Statistical calculations of the network build-up in the postgel stage of A$_2$-cyclotrimerization

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Summary

Statistical parameters for the postgel stage of an ideal A$_2$ polycyclotrimerization were derived and compared with the corresponding parameters for an A$_3$ homopolymerization. Both gel fraction and crosslink density increase less with conversion for the former case. This is due to the fact that branching units are present at a constant concentration from the beginning of the A$_3$ homopolymerization, but show a linear increase with conversion, from zero to the maximum value , for the A$_2$ polycyclotrimerization.

Introduction

The electronics industry is advancing toward increased circuit densities and commutating speeds. This requires the development of new materials offering very low dielectric losses and high service temperatures. Since they meet these requirements, and they display also a good toughness, polycyanurates have received increasing commercial interest over the past few years. The most frequently used monomer is the bifunctional 2,2'(4,4'dicyanato)-diphenylpropane, which cyclotrimerizes upon heating (1-4), leading to a polycyanurate network with triazine rings as branching units (Figure 1). Cyclotrimerization reactions are also possible with other monomers such as isocyanates or acetylene (5).

Several studies devoted to the polymerization of cyanates have recently been reported (1-4,6-10). They mostly deal with the reaction kinetics (catalyzed or uncatalyzed) or the approach to gelation (pregel stage of the cyclotrimerization). The postgel stage of the reaction has not received as much attention. Bauer et al (11) analyzed the network building process for a system consisting of dicyanates and diphenols where the cyclotrimerization competes with a chain extension reaction. Using cascade theory and a model of the multi-stage kinetics, the gel fraction as a function of the cyanate conversion was predicted. Simon and Gillham (8-9) also reported statistical calculations carried out for the postgel stage. These results do not differ from

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those obtained for the classical A_3 homopolymerization, a fact that cast some doubts about the validity of the equations derived.

Therefore, although statistical techniques valid for the postgel stage of the A_2 cyclotrimerization have been proposed in the literature (11), no analytical results are available, to our knowledge, for the crosslink density and the gel fraction as a function of conversion. These equations will be derived in what follows and the differences between an A_2 cyclotrimerization and an A_3 homopolymerization will be remarked.
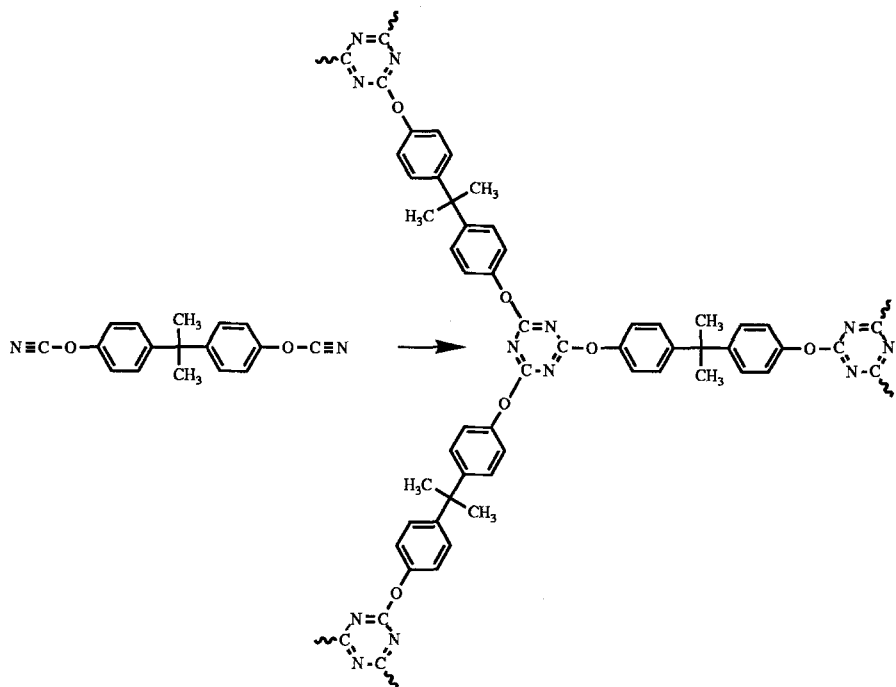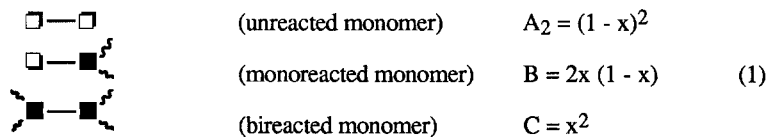

