Morphology control using core–shell type polymer microsphere

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Polymer microsphere composed of monodispersed poly(4-vinyl pyridine) core–polystyrene (PS) shell [poly(4-vinyl pyridine) 28 mol%; number-average molecular weight ($\bar{M}_n$) of shell chain, 8.0×10^4; arm number, 1400] was blended with poly(styrene-*b*-2-vinyl pyridine) diblock copolymer [poly(2-vinyl pyridine) 30 mol%; $\bar{M}_n$ of PS $= 2.0 \times 10^4$], poly(styrene-*b*-isoprene) diblock copolymer (polyisoprene 28 mol%; $\bar{M}_n$ of PS $= 2.6 \times 10^4$) or poly(styrene-*b*-4-vinyl pyridine) diblock copolymer [poly(4-vinyl pyridine) 17 mol%; $\bar{M}_n$ of PS $= 3.9 \times 10^5$]. The morphology of the blend was investigated by transmission electron microscopy. When $\bar{M}_n$ of the diblock copolymer was less than 3.2×10^4, a well-ordered arrangement of the microsphere and the spherical microdomains of block copolymer in the PS matrix was observed in two dimensions. The degree of order of the spherical microdomain was estimated using the radial distribution function.

(Keywords: morphology; binary blend; ordering)

INTRODUCTION

It has been reported that core–shell type polymer microsphere can be synthesized by crosslinking the spherical microdomain of microphase-separated film of diblock copolymer[1–4]. Poly(4-vinyl pyridine) (P4VP) core–polystyrene (PS) shell type polymer microsphere (AB05M) was synthesized by crosslinking the P4VP spherical microdomain of microphase-separated film of P(S-*b*-4VP) diblock copolymer (AB05; $\bar{M}_n = 11.0 \times 10^4$, P4VP 28 mol%) with dibromobutan (DBB)[5]. The diameter distribution ($\bar{D}_w/\bar{D}_n$) of the microsphere was monodispersed (< 1.03) and the core–shell structure was confirmed by transmission electron microscopy (TEM).

There was no specific regular structure of the P4VP spherical microdomain in the microphase-separated film of AB05. However, the AB05M microsphere formed a specific regular structure. In two dimensions (on the carbon substrate), the AB05M microsphere formed a well aligned hexagonal monolayer. In three dimensions (in the bulk of the film), the AB05M microsphere showed face-centred cubic packing[5], although the spherical microdomain of the block copolymer generally had body-centred cubic alignment[6]. This good ordering of the microsphere was explained by the structural similarity of the microsphere to star polymers[5].

The AB05M microsphere was blended with poly(styrene-*b*-2-vinyl pyridine) [P(S-*b*-2VP)] AB diblock copolymer, which formed a lamellar structure on its own[7]. As PS was chosen as the common sequence, the AB block copolymer formed vesicles around the microsphere with hexagonal ordering. Consequently, a well-ordered novel structure with three phases in two dimensions was obtained by blending. *Figure 1* shows the schematic structure of the previous novel morphology, which resulted in the ordered arrangement of the microsphere. From these results, it was suggested that microphase separation with three phases would be obtained by blending the microsphere and the block copolymer, although the block copolymer does not form a lamellar structure. Microphase separation with three phases can be obtained for an ABC triblock copolymer. The morphology of an ABC triblock copolymer has been suggested by Riess *et al.*[8]. An interesting morphology of microphase separation with three phases has been reported for ABC triblock copolymers[9–11]. On the other hand, Ishizu *et al.*[12] reported microphase separation with three phases in the blend system of AB micelles and AC diblock copolymers. In that blend, two spherical microdomains were placed at random. The AB05M microsphere used in this work forms an ordered structure easily on its own. Thus, the ordering of three phases is expected in this case.

The purpose of the work presented here was to control the morphology of microphase separation by blending the microsphere and block copolymer, which forms spherical microdomain in a matrix on its own. The AB05M microsphere was used because of its good ordering behaviour. PS was chosen as the common sequence for the microsphere and block copolymer. The morphology of the blend film was investigated by TEM.

