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A Kinetic Theory of Stepwise Cross-Linking Polymerization with Substitution Effect

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ABSTRACT: A kinetic model describing evolution of the molecular size distribution during stepwise homopolymerization of a trifunctional monomer reacting with substitution effect is presented. The model makes use of a Smoluchowski-like coagulation equation. It is shown that the pre-gel molecular size distribution in kinetically controlled polymerizations differs from that generated by the cascade theory (or any other equivalent statistical theory) except for the systems with equal and conversion independent reactivities of functional groups.

1. Introduction

In 1982, Mikeš and Dušek[1] published results of a Monte Carlo study on the network formation by stepwise homopolymerization of a trifunctional monomer.

In fact, their study aimed at showing that, in kinetically controlled stepwise polymerization, the size distribution of polymer molecules differs from that generated by the acknowledged statistical theories of Flory,[2] Stockmayer,[3] Gordon,[4] and others[5,6] except for the special case of the so-called *random* polymerization. In the random polymerization, all functional groups have equal and conversion-independent reactivities.

Mikeš and Dušek considered several *nonrandom* cases where the so-called *first-shell substitution effect* (FSSE)[7,8] was operative. With FSSE, a monomer has all its f functional groups equally reactive until one of the groups reacts. Then the remaining $f - 1$ groups become again equally reactive, but with different reactivity. The same applies to the $f - 2$ groups in a doubly connected unit, etc. Hence, the FSSE models the conversion dependence of reactivity of functional groups that is quite common in real polymerization processes.

This work deals with exactly the same system as considered by Mikeš and Dušek except that their Monte Carlo approach is replaced by a more straightforward analysis of the distribution of polymerization degrees. The techniques used in this work are very similar to those published by Kuchanov and Povolotskaya.[9,10] The analysis is based on a kinetic equation of the Smoluchowski type.[11] This equation (rederived in the Appendix section) is used to calculate various averages of the degree of polymerization as well as the time and conversion degree at the gel point for a number of nonrandom model systems of homopolymerization of a trifunctional monomer.

2. Statistical versus Kinetic Theory of Cross-Linking Polymerization with Substitution Effect

The following polymerization process is considered. At time $t = 0$, the system of constant volume contains $N \to \infty$ units, each having three functional groups. The groups of different units react *irreversibly* with each other to form bonds. No intramolecular reactions are allowed. The units with i reacted groups are referred to as i state.

While considering the FSSE, it is reasonable to assume additivity of activation energies.[7] Thus, the activation energy of reaction between two units (with i and j functional groups already reacted) is taken to be

$$\Delta E_{ij} = \Delta E^* + \psi(i) + \psi(j) \qquad (1)$$

where ΔE^* is the activation energy for the reaction of functional groups in a reference state and $\psi(\cdot)$ is the contribution of the unit substitution degree to the activation energy of reaction of its groups.

In terms of rate constants, eq 1 is equivalent to

$$K_{ij} = K^* K_i K_j \qquad (2)$$

so that the effects of substitution upon the reactivity of groups in two reacting units are separable.

The set of elementary reactions between units in homopolymerization of a trifunctional monomer is shown in Figure 1.

This set can be analyzed in two ways: by using a statistical or kinetic method.

A convenient statistical approach is the one developed by Gordon and Scantlebury.[7] In this approach, the distribution of molecular sizes is generated from the distribution of units by states. Thus, the fractions, α_i, of units with i reacted groups are calculated from the set of differential equations

$$-\mathrm{d}\alpha_i/K^*\,\mathrm{d}t = [(3-i)K_i\alpha_i - (3-i-1)K_{i-1}\alpha_{i-1}]\sum_{j=0}^{2}(3-j)K_j\alpha_j \qquad i = 0, 1, ..., 3; \quad \alpha_{-1} \equiv 0 \qquad (3)$$

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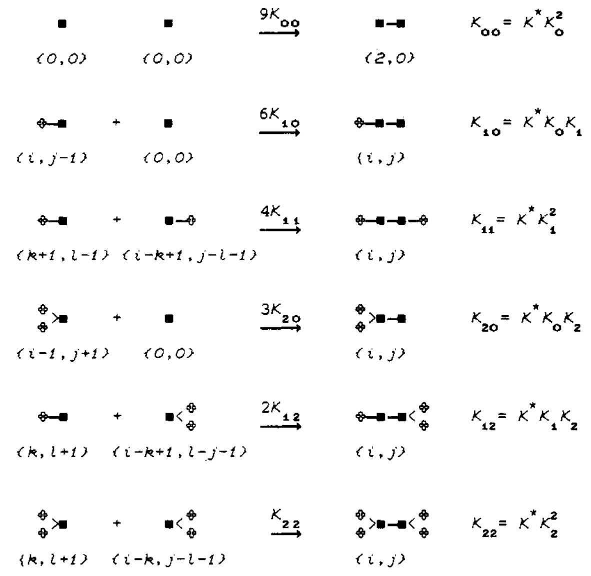

"■" denotes reacting unit and "⊕", the rest of molecule

Figure 1. Elementary reactions in homopolymerization of a trifunctional monomer with substitution effect.

