Hydrophobic Domain Structure of Water-Soluble Block Copolymer. 2. Transition Phenomena of Block Copolymer Micelles[1]

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ABSTRACT: Micelle formation and the hydrophobic domain structure of a water-soluble ABA-type block copolymer of hydrophobic poly(2-hydroxyethyl methacrylate) (PHEMA) and hydrophilic poly(ethylene oxide) (PEO) were investigated by means of small-angle X-ray scattering and a fluorometric analysis using fluorescent dyes as probes for the hydrophobic region. The emission λ_{max} of a fluorescent dye added to a block copolymer solution exhibits a distinct two-step blue shift with an increase in polymer concentration. The concentration at which the second transition takes place is consistent with the critical concentration for the intermolecular association determined from light scattering. The first transition in the emission λ_{max} indicates that the hydrophobic domain of the contracted PHEMA chain was formed within a molecule, suggesting the formation of a monomolecular micelle. Subsequent intermolecular association through PHEMA chains appears to bring about further aggregation of PHEMA chains within the hydrophobic domain. The fluorescence spectra exhibit a remarkable temperature dependence and the emission λ_{max} was shifted toward shorter wavelength on lowering the temperature in both the monomolecular and polymolecular micelles. As for the polymolecular micelle, X-ray scattering data reveal that a considerable extent of the intermixing phase exists in the interfacial region between the core and the shell and also that the width of the intermixing phase decreases with a lowering of the temperature. This suggests that a demixing of the constituent blocks results in an enhancement of the hydrophobicity of the PHEMA chains within the core of the micelle. The state of the PHEMA chains in the intermixing phase is discussed.

Introduction

In the previous article of this series,[3] we described the structure of the intermolecular associate of the water-soluble block copolymer in water, a selective solvent for the hydrophilic blocks. The water-soluble ABA-type block copolymer of hydrophobic poly(2-hydroxyethyl methacrylate) (PHEMA) and hydrophilic poly(ethylene oxide) (PEO)[4] forms an intermolecular associate through the aggregation of the insoluble PHEMA chains above a critical polymer concentration. We proposed a spherical micelle model with the intermixing phase of the unlike blocks around the core surface and investigated the structure of the intermolecular associate of the water-soluble block copolymer by means of small-angle X-ray scattering.[3] A considerable amount of the intermixing phase of the constituent blocks was found to exist in the interface between the aggregated core and the expanded shell of the polymolecular micelle.

A preliminary experiment was also made in an attempt to investigate the state of the hydrophobic chains within the block copolymer micelle by means of a fluorometric measurement using a hydrophobic probe. When the fluorescence characteristics of the probe bound to the hydrophobic chains were examined as a function of the polymer concentration, an unusual concentration dependence of the emission λ_{max} was observed, suggesting a change in conformation of the monomolecular block copolymer prior to the formation of the polymolecular micelle.

Extensive investigations were performed concerning the polymolecular micelle of the block copolymer.[5-12] However, there are few studies of the conformation of block copolymers dispersed molecularly in a selective solvent because of the lack of an effective experimental method. Only limited data for Pluronic copolymers were presented in which the inflection in the surface tension vs. concentration plot was related to the conformational change in the copolymer due to the formation of a monomolecular micelle.[13] Fluorometric measurement with a hydrophobic probe[14-19] is a powerful method to investigate the conformation of the water-soluble block copolymer since fluorescence characteristics of dyes which are bound onto the hydrophobic region reflect sensitively the change in the microenvironment.

We describe in this article the transition phenomena in the hydrophobic domain of a water-soluble block copolymer taking place during the course of micelle formation. The conformational change of hydrophobic blocks was investigated with two different fluorescent dyes, 1-anilinonaphthalene (AN) and 8-anilinonaphthalene-1-sulfonate (ANS), whose fluorescence characteristics should give information on the structure of the hydrophobic domain at different positions. The domain structure of the block copolymer was found to undergo a two-step variation in the association process. Prior to intermolecular association, intramolecular structural transition was considered to take place, resulting from the formation of the nonassociative monomolecular micelle which contains the hydrophobic core in an inner part of the whole chain from which the soluble chain is sufficiently excluded. The structure of the polymolecular micelle formed in the region above the critical polymer concentration was investigated by small-angle X-ray scattering using a spherical micelle model as previously reported. The temperature dependence of the association of the block copolymer and the structure of the polymolecular micelle was also investigated and is discussed in terms of the relation between the micellar structure and the domain hydrophobicity.

