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Draining Effects

Static and Dynamic Radii of Polystyrene in Ethylbenzene and Tetrahydrofuran

Alex M. Jamieson and K. Venkataswamy

Department of Macrom Molecular Science Case Western Reserve University, Cleveland, Ohio 44106, USA

Summary

Hydrodynamic radii, R_H^D and R_H^η, determined, respectively, from translational diffusion coefficients and intrinsic viscosities are compared with radii of gyration S_z for polystyrene of narrow molecular weight distribution in good-solvent systems, ethylbenzene and tetrahydrofuran. The S_z data indicate THF is of comparable solvating power to ethylbenzene which, in turn, based on literature data,is similar to benzene in its affinity for polystyrene. The ratios $\rho_1 = S_z/R_H^D$ and $\rho_2 = R_H^\eta/R_H^D$ are much larger for polystyrene in ethylbenzene than in tetrahydrofuran. These results are interpreted to indicate the presence of a large draining effect in the ethylbenzene system.

Introduction

This Communication summarizes some recent measurements of static and dynamic size parameters of polystyrenes of narrow molecular weight distribution in ethylbenzene and tetrahydrofuran. The relevant parameters are z-average radius of gyration, S_z, determined from light scattering intensities and hydrodynamic radius, $R_{h,f}$ and $R_{h,\eta}$ deduced, respectively, from the z-average translational diffusion coefficient obtained by dynamic light scattering, and the intrinsic viscosity. Our data are compared with literature data for polystyrene in benzene and toluene. The results are of interest, in view of current theoretical interpretations of the hydrodynamic properties of flexible chain molecules, since, as discussed below, they appear to clearly demonstrate the presence of significant draining effects.

Static and dynamic light scattering measurements were performed on two instruments; a custom-built system which has been described elsewhere (1), and utilizes a Coherent Radiation Model 42 Ar^+ laser (λ_o = 4880Å) with a Saicor digital correlator; and a Brookhaven Instruments Corp. spectrometer comprising a BI 2000 goniometer and BI 2020 correlator with SpectraPhysics 15 mW He/Ne laser (λ_o = 6328).

M_w and S_z were determined from square-root plots (2) of

$(K^*c/\Delta R_\theta)^{1/2}$ vs $\sin^2\theta + kc$ where K^* is the usual optical constant, c is polymer concentration in g/cc, ΔR_θ is the excess Rayleigh Ratio at scattering angle θ, and k is a convenient graphical constant; z-average diffusion coefficients were determined from photon correlation functions by the method of cumulants (3). Viscosity measurements were made using Ubbelohde viscometers chosen so that kinetic energy corrections were negligible.

Polystyrene standards were purchased from Toya Soda Ltd. and Pressure Chemicals (Tokyo). Weight-average molecular weights determined in our experiments in each case reproduced the specified values to within a few percent. Solvents used were of spectroscopic grade with measured values: for tetrahydrofuran: refractive index $\bar{n}^{30°C} = 1.403$, viscosity $\eta^{30°C} = 0.454$ cp, and refractive index increment with polystyrene solute $(d\bar{n}_D/dc)_{T = 30°C} = 0.2137$ cc/g; for ethylbenzene, $\bar{n}_D^{25°C} = 1.493$, $\eta_s^{25°C} = 0.619$ cp, and with polystyrene solute $(d\bar{n}_D/dc)_{T = 30°C} = 0.106$ cc/g.

Results

Table I summarizes our measurements, for polystyrene in ethylbenzene at 25°C, of single coil z-average translational diffusion coefficients, $D^o_{t,z}$, and intrinsic viscosities, $[\eta]$, as well as the equivalent hydrodynamic radii calculated from these quantities R_H^D, and R_H^η, respectively. Also listed are the weight-average molecular weights, M_w and z-average radii of gyration, S_z, determined from light scattering intensities, as well as the ratios $\rho_1 = S_z/R_H^D$ and $\rho_2 = R_H^\eta/R_H^D$. These data can be reproduced to within a few percent by the following relationships, determined by least squares fits:

