layers. The first technique that comes to mind for monitoring the complexes is dynamic light scattering, which has been applied to a diverse variety of systems.[29] It might be possible to verify eq 34 by measuring the translational diffusion coefficient of the complexes as a function of the ionic strength.

From an experimental point of view, our calculation rather severely restricts the range of values of the experimental parameters. More complex situations are of more practical interest. Hopefully, our results may be extended to other cases, a scaling approach being perhaps the most feasible extension.

Acknowledgment. The author thanks Professor Mandel for helpful discussions and Stichting Scheikundig Onderzoek Nederland for financial support.

References and Notes

(1) de Gennes, P. G. *Rep. Prog. Phys.* **1969**, *32*, 187.
(2) Lifschitz, I. M. *Zh. Eksp. Teor. Fiz.* **1968**, *55*, 2408 (translated in *Sov. Phys.-JETP* (*Engl. Transl.*) **1969**, *28*, 1280).
(3) Edwards, S. F. *Proc. Phys. Soc.* **1965**, *85*, 613.
(4) Jones, I. S.; Richmond, P. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 1062.
(5) Wiegel, F. W. *J. Phys. A* **1977**, *10*, 299.
(6) Dolan, A. K.; Edwards, S. F. *Proc. R. Soc. London, Ser. A* **1975**, *343*, 427.
(7) Richmond, P.; Lal, M. *Chem. Phys. Lett.* **1974**, *24*, 594.
(8) Joanny, J. F.; Leibler, L.; de Gennes, P. G. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1073.
(9) Chan, D.; Davies, B.; Richmond, P. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1584.
(10) DiMarzio, E. A.; Guttman, C. M.; *J. Res. Natl. Bur. Stand.* **1978**, *83*, 165.
(11) Freed, K. F. *Adv. Chem. Phys.* **1972**, *22*, 1.
(12) Lifschitz, I. M.; Grosberg, A. Yu.; Khokhlov, A. R. *Rev. Mod. Phys.* **1978**, *50*, 683.
(13) de Gennes, P. G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, N.Y., 1979.
(14) de Gennes, P. G. *J. Phys.* (*Paris*) **1976**, *37*, 1445.
(15) Vrij, A. *Pure Appl. Chem.* **1976**, *48*, 471.
(16) Yamakawa, H. *Pure Appl. Chem.* **1976**, *46*, 135.
(17) Edwards, S. F. *Proc. Phys. Soc.* **1967**, *91*, 513.
(18) Edwards, S. F. *J. Phys. A* **1968**, *1*, 15.
(19) Odijk, T. *Macromolecules* **1979**, *12*, 688.
(20) Berry, M. V.; Mount, K. E. *Rep. Prog. Phys.* **1972**, *35*, 315.
(21) Inomata, A.; Singh, V. A. *J. Math. Phys.* **1978**, *19*, 2318.
(22) Morse, P. M.; Feshbach, H. "Methods of Theoretical Physics"; McGraw-Hill: New York, 1953; Chapter 7.
(23) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
(24) Oosawa, F. "Polyelectrolytes"; Marcel Dekker: New York, 1971.
(25) Stigter, D. *J. Colloid Interface Sci.* **1975**, *53*, 296.
(26) Fixman, M. *J. Chem. Phys.* **1979**, *70*, 4995.
(27) Bender, C. M.; Orszag, S. A. "Advanced Mathematical Methods for Scientists and Engineers"; McGraw-Hill: New York, 1978; Chapter 10.
(28) Abramowitz, M.; Stegun, I. A. "Handbook of Mathematical Functions"; Dover: New York, 1970.
(29) Schurr, J. M. *CRC Crit. Rev. Biochem.* **1977**, *4*, 371.
(30) This is necessary only in those regions where $R(w)$ varies markedly. In the other regions, ϵ may be much larger than $|R(w)|$.
(31) Wiegel[5] derives an integral equation and then eq 1 by using the condition that the density profile varies sufficiently smoothly; i.e., $|\partial G/\partial \mathbf{r}|A \ll 1$. We note, however, that eq 1 cannot be exact for $\rho \rightarrow a$ since the boundary condition eq 6 implies that $G_N(\mathbf{r}, \mathbf{r}')$ varies markedly near the surface of the cylinder. As we remark in the Discussion, eq 28 cannot then be taken too literally, but the physically interesting collapse, as expressed by eq 34 and 35, is almost independent of the behavior of G_N near the surface.
(32) The ground-state eigenfunction f_0 "oscillates" for about half a period only and, of course, it has no nodes.
(33) In eq 22, 24, and 25, the integrand is related to the term $(-R(v))^{1/2}$. The negative sign arises because $S_0 = \int_{w_0}^{w} R^{1/2}(v)\,\mathrm{d}v = e^{3\pi i/2}\int_{w}^{w_0}(-R(v))^{1/2}\,\mathrm{d}v$. Hence, ${S_0}^{2/3}$ is negative so one needs the asymptotic behavior of Ai for negative arguments. See, e.g., ref 27.
(34) Even in the Manning approximation, one should perhaps use $\beta(\kappa) = 2[\kappa a K_1(\kappa a)]^{-1}$, where K_1 is the first-order modified Bessel function of the second kind. We have set $\kappa a K_1(\kappa a) \simeq 1$ whereas in the example of the Discussion, it is about 0.8. However, eq 27 is more in line with the Poisson–Boltzmann results in the region of physical interest. Moreover, our model is approximate anyway—we assume a uniform dielectric constant, a uniform charge density, etc.—so at this stage, errors of about 20% are not really severe.
(35) Equation 40 can be obtained by a mean-field argument. This is explained in ref 14 for the case of a polymer adsorbed onto a plane surface.
(36) Equations 34 and 35 are valid only when κ does not differ too much from κ_1; i.e., the binding should be weak and the thickness should be much larger than the segment length.

