From eq 60 it is seen that Θ-state dimensions are given by $\langle R^2\rangle_\Theta = N\langle l^2\rangle(1 + 5\zeta(3/2)/3\chi_2)$, where χ_2 is to be evaluated at the Θ temperature. For a purely repulsive potential all the moments vanish when the zeroth moment vanishes; for a repulsive–attractive potential these moments will not simultaneously vanish. In fact, the second moment will always be negative when the zeroth moment vanishes: the Θ chain is always swollen relative to its unperturbed reference state.

VIII. Conclusions

It is seen that purely repulsive potentials give a description of the Θ regime that is quantitatively similar to δ-function theory, except for certain correction terms of order $z/N^{1/2}$. Repulsive–attractive potentials give Θ behavior that is inconsistent with the Gaussian chain but that seems to be consistent with Monte Carlo results.

A few remarks are in order concerning the application of this method to topologically complex polymers, e.g., branched polymers. It is likely that the swelling of the Θ chain (relative to the unperturbed state) is dependent on polymer topology. In fact it might be expected that this swelling increases with the extent of branching. This would increase calculated values of Zimm–Stockmayer contraction factors. Let the radius of gyration for the branched polymer be $\langle S^2\rangle_\Theta{}^{\mathrm{b}} = \langle S^2\rangle_0{}^{\mathrm{b}}/(1 + \xi\phi)$. The contraction in dimensions at the Θ point is thus

$$\hat{g} \equiv \frac{\langle S^2\rangle_\Theta{}^{\mathrm{b}}}{\langle S^2\rangle_\Theta} = g(1 + (\xi - 3.27)\phi)$$

where g is the contraction factor in the unperturbed state. It has been implicitly assumed by many investigators that $\hat{g} = g$. This may be a good approximation if $g \sim 1$ but is known to be without merit for polymers with many circuits. An extreme example of the inapplicability of the unperturbed calculation occurs for networks—the phenomenon of network collapse.[28] Network collapse is characterized by $g \sim N^{-1}$, whereas physical considerations dictate that for real networks $g \sim N^{-1/3}$. The inclusion of an excluded volume potential is critical for networks.

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Excluded Volume Effects in the Θ Regime. 2. Extension of Perturbation Results to Arbitrary Potentials[†]

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ABSTRACT: The excluded volume effects treated in paper 1 are generalized to arbitrary interaction potentials by a moment expansion of the cluster function. In the first part of the paper the end-to-end vector is treated by a bond renormalization formulation that is shown to be essentially equivalent to first-order perturbation theory. These results show that perturbation theory is incorrect in one and two dimensions since no reference state is found in which the perturbation is small. The moment expansion method is shown to be qualitatively similar to three-body interaction theories but differs in its dependence on the excluded volume potential width. The formulation is extended to the second virial coefficient, and a relation is found between the dimensionless interaction width parameter introduced in paper 1 and the second moment of the cluster function. Finally, the results of the previous paper are presented as a three-parameter theory of Θ chains.

I. Introduction

In paper 1 a specific form of the excluded volume potential was used to obtain first-order perturbation theory results for polymers in the Θ regime. This approach to the excluded volume problem gave some interesting results for expansion factors, scattering functions, and second virial coefficients but lacked generality. In the present paper these results are generalized, via a moment expansion of the cluster function, to arbitrary well-localized interaction potentials.

In section II a heuristic bond renormalization approach is taken in the calculation of the first-order expansion

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factor for the end-to-end vector. The formulation shows that perturbation theory cannot be correct in one and two dimensions, since an appropriate reference state is not found. In the Appendix the bond renormalization approach is essentially verified by using ordinary first-order perturbation theory; both methods rely on a moment expansion of the cluster function. The equation in paper 1 for the expansion factor of the end-to-end vector is recovered when the cluster function of paper 1 is substituted into the expression derived here. Finally, the results of this moment expansion are compared to three-body interaction theories. It is found that for very narrow potentials three-body theories predict a divergence in Θ dimensions, whereas the present theory does not.

In section III this moment method is applied to the second virial coefficient. These results are found to agree with paper 1 and this prompts the general conclusion that the expansions (in the potential width) used in paper 1 are equivalent to the cluster function moment method. In this way previous results are generalized to arbitrary interaction potentials.

