

# Ordering structure of the microspheres in blend films

Reiko Saito\*, Shoutaro Tanaka and Koji Ishizu

Department of Polymer Science, Tokyo Institute of Technology, 2-12, Ookayama, Meguro-ku, Tokyo 152, Japan

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The blend films of poly(4-vinyl pyridine) (P4VP) core–polystyrene (PS) shell microsphere and poly(methacrylic acid) (PMAA) core–PS shell microsphere were prepared from benzene solutions. When the diameters of the two types of the microsphere were close, the two types were placed at random in the film. When the diameter of the P4VP core was much larger than that of PMAA core, the P4VP core–PS shell-type microspheres were ordered hexagonally in two-dimensional state in the solid state. However, an ordering regularity of the PMAA core–PS shell-type microspheres was not observed. © 1998 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

Ordering control of microspheres has been well investigated from the view-point of the application for the design of high functional materials<sup>1–3</sup>. We have synthesised monodispersed core–shell-type microspheres upon crosslinking of the spherical microdomains formed with diblock copolymers in solid state and in solution<sup>4–6</sup>. We also found that those core–shell-type microspheres formed the superlattice in solid state<sup>7</sup> and in solution above overlap concentration<sup>8</sup>. Theoretically<sup>9,10</sup>, the main driving force for ordering of the microspheres is a repulsive force between the microspheres due to the shell chains.

By blending linear polymers with our core–shell-type microspheres, novel morphologies of microphase separation were obtained<sup>11,12</sup>. It was because of this that the microspheres formed the superlattice, even in the blend system, and linear polymers filled the spaces where the segment densities of the microsphere were low. Such novel morphologies are very important for the design of high functional materials. It will be possible to obtain further novel morphology by blending two different types of microspheres. For this purpose, not only the repulsive force but also an attractive force between hetero-microspheres, should be controlled. When the inside texture of the microsphere is homogeneous, the following are considered to be disadvantages for the blending of the microspheres:

(1) no attractive interaction can be introduced because, if there is an attractive force between the hetero-microspheres, the repulsive force will vanish and, as a result, the microspheres will be precipitated;

(2) there is contact between the hetero-microspheres in the solid state.

On the other hand, for core–shell-type microspheres, the repulsive and attractive forces can be controlled independently, because the properties of the shell and core, which lead to the repulsive and attractive forces, respectively, can be changed independently. Moreover, the shell chains form a matrix even in the solid state.

The main purpose of this study is to investigate the possibility of the ordering control of the microspheres by using not only the repulsive but also attractive forces. Coulomb energy was chosen as the attractive force. For this purpose, two different types of microspheres, poly(4-vinyl pyridine) (P4VP) core–polystyrene (PS) shell-type and poly(methacrylic acid) (PMAA) core–PS shell-type microspheres were chosen. Additionally, in order to investigate the size effect of the microsphere blending on the ordering, two different sizes of the P(4VP) core–PS shell-type microspheres were synthesised. The ordering structures of the microspheres in 2- and 3-dimensional states were investigated by transmission electron microscopy and small-angle X-ray scattering methods, respectively.

## EXPERIMENTAL

### Materials

*P(4VP) core–PS shell-type microspheres (C1 and C2).* The microspheres were synthesised from poly(styrene-*b*-4-vinyl pyridine) (P(S-*b*-4VP)) diblock copolymers. The P(S-*b*-4VP) diblock copolymers were synthesised by a sequential additional anionic living polymerisation technique in THF at  $-78^{\circ}\text{C}$ <sup>13</sup>. Number-average molecular weights of PS precursors were determined with a Tosho HLC-8020 g.p.c. using THF as eluent at  $38^{\circ}\text{C}$ . A TSK-gel GMHXL column was used and flow rate was 1.0 ml/min. P4VP contents were measured with a Shimadzu Fourier transform infra-red spectroscope (FTi.r. 8020). The characteristics of the block copolymers are listed in *Table 1*. The microspheres were synthesised based on the synthetic method previously reported<sup>4</sup>. The properties of microspheres C1 and C2 are listed in *Table 2*.

