Kinetic Solution for Cyclotrimerization of A_2: Polymers of 2,2-Bis(4-cyanatophenyl)propane

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1. Introduction

A polymer of increasing commercial interest in the electronics and composite industry is that obtained by cyclotrimerization of the cyanate linkages.[1] The most frequently used monomer in this category is 2,2-bis(4-cyanatophenyl)propane,[1] which has two cyanate functional units on its ends. The main polymerization reaction, which is carried out at high temperatures (about 150 °C) in presence of transition-metal complex compounds as catalysts (such as zinc octate), is a trimerization reaction, wherein three cyanate functional groups combine to form the cyanurate ring.[1,2] The reaction is shown in Figure 1. The possibility of other reactions as suggested by some experimental evidence is currently being investigated.[3] Here we present a kinetic solution for the polymerization reaction based on the assumption that the trimerization is the only reaction.

2. Kinetic Solution

The kinetic solution consists of writing a reaction kinetic equation for the time rate of evolution of a typical polymeric molecule in terms of other polymeric species.[4] Thus, the equations are limited to the case of complete kinetic-controlled polymerization. This implies that molecules irrespective of their size have sufficient Brownian agitation such that any functional unit can react with any of the other functional units in the system, or, tantamountly, all functional units are "physically" equally reactive. The kinetic approach is one of the several mathematical approaches one might take within the mean-field paradigm. It is the most complete mathematical description and clearly highlights the biases of the underlying theory. The parameter of interest is the probability density function $P(\alpha,n)$, which is the probability that a randomly chosen polymer molecule in the system at a conversion α is of a certain size n. The size n refers to the number of connected monomers that constitute the polymer molecule in question. The theory does not predict any topological information about the polymers. Other approaches/techniques within the mean-field theory assumption of equal physical reactivity are statistical and yield certain parameters of $P(\alpha,n)$. For example, as the name probability generating function approach implies, this technique predicts the probability generating function of $P(\alpha,n)$, from which its moments can be evaluated.[5] Similarly the expectation value approach[6] predicts the expectation value of $P(\alpha,n)$, which is equivalent to the weight-averge degree of polymerization. The kinetic approach can, in principle, if the differential equations are tractable, be solved for the complete density function $P(\alpha,n)$ from which its parameters of interest can be evaluated. However, it is usually much easier, as we show here, to simply solve for the moments of $P(\alpha,n)$ by converting the kinetic equations to a moment equation.

The schematic of the chemistry is as shown in eq 1 with the cyanate functional units symbolized with A.

$$3A \xrightarrow{k} A_3 \tag{1}$$

For this chemistry any polymer molecule will have only an odd number of the monomer units. Thus we label P_{2n+1} as the number of polymeric molecules in the system of $2n+1$ monomeric size at a conversion α. P_{2n+1} normalized with respect to the total number of molecules in the system at a conversion α is the probability density function $P(\alpha,2n+1)$. The number of unreacted functional units on P_{2n+1} is $n+2$. Therefore, the kinetic rate equation for the evolution of P_{2n+1} is

$$\frac{dP_{2n+1}}{dt} = \frac{1}{3!}\sum_{\substack{0\le i\le\infty\\0\le j\le\infty\\0\le k\le\infty\\i+j+k=n-1}} (i+2)(j+2)(k+2)P_{2i+1}P_{2j+1}P_{2k+1} - \frac{1}{2!}(n+2)P_{2n+1}\sum_{\substack{0\le i\le\infty\\0\le j\le\infty}} (i+2)(j+2)P_{2i+1}P_{2j+1} \tag{2}$$