EXPERIMENTAL

Materials

Core–shell type polymer microsphere[5]. P(S-*b*-4VP) diblock copolymer [number-average molecular weight ($\bar{M}_n$) $= 1.1 \times 10^5$; 4VP $= 28$ mol%] film, 120 μm thick, was cast from 0.05 g ml^{-1} 1,1,2-trichloroethane (TCE) solution on a Teflon sheet. The film was dried slowly for

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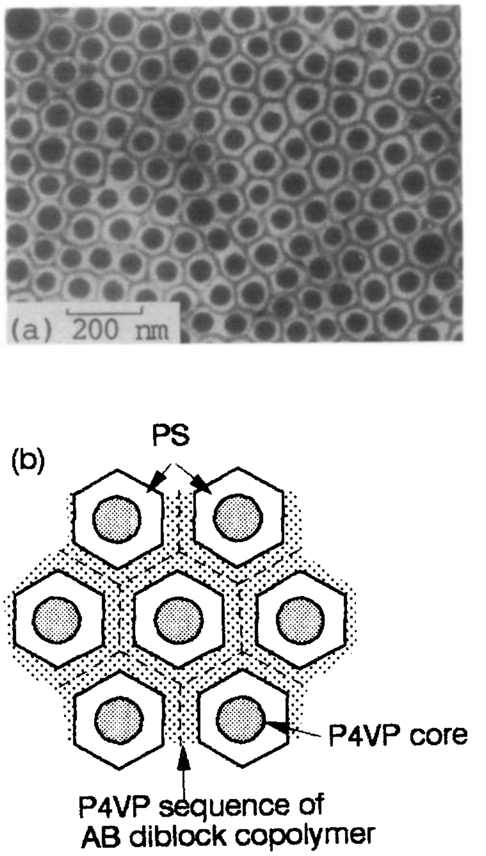

Figure 1 Microphase-separated structure of the blend of AB05M and AB100: (a) TEM micrograph; (b) schematic arrangement

Table 1 Characteristics of the P4VP core–PS shell type microsphere

	DQ[a] (mol%)	CD[b] (mol%)	Diameter (nm)[c] Core	External	f^d	M_{total}^e ($\times 10^{-8}$)
AB05M[f]	43.9	20.8	49.7	77.8	1400	1.5

[a] Degree of quaternization of P4VP core
[b] Crosslink density of PV4P core
[c] Estimated by TEM
[d] Aggregation number of block copolymer AB05 in a microsphere
[e] Molecular weight of a microsphere
[f] Microsphere of AB05 (see *Table 2*)

4 days at room temperature. Crosslinking of the segregated 4VP chains in the P4VP microdomains was carried out by quaternization with DBB vapour at 80°C for 24 h. Details concerning the crosslinking and characterization of microsphere have been given previously[5]. *Table 1* shows the characteristics of P4VP core–PS shell.

AB diblock copolymer. P(S-*b*-2VP) and P(S-*b*-4VP) were synthesized by the usual sequential anionic addition polymerization[13,14] using n-butyl lithium as an initiator in tetrahydrofuran (THF) at −78°C, poly(styrene-*b*-isoprene) [P(S-*b*-IP)] was synthesized in benzene[2] at 5°C. The $\bar{M}_n$ of precursor PS was determined with a Tosoh HLC-8020 g.p.c. with THF as eluent at 38°C, a TSK-gel GMHXL column and a flow rate of 1.0 ml min^{-1}. Weight-average molecular weight ($\bar{M}_w$) of block copolymer was determined by combining g.p.c. data and viscometric data in THF at 38°C. The styrene content in the block copolymer was determined by ^{1}H n.m.r. spectrometry (60 Hz, Hitachi R-24B n.m.r. spectrometer). The characteristics are listed in *Table 2.*

Blend of core–shell microsphere and block copolymer

Blending of the AB type diblock copolymers and the P4VP core–PS shell type microsphere was carried out from benzene solution at a polymer concentration of 1 wt%. The blend solution was dried slowly for 4 days.

