Ordered superstructure formation of core–shell type microspheres

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(Received 15 March 1993)

Poly(4-vinyl pyridine (P4VP) core–polystyrene (PS) shell type polymer microspheres were synthesized by crosslinking the P4VP spherical microdomains of poly(styrene-*b*-4-vinyl pyridine) (P(S-*b*-4VP)) diblock copolymers with 1,4-dibromobutane (DBB). The packing structures of well characterized microspheres, both on one layer and also in the bulk were investigated by transmission electron microscopy (TEM). For the AB05 microspheres (diameter of P4VP core = 40.7 nm, aggregation number = 1300), an ordered packing of the microspheres on to a hexagonal lattice was observed for one layer, while in the bulk of the film, AB05 ordered on to a face-centred cubic (f.c.c.) lattice.

(Keywords: microsphere; core–shell morphology; diblock copolymer)

INTRODUCTION

It is well known that block and graft copolymers with incompatible sequences undergo microphase separation as a result of the specific properties of the block and graft copolymers being considered. We have proposed a novel synthetic method for producing core–shell type polymer microspheres by crosslinking the segregated chains in the spherical microdomains of a microphase separated film[1]. Based on this concept, we have synthesized several core–shell type microspheres as follows; P4VP microspheres from P(S-*b*-4VP)[1–3], polyisoprene (PIP) microspheres from poly(styrene-*b*-isoprene) (P(S-*b*-IP))[4], poly(2-vinyl pyridine) (P2VP) microspheres from poly(styrene-*b*-2-vinyl pyridine) (P(S-*b*-2VP))[5] and poly(methacrylic acid) (PMAA) microspheres from poly(styrene-*b*-methacrylic acid) (P(S-*b*-MAA))[6]. It was possible to control the 'arm-number' of the P2VP core–PS shell type microspheres by 'cutting off' some of the shell chains from the microsphere[7].

The distributions of the diameters of the external shell and the internal core were monodispersed in all cases. In a good solvent for the shell sequences, none of the microspheres aggregated with each other, but formed single micelles with a solid core and a soluble shell structure. Such a core–shell structure is very similar to that of the so-called 'star-shaped model'[8]. Daoud and Cotton[9] have proposed a model giving the conformation of star-shaped polymers as functions of the arm-number, the degree of polymerization of the shell chain species, the excluded volume and the polymer concentration. From their model, it was reported that beyond a certain 'overlap' concentration (C^*), there was a region in which the shell chains did not penetrate, and the star in such a state behaved as an isolated entity. In fact, de la Cruz and Sanchez[10] calculated that an (AB)*n* type star block copolymer, which contained *n* arms of the A-type block copolymer, formed single polymer micelles with a core–shell structure by itself in solution, when *n* was large (> 20). In addition, these star block copolymers with a large number of arms are expected to form a crystalline array near the overlap concentration[11].

When comparing core–shell type microspheres and star block copolymers, it is found that they have similar structures. The region of the star-shaped polymer where the shell chains cannot penetrate corresponds to the core part of the core–shell type microsphere. Therefore, the crystalline arrangement of the microsphere is expected to be similar to that of the star-shaped copolymer.

Using this concept, the arrangement of a crystalline array of P4VP core–PS shell type polymer microspheres was investigated by casting samples from dilute solution on to carbon substrates[12]. Below a polymer concentration of 0.6 wt%, the P4VP core–PS shell type microspheres were well organized into hexagonal packing arrangement on the carbon substrate. The microspheres were well dispersed and did not form a film, as the polymer concentration used in the casting process was too dilute to allow formation of a segregated film of the microsphere.

The purpose of this study is to investigate the two- and three-dimensional structural arrangements of the P4VP core–PS shell microspheres in the condensed state. In order to achieve this, P4VP core–PS shell type microspheres with different characteristics (i.e. diameter of P4VP core, external diameter, and aggregation number) were synthesized from four different types of P(S-*b*-4VP) AB type diblock copolymers. The arrangement of the microspheres was then examined by TEM studies of carbon substrates containing cross-sections of films of the microspheres.

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0032-3861/94/08/1747–07

EXPERIMENTAL

Synthesis of diblock copolymers

A well defined poly(S-*b*-4VP) diblock copolymer was synthesized by the usual sequential anionic addition polymerization process, using n-butyl lithium as an initiator in tetrahydrofuran (THF) at −78°C. Details of the synthesis, purification and characterization of this block copolymer have been given previously[1]. The characteristics of the P(S-*b*-4VP) diblock copolymers are shown in *Table 1*.

Crosslinking of diblock copolymer films

A diblock copolymer film (thickness = 120 μm) was cast from a solution (0.05 g ml^{-1}), in either 1,1,2-trichloroethane (TCE) or chloroform/benzene 50/50 by volume), on to a Teflon sheet, and this was then gradually dried for 4 days at room temperature.

The crosslinking of the segregated 4VP chains in the P4VP microdomains was carried out by quaternization with the vapour of 1,4-dibromobutane (DBB) for 24 h at 80°C.

The degree of quaternization (DQ_1) of the P4VP chains was measured by using the Volhard titration method. The film was dissolved in benzene and the Br$^-$ ion in the system was titrated with aqueous $AgNO_3$ and KCNS. For the measurement of the pendant Br$^-$ anions, the total degree of quaternization (DQ_2) was measured by a similar titration using a benzene/triethylamine (TEA) mixture.

