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observed in the melting temperatures of these polymers should be attributed to the enthalpy rather than the entropy. It should be pointed out that since the sulfur atom has a much higher polarizability and interatomic attraction than the oxygen atom, the enthalpy of fusion of PTCMT should be higher than that of POCMT.[32] Molecular packing of the chains in the crystal that enhances S...S interactions would greatly increase the enthalpy of fusion of the alicyclic poly(thioformal).

Registry No. PTCMT (SRU), 99113-59-4; (*trans*-1,4-bis(mercaptomethyl)cyclohexane)·(paraformaldehyde) (copolymer), 99113-61-8.

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Remarks on A_2, Hydrodynamic Coil Expansion, and Concentration Dependence of the Diffusion Coefficient for Polystyrene in Toluene

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ABSTRACT: The approximation of the second virial coefficient by its expression for a hard sphere with a radius equal to the hydrodynamic radius R_H is investigated and shown to hold even for low molecular weights. The experimentally observed hydrodynamic expansion factor $\alpha_H^{\mathrm{exptl}} \equiv R_H(T)/R_H(\Theta)$, where $R_H(T)$ and $R_H(\Theta)$ are the hydrodynamic effective radii in toluene (T) and cyclohexane (Θ), is found to decrease below unity at low molecular weight. This effect is interpreted by the theory of Yamakawa and Fujii as being due to the difference in the characteristic parameters of the linear mass density m_L, the Kuhn length l_K, and the effective chain thickness d. The concentration dependence of the diffusion coefficient is in the high molecular weight region satisfactorily expressed by the parameter X in the theories of Akcasu and Benmouna and of Yamakawa. The theory of Pyun and Fixman is also considered and shown to give good agreement if the function $\kappa(A)$ is interpreted properly.

Relation between A_2 and Hydrodynamic Volume

It is often convenient to investigate the molecular weight and temperature dependence of the second virial coefficient A_2 in terms of reduced variables. A commonly used example is the interpenetration function $\psi(\bar{z})$ defined by

$$A_2 = 4N_A\pi^{3/2}(\langle S^2\rangle^{3/2}/M^2)\psi(\bar{z}) \qquad (1)$$

where the symbols have their usual meaning. Another example is the effective hard-sphere radius r defined by[1,2]

$$A_2M^2/N_A = 16\pi r^3/3 \qquad (2)$$

In the study of the concentration dependence of the diffusion coefficient, it is often convenient to introduce the ratio $X = r/R_H$, with R_H the hydrodynamic radius of an isolated chain, by the following equation:[3,4]

$$(A_2M^2/N_A)/V_H = 4X^3 \qquad (3)$$

with $V_H = (4\pi/3)R_H^3$ the hydrodynamic volume. The dimensionless variables $\psi(\bar{z})$ and X are then related to each other through

$$X = (3\pi^{1/2}/4)^{1/3}\rho(\psi(\bar{z}))^{1/3} \qquad (4)$$

where

$$\rho = \langle S^2\rangle^{1/2}/R_H \qquad (5)$$

In these equations R_H is measured via D_z by quasi-elastic

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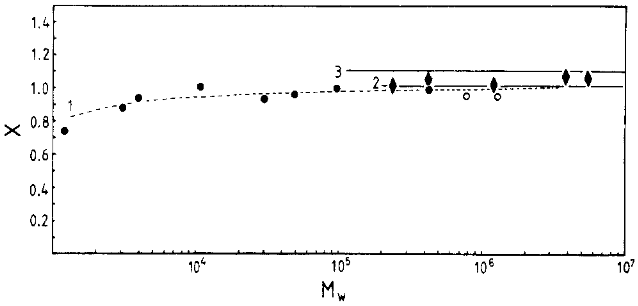

Figure 1. Molecular weight dependence of the parameter $X \equiv r/R_H$ in toluene, where r is defined by eq 2 and $R_H \equiv (kT/6\pi\eta D_z^0)$ is the hydrodynamic radius: (1) experimental dependence on M_w consistent with curve PF in Figure 5 (see text); (2) mean value of experimental data for $M_w > 2 \times 10^5$; (3) theoretical prediction by Barret[5] and Oono and Freed;[6] (●) our measurements; (○) experimental data of Bantle et al.;[11] (◆) experimental data of Varma et al.[27]

light scattering and $\langle S^2 \rangle$ and A_2 are measured by static light scattering and small-angle neutron scattering.

