) for A$_2$ + A.

Discussion

Conclusions Based on Experimental Results. Studies on the model compound CPP show that trimerization (Figure 1) is the principal reaction. The effective functionality for the trimerization reaction of bifunctional monomer is 3, and mean-field theory predicts that this system gels at 50% conversion. The side reaction as observed in model compound studies is most probably noncyclic and produces linear oligomers. For a noncyclic

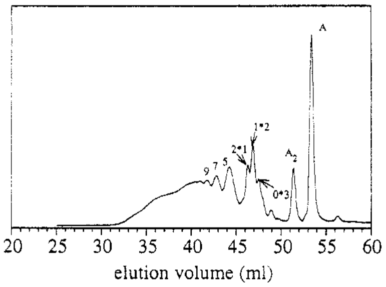


Figure 8. SEC trace of $^1/_2A_2 + A$. Oligomer size in monomer units as marked. The notation $a*b$ refers to the number of A_2 and A making a trimer respectively.

side reaction involving the opening of a triple bond the functionality of a bifunctional monomer is 4. Thus the side reaction produces more highly branched polymers and should cause gelation at even earlier conversions. If the side reaction occurs chainwise, as is most likely, gelation should also be at earlier conversion. These straight chain structures are approximately on the order of a few percent as seen in SEC spectra. Their concentration is too low for detection in NMR and IR. Therefore, side reactions cannot explain the observed gel conversion for BCP bulk polymerization.

For the sake of argument assume that cyclic dimerization occurs during cyanate polymerization along with the trimerization reaction (or any other kind of side reaction that has an effective functionality of 2). Then if α_1 is the functional conversion of groups through dimerization and α_2 the functional conversion through trimerization according to mean-field theory at gelation, $\alpha_1 + 2\alpha_2 = 1$. If gelation occurs when $\alpha_1 + \alpha_2 = {}^2/_3$, at the gel point half the converted groups must be dimerized and the other half are trimerized. This analysis shows that cyclic dimerization would have to be a reaction of equal importance to trimerization if mean-field theory was to explain the observed gel conversion. In these experiments no side reactions of this magnitude were found. Further the dimerization reaction is expected to be noncyclic in which case the effective functionality is 4 and not 2.

The purity of the monomer is very high (>99.5%); therefore, the effective monomer functionality is not in question. Further monomer functionality is not significantly lost during the reaction. This follows for two reasons: several different monomers have the same gel conversion and heat of reaction (see Table I), and neither IR nor NMR reveals any new structures resulting from loss of functionality during polymerization. A small shoulder on the monomer peak in SEC perhaps indicates some loss of functionality, but this is a small side reaction and cannot by itself explain the observed gel conversion.

The reactivity of the two functional groups on BCP is expected to be identical since the monomer structure is symmetric. The two cyanate functional groups are sufficiently separated on the monomer; therefore, the reactivity of a group is not influenced by the state of reaction of its twin. This deduction is further reinforced by noting that changing the backbone of the monomer does not effect the gel conversion (see Table I). Thus, chemical unequal reactivity, either inherent or induced, is not a plausible explanation of the delayed gel conversion. However, unequal reactivities can arise from other sources such as diffusion limitations or steric hindrances and these will be discussed further.

Studies on BCP show that the system does not gel until after 60% conversion. The conversion values were obtained through two different techniques and are accurate to 10%.

Applicability of Mean-Field Theory. The key assumption in any mean-field theory is that fluctuations within the range of interaction are negligible. In Flory's theory of polymerization the range of interaction is the entire reaction volume. Thus this theory implies that all functional sites are equally accessible to each other. During polymerization fluctuations in the local density of functional sites can arise from at least two sources. Large branched molecules have limited center of mass mobilities and therefore accessibility to other sites. Also the decoration of a functional site on a molecular geometry can be such that it is effectively screened from all or some other sites. The latter has been variedly discussed as "buried group"[37] phenomena or steric hindrances in the literature. The former effect is a match of reaction and diffusion times. It is difficult to separate the two effects either experimentally or theoretically. Some effort in that direction is made in the last section of this discussion.

