(23) Schaeffer, D. W.; Benedek, G. B.; Schofield, P.; Bradford, E. *J. Chem. Phys.* **1971**, *55*, 3884.
(24) Edmonds, A. R. "Angular Momentum in Quantum Mechanics"; Princeton University Press: Princeton, N.J., 1974.
(25) Tanford, C. "Physical Chemistry of Macromolecules"; Wiley: New York, 1961.
(26) Mandelkern, L.; Mattice, W. L. *Jerusalem Symp. Quant. Chem. Biochem.* **1973**, *5*, 121.
(27) Ookubo, N.; Komatsubara, M.; Nakajima, H.; Wada, Y. *Biopolymers* **1976**, *15*, 929.
(28) Maguire, J. F.; McTague, J. P.; Rondelez, F. *Phys. Rev. Lett.* **1980**, *45*, 1891.

Simulation of Polymer Network Formation by the Monte Carlo Method

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ABSTRACT: A Monte Carlo method for simulation of the stepwise polyreaction generating treelike polymer structures and admitting intramolecular reactions inside the largest particle (identified with the gel) has been developed. The method is equivalent to the kinetic theory of network formation applied to finite systems. The limiting properties of an infinite system are obtained by extrapolation; among those best accessible are the critical conversion of gelation and weight fractions of sol and gel. Polymerization of a trifunctional monomer with a first-shell substitution effect was used as an example to demonstrate that, with the exception of some special cases, the results obtained by the kinetic method are virtually identical with those provided by the statistical method based on the treelike model and cascade substitution.

Introduction

Network models are essentially graphlike and network formation from smaller building units is simulated either by percolation in D-dimensional space using Monte Carlo methods or by formation of (perturbed) treelike structures in $D = 1$, equivalent to percolation on the Cayley tree, which is usually given an anlytical solution.

The treelike models are based on the Flory–Stockmayer[1,2] approach, but the network formation can be treated in two different ways: either statistically (theory of branching processes (TBP) developed mainly by Gordon; cf., for example, ref 3 and 4), when the final assembly of molecules is generated from the building units, in which different numbers of functional groups have been converted into chemical bonds, or kinetically (kinetic theory), when the growth of molecules is considered as a chemical reaction occurring between two functional groups of any pair of existing molecules. Both methods are statistically nonequivalent because in the kinetic approach the integrity of the existing structures, and so information on the formation history, is preserved, while it is not so in the statistical TBP. This difference is irrelevant for equilibrium-controlled reaction (both approaches are equivalent) but may become serious in the case of kinetically controlled reactions.

To make the situation clearer, let us consider a simple case of a step polyaddition of a f-functional monomer with all functional groups of the same type but with a first-shell substitution effect (FSSE). FSSE means that the reactivity of an unreacted group depends on the number of reacted groups in the same monomer unit (called the reaction state of the unit) but not on reaction states of other units in the system.

The fractions of units in different reaction states (later called the distribution of units) are determined by kinetic differential equations based on the mass action law. If additivity of contributions to the activation energy is valid, the number of kinetic equations is $f + 1$. The distribution of units is thus a function of time and depends on the respective rate constants.

As shown below, it is to our advantage to express the fractions of units as a function of overall conversion of functional groups; the conversion is then an implicit function of time. Note that in the calculation of the distribution of units only their molar concentrations, i.e., the mass action law, are operative and not any other constraints coming, for example, from ring closure determined by chain flexibility or space embedding. Such constraints would alter the distribution of reaction states, although nothing changes from the point of view of chemical reactivity of the functional groups.

Up to this point, there is no difference between the methods (TBP and kinetic) and the distributions of units are identical.

In the theory of branching processes, the treelike molecules are generated from the distribution of units by applying the so-called cascade substitution procedure and generating functions (or an equivalent recursive procedure when the language of conditional probabilities is preferred[5]) which generates all possible treelike molecules with proper weighting compatible with random combination of reacted functional groups to form a bond. An example of detailed application of this procedure can be found, for example, in the paper by Gordon and Scantlebury.[6] It is important to note that the molecules are generated from monomer units at any extent of reaction anew. It is clear that there is no information stored on sequence order in the generated structures. To make the situation clearer, imagine that the monomer is colored and its color is time (conversion) dependent. In kinetically controlled reactions, the sequences of colors (although subjected to statistical fluctuations) must evidently depend on reactivities of functional groups. A strong positive substitution effect, for example, would yield long sequences of the same color.

The question is whether this lack of memory inherent in TBP may affect the distribution of sizes (masses) of the generated molecules, gelation, and sol–gel relation.

In the kinetic method, first used by Stockmayer[1] and later developed for a number of polymerization problems,[7,8] the distribution of units is not input information but is generated implicity in the course of the growth process. Instead of the $f + 1$ differential equations, one writes an inifinite number of differential equations, corresponding to a bimolecular reaction (without substitution effect)

$$Z_{ij} + Z_{kl} \rightarrow Z_{i+k,j+l-2}$$

where Z_{ij} represents a molecule composed of i monomer units and bearing j unreacted functional groups. The

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concentration of the species Z_{ij}, c_{ij}, is determined by a rate equation employing again the mass action law. The time change of c_{ij} is given by the rate of disappearance of Z_{ij}, in which Z_{ij} reacts with any other molecule in the system, and by formation of Z_{ij} by forming a bond between molecules of complementary sizes. The rates of these processes are proportional to the products of the number and reactivity of the functional groups of each of the two molecules involved in the reaction. The infinite set of differential rate equations can always be transferred into one partial differential equation for the time derivative of the generating function for the distribution c_{ij} (in the case of unequal reactivity of groups and/or substitution effect, j should be regarded as a vector).

