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Critical Conversions in Chain Network Polymerization

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SUMMARY: The kinetics of network polymerization are considered by the method of generating functions. The critical condition at gelation is defined as the conversion when the second moment of the distribution of macromolecules with respect to functionality $\Phi_{22}(t) \to \infty$. Relations for the critical conversions for polymerization with instantaneous and slow initiation, without and with the chain transfer and recombination are obtained.

Introduction

The equations for the critical conversion (gel point), α_{cr}, in polycondensation processes are well known. However, there are no analogous relations that relate the values of critical conversion (CC) with the reaction conditions and reactant amounts in chain network polymerizations (CNP). Some simple relations[1-4] show that for primary chains of weight average polymerization degree $\overline{P}_w$, $\alpha_{cr} \cdot \overline{P}_w \approx 1$. These relations were generated from the concept that CNP did not differ from a polycondensation or polyaddition.[5,6] However, this concept was postulated, but not proved.

In this work, we present the results of calculations of critical conversions for some types of polymerization: living polymerizations with instantaneous and slow initiation, with and without chain transfer reactions, and polymerizations with the chain termination by recombination.

Method of Calculation

To solve the problem, we use the method of generating functions. Let $R(i,j,l)$ be the concentration of chains possessing i structural units of any functionality, j functional groups and l active centers. The corresponding generation function $\Phi(\vec{q})$ will be:

$$\Phi(\vec{q}) = \sum_i \sum_j \sum_l q_1^i \cdot q_2^j \cdot q_3^l \cdot R(i,j,l) \qquad (1)$$

Vector $\vec{\mathbf{q}} \equiv \{q_1, q_2, q_3\}$, q_i are dummy variables.

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Based on the conventional polymerization scheme, including initiation, propagation, chain transfer and recombination and taking into account relation (1), it is possible to obtain the following system of differential equations for $R(i,j,l,)$ and $\Phi(\vec{q})$:

$$\begin{aligned}
\frac{\mathrm{d}R(0,0,1)}{\mathrm{d}t} &= k_i I - R(0,0,1)\cdot(k_p F + k_x X + k_t R) + k_x XR \\
\frac{\mathrm{d}R(i,j,l)}{\mathrm{d}t} &= -R(i,j,l)\cdot\{k_p(lF + jR) + k(k_x X + k_t R)\} + \\
&\quad + k_x X \cdot R(i,j,l+1) \\
&\quad + k_p \sum_{m,n,p}^{i,j,l} \{n(k-p)\cdot R(i-m, j-n+1, l-p) + \\
&\quad + p(j-n+1)\cdot R(i-m, j-n+1, l-p)\}\cdot R(m,n,p,)
\end{aligned} \tag{2}$$

$i,j,l = 1,2,3,\ldots$.

Then

$$\begin{aligned}
\frac{\partial\Phi(\vec{\mathbf{q}})}{\partial t} &= k_i q_3 I + k_p \cdot \left\{ \frac{\partial\Phi(\vec{\mathbf{q}})}{\partial q_2} \cdot \frac{\partial\Phi(\vec{\mathbf{q}})}{\partial q_3} - q_3 F \frac{\partial\Phi(\vec{\mathbf{q}})}{\partial q_3} - q_2 R \frac{\partial\Phi(\vec{\mathbf{q}})}{\partial q_2} \right\} + \\
&\quad + k_x X \cdot (1 - q_3) \cdot \frac{\partial\Phi(\vec{\mathbf{q}})}{\partial q_3} + k_t \cdot \left\{ \tfrac{1}{2} \cdot \frac{\partial\Phi(\vec{\mathbf{q}})}{\partial q_3} - q_3 R \right\} \cdot \frac{\partial\Phi(\vec{\mathbf{q}})}{\partial q_3}
\end{aligned} \tag{3}$$

Here I and X are the concentrations of initiator and transfer agent, respectively, k_i, k_p, k_x, and k_t are the kinetics rate constants of the reactions of initiation, propagation, transfer and termination, respectively.

