# Novel, ordered, microphase-separated structure of the blends of a core–shell-type polymer microsphere and AB diblock copolymers with a lamellar morphology

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*(Received 19 April 1993; revised 2 August 1993)*

Blending of a poly(4-vinylpyridine) core–polystyrene shell polymer microsphere with lamellar poly(styrene-*b*-4-vinylpyridine) block copolymers gave novel, microphase-separated films which were examined in two dimensions using transmission electron microscopy (TEM). The TEM results showed that the poly(styrene-*b*-4-vinylpyridine) block copolymer was arranged as a honeycomb-like bilayer around the ordered microspheres.

**(Keywords: core–shell microsphere; binary blend; AB diblock copolymer)**

## INTRODUCTION

Core–shell-type polymer microspheres can be synthesized by crosslinking the spherical microdomains of microphase-separated films of AB-type diblock copolymers[1–7]. The core–shell-type polymer microspheres obtained by this method have very narrow size distributions and are composed of crosslinked cores and shells of linear chains, each of which is connected to the surface of the core by one end. It is possible to introduce colloidal silver into the core part of the microsphere[8].

These core–shell microspheres have a similar structure to the $(AB)_n$-type star block copolymers. According to de la Cruz and Sanchez[9], the $(AB)_n$-type star block copolymers in solution form single-polymer micelles with the core–shell structure when the arm number is larger than 20. With much larger arm numbers[10], the formation of crystalline arrays of $(AB)_n$-type star block copolymers can be expected near the overlap concentration $C^*$. Owing to the structural similarity between the core–shell-type polymer microspheres and the $(AB)_n$-type star block copolymers, the formation of crystalline arrays of core–shell-type polymer microspheres can also be expected. If control of the arrangement of microspheres in two and three dimensions is possible, the core–shell-type microspheres should be very useful materials. In light of this supposition, the ordered arrangement of the poly(4-vinylpyridine) core–polystyrene shell polymer microspheres was investigated by transmission electron microscopy (TEM) in the solid state[11,12].

The poly(4-vinylpyridine) core–polystyrene shell microspheres form a hexagonally packed monolayer in two dimensions and a film with a face-centred cubic packing in three dimensions[11]. In the two-dimensional case, the distances between the centres of the microspheres increase with decreasing polymer concentration in the cast solution, while the ordered structure is maintained[12]. These well-ordered arrangements of core–shell polymer microspheres can be explained in terms of the formation of microsphere macrolattices in the solvent near $C^*$ upon concentration of the microsphere solution.

On the other hand, the core–shell polymer microspheres can be considered as the smallest units in the microphase-separated structure. The properties of the microsphere in the solvent are governed not by the core but by the shell chains in a good solvent for the shell. So, the core–shell polymer microsphere can be thought of as one spherical molecule with many branches in the solvent. Thus, core–shell polymer microspheres can be used as composite materials in blends for the introduction of spherical microdomains into a matrix. Core–shell polymer microspheres synthesized by emulsion polymerization are used industrially. However, the effect of the ordering of the microspheres on the morphology of the blend has not been investigated.

In our investigations, core–shell polymer microspheres easily form ordered arrangements. Thus, ordering of the microspheres was expected in blends of microspheres with lamellar block copolymers. The purpose of this study was to investigate the morphologies of blends of a well-ordered core–shell microsphere with lamellar, AB-type block copolymers. The poly(4-vinylpyridine) core–polystyrene shell polymer microsphere synthesized previously was used because of its tendency towards hexagonal packing in two dimensions and face-centred cubic packing in three dimensions. Lamellar poly(styrene-*b*-4-vinylpyridine)s (P(S-*b*-4VP)s), synthesized by anionic polymerization, were chosen as the AB diblock copolymer blend materials. The morphology of the binary blend was investigated by TEM for various weight fractions of the AB diblock copolymer in the blend.