This generating function is analogous to but in general not identical with the generating function obtained by cascade substitution. A simple reasoning may show that the kinetic treatment preserves the right sequential order of colors, if the color of monomers were time (conversion) dependent. However, a solution of the partial differential equation has been obtained only for a few simple cases involving the random case for $f \geq 2$ (equal and independent reactivities of groups) and linear polymerization with substitution effect for $f = 2$. For higher functionality and substitution effect, a solution of the respective partial differential equations has not been found yet.

In general, the solutions obtained by the cascade substitution and kinetic methods are not reducible. However, for the random case both methods have been shown[9] to yield identical generating functions and are, therefore, fully equivalent even beyond the gel point. There is not much known whether measurable differences can be found in the nonrandom case. Kuchanov[8] found considerable differences in the polydispersity of linear polymers calculated by both methods when a strong substitution effect was operative. It is, therefore, expected that differences also exist in the reaction of multifunctional monomers with a substitution effect.

In order to elucidate these differences and in view of the difficulties with a solution of the partial differential equations characteristic for the kinetic method, we have developed and used a Monte Carlo (MC) simulation, which by its logic of formation of molecules is equivalent to the kinetic method. MC is limited to finite systems and may be employed in an analysis of the effect of finiteness. An analogous exact statistical theory of finite systems[10] is restricted to relatively small assemblies of monomer units. In the limit of an infinite number of monomer units, the MC results are equivalent to the kinetic solution for the treelike model. The results were compared with those obtained using the theory of branching processes based on cascade substitution (CS).[3,4,6]

Theory of Branching Processes

Let us examine a system with a first-shell substitution effect. Let a monomer unit with i reacted functionalities be denoted with U_i; for the trifunctional monomer, i = 0–3.

Assuming the additivity of activation energies,[6] the rate constant k_{ij} of the reaction between U_i and U_j may be expressed through

$$k_{ij} = k^{+}(3 - i)K_i(3 - j)K_j \tag{1}$$

where K_i is a relative (dimensionless) rate constant (later called reactivity) of the reaction of the group of type i with a reference group and k^+ is the rate constant for the reaction of reference groups. If the unit U_i with $3 - i$ functionalities of type i characterized by the relative reactivity K_i reacts, it is transformed into the unit U_{i+1} with $3 - i - 1$ functionalities of type $i + 1$ characterized by K_{i+1}.

The composition of the system may be characterized by the number fractions a_i of the monomer units U_i. Their time dependence is given by a system of differential equations

$$\begin{aligned} -\mathrm{d}a_0/\mathrm{d}t &= 3K_0a_0S \\ -\mathrm{d}a_1/\mathrm{d}t &= 2K_1a_1S - 3K_0a_0S \\ -\mathrm{d}a_2/\mathrm{d}t &= K_2a_2S - 2K_1a_1S \\ -\mathrm{d}a_3/\mathrm{d}t &= -K_2a_2S \end{aligned} \tag{2}$$

where $S = k^{+}c^0(3K_0a_0 + 2K_1a_1 + K_2a_2)$; c^0 is a constant equal to the molar concentration of all monomer units at any time t.

The system may be considerably simplified by expressing a_i as a function of a_0 and using the ratios $\varkappa_1 = 2K_1/3K_0$ and $\varkappa_2 = K_2/3K_0$. After integration of system 2, we obtain

$$a_1 = [1/(1 - \varkappa_1)](a_0^{\varkappa_1} - a_0)$$

$$a_2 = [\varkappa_1/(1 - \varkappa_1)][(a_0 - a_0^{\varkappa_2})/(1 - \varkappa_2) - (a_0^{\varkappa_1} - a_0^{\varkappa_2})/(\varkappa_1 - \varkappa_2)]$$

$$a_3 = 1 - [\varkappa_1/(1 - \varkappa_1)][(\varkappa_2a_0 - a_0^{\varkappa_2})/(1 - \varkappa_2) - (\varkappa_2a_0^{\varkappa_1} - \varkappa_1a_0^{\varkappa_2})/(\varkappa_1^2 - \varkappa_1\varkappa_2)] \tag{3}$$

The fourth equation needed for the determination of the fractions a_i is a balance one:

$$a_1 + 2a_2 + 3a_3 = 3\xi \tag{4}$$

where ξ is the molar conversion of functional groups. The dependence of conversion ξ on time can be obtained, if necessary, by substitution of eq 3 and 4 into eq 2 and numerical solution. For the random case, $K_0 = K_1 = K_2$, the solution is simple because $\mathrm{d}\xi/\mathrm{d}t = K_0^2(1 - \xi)^2$ so $\xi/(1 - \xi) = K_0^2t$.

Systems 3 and 4 determine the link probability generating function (pgf) for units in the roots of trees generated by the theory of branching processes

$$F_0(\theta) = a_0 + a_1\theta + a_2\theta^2 + a_3\theta^3 \tag{5}$$

and the link pgf for units in higher generations

$$F_1(\theta) = (a_1 + 2a_2\theta + 3a_3\theta^2)/3\xi \tag{6}$$

The critical conversion was determined by the numerical solution to the equation

$$[\mathrm{d}F_1(\theta,\xi)/\mathrm{d}\theta]_{\theta=1} \equiv F_1' = (2a_2 + 6a_3)/3\xi = 1 \tag{7}$$

The distribution of the degrees of polymerization was characterized by the first three moments. The number-average P, P_{n}, is obtained from stoichiometric consideration; the weight average P, P_{w}, and the z-average P, P_z, were determined from the weight-fraction generating function (obtained by cascade substitution):

$$\begin{aligned} P_{\mathrm{n}} &= 2/(2 - 3\xi) \\ P_{\mathrm{w}} &= 1 + F_0'/(1 - F_1') \\ P_z &= \{3P_{\mathrm{w}} - 2 + 1/(1 - F_1')^2[F_0'' + F_0'F_1' + F_0'F_1''/(1 - F_1')]\}/P_{\mathrm{w}} \end{aligned} \tag{8}$$