Differentiation of equation (3) with respect to q_i leads to the first and the second moment of the generation function. $N = \Phi(\vec{1})$ is the total concentration of polymer chains, $F = \frac{\partial\Phi(\vec{1})}{\partial q_2} = \sum_{i,j,l} jR(i,j,l)$ is the total concentration of functional groups, the total concentration of active centers is $R = \frac{\partial\Phi(\vec{1})}{\partial q_3} = \sum_{i,j,l} lR(i,j,l)$ and the second moments are $\Phi_{ij} = \frac{\partial^2\Phi(\overline{\mathbf{q}})}{\partial q_i \partial q_j}$ at $\overline{\mathbf{q}} = \mathbf{1}$. Evidently the Φ_{ij} are functions of time, t. The gel condition is $\Phi_{22}(t) = \sum_{i,j,l} j(j-1)\cdot R(i,j,l) \to \infty$.

Results and Discussion

Analysis of the shape of the kinetics curves $\Phi_{22}(t)$ vs. t has shown$^{7)}$ that they have points of inflection over some very narrow range of conversion that depends on the initial conditions.

This character of the relationship has made it possible to obtain values of CC with high accuracy. Moreover, the value of the CC did not depend on $F(0)$, the initial functionality; α_{cr} was the function of $\Phi_{22}(0) \equiv \Phi_{22}(t)_{t=0}$ only.

The data showing the dependence of α_{cr} on $\Phi_{22}(0)$ for instantaneous initiation, (k_i=k_x=k_t= 0, $R = I_0$) are presented in Fig. 1a.

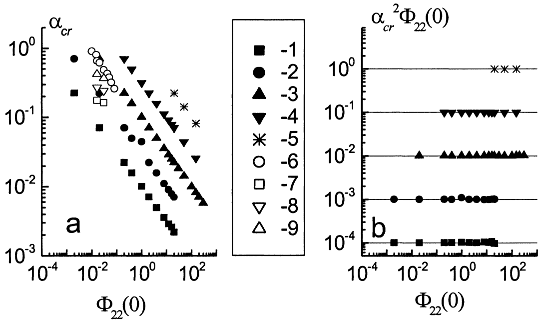

Fig. 1: Relations between α_{cr} and $\Phi_{22}(0)$ in living polymerizations with instantaneous initiation. I_0 /mol·l^{-1}: 10^{-4}(1); 10^{-3}(2); 10^{-2}(3); 10^{-1}(4); 1(5); 0.023(6); 0.0061(7); 0.0099(8); 0.034(9). 1–5 are calculated, and 6–9 are the experimental[8] data.

It can be seen that the relation $\alpha_{cr} \sim [\Phi_{22}(0)]^{-0.5}$ holds or, more precisely (as can be seen in Fig. 1b), $\alpha_{cr}^2 \cdot [\Phi_{22}(0)] = \text{const}$. Since the product $\alpha_{cr}^2 \cdot \Phi_{22}(0)$ is equal to the initiator concentration (Fig. 1b), it is possible to write the analytical formula expressing the relation between the CC and polymerization conditions:

$$\frac{\alpha_{cr}^2 \cdot \Phi_{22}(0)}{I_0} = 1 \tag{4}$$

The validity of relation (4) is established by the experimental data obtained for radical living polymerizations[8] (Fig. 1a). Some deviation of the data from the calculated values can be accounted for differences in actual and assumed reaction mechanisms.

The relation (4) has a clear physical meaning: the CC will be reached when at least two functional groups of one polyfunctional monomer per chain are converted. This condition differs from $\alpha_{cr} \cdot \overline{P}_w \approx 1$. Thus, the relations based on the supposition that CNP does not differ from a polycondensation or polyaddition are incorrect.