II. Bond Renormalization Approach

The bond renormalization formulation is intuitively pleasing but is certainly subject to criticism for the somewhat arbitrary steps taken in the derivation. For this reason exact results are given in the Appendix.

Using the sign convention of paper 1, define the cluster function in terms of the interaction potential $v(\mathbf{r}_{ij})$ where $\mathbf{r}_{ij}$ is the vector that runs from segment i to segment j on a linear polymer chain of $N + 1$ statistical segments.

$$\chi(\mathbf{r}_{ij}) = 1 - e^{-v(\mathbf{r}_{ij})/kT} \tag{1}$$

It is convenient to define a parameter $\epsilon \sim \delta r^{-2}$ that allows variation of the interaction width, δr. This parameter can be introduced into the cluster function in such a way that the binary cluster integral is held constant. In the theory of imperfect gases the binary cluster integral is defined as the zeroth moment of the cluster function. With the interaction width scaling parameter this gives

$$\beta = \epsilon^{m/2}\int \chi(\epsilon^{1/2}\mathbf{r})\, \mathrm{d}^m\mathbf{r} = \int \chi(\mathbf{s})\, \mathrm{d}^m\mathbf{s} \tag{2}$$

where m is the dimensionality of space and $\epsilon^{m/2}$ is the normalization that fixes β while allowing the interaction width to vary.

From eq 2 it is seen that β measures the excluded volume of two interacting molecules. The integral can be thought of as a difference between two Boltzmann factors; the first Boltzmann factor gives the spatial probability distribution for noninteracting bodies, and the second factor is the distribution for interacting bodies. The integral of this difference is a measure of nonideality. This interpretation of β can be generalized to segments on a polymer chain by introducing a weighting factor $P(\mathbf{r}_{ij})$ into the integral. This weighting factor accounts for the random flight part of the segment–segment interaction; clearly, an excluded volume interaction is of little importance if two segments rarely come into contact. In this way we define a dimensionless parameter

$$\beta_{ij} = \epsilon^{m/2}\int P(\mathbf{r}_{ij})\chi(\epsilon^{1/2}\mathbf{r}_{ij})\, \mathrm{d}^m\mathbf{r}_{ij} \tag{3}$$

where the probability distribution function for the ith and jth segments is given by the Gaussian

$$P(\mathbf{r}_{ij}) = \left(\frac{\gamma}{\pi|i-j|}\right)^{3/2} e^{-\gamma r_{ij}^2/|i-j|} \tag{4}$$

$$\gamma = 3/2a^2$$

and a is the root-mean-square step length. For a very localized interaction the β_{ij} fall off as the intervening polymer contour length to the $-3/2$ power. These β_{ij} can be used to compute an effective interaction contour length for the ith segment on the polymer chain.

$$s_i = \sum_{j<i}\beta_{ij}|i-j|a \tag{5}$$

Here, $|i-j|a$ is the chain contour length between segments i and j, and β_{ij} is proportional to the collision frequency between these monomers times their mutual excluded volume. To define a mean interaction length scale we simply average s_i over all i.

$$s = N^{-1}\sum_{1}^{N} s_i \tag{6}$$

Formally, the Gaussian bond length can be renormalized to absorb this factor by letting the Gaussian bond become comparable to this length. Denoting the renormalized chain parameters N and a by primes, a' must obey two limits: $\lim_{s\to 0} a' = a$ and $\lim_{s\to\infty} a' = s$. Since a' must also have the dimensions of length, we let $a' = a + s$. The mean square unperturbed (no excluded volume interactions) end-to-end vector, $\langle R^2\rangle_0$ is just Na^2. In terms of the renormalized parameters, the mean square perturbed end-to-end vector, $\langle R^2\rangle$, is $N'a'^2$. Fixing the chain contour length ($Na = N'a'$) gives an expression for the expansion factor of the end-to-end vector.

$$\alpha_R^2 \equiv \langle R^2\rangle/\langle R^2\rangle_0 = 1 + s/a \tag{7}$$

This expansion factor is relative to the arbitrary unperturbed reference state. This reference state is not the observed Θ state, as shown in paper 1, and eq 7 is therefore not the experimentally observed expansion factor.