The sol fraction, w_{s}, in the postgel stage of the reaction is determined by the extinction probability, v ($v = F_1(v)$)

$$w_{\mathrm{s}} = a_0 + a_1v + a_2v^2 + a_3v^3 \tag{9}$$

The characteristics of the sol are derived similarly to the pregel stage of the reaction by using the pgf's:

$$\hat{F}_0(\theta) = F_0(v\theta)/F_0(v)$$
$$\hat{F}_1(\theta) = F_1(v\theta)/F_1(v) \tag{10}$$

Monte Carlo Simulation

The simulation is carried out by choosing a pair of molecules and by joining them into a larger one. Assuming a first-shell substitution effect and additivity of the activation energies to be operative, the reaction probability p_i of a functionality i is proportional to its reactivity K_i. The probability of the choice of a molecule to react is then proportional to the sum of reactivities K_i of all the functionalities in the molecule.

In the course of the reaction, the size (degree of polymerization) of the largest molecule in the system begins to increase sharply near a certain conversion. Such behavior corresponds to a gelation of the infinite system at the critical conversion. The largest molecule beyond this conversion corresponds to the gel.

In the pregel stage of reaction, the treelike character of the structures is guaranteed by the fact that reactions between functionalities of the same molecule are forbidden, which perturbs the proportionality between p_i and K_i. The MC experiments showed, however, that for a sufficiently large system, where the number of monomer units N is higher than 10^3–10^4, the probabilities of such intramolecular reactions, given by the probability that the same molecule will be chosen twice for the reaction, are quite negligible. A similar experience has been made by Busnel and Bruneau.[11]

Beyond the gel point, intramolecular reactions were permitted in the largest molecule (representing the gel). Conformationally controlled cyclization is not considered; only bifunctional collisions respecting the mass action law are considered in this case. This allows us to respect the proportionality between p_i and K_i and allows the reaction to proceed to full conversion. This treatment is in accordance with the way of determining the coefficients of the link pgf in TBP and corresponds to the Flory model of gelation.

If cross-linking within the largest molecule were not allowed, the gel formation would correspond to the third model of Ziff and Stell.[12]

An important feature of the MC method consists in that it simulates finite systems, and therefore each independent MC experiment gives a somewhat different molecular size distribution. The values thus obtained are then subjected to scatter, especially important in the range of critical conversion. Extrapolation to an infinite size of the system requires a thorough statistical analysis, and the limiting values of parameters for $N \to \infty$ may be obtained only if the limiting behavior has been reached for them; i.e., they are independent of N.

The numerical simulation method is described in the Appendix.

Results and Discussion

MC Simulation. The main purpose of the MC simulation was to obtain data corresponding to the kinetic model and find its regions of convergence to and divergence from the TBP. Two problems have been examined: (a) testing of the accuracy of the computer program for simulation and (b) the speed of convergence of the parameters and their scatter with increasing size of the system (number of monomer units, N).

Two methods have been used for testing the program. The first one is universal and valid for any substitution effect: it involves a comparison of fractions of monomer units in different reaction states, a_i (cf. eq 3), which in the limit $N \to \infty$ should be the same irrespective of which method has been used. Table I shows that the sets of a_i extracted from the MC simulation converge rapidly to the solution given by eq 3 and 4.

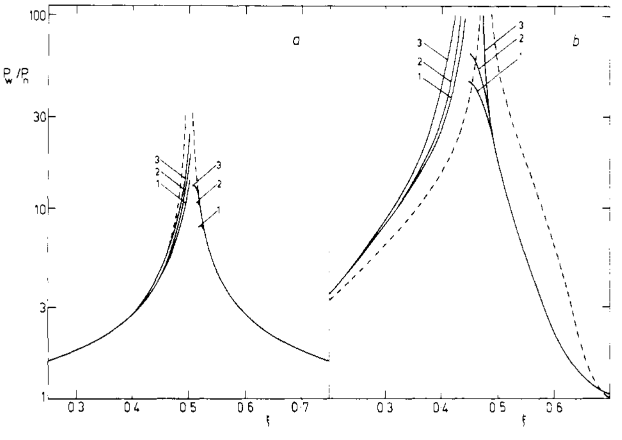

Figure 1. Dependence of the polydispersity, P_w/P_n, on the degree of conversion. Solid lines are Monte Carlo data for various N; the numbers of independent experiments used for construction of the curves are given in Table I. The broken line represents the dependence calculated from cascade substitution. (a) K_0:K_1:K_2 = 1:1:1: (1) N = 3000; (2) N = 10000; (3) N = 30000. (b) K_0:K_1:K_2 = 1:10:0.1: (1) N = 10000; (2) N = 30000; (3) N = 100000.

The second test involves a comparison of structural parameters like the degree-of-polymerization averages, the gelation threshold, and the gel fraction, calculated by TBP and MC simulation for the random case ($K_0 = K_1 = K_2$). For the random case, it has been proved analytically that TBP and the kinetic model (and, therefore, MC simulation in the limit $N \to \infty$) are identical.

The distribution of the degrees of polymerization and its moments are directly available from the MC experiment. The distribution in the sol beyond the gel point is obtained by excluding the largest molecule, which is an analogue of the gel. All parameters of the distribution function exhibit a scatter, which becomes larger the closer the system is to the gel point. Generally, the scatter is larger in the postgel stage of the reaction, obviously as a consequence of the reduced size of the sol at the expense of the gel.

