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Nonequilibrium Stochastic Theory of Polymerization Processes

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ABSTRACT: A new, nonequilibrium stochastic theory of polymerization processes is developed. For complex polymerization reactions as those involving cyclization, size dependent reactivity, or diffusion effects, existing statistical and kinetic theories do not predict equivalent results. In the present work a unified and internally consistent procedure is developed for the analysis of size distributions resulting from such complex polymerization reactions. Our starting point is the Kolmogorov stochastic differential equations with the generator depending explicitly on the transition matrix for multifunctional systems. The functional form of the generator is derived for systems with equal reactivity and then extended to systems with unequal reactivity. The solution to the equations yields the Flory–Stockmayer distributions when the assumption of equal reactivity is valid. Statistical and kinetic theories are re-covered as special cases of the present theory.

1. Introduction

Statistical[1-10] and kinetic[11-16] methods developed for the study of molecular size distributions resulting from polymerization reactions have been successfully applied to systems with equal reactivity. However, actual polymerization reactions involve a variety of side effects such as cyclization,[14,17-20,23-26] unequal reactivity,[16,21] and diffusion effects.[22-26] For these systems it is well-known that existing statistical and kinetic models do not predict equivalent distributions.

An advantage of statistical theories is that the distributions they predict are Markovian. Although this is what is also expected from kinetic theories, there is no direct way for the establishment of Markovian properties in species distributions obtained from kinetic equations. On the other hand, the kinetic equations afford distributions which are in agreement with the scaling properties predicted by percolation computer simulations.[16,27] More realistic computer simulations have been developed to account for cyclization effects.[28-30]

The present work aims at bridging the gap between statistical and kinetic theories, developing a unified approach for the investigation of size distributions. For this purpose the kinetic equations are replaced by a kind of kinetic–statistical equations, the stochastic differential equations.[31-33] The probabilities for a randomly selected monomer to belong to a molecule with degree of polymerization i are treated as quantities which change with time, rather than as equilibrium quantities.[2,3,13,15] It is then shown that statistical and kinetic theories form two equivalent representations of the more general stochastic theory.

2. Stochastic Equations for Polymerization Reactions

We start by rewriting the equations of mass conservation in a form suitable for polymerization reactions. A polymerization system is considered as a mixture of chemical species U_1, U_2, ..., U being the monomeric unit. We consider three successive instants t, t', and t'' and denote $M_i = M_i(t)$ the total number of monomeric units contained in molecules with degree of polymerization i at instant t (viz. being in state i at t). When $P_{ij}(t,t')$ is defined to be the fraction of monomeric units at t in state i which at t' are found to belong to molecules with degree of polymerization j, the number of monomeric units contained at t' in molecules with degree of polymerization j is obtained by summing over all contributions to state j:

$$M_j(t') = \sum_i M_i(t)P_{ij}(t,t') \qquad (1)$$

The number of monomeric units in state k at t'' may be calculated in two ways, the result being in both cases the same

$$\sum_i M_i(t)P_{ik}(t,t'') = \sum_j M_j(t')P_{jk}(t',t'') \qquad (2)$$

Substituting for $M_j(t')$ from eq 1 and rearranging we get

$$\sum_i [P_{ik}(t,t'') - \sum_j P_{ij}(t,t')P_{jk}(t',t'')]M_i(t) = 0 \qquad (3)$$

from which

$$\mathbf{P}(t,t'') = \mathbf{P}(t,t')\cdot\mathbf{P}(t',t'') \qquad (4)$$

where $\mathbf{P}(t,t')$ is the matrix with elements $P_{ij}(t,t')$.

The quantities P_{ij} appeared in the above discussion as fractions of monomers transferring from one species to another. To obtain their statistical counterpart, we consider the experiment in which, at a particular instant, monomeric units are randomly selected and the degree of polymerization of the molecule they belong to is examined. The degree of polymerization observed each time is a random quantity denoted X. The probability of selecting a monomeric unit belonging to a molecule with degree of polymerization i will be equal to the fraction

$$P(X=i) = \frac{iN_i}{M_0} = \frac{in_i}{X_n} = w_i \qquad (5)$$

where N_i is the number of molecules with degree of polymerization i, M_0 is the total number of monomeric units, X_n is the number average degree of polymerization, and w_i is the mass fraction of species i.

Similarly, the probabilistic counterpart of P_{ik} is obtained by considering the experiment in which at instant t a monomeric unit is randomly selected for study. If it belongs to a molecule with degree of polymerization i, then at instant t' the degree of polymerization of the molecule it belongs to is examined anew; else the trial is ignored. The probability of observing in this way a molecule with degree of polymerization k is given by the conditional probability on the left side of eq 6.

$$P(X(t') = k|X(t)=i) = \frac{M_i(t)P_{ik}(t,t')}{M_i(t)} = P_{ik}(t,t') \qquad (6)$$

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The reactant of a polymerization reaction is usually assumed to be a monomer or a mixture of monomers, which means that the conditional probability $P(X(t)=k|X(0)=1) = P_{1k}(0,t)$ coincides with the mass fraction of k.

Writing eq 4 in infinitesimal form, the equations of Kolmogorov[31-33] are obtained:

$$\left.\frac{\partial \mathbf{P}}{\partial t}\right|_{(\tau,t)} = \mathbf{P}(\tau,t)\cdot\mathbf{G}(t) \tag{7}$$

where

$$\mathbf{G}(t) = \lim_{\Delta t\to 0}\frac{1}{\Delta t}[\mathbf{P}(t,t+\Delta t) - \mathbf{I}] \tag{8}$$

is a matrix referred to as the process generator. For multifunctional polymerizations $\mathbf{G}$ is a function of $\mathbf{P}$, its functional form depending on the particular assumptions we associate with the polymerization process. In the next section the form of $\mathbf{G}$ is derived for systems with equal reactivity.

