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Comicellization of Diblock and Triblock Copolymers in Selective Solvents

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ABSTRACT: Comicellization of a diblock block copolymer polystyrene-*block*-hydrogenated polyisoprene, PS−HPI (M_w 1.05 × 10^5 g mol^{-1}, the weight fraction of styrene w_{PS} 0.34), and triblock copolymer polystyrene-*block*-hydrogenated polybutadiene-*block*-polystyrene, PS−HPB−PS (M_w 7.0 × 10^4 g mol^{-1}, w_{PS} 0.28), in selective solvents was investigated by static and dynamic light scattering methods at 25−70 °C. Decane was a selective solvent for HPI and HPB blocks and 1,4-dioxane for PS blocks. HPI and HPB blocks are incompatible. Only the diblock copolymer formed micelles in decane while the triblock was molecularly dissolved at low concentrations and the measurement temperatures. Both the copolymers formed micelles of different sizes in 1,4-dioxane solutions. Comicellization was observed at all weight fraction of PS−HPB−PS, *X*, in solutions of copolymer mixtures in both solvents. In contrast to mixtures of chemically identical diblock copolymers with different molecular weights of the constituent blocks in selective solvents, small changes of micellar parameters resulting from comicellization were found in the copolymer mixtures under study. This is due to different constitution of the copolymers and their partial incompatibility. The *X* dependence of the molecular weight and size of comicelles in decane at low values of *X* was successfully described by adsorption of the PS−HPB−PS copolymers on micelles of the PS−HPI copolymer. The large PS−HPI copolymers were accommodated in small micelles of the PS−HPB−PS copolymer in 1,4-dioxane solutions with an excess of the PS−HPI.

Introduction

Multicomponent nanoparticles are very important in many applications, e.g., for development of drug delivery systems,[1] paints, cosmetic, and oil recovery.[2] One of the promising ways for preparation of such nanoparticles is self-assembling different polymers and/or copolymers in solutions. While self-assembly of individual block copolymers in selective solvents has been frequently studied,[3] only several experimental studies have been devoted to association in solutions of mixtures of two or more copolymers.[4−12] Most of the investigations were on nonequilibrium systems. In our opinion, only four studies using light scattering methods for characterization of solutions have provided an insight into behavior of steady-state solutions of block copolymer mixtures.[9−12] The first study[9] investigated comicellization of two chemically identical diblock copolymers differing in molecular weights and block lengths. Mixtures of two poly(α-methylstyrene-*block*-2-(4-vinylphenyl)ethanol)s with only slightly different block lengths were investigated in benzyl alcohol. The critical micellization temperatures of the copolymers used were $T_1 = 24$ °C and $T_2 = 50$ °C. The comicellization behavior was observed at temperatures T where only one of the copolymers can form micelles in its pure solution, i.e., $T_1 < T < T_2$, and temperatures where both copolymers form micelles, i.e., $T < T_1$. Since block copolymers with only slightly different block lengths were used for the experiment, only minor changes of micellar parameters resulting from comicellization were found. The apparent molecular weight of mixed micelles was larger than that calculated for independent micellization while the hydrodynamic radius was influenced only slightly.

Comicellization of two commercial amphiphilic triblock copolymers, F127 ($E_{99}P_{69}E_{99}$) and B20-5000 ($E_{45}B_{14},E_{45}$), was studied in aqueous solution by light scattering methods.[10] E, P, and B are oxyethylene, oxypropylene, and oxybutylene, respectively, with the subscripts denoting the number of segmental units in the block. Both triblock copolymers tend to self-assemble into starlike micellar structures. The mixed block copolymer system provides a suitable model for studying comicelliztion.

Recently, comicellization of $E_{60}B_{12}$ and $E_{58}B_{20}E_{58}$ copolymers in water was published.[11] The micelle association number depended on the proportions of the two copolymers in solution. This dependence was rationalized by taking account of the triblock copolymer looping in the micelle.