*Quaternization of P(S-*b*-2VP) (AB02Q)*

P(S-*b*-4VP) was quaternized with ethyl bromide in a polymer/dimethylformamide solution (containing 2 wt% polymer) for 2 h at 50°C. The polymer was then precipitated in n-hexane, washed with the same solvent and dried. The degree of quaternization was found to be 46 mol% (by titration).

Morphological observations

Ultra-thin specimens of the starting block copolymers were prepared for TEM observations by placing a drop of a 1 wt% solution in TCE on to a copper grid coated with a carbon substrate, and then slowly evaporating off the solvent at room temperature. The specimens were then stained with OsO_4 (4 days at room temperature).

Specimens of the crosslinked products were prepared and stained with OsO_4 in the same way by using benzene solutions (0.05–1.00 wt%). For observation of the external shape of the crosslinked products, specimens cast from 0.05 wt% benzene solutions were shadowed with Cr at an angle of 20°. The morphological results were obtained by using a Hitachi H-500 transmission electron microscope operating at 75 kV. For observation of the packing state of the microspheres in the bulk ultra-thin films (thickness = 80 nm) were prepared by cutting the films with a microtome (Reinhert-Nissei Ultracut N); these were then stained with OsO_4. Microtomed specimens were observed with a Jeol 100CX transmisstion electron microscope operating at 100 kV. A side-entry goniometer and tilt–rotate specimen holder were used for tilting the specimens.

Table 1 Characteristics of poly(styrene-*b*-4-vinyl pyridine) diblock copolymers

Sample	$\bar{M}_n$ ($\times 10^{-5}$) PS[a]	$\bar{M}_n$ ($\times 10^{-5}$) Block[b]	4VP content (mol%)[c]	Diameter (nm)
AB01	3.9	4.7	17	68.0[d]
AB02	1.2	1.7	30	41.3[e]
AB04	0.7	1.0	36	34.5[e]
AB05	0.8	1.1	28	48.4[d]

[a] Determined by using gel permeation chromatography
[b] Determined by using membrane osmometry
[c] Estimated by using ^{1}H n.m.r. spectroscopy
[d] Obtained from TEM observations of the spherical P4VP microdomains in samples cast from TCE
[e] Obtained from TEM observations of the spherical P4VP microdomains in samples cast from benzene/chloroform solutions (50/50 by volume)

Observation of precipitation behaviour

A sample of polymer (0.05 g) was dissolved in 20 ml of THF in a cell at 25°C and water was then added dropwise with vigorous stirring. After each addition, the turbidity of the solution was measured spectroscopically at 600 nm with a single beam u.v.–vis. spectrophotometer (Hitachi Spectrophotometer Model 139).

Measurement of the external diameter of the microspheres in solution

This was carried out by dynamic light scattering, using a DLS-600 machine (Otsuka Electrics Co. Ltd).

RESULTS AND DISCUSSION

Block copolymers

The characteristics of the P(S-*b*-4VP) diblock copolymers are given in *Table 1*. All of the block copolymers showed narrow molecular-weight distributions, and had 4VP contents which were between 17 and 36 mol%. As reported previously[13], when the P4VP content of P(S-*b*-4VP) is larger than 30 mol%, a microphase separated film with P4VP spherical microdomains is obtained by casting from a benzene/chloroform solution (containing 50 vol% benzene). When the P4VP content is less than 30 mol%, such a structure is obtained by casting from a TCE solution. Thus, block copolymer samples AB01 and AB05 with 4VP contents less than 30 mol% were cast from TCE, while samples AB02 and AB04, with higher 4VP contents, were cast from benzene/chloroform mixtures.

Figure 1 shows a transmission electron micrograph of the block copolymer AB02 (4VP content = 30 mol%), cast from a benzene/chloroform mixture. Dark regions of the micrograph correspond to segregated P4VP chains, which have been selectively stained with OsO_4. The morphological structure consisted of P4VP spheres contained in a PS matrix. The number-average diameter of the P4VP spherical microdomains was 41.3 nm, with a narrow size distribution (1.01). Other block copolymers in this series also formed microphase separated films having this P4VP sphere–PS matrix morphology.

The number-average diameters ($\bar{D}_{n,4VP}$) of the P4VP microdomains, obtained from the TEM measurements, are listed in *Table 1*. For all of the films examined, the $\bar{D}_w/\bar{D}_n$ value (where $\bar{D}_w$ is the weight-average diameter) was less than 1.09. Thus, it was concluded that microphase separated films, having a P4VP sphere–PS matrix morphology, and a narrow size distribution, had been obtained.

