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A Kinetic Approach to the Network Formation in an Alternating Stepwise Copolymerization

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ABSTRACT: A Smoluchowski-like coagulation equation is used for calculating the molecular size distribution in kinetically controlled stepwise copolymerization of 3- and 2-functional monomers up to the gel point. In the systems where the reactivities of functional groups are affected by the substitution effect, the present method predicts different distributions and gel point conversions than the cascade theory.

1. Introduction

The theories of network formation in polymerization processes provide the means for calculating various molecular parameters, e.g., the averages of molecular weight, as they change with time or conversion up to, and beyond, the characteristic moment where gelation transition occurs. The statistical theories developed by Flory,[1] Stockmayer,[2] Gordon,[3] and others[4-8] dominated the field for many years and laid the groundwork for the understanding of the whole cross-linking process, including the transition at gelation. All these theories were essentially equivalent. They differed mainly in the mathematical language applied.

Gordon and co-workers[3,9,10] introduced to polymer science a particularly fruitful method based on the stochastic theory of branching processes.[11,12] With this method, from reaction paths and reactivities of species not only molecular size distribution but also the particle scattering factor,[13,14] configurational parameters,[15] elasticity of resulting networks,[16-18] etc., could be calculated without much difficulty.

In the mid-1970s, however, the classical statistical theories of network formation started to be criticized from two flanks. Stauffer[19,20] questioned the ability of the theories to predict correctly the behavior of systems near gelation. The blame was put on neglect of the long-range correlations and concentration fluctuations that seemed to play an important role in gelation transition. In fact, the first reproach was not strictly correct. There existed already the *spanning tree approximation* within the theory of branching processes[21] and the *rate theory* of Stepto et al.[22] that dealt with long-range correlations, while taking into account intramolecular cyclization in cross-linking polymerization.

The other criticized aspect of the classical theories was the statistical character of the majority of the methods used. Kuchanov and his co-workers[23,24] (see also Dušek[25]) pointed out that the statistical methods were appropriate to deal with equilibrium systems only and yielded incorrect molecular size distributions for kinetically controlled processes with the substitution effect (see below).

To illustrate this, Kuchanov and Povolotskaya[24] calculated molecular weight distributions in a kinetically controlled polymerization of a bifunctional monomer (RA_2 system) by using both statistical and kinetic methods. The latter was based on an original single kinetic equation describing the whole polymerizing system. Nota bene, nearly 40 years earlier, another kinetic equation, the Smoluchowski coagulation equation, was shown by Stockmayer[2] to produce the *equilibrium* molecular weight distribution for the kinetically controlled *random f*-functional polymerization (RA_f system) (see also ref 28). Kuchanov and Povolotskaya showed that when monomers reacted nonrandomly, with, say, the substitution effect, the distributions calculated with the two methods differed significantly.

Mikeš and Dušek[27] used Monte Carlo calculations to analyze the distribution of molecular sizes in kinetically controlled polymerization of an RA_3 monomer with functional groups reacting with the substitution effect. Their results were compared with those calculated by using the theory of branching processes. Significant differences were found, even in the position of gel point on the conversion scale. Identical conclusions were published simultaneously by Kuchanov and Povolotskaya[28] and confirmed later for the same RA_3 system.[29]

In this work, another model polymerization system is analyzed. An alternating stepwise copolymerization (copolycondensation) (RA_3 + $R'B_2$ system) is considered where the reactivities of functional groups are modified by the substitution effect. The classical statistical approach (section 3) is again compared with kinetic theory on the basis of a Smoluchowski-like equation (section 2). The conversion at gel point is calculated in section 4 as a function of monomer composition and the substitution effect. The number- and weight-average degrees of polymerization are discussed in section 5.

For the sake of simplicity, only the so-called *first-shell substitution effect*[10] is taken into account. With this effect, a monomer has its functional groups equally reactive until one group has reacted. Then, the remaining groups are again equally reactive, but with reactivity different than before. The same applies to the two groups in the once-reacted RA_3 unit.

2. Kinetic Theory

Consider a system in which a trifunctional monomer, RA_3, reacts with a bifunctional one, $R'B_2$. The A groups react only with B ones and vice versa. The reactivities of groups are altered by at most the first-shell substitution effect (mean-field approximation), and intramolecular reactions are disregarded (long-range correlations are neglected).

