Since $j_n(-z) = (-1)^n j_n(z)$, the first term in [...] in eq A1 is even for both s and s', whereas the second term is odd for both s and s'. Let us define

$$U^{e}(s,s',\xi,\tau) = \tfrac{1}{2}[U(s,s',\xi,\tau) + U(s,-s',\xi,\tau)]$$

$$U^{o}(s,s',\xi,\tau) = \tfrac{1}{2}[U(s,s',\xi,\tau) - U(s,-s',\xi,\tau)]$$

Since $Q(m,-s) = (-1)^m Q(m,s)$ and hence $U(-s,-s',\xi,\tau) = U(s,s',\xi,\tau)$, U^e and U^o are even and odd for both s and s', respectively. Then, from eq 4 and A1, we have for a weakly bending rod

$$G^1(\tau) = G_D(\tau)(4/L^2)\int\int_0^{L/2} \mathrm{d}s\, \mathrm{d}s' \int_0^1 \mathrm{d}\xi\, [U^e(s,s',\xi,\tau) \times \cos(Ks\xi) \sum_{\text{even } n} g_n{}^{e}(s',\xi,\tau) + U^o(s,s',\xi,\tau) \sin(Ks\xi) \sum_{\text{odd } n} g_n{}^{o}(s',\xi,\tau)] \qquad \text{(A2)}$$

For a rigid rod, we have $\langle \mathbf{q}_m{}^2 \rangle = 0$ and hence $\Phi_0 = 0$. By use of

$$\tfrac{1}{2}\int_{-1}^{1} P_n(\xi) \exp(iKs\xi)\, \mathrm{d}\xi = i^n j_n(Ks)$$

we have from eq 4 and 6

$$G^1(\tau) = G_D(\tau) \sum_{\text{even } n,l}\sum (2l+1)(i)^{n+l} \mathbf{W}_{nl}(\tau) b_n(k) b_l(k) \qquad \text{(A3)}$$

where for $k = KL/2$

$$b_n(k) = (1/k)\int_0^k j_n(z)\, \mathrm{d}z \qquad \text{(even } n\text{)}$$

$$b_n(k) = 0 \qquad \text{(odd } n\text{)} \qquad \text{(A4)}$$

Equation A2 was used for $0.5 \geq \gamma L \geq 1 \times 10^{-3}$ and eq A3 for $1 \times 10^{-3} > \gamma L \geq 0$.

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Determination of the Flory Interaction Parameters in Miscible Polymer Blends by Measurement of the Apparent Radius of Gyration

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Received March 27, 1985

ABSTRACT: It is shown that measurement by small-angle neutron scattering of the apparent radius of gyration of a blend of two polymers having sufficient scattering contrast allows determination of the interaction parameter χ with good precision. The influence of the polydispersity of the blend components has been examined. An implementation of this method is presented with poly(dimethylsiloxane) (H and D), for which χ is far from negligible ($\chi = 1.7 \times 10^{-3}$).

The interaction parameter χ in a polymer mixture is related to the thermodynamical interaction between chains of different natures. The traditional methods used for its determination have been therefore of a thermodynamical nature: cloud point determination, heat of mixing, or zero-angle scattering. In all these approaches the Flory–Huggins expression for the free energy of mixing has been

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0024-9297/85/2218-2437$01.50/0

used as the simplest thermodynamical model for a polymer mixture. If one uses the random-phase approximation technique as introduced by de Gennes,[1] one obtains an expression for the scattered intensity $S(q)$ by a polymer blend at any angle, which depends on χ. In fact, it is a generalization of the Flory–Huggins model, and at a zero scattering angle, i.e., for thermodynamic quantities, the results of the de Gennes and Flory–Huggins theories are identical. This gives the possibility of measuring χ for any value of the scattering vector q.[2]

We show in this paper that the measurement of the apparent radius of gyration by small-angle neutron scattering or X-rays gives a convenient and accurate method for measuring the interaction parameter χ, even on polydisperse systems.