Experimental Section

Materials. Reagent-grade AN and ANS were used without further purification. Water was distilled twice after refluxing in the presence of a small amount of potassium dichromate.

The HEMA–EO ABA-type block copolymer was prepared by the same procedure reported earlier,[4] so only brief details are given here. The amino-semitelechelic oligo-HEMA was prepared by radical telomerization of HEMA monomer with 2-aminoethanethiol as a chain-transfer reagent. 2,4-Tolylene diisocyanate was introduced at both ends of PEO. The amino-semitelechelic oligo-HEMA was allowed to react with the isocyanato-telechelic PEO in DMF–chlorobenzene to obtain the HEMA–EO ABA-type block copolymer. The results of the sample preparation are shown in Table I.

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Table I
Preparation and Analysis of the HEMA-EO ABA-Type Block Copolymer

M_n of prepolymers			HEMA mole fraction in block copolymer	
amino-semitelechelic oligo-HEMA[a]	hydroxy-telechelic PEO[b]	yield, %	found[c]	calcd[d]
1940	7210	69.8	0.104	0.153

[a] Value determined from amino group analysis. [b] Value determined from viscosity equation. [c] Value determined from hydroxyl group analysis. [d] Value calculated assuming of ABA architecture.

Fluorometric Analysis. Fluorometric measurements were carried out at different temperatures with a spectrofluorometer (Hitachi MPF4). Water from a thermostated bath was circulated through the jacket around the cell. The sample solutions containing ANS were prepared as follows. The desired amount of the block copolymer was dissolved in a 1.0×10^5 mol/L ANS solution to obtain a 1.0 g/dL stock solution. The stock solution was diluted with an ANS solution of the same concentration to prepare samples of a given polymer concentration. The fluorescence of ANS was excited by using incident light of 360 nm. The sample solutions containing AN were prepared as follows. The desired amounts of the block copolymer were dissolved in water to obtain aqueous solutions of the block copolymer of given polymer concentrations. AN, which is insoluble in water, was dispersed into aqueous solutions of the block copolymer from a small amount of methanol solution containing the desired amount of AN. The final concentration of AN dispersed into the block copolymer solutions was adjusted at 1.0×10^{-5} mol/L for each solution. The fluorescence of AN was excited by using incident light of 330 nm. Each sample was stored in a dark place until measurements were carried out.

Light Scattering. Light scattering measurements were carried out at different temperatures with a light scattering photometer (Union Giken LS-601). The instrument was calibrated with benzene, for which the Rayleigh ratio is known. Measurements were made with light of 632.8 nm at 23 angles from 30 to 150°. The refractive index increment of the sample solution was determined by using a differential refractometer (Union Giken RM-101). Test solutions of the block copolymer for the light scattering measurement were prepared as follows. Distilled water was purified by using filters of pore size 0.8 μm. A polymer solution of concentration 0.5 g/dL was prepared by mixing the polymer sample with water and then transferred into light scattering cells with ground-glass stoppers after sufficient centrifugation. An aliquot of the stock solution was separated to determine the concentration by UV spectroscopy. Sufficient purified water was added directly to the light scattering cells containing the purified stock solution to obtain sample solutions of concentration ranging from 0.1 to 0.5 g/dL. The concentration of each solution was calculated from the weight of the solution and the solvent.

Small-Angle X-ray Scattering. Small-angle X-ray scattering (SAXS) measurements were carried out with a Rigaku-Denki X-ray small-angle scattering apparatus using a Kratky slit. Copper radiation from an X-ray generator with a power of 35 kV and 26 mA was nickel filtered and detected by a scintillation counter with a pulse height analyzer. The incident X-ray source was collimated as described elsewhere.[20] Brass plates of 1-mm thickness having slits 30 mm × 5 mm were used as sample cells; both sides of the plates were covered with mica films of about 30-μm thickness as cell windows. The cell containing the sample solution was placed in a cell holder, around which water from a thermostated bath was circulated through the jacket to maintain the sample at a given temperature. The scattered intensity was measured at a fixed time of 2000 s from 0.16 to 0.04° by a step-scanning device with a step interval of 0.004°. Parasitic scattering from the slit system was negligible within the angular region in which measurements were carried out. The scattered intensity of the solvent was subtracted from that of the sample solution after correction for absorption. The values of electron density for the constituent blocks of the block copolymer were determined according to the same procedure described in the previous article.[3]

Results and Discussion

Structural Transition of the Water-Soluble Block Copolymer in Micelle Formation.

