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Small-Angle Neutron Scattering from Star-Branched Polymers in Dilute Solution

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ABSTRACT: We have investigated the dilute solution behavior of a series of linear and star-branched polyethylene molecules by small-angle neutron scattering. The measurements were made in a Θ solvent (biphenyl-d_{10}) and in a good solvent (toluene-d_8). An important feature of the work is a comparison of the present measurements with previous measurements on identical molecules in the molten state. At the Θ temperature the star molecules in solution are swollen compared with those in the melt. This swelling increases with the number of arms but is independent of arm length. For the Θ solvent, the expansion factor, defined as the ratio of the radius of gyration in solution to that in the melt, is consistent with a three-parameter theory based on the smoothed density model, in which the third parameter corresponds to ternary interactions between the polymer segments. The value of the third parameter calculated from the observed Θ expansions by the intramolecular theory is in very good agreement with that obtained with the corresponding intermolecular theory from second viral coefficient data for a 12-arm star measured at several temperatures on either side of the Θ temperature. In the good solvent both the expansion factors and the second viral coefficients are in satisfactory agreement with the two-parameter smoothed density model.

Introduction

Two distinct factors are responsible for the continuing interest that has been shown in star-branched polymers since the synthesis of the first well-characterized samples in 1962.[1] First, the star-shaped molecule is the simplest branched structure, and so understanding the behavior of model star polymers is the key to understanding all branched systems. Second, the local density of polymer segments within a branched polymer is larger than within a linear chain molecule of the same mass. This latter feature facilitates the testing of theories for intersegment interactions in solution, since the greater number of segment–segment contacts exaggerates their influence upon the molecule as a whole.

In a previous paper[2] we presented the results of a small-angle neutron-scattering study of the sizes and conformation of a series of star-branched polymers in the molten state. The results were analyzed with respect to the Gaussian (random walk) model of polymer conformation, which has been applied to branched polymers by Zimm and Stockmayer.[3] Although the Gaussian model scattering functions could be fitted to the small-angle spectra very well, the molecular radii of gyration were found to be larger than the predicted Gaussian radii. The magnitude of this swelling was found to be greatest for stars with many arms and low molecular mass. Here we report on a continuation of the neutron study in which the same samples were measured in dilute solution in a Θ solvent and in a good solvent.

The simplest solution theories describe the statistics of polymer chains in terms of two quantities, one related to the overall size of the molecule, and the other a measure of the effective interaction, or volume excluded, between two polymer segments. Such theories are known as two-parameter theories.[4] Long-range excluded volume interactions between segments on the same molecule destroy the Markoff nature of the chain and, in general, cause an expansion of the molecule with respect to the unperturbed, random-walk size.

Interactions between segments of different molecules are represented by the second virial coefficient, A_2, whose magnitude indicates deviations from Van't Hoff's law for the osmotic pressure of ideal solutions.[5] When the second virial coefficient is zero, the polymer solution almost behaves ideally (higher virial coefficients are still nonzero), and the temperature at which this occurs is referred to as the Θ temperature, Θ_{A_2}. A polymer solution at Θ_{A_2} is formally analogous to the state of a van der Waals gas at the Boyle temperature.[4]

It is conventional also to make reference to two other definitions of the Θ temperature. The temperature at which a polymer in solution has the same dimensions as an unperturbed, random-walk chain is denoted by Θ_0, while the mean-field theory of Flory and Huggins[5] leads to a Θ temperature, denoted simply by Θ, defined as the highest, or critical, temperature at which a polymer of infinite molecular mass just precipitates out of solution. Θ is also known as the Flory temperature. Within the framework of two-parameter theory the three temperatures Θ_{A_2}, Θ_0, and Θ are coincident, but more sophisticated theories referred to later show that this need not be the case. We merely note for the present that for a chain of infinite mass only binary interactions are important, because the extremely low local segment density renders three-body and higher body interactions highly unlikely. Thus, Θ corresponds to the temperature at which repulsive and attractive interactions between two polymer segments in solution exactly cancel and so depends only on the type of monomer and solvent molecule and not on the architecture of the polymer as a whole.

Two-parameter theories have also been applied to branched polymers. At the Θ temperature, polymers are expected to exhibit unperturbed dimensions irrespective of branching, but when excluded volume is present it has been shown that a branched polymer is more swollen than a linear chain of the same mass under identical thermodynamic conditions. This is a consequence of the more compact nature of a branched molecule; there is an increased likelihood of intramolecular segment–segment interactions as compared with a linear chain of the same mass.

A convenient parameter for assessing the effects of branching is g, defined by

$$g = \langle S^2 \rangle_{\rm br} / \langle S^2 \rangle_{\rm lin} \tag{1}$$

The ratio is evaluated for branched and linear polymers

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of equal molecular masses. Within the Gaussian model g is the ratio of the unperturbed squared radii and for star molecules is given by[3]

$$g_0 = (3f - 2)/f^2 \tag{2}$$

where f is the number of arms, or functionality, of the star.

A number of previous scattering studies have been made on star polymers in dilute solution. The approach adopted in the majority of these experiments was to measure the radius of gyration and second virial coefficient in Θ and good solvents and to compare the results with equivalent measurements made on a reference series of linear chains. Agreement between all the experiments has not been unanimous, but some general trends may be identified: (i) A_2 is not zero at Θ, and in all cases it has been found that $\Theta_{A_2} < \Theta$. Special effort was made by Roovers and Bywater[6] and by Bauer et al.[7] to study this phenomenon. (ii) For small f the value of g at the Θ temperature, g_Θ, is close to the Gaussian result, g_0. For $f \geq 6$, though, g_Θ is larger than g_0, with the expansion increasing with f. (iii) For a given functionality g_Θ is molecular mass dependent, with the largest value at low molecular mass. This is particularly noticeable in the studies of Bauer et al.[7] and of Huber et al.[8] (iv) In good solvents g tends to be larger than g_0, but in comparison with g_Θ it appears that for large molecular masses $g > g_\Theta$ and for small masses $g < g_\Theta$. It is clear that the most serious deviations from the two-parameter theory occur for polymers of low mass and high functionality. This observation suggests that structural effects around the branch point may be responsible for changes to the statistics not predicted by theory.