Theory

Let us assume that we have a blend of two polymers A and B having respectively n_A and n_B segments, all occupying the same volume V, regardless of their type. If the number of chains per unit volume is N_A and N_B in each component, by definition we have

$$N_An_A + N_Bn_B = N$$

where N is the total number of monomer units. The intensity $NS(q)$ scattered by such system at a given scattering vector q ($q = (4\pi/\lambda)\sin(\theta/2)$ where λ is the wavelength and θ is the scattering angle) can be written according to de Gennes[1] as

$$\frac{K}{NS(q)} = \frac{1}{S_A(q)} + \frac{1}{S_B(q)} - 2\chi \qquad (1)$$

where K is a constant depending on the difference between the square of the coherent scattering lengths of the two species as well as on the experimental working conditions and χ is the Flory interaction parameter. In this formula, $S(q)$ is the experimental scattered intensity and $S_A(q)$ is given by[3]

$$S_A(q) = (N_A/N)n_A^2P_A(qR_A)$$

where $P_A(qR_A)$ is the structure factor of a chain of type A ($P_A(0) = 1$). The same definition stands for $P_B(qR_B)$. In the case where segments A and B differ by their volume V, eq 1 can be generalized as detailed in the Appendix.

The generalization to polydisperse systems consists of modifying the expression of S_A and S_B in eq 1 according to

$$S_A(q) = \frac{\sum N_{i,A}n_{i,A}^2}{N}P_{i,A}(qR_{i,A})$$

and replacing the normalization conditions by

$$\sum N_{i,A}n_{i,A} + \sum N_{i,B}n_{i,B} = N$$

The expression of $S_A(q)$ and $S_B(q)$ can be written in a more compact way, particularly in the small-q region, by introducing the following notations. We define the weight-average degree of polymerization by the relation

$$n_{w,\alpha} = \frac{\sum_i N_{i,\alpha}n_{i,\alpha}^2}{\sum_i N_{i,\alpha}n_{i,\alpha}} \qquad \text{with } \alpha = \text{A or B}$$

and the "z-average" radius of gyration by

$$\langle R_{z,\alpha}^2\rangle = \frac{\sum_i N_{i,\alpha}n_{i,\alpha}^2R_{i,\alpha}^2}{\sum_i N_{i,\alpha}n_{i,\alpha}^2}$$

and introduce the number fraction of species A

$$\phi_A = \frac{\sum_i N_{i,A}n_{i,A}}{\sum N_{i,A}n_{i,A} + \sum N_{i,B}n_{i,B}}$$

Then in the limit of small q, we find

$$S_A(q) \simeq n_{w,A}\phi_A(1 - q^2R_{z,A}^2/3)$$

$$S_B(q) \simeq n_{w,B}(1 - \phi_A)(1 - q^2R_{z,B}^2/3)$$

In order to further simplify the results, we introduce an average molecular weight $\bar{n}_w$ and an heterogeneity parameter u defined by the equations

$$n_{w,A} + n_{w,B} = 2\bar{n}_w$$

$$n_{w,A} - n_{w,B} = 2\bar{n}_wu$$

leading to

$$n_{w,A} = \bar{n}_w(1 + u)$$

$$n_{w,B} = \bar{n}_w(1 - u)$$

In a similar way one defines R_z and v such that

$$\langle R_{z,A}^2\rangle = \langle R_z^2\rangle(1 + v)$$

$$\langle R_{z,B}^2\rangle = \langle R_z^2\rangle(1 - v)$$

The relation between the heterogeneity parameters u and v depends on the mass distribution of polymers A and B. If we identify the component with the larger molecular weight as "A" so that $n_{wA} > n_{wB}$, then the parameter u is positive by definition but v can have any sign. This can be shown in the case of Gaussian statistics, for which v can be written as

$$v = \frac{n_{z,A} - n_{z,B}}{n_{z,A} + n_{z,B}}$$

If the polydispersity of A and B is the same, $u = v$. If on the other hand, the polydispersities are very different, $n_{z,B}$ can, for instance, be larger than $n_{z,A}$, which makes u and v of opposite sign.

With these notations S_A and S_B can be written as

$$S_A(q) = \bar{n}_w(1 + u)\phi_A\left[1 - q^2\frac{\langle R_z^2\rangle}{3}(1 + v)\right]$$

$$S_B(q) = \bar{n}_w(1 - u)(1 - \phi_A)\left[1 - \frac{q^2\langle R_z^2\rangle}{3}(1 - v)\right]$$

