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Gelation in the cyclotrimerization of dicyanates considering substitution effects

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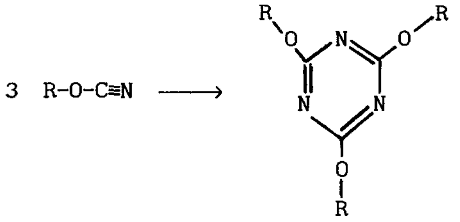
Summary

The cyclotrimerization of dicyanates to form polycyanurate networks has been analyzed using a pure kinetic model and a combined kinetic-recursive procedure. In both cases substitution effects were considered, i.e. the reactivity of OCN groups pertainning to clusters was assumed lower than the corresponding reactivity of the monomer groups. The gel conversion varied from 1/2 (no substitutions effects) to 2/3 (infinite substitution effects). The evolution of trimer concentration along the reaction constitutes a direct experimental evidence to decide whether the polymerization follows or not an ideal course, described by the mean-field theory.

Introduction

Polycyanurate networks are formed by the cyclotrimerization of cyanate ester monomers:



(1)

The use of aromatic dicyanates leads to excellent thermosetting polymers characterized by high values of thermal stability, glass transition temperature, moisture resistance and electrical insulating properties.

Although several studies dealing with this system have been recently reported (1-13), there still remains a controversy about the gel conversion (13). While J. Bauer, M. Bauer and coworkers (6,10-12) found gelation at 50% conversion (the value arising from mean-field theory for an ideal polymerization), other workers (13 and references therein) reported values in the range 60 % to 65 % conversion.

Our aim is to present a theoretical framework for the analysis of the network build-up in the presence of substitution effects, i.e. after

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*To whom offprints requests should be sent reaction of one OCN group of the monomer, the remaining functionality reacts at a lower rate. We will discuss if this effect can be invoked to explain gel conversions ranging from 0.6 to 0.65.

Kinetic model

Gupta (14) has recently provided the general kinetic equations to describe the ideal cyclotrimerization of an A_2 monomer. We call P_{2n+1} the cluster formed by (2n+1) monomers units (n=0,1,..), divided by the initial monomer concentration, A_2. Initially, $P_1=1$ and P_3, $P_5,\ldots=0$. Kinetic equations may be written in terms of a dimensionless time, $= k(A_2)^2 t$, where k is a specific rate constant for the cyclotrimerization. According to Gupta (14),

$$dP_1/d = - P_1 \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} (i+2)(j+2) P_{2i+1} P_{2j+1} \qquad (2)$$

$$n>=1,\ dP_{2n+1}/d = \frac{1}{3!} \sum_{\substack{i=0 \\ (i+j+k=n-1)}}^{\infty} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} (i+2)(j+2)(k+2) P_{2i+1} P_{2j+1} P_{2k+1}$$

$$- \frac{1}{2!} (n+2) P_{2n+1} \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} (i+2)(j+2) P_{2i+1} P_{2j+1} \quad (3)$$

The triple summation refers to all different polymer sizes that would, when any three of their several unreacted functional units trimerize, yield a molecule with size 2n+1. The double summation represents the disappearance term of a P_{2n+1} molecule. Factors like (i+2) arise from the number of free functionalities (OCN groups), available for reaction in the cluster P_{2i+1}.

This kind of kinetic model may be used to determine the relative concentration of different clusters along the polymerization, e.g. P_{2n+1} (n>=1) as a function of P_1. However, it cannot be expected to predict concentrations vs. time because the constitutive equation for kinetics does not necessarily agree with the reaction molecularity. In other words, k may be regarded as a function of the overall conversion, leading to a non-linear scale.

Using moment generating functions, Gupta (14) was able to obtain expressions for the number and weight average degrees of polymerization that agree with Flory-Stockmayer predictions,

$$\overline{DP}n = \frac{1}{1 - \frac{4}{3}x} \qquad (4)$$

$$\overline{DP}w = \frac{1+2x}{1-2x} \qquad (5)$$

where x is the conversion of OCN groups. For $x = x_{gel} = 0.5$, $\overline{DP}w \to \infty$.

The substitution effect may be now introduced into the ideal kinetic scheme. For example, it may be assumed that the reactivity of a free OCN group pertaining to any cluster P_{2n+1} ($n>=1$) is r times lower than the reactivity of an OCN group of the unreacted monomer ($0<r<1$). This hypothesis must be regarded as the simplest approach explaining a continuous decrease of r with the size of the cluster, n, due to diffusional restrictions.