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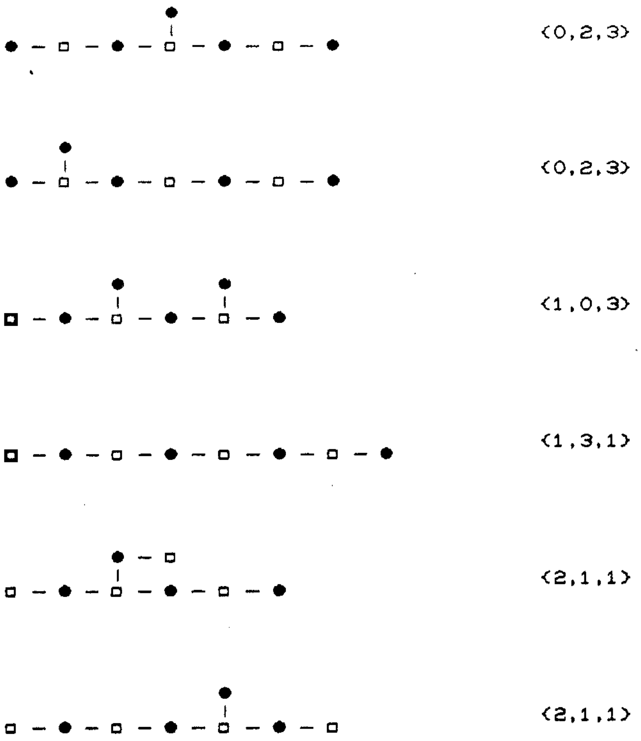

Figure 1. Several molecules of an alternating copolymer, $RA_3 + R'B_2$, with $n = 8$ units. The sets of three numbers on the right are sufficient enough to characterize the size of the molecules and the numbers of functional groups of a different kind (reactivity). Structural isomers, however, are indistinguishable.

For illustration, a few molecules containing $n = 8$ units are shown schematically in Figure 1. It is not difficult to see that, for any $n > 1$, one may write down the following relationships linking the size (n) or the number of bonds ($n - 1$) in an acyclic molecule with the numbers of units of a different substitution degree

$$\begin{aligned} n &= n_{A_1} + n_{A_2} + n_{A_3} + n_{B_1} + n_{B_2} \\ n - 1 &= n_{A_1} + 2n_{A_2} + 3n_{A_3} \\ n - 1 &= n_{B_1} + 2n_{B_2} \end{aligned} \qquad (1)$$

where n_{A_i} and n_{B_j} (i = 1–3, j = 1, 2) are the numbers of RA_3 or $R'B_2$ units with i or j reacted functional groups, respectively.

Elimination of n_{A_3} and n_{B_2} yields

$$n = 4n_{A_1} + 2n_{A_2} + 3n_{B_1} - 5 \qquad (2)$$

Hence, the set of just three numbers, n_{A_1}, n_{A_2}, and n_{B_1}, sufficiently characterizes the size of copolymer molecules. Furthermore, with these three numbers one knows exactly how many groups of various reactivities each molecule has.

Let the concentration of all molecules (structural isomers) that share the set (i,j,k) of numbers n_{A_1}, n_{A_2}, and n_{B_1} be denoted as c_{ikj} and defined as the number of these molecules divided by the total number, $N \to \infty$, of units in the system (volume is assumed to be constant). Let the concentrations of unreacted monomers RA_3 and $R'B_2$ (i.e., the numbers of these monomers divided by N) be X and Y, respectively (initially, at time zero $X = X_0$; $Y = Y_0$; $X_0 + Y_0 = 1$).

Now, consider all elementary reactions that may take place in the system. All these reactions are shown schematically in Figure 2. The reactions are irreversible; the polymerization process is kinetically controlled.

Relatively simple reasoning on the additivity of activation energies explains the product form of the rate constants.[10,27,29] Each rate constant consists of the substitution-independent term, k^*, and the contributions k_i and k_j (i = 0–2; j = 0, 1) related to the substitution degree of RA_3 and $R'B_2$ units, respectively. Since the k values are related to the functional groups only, the actual rate constants have to be premultiplied by the number of groups of a given type that may enter into the reaction.

