Statistical Polymer Method: Modeling of Macromolecules and Aggregates with Branching and Crosslinking, Formed in Random Processes

FREDDY A. ROMM[a,*] and OLEG L. FIGOVSKY[b]

[a]*Department of Chemical Engineering, Technion-IIT, Haifa, Israel;* [b]*Eurotech Ltd., Rochville, USA*

The statistical polymer method is based on the consideration of averaged structures of all possible macromolecules of the same weight. One has derived equations allowing evaluation of all additive parameters of macromolecules and their systems. The statistical polymer method allows modeling of branched crosslinked macromolecules and their systems in equilibrium or non-equilibrium. The fractal consideration of statistical polymer allows modeling of all kinds of random fractal and other objects studied by fractal theory. The statistical polymer method is applicable not only to polymers but also to composites, gels, associates in polar liquids and other aggregates.

Keywords: Branched polymers, Branched structures, Branched aggregates, Branching and crosslinking, Random chaos, Random structure, Random fractal, Non-equilibrium

INTRODUCTION

Theoretical description of branched crosslinked polymers, gels and aggregates formed in random processes was traditionally very problematic for polymer science and related disciplines because of difficulties of taking into account all possible structures. Classic methods elaborated by Flory for linear macromolecules [1] are not applicable, in most cases, to branched, especially crosslinked structures [2]. Moreover, if systems of branched crosslinked polymers are in non-equilibrium, their description is impossible without combination of special statistical methods [3,4] and non-linear dynamics of chaos [5].

The problem of modeling of branched crosslinked macromolecules and aggregates was solved recently by the statistical polymer method [3,4].

STATISTICAL POLYMER METHOD

Let us consider the statistical polymer method in the following order:

(1) modeling of separate macromolecules without crosslinking;

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* Corresponding author.

(2) modeling of equilibrium polymeric systems, evaluation of thermodynamic functions, first of all chemical potential;

(3) modeling of complex systems (crosslinking and/or non-equilibrium state, etc.);

(4) possible applications.

MAIN NOTIONS, DEFINITIONS AND EQUATIONS

Statistical Polymer

Statistical N-mer is defined as *the averaged structure formed by all possible structures of N-mers and exhibiting all possible structures of polymers containing the same number of monomeric units*. In the light of this definition, polymeric systems are considered as sets of assemblages possessing structures averaged on all polymers containing the same numbers of monomeric units – statistical polymers. All interactions in polymeric systems are considered as result of interactions of statistical polymers, and the evaluation of additive (extensive) parameters like energy, entropy etc. may be carried out through statistical polymers instead of branched crosslinked ones.

For large values of N, the number of possible structures is, obviously, much more than the number of monomeric units through the system, and most of the possible structures cannot realize, that could seem to be a drawback of the statistical polymer method. However, if the relaxation time of reactions is much shorter than the measurement duration, one may assume the dynamic equilibrium between various structures, that determines correctness of the statistical polymer method even for large enough N. Moreover, because of quantum effects the traditional description of macromolecules (as specified structures) is not exact, and this factor of eventual error caused by quantum features of the system allows application of the statistical polymer method for very large macromolecules.

Now, let us consider characteristics of statistical polymer which determine its ability to interact with other statistical polymers and monomers.

Vacancy of the statistical polymer is defined *as the capacity of the statistical polymer to capture a monomeric unit*. The number of vacancies is denoted as $V(N)$. It is obvious that the capture of an additional monomeric unit by statistical N-mer leads to the formation of $(N+1)$-mer.

Extreme unit of the statistical polymer is defined as *the monomeric unit which has one only bond with the main structure of the statistical polymer*. Let us denote the number of extreme units in statistical N-mer as $U(N)$. It is obvious that breaking of the bond of the extreme unit with the main structure of statistical N-mer leads to the formation of $(N-1)$-mer.

Processes of polymerization–destruction in a polymeric system are described as combinations of reactions of statistical polymers:

$$Pol(N) + M \Leftrightarrow Pol(N+1), \qquad (1)$$

$$Pol(N_1) + Pol(N_2) \Leftrightarrow Pol(N_1 + N_2), \qquad (2)$$
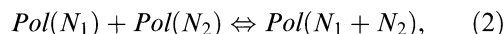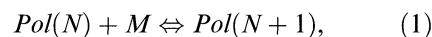
where $Pol(N)$ is the statistical polymer containing N units; M is a monomer. Since reactions (2), in their turn, can be written as combinations of reactions (1), these can be considered as independent reactions. Since the process of polymerization is determined by vacancies, whereas destruction – by extreme units, reactions (1) can be written in the following form:

$$Vac(N) + M \Leftrightarrow Ex(N+1), \qquad (3)$$
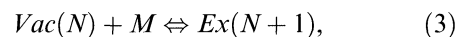
where Ex is the extreme unit. If no crosslink forms, the values of $V(N)$, $U(N)$ are given by the following recurrent equations [3]:

$$V(N+1) = V(N) + m - 1 = 2 + N \cdot (m-1), \quad (4)$$

$$U(N+1) = U(N) + 1 - \frac{mU(N)}{V(N)}$$

$$= 1 + U(N)\left[1 - \frac{m}{V(N)}\right], \qquad (5)$$

where m is the maximal number of possible branches (functionality minus one).