For faithfully reproduced chemistries the mean-field value of gel conversion is the lowest bound for homogeneous polymerization. All systems are expected to have higher deviations. Typically these deviations are small in stepwise polymerizations, and consequently mean-field models serve well as predictive tools for structure calculations. For cyanate polymerization it is found that the deviations are significantly higher. One simple cause of this could be vitrification of the sample. If the material becomes a glass before the gel point, the accessibility of reactive sites to one another is limited and therefore mean-field models are inapplicable. However, the glass transition temperature at a conversion of 60% is only 50 °C, while the reaction temperature is 200 °C.[17]

In the literature deviations from the mean-field prediction of gel conversion are customarily discussed in terms of cyclization.[31,32] In mean-field models because of equal accessibility assumption no loops are formed. This can be reasoned simply: in an infinite system a given functional unit on a finite molecule has a finite number of sites on itself and infinite choices on other molecules to choose its reactive partner; therefore, it shall never choose to form a loop.[38] Cycles will form if the spatial nature of polymerization is taken into account and if molecules have limited mobility, thus rendering functional sites on the same molecule more prone to reaction. In the literature many theoretical attempts to incorporate cycles exist.[31,32,39,40] These models can be useful but are inconsistent in as much as intermolecular reactions are still mean-field while intramolecular reactions are superimposed to some approximation. To properly account for the formation of cycles, questions of space and mobility of molecules must be addressed. Computer simulations of polymerization are spatial, and the effects of diffusion of molecules can be studied under some simplifying assumptions. Results from computer simulations (see the section on Monte Carlo simulations) reveal that if intermolecular reactions are treated in a non-mean-field way, cycles emerge naturally.[33]

Consider the following thought experiment. Tag a molecule in the system. Let t_{rxn} be the existence time of the molecule between two reactions. Let t_{dif} be the time it takes the tagged molecule to traverse across the dimensions of the reaction bath. If t_{dif} is much less than t_{rxn}, then any functional site on the tagged molecule, on an average, suffers collision from all the other sites before reacting, and, therefore, the resulting structure is mean-field. However, if t_{rxn} is much smaller than t_{dif}, then the functional site is limited in its choice of reactive partner to the sites it meets in the reaction time t_{rxn}. This effect may arise from slowing down of the center of mass motion.

In the above it is also assumptive that functional sites on the molecule are not sheltered. Alternately molecules could react in local neighborhoods because they are prevented from exploring the complete possibilities by the geometry of the growing molecules. In either case a functional site that is so impaired can only choose from neighboring sites.

Monte Carlo Simulation of Diffusional Effects. Computer simulations are useful as model systems for testing the applicability of different theories. Recently Monte Carlo simulations of A_f homopolymerization have been reported.[33] The simulations were devised to study the effects of relaxing the equal accessibility assumption in mean-field theory. Diffusional effects on the structure evolution during homopolymerization (through dimerization type of reactions) of A_3 were studied. While chemical reaction in these simulations is different from the cyanate reaction, the underlying physics of growth is the same. The simulations do not distinguish between diffusion limitations arising from local steric hindrances or global mobility slow down. Both of these are mimicked through the concept of a reactive radius. After the monomers are randomly decorated as unit radius spheres without excluded volume in a cube, reactions are allowed according to the following rule: if two randomly chosen unreacted functional sites are within a reactive radius r_h, the probability of their reaction is unity; otherwise, it is zero. r_h can be thought of as the average distance a functional unit traverses before reacting. Simulations with the entire computer bath as the reaction radius correspond to the mean-field limit. For more realistic simulations r_h should depend on both the chosen functional site and the degree of polymerization (r_h should decrease with progressive reaction). In the results discussed here r_h was kept a constant. In the work of Eichinger and co-workers[41] the reaction radius is allowed to increase with progressive reaction, which we believe is nonphysical. The usefulness of these simulations stems from the mapping of reactive radius to diffusion effects which was systematically varied to investigate the effect of diffusion limitations on polymerization.