The advantage of introducing the dimensionless variables $\psi(\bar{z})$ and X is that they depend on temperature and molecular weight less sensitively than A_2 itself and hence lend themselves better to approximations.

The large-$\bar{z}$ limit of X can be estimated in terms of the asymptotic values of ρ and ψ. The good solvent limit of ρ was calculated by Akcasu and Benmouna[3] as 1.86 using the fully swollen Gaussian chain model (maximum excluded volume effect). From the tables provided recently by Barrett[5] for the expansion factors α_H $(\equiv R_H(T)/R_H(\Theta))$ and α_S $(\equiv(\langle S_T^2 \rangle / \langle S_\Theta^2 \rangle)^{1/2})$ (where T and Θ refer to toluene and cyclohexane, respectively) obtained from computer results and analytical extrapolation formulas, we calculated the asymptotic value of ρ as 1.637. For ψ, Oono and Freed[6] predicted a value of 0.231, whereas Witten and Schäfer[7] calculated 0.268. Using $\rho = 1.637$ and $\psi = 0.231$, one obtains from eq 4 the asymptotic value $X = 1.104$. The variation of X with molecular weight of polystyrene (PS) in various good solvents is depicted in Figure 1; the experimental values of X vary from approximately 0.92 to 1.01 for a wider range of molecular weights. Apparently X is about unity, both theoretically and experimentally, in a wide molecular weight range in good solvents, indicating that the equivalent hard-sphere radius r is close to the hydrodynamic radius. This conclusion was also pointed out by Adam and Delsanti[8] and by Han and Akcasu.[9] To demonstrate this point directly we calculated A_2 from eq 2 using $r = R_H$ and compared it with the measured A_2 for a large molecular weight range of PS in toluene. The hydrodynamic radius R_H was inferred from the measured diffusion coefficient D in the experiments by Huber et al.,[10] Bantle et al.,[11] and Raczek,[16] using the Stokes–Einstein relationship $R_H = kT/(6\pi\eta D_z)$, with k the Boltzmann factor and η the solvent viscosity. The points in Figure 2 depicted with different symbols represent the calculated A_2 values under the assumption $r = R_H$. A satisfactory agreement with the experimental A_2 data is observed even in the range of short chains, where chain stiffness plays an important role and where A_2 is no longer represented by a simple exponential law

$$A_2 \sim M^{-\nu_A} \tag{6}$$

As is demonstrated by the solid curve in Figure 2, experimental A_2 behavior in toluene exhibits an asymptotic exponent of $\nu_A = 0.2$ that increases for lower M_w. The asymptotic exponent $\nu_A = 0.2$ is consistent with eq 3.

The physical mechanism for the observed $X \approx 1$ can be attributed according to eq 4 to a compensation of the change in $\psi(\bar{z})$, which increases toward lower molecular weights, by the experimentally observed decrease in ρ when M_w is decreased (Table I).