Therefore, the specific rate constant is given by $r^j k$, where j (=0,1,2 or 3) indicates the number of clusters other than the monomer, involved in the cyclotrimerization. Eqs. (2) and (3) were numerically solved in the pregel stage for different r values, using a finite number of clusters. Truncation errors were minimized by increasing the number of clusters with conversion. Values of $\overline{DPn}$, $\overline{DPw}$ and x were calculated as follows:

$$\overline{DPn} = \frac{1}{\sum_{n=0}^{\infty} P_{2n+1}} \qquad (6)$$

$$\overline{DPw} = \frac{\sum_{n=0}^{\infty} (2n+1)^2 P_{2n+1}}{\sum_{n=0}^{\infty} (2n+1) P_{2n+1}} \qquad (7)$$

$$x = 1 - \frac{1}{2} \sum_{n=0}^{\infty} (2n+1) P_{2n+1} \qquad (8)$$

It was verified that eq.(7) gave the same results as those predicted by eq.(5), for r=1, proving the accuracy of the numerical solution.

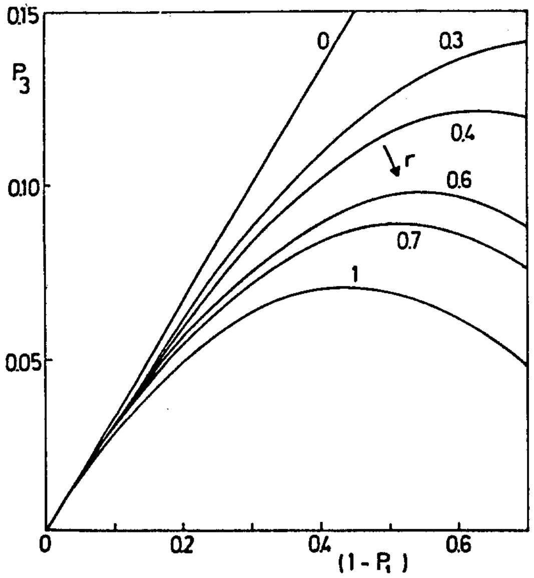

Fig. 1: Evolution of the trimer concentration, P_3 moles per initial mole of monomer, as a function of the monomer conversion, for several values of r.

Figure 1 shows predicted values of the trimer concentration, P_3 (number of moles per initial mole of monomer), as a function of the monomer conversion, $1-P_1$. For r=1 (ideal polymerization), the maximum trimer concentration predicted by the kinetic model is slightly higher than 7 % in moles (or 21.1% in mass), and takes place at a monomer consumption of 44%. Lower r values produce a higher trimer concentration with a maximum shifted to higher monomer conversions. For example, for r=0.4 the maximum P_3= 12.2% in moles (or 36.6 % in mass), and takes place at a monomer conversion close to 64%.

The high sensitivity of P_3 on r makes this a suitable way for an experimental verification of the presence of nonidealities in the network build-up. As shown by Gupta and Macosko (13), size-exclusion chromatography may be conveniently used to follow the trimer concentration along the polymerization. This may provide a solid argument to establish if the network build-up follows or not an ideal course.

Gelation in the presence of substitution effects

Let us call

□–□: P_1 (unreacted monomer)

□-■<: B (monoreacted monomer)

>■-■<: C (bireacted monomer)

where P_1, B and C represent dimensionless concentrations referred to the initial monomer concentration, A_2.

The cyclotrimerization is represented by the following reactions:

$$3\, P_1 \xrightarrow{k} 3\, B \qquad (9)$$

$$2\, P_1 + B \xrightarrow{rk} 2\, B + C \qquad (10)$$

$$P_1 + 2\, B \xrightarrow{r^2 k} B + 2\, C \qquad (11)$$

$$3\, B \xrightarrow{r^3 k} 3\, C \qquad (12)$$

This gives place to the following kinetic scheme:

$$-\, dP_1/d \;=\; 4\, P_1^3 + 4\, r\, P_1^2\, B + r^2\, P_1\, B^2 \qquad (13)$$

$$dB/d \;=\; 4\, P_1^3 + 2\, r\, P_1^2\, B - r^2\, P_1\, B^2 - r^3\, B^3/\, 2 \qquad (14)$$

$$dC/d \;=\; 2\, r\, P_1^2\, B + 2\, r^2\, P_1\, B^2 + r^3\, B^3/\, 2 \qquad (15)$$

In particular, eq. (13) results from eq.(2) by replacing

$B=\sum_{j=1}^{\infty}(j+2)\,P_{2j+1}$ (total number of unreacted functionalities in clusters $P_{2j+1}, j>=1$), and making use of the reactivity ratio, r.

