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Applicability of Statistical Theories of Network Formation

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Summary: The basis of the statistical method of generation of branched and crosslinked structures as a Markov process is analyzed with special emphasis on the effect of differences in reactivities of functional groups. For irreversible reactions, it is important that the transition probabilities are calculated kinetically and that bonds once formed are not allowed to be reformed. The statistical methods are often a good approximation of real situation even if not all approximations used in the model are fulfilled. Cyclization is still a serious problem in modeling; For practical application it is recommended to rescale calculated ring-free dependences against the experimental gel point.

Keywords: branching; network formation; polymer network; reactivity; theory

Introduction

Statistical generation of polymer structures in the course of their formation introduced by Flory was a great step forward in quantifying the distribution of degrees of polymerization (DDP) and the gelation threshold in a branching process. In 1940, Flory[1] derived the DDP of chains formed from bifunctional *units* in different *reaction states* where the state in the simplest case is defined by the number of reacted functional groups. A linear polymer chain is generated from units with one or two reacted functional groups at a given overall conversion of functional groups into bonds. Build-up of a chain in this way is a *Markov process* controlled by *transition probabilities*; *transition* here means a passage from k-meric sequence to $(k+1)$-meric sequence of units. For the simplest case of one kind of groups and equal and independent group reactivities, the independent variable of structure evolution is the conversion of functional groups into bonds, α. A randomly selected functional group is in the reacted state with probability α and in the unreacted state with probability $1-\alpha$, irrespective of states of other units. The molar fractions of bifunctional building units, n_i, are equal to coefficients of binomial expansion $(1-\alpha+\alpha)^{[2]}$.

$$n_0 = (1-\alpha)^2; \quad n_1 = 2\alpha(1-\alpha); \quad n_2 = \alpha^2 \tag{1}$$

The probability of adding to a reacted chain end units in state 1 and state 2 are equal to $p_1 = n_1/(n_1+2n_2) = (1-\alpha)$ and $p_2 = 2n_2/(n_1+2n_2) = \alpha$, respectively.

With some modification, this treatment is valid for unequal reactivities of functional groups as well as for functionality of unit higher than 2. However, these considerations have certain limits: (1) They are applicable to assemblage of molecules from units at equilibrium. This means that chains are assembled from units of different reaction states without recourse to history of previous connections between units. Real systems differ in that (1) the bond formed by kinetically controlled reactions remains intact when new bonds are formed; (2) when extending the considerations to polyfunctional case, the existence of the gel point and existence of sol and gel components are

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new phenomena; (3) the assumption of exclusive formation of acyclic structures should always be reconsidered for non-linear systems; cycles (circuits) always exist in the gel.

The statistical theories have been used most frequently in crosslinking studies because of their relative simplicity, ability to treat chemically complex systems, and closeness to the language polymer chemists speak. Their predictive power has been appreciated. Objections against correctness of statistical theories especially if used for kinetically generated branched and crosslinked systems include in addition to their "equilibrium" nature: (1) neglect of diffusion control for reactions between the largest clusters near the gel point and (2) neglect of the excluded volume effect on group reactivity (steric hindrance). In this paper, the validity of some assumptions used in statistical generation are analyzed and improvements are suggested for kinetically controlled network build-up in multicomponent system with non-equal reactivity of functional groups. The applicability of statistical theories is looked upon from the point of view of a user. Samples of papers related to the statistical method are represented by refs.[2–22]

Analysis of Statistical Network Build-up

Network Build-up as a Markov Process

The term *Markov process* is used here the 1st order Markov process: the transition probability (probability of formation of bond of a given type) depends only on the states of units the bond connects. The probability that the selected unit A in state i extends a bond to unit B in state j by reaction of groups p and r, respectively, is written as

$$p_{\mathrm{A}i\mathrm{p}\rightarrow\mathrm{rB}j} \equiv p_{\mathrm{A}i\mathrm{prB}j}; \qquad \sum_j \sum_{\mathrm{r}} p_{\mathrm{A}i\mathrm{prB}j} = 1 \tag{2}$$

Very often, less precise specifications of transition probabilities are used such that the states of units A and B are disregarded

$$p_{\mathrm{Ap}\rightarrow\mathrm{rB}} \equiv p_{\mathrm{AprB}} \quad \text{and} \quad \sum_{\mathrm{r}} p_{\mathrm{AprB}} = 1 \tag{3}$$

