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Correspondence Between the Theory of Branching Processes and the Kinetic Theory for Random Crosslinking in the Post-Gel Stage

Karel Dušek

Institute of Macromolecular Chemistry, Czechoslovak
Academy of Sciences, 162 06 Prague 6, Czechoslovakia

Summary

The kinetic theory of crosslinking by step reactions (KUCHANOV 1978) may be extended beyond the gel point, and the structure and amount of sol may be described. For random reactions, the kinetic theory yields results identical with the theory of branching processes based on cascade substitution (GORDON 1962, 1975, DOBSON 1965). The extension of the kinetic theory may be employed in order to compare deviations between the two theories expected for the dependent reactivities of functional groups.

The theory of branching processes and kinetic theory

The main theories used for the description of formation of crosslinked polymers are: (1) theory of branching processes based on the graph model of matter and on cascade substitution (GORDON 1962, 1975, DOBSON 1965), and (2) kinetic theory, describing the growth of chemical structures by kinetic differential equations (SAITO 1958, AMEMYIA 1969, PISMEN 1971, KUCHANOV 1978). In the theory of branching processes, which generalizes earlier combinatorial and similar approaches, chemical structures are represented by rooted trees; evolution of these trees also describes changes in the structure as a function of the extent of the crosslinking reaction. At each value of conversion, the trees are generated from smaller (starting) units, issuing various numbers of bonds. The generation of the trees occurs by means of probability generating functions (pgf) while respecting chemical and kinetic rules for bond formation. The apparatus used in the theory of branching processes is suitable for the description of structural changes in the pre- and post-gel stage.

The kinetic theory describes the formation and disappearance of an x-mer with unreacted functional groups as a second-order reaction. Changes of the respective concentration $c_{x,1}$ are described by an infinite system of differential equations. Saito's (SAITO 1958,

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AMEMYIA 1969) theory of random crosslinking (developed in connection with degradation and crosslinking caused by high-energy radiation) is based on several approximations (x=1 and direct proportionality of the conversion to time). Such approximations restrict the applicability of Saito's theory to very low reaction conversions (degrees of crosslinking) and may sometimes become a considerable drawback, especially beyond the gel point. Due to these approximations, the results of Gordon's and Saito's theories are different.

The independently developed Kuchanov's approach (PISMEN 1971, KUCHANOV 1978) is more perfect in that it takes into account the proportionality between the reaction rate of the particle and its number of unreacted functional groups (1), as well as the real dependence of conversion on time. In principle, the approach may also include the different or dependent (substitution effect) reactivities of functional groups, which makes the method attractive for its application in a number of important polycondensation and polyaddition reactions. The kinetic theory better simulates kinetically controlled polyreactions, since it preserves the connectivity of structures during their evolution.

Kuchanov's kinetic theory was applied only up to the gel point (PISMEN 1971, KUCHANOV 1978); its inapplicability beyond the gel point was explicitly stated (PISMEN 1971, IRZHAK 1978). Using a random reaction of an f-functional monomer (monodisperse primary chains) as an example, we demonstrate the possibility of extending Kuchanov's theory beyond the gel point, while respecting the kinetics of the process, and the full correspondence of this theory with Gordon's theory for random reactions beyond the gel point.

The extension of Kuchanov's kinetic theory beyond the gel point

A system of kinetic differential equations describing a process characterized by a change in the concentration, $c_{x,l}$, of particles composed of x units and bearing l unreacted groups may be written as

$$\partial c_{x,l}/\partial \tau = -l c_{x,l} \sum_{l=1}^{\infty} \sum_{x=1}^{\infty} l c_{x,l} +$$

$$+ (1/2) \sum_{j=0}^{l} \sum_{k=1}^{x-1} (j+1)(l-j+1) c_{k,j+1} c_{x-k,l-j+1} \qquad (1)$$

where τ is a dimensionless time. The first term expresses the rate of disappearance and the second one the rate of formation of particles with x units and l groups, x and l being interdependent. Such a system of differential equations may be transformed into a partial differential equation

$$\partial g/\partial \tau = -\mu r(\partial g/\partial r) + (1/2)(\partial g/\partial r)^2 \qquad (2)$$

for the generating function $g(s,r,\tau)$ with dummy variables s and r for the distribution of concentration $c_{x,l}(\tau)$

$$g(s,r,\tau) = \sum_l \sum_x c_{x,l}(\tau) s^x r^l \qquad (3)$$

the concentrations $c_{x,l}$ are related to the (structural) unit of the system,

$$\sum_l \sum_x x c_{x,l}(\tau) = 1$$

and the initial condition

$$g(s,r,0) = sr^f \quad \text{and} \quad d\mu/d\tau = -\mu^2,$$

where μ is the concentration of functional groups per unit. A solution employing the method of characteristics gives for the step polyaddition of an f-functional monomer ($l = f(x-2)-2$) the generating function

$$g(s,r,\tau) = s\xi^f - (1/2)fs\xi^{f-1}(\xi - r(1-\alpha)) \qquad (4)$$

where

$$\xi - \alpha s \xi^{f-1} = r(1-\alpha) \qquad (5)$$

and α is the conversion of functional groups ($\mu = f(1-\alpha)$).