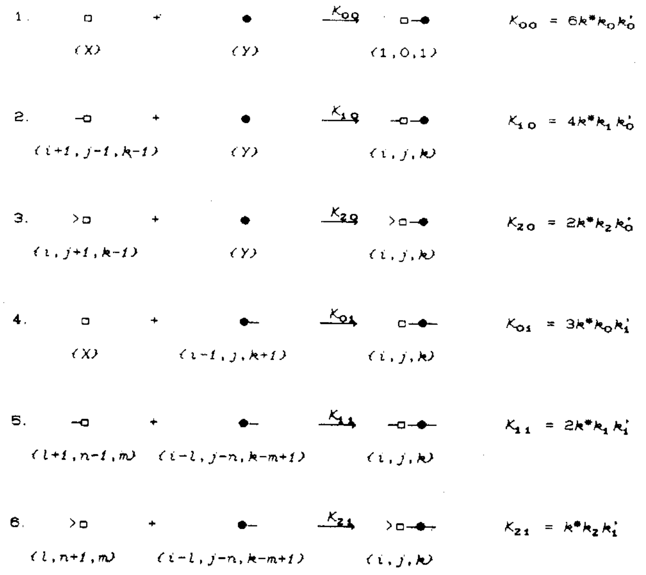

Figure 2. Six elementary reactions in alternating copolymerization and respective rate constants describing link formation between *units* (not functional groups or molecules) that are in different reaction states. The types of molecules that yield an $\{i,j,k\}$-mer are specified under each reaction scheme. The open squares and filled circles symbolize tri- and bifunctional units, respectively.

All reactions shown in Figure 2 are bimolecular. Therefore, it is possible to rescale the time by multiplying its units by $6k^*k_0k_0$ to have the rate constant in the first reaction in Figure 2 equal to 1. In this way, the reactivity of the whole system can be described in terms of not more than the following three reduced rate constants

$$\begin{aligned} a &= 2k_1/3k_0 \\ b &= k_2/3k_0 \\ c &= k_1'/2k_0' \end{aligned} \qquad (3)$$

(For example, the rate constant of the fourth reaction in Figure 2, in these new time units would simply be ac.)

The change in the distribution of the size of the molecules formed in copolymerization is conveniently analyzed by using a generating function of this distribution, say, the function

$$\mathcal{H}(\tau, x, y, z) = X(\tau) + Y(\tau) + \sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\sum_{k=0}^{\infty} c_{ijk}(\tau)\,[ax]^i[by]^j[cz]^k \qquad (4)$$

$$|x| \le 1/a, \quad |y| \le 1/b, \quad |z| \le 1/c$$

where $\tau = 6tNk^*k_0k_0'$ is the scaled time and x, y, and z are dummy variables used to transform the discrete distribution (set of c_{ijk}) into a continuous polynomial function in which the concentrations are the coefficients at respective powers of ax, by, and cz. The point in using ax, by, and cz instead of, say, x, y, z is that, in differentiation of $\mathcal{H}$ with respect to, say, x, all c_{ijk} become premultiplied by ai. The value of the derivative along the lines $x = 1/a$, $y = 1/b$, and $z = 1/c$ is the sum of terms aic_{ijk} that appear in the expressions describing the rates at which $\{i,j,k\}$-mers enter into reactions with one of their groups on a once-reacted RA_3 unit (there are i of such units in an $\{i,j,k\}$-mer and each contributes to the reaction rate with the relative rate constant a).

It is now left to the reader to verify that, in the copolymerization process with elementary reactions shown in Figure 2, generating function (4) changes with time τ according to the Smoluchowski-like equation

$$\frac{\delta\mathcal{H}}{\delta\tau} = \left(axX + by\frac{\delta\mathcal{H}}{\delta x} + \frac{\delta\mathcal{H}}{\delta y}\right)\left(czY + \frac{\delta\mathcal{H}}{\delta z}\right) - (X + \mathcal{H}_x + \mathcal{H}_y)\left(Y + cz\frac{\delta\mathcal{H}}{\delta z}\right) - (Y + \mathcal{H}_z)\left(X + ax\frac{\delta\mathcal{H}}{\delta x} + by\frac{\delta\mathcal{H}}{\delta y}\right) \quad (5)$$

where

$$\mathcal{H}_* = \delta\mathcal{H}/\delta^*|_{x=1/a,y=1/b,z=1/c} \quad (6)$$

(* stands for x, y, or z.)

The hint is to write down a general kinetic equation that includes terms for all reactions in which an $\{i,j,k\}$-mer may appear in, or disappear from, the system. On the right-hand side there should be 6 positive and 12 negative terms for the appearance and disappearance of molecules, respectively. These terms correspond to the "products" and "reagents" in the reactions presented in Figure 2. Multiplication of the thus obtained general kinetic equation by $[ax]^i[by]^j[cz]^k$ followed by summation over all i, j, and k yields eq 5 (cf. refs 29 and 30).

Equation 5 was derived in an identical manner to eq 12 in ref 29 and eq 4 in ref 24 where kinetically controlled homopolymerization of an RA_f monomer was considered. Although the resemblance of the form of eq 5 above to that of the original Smoluchowski equation[31] is not as striking as in the previous cases,[29,30] we still consider it to be Smoluchowski-like because the meaning of the terms in eq 5 is again the same as in the original Smoluchowski equation.