__Figure 1__ : Polycyclotrimerization of 2,2'(4,4'dicyanato)diphenylpropane

A_2 cyclotrimerization

The cyclotrimerization of dicyanates was found to be a step-growth reaction with ideal statistical behavior (1-2,11), a fact that was recently corroborated by us (10) working under inert atmosphere conditions. Then, the following assumptions will be considered valid :

(i)   all functional groups are equally reactive,

(ii)   all groups react independently of one another,

(iii)   no intramolecular reactions occur in finite species.

Under ideal polymerization conditions, the concentration of the different fragments along the reaction is given by (7) :


(unreacted monomer) $A_2 = (1 - x)^2$

(monoreacted monomer) $B = 2x (1 - x)$ (1)

(bireacted monomer) $C = x^2$

A_2, B and C represent dimensionless concentrations referred to the initial monomer concentration, $A_2(0)$; x is the conversion of cyanate groups.

The cyclotrimerization reaction is represented by :
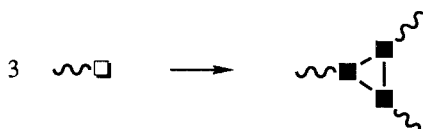
Using the formalism proposed by Miller and Macosko (12), we select a reacted group at random and call $P(F_{out}^A)$ the probability of finding a finite chain when looking out from its parent molecule, and $P(F_{in}^A)$ the corresponding probability when looking into its parent molecule.
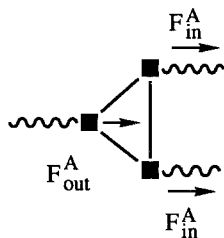
It is evident that :

$$P(F_{out}^A) = \left[P(F_{in}^A)\right]^2$$
(2)

To calculate $P(F_{in}^A)$, we must ask if the monomer which carries the selected A group is :

(i) a B-monomer, in which case there is no continuation to infinity,

(ii) a C-monomer, in which case the probability of finding a finite chain will depend on $P(F_{out}^A)$, stated for the other reacted group. Thus,

$P(F_{in}^A)$ = (fraction of reacted groups pertaining to B) $\times$ 1 + (fraction of reacted groups pertaining to C) $\times$ $P(F_{out}^A)$

$$P(F_{in}^A) = \frac{B}{B+2C} + \frac{2C}{B+2C} P(F_{out}^A) \tag{3}$$

Replacing eq (1) in (3), we get

$$P(F_{in}^A) = 1 - x + x P(F_{out}^A) \tag{4}$$

Solving eqs (2) and (4) yields

$$\begin{cases} P(F_{in}^A) = \dfrac{1-x}{x} \\ P(F_{out}^A) = \left(\dfrac{1-x}{x}\right)^2 \end{cases} \tag{5}$$
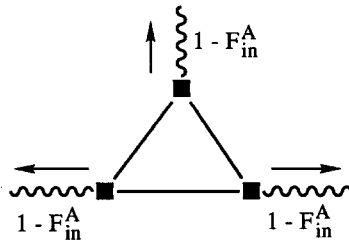
Concentration of triazine cycles (T)

Since a cycle result from the reaction of three functionalities, its concentration is $\frac{1}{3}$ of the concentration of the reacted groups :

$$T = A_2(0) \frac{B+2C}{3} = \frac{2}{3} A_2(0) x \tag{6}$$

Concentration of crosslink units (X)