Each of the fractions can be considered as the probability of finding a unit in the system with a given number of reacted groups. Hence, the fractions can be used as coefficients at powers of the dummy variable, θ, in the generating function

$$F_0(\theta) = \alpha_0 + \alpha_1\theta + \alpha_2\theta^2 + \alpha_3\theta^3 \tag{4}$$

The distribution of polymerization degrees is now implicitly given by the cascade substitution[1,4,7,8]

$$W(\theta) \equiv \sum_1^{\infty} w_i\theta^i = \theta F_0(\theta F_1(\theta F_1(...))) \tag{5}$$

where

$$F_1(\theta) = \frac{\mathrm{d}F_0(\theta)/\mathrm{d}\theta}{F_0'} = (\alpha_1 + 2\alpha_2\theta + 3\alpha_3\theta^2)/F_0' \tag{6}$$

and

$$F_0' = \left.\frac{\mathrm{d}F_0(\theta)}{\mathrm{d}\theta}\right|_{\theta=1} = \alpha_1 + 2\alpha_2 + 3\alpha_3 = 3\xi \tag{7}$$

(ξ is the conversion degree).

The coefficients at θ^i in $W(\theta)$ are the weight fractions of molecules containing exactly i units.

The alternative method of dealing with the polymerization system represented by Figure 1 is the method based on the Smoluchowski-like equation[11] (eq 12, below). In this method (referred to as the kinetic one), the time evolution of the whole distribution of polymerization degrees is considered.

The distribution is again implicitly given by the generating function

$$\mathbb{H}(\tau,x_1,x_2) = X_0 + \sum_{k=2}^{\infty}\sum_{l=0}^{\infty} c_{kl}[\varkappa_1x_1]^k[\varkappa_2x_2]^l \tag{8}$$

where $\tau = 3K^*K_0Nt$ is the scaled time, x_1 and X_2 are dummy variables, $X_0 = X_0(\tau)$ is the fraction of unreacted monomer (hence $X_0 = \alpha_0$ of eq 3), $\varkappa_1 = 2K_1/3K_0$, $\varkappa_2 = K_2/3K_0$, and $c_{kl} = c_{kl}(\tau)$ is divided by N, the number of molecules built of exactly k units with one reacted functional group and l units with two reacted functional groups.

The pair of numbers k and l sufficiently characterizes molecules that are formed in homopolymerization of a trifunctional monomer. For a molecule containing k, l, and m units with one, two, and three reacted groups, respectively, one can write down two relationships linking these numbers with the size of the molecule, n:

$$n = k + l + m \tag{9}$$

and

$$2(n - 1) = k + 2l + 3m \tag{10}$$

The first relationship is obvious. The second relates the number of links in an acyclic molecule, $n - 1$, with the number of all reacted groups in this molecule.

Elimination of m yields

$$n = 2k + l - 2 \tag{11}$$

As it is shown in the Appendix section, the generating function 8 changes with time according to the equation that both with form and meaning resembles the Smoluchowski coagulation equation[12]

$$\frac{\partial\mathbb{H}}{\partial\tau} = \frac{1}{2}\left[(\varkappa_1x_1)X_0 + (\varkappa_2x_2)\frac{\partial\mathbb{H}}{\partial x_1} + \frac{\partial\mathbb{H}}{\partial x_2}\right]^2 - (X_0 - X_1 + X_2)\left[X_0 + (\varkappa_1x_1)\frac{\partial\mathbb{H}}{\partial x_1} + (\varkappa_2x_2)\frac{\partial\mathbb{H}}{\partial x_2}\right] \tag{12}$$

where X_1 and X_2 denote the partial derivatives of $\mathbb{H}$ with respect to x_1 and x_2, respectively, calculated along the line $(\tau,1/\varkappa_1,1/\varkappa_2)$.

3. Moments of the Molecular Size Distribution

In the theory of branching processes applied to homopolymerization, the weight-average degree of polymerization is given by

$$P_{\mathrm{w}} = \left.\frac{\mathrm{d}W}{\mathrm{d}\theta}\right|_{\theta=1} \equiv M_2 \tag{13}$$

and for the reason explained below, it is defined to be the second rather than first moment of the molecular size distribution.