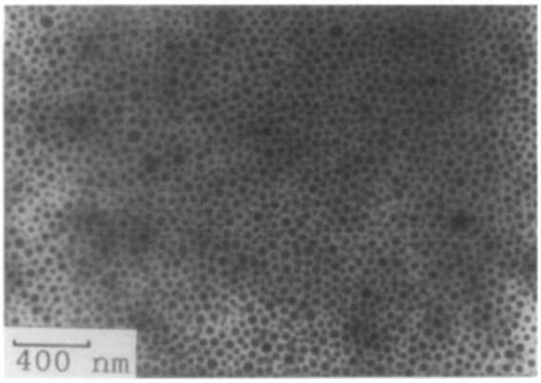


Figure 1 Transmission electron micrograph of the P(S-*b*-4VP) diblock copolymer AB02, cast from a 1 wt% benzene/chloroform mixture (50/50 by volume), and stained with OsO_4

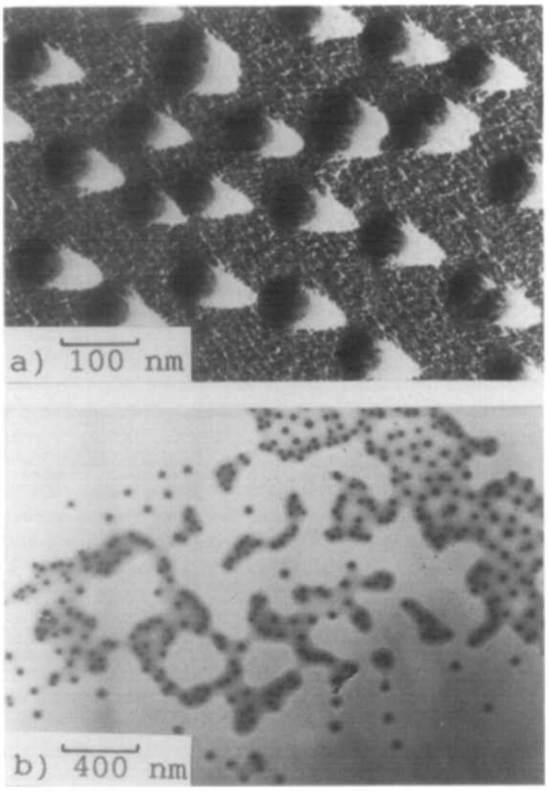


Figure 2 Transmission electron micrographs of the crosslinked products AB02M cast from benzene solution containing 0.5 wt% of polymer: (a) shadowed with Cr at an angle of 20°; (b) stained with OsO_4

Synthesis of P4VP core–PS shell microspheres

Crosslinking of the P4VP spherical microdomains with DBB was then carried out: all of the crosslinked products freely dissolved in benzene and THF. The degree of quaternization of the 4VP group with DBB (DQ_1) was measured by the Volhard titration method in benzene. The pendent Br groups in the 4VP sequences were quaternized with triethylamine, and the total degree of quaternization (DQ_2, including the pendant Br groups) was measured by titration in benzene/triethylamine mixtures. The crosslink density (CD) was calculated from the following equation:

$$CD = 2DQ_1 - DQ_2 \qquad (1)$$

Values of DQ_1 and the corresponding CDs are listed in *Table 2*. The minimum CD value was 16.7 mol%, indicating, therefore, that the P4VP spherical microdomains were tightly crosslinked.

In order to estimate both the shape and the size of the crosslinked products, TEM measurements of the crosslinked products, which had been shadowed with Cr and stained with OsO_4, were then carried out. *Figure 2* shows the transmission electron micrographs obtained for the crosslinked product AB02M when cast from benzene solution containing 0.5 wt% polymer. From the shadowed sample (see *Figure 2a*), it was found that the crosslinked products were spherical with $D = 61$ nm. It was also found that the distribution of the external diameters of the microspheres was very narrow (i.e. 1.01). From detailed examination of the internal texture of the microspheres (see *Figure 2b*), it was found that spherical P4VP microdomains (the dark regions, stained with OsO_4), 30 nm in diameter and with a narrow size distribution (1.01), were dispersed on the carbon substrate. PS shells (shown as grey regions in the micrograph) were observed around the P4VP core regions. Thus, the P4VP core–PS shell structure was clearly confirmed. It was therefore concluded that P4VP core–PS shell type spherical microspheres having narrow size distribution had been produced.

The diameters of the external shells and the P4VP cores of other microspheres were also estimated from TEM measurements, and are listed in *Table 2*. It was concluded that all of the crosslinked products were spherical in shape, with a narrow size distribution (<1.01), and had a P4VP core–PS shell type morphology.

From the diameter of the P4VP core, the arm-number of the PS shell, f, (the segregation number of the block copolymer) in a microsphere, and the molecular weight

Table 2 Conditions and results of crosslinking of microphase separated films

Sample[a]	DQ_1[b] (mol%)	CD[c] (mol%)	Diameter (nm)[d]		f[e]	M_{total}[f] ($\times 10^{-8}$)
			P4VP core	External		
AB01M	41.3	36.3	74.8(1.01)	111.4(1.00)	1800	8.5
AB02M	46.3	41.2	29.5(1.01)	60.7(1.00)	200	0.34
AB04M	23.6	16.7	40.4(1.00)	55.5(1.01)	690	0.69
AB05M	43.9	20.8	49.7(1.01)	77.8(–)	1400	1.5

