Properties of Poly(α-methylstyrene) in Toluene: A Comparison of Experimental Results with Predictions of Renormalization Group Theory

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ABSTRACT: Dilute solution properties of poly(α-methylstyrene) (PαMS) in toluene at 25 °C were studied by static and dynamic light scattering and intrinsic viscosity measurements. Some of the experimental values of universal ratios of static and dynamic quantities are found to be in agreement with theoretical calculations corresponding to the least-draining self-avoiding limit. In most cases, renormalization group calculations of Oono agree somewhat better with experimental findings than those results of the renormalized two-parameter theory of Douglas and Freed or the numerical quadrature analysis of Barrett. Experimental results for poly(styrene) in various good solvents are included in the comparison of theory and experiment. In those instances where good agreement with theory is not obtained, departures from the least-draining limit may be responsible, although it is possible that the self-avoiding limit is not reached even for the highest molecular weight PαMS samples investigated. In addition, the value of the conformational parameter, ρ, for PαMS/toluene was found to equal 1.54, whereas earlier results indicated $\rho = 2.0$ for the same polymer-solvent system. Reasons for this discrepancy are described.

I. Introduction

In a series of recent papers Oono and Kohmoto[1] and Oono[2,3] have presented a description of the properties inherent to "nondraining" macromolecules in solution. A general theoretical framework was developed by employing a renormalization group transformation and, ultimately, perturbation theory. In this way the preaveraging of the Oseen tensor in the Kirkwood–Riseman theory[4,5] was avoided, and calculations were performed from the Gaussian or unperturbed state to the good solvent or self-avoiding (SA) asymptotic limit.

In this framework, universal ratios of fundamental polymer properties such as the intrinsic viscosity, $[\eta]$, the translational friction coefficient, f, the radius of gyration, $\langle S^2\rangle_z^{1/2}$, the second virial coefficient, A_2, and the molecular weight, M, are defined as (1)–(3)

$$U_{A\eta} = A_2M/[\eta] \tag{1}$$

$$U_{fs} = (f/\eta_0)/\langle S^2\rangle_z^{1/2} \tag{2}$$

$$U_{\eta f} = \eta_0(M[\eta]/N_A)^{1/3}/f \tag{3}$$

$$U_{\eta s} = M[\eta]/N_A\langle S^2\rangle_z^{3/2} \tag{4}$$

and

$$U_{AS} = A_2M^2/\langle S^2\rangle_z^{3/2}N_A \tag{5}$$

where η_0 is the viscosity of the solvent and N_A is Avogardro's number. The ratios U_{fs} and $U_{\eta f}$ are related to the parameter P and the Flory–Scheraga–Mandelkern factor β, respectively.[6] $U_{\eta s}$ is related to the Flory–Fox viscosity constant Φ, and U_{AS} can be converted to the interpenetration factor Ψ.

A close examination of eq 1–5 reveals that the universal ratios are also proportional to various ratios of hydrodynamic and thermodynamic radii which may be calculated from pertinent parameters based on geometrical considerations. For example, the parameter $U_{A\eta}$ is proportional to R_T/R_V where the subscripts T and V refer to thermodynamic and viscometric radii, respectively. Similarly, the ratio U_{fs} is inversely proportional to the conformational parameter $\rho = \langle S^2\rangle_z^{1/2}/R_H$, where R_H is the hydrodynamic radius. The representation of experimental data in terms of U_{xy} ratios is considered to be more appropriate than representation based on calculated radii where geometrical constraints are invoked.

The presence of a measurable draining effect for high molecular weight flexible polymers in good solvents has been debated for many years.[1-3,6-9] The widely accepted consensus[6] has been that the draining effect is not important under these conditions. The degree of draining would, of course, be reflected in the values of the U_{xy} ratios (except for U_{AS}). Recently, Mulderije and Jalink[10] have shown that the term "nondraining" is inappropriate even for high molecular weight polymers at the Θ state where $[\eta]/M^{1/2}$ and $f/M^{1/2}$ are independent of M. In what follows, we will use the term "least-draining" instead of nondraining to refer to behavior characteristic of high molecular weight flexible chains at the Θ state. The issue thus becomes whether or not a significant enhancement of draining is exhibited in good solvents.

Prior to this work, only one paper has appeared[11] which directly compared experimental results to those calculated via the renormalization group scheme of Oono.[1-3] Data were obtained[11] for poly(styrene) (PS) in ethylbenzene and tetrahydrofuran (THF), both considered good solvents. Results in ethylbenzene, on averaging, yielded values of the ratios in agreement with theoretical calculations for the SA limit, whereas data obtained for THF solutions showed deviations from predicted SA results. Some possible reasons for the discrepancies between theory and experiment were advanced.

In this work, the solution properties of nearly monodisperse poly(α-methylstyrene) (PαMS) chains in toluene are examined. Although studies of this system have appeared in the literature (cf. Results), there are reasons to reexamine this polymer solvent pair. For example, results published by Selser[12] for PαMS/toluene indicate $\rho = 2.0$, which is at variance with recent theoretical[1,13,14] and extensive experimental results[11,15-24] on a variety of flexible

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Table I
Static Properties of the Poly(α-methylstyrenes)

sample	$10^{-4}\bar{M}_w$, g mol^{-1}	$10^4 A_2$, mL mol·g^{-2}	$10^{-4}\bar{M}_n$, g mol^{-1}	$\bar{M}_w/\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[b]	$\bar{M}_z/\bar{M}_w$[b]
PC-3	0.70		0.55	1.27	1.33	1.25
PL-19	2.01	8.05	1.93	1.04	1.03	1.03
PC-1	2.47	7.03	2.25	1.10	1.14	1.12
PL-55	5.90	5.54	5.38	1.10	1.13	1.11
PMS-3	6.31	5.29	6.03	1.05	1.05	1.02
PC-2	7.59	5.67	7.44	1.02	1.03	1.02
PC-4	11.8	4.63	11.5	1.03	1.03	1.03
PL-150	17.7	4.55	16.6	1.07	1.05	1.05
PC-6	30.5	3.73	28.9	1.06	1.07	1.06
PL-285	31.3	3.56	31.0	1.01	1.04	1.03
PC-17	66.5	2.90	59.4	1.12	1.09	1.06
PL-770	90.3	2.71			1.05	1.04
PC-16	114	2.56			1.11	1.08

[a] From osmometry and LALLS. [b] From SEC.

macromolecules in good solvents. An additional motivation for this work is to provide a further test of the renormalization group results of Oono and Kohmoto,[1-3] since the previous experimental study of poly(styrene) in ethylbenzene and THF by Venkataswamy and co-workers[11] was inconclusive.

