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Measurement of the Flory–Huggins Interaction Parameter between Unlike Polymers via Solution Light Scattering near the "Optical Θ" State

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ABSTRACT: The "optical Θ" technique proposed by Inagaki et al. for the measurement of the polymer–polymer interaction parameter via ternary solution light scattering was critically examined. A modification of their method through a combination of Flory–Krigbaum theory and Yamakawa theory was developed so that the technique can be applied to both symmetric and moderately asymmetric ternary systems. From the light scattering results of Inagaki et al., the Flory–Huggins interaction parameter between polystyrene and poly(methyl methacrylate) was determined to be 0.009 ± 0.001 at 30 °C.

I. Introduction

Over 30 years ago, Stockmayer and Stanley[1] measured the Flory–Huggins (F–H) interaction parameter between polystyrene (PS) and poly(methyl methacrylate) (PMMA) via a ternary (PS/PMMA/butanone) solution light scattering technique. The main difficulty of their method is that generally the contribution of solvent–polymer interactions to the second virial coefficient of the ternary solution is overwhelmingly larger than that of the polymer–polymer interaction, thus rendering the obtained polymer–polymer interaction parameter poor in accuracy. Another inadequacy of the method, as pointed out by Krigbaum and Flory,[2] lies in its mean-field or lattice-model theoretical frame,[3] which disregards totally the excluded volume effect. Recently, Inagaki et al.[4,5] devised an intriguing modification to the technique. Under the so-called "optical Θ" state achieved by using a solvent with refractive index intermediate to those of the polymers and carefully selecting operation conditions such as temperature, blend composition, and polymer molecular weights, the scattering components resulting from solvent–polymer interactions "exactly" cancel each other according to Stockmayer's theoretical scheme; thus the second virial coefficient becomes (presumably) proportional to the polymer–polymer interaction parameter and a better accuracy is realized. However, the excluded volume effect was still not considered during their theoretical development. Rather, the correction for the excluded volume effect was done after the preliminary values (based on Stockmayer's mean-field theoretical frame) of the polymer–polymer interaction parameter at different blend compositions and polymer molecular weights were obtained. The "symmetry" of the polymers used (PS and PMMA) with respect to the solvent (bromobenzene), i.e., the component polymers were not strongly interacting with each other and had similar expansion factors, chain lengths, and solvent–polymer interaction parameters, allowed the excluded volume effect to be taken into account by applying *binary* polymer solution theories. This ad hoc correction of excluded volume effect, although maybe in principle justifiable for their specific ternary system, imposes a severe constraint on the application of the technique due to the simultaneous requirements of "symmetry" and the "optical Θ" condition.

It is the attempt of this paper to examine more closely and then extend this "optical Θ" technique to less symmetric ternary systems by introducing corrections for excluded volume effect from the beginning of the theoretical development.

II. Theory

Assuming the segmental distribution of polymer chains to be Gaussian, Krigbaum and Flory[2] introduced the excluded volume effect into the classical mean-field frame and reached, for a dilute ternary solution of two monodisperse polymers (subscripts 1 and 2) in a solvent (subscript 0)

$$K^*c/R_0 = A_1 + 2A_2c \tag{1}$$

$$A_1 = (\xi_1^2 y_1 M_1 + \xi_2^2 y_2 M_2)^{-1} \tag{2}$$

$$A_2 = [\mu_1^2(1/2 - \chi_{01})F(X_{11}) + \mu_2^2(1/2 - \chi_{02})F(X_{22}) + \mu_1\mu_2(1 - \chi_{01} - \chi_{02} + \chi_{12})F(X_{12})]/V_0 \tag{3}$$

with

$$\mu_i = A_1 \xi_i y_i M_i v_i \tag{4}$$

$$X_{ij} = \left(\frac{3}{2\pi}\right)^{3/2} (\langle s^2\rangle_i + \langle s^2\rangle_j)^{-3/2} (1 - \chi_{0i} - \chi_{0j} + \chi_{ij}) M_i M_j v_i v_j (V_0 N_A)^{-1} \tag{5}$$

and

$$F(X_{ij}) = \frac{8}{3\pi^{1/2}} \int_0^\infty t^4 \exp[-t^2 - X_{ij}\exp(-t^2)]\,\mathrm{d}t \tag{6}$$

where K^* is the light scattering constant exclusive of the refractive index increment factor, R_0 is the reduced Rayleigh ratio at zero angle, c is the total concentration of polymers, V_0 is the molar volume of the solvent, N_A is the Avogadro number, χ_{ij} is the segmental F–H interaction parameter between species i and j, y_i is the weight fraction of polymer i in the blend, and ξ_i, $\langle s^2\rangle_i$, v_i, and M_i are the refractive index increment, mean-square radius of gyration in the solution, specific volume at liquid state, and molecular weight of polymer i, respectively. Imposing the proposed condition for the "optical Θ" state[5], i.e.

