PHYSICAL REVIEW B VOLUME 48, NUMBER 18 1 NOVEMBER 1993-II

Formation and structural ordering of micelles of block copolymers in a thin-film-homopolymer matrix

F. J. Esselink, A. N. Semenov,* G. ten Brinke, and G. Hadziioannou†
Department of Polymer Chemistery and Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

G. T. Oostergetel
BIOSON Research Institute, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

(Received 16 July 1993)

In this paper the segregation of block copolymer deuterated polystyrene 2-vinylpyridine micelles in a thin film homopolymer polystyrene matrix, observed by cross-sectional transmission-electron microscopy, is presented. The experimental results together with a theoretical analysis demonstrate that the micelles observed must have been formed already in the solution from which the films were prepared by spin coating. Annealing at temperatures above the glass-transition temperatures leads to preferential segregation of the micelles to existing interfaces. Furthermore at sufficiently high concentration, micelles are found to form clusters due to their mutual attraction. It is demonstrated that existing theories compare favorably with these experimental results.

INTRODUCTION

In the last decade block copolymer systems have become subjects of an increasing number of experimental and theoretical studies. Scientifically they constitute fascinating systems because of the almost infinite variety of structures, related to the particular molecular architecture, possible. This paper deals with the simplest of these architectures: the diblock copolymers. In fact we will focus on mixtures of diblock copolymers (A-B) in a matrix of homopolymers (hA). This turns out to be a complicated system already with complex time-dependent behavior. Besides being of interest from a purely scientific point of view, these types of systems are potentially of great practical importance. They are model systems for composites of two or more polymer components containing block copolymers as interface-active species. One of the drawbacks of using block copolymers for this purpose turns out to be the large amount ($>10\%$) of block copolymer that appears to be required in practice to obtain the desired (mechanical) properties. This amount is in general far above the critical micelle concentration. The main issue considered in the present paper is closely related to this and concerns the formation and the diffusion of block copolymer micelles in a homopolymer matrix.

Phase behavior of block copolymer (AB) + homopolymer (hA) mixtures have been studied extensively, experimentally,[1-6] as well as theoretically.[7-12] The effectiveness of copolymers as emulsifying agents in two-phase systems is based on the selective affinity the two blocks have for the two separate phases, thus reducing the interfacial tension[13,14] by segregating to the interface between these phases.[15,16] Obviously, micelle formation is detrimental to this goal and should be avoided if possible. Apart from this point of view, a detailed understanding of the behavior of block copolymer micelles is also essential in understanding the ordered morphologies formed in pure block copolymer melts.

In this study the effect of annealing time on the morphology of systems containing diblock copolymers of deuterated polystyrene (dPS) and poly(2-vinylpyridine) (P2VP) and homopolymers polystyrene (hPS) in confined space, e.g., in a thin film configuration, is considered in detail. The polystyrene block has been deuterated because of additional ion-beam experiments (nuclear reaction analysis and secondary ion mass spectroscopy) requiring this type of isotope substitution. Micelles were observed and followed as a function of annealing time by transmission electron microscopy (TEM), a direct technique which allows a molecular scale resolution. Micelles of dPS-P2VP were found to have characteristic core sizes of the order of 40–50 nm, a fact that is, as will be shown, difficult to reconcile with their formation in the homopolymer matrix during the time of the experiments. Most likely, they were present in the original solution in toluene from which the films are spin coated. This agrees with the results of Ref. 17 where the critical micelle concentration of these types of block copolymers in toluene is found to be considerably lower than the concentrations employed in the present study. For a homopolymer matrix of sufficiently high molecular weight block copolymer micelles are predicted to have a strong tendency to segregate to preexisting interfaces, a property that is confirmed by our electron microscopy results and previous work (direct and indirect).[18] Furthermore, at higher concentration, clustering of micelles occurs at the surface as well as at the silicon layer on which the polymer film is spin coated. At even longer annealing times a layer of micelles is formed at the polymer-silicon interface after several of these micelles have broken up, forming hemispheres (half-open cones) on top of the silicon, in this way stabilizing the row of micelles formed.

EXPERIMENT

The block copolymers used were diblock copolymers of deuterated polystyrene (dPS) and poly(2-vinylpyridine) (P2VP) with different degrees of polymerization for the P2VP blocks. These block copolymers were mixed in a polystyrene matrix with a molecular weight of 190 k. The polymers were made in our own laboratory by means of anionic polymerization. The overall polydispersities for all the polymers did not exceed 1.14.

The experimental results were obtained using two block copolymers differing by the molecular weights of the P2VP blocks. The first block copolymer system consisted of a PS block with a molecular weight of 75 k and a P2VP block of 102 k. For the second one the P2VP block had a molecular weight of 95 k. These block copolymer systems were together with the homopolymer dissolved in toluene with different relative block copolymer weight percent.

The thin specimens which are required for TEM were obtained by spin coating the polymer solutions on a suitable round substrate, made out of Epon, an electron microscopy embedding material. The diameter of this disk was 1 cm and the thickness was about 3 mm. In order to get a smooth surface, one side of these substrates was polished by means of diamond polish. A silicon layer was evaporated on to the polished surface, creating in this way a silicon layer on which the polymer solution can be spin coated. This is necessary because the Epon will interact with P2VP (but not with PS or dPS). The polymer solution was spin coated directly on the silicon-covered substrate. This facilitates the study of cross sections of the film and is comparable to the spin coating on Si wafers used for ion-beam techniques. The specimens were annealed under vacuum at 180 °C for a predescribed time. After annealing the samples were sectioned normal to the film surfaces by ultramicrotomy, using a Reichert-Jung Ultracut-E with a diamond knife. The thickness of these cross sections was about 70 nm. The sections were picked up on gold grids and stained in iodine vapor for about 1 h. The iodine selectively stains the P2VP units of the block copolymer by reacting with the pyridine rings forming an ammonium salt. Because of the higher electron density of the iodine atoms, the P2VP units will appear as dark areas. The grids were observed at 80 kV in a Philips EM-300 electron microscope. The particular block copolymers studied with TEM are given in Table I.

TABLE I. Used block copolymers in 190 k hPS matrix.