Solving eqs.(13) to (15), with the initial condition, $P_1=1$, $B=C=0$ at =0, the evolution of B and C as a function of P_1 may be obtained. These concentrations are related by:

$$P_1 + B + C = 1 \qquad (16)$$

$$x= 1 - P_1 - B/2 \qquad (17)$$

The gel condition may be obtained by stating a recursive procedure. Let us call W the average weight attached to a reacted functionality when looking out of the monomer to which it belongs. Three possibilities arise: i)It is joined to two B groups, probability = $B^2/(B+2C)^2$; ii)It is joined to one B and one C group, probability $=4BC/(B+2C)^2$; iii)It is joined two C groups, probability= $4C^2/(B+2C)^2$. Therefore, W is given by:

$$W= \frac{B^2}{(B+2C)^2}\,(2\,M_B) + \frac{4\,B\,C}{(B+2C)^2}\,(M_B+M_C+W) + \frac{4\,C^2}{(B+2C)^2}\,(2M_C+2W) \qquad (18)$$

where M_B and M_C are the molar masses of fragments B and C, respectively.

Solving for W, we get:

$$W= [2B^2M_B + 4BC(M_B + M_C) + 8C^2M_C] \;/\; [B^2-4C^2] \qquad (19)$$

Gelation occurs when $W \to \infty$, implying that:

$$B = 2\;C \quad \text{(gel condition)} \qquad (20)$$

Before solving the general case, two particular situations may be analyzed.

I) Ideal polymerization (r=1)

Now, the fraction of unreacted monomer at any conversion x is given by, $P_1= (1-x)^2$. Replacing in eqs. (16) and (17), we get $B = 2\,x\,(1-x)$ and $C = x^2$. From eq.(20), we obtain $x_{gel}=0.5$.

II) Infinite substitution effects ($r \to 0$)

In this case, P_1 is completely converted into B and only then the transformation of B to C takes place. From this time on, $B + C=1$, meaning that eq.(20) is verified when $B=2/3$ and $C= 1/3$. From eq.(17) with $P_1=0$ and $B=2/3$, we get $x_{gel}= 2/3$.

Therefore, depending on the significance of substitution effects, the gel conversion varies from $x_{gel}=0.5$ to $x_{gel}=2/3$. Figure 2 shows the gel conversion for the general case as a function of the reactivity ratio, r. For r values in the range 0.3 to 0.55, x_{gel} is located in the range of 60-65 % reported by several researchers (13).

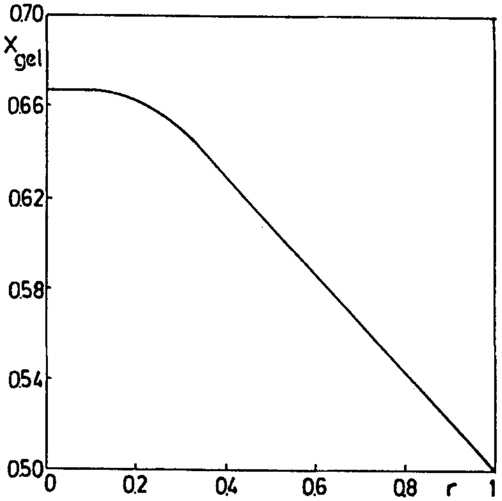

Fig. 2. Gel conversion vs r (parameter related to the substitution effects)

Conclusion

The evolution of trimer concentration along the reaction constitutes a direct experimental evidence to decide whether the cyclotrimerization of a dicyanate follows or not an ideal course, described by the mean-field theory. Use of the kinetic model developed for the ideal polymerization (14), leads to a maximum trimer concentration close to 7 % in moles per mole of monomer or 21.1 % in mass fraction. This maximum takes place at a monomer consumption of 44%. When confronting this theoretical prediction with experimental results, one may argue about the presence of non-idealities in the network build-up. For example, if the trimer concentration is higher than expected, a substitution effect may become operative explaining the delay in gelation. On the other hand, if the trimer concentration shows a lower value than expected for the ideal polymerization one may analyze whether there are other reactions than cyclotrimerization involved in the monomer conversion, e.g. formation of linear polymers. Experimental work aimed at following the trimer concentration along the polymerization is in progress.

Acknowledgements

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