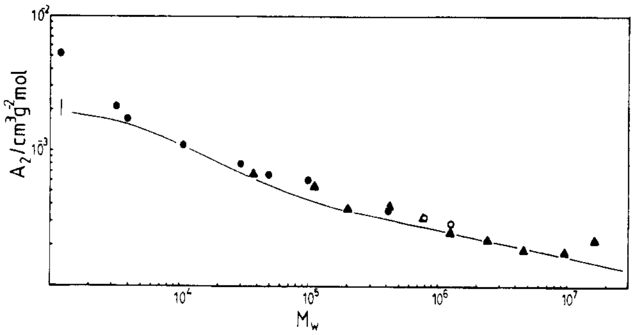

Figure 2. Molecular weight dependence of the second virial coefficient in toluene at 20 and 25 °C. Solid line represents experimental data from static light and neutron scattering.[10] The points are derived from eq 2 assuming $r = R_H$. Symbols represent the following data: (●) our measurements; (○) Bantle et al.;[11] (▲) Razcek.[16]

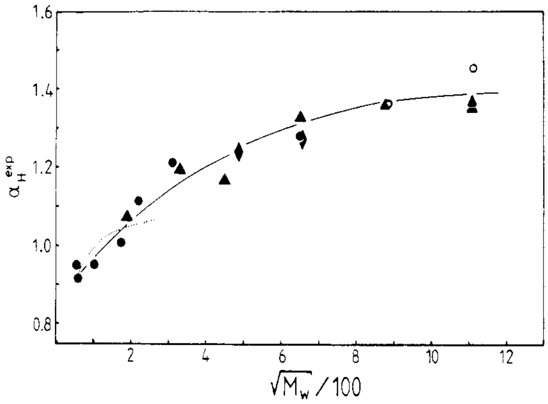

Figure 3. $\alpha_H^{\mathrm{exptl}} \equiv R_H(T)/R_H(\Theta)$, where T refers to toluene at 20 and 30 °C and Θ to cyclohexane at 35 °C. The dotted line was calculated with the YF theory, assuming $m_L(\Theta) = 390$ (g/mol nm), $l_K(\Theta) = 2$ nm, $d(\Theta) = 0.83$ nm and $m_L(T) = 450$ (g/mol nm), $l_K = 2.9$ nm, $d(T) = 0.62$ nm. For details see text. Symbols as in Figures 1 and 2.

Table I
X, $\psi(\bar{z})$, ρ, k^*_D, and k^*_f Calculated from Experimental Results[10] of PS in Toluene at 20 °C[a]

M_w	X	$\psi(\bar{z})$	ρ	k^*_D	k^*_f
1 200	0.74		0.73	−0.51	3.1
3 100	0.88	0.392	1.09	0.0	4.3
4 000	0.94	0.367	1.21	0.0	6.8
10 700	1.006	0.256	1.44	0.58	7.2
21 600		0.185			
30 200	0.929			0.86	5.4
48 500	0.957			1.25	5.6
97 000	0.996	0.244	1.45	1.42	6.4
424 000	0.993	0.214	1.51	1.87	5.9

[a] For comparison we add here the experimental values for ψ (∞) by Cotton[39] and Miyaki et al.,[40] who found 0.245 and 0.22, respectively.

Expansion Factor for R_H

Figure 3 exhibits the experimentally determined expansion factor of PS in toluene

$$\alpha_H^{\mathrm{exptl}} = R_H(T)/R_H(\Theta) \tag{7}$$

for the hydrodynamic radius R_H. The latter is calculated from the z-averaged experimental diffusion coefficient using the Stokes–Einstein relation where the unmodified solvent viscosity is used. It is noted that $\alpha_H^{\mathrm{exptl}}$ becomes

Table II
Diffusion Coefficients in the Low Molecular Weight Range according to Fits with Various Sets of Parameters m_L, l_K, and d in Comparison with Experimental Data of PS in Toluene

	$D/10^{-7}$, cm^2 s^{-1}				
	d = 0.62 nm			d = 0.83 nm	
M_w	l_K = 2.9 nm m_L = 450	l_K = 2.0 nm m_L = 390	exptl data	l_K = 2.9 nm m_L = 450	l_K = 2.0 nm m_L = 390
3100	29.28	29.08	28.5	26.72	26.80
4000	25.44	25.54	25.8	23.43	23.75
10700	14.86	15.48	15.1	14.08	14.78

