$$F(X) = h_0(z) = \Psi(\bar{z})/\bar{z} \qquad (27)$$

Registry No. PS (homopolymer), 9003-53-6; PMMA (homopolymer), 9011-14-7.

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Predictions of the Gambler's Ruin Model for Neutron Scattering by Semicrystalline Polymers

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Received August 12, 1985

ABSTRACT: In a recent paper we showed that the gambler's ruin model of semicrystalline chains predicts, first, that $R^2_{\mathrm{g,cry}} = [(2x_{\mathrm{a}} + x_{\mathrm{a}}^{-1})/3]R^2_{\mathrm{g,melt}}$ for the square radius of gyration of long semicrystalline chains, where x_{a} is the fraction of polymer segments in amorphous domains (one less the degree of crystallinity) and $R^2_{\mathrm{g,melt}}$ is the radius of gyration in the melt, and, second, that the chains follow anisotropic Gaussian distributions, elongated normal to the lamellar plane with aspect ratios x_{a}^{-1}. In this paper we extend those results to finite chains and consider scattering at higher angles. Two predictions are made: First, the static structure factors continue to follow a q^{-2} power law at higher scattering angles, but with a prefactor dependent on the anisotropy of the chains, and therefore on the degree of crystallinity. Second, at lower molecular weights the above formula becomes $R^2_{\mathrm{g,cry}} = [(2x_{\mathrm{a}} + x_{\mathrm{a}}^{-1})/3]R^2_{\mathrm{g,melt}} + l_{\mathrm{c}}^2/4$ for l_{c} the length of a crystalline stem.

Introduction

Neutron scattering experiments[1-8] indicate that lamellar semicrystalline polymer chains follow Gaussian statistics, with dimensions comparable to those of the melt. With only one exception,[4] gyration radii in both systems agree to within 10% or so and follow the $M^{1/2}$ power law indicative of Gaussian coils. The static structure factors often agree rather well also, at least over small and intermediate angles. Crystalline structure factors at intermediate angles often follow a q^{-2} power law,[1-4,7,8] also indicative of Gaussian behavior, which is usually numerically close to the melt structure factor. Only at larger scattering angles, when the crystalline structure becomes resolvable, are significant differences observed.

In a recent publication,[9] we demonstrated that the "gambler's ruin" model[10,11] of semicrystalline polymers predicts Gaussian behavior, in the limit of very long chains, with a gyration radius close to the melt value. The gambler's ruin model treats chains in the amorphous domains as random walks between two absorbing barriers. It requires 2/3 near-adjacent reentry and 1/3 random reentry to properly fill the amorphous domains. In the limit of long chains we derived

$$R^2_{\mathrm{g,cry}} = (2x_{\mathrm{a}} + x_{\mathrm{a}}^{-1})R^2_{\mathrm{g,melt}}/3 \qquad (1)$$

for $R_{\mathrm{g,cry}}$ and $R_{\mathrm{g,melt}}$ the semicrystalline and melt gyration radii, respectively, and x_{a} the amorphous fraction. Equation 1 implies $R_{\mathrm{g,cry}} \simeq R_{\mathrm{g,melt}}$ for x_{a} in the usual experimental range.

Another prediction of the gambler's ruin model is that the chains follow anisotropic Gaussian distributions, expanded by a factor $x_{\mathrm{a}}^{-1/2}$ normal to the lamellar plane and contracted by a factor $x_{\mathrm{a}}^{1/2}$ in the lamellar plane.[9] Since experimental samples are polycrystalline, the structure factor is spherically symmetric. However, the anisotropy should be evident, at least in principle, at higher scattering angles. In the next section we discuss the scattering structure factors for anisotropic Gaussian coils. The anisotropy is predicted to affect the form of the structure factor in the q^{-2} region.

Another prediction of the gambler's ruin model is that departures from the $M^{1/2}$ power law might be discernible at lower molecular weights.[9] All unperturbed coils obey

$$R_{\mathrm{g}}^2 = \alpha n + \beta + \mathcal{O}(n^{-1}) \qquad (2)$$

for n the number of bonds in the chain. This is simply an expansion in powers of n^{-1}. For flexible, molten-state chains, β is very small and the usual power law behavior is observed over all molecular weights. However, we show below that gambler's ruin predicts $\beta = l_{\mathrm{c}}^2/4$ for semicrystalline polymers, where l_{c} is the stem length. At low molecular weights, this term can be important, producing observable departures from the power law. In the third

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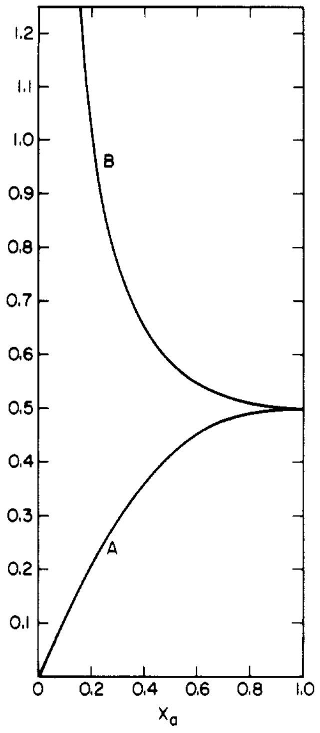

Figure 1. Variation in the parameters A and B of eq A20 with x_a, the amorphous fraction.

section and in the appendices we derive the above expression for β. In the fourth section we compare the predictions of this model with experiment. Finally, in the last section we summarize our findings and present some discussion.