We were not able to solve eq 5 explicitly to obtain the distribution function $c_{ijk}(\tau)$. It was possible, however, to extract moments of this distribution (cf. ref 28) or, even more conveniently, moments of the molecular size distribution. According to eq 2 the latter are defined thus

$$M_r(\tau) = X(\tau) + Y(\tau) + \sum\sum\sum[4i + 2j + 3k - 5]^r c_{ijk}(\tau) \quad (7)$$

The terms of the triple sum in eq 7 obtained by raising the bracketed expression to the rth power can be calculated as appropriate derivatives of $\mathcal{H}$ of order at most r with respect to x, y, and/or z evaluated at $x = 1/a$, $y = 1/b$, $z = 1/c$.

To illustrate this, let us consider the term $\sum\sum\sum i^2 c_{ijk}$. It can be written as $\sum\sum\sum i(i-1)c_{ijk} + \sum\sum\sum ic_{ijk}$ or $(1/a^2)\delta^2\mathcal{H}/\delta x^2|_{x=1/a,y=1/b,z=1/c} + (1/a)\delta\mathcal{H}/\delta x|_{x=1/a,y=1/b,z=1/c}$ or $\mathcal{H}_{xx}/a^2 + \mathcal{H}_x/a$. The derivatives $\mathcal{H}_{xx}$ and $\mathcal{H}_x$ as well as other derivatives of $\mathcal{H}$ are available after solving sets of ordinary differential equations resulting from differentiating eq 5. Details are presented in the Appendix.

3. Theory of Branching Processes

For the system $RA_3 + R'B_2$, the link probability generating function used by the theory of branching processes (cascade theory) is the vector function[3,11,15]

$$\mathbf{F}_0(\mathbf{s}) = (F_{0A}(\mathbf{s}), F_{0B}(\mathbf{s})) \quad (8)$$

which has the vectorial dummy argument $\mathbf{s} = (s_A, s_B)$. The components of F_0 are the link probability generating functions for RA_3 units

$$F_{0A}(\mathbf{s}) = p_0 + p_1 s_B + p_2 s_B^2 + p_3 s_B^3 \quad (9)$$

and $R'B_2$ units

$$F_{0B}(\mathbf{s}) = q_0 + q_1 s_A + q_2 s_A^2 \quad (10)$$

The coefficients p_i and q_j ($i = 0, ..., 3$; $j = 0, ..., 2$) are the time-dependent (or conversion-dependent) link probabilities. Thus, p_i (q_j) denotes the probability that an RA_3 ($R'B_2$) unit has i (j) reacted functional groups. Because of the alternating character of reaction, the link probability generating function for the RA_3 unit is a function of s_B only and vice versa. Indeed, any link emanating from the RA_3 unit leads necessarily to the $R'B_2$ one.

Clearly, the probabilities p_i and q_j can be identified with fractions of units having i and j reacted functional groups, respectively. Thus

$$p_0 = X/X_0; \quad p_1 = \mathcal{H}_x/aX_0$$

$$p_2 = \mathcal{H}_y/bX_0; \quad p_3 = 1 - p_0 - p_1 - p_2 \quad (11)$$

$$q_0 = Y/Y_0; \quad q_1 = \mathcal{H}_z/cY_0; \quad q_2 = 1 - q_0 - q_1 \quad (12)$$

where $X_0 = X(0)$ and $Y_0 = Y(0)$ are the initial concentrations of the RA_3 and $R'B_2$ units (i.e., at $\tau = 0$), respectively.

The moments of the molecular size distribution at certain a time or conversion are given by the standard equations[15]

$$M_0 = P_n^{-1} = 1 - (1/2)\,\mathbf{j}\mathbf{F}_0'\mathbf{n} \quad (13)$$

$$M_2 = P_w = \mathbf{j}[\mathbf{1} + (\mathbf{1} - \mathbf{F}_1')\mathbf{F}_0']\mathbf{n} \quad (14)$$

where $\mathbf{j} = (1,1)$, $\mathbf{n} = (X_0, Y_0)^T$; $\mathbf{1}$ is the 2×2 identity matrix, $\mathbf{F}_0'$ and $\mathbf{F}_1'$ are the 2×2 matrices of derivatives of $\mathbf{F}_0$ and $\mathbf{F}_1$ with respect to $\mathbf{s}$ and

$$\mathbf{F}_1(\mathbf{s}) = (F_{1A}(\mathbf{s}), F_{1B}(\mathbf{s})) \quad (15)$$

where

$$F_{1*} = \frac{dF_{0*}/ds_A + dF_{0*}/ds_B}{dF_{0*}/ds_A|_{s=1} + dF_{0*}/ds_B|_{s=1}} \qquad * = A, B \quad (16)$$

As shown in eqs 13 and 14, the moments of the molecular size distribution M_0 and M_2 are directly related to the number, P_n, and weight, P_w, average molecular weights in the system. More strictly $P_n = M_1/M_0$ and $P_w = M_2/M_1$, but, before gelation, $M_1 = 1$, by definition (eq 7).

