Evolution of Block Copolymer Micellar Size and Structure Evidenced with Cryo Electron Microscopy

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

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

Received July 9, 1997; Revised Manuscript Received January 5, 1998

ABSTRACT: The equilibration of spherical micelles formed by polystyrene−poly(2-vinylpyridine) (PS−PVP) diblock copolymers in toluene is studied by means of cryo electron microscopy. The evolution of the micelles in order to reach the equilibrium state involves the transformation of their structure and size and requires a considerable time. The micellar size distribution, which is relatively narrow after dissolution, becomes broader with time. The micellar structure changes with time toward a spherical form with narrow interfacial zone between the core and corona regions. The possible scenario of the equilibration process is discussed. The influence of the dilution on the micelles' evolution toward the equilibrium is investigated. It is found that strong dilution can lead to a decrease of the final size of the micelles. The reasons for this phenomenon are discussed.

Introduction

Due to their rich phase and structural behavior, block copolymers have received much attention from many research groups in the past.[1−11] Block copolymers are also important because of their scientific challenge and industrial relevance. This type of polymer has drawn the attention of the polymer scientists over the last 40 years with a much intensified activity over the last 10 years. In some respects, the diblock copolymers can be compared with surfactant molecules since they are capable of reducing the interfacial tension between two immiscible (homopolymer) phases.[12−15] Similarly to surfactant molecules, consisting of a polar headgroup and an apolar tail, dissolved in water, diblock copolymers also form micelles in a selective solvent.[1,16] Studying the behavior of these micelles can give much insight into the phenomena taking place in blends of a homopolymer and a diblock copolymer, and it can also help one to understand the genesis of the ordered morphologies of a diblock copolymer.

In this paper we discuss the behavior of a polystyrene−poly(2-vinylpyridine) (PS−PVP) diblock copolymer in toluene. Since the PS block is incompatible with the PVP block and toluene is a selective solvent for the PS block, spherical micelles consisting of a core built from PVP blocks and a corona built from PS blocks can be formed. The initial micelles formed directly upon dissolution do not necessarily correspond to the equilibrium ones. The process of reaching the equilibrium micellar size and structure can take a considerable time. It is accompanied by an increase of the average micellar size and may also involve structural transformations. The equilibration process can be influenced by many different factors such as block lengths, polymer concentration, quality of solvent, degree of incompatibility between the blocks, and so on. Thus the dilution of the solution can change considerably the equilibrium state of the micelles formed. The main aim of the present paper is to analyze the phenomena occurring under evolution of the system toward the equilibrium state, taking into account the influence of dilution.

The block copolymer solutions are studied with the help of transmission electron microscopy (TEM), allowing one to have a direct view of the micellar structures formed. This direct observation is a considerable advantage compared to the information that can be obtained by other experimental techniques. For instance, static and dynamic light scattering give an average value of the sizes of the micelles and, with the help of a model, information about the structure. TEM, however, due to the direct imaging, allows one to obtain more detailed information about the structure and the size distribution of the micelles.

This paper is organized in the following manner. In the next section the details of the experimental procedure and the results obtained are presented. Then, the possible scenario of the equilibration process will be proposed based on the experimental data and taking into account both dynamic and structural aspects of micelle formation. Finally, the effect of dilution on the equilibrium structures will be addressed. The reasons for the experimentally observed micellar size reduction upon dilution are analyzed theoretically, taking into consideration the effect of the translational entropy of the micelles.

Experimental Section

The diblock copolymer we used in this study consists of a polystyrene (PS) block which is deuterated and has a molecular weight of 75 000 and a poly(2-vinylpyridine) (PVP) block which is hydrogenated and has a molecular weight of 102 000. The overall polydispersity is 1.14. This diblock copolymer is dissolved in toluene to a concentration of 1 wt % and is subsequently stored in a sealed bottle at 4 °C. After storage for 19 months at this temperature, a part of this solution was diluted by a factor of 10 and another part was diluted by a factor of 100. The solutions obtained were then stored at −80 °C.

The solutions were all studied with the help of cryo-TEM.[17−19] For TEM it is necessary to have a very thin film of

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

S0024-9297(97)01011-5 CCC: $15.00
Published on Web 04/14/1998

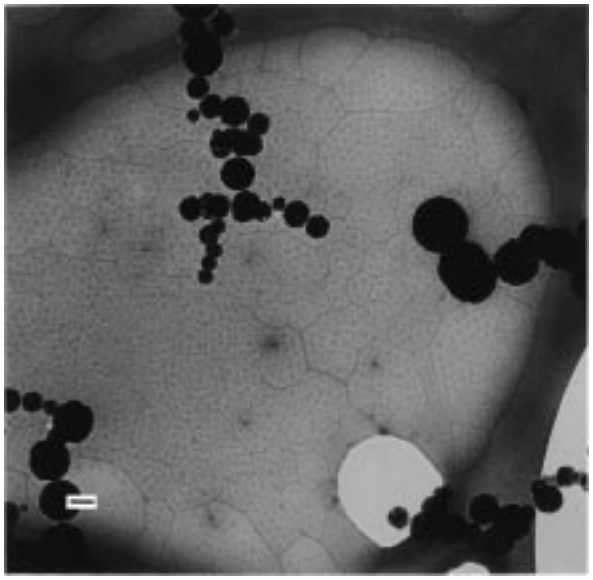

Figure 1. Cryo electron micrograph of a "fresh" solution of PS−PVP diblock copolymer in toluene. The scale bar indicates 200 nm.

the material of interest. Here we use special "holey" carbon-coated grids. These grids have a noncontinuous support film that looks like a spider web and contains holes of different sizes. For the preparation of the samples, the holey grids were covered with a droplet of the solution and subsequently blotted with filter paper to obtain a thin film of the solution. Directly after blotting, the grids were rapidly cooled to a temperature close to −196 °C by plunging them into liquid nitrogen. The preparation of these samples was normally performed inside a controlled environment vitrification system (CEVS)[20] in order to prevent the fast evaporation of toluene just before freezing. Furthermore, this CEVS makes it possible to prepare the samples at a specific temperature. More details on the cryo-TEM technique can be found in ref 19.

