Macromolecules **1998,** *31,* 4873−4878

Redistribution of Block Copolymer Chains between Mixed Micelles in Solution

F. J. Esselink, E. E. Dormidontova, and G. Hadziioannou*

Laboratory of Polymer Chemistry and Materials Science Centre, Chemistry Department, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Received February 10, 1998; Revised Manuscript Received May 26, 1998

ABSTRACT: The evolution of polymolecular micelles formed by two different poly(2-vinylpyridine)−polystyrene (PVP−PS) block copolymers dissolved in toluene is studied by means of transmission electron microscopy (TEM). The two PVP−PS diblock copolymers differ in composition, namely in the length of PVP block. Upon dissolution, a rapid formation of mixed polymolecular micelles takes place. As a result, the micellar size distribution observed is rather broad already at this initial stage. Due to the presence of two different diblock copolymers, the process of micellar growth involves not only the fusion of micelles but also the chain exchange between polymolecular micelles of different composition, which may slow the equilibration process. After a considerable aging time, the block copolymers seem to reach the equilibrium state, and an almost perfect bimodal size distribution is observed. According to the theoretical analysis given, both "pure" and "mixed" micelles constitute the micellar size distribution.

Introduction

In this paper we study, both experimentally and theoretically, the behavior of a mixture consisting of two diblock copolymers differing in molecular weight for one of the blocks, in a selective solvent. Many reports exist on experimental results and modeling approaches to systems of block copolymers forming micelles in solution or melts.[1−20] Besides the investigation of "pure" diblock copolymer melts,[7] diblock copolymers are studied in blends with homopolymers[6] because of their capability to act as an emulsifier between two immiscible phases. Some experiments were devoted to investigating the behavior of diblock copolymers in the presence of solvent, which was either selective[8−11] (i.e., a good solvent for one block but a poor solvent for the other block) or nonselective.[12,13]

Only a relatively small number of studies were devoted to mixtures of block copolymers in solution.[8,14−17,19] Several theoretical studies concerning polymer solutions containing two sorts of diblock copolymers have appeared.[14,16,21] In ref 21, 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. In ref 14, the insoluble blocks have the same length but are different in chemical nature, while the soluble blocks have the same chemical nature but have a different length. In ref 16, two different diblock copolymers having the same chemical nature but different composition are analyzed. Two cases have been studied: (i) the length of the soluble blocks is much larger than that of the insoluble blocks; (ii) the length of the soluble block of one block copolymer is much larger than that of the insoluble block, while the soluble block for the other diblock copolymer is much shorter than the insoluble block.

The main objective of the present paper, however, is to study experimentally the evolution of block copolymer micelles formed by a mixture of two diblock copolymers differing in length of insoluble block but having the same molecular weight for the soluble block, as well as to analyze theoretically the equilibrium state. The micellar evolution has been studied with the help of transmission electron microscopy (TEM). The specific features of the equilibration process will be discussed and compared with those for a solution of identical block copolymer molecules. It is found that upon reaching the equilibrium, the mixture of two diblock copolymers forms an almost perfect bimodal size distribution. To analyze the equilibrium state of the system, theoretical calculations have been performed for a model system in the strong segregation limit. The theoretical predictions are compared with the experimental observations.

Experimental Section

In this study two diblock copolymers differing in composition were used. Both block copolymers consist of (deuterated) polystyrene (PS) and poly(2-vinylpyridine) (PVP) blocks. The molecular weight of the PS block was 75 000 in both cases. The PVP block had a different molecular weight for each copolymer: 102 000 or 18 000. (The block copolymers are denoted 102−75 and 18−75, respectively.) Both block copolymers were dissolved in toluene. The concentration of the solution was 1 wt %, while the weight ratio of the diblock copolymers was 1:1. Toluene is a selective solvent for the PS blocks. Micelles are readily formed because of the very unfavorable interactions between PVP and toluene and between the PVP and PS blocks.[6]

The structures formed by the diblock copolymer mixture were studied by means of transmission electron microscopy. A small droplet of the solution was placed on a copper microscopy grid. Most of the solution was then removed by blotting with filter paper. In this way it is possible to obtain a micellar layer that is thin enough to be studied in the electron microscope. To enhance the contrast between the two different blocks, a small amount of iodine was added to the solution just before it was placed on the grid. Iodine forms a pyridinium salt with the PVP blocks. In this way the electron density is locally increased and thus the contrast.

Results

Ideally, the specimen to be investigated should consist of a monomicellar layer. This result, however, can only be obtained occasionally. Due to the blotting technique

---

* To whom correspondence should be sent. E-mail: hadzii@chem.rug.nl.