The triple summation refers to all the different polymer sizes that would, when any three of their several unreacted functional units trimerize, yield a molecule of size $2n+1$. The second double summation is the disappearance term for all other molecules that could react with a P_{2n+1} molecule. In order to solve this infinite set of differential equations (one for each n), we convert them to a moment equation. First, define the moment generating function as

$$\mu_m \overset{\text{def}}{=} \sum_{0\le n\le\infty} n^m P_{2n+1} \tag{3}$$

Then eq 2 can be rewritten in terms of μ_m. This is achieved by multiplying both sides of eq 1 with n^m and summing over all n. The rewritten equation reads

$$\frac{d\mu_m}{dt} = \frac{1}{3!}\sum_{p=0}^{m}\sum_{q=0}^{p}\sum_{r=0}^{q}\binom{m}{p}\binom{p}{q}\binom{q}{r}[\mu_{m-p+1}\mu_{p-q+1}\mu_{q-r+1} + 4\mu_{m-p+1}\mu_{p-q}\mu_{q-r} + 4\mu_{m-p}\mu_{p-q+1}\mu_{q-r} + 4\mu_{m-p}\mu_{p-q}\mu_{q-r+1} + 2\mu_{m-p+1}\mu_{p-q+1}\mu_{q-r} + 2\mu_{m-p}\mu_{p-q+1}\mu_{q-r+1} + 2\mu_{m-p+1}\mu_{p-q}\mu_{q-r+1} + 8\mu_{m-p}\mu_{p-q}\mu_{q-r}] - \frac{1}{2!}(\mu_{m+1}+2\mu_m)(\mu_1+2\mu_0)^2 \tag{4}$$

The total number of monomer molecules in the system is a constant; therefore

$$\sum_{n=0}^{\infty}(2n+1)P_{2n+1} = 2\mu_1 + \mu_0 = [A]_0/2 \tag{5}$$

where $[A]_0$ is the number of initial functional units, two per monomer. We can, therefore, normalize eq 4 by dividing each of the moments by $2\mu_1 + \mu_0$. We also eliminate time t in favor of conversion α. This is achieved by solving the kinetic equation for the schematic reaction (eq 1).

$$-\frac{1}{k}\frac{d[A]}{dt} = \frac{3}{3!}[A]^3 \tag{6}$$

First define a dimensionless time τ:

$$\tau \overset{\text{def}}{=} k[A]_0^2 t \tag{7}$$

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Then eq 6 rewritten in terms of conversion α reads

$$-\frac{d(1-\alpha)}{d\tau} = \frac{1}{2}(1-\alpha)^3 \tag{8}$$

for which the solution is

$$\frac{1}{(1-\alpha)^2} = 1 + \tau \tag{9}$$

Equation 4 can now be rewritten in the dimensionless form as

$$12(1-\alpha)^3\frac{d\mu_m}{d\alpha} = \sum_{p=0}^{m}\sum_{q=0}^{p}\sum_{r=0}^{q}\binom{m}{p}\binom{p}{q}\binom{q}{r} \times [\mu_{m-p+1}\mu_{p-q+1}\mu_{q-r+1} + 4\mu_{m-p+1}\mu_{p-q}\mu_{q-r} + 4\mu_{m-p}\mu_{p-q+1}\mu_{q-r} + 4\mu_{m-p}\mu_{p-q}\mu_{q-r+1} + 2\mu_{m-p+1}\mu_{p-q+1}\mu_{q-r} + 2\mu_{m-p}\mu_{p-q+1}\mu_{q-r+1} + 2\mu_{m-p+1}\mu_{p-q}\mu_{q-r+1} + 8\mu_{m-p}\mu_{p-q}\mu_{q-r}] - 3(\mu_{m+1} + 2\mu_m)(\mu_1 + 2\mu_0)^2 \tag{10}$$

For the zeroth moment μ_0 this reduces to

$$12(1-\alpha)^3\frac{d\mu_0}{d\alpha} = -2(2\mu_0 + \mu_1)^3 \tag{11}$$

This can be solved by substituting for μ_1, which is $(1 - \mu_0)/2$ in the dimensionless format to obtain the solution

$$\mu_0 = 1 - (4/3)\alpha \tag{12}$$

Thus the number-average degree of polymerization, which is the inverse of the zeroth moment in the present normalized context, is

$$(DP)_n = 1/[1 - (4/3)\alpha] \tag{13}$$

Either by directly solving for the first moment μ_1 or by using the fact that $2\mu_1 + \mu_0 = 1$, we obtain

$$\mu_1 = (2/3)\alpha \tag{14}$$

The equation for the second moment can be similarly written as

$$12(1-\alpha)^3\frac{d\mu_2}{d\alpha} = 30\mu_2\mu_1^2 + 24\mu_2\mu_0^2 + 72\mu_2\mu_1\mu_0 + 6\mu_2^2\mu_1 + 12\mu_2^2\mu_0 + 102\mu_1^2\mu_0 + 37\mu_1^3 + 60\mu_1\mu_0^2 + 8\mu_0^3 \tag{15}$$