To enhance the contrast between the polymer and the toluene, the solutions were stained in situ by means of iodine, which selectively stains the PVP blocks by reacting with the pyridine rings, forming a pyridinium salt and thus creating a higher electron density in the PVP domains. This staining was in all cases done just before putting the solution on the grid.

The micrographs were taken with a JEOL 1200-EX transmission electron microscope operated at 100 kV, while the temperature of the specimen was kept at −170 °C.

Results

In Figure 1 a micrograph of a thin film of a "fresh" 1 wt % PS−PVP diblock copolymer solution in toluene is shown. Clearly visible are the holes formed by the carbon support layer. Inside these holes polymolecular micelles are visible as small spheres. These micelles are surrounded by a frozen amorphous layer of toluene. The thickness of the film is of the order of the diameter of the micelles as explained in ref 18. The micelles are confined to a small volume bounded by the toluene-air interfaces and the carbon support surrounding the film. Only the interior of the micelles is visible as explained in refs 18 and 19. The average diameter determined from the micrograph for this interior part of the micelle is about 45 ± 5 nm, corresponding to an aggregation number of about 300. In the micrograph (Figure 1) we observe a hexagonal packing of the micelles, common for globules in two dimensions. The typical intermicellar distance is determined to be 60 ± 5 nm. This value can be interpreted as a total micellar diameter. The large black objects in Figure 1 are frost particles which are commonly seen in cryo specimens.

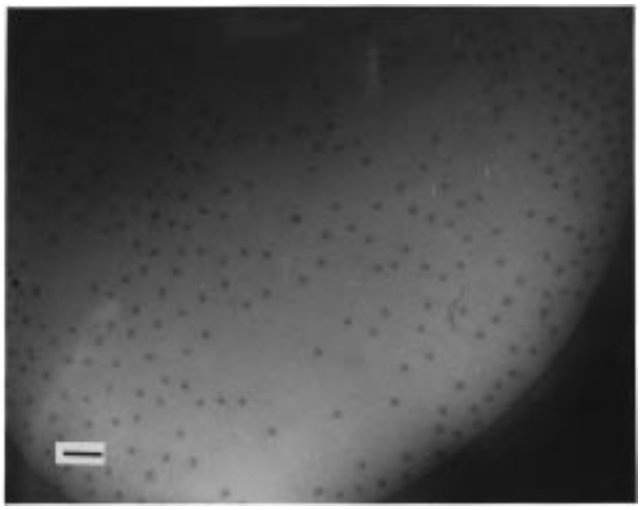

Figure 2. Cryo electron micrograph of a solution of PS−PVP diblock copolymer in toluene. The PVP block was stained with iodine. The scale bar indicates 200 nm.

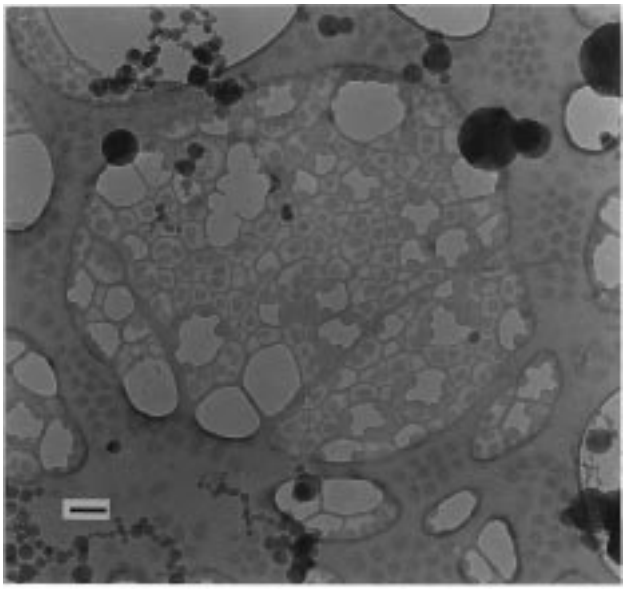

Figure 3. Cryo electron micrograph of a solution of PS−PVP diblock copolymer in toluene after aging for 18 months at 4 °C. The scale bar indicates 200 nm.

Figure 2 shows a micrograph of a thin film of a PS−PVP diblock copolymer stained with iodine in toluene. The contrast is enhanced, and the interiors of the micelles are now more clearly delineated from the surroundings. The sizes of the micelles are similar to that determined in Figure 1.

Figure 3 shows a micrograph of the same solution as in Figure 1, after aging for 18 months in a sealed bottle at 4 °C in a dark room. The first striking observation from this figure is that the micelles have grown considerably in size. On closer inspection, however, we see that the average size of the micellar cores has increased to about 51 ± 5 nm. Besides the appearance of larger micelles, also much smaller micelles are visible. The larger structures that are visible seem to be less spherical and slightly deformed within the holes.