To facilitate the comparison between theory and experiment, we have reexamined the results of ref 11 as well as other experimental results for PS in good solvents.[16-22] We have also included comparisons with theoretical results from the numerical quadrature study of Barrett[13] and from the renormalized two-parameter theory of Douglas and Freed.[14,25] Here we are primarily interested in determining which (if any) approach to calculating universal ratios best coincides with the bulk of experimental results.

This paper is organized as follows. In section II the sources of the PαMS samples and details of their characterization are described. Our results for static and dynamic properties of PαMS in toluene are compared to results of previous studies in section III. Evaluation of the universal ratios, including possible error sources and a comparison to the renormalization perturbation scheme of Oono,[1-3] is given in section IVA. The comparison is extended in section IVB to include experimental results for other systems and comparison to other theories. Pertinent conclusions are summarized in section V. An Appendix is included so that calculated radii and their ratios are directly available. A comparison of the latter values with theory is also made.

II. Experimental Section

The sources and preliminary characterization of most of the near-monodisperse poly(α-methylstyrene) samples have been previously described.[26] Additional samples of low and high molecular weights were obtained from Pressure Chemical Co. All samples were characterized by low-angle laser light scattering (LALLS), membrane osmometry (MO) (where possible), and size exclusion chromatography (SEC).[26] These results, which are summarized in Table I, indicate that all samples exhibit very narrow molecular weight distributions.

For the lowest molecular weight sample, PC-3, the number-average molecular weight, $\bar{M}_n$, was measured by vapor pressure osmometry using a Wescan Model 232A unit. This instrument operated in toluene at 50 °C and was calibrated by using benzil and sucrose octaacetate. The toluene used in this experiment (and for LALLS, MO, and viscosity measurements) was distilled-in glass grade from Burdick and Jackson.

Specific refractive index increments (dn/dc) were measured at a wavelength, λ, of 632.8 nm using the Chromatix KMX-16 unit or the C. N. Wood Model 6000 monophotometer equipped with the RF-500 attachment.

Intrinsic viscosities were measured in toluene at 25 ± 0.02 °C by using Ubbelohde viscometers. Intrinsic viscosities and Huggins coefficients, k_H, were evaluated from linear regression fits of η_{sp}/c versus c, where η_{sp} is the specific viscosity, for at least four concentrations of polymer. Concentrations were chosen so that the relative viscosity $\eta_r \leq 1.4$ for the highest concentrations used. Kinetic energy corrections were negligible and were not applied.

Apparent diffusion coefficients, $D_{app,z}$, were determined by using photon correlation spectroscopy (PCS) as described previously.[27] Briefly, incident radiation from a Jodon Model HN-50 helium–neon laser (λ = 632.8 nm) was directed by mirrors and focused to the center of a 10-mm diameter cylindrical cell. The cell was positioned in the center of a vat, 7.62 cm high by 10.2 cm in diameter, containing toluene. The vat was housed in a machined aluminum block specifically designed to allow optical access from 0 to 180° and equipped with a series of channels suitable for fluid circulation from an external bath (Forma Model 2095). All of the measurements were done at 25 ± 0.1 °C, as determined by a thermometer inserted in the index matching fluid.

Scattered light was detected at the angle of interest by an RCA C31034 photomultiplier tube housed in a magnetically shielded and thermoelectrically cooled cylinder, Pacific Model 3457. The detector assembly was equipped with an externally controllable camera shutter and was clamped to the rotating arm of a goniometer. The laser, detector, cell assembly, and optics were supported by a massive 5 ft by 9 ft optical bench.

High voltage to the PMT was supplied by a Fluke 415B power supply. The resulting pulses were shaped and amplified by using a Pacific AD-6 amplifier/discriminator. The TTL pulse train was routed directly into a Bookhaven BIC 2020 digital correlator equipped with 72 real time channels and 8 channels delayed 1028 in τ. The NIM output from the discriminator was routed into a counter gated at either 1 or 10 s. The counter was used to monitor the scattered light intensity during averaging of the correlation function and also during filtration, as described below.

Optical alignment was established by using a right angle prism and a pointer and, ultimately, by determining the scattered intensity (Rayleigh ratio) from a pure fluid. Measurements were principally confined to 20°, although some functions were collected at angles, Θ values, of 25 and 30°. No differences were observed in the measured parameters, indicating that scattering from extraneous sources was negligible.

Intensity correlation functions were converted to electrical correlation functions, $g'(\tau)$, by the relation of Siegert[28] and then analyzed by the method of cumulants;[29,30] to second order

$$b^{1/2}\frac{\ln g'(\tau)}{B} = \ln b^{1/2} - \bar{\Gamma}(\tau) + \frac{\mu_2(\tau)}{2} \tag{6}$$

where $b^{1/2}$ is an optical constant, B is the base line determined by calculation or from the eight channels delayed in τ, Γ is the decay constant, and μ_2 is the second moment and is related to the width of decay constants. The decay constant has been shown by Koppel[29] to lead to a z-average quantity; $\bar{\Gamma}$ is related to the z-average apparent diffusion coefficient by

$$\bar{\Gamma} = D_{app,z}q^2 \tag{7}$$

where q is the wave vector

$$q = \frac{4\pi n_0}{\lambda}\sin\frac{\theta}{2} \tag{8}$$

and n_0 is the refractive index of the solvent. Second moment values were always less than 0.1 and were typically between 0.025 and 0.08. These results fortify the SEC and absolute measurements (Table I) insofar as the narrow molecular weight distributions of these samples are concerned. Calculated and measured base lines differed by less than 0.01%.

Clarification of the solutions was accomplished by using a closed-loop filtration system. Filters of 0.2 or 0.45 μm were employed. Initially, toluene (Fisher spectrograde) was added to the system and filtration was begun at <0.3 mL min^{-1}. Filtration continued until a constant intensity was observed on the counter. This process was repeated by adding a known volume of polymer solution. Equilibrium times typically ranged from 10 to 15 min.

Diffusion coefficients at infinite dilution, D_z, were determined from measured values of $D_{app,z}$ according to[31,32]

$$D_{app,z} = D_z(1 + k_d c + ...) \tag{9}$$

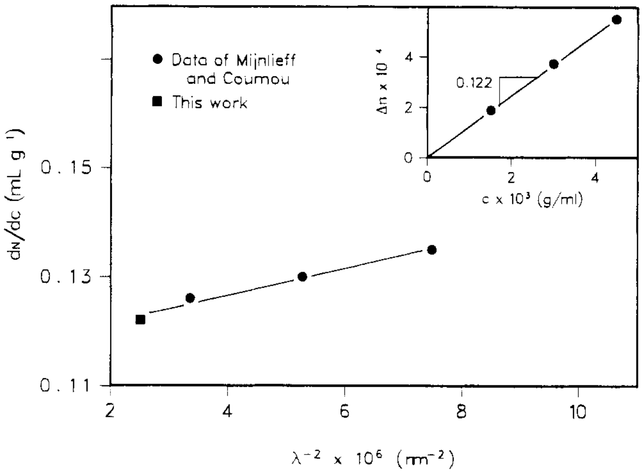

Figure 1. Specific refractive index increment, dn/dc against λ^{-2} for PαMS in toluene at 25 °C. Circles in the main plot correspond to the data in ref 34. The insert shows a typical dn/dc determination for PαMS PL-770.