S0024-9297(98)00206-X CCC: $15.00

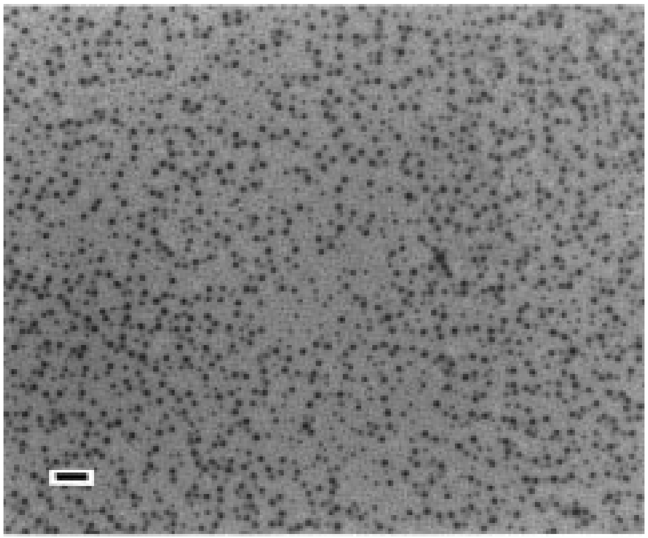

Figure 1. Electron micrograph of a mixture of two PVP–PS diblock copolymers (M_w 18k–75k and 102k–75k) after 1 h of aging. Scale bar represents 200 nm.

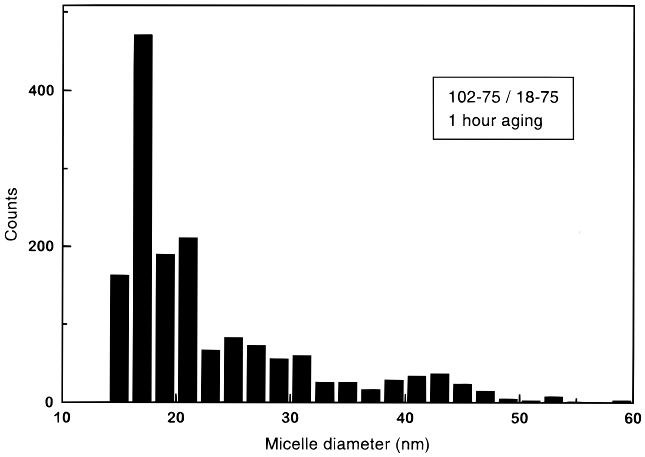

Figure 2. Histogram showing the size distribution belonging to Figure 1.

used for the preparation of a sufficiently thin specimen, it was not possible to obtain the same thickness for each specimen. Despite this experimental limitation it is possible to compare the formation and behavior of the block copolymer micelles in solution as a function of time.

Figure 1 shows an electron micrograph of a mixture of the two PVP–PS block copolymers after 1 h of aging. The polymolecular micelles are clearly visible as spheres. From this figure it is obvious that the micelles formed cover a broad range of sizes. There are small micelles having a diameter of about 15 nm, but much larger micelles having a diameter of about 45 nm are also visible. This latter size is also found in previous experiments where the behavior of the 102–75 diblock copolymer was investigated.[9,22] It is worthwhile to note that even the large polymer micelles are smaller than the equilibrium micelles in solution and much smaller than those in the melt, which indicates that dissolution does take place in the whole volume of the system. With the help of an image analysis program, it is possible to count the micelles that belong to a certain size range. Figure 2 shows a histogram of all the micelles visible in Figure 1. From this histogram it is clear that the micelles formed differ considerably in size at this initial stage.

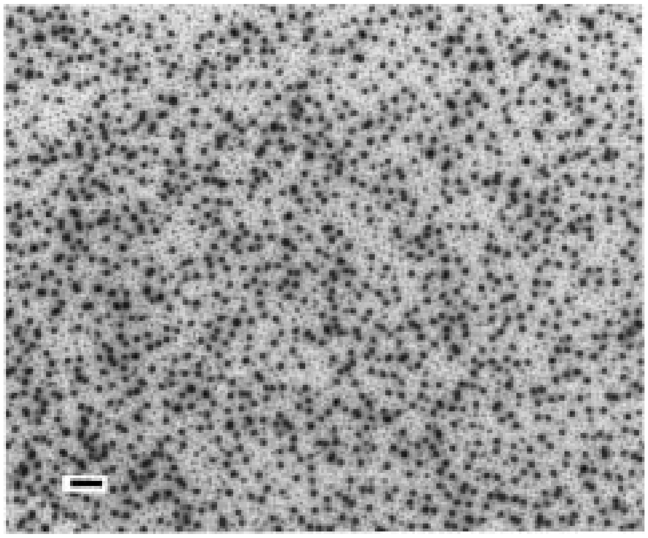

Figure 3. Electron micrograph of a mixture of two PVP–PS diblock copolymers (M_w 18k–75k and 102k–75k) after 38 days of aging. Scale bar represents 200 nm.