Our solution investigations differ from all previous ones in two important ways. First, in terms of the equivalent Kuhn chains the molecules studied were nearly all smaller than the smallest molecules previously measured, so we are in the least understood regime, and second, we have already measured the same polymers in the molten state where excluded volume is expected to be screened out.[9] The melt results are central to the interpretation of the dilute solution data, because a comparison of the conformation in dilute solution with the molten state makes it possible to isolate the purely solvent-dependent effects from the influences of nonidealities of structural origin and thereby enables a more reliable test of the theories of excluded volume than has hitherto been possible.

Experimental Section

Samples. The polymer samples were the same as those measured in the molten state.[2] These consisted of four linear molecules, five stars with $f = 3$, three with $f = 4$, five with $f = 12$, and one with $f = 18$. One extra linear polymer (S2E) of molecular mass 99 600 g mol^{-1} was also run.

Solvents. The Θ solvent for the neutron experiments was biphenyl-d_{10} ($C_{12}D_{10}$) purchased from Merck, Sharp and Dohme, and quoted as 99.2 at.% deuterated. The Θ temperature of linear polyethylene in biphenyl has been measured before,[10,11] and Θ values of 125 and 127.5 °C were reported. However, in view of the slightly branched microstructure of the saturated polybutadienes of the present study (it has been reported[12] that a small number of ethyl groups are attached to the backbone) and the fact that it was the Θ temperature in the *deuterated* solvent that was required, it was felt prudent to make an independent determination. This measurement is described below.

The good solvent was toluene-d_8 (C_7D_8) purchased from Fluorochem Ltd. and quoted as 99.6 at.% deuterated. The polymers were found to dissolve in toluene at temperatures in the range 54–62 °C.

Θ Temperature. The procedure used for measuring Θ was the phase equilibrium method of Shultz and Flory,[13] which follows directly from the definition of Θ as the critical precipitation temperature for a polymer of infinite mass.

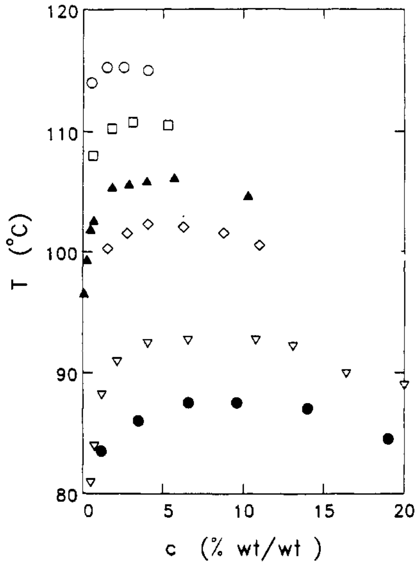

Figure 1. Phase curves for a series of six hydrogenated polybutadienes in biphenyl-h_{10}. The molecular masses (in g mol^{-1}) are 11 200 (●), 14 500 (▽), 33 300 (◇), 55 000 (▲), 99 600 (□), 200 000 (○).

Flory–Huggins theory[5] predicts that the phase boundary between the single- and two-phase regions exhibits a maximum, so there is a critical temperature, T_c, above which a polymer–solvent system is miscible over the whole composition range. The critical temperature is related to the molecular mass by

$$\frac{1}{T_c} = \frac{1}{\Theta}\left[1 + \frac{1}{\Psi}\left(\frac{1}{x^{1/2}} + \frac{1}{2x}\right)\right] \tag{3}$$

$$x = (M/m)\beta$$

where M and m are the molecular masses of the polymer and monomer, respectively, and β is the ratio of the partial molar volumes of the monomer and solvent molecule in solution. Ψ is a positive constant known as the entropy parameter.

Phase measurements were carried out on a series of six linear hydrogenated polybutadienes with molecular masses from 10 000 to 200 000 g mol^{-1}. The solutions were made up in 5-mL volumetric flasks and suspended in an oil bath. The temperature was varied with an electronic controller, and the precipitation temperature, T_p, was ascertained by heating the solution until all of the polymer dissolved and then slowly cooling until the solution just went cloudy. The temperature T_d where the precipitate redissolved on heating was also noted.

Figure 1 shows the measured phase curves for the solvent biphenyl-h_{10} ($C_{12}H_{10}$). All the phase boundaries exhibit the characteristic maxima expected from the theory, and T_c was taken as the temperature at the maximum. At the critical composition the transition was very sharp, $T_d - T_p$ being less than 0.5 °C, and T_c could be established to 0.25 °C. Two precautionary tests were made with respect to the phase measurements. First, a number of compositions were repeated in small flat cells (those used in the neutron-scattering measurements); T_p was found to be the same as for the volumetric flasks. Second, one solution was left at 120 °C for 3 weeks and periodically checked for the phase behavior. T_p was found to vary by less than 0.1 °C, demonstrating the good stability of the polyethylene–biphenyl system.

To measure Θ for the deuterated solvent, we shortened the procedure. Assuming that the critical composition for the protonated and deuterated solvents would be the same, we prepared only one solution (at the critical composition) for each polymer sample. Since the maxima in the phase curves are quite broad, any shift in the critical compositions leads to only a small error in the measured value of T_c. The solutions in biphenyl-d_{10} were made up in small, 0.5-mL flasks, and five of the six linear polymers were measured.

In Figure 2 the results are plotted according to eq 3. The values of T_c for the deuterated solvent were consistently about 2 °C higher than those for the protonated solvent. This is in accord with similar observations on the polystyrene–cyclohexane system.[14]

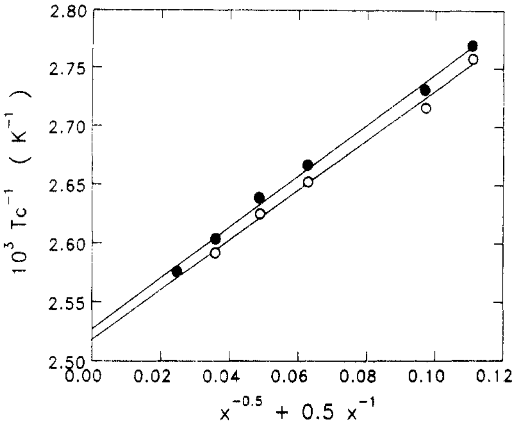

Figure 2. Determination of Θ by means of eq 3 with the critical precipitation temperatures of the hydrogenated polybutadienes in biphenyl-h_{10} (●) and biphenyl-d_{10} (○).