Morphological observations

An ultrathin specimen of the polymer for TEM observation was prepared by placing a drop of 1 wt% benzene solution on a copper grid coated with a carbon substrate, and evaporating the solvent as slowly as possible at room temperature. The specimens were stained with OsO_4 for 4 days at room temperature. The morphological results were obtained using a Hitachi H-500 TEM at 75 kV.

RESULTS AND DISCUSSION

Characteristics of core–shell type microsphere

Well characterized P4VP core–PS shell type polymer microsphere (AB05M) was employed in this work. *Figures 2a* and *b* show TEM micrographs of the inner texture of AB05M stained with OsO_4 and the external shape shadowed with chromium at an angle of 20°, respectively. The diameters of the particle and P4VP core of AB05M were 77.8 and 49.7 nm, respectively. It was found from dynamic light scattering measurements that the external diameter of this microsphere swollen in benzene was 180.5 nm. The overlap concentration[15], C^*, of AB05M in benzene was calculated to be 4.4 wt% from the external diameter in benzene and the total molecular weight of the microsphere.

Characteristics of block copolymers

In order to investigate the effect of chemical species of segments and molecular weight on the morphology of binary blends, three samples of block copolymers were synthesized. *Table 2* shows that P(S-*b*-2VP) and P(S-*b*-IP) had similar $\bar{M}_n$ values. The molecular weight dispersity of all block copolymers was narrow. The expected morphology was of spheres in a PS matrix for the diblock copolymers by themselves, because the PS content of all block copolymers was greater than 70 mol%.

Figure 3 shows the transmission electron micrographs of the cross-section of the AB diblock copolymers.

Table 2 Characteristics of diblock copolymers

Sample no.[a]	$\bar{M}_n$ ($\times 10^{-4}$) PS[b]	Block copolymer	PS content[c] (mol%)	Diameter[d] (nm)
SV	2.0	2.8	70.0	18
SI	2.3	3.2	72.5	10
AB01	39.0	47.0	83	68
AB05	8.0	11.0	72	48.4

[a] SV, poly(styrene-*b*-2-vinyl pyridine); SI, poly(styrene-*b*-isoprene); AB, poly(styrene-*b*-4-vinyl pyridine)
[b] Determined by g.p.c.
[c] Estimated by ^{1}H n.m.r.
[d] Diameter of spherical microdomain observed by TEM

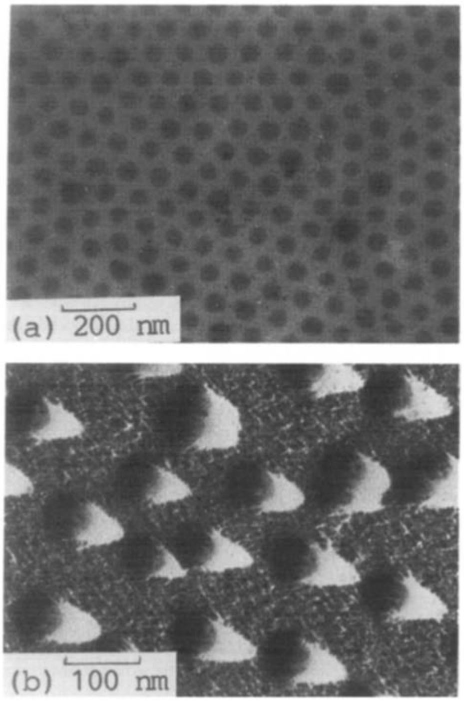

Figure 2 TEM micrographs of AB05M microsphere: (a) stained with OsO_4; (b) shadowed with Cr at an angle of 20°

The microphase-separated structures of all films were spheres in a PS matrix. The diameters of the spherical microdomains were approximately 10, 18 and 68 nm for SI, SV and AB01, respectively (see *Table 2* for polymer identification). The dispersities of the diameter for all films were less than 1.05.