M_w dPS-P2VP-block	wt %	Annealing time (h)
75–102 k	15	52
75–102 k	30	48
75–102 k	30	176
75–95 k	2	0
75–95 k	2	2
75–95 k	2	33

RESULTS

In Fig. 1 a TEM micrograph is shown of a 15 wt. % 75–102 k dPS-P2VP diblock copolymer in the 190 k hPS matrix. After spin coating, the sample was annealed for 52 h at 180 °C, far above the glass transition temperatures of the polymers used (which are in the range of 100–110 °C). The clearly visible dark spots correspond to the cores of the micelles formed by the iodine-stained P2VP blocks of the aggregated block copolymers. The figure shows that a layer of micelles is concentrated at the polymer-air interface. In this particular case the polymer film happens to be rather thick (about 2000 nm), but in a thinner film the same phenomenon is observed [Figs. 2(a) and 2(b)]. The difference in apparent core diameters between the micelles observed is probably caused by the fact that the cutting procedure will not necessarily cut a micelle in the middle. From these micrographs of annealed films it is possible to derive a characteristic value for the diameter D of the P2VP core of the micelles: $D = 50$ nm with a deviation of about 10%. These and related results that will be presented further on contain already a wealth of information that can only be appreciat-

FIG. 1. Cross-sectional view of a 15 wt % 75–102 k dPS-P2VP in 190 k hPS. Annealing time is 52 h at 180 °C. Layer thickness is 2000 nm. The micellar surface layer is clearly visible. (Bar indicates 400 nm, A = air, P = polymer layer, Si = silicon layer, E = epon substrate.)

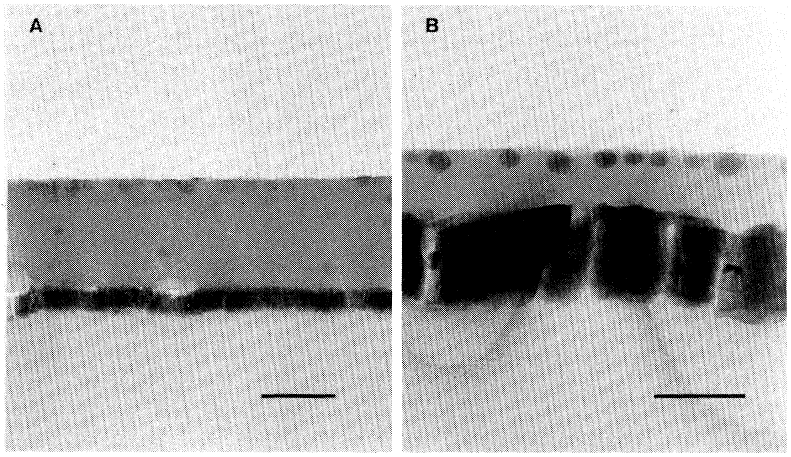

FIG. 2. (a) Cross-sectional view of a 15 wt % 75–102 k dPS-P2VP in 190 k hPS. Annealing time is 52 h at 180 °C. Layer thickness is 500 nm. (Bar indicates 300 nm.) (b) Same sample, but smaller layer thickness of approximately 150 nm (annealing time 48 h). (Bar indicates 200 nm.) Both cases show clear surface segregation.

ed after a more elaborate consideration of micelle formation, interaction, and diffusion.

Collapse of P2VP blocks

A convenient starting point for any discussion of micelles is the conformation of a single free PS-P2VP diblock copolymer in a PS matrix. As is well known, PS and P2VP are highly incompatible, which in the usual description is expressed in terms of the Flory-Huggins parameter χ. For the system considered $\chi=0.11$.[16] As a consequence, the P2VP block will be in a collapsed state provided the molecular weight of it, M_{P2VP}, is high enough: $M_{\mathrm{P2VP}} > M^*_{\mathrm{P2VP}}$, where M^*_{P2VP} is a critical molecular weight for which a rough estimate can be given in the following way. The interaction energy of the PS-P2VP block copolymer in the PS matrix is given by

$$F=\chi\int \phi_{\mathrm{PS}}\phi_{\mathrm{P2VP}}\frac{d^3r}{v}\ , \tag{1}$$

where ϕ_{PS} and ϕ_{P2VP} are the volume fractions of PS and P2VP and v is the volume per "link." Incompressibility is assumed:

$$\phi_{\mathrm{PS}}+\phi_{\mathrm{P2VP}}=1\ . \tag{2}$$

Equation (1) can be rewritten as

$$F=\mathrm{const}-\chi\int \phi^2\frac{d^3r}{v}\ , \tag{3}$$

where $\phi\equiv\phi_{\mathrm{P2VP}}(r)$, and the constant is given by $\mathrm{const}=\chi\int\phi_{\mathrm{P2VP}}(d^3r/v)=\chi\Gamma_{\mathrm{P2VP}}$ (Γ_{P2VP} is the total number of P2VP "links" in the system). This constant will be omitted below. Furthermore, the volume per link is given by $v\approx 160$ Å^3.

Next, the free energy per P2VP block in the coiled state will be compared with that of the collapsed state. In the coiled state the fraction of P2VP-P2VP interactions is very small and can be neglected. Therefore, the free energy of P2VP blocks in the coiled state (F_{coil}) is

$$F_{\mathrm{coil}}=0\ . \tag{4}$$

The free energy of a collapsed P2VP block can be roughly estimated as

$$F_{\mathrm{coll}}=F_v+F_s=-\chi N_{\mathrm{P2VP}}+4\pi R^2\gamma\ , \tag{5}$$

where $F_v=-\chi\int\phi_{\mathrm{P2VP}}(d^3r/v)=-\chi V_{\mathrm{P2VP}}/v=-\chi N_{\mathrm{P2VP}}$ is the volume interaction contribution (V_{P2VP} is the volume of the block) and $F_s=4\pi R^2\gamma$ is the surface contribution. Here

$$\gamma=\frac{a}{v}\chi^{1/2} \tag{6}$$

is the tension of the PS-P2VP interface,[19] $a\equiv 1/\sqrt{6}$ of the statistical segment, i.e., $a\sim 2.7$ Å and R is the radius of the P2VP globule,

$$\frac{4\pi}{3}R^3=vN_{\mathrm{P2VP}}\ . \tag{7}$$

Using Eqs. (4)–(7) we find that the collapsed state is more favorable ($F_{\mathrm{coll}}<F_{\mathrm{coil}}$) if $N_{\mathrm{P2VP}}>N^*_{\mathrm{P2VP}}$,

$$N^*_{\mathrm{P2VP}}\approx\frac{13}{\chi^{3/2}}\approx 400\ . \tag{8}$$

The corresponding molecular weight is $M^*_{\mathrm{P2VP}}\approx 40\times 10^3$. Thus P2VP blocks of isolated PS-P2VP diblock copolymers with $M_{\mathrm{P2VP}}\approx 10^5$ must be in a collapsed state. Next we proceed towards micelles.