[a] Crosslinked products AB0*X*M were synthesized from AB0*X*
[b] Degree of quaternization determined by the Volhard titration method
[c] Crosslink density calculated from DQ_1 and DQ_2 data
[d] Distributions (D_w/D_n) estimated from TEM measurements
[e] Aggregation number of the block copolymer in a microsphere, estimated from TEM measurements
[f] Molecular weight of a microsphere

of the microsphere, M_{total}, can be calculated by using the following equations:

$$f = (4\pi/3)R_{\mathrm{core}}^3 \rho_{\mathrm{P4VP}} N_{\mathrm{A}} / M_{\mathrm{P4VP}} \qquad (2)$$

$$M_{\mathrm{total}} = f M_{\mathrm{block}} \qquad (3)$$

where R_{core}, ρ_{P4VP}, N_{A}, M_{4VP} and M_{block} are the radius of the core, the density of P4VP, the Avogadro constant, the molecular weight of the P4VP sequence and the molecular weight of the block copolymer, respectively. The density of P2VP ($1.14 \times 10^3\ \mathrm{mol\ m^{-3}}$) is used as the value for P4VP[14]. The values of f and M_{total} are also given in *Table 2*. The minimum value of f was 200, for sample AB02M. Consequently, it was concluded that monodispersed P4VP core–PS shell type microspheres with many arms had been produced.

Properties of microspheres

In order to examine the physical state of the micropheres in solution, the precipitation behaviour of the AB02M material was investigated in THF–water systems. The core part of the microsphere consisted of partially quaternized 4VP, when DBB was used as the crosslinking agent. In order to investigate in detail the difference in the precipitation behaviour of an AB02M microsphere from its precursor block copolymer AB02, partially quaternized block copolymer AB02Q was synthesized from the corresponding precursor copolymer by using 1-bromoethane, which had the 'half-structure' of the crosslinking reagent DBB. The *DQ* of AB02Q was 46 mol%, which agreed well with the *DQ* of the AB02M microsphere.

Figure 3 shows the turbidimetric behaviour of the AB02 series of materials. All of the polymers freely dissolved in THF. By adding water, the AB block copolymer AB02 suddenly precipitated at a water content of 10 vol%, while the partially quaternized block copolymer AB02Q continued to dissolve in the system over the range of water contents between 0 and 30 vol%. This indicates that the AB02 species become amphiphilic (represented by AB02Q) as the result of the partial quaternization process. On the other hand, no effect of the quaternized P4VP in the core was observed for the microsphere AB02M, which consisted of the same chemical species as amphiphilic AB02Q. In fact, it became turbid in a similar way to that seen for AB02. This shows that the properties of the microspheres show a great dependence on the properties of the shell. It was therefore concluded that the properties of the microspheres were governed by the chains in the shell, while the chemical nature of the core did not have any effect on the properties of the microspheres.

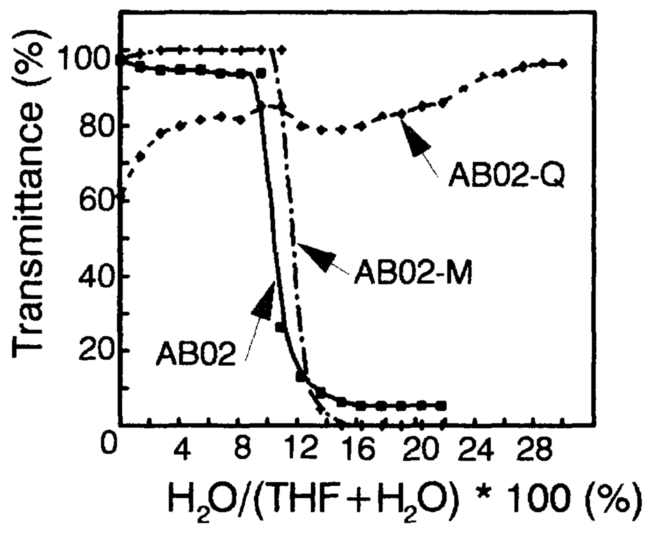


Figure 3 Turbidimetric behaviour of the AB02 series of materials in THF/water systems

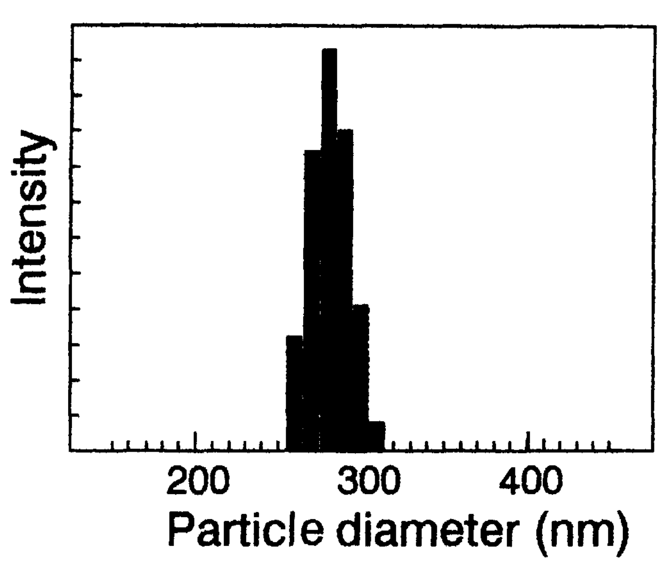


Figure 4 The intensity curve of the external diameter of AB01M microspheres, obtained by d.l.s. measurements in benzene

Table 3 Values of the external diameter and the overlap concentration C^* of the microspheres, measured in benzene at 25°C

