

Experimental Confirmation of Extent of Reaction at the Gel Point in a Polyisocyanurate

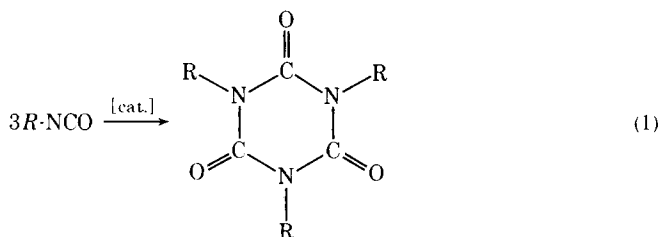
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Synopsis

Theoretical equations were developed to relate the extent of reaction at the gel point for a system where three functional groups trimerize to a ring structure during the polymerization reaction. Specific relationships were developed for a difunctional monomer where the two functional groups are of unequal reactivity and for a mixture of difunctional and monofunctional monomer where all three functional groups are of unequal reactivity. These two cases were tested experimentally by determining the extent of reaction at the gel point for the system isocyanate reacting to form isocyanurate. In the case of 4,4'-diisocyanatophenylmethane (MDI), the extent of reaction at gelation was determined experimentally to be 60%. When this data was analyzed according to the theory developed, a reactivity ratio of 2.38 was calculated for the rate of the first isocyanate group to react as compared to the second. Experiments were also performed with 2,4-toluene diisocyanate, which gave a 72% conversion at the gel point. The extents of reaction at the gel point for mixtures of MDI and phenyl isocyanate were also determined experimentally. An analysis according to the theory developed further supported the idea that all three isocyanate groups in this system have different reactivities. Theoretical relationships also were developed for a trifunctional isocyanate reacting to form isocyanurate. Experimentally, a crude MDI was used, and approximate relationships were used to analyze the results.

INTRODUCTION

There has been increased interest in recent years in isocyanurate polymers, particularly in the area of rigid foam insulation.¹⁻⁴ These materials are produced by the reaction of an isocyanate to form the six-membered isocyanurate (I) ring, and the reaction is usually catalyzed by tertiary amine or bases.⁵ The general reaction scheme is shown below:



More detailed discussions of the chemistry can be found in the literature.⁵⁻⁷

Because three equivalents of isocyanate are incorporated into one equivalent of isocyanurate, the usual equations⁸ predicting the conversion of reactant at the gel point are difficult to apply. However, Stein and LeGrand⁹ have used a statistical approach to calculate the degree of polymerization between crosslinks and the extent of conversion at the point of incipient gelation for the reaction

of perfluoroalkyl amidines to triazine type rings. This analysis was also used to investigate the mechanical and optical properties of these polymers by Stein and Kawai.¹⁰

THEORY

The original reference⁹ also included the case of monofunctional and difunctional amidines reacting to give different degrees of reaction at the gel point. The analysis of Stein and LeGrand⁹ showed that the critical degree of reaction X_2^* for ring formation depended on the monomer ratio of difunctional to monofunctional monomer according to equation (2):

$$X_2^* = \frac{1}{2} + \frac{1}{4(X_2 m_2 / X_1 m_1)} \quad (2)$$

where X_2 is the fraction of difunctional groups which have reacted, X_1 the fraction of monofunctional groups which have reacted, m_2 the number of molecules of difunctional monomer per cm^3 , and m_1 the number of molecules of monofunctional monomer per cm^3 .

It can be seen from eq. (2) that as the amount of difunctional monomer increases in a given mix to that of pure difunctional monomer, X_2^* will approach a value of 0.5. Thus for a system composed of only difunctional monomer reacting to isocyanurate rings, the extent of reaction at the gel point would be 50%. The extent of conversion at gelation for the total system would be >50% when monofunctional monomer is present as a more reactive species. The extent of conversion at gelation then would be given by eq. (2).

The analysis of Stein and LeGrand⁹ was extended to a trifunctional monomer forming a ring system. The expression relating the extent of reaction at the gel point for a trifunctional isocyanate is given in Appendix A. At gelation a trial and error solution gives the extent of reaction as 33%.