Formation of micelles

At first it may seem plausible that the micelles observed were formed during the annealing processes in the homopolymer matrix. This is probably not the case, however, for the following reasons.

(1) Small micelles can be readily formed in a blend during annealing because when two collapsed P2VP blocks meet they will unify and form one micelle without any difficulty. Therefore after a short time there will hardly be any "free" copolymer chains left in the blend: they will all be incorporated into small micelles. These micelles can then grow in size by fusion. However, this process assumes that the P2VP cores of two micelles must come close to each other (see Fig. 3) implying a deformation of micellar coronas. The activation energy of this

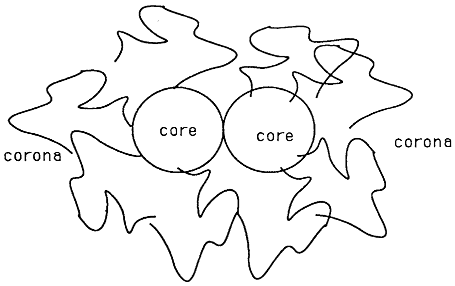

FIG. 3. Confluence of two micelles.

deformation can be estimated using the results of Ref. 20. From this it follows that the activation barrier for micellar fusion is probably too large to obtain micelles with a diameter of ~ 50 nm in a reasonable time span inside the highly viscous polymer matrix. However, this argument ceases to be valid in solutions, where the viscosity is much lower.

(2) Micelles were observed even for zero annealing time. This is demonstrated in Fig. 4(a), where a TEM picture of an unannealed 2 wt % 75–95 k block copolymer in 190 k homopolymer matrix is shown. Clearly, micelles, although admittedly of a somewhat smaller size than those in Figs. 1 and 2, are already present.

(3) Micelles of PS-P2VP diblock copolymers in toluene have been observed before at even lower concentration than employed here by dynamic light scattering.[17]

These facts demonstrate that the micelles must have been formed already in the solution before spin casting. As indicated, small micelles can readily be formed and they can increase their size by fusion which is more effective in solution than in the blend, since the viscosity of the solvent (toluene) is much smaller than that of the blend. To develop a feeling for the time scales involved in the formation of larger micelles by fusion of smaller ones, the kinetics of this process will be considered in some detail. Experimentally, the original solution consisted of a 3 wt % of the homopolymer PS in toluene together with 6×10^{-4}, 4.5×10^{-3}, and 9×10^{-3} wt % block copolymer for the three different block copolymer concentrations employed (Table I). The viscosity of the solution for all these systems is of the order of that for pure toluene:

$$\eta \sim 10^{-2}\ \mathrm{P}\ . \tag{9}$$

Toluene is a good solvent for PS and a bad solvent for P2VP, therefore, as discussed before, a micelle consists of a dense P2VP core and a swollen PS corona. An estimate of the final size of the (largest) micelles, containing Q block copolymers, that can appear in the solution after a time t_0 can be given provided the simplifying assumption that it is determined by fusion of two nearly equal micelles consisting of $Q/2$ chains each, is made:

$$Q/2+Q/2\rightarrow Q\ . \tag{9a}$$

The probability that a given $Q/2$ micelle will undergo this reaction can be estimated as