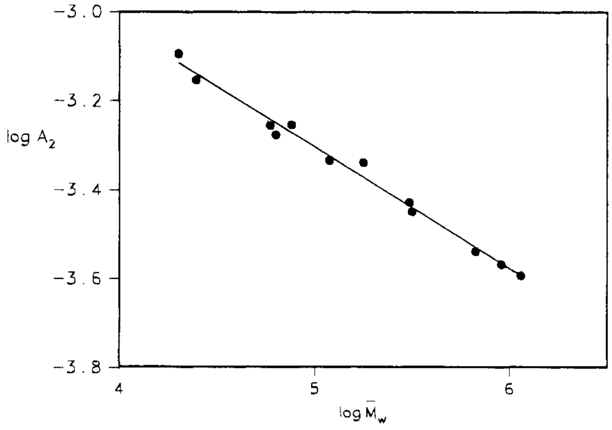

Figure 2. Dependence of the second virial coefficient on weight-average molar mass, $\bar{M}_w$, for PαMS in toluene at 25 °C. The line is the statistical fit to the data (eq 11).

where $k_d = 2A_2M - k_f - v_2$, with k_f the frictional virial coefficient and v_2 the partial specific volume of the polymer. No attempts were made to investigate the semidilute or concentrated regimes. Frictional coefficients, f, were calculated from the Stokes–Einstein relation

$$D_z = kT/f \tag{10}$$

where k is the Boltzmann constant, T is absolute temperature, and $f = 6\pi\eta_0 R_H$, with $\eta_0 = 0.5516$ cP at 25 °C for toluene.[33]

III. Results

A. Static Properties. Literature results[34] for dn/dc of poly(α-methylstyrene) in toluene and our average value at 632.8 nm are plotted as a function of λ^{-2} in Figure 1. The insert displays the dn/dc determination for sample PL-770. Neglecting sample PC-3, the average value of dn/dc is 0.122 mL g^{-1}. This result is in agreement with the value, 0.124 mL g^{-1}, obtained by extrapolation of the lower wavelength data. For sample PC-3, dn/dc = 0.107 mL g^{-1}; this lower value is consistent with the very low molecular weight of this sample. Selser[12] has previously reported dn/dc = 0.108 mL g^{-1} for a series of PαMS samples in toluene under the same conditions. The use of the lower dn/dc value results in an overestimation (about 25%) of weight-average molecular weights, $\bar{M}_w$, and is inconsistent with extensive literature data.[34-38]

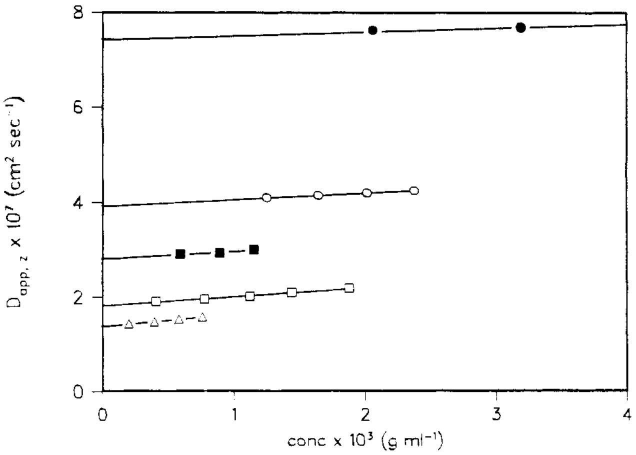

Figure 3. Plot of the apparent diffusion coefficient against solute concentration for some of the PαMS chains. Measurements were made in toluene at 25 °C and at a scattering angle of 20°. Symbols are as follows: ●, PL-55; ○, PL-150; ■, PL-285; □, PC-17; △, PL-770.

Table II
Transport Properties for PαMS in Toluene

sample	$10^{-4}\bar{M}_w$, g mol^{-1}	10^7D_z[a] cm^2 s^{-1}	k_d,[a] mL g^{-1}	k_f, mL g^{-1}	$[\eta]$, mL g^{-1}	k_H
PC-3	0.70	(19.55)	(1.12)		6.8	0.62
PL-19	2.01	12.9	6.0	26.7	12.7	0.48
PC-1	2.47	(10.6)	(4.63)	30.4	14.2	0.58
PL-55	5.90	7.43	11.3	54	24.1	0.58
PC-2	7.59	(6.10)	(15.5)	70	28.7	0.42
PC-4	11.8	(4.67)	(23)	86	40.3	0.32
PL-150	17.7	3.90	34	127	52.2	0.38
PC-6	30.5	(2.77)	(53)	174	79.5	0.41
PC-285	31.3	2.79	63	160	82.1	0.36
PC-17	66.5	1.81	107	279	139	0.34
PL-770	90.3	1.50	162	329	170	0.34
PC-16	114	1.36	201	383	198	0.34

[a] Values in parentheses from ref 12.

Results from LALLS, osmometry, and SEC experiments are collected in Table I. Second virial coefficients, A_2, obtained from LALLS data by using conventional plots of Kc/R_θ against c, are plotted as a function of $\bar{M}_w$ in Figure 2. Although some scatter is observed, log A_2 appears to vary linearly with log $\bar{M}_w$. The data are represented by the power law

$$A_2 = 1.15 \times 10^{-2}\bar{M}_w^{-0.273} \tag{11}$$

Equation 11 is in accord with the data of Kato et al.,[39] who found

$$A_2 = 8.9 \times 10^{-3}\bar{M}_w^{-0.282} \tag{12}$$

and the results of Siriani et al.[35]

$$A_2 = 9.65 \times 10^{-3}\bar{M}_w^{-0.298} \tag{13}$$

B. Transport Properties. Apparent diffusion coefficients for some of the samples are plotted against solute concentration in Figure 3. In all cases the variation of $D_{app,z}$ with polymer concentration is linear, thereby indicating that higher order terms in eq 9 are negligibly small. Values of D_z, diffusional and frictional virial coefficients, k_d and k_f, $[\eta]$, and k_H, respectively, are given in Table II.