Two additional cases originally considered by Stein and LeGrand⁹ were further extended. One consists of a difunctional monomer (reactive groups a and b) and a monofunctional monomer, where the reactivity of all groups, a , b , and monofunctional, are different. This analysis is given in Appendix B. At the gel point, the relationship is

$$4(m/m_0)X_a X_b = X_0 + (m/m_0)(X_a + X_b) \quad (3)$$

where m is the number of difunctional molecules per cm^3 , m_0 the number of monofunctional molecules per cm^3 , X_a the extent of reaction of group a on the difunctional molecule, X_b the extent of reaction of group b on the difunctional molecule, and X_0 the extent of reaction of the monofunctional group.

In the case of a difunctional reactant only, where the two groups are of unequal reactivity, eq. (4) reduces to (at the gel point)

$$4X_a X_b = X_a + X_b \quad (4)$$

Equations (2)–(4) were tested experimentally as described in the Experimental section. Since a pure trifunctional isocyanate was not available, a crude isocyanate was used, with some modification to the theory, as described below.

EXPERIMENTAL

The isocyanates used were phenyl isocyanate as the monofunctional monomer (Eastman); 4,4'-diisocyanato diphenyl methane (MDI, 125M Upjohn); 2,4-toluene diisocyanate (TDI, Hylene T, DuPont); and a crude MDI with isocyanate equivalent weight of 133 and a number-average functionality of 2.3 (by GPC). All isocyanates were used as received after first checking their purity by determining the isocyanate equivalent weight.¹¹

The isocyanurate reaction was run by using the isocyanate (or mixture of isocyanates) in a 40% (w/w) solution in *N,N*-dimethylformamide (DMF, Fisher, Certified ACS, stored over 3-Å sieves) as solvent. The catalyst used was 2,4,5-*tris*(dimethylaminomethyl)phenol (DMP-30, Rohm and Haas). The level of catalyst used was 20 drops in 100 g of total reaction solution (0.25 wt-% based on the isocyanate). The reaction mixture was kept at 50°C (thermostated oil bath) in a 200-ml resin kettle under a N₂ blanket; a mechanical stirrer was used. The conversion of the isocyanate was determined as a function of time by taking weighed aliquots of the reaction mixture and placing them into a preweighed quantity of a DMF solution of *N,N*-dibutylamine (Eastman), which was in excess. This would immediately react with any unreacted isocyanate. The solution was then back titrated with HCl, and the equivalents of reacted isocyanate could then be calculated. Since the equivalents of starting isocyanate in the reaction mixture had been similarly determined at time zero before the addition of catalyst, the extent of reaction could then be determined.

A plot of the extent of reaction versus time was made and extrapolated to the gel time. The gel time was observed visually as the point where the reaction mixture began to climb the stirring shaft and could no longer be stirred.

RESULTS AND DISCUSSION

Two typical conversion-time plots and the extrapolations to the gel point are shown in Figure 1 for a mixture consisting of 74.1% (equivalents) MDI with phenyl isocyanate (Run 017) and pure difunctional monomer, 2,4-TDI (Run

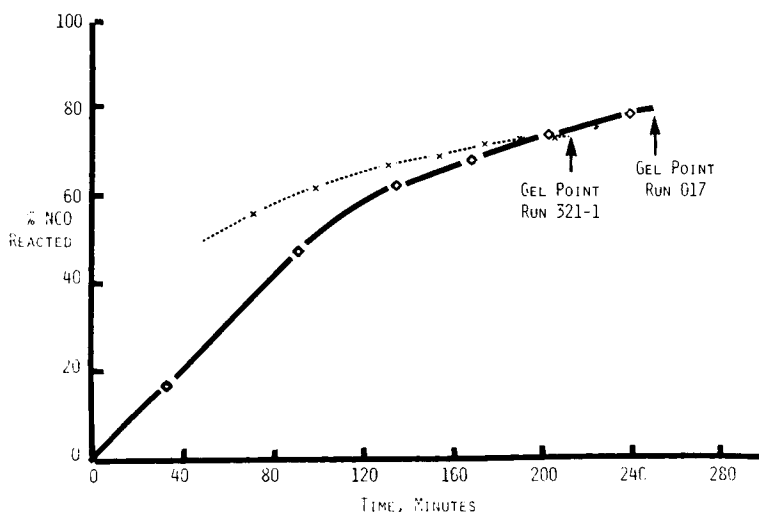


Fig. 1. Percent NCO converted versus reaction time for runs 017 (◊) and 321-1 (×).

