fusion can be explained with the help of a blob model.

Our results confirm that various concentration regimes exist in aqueous solutions of charged macromolecules in the absence of low molar mass electrolyte and can be detected by quasi-elastic light-scattering experiments. Much more systematic investigations are needed, together with further theoretical work, for even the qualitative understanding of these systems.

References and Notes

(1) Katchalsky, A. *Pure Appl. Chem.* **1971**, *26*, 327.
(2) de Gennes, P. G.; Pincus, P.; Velasco, R.; Brochard, F. *J. Phys. (Orsay, Fr.)* **1976**, *37*, 1461.
(3) Odijk, T. *Macromolecules* **1979**, *12*, 688.
(4) Odijk, T. *Polymer* **1978**, *19*, 989.
(5) (a) Levij, M.; de Bleijser, J.; Leyte, J. C. *Chem. Phys. Lett.* **1981**, *83* 183. (b) *Ibid.* **1982**, *87*, 34.
(6) Roots, J.; Nyström, B. *Polymer* **1981**, *22*, 573.
(7) Grüner, H.; Lehman, F. *J. Phys. A: Math. Gen.* **1981**, *24*, L307.
(8) Koene, R.; Mandel, M. *Macromolecules* **1983**, *16*, 220.
(9) Koene, R.; Nicolai, T.; Mandel, M. *Macromolecules* **1983**, *16*, 227.
(10) Koene, R.; Nicolai, T.; Mandel, M. *Macromolecules* **1983**, *16*, 231.
(11) Lee, W. J.; Schmitz, K. S.; Lin, S. C.; Schurr, J. M. *Biopolymers* **1977**, *16*, 583.
(12) Jamieson, A. M.; Presley, C. T. *Macromolecules* **1973**, *6*, 358.
(13) Mathiez, P.; Mouttet, C.; Weisbuch, G. *Biopolymers* **1979**, *18*, 1465.
(14) Mathiez, P.; Mouttet, C.; Weisbuch, G. *J. Phys. (Orsay, Fr.)* **1980**, *41*, 519.
(15) Mathiez, P.; Mouttet, C.; Weisbuch, G. *Biopolymers* **1981**, *20*, 2381.
(16) Fulmer, A.; Benbasit, J.; Bloomfield, V. *Biopolymers* **1981**, *20*, 1147.
(17) (a) Perrin, F. *J. Phys. Radium* **1934**, *5*, 497. (b) *Ibid.* **1936**, *7*, 1.
(18) Odijk, T. *J. Polym. Sc., Polym. Phys. Ed.* **1977**, *15*, 477.
(19) Skolnick, J.; Fixman, M. *Macromolecules* **1977**, *10*, 944.
(20) de Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572.
(21) Edwards, S. F.; Grant, J. W. *J. Phys. A: Math. Nucl. Gen.* **1973**, *6*, 1169, 1186.
(22) de Gennes, P. G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979; Chapter 8.
(23) Kratky, O.; Porod, G. *Recl. Trav. Chim. Pays-Bas* **1949**, *68*, 1106.

Static Light Scattering from Aqueous Poly(ethylene oxide) Solutions in the Temperature Range 20–90 °C

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ABSTRACT: Static light scattering from aqueous solutions of poly(ethylene oxide) has been recorded over the temperature range 20–90 °C and at eight different concentrations varying from 0.25% to 2% for a polymer of molecular weight 20 000. In spite of the low molecular weight, strong angular dependence of the scattering and a very high average particle weight M_w were found, indicating the presence of large aggregates of poly(ethylene oxide) in the aqueous solutions. The aggregation increases markedly upon heating; above 60 °C, however, a decrease in M_w occurs. At 40 °C minima and maxima in the angular distribution were observed that are characteristic of globular, fairly monodisperse structures. The dimensions of these globular particles were found to decrease with rising temperature, in contrast to the mean square radius of gyration $\langle S^2 \rangle_z$, which increases up to 70 °C. The second osmotic virial coefficient A_2 decreases with rising temperature as the system approaches its Θ temperature of 102 °C. Finally, the intrinsic viscosity in water is shown to be only slightly influenced by the presence of globular aggregates. These findings indicate the coexistence of high-density spherulites with low-density microgel aggregates and are discussed in terms of the hydrophobic interactions between the polymer and solvent.