Calculations based on the above equations are straightforward if we assume that the excluded volume potential is well localized ($\delta r < a$). In this case it is valid to expand the distribution function $P(\mathbf{r}_{ij})$ for small $\mathbf{r}_{ij}$. Keeping terms of order r_{ij}^2 and using eq 2 gives

$$\beta_{ij} = \mu^{-m/2}(\chi_0 - \pi\chi_2/\mu) \tag{8}$$

where χ_0 and χ_2 are dimensionless moments of the cluster function. Defining $\Delta = 1/\epsilon$, these moments are

$$\chi_0 = (\gamma/\pi)^{m/2}\int \chi(\mathbf{s})\, \mathrm{d}^m\mathbf{s} \tag{9}$$

$$\chi_2 = (\gamma/\pi)^{(m+2)/2}\Delta\int s^2\chi(\mathbf{s})\, \mathrm{d}^m\mathbf{s} \tag{10}$$

Substitution of this result into eq 6 with eq 7 gives an expression for the expansion factor:

$$\alpha_R^2 - 1 = N^{-1}\sum_{\mu=1}^{N}\frac{N-\mu}{\mu^{m/2}}(\mu\chi_0 - \pi\chi_2) \tag{11}$$

This can be compared with the exact first-order expression, valid to the second moment, from the Appendix.

$$\alpha_R^2 - 1 = N^{-1}\sum_{\mu=1}^{N}\frac{N-\mu}{\mu^{m/2}}\left(\mu\chi_0 - \frac{5}{m}\pi\chi_2\right) \tag{12}$$

These results are seen to agree to within a numerical prefactor in the second moment term. In the δ-function limit, where the second moment is zero, eq 11 is exact. For various dimensionalities the results are

$$m = 1: \qquad \alpha_R{}^2 - 1 = \frac{4}{5}\chi_0 N^{3/2} - \frac{20}{3}\pi\chi_2 N^{1/2}$$

$$m = 2: \qquad \alpha_R{}^2 - 1 = \frac{1}{2}\chi_0 N - \frac{5}{2}\pi\chi_2 \ln N$$

$$m = 3: \qquad \alpha_R{}^2 - 1 = \frac{4}{3}\chi_0 N^{1/2} - \frac{5}{3}\pi\zeta(3/2)\chi_2$$

$$m = 4: \qquad \alpha_R{}^2 - 1 = \chi_0 \ln N - \frac{5}{4}\pi\zeta(2)\chi_2$$

$$m = 5: \qquad \alpha_R{}^2 - 1 = \zeta(m/2 - 1)\chi_0 - \frac{5}{m}\pi\zeta(m/2)\chi_2$$

where $\zeta(x)$ is the Riemann ζ function. The δ-function result appears as the first term in each expression.

For a potential with a repulsive core followed by an attractive interaction, the second moment is always negative where the zeroth moment vanishes (in paper 1 this is identified as the Θ point). But it is readily seen that in one and two dimensions there is no temperature at which the expansion factor is independent of N unless these moments vanish simultaneously—this occurs only in the δ-function limit. The conclusion is that perturbation theory is incorrect in one and two dimensions since there is no suitable reference state where the perturbation is small for large N. In other words, $^1/_2$ cannot be the Θ-state exponent in these dimensions. This observation cannot come from a theory based on the δ potential. In fact, Oono[1] has shown that the Θ-state exponents for the radius are 1 and $^2/_3$ in one and two dimensions; this reiterates the conclusion that the one- and two-dimensional Θ states cannot be treated as a perturbation of a random walk.

In four dimensions there is a logarithmic swelling associated with the zeroth moment and in higher dimensions excluded volume effects amount to only a uniform swelling—a specific solvent effect. Hence, real chains are never ideal in one and two dimensions and are always ideal in five and higher dimensions.

Three dimensions is of greatest interest and is treated separately. It is clear that the expansion factor is independent of N when the segment binary cluster integral is zero. At this temperature the polymer is in a swollen state relative to the reference state, as described in paper 1, and this swelling is seen to decrease linearly with the square width of the potential. The Θ-state mean square end-to-end vector, $\langle R^2\rangle_\Theta$, is then just $Na^2\,(1 - {}^5/_3\pi\zeta(3/2)\chi_2)$. The experimentally observed expansion factor is relative to this dimension and is (for large N)

$$\tilde{\alpha}_R{}^2 - 1 = \frac{4}{3}\chi_0 N^{1/2} \Big/ \left(1 - \frac{5}{3}\pi\zeta(3/2)\chi_2\right) \tag{13}$$

where here χ_2 is evaluated at $T = \Theta$.