Sample	Diameter[a] (nm)	$\bar{D}_w/\bar{D}_n$	C^{*b} (wt%)
AB01M	283.9	1.08	6.2
AB02M	142.5	1.26	2.0
AB04M	154.2	1.05	3.2
AB05M	180.5	1.03	4.4

[a] External diameter measured by d.l.s.
[b] Overlap concentration calculated from $C^* = M_{\mathrm{total}}/(N_{\mathrm{A}} D_{\mathrm{n}}^3)$, where N_{A} is the Avogadro constant, and D_{n} is the external diameter

The diameters of the microspheres were measured in benzene using dynamic light scattering (d.l.s.). *Figure 4* shows a typical case of the intensity curve of the AB01M microsphere material. A single clear peak for the diameter could be observed at 280 nm; its size distribution was 1.08. The diameters of other microsphere systems (also measured in benzene) are listed in *Table 3*. A single peak, with a narrow size distribution, was observed in all cases. Therefore, it was concluded that P4VP core–PS shell microspheres could be dispersed in benzene, forming isolated micelles in the solution.

From the diameters of the P4VP core and the microsphere in the solution (measured by d.l.s.), the overlap concentrations (C^*) of the microspheres can be calculated. In the case of star-shaped polymers, C^* is one of the most important parameters used to describe their arrangement. According to Witten *et al.*[11], a structure for the crystalline array of the star-shaped polymer appears near C^*. When the polymer concentration is below C^*, molecules of the star-shaped polymer remain isolated in solution. Therefore, in order to achieve an arrangement of star-shaped polymer, the latter should be condensed from solution just below C^*. In order to obtain core–shell type microspheres with similar structures to the star-shaped polymers, formation of crystalline arrays in the solution near C^* is required. This concentration was calculated from the diameter of the microspheres in solution (determined by d.l.s.) and the total molecular weight of the microsphere (M_{total}), by using the following equation[15]:

$$C^* = M_{\text{total}}/[N_A(2R_h)^3] \tag{4}$$

where R_h is the hydrodynamic radius of a core–shell type microsphere. The calculated C^* values are listed in *Table 3*: a minimum C^* value of 2.0 wt% was found for the AB02M system. Below C^*, the microspheres remain isolated, as any arrangement of the microspheres in solution was expected near or above C^*. For this reason, the polymer concentration used for film preparation of the microspheres was set at 1 wt%.

Two-dimensional arrangement of the microspheres

As described above, an arrangement of a crystalline array of microspheres in solution was expected at a concentration near C^*. In general, it is well known that small-angle X-ray scattering (SAXS) measurements of films are useful for investigation of the lattice structure of microdomain packing for the bulk of the solution[16] and also the solid[17]. The diameters of the P4VP cores of the microspheres in this study were, however, too large to allow investigation of the three-dimensional structure by SAXS. Therefore, the arrangement of the microspheres in the solid state was investigated in this study, by using TEM; this was examined from both a two- and three-dimensional aspect.

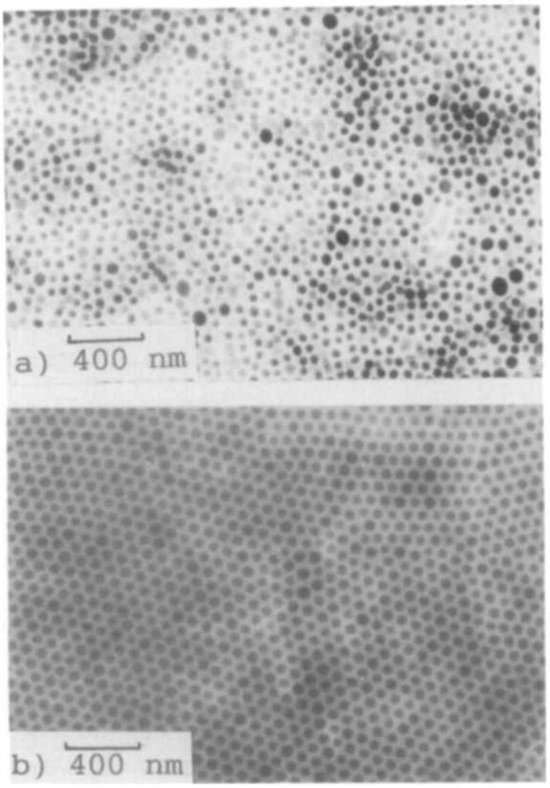


Figure 5 Transmission electron micrographs of samples of the AB05 series cast from solutions containing 1 wt% of polymer: (a) AB05 diblock copolymer cast from TCE and stained with OsO_4; (b) AB05M microsphere cast from benzene