Introduction

Poly(ethylene oxide) (PEO) is a simple polymer with rather remarkable properties.[1] It dissolves readily not only in a large number of organic solvents but also in water. Moreover, it exhibits both upper and lower critical solution temperature phenomena (UCST and LCST) in both *tert*-butyl acetate[2] and water.[2-4] However, these two systems are very different, for in the organic solvent the UCST lies well below the LCST but in the PEO–water system there is a closed miscibility loop, the UCST lying higher than the LCST. The former type of behavior is an example of the well-understood "free-volume" or "equation of state" effects discussed by Prigogine,[5] Patterson and Delmas,[6] and Flory and his co-workers.[7] Closed miscibility loops, however, are seen only in highly polar systems with strong orientation dependence of the molecular interactions.[8] Our interest in the solution behavior of PEO increased when we noticed that only a few light scattering measurements of PEO in water have been published.[2,9-14] The purpose of the present study was to measure the thermodynamic solution properties and, so far as possible, the conformational properties of the polymer in water as a function of temperature.

Experimental Section

Sample. Polywachs-20,000 from Chemische Werke Huls, Marl, Germany, was used. To remove possible traces of initiator the product was dissolved in benzene, filtered, precipitated with freshly distilled petroleum ether, and dried in a vacuum oven at 50 °C. Gel permeation chromatography (GPC) in *N*,*N*-dimethylacetamide, which was kindly performed by Peuscher and Eisenbach[15,16] in our institute, gave a molecular weight of $M_{\mathrm{GPC}} = 21\,400$ and a polydispersity of $M_w/M_n = 1.37$, while light scattering in acetonitrile gave a value of $M_w = 17\,000$, which agrees fairly well with the GPC values.[16]

Solution Preparation. A dilution series of eight concentrations ranging from 0.25% to 2% in increments of 0.25% was prepared at room temperature with freshly doubly distilled water. The solutions were centrifuged for optical clarification at 20 °C in a Spinco Model L ultracentrifuge at 40 000 rpm with a fixed angle Titan rotor. The upper two-thirds of a total of 25 mL were pipetted into cylindrical light scattering cells made of optical glass

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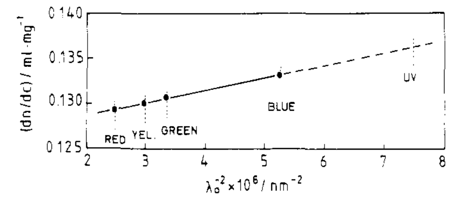

Figure 1. Plot of measured refractive index increments against $1/\lambda_0^2$. The wavelengths used are λ_0 = 633 nm (red), 578 nm (yellow), 546 nm (green), andd 436 nm (blue). Extrapolation is made for λ_0 = 365 nm (UV).

Table I
Refractive Index Increments of PEO in Water

temp, °C	dn/dc, mL/mg			
	λ_0 = 633 nm	λ_0 = 578 nm	λ_0 = 546 nm	λ_0 = 436 nm
20	0.1345	0.1352	0.1351	0.1379
30	0.1330	0.1332	0.1345	0.1357
40	0.1317	0.1318	0.1319	0.1338
50	0.1293	0.1301	0.1307	0.1331

transparent to near-UV light (λ_0 = 330 nm).