The Θ-state dimensions derived here are in sharp contrast with the effects predicted for three-body interactions. Defining a three-body parameter (we generalize this with the scaling parameter ϵ)

$$v_3 = -\epsilon^{3/2}\int \chi(\mathbf{s})\chi(\mathbf{s} - \mathbf{s}')\chi(\mathbf{s}')\ \mathrm{d}^3\mathbf{s}'\ \mathrm{d}^3\mathbf{s} \tag{14}$$

Oyama and Oono[2] derived an expression for the Θ-point swelling of a randomly coiling chain. Their result is

$$\frac{\langle S^2\rangle_\Theta}{\langle S^2\rangle_0} = \frac{6}{3^{1/2}}\left[\frac{1}{24} + \left(\frac{1}{24^2} + \frac{3v_3}{16\pi^2}\right)^{1/2}\right]^{1/2} \tag{15}$$

Keeping β constant, this swelling is seen to increase to infinity as the interaction width of the potential approaches zero. For very small Δ the swelling of root-mean-square dimensions is $\sim 1/\Delta^{3/8}$. This result contradicts the behavior predicted by first-order perturbation theory but could arise from higher order interactions. At any rate, these differing conclusions are certainly subject to Monte Carlo verification.

III. Moment Method for the Second Virial Coefficient

The cluster function moment expansion for the second virial coefficient is developed from the Zimm[3] expression for A_2.

$$A_2 = -\frac{N_\mathrm{A}}{2VM^2}\int F(1)F(2)[\prod_{i_1,i_2}(1 - \chi(\mathbf{r}_{i_1} - \mathbf{r}_{i_2})) - 1]\ \mathrm{d}(1)\ \mathrm{d}(2) \tag{16}$$

Here, $F(k)$ is the configuration distribution function for polymer k, $\mathrm{d}(k)$ is the $3N$-dimensional volume element for this polymer, and the integral of $F(k)$ over this volume element is V, the volume of solution. N_A is Avogadro's number and M is the polymer molecular weight. Expanding the product of cluster functions gives

$$A_2 = -\frac{N_\mathrm{A}}{2M^2}\sum_1^{N^2}(-1)^p b_p \tag{17}$$

where b_p denotes the contribution of the pth contact term to the virial coefficient (for convenience, we use a chain of N segments here). The single-contact term is seen to be related to the zeroth moment by integrating over the volume element $\mathrm{d}(1)\ \mathrm{d}(2)/\mathrm{d}\Delta\mathbf{r}_i$, where $\Delta\mathbf{r}_i$ is the vector that runs from the interacting segment on 1 to the interacting segment on 2.

$$b_1 = \sum_{i=1}^{N^2}\int \chi(\Delta\mathbf{r}_i)\ \mathrm{d}^3\Delta\mathbf{r}_i = N^2\beta \tag{18}$$

The double-contact term is obtained by integrating

$$\frac{1}{V}\int F(1)F(2)\chi(\Delta\mathbf{r}_i)\chi(\Delta\mathbf{r}_j)\ \mathrm{d}(1)\ \mathrm{d}(2) \tag{19}$$

over the volume element $\mathrm{d}(1)\ \mathrm{d}(2)/\mathrm{d}\Delta\mathbf{r}_i d\Delta\mathbf{r}_j$, where $\Delta\mathbf{r}_i$ is the first contact vector and $\Delta\mathbf{r}_j$ is the second contact vector in the double-contact graph. The result is in terms of the conditional probability distribution $P(\Delta\mathbf{r}_i|\Delta\mathbf{r}_j)$ (symmetric in its arguments)

$$b_2 = \sum\sum\int P(\Delta\mathbf{r}_i|\Delta\mathbf{r}_j)\chi(\Delta\mathbf{r}_i)\chi(\Delta\mathbf{r}_j)\ \mathrm{d}^3\Delta\mathbf{r}_i\ \mathrm{d}^3\Delta\mathbf{r}_j \tag{20}$$

$$P(\Delta\mathbf{r}_i|\Delta\mathbf{r}_j) = \left(\frac{\gamma}{\pi(\kappa + l)}\right)^{3/2} e^{-\gamma(\Delta\mathbf{r}_i - \Delta\mathbf{r}_j)^2/(\kappa+l)} \tag{21}$$

where the sums are over all double-contact terms. Here, κ is the number of Gaussian bonds between the interaction segments on polymer 1 (these, of course, interact with segments on polymer 2) and l is the corresponding quantity for polymer 2. Expanding the conditional probability to terms of order Δr^2 (the cluster functions are localized) and integrating gives

$$b_2 = 2\beta \sum_{\substack{\kappa=0 \\ \kappa+l>0}}^{N}\ \sum_{l=0}^{N} \frac{(N - \kappa)(N - l)}{(\kappa + l)^{3/2}}(\chi_0 - 2\pi\chi_2/(\kappa + l)) \tag{22}$$