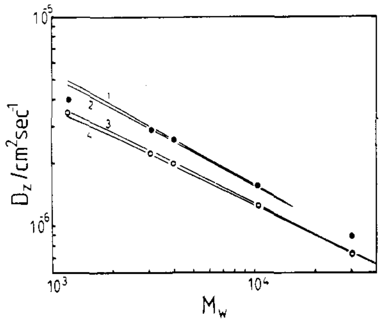

Figure 4. Translational diffusion coefficient for very low molecular weights of PS in toluene (●) and cyclohexane at T = 35 °C (○). Solid lines are calculated by the YF theory. 1 and 2 show the variation of the thickness between d = 0.59 and 0.65 nm in toluene with m_L = 450 (g/mol nm) and l_K = 2.9 nm; 3 and 4 show the variation of the thickness between d = 0.77 and 0.88 nm in cyclohexane with m_L = 390 (g/mol nm) and l_K = 2 nm.

less than unity for molecular weights $M_w < 20000$. Similar behavior was observed with poly(methyl methacrylate).[17] This unexpected result may be explained in terms of the wormlike chain model suggested by Yamakawa and Fujii[12] (YF). In this model m_L, d, and l_K are three independent parameters for a given solvent. As is shown in Figure 4, under Θ conditions a satisfactory description of the experiment can be achieved with values for the thickness d between 0.77 and 0.88 nm,[10] using m_L = 390 (g/mol nm) and l_K = 2 nm from Norisuye et al.[13] These numbers in general may be different under Θ conditions and in good solvents.

To interpret the molecular weight dependence of the chain properties such as $\langle S^2\rangle$ and R_H in toluene, these parameters again were estimated by using the YF theory of wormlike chains. Since this theory is only applicable to Θ systems, we have to assume that excluded volume effects are negligible for molecular weights up to 15 000. With this assumption, one can calculate R_H once the three parameters m_L, l_K, and d are specified.

A systematic curve fitting with three parameters in a restricted molecular weight range does not seem sensible to us. We therefore proceeded choosing reasonable values for m_L and l_K and estimating d. First the values of m_L =450 (g/mol nm) and l_K = 2.9 nm were used, which were estimated as reasonable numbers to interpret the A_2 vs. M_w data in an eariler work.[10] As is shown in Table II, $d \simeq 0.62$ nm provides good agreement between calculated and measured D_z. It is worth noting that agreement in toluene is achieved also with the Θ values of m_L and l_K but with a lower value of d = 0.62 nm. Apparently the thickness of the cylinder in the YF theory is sensitive to the quality of solvent. In this estimation we neglected the point in toluene for the lowest molecular weight.

In conclusion we consider the two sets of parameters m_L = 450 (g/mol nm), l_K = 2.9 nm, and d = 0.62 nm for the system polystyrene in toluene (set Tol) and m_L = 390 (g/mol nm), l_K = 2.0 nm, and d = 0.83 nm for the Θ system polystyrene in cyclohexane (set Θ) as reasonable values. Although these values represent the experimental data satisfactorily, they should be regarded as a display for the correct qualitative tendencies only.

As a further check, we calculated the draining parameter $h^* = \zeta/(b\pi(12\pi)^{1/2})$, where ζ is the friction coefficient of a bead of length b, entering in the Kirkwood–Riseman theory, from the discrete chain model, using

$$h^* = (3/\pi)^{1/2}(3/4)^{1/3}(d/2l_K)^{2/3} \qquad (8)$$

which we had proposed in an ealier communication to relate the parameters of continuous and discrete chain models.[37] In cyclohexane (Θ) we obtained $h^*(\Theta) = 0.311$ using the set Θ, whereas in toluene we obtain $h^*(T) = 0.200$ with the set Tol. The ratio of h^* in Θ and good solvents follows as $h^*(T)/h^*(\Theta) = 0.64$.[28] This result is consistent with the ratio $h^*(T)/h^*(\Theta) = 0.6$ calculated from values for $h^*(T)$ and $h^*(\Theta)$ reported by Johnson et al.[14] and Ferry[15] (however, see ref 41).

