Notes

Comicellization of Chemically Identical Diblock Copolymers with Different Molecular Parameters of the Constituent Blocks in a Selective Solvent

Čestmír Koňák*,† and Martin Helmstedt‡

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic, and Fakultät für Physik und Geowissenschaften, Universität Leipzig, Linnéstrasse 5, D-04103 Leipzig, Germany

Received March 7, 2001

Introduction

Formation of multicomponent nanoparticles by self-assembly of different macromolecules and/or copolymers is a very topical problem, particularly for development of drug delivery systems,[1] detergents, paints, cosmetics, oil recovery, etc.[2] On the other hand, selective interactions and self-organization of synthetic macromolecules are frequently used in the materials science to improve and modify properties of polymeric materials.[3−5] Binary blends of block copolymers offer a unique opportunity to produce a new class of polymeric materials having high flexibility in the choice of constituent components.[6]

Only a relatively small number of experimental studies were devoted to mixtures of two block copolymers in solutions.[7−10] Several theoretical studies concerning polymer solutions containing two sorts of diblock copolymers have also appeared.[11−14] Copolymer mixtures of block copolymers in solutions were studied by centrifugation,[7,8] transmission electron microscopy,[9] and static and dynamic light scattering methods.[10] In the last paper,[10] mixtures of two poly(α-methylstyrene-*block*-4-vinylphenethyl alcohol)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 has been 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., $T < T_1$. As for the theory, the formation of mixed micelles has been considered for the case where the insoluble blocks are identical, and the soluble blocks have the same length but are different in chemical nature.[11] In ref 12, 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 different length were investigated. In ref 13, two different diblock copolymers having the same chemical nature but different composition were analyzed. If the asymmetries in the sizes of the blocks of the two copolymers are not too large, the short copolymers are incorporated continuously in the large copolymer micelles and only mixed micelles are stable. If the asymmetries are large, mixed micelles and large copolymer micelles can coexist. In recent theory,[14] the micellization and comicellization in dilute solution mixtures of two chemically identical diblock copolymers with very long soluble blocks and insoluble blocks differing in length were analyzed. The conditions for the formation of pure micelles and comicelles were determined. Five different regimes were found.

In this work, solution properties of two chemically identical block copolymers in a selective solvent are presented. As a model system, mixtures of polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) copolymers differing in molecular weights and block lengths were investigated in mixed solvents *p*-cymene and toluene (a selective solvent for PS blocks). The light scattering methods were used for characterization of copolymer solutions.

Experimental Section

Block copolymers PS-*b*-PMMA were purchased from Polymer Source and Polysciences. The molecular weights of the constituent blocks of copolymers were the following: copolymer **1**−PS, 29 200; PMMA, 285 100; copolymer **2**−PS, 9100; PMMA, 7800. The copolymers were selected to have very different insoluble PMMA blocks. Mixed solvents of *p*-cymene and toluene (65 wt % *p*-cymene and 35 wt % toluene) were used as selective solvents for PS blocks.[15] Toluene is a thermodynamically good solvent for both the blocks while *p*-cymene is a good solvent for PS blocks[15] and Θ-solvent for PMMA blocks with Θ-temperature of 159.7 °C.[16]

Solutions were prepared by dissolving both copolymers in the selective solvent and heating for 1 h to 100 °C (above the critical micellar temperature of copolymers used) in sealed ampules. Since there were small changes of solution characteristics in the first hours after cooling from 100 °C to measurement temperature (30 °C), the measurements were made after 24 h but not later than after 48 h. For most of the experiments, dilute solutions with $c = 0.01$ g/mL have been used. The concentration was selected to allow a sufficiently accurate measurement at all mixture compositions.

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 $\theta = 30{-}150°$ and at 30 °C.

For the static light scattering experiments, the apparatus was calibrated with benzene at $\theta = 90°$. The processed data are represented by $R(0,c)/Kc$, where K is the optical constant which includes the square of the refractive index increment dn/dc, $R(\theta,c)$ is the Rayleigh ratio, proportional to the intensity of the light scattered from solutions, and c is the total copolymer concentration in g/mL. A model of solid spheres in the Rayleigh approximation was used to obtain zero-angle limits of $R(\theta,c)/Kc$.

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† Academy of Sciences of the Czech Republic.

‡ Universität Leipzig.

* Corresponding author. e-mail: konak@imc.cas.cz.