The elements of matrices $\mathbf{F}_0'$ and $\mathbf{F}_1'$ are defined as

$$\mathbf{F}_*' = \begin{bmatrix} F_{*A}{}^A & F_{*B}{}^A \\ F_{*A}{}^B & F_{*B}{}^B \end{bmatrix} \quad (17)$$

where $F_{*r}{}^u = dF_{*t}/ds_u|_{s=1}$ ($* = 0, 1$; t, u = A, B).

For the alternating system considered here $F_{*A}{}^A = F_{*B}{}^B = 0$ and eqs 13 and 14 take the following, simpler forms

$$M_0 = 1 - (1/2)(F_{0A}{}^B X_0 + F_{0B}{}^A Y_0) \quad (18)$$

$$M_2 = 1 + \frac{F_{0A}{}^B(F_{1B}{}^A + 1)X_0 + F_{0B}{}^A(F_{1A}{}^B + 1)Y_0}{1 - F_{1A}{}^B F_{1B}{}^A} \quad (19)$$

which can be used directly in calculations after expressing the probabilities appearing in F's in terms of the quantities defined by eqs 11 and 12.

4. Gel Point

The sets of 11 differential equations for the functions X and Y, $\mathcal{H}_x$, ..., $\mathcal{H}_{xy}$, $\mathcal{H}_{zz}$ (see the Appendix) were solved numerically by using a fifth-order Sehlberg method.[32] The

Table I
Critical Time, τ, and Conversion, ξ, at the Gel Point in Copolycondensation of 3- and 2-Functional Monomers, Calculated by Using the Smoluchowski-like Kinetic Equation 5 (Superscript "k") and by Using Statistical (Cascade) Theory (Superscript "s")[a]

X_0		$k_1 = 10$, $k_2 = 10$, $k_{1'} = 10$	$k_1 = 10$, $k_2 = 10$, $k_{1'} = 0.1$	$k_1 = 0.1$, $k_2 = 0.1$, $k_{1'} = 10$	$k_1 = 10$, $k_2 = 0.1$, $k_{1'} = 10$	$k_1 = 1$, $k_2 = 1$, $k_{1'} = 1$	$k_1 = 0.1$, $k_2 = 10$, $k_{1'} = 0.1$
0.3	τ_{cr}^{k}	0.6113	no gel	22.99	5.262	15.59	no gel
	τ_{cr}^{s}	0.6473	no gel	21.93	5.373	15.59	no gel
	$\xi_{A,cr}^{k}$	0.3023	no gel	0.6483	0.6918	0.8819	no gel
	$\xi_{A,cr}^{s}$	0.3227	no gel	0.6386	0.6934	0.8819	no gel
0.4	τ_{cr}^{k}	0.5773	21.87	27.66	3.580	12.07	326.5
stoichiometric mixture ($\xi_A = \xi_B$)	τ_{cr}^{s}	0.6125	21.49	27.27	4.221	12.07	398.1
	ξ_{cr}^{k}	0.2427	0.6681	0.6060	0.6048	0.7071	0.7005
	ξ_{cr}^{s}	0.2600	0.6859	0.6036	0.6267	0.7071	0.7242
0.5	τ_{cr}^{k}	0.5887	16.49	50.99	3.305	13.79	386.5
	τ_{cr}^{s}	0.6262	15.24	55.62	4.399	13.79	408.7
	$\xi_{B,cr}^{k}$	0.3041	0.7270	0.8610	0.7585	0.8660	0.8389
	$\xi_{B,cr}^{s}$	0.3261	0.7144	0.8739	0.8133	0.8660	0.8466

[a] X_0 is the initial molar fraction of the 3-functional monomer. The meaning of the rate constants is explained in the text. In all examples $k_0 = k_0' = 1$. ξ_A and ξ_B are the conversion degrees of 3- and 2-functional monomers, respectively ($\xi_B = \xi_A[3X_0/(2 - 2X_0)]$). The values related to the minor component are shown in the table.

calculations were made for different values of rate constants k_1, k_2, and k_1' and for several initial molar ratios of monomers, X_0/Y_0. The "kinetic" gel points were identified with the values at which the instability of calculations had been encountered. The instability corresponded to the divergence of the second derivatives of $\mathcal{H}$.