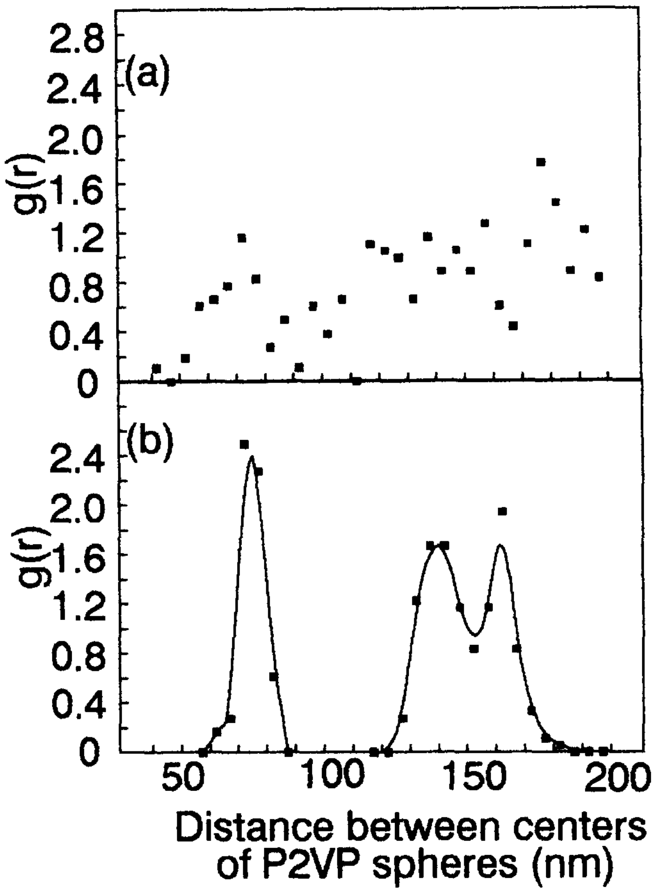


Figure 6 Distribution functions of the distances between the centres of P4VP spherical microdomains: (a) AB05 diblock copolymer; (b) AB05M microsphere

First, the two-dimensional arrangement of the microspheres was considered. *Figure 5* shows transmission electron micrographs of the samples AB05 and AB05M, cast from TCE and benzene, respectively, with both solutions containing 1 wt% of polymer. Packing structures for the spherical microdomains in microphase separated films of block copolymers[18,19] and blends of homopolymers and block copolymers have been well reported[20]. However, the P4VP microdomains of the AB05 material (see *Figure 5a*) do not appear to be arranged in any ordered fashion, and there seemed to be no rule for packing the P4VP microdomains in the film. On the other hand, the microspheres of the AB05M material formed a monolayer film, exhibiting a well ordered hexagonal arrangement on the carbon substrate (see *Figure 5b*).

In order to investigate the degree of ordering of the microspheres on the carbon substrate, the distribution of the distances between the centres of the P4VP spherical microdomains was measured (*Figure 6*). For the diblock copolymer film of AB05, only one wide peak was observed at ~75 nm. This indicates the distance between the nearest P4VP microdomains, namely the so-called 'domain spacing': other peaks could not be observed. Therefore, there is no clear regular arrangement in the packing of the P4VP microdomains of this copolymer film.

On the other hand, in the case of the AB05M microsphere material, three clear peaks appeared in the region below 200 nm, at distances of 79.9, 139.4 and 159.7 nm. When spheres are completely packed in an hexagonal fashion, the distances between the centres of

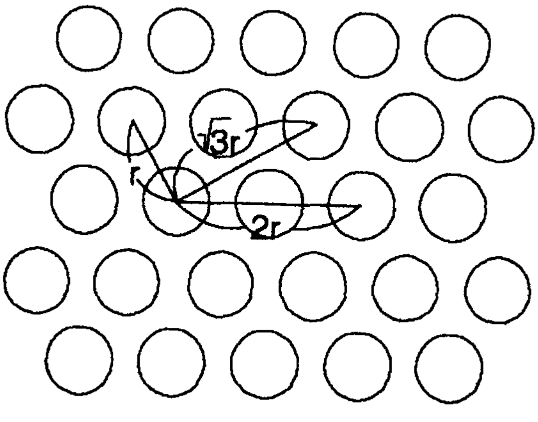


Figure 7 Schematic representation of microspheres showing a two-dimensional hexagonal packing arrangement

the spheres are $r, \sqrt{3}r$ and $2r$ for the first, second and third generation spheres, respectively (see *Figure 7*). The ratio of these distances for the peaks observed for AB05M were 1:1.75 (=139.4/79.9):2.00 (=159.7/79.9), values which agree well with the theoretical ratio of $1:\sqrt{3}:2$. Therefore, it was concluded that the microspheres were packed in a completely hexagonal arrangement on the carbon substrate.

According to Thomas *et al.*[18], the hexagonal lattice is the most favourable state for two-dimensional packing of the spherical microdomains in AB type diblock copolymers. In such a structure, chain conformation can be minimized by the interpenetrating shell chains uniformly filling the matrix space. In our case, the structure of the core–shell microsphere could not be changed by altering the thermodynamic conditions. The matrix space, however, must be uniformally filled with shell chains. The closed packing structure in two dimensions is hexagonal, and so, therefore, a hexagonal packing of microspheres was observed in this case.

This arrangement of an hexagonal array of microspheres is explained from the viewpoint of formation of crystalline arrays of microspheres in solution, at a concentration of $\sim C^*$, as follows; when the polymer concentration was $< C^*$, microspheres dispersed in the solvent at random, but when this polymer concentration was increased to $\sim C^*$, a crystalline array of microspheres was produced. Further increases in polymer concentration did not lead to any further changes in the arrangement of the microspheres, and a hexagonal array was thus observed on the carbon substrate.