The higher averages (or higher moments of the distribution) are extracted from $\mathrm{d}W/\mathrm{d}\theta$ by the operator[13] d/d ln θ. Thus,

$$M_3 = P_zP_{\mathrm{w}} = \frac{\mathrm{d}}{\mathrm{d}\ln\theta}\left(\frac{\mathrm{d}W}{\mathrm{d}\theta}\right)_{\theta=1} \tag{14}$$

$$M_4 = P_{z+1}P_zP_{\mathrm{w}} = \frac{\mathrm{d}}{\mathrm{d}\ln\theta}\left[\frac{\mathrm{d}}{\mathrm{d}\ln\theta}\left(\frac{\mathrm{d}W}{\mathrm{d}j}\right)\right]_{\theta=1} \tag{15}$$

etc., where P_z and P_{z+1} are the z and $z + 1$ average degrees of polymerization, respectively.

Since $W(\theta)$ is expressed in terms of α_0–α_3 only, all moments are also appropriate combinations of these values. More strictly, it is sufficient to know only three of them, since

$$\sum_{i=0}^{3}\alpha_i = 1 \tag{16}$$

The number-average degree of polymerization can easily be calculated following the reasoning of Stockmayer.[3] Each bond (formed by two reacting groups) reduces the number of molecules in the system by one. On average, there are F_0' groups in each unit that have reacted at a given stage of polymerization. Hence, the average number of units per molecule is

$$P_{\mathrm{n}} = 1/(1 - F_0'/2) \tag{17}$$

In the kinetic approach, it seems more practical to consider, instead of the weight fraction distribution, a function consistent with $\mathbb{H}$, say, the distribution function of the numbers of molecules of a given size divided by the total number of units in the system (cf. ref 9, 14, and 15).

The first moment of such a distribution (up to the gel point) is simply unity, whereas the number- and weight-average degrees of polymerization are $P_n = M_1/M_0 = 1/M_0$ and $P_w = M_2/M_1 = M_2$, respectively.

Therefore, in the kinetic approach, the moments are, according to eq 11, given by

$$M_r = X_0 + \sum_k \sum_l (2k + l - 2)^r c_{kl} \tag{18}$$

For a positive integer r, the moments can be expressed in terms of the derivatives of $\mathbb{H}$ with respect to x_1 and/or x_2 of the order, at most, r, calculated at $x_1 = 1/\varkappa_1$ and $x_2 = 1/\varkappa_2$. The first derivatives, X_1 and X_2, appeared already in eq 12.

Let X_{11}, X_{12}, X_{22}, X_{111}, etc., denote derivatives of $\mathbb{H}$ with respect to x_1 and x_1, x_1 and x_2, x_2 and x_2, x_1, x_1, and x_1, etc., respectively, calculated at $x_1 = 1/\varkappa_1$ and $x_2 = 1/\varkappa_2$. All X's are functions of time and can be calculated from eq 12 as follows (cf. ref 10).

The substitution $x_1 = x_2 = 0$ yields

$$\dot{X}_0 = -X_0(X_0 + X_1 + X_2) \tag{19a}$$

where the upper dot denotes the time derivative.

Differentiation of eq 12 with respect to x_1 and x_2 followed by the substitutions $x_1 = 1/\varkappa_1$ and $x_2 = 1/\varkappa_2$ leads to

$$\dot{X}_1 = -\varkappa_1(X_1 - X_0)(X_0 + X_1 + X_2) \tag{19b}$$

$$\dot{X}_2 = -\varkappa_2(X_2 - X_1)(X_0 + X_1 + X_2) \tag{19c}$$

since all second derivatives automatically cancel out.

It is not difficult to see that X_1 and X_2 are closely related to the fractions α_1 and α_2 of the units with one and two reacted functional groups, respectively:

$$X_1/\varkappa_1 = \sum\sum k c_{kl} = \alpha_1 \tag{20a}$$

$$X_2/\varkappa_2 = \sum\sum l c_{kl} = \alpha_2 \tag{20b}$$

Hence, together with $X_0 = \alpha_0$, the set of X's with one subscript is equivalent to the set of α_i's in eq 3.

Also the set 19 of differential equations is fully equivalent to eq 4 derived by Gordon and Scantlebury.[7] In fact, the sets are identical; the difference is merely in notation.

Further differentiation of eq 12 with respect to x_1 and/or x_2 followed by putting $x_1 = 1/\varkappa_1$ and $x_2 = 1/\varkappa_2$ yields the sets of differential equations for the second[10] derivatives

$$\dot{X}_{11} = A^2 - 2\varkappa_1 X_{11} H \tag{21a}$$

$$\dot{X}_{12} = AB - [(\varkappa_1 + \varkappa_2)X_{12} - \varkappa_2 X_{11}]H \tag{21b}$$

$$\dot{X}_{22} = B^2 - 2\varkappa_2(X_{22} - X_{12})H \tag{21c}$$

and third derivatives of $\mathbb{H}$

$$\dot{X}_{111} = 3A(X_{111} + X_{112}) - 3\varkappa_1 X_{111} H \tag{22a}$$

$$\dot{X}_{112} = 2A(\varkappa_2 X_{11} + X_{112} + X_{122}) + B(X_{111} + X_{112}) - [(2\varkappa_1 + \varkappa_2)X_{112} - \varkappa_2 X_{111}]H \tag{22b}$$