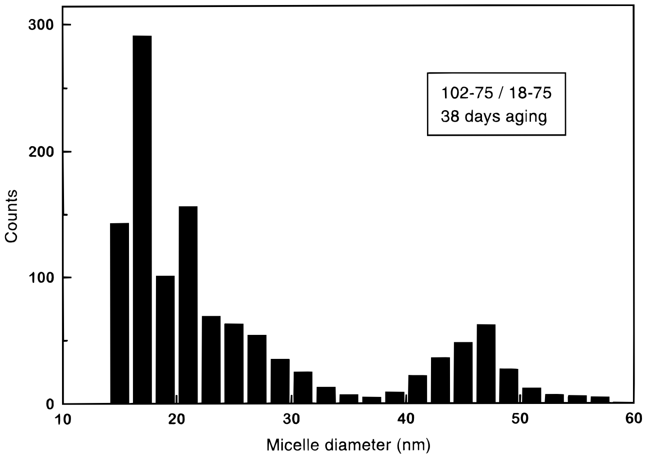

Figure 4. Histogram showing the size distribution belonging to Figure 3.

The solution used for the sample just discussed was stored in a sealed bottle at room temperature. Figures 3 and 4 show the result after 38 days of aging. A tendency of the system to decrease the variation in micellar size is observed. Two main micellar sizes can be distinguished. A comparison of Figures 2 and 4 shows that the number of micelles having a size between 30 and 40 nm has decreased slightly.

This evolution toward a smaller variation in size is even more obvious from Figures 5 and 6, where an electron micrograph and corresponding size distribution histogram of the same initial solution after aging for 4 months are shown. The comparison of Figure 5 (6) with Figures 1 and 3 (2 and 4) shows that the block copolymers in solution evolve toward two micellar populations, differing in size.

In addition, Figures 5 and 6 show that both populations move to higher values of micellar size during aging, indicating growth.

Discussion

Micellar evolution. The common scenario of micellar evolution encountered here, is similar to that occurring in a solution of identical block copolymer molecules.[20,22] As is discussed in ref 22, the equilibration process

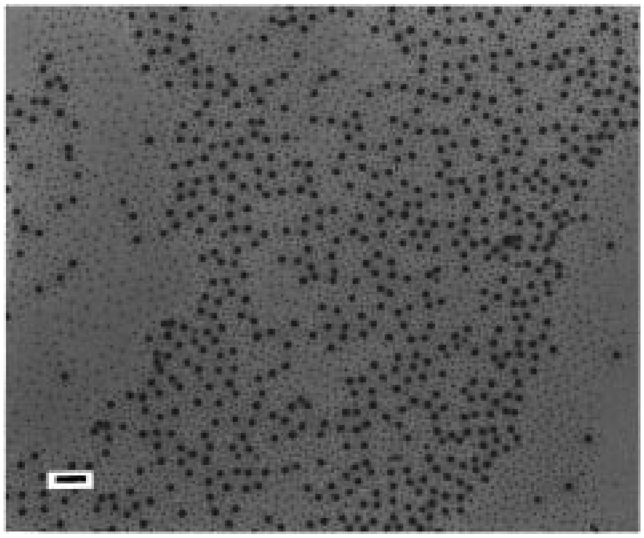

Figure 5. Electron micrograph of a mixture of two PVP−PS diblock copolymers (M_w 18k−75k and 102−75k) after 4 months of aging. Scale bar represents 200 nm.

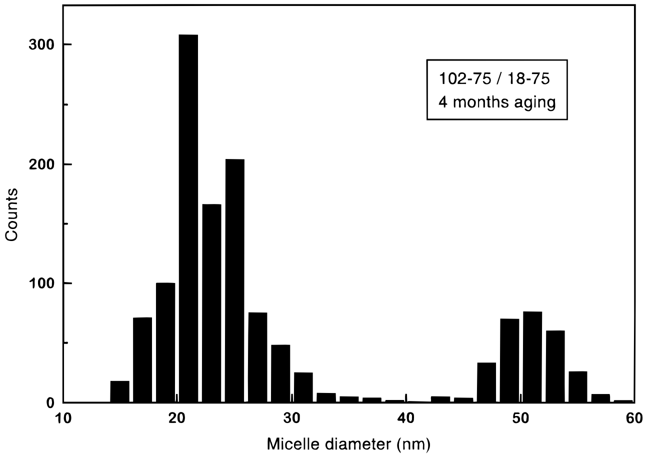

Figure 6. Histogram showing the size distribution belonging to Figure 5.

depends on many factors, such as the probability of micellar collisions, the composition and length of the block copolymer, quality of the solvent and so on. For instance, for diblock copolymers with a long (insoluble) PVP block, the final (equilibrium) micelle size is larger than that for block copolymers with a shorter PVP block. As a result, the formation of equilibrium micelles from long PVP−PS chains requires a much longer time, since for the equilibrium to be attained, a larger number of micellar collisions should occur and the energetic barrier to be overcome for micellar merging is also larger for micelles with a larger aggregation number. Thus, the comparison of two different solutions consisting of PVP−PS block copolymers of different lengths shows that for the shorter PVP−PS chains the equilibrium state can be reached faster and the final micellar size distribution is relatively narrower than that for a solution of longer block copolymers.