The straight lines in Figure 2 represent least-squares fits and yield the parameters Θ and Ψ for each solvent:

biphenyl-h_{10} $\Theta = 121.9 \pm 0.9$ °C

$\Psi = 1.19 \pm 0.04$

biphenyl-d_{10} $\Theta = 124.1 \pm 1.2$ °C

$\Psi = 1.19 \pm 0.05$

The Θ temperature in biphenyl-h_{10} is slightly lower than reported previously, but the entropy parameter is in good agreement with that from ref 11.

SANS Experiments. The neutron scattering was performed at the Institut Laue-Langevin, Grenoble, on the diffractometer D17.[15] For most of the experiments the instrument was set in exactly the same way as for the melt samples.[2] The geometry and 1.2-nm-wavelength neutrons transmitted by the 10% velocity selector provided a usable range of wavevector transfer of $0.13 \leq Q \leq 0.9$ nm^{-1}. Some small changes to the basic setup were made for two of the experiments, and these are described later.

The solutions were prepared in quartz disk cells, with 2-mm path lengths, which were then screwed into brass holders and inserted into the heating block as described previously. The temperature of the furnace could be maintained to 0.2 °C. To reduce the time required for the furnace to reach thermal equilibrium, the solutions were first heated in an identical heating block situated close to the diffractometer. The aluminum inserts holding the cells could then be transferred into the furnace with minimal heat loss.

The quantities of polymer and solvent were determined by mass, and concentrations in g cm^{-3} were calculated from the temperature-dependent densities of the solvents, which were measured to be

biphenyl-h_{10}

$$\rho(T)/\text{g cm}^{-3} = 0.992 - (8.35 \times 10^{-4})(T - 70), \quad 70 < T < 155\ ^\circ\text{C}$$

toluene-h_8

$$\rho(T)/\text{g cm}^{-3} = 0.867 - (9.54 \times 10^{-4})(T - 20), \quad 20 < T < 85\ ^\circ\text{C}$$

All the concentrations were in the range $0.001 < c < 0.02$ g cm^{-3}.

The experiments may be divided into three classes:

(i) Dilute Θ Solutions. One solution of very low concentration (0.001–0.004 g cm^{-3}) was run for each sample at a temperature of 125 °C. In addition to the solutions of protonated polymer in deuterated solvent, one sample of deuterated polymer was run in deuterated biphenyl. The purpose of this run was to check that the many-arm stars were uniformly deuterated.

(ii) Temperature Effects In Biphenyl-d_{10}. One 12-arm star sample, S12C, was chosen for a study of the change in solution properties with temperature near Θ. Four concentrations were prepared (0.28%, 0.71%, 1.45%, and 1.85% by mass) and measured at five different temperatures straddling the Θ temperature (100, 113, 125, 138, and 150 °C). For this series of measurements neutrons of wavelength 1.5 nm were used and the D17 detector was set back to 3.43 m. This arrangement was chosen to gain more information at the low-Q part of the spectrum.

(iii) Good Solvent. The measurements were made at 85 °C, which is well below the boiling point of toluene but sufficiently high so as to ensure complete solubility. Three or four concentrations were prepared for each sample, with the exception of the three-arm stars S3B, S3C, S3D, and S3E, for which no data were taken. All of the good solvent spectra were taken with a 25% velocity selector. Monte Carlo calculations showed that the resulting resolution broadening had no significant effect upon the scattering.

Measurements were also made on a sample of pure solvent, an empty cell, and a 1-mm-thick water sample. These runs were used to correct the scattering for the incoherent background and to obtain the coherent differential cross section in absolute units. The procedure followed was the same as that described by Ragnetti et al.[16]

Data Analysis. The coherent scattering at small Q for a dilute solution of flexible polymers was derived within the binary-contact approximation by Zimm:[17]

$$c^{-1}(\mathrm{d}\Sigma/\mathrm{d}\Omega) \approx KM_wP(Q)[1 - 2A_2cM_wP(Q)] \tag{4}$$

where $\mathrm{d}\Sigma/\mathrm{d}\Omega$ is the coherent partial differential cross section, and $P(Q)$ is the single chain scattering function normalized to unity at $Q = 0$. The constant K is a property of the polymer, solvent, and type of radiation. For neutron scattering K is given by

$$K = \frac{(b_p - \beta b_0)^2}{m^2}N_A \tag{5}$$

where b_p and b_0 are the coherent scattering lengths[18] of a monomer unit and a solvent molecule, respectively. We have determined β for protonated polybutadiene in both biphenyl-h_{10} and toluene-h_8 by finding the change in mass of a series of solutions of different concentration but constant volume. The results are

biphenyl-h_{10} $\beta = 0.113 \pm 0.004$

toluene-h_8 $\beta = 0.147 \pm 0.007$

To a very good approximation β should have the same values for the deuterated solvents too. From the known scattering lengths of the constituent nuclei we find K to be

biphenyl-d_{10} $K = 0.0093$ mol cm^2 g^{-2}

toluene-d_8 $K = 0.0074$ mol cm^2 g^{-2}

At the Flory temperature A_2 is expected to be very small, so the second term on the right of eq 4 can be neglected for dilute solutions. Thus, the coherent scattering is directly proportional to the single-chain scattering function. For the measurements in biphenyl at temperatures different from Θ and for the good solvent runs, A_2 is not zero, and $P(Q)$ must be determined from a series of concentrations extrapolated to $c = 0$. The method is straightforward; $P(Q)$ is obtained by linear regression of $c^{-1}\ \mathrm{d}\Sigma(Q)/\mathrm{d}\Omega$ as a function of c for each value of Q, and A_2 is found from the slope of the plot $c^{-1}\ \mathrm{d}\Sigma(0)/\mathrm{d}\Omega$ vs c. Figure 3 shows a typical series of concentrations on a Zimm plot together with the zero-concentration extrapolated curve.

To determine the radius of gyration of the polymer, we fitted the experimental $P(Q)$ curves with the Benoit scattering function[19] for Gaussian star polymers:

$$P_0(Q) = \frac{2}{y^2}\left[\frac{y}{f} - \frac{1}{f}(1 - e^{-y}) + \frac{(f-1)}{2f}(1 - e^{-y})^2\right] \tag{6}$$

$$y = \frac{f}{3f - 2}Q^2\langle S^2\rangle$$

As before with the melt data we found that eq 6 fitted the data extremely well, even for the good solvent where Gaussian statistics are not applicable. It must be assumed that although the polymers change their conformation from the unperturbed state, the expansion occurs relatively uniformly throughout the molecule.

