tional contribution, and the evaluation of the vibrational free energy requires a complete normal mode analysis of the crystal lattice. In addition, for actual crystals, the entropy term due to the crystal defect and incoherent molecular motion at high temperature may play an important role in the stabilization of the crystal.

In this paper, however, only the static potential energy term which would occupy the largest part of the free energy was discussed as a first approximation.

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Light-Scattering Studies of a Polystyrene–Poly(methyl methacrylate) Two-Block Copolymer in Mixed Solvents

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ABSTRACT: Light-scattering measurements were made on a two-block copolymer of polystyrene and poly(methyl methacrylate) whose molecular weight and styrene content by weight are 1.53×10^6 and 0.38, respectively. Mixtures of toluene and furfuryl alcohol of various compositions were used as solvent. They are both good as solvent for poly(methyl methacrylate) and isorefractive as well, but the latter is a nonsolvent for polystyrene. The results show that the mean-square radius of the polystyrene subchain in the isolated block copolymer always exceeds the value for the homopolystyrene of equal molecular weight. This result confirms the view that intramolecular contacts of dissimilar units do occur. The intermolecular micelle formation set in at a solvent composition between 36.7 and 38.9 wt % of toluene. The largest micelle formed at 19.8% comprised about 72 molecules. From the shape of the particle scattering function we have concluded that the polystyrene subchain forms a core of anisotropic shape in the beginning of aggregation but cores in larger micelles assume the shape of dense sphere. Solutions of isolated molecules and micelles both revealed an anomalous upsweep of the reciprocal scattering function at small scattering angles but the anomaly became more pronounced for larger micelles as evidenced by a longer correlation distance. This result suggests for the micelle such a conformation as the dense polystyrene core thickly surrounded by extended chains of poly(methyl methacrylate).

In the previous light-scattering study on a two-block copolymer of polystyrene (PS) and poly(methyl methacrylate) (PMMA),[1] we compared the size of the PS subchain with that of the isolated PS of equal molecular weight in solvents that are good solvents for both PS and PMMA and isorefractive as well to PMMA.[2] In the present work we have investigated the conformation of the two-block copolymer in poor solvents for PS. Of special interest to us is the investigation of the extent to which the size of the PS subchain is diminished in increasingly poor solvents before molecules undergo the intermolecular aggregation. It is also important to elucidate the size and conformation of the micelle in relation to the process of the domain formation in films cast from block copolymer solutions.[3] Krause found almost a decade ago[4] that three-block copolymers of PMMA–PS–PMMA form stable aggregates which are in a state of thermodynamic equilibrium. It may be interesting to investigate further the process of micelle formation by adopting the approach initiated by Leng and Benoit[5] and adopted also in our previous study, *i.e.*, to utilize as solvent a liquid giving a very low value of refractive index increment for PMMA. The analysis of the experimental angular variation of light scattering at infinite dilution is then straightforward. We thus decided to choose as solvent a mixture of two liquids which meet the following specifications: (1) they are both

Table I
Refractometric Constants Used for the Calculation of Numerical Results of Light-Scattering Measurements

Solvent	Temp (°C)	$\tilde{n}_0$ (5461 Å)	Density (g/dl)	(d$\tilde{n}$/dc) (ml/g, 5461 Å) PS	PMMA	BMM-313
Toluene	30	1.4950	0.8577	0.1096	0.0031	0.0443
Furfuryl alcohol	30	1.4867	1.1238	0.1175	0.010	0.0517

Table II
Light-Scattering Results on Polystyrene 13-a and RS-13 in the Mixed Solvents of Toluene and Furfuryl Alcohol at 30°

Solvent Composition (wt % of Toluene)	(d$\tilde{n}$/dc)^a (ml/g)	$M \times 10^{-4}$	$A_2 \times 10^4$ (g/ml)	$\langle S^2\rangle^{1/2}$ (Å)
	Polystyrene 13-a			
100	0.110	61.4	2.99	355
80.1	0.112	63.0	2.86	338
60.0	0.113	61.4	1.80	298
45.2	0.114	60.2	0.57	258
39.5	0.115	61.0	−0.71	237
	Polystyrene RS-13			
100	0.110	58.6	3.05	349
39.6	0.115	59.0	−0.32	236