For the polymer solution containing both short and long PVP−PS chains, the evolution toward the equilibrium state is more complicated than for solutions containing a single component. The initial micelles emerging immediately after dissolution are formed independently of the type of chains aggregated and, hence, can have different compositions. As is seen from Figures 1 and 2, the size distribution is already broad at this initial state, while for solutions of identical block copolymers the initial size distribution observed is rather narrow.[9,22,23] The main driving force for the formation of initial micelles is to minimize unfavorable PVP−PS and PVP−toluene contacts.

Further micellar evolution (mainly through collisions) becomes more and more dependent on the micellar composition as the micellar size increases. For large micelles, the chains (in corona and core regions) will be more extended. The balance between the tendency to minimize PVP−toluene contacts on one hand and the PS-block (and PVP-block) extension on the other hand determines the equilibrium state. Let us consider small and large micelles differing in composition. A small micelle with several long PVP−PS chains will tend to transfer these chains (or exchange these for shorter ones) to the large micelle in order to decrease the core surface and, hence, to minimize unfavorable contacts. Furthermore, the transfer of short chains from large micelles with a dominant fraction of long chains is favorable, since short chains will be less extended in a smaller micelle. Moreover, the transfer of a short chain will be easier than that of a long one. Thus, in contrast to the case of a solution of identical (small or large) micelles, the rate and the result of micellar evolution in a mixed system will strongly depend on the micellar composition. For instance, a collision of a large and a small micelle, each smaller than its equilibrium size, probably will not lead to merging when the micellar compositions are very different. Chain exchange is more probable in this case. Thus, micellar collisions will probably result in merging of micelles with similar composition or in chain exchange for micelles with different compositions. Chain exchange via small micelles (unimers) transfer[19,24] can also take place, especially if only a few chains should be removed from a large micelle (or exchanged with chains of another type).

Due to chain exchange involving micelles of different sizes and compositions, the equilibration process is slowed even for micelles entirely formed by chains having short PVP blocks. The corresponding size distribution remains broad, even after a long time (Figures 4 and 6). Another reason for this is the formation of equilibrium “mixed” micelles, which will be discussed in the next section. The other result of the evolution process is the formation of large micelles containing only long chains. The corresponding peak in the size distribution plots becomes more pronounced with time and the average micellar size increases (Figures 4 and 6).

As has been suggested recently,[22] it may be that the micelles have a “soft” character when the core and the corona are separated by a broad interface consisting of both blocks. Then, the evolution toward equilibrium will proceed more easily. However, regardless of the exact structure of the micelles, it is clear that the rate of equilibration in these systems is very slow. This means also that the system described here is not necessarily in its most favorable state after the time period studied.

As a result of the micellar evolution, the equilibrium state corresponding to the minimum of the free energy is reached. The equilibrium properties of polymer micelles that are formed in the diblock copolymer mixture are analyzed theoretically in the next section by considering the free energy of micelles in solution, taking the possibility of ”mixed” micelles formation into account.

“Equilibrium” Micelles. To analyze the results obtained after aging for 4 months, theoretical considerations are given for the equilibrium state expected. To this end, the model proposed in refs 14 and 16 is applied. We will consider two kinds of diblock copolymers A−B and C−B in solution. The B-block of both diblock copolymers is identical and the polymerization index is given by N_B. In the experimentally studied case $N_B = 670$, the B-block is similar to the PS sequence. The blocks A and C are of similar nature but have different lengths, $N_A \leq N_C$. These correspond to the PVP blocks in the experimentally studied case ($N_A = 171$ and $N_C = 971$).

We will assume that three types of micelles can be formed: “pure” PVP−PS 18−75 (denoted A-micelles), “pure” PVP−PS 102−75 (denoted C-micelles) and “mixed” A/C micelles. For the sake of simplicity, only identical “mixed” micelles are considered.

The equilibrium properties of the polymolecular micelles in the solution can be defined by analyzing the free energy[16] (in units of kT):

$$F = n_A^{\mathrm{mic}}(F_A + \ln \phi_A^{\mathrm{mic}}) + n_C^{\mathrm{mic}}\,(F_C + \ln \phi_C^{\mathrm{mic}}) + n_{\mathrm{mix}}^{\mathrm{mic}}(F_{\mathrm{mix}} + \ln \phi_{\mathrm{mix}}^{\mathrm{mic}}) \quad (1)$$

where n_i^{mic} and ϕ_i^{mic} are the number and volume fractions of micelles of type i (i = A, C, mix), respectively, and F_i is the corresponding free energy of the micelles. The logarithmic terms in eq 1 represent the translational entropy of the micelles. The contribution of these terms is smaller than from the other terms, but it can be important to take them into account for the determination of the fraction of “mixed” micelles in solution.