The kinetics of independent reactions like (1) is given by

$$W_+(N) = K_+[N(m-1)+2]C_N C_1,$$
$$W_-(N) = K_- U(N) \cdot C_N,$$
(6)

where W_+, W_-, and K_+, K_- are the rates and the rates constants of the direct and the inverse reactions, respectively, and C_N is the concentration (mole fraction) of the N-mer. For equilibrium,

$$W_+(N) = W_-(N+1) \Rightarrow \frac{C_{N+1}}{C_1 C_N}$$
$$= \frac{K_+[N(m-1)+2]}{K_- U(N+1)} = K_r(N).$$
(7)

$$K_+ = K_1 \cdot \exp\left(-\frac{E_{a1}}{R_g T}\right),$$
(8)

$$K_- = K_2 \cdot \exp\left(-\frac{E_{a2}}{R_g T}\right),$$
(9)

$$K_r(N) = K_0 \cdot \exp\left(-\frac{\Delta E}{R_g T}\right) \cdot \frac{V(N)}{U(N+1)},$$
(10)

where T – Temperature, R_g – gas constant;

$$K_0 = \frac{K_1}{K_2} \quad \text{and} \quad \Delta E = E_{a1} - E_{a2}.$$
(11)

For large values of N, one obtains

$$\lim_{N \to \infty} U(N) = \alpha N,$$

$$\alpha = \frac{m-1}{2m-1} \quad \text{(for } M = 1, \; m > 1),$$
(12)

$$K_r(n \to \infty) = \frac{K_+}{K_-}(2m-1).$$
(13)

The statistical polymer method can be employed also for the description of multicomponent systems, the relevant equations are derived in [4].

CROSSLINK FORMATION

Let us consider crosslink as the bond between two monomeric units inside the same macromolecule. Hence, crosslink can form only between monomeric units possessing vacancies. Each vacancy can

participate in the formation of crosslink with monomeric units which possess vacancies. Hence, the sum number of possibilities of ring formation is

$$C_r = \frac{1}{2}V(N)[N - 1 - B_0(N)],$$
(14)

where $B_0(N)$ is the number of monomeric units which have no vacancies. The value of $B_0(N)$ can be estimated from

$$B_0(N+1) = B_0(N) + B_1(N)/V(N)$$
(15)

taking into account that for monomeric units with s vacancies $(1 \le s \le (m-1))$:

$$B_s(N+1) = B_s(N) + (s+1) \cdot B_{(s+1)}(N)/V(N)$$
$$- s \cdot B_s(N)/V(N);$$
(16)
$$B_m(N) \equiv U(N).$$
(17)

The rate of reaction of crosslink formation is

$$W_{c+} = K_{c+} C_r.$$
(18)

The rate of reaction of crosslink destruction is

$$W_{c-} = K_{c-} G_r,$$
(19)

where $G_r(N)$ is the number of crosslinks, whereas K_{c+} and K_{c-} are the constants of crosslink formation and destruction, respectively.

In equilibrium:

$$W_{c+} = W_{c-} \Rightarrow K_{c+} C_r = K_{c-} G_r,$$
(20)

$$K_{cr} = \frac{K_{c+}}{K_{c-}} = \frac{G_r}{C_r} = \frac{2G_r}{V(N)[N - B_0(N) - 1]}.$$
(21)

The crosslink formation reduces the number of vacancies and extreme units:

$$V'(N) = (m-1)N + 2 - 2G_r,$$
(22)

$$U^{(c+1)}(N) = U^{(c)}(N) - mU^{(c)}(N)G_r(N)/V(N).$$
(23)

or

$$U(l) = U^0 \prod_{k=1}^{l}\left[1 - \frac{2m}{V^0 - 2(k-1)}\right],$$
(24)

where index "0" means the non-crosslinked state, l – the number of crosslinks.

The ring formation reduces both the number of vacancies and that of extreme units, therefore one may assume that the weak ring formation does not significantly influence the weight distribution of polymers.