$$S_z = 0.1503 \pm 0.005 M_w^{0.579 \pm 0.005} (\text{Å}) \qquad (1)$$

$$R_H^D = 0.1704 \pm 0.013 M_w^{0.535 \pm 0.007} (\text{Å}) \qquad (2)$$

and

$$R_H^\eta = 0.1875 \pm 0.013 M_w^{0.564 \pm 0.013} (\text{Å}) \qquad (3)$$

Our experimental results are, within experimental error, identical to those deduced by Miyaki et al for polystyrene in benzene (4), summarized by the relation

$$S_z = 0.1212 M^{0.595} (\text{Å}) \qquad (4)$$

Thus we infer that ethylbenzene is for polystyrene of solvating power comparable to benzene. Note S_z values for low molecular weights given in parentheses in Table I are computed by scaling from higher molecular weights using the Domb-Barrett equation, as described below. In eqs. (1)-(3), the difference in molecular weight scaling exponents for R_H^D, and R_H^η vs that for S_z has been ascribed to the existence in the R_H^D and R_H^η length scales of a relatively slow crossover in the chain statistical properties from gaussian behavior for short chains to the asymptotic limit of large excluded volume. Below we will argue that a substantial draining

Table I

Static and Dynamic Size Parameters of Polystyrene in Ethylbenzene

$M_w \times 10^{-6}$ g/mole	$D_t^o \times 10^{-7}$ cm^2/sec	$R_H^D(\mathring{A})$	$[\eta]$ cc/g	$R_H^{\eta}(\mathring{A})$	$S_z(\mathring{A})$ **	α_s^2 **	z **	S_z/R_H^D	$R_H^{\eta}/R^D{}_H$
0.093	4.54	77.8	41.5	84.9	(118)	(1.70)	(.856)	1.52	1.09
0.307	2.40	147	114	177	(223)	(1.84)	(1.555)	1.52	1.20
0.620	1.64	215	183	262	(338)	(2.10)	(2.210)	1.57	1.22
0.895	1.36	260	206	308	435	2.50	3.42	1.67	1.18
1.85	0.88	401	355	466	620	2.54	3.55	1.55	1.16
3.88	0.63	560	575	707	950	2.80	4.53	1.70	1.26
5.61	-	-	-	-	1188	3.06	5.65	-	-
8.46	-	-	-	-	1608	3.64	8.71	-	-

**Values in parentheses calculated from Domb-Barrett equation (see text).

effect must also be included to explain the larger hydrodynamic radii by polystyrene in THF.

In Table II, we list $D^{o}_{t,z}$ and R^{D}_{H} values for polystyrenes in tetrahydrofuran at 30°C determined from previous work (5,6). We also present $[\eta]$ and R^{η}_{H} values estimated from the experimental relation for polystyrene in THF by Appelt and Meyerhoff (7). Finally, S_z values determined in our laboratory for several polystyrenes in THF are given. Again, since we find these results to be numerically comparable to those obtained in ethylbenzene and benzene, it is clear that THF is a good solvent for polystyrene. Numbers in parentheses represent low molecular weight values again estimated by scaling for the experimental values at high molecular weights using the Domb-Barrett equation.

Discussion

First, we note that while our $[\eta]$ measurements for polystyrene in ethylbenzene are consistent with an earlier study (8a), our $D^{o}_{t,z}$ results are substantially different from previous literature values for this solvent (8b). The latter, however, represent weight-average quantities evaluated on relatively polydisperse samples. Also, our S_z values for ethylbenzene are the first reported for this solvent. Our S_z results for tetrahydrofuran are, on the other hand, in good agreement with the weight-average values S_w obtained by Bauman (9) for this system.

