(5) Michaeli, I. *J. Polym. Sci., Part C* **1968**, *16*, 4169.
(6) Crescenzi, V. *Adv. Polym. Sci.* **1968**, *5*, 358.
(7) Davenport, J. N.; Wright, P. V. *Polymer* **1980**, *21*, 287.
(8) Jortner, J.; Sololov, K. *J. Phys. Chem.* **1961**, *65*, 1633.
(9) Robinson, G. W. *J. Chem. Phys.* **1967**, *46*, 572.
(10) Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions", 2nd ed.; Butterworths: London, 1965.
(11) Harned, H. S.; Owen, B. B. "The Physical Chemistry of Electrolyte Solutions", 3rd ed.; Reinhold: New York, 1958.
(12) Verwey, E. J. W.; Overbeek, J. Th. G. "Theory of Stability of Lyophobic Colloids"; Elsevier: Amsterdam, 1948.
(13) Muresan, I.; Zador, L. *Stud. Univ. Babes-Bolyai, Chem.* **1973**, *18*, 89.
(14) Zador, L.; Muresan, I. *Rev. Roum. Chim.* **1974**, *19*, 353.
(15) Zador, L.; Muresan, I. *Stud. Univ. Babes-Bolyai, Chem.* **1979**, *24*, 3.
(16) Zador, L.; Muresan, I. *Stud. Univ. Babes-Bolyai, Chem.* **1979**, *24*, 47.
(17) Muresan, I.; Zador, L. *Bul. Inst. Politeh. sect. 2* **1980**, *26*, 59.
(18) Elisassaf, J. *J. Appl. Polym. Sci.* **1963**, *7*, S9.
(19) Wojtczak, Z. *Rocz. Chem.* **1968**, *42*, 1319.
(20) Wojtczak, Z. *Rocz. Chem.* **1971**, *45*, 237.
(21) Wojtczak, Z. *Rocz. Chem.* **1973**, *47*, 1703.
(22) Rossini, F. D.; Wagman, D. D.; Evans, W. H.; Levine, S.; Jaffé, I. "Selected Values of Chemical Thermodynamic Properties", National Bureau of Standards, Washington, D.C., Circular 500, 1952.
(23) Slansky, C. M. *J. Am. Chem. Soc.* **1940**, *62*, 2430.
(24) Price, E. In "The Chemistry of Non-aqueous Solvents"; Lagowski, J. J., Ed.; Academic Press: New York, 1966; Vol. I, Chapter 2.
(25) Henstock, H. *J. Chem. Soc.* **1934**, 1340.
(26) Stephen, H.; Stephen, T., Eds. "Solubilities of Inorganic and Organic Compounds"; Pergamon Press: London, 1963.
(27) *Encycl. Polym. Sci. Technol.* **1969**, *10*, 781 ff.
(28) Khokhlov, A. R. *J. Phys. A.: Math. Gen.* **1980**, *13*, 979.
(29) de Gennes, P.-G., "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(30) de Gennes, P.-G.; Pincus, P.; Velasco, R. M.; Brochard, F. *J. Phys. (Orsay)* **1976**, *37*, 1461.
(31) Odijk, T. *Macromolecules* **1979**, *12*, 686.
(32) Mandel, M. *Eur. Polym. J.* **1983**, *19*, 911.
(33) Oosawa, F. "Polyelectrolytes"; Marcel Dekker: New York, 1971.

Equivalence of Scaling Exponents from Static and Dynamic Measurements

Mohan Ramanathan

West Virginia University, Department of Physics, Morgantown, West Virginia 26506

Milton E. McDonnell*

Allied Chemical Corporation, Syracuse Research Laboratory, Solvay, New York 13209.

Received December 6, 1983

ABSTRACT: New dynamic light scattering measurements of the translational diffusion coefficient of relatively monodisperse samples of polystyrene in toluene indicate that at sufficiently high molecular weight, the hydrodynamic radius is directly proportional to the radius of gyration at infinite dilution. This observation constitutes a demonstration of the equality of the static scaling exponent ν and the hydrodynamic scaling exponent ν_H. In order to show the equality of the two scaling exponents, it is necessary to (1) use molecules of sufficiently high molecular weight, (2) have an adequately good solvent, (3) assess the effect of polydispersity, and (4) limit the scattering from intramolecular motion.