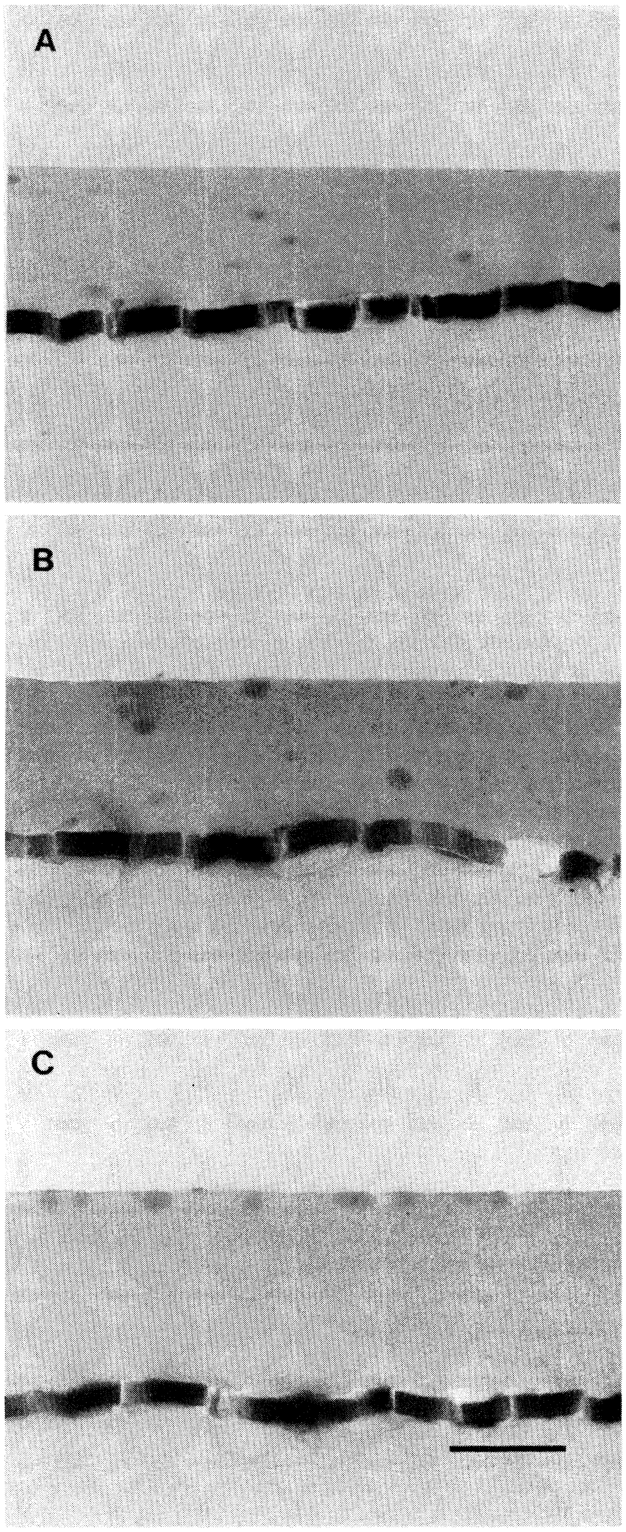

FIG. 4. Cross-sectional view of a 2 wt % 75–95 k dPS-P2VP in 190 k hPS, as cast (a), after 2 h annealing (b) and 33 h annealing (c) at 180°C. The migration of micelles towards the surface is obvious. (a) also demonstrates that the micelles must have been present in the solution. (Bar indicates 300 nm.)

$$p \sim \frac{t_0}{\tau_0} \phi_0 e^{-U} , \tag{10}$$

where τ_0 is the characteristic "micellar" time, i.e., the time of its displacement over a distance of the order of its diameter, D:

$$\phi_0^{2\ \mathrm{wt}\,\%} \approx 6\times 10^{-4} , \quad \phi_0^{15\ \mathrm{wt}\,\%} \approx 4.5\times 10^{-3} ,$$
$$\phi_0^{30\ \mathrm{wt}\,\%} \approx 9\times 10^{-3} \tag{11}$$

are the volume fraction of micelles (= volume fraction of block copolymers) for each specific block copolymer wt % and U is the activation energy (the height of the energy barrier due to deformation of micellar coronas, see Fig. 3).

The time τ_0 can be estimated as

$$\tau_0 \sim \frac{D^2}{D_m} , \tag{12}$$

where

$$D_m \sim \frac{kT}{3\pi\eta D} \tag{13}$$

is the diffusion constant of a micelle (which is estimated using Stokes equation).

For a given Q, the barrier U should depend on the degree of swelling of the corona: the larger the degree of swelling the higher the barrier. There is no experimental evidence for this degree of welling at present and we do not want to speculate on this point here. Asymmetric fusion, $Q_1+Q_2 \rightarrow Q$, is another important possibility, which has to be considered seriously since a detailed comparison between Figs. 4(a), 4(b), and 4(c) shows that the micelles grow somewhat during the first part of the annealing time. Since, roughly, the barrier $U \sim Q_1 Q_2$, its value can be decreased appreciably when a smaller micelle "reacts" with a larger one. In order to consider this possibility, the distribution of micellar sizes has to be taken into account. A more detailed study employing computer simulations will check this point. At this stage it seems that this is the type of phenomenon observed in Fig. 4; at any rate, no indications for symmetric fusion are present.

The elastic energy (energy of elongation of dPS blocks) of a micellar corona is[21]

$$W_Q \approx \frac{Qx^2}{12}(1-f^{1/3}) , \tag{14}$$

where

$$x = \frac{D}{2N_{\mathrm{P2VP}}^{1/2} a} \tag{15}$$

is the ratio of the core radius $R = D/2$ to the "Gaussian" radius of gyration of P2VP blocks; $f = N_{\mathrm{P2VP}}/(N_{\mathrm{PS}} + N_{\mathrm{P2VP}})$ is the block copolymer composition. Assuming that the core is densely filled by P2VP blocks, we get

$$Q = \frac{\pi}{6} \frac{D^3}{N_{\mathrm{P2VP}} v} \tag{16}$$

so that $x \propto Q^{1/3}$. The elastic corona energy in the critical (activation) state (see Fig. 3) should be nearly the same as for the final micelle. Thus, with this assumption, the activation energy is

$$U \approx W_Q - 2W_{Q/2} \approx 0.031 Qx^2(1-f^{1/3}) . \tag{17}$$

The typical size of the largest micelles that will appear in the solution during the "annealing time" t_0 can be estimated using the condition

$$p \sim 1 , \tag{18}$$

where p is the probability of "reaction" (9a). Using Eqs. (10), (13), and (15)–(18), the "final" size for $t_0 \sim 1$ week for the 75–102 k block copolymer ($\phi_0 \approx 4.5\times 10^{-3}$, i.e., the lowest concentration) is found to be $D \approx 49$ nm. For the 75–95 k block copolymer ($\phi_0 \approx 6\times 10^{-4}$), $D \approx 47$ nm for $t_0 \sim 1$ month. Both estimates are in fair agreement with the experimental results.

Having discussed the origin of the micelles we continue with a more detailed look at the dynamics of structure formation by diffusion of micelles. After spin coating, the micelles should be randomly distributed in the PS-homopolymer film. Since the incompatibility parameter $\chi N_{2\mathrm{VP}} \approx 100$ is large, nearly all block copolymers should be gathered in micelles. The behavior of these micelles during annealing is then governed by their interaction and diffusion.

Interaction of micelles

As was shown in Ref. 20, micelles must attract each other at large distances, provided that the homopolymer molecular weight is large enough: $N_h > N_h^*$, where N_h^* for spherical micelles is[21]

$$N_h^* \approx 0.66(1-f)^{4/3} N(\chi N)^{-1/9} f^{-2/9}$$
$$\times (1-f^{1/3})^{-2/3}(1.74-f^{1/3})^{2/9} . \tag{19}$$

For $N = N_{\mathrm{PS}} + N_{\mathrm{P2VP}} = 670+970 = 1640$ and $f = N_{\mathrm{P2VP}}/N = 0.59$ we find $N_h^* = 686$ for the 75–102 k block copolymer case. Homopolymers of much higher molecular weight, $N_h \approx 1900$, were used in the experiments. Therefore micelles should really attract each other. The maximum energy of attraction U_{attr} can be estimated using the results of Ref. 20 [cf. Eq. (A2)]:

$$U_{\mathrm{attr}} \approx 0.82 \frac{Da^2}{v} , \tag{20}$$

where D is the core diameter, $D \approx 50$ nm; thus

$$U_{\mathrm{attr}} \approx 18 . \tag{21}$$

This energy is quite enough to ensure irreversible bonding of micelles after they come into contact. The same type of estimation gives a similar or larger energy of attraction of a micelle to the surface of the film or to the interface. As a consequence, micelles will form three-dimensionally (3D) ordered closely-packed clusters at the free surface and at the interface provided they have enough time to diffuse to these surfaces and provided they did not meet each other before reaching the surfaces. Figure 5 shows the morphology of a 30 wt %