It should be remarked that some of the Pressure Chemical Co. samples evaluated here are the same samples employed by Selser, i.e., much of the data from Table I of ref 12 was supplied to us by Pressure Chemical Co. as characterization data for these samples. While we have noted the disparity in the earlier[12] dn/dc data, we believe the diffusion data reported by Selser to be accurate. The concurrence between our PCS results and those from the aforementioned study can be observed in Table II and

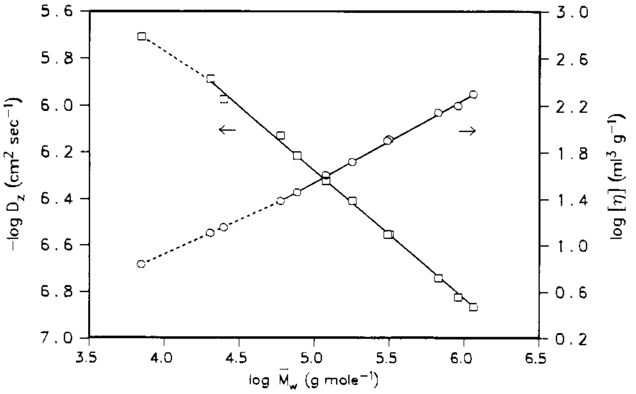

Figure 4. Power laws for the intrinsic viscosity and zero concentration diffusion coefficient against molecular weight. The solid lines are best represented by eq 14 and 19.

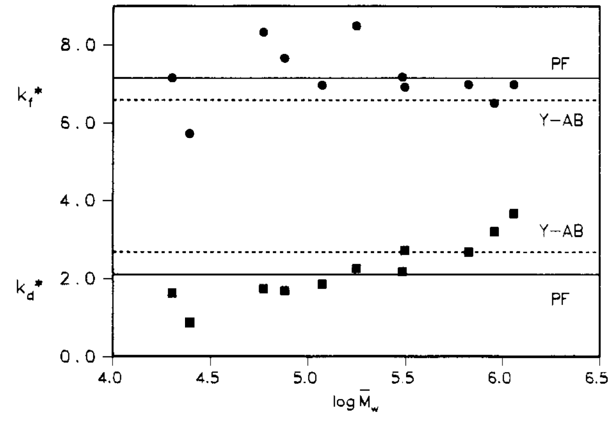

Figure 5. Reduced quantities K_d^* and K_f^* plotted against log $\bar{M}_w$. The symbols and lines denoted by Y-AB and PF correspond to theoretical expressions derived by Yamakawa[44] and by Akcasu and Benmouna[43] and those advanced by Pyun and Fixman,[45] reviewed in ref 72. Only one line is plotted for Y-AB since both their equations lead to essentially identical results.

Figures 4 and 5. Quantities in parentheses in the table are those reported previously by Selser.[12] The close agreement between the D_z and k_d results of comparable molecular weight samples (compare PL-285 and PC-6) confirms the validity of the earlier measurements.

Neglecting the lowest molar mass sample, the data of Figure 4 yield the following power law

$$D_z = 3.14 \times 10^{-4}\bar{M}_w^{-0.556} \qquad (14)$$

This expression is in excellent agreement with the data and corresponding power law from ultracentrifugation experiments of Noda and co-workers[40] for samples with $\bar{M}_w$ ranging from 2.04×10^5 to 7.47×10^6

$$D_z = 2.99 \times 10^{-4}\bar{M}_w^{-0.557} \qquad (15)$$

We have also calculated the scaling law from the data of Cowie and Bywater[41] at 37 °C within the range $1.5 \times 10^4 \leq \bar{M}_w \leq 8.45 \times 10^5$

$$D_z = 3.95 \times 10^{-4}\bar{M}_w^{-0.564} \qquad (16)$$

This last expression corresponds to measurements at small but finite concentrations; i.e., the data for sedimentation coefficients were not extrapolated to the zero concentration limit.

The lower than expected diffusion coefficient for sample PC-3 ($\bar{M}_w = 7000$) is thought to reflect chain swelling at low molecular weights. Cowie and Bywater[41] reported that $[f]$ for PαMS in toluene scaled as $\bar{M}_w^{0.5}$ for samples with molecular weights less than 10^4. Similar results have recently been reported for solutions of poly(methyl methacrylate) in acetone[24] and poly(styrene) in toluene.[42] In this latter work, accurate values of D_z were calculated by including the free draining term of the Kirkwood diffusion equation. The diffusion–molecular weight power law appears, therefore, to break down (approaching a slope of ca. $^1/_2$) at low molecular weights, a result similar to that observed for the Mark–Houwink–Sakurada, M–H–S, equation (see below). Reasons for this effect have been discussed.[24,41,42]

Diffusion and frictional virial coefficients are plotted as the reduced quantities

$$k_d^* = k_d(M/N_A V_H) \qquad (17)$$

$$k_f^* = k_f(M/N_A V_H) \qquad (18)$$

against $\bar{M}_w$ in Figure 5, where V_H is the hydrodynamic volume, $(^4/_3)\pi R_H^3$. The horizontal lines in Figure 5 are those based on the Akcasu–Benmouna (AB) parameter x[43] as applied to the theoretical expression of Yamakawa (Y),[44] Pyun and Fixman (PF),[45] and AB.[43] Calculated parameters from the Y and AB theories are quite close. Consequently, we have plotted common (averaged) lines labelled Y-AB. The large scatter in the experimental data precludes the complete acceptance of any pair of theoretical expressions. The k_f^* values, however, appear to be satisfactorily described by the PF expression. This tentative conclusion was previously reached by Noda and co-workers.[40] In general, for a number of flexible chain macromolecules in good solvents, k_f^* values agree quite favorably with theoretical predictions for spheres where values between 5 and 7 are predicted.[46–50] This is a curious result when one also considers the parameter ρ, which exhibits much larger values than theoretically predicted for spherical geometries. A tendency for k_d^* to increase with increasing $\bar{M}_w$ is also observed, contrary to theoretical predictions.

The M–H–S plot is given in Figure 4. Analysis of the results of $\bar{M}_w > 5 \times 10^4$ yields

$$[\eta] = 9.69 \times 10^{-3}\bar{M}_w^{0.713} \qquad (19)$$

This result is in agreement with a number of previous studies.[36,51,55] The exponent of the M–H–S expression, a, is related to the diffusion–molecular weight power law exponent, b, by

$$b = \frac{a+1}{3} \qquad (20)$$

The M–H–S exponent of 0.713 predicts $b = 0.571$, in fair agreement with eq 14.

As referred to above, the inability of a common power law to describe intrinsic viscosities measured in good solvents at both low and intermediate or high molecular weights, has been observed for poly(styrene),[56] poly(dimethylsiloxane),[57] and poly(methyl methacrylate).[58] The onset of linear behavior appears at somewhat higher molecular weight than in the diffusion power law. However, an additional factor that must be considered for PαMS chains is the known[26,39] increase in syndiotactic content for low molecular weight chains ($M < 5 \times 10^4$). No such effect has been observed for the other polymeric species cited above. Thus, for PαMS enhanced draining, a decrease of excluded volume effects *and*, possibly, tacticity variations affect the hydrodynamic behavior at low molecular weights.