In order to solve this equation, we substitute for μ_0 and μ_1 from eqs 12 and 14. The resulting equation after some simplification reads

$$9(1-\alpha)^2\frac{d\mu_2}{d\alpha} = 6\mu_2(3 + \alpha) + 9\mu_2^2 + 2(3 + 6\alpha - \alpha^2) \tag{16}$$

It can then be shown that a solution for the above equation is

$$\mu_2 = 2\alpha(\alpha + 1)/(3(1 - 2\alpha)) \tag{17}$$

from which finally we derive our weight-average degree of polymerization $(DP)_w$

$$(DP)_w = (1 + 2\alpha)/(1 - 2\alpha) \tag{18}$$

Using the expectation value approach, one can easily verify the above result. In Figure 2 a plot of $(DP)_w$ and $(DP)_n$ against conversion α is shown. As follows from eq 18, under the assumption that eq 1 is the only reaction and the polymerization step is controlled by kinetics, gel conversion of 50% is predicted.

Experimentally, through NMR, IR, and DSC, the current evidence suggests gelation between 60% and 65%.[7]

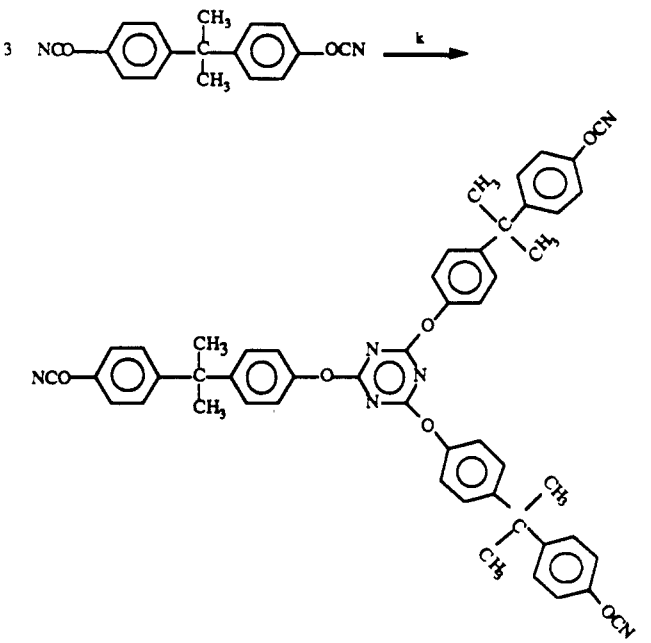

Figure 1. Trimerization reaction of 2,2-bis(4-cyanatophenyl)-propane.

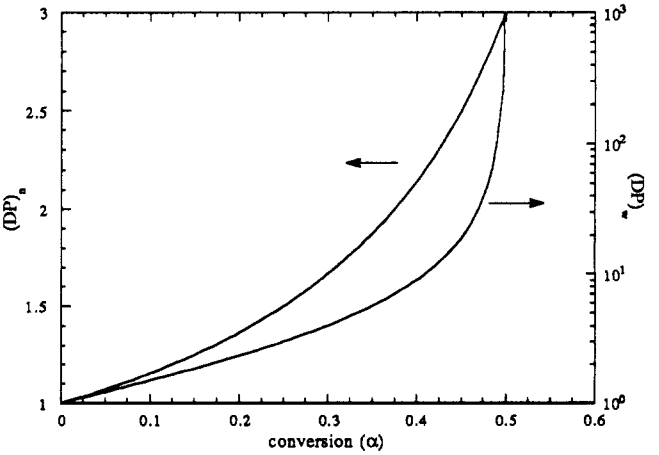

Figure 2. Weight-average and number-average degrees of polymerization against the conversion of cyanate groups, from eqs 18 and 13, respectively.