3. Solution to the Stochastic Equations for the Polycondensation of an f-Functional Monomer

In the present section the polycondensation of an f-functional monomer with similar functional groups reacting intermolecularly[1b,2,3,6,8,12,13] is treated according to the stochastic theory. The reaction mechanism is fully specified by the next two additional assumptions known as the postulate of equal reactivity:[1a]

1. Distinct functional groups belonging to the same molecule react independently from each other.

2. All functional groups present in the reaction place have an equal chance for reaction at any particular instant, no matter what the size is of the molecule they belong to.

Process Generator. The chance for reaction in $t,t+\mathrm{d}t$ coincides with the probability $b\mathrm{d}t$ for a randomly chosen functional group to react in this time interval. This is obviously given by the fraction of functional groups reacting in this time interval, i.e., $-\mathrm{d}F/F$, where F is the total number of functional groups at instant t. Expressing F in terms of the functionality conversion p gives

$$b\mathrm{d}t = \frac{\mathrm{d}p}{1-p} \tag{9}$$

When ϕ_j (it follows from assumption 2 that it does not depend on i) is denoted as the fraction of the $F_i b\mathrm{d}t$ i-functional groups which react during the interval $t,t+\mathrm{d}t$ with j-functional groups, the number of functional groups belonging to species i at t and reacting during the interval $t,t+\mathrm{d}t$ with j-functional groups is $F_i b\mathrm{d}t\phi_j$. From symmetry and the normalization condition on ϕ_j follows

$$\phi_j = F_j/F \tag{10}$$

Equation 10 expresses that at any particular instant the (conditional) probability for an i-functional group to react with a j-functional group (given that it does react) is equal to the functionality fraction of species j and it is independent of i.

We are now in the position to calculate the process generator $\mathbf{G}$. Recall that $X(t)$ is the degree of polymerization of the molecule to which a randomly selected (at instant t) monomeric unit belongs and $P(X(t')=j|X(t)=i) = P_{ij}(t,t')$ is the probability for the transition $i \to j$ in the time interval t,t'. The probability that a molecule with degree of polymerization i at t does not react during the interval $t,t+\mathrm{d}t$ is given by the probability that none of its functional groups react in this time interval. The latter, according to assumption 1 and the law of independent events, is $(1-b\mathrm{d}t)^{f_i}$, where $f_i = (f-2)i+2$ is the functionality of the molecule:

$$P(X(t+\mathrm{d}t)=i|X(t)=i) = (1-b\mathrm{d}t)^{f_i} = 1 - f_i b\mathrm{d}t \tag{11}$$

For $j \neq i$ the probability for a transition $i \to j$ in the interval $t,t+\mathrm{d}t$ is given according to the law of conditional probabilities by

$$P(X(t+\mathrm{d}t)=j|X(t)=i) = P(X(t+\mathrm{d}t)=j|X(t)=i,X(t+\mathrm{d}t)\neq i)P(X(t+\mathrm{d}t)\neq i|X(t)=i) \tag{12}$$

According to eq 11

$$P(X(t+\mathrm{d}t)\neq i|X(t)=i) = 1-(1-b\mathrm{d}t)^{f_i} = f_i b\mathrm{d}t \tag{13}$$

Transitions $i \to j$ are only possible through reaction of i-molecules with $(j-i)$-molecules, i.e. the first factor of the right-hand side of eq 12 is equal to the (conditional) probability that an i-molecule reacts with a $(j-i)$-molecule (given that the molecule with degree of polymerization i does react) (eq 10):

$$P(X(t+\mathrm{d}t)=j|X(t)=i,X(t+\mathrm{d}t)\neq i) = \phi_{j-i} \tag{14}$$

Combining eqs 12–14 we get

$$P_{ij}(t,t+\mathrm{d}t) = f_i b\mathrm{d}t\phi_{j-i} \qquad \text{for } j > i \tag{15}$$

The process generator $\mathbf{G}$ is calculated according to eq 8:

$$G_{ij}(t) = \begin{cases} -f_i b & \text{for } j = i \\ f_i\phi_{j-i}b & \text{for } j > i \\ 0 & \text{for } j < i \end{cases} \tag{16}$$

where $b = b(t)$ and $\phi_j = \phi_j(t)$.

The stochastic equations (7) read

$$\left.\frac{\partial P_{ik}}{\partial t}\right|_{(\tau,t)} = -f_k b(t)P_{ik}(\tau,t) + b(t)\sum_{j=1}^{k-1} f_j P_{ij}(\tau,t)\phi_{k-j}(t) \tag{17}$$

Mass Distribution. A system of differential equations for the mass distribution is obtained from eq 17 by letting $i = 1$ and $\tau = 0$ and replacing b by its expression from eq 9:

$$(1-p)\frac{\mathrm{d}w_k}{\mathrm{d}p} = -f_k w_k + \sum_{j=1}^{k-1} f_j\phi_{k-j}w_j \tag{18}$$

Equation 18 must be solved with the initial conditions $w_1 = 1$ and $w_k = 0$, $k > 1$, for $p = 0$.

The relationship between the mass and the functionality distributions is obtained from eqs 10 and 5:

$$\phi_k = \frac{f_k n_k N}{F} = \frac{f_k w_k}{kf(1-p)} \tag{19}$$

where N is the total number of molecules.

Introducing eq 19 into eq 18 and combining the first two terms of eq 18 into a single one through the substitution $y_k = w_k(1-p)^{-f_k}$ furnish a system for y_k which has the obvious solution $y_k = C_k p^{k-1}$ with C_k defined by the recursion relationship

$$C_k = \frac{1}{(k-1)f}\sum_{j=1}^{k-1}\frac{f_j f_{k-j}}{k-j}C_j C_{k-j} \qquad C_1 = 1 \tag{20}$$

from which we get the explicit relationship

$$C_k = \frac{f(kf-k)!}{(k-1)!f_k!} \tag{21}$$

The solution for the mass distribution is the classical Flory–Stockmayer distribution.[1b]

$$w_k = C_k p^{k-1}(1-p)^{f_k} \tag{22}$$

with C_k given by (21) or equivalently (20).