$$-\xi_1 y_1 M_1 v_1 = \xi_2 y_2 M_2 v_2 \tag{7}$$

or, equivalently

$$-\mu_1 = \mu_2 = \mu \tag{8}$$

we reached

$$K^* V_0 \phi / R_0 = A_{1\phi} + 2A_{2\phi}\phi \tag{9}$$

$$A_{1\phi} = \phi/(\psi_1^2 m_1 \phi_1 + \psi_2^2 m_2 \phi_2) \tag{10}$$

$$A_{2\phi} = \mu^2[(1/2 - \chi_{01})F_{11} + (1/2 - \chi_{02})F_{22} - (1 - \chi_{01} - \chi_{02} + \chi_{12})F_{12}] \tag{11}$$

with

$$\phi_i = w_i v_i / (w_0 v_0 + w_1 v_1 + w_2 v_2) \tag{12}$$

$$\phi = \phi_1 + \phi_2 \tag{13}$$

$$m_i = M_i v_i / V_0 \tag{14}$$

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$$\psi_i = \partial n / \partial \phi_i = \xi_i / v_i \qquad (15)$$

and

$$F_{ij} = F(X_{ij}) \qquad (16)$$

where w_i is the weight fraction of component i in the ternary solution.

Equations 9 and 10 are of the same form as those obtained by Inagaki et al.[5] The expression they had for $A_{2\phi}$ was, however

$$A_{2\phi} = -\mu^2 \chi_{12} \qquad (17)$$

which is true only when, as seen from eq 11

$$F_{11} = F_{22} = F_{12} = 1 \qquad (18)$$

Note also that their ad hoc correction scheme bore inherently the assumption

$$F_{11} = F_{22} = F_{12} = F \qquad (19)$$

so that

$$A_{2\phi} = -\mu^2 \chi_{12} F \qquad (20)$$

thus a correction using binary polymer solution theories to estimate F could proceed. Furthermore, eq 11 delineates the fact that, as long as eq 19 is not obeyed, the polymer–solvent interactions may still contribute to the second virial coefficient although eq 7 is satisfied. Accordingly, the criterion for the "optical Θ" condition should be, instead of eq 7

$$\mu_1^2(\tfrac{1}{2} - \chi_{01})F_{11} + \mu_2^2(\tfrac{1}{2} - \chi_{02})F_{22} + \mu_1\mu_2(1 - \chi_{01} - \chi_{02})F_{12} = 0 \qquad (21)$$

Thus, it is clear that the selection of experimental condition by eq 7 serves only as a first approximation to the nullification of interference from solvent–polymer interactions, and the calculation of χ_{12} should be carried out by way of eq 11 instead of eq 20 since a slight deviation from the true "optical Θ" state may sometimes allow a considerable contribution from solvent–polymer interactions to the second virial coefficient, thus rendering the latter route inappropriate, especially when χ_{12} is very small.

Although the Flory–Krigbaum (F–K) theory is considered qualitatively correct[6] and is selected as the basis of the theoretical discussion above since it has F–H interaction parameters conveniently built in its frame and has readily been developed to ternary systems, it suffers the disadvantage that the function defined by eq 6 agrees quantitatively with experimental data only when X_{ij} is small (say, $X_{ij} < 0.2$),[7] i.e., when the excluded volume effect is not very important. Yamakawa et al.[8-11] developed a binary dilute solution theory that described more closely the behavior of the second virial coefficient. Summarized as follows are the results of their first-order perturbation theory:

$$\alpha_b^2 = 0.541 + 0.459(1 + 5.62z)^{0.46} \qquad (22)$$

$$\alpha^2 = 0.541 + 0.459(1 + 6.04z)^{0.46} \qquad (23)$$

$$\Psi(\bar{z}) = 0.783(\alpha_b/\alpha)^3[1 - (1 + 4.454\bar{z})^{-0.2867}] \qquad (24)$$

with

$$z = (4\langle s^2 \rangle_0)^{-3/2} \beta n^2 \qquad (25)$$

and

$$\bar{z} = z / \alpha_b^3 \qquad (26)$$

where α is the expansion factor of a solitary chain, α_b is the expansion factor of a chain in contact with another and is somewhat smaller than α, $\langle s^2 \rangle_0$ is the mean-square radius of gyration of the chain in its unperturbed state, β is the binary-cluster integral of a pair of segments, and n is the number of segments in a chain. With α experimentally accessible, z can be calculated from eq 23, α_b from eq 22, $\bar{z}$ from eq 26, and $\Psi(\bar{z})$ from eq 24.