In a number of instances, units A bear groups a and units B bear groups b. Then, relation (3) is simplified to

$$\begin{aligned} & p_{\mathrm{Aa}\rightarrow\mathrm{bX}} \equiv p_{\mathrm{AabB}} \equiv \\ & \quad p_{\mathbf{AB}}\ \text{and}\ p_{\mathrm{AA}} + p_{\mathrm{AB}} = 1; \\ & \quad p_{\mathrm{BA}} + p_{\mathrm{BB}} = 1 \end{aligned} \tag{4}$$

For only A and B units having, respectively, groups a and b, when only bonds a-b are

$$\begin{aligned} & p_{\mathrm{Aa}\rightarrow\mathrm{bB}} \equiv p_{\mathrm{AabB}} \equiv p_{\mathrm{AB}} = 1; \\ & \quad p_{\mathrm{BA}} = 1 \end{aligned} \tag{5}$$

In this simplest case, the fraction of reacted groups **a** engaged in bonds **a-b** is equal to $\alpha_{\mathrm{A}} p_{\mathrm{AB}} = \alpha_{\mathrm{A}}$.

Nature of Statistical Generation of Branched Structures - the Random Case

For systems with equal and independent reactivities, the structural characteristics for formation controlled by equilibrium and kinetics are the same, independent of bond formation history.[19,20] In this case, the population of units in $f+1$ reaction states, n_i $(i = 0 - f)$, and the probability of adding a unit in state i to a reacted functional group, p_i, are equal to

$$\begin{aligned} n_i &= \frac{f!}{(f-i)!i!}(1-\alpha)^{(f-i)}\alpha^i; \\ p_i &= \frac{f!i(1-\alpha)^{(f-i)}\alpha^{i'}}{(f-i)!i!f\alpha} \\ &= \frac{(f-1)!(1-\alpha)^{(f-i)}\alpha^{i-1'}}{(f-i)!(i-1)!} \end{aligned} \tag{6}$$

For n_i i varies from 0 to f and in p_i, 1 to f. This distribution is conveniently expressed in the form a number-fraction generation function

$$F_{0n}(z) = \sum_{i=0}^{f} n_i z^i = \sum_{i=0}^{f} \frac{f!}{(f-i)!i!}(1-\alpha)^{(f-i)}\alpha^i z^i = (1-\alpha+\alpha z)^f \qquad (7)$$

The auxiliary variable, z, of the probability generating function (pgf) is associated with the number of bonds. The simple form on r.h.s. of Equation (7) just demonstrates that the building unit has f functional groups which are in reacted or unreacted states. Larger structures are generated from building units by combining reacted functional groups into bonds. The pgf for the distribution of the number of bonds additional to that by which the unit is already connected is obtained from pgf F_{0n}

$$F(z) = (\partial F_{0n}/\partial z)/(\partial F_{0n}/\partial z)_{z=1} = (1-\alpha+\alpha z)^{f-1} \qquad (8)$$

Thus, the distribution of fractions of larger structures are described by substitution of z successively by $F(z)$. The pgf

$$G_k(z) = F_{0n}\underbrace{F(F(.......F(z)....)))}_{k-1\text{times}} \qquad (9)$$

describes the distribution of the number of units in the topological distance of k units. and

$$W_k(z) = zF_{0n}(\underbrace{zF(zF(.......zF(z)....)))}_{k-1\text{times}} \qquad (10)$$

the distribution of fractions of sum of units from the selected unit up to the topological distance k. The change of the value of the derivatives $G'_k(1) = F'_{0n}(1)[F'(1)]^{k-1}$ $(G'_k(1) \equiv [\partial G_k(z)/\partial z]_{z=1})$ gets steeper at $F'(1) = 1$ with increasing k and changes discontinuously for $k \to \infty$. The limits for $k \to \infty$ give recursive equations and the distributions in implicit forms valid up to the gel point.

$$G(z) = F_{0n}(w); \quad w = F(w) \quad \text{and} \quad W(z) = zF_{0n}(u); \quad u = zF(u) \qquad (11)$$

and, the condition for the gel point and the weight-average degree of polymerization:

$$F'(1) = 1\,(\text{gel point}),\ W'(1) = P_w = 1 + \frac{F'_{0n}(1)}{1-F'(1)} \qquad (12)$$

Beyond the gel point, the bonds are formed by sol + sol → (larger)sol, sol + gel → (larger)gel and gel + gel → (denser)gel reactions. Surprisingly, the fractions of units in different reaction states found experimentally are close to that calculated for an unconstrained system, but not always (e.g., chain crosslinking copolymerization[21–23]). By gel-gel reactions, circuits are formed within the gel and their number expressed by cycle rank is related to the concentration of elastically active network chains (EANC). By the "reaction fractionation", the gel in comparison with sol is progressively richer in units with more functional groups. A difference exists already at the gel point.