The change in solute configuration and excluded volume effects observed in the M–H–S plot is also reflected in the Huggins coefficients (Table II). Values of k_H decrease from initially high values at low molecular weights to a constant

Table III
Calculated Universal Ratios for Poly(α-methylstyrene) in Toluene at 25 °C

sample	$10^{-4}\bar{M}_w$, g mol^{-1}	$U_{A\eta}$	$U_{\eta f}$	$U_{\eta s}$	U_{AS}	U_{fs}	ρ
PC-3	0.70	...	0.112				
PL-19	2.01	1.27	0.129				
PC-1	2.47	1.32	0.120				
PL-55	5.90	1.36	0.131				
PC-2	7.59	1.47	0.125				
PC-4	11.8	1.36	0.127				
PL-150	17.7	1.55	0.130				
PC-6	30.5	1.43	0.128	3.99	5.72	12.42	1.52
PL-285	31.3	1.36	0.131	4.04	5.52	12.18	1.53
PC-17	66.5	1.39	0.130	3.94	5.57	12.17	1.55
PL-770	90.3	1.44	0.127	3.86	5.57	12.33	1.54
PC-16	114	1.47	0.131	3.80	5.60	11.88	1.54
average		1.43 ±0.07	0.129 ±0.002	3.93 ±0.10	5.60 ±0.09	12.20 ±0.21	1.54 ±0.011
theory[1-3]		1.196	0.1297	4.078	4.86	12.067	1.562

value of 0.34 at higher molecular weights. Similar behavior has also been observed for other polymers in good solvents.[21,59] Unlike the diffusion virial coefficient, the theoretical representation of k_H does not lend itself to a simple analysis in terms of thermodynamic and frictional components.[60]

IV. Discussion

A. Universal Ratios and Comparison to the Theory of Oono. Table III lists universal ratios calculated via eq 1–5 as well as values of the parameter ρ and the theoretical results of Oono corresponding to the least-draining self-avoiding (SA) limit. In determining those ratios requiring the radius of gyration, we have invoked the empirical expression

$$\langle S^2\rangle_z^{1/2} = 1.48 \times 10^{-9}\bar{M}_w^{0.577} \qquad (21)$$

calculated from the results of Kato et al.[39] and valid for the molecular weight range from 2.04×10^5 to 7.47×10^6 g mol^{-1}.

At molecular weights greater than about 5×10^4 g mol^{-1}, the ratios are reasonably constant and scattered about their averages.[61] The lack of a molecular weight dependence, except perhaps for $U_{\eta s}$, suggests that the PαMS chains are either at the asymptotic SA limit or that the other ratios are insensitive to whether or not the SA limit has been reached. $U_{\eta s}$ appears to decrease slightly with increasing molar mass; this trend, however, may not be significant. Both $U_{\eta s}$ and U_{AS} will exhibit larger errors than the other ratios. The fact that U_{AS} does not change significantly with increasing molar mass may be due to some cancellation of errors. Alternatively, it is possible that $U_{\eta s}$ has not yet reached the asymptotic limit whereas the other parameters have. The largest molecular weight sample investigated here is slightly over 1×10^6 g mol^{-1}; therefore z, the excluded volume parameter from two-parameter theory, is, using any expansion factor expression, quite small.

The universal ratios $U_{\eta f}$ and U_{fs} and the conformational parameter ρ are in favorable agreement with the theoretical results reported by Oono. The ratio ρ is also consistent with other experimental and theoretical studies on monodisperse linear chains in good solvents. Our average value of 1.54 is much smaller than that quantity, 2.0, previously reported.[12] The smaller value is consistent with the earlier discussion concerning determination of the specific refractive index increment and with theoretical[1,13,14] and other experimental results[11,15-24] for ρ.

Discrepancies in the experimental and theoretical results for $U_{A\eta}$ and U_{AS} are not considered great and could arise from experimental errors in measuring A_2. Conversely, the generally satisfactory agreement between the experimental and theoretical values for the other ratios which do not contain A_2 may indicate that this thermodynamic parameter is theoretically underestimated. The argument could be advanced that the larger than theoretically predicted values of $U_{A\eta}$, along with the possible molecular weight dependence of $U_{\eta s}$, implies departures from the least-draining limit. Results below, however, indicate that by the current theoretical interpretations we cannot yet completely accept or reject the existence of enhanced draining at the higher molecular weights. We can say that if draining is responsible for the observed behavior, then other systems also exhibit similar effects.

We note that in the low molecular weight regime, $\bar{M}_w < 5 \times 10^4$, the quantities $U_{A\eta}$ and $U_{\eta f}$ decrease, with one exception, as the molecular weight is lowered. Additional work, including the measurement of $\langle S^2\rangle_z^{1/2}$, on low molecular weight samples, is required to relate directly the influence of solvent permeation upon the universal ratios. It appears safe to assume, however, that the ratios will exhibit molecular weight variations consistent with the degree of draining.

B. Further Comparison of Experiment with Theory. In light of the previous discussion, it is relevant to compare our results with those for other experimental systems and other theoretical studies. The experimental and theoretical ratios collected in Table IV correspond to chains in good solvents. The theoretical ratios, with the exception of $U_{\eta f}$ attributed to Barrett, were taken from the appropriate references and converted, if necessary, into the U_{xy} formalism. The value of $U_{\eta f}$ cited for ref 13 has been calculated via $U_{\eta f} = U_{\eta s}^{1/3}/U_{fs}$.

Experimental data for poly(styrene) in various good solvents were used to generate the experimental ratios in Table IV. Poly(styrene) is widely available in near-monodisperse form (generally $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w < 1.1$) and is known to exhibit chain flexibility comparable to PαMS.[26,64] To obtain all of the raw data required to calculate the various parameters, it was usually necessary to combine results from different laboratories. We have attempted to utilize only the highest quality experimental data and/or the most recent results.

