Macromolecules 1991, *24*, 5729–5731 **5729**

Static and Hydrodynamic Size of Polystyrene Coils in Various Solvents

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Received March 4, 1991;
Revised Manuscript Received May 29, 1991

Introduction

The hydrodynamic radius, R_h, of a polymer coil can be compared to the root-mean-square radius of gyration, R_g, in terms of the dimensionless parameter ρ.

$$\rho = R_g/R_h \qquad (1)$$

Although there exist some reports that this ratio does not change with coil swelling,[1-3] the majority of data and recent theoretical efforts indicate that the value of ρ varies with solvent quality.

For the Θ condition, where the segmental distribution of a polymer coil is well-defined so that more rigorous theoretical treatment is possible, there seems to exist a good experimental consensus that $\rho = 1.27$–1.30.[4-8] As for theory, the original treatment of Kirkwood[9] for a Gaussian chain gave a ρ value of 1.504 while Zimm[10] obtained 1.479. Recently the thermal blob theory[11-13] treated the transition from Θ to good solvent condition, but it did not change the prediction of ρ. The renormalization group (RG) theory, however, gave much closer predictions. Oono and Kohmoto[14] predict $\rho = 1.24$, while Douglas and Freed[15] obtained 1.29 at the non-free-draining Gaussian chain limit. Although there still remain some controversies concerning the validity of the RG treatments,[16,17] there is no question that their results are in better agreement with the experimental data.

Turning to the case of good solvents, there again exists a reasonable experimental consensus. For polystyrene, Nemoto et al.[18] reported 1.53 ± 0.03 in benzene, and Jamieson et al.[19,20] obtained 1.57 in ethylbenzene, while the values of 1.53 ± 0.04 and 1.5–1.7 can be deduced from the data of Varma et al.[8] and Appelt and Meyerhoff[21] in toluene, respectively. For other polymers, we can list 1.5 and 1.47 for poly(α-methylstyrene) in toluene by Noda et al.[1,2] and Kim et al.,[22] respectively, 1.50 for polyisoprene in cyclohexane by Tsunashima et al.,[23] and 1.555 for poly(methyl methacrylate) in acetone by ter Meer et al.[24]

According to the blob theories,[11-13] ρ increases smoothly with solvent quality up to the asymptotic value of 1.86 in a good solvent, which again differs from the experimental observation. Oono and Kohmoto[14] predict 1.562 in their RG calculation for a nondraining self-avoiding walk chain, which is in good agreement with the experimental data. On the other hand, recent RG treatments of Freed and co-workers[15] reached the conclusion that ρ would not change if the hydrodynamic interaction does not change with coil swelling; i.e., the large ρ values obtained in good solvents are due to the change of solvent draining. In a series of light scattering studies with polystyrene in tetrahydrofuran (THF), Jamieson and co-workers[19,20] reported the ρ value of 1.3, which is much smaller than that observed in other good solvents. They argued that the solvent draining in THF would be much smaller due to the more facile internal motion found in the system[25] and interpreted their results in favor of the RG theory of Freed et al.[15,17] This result implies that the hydrodynamic interaction in a polymer coil is dependent not only on the segmental distribution but also strongly on the nature of the solvent. In this paper, we present the results of static and dynamic light scattering studies with polystyrenes in a number of solvents with varying solvent quality and polarity in order to further pursue this problem.

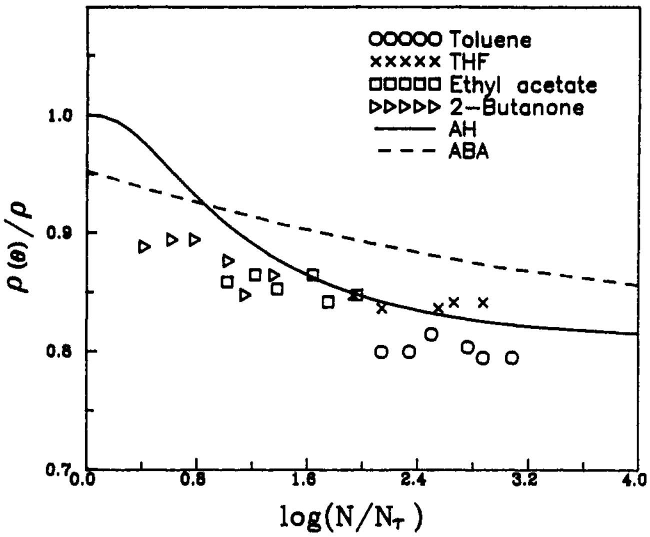

Figure 1. Variation of the ratio of the hydrodynamic radius to the radius of gyration (ρ) with solvent quality. The symbols represent the experimental data obtained from various solvents: ((○) toluene, (×) THF, (□) ethyl acetate, (▷) 2-butanone). The solid and dashed lines are from the blob theories by Akcasu and Han[11] (AH) and its modified version of Akcasu et al.[12] (ABA), respectively.