Fluorometric measurements were carried out at 30 °C on aqueous solutions of the HEMA–EO ABA-type block copolymer in the presence of extrinsic fluorescence probes for the hydrophobic region. Two different fluorescent dyes, AN and ANS, were used as extrinsic probes for the hydrophobic region. These dyes are bound preferentially to the hydrophobic region of polymers, resulting in enhancement of the fluorescence quantum yield and a shift of the emission maximum (λ_{max}) toward the blue. The fluorescence characteristics of these dyes bound to the polymer chain should reflect sensitively the structure of the hydrophobic region.

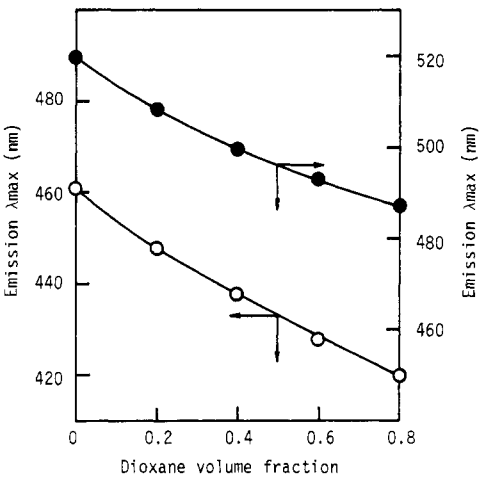

Figure 1. Solvent perturbation of the emission λ_{max} of AN (○) and ANS (●) in solvent mixtures of water and dioxane at 20 °C. [Dye] = 1.0×10^{-5} mol/L.

AN, a polycyclic aromatic compound, is quite insoluble in water. AN is solubilized into strongly hydrophobic regions[21-24] when dispersed into aqueous solutions from a small amount of organic solvent such as methanol. On the other hand, ANS, which is an amphiphatic compound having a sulfonate group, is freely soluble in water but insoluble in nonpolar solvents. An ANS molecule can be bound only to a hydrophobic region near the aqueous medium like the surface of a surfactant micelle or the hydrophobic cleft of globular proteins since a sulfonate group of an ANS molecule has to be in contact with the aqueous medium. The fluorescence characteristics of these dyes should give information on different regions of the hydrophobic domain because the binding ability of these dyes to the hydrophobic region has different requirements.

The fluorescence spectra of AN and ANS were measured in mixtures of water and dioxane and the relation between the emission λ_{max} and the solvent composition is shown in Figure 1. As the polarity of the solvent decreased, the emission λ_{max} of these dyes was shifted monotonously toward the blue, being accompanied by an increase in fluorescence intensity. The dependence of the λ_{max} on the polarity of the solvent is believed to result from the reorientation of the solvent shell around the chromophores when they are excited.[25] No difference was observed in

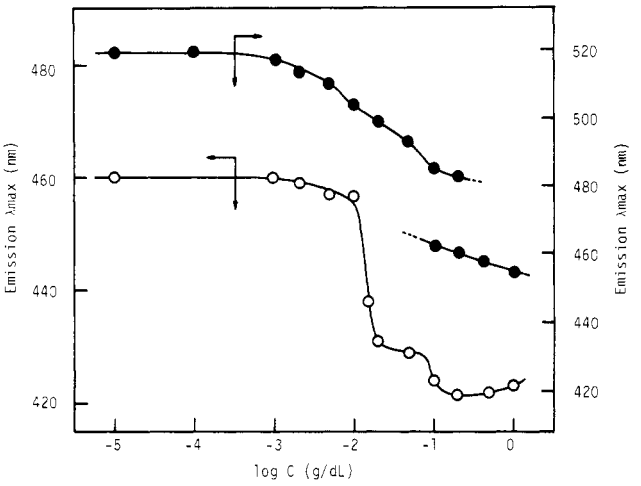

Figure 2. Polymer concentration dependence of the emission λ_{max} for aqueous solutions of the HEMA-EO block copolymer in the presence of a fluorescent dye at 30 °C. [Dye] = 1.0×10^{-5} mol/L. Fluorescent dye: (○) AN; (●) ANS.

the fluorescence characteristics of AN and ANS except that the λ_{max} of ANS was at a longer wavelength than that of AN due to the substituent effect of the sulfonate group.[26]

In Figure 2, the emission λ_{max} of the fluorescence spectra is plotted against the polymer concentration for aqueous solutions of the block copolymer in the presence of AN and ANS, respectively. The emission λ_{max} of these dyes exhibits a significant dependence on the polymer concentration. Moreover, ANS and AN differ in the concentration dependence of the emission λ_{max}.