In parallel calculations, the "statistical" gel points were calculated too by solving the equation

$$F_{1A}{}^{B}F_{1B}{}^{A} = 1 \tag{20}$$

at which, as follows from eq 19, the weight-average degree of polymerization diverges. This gelation condition is expressed in terms of the first derivatives of $\mathcal{H}$ only; the calculations were not accompanied by any numerical instability.

In the randomly reacting alternating copolymerization system, gelation may occur at the range of initial molar fractions of a trifunctional monomer, X_0, from $^1/_4$ to $^4/_7$ (cf. ref 1). Some of the results obtained in that range are presented in Table I. Except for the random case, the kinetic theory gave different critical times and conversions than the statistical approach. In some cases no gelation occurred for $X_0 = 0.3$. The weight average polymerization degree increased extremely slowly in calculations, allowing the conversion degree, ξ_A, to grow steadily and reach unity. This happened for the slow reaction of the second groups in a bifunctional monomer ($k_1' = 0.1$), with the monomer used in excess. Clearly, the reason was that small molecules were formed with branches terminated by slowly reacting bifunctional units. Before any large structures could be formed, all groups in the trifunctional monomer have been consumed.

In the homopolymerization of a trifunctional monomer analyzed previously,[29] the kinetic gel points were always at lower time or conversion degree than the statistical ones (except for the random case). The larger the differences in gel point conversion were, the higher the differences in reactivities of groups in mono- and disubstituted units (and none for the random polymerization). In the present case of alternating copolymerization, the kinetic gel points were not necessarily at lower times than the statistical ones. Higher critical conversions were obtained in kinetic calculations for the systems where the reactivity of functional groups in the minor component was substantially smaller than that of groups in the component used in excess (e.g., $k_1 = k_2 = 0.1$ and $k_1' = 10$ for $X_0 = 0.3$, $X_0 = 0.4$, or $k_1 = k_2 = 10$ and $k_1' = 0.1$ for $X_0 = 0.5$; see Table I). For other combinations of reactivities, the kinetic gel points were smaller than the statistical ones, similar to those for homopolymerization.[29]

It seems worthy of reminder at this point that the present method counts only acyclic, treelike structures. The waste of functional groups for cycle formation is considered to be the main reason for the shift of experimentally measured gel points toward higher conversions than predicted by statistical theories.[1,25]

5. Number- and Weight-Average Degrees of Polymerization

After $\mathbf{F}_0'$ is expressed in terms of p_i's and q_i's (eqs 8–10) and these in turn are expressed in terms of X and Y and the appropriate derivatives of $\mathcal{H}$ (eqs 11 and 12), eq 3 for the reciprocal number-average degree of polymerization reads

$$M_0 = 1 - (1/2)[(3X_0 - 3X - 2\mathcal{H}_x/a - \mathcal{H}_y/b) + (2Y_0 - 2Y - \mathcal{H}_z/c)] \tag{21}$$

It is not difficult to verify that the right-hand side of eq 21 fulfills the differential equation

$$\dot{\mathcal{H}} \equiv \delta\mathcal{H}/\delta\tau|_{x=1/a,y=1/b,z=1/c} = -(Y + \mathcal{H}_z)(X + \mathcal{H}_x + \mathcal{H}_y) \tag{22}$$

(use the set of eqs A-1–A-5 in the Appendix). This proves that the statistical and kinetic number-average degrees of polymerization are the same since eq 13 is equivalent to eq 7 with $r = 0$.

The weight-average degree of polymerization for the random copolymerization ($k_0 = k_1 = k_2 = k_0' = k_1' = 1$) can be calculated by using the well-known (statistical) equation derived by Stockmayer,[33] which for a stoichiometric mixture ($X_0 = {}^2/_5$, $Y_0 = {}^3/_5$), reduces to

$$P_w = 1 + (6/5)\frac{\xi(3\xi + 2)}{1 - 2\xi^2} \tag{23}$$

where $\xi = \xi_A = \xi_B$ is the conversion degree of functional groups.

As it should be, the same result is obtained from the cascade theory (eq 19). It is easy to verify, since then we get $F_{0A}' = 3\xi$, $F_{0B}' = 2\xi$, $F_{1A}' = 2\xi$, and $F_{1A}' = \xi$.