THERMODYNAMIC FUNCTIONS OF NON-CROSSLINKED STATISTICAL POLYMERS. NON-EQUILIBRIUM

From Eq. (10) one obtains

$$\frac{\Delta S^0}{R_g T} = \frac{\Delta H^0}{R_g T} + \ln K_0 - \frac{\Delta E_a}{R_g T} + \ln V_\Sigma(N)$$
$$- \ln U_\Sigma(N+1). \tag{25}$$

However, the heat effect of a reaction of polymerization

$$\Delta H^0 = \Delta E_a = 2\varepsilon_0, \tag{26}$$

where ε_0 is the energy of a vacancy (all vacancies are assumed to be equivalent!). From Eqs. (25) and (26) one obtains

$$\Delta S^0(N) = R_g[\ln K_0 + V_\Sigma(N) - \ln U_\Sigma(N+1)]. \tag{27}$$

However

$$\Delta S^0(1) = R_g[\ln K_0 + \ln V_\Sigma(1) - \ln U_\Sigma(2)]. \tag{28}$$

Taking into account that $V_\Sigma(1) = m+1$, and $U_\Sigma(2) = 2$ [3], one obtains

$$\ln K_0 = \frac{\Delta S^0(1)}{R_g} + \ln \frac{2}{m+1}, \tag{29}$$

$$\Delta S^0(N) = \Delta S^0(1) + R_g \ln \frac{2V_\Sigma(N)}{(m+1)U_\Sigma(N+1)}. \tag{30}$$

The chemical potential of statistical N-mer is given by

$$\mu^0(N) = \varepsilon_0 V_\Sigma(N) - T\left[NS^0(1) + N\Delta S^0(1) \right.$$
$$\left. + R_g \sum_{n=1}^{N} \ln \frac{2V_\Sigma(n-1)}{(m+1)U_\Sigma(n)} \right], \tag{31}$$

where C_N is the concentration of N-mer; $S^0(1)$-the entropy of monomer.

Now, let us consider a non-equilibrium chemical process in a polymeric system described in linear approximation:

$$\{C_{1n}\} \rightarrow \{C_{2n}\}, \tag{32}$$

where indexes "1" and "2" correspond to the initial and final states, respectively. The Gibbs' energy in these states is given by

$$\Delta G_1 = \sum_{n=1}^{\infty} \left(\mu_{1n}^0 + R_g T \ln C_{1n} \right) C_{1n}, \tag{33}$$

$$\Delta G_2 = \sum_{n=1}^{\infty} \left(\mu_{2n}^0 + R_g T \ln C_{2n} \right) C_{2n}. \tag{34}$$

The moving force of the process (32) is

$$\Delta G = \sum_{n=1}^{\infty} \left(\mu_n^0 + R_g T \ln C_n \right) C_n$$
$$= \sum_{n=1}^{\infty} \mu_n C_n = \sum_{n=1}^{\infty} \Omega_n, \tag{35}$$

where $\Omega_n = \mu_n C_n$.

Description of non-linear situations can be carried out in the same style, using methods of dynamic of chaos [5].

COMBINATION OF THE STATISTICAL POLYMER AND FRACTAL METHODS

Let us consider statistical N-mer $(N \rightarrow \infty)$ as the fractal with dimensionality D_f. Such approach can

be compared to the accepted practice of the construction of fractal clusters by the Monte-Carlo method of random addition of new units; only difference – the statistical polymer is automatically random and contains all possible structures of randomly constructed clusters (of course, if they contain the same number N of units). We may assume that the statistical N-mer can be considered as the averaged structure obtained after the infinite number of operations of constructions of N-meric clusters.

We note some obvious advantages of the statistical polymer approach in comparison with the Monte-Carlo method of the construction of cluster: (1) Monte-Carlo method is not strictly random, that causes several errors which are reduced and disappear only for ∞-meric clusters; (2) the application of the Monte-Carlo method to the 3-dimensional systems is too difficult, whereas the statistical polymer method is applicable in all situations, that offers much more freedom to the researcher; (3) the Monte-Carlo method furnishes numerical results, whereas the statistical polymer method allows the obtainment of analytical ones (at least, for all additive parameters of macromolecules and polymeric systems); (4) for the obtainment of the same result, the Monte-Carlo method requires much more calculations.

Since we consider statistical N-mers (at very large N) as random fractal-like objects, we need to define the characteristic dimension (size) of the fractal statistical polymer. Let us define the characteristic size of fractal statistical N-mer (at very large N) as follows:

$$Z(N) = d_0 \sum_{k=1}^{N} W_k(N),$$

$$W_k(N) = \begin{cases} 1 & \text{if } R_k(N) \geq 1, \\ R_k(N) & \text{for } R_k(N) < 1. \end{cases} \tag{36}$$

where d_0 is the characteristic size of monomeric unit ($d_0 = v_0^{1/3}$, v_0 is the volume of monomer unit), and the parameter $R_k(N)$ (presence) characterizes the distribution of monomeric units inside the statistical polymer [3]. Since the validity of the fractal

approach is assumed, the volume and the surface area of such N-mer are given by

$$V_f = V(N) \sim [Z(N)]^{D_f}, \tag{37}$$

$$A_f = A(N) \sim [Z(N)]^{D_f-1}, \tag{38}$$

where D_f is the fractal dimensionality.