Introduction

To date, reported measurements of the hydrodynamic radius R_H of isolated random-configurationed macromolecules in good solvents do not increase as quickly with molecular weight M as do the values of the radius of gyration $\langle S^2\rangle^{1/2}$; that is, the reported values of the hydrodynamic coefficient ν_H where $R_H \propto M^{\nu_H}$ are less than the static scaling exponent ν where $\langle S^2\rangle^{1/2} \propto M^{\nu}$.[1] Several authors have argued that this is a consequence of the hydrodynamic radius being more heavily weighted by short-chain segments which are distributed more compactly than the farther separated segments that are more prominent in the averaging of the radius of gyration.[2,3] This argument implies that macromolecules of much higher molecular weight must be used for hydrodynamic measurements to reach the asymptotic scaling limit where $\nu_H = \nu$. Here we present dynamic light scattering measurements of the translational diffusion coefficient of polystyrene in toluene indicating that this asymptotic limit is obtainable with commercially available samples. It is the lack of hydrodynamic data on sufficiently high molecular weight material with carefully controlled polydispersity at sufficiently low scattering vector that has obscured the experimental verification of the equivalence of ν and ν_H.

Methods and Materials

Five relatively monodisperse polystyrene standards with a molecular weight in the range $(1–20) \times 10^6$ produced and partially characterized by Toyo Soda Manufacturing Co. were obtained from Varian. The samples were dissolved in toluene with index of refraction $n = 1.491$, distilled in glass by Burdick and Jackson Laboratories. Dynamic light scattering measurements were made in a Chromatix KMX-6DC low-angle laser scattering photometer with radiation of a wavelength $\lambda = 6.328 \times 10^{-5}$ cm at an angle $\theta = 4.02°$ from the transmitted beam. The individual photons were analyzed in a 48-channel Malvern K7023 autocorrelator in the single-clipped mode. The experiment was performed at 23 °C.

Each sample was measured at five roughly equally spaced concentrations below $c^*/2$, where

$$c^* = 2.5[\eta]^{-1} \approx M/N_{Av}\langle S^2\rangle^{3/2} \quad (1)$$

is a concentration at which overlap of adjacent molecules becomes significant, $[\eta]$ indicates intrinsic viscosity, and N_{Av} is Avogadro's number. Solution concentrations are reported as a solute mass per solution volume of solution as in previous studies.[4] Samples were filtered into the scattering cell through a Millipore filter that had a pore size at least 6 times larger than the radius of gyration that Toyo Soda reported for the polymer in benzene at 30 °C.

Typically, 10^5–10^6 correlation functions over 2.5 decay periods were collected in the homodyne mode. The data were fit through the second cumulant with a variable base line.[5] A sample was

0024-9297/84/2217-2093$01.50/0

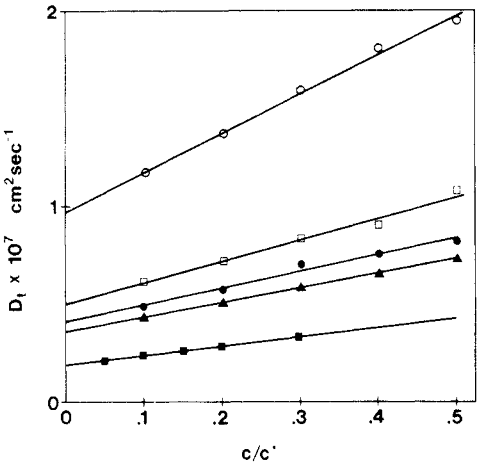

Figure 1. Translational diffusion coefficient as a function of reduced concentration for polystyrene in toluene at 23 °C for molecular weight 1.26 × 10^6 (○), 3.84 × 10^6 (□), 5.48 × 10^6 (●), 6.77 × 10^6 (▲), and 20.6 × 10^6 (■). Solid line indicates best least-squares fit.

considered acceptable if (1) the base line fell within 0.2% of its calculated position and on successive measurements (2) the first cumulant was reproducible to within 2%, (3) the second to within 30%, and (4) the correlation coefficient of the fit was greater than 0.8. Since the second and third cumulants are very small for samples with low polydispersity, it was judged better to set the third cumulant equal to zero rather than let the fitting routine irreproducibly distribute deviations from a single exponential between these terms on successive measurements.