The free energy (in units of kT) of a micelle of type i (i = A,C, mix) can be written in a standard way:[25]

$$F_i = F_{\mathrm{surf}} + F_{\mathrm{ext}} = c_1 Q_i^{2/3}(N_i v)^{2/3}\gamma + c_2 Q_i^{3/2} + c_3 Q_i^{5/3}\,N_i^{-1/3} \quad (2)$$

where γ is the surface free energy (in terms of kT) of micelles, describing the incompatibility of the PVP blocks with the solvent and PS blocks; Q_i and N_i are the aggregation numbers of the micelles and the number of monomer units of block i, respectively; c_j are numerical coefficients.

The first term in eq 2 represents the surface free energy, while the last two terms are connected with the free energy of extension of the PS or PVP blocks in the corona and core region, respectively. In solution, the extension of the PS blocks in the corona influences the properties of the micelles more than the extension of the PVP blocks in the core region[25] (that allows us to neglect the last term in the eq 2 in further considerations). This means that the equilibrium size of a micelle is determined mainly by the balance between surface free energy and the free energy of the PS block extension in the corona region.

For a “mixed” micelle the following relation between the radius of the micelle and the aggregation number takes place:

$$\frac{4\pi}{3}R_{\mathrm{mix}}^3 = (Q_{AB}^{\mathrm{mix}} N_A + Q_{CB}^{\mathrm{mix}} N_C)v = Q_{\mathrm{mix}} N_A v\left(1 + f_{CB}\left(\frac{N_C}{N_A} - 1\right)\right) \quad (3)$$

$$Q_{\mathrm{mix}} = Q_{AB}^{\mathrm{mix}} + Q_{CB}^{\mathrm{mix}}; \qquad f_{CB} \equiv \frac{Q_{CB}^{\mathrm{mix}}}{Q_{\mathrm{mix}}} \quad (4)$$

where $Q_{AB}{}^{\mathrm{mix}}$ and $Q_{CB}{}^{\mathrm{mix}}$ are the aggregation numbers of A−B (18−75) and C−B (102−75) copolymers in a “mixed” micelle, f_{CB} is the fraction of long (C−B) chains in a mixed micelle, and v is the volume per monomer unit of PVP blocks.

The free energy of a “mixed” micelle assumes the form of eq 2 (neglecting the last term) upon the replacement of Q_i by Q_{mix} and N_i by N_{mix}:

$$N_{\mathrm{mix}} = N_A\left[1 + f_{CB}\left(\frac{N_C}{N_A} - 1\right)\right] \quad (5)$$

N_{mix} can be considered as an “effective” length (number of monomer units) of an “averaged” block forming the core of a “mixed” micelle.

From eq 1 the free energy of the polymer system is seen to be a function of five variables, being the aggregation numbers of micelles Q_A, Q_B, and $Q_{\mathrm{mix},}$ the fraction of C−B chains in a “mixed” micelle f_{CB} and the volume fraction of “mixed” micelles in the solution $\phi_{\mathrm{mix}}^{\mathrm{mic}}$. Minimization of the free energy allows us to determine the equilibrium values of the variables. These calculations lead to the following expressions for micellar radii and aggregation numbers (i = A, C, mix):

$$R_i \sim (N_i v)^{3/5}\gamma^{2/5} \qquad Q_i \sim (N_i v)^{4/5}\gamma^{6/5} \quad (6)$$

As is seen from eq 6, independent of the presence or absence of “mixed” micelles, the size of “pure” micelles is expected to be the same as in a solution of only A−B (18−75) or C−B (102−75) block copolymer chains. On the basis of this theoretical prediction, the analysis of the experimental data presented in Figure 6 is attempted. The histogram of micellar size distribution contains two peaks with the average size of small and large micelles of about 22−23 and 51−52 nm, respectively. A comparison of these data with the observations made for two different solutions containing only 18−75 or only 102−75 block copolymer micelles (Figure 7a,b) shows that the peak of the histogram (Figure 6) corresponding to large micelles is probably only due to the presence of pure 102−75 micelles. The diameter of pure 102−75 micelles in the solution (Figure 7b) is about 53 nm, which is in accordance with the size observed for the 102−75/18−75 mixture (Figure 6). At the same time, the comparison of the average size for pure 18−75 micelles in solution[23] (≅17 nm, Figure 7a) with the size defined from the historgam in Figure 6 for small micelles (≅22−23 nm) indicates that the latter is definitely larger (even taking into account the range of uncertainty of the average values estimation) than the size of pure 18−75 micelles in solution. Thus, the peak of the histogram (Figure 6) for small micelles cannot evidently be explained only by the presence of pure 18−75 micelles.