Laplace Transforms of Species Distributions. The Laplace transform[32] of the mass distribution is defined by

$$W(p;s) = \sum_k w_k(p)e^{-ks} \qquad s \geq 0 \tag{23}$$

The Laplace transforms of the number and functionality distributions Γ and Φ, respectively, are defined similarly. Probability generating functions (denoted by the same letters) are obtained from the corresponding Laplace transforms setting $\theta = e^{-s}$.

For further reference we write down the transformed eqs 18, 5, and 19:

$$(1-p)\frac{\partial W}{\partial p} = -(1-\Phi)\mathcal{F}W \tag{24}$$

$$W = \mathcal{H}\Gamma' \tag{25}$$

$$f(1-p)\Phi = \mathcal{F}\Gamma' \tag{26}$$

with the degree of polymerization and functionality operators defined in the Laplace transform representation by $\mathcal{H} = -\partial/\partial s$ and $\mathcal{F} = 2 + (f-2)\mathcal{H}$. This terminology is due to the fact that the spectrum of these operators (defined on a suitable functional subspace) coincides with the set of allowable values for the degree of polymerization and functionality and the corresponding eigenfunctions represent sharply defined (monodisperse) states with degree of polymerization and functionality equal to the corresponding eigenvalue.

Degree of Polymerization Averages. From eq 29 below summing over k, an equation for X_n is obtained, which is easily solved to yield the number average DP:

$$X_n = 1/(1-q) \tag{27}$$

where $q = pf/2$ is the molecular conversion.

From eqs 19 and 29 we obtain a system for the functionality and mass average DP $X_f = \sum_k k\phi_k$ and $X_w = \sum_k kw_k$, respectively, which is solved for the mass average DP:[1-9]

$$X_w = \frac{1+p}{1-(f-1)p} \tag{28}$$

Kinetic Equations. Dividing both sides of eq 18 by k and using eq 19

$$f(1-p)^2\frac{dn'_k}{dp} = \frac{1}{2}\sum_j f_j f_{k-j} n'_j n'_{k-j} - f(1-p)f_k n'_k \tag{29}$$

where $n'_k = n_k/X_n$. Multiplying both sides of this equation by the number of monomers N_o and letting $k = b/F$ be the reaction constant between functional groups yield the kinetic equations in the form:

$$-\frac{dN_j}{dt} = \sum_{i=1}^{\infty} K_{ij}N_iN_j - \frac{1}{2}\sum_{i=1}^{j-1} K_{ij-i}N_iN_{j-i} \tag{30}$$

with $K_{ij} = kf_if_j$ (see refs 12, 13, and 16).

In eqs 29 and 30 reactions between functional groups are second order in species concentrations. This is also implicit in eq 18, as the postulate of equal reactivity is equivalent to second order reactions between functional groups: the reaction rate between *i*- and *j*-functional groups, $R_{ij} = -\mathbf{d}F_{ij}/dt$, ($-\mathbf{d}F_{ij}$ is the number of *i*-functional groups reacting in dt with *j*-functional groups) taking into account that $-\mathbf{d}F_{ij} = \phi_j F_i b dt$, is $R_{ij} = F_iF_j(b/F) = kF_iF_j$.

Deduction of the Branching Process Theory. Eliminating W and Γ from eqs 24–26 yields a partial differential equation for Φ

$$(1-p)\frac{\partial \Phi}{\partial p} - (f-2)(1-\Phi)\frac{\partial \Phi}{\partial s} = \Phi^2 - \Phi \tag{31}$$

which is solved by standard methods (Appendix A):

$$\Phi = \theta(1-p+p\Phi)^{f-1} \tag{32}$$

Equation 32 implies that Φ can be thought of as the probability generating function of all generations of a Galton–Watson branching procss[34] for which each generation has the probability generating function

$$F_2(\theta) = (1-p+p\theta)^{f-1} \tag{33}$$

The mass distribution W is obtained from eqs 24 and 32 with the method outlined in Appendix B:

$$W = \theta(1-p+p\Phi)^f \tag{34}$$

Equation 34 in view of eq 32 means that W can be conceived as the probability generating function of all generations of a Galton–Watson branching process for which the first generation has the probability generating function

$$F_1(\theta) = (1-p+p\theta)^f \tag{35}$$

and all other generations $F_2(\theta)$ (eq 33).

The probability generating functions F_1 and F_2 are the same as those used a priori by Gordon[6,7] in his branching process theory. The present theory offers, aside of a strict derivation of these functions, a physical interpretation to "dummy" variables:[6,7] Φ (u in ref 6) is the functionality distribution generating function.

4. Unequal Reactivity

For systems with equal reactivity the reaction rate R_{ij} between *i*- and *j*-functional groups is proportional to the corresponding functionality concentrations F_i and F_j, the proportionality coefficient being independent from i and j. In the most general case R_{ij} is a function of i, j, F_i, and F_j. The chance an *i*-functional group has to react in the interval $(t, t+dt)$, $b_i dt$, depends on i, and the probability that an *i*-functional group reacts in this time interval with a *j*-functional group is $b_{ij}dt = -\mathbf{d}F_{ij}/F_i = R_{ij}dt/F_i$. The process generator is determined in exactly the same way with systems having equal reactivity:

$$G_{ij}(t) = \begin{cases} -f_ib_i & \text{for } j=i \\ f_ib_{i,j-i} & \text{for } j>i \\ 0 & \text{for } j<i \end{cases} \tag{36}$$