In our previous paper,[12] solution properties of mixtures of two diblock polystyrene-*block*-poly(methyl methacrylate) (PS−PMMA) copolymers strongly differing in molecular weight and composition were investigated in a selective solvent for PS blocks (65 wt % *p*-cymene and 35 wt % toluene). Molecular weights of the constituent blocks were the following: copolymer 1-PS, 29 200; PMMA, 285 100 and copolymer 2-PS, 9100; PMMA, 7800. Copolymer 1 formed micelles while copolymer 2 was molecularly dissolved at 30 °C and $c = 0.01$ g/mL. The mixtures of copolymers were investigated by static and dynamic light scattering methods. Comicellization was observed in copolymer mixtures below the critical

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weight fraction of copolymer 2, X_c ($\approx$0.95). The hydrodynamic radius of mixed micelles varied from 47 nm at $X = 0$ to 119 nm at X_c. A partial decomposition of mixed micelles was observed above X_c.

Several theoretical studies devoted to comicellization were published.[13-16] The formation of mixed micelles has been considered for the case when the insoluble blocks are identical, and the soluble blocks have the same length but are different in chemical nature in ref 13. The reversed situation, mixtures of two diblock copolymers having the same length of insoluble blocks but different chemical nature and the soluble blocks of the same chemical nature but of different length, was investigated in ref 14. Two different diblock copolymers having the same chemical nature but different composition were analyzed in refs 15 and 16. The conditions for the formation of pure micelles and comicelles were determined.

In this work solution properties of mixtures of diblock copolymer polystyrene-*block*-hydrogenated polyisoprene (PS−HPI) and triblock copolymer polystyrene-*block*-hydrogenated polybutadiene-*block*-polystyrene (PS−HPB−PS) have been investigated by static and dynamic light scattering methods in a selective solvent for HPI and HPB (decane) and in a selective solvent for PS (1,4-dioxane). In decane at room temperature, the diblock forms micelles with the hydrodynamic radius, $R_h = 42$ nm, core radius, $R_c(\mathrm{PS}) = 13.8$ nm, and $M_w = 8.7 \times 10^6$ g/mol and in 1,4-dioxane with $R_h = 32$ nm, $R_c(\mathrm{HPI}) = 21.3$ nm, and $M_w = 2.6 \times 10^7$ g/mol.[17] The micelles are, after thermal treatment (for details see, e.g., refs 18 and 19), stable at temperatures up to 100 °C, and the cmc is below 1×10^{-6} g/mL.[18,19] The triblock copolymer in decane is already below the cmc (molecularly dissolved) at $c = 1 \times 10^{-3}$ g/mL, in accord with results in *n*-heptane solutions.[20] In 1,4-dioxane at room temperature, the triblock forms micelles with $R_h = 19.7$ nm, $R_c(\mathrm{HPB}) = 12.5$ nm, and $M_w = 4.8 \times 10^6$ g/mol.[21] Apart from that HPI and HPB blocks are slightly incompatible,[22] comicellization was observed for solutions of copolymer mixtures in both solvents under study in a broad range of mixing ratios.

Experimental Section

Copolymers. The triblock copolymer, polystyrene-*block*-poly(hydrogenated butadiene)-*block*-polystyrene, PS−HPB−PS (Shell product, Kraton G-1650), was fractionated, and the middle fraction, 15 wt % of the raw sample, was used in the study. The mass-average molar mass of the sample was $M_w = 7.0 \times 10^4$ g mol^{-1}, polydispersity $M_w/M_n = 1.05$, and weight fraction of styrene $w_{PS} = 0.28$.[21]

The diblock copolymer, polystyrene-*block*-hydrogenated polyisoprene, PS−HPI (also Shell product, Kraton G-1701), had $M_w = 1.05 \times 10^5$ g mol^{-1} and $w_{PS} = 0.34$.[17,18]

Preparation of Solutions. The solutions were prepared by dissolving the copolymers in a particular selective solvent and 1 h heating above the critical micellar temperature of the copolymers (110 °C) in sealed ampules. After cooling to temperature of measurement, the measurements were started only when the scattering intensity monitored at the scattering angle $\theta = 30°$ was reliably stabilized. A sample measured at room temperature was equilibrated at 25 °C for several months. After the time, no changes of particle parameters were found in a week interval. For most of the experiments, dilute solutions with $c = 1$ mg/mL have been used. The concentration was selected to allow a sufficiently accurate measurement at all mixture compositions.