For the change in the λ_{max} of ANS, the range of the polymer concentration could be classified into three categories. First is the region in which the emission λ_{max} is almost equal to that of the free ANS in water, independent of the polymer concentration (less than ca. 2×10^{-3} g/dL). Second is the region in which the emission λ_{max} undergoes a considerable blue shift with an increase in the polymer concentration (ca. 2×10^{-3} to ca. 0.1 g/dL). Last is the region in which a shoulder appears at a wavelength shorter than λ_{max}; this becomes predominant as the polymer concentration increases and is accompanied by a further blue shift (higher than ca. 0.1 g/dL).

As for the change in the λ_{max} of AN, the range of the polymer concentration could be also classified into three categories, though the concentration range and the mode of the concentration dependence which characterize the shift of the emission λ_{max} are significantly different from those of ANS. The λ_{max} of AN added to block copolymer solutions was found to undergo a distinct two-step blue shift with an increase in the polymer concentration. Following the concentration-independent region, the emission λ_{max} of AN was drastically shifted toward shorter wavelengths within the relatively narrow concentration range around 0.016 g/dL (the first transition). Further increase in the polymer concentration (around 0.1 g/dL) resulted in a further shift of the emission λ_{max} toward the blue (the second transition).

The critical concentration for intermolecular association of the block copolymer determined from light scattering was found to be in good agreement with the concentration at which the shoulder appeared in the fluorescence spectra of ANS and also with the concentration at which the second transition took place in the emission λ_{max} of AN. This indicates that the intermolecular association results in a structural change in the hydrophobic region of the block copolymer. Moreover, the anomalous concentration dependence of the λ_{max} below the critical concentration for intermolecular association indicates that the structure of the hydrophobic region changes with polymer concentration even in the state of monomolecular dispersion, suggesting that a conformational change of the block copolymer takes place within the molecule.

As shown in Figure 2, plots of both ANS and AN have a concentration-independent region in which the emission λ_{max} is almost equal to that of the free dyes. This indicates that the block copolymer has no hydrophobic domain able to bind these fluorescent probes in dilute aqueous solutions though it contains a hydrophobic chain within the molecule. This is obviously because the block copolymer adopts the quasi-random coil form; i.e., the PEO chain penetrates freely the water-swollen PHEMA chains.

An increase in the polymer concentration beyond a certain value appears to induce a structural change of the block copolymer within a molecule as shown by the anomalous blue shift of the emission λ_{max} of the fluorescent probes. The gradual blue shift in the emission λ_{max} of ANS above ca. 1.0×10^{-3} g/dL indicates that the microenvironment around the binding site for ANS becomes hydrophobic with an increase in polymer concentration. It should be noted that ANS does not bind to the hydrophilic PEO chains. Therefore, the fluorescence characteristics of ANS bound to the block copolymer chain are believed to be affected by the interpenetration of the constituent blocks. Enhancement in hydrophobicity of the binding site of ANS is presumably due to the segregation of the constituent blocks, i.e., the partial exclusion of the hydrophilic PEO chain from the water-swollen PHEMA chains. As for the emission λ_{max} of AN, the abrupt blue shift took place within a narrow range of the polymer concentration, higher than that for the beginning of the blue shift of ANS. This indicates the formation of a domain with strong hydrophobicity, sufficient to solubilize an AN molecule which is insoluble in water, suggesting that the drastic conformational transition of the block copolymer took place within this concentration range. This transition in the λ_{max} of AN is believed to be induced by the formation of a large hydrophobic domain resulting from intramolecular micelle formation prior to intermolecular association. Sufficient segregation of the constituent blocks with an increase in polymer concentration may cause this transition in the conformation of the monomolecular block copolymer. Such a domain formation within the PHEMA core seems to induce still more segregation around the surface of the hydrophobic domain as shown in the small but distinct shift in the emission λ_{max} of ANS at the first transition around 0.08 g/dL.