Technique of High-Concentration Tagging in Small-Angle Neutron Scattering: R_g for Bulk Polystyrene[†]

C. Tangari,[‡] G. C. Summerfield, and J. S. King*

Department of Nuclear Engineering, The University of Michigan, Ann Arbor, Michigan 48109

R. Berliner and D. F. R. Mildner

University of Missouri Research Reactor, Columbia, Missouri 65211. *Received May 7, 1980*

ABSTRACT: A demonstration of the use of high-concentration deuterated polymer samples at the new University of Missouri Research Reactor small-angle neutron scattering spectrometer is presented. Bulk polystyrene samples with 30 and 70% deuteration are measured for two molecular weights. The data are expressed as the sum of a single-chain factor $S_s(Q)$ and a total scattering factor $S_T(Q)$. It is found that $S_T(Q)$ is zero within experimental error.

Introduction

It has been customary in small-angle neutron scattering (SANS) measurements on polymer systems to use samples in which a few percent or less of the polymer molecules are "marked" by deuteration.[1,2] This is to avoid the effects of chain–chain interference and follows older methods of spectroscopy. As pointed out by us for bulk polymers,[3] and recently generalized to polymer solutions,[4] it is very useful to decompose the scattering cross section into a self-term, $S_s(Q)$, and a total scattering term, $S_T(Q)$. Because of a different dependence on concentration for the coefficients of $S_s(Q)$ and $S_T(Q)$, it is possible to subtract

---

[†] Work supported in part by National Science Foundation Grant No. DMR-78-80152.

[‡] Sponsored by Comissao Nacional de Energia Nuclear/Brazil.

Table I
Composition, M_w, and Polydispersity of Mixed-Isotope Samples

	deuterated number fraction		PSD		PSH	
sample	c	$c(1-c)$	M_w	M_w/M_n	M_w	M_w/M_n
HPSH3D7	0.684	0.216	194000	1.15	198000	1.06
HPSH7D3	0.285	0.204				
LPSH3D7	0.684	0.216	64000	1.05	53700	1.06
LPSH7D3	0.285	0.204				

out $S_T(Q)$ and obtain only the single-chain structure factor $S_s(Q)$. When this is possible, interference scattering can be removed, and high-concentration samples can be used with consequent high experimental intensities. This has already been demonstrated by Williams et al.[5] for polyelectrolytes, by Han, Kim, and Yu for polyisoprene,[4] and in the intermediate-Q region by Stamm et al.[6]

It is our purpose here to report further high-concentration results, taken at the new intermediate-intensity MURR-SANS spectrometer.[7] We have chosen to demonstrate the precision of the method by reproducing the results of low-concentration data on the radius of gyration of bulk atactic polystyrene. Extensive data were obtained by Cotton et al. on D11 at Grenoble and at Saclay[2] on samples with deuterated fractions near 1.0%. These data were extrapolated to zero concentration, although for the bulk samples no concentration dependence was observed. The value of R_g obtained and its variation with molecular weight were compared to companion data for low concentrations of PSD in good and poor solvents. We believe these data represent a standard in accuracy for the SANS method.