The stochastic equations for the mass distribution assume the form

$$\frac{dw_k}{dt} = -f_kb_kw_k + \sum_{j=1}^{k-1} f_jb_{j,k-j}w_j \tag{37}$$

Similarly, the kinetic equations read

$$-\frac{\mathrm{d}N_j}{\mathrm{d}t} = \sum_{i=1}^{\infty} R_{ij} - \frac{1}{2}\sum_{i=1}^{j-1} R_{i,j-i} \tag{38}$$

where $R_{ij} = R_{ij}(i,j,N_i,N_j)$. Two special cases can be distinguished for R_{ij}:

1. For size dependent reactivity $R_{ij} = K_{ij}N_iN_j$ with $K_{ij} = k_{ij}f_if_j$.[16]

2. For 2α order reaction between functional groups $R_{ij} = K_{ij}N_i^{\alpha}N_j^{\alpha}$.

The above equations cannot be solved to obtain explicitly the species distribution. Similarly, the probability generating functions do not satisfy simple equations such as eqs 32 and 34 and the mass average DP X_w cannot be expressed explicitly as function of p. However, X_n is still given by eq 27, a consequence of the fact that the number average DP is independent from the way polymer molecules combine with each other.

For the study of these distributions one has to resort to numerical integration of eq 37 or 38. These equations are quite general, and it can be shown that even if cyclization reactions are present, they retain their form. However, the form of R_{ij} is indeterminate if cyclization side reactions are present, and a more general problem involving an additional index to account for the degree of cyclization must be considered (see forthcoming publication).

5. Mixture of Monomers with Similar Functional Groups

We consider a mixture of two types of monomers denoted 1 and 2, with similar functional groups and functionality f and g, respectively. The molecular species of this system are characterized by a double index $\mathbf{i} = (j,k)$ where j and k are the number of monomeric units (referred to as partial DP) of types 1 and 2, respectively, contained in the molecule. The functionality of a (j,k)-molecule will be

$$f_{jk} = (f-2)j + (g-2)k + 2 \tag{39}$$

The partial mass fractions are obtained from the transition matrix $\mathbf{P}$ with elements $P_{ij;kl}(\tau,t)$:

$$w^1_{kl} = P_{1,0;k,l}(0,t) \tag{40a}$$

$$w^2_{kl} = P_{0,1;k,l}(0,t) \tag{40b}$$

The (total) mass fraction will be

$$w_{kl} = x_1w^1_{kl} + x_2w^2_{kl} \tag{41}$$

x_j being the mole fraction of monomer j.

Relationships between mass and mole fractions are obtained considering the following experiment. At instant t a monomeric unit is randomly selected for study; if it is of type 1 the partial DPs of the molecule to which it belongs are recorded; else the trial is ignored. The probability to observe a molecule with partial DPs k,l is

$$P_1(X_1{=}k,X_2{=}l) = kN_{kl}/\sum_i\sum_j iN_{ij} \tag{42}$$

In this equation X_1 and X_2 are the random variables representing the corresponding partial DPs and N_{kl} and n_{kl} are the number of molecules with partial DPs k and l, respectively, and the corresponding mole fraction. Using the equation $\sum_i\sum_j iN_{ij}{=}x_1N_o$ in (42) and rearranging give

$$x_1w^1_{kl} = kn'_{kl} \tag{43}$$

N_o is the total number of monomeric units, $n'_{kl} \equiv n_{kl}/X_n$, and $X_n = N_o/N$ is the number average DP. A similar relationship is valid for w^2_{kl}.

The functionality fraction ϕ_{kl} of the species (k,l) is defined as the fraction of functional groups belonging to this species:

$$\phi_{kl} = \frac{f_{kl}n'_{kl}}{f_n(1-p)} \tag{44}$$

where $f_n = x_1f + x_2g$ is the average functionality.

Stochastic Equations. The process generator $\mathbf{G}$ with matrix elements $\mathrm{G}_{ij;kl}$ is derived quite analogously to systems with one type of monomer:

$$G_{\mathrm{ij};kl}(t) = \begin{cases} -f_{ij}b & \text{for } k = i,\ l = j \\ f_{ij}\phi_{k-i,l-j}b & \text{for } k \geq i,\ l \geq j,\ (k,l) \neq (i,j) \\ 0 & \text{else} \end{cases} \tag{45}$$

where b is given by eq 9.

Substituting in eq 7 the above expression for $\mathbf{G}$ we get the stochastic differential equations:

$$\frac{\partial}{\partial t}P_{ij;kl} = -bf_{kl}P_{ij;kl} + b\sum_m\sum_n P_{ij;mn}f_{mn}\phi_{k-m,l-n} \tag{46}$$

The summation in eq 46 extends over $m = 0, 1, ..., k$ and $n = 0, 1, ..., l$, $(m,n) \neq (k,l), (0,0)$. Letting in eq 46 $\tau = 0$ and successively $i = 1, j = 0$ and $i = 0, j = 1$, we obtain a system of differential equations for the partial mass fractions, which is solved with the method described in section 3 to yield the classical Stockmayer distributions.[2–5,36]

Kinetic Equations. The Laplace transforms[32] of the mass distributions are defined analogously to systems involving one monomer:

$$W_i(p;\mathbf{s}) = \sum_{\mathbf{k}} w^i_{\mathbf{k}}(p)e^{-\mathbf{k}\cdot\mathbf{s}} \qquad i = 1, 2 \tag{47}$$

with $\mathbf{k} = (k_1,k_2)$, $\mathbf{s} = (s_1,s_2)$, $\mathbf{k}\cdot\mathbf{s} = k_1s_1 + k_2s_2$. Similar definitions hold for the functionality and mole number distributions.