*P(MAA) core–PS shell-type microspheres.* The microspheres were synthesised and characterised as described previously<sup>14</sup>. The properties of the P(MAA) core–PS shell microsphere (A1) are shown in *Table 2*. The TEM micrograph of A1<sup>14</sup> is shown in *Figure 1*. The dark and white regions are the PS and PMAA domains.

\* To whom correspondence should be addressed

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

Name	$M_n$ of PS <sup>a</sup> ( $\times 10^{-5}$ )	4VP content <sup>b</sup> (mol.%)	$D_n$ of P4VP domain (nm) <sup>c</sup>	$D_w/D_n^c$
B1	1.4	15.6	23.3	1.01
B2	4.5	23.2	64.0	1.05

<sup>a</sup>Number average molecular weight of the PS sequence determined by g.p.c.

<sup>b</sup>Determined by FTi.r.

<sup>c</sup> $D_n$ , (number average) and  $D_w$ , (weight average) diameters of the P4VP spherical microdomains determined by TEM


**Figure 1** TEM micrograph of A1 stained with OsO<sub>4</sub><sup>14</sup>

**Blending of the microspheres.** The microspheres were dissolved into benzene at a certain polymer concentration. The solution was then blended and dried gradually.

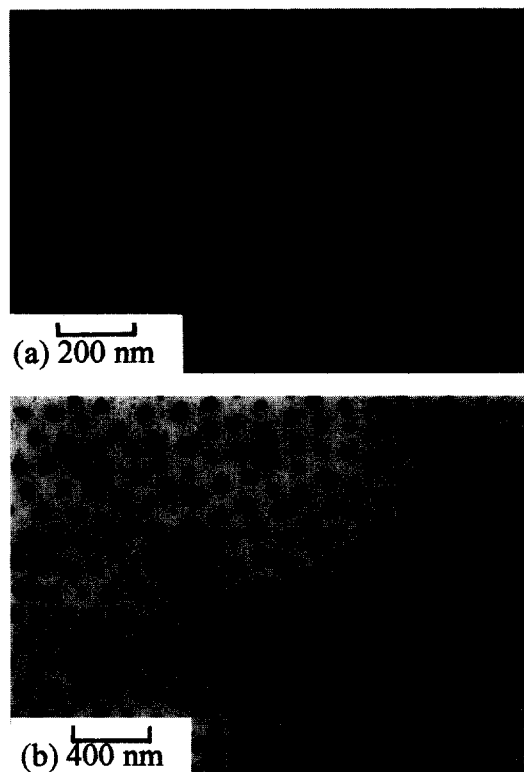
**Morphological observation.** The ultra-thin film specimens of the microspheres and blended solutions were prepared for transmission electron microscopy by placing one drop of polymer solution with a certain polymer concentration on a copper grid coated with carbon film, and then evaporating as gradually as possible at room temperature. In order to obtain the contrast for the film, the sequences were stained with OsO<sub>4</sub> or methyl iodide, by placing the specimen in OsO<sub>4</sub> or methyl iodide gas for 72 h at room temperature. The morphological results were obtained with a transmission electron microscope (Hitachi, H-500) at 75 kV.

**SAXS measurement.** The SAXS intensity distribution of the polymer film was measured with a rotating-anode X-ray generator (Rigaku Denki, Rotaflex RTP 300RC) operated at 40 kV and 100 mA. The X-ray source was monochromatized to Cu K $\alpha$  ( $\lambda = 1.52 \text{ \AA}$ ) radiation. The SAXS patterns were recorded with a fine-focused X-ray source using a flat-plate camera (Rigaku Denki, RU-100).