^{a} Values calculated from the Gladstone–Dale equation using the constants as described in the text.

isorefractive to PMMA; (2) they are similar in the goodness as solvent for PMMA; (3) for PS one is a good solvent and the other is a nonsolvent, and the mixture becomes a theta solvent for PS at a mixing ratio not far from 1:1. Toluene can readily be used as a solvent that is good for both PS and PMMA and isorefractive as well to the latter, but, as expected, some difficulties were encountered in finding a nonsolvent. After an extensive test of many liquids, we have found furfuryl alcohol suitable as the nonsolvent. Thus, by using as solvent the mixtures of toluene and furfuryl alcohol of various compositions and by analyzing the light-scattering data simply as the homopolymer-single solvent system, we obtained the size of the PS subchain while changing the goodness as solvent for PS at will.

Experimental Section

The sample of PS–PMMA two-block copolymer investigated in the present study is the same as used previously.[1] It was prepared by the anionic polymerization and designated as BMM-313. The molecular weight of the sample is 1.53 × 10^6 and its styrene weight fraction is 0.38. The sample is narrow in molecular weight distribution as verified by the sharp schlieren pattern of boundary sedimentation and contains no PS side chains from the PMMA subchain. A polystyrene sample of molecular weight identical with that of the PS subchain in the block copolymer was also prepared previously and designated as RS-13. Another polystyrene sample was purchased from the Pressure Chemical Co. (sample code, 13-a; cat. mol wt 0.67 × 10^6) and used without further treatment.

Reagent grade toluene and cyclohexane were purified as usual and distilled in a column just prior to use. Reagent grade furfuryl alcohol was dried over potassium carbonate for at least 3 days and distilled in a column under nitrogen. The boiling point of the collected fractions was 76–77° at 20 mm. The purity of the furfuryl alcohol thus prepared was checked on gas–liquid chromatograms taken with an analytical gas chromatograph Model GCG-220, Yanagimoto Manufacturing Co. Since furfuryl alcohol readily turns yellow through polymerization in air, it was added with a trace of *n*-butylamine and stored at −10° in a nitrogen atmosphere. Refractive indices of the solvents just before use were: toluene, $n^{25}{}_{\mathrm{D}}$ 1.49415; cyclohexane, $n^{25}{}_{\mathrm{D}}$ 1.42345; furfuryl alcohol, $n^{30}{}_{\mathrm{D}}$ 1.48293. The literature values to be compared with these are 1.49413, 1.42354, and 1.4801, respectively.[6]

The light-scattering photometer used and the procedure of the measurement were described elsewhere.[7,8] The scattered light intensity was measured in the angular range of 9–150°. Unless otherwise indicated, the measurements were made at 30° with vertically polarized incident light of 5461 Å. Test solutions of the block copolymer for the light-scattering measurement were prepared as follows. A polymer solution of concentration 0.2–1.2 g/dl was prepared first by mixing the thoroughly dried polymer sample with toluene in a sealed glass tube and by keeping the mixture overnight at 40° for the complete dissolution. The solution was then centrifuged for 120 min at 26,000 rpm in a Hitachi preparative centrifuge Model 55P in a fixed-angle rotor RP30. Right after the full stop of the rotor the solution was transferred carefully into a clean glass vial fitted with a ground-glass stopper. An aliquot of the solution was separated to measure the concentration by dry weight analysis. Toluene was made free of dust in the same manner. A longer period of centrifugation (5 hr) was necessary for furfuryl alcohol due to its high viscosity and density. The most concentrated test solution was prepared by adding the clean furfuryl alcohol at a desired weight ratio to the toluene solution gradually with stirring. The polymer concentration of the test solution was calculated from that of the toluene solution by using the mixing ratio and the density of the mixed solvent estimated as an algebraic sum of those of toluene and furfuryl alcohol. The volume change on mixing was neglected. When the light-scattering measurement on the solution was over, an aliquot of the solution was separated and mixed by weight with a mixed solvent to make a more dilute test solution. The mixed solvent had been prepared in advance by mixing furfuryl alcohol and toluene at the same weight ratio. Thus the light-scattering measurements were performed on at least five solutions of different concentration for each solvent composition. The absence of dust was checked on each test solution prior to the light-scattering measurement by viewing through a telescope at a small angle to the incident beam. The solutions were stable and did not show any time-dependent change of light scattering. We did not check whether the solution properties are affected by the manner of mixing the original toluene solution with furfuryl alcohol, but the results obtained indicate the solutions are kept at thermodynamic equilibrium, as referred to later.