Light Scattering Methods. Solution properties of copolymer in solutions were characterized by static and dynamic light scattering methods. Both the static and dynamic light scattering were simultaneously measured with an ALV goniometer in vertically polarized light at wavelength $\lambda_0 = 532$ nm in angular range $\theta = 30°-150°$.

(a) Static Light Scattering (SLS). For static light scattering measurements, the apparatus was calibrated with toluene at $\theta = 90°$. The processed data are represented (unless otherwise noted) as

$$Kc_t/R(\theta,c_t) = (M_w P(\theta))^{-1} + 2A_2 c_t \tag{1}$$

where M_w is the weight-average molecular weight, K is the optical constant which includes the square of the refractive index increment dn/dc, $R(\theta)$ is the Rayleigh ratio, proportional to the intensity of light scattered from solutions, A_2 is the second virial coefficient, and c_t is the total copolymer concentration in g mL^{-1}. $P(\theta)$ is the particle scattering function. A model of solid spheres in the Rayleigh approximation was used to obtain zero-angle limits of $R(\theta,c_t)/Kc_t = M_w^a$.

The refractive index increments, ν, for the copolymers mixtures were calculated as a weight-average of ν values for participating copolymers in a particular solvent: $\nu_1 = 0.120$ (546 nm) and 0.096 (546 nm) for copolymers PS−HPI in decane[19] and 1,4-dioxane, respectively. $\nu_2 = 0.118$ (546 nm) and 0.092 (546 nm) for copolymers PS−HPB−PS in decane and 1,4-dioxane,[21] respectively. The refractive index increments of PS−HPI in 1,4-dioxane and PS−HPB−PS in decane were measured with a Brice-Phoenix differential refractometer.

(b) Dynamic Light Scattering (DLS). Polarized DLS measurements were measured with an ALV 5000, multibit, multitau autocorrelator covering approximately 10 decades in the delay time τ. The correlation functions were analyzed with the REPES program,[23,24] which targets the inverse Laplace transformation

$$g^{(1)}(t) = \int A(\tau)\exp(-t/\tau)\,\mathrm{d}\tau \tag{2}$$

where $g^{(1)}(t)$ is the field correlation function. The REPES program is similar to the widely used program CONTIN,[25] except that REPES actually inverts the measured intensity correlation function $g^{(2)}(t) = 1 + C|g^{(1)}(t)|^2$, where C is an instrumental constant. Since a scattered light intensity distribution, $A(\tau)$, of decay times, τ, is expected for mixed micelles, the correlation functions were also fitted assumming the Pearson distribution of characteristic relaxation times, τ:[24]

$$z(\tau) = \tau_0^{\,p}\,\tau^{-p-1}\exp(-\tau/\tau_0)/\Gamma(p) \tag{3}$$

where τ_0 and p are parameters and $\Gamma(p)$ is the Gamma function of parameter p. The Pearson distribution was chosen for the simplicity of its mathematical treatment modeling of $A(\tau)$ as a generalized exponential function (GEX).[23]

The apparent hydrodynamic radius, R_h^a, was calculated from the diffusion coefficient, $D^a(\theta)$, using the Stokes−Einstein equation:

$$R_h^{\,a} = kT/6\pi\eta D^a \tag{4}$$

where k is the Boltzmann constant, T is absolute temperature, and η is the viscosity of solvents at temperature of measurement which were taken from literature.[26] The zero-angle limit of $D^a(\theta)$ was used for estimation of particle parameters (unless otherwise stated).

