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Association Phenomena in Macromolecular Systems—Influence of Macromolecular Constraints on the Complex Formation

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ABSTRACT: A theoretical model is presented to describe the association behavior of interacting units attached to a polymer chain. A polymer chain of i functional groups distributed statistically along the chain is considered. A mean field approach is used to derive the probability that the kth functional group forms a complex, if $k-1$ groups are already complexed. As a result of the fact that the associating units are linked to the polymer chain, the fraction of complexed units is reduced compared to the corresponding association behavior of low molecular weight compounds. The magnitude of these topological restrictions depends on the molecular weight, the concentration of the functional groups, the equilibrium constant for the "free" association, and the conformational properties of the chain.

Introduction

Since the pioneering work of Lundberg et al.[1-3] there has been increased interest in the structure-property relationships of ionomers. Strong physical associations between ion pairs lead to gel formation which is strongly dependent on dilution and temperature. Several theoretical approaches are reported in the literature to give a more general description of these systems.[4-6] One essential problem is the characterization of the ionic interactions. These may be ionic aggregates of different order (doublets, quadruplets, up to highly ordered clusters). Only few experimental results on ionomeric model systems, in order to characterize the cluster structure in detail, have been reported so far.[7,8] In most of the theoretical approaches[5,6] only the simplest case of two interacting sites is considered. Such types of noncovalent interactions also are observed in biopolymers, where hydrogen bonds are partly responsible for the formation of physical gels.[9,10] Corresponding theoretical work to describe the gel formation has been developed either on the basis of percolation theory[11,12] or

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on the cascade theory.[10,13] Biopolymer networks generally are complex systems. Gelation may be associated with helix-coil transitions and aggregation of helical strands by hydrogen bonding. Cooperative phenomena result.[10]

Similar synthetic model systems are attractive in order to test the limits of the theoretical predictions. The requirements for such model systems are a defined type of interaction, a possibility of variation of the number of interacting groups and a possibility of independent spectroscopic characterization of the interaction.

Hydrogen bond interactions in an nonpolar matrix may fulfill these requirements. A model system that is relatively easy to handle is the introduction of urazole groups into a diene elastomer via "ene"-reaction.[14,15] The reaction allows the defined variation of the amount of interacting groups. The number of urazole groups per polymer chain can be changed either by varying the primary molecular weight and keeping the degree of modification constant or by varying the degree of modification at constant primary molecular weight. The urazole groups form dimeric chelate-like hydrogen bond complexes. These hydrogen bond complexes strongly influence the dilute solution as well as the bulk properties.[16-18] In addition the amide-type hydrogen bonds can be characterized independently by IR spectroscopy.[19] Thus this type of system offers the opportunity of the correlation of molecular data directly with the macroscopic properties.

A detailed rheological characterization was performed on polybutadienes of narrow molecular weight distribution.[17,18] In accordance with the theoretical considerations on ionomer gels[4] it was found experimentally that the network formed by hydrogen bonding is not a "true" network with an equilibrium network modulus.[18,20] From the temperature dependence of the viscoelastic properties a strong increase of the apparent activation energy of flow was observed.[17,21] In addition, the terminal relaxation time in such modified polymers is greatly shifted to longer times.[18,21] Nevertheless it has been observed that neither the dependence of the activation energy nor the terminal relaxation time on the number of interacting groups per chain is consistent with simple considerations based on the formation of complexes in thermodynamic equilibrium. The apparent activation energy of flow should be correlated to the number of complexes between interacting groups. This will be true as long as these functional groups are not interrelated; i.e., there are no correlation effects along a single chain. In the case of cooperative processes a different behavior is observed.[10]

The discussion in the present paper focuses on noncooperative association processes of functional groups located statistically along a polymer backbone. In the case of complex formation of low molecular weight systems, the fraction of complexed units is given by the concentration of functional groups and by the equilibrium constant (section A.1). Using this approach Hermans[13] has applied cascade theory to describe thermoreversible gels.