Table I and Figure 1 show conversion intervals where P_w/P_n has reached the limit for $N = \infty$. In the vicinity of the actual gel point (ξ_c(MC)), P_w/P_n increases with increasing size of the system, N, and in the case of random reaction converges to the solution given by TBP, as has been predicted. However, for the nonrandom case (K_0:K_1:K_2 = 1:10:0.1), the MC ($N \to \infty$) and the TBP results are different, which points to the stochastic nonequivalency of the TBP and the kinetic methods.

The position of the gel point (critical conversion, ξ_c) can be determined only indirectly. It was found that the best procedure for determining ξ_c was that using the dependence of the weight fraction of the largest particle, w_M, on conversion. In the limit of infinite size of the system, $N \to \infty$, w_M assumes the meaning of the weight fraction of the gel, $w_g = 1 - w_s$. Table I shows how the size of the largest particle depends on N. From the part of the dependence of w_M, which has already reached the limiting behavior, an extrapolation is made to $w_g = 0$, which corresponds to the critical conversion. The procedure is demonstrated in Figure 2; the extrapolated part of the curve is dashed. In all the systems studied, the limiting behavior of w_M was already reached when N = 30000, comparatively close to the gel point (Figure 2). This is why

Table I
Parameters of Distribution Obtained by CS and MC Simulation and Their Dependence on System Size N^a

ξ	N	a_0	a_1	a_2	a_3	P_w/P_n	w_M
Random Case: $K_0 = K_1 = K_2$ ($\xi_c = 0.5$)							
0.20	3×10^3	0.5117	0.3852	0.0945	0.0086	1.402	0.00339
		(0.0043)	(0.0082)	(0.0038)	(0.0008)	(0.020)	(0.00059)
	10^4	0.5102	0.3877	0.0940	0.0081	1.392	0.00115
		(0.0028)	(0.0050)	(0.0019)	(0.0006)	(0.0017)	(0.00020)
	3×10^4	0.5112	0.3854	0.0954	0.0079	1.397	0.00048
		(0.0015)	(0.0031)	(0.0016)	(0.0006)	(0.010)	(0.00009)
	CS (∞)	0.5120	0.3840	0.0960	0.0080	1.400	0
0.45	3×10^3	0.1650	0.4103	0.3344	0.0903	4.27	0.0269
		(0.0053)	(0.0077)	(0.0050)	(0.0041)	(0.77)	(0.0061)
	10^4	0.1632	0.4127	0.3350	0.0891	4.28	0.0126
		(0.0022)	(0.0034)	(0.0014)	(0.0013)	(0.26)	(0.0025)
	3×10^4	0.1661	0.4087	0.3344	0.0908	4.72	0.0071
		(0.0011)	(0.0012)	(0.0020)	(0.0015)	(0.33)	(0.0031)
	CS (∞)	0.1664	0.4084	0.3341	0.0911	4.712	0
0.55	3×10^3	0.0891	0.3358	0.4110	0.1641	4.99	0.428
		(0.0046)	(0.0038)	(0.0097)	(0.0070)	(1.42)	(0.042)
	10^4	0.0897	0.3348	0.4113	0.1642	4.96	0.436
		(0.0012)	(0.0024)	(0.0033)	(0.0018)	(0.63)	(0.017)
	3×10^4	0.0915	0.3340	0.4074	0.1671	4.99	0.453
		(0.0007)	(0.0011)	(0.0025)	(0.0015)	(0.45)	(0.012)
	CS (∞)	0.0911	0.3341	0.4084	0.1664	4.712	0.4523
Nonrandom Case: $K_0:K_1:K_2 = 1:10:0.1$ (ξ_c(MC) = 0.440)							
0.20	10^4	0.6473	0.1069	0.2443	0.0015	3.55	0.00462
		(0.0014)	(0.0028)	(0.0017)	(0.0005)	(0.21)	(0.00094)
	3×10^4	0.6477	0.1059	0.2451	0.0013	3.48	0.00165
		(0.0008)	(0.0017)	(0.0010)	(0.0002)	(0.52)	(0.00019)
	10^5	0.6484	0.1049	0.2451	0.0017	3.54	0.00058
		(0.0003)	(0.0006)	(0.0004)	(0.0001)	(0.05)	(0.00007)
	CS (∞)	0.6484	0.1046	0.2455	0.0015	3.216	0
0.40	10^4	0.3711	0.0666	0.5535	0.0088	26.3	0.0398
		(0.0008)	(0.0016)	(0.0020)	(0.0010)	(5.3)	(0.0151)
	3×10^4	0.3717	0.0655	0.5540	0.0089	29.7	0.0193
		(0.0009)	(0.0013)	(0.0008)	(0.0006)	(0.6)	(0.0042)
	10^5	0.3723	0.0648	0.5537	0.0093	45.6	0.0146
		(0.0003)	(0.0003)	(0.0001)	(0.0002)	(7.6)	(0.0054)
	CS (∞)	0.3719	0.0654	0.5536	0.0091	15.557	0
0.50	10^4	0.2377	0.0428	0.7010	0.0184	16.37	0.581
		(0.0016)	(0.0036)	(0.0025)	(0.0007)	(7.7)	(0.042)
	3×10^4	0.2383	0.0415	0.7018	0.0182	16.8	0.604
		(0.0007)	(0.0009)	(0.0012)	(0.0009)	(4.1)	(0.050)
	10^5	0.2383	0.0419	0.7011	0.0186	20.0	0.595
		(0.0004)	(0.0010)	(0.0007)	(0.0002)	(2.0)	(0.009)
	CS (∞)	0.2382	0.0420	0.7012	0.0185	51.88	0.3209

[a] ξ is the molar conversion, $\{a_i\}$ is the distribution of reaction states of monomer units (coefficients of the link probability generating function), P_w/P_n is the polydispersity of the system before gelation and in the sol, respectively, and w_M is the weight fraction of the largest particle. The dispersion of the MC values is characterized by the mean quadratic deviation given in parentheses below the mean value. Number of simulations: random case, 6 for $N = 3 \times 10^3$ and 10^4 and 5 for $N = 3 \times 10^4$; nonrandom case, 4 for $N = 10^4$ and 10^5 and 5 for $N = 3 \times 10^4$.

the values of critical conversion are determined with relative reliability even in the case of a single experiment with N = 30 000.