Results and Discussion

Comicellization in Decane. The first step of investigation concentrated on behavior of the two block copolymers in decane. Micelles have been formed through aggregation of PS blocks only in the case of PS−HPI. Micelles were formed at all temperatures up to 104 °C. Characteristics of micelles at 25 °C and $c = 1 \times 10^{-3}$ g/mL were the following: $M_w^a = 4.8 \times 10^6$, hydrody-

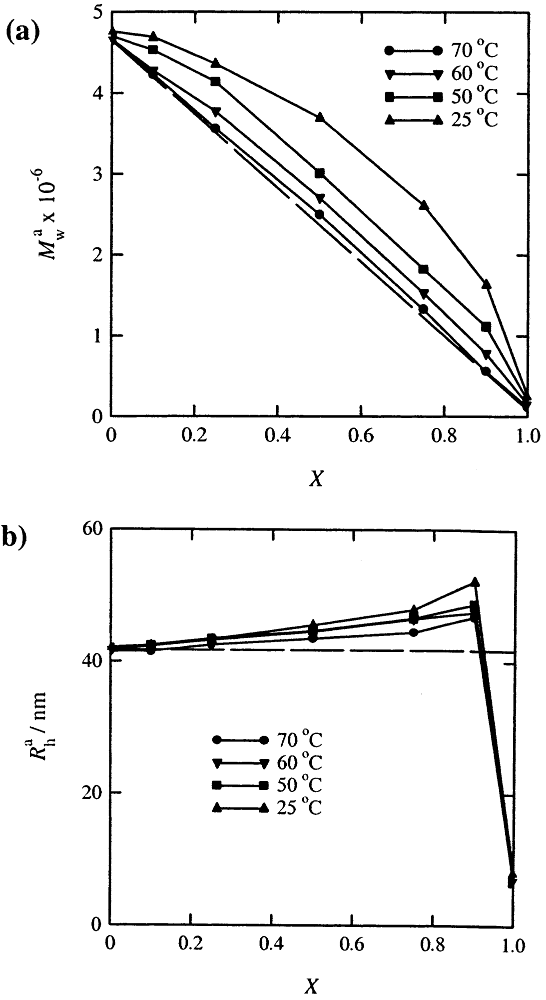

Figure 1. (a) M_w^a of micelles in decane plotted as a function of the weight ratio of PS−HPB−PS triblock copolymer, X, at indicated temperatures. (b) R_h^a of micelles in decane plotted as a function of the weight ratio of PS−HPB−PS triblock copolymer, X, at indicated temperatures.

namic radius $R_h^a = 42$ nm. Micellar parameters were stable for several months and independent of temperature up to 100 °C. The apparent molecular weight of micelles is close to the published value for the same concentration.[17] The PS−HPB−PS copolymer was molecularly soluble at all temperatures above room temperature. The hydrodynamic radius of diblock copolymer molecules was $R_h^a = 6.8$ nm at 25 °C.

Formation of mixed micelles was observed in a wide range of mixing ratios, X. The apparent molecular weight, M_w^a, and the hydrodynamic radius, R_h^a, of the micelles are plotted as a function of the weight fraction of the PS−HPB−PS copolymer, X, in parts a and b of Figure 1, respectively. As long as the PS−HPI copolymer micelles and PS−HPB−PS copolymer molecules were hypothetically noninteracting species, the M_w^a obtained from SLS should be the weight-average of molecular weights of both the scattering species. Then, the X dependence of such M_w^a should be a line connecting M_w^a of micelles with M_w^a of the triblock copolymer (dashed line in Figure 1a). Since PS−HPI micelles are dominant in the light scattering at least for low X values, R_h^a should be independent of X (dashed line in Figure 1b). It can be seen in Figure 1a that M_w^a of micelles deviates from the linear dependence. The deviation decreased with increasing temperature, being very close to the linear dependence for temperature 70 °C. R_h^a of micelles increases with increasing proportion of PS−HPB−PS copolymer in solution, X, up to the weight ratio $X = 0.9$, being more pronounced for the room temperature data. Small PS−HPB−PS molecules ($R_h^a \approx 6.8$ nm) can be distinguished by dynamic light scattering experiments in solutions at $X = 0.9$ (see Figure 2). The fraction of scattering intensity of PS−HPB−PS copolymer molecules relative to the total scattering intensity is very low, being practically negligible at room temperature and increases up to 0.1 at 70 °C. No trace of PS−HPB−PS copolymer was found by DLS at $X \leq 0.75$. Thus, the observed particle sizes are predominantly related to mixed micelles of both the copolymers, at least up to $X = 0.75$. An increase in R_h^a below $X = 0.9$ is probably due to solubilization of PS−HPB−PS molecules in micelles of the PS−HPI copolymer (comicellization). In contrast to mixtures of two chemically identical diblock polystyrene-*block*-poly(methyl methacrylate) (PS−PMMA) copolymers strongly differing in molecular weight, the comicellization effect is not so pronounced; this is due to the solution behavior of the triblock in a poor solvent for PS. Triblock chains must form loops to keep both the PS blocks in the same comicellar core, which is an energy-consuming process. Moreover, the incompatibility of HPI and HPB blocks in the micellar shell could also play a nonnegligible role.