Taking the Laplace transform of eqs 43 and 44 yields

$$x_iW_i = \mathcal{H}_i\Gamma' \qquad i = 1, 2 \tag{48}$$

$$f_n(1-p)\Phi = \mathcal{F}\Gamma' \tag{49}$$

with the partial DP and functionality operators $\mathcal{H}_i$ ($i = 1, 2$) and $\mathcal{F}$ defined by

$$\mathcal{H}_i = -\frac{\partial}{\partial s_i} \qquad \mathcal{F} = (f-2)\mathcal{H}_1 + (g-2)\mathcal{H}_2 + 2$$

The transformed stochastic equations are obtained from eq 46:

$$(1-p)\frac{\partial W_i}{\partial p} = -(1-\Phi)\mathcal{F}W_i \tag{50}$$

Combining eqs 48–50 we obtain the equation

$$\frac{\partial \Gamma'}{\partial p} = \frac{1}{2}f_n(\Phi^2 - 2\Phi) \tag{51}$$

which is alternatively written in the usual form of kinetic equations:

$$-\frac{\mathrm{d}N_{ij}}{\mathrm{d}t} = \sum_{m,n=0}^{\infty} kf_{mn}f_{ij}N_{mn}N_{ij} - \frac{1}{2}\sum_m\sum_n kf_{mn}f_{i-m,j-n}N_{mn}N_{i-m,j-n} \tag{52}$$

the summation on the second term of the right-hand side extends over $m = 0, 1, ..., i$ and $n = 0, 1, ..., j$, $(m,n) \neq (0,0)$, (i,j).

Probability Generating Functions. Applying the operator $\mathcal{F}$ on both sides of eq 51 and taking into account eq 49, we get a partial differential equation for Φ:

$$(1-p)\frac{\partial\Phi}{\partial p} - (f-2)(1-\Phi)\frac{\partial\Phi}{\partial s_1} - (g-2)(1-\Phi)\frac{\partial\Phi}{\partial s_2} = \Phi^2 - \Phi \quad (53)$$

Equation 53 is solved with the method outlined in Appendix A. The solution is easily generalized to any number of constituents:

$$\Phi = \sum_i \phi^{\circ}{}_i\theta_i(1 - p + p\Phi)^{f_i-1} \quad (54)$$

$\phi^{\circ}{}_i$ being the functionality fraction of the ith monomer initially and $\theta_i = \exp(-s_i)$. The mass generating functions are derived with the method of Appendix B. The overall mass (functionality) distribution w_k (ϕ_k), i.e. the mass (functionality) fraction of all species with DP k regardless of their partial DPs, is obtained from w_{ij} (eq 41) summing over all i,j with $i + j = k$. The corresponding generating functions are obtained by putting $\theta_1 = \theta_2 = ... = \theta$:[6,7]

$$W = \theta\sum_i x_i(1 - p + p\Phi)^{f_i} \quad (55)$$

$$\Phi = \theta\sum_i \phi^{\circ}{}_i(1 - p + p\Phi)^{f_i-1} \quad (56)$$

Equations 55 and 56 mean that W may be thought of as the probability generating function of all generations of a Galton–Watson branching process[34] with first generation generating function[6,7]

$$F_1(\theta) = \sum_i x_i(1 - p + p\theta)^{f_i} \quad (57)$$

and higher order generations generating function[6,7]

$$F_2(\theta) = \sum_i \phi^{\circ}{}_i(1 - p + p\theta)^{f_i-1} \quad (58)$$

The probability generating functions F_1 and F_2 are similar to those first used by Gordon[6,7] (see comment following eq 35).

DP Averages. Putting $\mathbf{s} = 0$ in eq 51 and integrating the resulting differential equation using the initial condition $X_n = 1$ for $p = 0$ give expression (27) with $q = pf_n/2$ for X_n. Once the mass and functionality probability generating functions have been derived, the methods of Gordon's branching process theory can be applied to obtain the corresponding DP averages.[6,7]

6. Monomers with Different Functional Groups

For simplicity of notation we consider a mixture consisting of two monomers, each bearing either functional groups type A or B and reacting through condensation reaction of functional groups type A with B. The monomers are denoted 1 and 2, and they are assumed to have functionalities f and g, respectively. The molecular species of this system are characterized by means of a double index $\mathbf{i} = (j,k)$, where j and k are the corresponding partial DPs. A (j,k)-molecule bears

$$f_{Ajk} = (f-1)j - k + 1 \quad (59a)$$

$$f_{Bjk} = -j + (g-1)k + 1 \quad (59b)$$

functional groups types A and B, respectively. Similarly, there are two types of functionality distribution:

$$\phi_{\alpha ij} = \frac{f_{\alpha ij}N_{ij}}{F_\alpha} = \frac{f_{\alpha ij}n'_{ij}}{f_{\alpha n}(1-p_\alpha)} \qquad \alpha = \mathrm{A, B} \quad (60)$$

where F_A and F_B are the total functionalities of type A and B, respectively, p_α is the conversion of functional groups type α = A, B, $p_A = p$, $p_B = rp$, $r = F_{Ao}/F_{Bo}$, $f_{An} = F_{Ao}/N_o$, and $f_{Bn} = F_{bo}/N_o$ are the average functionalities, and N_o is the total number of monomeric units.

The mass fractions are given by eqs 40 and 41. The mass and number distributions are related to each other through eq 43.