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0032-3861/94/08/1580–06

**Table 1** Characteristics of the P(S-*b*-4VP) diblock copolymers

| Sample | $10^{-4}\ \bar{M}_n$[a] PS | $10^{-4}\ \bar{M}_n$[a] Block | PS content[b] (mol%) | Morphology Shape[c] | Morphology $D$[d] (nm) |
|---|---|---|---|---|---|
| AB-100 | 1.6 | 2.4 | 68 | Lamellar | 10.8 |
| AB-200 | 5.6 | 7.6 | 73 | Lamellar | 24.0 |
| AB05 | 8.0 | 11.1 | 72 | Spherical 4VP | 48.4 |

[a] Number-average molecular weights determined from g.p.c. and n.m.r. data
[b] Estimated from $^1$H n.m.r. data
[c] Estimated by TEM for films cast from TCE solutions for AB-100 and AB05 and from a benzene/chloroform (1:1 v/v) mixture for AB-200
[d] Domain size of the P4VP phase, diameter of the sphere, or thickness of the lamella

**Table 2** Characteristics of the P4VP core–PS shell polymer microsphere

| Sample | Diameter (nm) 4VP core[a] | Diameter (nm) Internal[a] | Diameter (nm) External[b] | Crosslink density[c] (mol%) | $C^*$[d] (wt%) |
|---|---|---|---|---|---|
| AB05-M | 49.7 | 77.8 | 180.5 | 20.8 | 4.4 |

[a] Determined by TEM in the solid state
[b] Measured by dynamic light scattering in benzene at 20°C
[c] Measured by Volhard titration
[d] Overlap concentration in benzene calculated from the external diameter in benzene

## EXPERIMENTAL

### *Materials*

*Poly(styrene-*b*-4-vinylpyridine) diblock copolymers.* P(S-*b*-4VP) diblock copolymers were synthesized by the usual sequential anionic addition polymerization using n-butyllithium as the initiator in tetrahydrofuran (THF) at −78°C[13]. The number-average molecular weight ($\bar{M}_n$) of the polystyrene (PS) precursor was determined by gel permeation chromatography (g.p.c.) on a Tosoh HLC-8020 with THF as the eluent at 38°C through a TSK gel $GMH_{XL}$ column at a flow rate of 1.0 ml min$^{-1}$. The weight-average molecular weights ($\bar{M}_w$) of the block copolymers were determined by combining the g.p.c. data with viscometric data from studies in THF at 38°C. The styrene contents in the block copolymers were determined by $^1$H n.m.r. spectroscopy on a 60 MHz Hitachi R-24B spectrometer. The results are listed in *Table 1*.

*Core–shell polymer microsphere.* A P(S-*b*-4VP) diblock copolymer (AB05; $\bar{M}_n = 1.1 \times 10^5$, 4-vinylpyridine content of 28 mol%) film 120 μm thick was cast from a 0.05 g ml$^{-1}$ 1,1,2-trichloroethane (TCE) solution onto a Teflon sheet. The cast film was allowed to dry for four days at room temperature. Crosslinking of the segregated 4-vinylpyridine (4VP) chains in the poly(4-vinylpyridine) (P4VP) microdomains was achieved by quaternization with 1,4-dibromobutane (DBB) vapour at 80°C over 24 h. The details concerning the crosslinking and characterization of the microsphere are given elsewhere[11]. Some characteristics of the P4VP core–PS shell microsphere are shown in *Table 2*.

### *Blends of the core–shell microsphere with block copolymers*

The blends of the AB-type diblock copolymers with the P4VP core–PS shell microsphere were prepared from benzene solution at 1 wt% and 5 wt% polymer concentrations.

### *Morphology examinations*

Ultrathin specimens of the block copolymers and the blend were prepared for TEM by allowing a drop of a benzene solution on a copper grid coated with a carbon substrate to evaporate very slowly at room temperature. The specimens were stained with $OsO_4$ over four days at room temperature. The morphology examinations were performed with a Hitachi H-500 transmission electron microscope at 75 kV.