Monte Carlo results show that reactions in local neighborhoods lead to smaller average structures (than mean-field) and thus higher gel conversions. It was found that for A_3 homopolymerization with a reactive radius of 2 monomer sizes gel conversion was 68% (in these simulations the average distance between two monomers is about a monomer size). The mean-field gel conversion is 50%. Studies of different reactive radii reveal important trends. Mobilities within a small reactive radius (typically four monomer sizes) result in structures that are indistinguishable from the mean-field limit (see Figure 9). This helps explain the success of mean-field models which at first glance appear to be highly unrealistic. It is reasoned that even small mobilities as those in which a functional site only probes, on an average, four nearest monomer neighbors are comparable for structural features like gel conversion, to the case where molecular diffusion is unlimited compared to reaction rates.

The importance of cycles was studied by comparing results with and without cycles for a reactive radius r_h = 2 and population of 100 000 monomers. It was found that approximately $^2/_3$ of the difference between mean-field gel conversion (50%) and gel conversion for r_h = 2 polymerization (68%) comes from intramolecular reactions. The additional $^1/_3$ reactions were intermolecular (see Figure 10). Thus cycles are not the only cause of approximation in mean-field theory. In mean-field theory the probability of two large molecules reacting together is much higher than that of two small, or one large and one small molecule. This follows because large molecules have many more unreacted sites and any two sites can react randomly. However, when reactions are limited to a small reactive radius, large molecules will only react together when they have grown big enough to overlap spatially. The dramatic behavior at gelation corresponds to reactions of large molecules since these make the major contribution to M_w. Thus the average structures in diffusion-limited growth are smaller than the mean field, which physically is the fastest (in terms of functional conversion) growth theory. The $(DP)_w$ for these three cases is shown in Figure 10.

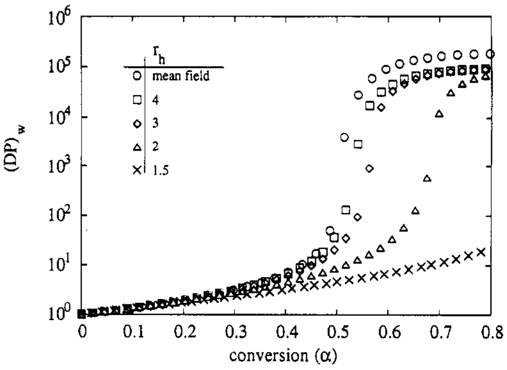


Figure 9. Weight-average degree of polymerization as a function of the reactive radius for A_3 homopolymerization. Reactive radius r_h is the radius within which two functional units must reside for the reaction to occur. All results are averaged over 10 runs and for a population size of 100 000 monomers (except the mean-field case which is for 200 000 monomers). Reproduced from ref 33.

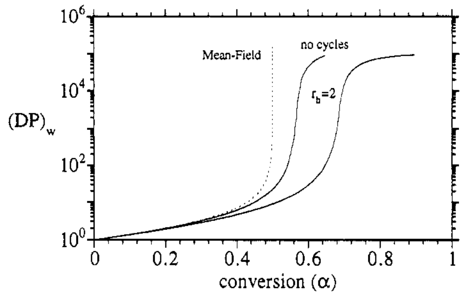


Figure 10. Effect of cycles on weight-average degree of polymerization from Monte Carlo simulations. The result for a reactive radius of 2 monomer sizes is compared with the analytical mean-field result. The results with (right-most curve) and without cycles as depicted. All results averaged over 10 runs and for 100 000 monomers.

Monte Carlo simulations allow us to probe other structural features. Consider the number fraction of monomers, dimers, trimers, tetramers, and so on during polymerization. The dependence of the first four species on conversion for the mean-field limit and polymerization with a reactive radius of 2 monomer sizes is shown in Figure 11. Until about 50% conversion the two cases are indistinguishable, but they begin to differ increasingly thereafter. In the mean-field case growth is symmetric about the gel conversion which is 50% for A_3. In mean-field polymerization large molecules have a higher probability of reacting; therefore, the concentration of monomers is high, while, correspondingly, the concentration of other species is lower after gelation, in comparison to the case where reactions only occur in local neighborhoods. After gelation the sol fraction is rapidly shrinking, with bigger molecules reacting with the gel sooner. This can be a critical experimental test for checking if growth is