In establishing the best fit we treated the background level as an adjustable parameter. We justify this procedure by the fol-

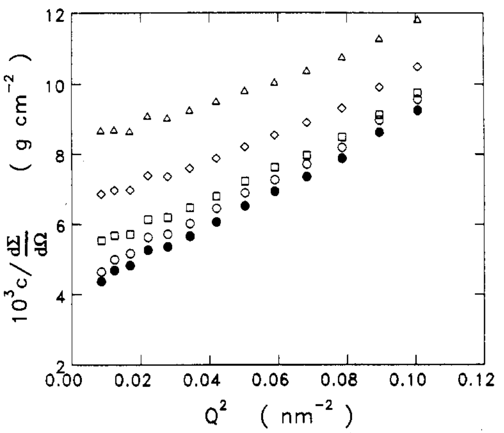

Figure 3. Zimm plot of the low-Q scattering from four solutions of the sample S12C. The concentrations are (in mg cm^{-3}) 12.1 (△), 7.6 (◇), 3.1 (□), 1.4 (○), and extrapolated zero concentration (●).

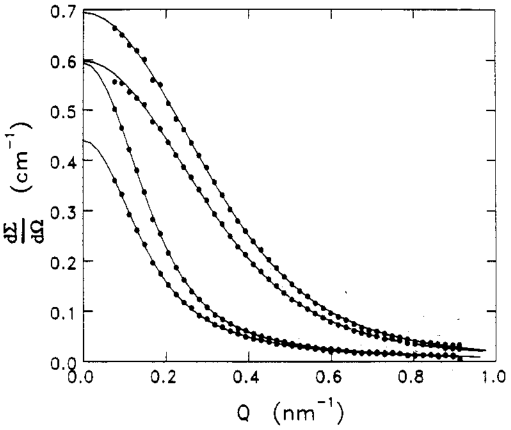

Figure 4. Coherent neutron-scattering spectra for the samples S2D, S4C, S12C, and S18A in dilute solution in the Θ solvent biphenyl-d_{10}. The continuous curves are least-squares fits to the Benoit function, eq 6.

lowing remarks: (i) The adjustment was typically a few percent of the incoherent signal and did not exceed the uncertainty in the background level calculated from the measured pure solvent scattering. (ii) The best-fit criterion provides a systematic way of treating all the polymer samples. The choice of obtaining $\langle S^2 \rangle$ from the best fit with variable background for both the melt and solution experiments eliminates the possibility of introducing any systematic differences between the two sets of results caused by an incorrect background subtraction in one of them. (iii) While changing the subtracted background may greatly improve the quality of the fit, it has relatively little effect on the values of the fitting parameters.

Figures 4 and 5 show representative fits to some of the Θ solution and good solvent spectra. With this method we found that we could determine the radius of gyration with a precision of better than 1%. However, we found that the values for the same sample measured on different visits to the ILL were not reproducible to this accuracy. The ratios of the radii of gyration of a set of melt samples which we used as standards *did* remain substantially the same. We therefore used these values to scale all the results on the same visit by a constant factor; these corrections were always less than 1.5% of the radius of gyration for the samples measured under identical conditions and were no more than 5% for the runs with poorer resolution.

Molecular Masses. With the neutron-scattering spectra calibrated in absolute units we were able to estimate the molecular masses from the extrapolated zero-Q intensity and the known constants K. In general the SANS values for M_w were in good agreement with those measured by gel permeation chromatography (GPC) on the original PBD stars. But for the 18-arm star, which was measured three times in solution, we obtained M_w values nearly twice that of the GPC result. The origin of this discrepancy is not understood, and a repeat of the GPC characterization on the saturated molecule confirmed the original measurement. In this paper we have used the same molecular masses as in the melt paper, namely, the GPC masses.

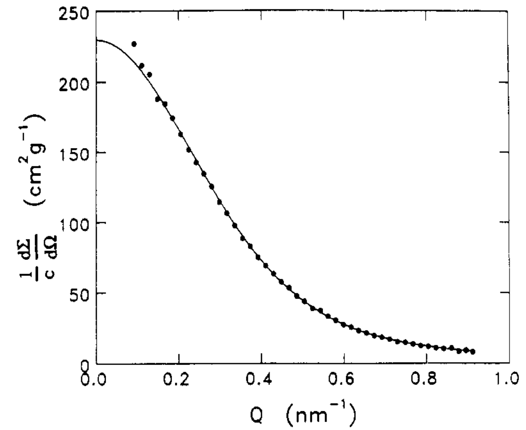

Figure 5. Benoit function fit to the extrapolated zero concentration spectrum of S12C in toluene-d_8.

Table I
Expansion Factors in Dilute Solution in Biphenyl-d_{10} at the Temperature Θ

sample	$M_w/10^3$	$\langle S^2 \rangle^{1/2}$/nm^a	α_{Θ_s}	mean^b α_{Θ_s}
linear				
S2A	11.2	4.78	1.023	
S2B	14.5	5.82	1.016	1.029 (7)
S2C	33.3	8.64	1.026	
S2D	55.0	10.26	1.050	
3 arm				
S3A	5.7	3.02	1.006	
S3B	7.1	3.45	1.043	1.023 (7)
S3C	9.2	3.98	1.023	
S3E	41.3	7.79	1.018	
4 arm				
S4A	9.9	4.04	1.033	
S4B	23.1	6.01	1.023	1.026 (3)
S4C	65.0	9.28	1.023	
12 arm				
S12A	9.3	3.15	1.082	
S12B	11.5	3.40	1.049	
S12C	29.3	4.77	1.056	1.059 (5)
S12D	68.9	6.70	1.052	
S12E	193.0	10.99	1.056	
18 arm				
S18A	23.9	4.60	1.073	1.073 (3)
DS18A^c	25.0	4.46	1.041	

^{a} The fitting error on $\langle S^2 \rangle^{1/2}$ is typically 0.5%. ^{b} The error in the mean, quoted in parentheses, corresponds to the scatter of the α_{Θ_s} values, except sample S18A, for which the error was estimated from the fitting error on the radii of gyration. ^{c} Deuterated 18-arm star.