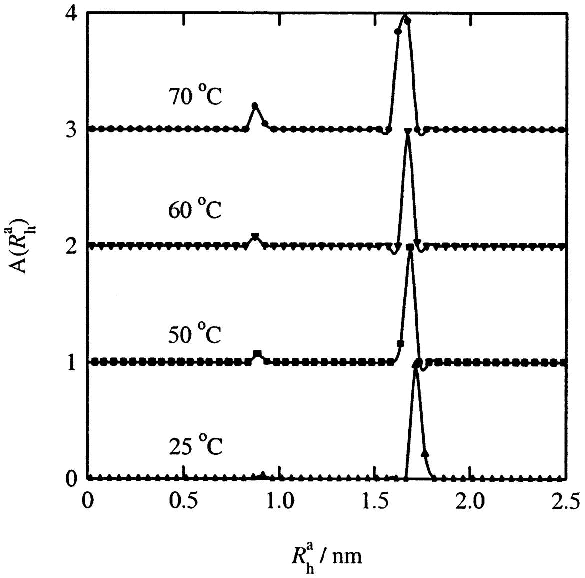

Figure 2. R_h^a distribution of particles observed at $X = 0.9$ and at indicated temperatures. Calculated from time correlation functions measured at $\theta = 90°$.

Since the changes of M_w^a due to comicellization of the copolymers are not very pronounced, we can assume that a reservoir of diblock micelles is available in mixed solutions and that the driving force of comicellization of the triblock copolymer is weak. Then, one can treat the micelles as a separate phase and write rate of comicellization = $k_c c_2(1 - f_c)$ and rate of decomicellization = $k_{dc} f_c$, where f_c represents the fraction extent of comicellization which is directly proportional to the weight of PS−HPB−PS copolymer in a mixed micelle, ΔM_w^{tr}, k_c, and k_{dc} are the corresponding rate constants, and c_2 is the concentration of free PS−PHB−PS molecules in solution. Under equilibrium conditions

$$f_c = bc_2^e/(1 + bc_2^e) \quad (5)$$

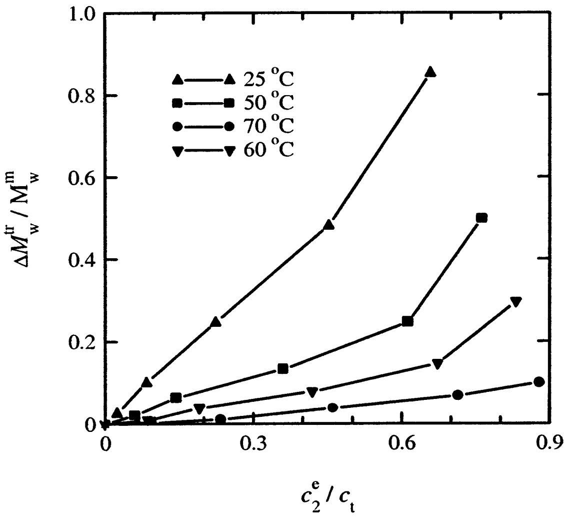

Figure 3. Increase in the molecular weight of micelles of the PS−HPI diblock copolymer due to comicellization with the PS−HPB−PS triblock copolymer, ΔM_w^{tr}, plotted as a function of the equilibrium weight concentration of PS−HPB−PS, c_2^e, at indicated temperatures; M_w^m is the molecular weight of micelles of the neat diblock copolymers.

where $b = k_c/k_{dc}$ is the temperature-dependent coefficient and c_2^e is the equilibrium weight concentration of PS−HPB−PS in solution.