The specific refractive index increments for the polymer solutions tested were determined by calculation, for the same reason as described earlier, from the Gladstone–Dale equation

$$d\tilde{n}/dc = R_2 - [(\tilde{n}_0 - 1)/\rho_2] \qquad (1)$$

The same values were used for the constant R_2 and the polymer density ρ_2 as used in the previous study,[1] *i.e.*, 0.5810 and 1.05 respectively for PS and 0.4156 and 1.20 respectively for PMMA. The refractive index $\tilde{n}_0$ of each mixed solvent was calculated as an algebraic sum of the values for toluene ($n^{30}{}_{546\ \mathrm{m}\mu}$ 1.4950) and furfuryl alcohol ($n^{30}{}_{546\ \mathrm{m}\mu}$ 1.4867). The physical constants used for the calculation of the light-scattering results are summarized in Table I.

Experimental Results

In order to determine the solvent composition[9] where PS exists in a θ state, a series of light-scattering measurements were performed on the narrow distribution PS, 13-a. The results are summarized in Table II, and the changes of the second virial coefficient and the root-mean-square radius with the solvent composition are shown in Figure 1. The molecular weight of 13-a was determined as 61.4 × 10^4, which is very close to the value for RS-13. In fact both samples yielded very similar light-scattering results as shown in Table II, and they can essentially be re-

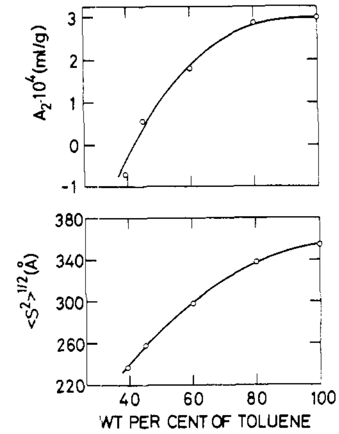

Figure 1. Dependences of the second virial coefficient and the root-mean-square radius of polystyrene 13-a on the composition of the mixed solvent of toluene and furfuryl alcohol at 30°.

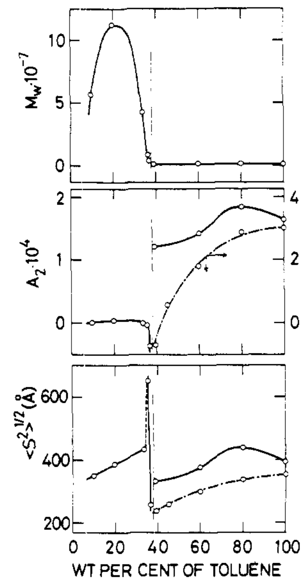

Figure 2. Light-scattering results on the two-block copolymer BMM-313 of polystyrene and poly(methyl methacrylate) as a function of the composition (wt % of toluene) of the mixed solvent of toluene and furfuryl alcohol at 30°. The chain curves represent the data for homopolystyrene sample 13-a.

Table III
Light-Scattering Data on a Two-Block Copolymer BMM-313 of Polystyrene and Poly(methyl methacrylate) in Mixed Solvents of Toluene and Furfuryl Alcohol at 30°

Solvent Composition (wt % of Toluene)	$(d\tilde{n}/dc)^a \times 10^2$ (ml/g)	$M \times 10^{-6}$	$A_2 \times 10^4$ (ml/g)	$\langle S^2 \rangle^{1/2}$ (Å)
100	4.51	1.53	1.65	394
80.1	4.58	1.52	1.84	439
60.0	4.73	1.55	1.42	374
38.9	4.88	1.53	1.20	332
36.7	4.9	4.00	−0.36	256
35.7	4.91	14.3	−0.043	651
33.6	4.92	42.7	0.0083	433
19.8	5.02	111	0.044	373
9.94	5.1	56.9	0.0081	351

[a] Values calculated from the Gladstone–Dale equation using the constants as described in the text.