TABLE I
Conversions of Isocyanate at the Gel Point

Run	Equivalent Fraction Isocyanate				Fraction Extent of Reaction at Gelation, Total NCO
	Phenyl	MDI	TDI	Crude MDI	
392	0	1.00	0	0	0.59
033	0	1.00	0	0	0.60
035	0	1.00	0	0	0.60
028	0.13	0.870	0	0	0.63
017	0.259	0.741	0	0	0.80
144-1	0.332	0.668	0	0	0.87
138-1	0.425	0.575	0	0	0.93
136	0.480	0.520	0	0	No gel, $\eta_{inh}(0.5 \text{ DMF}) = 0.08$
318	0	0	100	0	0.72
321-1	0	0	100	0	0.72
189	0	0	0	100	0.44

321-1). The conversions at the gel point for the various runs are given in Table I.

From Table I the runs for MDI (392, 033, 035) gave conversions at gelation of 0.59, 0.60, and 0.60, respectively. According to eq. (2), if both isocyanate groups are of equal reactivity, the conversion at gelation should be 0.50. In order to investigate this further, the data can be plotted (Fig. 2) as the percent total NCO reacted at the gel point versus equivalent fraction MDI, for the MDI/phenyl isocyanate mixtures. Figure 2 also contains two theoretical plots (solid lines) plotted according to eq. (2). One of them, shown as curve 1, is for the case where all the isocyanate groups would be of equal reactivity. The other, curve 2, is for

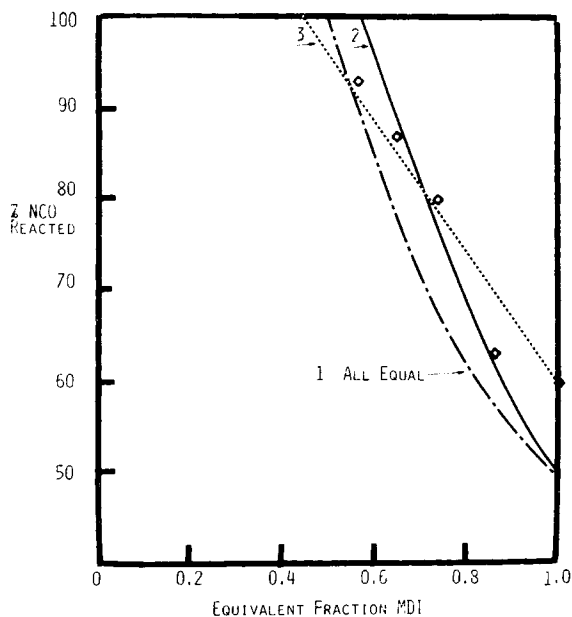


Fig. 2. Percent isocyanate (total) reacted at the gel point vs equivalent fraction MDI.

the case where the isocyanate groups on the difunctional monomer (MDI) are of equal reactivity but of different reactivity from the isocyanate group on the monofunctional monomer (specifically tested for the case where the difunctional rate is 0.8 times the monofunctional). Although the theoretical curves are shifted towards the experimental data, they still show an extent of reaction of 0.5 for pure MID rather than the 0.59–0.60 measured experimentally. Thus if no factors other than reactivity account for this difference and we assume that the isocyanate groups on MDI are of unequal reactivity, then we can apply eqs. (3) and (4).