Structure Factor of Anisotropic Gaussian Coils

In Appendix 1 we derive an expression, eq A19, for the structure factor of anisotropic Gaussian coils which are assumed to be elongated normal to the lamellar plane and contracted within the lamellar plane by factors $x_a^{1/2}$ and $x_a^{-1/2}$, respectively, and for which all possible orientations of the lamellar plane are allowed. It is, of course, necessary to assume an anisotropic Gaussian distribution, Equation A1, between different polymer segments, invalidating the equation at high wavenumbers. It should do well, however, in the Guinier and q^{-2} regions for sufficiently long chains. The expression exhibits the q^{-2} behavior at intermediate angles expected of any Gaussian distribution, isotropic or not, as displayed in eq A20–A22. The precise form of the structure factor in the q^{-2} region, however, depends on the anisotropy and therefore on the amorphous fraction or the degree of crystallinity. The values of A and B differ from the value $^1/_2$ that they would assume in an isotropic system at all values of $x_a \neq 1$, as shown in Figure 1. This variation of A and B with x_a provides an experimental method, at least in principle, of detecting the anisotropy.

In Figures 2 and 3 we display structure factors calculated for various x_a values according to eq A19. One important point to note is that the structure factors for degrees of crystallinity less than about a half are predicted to lie rather close to the structure factors expected for isotropic coils.

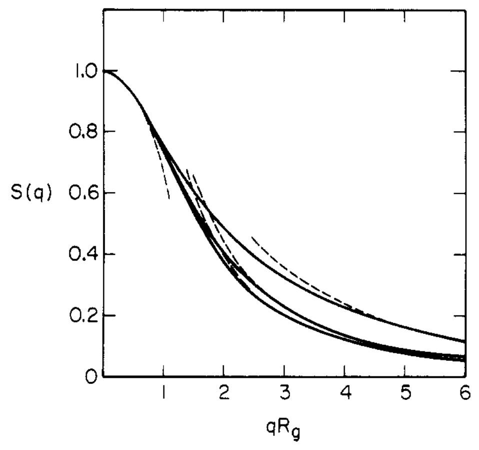

Figure 2. Change in the structure factor, as predicted by the present model, with x_a, the amorphous fraction. The solid curves represent the exact expression for $S(q)$ at x_a = 0.2, 0.5, and 1, reading from top to bottom. The dashed curves represent the approximations $1 - q^2R_g^2/3$ and $[Aq^2R_g^2 + B]^{-1}$, valid at low and high q, respectively.

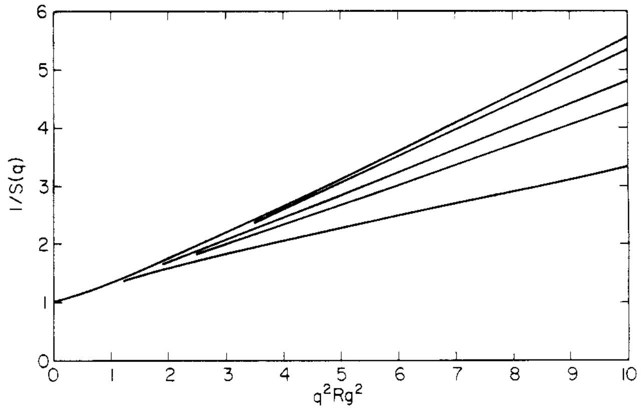

Figure 3. Change in structure factor, plotted as $[S(q)]^{-1}$ vs. $(qR_g)^2$, as predicted by the present model, with x_a, the amorphous fraction. x_a values, reading from top to bottom, are 1, 0.707, 0.5, 0.4, and 0.2.

Radius of Gyration of Finite Chains

In Appendix 2 we discuss the linearity, eq A43 and A44, between either $\langle R^2 \rangle$ or R_g^2 and the degree of polymerization. We show that $\langle R^2 \rangle$ is linear in n for any chain having negligible directional correlation between the bonds at either end, while R_g^2 is linear in n when terms of order n^{-1} can be neglected. We also establish the relationship, eq A42, between the two sets of parameters. Although we only consider chains in which all the bonds are statistically equivalent, the above-cited findings are expected to hold generally. In Appendix 3 we derive the parameter β of eq A44, obtaining $\beta = l_c^2/4$ for l_c the length of a crystalline stem.

The results of Appendix 3, specifically eq A55 and A56, are derived for an ensemble in which the number of virtual bonds, n, is fixed. However, the results are expected to apply generally.[9] In particular, β, being a constant independent of molecular weight, is expected to be independent of any particular chain ensemble or molecular weight distribution.

At lower molecular weights, since l_c and R_g both have magnitudes on the order of 10^2 Å, the second term of eq A43 becomes important. However, since eq A43 involves neglect of terms of $\mathcal{O}(n^{-1})$ and lower, additional terms are not expected to be important at any molecular weight usually encountered.

Comparison with Experiment

1. Isotactic Polystyrene. Guenet et al.[4] report experiments on isotactic polystyrene, in which deuterated samples of molecular weights from 2.5×10^5 to 7×10^5 were suspended in protonated matrices of $M_w = 4 \times 10^5$ or 1.75×10^6. They obtained anomalous behavior for the

Table I
Experimental Results of Guenet et al.[4] for Isotactic Polystyrene Compared with Predictions of the Present Model[a]

M_w	5×10^5	7×10^5
$R_{g,am}$ Å	165	195
$R_{g,cry}$ Å	150	177
$R^2_{g,cry}/R^2_{g,am}$(exptl)	0.83	0.82
$R^2_{g,cry}/R^2_{g,am}$(pred)	0.95	0.95
$[q^2S(q)]_{am}/[q^2S(q)]_{cry}$(exptl)	0.86	
$[q^2S(q)]_{am}/[q^2S(q)]_{cry}$(pred)	0.88	

[a] Crystalline samples had $x_a = 0.65$.