The experimental results obtained for the urazole-modified polybutadienes indicate that the actual fraction of complexed groups is less than predicted from thermodynamic equilibrium considerations.[21] It is the purpose of this paper to develop a simple model which takes into account the topological restrictions acting on a functional group in a polymer chain, if other groups in the same chain are complexed. The situation is shown schematically in Figure 1. A polymer chain with a certain number of functional groups is considered. If some of the functional groups of the polymer chain are complexed, the free groups will be restricted to a certain volume defined by a radius

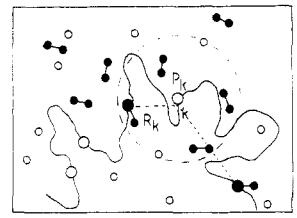

Figure 1. Schematic representation of a chain within a matrix of complexed (filled circles) and free (open circles) functional groups. The large circles correspond to the functional groups of the chain under consideration, while the smaller circles are attached to chains in the matrix which are not shown explicitely. If $k-1$ groups of the chain are complexed, the kth unit is restricted to the volume V_k, defined by the distance R_k to the next complexed unit.

R_k to find a partner for complexation. The problem is to calculate the influence of the chain topology on the association behavior.

A.1. Complex Formation without Topological Restrictions

The mole fraction x_2 of hydrogen bond complexes U_2 formed by the reaction

$$U + U \xrightarrow{K_0} U_2 \tag{1}$$

is given by the equilibrium constant K and the total concentration of functional groups in the systems $[U_0]$ (eq 2)

$$x_2 = -a/2 \pm ((-a/2)^2 - 1)^{1/2} \tag{2}$$

with

$$a = -(2 + 1/(2K_0[U_0]))$$

According to Le Chateliers principle, an increase in the concentration $[U_0]$ will increase the fraction of complexed units x_2. Thus the number of hydrogen bond complexes will increase more than linearly with increasing concentration. The probability for the formation of a complex by a functional group (p_2^0) is given by x_2^0. The symbol ^{0} indicates the absence of any restriction.

Thermodynamic equilibrium is determined only by the enthalpy and the entropy of complex formation, ΔH^f and ΔS^f. While ΔH^f is negative and thus favors complex formation, the entropy change ΔS^f is positive.

A.2. Complex Formation with Topological Restrictions

If the functional groups are bound to a polymer chain, the number of complexes may be reduced, compared to the case of associating groups in low molecular weight molecules. In general we may write

$$x_2^{\text{eff}} = x_2^0 f_{\text{red.}} \tag{3}$$

where $f_{\text{red.}} \leq 1$ describes the reduced probability of complex formation in the case of polymer bound functional groups. Thus, $f_{\text{red.}}$ expresses a polymer-specific excess entropy contribution to the complex formation. This is an entropy contribution because it depends on the spatial arrangement of functional units. To obtain a mathematical expression for $f_{\text{red.}}$ the following assumptions are made: the polymer molecules with average degree of polymerization n are monodisperse; the fraction of complexed groups per chain is the same as the overall fraction of complexed groups (mean field approximation); the groups are introduced in a statistical process; i.e., the number of functional groups per chain is given by a Bernoullion distribution.

For sake of simplicity, the model is explained for a polymer containing a defined number of groups per chain. The distribution of the number of functional groups can

be introduced without altering the preceding conclusions.

A hypothetical chain with i units of functional groups is placed into a matrix with $x_2^{eff}[U_0]$ complexed groups. The probability that the kth unit of this chain will form a complex if $j = k - 1$ groups are already complexed is represented by $p(k)$.