Under the assumption of a low extent of comicellization ($bc_2^e \ll 1$), relation 5 can be simplified:

$$\Delta M_w^{tr}/M_w^m = b'(c_2^e/c_t) \qquad (6)$$

where M_w^m is the weight-average molecular weight of micelles of neat PS−HPI copolymer at $X = 0$.

ΔM_w^{tb} and c_2^e values are not directly accessible from the light scattering experiments but they can be estimated from M_w^a values under the assumption that the number concentration of micelles in mixed solutions is proportional to dilution with the triblock copolymer, 1-X. The assumption is valid at least at low values of c_2^e, where the extent of comicellization is low. The calculation procedure is described in the Appendix. The calculated values of $\Delta M_w^{tb}/M_w^m$ are plotted as a function of c_2^e in Figure 3.

The found linear c_2^e dependences of $\Delta M_w^{tr}/M_w^m$ at small c_2^e values and at all temperatures of measurement were in accord with expectations. The higher temperature of measurement, the broader is the range of c_2^e where the dependence is linear. The failure of the calculation procedure manifests itself in positive deviations from the linear dependence observed at high values of c_2^e. The values of equilibrium constant, b', estimated from slopes of linear parts in Figure 3 are plotted as a function of temperature of measurement in Figure 4. b' decreases with increasing temperature, asymptotically approaching zero. Comicellization at 80 °C is practically negligible, amounting to the experimental limit of SLS measurements. This temperature can be understood as a critical temperature of comicellization. Above this temperature, comicellization is not observable by light scattering methods. The critical temperature of comicellization is lower than the critical micellar temperature, cmt, of PS−HPI copolymer, which is about 104 °C.[18]

Comicellization in 1,4-Dioxane. Comicellization was also observed in a mixture of two copolymer micelles of di- and triblock copolymers in 1,4-dioxane. The apparent molecular weight, M_w^a, and hydrodynamic radius, R_h^a, of the micelles are plotted as a function of the weight fraction of the PS−HPB−PS copolymer X in parts a and b of Figure 5, respectively. While values M_w^a and R_h^a of PS−HPI micelles ($X = 0$) are independent of temperature, a small M_w^a decrease of PS−HPB−PS micelles ($X = 1$) was observed on heating. The dashed line in Figure 5a again corresponds to M_w^a of hypothetical noninteracting micelles in solution. Contrary to previous results in decane, the temperature effect is small and practically negligible in the investigated range. It can be seen in Figure 5a that M_w^a of micelles deviates from the linear dependence. The positive deviations from linear dependence were found at $X < 0.5$ and negative deviation at $X \geq 0.5$. The intensive comicellization was also found for $X \geq 0.75$. Such a behavior is rather surprising since it is hard to imagine how long HPI chains of the diblock can be built into a smaller core of short HPB blocks of the triblock copolymer. The answer to the question provides Figure 5b. While R_h^a follows changes of M_w^a at small values of X, a strong increase in R_h^a with decreasing X is observed at high values of X in the region, where M_w^a changes only slightly. This means that incorporation of large PS−HPI molecules into small micelles of PS−HPB−PS copolymers results in an extensive swelling of micelles, including probably also effective swelling of cores. It was also found that any bimodal distribution of hydrodynamic radii could not be distinguished by dynamic light scattering experiments at all X values including $X = 0.5$, where such a situation could be expected and could also be well detectable by DLS. Thus, only mixed micelles were detected by light scattering experiments.