Beyond the gel point, the statistical theories distinguish bonds with finite or infinite continuation if one proceeds through sequences of bonds and units. The probability that an existing bond has finite continuation is called *extinction probability*. Its value is determined by a logical condition stating: if we look into the unit through a incoming bond with finite continuation, all outgoing bonds must have finite continuations. By calculating the populations of units with different number of bonds with infinite continuation, the composition of the reacting system (e.g., sol, gel, dangling chains, elastically active network chains) is established. The validity of the assumption of independence of the probabilities for a bond in the gel to have finite or infinite continuation of the state of other bonds should be analyzed.

The statistical generation of various finite branched substructures within the gel is formally possible and could characterize the fluctuations of bond densities in the gel already predicted and observed.[24] However, a straightforward generation of fluctuations is biased by the fact that circuits do exist in the gel and that the cascade substitutions cannot hold any longer (overcrowding of space).

sidered to be the same. For irreversible second-order reactions, this distribution is obtained by solution of a system of kinetic differential equations where the dependence of concentrations $[\mathrm{A}]_i$ on time can be transformed into dependence of concentrations $[\mathrm{A}]_i$ on conversion α. According to mass-action law

$$\begin{aligned}
\frac{d[\mathrm{A}_0]}{dt} &= -[\mathrm{A}_0]((9/2)k_{00}[\mathrm{A}_0] + 6k_{01}[\mathrm{A}_1] + 3k_{02}[\mathrm{A}_2]) \\
\frac{d[\mathrm{A}_1]}{dt} &= [\mathrm{A}_0](9k_{00}[\mathrm{A}_0] + 6k_{01}[\mathrm{A}_1] + 3k_{02}[\mathrm{A}_2]) - [\mathrm{A}_1](6k_{01}[\mathrm{A}_0] + (4/2)k_{11}[\mathrm{A}_1] + 2k_{12}[\mathrm{A}_2]) \\
&\vdots \\
[\mathrm{A}_0]_0 &= [\mathrm{A}_0] + [\mathrm{A}_1] + [\mathrm{A}_2] + [\mathrm{A}_3]; \quad 3\alpha = ([\mathrm{A}_1] + 2[\mathrm{A}_2] + 3[\mathrm{A}_3])/[\mathrm{A}_0]_0
\end{aligned} \tag{14}$$

Single-Component System with Substitution Effect

When the reactivities of the same type of groups are different, the analytical equivalence of statistical and kinetic treatments is lost. The unequal reactivity effect can be treated statistically on several levels as demonstrated by crosslinking of a trifunctional monomer with substitution effect: The monomer unit has three **a** groups, the reactivity of one group depends on how many groups have already reacted (Figure 1)

The basic information is expressed in the form of pgf $F_{0n}(z)$.

$$F_{0n}(z) = a_0 + a_1 z + a_2 z^2 + a_3 z^3 \tag{13}$$

The substitution effect is reduced to a modification of distribution of reaction states of units, a_i, all bonds A-A are considered to be the same.

From Equation (13), one gets

$$F(z) = \frac{a_1 + 2a_2 z + 3a_3 z^2}{a_1 + 2a_2 + 3a_3} \tag{15}$$

and one proceeds as outlined for the equal-reactivity system.

The magnitude of the approximation arising from the absence of connectivity correlations in the structure growth, Equation (13), was tested against the exact solution by the kinetic theory.[25–27] Except of cases of large differences between rate constants k_{ij} and their unusual combinations, the differences between the values of gel point conversions obtained by kinetic and statistical theories (Equation (13)) are small, i.e., the statistical generation described by distribution (13) is a good approximation.