$$\dot{X}_{122} = A(\varkappa_2 X_{11} + X_{112} + X_{122}) + 2B(2\varkappa_2 X_{12} + X_{122} + X_{222}) - [(\varkappa_1 + 2\varkappa_2)X_{122} - 2\varkappa_2 X_{112}]H \tag{22c}$$

$$\dot{X}_{222} = 3B(2\varkappa_2 X_{12} + X_{122} + X_{222}) - 3\varkappa_2(X_{222} - X_{122})H \tag{22d}$$

where

$$H = X_0 + X_1 + X_2 \tag{23a}$$

$$A = \varkappa_1 X_0 + X_{11} + X_{12} \tag{23b}$$

$$B = \varkappa_2 X_1 + X_{12} + X_{22} \tag{23c}$$

Table I
Moments of the Molecular Size Distribution in Homopolymerization of a Trifunctional Monomer As Derived from Equation 12 (Kinetic Approach) and from Equation 13, 14 and 17 (Cascade Theory)

kinetic theory	cascade theory
$P_n = 1/M_0 = 1/\mathbb{H}(\tau,1/\kappa_1,1/\kappa_2)$	$(1/2)(3X_0 + 2X_1/\varkappa_1 + X_2/\varkappa_2 - 1)$
Gel Point	
no explicit expression was found	$3X_0 + 4X_1/\varkappa_1 + X_2/\varkappa_2 = 1$
$P_w = M_2$	
$3X_0 - 2 - (1/\varkappa_2)X_2 + (2/\varkappa_1)^2 X_{11} + 2(2/\varkappa_1)(1/\varkappa_2)X_{12} + (1/\varkappa_2)^2 X_{22}$	$1 + [(2/\kappa_1)X_1 + (1/\varkappa_2)X_2 - 3(1 - X_0)]^2/[(4/\varkappa_1)X_1 + (3/\varkappa_2)X_2 - 3(1 - X_0)]$
$P_wP_z = M_3$	
$4 - 3X_0 + (3/\varkappa_2)X_2 - (6/\varkappa_1\varkappa_2)X_{12} - (3/\varkappa_2)^2 X_{22} + (2/\varkappa_1)^3 X_{111} + 3(2/\varkappa_1)^2(1/\varkappa_2)X_{112} + (6/\varkappa_1)(1/\varkappa_2)^2 X_{122} + (1/\varkappa_2)^3 X_{222}$	$1 - 3[(2/\varkappa_1)X_1 + (1/\varkappa_2)X_2 - (1 - X_0)][[(2/\kappa_1)X_1 + (1/\varkappa_2)X_2 - 3(1 - X_0)]/[(4/\varkappa_1)X_1 + (3/\varkappa_2)X_2 - 3(1 - X_0)]]^3$

The expressions for the *kinetic* moments of the molecular size distribution that involve appropriate X derivatives are presented in Table I together with expressions for the *statistical* moments, calculated according to the theory of branching processes (eq 13–15 and 17). For the sake of comparison, the statistical moments are expressed in terms of X_0–X_2, with α_3 eliminated by using eq 16.

The set of differential equations comprising eq 19a, 21, and 22 was solved numerically by using the standard fourth-order Runge–Kutta procedure with automatically adjusted length of integration step. Equations 19b and 19c were not included in the set since X_1 and X_2 are analytically expressible in terms of X_0 (cf. ref 1 and 7)

$$X_1 = \frac{\varkappa_1}{1 - \varkappa_1}[X_0^{\varkappa_1} - X_0] \tag{24a}$$

$$X_2 = \varkappa_1\varkappa_2\left[\frac{X_0}{(1 - \varkappa_1)(1 - \varkappa_2)} + \frac{X_0^{\varkappa_1}}{(1 - \varkappa_1)(\varkappa_2 - \varkappa_1)} + \frac{X_0^{\varkappa_2}}{(1 - \varkappa_2)(\varkappa_2 - \varkappa_1)}\right] \tag{24b}$$

For a given pair of $\varkappa_1$ and $\varkappa_2$, the X's with two or three subscripts were found to diverge all at the same time $\tau_{cr} > 0$. This time was identified with the gel point.[10] To approach in calculations this critical time as closely as possible, all X's were, shortly before it, replaced by their reciprocals (and eq 21 and 22 modified accordingly). The singularities were not removed in this way, but the gelation times (corresponding to numerical instability of calculations) were slightly higher than those obtained from the original equations or from equations with log X substituting X.