For this simple system the coherent elastic differential cross section reduces to

$$S(Q) = [a_H + (a_D - a_H)c]^2 S_T(Q) + c(1-c)[a_H - a_D]^2 N S_s(Q) \quad (1)$$

where a_H and a_D are the scattering lengths of PSH and PSD monomers, respectively, N is the total number of molecules in the sample, and c is the number fraction of deuterated monomers. The single-chain structure factor, $S_s(Q)$, which we wish to measure and the total scattering term, $S_T(Q)$, which we wish to eliminate are

$$S_s(Q) = |\sum_j e^{i\mathbf{Q}\cdot\mathbf{r}_j}|^2 \quad (2a)$$

$$S_T(Q) = |\sum_{M,j} e^{i\mathbf{Q}\cdot(\mathbf{R}_M+\mathbf{r}_j)}|^2 \quad (2b)$$

where $\mathbf{R}_M$ is the position of the com of the Mth molecule and $\mathbf{r}_j$ is the position relative to $\mathbf{R}_M$ of the jth monomer of the Mth molecule. The condition for validity of eq 1 is that the PSD and PSH molecules look identical in all respects (except, of course, the neutron scattering lengths), including molecular weight. If, in addition, the system is incompressible, it is anticipated that $S_T(Q)$ should vanish.

Experimental Section

Two molecular weights were used and four bulk mixtures were prepared for each weight by freeze-drying particles from 5.0% benzene solutions, followed by vacuum drying for 12 h at 70 °C. Clear wafers 2.0 cm in diameter by 0.12 cm thick were produced by heating the powders to 120–140 °C for 2.0 h in a vacuum mold pressurized to approximately 1000 psi. The four weight fractions of deuterated polymer were 1.00, 0.70, 0.30, and 0.0 for both molecular weights.

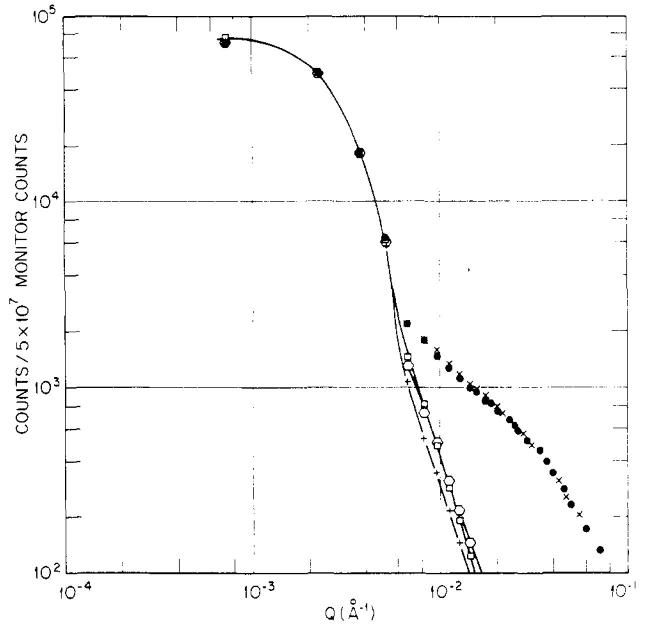

Figure 1. Transmission-corrected counts for medium-resolution geometry of the MURR-SANS spectrometer. Data points correspond to the open beam (+) and to the low molecular weight samples of Table I: (□) 100% PSD; (○) 100% PSH; (●) 70% PSD–30% PSH; (×) 30% PSD–70% PSH. A semitransparent beam stop extends to $Q = 0.006$ Å^{-1}.

Table I gives the characteristics of the components of the mixtures as reported by our sources.[8] It is seen that the weight match for the low-mass molecules is less than desired. This difference can be accounted for in the scattering law. We have elected instead to take an average M_w of 58800 because the error from this approximation is small and the approximation keeps our analysis simple. The observed scattered intensities $I(Q)$ are proportional to $S(Q)$. Using the concentrations of Table I and the values $a_H = +2.328 \times 10^{-12}$ cm and $a_D = +10.656 \times 10^{-12}$ cm, we obtain from eq 1 for both high- and low-M_w mixtures

$$\frac{1}{K}\left[\frac{I(Q)}{c(1-c)}\right]_{\mathrm{H3D7}} = 4.30 S_T(Q) + N S_s(Q) \quad (3a)$$

$$\frac{1}{K}\left[\frac{I(Q)}{c(1-c)}\right]_{\mathrm{H7D3}} = 1.56 S_T(Q) + N S_s(Q) \quad (3b)$$

where K is a constant.