We now introduce the mean square "apparent radius of gyration" $\langle R_{ap}^2\rangle$ for the whole system with two components by

$$S(q) = S(0)\left[1 - q^2\frac{\langle R_{ap}^2\rangle}{3}\right] \qquad (2)$$

where $S(0)$ is the intensity scattered at $q = 0$. From eq 1 we find

$$\frac{\bar{n}_w}{S(0)} \propto \frac{1}{\phi_A(1 + u)} + \frac{1}{(1 - \phi_A)(1 - u)} - 2\chi\bar{n}_w \qquad (3)$$

$$\langle R_{ap}^2\rangle = \langle R_z^2\rangle\left[\frac{1 + v}{\phi_A(1 + u)} + \frac{1 - v}{(1 - \phi_A)(1 - u)}\right]\bigg/\frac{\bar{n}_w}{S(0)} \qquad (4)$$

or in a form more suitable for the calculations

$$\langle R_{ap}^2\rangle = \langle R_z^2\rangle\frac{(1 - u)(1 + v) + 2\phi_A(u - v)}{1 + u(2\phi_A - 1) - 2\bar{n}_w(1 - u^2)\phi_A(1 - \phi_A)\chi} \qquad (5)$$

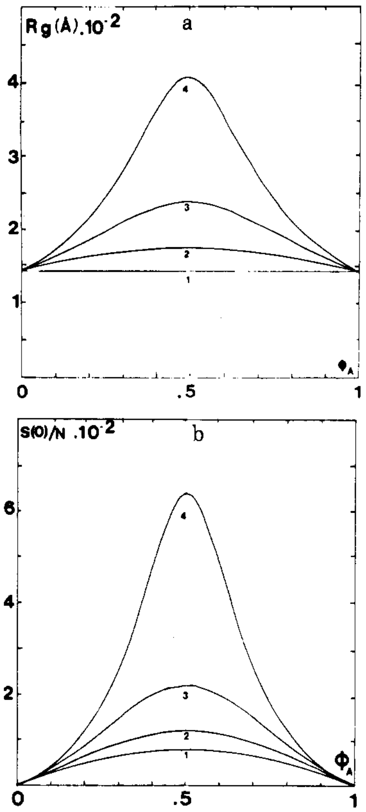

Figure 1. (a) Apparent radius of gyration and (b) scattered intensity at $q = 0$ plotted against the number fraction of species A when $R_{z,A} = R_{z,B}$ for different values of $\chi\tilde{n}_w$: (1) $\chi\tilde{n}_w = 0$ ($\chi = 0$); (2) $\chi\tilde{n}_w = 0.64$ ($\chi = 2 \times 10^{-4}$); (3) $\chi\tilde{n}_w = 1.27$ ($\chi = 4 \times 10^{-4}$); (4) $\chi\tilde{n}_w = 1.75$ ($\chi = 5.5 \times 10^{-4}$).

In the particular and theoretical case of identical polymers ($u = v = 0$; $n_{w,A} = n_{w,B} = n_w$; $\langle R_{z,A}^2\rangle = \langle R_{z,B}^2\rangle = \langle R_z^2\rangle$), (5) reduces to

$$\langle R_{ap}^2\rangle = \langle R_z^2\rangle[1 - 2\tilde{n}_w\phi_A(1 - \phi_A)\chi]^{-1} \qquad (6)$$

which simplifies to $R_{ap}^2 = R_z^2$ in the case of a noninteracting polymer ($\chi = 0$).

Figure 1 displays for that particular case the effect of χ on $\langle R_{ap}^2\rangle^{1/2}$ and $S(0)$ as a function of the volume fraction of polymer A.

Figure 2, in the same representation, concerns the case of two different polymers corresponding to the experimental situation under investigation (PDMS(H) + PDMS(D)). The shape of the curves shows a strong dependence on the parameter χ. In the dissymetrical case ($n_{w,A} \neq n_{w,B}$), $\langle R_{ap}^2\rangle^{1/2}$ exhibits two different types of behavior (continuous decrease or maximum), depending on the value of the interaction parameter χ.

Many authors[4,5] have used previously the variation of $S(0)$ or $S_{tot}(q)$ for the determination of χ, but Figures 1 and 2 show that the analysis of $\langle R_{ap}^2\rangle$ as a function of ϕ_A is a more appropriate approach for this purpose. The main advantage is that the measurement of $\langle R_{ap}^2\rangle$, which does not require absolute calibration, is always more precise than the measurement of the intensity $S(0)$. This advantage will be illustrated by the experimental example that is presented in the following section.

Obviously, in order to fit the experimental points with a value of χ, one has to know the quantities $\tilde{n}_w$, u, and v with good precision. We also discuss in the experimental part how the precision on these parameters affects the precision on χ measurements by considering a specific example.