## RESULTS AND DISCUSSION

### *AB-type diblock copolymers and the microsphere*

Some characteristics of the P(S-*b*-4VP) diblock copolymers are shown in *Table 1*. The block copolymer AB05 for the microsphere has been synthesized previously[11]. The block copolymers for the blends, AB-100 and AB-200, were synthesized for the first time in this study.

The number-average molecular weights ($\bar{M}_n$) of the PS precursors of AB-100 and AB-200 were $1.6 \times 10^4$ and $5.6 \times 10^4$, respectively, and both of these values are smaller than the $\bar{M}_n$ of the PS chains in the shell of the microsphere (PS of AB05; $\bar{M}_n = 8.0 \times 10^4$). The P4VP contents were 32 and 27 mol% for AB-100 and AB-200, respectively. It is known that the lamellar morphology can be obtained for P(S-*b*-4VP) diblock copolymers with 4VP contents in the range 28–68 mol% when cast from TCE or a benzene/chloroform mixture[14]. Thus, the lamellar morphology was expected for AB-100 and AB-200.

*Figure 1* shows the transmission electron micrographs of AB-100 and AB-200 cast from TCE and a

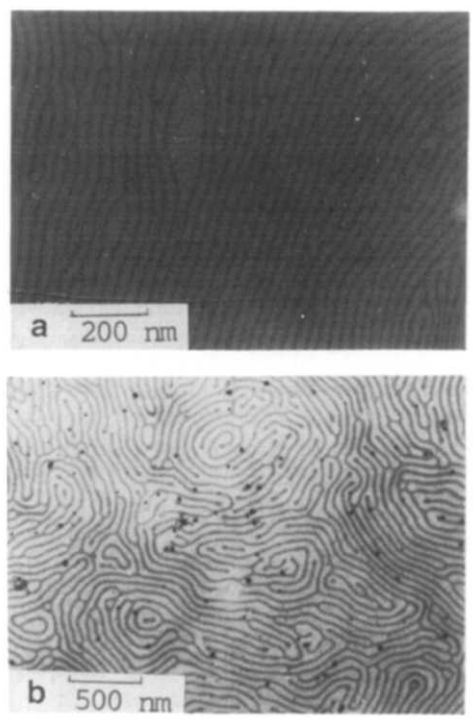


**Figure 1** TEM micrographs of P(S-*b*-4VP) diblock copolymers stained with $OsO_4$: (a) AB-100; (b) AB-200

benzene/chloroform (1:1 v/v) mixture, respectively, onto a carbon substrate. The dark regions in the micrographs are the segregated P4VP chains selectively stained with $OsO_4$. For both AB-100 and AB-200, the lamellar structure was observed. For AB-100, the lamellar thicknesses were 10.8 nm and 20 nm for the P4VP and PS phases, respectively. For AB-200, the lamellar thicknesses were 24 nm (P4VP) and 32 nm (PS). Consequently, two types of lamellar P(S-*b*-4VP) diblock copolymers with different molecular weights were obtained.

Some characteristics and TEM micrographs of the microsphere AB05-M, synthesized by the crosslinking of AB05, are shown in *Table 2* and *Figure 2*, respectively. The spherical shapes can be observed in the TEM of a sample cast from a dilute solution at a polymer concentration of 0.05 wt% and shadowed with Cr at an angle of 20° (*Figure 2a*). It was confirmed that one P4VP core (the dark region stained with DBB) exists in each microsphere (*Figure 2b*). When the TEM specimen was cast at a 1 wt% polymer concentration, the microspheres formed a monolayer with hexagonal packing in two dimensions (*Figure 2c*).

As described in a previous paper[11], the microsphere AB05-M has a soluble PS shell and a crosslinked P4VP core 49.7 nm in diameter. The P4VP core is tightly crosslinked (crosslink density of 20.8 mol%) and the structure of the microsphere is fixed in a good solvent for both P4VP and PS. From the P4VP core diameter in the solid state, the arm number was calculated as 1400. The overlap concentration $C^*$ of the microsphere in benzene, above which the microsphere will form a macrolattice[10], was calculated as 4.4 wt% from the equation[15]

$$C^* = M_{total}/N_A d^3$$

where $M_{total}$, $N_A$ and $d$ are respectively the total molecular weight of the microsphere, Avogadro's number and the external diameter of the microsphere as measured by dynamic light scattering in solution. To investigate the effect of $C^*$ on the macrolattice formation of the microsphere in solution, the microsphere and AB diblock copolymers were blended above and below $C^*$.