Light Scattering. A Sofica 4200 goniometer fitted with quartz optics and a special 500-W high-pressure air-cooled mercury lamp was used. The instrument allowed measurement at wavelengths of λ_0 = 546 (green), 436 (blue), and 365 nm (near UV). The angular range was varied from 20° to 150° in increments of 5°. For the determination of the Rayleigh ratio we calibrated a glass standard using the Rayleigh ratios for benzene at different temperatures as determined by Benoit and co-workers.[17]

Refractive Index Increment. Values of dn/dc were measured for λ_0 = 436, 546, 578, and 633 nm in a Brice-Pheonix differential refractometer. The data for each temperature were plotted against $1/\lambda_0^2$, according to a normal dispersion behavior, and were linearly extrapolated to λ_0 = 365 nm where no direct measurements were possible. Figure 1 gives an example of such a plot for 50 °C. The other data are collected in Table I.

Results

The light scattering experiments were carried out at eight temperatures from 20 to 90 °C in 10 °C increments. A single Zimm plot was constructed for each temperature from the measurements at the three different wavelengths by plotting Kc/R_θ against $q^2 = (n_s4\pi/\lambda_0)^2 \sin^2(\theta/2)$ rather than $\sin^2(\theta/2)$ as is usually done. The three curves did not lie exactly on top of one another but were very close. The deviations very likely result from differences in back-reflection from the primary beam. Such reflection occurs at the interface between the aqueous solution and the glass wall of the cell and is wavelength dependent because of the different dispersions of water and glass. The influence of backscattering is small for molecules of low molecular weight but can become appreciable when pronounced angular dependence of the scattered light is observed. The curves shown in Figure 2 were obtained by multiplying the Kc/R_θ values of the green and near-UV measurements by a constant factor (deviations from unity at most 2%) to align them with the blue measurements.

In Figure 2 one notices a very pronounced angular distribution of scattering intensities and a characteristic change in behavior with rising temperature. Most striking is the occurrence of two minima and maxima, which is most clearly seen at 40 °C. These extrema are certainly not artifacts because they appear for all three wavelengths at the same value of q. However, this value of $q = (n_s4\pi/\lambda_0)\sin(\theta/2)$ corresponds to very different scattering angles for the three wavelengths used.

The analysis of the Zimm plots was difficult and was performed as follows. We used the Guinier approximation for the small-angle portion of the scattering curves, i.e., $i(\theta) \cong i(0)\exp(-q^2\langle S^2\rangle_z/3)$, and determined $Kc/R_{\theta\to0}$ and $\langle S^2\rangle_z$ by a best fit of the curves. The results for the molecular weight and mean square radius of gyration appeared to depend on the number of points taken (but not systematically). We therefore made several fits with differing numbers of data points and calculated the average with its mean standard deviation.

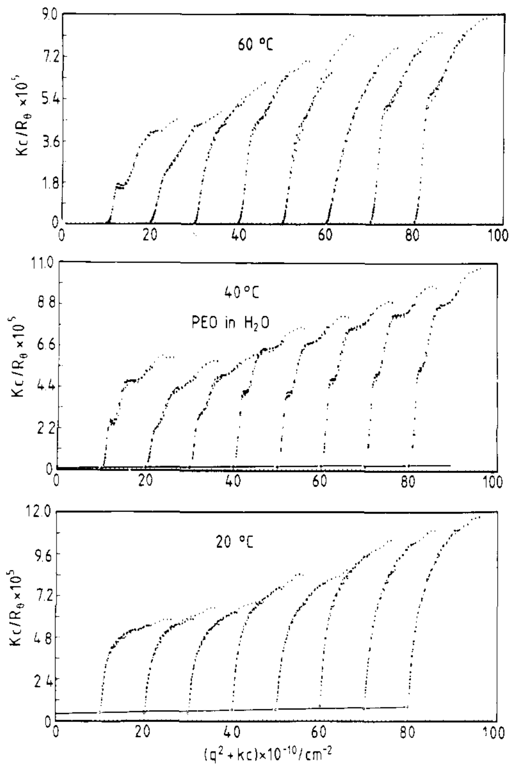

Figure 2. Zimm plots of light scattering measurements from a poly(ethylene oxide) sample, M_{GPC} = 21 400, in water at 20, 40, and 60 °C.