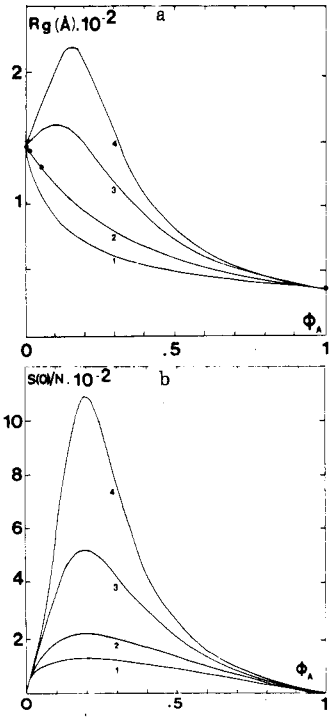

Figure 2. (a) Apparent radius of gyration and (b) scattered intensity at $q = 0$ plotted against the number fraction of species A for $n_{wB} = 195$, $n_{wA} = 3296$, $R_{z,B} = 34$ Å, and $R_{z,A} = 147$ Å at different values of $\chi\tilde{n}_w$: (1) $\chi\tilde{n}_w = 0$ ($\chi = 0$); (2) $\chi\tilde{n}_w = 2.97$ ($\chi = 1.7 \times 10^{-3}$); (3) $\chi\tilde{n}_w = 5.23$ ($\chi = 3 \times 10^{-3}$); (4) $\chi\tilde{n}_w = 6.11$ ($\chi = 3.5 \times 10^{-3}$).

Table I
Average Molecular Weights of PDMS(H) and PDMS(D) Determined by GPC-Light Scattering On Line

	M_n	M_w	M_w/M_n	n_w
PDMS(H)	9300	14600	1.57	195
PDMS(D)	178000	267000	1.50	3296

Experimental Section

Small-angle neutron scattering (SANS) experiments were carried out on a mixture of hydrogenated poly(dimethylsiloxane) (PDMS(H)) and deuterated poly(dimethylsiloxane) (PDMS(D)). In the following, subscripts D and H will correspond to A and B.

The synthesis of PDMS has been described[6] elsewhere. The molecular parameters were determined by GPC–light scattering on line[7] and are summarized in Table I.

Two blends with deuterated number fractions of 0.06 and 0.009 were investigated by SANS. The measurements were performed on the D11 spectrometer of the Institute von Laue Langevin (Grenoble, France).

The sample–detector distance was 10 m, and the wavelength was 10 Å ($\Delta\lambda/\lambda = 10\%$) allowing measurements in a range of momentum transfer ($q = (4\pi/\lambda) \sin(\theta/2)$) between 0.5×10^{-2} and 0.17×10^{-1} Å^{-1}.

The blends were placed in 1-mm-thick quartz cells; data were reduced in the classical way: subtraction of the appropriate incoherent background followed by normalization by an incoherent flat scatterer (pure water) in order to correct for detector efficiency.

Results and Discussion

The apparent radius of gyration was determined by using the classical Zimm representation. Figure 3 shows the results obtained for the two blends under investigation. The linear regression of the initial part of the curves leads to values of 142 and 129 Å respectively for $\phi_D = 0.009$ and $\phi_D = 0.06$.

Concerning the radii of gyration of the short (H) and long (D) PDMS chains in the very dilute regime (ϕ_D and

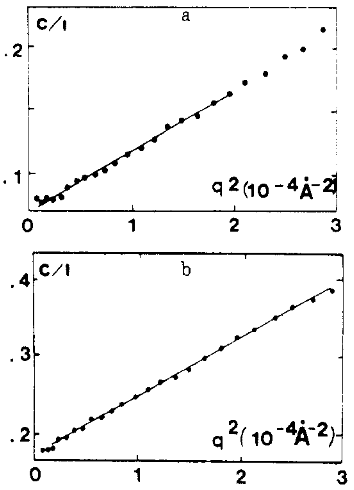

Figure 3. Inverse scattered intensity against q^b for two blends: (a) $\phi_A = 0.009$; (b) $\phi_A = 0.06$.

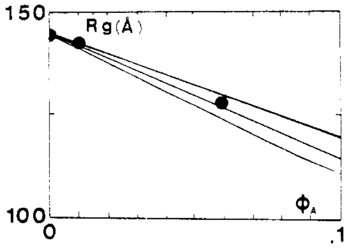

Figure 4. Apparent radius of gyration plotted against the number fraction of species A for the same molecular parameters as in Figure 2 for different values of $\chi\bar{n}_w$: (1) $\chi\bar{n}_w = 2.62$ ($\chi = 1.5 \times 10^{-3}$); (2) $\chi\bar{n}_w = 2.97$ ($\chi = 1.7 \times 10^{-3}$); (3) $\chi\bar{n}_w = 3.31$ ($\chi = 1.9 \times 10^{-3}$).