Listing of the experimental ratios in Table IV is arbitrary. Standard deviations, except for those reported in ref 11, were calculated for all the available U_{xy} ratios. This procedure can be considered satisfactory unless inherent trends exist in the data.[61] In such a case, the ultimate averages could be misleading. To ascertain the existence of such trends, an additional plot is presented below which has aided in the evaluation of the results and the possible

Table IV
Comparison of Theoretical and Experimental Results for Universal Ratios

theory								
author	type	$U_{\eta s}$	U_{AS}[a]	$U_{A\eta}$	U_{fs}	$U_{\eta f}$	ρ	ref
Oono/Kohmoto	renormalization	4.078	4.88	1.196	12.07	0.1297	1.562	1–3
Barrett	numerical quadrature	4.05	5.35	1.167	10.92	0.1320	1.64	13
Douglas/Freed	renormalization	5.47	5.98	1.10	14.65	0.120	1.50	14, 25

experiment									
system	temp, °C	$10^{-6}M_w$ range	$U_{\eta s}$	U_{AS}[a]	$U_{A\eta}$	U_{fs}	$U_{\eta f}$	ρ	ref
PS/THF	30	0.165–5.7	3.69 ± 0.76	4.38 ± 0.88	1.19 ± 0.08	12.66 ± 0.87	0.122 ± 0.003	1.49 ± 0.097	18, 19
PS/THF	30	0.9–8.5	5.083 ± 0.71	7.08 ± 0.61	1.54 ± 0.05	14.42 ± 0.00	0.121 ± 0.01	1.35 ± 0.06	11
PS/benzene	30	0.775–13.4	4.16 ± 0.07	4.75 ± 0.11	1.16 ± 0.05	12.19 ± 0.48	0.130 ± 0.01	1.58 ± 0.06	20–22
PS/ethylbenzene	25	0.9–8.5	3.99 ± 0.64	4.72 ± 0.51	1.07 ± 0.08	11.38 ± 0.52	0.1318 ± 0.005	1.61 ± 0.078	11
PS/toluene	25	0.513–29.6	3.74 ± 0.41	5.23 ± 0.43	1.41 ± 0.10	13.33 ± 0.31	0.117 ± 0.002	1.43 ± 0.032	16, 17
PαMS/toluene	25	0.305–1.14	3.93 ± 0.10	5.60 ± 0.09	1.43 ± 0.07	12.20 ± 0.21	0.129 ± 0.002	1.54 ± 0.011	this work, 39

[a] des Cloizeaux, J. *J. Phys.* **1981**, *42*, 635 obtained $U_{AS} = 5.99$, in excellent agreement with the value of Douglas and Freed.

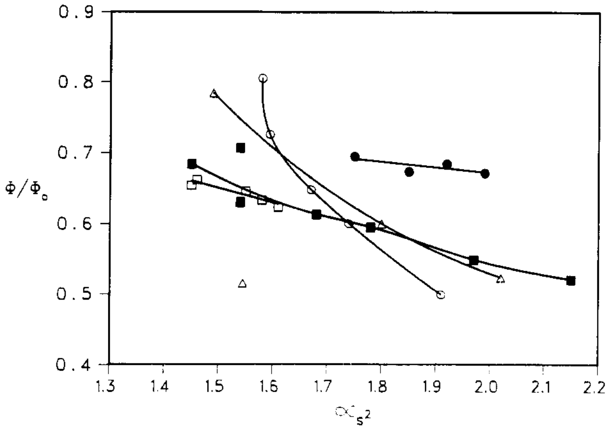

Figure 6. Plot of the universal ratio Φ/Φ_0 against the expansion factor for the root-mean-square radius of gyration, α_s^2. Symbols are as follows: ●, poly(styrene) in benzene;[20-22] ○, PS in ethylbenzene;[11] △, PS in THF;[18,19] ■, PS in toluene;[16,17] □, poly(α-methylstyrene) in toluene (this work and ref 39). One data point for PS/THF falls outside the trend observed for other data obtained for this system. The decreasing values of Φ/Φ_0 are believed to correspond to increasing solvent mobility within the coils.

establishment of empirical correlations.

Examination of the theoretical results in Table IV indicates some agreement between the renormalization theory of Oono[1-3] and the quadrature analysis reported by Barrett.[13] Numerical quantities of the ratios $U_{\eta s}$, $U_{A\eta}$, and $U_{\eta f}$ are all similar, whereas the ratios U_{AS} and U_{fs}, and the conformational parameter ρ exhibit discrepancies. The work of Douglas and Freed[14] yields some U_{xy} values which are inconsistent with the other theoretical studies. Differences in $U_{A\eta}$ and ρ are not considered significant. For U_{AS}, the result of Douglas and Freed is in good agreement with the experimental results for PαMS/toluene. Recent light scattering and viscosity experiments for poly(butyl methacrylate) in butanone[62] also agree quite favorably with this latter renormalization approach. There is however considerable variation in theoretical values of U_{AS}, as well as in the experimental results.

Serious discrepancies are noted in comparing the recently published[11] and earlier results[18,19] for poly(styrene) in tetrahydrofuran. Standard deviations from both studies are somewhat larger than those of the other experimental studies and could arise, as has been mentioned elsewhere,[11] from the properties of the solvent (THF is known to be quite hygroscopic). $U_{\eta f}$ values from both studies are essentially identical; consequently, it seems likely that the transport properties $[\eta]$ and D_z have been determined satisfactorily. The low average ρ value reported by Venkataswamy and co-workers[11] may indicate that their radii of gyration are underestimated, leading to the unusual results for U_{AS}, $U_{\eta s}$, and U_{fs}. Furthermore, the large values of $U_{A\eta}$ and U_{AS} as compared to the earlier work may signify problems with reported virial coefficients.

The earlier data for PS/THF[18,19] appear to be more consistent with the theoretical calculations and with other experimental results. Average quantities for ρ and $U_{\eta f}$ are in best agreement with the work of Douglas and Freed.[14] The other parameters, when the standard deviations are considered, are in good agreement with the theory of Oono. The lower value of $U_{\eta s}$ compared to that of Barrett or Oono and, most assuredly, that cited by Douglas and Freed could reflect draining.

Experimental results for PS in benzene and in ethylbenzene are in excellent accord with theoretical values advanced by Oono. The larger standard deviations of $U_{\eta s}$ in ethylbenzene may reflect a systematic variation with molecular weight. Attempts to extend the comparison of the average ratios to measurements in toluene is unsatisfying. It is perhaps relevant to mention that results obtained in this last solvent are among the poorest insofar as agreement with theory is concerned, although PS/toluene is among the most extensively studied systems.

Some comments regarding these last results are required. It should be mentioned that a power law for the translational diffusion coefficient at 25 °C over the molecular weight range from 5.13×10^5 to 2.36×10^7 g mol^{-1} is unavailable. The measurements reported by Appelt and Meyerhoff[63] were made with ultrahigh molecular weight samples of much broader polydispersity than the samples upon which the static results were obtained. Other determinations[42] at 20 °C were confined to a lower (3×10^4 to 5×10^5) molar mass regime. Consequently, we have employed the results from the ultracentrifugation experiments of Roovers and Toporowski,[17] corrected to 25 °C. The power law obtained is similar to that reported by Huber and co-workers,[42] however the molar mass range is somewhat larger. As a result, the average values of ρ, $U_{\eta f}$, and U_{fs} reported in toluene are thought to be accurate. The lack of direct measurements at the temperature and molecular weight range of interest precludes the total acceptance of the values in Table IV; however, as discussed below, the values are consistent with the overall solution properties in toluene.