4. Gel Point

The cascade theory predicts the gel point conversion to be at[1,4,7,8,13]

$$F_1' = F_0''/F_0' = 1 \tag{25}$$

As one can easily verify, this condition reduces for $f = 3$ to

$$3\alpha_3 = \alpha_1 \tag{26}$$

and states that no infinite molecule appears in the system

Table II
Some Explicit Expressions for the Random Homopolymerization of a Trifunctional Monomer ($K_0 = K_1 = K_2 = 1$): y Stands for $\tau/3$

X_0	$1/(1 + y)^3$
X_1	$2y/(1 + y)^3$
X_2	$y^2/(1 + y)^3$
X_{11}	$4y/[3(1 + y)^4(1 - y)]$
X_{12}	$4y^2/[3(1 + y)^4(1 - y)]$
X_{22}	$4y^3/[3(1 + y)^4(1 - y)]$
ξ	$y/(1 + y)$
$P_n = 1/M_0$	$2(1 + y)/(2 - y)$
$P_w = M_2$	$(1 + 2y)/(1 - y)$
$P_z = M_3/M_2$	$1 - y + 3y(3 - y^2)/(1 - y)^3$

until the number of bonds emanating from branching units ($3\alpha_3$) reaches the number of units terminating the branches (α_1). As soon as $3\alpha_3 > \alpha_1$, there are not enough terminating units to saturate all branches and an infinite molecule must be formed.

With this reasoning, the length of branches and hence the number of units in the linear portions of molecules (units with two reacted functional group) is irrelevant.

At the gel point, all moments of the molecular size distribution higher than M_2, inclusive, diverge. Indeed, in the expressions for the *statistical moments*, M_2, M_3, etc., $1 - F_1'$ $(=(4/\varkappa_1)X_1 + (3/\varkappa_2)X_2 - 3(1 - X_0))$, appears in the denominator (cf. Table I).

For the kinetic moments, the situation is slightly different. Here, the *components* of the sums for M_2 and M_3 diverge.[10] Mathematically, the singularities correspond to the lack of convergence of the sum eq 8.

As expected, for the random case $K_0 = K_1 = K_2 = 1$, the gel point as well as the moments of molecular size distribution calculated by using the kinetic method is exactly the same as the respective quantities obtained by applying the cascade theory (or another statistical method). Some explicit expressions for this case are listed in Table II. In particular, one notices that X_{11}, X_{12}, and X_{22}, as well as M_2, diverge at $\tau_{cr} = 3$ (conversion degree, $\xi_{cr} = 0.5$) with the exponent $-\gamma = -1$, typical for the classical, mean-field theories of critical phenomena.[15] The z-average degree of polymerization, P_z (termed also the typical cluster size[16]), diverges with the exponent -2 (i.e., with the classical value of $\sigma = {}^1/_2$).

The gel points calculated for different sets of K_0, K_1, and K_2 by using both the statistical (eq 25) and kinetic (singular points on the time scale) methods are shown in Table III.

As can be seen, in all nonrandom cases, the gel points calculated kinetically are smaller than the statistical ones. The differences between τ^k and τ^s (or between ξ^k and ξ^s) in Table III are small or negligible for small substitution effects but become significant when the rate of formation of doubly reacted units (K_1) is high, while the formation of branching points (K_2) is suppressed, or vice versa.

It seems that, in the kinetic approach, the contribution of units that form linear portions of molecules is not irrelevant anymore; the doubly reacted units present in a great excess may contribute significantly to the appearance of a gel molecule. The same happens when trifunctional units are formed much faster than bifunctional ones.

The numbers in parentheses in the last column of Table III are the gel points calculated by Mikeš and Dušek in their Monte Carlo study.[1] Although their systems were limited in size (30 000 to 300 000 units), the gel conversions calculated by them remarkably well agree with the values obtained by using eq 12.

Similarly as for the random case, in all nonrandom cases studied in this work, the gel points were approached with the classical exponents $\gamma = 1$ and $\sigma = {}^1/_2$.