It is assumed that $p(1)$, i.e. the probability that the first unit forms a complex, is given by the equilibrium probability

$$p(1) = x_2^0 \tag{4}$$

For any further unit the probability of complexation will be reduced by the fact that only a restricted volume is available in which another free functional group for complexation may be found. For the second unit it follows that

$$p(2) = x_2^0 Q(2) \tag{5}$$

and that for the kth unit in a chain with i functional groups

$$p(k) = x_2^0 Q(k) \tag{6}$$

Thus, the effective number of complexed groups is given by

$$x_2^{eff} = x_2^0(1/i)(1 + \sum_{k=2}^{i} Q(k)) \tag{7}$$

$Q(k)$ is the probability that a unit, restricted to a certain volume V_k, will find a partner to form a complex compared to a unit which is not restricted by topological constraints to a certain volume (Figure 1).

$Q(k)$ depends on the density (concentration) of free groups and on the volume V_k, which is assumed to be spherical for simplicity and given by a corresponding radius R_k.

The kth group performs a random walk starting at P_k^0. The probability that this group will find a free group to form a complex within the volume of the boundary R_k is given in accordance with the diffusion process in gases by the probability integral

$$W(R_k) = \int_0^{R_k} w(r)\, dr \tag{8}$$

with

$$w(r)\, dr = (\beta/(\pi)^{1/2})^3 e^{-\beta^2 r^2} 4\pi r^2\, dr \tag{9}$$

The term β is determined by the breadth of the distance distribution between free units and is given by

$$\beta = 1/d_u \tag{10}$$

where d_u is the average distance between free groups, i.e. the density of uncomplexed units (see Appendix B.1). Thus, β depends on the concentration $[U_0]$ and the mole fraction of effectively bonded functional groups x_2^{eff}.

R_k, which defines the available volume for the kth unit, when $k - 1$ units are complexed, is determined by the conformational properties of the parent polymer chain (Appendix B.2.). The first-order estimation for R_k that is used throughout the following calculations is given by eq 11

$$R_k^2 = \bar{m} l^2 C^\infty \tag{11}$$

with

$$\bar{m} = n/(2(k - 1) + 1) \tag{12}$$

In Figure 2, the integral probability $W(R)$ is plotted versus R for two different concentrations of urazole groups. From these curves the values of $Q(k)$ are obtained as the integral probability at R_k. In Figure 2, the corresponding radii for different values of k are shown. For small values

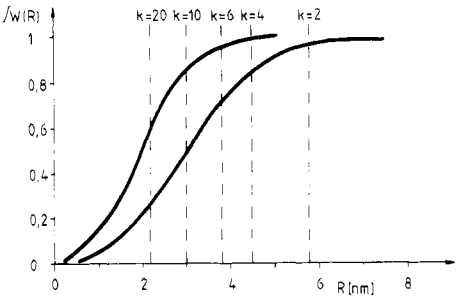

Figure 2. Integral probability $W(R)$ for two different concentrations of functional groups. The vertical lines indicate the locations of R_k for different values of k. Computational parameters: chain length n, 500; concentrations, 0.83 and 0.33 mol/L; fraction of complexed groups, 0.47 and 0.31 (first calculating cycle).

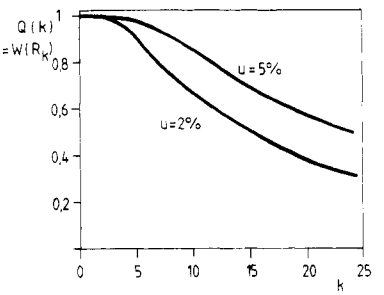

Figure 3. Reduction parameter $Q(k) = W(R_k)$ as a function of k for two different degrees of modification (parameters as in Figure 2).

of k, $Q(k)$ reaches the limiting value of 1; i.e., the probability for a certain group of finding a free partner is the simple thermodynamic probability given by x_2^0. For increasing values of k, $W(R_k) = Q(k)$ is reduced. In Figure 3 the variation of $Q(k)$ with increasing k is plotted for two degrees of modification. It is evident that, for a certain value of k, $Q(k)$ decreases with decreasing modification. This is a consequence of the lower density of free units. The quantity, which determines the fraction of effective complexes, is $f_{red.}$, given by eq 13 (from eq 3 and 7).