The fact that the second transition in the λ_{max} of AN took place at the same concentration as the intermolecular association indicates that the intermolecular aggregation of the PHEMA chains leads to the formation of a dense core within the interior of the hydrophobic domain of the block copolymer micelle. In the fluorescence spectra of ANS, moreover, a shoulder at a wavelength shorter than λ_{max} appeared at the same concentration, suggesting that the intermolecular aggregation of the PHEMA chains seems to also induce sufficient exclusion of the hydrophilic PEO chains from the hydrophobic domain as well as the formation of a PHEMA dense core within the hydrophobic domain.

Temperature Dependence of the Micellar Structure. Light scattering measurements were carried out at different temperatures on aqueous solutions of the block copolymer. The angular distribution of the scattered intensity was measured at four different concentrations and the reduced scattered intensity (Kc/R_θ) was extrapolated

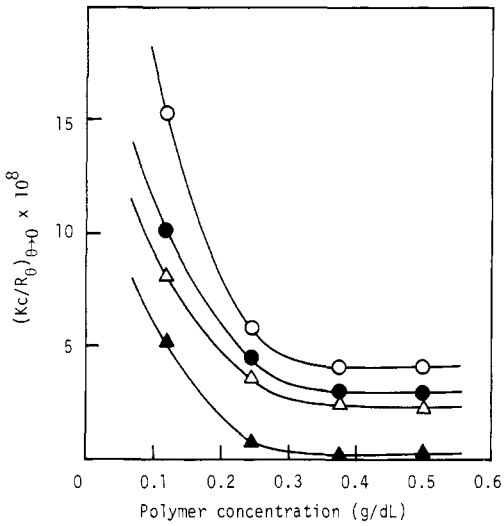

Figure 3. Plot of the reduced scattering intensity $(Kc/R_\theta)_{\theta\to 0}$ vs. polymer concentration for aqueous solutions of the HEMA–EO block copolymer. Temperature: (○) 21.0 °C; (●) 28.7 °C; (△) 36.9 °C; (▲) 50.5 °C.

to zero angle. As shown in Figure 3, each plot of $(Kc/R_\theta)_{\theta\to 0}$ vs. polymer concentration deviated upward from linearity below a concentration of about 0.3 g/dL, irrespective of temperature. The curvature of these plots indicates that the apparent molecular weight of the block copolymer increases with increasing polymer concentration in this concentration range, corresponding to a process of intermolecular association of the block copolymer. Intermolecular association appeared to set in at least at a concentration of ca. 0.1 g/dL, though it was difficult to perform the experiment at lower concentration because of the considerable decrease of scattered intensity. The intercept values, extrapolated from the concentration range in which plots seem to obey a linear relationship, decreased with rising temperature. This means that the molecular weight of the intermolecular associate of the block copolymer increased with rising temperature. The concentration ranges at which the $(Kc/R_\theta)_{\theta\to 0}$ values begin to deviate upward from linearity are almost constant independent of temperature. This shows that the critical concentration for the intermolecular association does not depend on temperature. The increase in the molecular weight of the polymolecular micelle with rising temperature suggests that the intermolecular association may arise mainly from the hydrophobic interaction between the PHEMA chains since this is generally enhanced at higher temperatures.[27]

In Figure 4, the temperature dependence of the emission λ_{max} of ANS was plotted against the logarithm of the polymer concentration. At the lower concentrations, the emission λ_{max} exhibits only a slight temperature dependence, resulting from the intrinsic fluorescence characteristics of ANS. The concentrations at which a significant blue shift sets in move lower on lowering the temperature and the extent of the blue shift increases. This indicates that hydrophobicity around the binding site of ANS is enhanced, probably due to a conformational change of the block copolymer. The constituent blocks of the block copolymer are believed to undergo demixing, leading to a substantial increase in the hydrophobic segment rich regions. The concentrations at which the shoulder appeared at a wavelength shorter than λ_{max} are ca. 0.1 g/dL at each temperature. This is in good agreement with the temperature-independent critical concentration for the intermolecular association determined from light scattering.