An analysis of the pure MDI data using eq. (4) would give $X_a = 0.845$ and $X_b = 0.355$ at the gel point. If the ratio of the extents of reaction for the two NCO groups is equal to the ratio of the rate constants for the two isocyanates in this reaction, one obtains 2.38 as the ratio of the rate constants. This is in fair agreement for data in the literature¹² for urethane formation, where the rate constant of the first isocyanate to react is 2.91 times that of the second isocyanate group (after the first has reacted). Using these ratios for the two isocyanate groups ($K_a/K_b = 2.38$) and using $K_a/K_0 = 0.9$, curve 3 was calculated in Figure 2. Analyzed in this manner the MDI/phenyl isocyanate data suggests that all isocyanate groups are of unequal reactivity.

As a further rough correlation, one can analyze run 136, where gelation did not occur, even though the equivalent fraction of MDI was greater than phenyl isocyanate. If the isocyanate groups were all of equal reactivity, gelation would still occur at a reaction extent of 0.50. Equation (B2) in Appendix B can be rearranged to give N_0/N , which would be the fraction of triphenyl isocyanurate groups in the MDI/phenyl isocyanate system. Since this reaction mixture (run 136) did not gel, all isocyanate groups were fully reacted (this was confirmed by infrared analysis). Therefore, $X_a = X_b = X_0 = 1.0$, and eq. (A14) reduces to

$$N_0/N = m_0/(m_0 + 2m) \quad (5)$$

Run 151 was made with 20 g phenyl isocyanate and 20 g MDI, which have molecular weights of 119 and 250, respectively. Using these values and eq. (5), one obtains 13.4% triphenylisocyanurate. The amount of triphenylisocyanurate in run 151 was determined by GPC to be 11.5% by comparison with a calibration based on pure triphenylisocyanurate. This value is in close agreement with theory and supports the general statistics of the analysis.

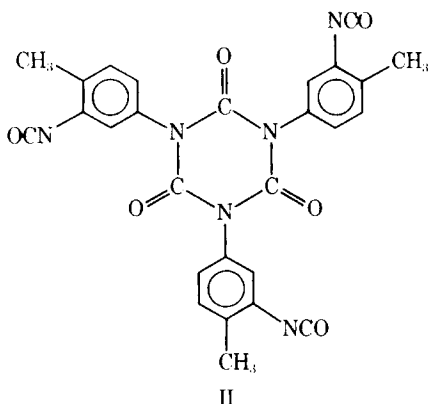
A possible reason for the differences between the experimentally determined extent of reaction at gelation for MDI (assuming equal reactivity of both isocyanates) is reaction with the catalyst, which contains a phenolic hydroxyl group. However, the catalyst could, at most, only account for 1% isocyanate conversion.

Side reactions with the solvent were checked by running a reaction in DMF with no catalyst at 50°C for 300 min. The method of analysis showed that the isocyanate was still present in >99% of the original amount (<1% reacted); thus this cannot account for these differences.

Other than unequal reactivity of the isocyanates, one other possibility is the formation of microgel particles prior to the formation of an infinite three-dimensional network, as suggested by Bobalek et al.¹³ Unfortunately, the methods of analysis used in the present research could not distinguish the formation of microgels. However, the research of Bobalek et al.¹³ found differences of ap-

proximately 4% (based on the calculated values) between the extent of reaction at the observed gel point compared to the extent of reaction when the microgel was formed. Since in this research the difference between the extent of reaction at the observed gel point and the calculated value was 20% (based on the calculated value), it would appear that the formation of microgel alone cannot account for all of the differences.

When pure 2,4-TDI alone was used as the diisocyanate, the extent of reaction at the gel point was measured as 72% (runs 318 and 321-1, Table I). This is in agreement with the literature for the difference in reactivity of the 2- and 4-position isocyanate of 2,4-TDI.¹² Furthermore, if one does the thought experiment and takes the 4-position isocyanate as preferentially reacting first to give the structure shown below as II,



then up to this point there would have been 50% conversion of the total isocyanate groups. Considering II as a new monomer which is trifunctional, then eq. (A12) would predict the gel point to occur at $33\frac{1}{3}\%$ conversion of II. Thus the overall conversion would be $66\frac{2}{3}\%$ (0.667 fraction) at the gel point. Since the observed gel point is 72%, it would appear that some of the effective crosslinks counted by the theory are not in fact truly effective. That is, it appears that some of the unreacted isocyanate groups in the growing branched polymer cannot react and hence become "lost."