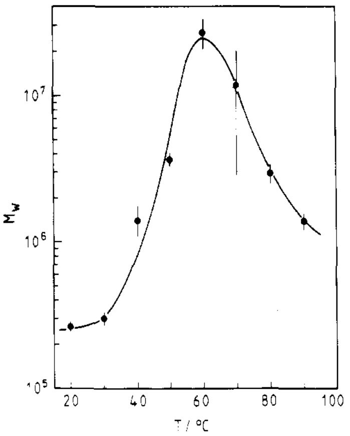

Figure 3. Temperature dependence of the measured particle weight, M_w, of the PEO sample in water. The bars indicate the experimental error.

Figure 3 shows the dependence of M_w on temperature. Most noticeable is the dramatic increase in M_w from about 260 000 at 20 °C up to 26×10^6 at 60 °C (a factor of 100!) and then a decrease on further heating to about 1.3×10^6 at 90 °C.

The temperature dependence of $\langle S^2\rangle_z$ is given in Figure 4 and that for the second virial coefficient in Figure 5.

Discussion

In an extension study of the solution behavior of PEO by vapor pressure osmometry and light scattering tech-

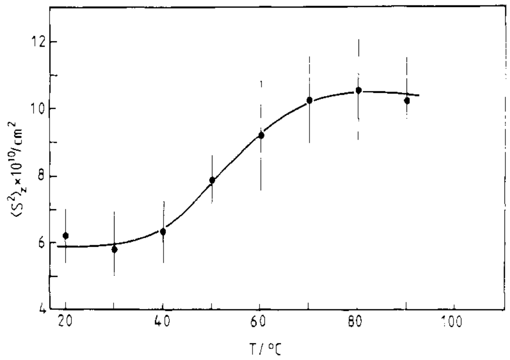

Figure 4. Temperature dependence of the mean square radius of gyration, $\langle S^2\rangle_z$, of the PEO sample in water.

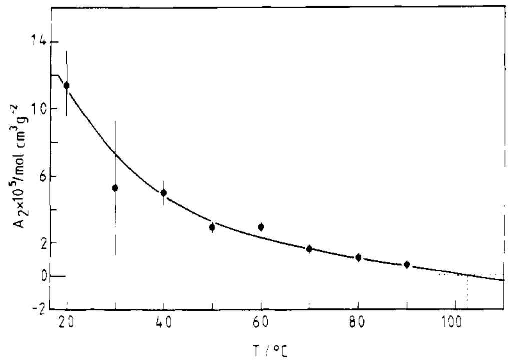

Figure 5. The second virial coefficient A_2 as a function of the temperature. The dotted lines indicate the position of $A_2 = 0$, which is at $T = \Theta = 102$ °C.

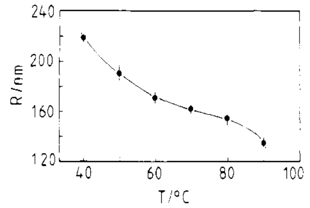

Figure 6. Variation of the sphere radius, R, with temperature. R has been calculated from the position of the first maximum of the lowest concentration in Figure 2 by use of eq 2.

niques, Elias and Lys[12] came to the conclusion that the polymer forms no aggregates in three of the seven solvents investigated, water, methanol, and *N*,*N*-dimethylformamide. Their conclusion is in remarkable disagreement not only with our light scattering results and the recent measurements by Bortel and his co-workers[18] but also with those by Strazielle,[19] who noticed a strong downturn at low scattering angles in methanol. It appears likely that many authors neglected the downturn in scattering intensity at small angles and used only the flat linear part at larger angles as a basis for their calculations. Indeed, if we proceed in this manner for the measurements at 20 °C and if we take only the lowest concentrations, we obtain a molecular weight of $M_w = 23000$, which is close to the value of 21 400 determined by GPC. Downturns in Zimm plots are commonly interpreted as being caused by "dust", which in fact is often difficult to remove from water. The downturn observed in this case cannot be caused by dust, since common dust does not aggregate and dissociate reversibly to such a large extent upon changes in temperature. We therefore regard the pronounced angular distribution of scattered light as a real effect of PEO aggregation in water.