Stochastic Equations. Denoting $b_\alpha\mathrm{d}t$ the chance a functional group of type α = A, B has to react in the infinitesimal time interval $(t,t+\mathrm{d}t)$ and proceeding as in the one monomer case

$$b_\alpha\mathrm{d}t = \mathrm{d}p_\alpha/(1-p_\alpha) \quad (61)$$

The probability that a molecule with partial DPs i,j and f_{Aij} ($\equiv\lambda$), f_{Bij}($\equiv\mu$) functional groups type A and B, respectively, does not react in the interval $(t,t+\mathrm{d}t)$ equals the probability that none of its functional groups type A or B react in this interval, i.e. $(1 - b_A\mathrm{d}t)^\lambda(1 - b_B\mathrm{d}t)^\mu$:

$$P_{ij;ij}(t,t+\mathrm{d}t) = 1 - f_{Aij}b_A\mathrm{d}t - f_{Bij}b_B\mathrm{d}t \quad (62)$$

The probability that a functional group type A (B) reacts in $(t,t+\mathrm{d}t)$ is $1 - (1 - b_A\mathrm{d}t)^\lambda = f_{Aij}b_A\mathrm{d}t(f_{Bij}b_B\mathrm{d}t)$. As only reactions between functional groups type A and B are permissible and a molecule can react either through reaction of a functional group type A or B

$$P_{ij;kl}(t,t+\mathrm{d}t) = f_{Aij}b_A\mathrm{d}t\phi_{Bk-i,l-j} + f_{Bij}b_B\mathrm{d}t\phi_{Ak-i,l-j} \quad (63)$$

From eqs 62 and 63 the process generator is obtained:

$$G_{ij;kl} = \begin{cases} -(f_{Aij}b_A + f_{Bij}b_B) & \text{for } k = i,\ l = j \\ f_{Aij}b_A\phi_{Bk-i,l-j} + f_{Bij}b_B\phi_{Ak-i,l-j} & \text{for } k \geq i,\ l \geq j \\ 0 & \text{else} \end{cases} \quad (64)$$

The stochastic equations are obtained by substituting in eq 7 the above expression for **G**.

Kinetic Equations. The transformed stochastic equations read

$$\frac{\partial W_i}{\partial p} = -\left[\frac{(1-\Phi_B)}{1-p}\mathcal{F}_A + \frac{r(1-\Phi_A)}{1-rp}\mathcal{F}_B\right]W_i \qquad i = 1, 2 \quad (65)$$

with the functionality operators given by eqs 59 with the substitutions $j \rightarrow \mathcal{H}_1$, $k \rightarrow \mathcal{H}_2$, $f_{Ajk} \rightarrow \mathcal{F}_A$, $f_{Bjk} \rightarrow \mathcal{F}_B$. Equation 60 transforms to

$$f_{\alpha n}(1-p_\alpha)\Phi_\alpha = \mathcal{F}_\alpha\Gamma' \qquad \alpha = \mathrm{A, B} \quad (66)$$

and eq 48 remains valid as it is.

Combining eqs 65, 66, and 48

$$\frac{\partial\Gamma'}{\partial p} = f_{An}(\Phi_A\Phi_B - \Phi_A - \Phi_B) \quad (67)$$

Equation 67 represents the Laplace-transformed kinetic equations (see eq 52 above).

Probability Generating Functions. Applying on both sides of eq 67 the operators $\mathcal{F}_A$ and $\mathcal{F}_B$ successively and taking into account eq 66 a system of partial differential equations for Φ_A and Φ_B is obtained:

$$\frac{1}{r}\lambda_A\lambda_B\frac{\partial\Phi_A}{\partial p} + \sum_i[\lambda_B(\Phi_B - 1)Q_{Ai} + \lambda_A(\Phi_A - 1)Q_{Bi}]\frac{\partial\Phi_A}{\partial s_i} = \lambda_A\Phi_A(\Phi_A - 1) \quad (68)$$

where $\lambda_A = r(1 - p)$, $\lambda_B = 1 - rp$, and

$$\mathbf{Q} = \begin{bmatrix} Q_{A1} & Q_{A2} \\ Q_{B1} & Q_{B2} \end{bmatrix} = \begin{bmatrix} f-1 & -1 \\ -1 & g-1 \end{bmatrix}$$

A similar differential equation holds for Φ_B with λ_B in place of λ_A on the right-hand side of eq 68.

These differential equations are solved by following the procedure outlined in Appendix A. The results are easily extended to a mixture of $a + b$ monomers denoted $i = 1, 2, ..., a$, bearing functional groups type A and having functionality f_i and $j = 1, 2, ..., b$ bearing functional groups type B and functionality g_j. A molecule characterized by a multiindex $\mathbf{i} = (i_1, i_2, ..., i_a; j_1, j_2, ..., j_b)$ will have functionalities

$$f_{A\mathbf{i}} = \sum_A(f_k - 1)i_k - \sum_B j_k + 1 \quad (69a)$$

$$f_{B\mathbf{i}} = -\sum_A i_k + \sum_B(g_k - 1)j_k + 1 \quad (69b)$$

The solution for the functionality distributions will be[7] (Appendix A)

$$\Phi_A = \sum_A \phi^{\circ}{}_{Ai}\theta_i(1 - p + p\Phi_B)^{f_i-1} \quad (70a)$$

$$\Phi_B = \sum_B \phi^{\circ}{}_{Bj}\theta_j(1 - rp + rp\Phi_A)^{g_j-1} \quad (70b)$$

From the solution for Φ_A, Φ_B the mass distributions are calculated[7] (Appendix B):

$$W = \sum_A x_i\theta_i(1 - p + p\Phi_B)^{f_i} + \sum_B x_j\theta_j(1 - rp + rp\Phi_A)^{g_j} \quad (71)$$

The (overall) mass average DP and the critical point are given by eqs 75 and 76 below with $\rho = 0$.[4,5,7,36]

7. Monomers with Both Types of Functional Groups

We consider the polycondensation of a mixture of two monomers denoted 1 and 2 bearing f_1,g_1 and f_2,g_2 functional group types A and B, respectively. The functionalities of type A and B of a (j,k)-molecule are given by

$$f_{Ajk} = (f_1 - 1)j + (f_2 - 1)k + 1 \quad (72a)$$

$$f_{Bjk} = (g_1 - 1)j + (g_2 - 1)k + 1 \quad (72b)$$

The functionality distributions are given by eq 60. Equation 61, the process generator, and the stochastic equation (65) remain unaltered, provided that f_{Ajk} and f_{Bjk} are given by eqs 72. The functionality operators are obtained from eqs 72 with the substitutions $j \rightarrow \mathcal{H}_1$, $k \rightarrow \mathcal{H}_2$, $f_{Ajk} \rightarrow \mathcal{F}_A$, $f_{Bjk} \rightarrow \mathcal{F}_B$.