It is important to mention that for a given chemistry the gel point predicted by mean-field theory shall always be the lowest possible value. Thus if trimerization is the main reaction but diffusion limitations are present, gelation would happen at higher conversion. Mobility or diffusion limitations, steric hindrances being an alternate expression for such limitations, shall result in extensive cyclization, as on an average a functional unit that is frozen is closer to the other functional units on the same molecule. Also, as Monte Carlo simulations suggest, even if cycles were disallowed, gelation would still be delayed if units were allowed to react only in their respective neighborhoods.[8] Physically diffusion limitation promotes generation of several comparable size clusters, without accelerating the growth of any one of them, which is what happens at gelation. Gelation finally occurs for the case of diffusion limitation when two of these clusters begin to overlap.

For the present case, a secondary reaction, that of dimerization of cyanate units which has been suggested,[9] would also explain the experimental evidence. It can be shown by the expectation value technique that, if α_1 is the dimerization conversion and α_2 the trimerization conversion,

then the weight-average degree of polymerization is given by

$$(DP)_w = (1 + \alpha_1 + 2\alpha_2)/(1 - \alpha_1 - 2\alpha_2) \qquad (19)$$

which depending on the ratio between the kind of reacted units would vary between 50% and 100%.

We have studied the details of the kinetics of the reaction and structure buildup using the monofunctional model compound 2-(4-cyanatophenyl)-2-phenylpropane. The synthesis work was done under four different transition-metal catalysts and without a catalyst. SEC and ^{13}C NMR were used for characterization of the reaction products. The complete details of this study shall be reported separately.[10] We found that trimerization was the dominant reaction (>80%). Dimerization was found to be a small side reaction (typically <1%). We also found four- and five-membered species, which are most likely to be straight-chain oligomers. Thus we concluded that other than the trimerization reaction a small side reaction that produces straight-chain molecules is also prevalent. In the present context this implies that the additional chemistry, which produces four branch nodes for growth, would predict even faster growth and gelation. Thus the side reactions do not explain the experimentally observed gel point. The higher gel conversion is most likely to be due to diffusion limitations, which would cause the reactivity of branch nodes to decrease, because of both the shape and size of the growing molecules.

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References and Notes

(1) Shimp, D. A.; Christenson, J. R.; Ising, S. J. *Cyanate Ester Resins-Chemistry, Properties & Applications*; Hi-Tek House Publication: Louisville, KY, 1989.
(2) Grigart, E.; Putter, R. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 206.
(3) Some experimental evidence, from SEC traces, suggests that polymerization also involves a dimerization reaction (communication with D. Shimp, Hi-Tek Polymers). Also see ref 10 below.
(4) (a) Stockmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45. (b) Ziff, R. M.; Stell, G. *J. Chem. Phys.* **1980**, *73*, 3492.
(5) Gordon, M. *Proc. R. Soc. London, A* **1962**, *268*, 240.
(6) Miller, D. R.; Macosko, C. W. *Macromolecules* **1976**, *9*, 206.
(7) For reasons that are not entirely understood at this stage, gel point at 50% conversion has also been reported for the same monomer. Bauer, M.; Bauer, J.; Kuhn, G. *Acta Polym.* **1986**, *37*, 715.
(8) Gupta, A. M.; Hendrickson, R. C.; Macosko, C. W. Monte Carlo Description of A_f Homopolymerization: Diffusional Effects, submitted to *J. Chem. Phys.* (Dec 1990).
(9) Korshak, V. V. *J. Polym. Sci.* **1974**, *A16*, 1066.
(10) Gupta, A. M.; Macosko, C. W., to appear in the symposium issue of *Macromol. Chem.*, Network '90, Jerusalem.

Registry No. 2,2-Bis(4-cyanatophenyl)propane, 1156-51-0; 2-(4-cyanatophenyl)-2-phenylpropane, 110215-65-1.