Table II
Parameters with Error Domains Necessary To Determine $\langle R_{ap}^2\rangle$

$\bar{R}_z$, Å	$\bar{n}_w$	u	v
107 ± 5	1745 ± 88	0.89 ± 0.01	0.90 ± 0.02

$\phi_H \sim 0$), values were obtained from the compilation of data of Beltzung[6] and Haug[8] that lead to a molecular weight dependence of athermal solvents.

$$\langle R_\Theta^2\rangle^{1/2} = 0.285 M_w^{1/2}$$

This leads to 34 and 147 Å for the two PDMS species. From these two values and those given in Table I, the parameters required for the theoretical calculation of $\langle R_{ap}^2\rangle$ (relation 5) can be obtained. They are listed in Table II.

The theoretical variation of $\langle R_{ap}^2\rangle^{1/2}$ given by relation 5 is represented in Figure 2a as a function of ϕ_D for different values of χ. On the same figure appear the experimental data that fit the theoretical prevision corresponding to $\chi = 1.7 \times 10^{-3}$. The enlargement of the range corresponding to our experimental investigations is given in Figure 4 which shows, in more detail, the theoretical curves resulting from a small deviation of χ ($\pm 0.2 \times 10^{-3}$) around the experimental value. At first sight, it seems that our precision on χ is within $\pm 0.2 \times 10^{-3}$. This has to be discussed in more detail since the value of χ depends on the experimental parameters introduced in relation 5, mainly R_z, n_w, u, and v. Therefore, the inaccuracies in the values of these parameters will affect the precision on χ.

In order to discuss this point more quantitatively, we first remark that in the range of ϕ_D values that have been used, $\langle R_{ap}^2\rangle^{1/2}$ is a linear function of ϕ_D

$$\left[\frac{R_{ap}^2}{R_z^2}\right]^{1/2} = (1+v)^{1/2}\left\{1 + \phi_D \frac{1+u}{1-u}\left[\chi\bar{n}_w(1-u) - \frac{v}{1+v}\right]\right\}$$

The experimental quantity of interest is the coefficient of ϕ_D, which will be called m. From Figure 4, the precision on m can be estimated as 5%. Knowing the precision on u, v, and n_w and by using the values that maximize or minimize m, one can conclude that χ is determined with a precision of the order of 10%. Therefore, one can write $\chi = (1.7 \pm 0.2) \times 10^{-3}$.

The theoretical calculations used for the evaluation of χ have been carried out by using for the radius of gyration of the deuterated and hydrogenated components the unperturbed dimensions measured by neutron scattering. This involves an approximation since the theory[2] and the experiments[9] predict changes of the radius of gyration when the molecular weights of the two components are different even if $\chi = 0$. In this case it has been shown that this effect has to be taken into account for the larger constituent A only if $(M_A)^{1/2}/N_B \ll 1$. Concerning the case presented here, the correction can be considered to be negligible. Qualitatively it seems that this effect should be less important for positive χ values and for the system compositions close to $\phi = {}^1/_2$.

Moreover, the use of eq 1 gives for each experimental condition a given value of χ. It is well-known that χ can be composition and molecular weight dependent. If that would occur, it would be impossible to fit all the data with a simple theoretical curve. Each point would give the χ value corresponding to the case concerned by the experimental conditions. The present case described in this work corresponds to a dilute solution of PDMS(D) in PDMS(H). Further work could allow a precise determination of the volume fraction dependence of χ.

Conclusion

We have demonstrated how the interaction parameter χ may be determined with good precision from the measurement of the apparent radius of gyration of a blend of two polymners having sufficient coherent scattering contrast. This type of measurement does not require absolute scattering calibration and could be adopted for the study of practical systems. This work also points out the important effect of the mass polydispersity for the evaluation of χ. Furthermore, we have shown that, for the PDMS(D)/PDMS(H) system, the interaction parameter χ is far from being negligible. This point has been discussed by Koningsveld et al.[10] on the basis of the results of Kirste et al.[9] The average χ value proposed is in good qualitative agreement with our result. Due to the lack of precision of the Kirste data and to the approximations involved in the molecular models, a more precise determination of χ was not possible. It should be noted also that Strazielle et al.[11] have found different values for the Θ point of deuterated and ordinary polystyrene; this can be explained only by assuming a χ value different from 0. If our result is correct, phase separation should occur for large molecular weights. It is known that the critical value for phase separation is given by $\chi n = 2$ when the system is symmetrical ($n_A = n_B = n$). Consequently as soon as M_w is larger than 100 000, one should observe phase separation at room temperature. This point and the temperature dependence of χ for such a PDMS(H)/PDMS(D) system will be studied in a forthcoming publication.