Last, we calculated the molecular weight dependence of $\alpha_{YF} \equiv R(T)_{YF}/R_{YF}(\Theta)$ on the basis of the YF theory, using these two sets, set Θ and set Tol, respecitvely, up to M_w = 15 000, neglecting the effect of excluded volume. As is shown in Figure 3, $\alpha_H^{\text{exptl}} < 1$ is now predictable by the YF theory. The observed decrease of α_H^{exptl} below 1 in the very low molecular weight range evidently arises from the difference in the two sets of parameters m_L, l_K, and d. Again the lowest molecular weight of 1200 was not taken into account.

Molecular Weight Dependence of k_D

The concentration dependence of the translational diffusion coefficient D_c and the friction coefficient f_c can for low concentrations be described by the two linear relationships

$$D_c = D_z(1 + k_D c) \qquad (9)$$

$$f_c = f_0(1 + k_f c) \qquad (10)$$

The coefficient k_D is related to A_2 and k_f by irreversible thermodynamics as

$$k_f = 2A_2M_w - k_D - v_2 \qquad (11)$$

where v_2 is the partial molar volume of the solvent.

All quantities besides v_2 on the right of eq 11 are measurable by static and dynamic light scattering. For k_f various theories have been derived. In the hard-sphere limit $2A_2M \sim V_HN_A/M_w$, and thus also k_f and k_D are proportional to the ratio N_AV_H/M_w. This suggests that the reduced coefficients

$$k^*_D \equiv k_D(M_w/N_AV_H) \qquad (12a)$$

$$k^*_f \equiv k_f(M_w/N_AV_H) \qquad (12b)$$

should be considered rather than the coefficients themselves. Since A_2 is conveniently expressed by the parameter $X \equiv (V_m/V_H)^{1/3}$ we rewrite k^*_f and k^*_D in terms of this

Table III
Theoretical Expressions for k^*_f and k^*_D according to PF,[18] Y,[19] and AB[3]

k^*_f	$k^*_f{}^a$	k^*_D	$k^*_D{}^a$	ref
$7.16 - \kappa(A)$	7.16	$8X^3 - (7.16 - \kappa(A))$	1.18	18
$4.8X^3 + 1$	5.94	$3.2X^3 - 1$	2.34	19
$6X^2$	6.26	$8X^3 - 6X^2$	2.17	3
	6.33		2.02	exptl[b]

[a] Values for k^*_f and k^*_D calculated with the experimentally found asymptote $X = 1.014$ and $\kappa(A) = 0$. [b] Values calculated from experimental data of Figures 5 and 6 in the M_w range $2 \times 10^5 - 10^7$.

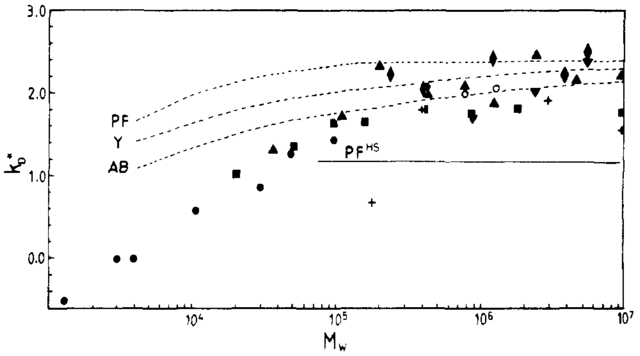

Figure 5. Molecular weight dependence of k^*_D of PS in toluene in various good solvents (eq 12a) according to measurements of Huber et al.[10] (●), Bantle et al.[11] (○), Varma et al.[27]. (◆), Raczek et al.[16] (▲), Mandema et al.[31] (■), Nemoto et al.[32] (▼), and Yu et al.[33] (+). Theories: Yamakawa[19] (Y); Pyun and Fixman[18] (PF); Akcasu and Benmouna[3] (AB); hard-sphere limit by Pyun and Fixman[18] (PF^{HS}) using 1.014 as an asymptotic value for X.