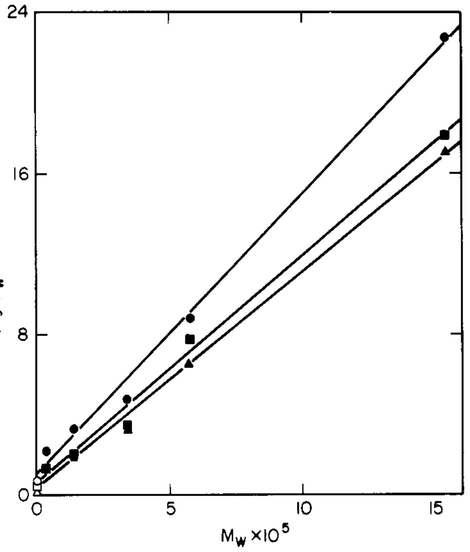

Figure 4. Plot of $\langle R_g^2 \rangle_w$ vs. M_w for the isotactic polypropylene data of Ballard et al.[2] for quenched (▲), annealed (■), and isothermally crystallized (●) samples. Open symbols represent the predicted intercepts.

Table II
Experimental Results of Ballard et al.[2] for Isotactic Polypropylene[a]

	quenched	annealed	isothermally crystallized
$\alpha n_w/M_w$, A^2	0.108 ± 0.005	0.113 ± 0.006	0.139 ± 0.006
$\beta \times 10^3$, Å^2	3.5 ± 2.6	5.7 ± 3.1	10.2 ± 3.4
l_c, Å	68	126	171
$l_c^2/4$, Å^2	1.2×10^3	4.0×10^3	7.3×10^3
$(2x_a + x_a^{-1})/3$	1.04 ± 0.02	1.13 ± 0.02	1.27 ± 0.03

[a] n_w is the weight-average number of bonds in the backbone.

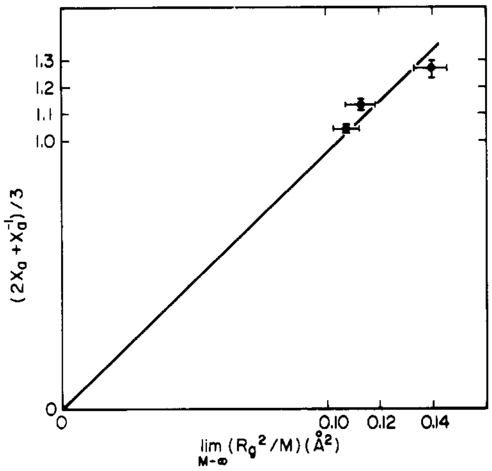

Figure 5. Plot of $(2x_a + x_a^{-1})/3$ vs. $\lim_{M_w\to\infty} \langle R_g^2 \rangle_w/M_w$ for the isotactic polypropylene data of Ballard et al.[2] for x_a, the amorphous fraction. These two quantities are predicted to be proportional by the present model. Individual points represent quenched, annealed, and isothermally crystallized samples. The solid curve is the best-fit line constrained to pass through the origin and has slope 9.55.

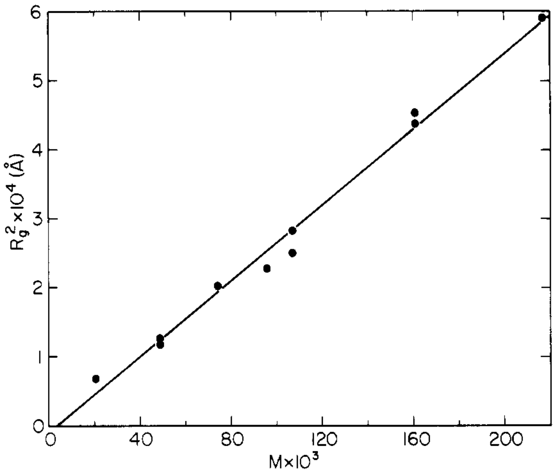

Figure 6. Plot of R_g^2 vs. M for the hydrogenated polybutadiene data of Tanzer et al.[8]

lower molecular weight matrix, with $R_g \sim M^{0.8}$, which has not been observed in any other system. However, a few results reported for the higher molecular weight matrix agree with the predictions of the present model. These are summarized in Table I. The ratios of crystalline and amorphous square gyration radii are 0.83, as compared with 0.95 predicted by eq 1. (For these samples, $x_a = 0.65$.) The ratios of $q^2S(q)$ on a Kratky plot are predicted by eq A22 and 1 to be 0.88, in good agreement with the experimental value of 0.86. This latter result is not strong evidence for the anisotropy predicted here, however, since the experimental ratio is also consistent with the experimental gyration radius ratio.[4] In any case, we expect it to be difficult to observe anisotropy at such low crystallinities, as is obvious from Figures 2 and 3.

2. Isotactic Polypropylene. Ballard et al.[2] performed experiments on isotactic polypropylene, examining samples that were either quench crystallized, quench crystallized and then annealed, or isothermally crystallized at elevated temperatures. As previously remarked,[6] their data can be fit with eq 2, as shown in Figure 4. The experimental values of α and β, obtained by linear least-squares regression, are given in Table II. Also in Table II we display l_c, the stem length, calculated from low-angle X-ray long spacing and degree of crystallinity data tabulated by Ballard et al.[2] The tabulated values of l_c assume a zero tilt angle and so actually represent a lower bound to l_c. Also in Table II are experimental values of the proportionality factor of eq 1, $(2x_a + x_a^{-1})/3$. (The tabulated uncertainties in these values are generated by the scatter in the crystallinities over the molecular weight series.) The values $l_c^2/4$ are consistently smaller than the best-fit β values[12] but nonetheless agree to within the rather large experimental error of the latter. Also, we expect a direct proportionality between α and $(2x_a + x_a^{-1})/3$, which is confirmed in Figure 5, at least to within experimental error. The agreement shown in Figure 5 is remarkable not only on account of the rather large variation in l_c values from one set of samples to the next but also because of our prediction[9] that eq 1 might only be valid for quench-crystallized samples.