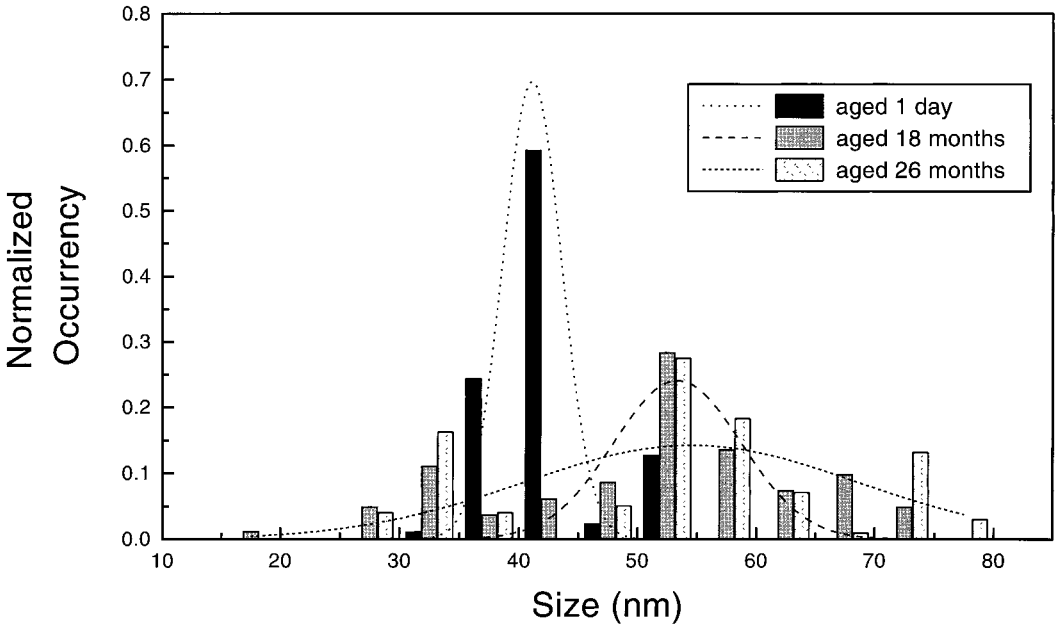

Figure 4. Histograms showing the size distribution for a 1 wt % PS−PVP solution after aging for 1 day, for 18 months, and for 26 months at 4 °C.

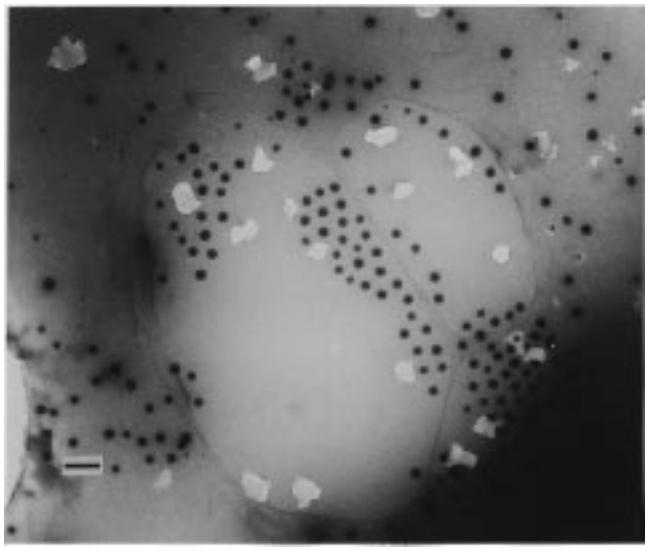

Figure 5. Cryo electron micrograph of a solution of PS−PVP diblock copolymer in toluene after aging for 26 months at 4 °C. The PVP block was stained with iodine. The scale bar indicates 200 nm.

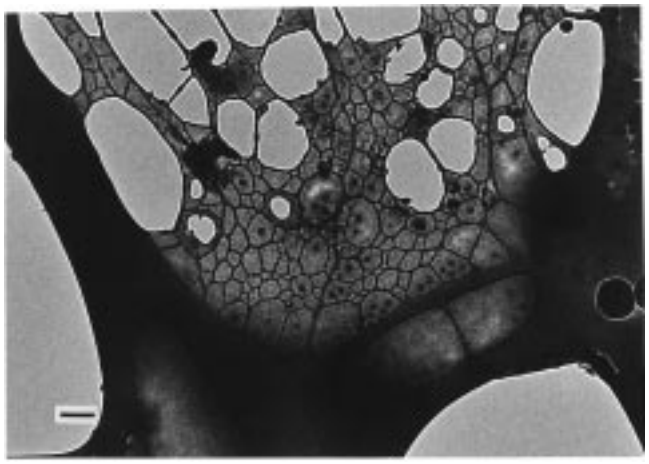

Figure 6. Cryo electron micrograph of a 0.01 wt % solution of PS−PVP diblock copolymer in toluene obtained by dilution of the 18-months-aged solution shown in Figure 3. The scale bar indicates 200 nm.

Figure 4 shows a histogram of the size distributions obtained from cryo-TEM micrographs of a 1 wt % PS−PVP solution in toluene after aging for 1 day, 18 months, and 26 months. The width of each histogram bar is 5 nm. It is clear that in the course of time the average size increases, which is accompanied by a broadening of the size distribution. After long-time aging, the sizes are in the range of about 20 to 70 nm.

Figure 5 shows a cryo electron micrograph of the diblock copolymer in toluene aged for 26 months. The average size is determined to be about 50 nm. In this case the solution has been stained by adding a small amount of iodine after aging. As was the case in Figure 3, a rather broad size distribution is visible. However, the micelles are more spherical compared to those visible in Figure 3.

Figure 6 shows a micrograph of the 100-fold diluted solution after 2 more days of aging at −80 °C. The average size for the micellar cores is reduced and determined to be about 42 nm. This size compares to the size of the polymolecular micelles in the original preparation shown in Figure 1.

In Figure 7, histograms of the size distributions for the 100-fold diluted solution after 2 days and 6 months are shown. From this figure it is clear that the sizes of the micelles are reduced compared to those of the aged undiluted solution (Figures 3−5) and that the width of the size distribution has decreased. The 10-fold diluted solution did also show a small reduction in the micellar size but, due to the experimental error in size determination and statistical limitations, a precise value cannot be given.