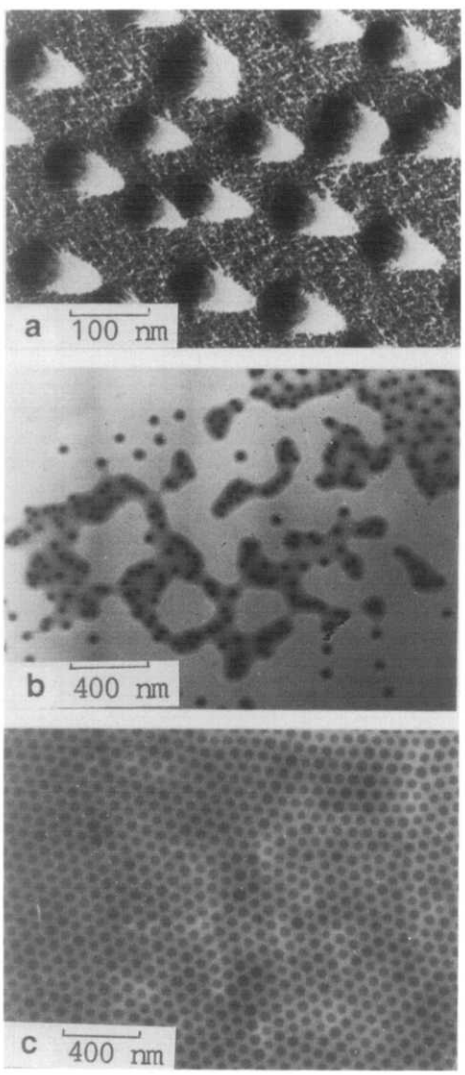


**Figure 2** TEM micrographs of AB05 microspheres cast from benzene: (a) at a 0.05 wt% polymer concentration and shadowed with Cr at an angle of 20°; (b) at a 0.05 wt% polymer concentration; (c) at a 1 wt% polymer concentration

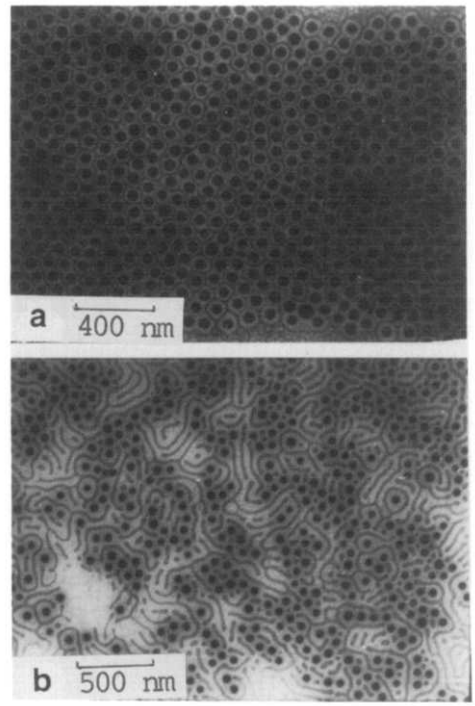


**Figure 3** TEM micrographs of the binary blends of diblock copolymers with the microsphere at $r=0.5$: (a) with AB-100; (b) with AB-200

*Binary blends of the microsphere with AB-type diblock copolymers*

As described above, the $C^*$ of the AB05-M microsphere is 4.4 wt%. First, in order to sidestep the effect of polymer concentration on the morphology, the microsphere AB05-M was blended with AB-100 or AB-200 below $C^*$ (1 wt%). The weight fraction $r$ of the AB diblock copolymer in the blend was 0.5.