Kratky plots of the Ballard et al.[2] polypropylene data indicate that the structure factor follows q^{-2} behavior at intermediate angles, an indication of Gaussian behavior. The A^{-1} values determined from the plots are tabulated in their paper, but the experimental uncertainty in these values seems too large to make a meaningful analysis.

3. **Hydrogenated Polybutadiene.** This polymer has been studied by Crist et al.[7] and by Tanzer et al.[8] Figure 6 displays a plot of R_g^2 vs. M. The graph is linear, with least-squares estimates of 0.27 ± 0.01 Å^2 and (−11 ± 6) × 10^3 Å^2 for the slope and intercept, respectively. The least-squares intercept has a sign inconsistent with eq A57, but experimental uncertainty appears sufficiently large that this fact should not be too alarming. The authors successfully fit scattering data for these polymers to the standard formula[13] for the structure factor of isotropic Gaussian chains, but at such low crystallinities (near 40%) we would expect the structure factor of anisotropic Gaussian coils to provide an equally adequate fit, as shown in Figures 2 and 3.

4. **Polyethylene.** Schelten et al.[1] have reported studies of this polymer. They find that molten and crystalline radii are comparable, but the experimental uncertainty is too large for fits to eq A43 to be meaningful. Kratky plots exhibit q^{-2} behavior at intermediate angles and yield A^{-1} values of ca. 2.3, somewhat smaller than the ca. 3 predicted by eq A20 for the observed crystallinity of 65%. This may not be unreasonable, however, given the experimental uncertainties accompanying measurements at these angles, such as low scattering intensity and uncertainty in the background scattering.

Summary

In this paper we discuss two predictions of the gambler's ruin model of semicrystalline polymers, in addition to the prediction, eq 1, derived earlier. The first prediction is that chain anisotropy gives rise to a structure factor, eq A19, different from the structure factor predicted for isotropic coils. The second prediction is that at finite molecular weights the radius of gyration is given by eq A43 and A57. These predictions do not seem to be inconsistent with experiment, although in many cases experimental uncertainties appear too large to exclude other possibilities.

It is probably important to point out the assumptions involved in the derivations given here and in our previous paper[9] on this subject. Inherent in the gambler's ruin model is the assumption that amorphous chains obey random walk statistics. The possibility that some partial ordering of the amorphous material might be generated during solidification is not considered. It is also assumed that the statistical segment length of the amorphous chains is much smaller than the thickness of the amorphous domains and that both phases have the same density. Each of the latter two assumptions could generate errors on the order of 10% or so. Therefore, one should not expect precise agreement with the predictions of this model.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Computation facilities were provided in full by the Computer Science Center of the University of Maryland.

Appendix 1. Structure Factor Derivation

Adopt a coordinate system with the z axis normal to the lamellar plane. Let the distribution function of $\mathbf{r}_{jl} = (x,y,z)$, the displacement vector between segments j and l, be

$$(\Lambda/\pi)^{3/2}(a_1^2a_3)^{-1}\exp\{-\Lambda[(x/a_1)^2 + (y/a_1)^2 + (z/a_3)^2]\} \tag{A1a}$$

where

$$\Lambda = 3/2|l - j| \tag{A1b}$$

The above distribution yields

$$\langle r_{jl}^2\rangle = |l - j|(2a_1^2 + a_3^2)/3 \tag{A2}$$

so that by taking a_1 and a_3 proportional, respectively, to $x_a^{1/2}$ and $x_a^{-1/2}$, this distribution should give the structure factor predicted by the gambler's ruin model, at least in the Guinier and q^{-2} regions. An integration over eq A1 yields

$$\langle e^{i\mathbf{q}\cdot\mathbf{r}_{jl}}\rangle = \exp\{-(1/4\Lambda)(a_1^2q_x^2 + a_1^2q_y^2 + a_3^2q_z^2)\} \tag{A3}$$

The structure factor in the reference frame attached to the lamellar plane is

$$[S(q)]_{\text{lam}} = N^{-2}\sum_{j,l}^{N}\langle e^{i\mathbf{q}\cdot\mathbf{r}_{jl}}\rangle \tag{A4}$$

for N the number of segments. The sum in eq A4 can be written down directly through comparison with the formula for the structure factor of isotropic Gaussian coils,[13] since both require a sum of the form

$$N^{-2}\sum_{j,l}^{N}\exp[-f|l - j|] \tag{A5}$$

where f is a function independent of l or j. In other words, if we were to replace $a_1^2q_x^2 + a_1^2q_y^2 + a_3^2q_z^2$ in eq A3 with a^2q^2, we would obtain the analogous expression for isotropic coils. It follows that the sum in eq A4 can be obtained by replacing $a^2q^2 = 6q^2R_g^2/N = 6u/N$ in

$$(2/u^2)(e^{-u} + u - 1) \tag{A6}$$

with $a_1^2q_x^2 + a_1^2q_y^2 + a_3^2q_z^2$. Therefore, the sum in eq A4 becomes

$$[S(q)]_{\text{lam}} = 12/N\kappa - 72/N^2\kappa^2 + (72/N^2\kappa^2)\exp(-N\kappa/6) \tag{A7}$$