Substituting this result into eq 17 gives the double-contact expression for the second virial coefficient (m_s is the segment molecular weight)

$$A_2 = \frac{N_\mathrm{A}\beta}{2m_\mathrm{s}{}^2}(1 + 4\pi\zeta(3/2)\chi_2 - 2.865\chi_0 N^{1/2}) \tag{23}$$

It is seen that very near the Θ temperature A_2 depends on the product of the binary cluster integral times a dimensionless factor that is always less than 1 and that decreases as the interaction width increases. Higher moments will also make contributions to this term, so it should be considered valid only for small Δ.

IV. A Generalized Three-Parameter Theory

In paper 1 the excluded volume potential was taken to be

$$-kT \ln \left(1 + \sigma\left(\frac{\gamma\epsilon}{\pi}\right)^{3/2}(e^{-\epsilon\gamma r^2} - 8^{1/2}ce^{-2\epsilon\gamma r^2})\right) \quad (24)$$

where σ is an amplitude parameter and c is a temperature-dependent parameter which is just 1 when $\beta = 0$. The second moment of the cluster function of this potential is $-(3/4\pi)(\gamma/\pi)^{3/2}(\sigma - \beta)$ and when substituted into eq 13 gives agreement with the formula for the expansion factor derived in paper 1. Too, when this moment is substituted into the expression for the second virial coefficient, agreement is found with the corresponding formula in paper 1.

By way of review, the expressions obtained in paper 1 are exact to terms of order Δ. But it is seen from eq 16 that the cluster function used in those calculations is just of the form $\epsilon^{3/2}\chi(\epsilon^{1/2}r)$. Clearly, ϵ is just the width scaling parameter defined above. Since the $2m$th moment of the cluster function scales like ϵ^{-m}, terms of order Δ^m in paper 1 must correspond to just the $2m$th moment. This is providing, of course, that the moments appear linearly in the moment expansions, as is indeed the case for the expansion factors for the radius of gyration and the end-to-end vector and for the second-order expression for the virial coefficient. In effect, ϵ can be thought of as a dummy parameter that is used only to relate cluster function moments to terms in the expansions of paper 1.

The results of paper 1 can now be generalized to arbitrary interaction potentials. In doing this, we adopt the notation of paper 1; let $z = \chi_0 N^{1/2}$ be the excluded volume parameter, and let $\phi = (-4\pi/3)\chi_2$. The generalized three-parameter theory is then summarized in the following equations, all of which appear in paper 1. Θ-state dimensions are predicted to be

$$\frac{\langle S^2\rangle_\Theta}{\langle S^2\rangle_0} = \frac{\langle R^2\rangle_\Theta}{\langle R^2\rangle_0} = 1 + \frac{5}{4}\zeta(3/2)\phi \cong 1 + 3.27\phi$$

$$\frac{\langle a_h\rangle_\Theta{}^2}{\langle a_h\rangle_0{}^2} = 1 + 3.45\phi$$

and the results for expansion factors and A_2 are

$$\tilde{\alpha}_R{}^2 - 1 = \frac{4}{3}\Big/(1 + 3.27\phi)$$

$$\tilde{\alpha}_S{}^2 - 1 = \frac{134}{105}\Big/(1 + 3.27\phi)$$

$$\tilde{\alpha}_h{}^2 - 1 = 1.218/(1 + 3.45\phi)$$

$$A_2 = \frac{N_A\beta}{2m_s{}^2}(1 - 7.84\phi - 2.865z)$$

where the expansion factors are now relative to the Θ dimensions, and a_h is the hydrodynamic radius in the Kirkwood[4,5] nondraining limit. The generalized expression for the hydrodynamic radius must be considered a conjecture; it is difficult to prove. Still, this second-moment generalization seems reasonable enough, given the other results.