It is not really clear whether the micelles are in the equilibrium state after 4 months of aging, but the

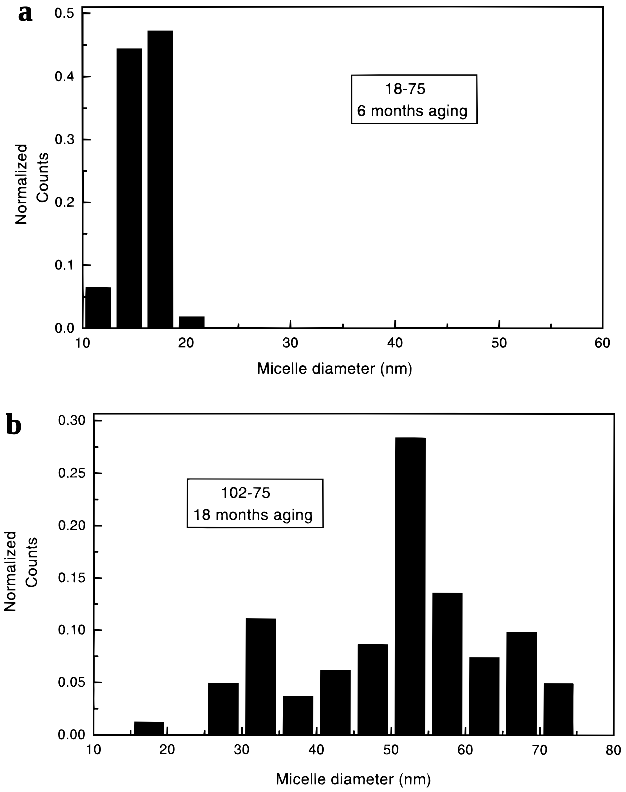

Figure 7. Normalized histogram showing the size distribution for 18–75 PVP–PS micellar solution (a) and for 102–75 PVP–PS micellar solution (b)

common tendency observed from comparison of Figures 2, 4, and 6 is the increase in the average size for the small micelles. Hence, it is possible to assume that only "mixed" micelles contribute to the histogram peak. The average size for "mixed" micelles can be estimated using eq 6. The equilibrium value of the effective length of an "averaged" block forming the core of a "mixed" micelle, N_{mix} (which determines the size of "mixed" micelles), can be evaluated from the minimization of the free energy:

$$N_{\mathrm{mix}} \cong N_{\mathrm{C}}\left[\frac{2}{5}\,\frac{1-\dfrac{N_{\mathrm{A}}}{N_{\mathrm{C}}}}{1-\left(\dfrac{N_{\mathrm{A}}}{N_{\mathrm{C}}}\right)^{2/5}}\right]^{5/3} \qquad (7)$$

In the limit where C–B chains are only a bit larger than A–B chains ($N_{\mathrm{C}} \rightarrow N_{\mathrm{A}}$), the effective length N_{mix} tends to N_{A}. If the difference in chain length between *A* and *C* blocks is large, the fraction of C–B copolymer in a "mixed" micelle f_{CB} tends to $N_{\mathrm{mix}}/N_{\mathrm{C}} \rightarrow (2/5)^{5/3}$ (≈ 0.22). The dependence of $Q_{\mathrm{CB}}{}^{\mathrm{mix}}/Q_{\mathrm{mix}}$ on the ratio $N_{\mathrm{C}}/N_{\mathrm{A}}$ is shown in Figure 8. The fraction of long chains (C–B) in a "mixed" micelle is smaller than the fraction of short chains (A–B). For the case under consideration, the fraction of long chains is given by $Q_{\mathrm{CB}}{}^{\mathrm{mix}}/Q_{\mathrm{mix}} \approx 0.39$.

The reasons why incorporation of long chains into a micelle consisting of mainly short chains is preferable for the polymer system can be made clear from the following qualitative considerations. The incorporation of a long chain (C–B) into a "small" micelle leads to a decrease in extension of the blocks of the long chain in both core and corona regions, since the aggregation number of such a "small" micelle is small. However, it results also in an increase of the core surface and thus in unfavorable contacts. Hence, the addition of long chains is possible until the increase in surface free energy reaches a certain limit. On the contrary, when a short chain (A–B) enters a "large" micelle, an additional extension of the blocks of the short chain occurs (since the radius and aggregation number of a "large" micelle is large). This makes the formation of large "mixed" micelles with participation of a few short chains unfavorable. Thus, only small "mixed" micelles consisting mainly of short chains with a small fraction of long chains are preferable.