where

$$\kappa = a_1^2q_x^2 + a_1^2q_y^2 + a_3^2q_z^2 \tag{A8}$$

The laboratory frame structure factor is obtained by averaging eq A7 over all orientations:

$$[S(q)]_{\text{lab}} \equiv S(q) = (4\pi)^{-1}\int_0^{\pi}\sin\theta\,\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\phi\,[S(q)]_{\text{lam}} \equiv (4\pi)^{-1}\int\mathrm{d}\Omega\,[S(q)]_{\text{lam}} \tag{A9}$$

where

$$\begin{aligned} q_x &= q\sin\theta\cos\phi \\ q_y &= q\sin\theta\sin\phi \\ q_z &= q\cos\theta \end{aligned} \tag{A10}$$

We will now carry out the integrals in eq A9 term by term. The integral over κ^{-1} reduces to

$$\int\mathrm{d}\Omega\,\kappa^{-1} = (2\pi/q^2)\int_{-1}^{1}\mathrm{d}t(a_1^2 + d^2t^2)^{-1} = (4\pi/q^2a_1d)T \tag{A11}$$

where

$$d^2 = a_3^2 - a_1^2 \tag{A12}$$

and

$$T = \tan^{-1}(d/a_1) \tag{A13}$$

The integral over κ^{-2} becomes

$$\int\mathrm{d}\Omega\,\kappa^{-2} = (2\pi/q^4)\int_{-1}^{1}\mathrm{d}t\,(a_1^2 + d^2t^2)^{-2} = 2\pi Q/q^4 \tag{A14}$$

where

$$Q = a_1^{-2}a_3^{-2} + a_1^{-3}d^{-1}T \tag{A15}$$

The integral over $\kappa^{-2}\exp(-N\kappa/6)$ becomes

$$\int \mathrm{d}\Omega\, \kappa^{-2}\exp(-N\kappa/6) = (4\pi/q^4)\int_0^1 \mathrm{d}t\, (a_1^2 + d^2t^2)^{-2}\exp\{-(Nq^2/6)(a_1^2 + d^2t^2)\} \tag{A16}$$

Equation A16 cannot be further reduced and must be integrated numerically.

We now express the above in terms of the reduced variable

$$u = q^2/R_g^2 = Nq^2(2a_1^2 + a_3^2)/18 \tag{A17}$$

Also, remembering the proportionality between a_1 or a_3 and $x_a^{\pm 1/2}$, we may write

$$a_1 = zx_a^{1/2} \tag{A18a}$$

$$a_3 = zx_a^{-1/2} \tag{A18b}$$

where z can be thought of as an arbitrary proportionality constant that does not appear in the final expression. We finally obtain

$$S(q) = F/u + (G - H)/u^2 \tag{A19a}$$

with

$$F = 2J\epsilon_1 \tag{A19b}$$

$$G = 2\epsilon_1^2 I \tag{A19c}$$

$$H = \epsilon_1^2\epsilon_3/x_a^2 \tag{A19d}$$

$$\epsilon_1 = (1 + 2x_a^2)/3 \tag{A19e}$$

$$\epsilon_2^2 = 1 - x_a^2 \tag{A19f}$$

$$\epsilon_3 = 1 + J \tag{A19g}$$

$$I = \int_0^1 \mathrm{d}t\, (x_a^2 + \epsilon_2^2t^2)^{-2}\exp[-u(x_a^2 + \epsilon_2^2t^2)/\epsilon_1] \tag{A19h}$$

and

$$J = (x_a\epsilon_2)^{-1}\tan^{-1}(\epsilon_2/x_a) \tag{A19i}$$

Consider the limit $x_a \rightarrow 1$. Then $J \rightarrow 1$, $\epsilon_3 \rightarrow 2$, $\epsilon_2 \rightarrow 0$, $\epsilon_1 \rightarrow 1$, $I \rightarrow e^{-u}$, $H \rightarrow 2$, $G \rightarrow 2e^{-u}$, and $F \rightarrow 2$. Then eq A19a becomes eq A6 as expected.

At large scattering angles ($u \rightarrow \infty$), $I \rightarrow 0$. Then

$$S^{-1}(q) = Au + B + \mathcal{O}(u^{-1}) \tag{A20a}$$

with

$$A = F^{-1} \tag{A20b}$$

and

$$B = HF^{-2} \tag{A20c}$$

The above expressions, of course, are appropriate only for monodisperse molecular weight distributions. If we assume that all molecular weight species present in a polydisperse sample obey eq A20 with the same values of A and B and that they are all sufficiently long to obey $R_g^2 \sim M$ (this may not always be the case; see above), then the polydisperse sample obeys

$$S^{-1}(q) = Aq^2\langle R_g^2\rangle_w + (M_w/M_n)B + \mathcal{O}(q^{-2}) \tag{A21}$$

Then in Kratky representation, we have

$$q^2\langle R_g^2\rangle_w S(q) = A^{-1} - (M_w/M_n)BA^{-2}(q^2\langle R_g^2\rangle_w)^{-1} + \mathcal{O}(q^2\langle R_g^2\rangle_w)^{-2} \tag{A22}$$

Appendix 2. Series Expressions for $\langle R^2\rangle$ and R_g^2 for Finite Unperturbed Chains