parameter. This can be performed easily for most of the theories with the exception of the theory of Pyun and Fixman[18] (PF). In this theory a function $\kappa(A)$ is introduced, which is given by eq 13

$$\kappa(A) = 6.39/(A + 2.6)^{1/2} \tag{13}$$

with

$$A = 3n^2\beta/8\pi R_H{}^3 \tag{14}$$

where n is the degree of polymerization and β the excluded volume integral for a monomeric unit. Nevertheless it is possible to express A as a function of X graphically within a given model, e.g., the uniform-density sphere model as was outlined previously.[4]

Here we calculate A directly, using experimental results for the geometric coil expansion α_S, which involves the crucial parameter β appearing in eq 14. A similar way to determine A was chosen by Van den Berg et al.[38] For β, a value of 0.04 nm^3 has been used,[25] which yields $\kappa(A) = 1.22$ if $M_w = 8 \times 10^6$. This still is significantly higher than 0.

The relationships for k^*_D and k^*_f are listed in Table III. This table also contains in columns 2 and 4 values for k^*_f and k^*_D calculated with $X = 1.014$, which corresponds to the mean value of X received from experimental data in the high molecular weight range $2 \times 10^5 < M_w < 10^7$.

The M_w dependence of X, derived from measurements of A_2, is shown in Figure 1. A molecular weight dependence becomes noticeable below $M_w \simeq 10^4$; at larger molecular weights, X *apparently* remains constant. If the constant value of $X = 1.014$ is used in the PF theory for an estimation of k^*_D as a function of molecular weight, a significant decrease of k^*_D with increasing M_w, in contradiction to experiment, is predicted in the range $2 \times 10^5 < M_w < 10^7$ since $\kappa(A)$ still decreases. A constant k^*_D, however, is also obtained in the PF theory (see curve PF in Figure 5) if a slight increase of X from 0.99 at $M_w = 10^5$ to 1.014 at $M_w = 10^7$ is assumed (curve 1 in Figure 1). This increase is in fact completely compatible with the experimental error as indicated in Figure 1. Figure 5 also contains the M_w dependence of k^*_D derived by Akcasu and Benmouna[3] (AB) and by Yamakawa[19] (Y) using the dashed curve in Figure 1 for the experimental X values.

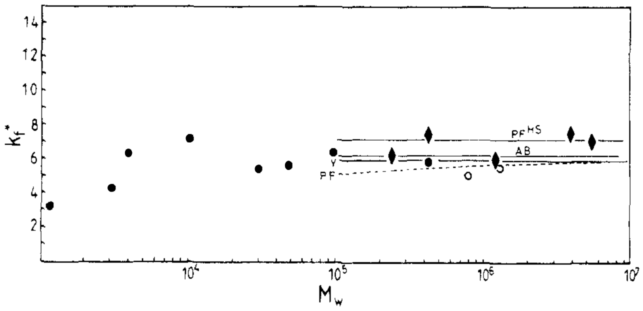

Figure 6. Molecular weight dependence of k^*_f (eq 12b) of PS in toluene. Symbols and notation as in Figure 5.

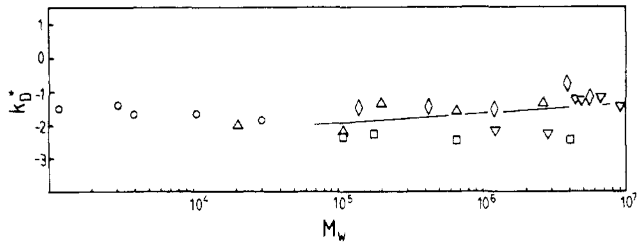

Figure 7. Molecular weight dependence of k^*_D (eq 12b) of PS in cyclohexane at T = 35 °C according to measurements of Huber et al.[10] (○), King et al.[34] (△), Han et al.[35] (□), Varma et al.[27] (◇), and Jones et al.[36] (▽).