Blending microsphere and block copolymer

The three block copolymers were blended with the AB05M microsphere. For the star block copolymer, the macrolattice formation of the microdomain, which will lead to the ordering of the microdomain, is expected[16] at about C^*. To form the macrolattice with microsphere on drying the blend solution, the polymer concentration of the blending solution was at 1 wt%, i.e. below C^*.

Figure 4 shows TEM micrographs of the blend film of AB05M with SV, SI and AB01 with blending ratio [diblock copolymer]/[AB05M] = 1/1 (wt/wt) on carbon substrate (in two dimensions). The dark regions in the micrographs are P4VP, P2VP and PIP microdomains selectively stained with OsO_4. In all micrographs, two types of spherical microdomain with different diameters were observed.

When the $\bar{M}_n$ of the block copolymer (SI) was smaller than the PS shell of the microsphere (*Figure 4a*), an interesting morphology was observed. Six small

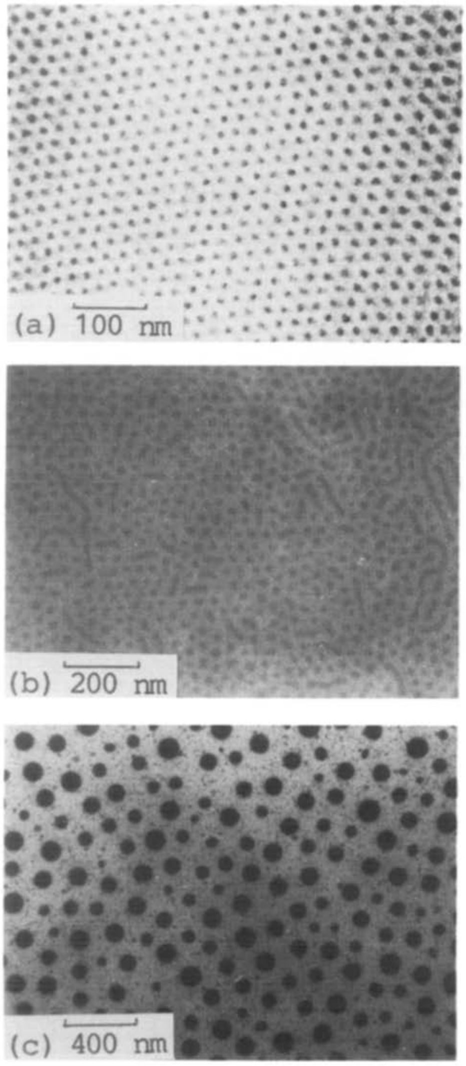

Figure 3 TEM micrographs of the blend of block copolymer and microsphere: (a) SI; (b) SV; (c) AB01

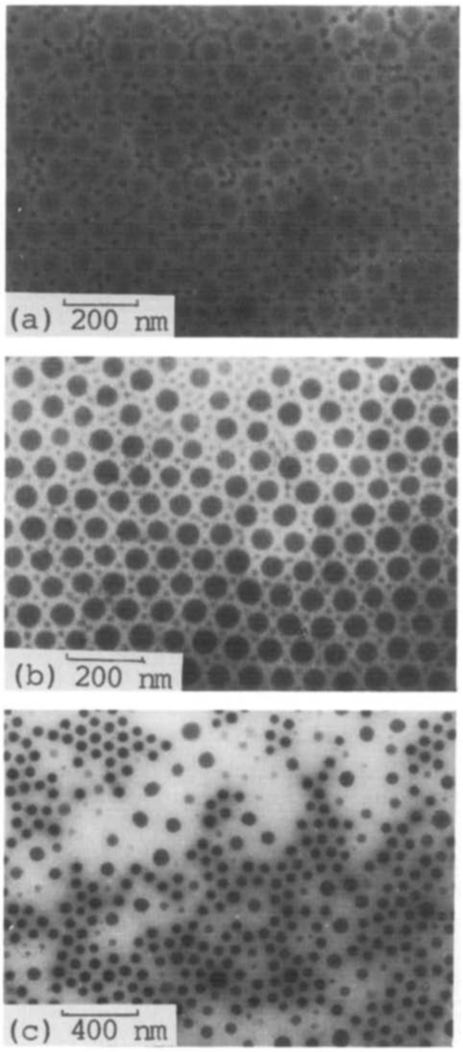

Figure 4 TEM micrographs of the blend of AB05M microsphere with (a) SI, (b) SV, (c) AB01