Probability Generating Functions. The system of partial differential equations (68) is valid with

$$\mathbf{Q} = \begin{bmatrix} Q_{A1} & Q_{A2} \\ Q_{B1} & Q_{B2} \end{bmatrix} = \begin{bmatrix} f_1-1 & f_2-1 \\ g_1-1 & g_2-1 \end{bmatrix}$$

Equation 68 is solved with the initial conditions $\Phi_A = \phi^{\circ}{}_{A1}\theta_1 + \phi^{\circ}{}_{A2}\theta_2$ and $\Phi_B = \phi^{\circ}{}_{B1}\theta_1 + \phi^{\circ}{}_{B2}\theta_2$ for $p = 0$, where $\phi^{\circ}{}_{Ai} = x_if_i/\sum_jx_jf_j$, $\phi^{\circ}{}_{Bi} = x_ig_i/\sum_jx_jg_j$, $i = 1, 2$ (Appendix A). The solutions for Φ_A and Φ_B are

$$\Phi_A = \sum_i \phi^{\circ}{}_{Ai}\theta_i(1 - rp + rp\Phi_A)^{g_i}(1 - p + p\Phi_B)^{f_i-1} \quad (73a)$$

$$\Phi_B = \sum_i \phi^{\circ}{}_{Bi}\theta_i(1 - rp + rp\Phi_A)^{g_i-1}(1 - p + p\Phi_B)^{f_i} \quad (73b)$$

Equations 73 are valid for an arbitrary number of constituents. The mass distribution reads

$$W = \sum_j x_j\theta_j(1 - rp + rp\Phi_A)^{g_j}(1 - p + p\Phi_B)^{f_j} \quad (74)$$

DP Averages. The number average DP is given as previously by eq 27. The mass average DP is derived as described above:

$$X_w = 1 + q\frac{2(1 - \rho p) + (f_\varphi - 1)p + (g_\varphi - 1)rp}{(1 - \rho p)^2 - (f_\varphi - 1)(g_\varphi - 1)rp^2} \quad (75)$$

with $\rho = (2r/f_s)\sum_jx_jf_jg_j$, $f_\varphi = \sum_j\phi^{\circ}{}_{Aj}f_j$, and $g_\varphi = \sum_j\phi^{\circ}{}_{Bj}g_j$. The critical point is given by

$$1/p_c = \rho + [r(f_\varphi - 1)(g_\varphi - 1)]^{1/2} \quad (76)$$

Equations 75 and 76 represent generalizations of previously derived results for simpler systems.[1,36]

8. Discussion

A number of properties are characteristic of the distributions derived above:

(P1) They represent time Markov processes.

(P2) They represent spatial Markov processes (Galton–Watson branching processes).

(P3) They satisfy kinetic equations.

For systems satisfying the postulate of equal reactivity it was shown that (P2) is a consequence of (P1) and that description of these systems either as Markov processes or through kinetic equations are alternate representations of the same physical situation.

The physical grounds underlying the fundamental property of these distributions being simultaneously both time and spatial Markov processes are understood considering the (conditional) probability that an i-mer reacts with a j-mer (given that the i-mer does react). It was shown that if the postulate of equal reactivity is valid, this probability is equal to the functionality fraction of j, i.e., ϕ_j.

From the spatial point of view, selecting for study an i-functional group, the probability that a neighboring functional group belongs to a j-mer is obviously given by the fraction of neighboring j-functional groups and assuming that the spatial distribution of functional groups is homogeneous; this equals ϕ_j. Therefore, the same stochastic equations and consequently species distributions would have been derived, had we used the assumption of spatial homogeneity in place of the postulate of equal reactivity. Thus the next three statements are equivalent formulations of the postulate of equal reactivity:

(F1) All functional groups have an equal chance for reaction.

(F2) Functional groups are homogeneously distributed in space.

(F3) Reaction rates are second order in species concentrations with size independent reaction constants.

The equivalence of (F1), (F2), and (F3) is reflected in the properties of the species distributions (P1), (P2), and

(P3). Apparently, systems with size dependent reactivity are necessarily spatially inhomogeneous and functional group diffusion plays a role in the overall reaction process. Diffusion controlled reactions are important, especially for free radical polymerizations, and their effect on the species distributions will be the subject of a forthcoming publication.

9. Conclusions

A new, nonequilibrium stochastic theory of polymerization processes has been developed. The starting point for this theory is the Kolmogorov stochatic differential equations (7) with the process generator **G** given by (8). The functional dependence of **G** on the transition matrix **P** has been derived for systems with equal (eqs 16, 45, and 64) and unequal (eq 36) reactivity.

The mass distribution obeys eqs 18 and 37, respectively. Solution of the equations yielded the Flory–Stockmayer distributions for systems with equal reactivity. Statistical and kinetic theories have been recovered as special cases of the present theory. For systems with uequal reactivity, however, the statistical equations following from the stochastic theory do not obey the simple branching process equations.

The prominent advantage of the stochastic theory is the unification of statistical and kinetic theories it implements. Size distributions can thus be treated in a unified manner, the particular model (statistical or kinetic) applied being immaterial for the final results. Kinetically controlled effects are inherently accounted for, as they are the starting point for the derivation of the process generator. With the stochastic theory statistical models are no longer inappropriate to deal with kinetically controlled effects.[35]

The lengthy derivation of **G** might appear as a disadvantage of the present theory. However, once the expression for **G** has been derived for systems with equal reactivity, generalization to complex systems is immediate.