Natural questions to ask are what kinds of forces hold these molecules together in such large aggregates and what structures do the aggregates assume. In spite of considerable experimental error, we observed a continuous decrease of the second virial coefficient, i.e., the reduction of the solvent power of water, with increasing temperature. Such behavior is rare for polymers in common organic solvents except when there is a large "free volume" difference between the components. In aqueous polymer solutions, however, the clustering of molecules likely involves hydrogen bonding, the structure of water, and the "hydrophobic effect".[8,20-23] In such cases, both the excess entropy and enthalpy of dilution are negative,[4] unlike most common polymer solutions in organic solvents.[7,24,25]

A Θ state should be passed near the boiling point of water and before phase separation commences. Extrapolation of the second virial coefficient to $A_2 = 0$ yields a Θ-temperature of 102 °C, which is a little lower than the LCST of 110 °C for a PEO sample of molecular weight 30 000 observed by Bailey and Callard[9] and slightly higher than the LCST for a polymer of molecular weight 21 000 observed by Saeki et al.[2] For molecular weights as large as 1.02×10^6 and 7×10^6, LCSTs of 98.2 and 95 °C, respectively, were observed by the authors.

In their study of aqueous PEO solutions, Bortel and Kochanowski[18] also did not obtain linear Zimm plots for high molecular weight PEO in water, but they found very nice linear behavior in 0.1 M HCl aqueous solutions. This observation supports our interpretation that it is the hydrophobic interaction that brings about the cluster formation, for the addition of a strong electrolyte produces a complete change in the order of the water structure and breaks down the hydrophobic interaction.[23]

While the hydrophobic interaction offers an explanation for the decrease in A_2 with rising temperature, it does not at first sight account for the formation of large PEO clusters. Two observations suggest an interpretation for this phenomenon: (i) Two prominent minima and maxima appear in the angular distribution of the scattered light around 40 °C, which indicate the presence of globular structures of rather low polydispersity. (ii) The aggregates seem to dissociate at about 60 °C. Godovsky et al.[26] found a melting temperature of $T_m = 70$ °C for PEO of infinitely large molecular weight and $T_m = 68.6$ °C for $M_w = 6 \times 10^6$. For lower molecular weight an even lower T_m is expected. It therefore is tempting to regard the rather monodisperse globular structures as crystalline spherulites of PEO that melt around 60 °C. Actually, however, the problem is far more complex, as may be recognized from the following observations:

(1) The mean square radius of gyration increases with temperature up to about 70 °C and then remains constant. A decrease of $\langle S^2\rangle_z$ would be expected if the maximum in Figure 3 were entirely due to spherulite melting.

(2) The position of the first maximum in the angular dependence of the scattering light, which first becomes noticeable at 40 °C and can be observed through 90 °C, allows an estimation of the spherulite radii. Assuming the validity of the Rayleigh particle scattering factor of homogenous hard spheres in this case we have[27-31]

$$P(q) = [(3/X^3)(\sin X - X \cos X)]^2 \qquad (1)$$

with

$$X = Rq \qquad (2)$$

where R is the sphere radius. The first minimum of the reciprocal particle scattering factor of a slightly polydisperse system should occur when the first derivative of eq 1 with respect to X becomes zero, i.e., at $X_{\max} = 2.029$, which together with eq 2 allows the determination of R.

The result of this estimation is shown in Figure 6. Surprisingly, the radius of the spherulite globular structures decreases continuously. At low temperatures the radius of gyration approximately coincides with the spherulite radius, but at high temperatures the radius of gyration is about 2.4 times larger than the radii of the supposed spherulites.

(3) The striking extrema in the angular distribution gradually smooth out with increasing concentration. This effect is more evident at higher temperatures.