Results and Discussion

Dilute Θ Solutions. In Table I we list the results for the radii of gyration measured at the Flory temperature. We assume that the swelling observed in the molten state is architectural in origin and is therefore present to the same degree in solution. Since the sizes of branched polymers in solution are influenced by both excluded volume and structural effects, the g parameter introduced in eq 1 is not a useful one for the comparison of the present results with excluded-volume theories. Accordingly, we define the expansion factor, α_s, by

$$\alpha_s^2 = \langle S^2 \rangle / \langle S^2 \rangle_m \qquad (7)$$

where $\langle S^2 \rangle$ is the mean-squared radius of gyration in the solution, and $\langle S^2 \rangle_m$ is the corresponding quantity in the melt. It is clear from the table that the polymers are expanded with respect to the molten state and that α_s

increases with the degree of branching but does not seem to depend on molecular mass. Two-parameter theory cannot account for this "anomalous" Θ expansion, and to gain some insight into the possible origins of the effect we must consider theories that include a third parameter.

The simplest calculations of α_s are mean-field theories based upon the smoothed density model, in which the local segment density at a particular point is taken to be the same as the average segment density at that distance from the center of mass. The distribution of segments about the center of mass is assumed Gaussian. Orofino and Flory[20] modified the smoothed density model calculation of α_s by retaining a term cubic in concentration in the free energy of the solution. This term may be interpreted as being due to three-body interactions between the polymer segments. Candau et al.[21] applied the same procedure to star polymers and deduced the result

$$\alpha_{\Theta_s}^8 - \alpha_{\Theta_s}^6 = A/g_0^3 \tag{8}$$

where A is a constant independent of temperature, functionality, and molecular mass.

A second three-parameter theory was developed later by Vrij.[22] This time the third parameter arises from the change in the mean segment density over the nonzero range of the segment–segment potential. The theory of Vrij was extended to the case of star polymers by Casassa[23] and predicts the Θ expansion to be

$$\alpha_{\Theta_s}^7 - \alpha_{\Theta_s}^5 = B/(M^{1/2}g_0^{5/2}) \tag{9}$$

where, once again, the constant B is independent of T, f, and M.

It is clear from Table I that the experimental data are not consistent with the theory of Vrij and Casassa, because no dependence of α_s on molecular mass is observed. The expression of Candau et al. *is* independent of molecular mass but has been criticized[24] because it gives an incorrect scaling dependence on f. The scaling theories developed by Daoud and Cotton[25] and by Birshtein and Zhulina[24] show that for large f we must have

$$\alpha_{\Theta_s} \sim f^{1/4} \tag{10}$$

whereas eq 8 gives $\alpha_{\Theta_s} \sim f^{3/8}$. The reason for this discrepancy is that Candau et al. have used the elastic free energy of a *linear chain* rather than that of a *star* to calculate the expansion factor.

To include the elastic free energy of a star, we must find an expression appropriate to star molecules for $P(S)$, the probability distribution function for the radius of gyration. We follow a similar approach to that of Flory and Fisk[26] and choose the closed form

$$P(S) \sim \left(\frac{S}{\langle S^2\rangle^{1/2}}\right)^{(7/G)-1} \exp\left(-\frac{7}{2G}\frac{S^2}{\langle S^2\rangle}\right) \tag{11}$$

The distribution function (11) can be made to have the same second and fourth moments as the exact moments for a Gaussian star[27] if G is given by

$$G = (15f - 14)/(3f - 2)^2 \tag{12}$$

Equations 11 and 12 reduce to the Flory–Fisk distribution for linear chains when f = 1 or 2, as required.

If the modified $P(S)$ is used in the mean-field calculation, then the expansion factor is given by

$$\alpha_s^5 - \alpha_s^3 = \frac{3^{5/2}G}{14g_0^{3/2}}z + \frac{2}{7}\frac{AG}{g_0^3\alpha_s^3} \tag{13}$$

where z is the conventional excluded-volume parameter.

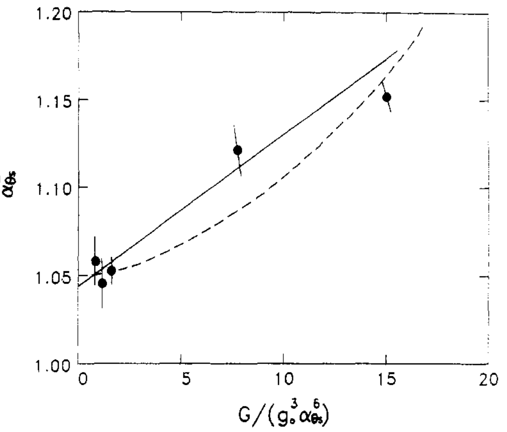

Figure 6. Mean Θ expansion factors for the five different star functionalities, plotted according to the three-parameter theory from which eq 15 was derived. The value $C = 0.15 \pm 0.02$ is obtained for the third parameter from the gradient and intercept of the straight line. The broken curve is the theory of Candau et al., eq 8, fitted to the data and plotted on the same axes.

The constant A (the same as in eq 8) is related to Orofino and Flory's third parameter, $C = (^1/_3) - \chi_2$, by

$$A = \frac{3^{5/2}}{(2\pi)^3}\frac{\bar{v}^3}{2v_0N_A^3}\left(\frac{M}{\langle S^2\rangle_\Theta}\right)^3_{\text{lin}} C \tag{14}$$

where $\bar{v}$ is the polymer partial specific volume and v_0 is the molecular volume of the solvent. The value of the coefficient of z in eq 13 is about 20% lower than the exact result calculated from first-order perturbation theory[4] but has the correct f dependence at large f. At the Θ temperature (z = 0), eq 13 gives the relation

$$\alpha_{\Theta_s}^8 - \alpha_{\Theta_s}^6 = \frac{2}{7}\frac{AG}{g_0^3} \tag{15}$$

which leads to a slower expansion with f than is predicted by the equation of Candau et al.; α_{Θ_s} now has the correct $f^{1/4}$ scaling form at large f.

To test eq 15, we plot $y = \alpha_{\Theta_s}^2$ against $x = G/(g_0^3\alpha_{\Theta_s}^6)$. If the relation in (15) holds, then we should obtain a straight line $y = mx + c$, with $m = 2A/7$ and $c = 1$. The experimental values are shown in Figure 6, and, within the limitations of the data, the points do lie on a straight line. The experimental gradient and intercept are $m_0 = 0.0081 \pm 0.0011$, and $c_0 = 1.045 \pm 0.008$.