10.1021/ma010411f CCC: $20.00

The refractive index increments, d*n*/d*c*, for the copolymers were calculated as linear combinations of d*n*/d*c* values for participating blocks: $dn/dc = 0.0185$ and 0.063 for copolymers **1** and **2**, respectively. The refractive index increments for PS and PMMA in *p*-cymene and toluene were taken from the literarture.[15,16]

Polarized DLS measurements were made with an ALV 5000, multibit, multitau autocorrelator covering approximately 10 decades in the delay time τ. The correlation functions were analyzed with the program REPES,[17,18] to determine the inverse Laplace transformation of the electric field correlation function, $g^{(1)}(t)$. The program REPES is similar to the widely used program CONTIN,[19] 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 analyzed by modeling $A(\tau)$ as a generalized exponential function (GEX).[18]

The apparent average hydrodynamic radius, R_h^a, was calculated from the diffusion coefficient, $D^a(\theta)$, using the Stokes–Einstein relationship. Viscosity of the mixed selective solvent used (65 wt % *p*-cymene and 35 wt % toluene) at 30 °C was determined with a capillary viscometer ($\eta = 0.662$ mPa s). The zero-angle limit of $D^a(\theta)$ was used for estimation of particle parameters (unless otherwise stated).

Results and Discussion

The first step of investigation was concentrated on behavior of the two block copolymers (**1** and **2**) in a mixed selective solvent containing 65 wt % *p*-cymene and 35 wt % toluene. The solvent composition was selected according to the experimental results of Kotaka et al.[15] Micelles have been formed through aggregation of PMMA blocks only in the case of copolymer **1**. Micelles started to form around 55 °C under cooling at a rate of 2 °C/20 min. Characteristics of the copolymer **1** micelles at 30 °C were the following: $M_w^a = 4.6 \times 10^7$, radius of gyration $R_g = 36$ nm, $R_h^a = 47$ nm, and association number $N_a = 150$. Micellar parameters were stable for several months and practically insensitive to dilution down to $c = 1 \times 10^{-4}$ g/mL. The symmetrical copolymer **2** was molecularly soluble at all temperatures above the room temperature. Since a tendency to slow aggregation (association) was observed at room temperature (20–22 °C), the measurements were performed at 30 °C where the effect of aggregation was not detectable after 2 weeks. The hydrodynamic radius of copolymer **2** molecules was $R_h^a = 3.6$ nm at 30 °C.

Formation of micelles was observed in a wide range of mixing ratios. The hydrodynamic radius, R_h^a, and $R(0,c)/Kc$ of the micelles, as determined by light scattering methods, are plotted in Figure 1a,b as a function of the weight ratio of copolymer **2**, X. It can be seen in Figure 1 that both the R_h^a and $R(0,c)/Kc$ of micelles increases with increasing proportion of low-molecular-weight copolymer in solution, X, up to the critical weight ratio, X_c, about 0.95. Above X_c, the values of both the parameters sharply decrease, and small copolymer **2** molecules ($R_h^a \approx 3.5$ nm) can be distinguished by dynamic light scattering experiments in solutions. Fractions of scattering intensity of copolymer **2** molecules relative to the total scattering intensity were very low, of the order of 0.01. In the case of a hypothetical independent micellization, R_h^a of micelles should be independent of X and $R(0,c)/Kc$ should decrease with increasing X. An increase of both R_h^a and $R(0,c)/Kc$ below X_c is probably due to solubilization of low-molecular-weight copolymer **2** in micelles of copolymer **1** (comicellization). Thus, copolymer **2** molecules can be preferentially bound in micelles instead of being molecularly dissolved. This conclusion is in agreement with the experimental results published by Honda et al.[10] In the temperature region where only long chain copolymers form micelles while short chain copolymers alone are nonaggregating, comicellization was also observed. Since block copolymers with only slightly different block lengths were used for the experiment, only minor changes of micellar parameters were found. The apparent molecular weight of mixed micelles was larger than that calculated for independent micellization while hydrodynamic radius was influenced only slightly. An analogous situation was also discussed in the recent theory of Borovinskii et al.[14] (regime III). According to the results, copolymers with short blocks should be incorporated into the large copolymer micelles at concentrations below critical micellar concentration (or temperature) for these copolymers. The calculated distribution function exhibits two maxima corresponding to the existence of comicelles and unimers of copolymers with short blocks. Copolymers with long chains do not form "pure" micelles, but all of them should be incorporated into the comicelles in this regime. Unfortunately, the assumption of very long soluble blocks is not fulfilled in our experiments; therefore, the theory can be applied only qualitatively.