V. Conclusions

It is found that the results of paper 1 can be generalized to arbitrary interaction potentials through a moment expansion of the cluster function. A three-parameter theory is proposed for dilute polymers in the Θ regime, and the third parameter is seen to be related to the second moment of the cluster function. The theory predicts that the Θ chain will be swollen relative to the unperturbed state, much the same as three-body theories. Quantitatively, however, the predictions differ; three-body theories predict that the swelling will become infinite as the width of the potential vanishes, but the present theory predicts that the swelling will vanish in this limit. Again, Monte Carlo studies may be able to sort this out, but the studies must be made in the very narrow interaction limit, where the current theory applies.

An upper bound on the range of applicability is obvious from the expression for A_2: $\phi < 1/(3\zeta(3/2))$. In terms of the Θ-point swelling of the mean square radius, this gives $\langle S^2\rangle_\Theta/\langle S^2\rangle_0 \ll 5/3$. This limited range will tend to make Monte Carlo verification of these results difficult.

Appendix

The cluster function moment expansion of the single-contact expansion factor for the end-to-end vector requires the perturbed distribution[6]

$$P(\mathbf{R}_{1N}) = P_0(\mathbf{R}_{1N}) + \sum_{k<l} Q(\mathbf{R}_{1N}, k - l) \quad \text{(A-1)}$$

where $\mathbf{R}_{1N}$ is the end-to-end vector for a chain of $N - 1$ segments, and the subscript zero denotes the unperturbed distribution. The function $Q(\mathbf{R}_{1N}, k - l)$ is the contribution to the perturbation from the k–l contact graph. It can be shown in a straightforward way that

$$Q(\mathbf{R}_{1N}, k - l) = \int \chi(\mathbf{R}_{kl})[P_0(\mathbf{R}_{1N})P_0(\mathbf{R}_{kl}) - P_0(\mathbf{R}_{1N},\mathbf{R}_{kl})]\ \mathrm{d}^m\mathbf{R}_{kl} \quad \text{(A-2)}$$

$$P_0(\mathbf{R}_{1N}) = \left(\frac{\gamma}{\pi(N-1)}\right)^{m/2} e^{-\gamma R_{1N}{}^2/(N-1)} \quad \text{(A-3)}$$

where $\mathbf{R}_{kl}$ is the vector that connects the kth and lth segments. In the usual way we factor the joint distribution $P(\mathbf{R}_{1N},\mathbf{R}_{kl})$ into $P(\mathbf{R}_{1N}|\mathbf{R}_{kl})P(\mathbf{R}_{kl})$, which includes the conditional probability

$$P_0(\mathbf{R}_{1N}|\mathbf{R}_{kl}) = \left(\frac{\gamma}{\mu\xi}\right)^{m/2} e^{-\gamma\Delta R^2/\xi} \quad \text{(A-4)}$$

$$\xi = N - 1 - |k - l|$$

$$\Delta\mathbf{R} = \mathbf{R}_{1N} - \mathbf{R}_{kl}$$

and the distribution

$$P_0(\mathbf{R}_{kl}) = \left(\frac{\gamma}{\pi|k - l|}\right)^{m/2} e^{-\gamma R_{kl}{}^2/|k-l|} \quad \text{(A-5)}$$

From eq A-1 the expansion factor is just

$$\alpha_R{}^2 - 1 = \frac{1}{a^2(N-1)}\sum_{k<l}\int Q(\mathbf{R}_{1N}, k - l)R_{1N}{}^2\ \mathrm{d}^m\mathbf{R}_{1N} \quad \text{(A-6)}$$

Integration over $\mathrm{d}^m R_{1N}$ gives

$$\frac{1}{(N-1)a^2}\sum_{\mu=1}^{N}\left(\frac{\gamma}{\pi\mu}\right)^{m/2}(N - \mu) \times \int \chi(\mathbf{R})e^{-\gamma R^2/\mu}(a^2\mu - R^2)\ \mathrm{d}^m\mathbf{R} \quad \text{(A-7)}$$

Expansion of the Gaussian to terms of order R^2 and integration over $d^m\mathbf{R}$ gives the final result, eq 12.