On the other hand, the same parameters are easily estimated from the total number of monomeric units:

$$V_p = V(N) = Nv_0, \tag{39}$$

$$A_p = A(N) = Na_0 = \alpha_s N(v_0)^{2/3}, \tag{40}$$

where a_0 is the surface area per monomeric unit, and α_s a normalization coefficient.

According to assumptions made above, Eqs. (36)–(38) should be correct at very large N, while for low and moderate values of N, they should not. This means that the total divergence between the values obtained from Eqs. (37)–(40) is large at small N and reduces at infinite N, that is characterized by the following functional ref. [4]:

$$\Phi_v = \Phi_v(N_1, N_2) = \frac{1}{4(N_2 - N_1 + 1)}$$
$$\times \sum_{N=N_1}^{N_2} \left[\frac{V_f(N)}{V_p(N)} - \frac{V_p(N)}{V_f(N)} \right]^2, \tag{41}$$

$$\Phi_A = \Phi_A(N_1, N_2) = \frac{1}{4(N_2 - N_1 + 1)}$$
$$\times \sum_{N=N_1}^{N_2} \left[\frac{A_f(N)}{A_p(N)} - \frac{A_p(N)}{A_f(N)} \right]^2. \tag{42}$$

Functional (41) was applied to the computer treatment of Eqs. (36), (37), (39) at various m, with minimization of the functional (41); the varied parameter of optimization was D_f.

The general correlation between values of $V(N)$ estimated from Eqs. (36), (39) at $m = 3$, $N_1 = 500$, $N_2 = 2000$, is presented in Fig. 1.

We see that the relative divergence between curves $V_f(N)$ and $V_p(N)$ is very large at small N, but decreases at large N. The relative square dispersion is $(\Phi_v)_{min} = 0.052$ (relative error about

Dimension of Macromolecule: Statistical Polymer (–) and Fractal Approach(o)
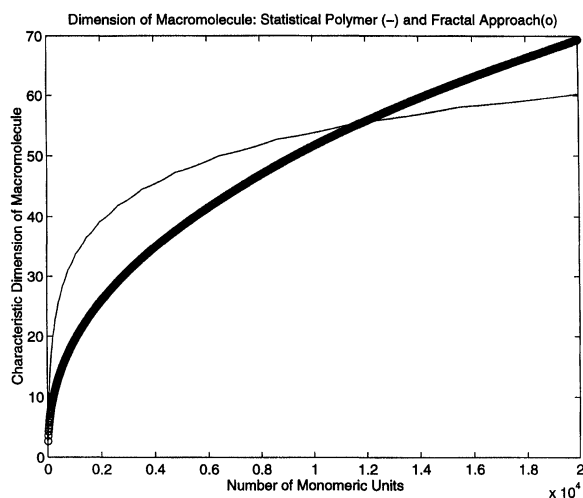

FIGURE 1

0.24) and is caused mostly by the initial parts of both curves, that is enough good for the correlation with single optimization parameter.

In this case, the fractal dimensionality $D_f = 2.32$.

In the general case, of course, the fractal dimensionality depends on m:

$$\lim_{m \to 1} D_f = 1, \qquad \lim_{m \to \infty} D_f = 3.$$

APPLICABILITY OF THE STATISTICAL POLYMER METHOD

The statistical polymer method allows modeling of not only polymers but also gels, several composites, associates in polar liquids, etc.

The combined fractal–statistical polymer method is applicable to all objects described by fractal theory, first of all random fractals.

The statistical polymer method can be very effective for the solution of numerous problems of materials science, because many of widespread materials exhibit macromolecule-like fragments. However, in such cases one should take into account that there are two kinds of interactions: inside macromolecule-like fragments ("strong" interactions) and between them ("weak" interactions). "Weak" interactions determine first of all mechanical stability, permeability and sometimes adhesion properties of the material.

CONCLUSIONS

The statistical polymer method is based on the consideration of averaged structures of all possible macromolecules of the same weight. One has derived equations allowing evaluation of all additive parameters of macromolecules and their systems. The statistical polymer method allows modeling of branched crosslinked macromolecules and their systems in equilibrium or non-equilibrium. The fractal consideration of statistical polymer allows modeling of all kinds of random fractal and other objects studied by fractal theory. The statistical polymer method is applicable not only to polymers but also composites, gels, associates in polar liquids and other aggregates.

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