The results presented in this section seem to prove that the MC simulation method described here works well and is able to supply results equal to those expected from the kinetic theory.

Comparison of the Results Obtained by MC and CS. Critical conversion is the most important criterion used in the comparison of the kinetic MC simulation with the statistical theory of branching processes based on cascade substitution (CS). Table II gives ξ_c values obtained by MC and CS for several ratios of the relative rate constants. As in the random case and in most other cases, both methods yield virtually the same values, even at the extreme substitution effects characterized by the ratios 1:10:100 and 100:10:1. An important difference may be observed only for systems approaching the case of linear polymerization (suppressed K_2 constant), but with a positive substitution effect in the first step. This case may be characterized by the inequalities $K_1/K_0 > 1$ and $K_2/K_1 < 1$ (Table II).

The most reliable parameter which characterizes the postgel reaction stage is the weight fraction of the largest particle, w_M, which readily reaches the limiting behavior. An important finding is that allowance of the mass action law controlled intramolecular reactions (Flory's approach) in the gel particle dose not lead in most cases to any variance with the theory of branching processes. If the gel points coincide, w_M also converges to the statistical value of w_g as shown in Figure 2 for the ratio 1:2:4. Excellent agreement was also found at the ratios 1:1:1 (where the equivalency between the statistical and kinetic approaches may be proved analytically[9]), 4:2:1, and 100:10:1.

A system possessing a strong positive substitution effect given by the ratio $K_0:K_1:K_2$ = 1:10:100 suggests some differences in w_M (w_g) between the MC and CS results

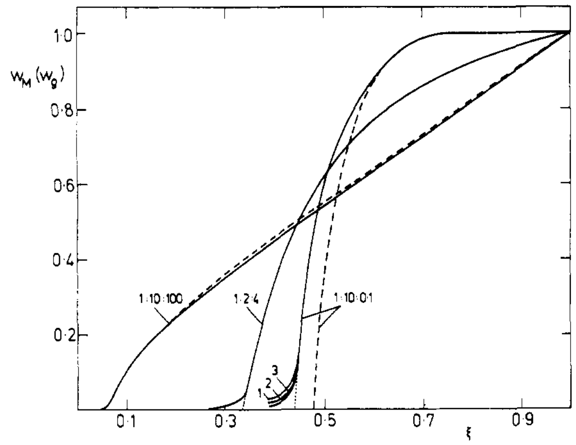

Figure 2. Dependence of the weight fraction of the largest molecule in the system on conversion: (——) MC data; (···) extrapolated MC dependences; (---) CS dependences. The numbers of independent MC experiments are given in parentheses. K_0:K_1:K_2 = 1:10:100 for N = 30 000 (4), N = 100 000 (3), and N = 300 000 (2); all MC curves coincide. K_0:K_1:K_2 = 1:2:4 for N = 30 000 (2); MC and CS curves coincide. K_0:K_1:K_2 = 1:10:0.1 for N = 10 000 (4) (curve 1), N = 30 000 (5) (curve 2), and N = 100 000 (4) (curve 3).

Table II
Critical Degrees of Conversion (Gel Points) for Various Reactivity Ratios As Determined by Monte Carlo, ξ_c(MC), and Cascade Substitution, ξ_c(CS)[a]

K_0	K_1	K_2	ξ_c(CS)	ξ_c(MC)	N_{max}
1	1	1	0.500	0.501	100 000 (2)
1	2	4	0.334	0.333	30 000 (2)
4	2	1	0.586	0.582	30 000 (2)
1	10	100	0.062	0.061	300 000 (2)
100	10	1	0.633	0.630	30 000 (1)
1	10	10	0.132	0.132	30 000 (2)
1	2	0.5	0.504	0.503	30 000 (1)
1	4	0.25	0.496	0.488	30 000 (1)
1	10	1	0.284	0.267	30 000 (2)
1	10	0.1	0.477	0.440	100 000 (4)
1	10	0.01	0.609	0.578	100 000 (2)
1	100	0.1	0.253	0.167	300 000 (2)

[a] N_{max} is the maximum number of monomer units at which the MC experiments were performed. The number of independent MC experiments by N_{max} is given in parentheses.

(Figure 2). The behavior of a system strongly deviating from the theory of branching processes (ratio of relative reactivities being 1:10:0.1) is shown in Figures 1 and 2.

The present study shows that the stochastically nonequivalent kinetic theory and the theory of branching processes yield in the majority of practically important cases experimentally indistinguishable results. Significant deviations can be found only for certain combinations of substitution effects. It is to be noted, however, that these limits may be dependent on the assumption of additivity of activation energies.

Appendix. Numerical Method of Simulation

Method of Information Storage. Let N monomer units form M molecules. The composition of a treelike molecule from the point of view of chemical kinetics is completely characterized by numbers of different unreacted functionalities and no information on topology is needed. In the case of a trifunctional monomer, there are three types of unreacted functionalities, i = 0, 1, and 2, with reactivities K_i. A simplification is possible due to the fact that monomers bear type 0 functionalities only and higher polymerization degrees functionalities types 1 and 2. Thus, the composition of a monomer is given by a single number ($n_{10}{}^g$ = 3) and the composition of any other molecule is given by a vector (n_{i1}, n_{i2}), where n_{ij} is the number of functionalities of type j in the ith molecule.