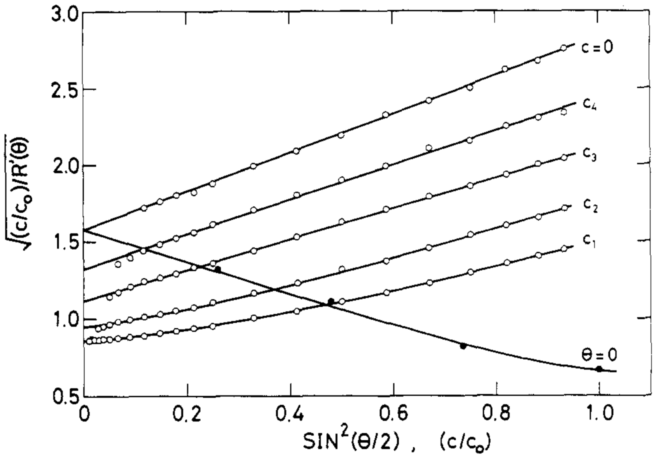

Figure 3. The square-root plot of the reciprocal scattering function of BMM-313 in a mixed solvent of toluene and furfuryl alcohol (toluene, 36.7 wt %). Filled circles represent the data extrapolated to zero angle and plotted versus the relative concentration (c/c_0): c_1, 1.00; c_2, 0.738; c_3, 0.479; c_4, 0.259. The concentration c_0 is 0.509×10^{-2} g/ml, and the apparent reduced scattered intensity R' is converted to the real value by multiplying by the apparatus constant of 1.54×10^{-3}.

garded as identical samples. From Figure 1 the so-called theta composition and the unperturbed root-mean-square radius were determined by interpolation as 42% and 247 Å, respectively. The latter value agrees well with the data of 234 Å obtained in cyclohexane at 34.8° (θ temperature). This result indicates that the micelle formation of the block copolymer may not take place above 42% because of the enhancement of the intermolecular repulsion by the incompatibility between PS and PMMA units.

Figure 2 shows the light-scattering results obtained on the two-block copolymer BMM-313 as a function of the solvent composition. The numerical data are summarized in Table III. In agreement with the expectation stated above the intermolecular micelle formation is seen to set in at a composition between 38.9 and 36.7%. It is also evidently seen that as long as the block copolymer remains molecularly dispersed in the solution the size of the PS subchain always exceeds that of the homopolystyrene of equal molecular weight. We also note that the second virial coefficient, as well as the root-mean-square radius, initially increases as the content of furfuryl alcohol increases and then decreases with a tendency to level off, while, in contrast, the data for the homopolystyrene 13-a reveal a normal decrease. The block copolymer solutions yielded in this range of the solvent composition similar dependences of the reciprocal scattering function on the scattering angle and concentration to those observed previously in pure toluene,[1] *e.g.*, the upsweep of the reciprocal scattering function at small scattering angles and at finite solute concentrations, and the negative third virial coefficient.

On the formation of the micelle the second virial coefficient of the block copolymer solution suddenly drops to a negative value like the first-order transition. It then increases with decrease in toluene content to a very small positive value and remains essentially constant thereafter. In this composition region the molecular weight of the micelle is seen to increase but not without limit. A substantial decrease is observed again at 9.94%. The decrease might have occurred as a consequence of the enhanced energy of interaction among PMMA subchains extending from the small PS core of the micelle. The largest molecular weight observed for the micelle was 111 million, meaning an aggregate of more than 70 block copolymer molecules.