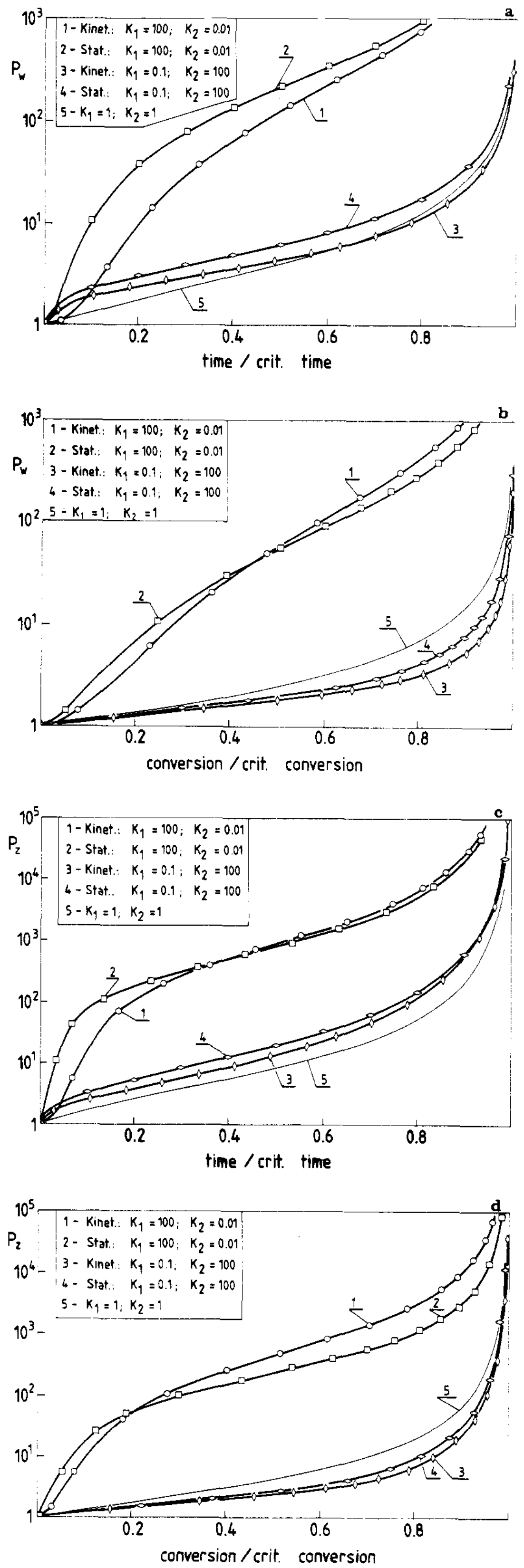

Figure 2. Weight- (a,b) and z-average (c,d) polymerization degrees in homopolymerization of a trifunctional monomer versus time (a,c) or conversion degree (b,d) relative to the gel point time or conversion, respectively. The curves were calculated by using the cascade (statistical) or kinetic theory.

5. Evolution of the Molecular Size Distribution

The calculated evolutions of weight- and z-average degrees of polymerization for kinetically controlled stepwise homopolymerization of a trifunctional monomer are presented in Figure 2. The calculations were performed

Table III
Time (τ) and Conversion Degree (ξ) at Gelation in the Stepwise Polymerization of a Trifunctional Monomer Calculated According to the Cascade Theory (Superscript s) and from the Kinetic Equation 12 (Superscript k)[a]

K_1	K_2	τ_{cr}^{s}	τ_{cr}^{k}	ξ_{cr}^{s}	ξ_{cr}^{k}
100	100	0.01732	0.01674	0.01546	0.01458
100	10	0.03908	0.3467	0.04088	0.03627
100	1	0.1018	0.07414	0.1069	0.07809
100	0.1	0.3122	0.1685	0.2534	0.1571 (0.167)
100	0.01	1.110	0.365	0.4593	0.2866
10	100	0.09062	0.08977	0.06226	0.06074 (0.061)
10	10	0.1829	0.1780	0.1324	0.1272 (0.132)
10	1	0.4397	0.4028	0.2836	0.2628 (0.267)
10	0.1	1.303	1.021	0.4771	0.4351 (0.440)
10	0.01	5.185	3.187	0.6089	0.5748 (0.578)
1	100	0.8119	0.8021	0.2836	0.2802
1	10	1.166	1.163	0.3467	0.3451
1	1	3.000	3.000	0.5000	0.5000 (0.501)
1	0.1	11.06	11.06	0.6171	0.6171
1	0.01	53.94	53.90	0.6569	0.6569
0.1	100	28.96	16.37	0.4979	0.4433
0.1	10	30.99	19.49	0.5006	0.4538
0.1	1	56.30	44.57	0.5217	0.4902
0.1	0.1	231.7	207.0	0.5772	0.5619
0.1	0.01	1090	1044	0.6331	0.6302 (0.630)
0.5	0.25	14.40	14.15	0.5866	0.5835 (0.582)
2	0.5	2.172	2.144	0.5038	0.5002 (0.503)

[a] The values in parentheses are Monte Carlo data from ref 1. In all examples, $K_0 = 1$.

for three different systems: the random one, $K_0 = K_1 = K_2 = 1$; the system with a rapid growth of linear fragments, $K_1 = 100$, and branch formation suppressed, $K_2 = 0.01$; and, finally, the system with branching much favored, $K_2 = 100$, and reduced growth to linear structures, $K_1 = 0.1$. In the last two cases, the "reference" reactivity of the first functional group of a unit was taken to be unity, $K_0 = 1$.

For each set of K_0, K_1, and K_2, the average degress of polymerization were calculated by using the cascade theory (statistical method) and from eq 18 (kinetic method) (cf. Table I).