Figure 8 shows a cryo electron micrograph of the 100-fold diluted solution. The solution was aged for 13.5 months at −80 °C after dilution. In this case the PVP blocks were stained with a small amount of iodine. We can compare Figures 3 and 5 with Figures 6 and 8, respectively. In both cases, stained and nonstained solutions, there is a clear change in size distribution

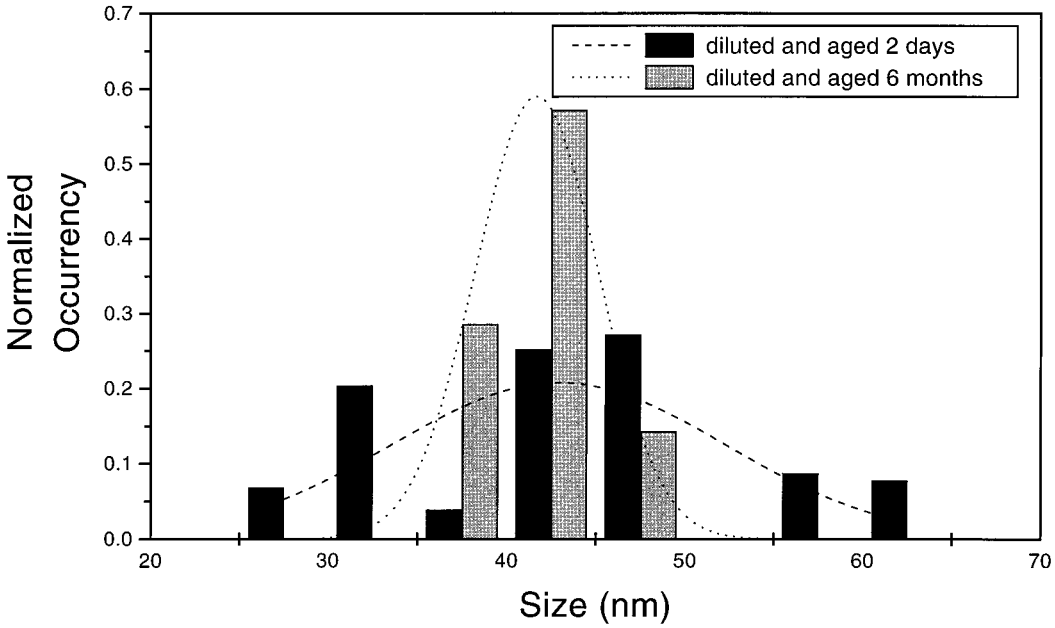

Figure 7. Histograms showing the size distribution for a 0.01 wt % PS−PVP solution after aging for 2 days and for 6 months at −80 °C.

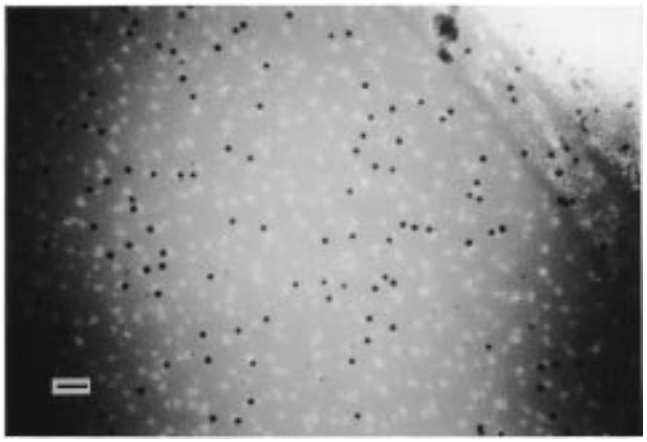

Figure 8. Cryo electron micrograph of a 0.01 wt % solution of PS−PVP diblock copolymer in toluene obtained by dilution of an 18-months-aged solution and further aging for 13.5 months at −80 °C. The PVP block was stained with iodine. The scale bar indicates 200 nm.

upon dilution. In the case of the stained solutions, however, the micelles seem to have a more spherical shape than in the unstained ones.

Discussion

The Genesis of Micelles and Their Evolution. As discussed above, the driving force ensuring the formation of the PS−PVP micelles in solution is the incompatibility of the blocks on one hand and the incompatibility of PVP block with the solvent on the other hand. As a result, PVP blocks tend to aggregate in order to minimize the contacts with both PS blocks and solvent (toluene). Due to chemical connectivity of PS and PVP blocks, ordinary macrophase separation is impossible, and the tendency to segregate can be resolved by the formation of micelles.

The micelles formed directly after dissolution will be unimolecular micelles. The internal structure of these micelles depends on many factors: one of them is the degree of incompatibility between the blocks and between the insoluble block and the solvent. For instance, if the monomer units of the insoluble block prefer to have contact with solvent rather than with the other block, as is the case for PVP−PS diblock copolymer in toluene, the initial unimolecular micelle resembles a surfactant molecule with a dense headgroup formed by the PVP block and a tail formed by the PS block swollen in toluene. The structure of these unimolecular micelles differs considerably from the "classical" model of a micelle with a clearly defined core and corona region. The latter structure is formed as a result of the equilibration processes. As a matter of fact, the solution of unimolecular micelles is only the very initial state of the evolution process. Since the number of unfavorable contacts between insoluble block and solvent is large in a unimolecular micelle, the aggregation of unimers resulting in a decrease in the number of unfavorable contacts becomes the leading process:

$$M_1 + M_1 \rightarrow M_2 \qquad (1)$$

Of course not only two, but also three or more unimolecular micelles can merge. This merging process is schematically drawn in Figure 9a. However, the probability of a collision between a large number of unimers is rather small. Hence the initial aggregation probably proceeds via successive incorporation of unimolecular micelles. Unimer aggregation is a very quick process starting just after unimer formation. As a result, a micelle size distribution will arise very soon after dissolution. This is the size distribution observed in PS−PVP solutions almost immediately after preparation (Figures 1, 2, and 4).