The overall size of the PS subchains in the micelle exhibits a complicated change as shown in the bottom of

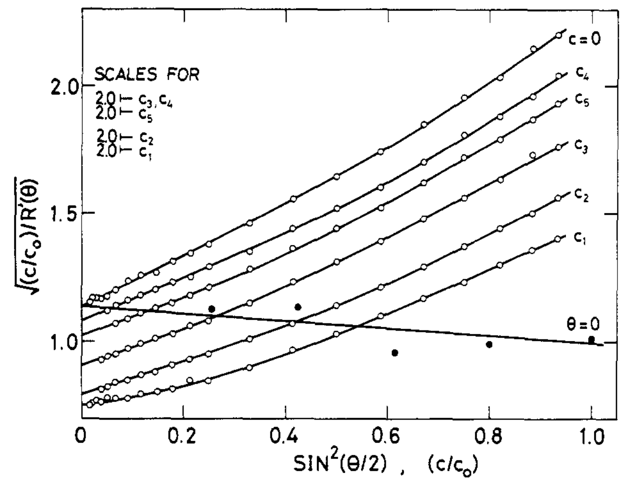

Figure 4. The square-root plot of the reciprocal scattering function of BMM-313 in the mixed solvent containing 35.7 wt % of toluene. For the symbols, see the legend to Figure 3. The concentration c_0 is 0.210 × 10^{-2} g/ml, and the relative concentrations are: c_1, 1.00; c_2, 0.799; c_3, 0.618; c_4, 0.424; c_5, 0.256. The ordinate scale is displaced as indicated in the figure for the clear representation.

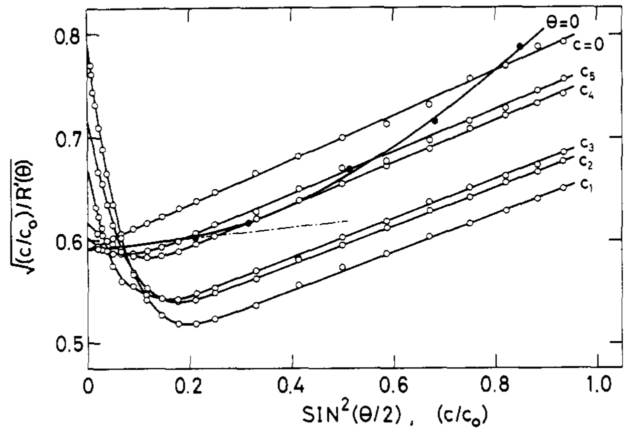

Figure 5. The square-root plot of the reciprocal scattering function of BMM-313 in the mixed solvent containing 33.6 wt % of toluene. For the symbols, see the legend to Figure 3. The concentration c_0 is 0.261 × 10^{-2} g/ml and the relative concentrations are: c_1, 0.851; c_2, 0.683; c_3, 0.515; c_4, 0.318; c_5, 0.213.

Figure 2. When a micelle is formed first by a few molecules in the solvent of 36.7% the root-mean-square radius suddenly drops to 256 Å which is close to the value for the homopolystyrene 13-a in the θ state, indicating the abrupt contraction of PS subchains upon the micelle formation. This change is not unexpected at all, because the domain exclusive of styrene units might be formed in the micelle against the repulsion between dissimilar segments. Within the following decrease of the solvent composition of only a few per cent it rises to a value as large as 650 Å and drops again to 430 Å. Below the solvent composition of 33.6% the root-mean-square radius decreases by only a small amount in a linear fashion. The discontinuous change obtained seems to indicate that the conformations of the micelles formed at various compositions are not identical. Indeed, the experimental results of the particle scattering function provide a support to this view as illustrated in the following.

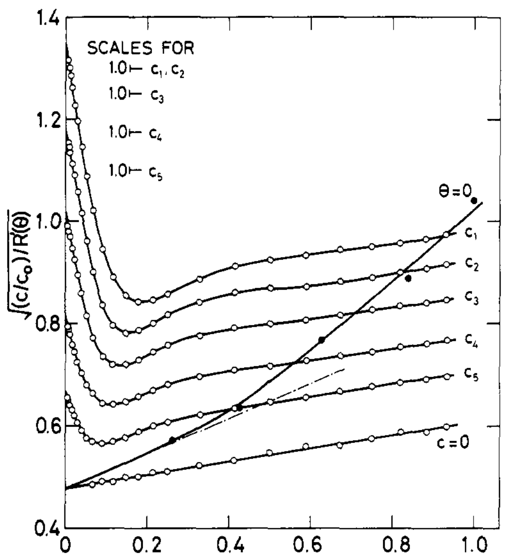

Figure 6. The square-root plot of the reciprocal scattering function of BMM-313 in the mixed solvent containing 19.8 wt % of toluene. For the symbols, see the legend to Figure 3. The concentration c_0 is 0.148 × 10^{-2} g/ml and the relative concentrations are: c_1, 1.00; c_2, 0.838; c_3, 0.640; c_4, 0.426; c_5, 0.260.