*Figure 3* shows the two-dimensional TEM micrographs of the binary blends of AB05-M with AB-100 and AB-200 cast onto carbon substrates and stained with $OsO_4$. For both blends, spheres and lines of P4VP (the dark regions) are observed.

The diameter of the spherical microdomain was 48 nm for both samples. The widths of the dark lines were 11 nm and 22 nm for the blends with AB-100 and AB-200, respectively. The diameter of the spherical microdomain agrees well with the diameter of the P4VP core of the microsphere. The widths of the lines also agree well with

the lamellar thicknesses of the block copolymers. From these values, it was concluded that the spherical microdomains were the P4VP cores of the microspheres and the P4VP lines were one lamellar phase (a bilayer) formed from the P4VP of the AB-type diblock copolymer in the blend.

Detailed observation of the blend of AB05-M with AB-100 (*Figure 3a*) reveals an interesting and novel morphology. This morphology can be described as follows. The P4VP cores of the microspheres form a regular structure, and the P4VP bilayer surrounds each microsphere with a honeycomb-like structure similar to a cell wall. Similar structures have been observed for ABC triblock copolymers[16]. However, the morphology of the ABC triblock copolymer is cylindrical rather than spherical. Also, our case is observed in the monolayer. Thus, the morphology in this study is novel.

On the other hand, in the blend of the microsphere with AB-200 (*Figure 3b*), no specific ordered structure can be observed. This suggests that the $\bar{M}_n$ of the block copolymer affects the morphology. Indeed, it is well known that the molecular weight of the polymer has an effect on the morphology[17,18]. However, to remove the problem of the chain conformation, more information is required, because the conformation of the PS shell of the microsphere changes gradually from the surface to the core[19]. Thus, a detailed investigation of the effect of the molecular weight of the AB diblock copolymer on the morphology was not carried out in this study.

It was concluded that the novel and interesting morphology was obtained by blending the microsphere with the AB-type diblock copolymer.

*The weight fraction of AB diblock copolymer in the blend*

In order to investigate the arrangement of the chains in the novel ordered structure, the novel morphology was investigated in detail by varying the weight fraction $r$ of AB-100 in the blend from 0.33 to 0.66 (*Figure 4*).

*Figure 4* shows that the P4VP spherical core microdomains and the P4VP linear microdomains of AB-100 did not separate at any of the weight fractions studied. The diameter of the P4VP core and the thickness of the P4VP layer did not change with the weight fraction.

When $r$ was 0.33, the P4VP layer surrounded some microspheres in groups. The average number of microspheres in one domain surrounded by the P4VP layer ($K$) was 2.48. This indicates that the amount of AB-100 was insufficient to surround each microsphere separately. However, this structure is strange. As described above, the effect of the P4VP core on the microsphere can be neglected. Thus, the microsphere can be thought of as a PS microsphere.

In general, the morphologies of blends of A homopolymer and lamellar AB diblock copolymer can be divided into two cases: (i) the AB diblock copolymer forms a spherical microdomain of B in the blend when the AB diblock copolymer and A homopolymer are mixed homogeneously and the composition of the B block in the blend is less than 25 vol%; or (ii) the AB diblock copolymer forms the onion-ring structure in the blend[20]. In this study, neither the usual onion-ring structure nor the spherical microdomain of P4VP from AB-100 was observed at $r=0.33$.

For $r=0.5$, as described above, most microspheres were surrounded by a P4VP layer similar to a cell wall. $K$ was 1.08 for $r=0.5$, and each microsphere was surrounded with a P4VP layer. For $r=0.66$ (*Figure 4c*), all