As soon as there are different micelles in the solution, the further evolution toward equilibrium proceeds through the collisions between and merging of micelles. The frequency of collision, ω, between two micelles with aggregation numbers Q_1 and Q_2 can be estimated as

$$\omega \sim \frac{n_{Q_1} v}{V} \frac{n_{Q_2} v}{V} \qquad (2)$$

where n_i is the number of polymer micelles with

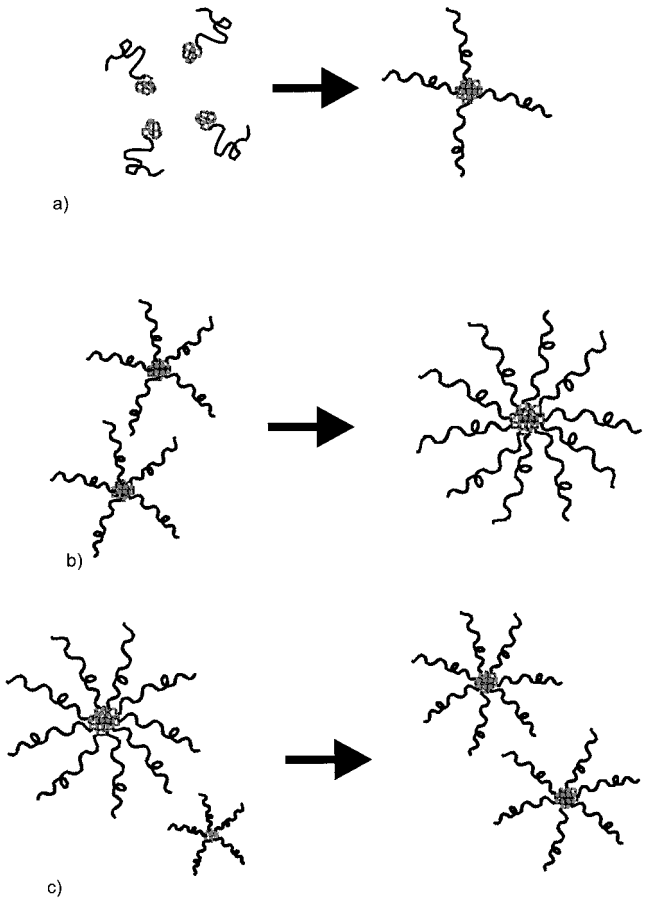

Figure 9. Evolution of micellar sizes: (a) formation of polymolecular micelles from unimers; (b) fusion of polymolecular micelles; (c) redistribution of block copolymer chains over polymolecular micelles.

aggregation number i in the system, v is the volume per monomer unit, and V is the volume of the system. The larger the number of micelles with given aggregation number, the larger the probability that they will come into collision with the same or other micelles and, consequently, participate in the micellar growth process. The number of unimolecular micelles is large at the beginning of the evolution process. However, with time their number decreases considerably. As a result, the process of micellar growth visible in Figures 3−5 occurs mainly by fusion of polymolecular micelles:

$$M_{Q_1} + M_{Q_2} \rightarrow M_{Q_1+Q_2} \tag{3}$$

Merging of micelles is schematically shown in Figure 9b. To form such a combined micelle, the cores of two micelles taking part in the collision must come into contact. This implies the deformation of the soluble blocks forming the corona regions of the micelles. This energy of deformation can be estimated as the free energy of chain extension in the corona region:[21−24]

$$U \sim \kappa Q^{3/2} \tag{4}$$

where κ is a numerical constant.

It is worth noting that eq 4 is obtained for the model of "classical" micelles with a well-defined core and corona region with a narrow interface between them. As mentioned above, this does not necessarily apply to unimolecular micelles or to micelles with a small aggregation number. For these micelles only a small part of the surface between soluble and insoluble blocks can be covered by junction points. The rest of the surface can be covered by solvent (see Figure 9a). This facilitates the contact between the cores ("headgroups") of the (unimolecular) micelles. As a result, the energy of deformation is rather small for unimers or micelles with small aggregation numbers, and the initial aggregation occurs very quickly. When the aggregation number increases, the structure of a micelle becomes more similar to the "classical" picture with core and corona regions and a narrow interface (Figure 9b). For such micelles the energy of deformation may be large, in accordance with eq 4.

As discussed above, equilibration is a rather slow process. The average time required to form the micelle with an equilibrium aggregation number Q_{eq} can be estimated as[8,18]

$$t^{eq} \sim (1/\omega) \exp(\kappa Q_{eq}^{3/2}) \tag{5}$$

The larger the aggregation number of a micelle, the more collisions between micelles have to occur and, hence, the more time will be needed to reach the equilibrium state. The "equilibration" time depends on the frequency of collisions, which is a function of the number of micelles in solution. Due to fusion reactions, the number of micelles (and hence the probability of collisions) decreases with time, slowing down the equilibration process.

According to the experimental observations, the "initial" size distribution, probably formed mainly by fusion of (unimers and/or) small micelles, appears very quickly, while the further evolution of the distribution occurs rather slowly. The only discernible features of the equilibration process are the increase of the average aggregation number and "broadening" of the size distribution. This latter phenomenon can be explained by collisions between micelles of different sizes. The larger the number of micelles of a given type is, the larger the probability of collision in which such micelles are involved. Since the fraction of small micelles is not large in comparison with that of micelles having an average size, the probability of collisions in which they participate will be small, and as a result, small micelles will exist for a relatively long time. It is one of the reasons why the size distribution remains broad (Figures 3−5).