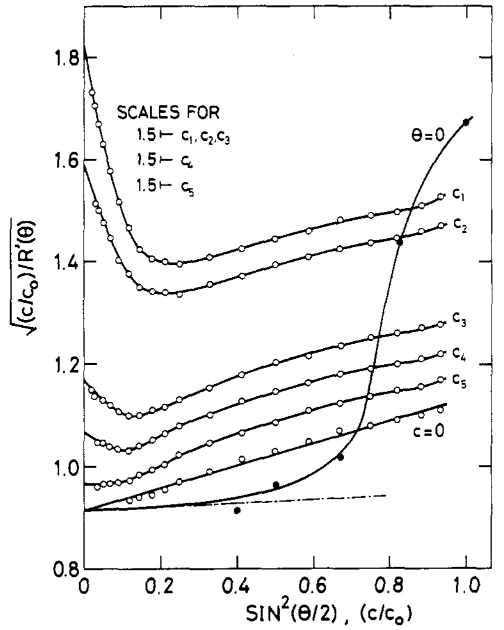

Figure 7. The square-root plot of the reciprocal scattering function of BMM-313 in the mixed solvent containing 9.94 wt % of toluene. For the symbols, see the legend to Figure 3. The concentration c_0 is 0.764 × 10^{-3} g/ml and the relative concentrations are: c_1, 1.00; c_2, 0.831; c_3, 0.674; c_4, 0.505; c_5, 0.400.

Figure 3 shows the square-root plot of the reciprocal scattering function for BMM-313 in the solvent of 36.7%. The angular dependence resembles that obtained in pure toluene but the second virial coefficient is negative. Figure 4 shows the similar data for the solvent of 35.7%. The angular variation concave upward suggests the sphere or the ellipsoid of revolution for the conformation of the PS aggregate in the micelle. Figure 5 shows the similar result in the solvent of 33.6%. The square root of the reciprocal scattering function follows a straight line except for the range of small scattering angles where it reveals an extraordinarily sharp increase at higher solute concentrations. This type of increase may be interpreted by the theory developed in part I[1] as indicative of a conformation of the tightly coiled PS core surrounded by a number of PMMA subchains from the core. The points for values extrapolated at zero-scattering angle reveal a pronounced

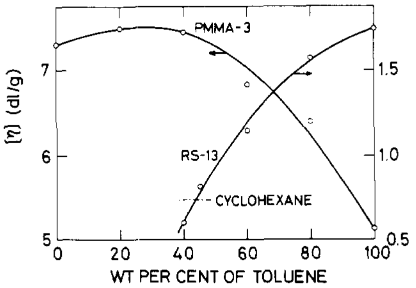

Figure 8. Plots of intrinsic viscosity *vs.* the solvent composition for polystyrene RS-13 and a poly(methyl methacrylate) sample PMMA-3. The latter was prepared by the anionic polymerization, and its sedimentation constant measured in acetone at 20° was 56.2 S. The molecular weight estimated by using the relation of Eriksson[9] was 1.53×10^6. The viscosity measurements were made at 30° in a Ubbelohde viscometer.

upward curvature when plotted *vs.* the relative concentration (c/c_0) but the initial slope indicated by the chain straight line remains very small.