However, according to eq 15 the intercept c is not a variable and must be unity. Since the melts and Θ solutions were run at different temperatures, we would expect the α_{Θ_s} values to include a multiplicative factor originating from the different thermal populations of trans and gauche bonds along the backbone.[28] The plot in Figure 6 remains a straight-line relation when each α_{Θ_s} value is multiplied by a constant, so if we take this constant to be $c_0^{-1/2}$ = 0.978, then c has the required value of unity, and the slope becomes $m = m_0/c_0^4$. This reduction of the α_{Θ_s} values by 2.2% is consistent within experimental error with the accepted temperature variation of the unperturbed dimensions of polyethylene.[28] Equating m_0/c_0^4 to $2A/7$ gives

$$A = 0.024 \pm 0.004$$

If the physical constants $\bar{v} = 1.31$ cm^3 g^{-1}, $v_0 = 2.70 \times 10^{-22}$ cm^3 (at 125 °C), and $\langle S^2\rangle_{\Theta,\text{lin}} = (0.195 \pm 0.008) \times 10^{-16}M_w$ cm^2 (deduced from the five linear samples at the Θ temperature), together with the above value of A, are inserted into eq 14, then the value of the third parameter is

$$C = 0.15 \pm 0.02 \tag{16}$$

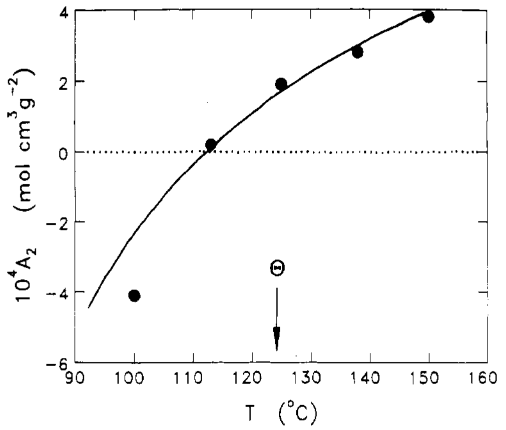

Figure 7. Temperature dependence of the second virial coefficient of the 12-arm star S12C. The temperature at which A_2 vanishes is clearly below Θ. The continuous curve was obtained by fitting eq 18 to the experimental data with Θ_{A_2} fixed at 112 °C.

Finally, with reference to the sample of deuterated S18A run at the Θ temperature we remark that the radius of gyration differs from the protonated sample by only 3%. We conclude that any nonuniformity of the deuteration within the molecule is very small and note that if the outside of the star were more heavily labeled than the inside, then the apparent melt size would be larger than the actual size. Correction for this effect would yield slightly *increased* expansion factors for the many-arm stars.

Measurements in Biphenyl as a Function of Temperature. The second virial coefficients for the 12-arm star S12C are shown in Figure 7 as a function of temperature. Over the same range of temperature the variation in radius of gyration was less than 0.2 nm.

The temperature at which A_2 vanishes is significantly lower than Θ, in accord with the earlier experiments on stars:

$$\Theta_{A_2} = 112.0 \pm 0.5\ °\mathrm{C} \qquad (17)$$

Both of the three-parameter approaches discussed in the preceding section have been used to derive expressions for $A_2(T)$. The order $\Theta < \Theta_{A_2}$ arises from the theory of Vrij, and this is clearly at variance with all the experimental results. The theory of Orofino and Flory, on the other hand, yields the equation

$$A_2(T) = \frac{16\pi}{3^{3/2}} \frac{N_A \langle S^2\rangle^{3/2}}{M^2} \ln\left[1 + \frac{3^{3/2}\pi^{1/2}}{4}\bar{z} + X_2\right] \qquad (18)$$

in which

$$X_2 = \pi^{3/2}\left(\frac{3}{4\pi}\right)^4 \frac{\bar{v}^3}{v_0 N_A{}^3}\left(\frac{M}{\langle S^2\rangle}\right)^3 C \qquad (19a)$$

$$\bar{z} = \frac{z}{\alpha_{0s}{}^3} = \frac{1}{4\pi^{3/2}} \frac{\bar{v}^2}{v_0 N_A{}^2}\left(\frac{M}{\langle S^2\rangle}\right)^{3/2} \Psi(1 - \Theta/T)M^{1/2} \qquad (19b)$$

$$\alpha_{0s}{}^2 = \langle S^2\rangle / \langle S^2\rangle_0 \qquad (19c)$$

$\langle S^2\rangle_0$ being the mean-squared radius of gyration for an unperturbed, random-walk chain. It follows from eq 19 that Θ and Θ_{A_2} are related by

$$\frac{\Theta}{\Theta_{A_2}} - 1 = \frac{3^{5/2}}{16\pi^{3/2}} \frac{\bar{v}}{\Psi N_A} \frac{1}{M^{1/2}}\left(\frac{M}{\langle S^2\rangle}\right)^{3/2} C \qquad (20)$$

Equation 20 implies the order $\Theta_{A_2} < \Theta$, if C is positive. When the values of Θ, Θ_{A_2}, the radius of gyration, and the molecular mass of S12C are inserted into eq 20, the third parameter is found to be

$$C = (0.31 \pm 0.03)\Psi \qquad (21)$$

In the mean-field theory the entropy parameter Ψ is independent of branching and appears both in the expressions for $A_2(T)$ and for the phase curves, eq 3. However, it has been observed[13,29] with the polystyrene/cyclohexane system that the experimental values of Ψ derived from each of these measurements are rather different. It is consistent with the present analysis to take Ψ from the $A_2(T)$ measurements, and the continuous curve through the points in Figure 7 is a fit of eq 18 to the data with Θ_{A_2} fixed at the result (17). The value of Ψ from this fit is

$$\Psi = 0.55 \pm 0.05 \qquad (22)$$

(This differs considerably from the value of 1.19 from the phase measurements and so confirms the earlier observations.) The combination of results (21) and (22) gives for the third parameter

$$C = 0.17 \pm 0.02 \qquad (23)$$

The good agreement between the values in (16) and (23) indicates a consistency between the intra- and intermolecular theories, which provides strong evidence for a ternary interaction model.