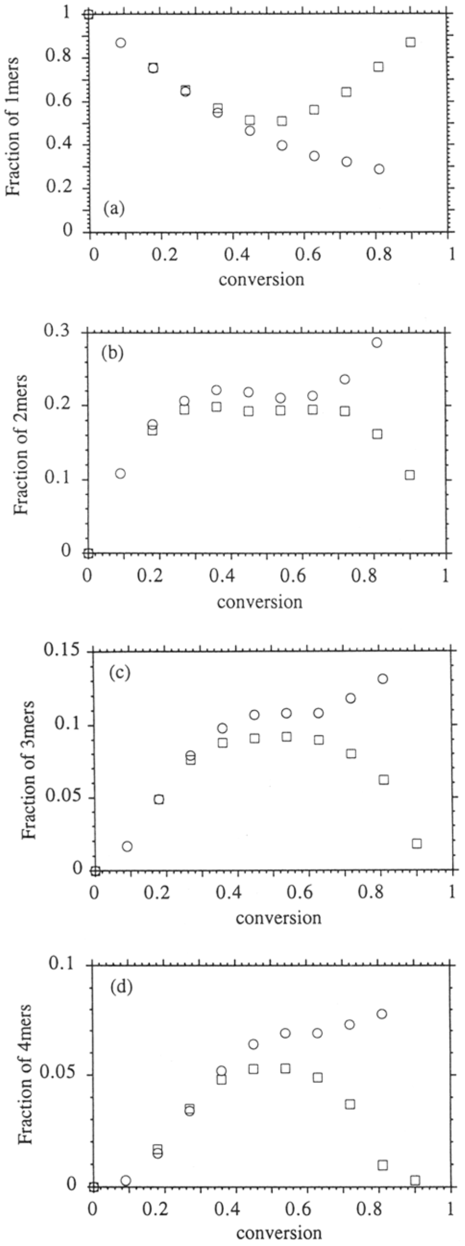


Figure 11. Number fraction of monomers, dimers, trimers, and tetramers obtained from Monte Carlo simulations of A_3 homopolymerization: (○) results when reactions are only allowed within a reactive radius of 2 monomer sizes; (□) the mean-field case.

mean-field. In principle SEC on the sol fraction should allow us to obtain the fraction of different species as a function of conversion.

Experimental Test of Diffusion Limitations. It is speculated that the cyanate structures are reacting in local neighborhoods. This could be due to steric hindrances or center of mass diffusion limitations or both. A number of experiments could further test this hypothesis and also help distinguish between these two causes.

It is to be expected that making the monomer backbone longer would overcome steric hindrances. In at least one such experiment (see Table I) the addition of another aromatic ring to the backbone of the monomer BCP did not affect the gel conversion.[20] However, this small change in monomer backbone (see Table I) may not be enough to cause an appreciable change in the packing of functional groups in large branched molecules. A better experiment would be to use a long-chain aliphatic backbone with end-functionalized cyanates. However, it is expected that the cyanate groups would lose their functionality unless they are directly on an aromatic ring.

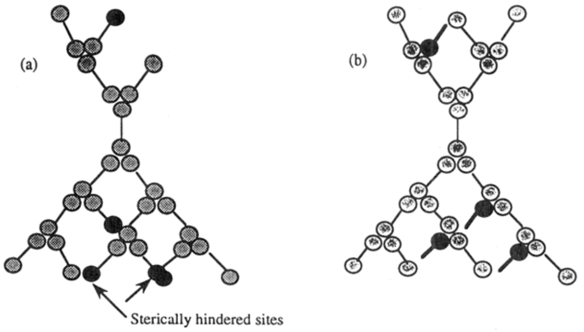


Figure 12. Illustration of how spacers ease steric hindrances. On the left, polymer formed by bifunctional cyanate monomers only. The dark-shaped functional units cannot form triazine rings because of steric hindrances. On the right, polymer formed with a mixture of monofunctional (black-shaded monomers) and bifunctional monomers.