In view of these seemingly inconsistent findings, caution is prescribed in making a definite interpretation. Yet a few illuminating conclusions can be drawn without speculation. We assume that the various structures present in solution are close to thermodynamic equilibrium, because approximately the same scattering behavior is recovered when the solutions are cooled down again. If we accept this premise, then we must conclude that highly swollen noncrystalline aggregates coexist with the spherulites in the system. These microgels, as we tentatively call them, would not show extrema in the angular distribution, even if they were strictly monodisperse.[32] The mass fractions of spherulites and microgels change in favor of the microgels with rising temperature and evidently also with increasing concentration. Apparently the spherulites partially melt, and large microgels of a much lower density are formed. This follows from the opposite behavior of $\langle S^2\rangle_z$ and R with changes in temperature.

A conclusion concerning the microgel size and weight fraction can be drawn from the maximum in M_w near 60 °C. At this point the weight-average particle weight M_w is about 1300 larger than the molecular weight M_1 of molecularly dispersed PEO; thus, we can neglect the contribution of the latter to the aggregates; i.e., we can assume

$$M_w = w_a M_{wa} \tag{3}$$

where M_{wa} is the weight-average particle weight of all types of aggregates in the system and w_a is the corresponding mass fraction. An increase in M_w as a function of rising temperature can occur only if both w_a and M_{wa} change in the same manner. For the temperature range of 20 to 60 °C this seems to be the case. Beyond 60 °C, however, the product of w_a and M_{wa} decreases, yet the mean square radius of gyration $\langle S^2\rangle_z$ remains almost constant, indicating that the microgel particle weight remains almost constant and only the mass fraction w_a decreases. It may be of interest in this connection that aggregates of poly(vinylpyrrolidone) (PVP) have been found[33,34] in aqueous solutions with radii of about 270 nm, and they remained unchanged in size as the molecular weight of the polymer sample was increased; the mass fraction w_a increased approximately linearly with M_1 of the molecularly dispersed PVP. The extent of association is much less for PVP than for PEO, probably because of the greater hydrophilic character of PVP. Also, no spherulites were observed for PVP; crystallization occurs in aqueous PEO solutions because of its very regular chain structure.

Aggregation even to the point of phase separation of hydrophobic compounds on heating, seems to be a general phenomenon of the hydrophobic interaction and was documented by small-angle X-ray scattering from *tert*-butyl alcohol/water mixtures by Bale et al.[35] and by electron micrographs from poly(vinylpyrrolidone) (PVP) and hydroxyethyl starch (HES) solutions by Franks et al.[36] Strong self-assembling of tubulin and tobacco mosaic virus peptides on heating has long been known.[38,37] An attempt to provide a detailed thermodynamic description of the hydrophobic interactions in PEO solutions was recently reported by Kjellander and Florin.[39]

Finally we wish to comment on the apparent insensitivity of the intrinsic viscosity of PEO in water to the presence of globular aggregates. The large microgel particle observed among the molecularly dispersed PEO by light scattering techniques might be thought to raise the viscosity of an aqueous PEO solution substantially. However, the size of these particles is measured by a z-average, which heavily weights particles of larger size. When the free draining contribution is neglected, the intrinsic viscosity of a polydisperse system may be expressed[40] as

$$[\eta] = \Phi \frac{[\langle S^2\rangle^{3/2}]_n}{M_n} \tag{4}$$

where the subscript n denotes the number average, thus counting the molecularly dispersed PEO with relatively greater weight. The aggregates therefore play a much larger role in the particle size observed by light scattering experiments than in viscosity measurements because of the different averages involved. This effect is nicely illustrated by some classical results of Muus and Billmeyer,[41] who observed a 10-fold increase in apparent weight-average molecular weight and a 3-fold increase in $\langle S^2\rangle_z^{1/2}$ from the presence of particulate matter in their light scattering experiments on branched polyethylene in α-chloronaphthalene, while recording an increase of only about 10% in intrinsic viscosity. Since the effects of aggregation are small, viscosity measurements on PEO in water may be used to determine the molecular weight of the nonassociated PEO molecules according to a Mark–Houwink relation based on molecular weight measurements performed in another solvent in which association does not occur.