Experimental Section

We used two light scattering instruments. One is a commercial instrument (Malvern, Model 4700) equipped with a 64-channel, 8-bit digital correlator and operated with a 488.0 nm line of an Ar ion laser (Coherent, Model 90-3). The other instrument described elsewhere[26] uses a He/Ne laser (Spectra-Physics, Model 127-35) as the light source. For most of the static measurements, the latter instrument was used. All the measurements were carried out at the temperature of 25.0 ± 0.1 °C.

Solvents were reagent grade (Aldrich) and further purified by fractional distillation after drying with proper reagents.[27] Six commercial polystyrene samples were used, and their characteristics are listed in Table I. At least four different concentrations were prepared by weight and clarified by slow filtration through PTFE membrane filters (Gelman) whose pore size was at least 4 times larger than the R_g of the polymer. With our clarification procedure, we found no change in molecular weight and polydispersities, indicating sample degradation.

Static light scattering data were analyzed by the square-root plot[28] in the Guinier region, i.e., at the scattering angle $qR_g < 1$, where q is the magnitude of the scattering wave vector. The Rayleigh factors were calculated from the scattered intensities by use of purified toluene (Rayleigh factor: 10.0×10^{-6} cm^{-1} (V_V)[29] at 632.8 nm) as the reference material and an n^2 refraction correction.[30]

Autocorrelation functions were obtained from the same samples at more than five scattering angles within the Guinier region in order to check the angular dependence of the decay time constants. The nonlinear regression method was used to fit the autocorrelation function to the second-order cumulant model function,[31] and the subsequent analysis scheme to deduce R_h was similar to that of other works.[8,19]

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Table I
R_g, R_h, and ρ of Polystyrenes in Different Solvents

sample	M_w[c]	M_w/M_n[c]		toluene	THF	CCl_4	MEK	EA
F-80[a]	706	1.05	M_w (×10^3)	697	710	721	695	719
			R_g (nm)	39.2	39.5	38.7	30.7	30.0
			R_h (nm)	24.7	26.3	24.7	20.8	21.0
			ρ	1.59	1.50	1.59	1.48	1.43
F-128[a]	1090	1.08	M_w (×10^3)	1130	1120	1150	1190	1160
			R_g (nm)	50.2	51.4	49.0	39.2	38.1
			R_h (nm)	31.6	33.8	30.5	26.7	26.8
			ρ	1.59	1.52	1.61	1.47	1.42
P-180[b]	1800	1.06	M_w (×10^3)	1650	1650	1650	1600	1650
			R_g (nm)	61.9	64.3	60.7	47.7	46.0
			R_h (nm)	39.6	41.7	39.7	32.0	32.5
			ρ	1.56	1.54	1.53	1.49	1.42
F-288[a]	2890	1.09	M_w (×10^3)	2930	2950	2980	2910	2960
			R_g (nm)	89.2	91.7	88.7	67.7	64.6
			R_h (nm)	56.3	60.2	55.0	45.9	44.5
			ρ	1.58	1.52	1.61	1.47	1.45
F-380[a]	3840	1.04	M_w (×10^3)	3840	3710	3970	3930	3890
			R_g (nm)	104	105	102	79.2	77.2
			R_h (nm)	65.0	69.5	64.2	52.3	51.6
			ρ	1.60	1.51	1.59	1.51	1.50
F-700[a]	6770	1.14	M_w (×10^3)	6070	6270	6310	6060	6300
			R_g (nm)	137	138	135	105	101
			R_h (nm)	85.4	91.1	84.4	70.0	68.6
			ρ	1.60	1.51	1.60	1.50	1.47
mean			ρ	1.59 ± 0.01	1.52 ± 0.01	1.59 ± 0.03	1.49 ± 0.01	1.45 ± 0.03

[a] From the Tosoh Corp. [b] From Polymer Laboratories, Ltd. [c] Manufacturer's value.

Results and Discussion

Most of the parameters used conform to the values in the literature[32] except the dn/dc value of CCl_4 at the wavelength of 632.8 nm. We measured 0.146 mL/g while the literature value is 0.156.[32,33] We have no explanation for this discrepancy, but the molecular weight in CCl_4 would yield consistently values smaller by about 10% than those determined in other solvents if we used the literature value.[32,33] Also the literature values[32] at other wavelengths are consistent with the value measured in this work in terms of the dispersion relation.