Another series of experiments involve polymerization of monofunctional and bifunctional monomers. Use of monofunctional monomers would ease steric hindrances by reducing the crowding of functional sites (see Figure 12). These experiments clearly indicate that polymerizations with an increased ratio of monofunctional monomers are better described by mean-field theory (see Figure 6). These experiments argue in favor of local hindrances as the cause of the observed gel conversion as opposed to the limited global mobility of molecules. The change to monofunctional monomers is not expected to effect the center of mass mobility significantly.

Steric hindrances lead to sheltering of some functional sites on a molecule. This reduces the accessibility of these sites. If some sites are completely screened, the average branch functionality is reduced and the gel conversion is delayed. In the work reported by Price et al.[37] this effect was interpreted from a kinetic slow down. They found that for solution polymerization of adipoyl chloride (AC) and trimethylethane (TME) the rate of reaction of TME slowed down by 2 orders of magnitude well before gelation. AC sites were still present as was shown by addition of small-molecule alcohols. When these small molecules were added the rate picked up an order of magnitude but was still slower than the original rates. This suggests that some sites are partially accessible to small molecules and not to big molecules, while others are not accessible even to small molecules. For cyanate polymerization no kinetic slow down is observed.[14] Therefore, this kind of burying of functional groups from steric hindrances is unlikely to be operative. It is speculated that steric hindrances are such that functional sites do react albeit only in local domains.

The effect of mobility of molecules can also be deduced from polymerizations conducted at different temperatures. Table I shows results for reaction temperatures from 120 to 200 °C. The gel conversion appears to be unaffected by the reaction temperature in this range. These results also argue in favor of local mobility limitations or partial steric hindrances. It is reasonable to suppose that temperature would not affect the steric constraints as significantly as it would the center of mass motion. Thus it is concluded that polycyanate growth is not controlled by the mobility of the molecules but by steric hindrances of functional sites.

Polycyanates based on the monomer BCP are different from stepwise polymers like typical polyesters, polysiloxanes, polyepoxies, and polyurethanes in that they are rigid and tightly branched. The rigidity of the polymer can result in liquid crystalline behavior. It is speculated that the rigidity of the polymer is responsible for the experimental results reported in this study. If functional sites are attached to rigid appendages, they can get trapped in the core of the growing molecule and thus they are not readily accessible to all other sites. Consequently such sites can only react with other neighboring sites. Few studies on the growth of rigid networks are available, though some studies on the final properties of rigid networks based on polyamides have appeared recently.[42] It is hoped that this study and the anomalous results reported here would motivate systematic studies on these and other rigid networks.

Summary

The formation of network polymers based on cyanate functional groups has been studied. Synthesis and characterization of polymers based on monofunctional monomer CPP and bifunctional monomer BCP are reported. Model studies on the monofunctional monomer prove that trimerization occurs in excess of 90%. Reaction kinetics are sensitive to the presence of impurities. The side reactions lead to the formation of dimers as well as higher oligomeric species. These reactions are not insignificant. They suggest a functionalility of cross-linking higher than 3. Studies of the bifunctional monomer show that the polymers are not described by the mean-field theory of polymerization. This is primarily deduced from a higher gel conversion of 60–65%. Studies of mixed synthesis show that increasing amounts of monofunctional monomers result in better agreement with the mean-field theory. The experimental results are interpreted in light of Monte Carlo simulation results of diffusional effects for A_3 homopolymerization. Monte Carlo simulations have shown that diffusion limitations result in higher gel conversion. Therefore, it is speculated that the reason for the 60% gel conversion of the cyanate resin is the fact that, on the average, reactions are only occurring in local neighborhoods. This is mainly due to steric hindrances which limit reactions to local domains. There are two peculiarities to the cyanate chemistry which may contribute to this effect. The first is that the reaction can be trimolecular as opposed to two-body collisions (the reaction mechanism is not understood at present). The second is that the cyanate molecules are extremely rigid on account of the double aromatic ring and the triazine ring.

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