spherical microdomains were arranged around each large spherical microdomain. The large spherical microdomains were hexagonally packed in two dimensions. The diameters of spherical microdomains were approximately 10 and 50 nm. These diameters agreed well with those of the PI spherical microdomain and P4VP core by themselves. Moreover, the small spheres were darker than the large spheres. Since PI is stained with OsO_4 more easily than P4VP, it was concluded that the small spherical microdomain was PI and the large one was the P4VP core.

A similar morphology was observed for blending AB05M and SV (*Figure 4b*). In this micrograph, all spheres were stained homogeneously. There were two types of spheres in the matrix. It was determined that the large spheres were P4VP cores and the small spheres were composed of P2VP from SV diblock copolymer, because their diameters, 18 and 50 nm, were approximately the same as those of the P2VP spherical microdomain of SV and P4VP core of AB05M, respectively.

For the block copolymer AB01 (*Figure 4c*), two types of spherical microdomain were observed. The spherical microdomains with diameters of 50 and 70 nm correspond to the P4VP core of the microsphere and the spherical microdomain of AB01 diblock copolymer. Consequently, it was concluded that the diameters of the spherical microdomains of AB diblock copolymer and P4VP core did not change by blending with any diblock copolymer.

When AB01 was blended, no regular structure could be observed. The P4VP core and P4VP spherical microdomain of AB01 exist at random. SV and SI, which formed an ordered structure upon blending, have similar $\bar{M}_n$ values to AB100 ($\bar{M}_n = 2.4 \times 10^4$) which formed a novel ordered structure by blending with AB05M. The $\bar{M}_n$ of AB01 was six times larger than that of the PS shell of the AB05M microsphere. This suggests that the super-ordering structure formation depends not on the chemical species but on the $\bar{M}_n$ of the AB diblock copolymer. There are two possible explanations for the ordered arrangement of the spherical microdomain when blended with AB diblock copolymer with small $\bar{M}_n$.

First, the short chain can be dispersed easily in the polymer matrix. Noolandi and Hong[17] calculated the conformation of the corona chain of polymer micelles in the blend of polymer micelle and homopolymer. When $\bar{M}_n$ of the homopolymer was smaller than that of the corona chain, the corona chain was expanded in the system and the homopolymer chain could be dispersed in the corona chain. The $\bar{M}_n$ of block copolymer was much smaller than that of the PS shell, thus the diblock copolymer dispersed between the microspheres and formed the spherical microdomain.

On the other hand, regarding the packing of the microspheres, the size factor should be taken into account. At equilibrium, microspheres should prefer to retain their symmetric spherical shape, thus leaving gaps filled by block copolymer chains. The second explanation proposed is that the smaller microdomain, owing to the smaller $\bar{M}_n$ of the block copolymer, would be comfortable for the size problem (leaving gaps). In order to investigate the size problem, the packing pattern of microdomains was investigated.

Degree of order of the microdomains

In order to investigate the packing pattern, the degree of order of the microdomains was investigated using the radial distribution function *gnm*(*r*) from sphere *n* to sphere *m*.

Figure 5 shows the radial distribution functions of the blend of AB05M and SV in two dimensions. For the radial distribution function, 1 and 2 indicate the P4VP core and the P2VP spherical microdomain, respectively. From TEM observation, the arrangement of the spheres was assumed to be as follows: the P4VP cores were packed hexagonally, and six P2VP spheres were arranged on top of the hexagons surrounding the P4VP spheres. *Figure 6* shows the schematic arrangement of the spheres in this blend system.