Consider an unperturbed polymer chain with end-to-end vector

$$\mathbf{R} = \sum_{j=1}^{n}\mathbf{r}_j \tag{A23}$$

for n the number of bonds and for $\mathbf{r}_j$ the jth bond vector. Further, suppose that $\langle \mathbf{r}_j\cdot\mathbf{r}_k\rangle = t_{|j-k|}$, i.e., is a function only of $|j - k|$. This limits us formally to chains in which all bonds are statistically equivalent but is nevertheless adequate for our needs. The following equation holds exactly:

$$\langle R^2\rangle = \sum_{j=1}^{n}\sum_{k=1}^{n}\langle \mathbf{r}_j\cdot\mathbf{r}_k\rangle = \sum_{j=1}^{n}\sum_{k=1}^{n}t_{|k-j|} \tag{A24}$$

Note that the sum over j can be broken up as follows:

$$\langle R^2\rangle = \sum_{k=1}^{n}t_{|k-1|} + \sum_{j=2}^{n-1}\sum_{j=1}^{n}t_{|k-j|} + \sum_{k=1}^{n}t_{|k-n|} \tag{A25}$$

The sum over k can also be broken:

$$\langle R^2\rangle = \sum_{k=1}^{n}t_{|k-1|} + \sum_{j=2}^{n-1}\Big(\sum_{k=1}^{j-1}t_{|k-j|} + t_0 + \sum_{k=j+1}^{n}t_{|k-j|}\Big) + \sum_{k=1}^{n}t_{|k-n|} \tag{A26}$$

The above becomes

$$\langle R^2\rangle = nt_0 + 2\sum_{k=1}^{n-1}t_k + \sum_{j=2}^{n-1}\sum_{k=1}^{j-1}t_k + \sum_{j=2}^{n-1}\sum_{k=1}^{n-j}t_k \tag{A27}$$

For any unperturbed chain t_k decays exponentially, and $\sum t_k$ converges over several persistence lengths. Let

$$T = \sum_{k=1}^{\infty}t_k \tag{A28}$$

and let u_j represent the difference between finite and infinite sums:

$$\sum_{k=1}^{j}t_k = T - u_j \tag{A29}$$

defined so that $u_\infty = 0$. Clearly, u_j also exhibits exponential decay over a range comparable to the persistence length. Then eq A27 becomes

$$\langle R^2\rangle = nt_0 + 2(n - 1)T - 2\sum_{j=1}^{n-1}u_j \tag{A30}$$

Now, through definitions similar to those given above, we let

$$\sum_{k=1}^{j}u_k = U - v_j \tag{A31}$$

with U and v_j defined such that $v_\infty = 0$. Of course, v_j also decays exponentially over several persistence lengths. Equation A30 finally becomes

$$\langle R^2\rangle = n\alpha' + \beta' + 2v_{n-1} \tag{A32}$$

where

$$\alpha' = 2T + t_0 \tag{A33}$$

and

$$\beta' = -2(T + U) \tag{A34}$$

To develop a series for R_g^2, we start with the standard expression

$$R_g^2 = (n + 1)^{-2}\sum_{0\le i<j\le n}\langle R_{ij}^2\rangle \tag{A35}$$

This becomes, using eq A32

$$R_g^{\ 2} = (n + 1)^{-2}\{\sum_{i=0}^{n-1} \sum_{j=i+1}^{n} [(j - i)\alpha' + \beta' + 2v_{j-i-1}]\} \qquad \text{(A36)}$$

When $j = i + 1$, eq A36 involves the undefined quantity v_0. This ambiguity results from an attempt to obtain $\langle R^2_{i,i+1} \rangle = t_0$ by setting $n = 1$ in eq A32, while eq A32 is valid only for $n > 1$. Note, however, by letting $v_0 = U$, eq A32 becomes valid at $n = 1$. Therefore we can proceed if we remember to substitute U everywhere for the undefined v_0. Therefore, we obtain

$$R_g^{\ 2} = (n + 1)^{-2}\{\sum_{i=0}^{n-1}[(n - i) \times (n - i + 1)\alpha'/2 + (n - i)\beta' + 2U + 2V - 2w_{n-i-1}]\} \qquad \text{(A37)}$$

where we define V and w_j such that

$$\sum_{k=1}^{j} v_k = V - w_j; \qquad w_\infty = 0 \qquad \text{(A38)}$$

When $i = n - 1$, we encounter the undefined quantity w_0, and as before, we may remove the ambiguity by defining $w_0 = V$. (When $i = n - 1$, the quantity in square brackets in eq A37 is just $\langle R^2_{n-1,n} \rangle$ and must equal t_0.) Finally, eq A37 becomes

$$R_g^{\ 2} = (n + 1)^{-2}\{\alpha' n^3/6 + (\alpha' + \beta')n^2/2 + (\alpha'/3 + \beta'/2 + 2U + 2V)n - 2V - 2W + 2x_{n-1}\} \qquad \text{(A39)}$$

where

$$\sum_{k=1}^{j} w_j = W - x_j; \qquad x_\infty = 0 \qquad \text{(A40)}$$

Expanding eq A39 in powers of n^{-1} yields

$$R_g^{\ 2} = n\alpha + \beta + \mathcal{O}(n^{-1}) \qquad \text{(A41)}$$

where

$$\alpha = \alpha'/6 \qquad \text{(A42)}$$

and

$$\beta = \alpha + \beta'/2$$

Note that to a good approximation, the mean-square end-to-end distance and square radius of gyration of unperturbed polymer chains are both linear in the number of bonds:

$$R_g^{\ 2} = n\alpha + \beta \qquad \text{(A43)}$$

$$\langle R^2 \rangle = n\alpha' + \beta' \qquad \text{(A44)}$$

Equation A43 involves the neglect of terms of order n^{-1} and smaller, and eq A44 involves neglect of the term $2v_{n-1}$ in eq A32, which is expected to decay exponentially about as quickly as t_{n-1} and should therefore be negligible whenever the bonds at either end of the chain are negligibly correlated. This linearity seems not to have been fully appreciated in the past.