## RESULTS AND DISCUSSIONS

### Synthesis of cationic core-type microspheres

First, P(S-b-4VP) diblock copolymers, B1 and B2, were synthesized as the original materials for the microsphere synthesis. Their characteristics are listed in Table 1. The P4VP contents of B1 and B2 were less than 25 mol.%. Based on Molau's law<sup>15</sup>, P4VP spheres in a PS matrix-type microphase-separated structure were expected. As expected, P4VP spherical microdomains were observed in PS matrices for both block copolymers. The distribution indexes of the diameters of P4VP spherical microdomains were less than 1.1. Thus, these B1 and B2 block copolymers were suitable for microsphere synthesis.


**Figure 2** TEM micrographs of C series stained with OsO<sub>4</sub>. (a) Microsphere C1; (b) microsphere C2

**Table 2** Characteristics of the microspheres<sup>14</sup>

Name	$D_n$ in Bz (nm) <sup>a</sup>	$f^b$	$D_n$ of core (nm) <sup>c</sup>	$c^*$ (wt./vol.%) <sup>d</sup>
C1	122.2	246	25.7	7.3
C2	361.5	969.3	67.8	3.4
A1 <sup>14</sup>	96.5	226.4	21.8	8.1

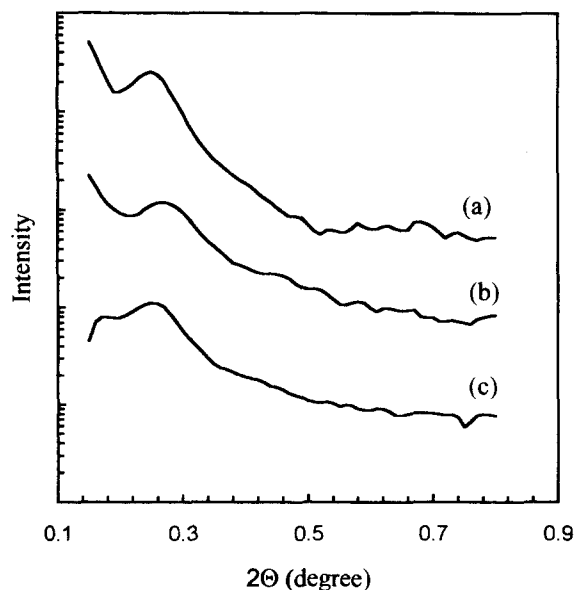
<sup>a</sup>Hydrodynamic diameter of microsphere in benzene at 20°C

<sup>b</sup>Arm number of shell in a microsphere

<sup>c</sup>Number average diameter of core determined by TEM

<sup>d</sup>Overlap concentration of the microspheres in benzene at 20°C

Then, the P4VP chains in the P4VP microdomains were crosslinked with dibromobutan and P4VP core-PS shell-type microspheres, C1 and C2, were synthesized. Microsphere C1 was produced from B1, and C2 from B2. Figure 2 shows the TEM micrographs of C1 and C2. The dark regions are the P4VP microdomains selectively stained with OsO<sub>4</sub>. From these micrographs, it was confirmed that C1 and C2 were P4VP core-PS shell-type microspheres. Additionally, C1 and C2 showed good ordering in two dimensions since they were hexagonally packed. The characteristics of C1 and C2 are listed in Table 2. The diameters of the P4VP cores agreed well with those of the P4VP spherical microdomains before crosslinking. These



**Figure 3** SAXS intensity profiles of the polymer films. (a) The C1 film; (b) the A1 film<sup>14</sup>; (c) C1/A1 blend film

microspheres were monodispersed in benzene. Therefore, it was concluded that monodispersed P4VP core-PS shell-type microspheres were obtained.