The beam geometry of the MURR-SANS spectrometer was fixed by a source iris of 2.0-cm diameter, a sample iris of 1.0-cm diameter, an effective detector element area of 1.27 × 0.5 cm^2, and equal flight paths of 4.5 m between source and sample and between sample and area detector. The wavelength λ was 4.75 Å and $\Delta\lambda/\lambda$ was approximately 5%.[7] A semitransparent gadolinium beam stop 4.0 cm in diameter was used. The beam stop attenuates the direct beam by a factor of approximately 200 and, for the geometry used, closely masks the direct beam. Figure 1 is a plot of transmission-corrected data from all four samples of low M_w as well as from the open beam. The radial limits of the beam stop and direct beam are equal and correspond to $Q = 0.006$ Å^{-1}. An unattenuated profile can be produced by multiplying the first four points by 200; the integrated direct beam count is 9900 cps. The conditions of Figure 1 provide a good picture of the present capability of the MURR-SANS spectrometer for detecting low-Q data from medium-weight polymer samples. In the present experiment each of the eight samples was run for 3 h. The statistical error of the radially averaged data is less than 1.0% for all mixed samples and varies from 1 to 4% for the pure-PSH and -PSD samples.

Results and Conclusions

The low-Q data for the samples of both molecular weights are presented as Zimm plots in Figures 2 and 3. The fractional intensities for the pure-PSH and -PSD samples have been subtracted from each of the PSD–PSH mixtures, after correcting all data to 100% transmission.

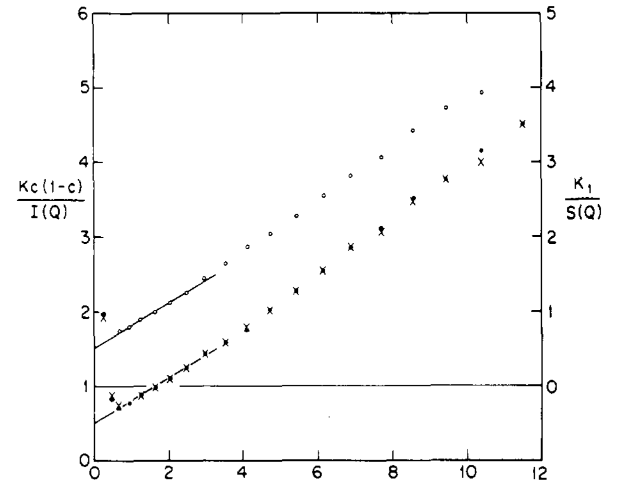

Figure 2. Zimm plots for samples HPSH3D7 (●) and HPSH7D3 (×) and the difference curve (○).

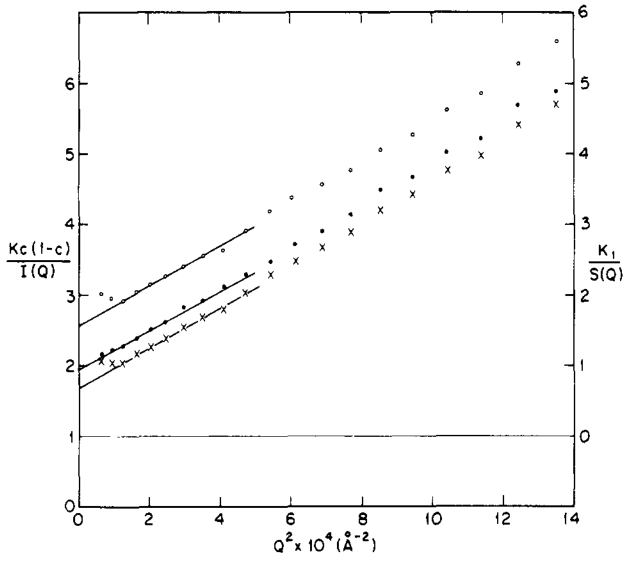

Figure 3. Zimm plots for samples LPSH3D7 (●) and LPSH7D3 (×) and the difference curve (○).

Sample-thickness corrections are also made but are small, of the order of 1.0%. The net intensities are plotted as $Kc(1 - c)/I(Q)$ vs. Q^2. With particular attention to the high-M_w data, which should be the most reliable, we observe the following results:

A. The two mixtures of Figure 2 give almost identical, overlapping curves and intercepts. Equations 3a and 3b, by contrast, give very large differences unless $S_T(Q) \ll NS_s(Q)$. For this condition a difference curve which eliminates $S_T(Q)$ will, within a constant, look exactly like either curve of Figure 2. This is plotted as $K_1/S_s(Q)$ vs. Q^2.