Comparison between the Yamakawa and F–K theories shows (see Appendix) that

$$F_{ii} = [\Psi(\bar{z})/\bar{z}]_i \qquad (27)$$

It is thus a logical choice to evaluate F_{ii} from eq 27 instead of eq 5 and 6. As for F_{12}, since the Yamakawa theory has not been extended to ternary systems yet, we chose quite arbitrarily to take, when $\bar{z}_1$ and $\bar{z}_2$ are not too far apart

$$F_{12} = [\Psi(\bar{z})/\bar{z}]_{\bar{z}=(\bar{z}_1\bar{z}_2)^{1/2}} \qquad (28)$$

with the assumption that the polymer–polymer interactions are comparatively very weak so that the dimensions of chains are not significantly different from those in binary solutions. Note that Inagaki et al., based on a puzzling qualitative argument, suggested[5]

$$F = [\partial \Psi(\bar{z})/\partial \bar{z}]_{\bar{z}=(\bar{z}_1\bar{z}_2)^{1/2}} \qquad (29)$$

instead of eq 28 for the correction of the excluded volume effect.

III. Calculations

1. Molecular Characteristics of PS and PMMA Samples in Bromobenzene: Binary Solutions. The values of the F–H interaction parameters between polymers and the solvent were not needed in Inagaki's approach. In the present modification, however, we must have these values with reasonable accuracy. Fortunately, some experimental clues about the related second virial coefficients, in addition to values of molecular weights, molecular weight distributions, and z-average radii of gyration $\langle s^2 \rangle_z^{1/2}$ of the polymer samples were given in ref 5 and thus allow the calculation of polymer–solvent interaction parameters.

The reported values of $\langle s^2 \rangle_z^{1/2}$ were converted to $\langle s^2 \rangle_w^{1/2}$ by assuming the molecular weight distribution of the samples to be of the Shultz–Flory type,[12] i.e.

$$M_w/M_n = (1 + k)/k \qquad (30)$$

$$M_z/M_w = (2 + k)/(1 + k) \qquad (31)$$

where k is a parameter related to polydispersity. To estimate $\langle s^2 \rangle_w^{1/2}$ values for samples lacking experimental data, it is further assumed that

$$\langle s^2 \rangle_w^{1/2} \sim M_w^{\nu} \qquad (32)$$

and

$$\langle s^2 \rangle_z^{1/2} \sim M_z^{\nu} \qquad (33)$$

Linear regression analyses yielded

$$\langle s^2 \rangle_w^{1/2} = 0.1496 M_w^{0.574}\ \text{Å} \quad \text{(for PS)} \qquad (34)$$

and

$$\langle s^2 \rangle_w^{1/2} = 0.1497 M_w^{0.566}\ \text{Å} \quad \text{(for PMMA)} \qquad (35)$$

As pointed out long ago by Flory and rephrased more recently by scaling theory,[13] ν should be 0.5 for a Θ solvent and 0.6 for good solvents. Since bromobenzene is not really a very good solvent for both PS and PMMA as judged from the solvent–polymer interaction parameters (Table I) and actually only two or three experimental points for each polymer were available, the correlations obtained are considered in satisfactory agreement with the theoretical

Table I
Molecular Characteristics of Polymer Samples[a]

sample	$M_w \times 10^{-4}$	M_w/M_n[b]	$A_2 \times 10^4$, mol mL/g^2	$\langle s^2 \rangle_z^{1/2}$, Å	$\langle s^2 \rangle_w^{1/2}$,[d] Å	α_w^2[d]	χ_{0i}
			Polystyrene				
PC200	242	1.30	2.05	770	683	2.23	0.4242
F80	80.6, 77.5[c]	1.01	2.71	370	368	1.94	0.4126
57H	32.4, 32.2[b]	1.02	3.45	218	216	1.67	0.4058
49H	28.3[b]	1.10	3.56[d]		201	1.66	0.4033
39H	2.45[c]	1.27	6.69[d]		49.4	1.14	0.3932
			Poly(methyl methacrylate)				
75M	219, 214[c]	1.35	1.57	660	579	2.40	0.4184
78M	62.5, 62.7[c]	1.45	2.33	334	287	2.06	0.3952
31M	20.2, 21.1[c]	1.27	2.89		151	1.75	0.3906
91M	2.45[b]	1.04	5.17[d]		45.8	1.35	0.3590