Run 189, Table I, was made with a crude MDI, which has a number-average functionality of approximately 2.25 and a weight-average functionality of 2.61 (both by GPC). One would estimate the conversion at the gel point (based on $1/F$) to be 44.4% based on the number-average and 38.3% based on the weight-average functionality. Since the gel point should depend more on weight-average properties, the 38.3% figure is probably a closer approximation to the actual theoretical value, which would have to be calculated from an analysis similar to that in Appendix A. The observed extent of reaction of 44% is probably high for reasons similar to that for the pure 2,4-TDI experiment.

CONCLUSIONS

In summary, the extent of reaction for difunctional monomers and for mixtures of difunctional and monofunctional monomers at the gel point in a trimerization reaction can be predicted using a statistical method based on the unequal reactivity of the functional groups.

The general method has also been extended to a trifunctional monomer where the reactivity of all three groups is equal. An approximation can be used for the extent of reaction at the gel point as $1/F$, where F is the functionality of the reacting species, for cases where the functionality is not a whole number.

APPENDIX A. TRIFUNCTIONAL MONOMER

This analysis follows directly from that of Stein and LeGrand,⁹ with the following quantities defined:

M_3 = number of molecules of trifunctional monomer per cm^3

X_3 = fraction of groups on trifunctional monomer which react, then;

N = the number of rings formed per cm^3 is

$$N = X_3 M_3 \quad (\text{A1})$$

These rings may be divided into the following numbers of rings:

$$\text{All six pendant groups react further: } N_6 = NX_3^6 \quad (\text{A2})$$

$$\text{Five pendant groups react: } N_5 = 6NX_3^5(1 - X_3) \quad (\text{A3})$$

$$\text{Four pendant groups react: } N_4 = 15NX_3^4(1 - X_3)^2 \quad (\text{A4})$$

$$\text{Three pendant groups react: } N_3 = 20NX_3^3(1 - X_3)^3 \quad (\text{A5})$$

$$\text{Two pendant groups react: } N_2 = 15NX_3^2(1 - X_3)^4 \quad (\text{A6})$$

$$\text{One pendant group reacts: } N_1 = 6NX_3(1 - X_3)^5 \quad (\text{A7})$$

$$\text{No pendant groups react further: } N_0 = N(1 - X_3)^6 \quad (\text{A8})$$

The molecules in groups N_6 , N_5 , N_4 , and N_3 will produce crosslinks in the system, while those in N_2 will serve as connecting linkages. The N_1 molecules will terminate chains, while the N_0 molecules will not be incorporated into the chain.

Thus the number of effective crosslinks V_e will be equal to the number of crosslinks V minus the number of terminated chains V_t , all divided by 2, since all chains are counted twice:

$$V_e = (V - V_t)/2 \quad (\text{A9})$$

Substituting from eqs. (A2)–(A5) with the appropriate factors, since there are six ways for the N_6 molecules to react further, five ways for the N_5 , etc., we have

$$V_e = \frac{6N_6 - V_t}{2} + \frac{5N_5 - V_t}{2} + \frac{4N_4 - V_t}{2} + \frac{3N_3 - V_t}{2} \quad (\text{A10})$$

Since $V_t = N_1$ and substituting from (A7) into (A10) and from $N = X_3 M_3$, we obtain after rearrangement

$$V_e = 3M_3 X_3^2 [X_3^6 + 5X_3^4(1 - X_3) + 10X_3^3(1 - X_3)^2 + 10X_3^2(1 - X_3)^3 - 4(1 - X_3)^5] \quad (\text{A11})$$

Since V_e must be positive for a three-dimensional network, then at the gel point the quantity in brackets must equal zero.

When this is done, and using a trial and error solution, one obtains

$$X_3 = 0.334 \quad (\text{A12})$$

for the extent of reaction at the gel point.