Consequently, it was therefore concluded that a hexagonal packing arrangement of microspheres could be obtained in two dimensions, although its precursor block copolymer did not form any ordered structures in the microphase separated film.

Three-dimensional arrangement of the microspheres

The three-dimensional lattice structure of the microspheres was investigated by the use of TEM on samples of microtomed film. A single, three-dimensional image can be obtained by combining the TEM images obtained for essentially two-dimensional projections[21]. *Figure 8* shows the transmission electron micrographs of a cross-section of an AB05M film which had been cast from benzene and tilted to the y-axis: *Figure 8b* is the sample shown in *Figure 8a*, tilted at an angle of 45° to the y-axis. From micrographs of a sample tilted at different angles, according to Ma and Fukutomi[22], the coordinates of each microsphere in three dimensions can be deduced. The coordinates of sphere i, $a_i(x_0, y_0, z_0)$ become $a_i'(x_1, y_0, z_1)$ by tilting the sample about the (010) direction at an angle of θ, with the coordinates, x_0, y_0 and z_1 being obtained from the figures. By assuming that the angle that the sphere makes with the y-axis is θ_0, the values of z_0 and z_1 can be calculated. Using the coordinates for each microsphere, the distance and the angle between the spheres were calculated. From this calculation, it was found that the spheres were on the same plane, and *Figure 8c* shows the rearrangement of the spheres on this plane. The average distances between the centres of the microspheres are 57.3 and 80.0 nm for the a- and b-axis, respectively. The ratio of these values is $80/57.3 = 1.40 = \sqrt{2}$. This value agreed well with the packing pattern of a (110) plane in a f.c.c. structure. Thus, the conclusion was made that the packing structure of the microsphere was face-centred cubic.

In general, when a block copolymer forms a highly ordered microphase separated structure, the spherical microdomains can be packed into one of the three following cubic forms: simple (s.c.), face-centred (f.c.c.) and body-centred (b.c.c.). According to Ohta and Kawasaki[23], a b.c.c. arrangement is only slightly more favoured than the f.c.c. arrangement. In fact, many b.c.c. lattice formations have been reported for AB type diblock copolymers and blends of homopolymer/block copolymer systems[18,24–26].

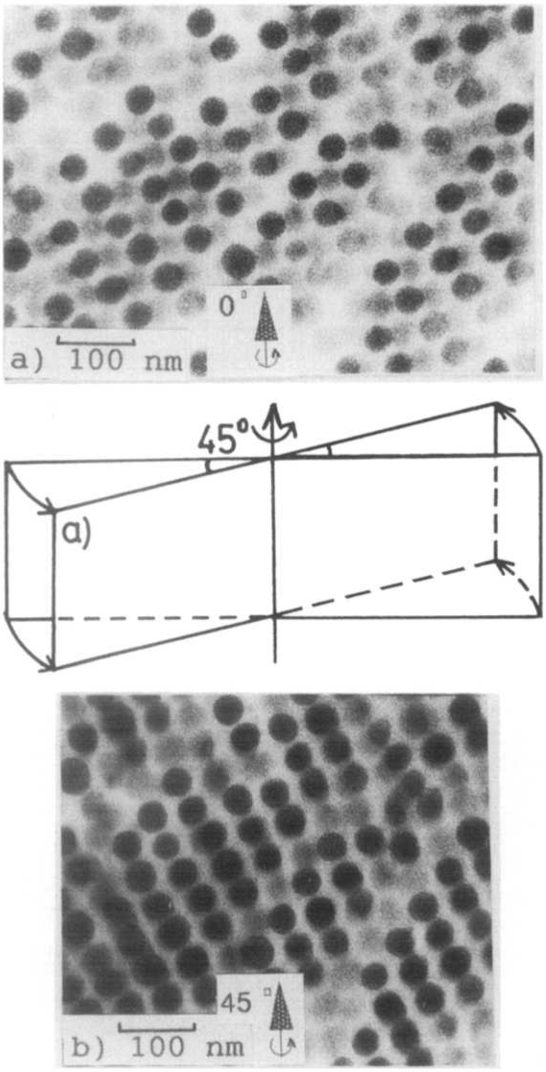
In our case, however, the microspheres were packed as a f.c.c. structure, with the packing of the microspheres resulting from the structural effects of the latter. The most important feature of the microspheres is that they do not change their shape in any state. Thus, the microspheres cannot replace their shell chains in the microphase separated film by changing their structure in order to minimize the thermodynamic energy.

CONCLUSIONS

Microphase separated films with a poly(4-vinyl pyridine) (P4VP) sphere–polystyrene (PS) matrix morphology were formed from poly(styrene-*b*-4-vinyl pyridine) (P(S-*b*-4VP)) diblock copolymers with 4VP contents which were less than 38 mol%. The size distributions of the P4VP spherical microdomains were narrow.

By crosslinking the P4VP spherical microdomains of microphase separated films with 1,4-dibromobutane (DBB) vapour, and dissolving in a good solvent for PS, P4VP core–PS shell type microspheres were synthesized. The size, the shape and the inner texture of the microspheres were confirmed by TEM for samples shadowed with Cr, or stained with OsO_4. As the crosslink densities of the P4VP cores were larger than 40 mol%, and closed to further effects of the quaternization, it was found that these cores were tightly crosslinked.