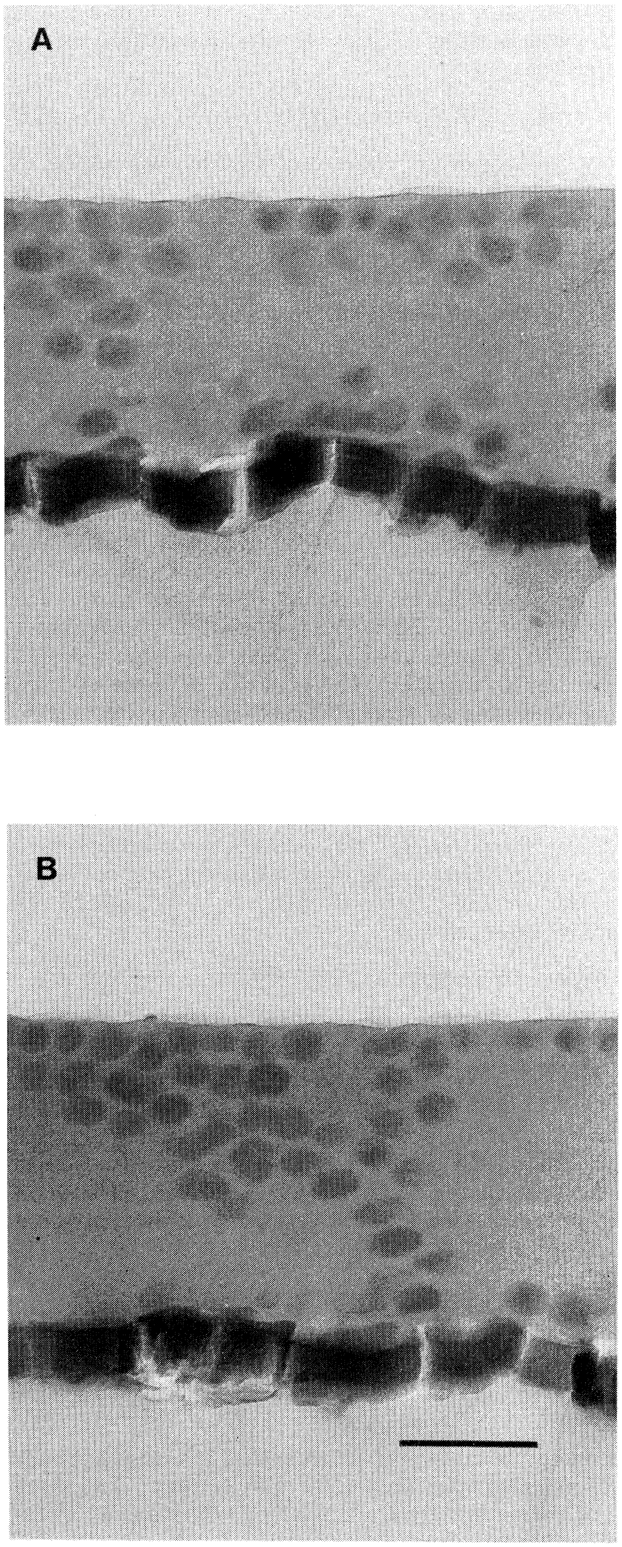

FIG. 5. Cross-sectional view of a 30 wt % 75–102 k dPS-P2VP in 190 k hPS. (a) Annealed for 48 h at 180 °C. Cluster formation at surface as well as interface. (b) Same procedure, junction between cluster at surface and interface. (Bar indicates 200 nm.)

75–102 k block copolymer in a 190 k homopolymer matrix, annealed for 48 h. The micelles have indeed formed a densely packed 3D structure at the free surface and at the polymer-silicon interface, indicating that the conditions set out have been met. Next we will take a closer look at the diffusion process itself.

Diffusion of micelles

The homopolymer matrix is highly entangled, since $N_h/N_e = 1860/200 \gg 1$. The characteristic pore size of the entangled network is

$$d_e \sim \sqrt{6} a N_e^{1/2} \approx 9 \text{ nm} , \tag{22}$$

that is, the pores are much smaller than the core size of the micelles ($D \sim 50$ nm). This implies that the micelles can hardly penetrate the pores and thus their diffusion must be governed by the entanglement relaxation time. In order to estimate the diffusion constant of a micelle Stokes equation is used:

$$D_m \sim \frac{kT}{3\pi\eta D} \tag{23}$$

with η being the viscosity of the homopolymer melt, $\eta \sim 10^{5.665}$ P (Ref. 22) for $T = 180\,^{\circ}\mathrm{C}$ and $M_h = 186 \times 10^3$. The typical displacement of a micelle during annealing time t_a is

$$L_t \sim (2 D_m t_a)^{1/2} . \tag{24}$$

This means $L_t \sim 300$ nm when $t_a = 48$ h. At low concentrations, the typical "free" displacement of a micelle (i.e., the displacement before it will contact with another micelle) is

$$L_\phi \sim \frac{D}{\phi_c^{1/2}} , \tag{25}$$

where ϕ_c is the volume fraction of block copolymer in the blend. This means $L_\phi = 350$ nm for the 2 wt % 75–95 k block copolymer case. The same expression gives for the 15 and 30 wt % 75–102 k block copolymer case $L_\phi = 130$ nm and $L_\phi = 90$ nm, which should be considered as an upper limit. We are now in a position to analyze the final structure of the film as a function of annealing time.