Table II
Expansion Factors and Second Virial Coefficients Measured in Toluene-d_8

sample	α_s	10^4A_2/mol cm^3 g^{-2}
linear		
S2A	1.11	16.0[a]
S2B	1.09	14.5
S2C	1.13	11.8
S2D	1.11	10.0
S2E	1.24	9.4
3 arm		
S3A	1.15	20.0
4 arm		
S4A	1.10	12.7
S4B	1.10	11.3
S4C	1.15	9.0
12 arm		
S12A	1.09	10.2
S12B	1.06	11.7
S12C	1.14	8.3
S12D	1.20	7.1
S12E	1.32	4.6
18 arm		
S18A	1.16	8.5

[a] We estimate the uncertainty in the values of A_2 to be about 10%.

Good Solvent Results. The expansion factors and second virial coefficients measured in toluene-d_8 are listed in Table II. We note first of all that there is a tendency for the many-arm stars to be more swollen and to have a smaller second virial coefficient than linear samples of the same mass. These general observations are in qualitative agreement with two-parameter theory.

One of the fundamental aspects of two-parameter theory is that the excluded volume parameter contains no dependence upon the polymer architecture, so should be equal for all molecules of a given mass. Specifically, z is proportional to the square root of the mass:

$$z = kM^{1/2} \qquad (24)$$

A good test of theory is to calculate z from a measured quantity and check for the dependence on molecular mass.

There are many possible versions of the two-parameter theory that might be tested in this way. We choose only

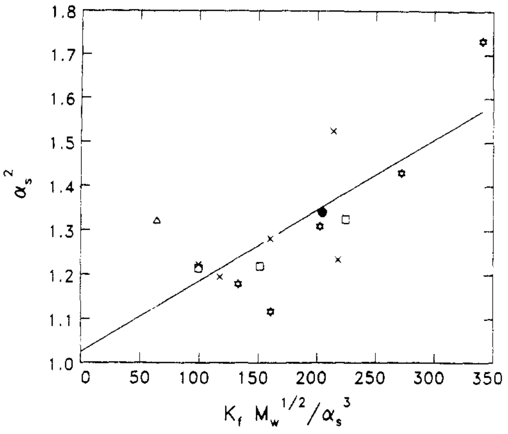

Figure 8. Test of the molecular mass dependence of the expansion factor of the molecules in the good solvent toluene-d_8. The symbols are as follows: $f = 2$ (×), $f = 3$ (△), $f = 4$ (□), $f = 12$ (☆), $f = 18$ (●). The plot assumes the two-parameter result, eq 24, and shows that there is uniform mixing of points for all functionalities and that the scatter is consistent with the proportionality predicted by the smoothed density model. From the linear fit we deduce that the excluded-volume parameter $z = (0.0015 \pm 0.0004)M^{1/2}$.

one, the smoothed density model, because the data are not precise enough to resolve the subtle differences between all the theories and because when modified to agree with first-order perturbation theory at small excluded volume this theory has been very successful in describing linear polymers in dilute solution. The smoothed density model results for α_s and A_2 for star polymers are

$$\alpha_s^5 - \alpha_s^3 = K_f z \qquad (25)$$

$$A_2 = \frac{2\pi^{3/2}N_A\langle S^2\rangle^{3/2}}{M^2 g_0^{3/2}C_f}\ln(1 + 2C_f\bar{z}) \qquad (26)$$

where K_f and C_f are the first-order perturbation theory coefficients for stars.[4] Equation 25 is numerically very similar to eq 13 if only the two-body term is retained in the latter.

In Figure 8 the measured expansion factors have been plotted to test eq 25. Once again the plot remains linear when each value of α_s is multiplied by a constant factor. Although the points are too scattered to establish eq 25 unequivocally, there are no obvious trends with functionality, and the data are consistent with a linear relationship. A linear regression fit gives a value for k in eq 24, independent of branching, of

$$k = 0.0015 \pm 0.0004\ \mathrm{mol}^{1/2}\ \mathrm{g}^{-1/2} \qquad (27)$$

Before carrying out a similar analysis for the second virial coefficient we may note that the definition of $\bar{z}$, eq 19b, involves α_{0s} (the swelling relative to the random-walk size) rather than α_s (the swelling relative to the melt size) as was used in the expression for the expansion factor, eq 7. This is appropriate because the mean-field calculation of A_2 assumes a monomer distribution derived from the random-walk model, whereas the molecules in the present study are swollen in comparison to random-walk stars. Following the precedent of earlier investigators,[4] we have applied the same closed form for A_2 to our swollen polymers but replaced the random-walk radius of gyration by the measured radius of gyration. Physically this corresponds to the assumption that the molecules are expanded uniformly from the random-walk state.

In Figure 9 we plot the values of z derived by means of eq 26 from the experimental data for A_2 and $\langle S^2\rangle$ and the calculated random-walk sizes. Once again the relationship is independent of functionality and consistent with z being proportional to $M_w^{1/2}$. From the straight line

$$k = 0.0015 \pm 0.0002\ \mathrm{mol}^{1/2}\ \mathrm{g}^{-1/2} \qquad (28)$$

This is in good agreement with the k value derived from the expansion factor measurements.

A good model for polymers in solution must be able to describe both inter- and intramolecular interactions simultaneously. The results (27) and (28) indicate that the smoothed density model is complete in this way. However, we can illustrate more directly the self-consistency of the inter- and intramolecular results by eliminating the phenomenological parameter z and expressing A_2 directly in terms of α_s. The amalgamation of eq 25 and 26 yields

$$y = \ln(1 + r) \qquad (29)$$

where we have defined the dimensionless quantities

$$y = \frac{M^2 g_0^{3/2}C_f A_2}{2\pi^{3/2}N_A\langle S^2\rangle^{3/2}}$$

$$r = \frac{2C_f}{K_f}(\alpha_s^2 - 1)\left(\frac{\langle S^2\rangle_0}{\langle S^2\rangle_m}\right)^{3/2}$$

In Figure 10 we plot y against $\ln(1 + r)$, which according

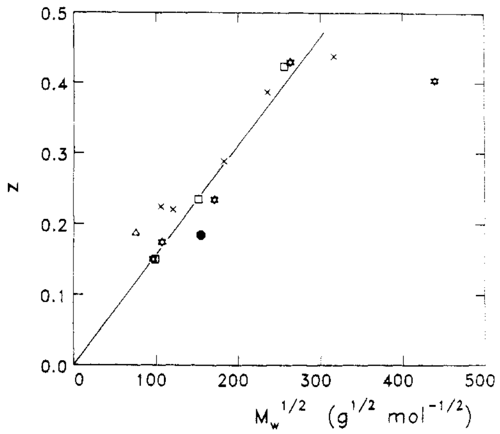

Figure 9. Molecular mass dependence of z derived from the measured second virial coefficients in toluene-d_8 by means of the smoothed density model result, eq 25. The functionalities are uniformly distributed, and the points are consistent with a straight line through the origin. From the gradient of the fit we find $z = (0.0015 \pm 0.0002)M^{1/2}$. The symbols are as in Figure 8.