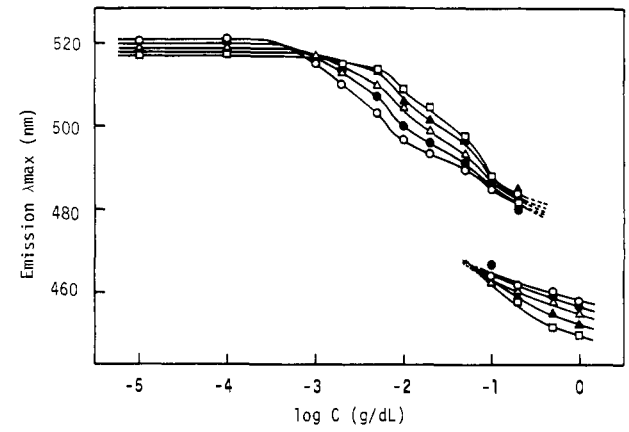

Figure 4. Polymer concentration dependence of the emission λ_{max} for aqueous solutions of the HEMA–EO block copolymer in the presence of ANS. [ANS] = 1.0×10^{-5} mol/L. Temperature: (○) 10 °C; (●) 20 °C; (△) 30 °C; (▲) 40 °C; (□) 50 °C.

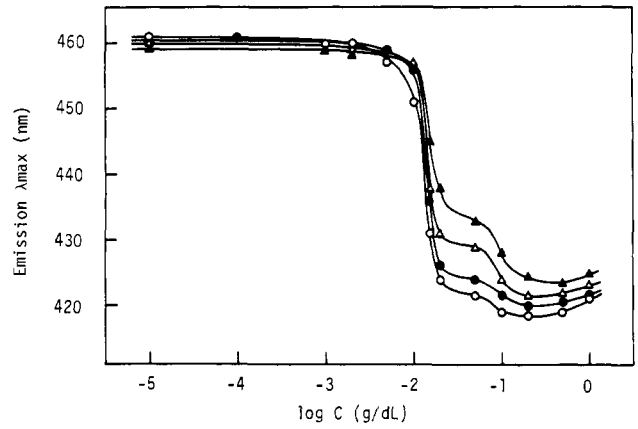

Figure 5. Polymer concentration dependence of the emission λ_{max} for aqueous solutions of the HEMA–EO block copolymer in the presence of AN. [AN] = 1.0×10^{-5} mol/L. Temperature: (○) 10 °C; (●) 20 °C; (△) 30 °C; (▲) 40 °C.

However, above 0.1 g/dL, the blue shift increases with rising temperature. This suggests a difference between polymolecular and monomolecular micelles in the PHEMA chains within the hydrophobic domain. The structure of the polymolecular micelle will be discussed in detail in the following section, which is concerned with the SAXS data.

In Figure 5, the temperature dependence of the λ_{max} of AN was plotted against the logarithm of the polymer concentration. Each plot exhibits an unambiguous two-step variation with an increase in the polymer concentration, irrespective of the temperature. At both the first and second transitions, the λ_{max} blue shift increases with decreasing temperature. As for the extent of the blue shift, the larger is at the first transition, the smaller at the second transition.

The temperature dependence of the λ_{max} at these two transitions indicates that a temperature-dependent structural change took place in the hydophobic domains of the block copolymer. This phenomenon is believed to arise from the extent of the intrachain segregation of the constituent blocks. Because of their incompatibility, the hydrophilic PEO chain is sufficiently excluded from the PHEMA core at the lower temperatures, leading to the formation of the dense core of the PHEMA blocks at the first transition, i.e., the formation of a monomolecular micelle. Elevating the temperature may cause a partial penetration of the PEO chain into the hydrophobic PHEMA core due to the active motion of the segments, resulting in a decrease of the density of the hydrophobic

segments within the hydrophobic domain. The above descriptions were also supported by the data in Figure 4, which show that a larger λ_{max} blue shift of ANS occurred at lower temperatures, presumably because of the partial demixing of the constituent blocks.

As stated above, the larger the blue shift at the first transition, the smaller it is at the second transition. This means that intermolecular association seems to induce no significant change in the state of the PHEMA chains within the hydrophobic domain when a sufficiently dense core was formed in the first transition at the lower temperatures.

Further increase in the polymer concentration resulted in a slight red shift of λ_{max}, irrespective of the temperature, indicating that the microenvironment around the binding site of AN becomes hydrophilic. This unexpected result contrasts with that obtained from ANS, and its significance is unknown.