The agreement with the exact values in the whole range of rate constants k_{ij} was much better when the structure was

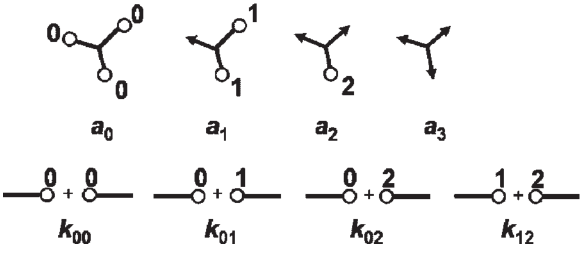

Figure 1.
Reaction states of trifunctional units with substitution effect. Numbers at unreacted groups characterize their reactivities; k_{ij} rate constants for selected pairs.

generated from fragments larger than monomer unit,[18] however, at the expense of larger complexity of the treatment. Similar improvement would be achieved by generation using rigorous 2nd order Markov process corresponding to penultimate effect in linear polymerizations.- Using a different, less complicated approach, one can incorporate information about the connectivity as developed in time. by distinguishing connections between A_i units as developing in time (16).

$$\begin{aligned} F_{0n}(\mathbf{z}) &= a_0 + a_1\zeta_1 + a_2\zeta_2 + a_3\zeta_3 \\ \zeta_1 &= p_{11}z_{11} + p_{12}z_{12} + p_{13}z_{13}; \\ \zeta_2 &= (p_{11}z_{11} + p_{12}z_{12} + p_{13}z_{13}) \\ &\quad \times (p_{21}z_{21} + p_{22}z_{22} + p_{23}z_{23};); \\ \zeta_3 &= (p_{11}z_{11} + p_{12}z_{12} + p_{13}z_{13}) \\ &\quad \times (p_{21}z_{21} + p_{22}z_{22} + p_{23}z_{23}) \\ &\quad \times (p_{31}z_{21} + p_{32}z_{22} + p_{33}z_{23}); \end{aligned} \tag{16}$$

In the construction (16), each building unit has a certain history in the reactions with another unit: When the first group of a unit reacted, it may have reacted with the 1st, 2nd, or 3rd group of the other unit. Also, a unit with three reacted groups was once in the state 1 and later in the state 2 before it was transformed into the state 3. The transition probabilities p_{ij} can be calculated from dyad concentrations, [11], [21] = [12], [22], [31] = [13], [33], [23] = [32], for a given reaction time (conversion α). The dyad concentration can be calculated by solving the system of differential equations similar to that used for calculation of concentration of units $[A]_i$. The effect of this refinement has not been analyzed as yet.

Multicomponent Systems with Groups of Different Types and Reactivities

Components with groups of intrinsically different reactivities are very important in practice for control of gelation time and conversion. As soon as the number of components increases, there exist more ways how to form branched and crosslinked structures. We will consider two-component systems. Among the simplest systems are those of $A_f + B_g$, i.e., composed of monomers having f groups **a** and g groups **b**. For equal and independent reactivity of **a** and **b** groups, respectively, the distribution of reaction states and bond types, expressed by a pgf is

$$\begin{aligned} F_{0n}(\mathbf{z}) &= n_A(1 - \alpha_A + \alpha_A\zeta_A)^f \\ &\quad + n_B(1 - \alpha_B + \alpha_B\zeta_B)^g \end{aligned} \tag{17}$$

$$\mathbf{z} = (z_{aa}, z_{ab}, z_{ba}, z_{bb})$$

where ζ_A and ζ_B, describe possible reaction paths and their relative intensities

$$\begin{aligned} \zeta_A &= p_{aa}z_{aa} + p_{ab}z_{ab}; \\ \zeta_B &= p_{ba}z_{ba} + p_{bb}z_{bb} \end{aligned} \tag{18}$$

for an alternating system $p_{aa} = p_{bb} = 0$; $p_{ab} = p_{ba} = 1$; $\zeta_A = z_{ab}$; $\zeta_B = z_{ba}$. All structural parameters are only a function of conversion, irrespective of whether the network build-up is controlled by equilibrium or by kinetics.

For the general case of Equation (18), the reaction rate constants for formation of **a-a**, **a-b**, and **b-b** bonds are different and the transition probabilities controlling bond distribution for the equilibrium case are equal to

$$\begin{aligned} p_{aa} &= \frac{n_A f\alpha_A}{n_A f\alpha_A + n_B g\alpha_B} \quad p_{bb} = \frac{n_B g\alpha_B}{n_A f\alpha_A + n_B g\alpha_B}; \\ p_{ab} &= \frac{n_B g\alpha_B}{n_A f\alpha_A + n_B g\alpha_B} \quad p_{ba} = \frac{n_A f\alpha_A}{n_A f\alpha_A + n_B g\alpha_B} \end{aligned} \tag{19}$$