For the random case, $K_0 = K_1 = K_2 = 1$, both methods led to the same results (thin curves). Different results were obtained for the other two sets of rate constants. Since the positions of gel points calculated by the two methods were also different (see Table III), the average polymerization degrees were plotted against time (Figure 2a,c) or conversion (Figure 2b,d) relative to respective critical values at the gel point.

6. Discussion

The results presented in sections 4 and 5 fully confirm the conclusions of Kuchanov and Povolotskaya[9,10,14] and of Mikeš and Dušek[1] (see also ref 17) about differences in molecular size distribution generated by statistical and kinetic methods. This means that, indeed, the statistical methods, including the cascade theory, are *not appropriate* to deal with kinetically controlled polymerization processes, except for the rather rare systems with equal and conversion-independent reactivities of functional groups. The reason for this has been explained by Dušek[17] and can be summarized as follows.

The statistical methods generate the molecular size distribution from the distribution of unit reaction states. At each moment of time (or conversion degree) the distribution is calculated anew and the method does not relate this distribution to what has or will happen to the system. With the Smoluchowski-like equation (eq 12), the situation is different. It keeps track of the whole distribution (or rather its generating function) as it changes with time.

It seems worthwhile to point out that the cascade theory and Smoluchowski-like approach yield identical distribution of units by states of their reactive groups; the sets of differential equations deduced by Gordon and Scantlebury[7] follow automatically from eq 12.

Obviously, the kinetic model presented in this work is too simplified to be verified against any particular real system. It is known that real systems gel at even higher conversions than predicted by the cascade theory. The shift in the gel point toward high conversion is believed to be caused mainly by cyclization and, in some cases, by steric hindrances.[17,18] These were not considered in this work.

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Appendix

Equation 12 was derived by using a method similar to that applied to the original Smoluchowski equation[12] by Kuchanov and Povolotskaya,[9,10] Kuchanov,[14] Ziff,[19] Dušek,[20] and others.[21] The method consists of writing down all possible rates at which an acyclic molecule built of i units with one reacted functional group and j unit with two reacted functional groups (shortly an (i,j)-mer) appears in or disappears from the system.[22]

For a trifunctional monomer, there are six different rates at which a molecule (including monomer) may disappear. The total disappearance rate is the sum of all these rates (the inappropriate terms cancel out automatically).

$$-\left(\frac{\mathrm{d}c_{ij}}{\mathrm{d}\tau}\right)_{\text{disapp}} = X_0(\varkappa_1 i c_{ij} + \varkappa_2 j c_{ij}) + c_{ij}[\varkappa_1 i(\sum_k\sum_l \varkappa_1 k c_{kl} + \sum_k\sum_l \varkappa_2 l c_{kl}) + \varkappa_2 j(\sum_k\sum_l \varkappa_1 k c_{kl} + \sum_k\sum_l \varkappa_2 l c_{kl})] \quad \text{(A-1)}$$

The reactions in which an $\{i,j\}$-mer is formed are shown in Figure 1. The types of molecules that react are specified under each of the six reaction schemes. The total rate of the appearance of i,j-mer is

$$\left(\frac{\mathrm{d}c_{ij}}{\mathrm{d}\tau}\right)_{\text{app}} = X_0[\varkappa_1 i c_{ij-1} + \varkappa_2(j+1)c_{i-1,j+1}] + \frac{1}{2}\sum_{k=2}^{i-2}\sum_{l=1}^{j-1}\varkappa_1^2(k+1)(i-k+1)c_{k+1,l-1}c_{i-k+1,j-l-1} + \sum_{k=2}^{i-2}\sum_{l=0}^{j-1}\varkappa_1\varkappa_2(i-k+1)(l+1)c_{kl+1}c_{i-k+1,j-l-1} + \frac{1}{2}\sum_{k=2}^{i-2}\sum_{l=0}^{j-1}\varkappa_2^2(l+1)(j-l+1)c_{kl+1}c_{i-k,j-l+1} \quad \text{(A-2)}$$

with an additional term, $^1/_2X_0^2$, for dimer ($\{2,0\}$-mer) only.

The $^1/_2$'s take care for double counting while considering the symmetric reactions.

Now, multiplication of $(A-1) + (A-2)$ by $(\varkappa_1 x_1)^i(\varkappa_2 x_2)^j$ followed by summing over all i's and j's yields eq 12.