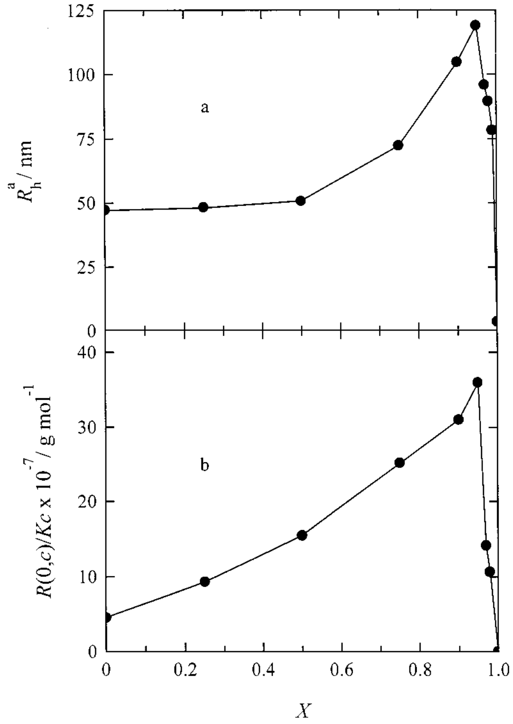

Figure 1. R_h^a(a) and $R(0,c)/Kc$ (b) plotted as a function of the weight ratio of copolymer **2**, X.

Above X_c, where concentration of copolymer **1** is more than 20 times smaller than those of copolymer **2**, mixed micelles are partly decomposed, and a mixture of micelles and small copolymer **2** molecules was observed. We suppose that micelles are approaching their cmc with increasing X (decreasing their concentration). In terms of the theory,[14] the copolymer system is approaching the boundary between regime III and regime I. In regime I, both the copolymers should be molecularly dissolved. Honda et al.[10] also found that, in solutions with high contents of the short nonaggregating copolymer, there remains a great amount of the free

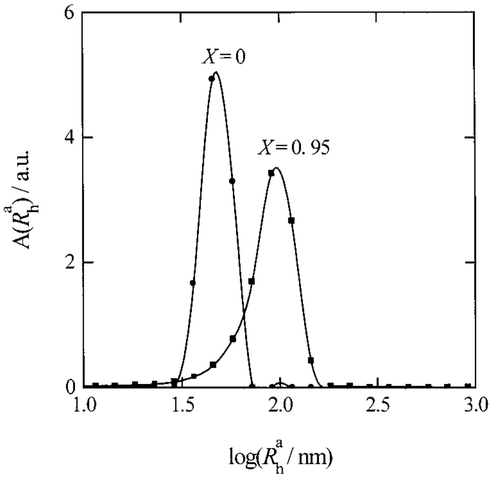

Figure 2. R_h^a distribution of micelles observed at $X = 0$ (single copolymer **1** micelles) and $X_c = 0.95$ (mixed micelles) as indicated. Calculated from time correlation functions measured at $\theta = 90°$.

short-chain copolymer which is not involved in any micelles. The mixed micelles are less stable than "pure" copolymer **1** micelles that are still outliving at concentration of 1×10^{-4} g/mL.

The R_h^a distribution of micelles also changes when approaching X_c. While sharp distributions were observed at $X = 0$ (copolymer **1** micelles), a broad distribution with tailing at smaller R_h^a values was observed at $X_c = 0.95$ (see Figure 2). The tailing evidences a starting decomposition of mixed micelles at X_c which is continues at $X > X_c$ (cf. Figure 1). Analyzing DLS data cannot reliably prove the coexistence of two kinds of micelles at X_c.

Conclusions

Solution properties of mixtures of two polystyrene-*block*-poly(methyl methacrylate) copolymers differing in molecular weights and block lengths were investigated in a selective solvent for PS blocks (65 wt % *p*-cymene and 35 wt % toluene) by light scattering methods. Comicellization was observed in copolymer mixtures below the critical weight ratio of copolymer **2**, X_c (≈ 0.95), and a partly decomposition of mixed micelles above X_c. The hydrodynamic radius of mixed micelles varied from 47 nm at $X = 0$ to 119 nm at X_c.

Acknowledgment. Č.K. acknowledges financial support of the Alexander von Humboldt Foundation, the Grant Agency of the Academy of Sciences (A4050902), and the Grant Agency of the Czech Republic (No. 203/99/0573). M.H. thanks the Deutsche Forschungsgemeinschaft (SFB 294) for financial support.

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MA010411F