Beyond the gel point, Eq.(1) is still valid, if $c_{x,l}$ are related only to particles in the sol: from here onwards, the particle concentration changes by combining finite particles through reaction of their unreacted functional groups, but finite particles also disappear by reacting with functional groups in the gel. Hence, Eq.(1) may be rewritten to yield

$$\partial c_{x,l}/\partial \tau = -l c_{x,l}\left(\sum_l \sum_x l c_{x,l} + \mu_g w_g\right) +$$

$$+ (1/2)\sum\sum (j+1)(l-j+1)c_{k,j+1}c_{x-k,l-j+1} \qquad (6)$$

where μ_g is the concentration of unreacted groups in the gel per unit in the gel, and w_g is the weight fraction of the gel. In addition to sol-sol and sol-gel reactions, there occur reactions between functional groups in the gel, which however are irrelevant for changes described by Eq.(6). It holds, also, that

$$\sum_x \sum_l l c_{x,l} = \mu_s w_s \qquad \text{and} \qquad \mu_s w_s + \mu_g w_g = \mu$$

so that the solution of Eqs (1) and (6) is the same, leading through Eq.(2) to Eqs (4) and (5).

The solutions of (4), (5) allow us to obtain the sol fraction and the degrees of polymerization averages (e.g., the number average P_n and the weight average P_w) of the sol

$$\hat{P}_n = w_s/g(1,1,\tau) \tag{7}$$

$$w_s = g^s(1,1,\tau) \tag{8}$$

$$\hat{P}_w = g^{ss}(1,1,\tau)/g^s(1,1,\tau) + 1 \tag{9}$$

where g^s and g^{ss} respectively are the first and second derivative of g with respect to s. The correspondence of this solution with that offered by the theory of branching processes follows already from the structure of Eq.(5) for r=s=1. If we put $\xi^{f-1} = v$, Eq.(5) becomes

$$v = (1-\alpha + \alpha v)^{f-1} \tag{10}$$

which is the equation for the extinction probability, v, derived in Gordon's theory from the link probability generating function (lpgf) F_1 for units in the first generation, $v = F_1(v)$, and

$$\hat{P}_n = 1/(1-F_o'/2) \tag{11}$$

$$\hat{P}_w = 1 + F_o'/(1-F_1') \tag{12}$$

$$w_s = F_o(v) \tag{13}$$

where F_o is lpgf for the number of bonds issuing from the root, and $F' = (\partial F(\theta)/\partial\theta)_{\theta=1}$.

Both procedures (Eqs (7-9) and (11-13)) lead to the same result expressed e.g. through v

$$\hat{P}_n = 1/\left[1-fv\alpha/2(1-\alpha+\alpha v)\right] \tag{14}$$

$$\hat{P}_w = \left[f\alpha v/(1-\alpha+\alpha v)\right]/\left[1-(f-1)\alpha v/(1-\alpha+\alpha v)\right] \tag{15}$$

$$w_s = v(1-\alpha+\alpha v) \tag{16}$$

Likewise, for the distribution of functionalities (crosslinking of primary chains) Eq.(1) under initial condition

$$g(s,r,0) = N_o(sr)$$

yields a relation for ξ in the form

$$r(1-\alpha) = \xi - \alpha W_o(\xi s)/\xi \tag{17}$$

which, with $\xi = 1-\alpha+\alpha u$, leads to the recurrent relation of cascade substitution

$$u = W_o(\xi s)/\xi = \sum_x w_x^o s^x(1-\alpha+\alpha u)^{x-1} \tag{18}$$

when N_o and W_o respectively are pgfs for the number and weight fraction of the primary distribution.

The equivalency of both procedures in random crosslinking is very important for the analysis of crosslinking polyreactions of compounds bearing groups with dependent reactivity. Kuchanov (1978) has found that the kinetically controlled stepwise polyaddition of a bifunctional monomer with the first-shell substitution effect yields chains obeying non-Markovian statistics. An exact distribution of the degrees of polymerization cannot therefore be obtained by cascade substitution with the Markovian finite-order statistics. It may be expected, consequently, that for non-random crosslinking polyreactions too the kinetic theory and the theory of branching processes will not give identical results. It is namely possible, even for unequal and dependent reactivities of functional groups, to extend the kinetic theory beyond the gel point while observing the general structure of Eq.(1). The terms corresponding to the first term on the right-hand side of Eq.(6) should have the form

$$-{}^{1}_{i}c_{x,1}\left[\sum_{i}\sum_{x}\sum_{j}k_{ij}({}^{1}_{j}c_{x,1}+\mu_{j}w_{g})\right]$$

where k_{ij} are the relative dimensionless rate constants of a reaction between functional groups of type i and j. The term in square brackets obviously depends only on τ.

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