Conclusion

Full interpretation of the above findings is not yet possible, but some conclusions concerning the behavior of PEO in aqueous solution may be drawn without speculation. (i) Aggregates of high and low density coexist with molecularly dispersed PEO. The high-density particles are probably spherulites, and the low-density aggregates are noncrystalline microgel particles. (ii) On heating, the spherulites melt, causing the weight fraction of microgel to increase. (iii) The microgel particles appear to have dimensions that are rather insensitive to changes in temperature, but their weight fraction gradually decreases as the temperature rises above 60 °C. (iv) The decrease of A_2 is consistent with the concept of hydrophobic interactions, i.e., the increase in the order of water molecules in the neighborhood of PEO molecules. (v) The intrinsic viscosity of aqueous PEO solutions is only slightly influenced by the presence of globular aggregates.

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Registry No. Poly(ethylene oxide), 25322-68-3.

References and Notes

(1) Bailey, F. E.; Koleske, J. V. "Poly(ethylene oxide)"; Academic Press: New York, 1976.
(2) Saeki, S.; Kuwahara, N.; Nakata, M.; Kaneko, M. *Polymer* **1976**, *17*, 685.
(3) Cox, H. L.; Cretcher, L. H. *J. Am. Chem. Soc.* **1926**, *48*, 451.
(4) Malcolm, G. N.; Rowlinson, J. S. *Trans. Faraday Soc.* **1957**, *53*, 921.

Macromolecules 1983, 16, 982–992

(5) Prigogine, I.; Defay, R. "Chemical Thermodynamics"; Longmans, Green and Co.: London, 1954.
(6) Patterson, D.; Delmas, G. *Discuss. Faraday Soc.*, **1970**, *49*, 98.
(7) Flory, P. J. *Discuss. Faraday Soc.* **1970**, *49*, 7.
(8) Rowlinson, J. S. "Liquid and Liquid Mixtures", 2nd ed.; Butterworth: London, 1969; p 167–170.
(9) Bailey, F. E.; Callard, R. W. *J. Appl. Polym. Sci.* **1959**, *1*, 56, 373.
(10) Bailey, F. E.; Kucera, J. L.; Imhof, L. G. *J. Polym. Sci.* **1958**, *32*, 517.
(11) Ring, W.; Cantow, H.-J.; Holtrup, W. *Eur. Polym. J.* **1966**, *2*, 151.
(12) Elias, H.-G.; Lys, H. *Makromol. Chem.* **1966**, *92*, 1.
(13) Liu, K.-J.; Parsons, J. *Macromolecules* **1969**, *2*, 529.
(14) Koenig, J.; Angood, A. *J. Polym. Sci., Polym. Phys. Ed.* **1970**, *8*, 1787.
(15) Eisenbach, C. D.; Peuscher, M. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 105.
(16) Peuscher, M. Ph.D. Thesis, University of Freiburg, Freiburg, 1982.
(17) Ehl, P. J.; Loucheux, C.; Reiss. C.; Benoit, H. *Makromol. Chem.* **1964**, *75*, 35.
(18) Bortel, E.; Kochanowski, A. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 205.
(19) Strazielle, C. *Makromol. Chem.* **1968**, *119*, 50.
(20) Nemethy, G.; Scheraga, H. A. *J. Phys. Chem.* **1962**, *66*, 1773; **1963**, *67*, 2888.
(21) Nemethy, G.; Scheraga, H. A. *J. Chem. Phys.* **1962**, *36*, 3382, 3401.
(22) Frank, H. S. In "Water: A Comprehensive Treatise"; Franks, F., Ed.; Plenum: New York, 1972; Vol. 1, Chapter 14.
(23) Tanford, C. "The Hydrophobic Effect"; Wiley: New York, 1973.
(24) Flory, P. J. "Principls of *Polymer Chemistry*"; Cornell University Press: Ithaca, NY, 1953.
(25) Tompa, H. "Polymer Solutions"; Butterworth: London, 1956.
(26) Godovsky, Yu. K.; Slonimsky, G. L.; Garbar, N. M. *J. Polym. Sci., Part C* **1972**, *38*, 1.
(27) Rayleigh, J. W. *Proc. R. Soc. London, Ser. A.* **1914**, *90*, 219.
(28) van de Hulst, H. C. "Light Scattering by Small Particles"; Wiley: New York, 1957.
(29) Kerker, M. "The Scattering of Light"; Academic Press: New York, 1969.
(30) Huglin, M. B. "Light Scattering from Polymer Solutions"; Academic Press: New York, 1972.
(31) Burchard, W. In "Applied Fibre Science"; Happey, F., Ed.; Academic Press: New York, 1978; Chapter 10.
(32) Burchard, W.; Kajiwara, K.; Nerger, D. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 157.
(33) Burchard, W., Thesis (Habilitation), University of Freiburg, Freiburg, 1966.
(34) Franks, F.; Asquith, M. H.; Hammond, C. C.; Skaer, H. L. B.; Echlin, P. *J. Microsc.* (*Oxford*) **1977**, *110*, 223.
(35) Bale, H. D.; Shepler, R. E.; Sorgen, D. K. *Phys. Chem. Liq.* **1968**, *1*, 181.
(36) Franks, F.; Asquith, M. H.; Hammond, C. C.; Skaer, H. B.; Echlin, P. *J. Micros.* (*Oxford*) **1977**, *110*, 223, 239.
(37) Dustin, P. "Microtubules"; Springer-Verlag; Heidelberg, 1978.
(38) Fraenkel-Conrad, H. "Chemie und Biologie der Viren"; G. Fischer Verlag: Stuttgart, 1974.
(39) Kjellander, K.; Florin, E. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2053.
(40) Newman, S.; Krigbaum, W. R.; Laugier, C.; Flory, P. J., *J. Polym. Sci.* **1954**, *14*, 451.
(41) Muus, L. T.; Billmeyer, F. W. *J. Am. Chem. Soc.* **1957**, *79*, 5079.