[a] In bromobenzene at 30 °C unless indicated otherwise. [b] GPC values. [c] In butanone at 30 °C. [d] Estimated as described in the text.

prediction. From the values of $\langle s^2 \rangle_w^{1/2}$ obtained as described above, values of the weight-average expansion coefficient, defined as

$$\alpha_w = (\langle s^2 \rangle_w / \langle s^2 \rangle_{w,0})^{1/2} \tag{36}$$

with[5]

$$\langle s^2 \rangle_{w,0}^{1/2} = 0.294 M_w^{0.5} \text{ Å} \quad \text{(for PS)} \tag{37}$$

$$\langle s^2 \rangle_{w,0}^{1/2} = 0.253 M_w^{0.5} \text{ Å} \quad \text{(for PMMA)} \tag{38}$$

were then calculated.

The second virial coefficients of some of the polymer samples were estimated, based on the available values of other samples, by assuming

$$A_2 \sim M_w^{-\gamma} \tag{39}$$

Routine linear regression analyses yielded

$$A_2 = 9.068 \times 10^{-3} M_w^{-0.258} \text{ mL mol/g}^2 \text{ (for PS)} \tag{40}$$

and

$$A_2 = 7.206 \times 10^{-3} M_w^{-0.261} \text{ mL mol/g}^2 \text{ (for PMMA)} \tag{41}$$

On the basis of Flory's suggestion[14] that, at the dilute limit, a chain in a good solvent behaves like a hard sphere, it has been suggested that[13]

$$A_2 \sim \langle s^2 \rangle^{3/2} M^{-2} \tag{42}$$

Combination of eq 42 and 32 yields

$$\gamma = 2 - 3\nu \tag{43}$$

Following eq 43, the predicted values for γ_{PS} and γ_{PMMA} are 0.278 and 0.301, respectively. The agreement between these values and the regression results given in eq 40 and 41 is not too bad considering only three second virial coefficient data were available for each homologue series and each value of ν was also based on essentially only two or three data points, not to mention the fact that bromobenzene is only a fair solvent for the polymers. A further justification in using eq 39 can be found through a compilation of light scattering data[5,15-19] of more or less narrowly distributed polymers in various solvents. As shown by Figure 1, eq 39 is fairly well obeyed except for PS in butanone at 25 °C,[17] for which the point corresponding to the lowest molecular weight sample is somewhat doubtful as compared to the more elaborate data of Outer et al.[15] for the same system at 22 °C. If that point is discarded, the correlation of eq 39 sustains.

Listed in Table I are the characteristics of the binary solutions, including the solvent–polymer interaction parameters calculated from

$$\chi_{0i} = \tfrac{1}{2} - A_{2,i} V_0 \bar{z} v_i^{-2} [\Psi(\bar{z})]^{-1} \tag{44}$$

where $A_{2,i}$ is the second virial coefficient obtained from a routine Zimm plot for binary solutions. It is noted that the estimated $\langle s^2 \rangle_w^{1/2}$ and α_w^2 values are somewhat different from those of Inagaki et al.[5] Since they did not describe explicitly their method of estimation, we are not able to comment on the differences except that the calculated χ_{12} values were not greatly altered as shown later.