Second, we reiterate that our S_z values for polystyrene in ethylbenzene and tetrahydrofuran, when compared with literature values for polystyrene in benzene (eq. (4)), indicate that, based on S_z data, all these solvents are of comparably good solvating power for polystyrene. Specifically, we estimated the binary cluster integral, β_1 for ethylbenzene and tetrahydrofuran by comparing our results with the Domb-Barrett equation (10) for the chain expansion parameter, α_s. We utilized the asymptotic form of the latter, suggested by Miyaki et al (4), valid for $\alpha_s^2 \gtrsim 1.7^2$, viz.

$$\alpha_s^2 = 1.53z^{2/5} \qquad (5)$$

where the excluded volume parameter $z = (4\pi)^{-3/2}(M/M_o)^2\langle S^2\rangle_o^{-3/2}\beta$, and M_o is the monomer molecular weight with $\langle S^2\rangle_o$ the unperturbed radius of gyration. In calculating α_s^2 and $\langle S^2\rangle_o$, we used the relation

$$\langle S^2\rangle_o^{1/2} = 0.290\ M_w^{1/2}(\text{Å}) \qquad (6)$$

suggested by Ter Meer et al (11) based on a summary of theta solvent data. For ethylbenzene, we determine $\beta = 33 \pm 5 \times 10^{-24}$cc, and for THF, we obtain $\beta = 25 \pm 5 \times 10^{-24}$cc, which compare with $\beta = 34 \times 10^{-24}$cc reported for benzene by Miyaki et al (4). Within experimental error, ethylbenzene, benzene, and THF are equally good solvents for polystyrene. α_s and S_z quantities in parentheses in Tables I and II are calculated by using equations (5) and (6) and the experimental results for β. For $\alpha_s^2 < 1.7$, the complete form of the Domb-Barrett equation was used to estimate S_z values. For

Table II

Static and Dynamic Size Parameters of Polystyrene in Tetrahydrofuran

$M \times 10^6$ g/mole	$D_t^o \times 10^7$ cm^2/sec	R_H^D(Å)	R_H^η(Å) *	S_z(Å) **	α_s^2 **	z **	S_z/R_H^D	R_H^η/R_H^D
0.037	8.81	55.8	52.7	(68.3)	(1.48)	(0.41)	1.22	0.94
0.051	8.02	61.3	63.3	(79.6)	(1.50)	(0.47)	1.30	1.03
0.110	4.92	99.9	98.1	(123)	(1.64)	(0.70)	1.23	0.98
0.180	3.25	150	130	(162)	(1.73)	(0.90)	1.08	0.87
0.39	2.48	198	202	(250)	(1.91)	(1.33)	1.26	1.02
0.411	2.51	196	208	(258)	(1.92)	(1.36)	1.32	1.06
0.600	1.93	254	259	(318)	(2.00)	(1.64)	1.25	1.02
1.8	1.05	468	489	(594)	(2.33)	(2.85)	1.27	1.04
3.00	0.813	605	649	(807)	(2.58)	(3.68)	1.33	1.07
3.76	-	748$^+$	740	945	2.77	4.16	1.26	0.99
5.61	0.56	860	930	1146	2.85	4.97	1.23	1.08
7.6	0.435	1130	1104	(1408)	(3.10)	(5.85)	1.25	0.98

+Values calculated from $D_t^o = 3.4 \times 10^{-4} M_w^{-0.56}$ (least squares fit to data in column 2).

*Values calculated from $[\eta] = 1.363 \times 10^{-} M_w^{0.71}$ (cc/g) (ref. 7).

**Values in parentheses calculated from Domb-Barrett equation (see text).

ethylbenzene, the calculated values in parentheses are consistent with equation (4) which has been demonstrated (4) to be accurate for molecular weights down to $M_w = 250{,}000$.

Our observations indicate, as evident in the ratios $\rho_1 = S_z/R_H^D$ and $\rho_2 = R_H^{\eta}/R_H^D$ in Tables I and II, that, while the static size, S_z, is similar, within experimental error, for polystyrene in THF and ethylbenzene (and benzene), there is a considerable difference in hydrodynamic properties between the two solvents.