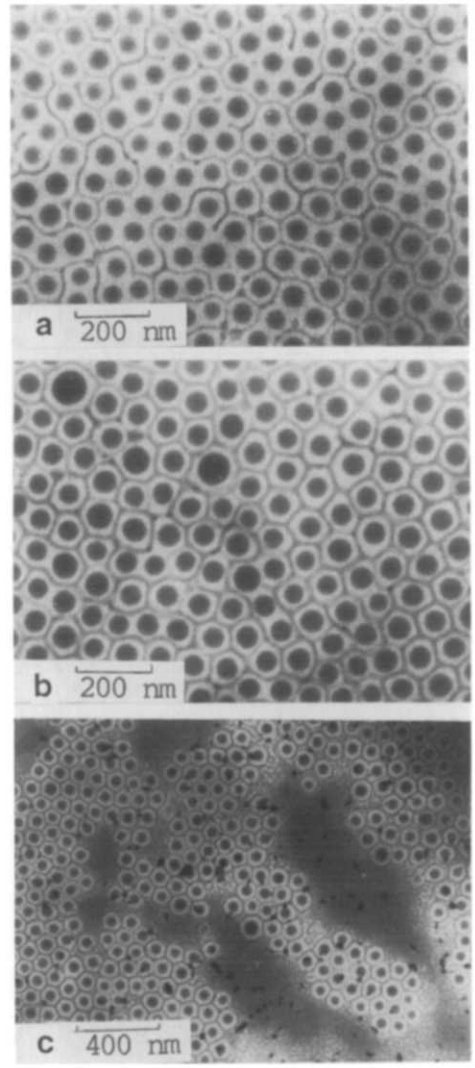


**Figure 4** TEM micrographs of the binary blend AB05-M/AB-100 on a carbon substrate (polymer concentration 1 wt%): (a) $r=0.33$; (b) $r=0.5$; (c) $r=0.66$

microspheres were surrounded with an AB-100 P4VP layer, and the P4VP spherical microdomains were locally ordered in a honeycomb-like P4VP layer. However, wide, dark regions of P4VP were observed. These regions were horizontally oriented lamellar microdomains of AB-100, resulting in a minimization of the air/polymer surface tension[21]. It was confirmed that the AB-100 was in excess to the microsphere AB05-M at $r=0.66$.

In order to investigate the packing state of the microspheres, the radial distribution function $g(D)$ of the P4VP spherical microdomain was measured and is shown in *Figure 5*. As shown in *Figure 2c*, the microsphere AB05-M itself packs hexagonally. When all spheres are packed hexagonally, the peaks must appear at $D=b, \sqrt{3}b$ and $2b$ for the first, second and third generations, respectively. Narrow peaks appear at $D=79.9$ nm, 139.4 nm and 159.7 nm, and the ratio of $D$ for these peaks is $1:\sqrt{3}:2$ (*Figure 5a*).

At $r=0.33$ (*Figure 5b*), the three peaks are wide. This indicates that the packing structure of the microspheres was less ordered. For the blend at $r=0.5$ (*Figure 5c*), three narrow peaks appear. The $D$ values for the peaks are 88 nm, 158 nm and 178 nm, and the ratio of $D$ for these peaks is 1:1.80:2.02. Thus, the microspheres were packed hexagonally, even though AB-100 was blended