Appendix

Let us consider a mixture of two polymers A and B differing by their specific volume $\bar{v}_A$ and $\bar{v}_B$. The intensity $I_{V_0}(q)$ scattered by a given reference volume V_0 is written as

$$\frac{(a-b)^2}{I_{V_0}(q)} = \frac{1}{\phi_A n_A P_A(q)} + \frac{1}{\phi_B n_B P_B(q)} - 2\chi \qquad \text{(1a)}$$

where a and b are the coherent scattering length of A and B corresponding to the same volume V_0. n_A and n_B do not need to be the number of monomer units. They will be defined now as the number of segments having a volume V_0 such that

$$n_A = \frac{M_A \bar{v}_A}{\mathcal{N} V_0} \qquad n_B = \frac{M_B \bar{v}_B}{\mathcal{N} V_0}$$

($\mathcal{N}$ = Avogadro's number)

By introducing the intensity scattered per unit volume $I(q) = I_{V_0}/V_0$ and using these notations, one can write (1a)

$$\frac{(a-b)^2}{I(q)V_0} = \frac{aV_0}{\phi_A M_A \bar{v}_A P_A(q)} + \frac{aV_0}{\phi_B M_B \bar{v}_B P_B(q)} - 2\chi \qquad \text{(2b)}$$

If a_0 and b_0 are the coherent scattering lengths per unit volume, (2b) becomes

$$\frac{(a_0-b_0)^2}{\mathcal{N} I(q)} = \frac{1}{\phi_A M_A \bar{v}_A P_A(q)} = \frac{1}{\phi_A M_A \bar{v}_A P_A(q)} + \frac{1}{\phi_B M_B \bar{v}_B P_B(q)} - \frac{2\chi}{\mathcal{N} V_0} \qquad \text{(3b)}$$

This expression differs from eq 1a by the fact that instead of using the scattering lengths and the χ parameter per monomeric unit one uses these values per unit volume. ϕ_A and ϕ_B can be expressed in terms of experimental quantities such as weight concentrations c_A and c_B.

$$\phi_A = \frac{c_A \bar{v}_A}{c_A \bar{v}_A + c_B \bar{v}_B}$$

$$\phi_B = \frac{c_B \bar{v}_B}{c_A \bar{v}_A + c_B \bar{v}_B}$$

Generally, the difference between specific volumes of two polymers is rather small. Taking it into account will not alter strongly the conclusion drawn by assuming the simplification $\bar{v}_A = \bar{v}_B$ and will improve the determination of χ.

Registry No. Neutron, 12586-31-1.

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Radius of Gyration of an Excluded Volume Polymer with Attached End Chains and Its Application to the Static Structure Factor[†]

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ABSTRACT: The Domb–Joyce model is the basis of an approximate expression for the expansion factor of the radius of gyration of a linear polymer with attached end chains. The resulting function is used to estimate the effect of end chains on the static structure factor for a chain with excluded volume. A comparison is made with available experimental data.

1. Introduction

The relatively recent development of new scattering techniques, with both laser light and neutrons, has permitted experimental investigation of polymers in previously inaccessible regimes. At the same time, theoretical advances interpret the new experimental results more clearly than ever before. In particular, it is now possible to measure the dimensions of chains, or portions of chains, which exhibit strong excluded volume effects; moreover, there exist models that can usefully interpret these measurements. Nonetheless there are gaps. For example, it is common to interpret the results of light scattering experiments using the familiar Debye[1] structure factor, but there is no precise expression for the structure factor for portions of chains or for chains that exhibit excluded volume effects. It is therefore not clear how experiments on such chains should be analyzed.

There have been a number of attempts to deal with the effect of excluded volume on the structure factor. In 1955 Peterlin[2] devised a famous model in which the expansion factor of a part of the polymer is proportional to the chemical length of that part raised to a power and applied the model to the structure factor. Thirteen years later Sharp and Bloomfield[3] combined the Peterlin model with

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[†] This work has been supported, in part, by CRAD, Grant 3610-656.