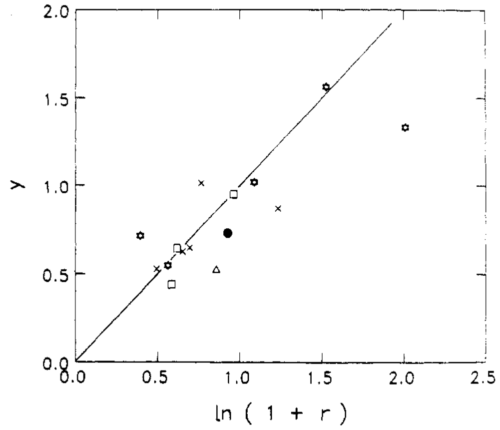

Figure 10. Test of the correlation between the intra- and intermolecular smoothed density model results as determined by the measured expansion factors and radii of gyration of the linear and star polymers. The straight line has gradient unity, as predicted by eq 28, and once again there is a uniform mixing of functionalities. The symbols are as in Figure 8.

to the smoothed density model should be a straight line of gradient unity passing through the origin for all functionalities. Within the scatter of the data this prediction is confirmed.

We have also tried to compare our good solvent data with the recent renormalization group (RG) theory calculations of Douglas and Freed.[30] These authors have identified three representations of RG theory for polymers. One is in terms of a "natural" crossover scaling variable η, and the other two are in terms of a new crossover variable which reduces to the excluded volume parameter $\bar{z}$ of traditional two-parameter theory in the limit of small excluded volume. The latter two representations differ in that the first-order coefficients are derived respectively from first-order RG theory and from traditional perturbation theory. We find, however, that there is a discrepancy between the coefficients in these two representations that becomes steadily worse as the number of arms increases. Also, the excluded volume limiting ratios g^*, y^*, and $g_{A_2}^*$ (the ratio of the A_2 values of a star and a linear molecule) predicted by the three representations are in serious disagreement for large f. It is likely that the neglect of higher order terms in the ϵ expansion is responsible for these differences.

Thus, it is not clear which of the RG theory representations is the most appropriate for star polymers, and when we made plots equivalent to Figures 8–10 we usually found that the data did not fit onto universal curves. We conclude that first-order RG theory is not sufficiently accurate to describe the statistics of star polymers and that calculations must be taken to higher orders to bring the three representations into line.

Conclusions

We can summarize the findings of this work as follows:

At the Θ temperature the behavior of star polymers in dilute solution can be described by a three-parameter theory based on the smoothed density model in which the third parameter corresponds to ternary interactions between the segments.

In good solvents the traditional two-parameter models are sufficient to explain the experimental results.

Care must be taken when the theories are applied to cases where the molecules are affected by factors of structural origin. The excluded-volume expansion must be referred to the melt size and not to the theoretical unperturbed size calculated from the size–mass relationship for linear polymers.

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References and Notes

(1) Morton, M.; Helminiak, T. E.; Gadkary, S. D.; Bueche, F. *J. Polym. Sci.* **1962**, *57*, 471.
(2) Horton, J. C.; Squires, G. L.; Boothroyd, A. T.; Fetters, L. J.; Rennie, A. R.; Glinka, C. J.; Robinson, R. A. *Macromolecules* **1989**, *22*, 681.
(3) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(4) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(5) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(6) Roovers, J. E. L.; Bywater, S. *Macromolecules* **1974**, *7*, 443.
(7) Bauer, B. J.; Hadjichristidis, N.; Fetters, L. J.; Roovers, J. E. L. *J. Am. Chem. Soc.* **1980**, *102*, 2410.
(8) Huber, K.; Burchard, W.; Fetters, L. J. *Macromolecules* **1984**, *17*, 541.
(9) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(10) Stacy, C. J.; Arnett, R. L. *J. Phys. Chem.* **1965**, *69*, 3109.
(11) Nakajima, A.; Hamada, F.; Hayashi, S. *J. Polym. Sci., Part C* **1966**, *15*, 285.
(12) Rachapudy, H.; Smith, G. G.; Raju, V. R.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1211.
(13) Shultz, A. R.; Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 4760.
(14) Strazielle, C.; Benoit, H. *Macromolecules* **1975**, *8*, 203.
(15) Guide to Neutron Research Facilities at the ILL, Dec 1988; pp 34.
(16) Ragnetti, M.; Geiser, D.; Höcker, H.; Oberthür, R. C. *Makromol. Chem.* **1985**, *186*, 1701.
(17) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1093.
(18) Lovesey, S. W. *Theory of Neutron Scattering from Condensed Matter*; Oxford University Press: New York, 1984; Vol. 1.
(19) Benoit, H. *J. Polym. Sci.* **1953**, *11*, 507.
(20) Orofino, T. A.; Flory, P. J. *J. Chem. Phys.* **1957**, *26*, 1067.
(21) Candau, F.; Rempp, P.; Benoit, H. *Macromolecules* **1972**, *5*, 627.
(22) Vrij, A. *J. Polym. Sci., Part A2* **1969**, *7*, 1627.
(23) Casassa, E. F. *J. Polym. Sci., Part A2* **1970**, *8*, 1651.
(24) Birshtein, T. M.; Zhulina, E. B. *Polymer* **1984**, *25*, 1453.
(25) Daoud, M.; Cotton, J.-P. *J. Phys. (Paris)* **1982**, *43*, 531.
(26) Flory, P. J.; Fisk, S. *J. Chem. Phys.* **1966**, *44*, 2243.
(27) Zimm, B. H.; Kilb, R. W. *J. Polym. Sci.* **1959**, *37*, 19.
(28) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Wiley: New York, 1969.
(29) Berry, G. C. *J. Polym. Sci., Part A2*, **1971**, *9*, 687.
(30) Douglas, J. F.; Freed, K. F. *Macromolecules* **1983**, *16*, 1800; **1984**, *17*, 1854; **1984**, *17*, 2344.