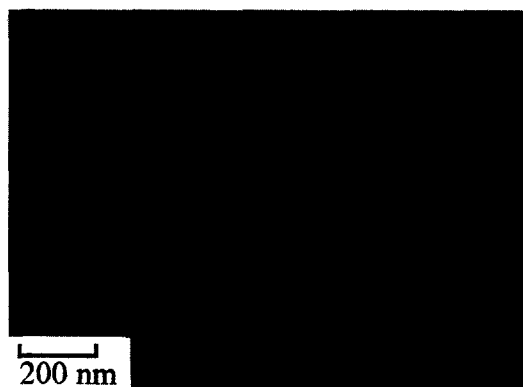
The diameter in benzene and the arm number of C1 were close to those of A1 (anionic core-type microsphere; PMAA core-PS shell-type microsphere). It was concluded that the architecture of C1 was similar to that of A1, except for the chemical species of the core sequences. Thus, the size effect between C1 and A1 can be neglected, and the arrangement of the microspheres between C1 and A1 should be governed by the Coulomb energy of these cores.

#### *Ordering structures of the microspheres using the Coulomb energy*

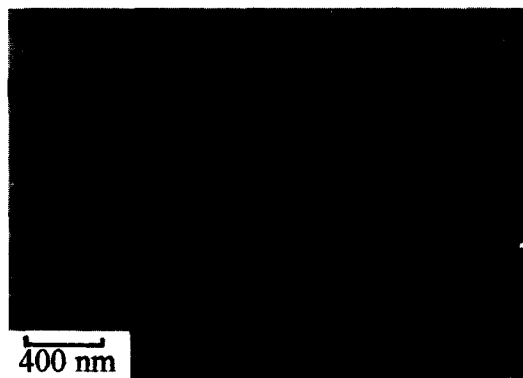
Before the investigation of the blend of C1 and A1, the 3-dimensional arrangement of microsphere C1 was investigated by SAXS measurement. Previous investigations<sup>7,8,14</sup> reported that the core-shell-type microspheres form an FCC lattice in the solid state. Thus, FCC lattice formation is expected for microsphere C1. *Figure 3a* shows the intensity profile of C1 in the solid state. Peaks are observed at 0.25, 0.41, 0.48, 0.58 and 0.63. These peaks indicate that the FCC lattice with  $d1 = 39.3$  nm was formed in the matrix. Therefore, microsphere C1 formed an FCC lattice in the solid state. In *Figure 3b*, the SAXS profiles of A1<sup>14</sup> are also shown. As reported previously<sup>14</sup>, the lattice structure of the A1 was FCC.

Microspheres C1 and A1 were then blended. The molar ratio of C1 to A1 in the blend was 1 since their diameters were very close. *Figure 3c* shows the SAXS intensity profiles of the blend film. Many peaks were clearly observed. However, it was impossible to determine the lattice structure of the microspheres in the film from these peaks. The first peak of the blend matched the first peak of A1. However, other peaks of the blend film did not match the peaks of either C1 or A1. This indicates that the lattice structures of both C1 and A1 did not remain in the blend film.

The arrangement of both microspheres in the blend was observed by TEM. *Figure 4* shows the TEM micrograph of the blend film of C1 and A1. The black, grey and white regions are the P4VP, PS and PMAA microdomains,