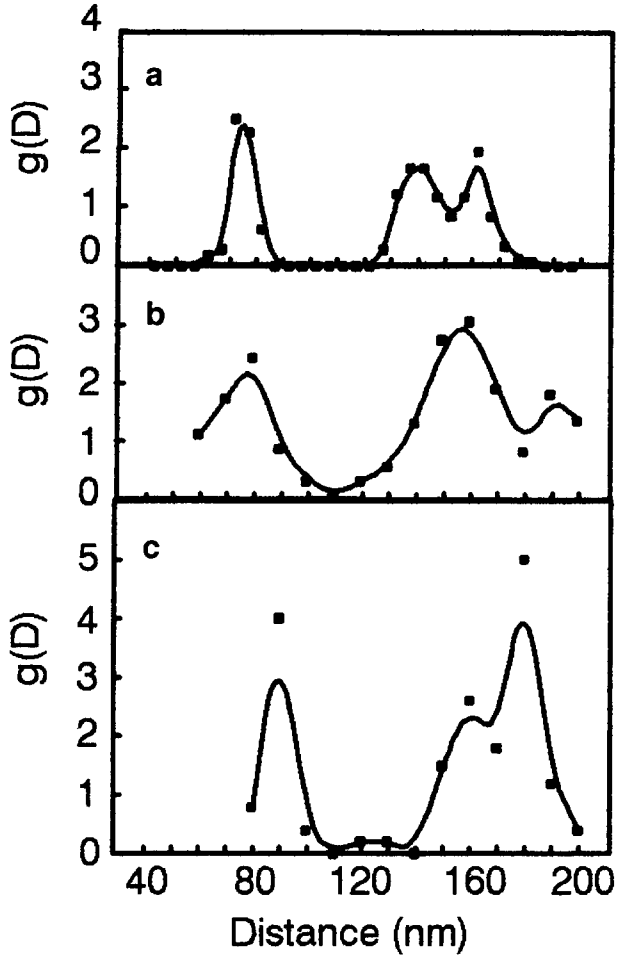


**Figure 5** Distribution functions of the microspheres of the AB05-M/AB-100 blend: (a) microsphere AB05-M; (b) binary blend at $r=0.33$; (c) binary blend at $r=0.5$

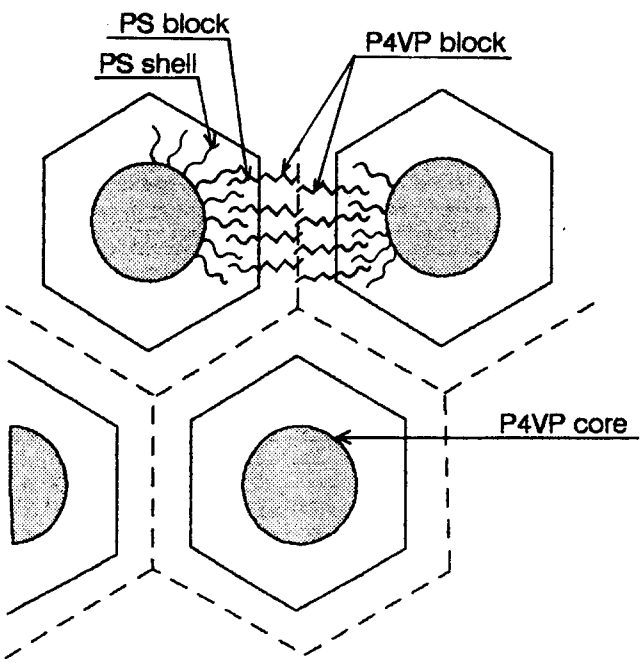


**Figure 6** Schematic of the two-dimensional chain conformations of the block copolymer and the microsphere in the binary blend

into the system. For the first generation, the $D$ value of the blend was 8 nm larger than that of AB05-M itself. This 8 nm approximately agrees with the thickness of the P4VP lamellar phase (10 nm). The increase in $D$ through blending was due to the presence of one P4VP lamellar phase between the microspheres. Consequently, it was concluded that the novel morphology observed for the AB05-M/AB-100 blend with $r=0.5$ had a completely ordered structure with hexagonal packing of the microspheres in two dimensions.

From a detailed observation of *Figure 4b*, it was found that the cell of the microsphere was hexagonal, and the AB-type diblock copolymer formed a bilayer between the microspheres. The hexagonal surrounding with a P4VP bilayer indicates that the unit cell of the microsphere was hexagonal in two dimensions. Thomas *et al.*[22] and Birshtein and Zhulina[23] have proposed that the unit cell of the spherical microdomain of the microphase-separated film is hexagonal in two dimensions.

From these results, the chain arrangement in this novel morphology with a honeycomb-like structure can be proposed, as shown in *Figure 6* schematically. The cell of the microsphere has a hexagonal surface, and the AB-type diblock copolymer forms a bilayer between the microspheres. From the schematic rearrangement of the chains (*Figure 4*), the $r$ value for a completely ordered morphology was calculated as 0.46. This value agrees well with the value $r=0.5$, at which the blend showed a completely ordered morphology. Thus, it was concluded that the core–shell polymer microsphere and the AB diblock copolymer were arranged as shown in *Figure 6*.