The data for 19.8% are similar in the concentration dependence of the reciprocal scattering function extrapolated at zero-scattering angle but the angular dependence at finite concentrations reveals a more complicated feature as shown in Figure 6. The sharp increase at small angles resembles the previous data but the plotted points at higher angles do not increase linearly but seem to oscillate about a straight line. The theory developed in part I predicts for such a result a substantially long correlation distance for the intermolecular interaction of the PS subchains. The micelle at this solvent composition contains as many as 72 block copolymer molecules on the average, but the overall size of the PS subchains in the micelle remains at a value comparable to the size of the single PS subchain in the isolated molecule. Figure 7 shows the light-scattering result in a solvent which contains the largest amount of furfuryl alcohol studied in the present investigation. The oscillation seen in Figure 6 at high scattering angles can again be detected. We also note that the apparent molecular weight sharply increased as the polymer solution was diluted as indicated by the abrupt decrease with decreasing concentration of the reciprocal scattering function extrapolated to zero scattering angle. It will be an interesting subject of further study whether this type of concentration-dependent transition is a phenomenon universal to block copolymer micelles.

Discussion

The present light-scattering results obtained on the isolated two-block copolymer confirm the conclusion of the previous study[1] that the intramolecular contacts of dissimilar segments do occur. At the theta composition, where the net interaction between PS units vanishes, the mean-square radius of the PS subchain is about 1.8 times larger than the unperturbed one. The maximum revealed at a solvent composition near 80% seems to have appeared as a consequence of the counter action of furfuryl alcohol as solvent to PS and PMMA, *i.e.*, PMMA is more expanded in furfuryl alcohol than in toluene, while the former is a nonsolvent for PS. The viscosity results shown in Figure 8 verify this view.

Next we discuss the particle-scattering function obtained at the solvent composition of 35.7% in terms of the conformation of the PS subchain in the micelle. Effects of heterogenieties in size and shape of the micelle are ignored in this discussion. Let us consider first the volume per unit mass for the PS core. Figure 9 plots $\langle S^2\rangle^{3/2}/M$ for the PS core against the solvent composition as a measure of this quantity, together with the number of molecules n comprising a micelle. It is seen that, except for the micelle at 35.7%, this quantity reveals a smooth change and the values are very small. Therefore, a spherically symmetric segment distribution or even a rigid sphere might be suggested for the conformation of these PS cores. These conformations are quite unlikely, however, for the micelle formed at 35.7% in view of the fact that within a slight change of the solvent composition from 36.7 to 35.7% the core volume per unit mass increased by 4.6 times. Correspondingly, the average micelle size increased from 2.61 to 9.35.

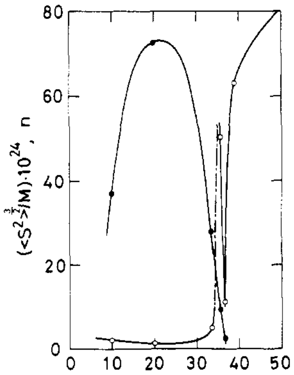

Figure 9. Plots of $\langle S^2\rangle^{3/2}/M$ for the polystyrene core in the micelle (open circles) and the number of block copolymer molecules n being comprised by a micelle (closed circles) as a function of the solvent composition.

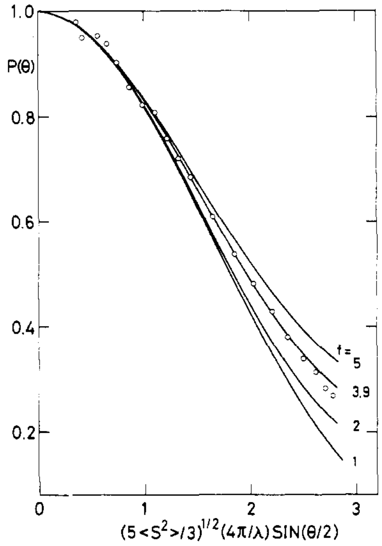

Figure 10. The particle scattering function obtained at the solvent composition of 35.7% (open circles) and the theoretical curves for the prolate ellipsoid of revolution of the axial ratio *f*.

Let us suppose that the PS core at 35.7% was formed by the linear association of the spherical PS core formed at 36.7% without a notable change of its size and assume its shape by a prolate ellipsoid of revolution with an axial ratio of 3.58 (= 9.35/2.16). Then the ratio of the quantity $\langle S^2\rangle^{3/2}/V$ for the ellipsoid of revolution to that for the sphere is calculated as 3.07. Here V signifies the volume of the particle. This value is comparable to 4.6. The particle-scattering function obtained by the experiment supports the model quite satisfactorily as shown in Figure 10. The axial ratio obtained from the comparison of theory[11] and experiment is 3.9 which stands in close proximity to the above value of 3.58. Thus we may conclude that in the initial stage of aggregation PS subchains form a core of anisotropic shape but the core changes into a more tightly coiled sphere with increase of the micelle size in poorer solvents.