Table III
Composition of Molecules of Groups G_1-G_7[a]

group	p	$n_{i0}{}^g$	$n_{i1}{}^g$	$n_{i2}{}^g$
G_1	1	3		
G_2	2		4	0
G_3	3		4	1
G_4	4		4	2
G_5	4		6	0
G_6	5		4	3
G_7	5		6	1

[a] p is the degree of polymerization and $n_{ij}{}^g$ is the number of functionalities of type j in the molecule of group G_i.

Molecules of a low polymerization degree occur in the reacting system with a high frequency. In our program, identical molecules up to pentamers are grouped together in the computer memory. There are 7 groups designated G_i, i = 1, 2, ..., 7; tetramers and pentamers participate with two isomeric structures. For every group G_i, the number of grouped molecules m_i must be known. The composition of grouped molecules, ($n_{i1}{}^g$, $n_{i2}{}^g$), is given in Table III.

The grouping of some low polymerization degree molecules saves considerable computer memory and speeds up computation. On the other hand, each group structure considerably complicates the program. For higher degrees of polymerization, the grouping loses its efficiency because the number of isomers grows rapidly, requiring an enormous amount of programming.

In the reacting system, there remain $Q = M - \sum_{i=1}^{7} m_i$ molecules. Each of them is designated A_i, i = 1, 2, ..., Q. These molecules are treated individually. The composition of a molecule A_i is given by the vector ($n_{i1}{}^a$, $n_{i2}{}^a$), where $n_{ij}{}^a$ are the numbers of functionalities of type j in the molecule A_i. In what follows, groups G_i are treated as a whole. Hence, the discernible objects are, on the one hand, groups G_i, and, on the other, the individual molecules A_i. The reactivity of the object X, which is denoted with r(X), is given by the sum of reactivities K_j of the individual functionalities, so for monomers (group G_1) it holds

$$r(G_1) = n_{10}{}^g K_0 m_1 = 3K_0 m_1 \qquad \text{(A-1)}$$

The reactivity of the other objects is given by the sum of the contributions of the functionalities of type 1, r_1(X), and the contributions of the functionalities of type 2, r_2(X):

$$r(G_i) = r_1(G_i) + r_2(G_i) = n_{i1}{}^g K_1 m_i + n_{i2}{}^g K_2 m_i \qquad i = 2, 3, ..., 7 \quad \text{(A-2)}$$

$$r(A_i) = r_1(A_i) + r_2(A_i) = n_{i1}{}^a K_1 + n_{i2}{}^a K_2 \qquad i = 1, 2, ..., Q \quad \text{(A-3)}$$

Information is stored in the computer memory in terms of reactivities; i.e., for monomers it is a scalar $r(G_1)$ and for the other objects a vector (r_1(X), r_2(X)), where X is either a group G_i or a molecule A_i.

The initial state of the system is defined by $m_1 = N$, $m_{i>1}$ = 0, and Q = 0.

Rules for the Choice of the Molecule and Its Functionality for Entering the Reaction. The molecule may be chosen from one of the groups G_i, an event denoted by $s(G_i)$, or the molecule A_i may be chosen, an event denoted by $s(A_i)$. The choice is accomplished by using the Monte Carlo method. The sample space is defined by the set of all possible choices:

$$\Omega = \{s(G_1),s(G_2),...,s(G_7),s(A_1),s(A_2),...,s(A_Q)\}$$

The respective probabilities w(X) of the event s(X) are determined by the values of normalized reactivities:

$$w(\mathrm{X}) = r(\mathrm{X})/r_\mathrm{T}$$

$$r_\mathrm{T} = \sum_{i=1}^{7} r(\mathrm{G}_i) + \sum_{i=1}^{Q} r(\mathrm{A}_i) \qquad \text{(A-4)}$$

The selection is performed by transformation of random (pseudorandom) numbers of a uniform distribution to the discrete distribution $w(\mathrm{X})$. Two basic methods[13] are available: (a) Piecewise fitting (PF) and (b) the rejection technique (RT). We combined both methods to take advantage of each of them in the appropriate part of the sample space Ω. For this purpose, the set of individual molecules is periodically sorted with respect to $r(\mathrm{A}_i)$ values to give $r(\mathrm{A}_{i+1}) \leq r(\mathrm{A}_i)$, the QUICKSORT[14] procedure being used. The sample space Ω is then divided into two subspaces: $\Omega_1 = \{s(\mathrm{G}_1),...,s(\mathrm{G}_7),s(\mathrm{A}_1),s...,s(\mathrm{A}_B))\}$ and $\Omega_2 = \{s(\mathrm{A}_{B+1}),...,s(\mathrm{A}_Q)\}$, where the subscript B indicates the position for procedure switch over.

Ω_1 includes groups and the largest molecule, which is the most reactive part of the system. PF is applied there; the method consists in stepwise testing of inequalities. In the first stage it is searched for the group G_i:

$$\sum_{k=1}^{i-1} r(\mathrm{G}_k) < \epsilon r_\mathrm{T} \leq \sum_{k=1}^{i} r(\mathrm{G}_k) \qquad \text{(A-5)}$$

If the inequality is not satisfied for any $i = 1, 2, ..., 7$, it is searched for the molecule A_i, $i = 1, 2, ..., B$:

$$Y + \sum_{k=1}^{i-1} r(\mathrm{A}_k) < \epsilon r_\mathrm{T} \leq Y + \sum_{k=1}^{i} r(\mathrm{A}_k)$$

$$Y = \sum_{k=1}^{7} r(\mathrm{G}_k) \qquad \text{(A-6)}$$

ϵ is a random number from a uniform distribution in the interval (0, 1). The ordering of $r(\mathrm{A}_i)$ values in the descending order makes the method more effective. PF is a powerful method for not too extensive sample spaces and is especially convenient if large differences exist between the individual probabilities $w(\mathrm{X})$, as is our case.