In order to investigate the behaviour of microspheres in solvent, turbidimetric titration in THF/water systems, and d.l.s. measurements in benzene were carried out. The precipitation behaviour of the microspheres was similar to the original precursor block copolymer and not the quaternized block copolymer material. It was found that the solubility of the core–shell type microspheres depended on the PS shell and not on the core. The diameters of the microspheres in benzene were measured by the d.l.s. method. All microspheres were expanded in



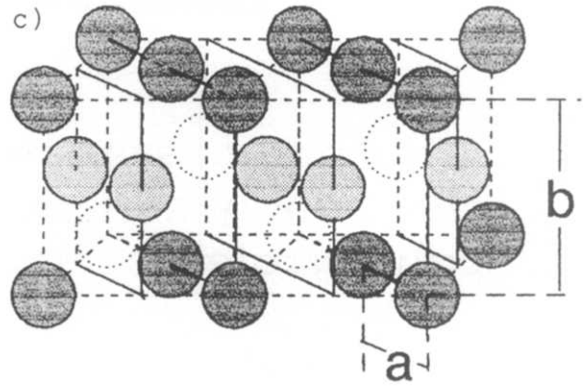


Figure 8 Transmission electron micrographs of cross-sections of AB05M films: (a) without any tilt; (b) tilted at an angle of 45° to the *y*-axis. (c) Schematic representation of the rearranged microsphere after tilting

this solvent and had narrow size distributions. Thus, it was concluded that the P4VP core–PS shell type microspheres were well dispersed in benzene and formed isolated micelles, with narrow size distributions, in the solution.

From the d.l.s. results, the overlap concentration, C^*, of the microspheres in benzene was also calculated. Microspheres were cast from solutions containing 1 wt% of polymer, i.e. at a level which was below C^*.

From two-dimensional analysis, it was found that the P4VP core–PS shell type microspheres were arranged with hexagonal packing in one layer, although the precursor diblock copolymer did not form any regular structure. By three-dimensional analysis of cross-sections of microsphere films, the packing structure of the microspheres in the bulk was found to be face-centred cubic.

ACKNOWLEDGEMENTS

This work was supported by Shorai Kagaku Gijutsu Shinkou Zaidan. The authors would like to thank Mr R. Oki and Mr T. Chiba, Faculty of Engineering, Tokyo Institute of Technology, for their help with the TEM sample preparation.

REFERENCES

1 Ishizu, K. and Fukutomi, T. *J. Polym. Sci., Polym. Phys. Edn* 1988, **26**, 281
2 Ishizu, K. *Polymer* 1989, **30**, 793
3 Ishizu, K. *Polym. Commun.* 1989, **30**, 209
4 Ishizu, K. and Önen, A. *J. Polym. Sci., Polym. Chem. Edn* 1989, **27**, 3721
5 Saito, R., Kotsubo, H. and Ishizu, K. *Polymer* 1992, **33**, 1073
6 Saito, R., Kotsubo, H. and Ishizu, K. *Eur. Polym. J.* 1991, **27**, 2501
7 Saito, R., Kawachi, N. and Ishizu, K. *Polymer* in press
8 Tanaka, T., Kotaka, T. and Inagaki, H. *Polym. J.* 1972, **3**, 338
9 Daoud, M. and Cotton, J. P. *J. Phys.* 1982, **43**, 531
10 de la Cruz, M. O. and Sanchez, I. C. *Macromolecules* 1986, **19**, 2501
11 Witten, T. A., Pincuc, P. A. and Cates, M. E. *Europhys. Lett.* 1986, **2**, 137
12 Ishizu, K. *J. Colloid Interface Sci.* 1993, **156**, 299
13 Ishizu, K., Inagaki, K. and Fukutomi, T. *J. Polym. Sci., Polym. Chem. Edn* 1985, **23**, 1099
14 Berkowitz, J. B., Yamin, M. and Fuoss, R. M. *J. Polym. Sci.* 1958, **28**, 69
15 Glaessley, W. W. *Adv. Polym. Sci.* 1974, **16**, 1
16 Plestil, J. and Baldrian, J. *Makromol. Chem.* 1975, **176**, 1009
17 Hashimoto, T., Nagatoshi, K., Toda, A., Hasegawa, H. and Kawai, H. *Macromolecules* 1974, **7**, 364
18 Thomas, E. L., Kinning, D. J., Alward, D. B. and Henkee, C. S. *Macromolecules* 1987, **20**, 2934
19 Gallot, B. R. M. *Adv. Polym. Sci.* 1979, **29**, 85
20 Kinning, D. J., Thomas, E. L. and Fetters, L. J. *J. Chem. Phys.* 1989, **90**, 5806
21 Spontak, R. J., Williams, M. C. and Agard, D. A. *Polymer* 1988, **29**, 387
22 Ma, G. H. and Fukutomi, T. *Macromolecules* 1992, **25**, 1870
23 Ohta, T. and Kawasaki, K. *Macromolecules* 1986, **19**, 2621
24 Hashimoto, T., Fujiura, M. and Kawai, H. *Macromolecules* 1980, **13**, 1660
25 Roe, R. J., Kishkis, M. and Chang, V. C. *Macromolecules* 1981, **14**, 1091
26 Richards, R. W. and Thomason, J. L. *Polymer* 1981, **22**, 581