$$f_{red.} = (1/i)(1 + \sum_{k=2}^{i} Q(k)) = x_2^{eff}/x_2^0 \tag{13}$$

The calculation of x_2^{eff} according to eq 7 is not possible because x_2^{eff} also enters the right side of eq 7 through β. The solution of eq 7 is possible by an iterative procedure. In the first calculation cycle the distance between free units d_u is calculated by using x_2^0. Thus, the value calculated for x_2^{eff} is too small. In the second cycle this value of x_2^{eff} is used to calculate d_u. This procedure is repeated, until a self-consistent result is obtained. The number of computational cycles depends on the chain length and the concentration of functional groups. The value of $f_{red.}$ depends on the chain length, the number of functional units per chain (= degree of modification, concentration) and the chain flexibility C^∞. The chain length dependence is only observed for very short chains. With increasing chain length $f_{red.}$ converges rapidly. The following calculations were performed for a long chain length. The characteristic ratio was kept constant (l = 0.45 nm, $C^\infty = 1$, $n > 500$).

In Figures 4 and 5 the mole fractions x_2^0 and x_2^{eff} are shown for various degrees of modification for two equilibrium constants K_0 (1 and 10). The degree of modification u is defined as the fraction of monomer units that carry functional groups. In addition, an effective equilibrium constant K, calculated from x_2^{eff}, is shown. With increasing degree of modification, the increase in the fraction of complexed units is less than that predicted from

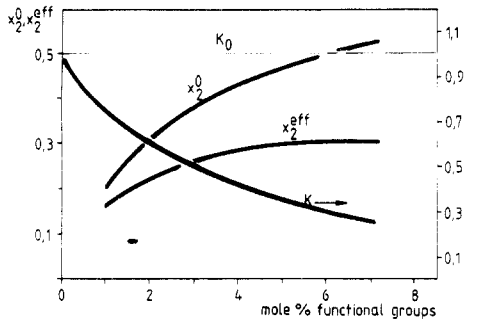

Figure 4. Mole fractions x_2^0 and x_2^{eff} (left axes) as a function of the degree of modification (fraction of substituted repeating units) for $K_0 = 1$. The curve corresponding to the right axes shows the change in the equilibrium constant with concentration calculated from x_2^{eff}.

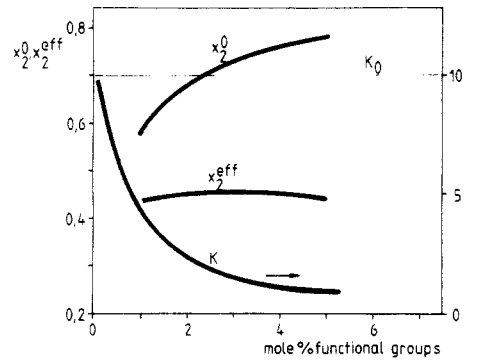

Figure 5. Mole fractions x_2^0 and x_2^{eff} (left axes) as a function of the degree of modification (fraction of substituted repeating units) for $K_0 = 10$. The curve corresponding to the right axes shows the change in the equilibrium constant with concentration calculated from x_2^{eff}.

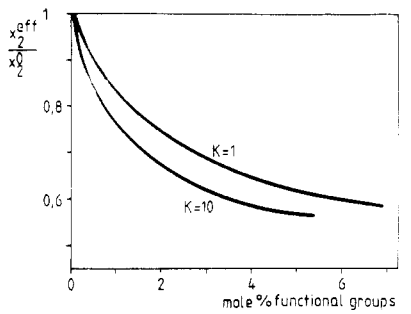

Figure 6. Reduction factor $f_{red.} = x_2^{eff}/x_2^0$ as a function of the degree of modification for two values for the equilibrium constant K_0 (high molecular weight limit).

thermodynamic considerations without topological restrictions. For $K_0 = 10$ a decrease in the fraction of complexed units is calculated for higher degrees of modification. Such behavior has been observed experimentally by IR spectroscopy for a modified polybutadiene with a high degree of modification.[22] Consequently, the effective K drops with increasing modification. In Figure 6 the reduction factor $f_{red.}$ is plotted versus the degree of modification for these equilibrium constants. The deviation of f_{red} from unity increases with modification and with increasing equilibrium constant. The variation of $f_{red.}$ with the equilibrium constant K_0 for a constant degree of modification (1%) is shown in Figure 7. The value for $f_{red.}$ reaches a limiting value for high values of K_0. This means, that in this region the formation of complexes is only controlled by the topological restrictions and not by the enthalpy of complex formation.