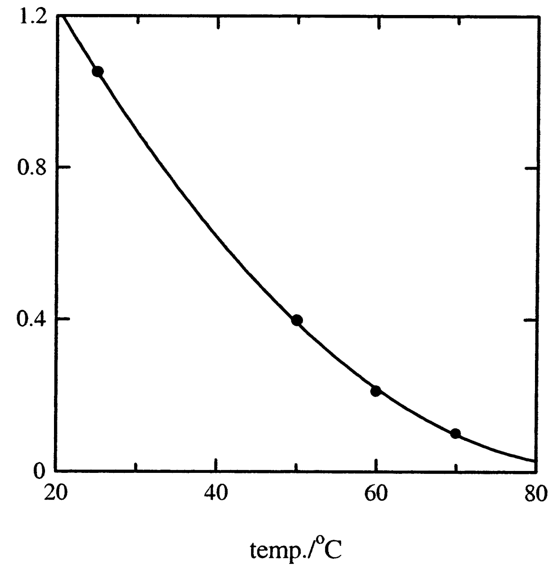

Figure 4. Initial slope, b', of $\Delta M_w^{ad}(X)/M_{wm}$ functions in Figure 3 plotted as a function of temperature.

Conclusions

Comicellization of a diblock block copolymer, PS−HPI, and triblock copolymer, PS−HPB−PS, in selective solvents (decane and 1,4-dioxane) was investigated by static and dynamic light scattering methods at 25−70 °C. Decane is a selective solvent for HPI and HPB blocks and 1,4-dioxane for PS blocks. HPI and HPB blocks are incompatible. Only the diblock copolymer formed micelles in decane while triblock was molecularly dissolved

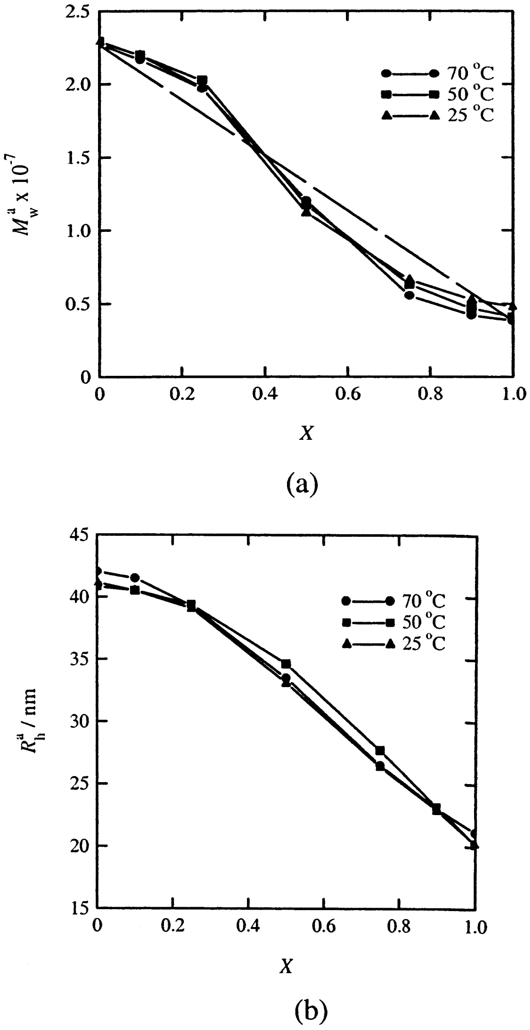

Figure 5. (a) M_w^a of micelles in 1,4-dioxane plotted as a function of the weight ratio of the PS−HPB−PS triblock copolymer, X, at indicated temperatures. (b) R_h^a of micelles in 1,4-dioxane plotted as a function of the weight ratio of the PS−HPB−PS triblock copolymer, X, at indicated temperatures.

at low concentrations and the measurement temperatures. Both the copolymers formed micelles of different sizes in 1,4-dioxane solutions.

Comicellization was observed in both solutions of copolymer mixtures at all weight ratios of PS−HPB−PS, X. In contrast to mixtures of chemically identical diblocks with different molecular parameters of the constituent blocks in selective solvents, smaller changes of micellar parameters resulting from comicellization were found in the mixtures under study, which is due to different constitution of the copolymers and their partial incompatibility.