First, the radial distribution function between P4VP cores in the blend, *g*11(*r*), was estimated. As reported

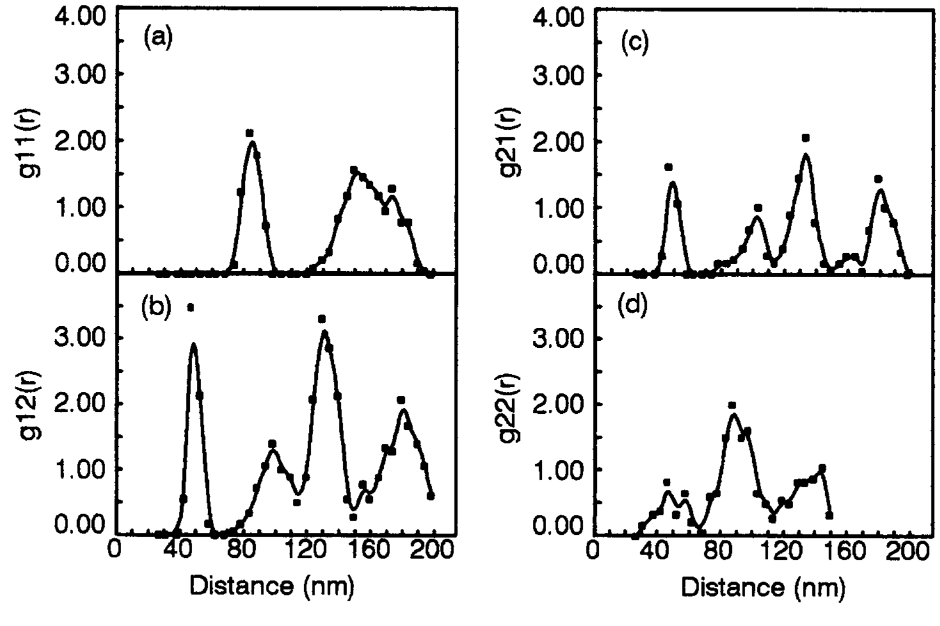

Figure 5 Radial distribution functions: (a) between the P4VP cores of the microsphere; (b) from P4VP core to P2VP spherical microdomain; (c) from P2VP spherical microdomain to P4VP core; (d) between the P2VP spherical microdomains

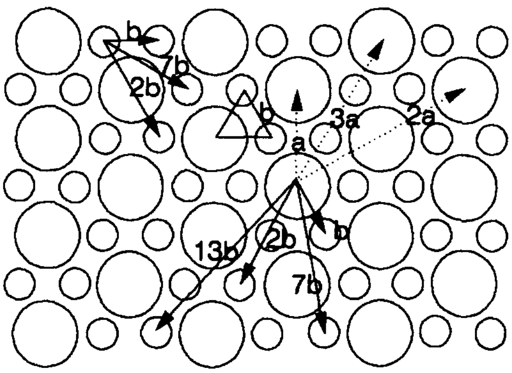

Figure 6 Schematic arrangement of the microdomains of microsphere and diblock copolymer

previously, the P4VP cores were arranged hexagonally in two dimensions by themselves. For the $g11(r)$ in the blend system (*Figure 5a*) three peaks are observed. When the spheres are packed in the schematic arrangement (*Figure 6*), the peaks of $g11(r)$ will appear at a, $\sqrt{3}a$ and $2a$ for first, second and third generation, respectively. Three peaks were observed at $a = 85.2$, 146.4 and 170.9 nm, and the ratio of r of these peaks was 1:1.72:2.01. These values agreed well with the values calculated from the schematic arrangement. Thus, it was found that the P4VP cores were arranged completely hexagonally, as shown in *Figure 6*, although the block copolymer was blended with the microsphere. The r value at the first generation between P4VP cores (*Figure 5a*) was 85.2 nm. By comparison with the distance between P4VP cores without blending (79.9 nm), the distance between P4VP cores increased from 79.9 to 85.2 nm with blending. However, the packing state of the P4VP cores was not destroyed by blending the block copolymer.