If the selection was not found within Ω_1, it is to be performed within Ω_2. Ω_2 comprises the small ($p > 5$) and medium-size molecules and includes the major part of the set $\{\mathrm{A}_i\}$; RT is used there. This method consists of two steps: in the first step the subscript i is chosen with equal probability according to the equation

$$i = B + 1 + \mathrm{Floor}\,[\epsilon(Q - B)] \qquad \text{(A-7)}$$

Floor (x) takes the nearest lower integer to x. In the second step, the choice is either accepted or rejected according to the criterion

$$r(\mathrm{A}_i)/r_\mathrm{max} \geq \epsilon \qquad \text{(A-8)}$$

where r_max is the maximum value $r(\mathrm{A}_i)$ in the subspace Ω_2. If the choice is not successful, the procedure is repeated until inequality A-8 is satisfied. RT is suited for distributions approaching the uniform one and for extensive sample spaces.

The separation of Ω into Ω_1 and Ω_2 according to B should be determined empirically from the dependence of time requirements on B. If such analysis has not been performed, an optimum may be expected at B/N = 0.001–0.01.

After the molecule has been selected, PF is used to determine the functionality by testing the inequality (with the exception of monomers):

$$\epsilon r(\mathrm{X}) \leq r_1(\mathrm{X}) \qquad \text{(A-9)}$$

If inequality A-9 is satisfied, then a functionality of type 1 reacts; otherwise type 2 reacts.

Reaction Rules. After two molecules and its functionalities have been selected for reaction, they are joined to form a larger molecule. This reaction step is reflected in the change of the space of selections Ω, probabilities $\{w(\mathrm{X})\}$, r_T, and r_max. The reaction rules depend on the functionalities which enter the reaction. The following pairs of functionalities can react: (0, 0), (0, 1), (0, 2), (1, 1), (1, 2), (2, 2). If the molecule is characterized by the vector (n_{i1}, n_{i2}), which gives the numbers of functionalities of type 1 and 2, respectively (except for monomers), then we can write the general scheme for the formation of the new molecule:

$$\text{monomer} + \text{monomer} \xrightarrow{(0,\,0)} \text{dimer } (4, 0)$$

$$\text{monomer} + (n_{i1}, n_{i2}) \xrightarrow{(0,\,1)} (n_{i1}, n_{i2} + 1)$$

$$\xrightarrow{(0,\,2)} (n_{i1} + 2, n_{i2} - 1)$$

$$(n_{i1}, n_{i2}) + (n_{j1}, n_{j2}) \xrightarrow{(1,\,1)} (n_{i1} + n_{j1} - 4, n_{i2} + n_{j2} + 2)$$

$$\xrightarrow{(1,\,2)} (n_{i1} + n_{j1} - 2, n_{i2} + n_{j2})$$

$$\xrightarrow{(2,\,2)} (n_{i1} + n_{j1}, n_{i2} + n_{j2} - 2)$$

In addition, the algorithm must include the following rules for placing the new molecule:

$$\mathrm{G}_1 + \mathrm{G}_1 \rightarrow \mathrm{G}_2$$

$$\mathrm{G}_1 + \mathrm{G}_2 \rightarrow \mathrm{G}_3$$

$$\mathrm{G}_1 + \mathrm{G}_3 \xrightarrow{(0,\,1)} \mathrm{G}_4$$

$$\xrightarrow{(0,\,2)} \mathrm{G}_5$$

$$\mathrm{G}_1 + \mathrm{G}_4 \xrightarrow{(0,\,1)} \mathrm{G}_6$$

$$\xrightarrow{(0,\,2)} \mathrm{G}_7$$

$$\mathrm{G}_2 + \mathrm{G}_2 \rightarrow \mathrm{G}_4$$

$$\mathrm{G}_2 + \mathrm{G}_3 \xrightarrow{(1,\,1)} \mathrm{G}_6$$

$$\xrightarrow{(1,\,2)} \mathrm{G}_7$$

All other combinations of groups result in the formation of a molecule A_i, which is placed at the end of the set $\{\mathrm{A}_i\}$:

$$\mathrm{G}_i + \mathrm{G}_j \rightarrow \mathrm{A}_{Q+1};\ Q \leftarrow Q + 1,\ m_i \leftarrow m_i - 1,\ m_j \leftarrow m_j - 1$$

In the remaining cases, the existing molecule A_i becomes larger:

$$\mathrm{G}_j + \mathrm{A}_i \rightarrow \mathrm{A}_i;\ m_j \leftarrow m_j - 1$$

$\mathrm{A}_i + \mathrm{A}_j \rightarrow \mathrm{A}_i$ (provided $i < j$); A_j is deleted ($\mathrm{A}_j \leftarrow (0, 0)$)

$\mathrm{A}_i + \mathrm{A}_i \rightarrow \mathrm{A}_i$; allowed only for the largest particle beyond the gel point

In every reaction step, the respective reactivity vector $(r_1(\mathrm{X}), r_2(\mathrm{X}))$ and the sum r_T must be calculated. If a group is selected, the change occurs immediately, but in other cases it occurs after completing the reaction step. If RT is used, the maximum value of $r(\mathrm{A}_i)$ for $i = B + 1$, $B + 2$, ..., Q, r_max must be tested and possibly increased.

The distribution function of polymerization degrees is evaluated after each predetermined set of reaction steps, and all other characteristics are derived from it. At the same time, the sorting of the set $\{\mathrm{A}_i\}$ is being performed.

The set of 10^7 pseudorandom numbers, $\{\epsilon_i\}$ from the interval $\langle 0, 2^{31} - 1\rangle$ was obtained by mixing the set 1 of

10^6 statistically verified pseudorandom numbers, $\{\epsilon_j^1\}$ and the set 2 of 10^5 random numbers $\{\epsilon_k^2\}$ generated physically. The mixing was done by applying the algorithm

$$\epsilon_i = (\epsilon_j^1 + \epsilon_k^2) \bmod (2^{31} - 1)$$

Possible repetition of the same pairs (j, k) has been algorithmically excluded.