Crosslinks are cycles with three arms going to infinite :

Thus, the crosslink density can be calculated as :

$$X = T \left[1 - P(F_{in}^A)\right]^3 = \frac{2}{3} A_2(0) \frac{(2x-1)^3}{x^2} \tag{7}$$

Sol and gel fractions (w_s, w_g)

The soluble material is constituted by the fraction of monomeric units with finite arms. Summing for all the species, we get :

$$w_s = A_2 + B \, P(F_{out}^A) + C \left[P(F_{out}^A)\right]^2 \tag{8}$$

Replacing eq (5) in (8) gives :

$$w_s = \left(\frac{1-x}{x}\right)^2 \tag{9}$$

and

$$w_g = 1 - w_s = \frac{2x-1}{x^2} \tag{10}$$

A3 homopolymerization

Statistical parameters for this case are reported in the literature (12). The crosslink density and the gel fraction are given by :

$$X = A_3(0) \left(\frac{2x-1}{x}\right)^3 \tag{11}$$

$$w_g = 1 - \left(\frac{1-x}{x}\right)^3 \tag{12}$$

Comparison : A2 cyclotrimerization and A3 homopolymerization

Comparing the expressions for the crosslink density in both cases (eqs (7) and (11)), it arises that there is a different dependence on conversion resulting from the fact that the concentration of branching units is constant for the A3 homopolymerization ($A_3(0)$), and increases linearly with conversion for the A2 cyclotrimerization (T). So, both X and w_g increase less with conversion for the A2 cyclotrimerization case (full line) than for the A3 homopolymerization case (dashed line) (see Figure 2).
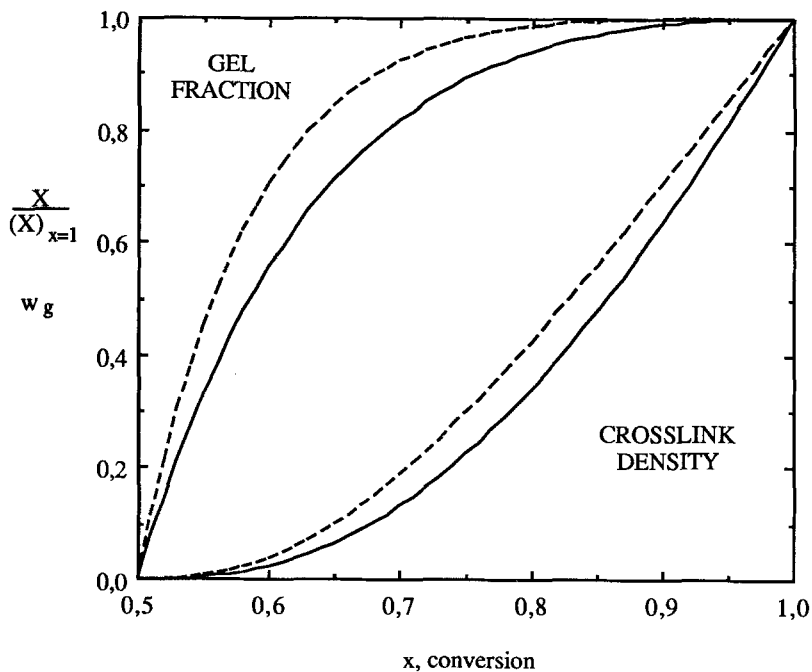
Figure 2 : *Crosslink density (referred to the maximum value) and gel fraction, as functions of conversion for A2 polycyclotrimerization (——) and A3 homopolymerization (– –)*

Conclusions

Statistical parameters for the postgel stage of an ideal A_2 polycyclotrimerization were derived and compared with the corresponding parameters for an A_3 homopolymerization. Both gel fraction and crosslink density increase less with conversion for the former case. This is due to the fact that branching units are present at a constant concentration from the beginning of the A_3 homopolymerization, but show a linear increase with conversion, from zero to the maximum value, for the A_2 cyclotrimerization.

Acknowledgements

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