Small-Angle Neutron Scattering Study of Block Copolymer Morphology

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ABSTRACT: Small-angle neutron scattering has been used to investigate the structural features of styrene–isoprene block copolymers. A wide range of molecular weight and composition has been investigated, encompassing the spherical, cylindrical, and lamellar morphologies of styrene domains chiefly. Apart from domain separation and packing, domain size has been determined by using copolymers with fully deuterated styrene blocks to improve contrast. While domain sizes are in some agreement with statistical thermodynamic theory no such agreement is found for domain separation. Possible reasons for this are discussed, especially for those copolymers with spherical morphology. Results also indicate that thermal annealing of the copolymers increases the grain size rather than improving the packing of domains with respect to each other.

Introduction

Structural investigations of the polymeric solid state over large length scales have used the techniques of electron microscopy and small-angle X-ray scattering (SAXS). Each of these suffers from disadvantages that make them unsuitable for studying structure over the range from supramolecular organization down to individual polymer molecules. Electron microscopy (EM) requires thin samples which have to be stained or replicated to produce observable images and this process may produce artifacts.[1] SAXS also requires thin samples (but not so thin as in EM); additionally, contrast in this technique relies on a good electron density difference between the matrix and the species being investigated,[2] and for many organic polymers the electron density difference cannot be enhanced sufficiently without drastic chemical modifications. Small-angle neutron scattering (SANS) is a relatively new technique[3–6] for the investigation of polymer structure and supramolecular organization but has produced definitive data for the critical evaluation of molecular theories of polymer structure and has contributed much to the debate on crystalline polymer structure.[7] The greater contribution of SANS in such a short time arises from the large neutron scattering cross section of hydrogen atoms and the considerable difference in scattering cross section for hydrogen and deuterium atoms. It is this difference that generates a contrast enabling "individual molecules" to be observed and their dimensions measured. The majority of work published thus far deals with the use of SANS in the determination of radii of gyration in homogeneous polymer systems. It is only recently that extensions to heterogeneous systems have been attempted. Styrene–diene block

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