Analysis of the Polymolecular Micelle Structure by Small-Angle X-ray Scattering. For the polymolecular micelle, we propose a spherical micelle model with a boundary region resulting from a partial mixing of the constituent blocks as described previously.[3] Here, we consider a spherical micelle of total radius R. The PHEMA blocks form a spherical core of radious γR and the PEO blocks form the shell of the micelle, where γ ($0 < \gamma < 1$) is defined as the ratio of the core radius to the total radius R. The aggregated PHEMA chains are assumed to be uniformly distributed within the spherical core. The PEO chains obey random-flight statistics and are fully excluded from a hard core of radius γR. When partial mixing of the constituent blocks takes place in the interfacial region between the core and the shell, AB chemical junction points on the core surface are assumed to be distributed in the radial direction within the boundary of width $2\alpha\gamma R$ ($0 < \alpha < 1$) around the center γR, where 2α is defined as the ratio of the boundary width to the core radius γR. The electron density distribution of constituent blocks within the intermixing phase is approximated by the boundary function as defined previously. In this micelle model, a radial electron density distribution function $\rho(r)$ is separated into ρ_c and ρ_s, those of the core and the shell, respectively. Both $\rho_c(r)$ and $\rho_s(r)$ are divided into two parts, i.e., the region consisting of a single component and the intermixing region, as expressed in the following equations:

$$\rho_c \begin{cases} \rho_1(r) = 1 \quad (0 < r < (1-\alpha)\gamma R) & (1) \\ \rho_2(r) = \frac{1}{2\pi}[-\sin(r-\gamma R)\frac{\pi}{\alpha\gamma R} - (r-\gamma R)\frac{\pi}{\alpha\gamma R} + \pi] \\ \qquad ((1-\alpha)\gamma R < r < (1+\alpha)\gamma R) & (2) \end{cases}$$

$$\rho_s \begin{cases} \rho_3(r) = \frac{1}{2\pi}[\sin(r-\gamma R)\frac{\pi}{\alpha\gamma R} + (r-\gamma R)\frac{\pi}{\alpha\gamma R} + \pi] \\ \qquad ((1-\alpha)\gamma R < r < (1+\alpha)\gamma R) & (3) \\ \rho_4(r) = \exp[-(\frac{r-(1+\alpha)\gamma R}{R-(1+\alpha)\gamma R})^2] \\ \qquad ((1+\alpha)\gamma R < r < R) & (4) \end{cases}$$

Thus, the structure factor $F(h)$ is represented as

$$F(h) = N_c\int_0^{(1+\alpha)\gamma R} \rho_c^*(r)\frac{\sin(hr)}{hr}4\pi r^2\,dr + N_s\int_{(1-\alpha)\gamma R}^{R} \rho_s^*(r)\frac{\sin(hr)}{hr}4\pi r^2\,dr \quad (5)$$

where $h = (4\pi/\lambda)\sin(\theta/2)$ is the scattering vector, λ is the X-ray wavelength, θ is the scattering angle, N_c and N_s are the total excess electron numbers of the core and the shell, respectively, and functions with an asterisk are normalized within the integrated region. The theoretical scattering intensity I was smeared according to the weighting function[28] calculated for the collimation system used in this study in order to compare the observed scattering intensity.

Table II
Summary of SAXS Results on the Polymolecular Micelle for the HEMA-EO ABA-Type Block Copolymer in Water

	temperature		
	15 °C	30 °C	45 °C
γ	0.31	0.33	0.36
α	0.20	0.30	0.40
radius of gyration (S), Å	522	591	638
total radius (R), Å	852	957	1018
core radius (γR), Å	264	316	367
boundary width ($2\alpha\gamma R$), Å	106	189	293

Small-angle X-ray scattering measurements were carried out at different temperatures on the polymolecular micelle of the water-soluble block copolymer. The radii of gyration S were determined from a Guinier plot of the scattered intensity, and the experimental particle scattering functions $P(\theta)$ were obtained. The shapes of the experimental curves are remarkably different from one another, indicating that the structure of the polymolecular micelle changes depending on temperature. The theoretical $P(\theta)^{-1}$ derived from this micelle model was compared with the experimental $P(\theta)^{-1}$ to evaluate the structural parameters γ and α. The values obtained for the structural parameters and the characteristics of the polymolecular micelle are shown in Table II together with the radious of gyration S and the total radius R evaluated from both the structural parameters and the values of the observed S.

The values of both the total radius and the core radius increase with rising temperature.[29] This increase in the size of the polymolecular micelle is believed to be attributable to an increase in the molecular weight of the block copolymer micelle as estimated from light scattering. A large part of the increased value of the total radius seems to be due to an increase in the core radius resulting from the interchain association of the hydrophobic PHEMA chains.