Data

The first cumulant Γ is divided by the solvent volume fraction to convert to the solvent fixed frame of reference, and an apparent diffusion coefficient D_{app} is obtained by dividing by the square of the scattering vector

$$q = \left(\frac{4\pi n}{\lambda}\right) \sin(\theta/2)$$

This coefficient is labeled apparent because it gives information on both the translational diffusion coefficient D_t and intramolecular motion. Low-angle measurements are desirable in this investigation because the contribution to D_{app} from internal motion becomes negligible at a sufficiently small scattering vector. The effect of the intramolecular motion was evaluated for monodisperse linear random coils with a preaveraged hydrodynamic interaction to be

$$D_{\text{app}}/D_t = 1 + 2q^2\langle S^2\rangle/15 + \mathcal{O}(q^4\langle S^2\rangle^2)$$

by Burchard et al.[6] Using this equation with the relation between the radius of gyration and the molecular weight of polystyrene in toluene at 25 °C

$$\langle S^2\rangle^{1/2} = (1.101 \times 10^{-9})M^{0.605} \text{ cm} \qquad (2)$$

that was found by Appelt and Meyerhoff,[7] one can calculate the translational diffusion coefficient. This correction varies from a 0.04% to 1.2% reduction in the apparent diffusion coefficient, which is smaller than the accuracy of the measurements.

In Figure 1 the average values of the translational diffusion coefficient are plotted as a function of c/c^*, where c^* is given by eq 1 with the intrinsic viscosity calculated by the Mark–Houwink equation determined by Oth and Desreux[8] for high molecular weight polystyrene in toluene. The values of the translational diffusion coefficient at infinite dilution, $D_t°$, the concentration dependence, $\mathrm{d}D_t/\mathrm{d}c$, and the average weighted second cumulant, μ_2/Γ^2, are collected in Table I. The linear regression coefficients of lines in Figure 1 are greater than 0.99. No systematic variation of weighted second virial coefficients with concentration was noted.

Table I
Values of $D_t°$, $\mathrm{d}D/\mathrm{d}c$, and μ_2/Γ^2 for Polystyrene in Toluene at 23 °C

$M_w \times 10^{-6}$	$D_t° \times 10^8$, cm^2/s	$\mathrm{d}D/\mathrm{d}c \times 10^5$, cm^5/(g-s)	μ_2/Γ^2
1.26	9.7	2.2	0.027
3.84	5.0	2.8	0.027
5.48	4.1	2.9	0.044
6.77	3.6	3.0	0.048
20.6	1.85	4.1	0.034

Table II
Comparision of the Polydispersity Measured by GPC and Light Scattering

	M_w/M_n	
$M_w \times 10^{-6}$	GPC	LS
1.26	1.05	1.08
3.84	1.04	1.08
5.48	1.15	1.14
6.77	1.14	1.15
20.6		1.10

Analysis

We seek a relation between the diffusion coefficient and the molecular weight of the form

$$D_t° = KM^{-\nu_H} \qquad (3)$$

where K and ν_H are to be experimentally determined. In order to correlate the diffusion coefficient and the molecular weight, it is necessary to compare appropriate averages of each quantity. The first cumulant gives the Z-average diffusion coefficient. If the molecular weight distribution is assumed to follow a Schulz distribution in terms of parameters y and h

$$f(M) = y^{h+1}M^h e^{-yM}/\Gamma(h+1)$$

the corresponding diffusion-average molecular weight M_D is[9]

$$M_D = \frac{M_w}{h+1}\left[\frac{\Gamma(h+2)}{\Gamma(h+2-\nu_H)}\right]^{1/\nu_H} \qquad (4)$$

where $\Gamma(Z)$ is the gamma function of argument Z.