Recently, it was shown[11] that the form of eq 12 does not change for homopolymerization of an f-functional monomer with an arbitrary $f > 2$. Then the size distribution generating function takes the form

$$\mathbb{H}(\tau,x_1,x_2,\ldots,x_{f-1}) + X_0(\tau) + \sum_{n_1=2}^{\infty}\sum_{n_2=0}^{\infty}\ldots\sum_{n_{f-1}=0}^{\infty} c_{\mathbf{n}}(\tau)\prod_{r=1}^{f-1}(\varkappa_r x_r)^{n_r} \quad \text{(A-3)}$$

and its time evolution is described by

$$\frac{\partial \mathbb{H}}{\partial \tau} = \frac{1}{2}\left[(\varkappa_1 x_1)X_0 + (\varkappa_2 x_2)\frac{\partial \mathbb{H}}{\partial x_1} + \ldots + (\varkappa_{f-1}x_{f-1})\frac{\partial \mathbb{H}}{\partial x_{f-2}} + \frac{\partial \mathbb{H}}{\partial x_{f-1}}\right]^2 - (X_0 + X_1 + \ldots + X_{f-1})\left[X_0 + (\varkappa_1 x_1)\frac{\partial \mathbb{H}}{\partial x_1} + \ldots + (\varkappa_{f-1}x_{f-1})\frac{\partial \mathbb{H}}{\partial x_{f-1}}\right] \quad \text{(A-4)}$$

with the meaning of symbols being analogous to those in eq 8 and 12. $\mathbf{n} = (n_1,n_2,\ldots,n_{f-1})$ is the vector with the number of units in the molecule having 1, 2, ..., f–1 reacted functional groups.

The moments of distribution

$$M_k = X_0 + \sum\sum\ldots\sum\{[(f-1)n_1 + (f-2)n_2 + \ldots + n_{f-1}]/(f-2)\}^k c_{\mathbf{n}} \quad \text{(A-5)}$$

can be extracted from (A-4) in exactly the same way as for $f = 3$.

From the practical point of view, however, more important seems to be the possibility of applying the present kinetic approach to multicomponent systems, too. The merit is in the proper choice of the generating function $\mathbb{H}$.

For an alternating copolymerization of a trifunctional monomer with a bifunctional one, the choice of $\mathbb{H}$ might be

$$\mathbb{H}(\tau,x_1,x_2,y) = X + Y + \sum_{i=1}^{\infty}\sum_{j=0}^{\infty}\sum_{k=0}^{\infty} c_{ijk}[\varkappa_1 x_1]^i[\varkappa_2 x_2]^j[ny]^k \quad \text{(A-6)}$$

and the kinetic equation might be

$$\frac{\partial \mathbb{H}}{\partial \tau} = \left(\varkappa_1 x_1 X + \varkappa_2 x_2 \frac{\partial \mathbb{H}}{\partial x_1} + \frac{\partial \mathbb{H}}{\partial x_2}\right)\left(\eta y Y + \frac{\partial \mathbb{H}}{\partial y}\right) - (X + \mathbb{H}_x + \mathbb{H}_y)\left(y + \eta y \frac{\partial \mathbb{H}}{\partial y}\right) - (y + \mathbb{H}_y)\left(X + \varkappa_1 x_1 \frac{\partial \mathbb{H}}{\partial x_1} + \varkappa_2 x_2 \frac{\partial \mathbb{H}}{\partial x_2}\right) \quad \text{(A-7)}$$

where X and Y are the fractions of unreacted tri- and bifunctional monomer, respectively, $\mathbb{H}_* = \partial \mathbb{H}/\partial *|_{x_1=1/\varkappa_1,x_2=2/\varkappa_2,y=1/\eta}$, and $\varkappa_1 = 2K_{1x}/3K_{0x}$, $\varkappa_2 = K_{2x}/3K_{0x}$, and $\eta = K_{1y}/2K_{0y}$ are the ratios of the appropriate contributions of the unit substitution states to the rate constants of reacting groups.

Further details on the application of eq A-7 will be published separately.

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(22) The equation analogous to (A-4)

$$\frac{\partial g}{\partial t} = N\sum_{i=0}^{f-1}\sum_{j=0}^{f-1}\tilde{k}_{ij}\{-\lambda_i s_j S_j + (1/2)s_{i+1}s_{j+1}S_iS_j\} \quad (*)$$

was derived in ref 9 for the generating function $g(\mathbf{s},t) = \sum_{\mathbf{l}} c(\mathbf{l},t)\prod_{i=0}^{f} s_i^{l_i}$, where $c(\mathbf{l},t)$ is the concentration of molecules that share the numbers $\mathbf{l} = l_0, l_1, \ldots, l_f$ of units with 0, 1, ..., f reacted functional groups; $\mathbf{s} = s_0, s_1, \ldots, s_f$ is dummy variable; t is time; $\tilde{k}_{ij} = (f-i)(f-j)k_{ij}$ are rate constants; $S_i = \partial g/\partial s_i$, and $\lambda_i = S_i(\mathbf{l},t)$. The equation of Kuchanov and Povolotskaya has $2f^2$ terms as compared with $f(f+1)$ terms of eq A-4, and it seems to underestimate the rates of appearance of some molecules. Full equivalence between eq A-4 and * is regained by substituting $^1/_2$ in eq * by $1/(1+\delta_{ij})$ where δ_{ij} is the Kronecker δ function.