The equilibrium formulation was used in the past as approximation for irreversible bond formation (cf., e.g.,[3,4,13,14,28–32]), For a kinetically controlled system, the dependence of transition probabilities on structure evolution parameter (time, conversion) is different. For irreversible reactions, bonds once formed remain intact as the reaction proceeds and cannot be transformed into bonds of other types, a process possible in reversible reactions including the equilibrium state. Then,

$$\begin{aligned} p_{aa} &= \frac{[aa]}{[aa] + [ab]} \quad p_{bb} = \frac{[bb]}{[bb] + [ba]}; \\ p_{ab} &= \frac{[ab]}{[aa] + [ab]} \quad p_{ba} = \frac{[ba]}{[bb] + [ba]} \\ [ab] &= [ba] \end{aligned} \tag{20}$$

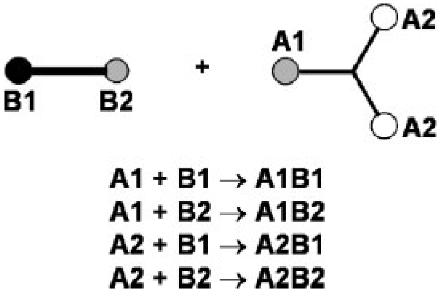

Figure 2.
Reaction scheme for monomers A1(A2)$_2$ with B1B2.

The concentrations of dyads [xy] are determined by differential equations of chemical kinetics. For instance, for simple second order kinetics

$$\frac{d[\mathrm{aa}]}{dt} = k_{\mathrm{aa}}[\mathrm{a}][\mathrm{a}] \quad \frac{d[\mathrm{ab}]}{dt} = k_{\mathrm{ab}}[\mathrm{a}][\mathrm{b}]$$
$$\frac{d[\mathrm{bb}]}{dt} = k_{\mathrm{bb}}[\mathrm{b}][\mathrm{b}]$$
$$-\frac{d[\mathrm{a}]}{dt} = \frac{1}{2}k_{\mathrm{aa}}[\mathrm{a}][\mathrm{a}] + k_{\mathrm{ab}}[\mathrm{a}][\mathrm{b}]$$
$$-\frac{d[\mathrm{b}]}{dt} = \frac{1}{2}k_{\mathrm{bb}}[\mathrm{b}][\mathrm{b}] + k_{\mathrm{ab}}[\mathrm{a}][\mathrm{b}] \tag{21}$$

with boundary conditions

$$[\mathrm{aa}]_0 = [\mathrm{ab}]_0 = [\mathrm{bb}]_0 = 0; \quad [\mathrm{a}] = [\mathrm{a}]_0, \quad [\mathrm{b}] = [\mathrm{b}]_0 \quad \mathrm{at}\, t = 0$$
$$\alpha_{\mathrm{A}} = \frac{[\mathrm{a}]_0 - [\mathrm{a}]}{[\mathrm{a}]_0}, \quad \alpha_{\mathrm{B}} = \frac{[\mathrm{b}]_0 - [\mathrm{b}]}{[\mathrm{b}]_0} \tag{22}$$

The alternating reaction of trifunctional monomer **A1 (A2)$_2$** with bifunctional monomer **B1B2 is a**nother example important for practice[33] (Figure 2). The functional groups **A1** and **A2** have intrinsically different reactivity and the same is true for groups **B1** and **B2**. (Figure 2). Chemically, the system refers to the crosslinking reaction of N-diisopropanolamine (DIPA) with a diisocyanate having NCO groups of different reactivity. The difference between the reactivity of secondary amine group of DIPA and its secondary OH group towards isocyanates groups is very large, so from these two monomers, molar ratio 1:1 a hyperbranched monomer could be formed as an intermediary product.

A classical treatment considers only reactions between groups of **A** and **B** type and the effect of unequal reactivity is reduced to the non-random distribution of units **A** and **B** units in different reaction states. A better approximation is to consider the difference in bonds (4 types of dyads, 8 types of oriented bonds). The population of bonds expressed by transition probabilities is proportional to the relative fractions of the respective partners groups (left-hand side of Equation (23))