To use eq 4 to assess M_D, the polydispersity $P = 1 + h^{-1}$ must be known. This is available from the weighted second cumulant, which corresponds to[10]

$$\mu_2/\Gamma^2 = [\langle D^2\rangle_Z/(D_Z)^2] - 1$$

Again assuming a Schulz distribution and a power law relation between D and M we find

$$\mu_2/\Gamma^2 = \frac{\Gamma(h+2-2\nu_H)\Gamma(h+2)}{[\Gamma(h+2-\nu_H)]^2} - 1 \qquad (5)$$

Thus the evaluation of the constants ν_H and K of eq 3 demands that the diffusion coefficients of Table I be related to the molecular weight average of eq 4 where h of each sample can be obtained from eq 5. This is easy to do since the calculated values of h from eq 5 are not very sensitive to ν_H. Taking the self-consistent value of ν_H = 0.587, the measured values of the weighted second cumulant become a measure of polydispersity. These polydispersity calculations are collected in Table II along with the GPC measurements made by Toyo Soda for lower molecular weight samples. The important features to note

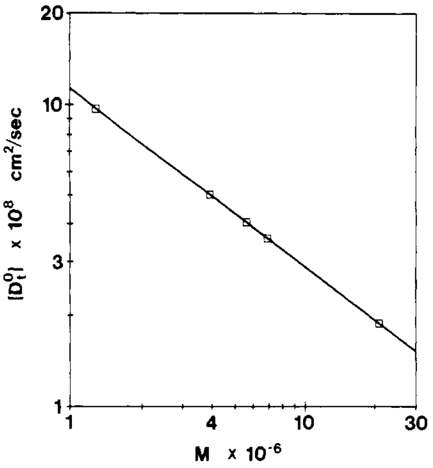

Figure 2. Translational diffusion coefficient at infinite dilution as a function of the molecular weight.

are that (1) there is good agreement between the GPC and dynamic light scattering measurements of polydispersity and (2) the polydispersity of the high molecular weight sample is comparable to that of the lower ones. The range in polydispersity between samples corresponds to a variation of h from 6.5 to 12. Applying this range of h to eq 3 indicates that the value of M_D varies from 2.8% to 1.6% larger than the M_w measured by light scattering by Toyo Soda. We apply this systematic correction although we note that it is less than the accuracy of the molecular weight determinations.

The Z-average translational diffusion coefficient is plotted as a function of the diffusion-average molecular weight on a double-logarithmic plot in Figure 2. The points also would correspond to the diffusion coefficient of truly monodisperse samples of mass $M = M_D$. The points are best described by the equation

$$D_t^\circ = (3.7 \pm 0.1) \times 10^{-4} M^{-(0.587 \pm 0.002)} \text{ cm}^2/\text{s} \qquad (6)$$

where the uncertainties are the standard deviation of the fit parameter for the data to the given model. It is important to realize that even though the measurements of D and M may only be accurate to within 2% and 4%, respectively, ν_H can be measured to within 0.3%. This follows from eq 3 where for each set of data

$$\Delta\nu_H = [(\Delta D_t^\circ/D_t^\circ)^2 + (\Delta M/M)^2]^{1/2}/\ln M$$

The $\ln M \simeq 16$ in the denominator permits the relative accuracy of ν_H to greatly exceed those of D_t° and M.

The correlation coefficient of the fit to eq 6 is 0.998. Omitting the point on either extreme of molecular weight does not alter the exponent more than 0.001, which indicates that ν_H is not varying strongly with molecular weight over this range. Finally we wish to point out that although we have carefully tried to assess the effect of polydispersity and internal modes, the experiment has been designed to minimize the contribution of each effect. Were either or both corrections ignored the change in the value of ν_H would be 0.001 or less.