Appendix A. Solution to the Partial Differential Equation for the Functionality Distribution

Considering the most complex case of a system involving mixed monomers, we start from the system of ordinary differential equations

$$\frac{\mathrm{d}p}{(1-p)(1-rp)} = \frac{\mathrm{d}s_i}{(\Phi_B - 1)(1-rp)Q_{Ai} + (\Phi_A - 1)r(1-p)Q_{Bi}} = \frac{\mathrm{d}\Phi_A}{r(1-p)\Phi_A(\Phi_A - 1)} = \frac{\mathrm{d}\Phi_B}{(1-rp)\Phi_B(\Phi_B - 1)} \quad \text{(A-1)}$$

with independent solutions

$$(1-rp)(1-\Phi_A){\Phi_A}^{-1} = C_1 \; (1-p)(1-\Phi_B){\Phi_B}^{-1} = C_2 \quad \text{(A-2)}$$

$${\Phi_B}^{f_1-1}{\Phi_A}^{g_1-1}\exp(-s_1) = C_3{\Phi_B}^{f_2-1}{\Phi_A}^{g_2-1}\exp(-s_2) = C_4 \quad \text{(A-3)}$$

The general solution to the system (68) has the form

$$G_1(C_1,C_2,C_3,C_4) = 0 \qquad G_2(C_1,C_2,C_3,C_4) = 0 \quad \text{(A-4)}$$

satisfying the initial conditions

$$\Phi_A = \phi^o{}_{A1}\exp(-s_1) + \phi^o{}_{A2}\exp(-s_2), \quad \Phi_B = \phi^o{}_{B1}\exp(-s_1) + \phi^o{}_{B2}\exp(-s_2)$$

for $p = 0$.

Combining the solutions (A–2) and (A–3) (for $p = 0$) to obtain the equations expressing the initial conditions, we find that G_1 and G_2 must have the forms

$$G_1(C_1,C_2,C_3,C_4) = \phi^o{}_{A1}(C_1+1)^{g_1}(C_2+1)^{f_1-1}C_3 + \phi^o{}_{A2}(C_1+1)^{g_2}(C_2+1)^{f_2-1}C_4 - 1 \quad \text{(A-5a)}$$

$$G_2(C_1,C_2,C_3,C_4) = \phi^o{}_{B1}(C_1+1)^{g_1-1}(C_2+1)^{f_1}C_3 + \phi^o{}_{B2}(C_1+1)^{g_2-1}(C_2+1)^{f_2}C_4 - 1 \quad \text{(A-5b)}$$

Replacing in eqs A–5 the expressions for C_1, C_2, C_3, and C_4 by eqs A–2 and A–3 and performing obvious rearrangements, we arrive at eqs 73.

Appendix B. Derivation of the Mass Distribution

Equations 73 are written in the form

$$\Phi_A = \sum_i \phi^o{}_{Ai}\,\mathrm{e}^{-s_i}Z^{g_i}T^{f_i-1} = \sum_i \phi^o{}_{Ai}e^{-s_i}Z^{g_i}(\phi T^{f_i}/\partial p)(1/f_iT_p) \quad \text{(B-1a)}$$

$$\Phi_B = \sum_i \phi^o{}_{Bi}\mathrm{e}^{-s_i}Z^{g_i-1}T^{f_i} = \sum_i \phi^o{}_{Bi}\mathrm{e}^{-s_i}(\partial Z^{g_i}/\partial p)(1/g_iZ_p)T^{f_i} \quad \text{(B-1b)}$$

with $Z = 1 - rp + rp\Phi_A$, $T = 1 - p + p\Phi_B$, $Z_p = \partial Z/\partial p$, and $T_p = \partial T/\partial p$. From eqs B–1 we get

$$\bar{f}T_p\Phi_A = \sum_i x_i\mathrm{e}^{-s_i}Z^{g_i}(\partial T^{f_i}/\partial p) \quad \text{(B-2a)}$$

$$\bar{g}Z_p\Phi_B = \sum_i x_i\mathrm{e}^{-s_i}(\partial Z^{g_i}/\partial p)T^{f_i} \quad \text{(B-2b)}$$

with $\bar{f} = \sum_i x_if_i$ and $\bar{g} = \sum_i x_ig_i$. From eqs B–2 we get

$$\bar{f}T_p\Phi A + \bar{g}Z_p\Phi_B = \frac{\partial\Omega}{\partial p} \quad \text{(B-3)}$$

with $\Omega = \sum_i x_i\mathrm{e}^{-s_i}Z^{g_i}T^{f_i}$. Performing obvious operations

$$\bar{f}T_p\Phi_A + \bar{g}Z_p\Phi_B = \bar{f}[-\Phi_A - \Phi_B + \Phi_A\Phi_B + \partial(p\Phi_A\Phi_B)/\partial p] \quad \text{(B-4)}$$

The right-hand side of eq B–4 in view of eq 67 and $\bar{f} = f_{An}$ yields $(\partial/\partial p)(\Gamma' + q\Phi_A\Phi_B)$. From eqs B–3 and B–4, evaluating the arbitrary integration function from the condition $\Gamma' = \sum_i x_i\mathrm{e}^{-s_i}$ for $p = 0$, we obtain

$$\Gamma' + q\Phi_A\Phi_B = \Omega \quad \text{(B-5)}$$

Similarly, taking the derivative on the right of (B–1) with respect to s_k rather than p and following the above procedure, we obtain the relationship

$$\frac{\partial}{\partial s_k}(q\Phi_A\Phi_B) = \frac{\partial\Omega}{\partial s_k} + x_k\mathrm{e}^{-s_k}Z^{g_k}T^{f_k} \quad \text{(B-6)}$$

Differentiating eq B–5 with respect to s_k and taking into account eq B–6, we obtain the expression for the partial mass distribution

$$W_k = \mathrm{e}^{-s_k}Z^{g_k}T^{f_k}$$

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