$$p_{\mathrm{A1}\to\mathrm{B1}} = p_{\mathrm{A1B1}} = \frac{n_{\mathrm{B1}}\alpha_{\mathrm{B1}}}{n_{\mathrm{B1}}\alpha_{\mathrm{B1}} + n_{\mathrm{B2}}\alpha_{\mathrm{B2}}}$$
$$p_{\mathrm{A1}\to\mathrm{B2}} = p_{\mathrm{A1B2}} = \frac{n_{\mathrm{B2}}\alpha_{\mathrm{B2}}}{n_{\mathrm{B1}}\alpha_{\mathrm{B1}} + n_{\mathrm{B2}}\alpha_{\mathrm{B2}}}$$
$$p_{\mathrm{A2}\to\mathrm{B1}} = p_{\mathrm{A2B1}} = \frac{n_{\mathrm{B1}}\alpha_{\mathrm{B1}}}{n_{\mathrm{B1}}\alpha_{\mathrm{B1}} + n_{\mathrm{B2}}\alpha_{\mathrm{B2}}}$$
$$p_{\mathrm{A2}\to\mathrm{B2}} = p_{\mathrm{A1B2}} = \frac{n_{\mathrm{B2}}\alpha_{\mathrm{B2}}}{n_{\mathrm{B1}}\alpha_{\mathrm{B1}} + n_{\mathrm{B2}}\alpha_{\mathrm{B2}}}$$
$$p_{\mathbf{B}1\to\mathrm{A1}} = p_{\mathrm{B1A1}} = \frac{n_{\mathrm{A1}}\alpha_{\mathrm{A1}}}{n_{\mathrm{A1}}\alpha_{\mathrm{A1}} + n_{\mathrm{A2}}\alpha_{\mathrm{A2}}}$$
$$p_{\mathbf{B}1\to\mathrm{A2}} = p_{\mathrm{B1A2}} = \frac{n_{\mathrm{A2}}\alpha_{\mathrm{A2}}}{n_{\mathrm{A1}}\alpha_{\mathrm{A1}} + n_{\mathrm{A2}}\alpha_{\mathrm{A2}}}$$
$$p_{\mathbf{B}2\to\mathrm{A1}} = p_{\mathrm{B2A1}} = \frac{n_{\mathrm{A1}}\alpha_{\mathrm{A1}}}{n_{\mathrm{A1}}\alpha_{\mathrm{A1}} + n_{\mathrm{A2}}\alpha_{\mathrm{A2}}}$$
$$p_{\mathbf{B}2\to\mathrm{A2}} = p_{\mathrm{B2A2}} = \frac{n_{\mathrm{A2}}\alpha_{\mathrm{A2}}}{n_{\mathrm{A1}}\alpha_{\mathrm{A1}} + n_{\mathrm{A2}}\alpha_{\mathrm{A2}}}$$
$$\text{calculated from conversions}$$
$$\alpha_{\mathrm{A1}}, \alpha_{\mathrm{A2}}, \alpha_{\mathrm{B1}}, \alpha_{\mathrm{B2}} \tag{23}$$

In this presentation, the probability that an **A1** group has reacted and the bond extends to a **B2** group is equal to $\alpha_{\mathrm{A1}}p_{\mathrm{A1B2}}$. We need 8 transition probabilities corresponding to 4 dyads. This form of transition probabilities corresponds rather to the equilibrium case, because, for instance, a part A1–B1 bonds is allowed to dissociate when A2 groups start reacting. In reality, it is not so, the A1-B1 bonds once formed remain intact. Therefore, the transition probabilities should reflect this fact and should be based on dyad concentration.

$$
\begin{aligned}
P_{A1\to B1} &= p_{A1B1} = \frac{[A1B1]}{[A1B1]+[A1B2]}\\
P_{A1\to B2} &= p_{A1B2} = \frac{[A1B2]}{[A1B1]+[A1B2]}\\
P_{A2\to B1} &= p_{A2B1} = \frac{[A2B1]}{[A2B1]+[A2B2]}\\
P_{A2\to B2} &= p_{A2B2} = \frac{[A2B2]}{[A2B1]+[A2B2]}\\
P_{\mathbf{B}1\to A1} &= p_{B1A1} = \frac{[B1A1]}{[B1A1]+[B1A2]}\\
P_{B1\to A2} &= p_{B1A2} = \frac{[B1A2]}{[B1A1]+[B2A2]}\\
P_{\mathbf{B}2\to A1} &= p_{B2A1} = \frac{[B2A1]}{[B2A1]+[B2A2]}\\
P_{B2\to A2} &= p_{B2A2} = \frac{[B2A2]}{[B2A1]+[B2A2]}
\end{aligned}
\qquad (24)
$$

calculated from dyads $[A2B1] = [B1A2]$, etc.