**Figure 4** TEM micrograph of the C1/A1 blend stained with OsO<sub>4</sub>

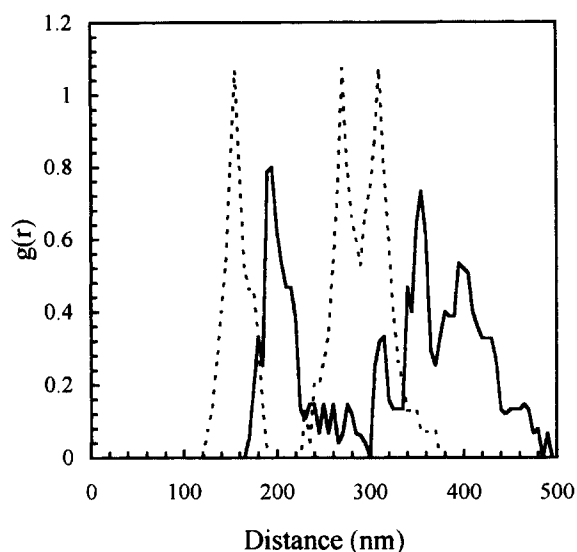


**Figure 5** TEM micrograph of the C2/A1 blend stained with methyl iodide

respectively. It was found that the microspheres of C1 and A1 did not segregate each other, and they existed at random in the solid state. Therefore, the lattice structure could not be determined by SAXS. This random arrangement of these microspheres suggests that the Coulomb energy of the microspheres did not work as a driving force for the arrangement. This could be due to the low dielectric polarization of benzene, which was used as the solvent for blending. Moreover, strictly, the diameters of the microspheres were slightly different. As a result, the microspheres of C1 and A1 mixed at random and destroyed the superlattice structure. This also indicates that the microspheres did not recognise the difference of the core species in the microspheres under these conditions. In order to introduce a Coulomb energy for these systems, a thinner shell or a good solvent with a high dielectric dipolarization are required.

#### *Effect of the size factor on the ordering of the microspheres*

Next, the size effect of the microspheres on ordering was investigated for the blend of C2 and A1. As described above, the Coulomb energy between the cationic and anionic microspheres can be neglected when the blending is carried out in benzene. Based on their diameters, the blend ratio of A1 to C2 was 2 (mol/mol). The SAXS profiles of the C2 series could not be obtained since the diameter of C2 was too large to be measured. Thus, the ordering behavior was estimated from TEM micrograph. *Figure 5* shows the TEM micrograph of the blend of C2/A1. The black, grey and white regions are the P4VP core, PS shell and PMAA core, respectively. The clear segregation of C2 and A1 was not observed. The P4VP cores seem to be arranged hexagonally



**Figure 6** Radial distribution functions of microsphere C2 series in two dimensions. Dashed line, C2; solid line, the C2/A1 blend

in two dimensions. The PMAA cores surrounded the P4VP cores.

In order to estimate the ordering of the P4VP cores quantitatively, the radial distribution functions of the P4VP cores were measured (Figure 6). Before blending with A1 (Figure 6a), three clear peaks appeared at 155.2, 268.9 and 310.4 nm, and the ratios of distances are 1, 1.73 ( $=\sqrt{3}$ ) and 2, respectively. This pattern indicates that the P4VP cores were arranged hexagonally outside A1. After the blending of A1, the three peaks shifted to a larger distance. The ratios of the distances were still 1, 1.79 ( $=351/196.2$ ) and 2.06 ( $=430.5/196.2$ ), respectively. The peaks became broader. Thus, it was concluded that the P4VP cores were packed hexagonally even with A1; however, the regularity of the ordering was decreased. Murakami et al. reported the good arrangement of hetero-microgels when the blend ratio was strictly controlled<sup>16</sup>. In this study, the blend ratio was not strictly calculated from the ratio of the diameters. Thus, the ordering of A1 could not be observed. However, the P4VP spheres showed a good arrangement. This could be due to

the buffering action of the soft shell of microsphere C2. For complete ordering, strict control of the blend conditions will be required.

## CONCLUSIONS

Two types of the core-shell-type microspheres with cationic P4VP cores were synthesised. From SAXS and TEM investigations, the microspheres formed an FCC lattice and a hexagonal lattice in three and two dimensions, respectively. The microspheres with cationic cores were then blended with the core-shell-type microspheres with anionic cores. When the diameters of the microspheres in the solvent were close, the microspheres were arranged at random. This was because the polarity of the solvent (benzene) was too low to introduce the Coulomb energy for arrangement. When the diameters of the microspheres were different, it was possible to arrange the large microspheres in the blend; however, the regularity of the ordering was decreased.

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