The R_g and R_h thus obtained are listed in Table I. The molecular weight relationships of R_g and R_h were as follows:

$$\begin{aligned} R_g &= 0.0150M^{0.583\pm0.022}\ \text{nm (toluene)} \\ &= 0.0160M^{0.580\pm0.015}\ \text{nm (THF)} \\ &= 0.0144M^{0.585\pm0.029}\ \text{nm (CCl}_4\text{)} \\ &= 0.0140M^{0.570\pm0.024}\ \text{nm (2-butanone, MEK)} \\ &= 0.0148M^{0.562\pm0.031}\ \text{nm (ethyl acetate, EA)} \end{aligned}$$

$$\begin{aligned} R_h &= 0.0103M^{0.577\pm0.015}\ \text{nm (toluene)} \\ &= 0.0106M^{0.579\pm0.020}\ \text{nm (THF)} \\ &= 0.0104M^{0.576\pm0.033}\ \text{nm (CCl}_4\text{)} \\ &= 0.0109M^{0.560\pm0.027}\ \text{nm (2-butanone)} \\ &= 0.0139M^{0.542\pm0.019}\ \text{nm (ethyl acetate)} \end{aligned}$$

Our results are in good agreement (within 4%) with available literature values in toluene[8,21,34] and 2-butanone.[8,35] We could not find a reasonable set of literature values in ethyl acetate and in CCl_4 to compare with our results. On the other hand, our results in THF are somewhat different from those of Jamieson and co-workers. We will come back to this later.

The ρ values are listed in Table I. For a given solvent, the ρ values fluctuate a little with the molecular weight of the polymer and do not exhibit a clear trend with molecular weight as predicted by the blob theory. This is probably due to the relatively narrow molecular weight range of polystyrenes used in this study and the experimental uncertainties aggravated by taking the ratio of two size parameters. In Figure 1 we plot our results together with theoretical curves from the blob theory of Akcasu and Han (AH) and its modified version of Akcasu et al. (ABA). In this plot, we set $\rho(\theta) = 1.27$[4] at $N/N_\tau = 1$, which yields $\rho(\theta)/\rho = 0.808$ in the high N/N_τ limit, adopting N_τ values from Han and Schafer,[36] which were obtained by fitting dynamic light scattering results to the AH blob theory. As shown in the figure, most of our data points fall below the theoretical predictions. A similar trend was also found by Varma et al.[8] Since our ρ values do not exhibit a clean molecular weight dependence, quantitative evaluation of N_τ for a better fit was not attempted, but about a factor of 3 reduction of N_τ will bring about better agreements with the AH theory for 2-butanone and ethyl acetate data. Also it may be worth mentioning that several attempts to test the blob theories show disparate results in N_τ values.[8,11,36-38] The ABA theory appears to be better in terms of smoother transition with solvent quality but worse in absolute values.

Anyhow, it is clear that ρ increases monotonically with solvent quality and that the ρ values found in good solvents are in good agreement with the RG predictions for the self-avoiding chain limit. With these results alone, however, it is difficult to conclude whether the increase of ρ with solvent quality is due to the increase of draining with coil swelling.[15,17] We are only able to say that the hydrodynamic interaction is mainly a function of the segmental distribution, and the dependence on the nature of solvents appears to be minor for the five solvents tested in this study. This means that we could not positively reproduce the anomalous behavior reported for THF solutions.[19,20] Although our results from THF solution show indeed a little larger R_h values compared to other good solvents and thus give consistently smaller ρ values, the effect is weaker than reported previously, only slightly beyond experimental uncertainty. The difference in two sets of THF solution data comes from the fact that R_h

values by Jamieson and co-workers[19] are slightly larger (~6%) than ours while their R_g values[20] are about 15% smaller than ours. Although the available R_g data of polystyrene in THF are not enough to resolve the problem, we are afraid that their R_g values are too small compared to existing R_g values in THF[39] and in other good solvents.[8,18,21,40] Also we note that the apparently facilitated internal motion observed in THF solution[25] cannot be a sufficient condition to observe the anomalously small ρ value since the work of Tsunashima et al. with polyisoprene in cyclohexane[23] showed a similar behavior at high scattering angles while it gave the ρ value of 1.5, which is consistent with our value in THF solution.

There exists a similar difficulty on the theoretical side. The problems involved in Zimm's Monte Carlo results[7] and the RG calculation by Oono and Kohmoto[14] were addressed.[16] It has even been argued by Fixman that universality of $\rho(\theta)$ does not exist.[41] Therefore our present knowledge is still far from complete and further studies are required to elucidate the single-coil properties in dilute solution theoretically and experimentally.

Acknowledgment. This work was supported in part by grants from the Korean Science and Engineering Foundation and from the Korea Ministry of Education. We also appreciate the helpful comments from reviewers.

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Registry No. Polystyrene, 9003-53-6.