In addition to the prediction of Pyun and Fixman,[18] Figure 6 contains the k^*_f values derived by Akcasu and Benmouna[3] (AB) and Yamakawa[19] (Y) using $X = 1.014$. For comparison the hard-sphere limit of the PF theory, i.e., $\kappa(A) = 0$ (PF^{HS}), with $X = 1.014$ is included in Figures 5 and 6.

In conclusion it can be noted that all three theories (PF, Y, and AB) yield k^*_f and k^*_D values that lie close together. A best fit is obtained with the AB theory, but the experimental error does not allow a definite distinction among the three. Values of k^*_f for hard spheres (i.e., $X = 1$) have been calculated also by Altenberger and Deutch[20] (6.0), Felderhof[21] (6.44), Harris[22] (5.0), Batchelor[23] (6.66), and Hess and Klein[24] (7.00). On the whole the values agree quite satisfactorily.

A few remarks concerning a proper application of the PF theory may be useful. The *hard-sphere* limit of this theory yields slightly too high a value for k^*_f and clearly too low a value for k^*_D with regard to the M_w range between 2×10^5 and 10^7. Evidently, even at such a high M_w, it is not permissible to assume $\kappa(A) = 0$. Actually $\kappa(A)$ approaches this hard-sphere limit very slowly ($\sim n^{-0.1}$), if β is constant such that in the above-mentioned M_w range the coil behaves, in the picture of PF, *only approximately* as a hard sphere. In calculating asymptotic k^*_D one therefore has to use the corresponding asymptotic value for X, which may be slightly larger than 1.014. Assuming $X \rightarrow 1.06$, the hard-sphere limit of the PF theory is 2.1, whereas it is 2.7 in the Y theory and 2.65 in the AB theory.

Finally, it is instructive to compare $k^*_D(T)$ with $k^*_D(\Theta)$ obtained from measurements in cyclohexane. The high-M_w region has been discussed previously in some detail by Nemoto et al.[29] Figure 7 shows (the solid line) the results of their best fit which follows for the nonreduced k_D a power law of

$$k_D = 0.13M_w^{0.43} \quad (\mathrm{cm}^3/\mathrm{g}) \tag{15}$$

To obtain the reduced values, we used the relationship $R_H = 0.0229M_w^{0.5}$ published by Schmidt et al.[30] The line for k^*_D agrees indeed satisfactorily with the high molecular weight data. Here we only wish to draw attention to the low-M_w region, where k_D apparently increases slightly with reducing M_w.

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Registry No. PS (homopolymer), 9003-53-6; toluene, 108-88-3.

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Small- and Intermediate-Angle Neutron Scattering from Stereoregular Poly(methyl methacrylate)

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ABSTRACT: Small- and intermediate-angle scattering (Q = 0.005–0.28 Å^{-1}) from amorphous poly(methyl methacrylate) (PMMA) of various stereoregularity was measured. The measured radii of gyration and characteristic ratios compare favorably with rotational isomeric state calculations (RIS). Isotactic PMMA shows a Debye-like scattering function, whereas the syndiotactic and atactic samples show a maximum in the scattering function. These results are similar to the RIS calculations for polymers of similar tacticities.

Introduction

Studies to ascertain the effect of stereoregularity on glass structure and on the physical properties of poly(methyl methacrylate) (PMMA) have been extended to include the technique of small-angle neutron scattering (SANS). Samples analyzed by this technique consist of a matrix of hydrogenous polymer molecules in which a fraction of isotopically substituted (deuterium labeled) molecules are dissolved. The difference in coherent scattering length b

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