Until now it has been assumed that every polymer chain bears i functional units. A more realistic model has to take

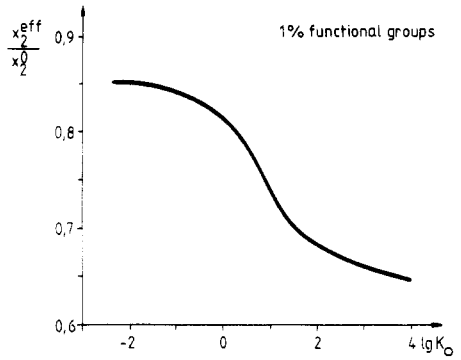

Figure 7. Reduction factor $f_{red.} = x_2^{eff}/x_2^0$ for a 1% modified polymer (1 functional group per 100 repeating units) as a function of the equilibrium constant K_0.

into account the distribution of the number of functional groups per chain. For a statistical modification $P_i(P_n;i,u)$ is the probability that a chain with degree of polymerization P_n carries i functional groups, if the degree of modification is u. For $u \ll 1$ the Bernoullian distribution $P_i(P_n;n,u)$ simplifies to the Poisson distribution, i.e.

$$P_i = N^i/i!\ \exp(-N) \tag{14}$$

where N is the average number of functional groups $N = uP_n$ as defined above.

Thus the final equation to calculate the fraction of effectively bound functional units in dimer complexes is

$$x_2^{eff} = \sum_{i=1}^{\infty} P_i(x_2^0/i)\left(1 + \sum_{k=2}^{i} Q(k)\right) \tag{15}$$

The results that are obtained, if eq 15 is used to calculate the influence of topological restrictions on the association behavior, are the same as if the average number of functional groups per chain is used. Nevertheless eq 15 must be used, when low degrees of modification and short polymer chains are considered.

The model presented so far is a simple approach to take into account the topological restrictions imposed on associating functional groups bound to a polymer. These restrictions are of a "long-range" type, since they arise from a limited spatial mobility of the functional groups. No attempt has been made to discuss changes in the local entropy of complex formation. Due to the direct linking of a functional group to the polymer, additional short-range restrictions may become important. The model calculations presented in this paper showed that noncooperative topological phenomena may play an important role in systems with high functionality and large equilibrium constants. It must be stated that the physical nature of these topological restrictions does not allow an analysis according to ideas that have has been developed to describe the protein–ligand or DNA–protein interactions.[23,24] In a protein every monomer unit can act as a binding site, either intramolecularly to form a helix or to another ligand molecule. If the ligand can bind several sites of the chain, these must be arranged in the correct conformational order. The main theoretical discussion of this problem deals with the cooperativity or noncooperativity, in which succeeding ligands react with the highly ordered biological macromolecule. In the discussion presented in this paper, the random configuration of the polymer chain determines the limit of the degree of association, while in the ligand binding in biopolymers the random attachment of a ligand which complexes n sites of a chain with N repeating units is considered.

Besides the simple binary association discussed in this paper, other types of associations that are more realistic

Figure 8. One complexed group (filled circle) at the chain end, the free group (cross) located anywhere along the chain.

for ionomers may be treated in a similar way. A closely related approach may be used to calculate the limiting extent of reaction in an end-linking process. More interesting in the context of thermoreversible gelation may be the application of this concept to the cascade theory.[9,10,13] The following different situations may be treated: gelation in bulk, gelation in the presence of a nonpolar solvent, and gelation when the solvent also may form a complex with the functional group.