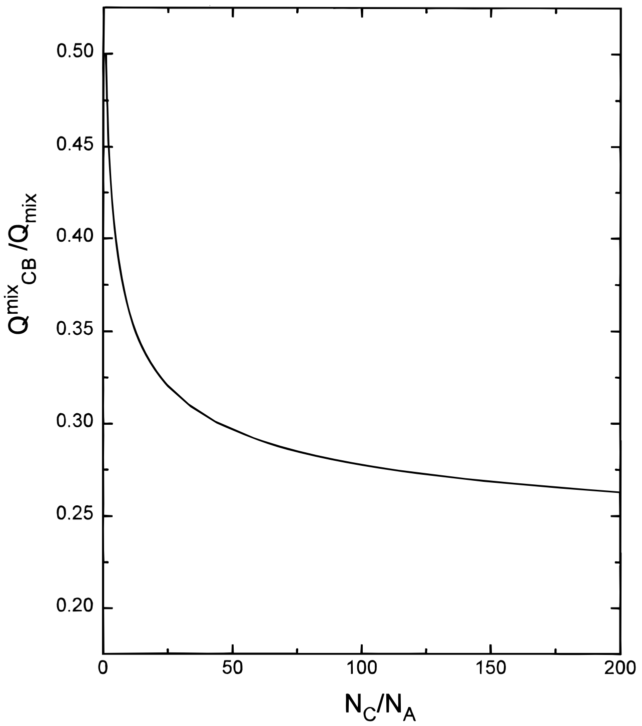

Figure 8. Fraction of long chains (C–B), $Q_{\mathrm{CB}}{}^{\mathrm{mix}}/Q_{\mathrm{mix}}$, in a "mixed" micelle as a function of the length ratio between long and short blocks ($N_{\mathrm{C}}/N_{\mathrm{A}}$).

For the experimental system under consideration the ratio $N_{\mathrm{mix}}/N_{\mathrm{C}}$ is about 0.5; thus, the "effective" length of an average block in "mixed" micelles is half that for the 102–75 micelle. The size of "mixed" micelles can be estimated using the ratio

$$\frac{R_{\mathrm{mix}}}{R_{\mathrm{CB}}} \sim \left(\frac{N_{\mathrm{mix}}}{N_{\mathrm{C}}}\right)^{3/5} \cong \frac{2}{5}\,\frac{1-\dfrac{N_{\mathrm{A}}}{N_{\mathrm{C}}}}{1-\left(\dfrac{N_{\mathrm{A}}}{N_{\mathrm{C}}}\right)^{2/5}} \qquad (8)$$

Based on a value of 51 nm for pure 102–75 micelles, the size of "mixed" micelles is expected to be about 33 nm, which is much larger than the average size obtained from the histogram. Thus, it is clear that this peak of the histogram cannot be explained by the presence of either only pure 18–75 or only "mixed" micelles. However, both types of micelles possibly contribute to the same peak, since the difference in sizes for "mixed" and "pure" 18–75 micelles is not large: $R_{\mathrm{mix}}/R_{\mathrm{AB}} \cong 1.87$.

To check this assumption, we need to estimate the fraction of “mixed” micelles. The minimization of the free energy (eq 1) leads to the following expression for the volume fraction of “mixed” micelles, ϕ_{mix}:

$$\phi_{\mathrm{mix}} \sim \phi_{\mathrm{A}}^{(Q_{\mathrm{mix}}/Q_{\mathrm{A}})^{3/2}} = \phi_{\mathrm{A}}^{(N_{\mathrm{mix}}/N_{\mathrm{A}})^{6/5}} \qquad (9)$$

where ϕ_{A} is the volume fraction of “pure” A−B micelles. For the experimental system under investigation we obtain (using eq 9) $\phi_{\mathrm{mix}} \sim \phi_{\mathrm{A}}^{3.5}$. Hence, the volume fraction of “mixed” micelles is much smaller than that for pure 18−75 micelles. However, in comparison with the fraction of pure 102−75 micelles, $\phi_{\mathrm{C}} \cong \phi_{\mathrm{A}}{}^{8}$, the fraction of mixed micelles is noticeable.

As follows from eq 9, an increase in the “effective” chain length (due to an increase in the fraction (or length) of long chains), results in the decrease of the volume fraction of “mixed” micelles. When the C−B chains are very long, the volume fraction of “mixed” micelles tends to zero and only “pure” micelles are in the solution. In such a case the incorporation of a long chain into a small micelle results in a huge increase of micellar surface and “mixed” micelle formation becomes unfavorable. In the limit where $N_{\mathrm{eff}} \rightarrow N_{\mathrm{A}}$ the volume fraction of “mixed” micelles, ϕ_{mix}, tends to ϕ_{A}; i.e. the concentration of “pure” A−B and “mixed” micelles becomes the same. In this limit, “mixed” and “pure” micelles become identical.

On the basis of eq 9, the average size for small micelles can be estimated by assigning the contribution of both pure 18−75 and “mixed” micelles to the same peak of the histogram. If P_{A} is the probability to find a pure A-micelle, the probability to find a “mixed” micelle (i.e., the fraction of “mixed” micelles in a mixture of pure A-micelles and “mixed” ones) is $P_{\mathrm{mix}} \cong P_{\mathrm{A}}{}^{3.5}$ (eq 9). Since the sum of the probabilities should be equal to $P_{\mathrm{mix}} + P_{\mathrm{A}} = 1$, the fraction of pure 18−75 micelles can be estimated as 70% and consequently the fraction of “mixed” micelles is 30%. Then the average micellar size for an 18−75/”mixed” micelles mixture is 22 nm (using the values of 17 nm for 18−75 micelles and 33 nm for “mixed” micelles). This result is in good agreement with experimentally observed data (22−23 nm). Hence, as follows from the theoretical calculations and experimental observations, all three types of micelles, pure large (102−75), pure small (18−75), and “mixed” micelles, are present in the solution and contribute to the histogram obtained (Figure 6). (It is worthwhile to remember that the theoretical calculations have been made under the assumption that all “mixed” micelles are identical.) Because the difference in the size of small (18−75) and “mixed” micelles is not very large, they cannot be distinguished as two separate peaks in the histogram (but the presence of “mixed” micelles noticeably increases the average size for “small” micelles) and as a whole the histogram has bimodal character.