*Effect of C* on the formation of the ordered structure*

The ordered structure could be obtained by blending AB05-M and AB-100 at a concentration of 1 wt%. As described in a previous paper, this ordered structure would result in the formation of a macrolattice of microspheres near the overlap concentration $C^*$. It was supposed that the ordered superstructure shown in *Figure 4* was the result of macrolattice formation in the solution near $C^*$.

To investigate the effect of the ordering of the microsphere on the ordered microphase separation of the blend, AB05-M and AB-100 were blended at 5 wt%, i.e. at a concentration higher than $C^*$ (4.4 wt%), at which ordering of the microspheres would occur. The blended film was annealed for three days at 120°C.

*Figure 7* shows the TEM micrograph of the blend of AB05-M and AB-100 obtained from a 5 wt% solution with $r=0.5$. In spite of the annealing of the blend, macrophase separation of the lamellar phases and spherical microdomains was observed, and the ordered structure could not be obtained. This shows that the

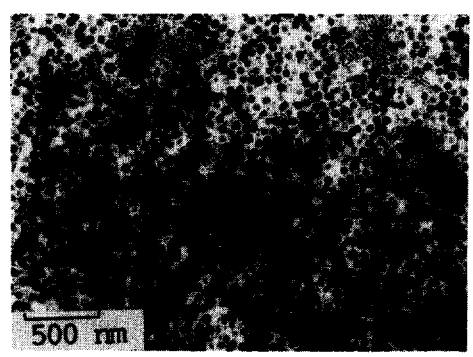


**Figure 7** TEM micrograph of the binary blend of AB-100 and the microsphere blended at a 5 wt% polymer concentration

ordered superstructure of the blend was formed below the overlap concentration of the microsphere and maintained during the drying process. Consequently, it was concluded that to form the ordered morphology of the blend of the microsphere and the AB diblock copolymer, the blending must be carried out at a concentration below the overlap concentration of the microsphere.

## CONCLUSIONS

Blending of the P4VP core–PS shell polymer microsphere with lamellar P(S-*b*-4VP) diblock copolymers was carried out, and the morphology of the microphase-separated blend in two dimensions on a carbon substrate was investigated by TEM.

For both blends of the microsphere with the diblock copolymers, the diameter of the P4VP spherical core microdomain and the lamellar thicknesses of the P4VP phases of the AB diblock copolymers were not changed by blending. The P4VP sequences of the block copolymers did not segregate with the P4VP core of the microsphere. When the $\bar{M}_n$ of the block copolymer was $7.6 \times 10^4$ (AB-200), macrophase separation of the core–shell polymer microsphere and the block copolymer was observed. When the $\bar{M}_n$ of the block copolymer was $2.4 \times 10^4$ (AB-100), uniform solubilization of the microsphere and the block copolymer occurred. Subsequently, the novel structure was obtained for the blend of AB05-M and AB-100.

At a weight fraction $r = 0.5$ for AB-100 in the blend, a honeycomb-like structure for the P4VP phase was observed in the PS matrix, and one spherical P4VP microdomain (P4VP core of the microsphere) was present in each hexagon. By measuring the distribution function of the P4VP cores in such a novel structure, it was found that the P4VP cores were ordered hexagonally on the carbon substrate. The AB diblock copolymer AB-100 formed a bilayer between the microspheres. When the polymers were blended above the overlap concentration of the microsphere, the ordered structure did not occur. This suggests that the ordered structure of the blend was formed below the overlap concentration of the microsphere and maintained during the drying process.

## ACKNOWLEDGEMENTS

This work was supported by Shorai Kagaku Gijutus Zaidan. The authors thank Mr R. Oki and Mr T. Chiba of the Faculty of Engineering, Tokyo Institute of Technology, Tokyo, for the TEM sample preparations.

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