Specifically, for ethylbenzene the data in Table I correspond to mean values $\rho_1 = 1.59 \pm 0.07$ and $\rho_2 = 1.19 \pm 0.05$, while for THF, Table II indicates $\rho_1 = 1.27 \pm 0.04$ and $\rho_2 = 1.02 \pm 0.04$. It is further relevant to note that our results for ethylbenzene are consistent with literature values for chemically-similar solvents, benzene and toluene. For benzene, light scattering data of Kurata et al (12) and Adams and Delsanti (13) lead to $\rho_1 = 1.50$, and, when combined with viscometric data of Fukuda et al (14), $\rho_2 = 1.12$. For toluene, data of Appelt and Meyerhoff (15) and Utiyama (16) are summarized by $\rho_1 = 1.48$ and $\rho_2 = 1.15$. Also, we note that diffusion coefficients reported for polystyrene in THF by Mandema and Zeldenrust (17) produce hydrodynamic radii, R_H^D similar to our values. Since the static radii, S_z, indicate all four solvents are good solvents for polystyrene, the differences in ρ_1 and ρ_2 observed for THF suggest that polystyrene has a different hydrodynamic behavior in this solvent in comparison to the other three. Since larger hydrodynamic radii are observed for THF, polystyrene appears to have less of a draining effect in this solvent.

Unfortunately current theoretical analyses of single-coil hydrodynamics have not led to conclusive predictions. Most current efforts in this area are developments of the original bead-spring analysis of Kirkwood and Riseman (18). The latter derived results, utilizing configurational preaveraging of the hydrodynamic interactions between beads, which correspond in the non-draining limit to $\rho_1 = 1.51$ and $\rho_2 = 1.31$. More recently Monte Carlo simulations by Zimm (19), which utilize the KR equation of motion but avoid the preaveraging assumption, lead to $\rho_1 = 1.28$ and $\rho_2 = 1.075$, again in the non-draining limit. Our results for THF are consistent with the Zimm calculation. Literature values for ρ_1 and ρ_2 consistent with the Zimm theory are reported for polystyrene in theta solvents. Thus, Schmidt and Burchard (20) report $\rho_1 = 1.28$ summarizes results for polystyrene in a variety of theta solvents. Also, literature data for polystyrene in cyclohexane at 35°C, viz. (21)

$$D_t^o = 1.3 \times 10^{-4} M_w^{-0.5} (\mathrm{cm}^2/\mathrm{sec})$$

and (22)

$$[\eta] = 8.4 \times 10^{-2} M_w^{0.5} (\mathrm{cc/g})$$

when combined with a solvent viscosity $\eta_o = 0.75$ cp lead to a value $\rho_2 = 1.017$, i.e. consistent with our result for THF and the Zimm calculation (19).

An alternative theoretical route to calculate R_H^D and R_H^{η} is via the porous sphere hydrodynamic model (23,24). The possibility of a substantial draining effect in the transport properties of chain molecules has been previously suggested, based on comparisons of experiment versus the porous sphere theory (25,26). By applying the model formulated by Wiegel and Mijnlieff (25), we obtained (26) an expression for the ratio ρ_2 as a function of the dimensionless parameter

$$\alpha = 2S_z^2/3K \tag{7}$$

where K is the permeability at the center of a macromolecule in its average configuration. From Fig. 1 of reference 22, using the above determined average values of ρ_2, we obtain $\alpha = 18$ for polystyrene in THF and $\alpha = 5.5$ for polystyrene in ethylbenzene, This result indicates that polystyrene is approximately three times less permeable to THF than to ethylbenzene, or, correspondingly, benzene or toluene.

In summary, the data presented here indicate a significant draining effect for polystyrene in ethylbenzene when compared with tetrahydrofuran. The latter appears to conform closely to the non-draining limit and in this respect is similar to literature data for polystyrene in theta solvents. It is tempting to suggest the non-draining behavior is most likely to be observed for compact coils near the theta temperature and that as chain expansion occurs the coils become more porous. Such behavior has, in fact, been suggested recently, based on theoretical analysis (27). A more detailed molecular interpretation of our results may be anticipated through development of current theoretical efforts. Two approaches seems particularly promising, viz. the application of renormalization group techniques (27,28), and the utilization of Monte Carlo simulation methods (19,29). Our observations indicate that, to achieve a meaningful description of the transport properties of polystyrene solutions, the theoretical model will need to include an appropriate treatment of solvent draining effects.

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