Discussion

The importance of the exponent in eq 6 is that this value of $\nu_H = 0.587 \pm 0.002$ is essentially equal to the most accurate theoretical calculation of $\nu = 0.588$.[11] It compares favorably with the experimentally determined values of $\nu = 0.595 \pm 0.005$[12] and 0.58[13] for the dependence of the radius of gyration on the molecular weight dependence of relatively monodisperse samples of polystyrene in benzene and $\nu = 0.58$[4] from the concentration dependence of scattered light intensity from semidilute solutions of polystyrene in toluene. The agreement with the value of $\nu = 0.605$[7] for polystyrene in toluene in eq 2 is not as close, but we judge this determination of ν to be less accurate since relatively large polydispersity corrrections were made in the course of the evaluation.

Reviewing reported values of the Flory parameter χ of different solutions reveals that polystyrene in toluene is the system described by the asymptotic value of ν_H at the lowest molecular weight.[1] Meyerhoff[14,15] reported $\nu_H = 0.574$ for this system from diffusion coefficients measured in the ultracentrifuge. The samples had varying polydispersities up to 1.5 and only one of the samples had a molecular weight in excess of one million. We observe that since the range of molecular weight studied was less than that of the current data the values are not inconsistent.

More recently, Appelt and Meyerhoff[7] reported $\nu_H = 0.577$ for polystyrene samples in the molecular weight range of 10–40 million. They concluded that ν_H gave negligible variation from the low molecular weight value previously studied.[14,15] For the high molecular weight studies the polydispersity varied from 1.2 to 2.0 and the diffusion coefficients were measured at higher scattering angles than those of the present study and extrapolated to $\theta = 0°$.[7] Because of the two relatively large extrapolations it is difficult to assess the accuracy of their determination of ν_H. The current measurements avoid these. We note that several other dynamic light scattering measurements of the diffusion coefficient of polystyrene in toluene have been reported,[16] but they use either too low a molecular weight or insufficiently describe measuring conditions to examine asymptotic behavior.

Conclusion

The hydrodynamic radius and the radius of gyration are proportional to one another in systems that are experimentally accessible. In order to see this relation the molecular weight must be sufficiently high and the solvent adequately good. The effect of polydispersity must be assessed and if the hydrodynamic radius is measured by dynamic light scattering (which permits the highest accuracy), measurements must be made at a very low scattering vector.

Acknowledgment. This work was supported by National Science Foundation Grant ISP-8011453.

Registry No. Polystyrene (homopolymer), 9003-53-6.

References and Notes

(1) Schaefer, D. W.; Han, C. C. Sandia Report 0815, Sandia National Laboratories, Albuquerque, NM, 1982.
(2) Akcasu, A. Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276.
(3) des Cloizeaux, J.; Weill, G. *J. Phys.* (*Paris*) **1979**, *40*, 99.
(4) Amirzadeh, J.; McDonnell, M. E. *Macromolecules* **1982**, *15*, 927.
(5) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.
(6) Burchard, W.; Schmidt, M.;Stockmayer, W. H. *Macromolecules* **1980**, *13*, 580.
(7) Appelt, B.; Meyerhoff, G. *Macromolecules* **1980**, *13*, 657.
(8) Oth, J.; Desreux, V. *Bull. Soc. Chim. Belges* **1954**, *63*, 285.
(9) Ford, N. C.; Gabler, R.; Karasz, F. E. *Adv. Chem. Ser.* **1973**, *No. 125*, 25.
(10) Brown, J. C.; Pusey, P. N. *J. Phys. D* **1974**, *7*, L31.
(11) Le Guillou, J. C.; Zinn-Justin, J. *Phys. Rev. Lett.* **1977**, *39*, 95.
(12) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180.
(13) Fukuda, M.; Fukutomi, M.; Kato, Y.; Hashimoto, T. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 871.
(14) Meyerhoff, G. *Z. Phys. Chem.* (*Frankfurt am Main*) **1960**, *23*, 100.
(15) Nachtigall, K.; Meyerhoff, G. *Z. Phys. Chem.* (*Frankfurt am Main*) **1961**, *30*, 35.
(16) Pusey, P. N.; Vaughan, J. M.; Williams, G. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1696.