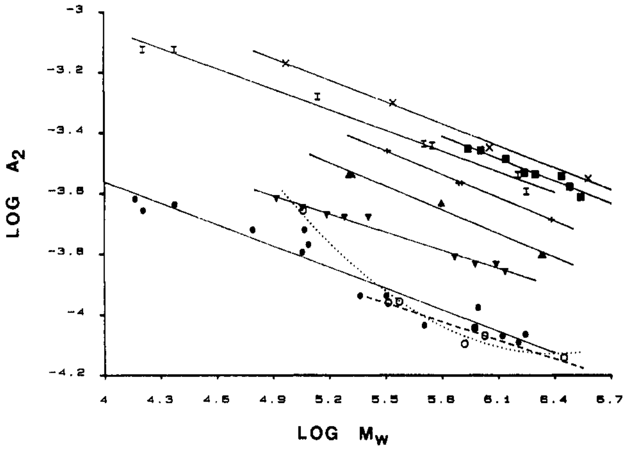

Figure 1. Dependence of second virial coefficient A_2 (mol mL/g^2) on molecular weight for some polymers of relatively narrow molecular weight distributions in various solvents. Solid lines are the least-squares correlations. The dotted line is the third-order polynomial fit of the data of Oth and Desreux,[17] while the dashed line is the least-squares correlation when the point corresponding to their lowest molecular weight sample is disregarded. The values of γ range from 0.20 to 0.26 in these binary solutions: (○) PS in butanone at 22 °C, ref 15; (I) PS in methylene chloride at 22 °C, ref 15; (●) PS in butanone at 25 °C, ref 17; (×) PS in toluene at 30 °C, ref 19; (+) PS in bromobenzene at 30 °C, ref 5; (▼) PMMA in acetone at 25 °C, ref 16; (▲) PMMA in bromobenzene at 30 °C, ref 5; (■) poly(vinyl acetate) in butanone at 25 °C, ref 18.

2. Calculation of χ_{12}: Ternary Solutions. To facilitate the comparison between the present approach and the one of Inagaki,[5] three methods were used to calculate χ_{12}.

Method 1. Following Inagaki's suggestion

$$\chi_{12} = \chi_{12,\text{app}} / [\partial \Psi(\bar{z}) / \partial \bar{z}]_{\bar{z} = (\bar{z}_1 \bar{z}_2)^{1/2}} \tag{45}$$

where $\chi_{12,\text{app}}$ is the F–H interaction parameter obtained without considering the excluded volume effect.

Method 2. Following Inagaki's inherent assumption of eq 19 and, as discussed in Theory, with

$$F = [\Psi(\bar{z}) / \bar{z}]_{\bar{z} = (\bar{z}_1 \bar{z}_2)^{1/2}} \tag{46}$$

then

$$\chi_{12} = \chi_{12,\text{app}} / [\Psi(\bar{z}) / \bar{z}]_{\bar{z} = (\bar{z}_1 \bar{z}_2)^{1/2}} \tag{47}$$

Table II
Light Scattering Results for PS/PMMA/Bromobenzene Ternary Solutions at 30 °C

blend				χ_{12}			
PS	PMMA	y_{PS}	$\chi_{12,\mathrm{app}}$	Inagaki et al.	method 1	method 2	method 3
PC200	75M	0.455	0.0026	0.024	0.021	0.0082	0.0083
F80	78M	0.427	0.0030	0.022	0.019	0.0082	0.0076
49H	31M	0.407	0.0040	0.021	0.019	0.0092	0.0088
39H	91M	0.479	0.0117	0.031	0.024	0.0172	0.0104
			0.007 ± 0.004	0.026 ± 0.005	0.022 ± 0.003	0.013 ± 0.005	0.009 ± 0.001

Method 3. Recover $A_{2\phi}$ from $\chi_{12,\mathrm{app}}$ (see eq 17) and then calculate χ_{12} from eq 11 with

$$F_{ij} = [\Psi(\bar{z})/\bar{z}]_{\bar{z}=(\bar{z}_1\bar{z}_2)^{1/2}} \qquad (48)$$

Values of χ_{12} obtained by these methods are listed in Table II.

IV. Results and Discussion

From Table II, it can be immediately observed that method 1 yielded χ_{12} values similar to those of Inagaki et al.[5] but significantly different from the values obtained by the other two methods. This confirms, first, our earlier statement that slight differences in estimated values of α_w^2 do not affect the result much and, second, our speculation on the validity of eq 45. The argument of Inagaki et al. in reaching eq 45, examined more closely, was actually based on the assumption of very small values of χ_{12}, $\chi_{12,\mathrm{app}}$, $\bar{z}$, and $\Psi(\bar{z})$. The requirement for small $\bar{z}$ and $\Psi(\bar{z})$ is certainly not satisfied in the present ternary system.

It also can be noted that, for the three higher molecular weight pairs, methods 2 and 3 yielded essentially the same χ_{12} value, as these pairs are rather symmetric. For the pair with the lowest molecular weights, the symmetry is relatively poor as observed from Table I, and method 2 yielded a value of χ_{12} significantly larger than that obtained by method 3. Although the χ_{12} value calculated from method 3 for this pair is still somewhat larger than values obtained for the first three pairs, the agreement between them is judged good considering the estimations of $\langle s^2\rangle_w^{1/2}$ and A_2 involved.