In later stages of the evolution process, additional obstacles for micellar growth arise. Indeed, upon the fusion of micelles, the common surface between core and corona region (and hence the number of unfavorable contacts) decreases. On the other hand, the soluble blocks become more extended in the corona region. The balance between these two tendencies determines the equilibrium size. When the average size of micelles in solution becomes comparable with (but is still smaller than) the equilibrium size, the collision of such average micelles can result in the formation of one large micelle with an aggregation number (much) larger than that for the equilibrium one. The free energy of such a micelle is larger than that for the equilibrium micelles, since the latter corresponds to the minimum of the free energy. As a result, such a large micelle will tend to decrease the aggregation number (size) by chain transfer to another small micelle via a collision process. Thus, the collision between a large micelle and a smaller micelle can lead to a redistribution of the chains in such a way that the final sizes of both micelles are closer to

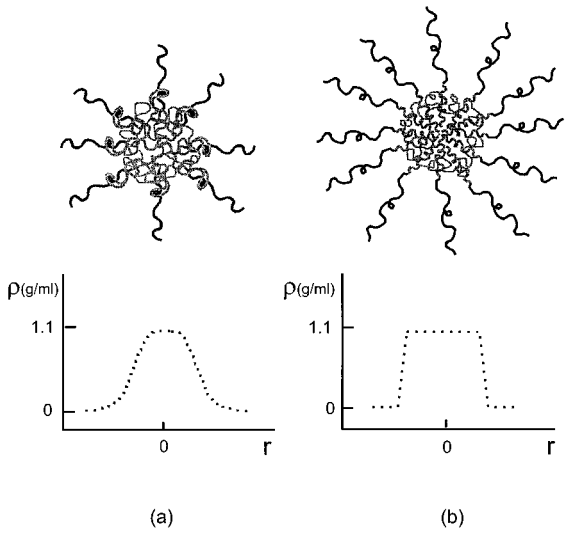

Figure 10. Plot showing the structure and segment density (ρ) of insoluble blocks of (a) a "fluffy" and (b) a "classical" block copolymer micelle.

the equilibrium size.

$$M_{Q_1} + M_{Q_2} \rightarrow M_{Q_1+x} + M_{Q_2-x} \qquad (6)$$

This is schematically shown in Figure 9c. At the same time, small micelles tend to increase their size by the collisions with other micelles. Thus, the collisions involving small micelles seem to be the mechanism toward the equilibrium in the final stage of the micellar evolution.

The scenario of micellar evolution considered above started from the picture of surfactant-like unimolecular micelles. However, the structure of initial unimers can be different depending on the incompatibility parameters. For instance, if the incompatibility of the insoluble block with solvent is stronger than with the other block, a unimolecular micelle can be formed in such a way that the "surface" of the micelle is completely covered by the soluble block only in order to screen the interactions between solvent and insoluble block. In this case a relatively broad intermediate layer between core and corona regions, formed by both sorts of blocks, can arise. The structure and the density distribution of the insoluble blocks of such a "fluffy" micelle is shown schematically in Figure 10 and compared with that of a micelle emerging from the "classical" picture. Fusion occurs more easily for "fluffy" micelles than for "classical" ones, since the corona region and hence the deformation energy are smaller for a "fluffy" micelle. On the other hand, the fusion of surfactant-like micelles (considered before) can occur more easily than that of "fluffy" ones, since the cores of surfactant-like micelles can come into contact with minimal (or without any) deformation of soluble blocks.

It is worth emphasizing that both these models of surfactant-like and "fluffy" micelles are applicable only to unimers or small micelles formed in the first stage of the equilibration process. As soon as the aggregation number of a micelle becomes large enough, the micelle structure corresponds to the "classical" picture with a well-defined core and corona region with a narrow interface.

Besides the above-mentioned collision scenario, it is also possible to think of the micellar growth proceeding via a second scenario, consisting of a two-step process during which a polymolecular micelle expels one (or more) block copolymer chain(s) which is (are) then reabsorbed by a second polymolecular micelle.[25] However, this latter scenario involves the diffusion of copolymer chains out of the polymolecular micelles into the solution. This implies a considerable increase in surface free energy, due to the formation of a small (possibly unimolecular) micelle. Thus, the second scenario is less favorable than the first one.

Effect of Dilution on the Size of Aged Micelles. Let us consider the phenomena taking place when the polymer solution is diluted. Under the conditions described in the Experimental Section, the PS−PVP solution stored for 18 months was diluted 10 and 100 times. After dilution these solutions were stored at −80 °C. Figures 6−8 suggest that a reequilibration process occurs, i.e., the size distribution obtained after 18 months aging before dilution is changed by 100-fold dilution in such a way that the average micellar size decreases and the size distribution becomes more narrow (Figures 6−8). For the 10-fold diluted solution, no noticeable changes in the distribution occurred. The conclusion which can be drawn on the basis of these observations is that upon dilution a completely new equilibrium is established. The equilibrium size of the micelles in the diluted solution is certainly smaller than in the undiluted case. To reach the new equilibrium, chain exchange between the micelles has to occur in such a way that upon collision of a small and a large micelle, the latter tends to decrease its aggregation number by chain transfer to the small one. This is also schematically represented in Figure 9c. During the equilibration process induced by dilution, the influx of (unimolecular) micelles is smaller than the outflux:

influx: $M_{n-x} + M_x \rightarrow M_n$ (Figure 9b)

outflux: $M_n \rightarrow M_{n-y} + M_y$

or

$M_n + M_x \rightarrow M_{n-y} + M_{x+y}$ (Figure 9c)

Thus, in contrast to the micellar growth discussed above, the opposite process of micelle "dissociation" takes place until the new equilibrium is reached.

Now, let us discuss the factors leading to a decrease of the average micellar size. First, it is important to note that besides dilution, cooling of the solution took place. Both of these factors could influence the final micellar size. Indeed, cooling leads to a decrease in the compatibility of the soluble block with the solvent. However, the 10-fold solution shows no substantial changes in micellar size distribution. This means that toluene is still a good solvent for PS blocks. Hence, the main difference between the 10- and 100-fold solutions is only the degree of dilution, which therefore is the reason for the micellar size reduction. This phenomenon can be connected with the phase behavior of the micellar solution.