B. Appendix

B.1. Estimation of the Mean Distance between Free Functional Groups. The number density of free groups per unit volume is given by

$$\rho_{ul} = (1 - x_2^{eff})\rho_u \tag{B-1}$$

where ρ_u is the number density of functional groups (number of groups per unit volume). Thus the average volume per free group V_{ul} is given by eq B-2.

$$V_{ul} = 1/\rho_{ul} \tag{B-2}$$

Assuming a homogeneous distribution of free groups, the average distance d_u between free groups is taken as twice of the radius of a sphere of the volume V_{ul}:

$$d_u = 2(^3/_4 V_{ul}/\pi)^{1/3} \tag{B-3}$$

The average distance between free groups will decrease with increasing degree of modification and decreasing effective complexation.

B.2. Estimation of the Average Radius R_k. Consider a chain of degree of polymerization n, carrying i functional groups. In order to determine the average available volume V_k of the kth functional group, if $k - 1$ groups are already complexed, the following assumptions are made: 1. The volume V_k is taken as spherical, and the corresponding radius is R_k (Figure 1). 2. The volume in which the kth functional group can move is determined only by the distance to the next complexed group along the chain. 3. The distance to the next complexed groups is given by the number of segments m_k. 4. Gaussian behavior is assumed for all subchains between functional groups. From assumptions 3 and 4, we can write

$$R_k^2 = m_k l^2 C^\infty \tag{B-4}$$

The problem thus reduces to the estimation of the average number of chain segments between the kth functional group which is free and the next complexed functional group along the chain. In order to solve this problem, two simple cases will first be considered. In the first case, one complexed group is located at one chain end, while the free group is located anywhere along the chain contour. The second case to be considered is that in which the complexed group is located statistically along the chain and the free group is located anywhere else along the chain contour.

After this discussion a more general solution will be presented on the basis of these simple limits.

B.2.1. The Complexed Unit Located at the Chain End. A schematic picture is shown in Figure 8. The complexed group (filled circle) is at one chain end (monomer unit 1) and the free group (cross) is a distance of j monomer units away. j can take any value between 2 and n (the degree of polymerization). Thus the average distance $\bar{m}$ between the free and the complexed group is given by eq B-5.

Figure 9. One complexed group (filled circle) located anywhere along the chain, the free group (cross) anywhere else along the chain.

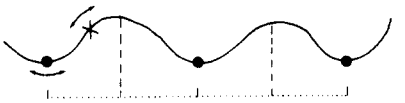

Figure 10. $k - 1$ complexed groups (filled circles) located along the chain. The chain is divided into $k - 1$ equally sized subchains. The free group is located in one of these subchains and can be treated as the free groups of Figure 9.

$$\bar{m} = \frac{\sum_{j=2}^{n} j - 1}{n - 1} = (n - 1)/2 \simeq n/2 \tag{B-5}$$

For $n \gg 1$, the average distance between any position in the chain and one distinct chain end is $n/2$ monomer units.

B.2.2. The Complexed Unit Located Statistically along the Chain. The situation is slightly more complicated if the complexed group can be positioned anywhere along the chain, as is shown schematically in Figure 9. If the complexed group is located at position i and the free group at position j ($j \neq i$), the average distance $\bar{m}$ is given by eq B-6.

$$\bar{m} = \frac{\sum_{i=1}^{n} \sum_{j=1, j\neq i}^{n} |j - i|}{n(n - 1)} = (n + 1)/3 \simeq n/3 \tag{B-6}$$

If the double summation of B-6 is evaluated, $\bar{m} = n/3$ is obtained as a result for the average number of monomer units between the complexed and the free group. Compared to the situation discussed in B.2.1., the chain has been divided in two parts (left and right to the complexed group). The free group is located in one of these parts.