Film structure after annealing

The micellar distribution depends on the film thickness H. If the thickness of the film is not too large, so that $H/2 \le L_t$, i.e., the largest initial distance between a micelle and the free surface (interface) is smaller than the typical displacement during annealing time, most of the micelles will come to the surfaces and form partially ordered clusters. The average number of layers n near the surface is determined by the total film thickness and copolymer volume fraction:

$$n \sim \frac{H\phi_c}{2D} . \tag{26}$$

Only a mirror part of the micelles will remain in the bulk after annealing. This is clearly demonstrated experimentally in Figs. 2 and 4(c). However, when the film is thick, $H \gg L_t$, most of the micelles will not have enough time to reach the surface or interface and remain in the bulk as isolated particles or as pairs. A pair of micelles will be formed if two micelles contact each other by chance during diffusion; it is stable since the "bonding" energy is large. The probability of pair formation is quite appreciable since $L_\phi \approx L_t$ [see Eqs. (24) and (25)]. Yet, for the low-concentration (2 wt %) case large clusters of micelles are not likely to appear in the bulk since cluster formation requires a longer time $L_t \gg L_\phi$. Micelles initially close at the surface or interface might "fall" on these surfaces during annealing and form clusters, the averaged number of layers being

$$n \sim \frac{L_t \phi_c}{D} . \tag{27}$$

Again this picture is in qualitative agreement with the experimental results shown in Figs. 4 and 5. In Fig. 6 a micrograph is shown for the same system annealed for 5.1 days at 180 °C. From this figure it is clear that the micelles have formed a more closely packed structure. This may well lead to a hexagonal packing at complete equilibrium. Besides this closer packing at the polymer-air interface a row of micelles is formed at the polymer-silicon interface. Although not clearly visible, this row is stabilized over the whole area by a row of surface micelles in the form of hemispheres.

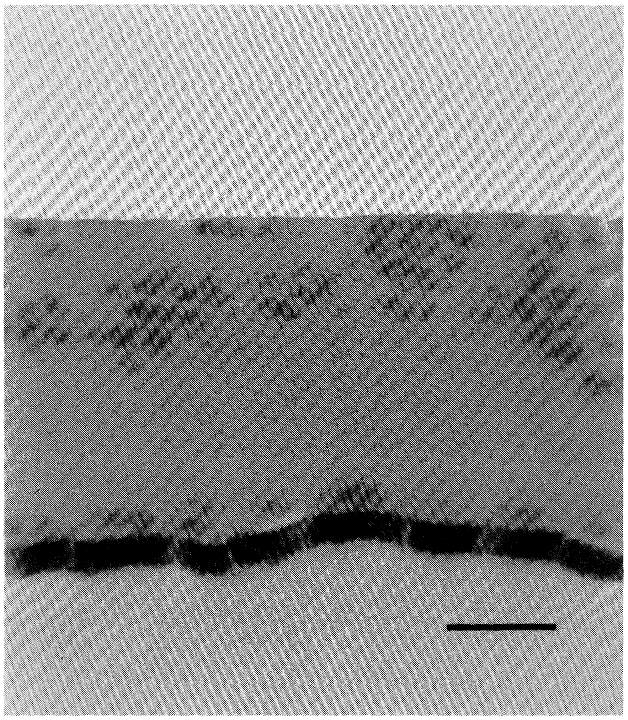

FIG. 6. Cross-sectional view of same sample as Fig. 5. Annealing time 5.1 days at 180 °C. Formation of a micellar layer at interface is clearly visible. (Bar indicates 300 nm.)

SUMMARY

In this paper, the structure formation by micelles consisting of block copolymers is reported. The micelles tend to segregate to the free surface and the polymer-silicon interface during annealing above the glass transition temperatures. At sufficiently high concentration of block copolymer the micelles form 3D structures. The experimental observations agree very well with the recently proposed theories of interaction and diffusion of micelles in a homopolymer matrix. Furthermore, it is shown that the micelles must have been formed already in the solutions used to prepare the polymer films.

ACKNOWLEDGMENTS

Discussions with Professor H. Benoit during the course of this work are gratefully acknowledged. R. Gill and J. Wildeman are acknowledged for the synthesis of the polymers used. Furthermore, the experimental assistance by H. Kuipers and S. Bakker from the physics department is well appreciated.

---

*Permanent address: Physics Department, Moscow State University, Moscow 117234, Russia.

†Author to whom correspondence should be addressed.

[1] R. J. Roe and W. C. Zin, Macromolecules **17**, 189 (1984).

[2] T. Hashimoto, H. Tanaka, and H. Hasegawa, Macromolecules **23**, 4378 (1990).

[3] H. Tanaka, H. Hasegawa, and T. Hashimoto, Macromolecules **24**, 240 (1991).

[4] K. I. Winey, E. L. Thomas, and L. J. Fetters, J. Chem. Phys. **95**, 9367 (1991).

[5] C. V. Berney, P. L. Cheng, and R. E. Cohen, Macromolecules **21**, 2235 (1988).

[6] G. Hadziioannou and A. Skoulios, Macromolecules **15**, 271 (1982).

[7] K. M. Hong and J. Noolandi, Macromolecules **16**, 1083 (1983).

[8] M. D. Whitmore and J. Noolandi, Macromolecules **18**, 2486 (1985).

[9] J. Noolandi, Ber. Bunsen-Ges. Phys. Chem. **89**, 1147 (1985).

[10] M. Olvera de la Cruz and I. C. Sanchez, Macromolecules **20**, 440 (1987).

[11] L. Leibler and P. Pincus, Macromolecules **17**, 2922 (1984).

[12] A. M. Mayes and M. Olvera de la Cruz, Macromolecules **21**, 2543 (1988).

[13] P. Gaillard, M. Ossenbach-Sauter, and G. Reiss, Makromol. Chem. **1**, 771 (1980).

[14] S. H. Anastasiadis, I. Gancarz, and J. T. Koberstein, Macromolecules **22**, 1449 (1989).

[15] R. Fayt, R. Jerome, and Ph. Teyssie, J. Polymer Sci. Polymer Phys. Ed. **20**, 2209 (1982).

[16] K. R. Shull, E. J. Kramer, G. Hadziioannou, and W. Tang,

Macromolecules **23**, 4780 (1990).

[17] W. T. Tang, G. Hadziioannou, P. M. Cotts, and B. A. Smith, Polymer Preprints Am. Chem. Soc. **27**, 107 (1986).

[18] K. R. Shull, K. I. Winey, E. J. Thomas, and E. J. Kramer, Macromolecules **24**, 2748 (1991).

[19] E. Helfand, Macromolecules **17**, 552 (1975).

[20] A. N. Semenov, Macromolecules **25**, 4967 (1992).