To analyze the phase behavior, let us consider the solution of identical micelles with the aggregation number Q. Such a system can be a model of a real system if Q corresponds to the average aggregation number of the micellar distribution. The free energy of the model system can be written in the following form:

$$F = \frac{\phi}{Q(N_{PVP} + N_{PS})}[\ln \phi + f_{mic}(Q)] + (1 - \phi)\ln(1 - \phi) + \chi\phi\frac{N_{PS}}{N_{PVP} + N_{PS}}(1 - \phi) \quad (7)$$

Here, Q and ϕ are the average aggregation number and volume fraction of the block copolymer micelles respectively, N_{PVP} (N_{PS}) is the number of monomer units per PVP (PS) block, and χ is the interaction parameter between PS blocks and solvent. The terms containing $\ln \phi$ and $\ln(1 - \phi)$ in eq 7 correspond to the translational entropy of the block copolymer micelles and solvent, respectively. The last term describes the volume interactions between PS blocks and solvent molecules. $f_{mic}(Q)$ is the micellar free energy:[26]

$$f_{mic}(Q) = c_1(N_{PVP}vQ)^{2/3}\gamma + c_2Q^{3/2} + c_3Q^{5/3}N_{PVP}^{-1/3} \quad (8)$$

where γ is the surface free energy, v is the volume per monomer unit, and c_i are numerical coefficients ($c_2 \equiv \kappa$, eq 4).

Dilution, i.e., a decrease in micellar volume fraction, can lead to instability of the system unless the aggregation number of the micelles changes. Indeed, the model polymer system becomes unstable with respect to macrophase separation in the region where $\partial^2F/\partial\,^2\phi < 0$.

$$\frac{\partial^2 F}{\partial^2 \phi} = \frac{1}{Q\phi(N_{PVP} + N_{PS})} + \frac{1}{1 - \phi} - 2\chi\frac{N_{PS}}{N_{PVP} + N_{PS}} < 0 \quad (9)$$

As can be seen from eq 9, the instability region becomes broader when the aggregation number of the micelles increases. The critical point of the spinodal, i.e., the point corresponding to the minimum values of χ and ϕ at which the system becomes unstable, also depends on the aggregation number:

$$\phi_{cr} = \frac{1}{1 + \sqrt{Q(N_{PVP} + N_{PS})}} \quad (10)$$

$$\chi_{cr} = \frac{1}{2}\frac{N_{PVP} + N_{PS}}{N_{PS}}\left(1 + \frac{1}{\sqrt{Q(N_{PVP} + N_{PS})}}\right)^2 \quad (11)$$

A qualitative plot of the spinodal curve for a solution of identical block copolymer micelles is given in Figure 11 for two values of the aggregation number. For the solution of micelles with smaller aggregation number, the region of instability is smaller. A decrease in the aggregation number results in an increase in the translational entropy of the micelles, which can lead to stabilization of the system as a whole. The critical point shifts to larger values of polymer volume fraction and χ parameter.

Thus, a decrease in the aggregation number of micelles may be preferred for polymer systems in very dilute solutions. In this region, the translational entropy of micelles can become important enough to influence the value of the equilibrium aggregation number. In contrast to the ordinary situation occurring in dilute (or semidilute) regions when the equilibrium value of the aggregation number is defined by the balance of surface free energy and elastic free energy,[26] i.e., by the competition of the tendencies to minimize unfavorable contact and chain stretching, the additional

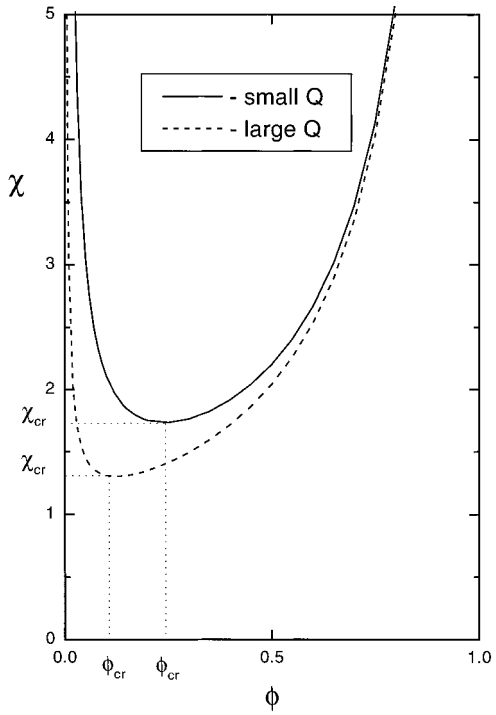

Figure 11. Plot of the spinodal curves for solutions of block copolymer micelles for large and small aggregation number.

factor of translational entropy of micelles comes into play in the very dilute region. Minimization of the free energy (eq 7) with respect to the aggregation number of micelles yields the following expression for the equilibrium aggregation number:

$$Q \approx Q_0\left(1 + c\frac{\ln \phi}{Q_0^{3/2}}\right) \quad (12)$$

Here $Q_0 \approx (N_{PVP}v)^{4/5}\gamma^{6/5}$ is the aggregation number obtained without taking translational entropy into account and c is a constant.

According to eq 12, dilution can really result in a noticeable reduction in the micellar size if the micellar volume fraction becomes smaller than some critical value. The smaller the micellar volume fraction, the more important the influence of translational free energy and the smaller the equilibrium micellar size.

In the experimentally studied case, the 100-fold diluted solution yields a polymer volume fraction at which the decrease of the average micelle size became clearly visible (Figures 6−8). For the 10-fold diluted solution, no such decrease in micelle size was found, suggesting that the concentration is still too high for the translational entropy to become an important factor and reduce the micellar size.

Conclusions

In the present study, the evolution of PS−PVP diblock copolymer micelles has been investigated with the help of cryo transmission electron microscopy (TEM), which is an effective tool to observe changes in micellar structure, average size and especially in size distribution with aging. On the basis of the experimental results obtained, the following scenario of micellar evolution toward equilibrium is proposed.