A program for simulation of the polymerization has been written in PL/1 for the IBM/370 computer, Model 135. The use of the described method of information storage allowed systems to be computed with a starting number of monomer units up to approximately $N = 5 \times 10^5$ (depending on the reactivities K_i) with 520 kilobytes of core memory. It is higher by more than one order of magnitude compared to the method storing separately each monomer unit.[11] The time consumption for a random reaction ($K_0 = K_1 = K_2$) and for the system size $N = 30\,000$ is 350 s for $B = 10$, 301 s ($B = 30$), and 451 s ($B = 300$); for $N = 100\,000$ it is 1250 s for $B = 100$.

References and Notes

(1) Stockmayer, W. H. *J. Chem. Phys.* **1973**, *11*, 45.
(2) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1950.
(3) Gordon, M. *Proc. R. Soc. London, Ser. A* **1962**, *268*, 240.
(4) Gordon, M.; Ross-Murphy, S. B. *Pure Appl. Chem.* **1975**, *43*, 1.
(5) Macosko, C. W.; Miller, D. R. *Macromolecules* **1976**, *9*, 199.
(6) Gordon, M.; Scantlebury, G. R. *J. Polym. Sci., Part C* **1968**, *16*, 3933.
(7) Ray, W. H. *J. Macromol. Sci., Rev. Macromol. Chem.* **1972**, *C8*, 1.
(8) Kuchanov, S. I. "Methods of Kinetic Calculations in Polymer Chemistry"; Khimiya: Moscow, 1978 (in Russian).
(9) Dušek, K. *Polym. Bull.* **1979**, *1*, 523.
(10) Donoghue, E.; Gibbs, J. H. *J. Chem. Phys.* **1979**, *70*, 2346.
(11) Busnel, J. P.; Bruneau, C. M. *C. R. Hebd. Seances Acad. Sci.* **1975**, *281*, 987.
(12) Ziff, R. M.; Stell, G. *J. Chem. Phys.* **1980**, *73*, 3492.
(13) Fluendy, M. In "Markov Chains and Monte Carlo Calculations in Polymer Science"; Lowry, G. G., Ed.; Marcel Dekker: New York, 1970; Chapter 3.
(14) Wirth, N. "Algorithms + Data Structures = Programs"; Prentice-Hall: Englewood Cliffs, N.J., 1976.

Elastic Activity of Imperfect Networks

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ABSTRACT: The number of elastically effective chains in an elastomeric network is $\nu_{\text{eff}} = 2\xi$, where ξ is the number of independent circuits, or the cycle rank of the network. This universal measure of network connectivity applies regardless of the functionalities of the junctions, of their statistical distribution, and of the distribution of free ends of chains in an imperfect network. It is unambiguously related according to $\xi = \nu_a - \mu_a$ to the number μ_a of "active" junctions arbitrarily identified as those joined by three or more paths to the network and the number ν_a of active chains attached at both ends to active junctions. The number ν_a of active chains thus defined is not, however, a proper substitute for ν_{eff}.

Introduction

The stored elastic free energy of a phantom network[1] of Gaussian chains is expressed rigorously by[2,3]

$$\Delta A_{\text{el}} = (\xi/2)kT(\sum_{i=1,2,3} \lambda_i^2 - 3) \qquad (1)$$

where λ_1, λ_2, and λ_3 are extension ratios along principal axes of the strain relative to the undeformed state of reference and ξ is the cycle rank of the network[3,4] or the number of independent circuits it contains. These circuits are assumed to be long, many chains being included in each of them. Otherwise stated, this qualification on the use of ξ as a universal measure of network connectivity requires that the number of short, circuitous paths shall be negligible, a condition usually fulfilled in densely interpenetrating networks.[4] The elastic response of the network is then uniquely determined by ξ; the number of junctions, their functionalities, and imperfections due to free (unattached) ends of chains are subsumed in ξ.

The cycle rank can be equated to the difference between the number ν of chains and the number ψ of labeled points in the network. These quantities are more fully defined in Figure 1. Junctions are represented in this figure by filled circles, free ends of chains by open circles. Their sum is ψ, the total number of labeled points. Junctions may be of any functionality $\phi \geq 2$. Labeling of bifunctional "junctions" is optional; inclusion of those with $\phi > 2$ is obligatory.

A chain is defined, in the usual way,[5,6] as the sequence of units bounded by consecutively labeled points along the given path. In the terminology of graph theory, the chains are edges and the labeled points are vertices of a connected graph. It follows that

$$\xi = \nu - \psi + 1$$

or, for a macroscopic network,

$$\xi = \nu - \psi \qquad (2)$$

The quantities ν and ψ refer exclusively to the network; coexisting material (sol) of finite molecular size is not to be included in their evaluation.

Scanlan[7] and Case[8] have defined an active junction as one joined by at least three paths to the gel network; see Figure 1. A junction connected to the network by only one path imposes no constraints that cannot be dissipated by diffusional relaxations. One with two paths to the network merely subdivides a chain into two chains without imposing permanent constraints beyond those due to the junctions at the ends of the undivided chain. Junctions with only two paths to the network are therefore relegated to the inactive category according to the Scanlan–Case criteria. Scanlan[7] and Case[8] define an active chain as one terminated by active junctions at both of its ends.

Pearson and Graessley[9] have shown that for a randomly interconnected network whose junctions are of even functionality (ϕ even[10])

$$\xi = \nu_a - \mu_a \qquad (3)$$

where ν_a and μ_a are the numbers of "active" chains and "active" junctions as defined by Scanlan[7] and Case.[8] The

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