For this same stoichiometric random case we were able to find analytical solutions for all derivatives of $\mathcal{H}$ needed for calculating M_2 (see Table A-2 in the Appendix). The

Table II
Functions Appearing in the Differential Equation A-6

t	u	$\mathcal{P}$	$\mathcal{Q}$	$\mathcal{R}$	$\mathcal{S}$
x	x	$-2a\mathcal{H}_{xx}$	0	$aX + \mathcal{H}_{xx} + \mathcal{H}_{xy}$	$\mathcal{H}_{xz}$
x	y	$b\mathcal{H}_{xx} - (a + b)\mathcal{H}_{xy}$	0		
x	z	$-a\mathcal{H}_{xz}$	$-c\mathcal{H}_{xz}$		
y	y	$2b(\mathcal{H}_{xy} - \mathcal{H}_{yy})$	0	$b\mathcal{H}_x + \mathcal{H}_{xy} + \mathcal{H}_{yy}$	$\mathcal{H}_{yz}$
y	z	0	$-c\mathcal{H}_{yz}$		
z	z	0	$-2c\mathcal{H}_{zz}$	$\mathcal{H}_{xz} + \mathcal{H}_{yz}$	$cY + \mathcal{H}_{zz}$

Table III
Functions Fulfilling the Set of Equations A-1–A-6 for the Random ($a = {}^2/_3$, $b = {}^1/_3$, $c = {}^1/_2$) and Stoichiometric ($X_0 = {}^2/_5$, $Y_0 = {}^3/_5$) Alternating Copolymerization of Tri- and Bifunctional Monomer[a]

$\xi = \tau(\tau + 5)$	$X = (1/5)(1 - \xi)^3$
$y = (3/5)(1 - \xi)^2$	$\mathcal{H}_x = (4/5)(1 - \xi)^2\xi$
$\mathcal{H}_z = (3/5)(1 - \xi)\xi$	$\mathcal{H}_y = (2/5)(1 - \xi)\xi^2$
$\mathcal{H}_{xx} = (8/15)\dfrac{(1 - \xi)^4\xi^2}{1 - 2\xi^2}$	$\mathcal{H}_{xz} = (2/5)\dfrac{(1 - \xi)^3\xi}{1 - 2\xi^2}$
$\mathcal{H}_{xy} = (8/15)\dfrac{(1 - \xi)^3\xi^3}{1 - 2\xi^2}$	$\mathcal{H}_{yz} = (2/5)\dfrac{(1 - \xi)^2\xi^2}{1 - 2\xi^2}$
$\mathcal{H}_{yy} = (8/15)\dfrac{(1 - \xi)^2\xi^4}{1 - 2\xi^2}$	$\mathcal{H}_{zz} = (3/5)\dfrac{(1 - \xi)^2\xi^2}{1 - 2\xi^2}$

[a] $\xi = \xi_A = \xi_B$ is the conversion of functional groups, and τ is the time.

terms of the sum required by eq 7 for $r = 2$ add up nicely to yield eq 23, again.

For the random copolymerization with different initial monomer compositions, identical weight-average degrees of polymerization were obtained in numerical calculations carried out by using both the kinetic and statistical approaches. As, however, the substitution effect became operative, the two methods of calculation yielded different results, similar to those in the homopolymerization of a trifunctional monomer.[29]

The reason for differences in the results obtained by using the alternative models seems now to be well understood.[25–28] The statistical approach is appropriate to the description of equilibrium processes, whereas the kinetic model is good for irreversible (kinetically controlled) polymerizing systems. For the random cases only the two models are equivalent.[2,25,26] The statistical analysis consists of the building up of the size distribution of a *single* molecular tree by compounding probabilities of link formation. In an equilibrium system only, every molecule may have the distribution calculated in that way (we mean, of course, the model system fulfilling all simplifying assumptions).

On the other hand, the kinetic calculations based on Smoluchowski-like equations keep track of the whole size distribution in an infinite system as the links are gradually added. No link rearrangement is possible.

Detailed considerations on the mathematical models underlying the statistical and kinetic approaches will be published separately.[34]

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Appendix

The moments of the molecular size distribution are expressed in terms of the partial derivatives of $\mathcal{H}$ calculated along the line $x = 1/a$, $y = 1/b$, and $z = 1/c$. These derivatives can be evaluated by solving the sets of ordinary differential equations obtained by differentiating eq 5 with respect to x, y, and/or z followed by substituting = $1/a$, $y = 1/b$, and $z = 1/c$. Note that after this substitution is made, the second partial derivatives obtained in the differentiation nicely cancel out. The set of first derivatives thus obtained (the overhead dot denotes the time derivative)

$$\dot{\mathcal{H}}_x = -a(\mathcal{H}_x - X)(Y + \mathcal{H}_z) \tag{A-1}$$

$$\dot{\mathcal{H}}_y = -b(\mathcal{H}_y - \mathcal{H}_x)(Y + \mathcal{H}_z) \tag{A-2}$$

$$\dot{\mathcal{H}}_z = -c(\mathcal{H}_z - Y)(X + \mathcal{H}_x + \mathcal{H}_y) \tag{A-3}$$

is supplemented by the two additional equations

$$\dot{X} = -X(Y + \mathcal{H}_z) \tag{A-4}$$

$$\dot{Y} = -Y(X + \mathcal{H}_x + \mathcal{H}_y) \tag{A-5}$$

obtained either by substituting $x = y = z = 0$ into eq 5 or by examining the rates at which monomers react. All the eqs A-1–A-5 can be deduced directly by examining the rates at which various types of units react. The set analogous to A-1–A-5 was obtained in that way by Gordon and Scantlebury.[10]