B. The overlap of the two curves for the low-M_w mixtures of Figure 3 is somewhat less precise, showing a difference in intercept of 11%. We attribute this to less precise background correction and to our approximate treatment of the differences in M_w, and not to the appearance of a small but finite $S_T(Q)$.

C. From the slope–intercept treatment of the low-Q region of Figure 2 we obtain an R_z of 132 Å. After a small correction for polydispersity[2] we obtain a best value of $R_w = 129 \pm 5$ Å. From Figure 3 we obtain two values, R_z = 67.0 Å and R_z = 70.3 Å. The difference curve from eq 3a,b gives R_z = 72.6 Å. We assign an average best value $R_w = 69 \pm 4$ Å. These values of R_w are shown as open circles in Figure 4, which is reproduced from Figure 8 of Cotton's paper.[2] Our value of $(R_w^2/M_w)^{1/2}$ is 0.28 ± 0.01. (Kratky plots are very well fit by Gaussian functions over the detector range $0.01 < Q < 0.085$ Å^{-1} but require R_w values about 11% lower than the Zimm values.)

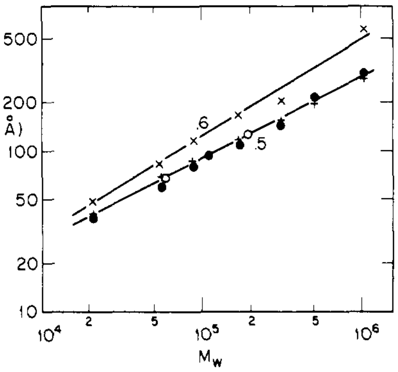

Figure 4. Reproduction of Figure 8 of ref 2 with present data superposed. Symbols correspond to bulk PSD/PSH (●), PSD in cyclohexane at 36 °C (+), PSD in CS$_2$ (×), and present data (○).

D. The ratio of intercepts for the $Kc(1 - c)/I(Q)$ curves of Figures 2 and 3 should be inversely proportional to the ratio of the two M_w. The nominal M_w ratio is 3.36 ± 0.34. The ratio of the average intercepts from Figures 2 and 3 is 3.45 ± 0.25.

Two conclusions may be drawn from the above results. First, the high-concentration method is quite precise when M_w for both protonated and deuterated components are well matched. Second, the magnitude of $S_T(Q)$ in bulk PSH/PSD is everywhere zero within our experimental limits. This is consistent with the observations of ref 2 and, in fact, confirms that Cotton et al. were seeing $S_s(Q)$ only.

Acknowledgment. We thank S. J. Bai and R. Ullman for their help in sample preparation and O. A. Pringle for his assistance in the SANS data acquisition.

Note Added in Proof. The present improvement in beam spreading of MURR-SANS at lowest Q easily distinguishes the scattering from pure-PSD vs. -PSH samples. This does not alter the sense of the present data.

References and Notes

(1) Wignall, G. D.; Ballard, D. G. H.; Schelten, J. *Eur. Polym. J.* **1974**, *10*, 861.
(2) Cotton, J. P.; Decker, D.; Benoit, H.; Farnoux, B.; Higgins, J.; Jannink, G.; Ober, R.; Picot, C.; des Cloizeaux, J. *Macromolecules* **1974**, *7*, 863.
(3) Summerfield, G. C.; King, J. S.; Ullman, R. *J. Appl. Crystallogr.* **1978**, *11*, 548.
(4) Akcasu, A. Z.; Summerfield, G. C.; Jahshan, S. N.; Han, C. C.; Kim, C. Y.; Yu, H. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 863.
(5) Williams, C. E.; Nierlich, M.; Cotton, J. P.; Jannink, G.; Boue, F.; Daoud, M.; Farnoux, B.; Picot, C.; de Gennes, P. G.; Rinaudo, M.; Moan, M.; Wolff, C. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 379.
(6) Stamm, M.; Fischer, E. W.; Dettenmaier, M. *Faraday Discuss. Chem. Soc. No. 68*, in press.
(7) Mildner, D. F. R.; Berliner, R.; Pringle, O. A.; King, J. S. "The Small Angle Neutron Scattering Spectrometer at the University of Missouri Research Reactor", to be published.
(8) The PSH material was supplied by Pressure Chemical Co. through L. Rosen; the PSD material was prepared and characterized by Dr. L. Fetters, The University of Akron.