Appendix 3. Dimensions of Semicrystalline Chains

In this appendix, we apply the results of our previous work[9] to determine the parameters β and β' of eq A43 and A44 for the gambler's ruin model of semicrystalline polymers. Let N_a and N_c be the thickness, respectively, of the amorphous and crystalline domains, measured in statistical segment lengths. Let ϵ and δ be respectively the probabilities that a chain emerging from the crystal and entering the melt returns to either the same or the neighboring crystallite. Then $\epsilon + \delta = 1$, while gambler's ruin predicts $\delta = (3N_a)^{-1}$. We decompose the chain into a set of virtual bonds, $\mathbf{V}_j$, where each virtual bond extends from one point at which the chain enters a crystallite to the next point at which it again enters either the same or a neighboring crystallite. We restrict ourselves to an ensemble in which the number of virtual bonds, n, is fixed. Then

$$\langle R^2 \rangle = \sum_{j=1}^{n} \sum_{k=1}^{n} \langle \mathbf{V}_j \cdot \mathbf{V}_k \rangle \qquad \text{(A45)}$$

In ref 9 we showed that

$$\langle \mathbf{V}_j \cdot \mathbf{V}_k \rangle = 4\epsilon N_a/9 + \epsilon N_c^{\ 2} + 2\delta N_a^{\ 2}/3 + \delta(N_a + N_c)^2 \qquad \text{(A46)}$$

if $j = k$, or

$$\langle \mathbf{V}_j \cdot \mathbf{V}_k \rangle = \mathbf{A} \cdot \mathbf{T}^{|j-k|} \cdot \mathbf{B} \qquad \text{(A47)}$$

if $j \neq k$, where

$$\mathbf{A} = [\epsilon N_c \ \delta(N_a + N_c)] \qquad \text{(A48)}$$

$$\mathbf{T} = \begin{bmatrix} -\epsilon & \delta \\ -\epsilon & \delta \end{bmatrix} \qquad \text{(A49)}$$

$$\mathbf{B} = \begin{bmatrix} N_c \\ N_a + N_c \end{bmatrix} \qquad \text{(A50)}$$

Let $C_{|j-k|} = \langle \mathbf{V}_j \cdot \mathbf{V}_k \rangle$. Then eq A45 becomes

$$\langle R^2 \rangle = nC_0 + 2\sum_{j=1}^{n}(n - j)C_j \qquad \text{(A51)}$$

$$= n(C_0 + 2\sum_{j=1}^{n} C_j) - 2\sum_{j=1}^{n} jC_j \qquad \text{(A52)}$$

For sufficiently long chains, the upper limit on the sums in eq A52 can be set at ∞. Such a step is, of course, equivalent to neglecting the $2v_{n-1}$ term in eq A32. The following equations hold:

$$\sum_{j=1}^{\infty} \mathbf{T}^j = \mathbf{T} \cdot (\mathbf{1} - \mathbf{T})^{-1} = (2\epsilon)^{-1}\mathbf{T} \qquad \text{(A53)}$$

$$\sum_{j=1}^{\infty} j\mathbf{T}^j = \mathbf{T} \cdot (\mathbf{1} - \mathbf{T})^{-2} = (2\epsilon)^{-2}\mathbf{T} \qquad \text{(A54)}$$

where **1** represents the unit matrix of order 2. Combining all the above yields

$$\langle R^2 \rangle = n(N_a + N_c)(2x_a + x_a^{\ -1})/3 + N_c^{\ 2}/2 \qquad \text{(A55)}$$

where $x_a = N_a/(N_a + N_c)$. The factor $n\ (N_a + N_c)$ is equal to $\langle R^2 \rangle_{\text{melt}}$,[9] and so the first term in eq A55 yields eq 1. The second term represents the β' parameter of eq A44.

We are also able to compute an expression similar to eq A55 but in the presence of tilt of the lamellar chain stems. The leading order term is given elsewhere,[9] and we find that the parameter β' is equal to the crystalline stem length, not the lamellar thickness:

$$\beta' = l_c^{\ 2}/2 \qquad \text{(A56)}$$

The parameter α is a number on the order of the radius of gyration divided by the degree of polymerization and is therefore much smaller than $l_c^{\ 2}$. Therefore, we may write, using eq A42,

$$\beta = \beta'/2 = l_c^{\ 2}/4 \qquad \text{(A57)}$$

Registry No. Isotactic polystyrene, 25086-18-4; isotactic polypropylene, 25085-53-4; polyethylene, 9002-88-4; neutron, 12586-31-1.

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Mean Square Dipole Moment of Excluded Volume Polymers

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ABSTRACT: A first-order excluded volume perturbation expansion that includes finite-chain effects is derived for the mean square dipole moment of a polymer chain. In the long-chain limit the Nagai–Ishikawa–Doi expression $(\alpha_\mu^2 - 1)/(\alpha_r^2 - 1) = \langle \mu\cdot\mathbf{r}\rangle_0^2/\langle \mu^2\rangle_0\langle r^2\rangle_0$ is obtained. A finite-chain correction term proportional to $N^{-1/2}$ is also present. The discrepancy between Monte Carlo calculations and the Nagai–Ishikawa–Doi formula is attributed to this correction term. We also conclude that when $\langle \mu\cdot\mathbf{r}\rangle_0 = 0$, $\langle \mu^2\rangle$ exhibits a weak excluded volume effect, with α_μ tending to a constant not equal to 1.