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Polymer Self-Diffusion: Dynamic Light Scattering Studies of Isorefractive Ternary Solutions†

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ABSTRACT: Dynamic light scattering measurements are reported for the ternary system poly(vinyl methyl ether) (PVME)/polystyrene (PS)/toluene. PVME is index matched by toluene, and hence scatters very little light, over a wide concentration range. Thus it is shown that dynamic light scattering can be used to measure the self-diffusion coefficient of PS ("optically labeled") chains. Since PS is chemically different from PVME, a scaling treatment is given for the concentration and molecular weight dependence of D in ternary systems. Simple power law behavior is not found for the concentration dependence but the molecular weight dependence is predicted to be $D \sim M^{-9/5}$. The scaling analysis also shows a crossover, beyond the semidilute crossover, from Stokes–Einstein diffusion to reptation. This dynamical crossover depends on the relative molecular weights of the labeled and "solvent" chains and is derived for chemically identical and nonidentical chains in both good and Θ solvents. The experimental data substantiate the scaling results; the crossover to reptation for the ternary system studied is at ca. 15% volume fraction PVME whereas the semidilute crossover for PVME was found from viscosity data to be at a volume fraction of 4%.

Introduction

The reptation model[1] provides a simple and appealing description of the diffusion of polymers in highly congested solutions. To date there have been a number of experiments which indicate that reptation ideas are essentially correct. The methods brought to bear on this problem are extensive: forced Rayleigh scattering,[2] pulsed field gradient nuclear magnetic resonance,[3,4] luminescence quenching,[5] slow-mode analysis of dynamic light scattering data,[6,7] radioactive tracers,[8,9] and infrared spectroscopy from deuterium-labeled chains.[10] The purpose of this paper is to introduce a new method for the study of the dynamics of highly entangled labeled chains: dynamic light scattering from isorefractive ternary solutions. The idea of optically labeled chains is simple enough and is certainly not new,[11] but the application of dynamic scattering techniques to such systems has not been reported in the literature.

Isorefractive scattering is the optical analogue of neutron scattering from deuterium-labeled chains; the ternary system consists of a solvent (toluene), a large concentration of index-matched polymer (poly(vinyl methyl ether) (PVME)), and a very small concentration of "labeled" polymer (polystyrene (PS)) with a large refractive index increment. There are, of course, some considerations in devising such a system. First, the ternary system must be compatible over a wide range of index-matched polymer concentration. Second, the index-matched polymer must be index matched over this concentration range. The system PS/PVME/toluene fulfills these requirements quite well, being much more compatible than the system PS/PMMA/toluene, for which static light scattering data have been reported[12].

Dynamic light scattering is ideally suited to the study of single-chain dynamics and offers some advantages over other techniques. First, a very broad spatial (ca. 25–500 nm) and temporal range (ca. 1 μs to 1 s) can be probed. Thus not only can reptation be investigated, but internal modes of entangled single chains can be studied—an experiment that previously has only been possible with spin-echo neutron scattering.[13] Second, the measurements are quickly and easily made, and samples are easily prepared, requiring only filtering and mixing. It should be pointed out, however, that there is an important disadvantage in working with ternary systems; power law scaling behavior does not hold for some of the properties of these chemically nonidentical chains (see below).

In this paper preliminary results are given for the concentration and wavevector dependence of the apparent diffusion coefficient in a system in which the labeled chains (M_n = 900 000) are longer than the isorefractive chains (M_v ~ 110 000). The applicability of scaling results to this system is discussed, with particular consideration given to thermodynamic screening and the crossover from Stokes–Einstein diffusion to reptation. Power law behavior is not expected for the concentration dependence of D but is predicted for the molecular weight dependence, with minor alteration of the exponent. Too, the crossover to reptation is predicted to occur well beyond the semidilute crossover for the semidilute chains. This prediction is verified by the experimental data.

Experimental Section

Equipment. Self-diffusion coefficients were determined on a photon correlation spectrometer that has not yet been described in the literature. The apparatus consists of the following components: a Spectra-Physics Model 125A He–Ne laser, a Spectra-Physics Model 164 argon ion laser, an Aerotech goniometer (which can be step scanned to a resolution of 0.9 MOA), a Malvern photomultiplier tube housing, an amplifier–discriminator unit, an index-matched sample cell assembly, an ITT FW130 photomultiplier tube (selected for low after-pulsing), a 72 hardware channel Model 1096 Langley-Ford correlator, and a DEC LSI 11/23 computer. The purpose of the computer is twofold: analysis of the data (single- and double-exponential decay nonlinear fitting routines, with or without a floating base line, and a cumulants

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