The second derivatives required for evaluating the kinetic second moment of molecular size distribution were calculated by using the general equation

$$\dot{\mathcal{H}}_{tu} = \mathcal{P}_{tu}(Y + \mathcal{H}_z) + \mathcal{Q}_{tu}(X + \mathcal{H}_x + \mathcal{H}_y) + \mathcal{R}_t\mathcal{S}_u + \mathcal{R}_u\mathcal{S}_t \tag{A-6}$$

with the functions $\mathcal{P}$, $\mathcal{Q}$, $\mathcal{R}$, and $\mathcal{S}$ presented in Table II. This equation was again obtained from eq 5 by differentiating it with respect to t and u (t, u = x, y, z) followed by substituting $x = 1/a$, $y = 1/b$, and $z = 1/c$.

Analytical solutions of differential eqs A-1–A-6 for the random and stoichiometric case are presented in Table III.

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Size Effect of Compliant Rubbery Particles on Craze Plasticity in Polystyrene

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ABSTRACT: Blends of polystyrene containing concentric spherical shell particles produced from KRO-1 resin by means of a morphological transformation discussed earlier by Gebizlioglu et al.[7] were disassembled to harvest the particles. These particles were in turn separated into two nearly nonoverlapping populations of average sizes of 0.32 and 2.3 μm and were subsequently reassembled by solvent blending into homo-PS to create two separate sets of heterogeneous polymers of large and small particles at particle weight fractions of 0.05 and 0.15, respectively. It was found that the craze flow stress increases systematically with decreasing particle volume fraction at constant particle size and that the blends with the small particles that are less potent craze initiators have substantially higher flow stresses than blends with the large particles. Definitive theoretical models for the cutoff particle size below which crazes cannot be initiated and for the craze flow stress are in substantial agreement not only with the results of the present study but also with particle size effects previously reported by us and other investigators.

I. Introduction

The incorporation of rubber particles with certain morphology into a normally brittle glassy polymer can substantially increase its toughness.[1–3] This approach has been used for decades in the production of tough polymers such as high-impact polystyrene (HIPS) or acrylonitrile–butadiene–styrene (ABS). In these polymers the particles act as potent craze initiators, and the source of the toughness is the extensive dilatational plasticity that results from the initiated crazes.[4,5] It has been stated that for particles to be effective they must be very compliant, must have a size exceeding a critical value, and finally, must be adhering well to the surrounding glassy polymer so they can eventually become fully load bearing when that becomes necessary.

Recent studies conducted on blends of polystyrene with polystyrene/polybutadiene (PS/PB) copolymers by Gebizlioglu et al.[6,7] have shown that the effectiveness of particles as craze initiators is governed not only by rubber content but even more importantly by particle morphology. The incorporation of low molecular weight PB into the KRO-1 type PS/PB block copolymer particles transformed their morphology from randomly interwoven rods of PB embedded in PS to a morphology comprised of concentric spherical shells of PS and PB. This morphological transformation accomplished by a small addition of rubber was found to result in a large increase of particle compliance and therefore in a significant increase of toughness.[6,7]

The effect of particle size on the mechanical properties of rubber-toughened polymers has been studied by a number of investigators.[1,3,8–11] There is agreement that rubber particles of a size less than some critical value are ineffective as craze initiators.[1,3] The critical size of particles, however, depends on the mechanical properties of both the matrix and the particles. Most studies of particle size effect on rubber-toughened PS concern mainly HIPS. Boyer and Keskkula[9] found that the optimum particle size for HIPS is within the range 1–2 μm, while Donald and Kramer[10] reported that particles of diameter <0.8 μm do not initiate crazes in HIPS. Bragaw[3] stated that particle size should be larger than the thickness of a craze to be effective as craze initiators. Similar observations concern also PS toughened with block copolymer particles of PS/PB. For such systems Gebizlioglu et al.[6,7] determined that particles of diameter less than a critical value do not initiate crazes but found that the critical cutoff size ranged from 0.1 to 0.4 μm for concentric spherical shell particles, while KRO-1 particles of much higher stiffness did not appear to initiate crazes even when exceeding 10 μm in size.

Uncertainty in the determination of the role of the particle size on toughening of the glassy matrix originates from the difficulties of controlling particle size without

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