The analysis of other polymerization processes with more complicated mechanisms validates this conclusion. Thus, the results calculated for slow initiation ($k_i \neq 0$, $k_x = k_t = 0$) are presented in Fig. 2. As can be seen, the relation between α_{cr} and $\Phi_{22}(0)$ is expressed as $\alpha_{cr} \sim [\Phi_{22}(0)]^{-0.67}$ or (cf. Fig. 2b):

$$\alpha_{cr}^3 \cdot \Phi_{22}^2(0) = \frac{k_i I_0}{k_p} \tag{5}$$

The form of equation (5) shows that in the case of slow initiation, at least three functional groups of two polyfunctional monomers per chain have been converted at the critical point. Obviously, this condition is stronger than $\alpha_{cr} \cdot \overline{P}_w \approx 1$.

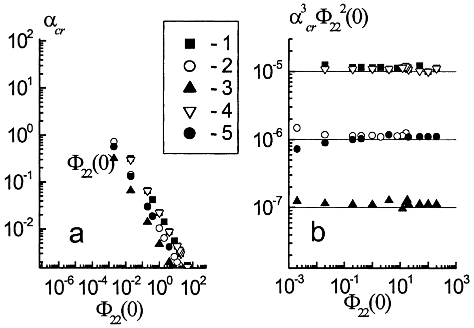

Fig. 2: Relations between α_{cr} and $\Phi_{22}(0)$ in living polymerizations with slow initiation. I_0 /mol·l^{-1}: 1(1); 10^{-1}(2); 10^{-2}(3,4); 10^{-3}(5); k_i/k_p: 10^{-5} (1-3); 10^{-3}(4,5).

In both of the cases of living polymerization considered, the critical probabilities are related to the chain concentration (initiator concentration in the first case and the rate of initiation in the second). This dependence is also evident when chain transfer reactions occur. The results of calculations are shown in Fig. 3a (instantaneous initiation) and Fig. 3b (slow initiation).

As can be seen, all points form master curves in rather complex coordinate systems. Nevertheless, analytical relations can be written for limiting cases. Simple relation describes the left-hand parts of the curves in both kinetics regimes of instantaneous and slow initiation. The gel point is defined by the ratio of rates of chain accumulation and propagation via polyfunctional monomers, or, in essence, via chain branching.

$$\alpha_{cr} = \frac{1}{2} \frac{k_x X_0}{k_p \Phi_{22}(0)} \tag{6}$$

For the right-hand part of the curves, on the other hand, the relations (4) and (5) turn out to be valid.

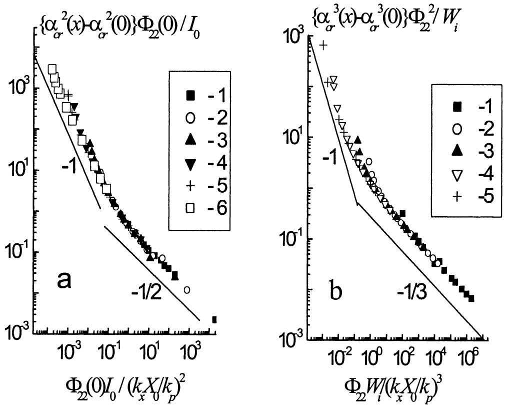

Fig. 3: The dependence of α_{cr} on polymerization conditions for living polymerization with chain transfer and instantaneous (a) and slow (b) initiation. Straight lines and associated numbers show the slopes. $\alpha_{cr}(0)$ is the CC at given $\Phi_{22}(0)$ and $X_0=0$. **a**: $I_0 = 10^{-4}$ mol·l^{-1}; $X_0=1$ mol·l^{-1}; k_x/k_p: 10^{-3}(1); $5\cdot10^{-3}$(2); 10^{-2}(3); $5\cdot10^{-2}$ (4); 10^{-1}(5); 0,5(6). **b**: $W_i \equiv k_iI_0/k_p = 10^{-4}$ mol^{2}l^{-2}; $X_0=1$ mol/l; k_x/k_p: 10^{-3}(1); $5\cdot10^{-3}$(2); 10^{-2}(3); $5\cdot10^{-2}$ (4); 10^{-1}(5).