B.2.3. $k - 1$ Functional Units Located Statistically along the Chain. To solve this case, the procedure described in B.2.2. could be continued and an additional complexed unit must be added to calculate the distance between the free functional group k and the complexed units. However, this would give information about the average distance between the free group and all complexed groups. The problem of interest is to determine the average distance between the kth group (free) and the next complexed functional group, because this complex will primarily restrict the kth unit.

The simplified schematic model that accounts for this complicated case is shown in Figure 10. The $k - 1$ complexed units are assumed for the moment to be distributed equidistantly along the chain. Thus a set of $(k - 1)$ subchains is generated with the complexed group located anywhere within the subchain and the free unit k located in one of these subchains. If the $k - 1$ groups would be fixed at the end of one of the subchains, the average distance $\bar{m}$ then would be $n/(2(k - 1))$. According to the averaging procedure given in B.2.2. the fact that the next functional group is not fixed must be taken into account. If the subchains are independent, the average number of monomer units between the kth group which is free and the next complexed group is given by eq B-7 (=12).

$$\bar{m} = n/(2(k - 1) + 1) \tag{B-7}$$

This equation has been used throughout the model calculations presented in this paper. It should be mentioned that this equation for $\bar{m}$ gives the upper limit of the volume V_k. In the real system the topologically next neighbor as well as the next neighbor in the other chain direction (Figure 1) will hinder the spatial mobility of the kth unit. Thus the efficient available volume would be even smaller. However, complexed junctions are not fixed but fluctuate around mean positions, similar to junction fluctuations in covalent polymer networks.[23] Such a fluctuation increases V_k and thus may partly compensate for neglecting the influence of both nearest neighbors.

Symbols

β	parameter that describes the breadth of the distance distribution between free functional groups
C^∞	characteristic ratio
d_u	average distance between two free functional groups
$f_{red.}$	factor by which the mole fraction of complexed units is reduced due to topological restrictions
i	number of functional groups per chain
K_0	equilibrium constant
l	length of monomer repeating unit
m	average number of monomer units between the kth functional group and the next complexed group
n	degree of polymerization
P_i	probability that a chain has i functional groups
$p(k)$	probability of the kth functional group of a chain to form a complex when $k-1$ functional groups are complexed
$Q(k)$	$W(R_k)$ = reduced probability for the kth functional group of a chain to form a complex if $k-1$ groups are complexed
ρ	number of functional groups per unit volume
R_k	average radius that defines the sphere in which the kth functional group can move
$[U_0]$	concentration of functional groups (mol/L)
u	degree of modification (fraction of monomer units that carry functional groups)
V_k	volume available for the kth unit
x_2^0	mole fraction of complexed functional groups without topological restrictions
x_2^{eff}	mole fraction of complexed functional groups

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A Continuum Gambler's Ruin Model

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ABSTRACT: A continuum version of the gambler's ruin model is presented. The following functions are derived: end-to-end vector distributions of both loops and ties and their Fourier transforms, chain length distributions of both loops and ties, and their Laplace transforms. A few of the lower moments of these distributions are also calculated. Gambler's ruin models lack sufficient detail to accurately predict the degree of adjacent reentry but nevertheless predict that most chains return to the crystal very near the point of departure. For example, on the basis of this model, we predict that $^3/_4$ of the chains in polyethylene return to the same crystallite within about 14 Å.

Introduction

The statistics of random walks between two absorbing parallel planes provides an important model of the amorphous domains of semicrystalline polymers. This model is admittedly deficient in accounting for the detailed packing of chains in the amorphous domains but has the benefit of mathematical tractability and accounts for chain packing in a certain mean-field sense in that it yields a uniform segment density throughout the amorphous domain.[1-3] Guttman, DiMarzio, and Hoffman[1,2] were the first to apply the concept to semicrystalline polymers, adopting the expression "gambler's ruin" model. The gambler's ruin model is expected to be valid and useful to the extent that polymer chains in the amorphous domains are ideal random walks.

Guttman, DiMarzio, and Hoffman first considered random walks on the simple cubic lattice[1] and later extended these results to more general random walks.[2] In

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