[21] A. N. Semenov, Macromolecules **26**, 2273 (1993).

[22] G. B. McKenna, G. Hadziioannou, P. Lutz, G. Hild, C. Strazielle, C. Straupe, P. Rempp, and A. J. Kovacs, Macromolecules **20**, 498 (1987).

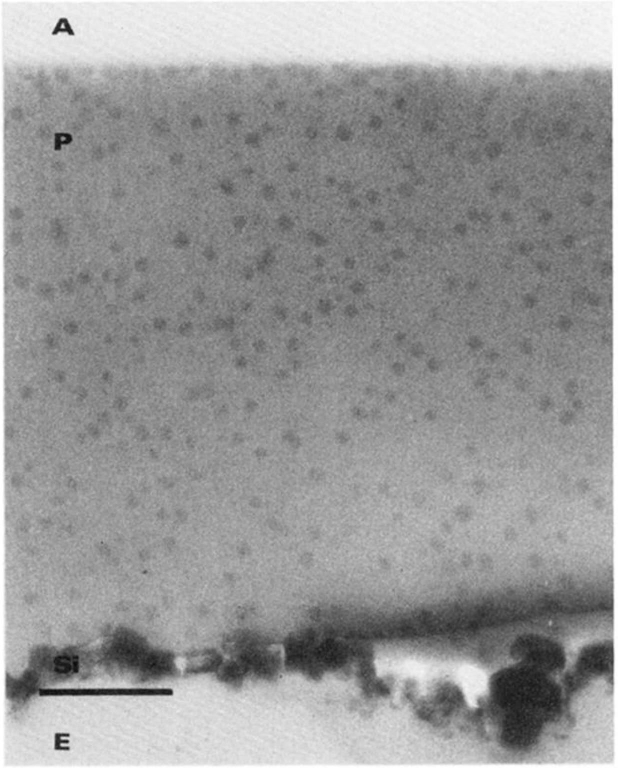

FIG. 1. Cross-sectional view of a 15 wt% 75–102 k dPS-P2VP in 190 k hPS. Annealing time is 52 h at 180 °C. Layer thickness is 2000 nm. The micellar surface layer is clearly visible. (Bar indicates 400 nm, A = air, P = polymer layer, Si = silicon layer, E = epon substrate.)

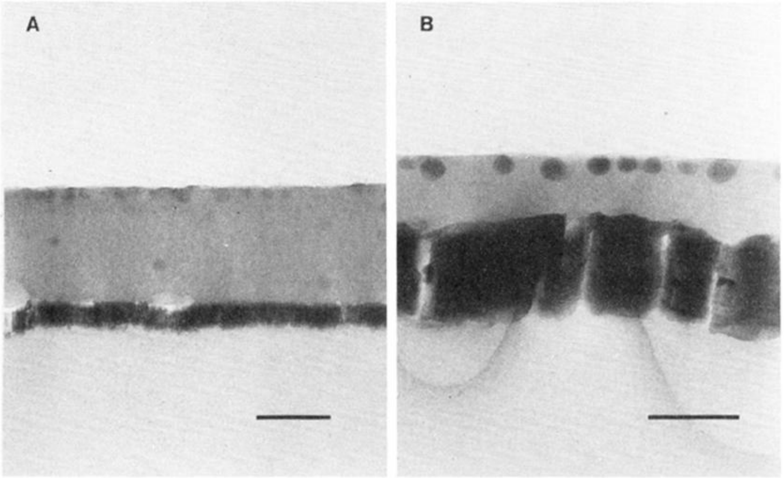

FIG. 2. (a) Cross-sectional view of a 15 wt % 75–102 k dPS-P2VP in 190 k hPS. Annealing time is 52 h at 180 °C. Layer thickness is 500 nm. (Bar indicates 300 nm.) (b) Same sample, but smaller layer thickness of approximately 150 nm (annealing time 48 h). (Bar indicates 200 nm.) Both cases show clear surface segregation.