It has been reported[20] that, at ambient temperature, monodisperse PS samples with $M \geq 9600$ were incompatible with high molecular weight ($M_v \geq 10^6$) PMMA samples, while lower molecular weight ($M \leq 3100$) PS samples could be compatible with the PMMA samples within limited composition ranges. Thus, the mixture of a high molecular weight PMMA and PS that have a critical temperature around ambient conditions should correspond to a PS molecular weight between 3100 and 9600. On the basis of F-H theory[21] that

$$\chi_{12,c} = (m_1^{-1/2} + m_2^{-1/2})^2/2 \qquad (49)$$

and with the assumption of negligible molecular weight dependence of χ_{12}, we estimated, around ambient temperature, $0.007 < \chi_{12} < 0.021$, which seems to agree well with the result of our calculations, i.e., $\chi_{12} = 0.009 \pm 0.001$, compared to that obtained by Inagaki et al., $\chi_{12} = 0.026 \pm 0.005$ (or by us using their method (method 1) $\chi_{12} = 0.022 \pm 0.003$). Another independent estimation, based on compatibility measurements[22] on PS/PMMA/benzene solution at room temperature and Scott's theory,[23] was cited by Stockmayer and Stanley.[1] Their estimation corresponds to, when taking the lattice volume to be that of a bromobenzene molecule, $0.009 < \chi_{12} < 0.018$, which is in good agreement with the estimation above.

As a final remark, we would like to point out that the main deficiency of the present modification lies in the estimation of F_{12} by eq 28, which limits the application of the technique to, at most, moderately asymmetric polymer pairs. An adequate ternary dilute solution theory is needed to extend the applicability of this "optical Θ" technique to badly asymmetric systems.

V. Conclusion

The "optical Θ" technique proposed by Inagaki et al. for the measurement of the polymer–polymer interaction parameter via ternary solution light scattering is critically examined. Modification of their method through a combination of F–K theory and Yamakawa theory shows that the criterion Inagaki et al. proposed for "optical Θ" state is applicable only to symmetric systems and, in general, should be considered only as a first approximation to the true "optical Θ" state and that their method of correcting excluded volume effect is applicable to symmetric systems but the correction factor should be $[\Psi(\bar{z})/\bar{z}]_{\bar{z}=(\bar{z}_{12})^{1/2}}$ instead of, as they suggested, $[\partial\Psi(\bar{z})/\partial\bar{z}]_{\bar{z}=(\bar{z}_1\bar{z}_2)^{1/2}}$.

The present modification seems to be able to give reasonable results for both symmetric and moderately asymmetric polymer pairs. The interaction parameter between PS and PMMA at 30 °C, determined by this modified approach, is 0.009 ± 0.001, in good agreement with estimations based on independent experimental compatibility studies. As for the extension of the "optical Θ" technique to general asymmetric systems, an adequate ternary dilute solutions theory is in need.

Appendix: Derivation of Eq 27

For the sake of easy comparison, some of the following equations were taken from a single source[11] and italic equation numbers correspond to the numbering system there.

The second virial coefficient of a binary polymer solution can be expressed as

$$A_2 = 4\pi^{3/2}\langle s^2\rangle^{3/2}M^{-2}\Psi(\bar{z}) \qquad (\mathit{21.17})$$

or

$$A_2 = (n^2\beta/2M^2)h_0(z) \qquad (\mathit{20.19})$$

where

$$\Psi(\bar{z}) = \bar{z}h_0(z) \qquad (\mathit{21.18})$$

If the molar segmental volume is taken to be the molar volume of the solvent, we can write

$$n = vM/V_0 \qquad (\mathrm{A1})$$

and, from eq *20.46*

$$\beta = 2V_0(0.5 - \chi) \qquad (\mathrm{A2})$$

Substitution of eq A1 and A2 into eq *20.19* yields

$$A_2 = (v^2/V_0)(0.5 - \chi)h_0(z) \qquad (\mathrm{A3})$$

while the F–K theory[14] gives

$$A_2 = (v^2/V_0)(0.5 - \chi)F(X) \qquad (\mathrm{A4})$$

Thus, by comparison between eq A3 and A4 and the application of eq *21.18*

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

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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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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