Lastly we consider the complicated angular dependence of the reciprocal scattering function for the PS core of the largest micelle obtained by the present investigation. If its shape is assumed as a rigid sphere its diameter is calculated from the mean-square radius as 960 Å. To this core are linked 72 PMMA subchains of molecular weight 0.94 million most probably in a spherically symmetric fashion. Therefore, the PS core may be thickly surrounded by PMMA subchains so much that direct contacts of PS cores are rare. Evidence supporting this view is provided by the large correlation distance $\langle r^2\rangle^{1/2}$ of 4400 Å for the intermolecular interaction of the PS core. This quantity was evaluated according to the procedure described in Part I. The correlation distance estimated at finite concentrations revealed a negative concentration dependence in agreement with the previous results, but the product $\langle r^2\rangle^{3/2}c$ increased with concentration consistent with the result of the positive second virial coefficient.

As explained in Part I the angular dependence of the light-scattering results is compared with theory in terms of the quantity $\Psi(\theta)$ defined by

$$\Psi(\theta) \equiv \lim_{c\to 0} \psi(\theta)/\lim_{\substack{c\to 0\\ \theta\to 0}} \psi(\theta) \tag{2}$$

where

$$\Psi(\theta) \equiv \left\{\frac{[Kc/R(\theta)]}{\lim\limits_{c\to 0} [Kc/R(\theta)]} - 1\right\}\frac{1}{c} \tag{3}$$

It will be legitimate to call this function the intermolecular interference function. The experimental results are plotted in Figure 11 as a function of sin $(\theta/2)$. Theoretically, $\Psi(\theta)$ is given by $\langle(\sin hr)/hr\rangle$ which is defined as

$$\left\langle\frac{\sin hr}{hr}\right\rangle = \frac{\int_0^\infty [1 - \exp(-U(r)/kT)]4\pi r^2(\sin hr/hr)\mathrm{d}r}{\int_0^\infty [1 - \exp(-U(r)/kT)]4\pi r^2\mathrm{d}r} \tag{4}$$

where $U(r)$ signifies the spherically symmetric potential of intermolecular interaction between PS cores and h is $(4\pi/\lambda)$ sin $(\theta/2)$. Judging from the shape of $\Psi(\theta)$ obtained by the experiment it is expected that the previous theory may reproduce the result quite well, if not quantitatively. For the present micelle we may approximate $U(r)$ by the hard sphere potential of diameter b based on the discussion stated above concerning the micelle shape, because the magnitude of A used in eq 8 of part I should be very close to unity. The b value can be determined by calculation from the correlation distance obtained above as 5680 Å. Theoretical values of the intermolecular interference function thus calculated according to the theory are shown in Figure 11 by the full curve. Neither an adoption of the A value smaller than unity nor the use of the potential of exponential repulsion were found to yield better agreement. In any case, detailed comparison of theory and experiment may have to be withheld at the present stage of investigation.

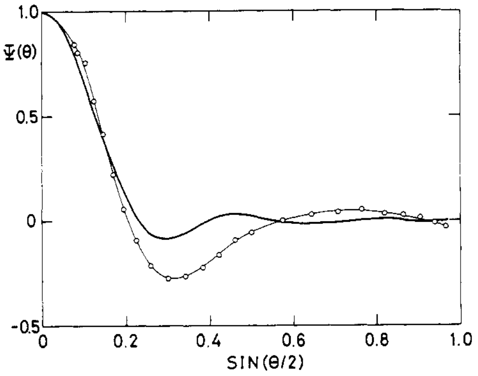

Figure 11. Plots of the intermolecular interference function $\Psi(\theta)$ obtained for the PS core of the micelle at 19.8% *vs.* sin $(\theta/2)$. The curve represents the theory for the hard sphere potential of a diameter of 5680 Å.

References and Notes

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