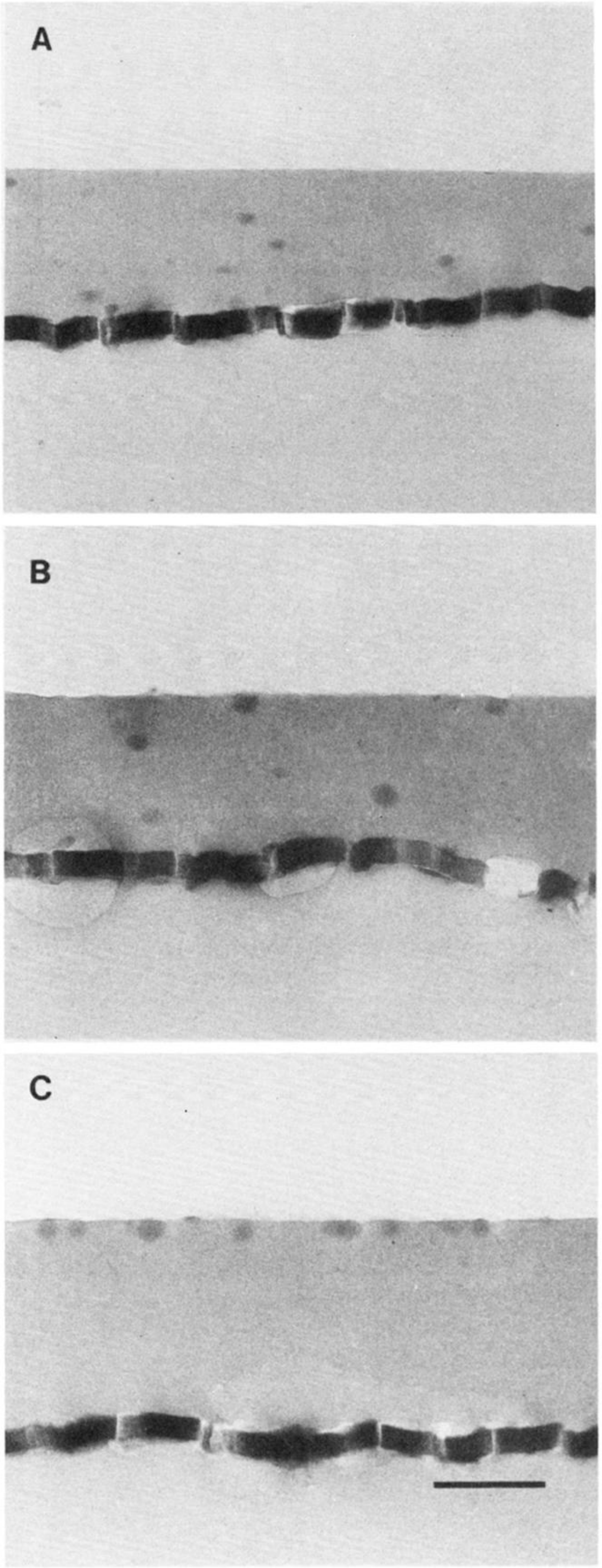

FIG. 4. Cross-sectional view of a 2 wt % 75–95 k dPS-P2VP in 190 k hPS, as cast (a), after 2 h annealing (b) and 33 h annealing (c) at 180°C. The migration of micelles towards the surface is obvious. (a) also demonstrates that the micelles must have been present in the solution. (Bar indicates 300 nm.)

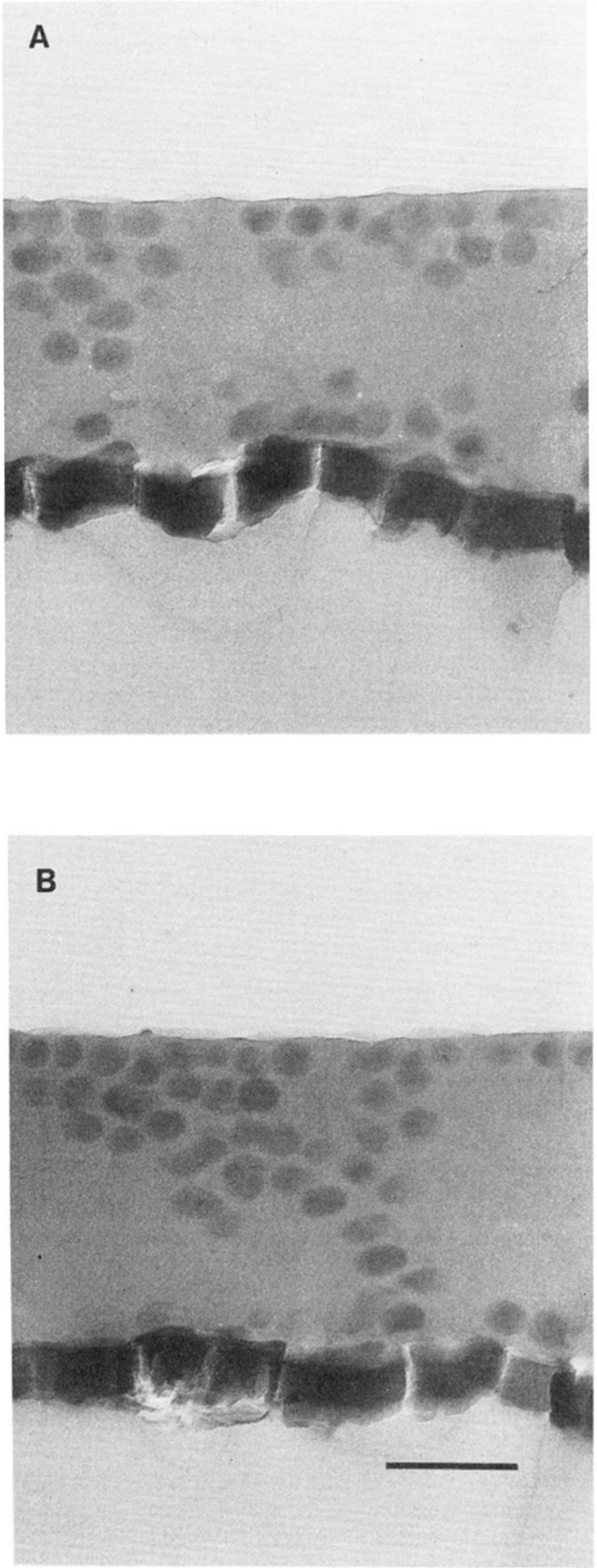

FIG. 5. Cross-sectional view of a 30 wt % 75–102 k dPS-P2VP in 190 k hPS. (a) Annealed for 48 h at 180 °C. Cluster formation at surface as well as interface. (b) Same procedure, junction between cluster at surface and interface. (Bar indicates 200 nm.)

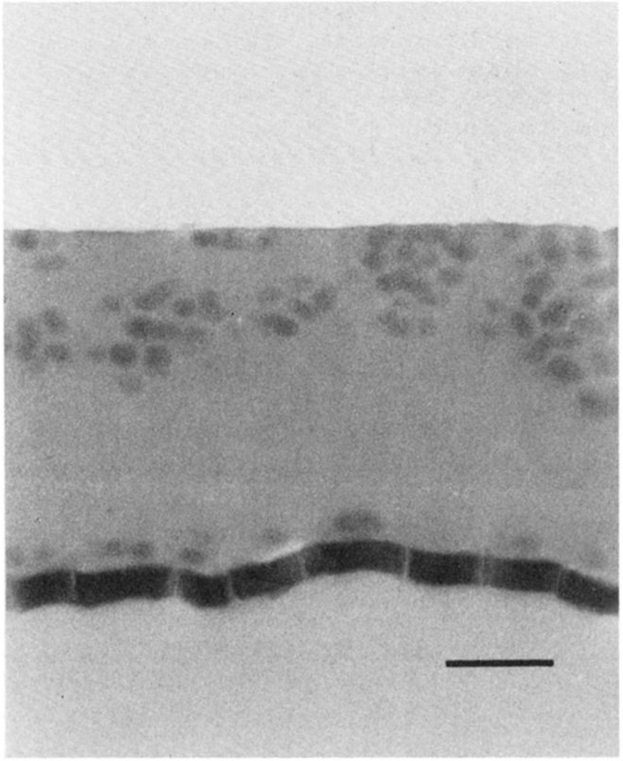

FIG. 6. Cross-sectional view of same sample as Fig. 5. Annealing time 5.1 days at 180 °C. Formation of a micellar layer at interface is clearly visible. (Bar indicates 300 nm.)