The dyad concentration is calculated by solving the system of differential equations

$$
\begin{aligned}
&\frac{d[A1B1]}{dt} = k_{A1B1}[A1][B1];\\
&\frac{d[A1B2]}{dt} = \cdots \text{ etc..}\\
&\frac{d[A1]}{dt} = -[A1](k_{A1B1}[B1] + k_{A1B2}[B1];\\
&\frac{d[A2]}{dt} = \cdots \text{ etc.}\\
&t = 0 \quad [A1] = [A1]_0,\ [A2] = [A2]_0,\\
&[B1] = [B1]_0,\ [B1] = [B1]_0,
\end{aligned}
\qquad (25)
$$

The basic distribution of units and bonds is stored in the pgf

$$
\begin{aligned}
F_{0n}(\mathbf{z}) = {} & n_A(1-\alpha_{A2}+\alpha_{A2}\zeta_{A2})^2\\
& \times (1-\alpha_{A1}+\alpha_{A1}\zeta_{A1}) + n_B\\
& \times (1-\alpha_{B1}+\alpha_{B1}\zeta_{B1})\\
& \times (1-\alpha_{B1}+\alpha_{B1}\zeta_{B2})\\
\zeta_{A1} &= p_{A1B1}z_{A1B1} + p_{A1B2}z_{A1B2};\\
\zeta_{A2} &= p_{A2B1}z_{A2B1} + p_{A2B2}z_{A2B2};\\
\zeta_{B1} &= p_{B1A1}z_{B1A1} + p_{B1A2}z_{B1A2};\\
\zeta_{B2} &= p_{B2A1}z_{B2A1} + p_{B2A2}z_{B2A2};
\end{aligned}
\qquad (26)
$$

There are 8 variables z related to bond types and 8 functions F for distribution of the number of outgoing bonds. The results obtained by using "equilibrium" and "kinetics" formulation of transition probabilities are compared in Figure 3. This figure shows the excess of the A groups over the B groups, $r_A = [A]_0/[B]_0$, necessary to keep the system below the gel point and prepare a highly-branched prepolymer with functional groups A. This critical ratio is dependent on difference in group reactivities. The additivity of activation energies is assumed:

$$\kappa_A = k_{A1BX}/k_{A2BX}; \quad \kappa_B = k_{B1AX}/k_{B2AX};$$

where AX and BX are reference groups.

This figure clearly demonstrates that the "equilibrium" and "kinetics" formulations of transition probabilities give different results but also that in a certain range ($\kappa = 1$–10) they differ below experimental error. The other conclusion is that data in the literature obtained by using the equilibrium approach to systems of unequal group reactivity should be reviewed before conclusion about the magnitude of the substitution effect, cyclization, gelation threshold and evolution of other network parameters are made.

The statistical method plays a key role in the so-called *combined method* in which the finite molecules and the gel are generated from *fragments* or *superspecies* larger than monomer unit (e.g., [10]- [12], [14], [32]). These fragments or superspecies are then building units in a branching process. They were formed from monomer units and their fragments by a process that could not be described adequately by a statistical method and are later recombined into sol and gel by a statistical procedure. Copolymerizations involving a monounsaturated and a bisunsaturated monomer by living or free-radical mechanisms are examples.[11,32] The combined methods consists of three stages: (1) in a polyfunctional monomer, the connections between groups of independent reactivity are cut and the points of cut labeled, (2) linear chains (fragment, superspecies) are generated using the kinetic method, and (3) the points of cut recombined quantitatively using the statistical

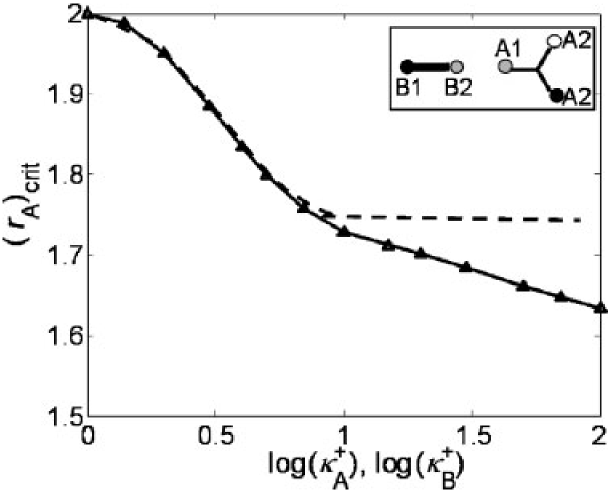

Figure 3.