Between the P4VP core and P2VP sphere, two radial distribution functions, $g12(r)$ and $g21(r)$ were obtained (*Figures 5b* and *c*). For both cases, the peaks appeared at the same r values. For the schematic packing, the peaks appeared at $r = b$, $2b$, $\sqrt{7}b$ ($= 2.645b$) and $\sqrt{13}b$ ($= 3.606b$), for the first, second, third and fourth generations, respectively (see *Figure 6*). For both $g12(r)$ and $g21(r)$, the peaks were observed at 49, 98, 130 and 177 nm. The ratio of the distances was 1:2:2.65:3.61. These values agreed well with the values calculated from the schematic arrangement. Moreover, from the schematic arrangement structure, the ratio of the particle number of the P2VP spherical microdomain to the P4VP core was calculated as 2. The peak heights of $g12(r)$ were twice as large as those of $g21(r)$. These results support the schematic arrangement of the spheres shown in *Figure 6*.

For the P2VP spherical microdomains [$g22(r)$, *Figure 5d*], many peaks appeared. The r value of the first peak, 48.7 nm, agreed well with the r values of the first peaks of the $g12(r)$ and the $g21(r)$. The agreement of these r values indicated that the two P2VP spherical microdomains and one P4VP core formed an equilateral triangle. For the schematic structure, the equilateral triangle must be formed with two P2VP spherical microdomains and one P4VP core. Consequently, the spherical microdomains were arranged on the same packing pattern as the schematic arrangement. However, the peaks of $g22(r)$ for more than the second generation were not clear. This suggests that there will be less interaction between P2VP spherical microdomains.

The ratio a/b is $85.3/49 = 1.738$. This indicates that the P2VP spherical microdomain existed at the centre of the equilateral triangle formed with three P4VP cores. Phase equilibria in the AB block copolymer + A homopolymer blend were investigated theoretically in the strong segregation limit. Semenov[18] reported the phase equilibria in a blend of AB block copolymer micelle and A homopolymer, which was a similar blend system to that considered here. According to Semenov, when the micelle formed an ordered structure, there were four regions: B core of micelle, A corona, interface between stretched A block and A homopolymer, and interstitial region filled by A homopolymer chain. The interstitial region was formed at the centre of the equilateral triangle formed by the three micelles. In our case, to retain the ordered structure of the microsphere after blending, the spherical microdomain of the blended AB diblock copolymer SV or SI would be smaller than the interstitial region.

Based on this assumption, the sizes of the interstitial region of AB05M blend system and the spherical microdomain of blended AB diblock copolymer were compared. To simplify the problem, the size of the micelle is taken as the external diameter of the AB05M microsphere (77.8 nm). From these values, the maximum diameter of the sphere that can exist in the interstitial region is calculated as 12 nm. This value agrees approximately with the diameters of spherical microdomain of SV (18 nm) and SI (10 nm). This suggests that when the spherical microdomain of AB diblock copolymer is smaller than the interstitial region, the AB diblock copolymer does not destroy the ordered structure of the microsphere and forms the spherical microdomain between microspheres.

CONCLUSION

The morphology of blends of P4VP core–PS shell type polymer microsphere and AB diblock copolymers with PS sequence was investigated. Three AB block copolymers, P(S-*b*-2VP), P(S-*b*-IP) and P(S-*b*-4VP) with different molecular weights were used.

When the $\bar{M}_n$ of block copolymer was less than 3.2×10^4, a well-ordered arrangement of the microdomains was obtained, and the morphology did not depend on the chemical species of the block copolymer. The ordered morphology was that the P4VP core of the microsphere was packed hexagonally in two dimensions, and six spherical microdomains of the AB diblock were positioned around each microsphere.

The degree of order of the packed microdomains was estimated by using the radial distribution function, which revealed that the microsphere was packed completely hexagonally, and the spherical microdomains filled the interstitial region between the microspheres.

When the domain size of the block copolymer by itself becomes larger than the size of the interstitial region, i.e. when the $\bar{M}_n$ of the block copolymer was 4.7×10^5, the block copolymer micelle would break the order of the microsphere packing.

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