The process of equilibration of polymer micelles can be subdivided in three main stages. In the first stage (almost immediately after dissolution) the initial mi-

cellar distribution is formed. In this stage micellar formation occurs mainly through aggregation of unimers (Figure 9a). Since unimer aggregation practically does not involve any deformation (elongation) of the soluble blocks, the process of initial micellar formation is rather fast and the micellar size distribution observed almost immediately after dissolution is rather narrow (Figures 1, 2, and 4).

The second stage of micellar evolution involves fusion of micelles (Figure 9b) through a collision mechanism, where the cores of the two micelles participating in the collision have to come into contact to form a large micelle. To this end, the soluble blocks of the corona regions have to be deformed, implying that some energetic barrier has to be overcome. The rate of micellar growth in this stage depends on the probability of collisions and on the size of the micelles. As a result, the larger the final size of a micelle is, the longer the time that is required for its formation. The micellar size distribution formed after multistage collisions involving micelles differing in size, can be rather broad (Figures 3−5). The larger the equilibrium micelle size, the broader the size distribution that can be expected.

In the last stage, the equilibration process involves a redistribution of chains between the micelles with a size exceeding the average size and smaller micelles (Figure 9c). This is an even slower process than micellar fusion, since it involves a large energy of chain deformation. Furthermore, the number of relatively small micelles is rather small.

Besides an increase of micellar size, the evolution process can also be accompanied by structure transformations. The structure of unimers (or even small initial micelles) may be surfactant-like (Figure 9a) or may correspond to a "fluffy" micelle structure (with a broad interface region formed by both blocks between the core and the corona) (Figure 10a). With an increase in the micellar aggregation number, the micellar structure becomes more and more similar to the "classical" micelle model with a well-defined core and corona region with a narrow interface (Figure 10b).

Dilution of the micelle solution influences the evolution process, resulting in the decrease of the average micellar size (Figures 6−8). In contrast to micellar growth, the opposite process of micellar "dissociation" takes place until the equilibrium state is achieved. During this dissociation process, micelles tend to transfer chains to smaller micelles. The final size distribution is more narrow than for the undiluted case. According to theoretical calculations, the reason for the equilibrium micelle size reduction is the translational entropy that is gained upon dilution. The translational entropy of micelles becomes especially important in the very dilute region, where a decrease in the average micelle size prevents the instability of the micellar solution.

Acknowledgment. We thank the FOM-SON Quantum Chemionics Project for financial support, Prof. G. ten Brinke and Prof A. N. Semenov for helpful discussions, and Dr. P. F. van Hutten for critically reading and correcting 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) Zhou, Z.; Chu, B. *J. Interface Sci.* **1988**, *126*, 171.
(6) Xu, R.; Winnik, M. A.; Riess, G.; Chu, B.; Croucher, M. D. *Macromolecules* **1992**, *25*, 644.
(7) Hadziioannou, G.; Skoulios, A. *Macromolecules* **1982**, *15*, 271.
(8) Esselink, F. J.; Semenov, A. N.; ten Brinke, G.; Hadziioannou, G.; Oostergetel, G. T. *Phys. Rev. B* **1993**, *48*, 13451.
(9) Tian, M.; Qin, A.; Ramireddy, C.; Webber, S. E.; Munk, P.; Tuzar, Z.; Prochazka, K. *Langmuir* **1993**, *9*, 1741.
(10) Honda, C.; Hasegawa, Y.; Hirunuma, R.; Nose, T. *Macromolecules* **1994**, *27*, 7660.
(11) *Solvents and self-organization of polymers*; Webber, S. E., et al., Eds.; NATO ASI Series E: Applied Sciences 327; Kluwer: Dordrecht, The Netherlands, 1996.
(12) Gaillard, P.; Ossenbach-Sauter, M.; Riess, G. *Makromol. Chem.* **1980**, *1*, 771.
(13) Anastasiadis, S. H.; Gancarz, I.; Koberstein, J. T. *Macromolecules* **1989**, *22*, 1449.
(14) Fayt, R.; Jerome, R. Teyssie, Ph. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 2209.
(15) Shull, K. R.; Kramer, E. J.; Hadziioannou, G.; Tang, W. *Macromolecules* **1990**, *23*, 4780.
(16) Tang, W. T.; Hadziioannou, G.; Cotts, P. M.; Smith, B. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27*, 107.
(17) Cohen, Y.; Talmon, Y.; Thomas, E. L. *Physical Networks*; Elsevier: Amsterdam, 1990, Chapter 12.
(18) Esselink, F. J.; Semenov, A N.; ten Brinke, G.; Hadziioannou, G.; Oostergetel, G. T. *Macromolecules* **1995**, *28*, 3479.
(19) Oostergetel, G. T.; Esselink, F. J.; Hadziioannou, G. *Langmuir* **1995**, *11*, 3721.
(20) Bellare, J. R.; Davis, H. T.; Scriven, L. E.; Talmon, Y. *Electron Microsc. Tech.* **1988**, *10*, 87.
(21) Semenov, A. N. *Macromolecules* **1992**, *25*, 4967.
(22) Daoud, M.; Cotton, J. P. *J. Phys. Fr.* **1982**, *43*, 531.
(23) Witten, T. A.; Pincus, P. A. *Macromolecules* **1986**, *19*, 2509.
(24) Semenov, A. N.; Joanny, J.-F.; Khokhlov, A. R. *Macromolecules* **1995**, *28*, 1066.
(25) Wang, Y.; Kausch, C. M.; Chun, M.; Quirk, R. P.; Mattice, W. L. *Macromolecules* **1995**, *28*, 904.
(26) Birshtein, T. M.; Zhulina, E. B. *Polymer* **1989**, *30*, 170.

MA971011O