Introduction

The mean square dipole moment of a polymer molecule in dilute solution is useful in polymer characterization, and so naturally its excluded volume behavior is of interest. For some time it has been accepted that the mean square dipole moment of any polymer for which $\langle \mathbf{r}\cdot\mu\rangle_0$ is zero, e.g., a polymer whose individual dipole moments lie perpendicular to the chain contour in the unperturbed state, would not exhibit excluded volume effects.[1-3] In 1971 Nagai and Ishikawa[4] derived the following equation:

$$\alpha_\mu^2 - 1 = [\langle \mathbf{r}\cdot\mu\rangle_0^2/\langle r^2\rangle_0\langle \mu^2\rangle_0](\alpha_r^2 - 1) \qquad (1)$$

Here $\mathbf{r}$ and μ represent the end-to-end vector and molecular dipole moment vector, respectively, $\langle\ \rangle$ and $\langle\ \rangle_0$ represent averages over perturbed and unperturbed chain ensembles, respectively, and $\alpha_\mu^2 = \langle \mu^2\rangle/\langle \mu^2\rangle_0$ and $\alpha_r^2 = \langle r^2\rangle/\langle r^2\rangle_0$ are the dipole moment and end-to-end vector expansion factors, respectively. Nagai and Ishikawa argued that the above equation holds at least through third order in the excluded volume perturbation expansion, and subsequently, Doi[5] argued that it holds to all orders. However, Mattice and Carpenter[6] reported Monte Carlo calculations of model polymers that violate eq 1. Mattice and coworkers[7] later argued that this discrepancy is due to a flaw in the Nagai–Ishikawa and Doi arguments, namely that the unperturbed bivariate distribution function $P(\mathbf{r},\mu)$ is non-Gaussian. In this paper we make a different assertion, namely that $P(\mathbf{r},\mu)$ is Gaussian, that eq 1 is correct in the long-chain limit, and that the discrepancy between the Monte Carlo results[6,7] and eq 1 is the result of finite-chain corrections to eq 1.

Since eq 1 holds in the long-chain limit, we conclude that $\langle r^2\rangle$ and $\langle \mu^2\rangle$ exhibit the same scaling behavior for large N whenever $\langle \mathbf{r}\cdot\mu\rangle \neq 0$. However, when $\langle \mathbf{r}\cdot\mu\rangle_0 = 0$, eq 1 does not require $\alpha_\mu = 1$ at large N since α_r diverges. The first-order perturbation expansion developed here indicates that $\alpha_\mu \neq 1$ even though $\langle \mathbf{r}\cdot\mu\rangle_0 = 0$, implying a weak excluded volume effect even when $\langle \mathbf{r}\cdot\mu\rangle_0 = 0$.

Mean Value Theorem

The mean value theorem assures that the end-to-end vector of a flexible polymer chain obeys Gaussian statistics. This theorem follows from the convolution integral

$$P(\mathbf{r},N) = \int d\mathbf{r}'\, P(\mathbf{r}',j)P(\mathbf{r}-\mathbf{r}',N-j) \qquad (2)$$

where $P(\mathbf{r},\mathrm{N})$ represents the distribution function of the end-to-end vector, $\mathbf{r}$, of an unperturbed chain of length N.[8] Equation 2 is a result of chain flexibility, expressing the fact that the chain is equivalent to two shorter chains joined through a flexible link. However, an analogous convolution integral can be written for the bivariate distribution function of $\mathbf{r}$ and μ, and it must follow that $P(\mathbf{r},\mu)$ is Gaussian in the long-chain limit. The most general form of $P(\mathbf{r},\mu)$ is[4]

$$P(\mathbf{r},\mu) = (3/2\pi)^3 D^{-3/2} \exp(-3Q/2D) \qquad (3a)$$

where

$$Q = \langle r^2\rangle_0\mu^2 - 2\langle \mathbf{r}\cdot\mu\rangle_0\mathbf{r}\cdot\mu + \langle \mu^2\rangle_0 r^2 \qquad (3b)$$

and

$$D = \langle r^2\rangle_0\langle \mu^2\rangle_0 - \langle \mathbf{r}\cdot\mu\rangle_0^2 \qquad (3c)$$

It follows from eq 3 that the distribution function of μ for an unperturbed ring polymer (obtained by setting $\mathbf{r} = 0$ in eq 3 and renormalizing) is also Gaussian with characteristic ratio, $C_\mu^{(\mathrm{ring})} = \langle \mu^2\rangle_0^{(\mathrm{ring})}/N$, given by

$$C_\mu^{(\mathrm{ring})} = C_\mu^{(\mathrm{linear})} - \langle \mathbf{r}\cdot\mu\rangle_0^2/N\langle r^2\rangle_0 \qquad (4)$$

where $C_\mu^{(\mathrm{linear})}$ is the characteristic ratio of the linear chain, N is the number of bonds in either the ring or linear chain, and the averages shown in the right-most term are taken over a linear chain of length N. All the quantities appearing on the right side of eq 4 can be easily calculated by the usual matrix techniques for unperturbed model polymers,[9,10] so that $C_\mu^{(\mathrm{ring})}$ is calculable. This result will be used below.

Non-Gaussian Contributions to $\langle r^2\rangle_0$ and $\langle \mu^2\rangle_0$

For all but the shortest linear chains,[11] the following equations hold:

$$\langle r^2\rangle_0 = NC_r + D_r \qquad (5a)$$

$$\langle \mu^2\rangle_0 = NC_\mu^{(\mathrm{linear})} + D_\mu^{(\mathrm{linear})} \qquad (5b)$$

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