Dependence of the critical initial molar ratio of A to B groups for the system $A1(A2)_2 + B1B2$ on the ratio of rate constants κ_A, κ_B (here, $\kappa_A = \kappa_B$, assumed).

method. This method can circumvent the complicated kinetic method applied to the whole system and to get access to parameters characterizing the gel structure. It was claimed by several groups that the recombination of points of cut can be random if the reactivities are independent. However, the recombination of points of cut should be controlled by kinetically obtained transition probabilities similarly as in the $A1(A2)_2 + B1B2$ case. In a number of systems (substitution effect in polyfunctional units), conversion dependent degree of polymerization of primary chains) random combination of fragments (by joining points of cut) is only an approximation. To remove this randomness of recombination, recombination probabilities were made dependent on conversion and network build-up was solved as a multistage process.[17] The bond formation is then classified according to the time (conversion) at which the bond was formed. This corresponds to sets of variables of probability generating functions. This is hardly applicable beyond the gel point (corresponding sets of extinction probabilities) and is of complexity of a fully kinetic approach.

Other Information Offered by Statistical Theories

The branching theories have been applied to characterize many other structural features of crosslinked systems. One of the most important advantages of statistical assemblage is the possibility to characterize special features of the gel and sol. Because of the limited size of the contribution, we can only briefly comment on the topic and give references to more detailed discussions

- classifying units with respect to the number of *bonds with finite and infinite continuation*, one can assemble *substructures* such as sol (all bonds with finite continuation), in the dangling chains (one bond with infinite continuation), elastically active network chains (two bonds with infinite continuation), and elastically active network junctions (three and more bonds with infinite continuation).[8,34,35]
- *polydispersity* of precursors with respect to the number of *functional groups* and *molecular mass*. is easy to handle with statistical theories. The distributions are very important for incipience of gelation and magnitude of the sol fraction.

- *internal branching* in some precursors (e.g., functional copolymers, hyperbranched polymers, off-stoichiometric highly-branched polymers). the branch points get gradually activated beyond the gel point and start contributing to the concentration of EANCs.[36] The existence of internal branch points has no effect on gelation which is only a function of precursor functionality.
- Characterization of magnitude of *chemical clusters* of like units, classifying bonds between like and unlike units.[37] For example, hard units in contrast to soft units in a polyurethane system. Existence of hard clusters and their size distribution affect the mechanical and optical properties.
- *Transient (physical) networks* is the domain most suitable for implementation of a statistical theory because of reversibility of the crosslinking reaction and independence of the history of structure build-up, Also attractive is the possibility of coupling gelation and phase separation[38–40]
- *Multistage network formation* is a process which can be very well described by statistical theories distinguishing bonds formed within different stages. The products in one stage are converted to starting components of the following stage.[41]
- *Cyclization* is an important phenomenon which can be treated with great difficulty because one has to find the probabilities that two specified functional groups chemically bonded to various polymer structures of the crosslinking system meet in space. Sums of these probabilities should be taken relative to the probability of formation of intermolecular bonds. Cyclization is a long-range correlation in reactivity which also affects the intermolecular reaction. The statistical theories are not equipped for treatment of such long-range correlations but they can be modified to take into account cyclization as perturbation of the ring-free case.[42,43] One of the variants is called *spanning-tree approximation* in which the bonds issuing from a unit are classified as *branching* or *ring forming*.[4,44] In some reactions (like free-radical crosslinking copolymerization, cyclization can be very strong and the perturbation treatment cannot be used.

Conclusions

Statistical assemblage of branched and crosslinked structures is relatively simple. Manipulation with building units is close to polymer chemist who builds up large structures from small molecules and to physical chemists who thinks in terms of kinetics and mechanism of bond formation and group reactivity as affected by electronic interactions and steric hindrance. One can expect that the application of statistical theories will be successful in a wide range of reaction mechanisms of bond formation and conversions of functional groups including the position of the gel point. It is not suitable for simulation of processes in the critical region of incipient gelation (critical exponents) because the simulation results are determined by the statistical nature of assemblage rather than by the actual physical mechanism of gelation. Cyclization is a serious problem. The models are not at the stage where extent of cyclization can simply be predicted from available information about the structure of connecting paths. In many practical systems, the fraction of bonds lost in cycles (elastically inactive cycles) varies between 10 and 40% of total bonds. It has been observed, however, that some dependences look similar to each other if rescaled against the gel point. This observation can be utilized is such a way that critical conversion of groups is found experimentally and structural parameters calculated using a ring-free model are rescaled. A check can be made whether extrapolation of the dependence of the gel point conversion to hypothetic ‘‘infinite density’’ gives the ‘‘ring-free’’ value of critical conversion.

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