The X dependence of the molecular weight and size of comicelles in decane could be described by adsorption of PS−HPB−PS copolymers on the diblock PS−HPI micelles at low values of X. The critical temperature of comicellization was determined by analysis of results. Above this temperature, no adsorption of PS−HPB−PS molecules takes place, and consequently, comicellization is impossible. This critical temperature of comicellization is lower than the critical micellar temperature, cmt, of PS−HPI copolymer, which is ca. 104 °C.

Incorporation of large PS−HPI copolymers into small micelles of PS−HPB−PS copolymer observed in 1,4-dioxane solutions with an excess of PS−HPI results in an extensive swelling of micelles including probably also an effective swelling of cores. It was also found that a bimodal distribution of hydrodynamic radii cannot be distinguished by dynamic light scattering experiments at all X values, including $X = 0.5$, where such a situation could be expected. Thus, only mixed micelles were detected by light scattering experiments.

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Appendix

Calculation of the Amount of Adsorbed PS−HPB−PS Copolymer on Micelles of PS−HPI Micelles. The apparent molecular weight, M_w^a, was calculated by

$$R(0) = Kc_tM_w^a \tag{A1}$$

where $c_t(X) = c_1(X) + c_2(X)$, $c_1(X) = c_t(1 - X)$ is a concentration of PS−HPB copolymer, $c_2(X) = c_tX$ is the concentration of PS−HPB−PS copolymer, and K is optical constant (see Static Light Scattering).

The comicellization of PS−HPI copolymer micelles with PS−HPB−PS molecules causes changes in K, c_1, c_2, and the molecular weight of micelles. If we assume that the major amount of PS−HPI copolymer is incorporated into micelles

$$R(0) = K_1^{cm}c_1^{cm}M_w^{cm} + K_2c_2^eM_{w2} \tag{A2}$$

where M_{w2} is the molecular weight of PS−HPB−PS copolymer, M_w^{cm} is the molecular weight of comicelles, and K_1^{cm} and K_2 are opptical constants of comicelles and PS−HPB−PS copolymer, respectively.

$$M_w^{cm} = M_w^m[1 + (\Delta M_w^{tr}/M_w^m)] \tag{A3}$$

$$c_1^{cm} = c_t(1 - X)[1 + (\Delta M_w^{tr}/M_w^m)] \tag{A4}$$

$$c_2^e = c_t - c_1^{cm} \tag{A5}$$

$$K_1^{cm} = K_1(\nu_1^{cm}/\nu_1)^2 \tag{A6}$$

$$\nu_1^{cm} = (M_w^m\,\nu_1 + \Delta M_w^{tr}\,\nu_2)/M_w^{cm} \tag{A7}$$

where ν_1 and ν_2 are refractive index increments of PS−HPB and PS−HPB−PS copolymers, respectively, ΔM_w^{tr} is the amount of PS−HPB−PS copolymer contained in a comicelle, and K_1 is the optical constant of PS−HPB copolymer.

Because the differences between the refractive index increments of the copolymers in decane are small, $\Delta M_w^{tr}/M_w^m$ can be calculated neglecting them. From that it follows

$$\left(1 + \frac{\Delta M_w^{tr}}{M_w^m}\right)^2 - \frac{M_{w2}}{M_w^m}\left(1 + \frac{\Delta M_w^{tr}}{M_w^m}\right) - \frac{M_w^a - M_{w2}}{M_w^m(1 - X)} = 0 \tag{A8}$$

The correct value of $\Delta M_w^{tr}/M_w^m$ can be obtained by solving the quadratic equation (A8) with the variable $z = [1 + (\Delta M_w^{tr}/M_w^m)]$.

The equilibrium concentration of free PS−HPB−PS molecules in solution calculated from (A5) is

$$c_2^e = c_t\left[X - (1 - X)\frac{\Delta M_w^{tr}}{M_w^m}\right] \tag{A9}$$

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