The SAXS data also reveal that a temperature increase causes a significant increase in the intermixing phase of the constituent blocks in the interfacial region between the aggregated core and the peripheral shell. The parameter α, which represents the extent of the interpenetration of the PEO chain into the hydrophobic core, attains a value of ca. 0.4 at 40 °C. This increase in the width of the intermixing phase is believed to result from the active segmental motion at the higher temperatures.

It is difficult to evaluate accurately the change in the segment density distribution of the PHEMA chains within the hydrophobic domain since the absolute intensity of the incident X-ray beam was not determined. The fluorometric data concerning AN, however, indicate that the interior region within the hydrophobic domain of the polymolecular micelle becomes more hydrophobic with a lowering of the temperature. This implies that the demixing of the constituent blocks in the interfacial region between the core and the shell results in a substantial increase in the density of the hydrophobic segments within the hydrophobic domain.

As shown in Figure 4, on the other hand, the emission λ_{max} of ANS in the range of the polymolecular micelle is

shifted further toward the blue with rising temperature, though the extent of the intermixing of the constituent blocks increases as indicated by the SAXS data. This tendency contrasts with the results obtained from fluorescence spectra of AN solubilized into the hydrophobic core of the micelle. Intermolecular association may induce a change in the state of the PHEMA chains within the intermixing phase since the number of chains participating in the formation of the polymolecular micelle increases with rising temperature.

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(29) The pure core radius, defined as $\gamma R - \alpha\gamma R$, reaches ca. 200 Å. The values seem to be too large for the PHEMA blocks to reach from the center of the inner core to its outer limit. This may arise from difficulty in determining the correct values of the boundary width since a partial mixing of the blocks continuously diminishes at the fringes of the boundary region. The values of the pure core radius are probably smaller than the values estimated from SAXS data.

Solvent-Dependent Conformations in Gels of Isotactic Polystyrene

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ABSTRACT: Using bulky hydrocarbon and substituted aromatic solvents, gels of isotactic polystyrene (iPS) were prepared by quenching the solution formed at high temperatures. It was found that the hydrocarbons induced the extended conformation, whereas either the threefold conformation or a mixture of threefold and extended conformations was obtained from aromatic solvents. Variations in the *d* spacings of the threefold helix structure were noted with the aromatic solvents. The observations are qualitatively explained on the basis of short-range interaction between adjacent phenyl groups.

Theoretical calculations on isotactic polystyrene (iPS) have shown that the nonstaggered conformations close to the tt state of the contiguous skeletal bonds are accessible without steric overlap.[1,2] This feature was shown to be common to most isotactic vinyl chains with planar substituents, including poly(*N*-vinylcarbazole).[3] The rotations $\Delta\phi_i$ and $\Delta\phi_{i+1}$ from perfect staggering (defined by (0°,0°) for the tt state) required to relieve the overlaps were of the order of 15–20°, and the signs of the rotations fell into two classes: (+,+) or (−,−) for monosubstituted chains and (+,−) or (−,+) for disubstituted chains, as shown in Figure 1. Calculations on iPS showed that without the adjustments adopted to include the solvent effects,[1] the energy of the tt state was lower than that of the tg state. However, it is known that in the crystalline state iPS adopts a threefold helical conformation, with a repeat distance of 6.6 Å along the chain, and that this helical character is substantially maintained in good solvents.[4]

Keller et al.[5,6] reported a new X-ray diffraction pattern from gels of iPS prepared from *trans*-decalin. The characteristic features were a meridional reflection of 5.1-Å spacing and a layer line distance of 30.6 Å. Calculations of several authors[2,7-9] showed that this pattern could be accounted for by a helix containing 12 monomers within the repeat distance of 30.6 Å. The conformations of the skeletal bonds would then correspond to the nonstaggered tt state.

Wellinghoff et al.[10] studied the gelation of isotactic and atactic polystyrenes from various solvents as a route to preparing glassy polymer films. The interesting feature of these films is the fringe-micellar aggregation of the extended-chain domains, giving rise to a glassy film with microcrystalline regions. Using various types of solvents with differing solubility parameters, they concluded that dispersion forces control the solution behavior of these systems.

The gels of iPS are prepared by quenching the solution rapidly below the spinodal line. In the poor-solvent regime, segmental interaction of the polymer chain becomes operative. In the concentration range used for the gelation experiments, interchain forces also might play a role. In the threefold helical conformation of iPS, which is char-

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