The ratio $U_{\eta s}/U_{\eta s}{}^0$, equivalent to Φ/Φ_0, is plotted against the expansion factor $\alpha_s{}^2$ in Figure 6. For PS the well established value of 6.1 for $U_{\eta s}$[64] was employed; also, quantities of the expansion factor have been based on the power law

$$\langle S^2\rangle_z^{1/2} = 0.029\bar{M}_w^{0.5} \qquad (22)$$

compiled by Schmidt and Burchard[65] from a number of experimental studies. Additional qualifications for PαMS are discussed below.

One important factor regarding Figure 6 involves the possible experimental errors for $U_{\eta s}$. This ratio, as well as U_{AS}, will exhibit larger errors than $U_{\eta f}$, U_{fs}, $U_{A\eta}$, and ρ. Consequently, the ultimate values of Φ/Φ_0 may be biased to some extent, and the relative positions of the various systems with respect to one another may be uncertain. In any event, it is difficult to understand how random errors associated with $U_{\eta s}$ could result in what appear to be systematic trends. We therefore consider the data in Figure 6 to be of significance. We feel that analysis of data via the format of Figure 6 may offer advantages over the universal plots proposed by Oono,[2,3] where U_{AS} is plotted on the x axis. We have already pointed out that evaluation of U_{AS} is subject to large experimental errors.

Values of the ratio Φ/Φ_0 in benzene are essentially constant, indicating that the chains have reached an asymptotic limit. Further evidence of this condition, the ratios of ρ and $U_{\eta f}$, can be observed in Table IV. The data in Figure 6 for PS in the other solvents reveal that the chains have not yet reached the limiting regime. Clearly, the slope for the data obtained in ethylbenzene is more negative than that observed in toluene and in benzene.

According to Freed,[66] the ratio Φ/Φ_0 for a nondraining coil in the self-avoiding limit is 0.89, in good agreement with 0.87 calculated by Rey et al.[67] The renormalization theory of Oono and Kohmoto[3] yields 0.707 whereas Barrett's calculations[13] establish the value of Φ/Φ_0 at 0.66. This lack of theoretical agreement (Table IV), although not surprising when one considers the complexities of the problem, requires additional attention.

Some results from the work of Barrett[13] and of that reported by Wang and co-workers[68,69] are available to aid in the analysis of Figure 6. Qualitatively both approaches predict a lower limiting value of Φ/Φ_0, assuming the asymptote can be reached, and a larger, more negative decline with increasing z as the permeation of solvent within the coil is increased. In this regard, we believe that the curves in toluene, THF, and ethylbenzene correspond to increased solvent permeation.[70] Although additional measurements are needed, it appears that draining in PS depends on the size of the solvent molecule, at least for the substituted benzene solvents. Whether or not the data in benzene corresponds to the self-avoiding limit may be open to question; however, the good agreement with the theory of Oono and with some of the ratios due to Barrett seems to indicate that the chains are at the least-draining limit.

Comparison of the average universal ratios and standard deviations in Table IV with Figure 6 is illuminating. The results in ethylbenzene are more realistically depicted in a graphical manner. Ratios in toluene and, to a lesser extent, in THF are generally consistent with draining. The ρ value in toluene implies a compact configuration. In this solvent the parameters U_{AS} and $U_{A\eta}$ are somewhat larger than those predicted by Oono and Kohmoto.[1] For the former ratio the experimental average is within the other theoretical estimates. The quantity 1.41 for $U_{A\eta}$ is outside all theoretical estimates and is only similar to the experimental value for PαMS in toluene.

In calculating the ratio Φ/Φ_0 for PαMS we have employed a value of 6.1 for $U_{\eta s}{}^0$. This value is taken from the work of Cowie and co-workers[53] and is consistent with experimental results for poly(styrene) (and other) chains[64] and with the Monte Carlo results of Zimm.[71]

Table V
Viscometric, Thermodynamic, and Hydrodynamic Radii for PαMS in Toluene

sample	$10^{-4}\bar{M}_w$, g mol	R_V, nm	R_T, nm	R_H, nm	R_V/R_H	R_T/R_H
PC-3	0.70	1.96		2.02	0.97	
PL-19	2.01	3.43	3.18	3.07	1.12	1.04
PC-1	2.47	3.82	3.49	3.73	1.02	0.94
PL-55	5.90	6.08	5.76	5.33	1.14	1.08
PMS-3	6.31		5.93			
PC-2	7.59	7.01	6.83	6.49	1.08	1.05
PC-4	11.8	9.09	8.61	8.32	1.09	1.03
PL-150	17.7	11.3	11.2	10.1	1.12	1.11
PC-6	30.5	15.6	15.1	14.3	1.09	1.06
PL-285	31.3	16.0	15.1	14.2	1.13	1.06
PC-17	66.5	24.4	23.3	21.9	1.11	1.06
PL-770	90.3	28.9	28.0	26.4	1.09	1.06
PC-16	114	32.9	32.1	29.1	1.13	1.10

Comparison of the universal ratios for PS and PαMS is hindered somewhat by the limited number of very high molecular weight samples employed in this work. In general, it is seen that the universal ratios for PαMS in toluene are quite similar to values found for PS in various good solvents. It appears likely, based on Figure 6, that at least some departure from the least-draining limit is involved for all the systems studied, except perhaps for PS in benzene. Although the agreement with Oono's theory for PαMS and PS are adequate, the existence of enhanced draining would indicate some fortuitous agreement. The least-draining theory requires that all the data reduce to a single universal curve, and this is definitely not observed in Figure 6. Again, we note that additional data for PαMS as well as PS samples of higher molecular weights are desirable. Further analysis of the results in Table IV, and Figure 6 is in progress.

V. Conclusions

In summary, static and dynamic results reported in this paper for PαMS in toluene are consistent with results from a number of previous studies. Diffusion coefficients measured in this work are shown to be in agreement with the results of Selser,[12] once the previously reported $\bar{M}_w$ values are corrected by using the proper value of dn/dc.

The break in the M-H-S plot at low molecular weights, presumably caused by enhanced draining, is accompanied by an increase in Huggins coefficient. The corresponding diffusion power law also breaks down, but at lower molecular weights. A change in PαMS tacticity at low molecular weights may also play a role.

Data for $k_d{}^*$ and $k_f{}^*$ are scattered, but the $k_f{}^*$ values seem to support the Pyun-Fixman[45] theory over the theories of Akcasu and Benmouna[43] and Yamakawa.[44]

The universal parameters $U_{\eta f}$, U_{fs}, and ρ all agree quite favorably with the theory of Oono and Kohmoto.[1-3] Large values of $U_{A\eta}$ and a possible weak molecular weight dependence on $U_{\eta s}$ may indicate departure from the least-draining limit. Alternatively, theoretical values for A_2 may be underestimated. Comparison to other theories applicable to the least-draining SA limit[13,14,25] reveals that the Oono theory[1,3] best describes the bulk of the PαMS solution properties in toluene. For low molecular weight samples, $U_{\eta f}$ and $U_{A\eta}$ decrease with increasing solvent permeation.