The crossover conditions are:

$$\frac{k_p\Phi_{22}(0)}{k_xX_0} \approx \begin{cases} \dfrac{k_xX_0}{k_pI_0} & \text{in the first case} \\ \dfrac{(k_xX_0)^2}{k_pk_iI_0} & \text{in the second case} \end{cases} \tag{7}$$

Therefore, as $k_x/k_p \approx 1$ and $X_0 \approx I_0$ it is necessary to use relation (6), if $\Phi_{22}(0) < X_0$, and relation (4) or (5) in the contrary case. However, from equation (7) it is seen that if $\Phi_{22}(0) < X_0$ then α_{cr} might exceed 1, hence gel point cannot be reached. Consequently, equations (4) and (5) are the ones that precisely define the critical conditions.

Consider now the case of terminated polymerizations. The results of calculations are presented in Fig. 4. The master curve was in this case obtained as in the previous ones. The left-hand part of the curve is expressed by the relation similar to equation (6)

$$\alpha_{cr} \approx \frac{1}{3}\frac{k_tR}{k_p\Phi_{22}(0)} \tag{8}$$

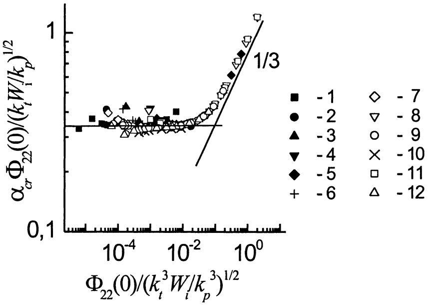

Fig. 4: The dependence of α_{cr} on the conditions of terminated chain polymerizations. $W_i \equiv k_iI_0/k_p$ /mol^{2}l^{-2}: 10^{-5} (1,2,3,4,11,12), $5{\cdot}10^{-5}$ (8,9,10), 10^{-4} (5,6,7); k_t/k_p: 10^3 (4,5,8), $2{\cdot}10^3$ (11,12), $5{\cdot}10^3$ (3,6), 10^4 (1,7,9), $5{\cdot}10^4$ (2), 10^5 (10).

The right-hand part is described by equation (6). The crossover point in this case is defined by the relation:

$$\frac{k_p\Phi_{22}(0)}{k_tR} \approx \frac{k_t}{k_p} \tag{9}$$

Thus, as far as the right-hand side of equation (9) is equal to about 10^4 and $\Phi_{22}(0)<1$, α_{cr} is to be defined by relation (8); relation (5) should be used when $\Phi_{22}(0)>1$. For example, the polymerization of dimethacrylates is characterized by the following parameters:2) $\Phi_{22}(0)=20$ mol l^{-1}, $k_p \approx 10^3$ l mol^{-1} s^{-1}, $k_t \approx 10^5$ l mol^{-1} s^{-1} and as a rule the initiation rate falls within the broad range between 10^{-9} and 10^{-6} mol l^{-1} s^{-1}. The conditions mean that relation (8) is valid. Therefore, $10^{-5} > \alpha_{cr} > 10^{-4}$.

The typical radical CNP can be compared with a living one. In the latter $10^{-2} < I_0 < 1$. Therefore, according to equation (4): $2{\cdot}10^{-2} > \alpha_{cr} > 2{\cdot}10^{-1}$. Hence, the gel point in the case of living polymerization occurs at much higher conversion then in the radical CNP; higher than by more than 2 orders of magnitude; for this reason the value of CC can serve as evidence of the living regime in a polymerization.

Conclusion

The fact that CNP with chain transfer and termination is described by equations (4) and (5), as if they are simple living polymerization processes, is the consequence of the kinetics peculiarities of CNP. Actually, when the concentration of multifunctional monomers is high, the rate of branching has to be higher than rate of chain transfer or termination; therefore, the chain length does not play role in defining of the gel point. The chain length is important only when the concentration of the multifunctional monomer is small and hence the number of pendant groups in primary chains is not too high. The main factor, however, that determines the critical conversion is the weight average functionality of the initial monomer mixture.

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