APPENDIX B. DIFUNCTIONAL MONOMER AND MONOFUNCTIONAL MONOMER—ALL GROUPS OF UNEQUAL REACTIVITY

We have the following:

M_0 = number of molecules of monofunctional monomer per cm^3 ,

M = number of molecules of difunctional monomer per cm^3 ,

X_0 = fraction of groups on monofunctional monomer which react,
 X_a = fraction of a groups on difunctional monomer which react, and
 X_b = fraction of b groups on difunctional monomer which react.

By an analysis similar to that of Appendix A,

$$N = (X_0M_0 + X_aM + X_bM)/3 \quad (\text{B1})$$

The number of rings composed of three reacted monofunctional groups N_0 is

$$N_0 = NF_0^3 \quad (\text{B2})$$

where F_0 , the probability that a monomer group selected randomly from the mixture is monofunctional, is

$$F_0 = X_0M_0/(X_0M_0 + X_aM + X_bM) \quad (\text{B3})$$

Again counting the number of rings composed of the various reacted groups, we have two monofunctional groups reacted with one a group:

$$N_{1a} = 3NF_0^2F_a \quad (\text{B4})$$

and two monofunctional groups reacted with one b group:

$$N_{1b} = 3NF_0^2F_b \quad (\text{B5})$$

Of these, N_{1a}^+ will have the second group of the difunctional react and be incorporated into the chains as terminating species:

$$N_{1a}^+ = X_bN_{1a} + X_aN_{1b} \quad (\text{B6})$$

Similarly, N_2 molecules will consist of one monofunctional and two difunctional:

$$N_2 = X_0M_0M(X_a + X_b)^2/(X_0M_0 + X_aM + X_bM)^2 \quad (\text{B7})$$

Of these N_2 rings, both, one, or none of the pendant groups can react further.

If both react further, then there are N_2^+ of these:

$$N_2^+ = 4M_0M^2X_0X_a^2X_b^2/(X_0M_0 + X_aM + X_bM)^2 \quad (\text{B8})$$

If one of the groups react further,

$$N_2^* = \frac{4M_0M^2X_0X_a^2X_b(1 - X_b) + 4M_0M^2X_0X_aX_b^2(1 - X_a)}{(X_0M_0 + X_aM + X_bM)^2} \quad (\text{B9})$$

The number of rings consisting of three groups is

$$N_3 = NF_a^3 + NF_a^2F_b + NF_aF_b^2 + NF_b^3 \quad (\text{B10})$$

where F_a is the probability of selecting an a group, etc. If all three pendant groups react further, then there will be N_3^+ of these:

$$N_3^+ = \frac{8}{3} \frac{M^3X_a^3X_b^3}{(X_0M_0 + X_aM + X_bM)^2} \quad (\text{B11})$$

If only one pendant group reacts further, this will cause termination. There will be N_3^{**} of these:

$$N_3^{**} = \frac{2M^3X_a^3X_b(1 - X_b)^2 + 4M^3X_a^2X_b^2(1 - X_a)(1 - X_b) + 2M^3X_aX_b^3(1 - X_a)^2}{(X_0M_0 + X_aM + X_bM)^2} \quad (\text{B12})$$

The number of terminated chains V_t is now

$$V_t = N_{1a}^+ + N_2^* + N_3^{**} \quad (\text{B13})$$

and the number of effective crosslinks is

$$V_e = \frac{3}{2}N_3^+ - \frac{1}{2}V_t \quad (\text{B14})$$

Substituting eqs. (B6), (B9), and (B11)–(B13) into (B14) gives, after rearrangement and simplification,

$$V_e = MX_aX_b \left[\frac{4MX_aX_b}{X_0M_0} \left(\frac{1}{(1 + R)} \right) - 1 \right] \quad (\text{B15})$$

where $R = M(X_a + X_b)/X_0M_0$. Again, at the gel point the quantity in brackets [] must equal zero. Thus

$$4 \left(\frac{M}{M_0} \right) X_a X_b = X_0 + \left(\frac{M}{M_0} \right) (X_a + X_b) \quad (\text{B16})$$

Note that in the absence of any monofunctional monomer, eq. (B16) reduces to

$$4X_a X_b = X_a + X_b \quad (\text{B17})$$

for the case of a difunctional monomer where the a and b groups are of unequal reactivity.

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