When the data are evaluated for poly(styrene) in various solvents, it appears likely that only in benzene are the chains at the least-draining limit. A plot of Φ/Φ_0 against $\alpha_s{}^2$ suggest that enhanced draining is present for toluene solutions and increases further on going to ethylbenzene. Similar data for the PS/THF system are scattered and, consequently, inconclusive. With regard to the PS/THF system, the older data[18,19] appear to be more reliable than results from a recent study.[11]

Even with the apparent presence of some draining at high molecular weights, the bulk of the universal ratio data suggests that the Oono theory[1,3] for least-draining coils provides at least semiquantitative agreement with experimental results. We are currently conducting a more rigorous study of draining effects in the high molecular weight SA limit using the methods suggested by Wang et al.[9] This analysis may prove useful in resolving the longstanding questions about the importance of draining on polymer properties.

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Appendix. Thermodynamic and Viscometric Radii for PαMS in Toluene

Size ratios, such as R_T/R_H, R_V/R_H, etc., can be calculated from the appropriate universal ratios. The purpose of this section is to tabulate viscometric and thermodynamic radii (R_V and R_T) for PαMS in toluene and to compare these results with other experimental and theoretical findings. If we assume that flexible polymer chains in good solvents may be modeled approximately as hard spheres of volume V,[6] the intrinsic viscosity and second virial coefficient are given as

$$[\eta] = {}^5\!/_2 N_A V/M \tag{A-1}$$

$$A_2 = 4N_A V/M^2 \tag{A-2}$$

Equations A-1 and A-2 lead directly to

$$R_V = 5.41 \times 10^{-9}(M[\eta])^{1/3} \tag{A-3}$$

$$R_T = 4.63 \times 10^{-9}(M^2A_2)^{1/3} \tag{A-4}$$

The calculated radii, including results for R_H, are tabulated in Table V. These values lead to the following power law relationships

$$R_V = 1.14 \times 10^{-2}\bar{M}_w^{0.572} \tag{A-5}$$

$$R_T = 1.04 \times 10^{-2}\bar{M}_w^{0.576} \tag{A-6}$$

$$R_H = 1.26 \times 10^{-2}\bar{M}_w^{0.556} \tag{A-7}$$

Equation A-5 is based on samples where $\bar{M}_w > 5 \times 10^4$, and eq A-7 excludes sample PC-3 ($\bar{M}_w = 7000$). The decision to omit low molecular weight samples is based on the curvature seen in Figure 4 at low molecular weights. No such curvature was observed for the thermodynamic parameter (Figure 2).

The values of the power law exponents are seen to be slightly lower than the theoretical value of 0.588.[73] The exponent for the R_H based expression is lower than for the others but is in excellent agreement with that found for polystyrene in good solvents where $R_H \alpha M^{0.55}$ over a broad molecular weight range.[20,74]

The size ratios of Table V yield average values for R_V/R_H and R_T/R_H of 1.09 and 1.05, respectively. Both parameters appear to be insensitive to molecular weight.

The values reported here are in general accord with experimental results on other flexible polymers in good solvents.[23] In addition, our values are quite close to values of 1.14 and 1.04 predicted by Oono[2] for R_V/R_H and R_T/R_H, respectively. Both ratios are greater than unity, the theoretical value for spheres.[6]

Registry No. Poly(α-methylstyrene), 25014-31-7; toluene, 108-88-3.

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Solution Properties of Exocellular Microbial Polysaccharides. 3. Light Scattering from Gellan and from the Exocellular Polysaccharide of *Rhizobium trifolii* (Strain TA-1) in the Ordered State

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ABSTRACT: Exocellular microbial polysaccharides (EPS) from *Rhizobium trifolii* strain TA-1 (TA-1-EPS) and from *Pseudomonas elodea* (Gellan) have been studied in dilute aqueous salt solutions by static and dynamic light scattering (LS) under conditions where the two polysaccharides are in the ordered (helical) state. The two polymers show pronounced chain rigidity. Their LS behavior has been evaluated from static and dynamic Zimm plots, i.e., Kc/R_θ versus q^2 and $D_{\mathrm{app}}(q) = \Gamma/q^2$ versus q^2, and from Holtzer plots, i.e., $qR_\theta/(Kc)$ versus $q = (4\pi/\lambda) \sin \theta/2$. From the two types of Zimm plots the common molecular parameters, i.e., molecular weight M_w, radius of gyration $R_g = \langle S^2\rangle_z^{1/2}$, and translational diffusion coefficient D_Z, were obtained. The Holtzer plots exhibit a clear asymptotic rod behavior. The value of the asymptotic plateau at large q gives the linear mass density (=mass per unit length) $M_L = M/L$. Comparison of the experimentally observed data to those calculated for a single-stranded helix allowed determination of the number of laterally associated strands which were found to be $n = 3.02 \pm 0.07$ and $n = 1.85 \pm 0.02$ for TA-1-EPS and Gellan, respectively. The Kuhn segment lengths could be estimated from the ratio of the heights of the maximum and asymptotic plateau in the Holtzer plot and were found to be $l_k = 152$ nm for TA-1-EPS and $l_k = 322$ nm for Gellan. These large values lie in the same range as the Kuhn segment lengths for other microbial polysaccharides. The observed angular dependence was checked with the predictions by Koyama for stiff chains and by Benoit et al. for flexible chains with large excluded volume. A good agreement was found with Koyama's prediction whereas application of the relationship for chains with large excluded-volume effect produces strong deviations. The large chain stiffness is confirmed by the value of the ρ-parameter R_g/R_h, where R_h is the hydrodynamically effective radius.

Introduction

In recent years a number of exocellular microbial polysaccharides (ESP) have aroused keen interest because of their unique solution and gelling properties.[1] In many instances, these properties have already opened avenues to the industrial utilization of such biopolymers,[2] while new species continue to appear as additional, interesting candidates for both basic and applied researches.[3]

A feature which seems to be in common to all EPSs so far studied is that in very dilute aqueous solution more or less disordered chains (probably, but not necessarily, single chains) would prevail. However, upon increasing polymer concentration and with added salt the EPS chains almost invariably undergo conformational disorder–order transitions. Because of the often highly cooperative character, this transition can be easily monitored by common physical–chemical techniques, e.g., chiroptical, calometric, and viscometric techniques.[4,5]

None of these experimental approaches can give, however, an unambigious answer to the central question of the final ordered conformation for the chains in each case (e.g., single helix or multiple-stranded helix). Kinetic measurements can be of valuable help in elucidating this important point.[6,7] In the context, radiation scattering (i.e., small-angle X-ray, small-angle neutron, and laser light scattering) appears quite naturally the most appropriate

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