Conclusions

The behavior of a mixture of two PVP−PS diblock copolymers (102−75 and 18−75) in a selective solvent was studied with the help of TEM. Initially, “mixed” micelles containing both diblock copolymer chains are formed and the corresponding size distribution is broad (Figure 2). Further evolution proceeds probably mainly via micellar collisions (unimer exchange is also possible, however). The result of micellar collisions, micellar merging, or chain exchange, depends on the composition of the micelles that collide.

The evolution of the system toward equilibrium is a very slow process, leading to the formation of a bimodal size distribution (Figures 4 and 6). The average size of the large micelles corresponds to that for micelles in a solution of long (102−75) diblock copolymers only. The other peak of the bimodal size distribution indicates the presence of small micelles with an average size larger than that found for “pure” 18−75 PVP−PS diblock copolymer micelles. Theoretical considerations predict that both “pure” and “mixed” micelles can exist at equilibrium. However, the size of such a “mixed” micelle is only somewhat larger than the size of a “pure” small (18−75) micelle. As a result, both “mixed” and “pure” micelles belong to the same peak in the size distribution histograms.

Acknowledgment. We would like to thank FOM-SON Quantum Chemionics Project for financial support. Dr. P. van Hutten is gratefully thanked for critically reading the manuscript.

References and Notes

(1) Tuzar, Z.; Kratochvil, P. *Surface Colloid Sci.* **1993**, *15*, 1.

(2) Noolandi, J.; Hong, K. M. *Macromolecules* **1983**, *16*, 1443.

(3) Nagarajan, R.; Ganesh, K. *J. Chem. Phys.* **1989**, *90*, 5843.

(4) Leibler, L.; Orland, H.; Wheeler, J. C. *J. Chem. Phys.* **1983**, *79*, 3550.

(5) Hadziioannou, G.; Skoulios, A. *Macromolecules* **1982**, *15*, 271.

(6) Esselink, F. J.; Semenov, A. N.; ten Brinke, G.; Hadziioannou, G.; Oostergetel, G. T. *Phys. Rev. B* **1993**, *48*, 13451 (and references therein).

(7) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525 (and references therein).

(8) Quintana, J. R.; Villacampa, M.; Katime, I. *Polym. Int.* **1995**, *36*, 325.

(9) Esselink, F. J.; Semenov, A. N.; ten Brinke, G.; Hadziioannou, G.; Oostergetel, G. *Macromolecules* **1995**, *28*, 3479.

(10) Bednár, B.; Karásek, L.; Pokorný, J. *Polymer* **1996**, *37*, 5261.

(11) Honda, C.; Abe, Y.; Nose, T. *Macromolecules* **1996**, *29*, 6778.

(12) Balsara, N.; Stepanek, P.; Lodge, T. P.; Tirell, M. *Macromolecules* **1991**, *24*, 6227.

(13) Liu, Z.; Pan, C.; Lodge, T. P.; Stepanek, P. *Macromolecules* **1995**, *28*, 3221

(14) Shim, D. F. K.; Marques, C.; Cates, M. E. *Macromolecules* **1991**, *24*, 5309.

(15) Pacovská, M.; Procházka, K.; Tuzar, Z.; Munk, P. *Polymer* **1993**, *34*, 4585.

(16) Sens, P.; Marques, C. M.; Joanny, J.-F. *Macromolecules* **1996**, *29*, 4880.

(17) Cantú, I.; Corti, M.; Salina, P. *J. Phys. Chem.* **1991**, *95*, 5981.

(18) Procházka, K.; Bednar, B.; Mukhtar, E.; Svoboda, P.; Trena, J.; Almgren, M. *J. Phys. Chem.* **1991**, *95*, 4563.

(19) Tian, M.; Qin, A.; Ramireddy, C.; Webber, S. E.; Munk, P.; Tuzar, Z.; Procházka, K. *Langmuir* **1993**, *9, 1741*.

(20) Haliloglu, T.; Bahar, I.; Erman, B.; Mattice, W. L. *Macromolecules* **1996**, *29*, 4764.

(21) Halperin, A. *J. Phys. Fr.* **1988**, *49*, 131.

(22) Esselink, F. J.; Dormidontova, E.; Hadziioannou, G. *Macromolecules* **1998**, *31*, 2925.

(23) Esselink, F. J.; Hadziioannou, G. Unpublished results.

(24) Halperin, A.; Alexander, S. *Macromolecules* **1989**, *22*, 2403.

(25) Birshtein, T. M.; Zhulina, E. B. *Polymer* **1989**, *30*, 170.

MA9802069