Surface changes on block copolymers by crosslinking of spherical microdomains

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Well-defined poly(styrene(S)-b-4-vinylpyridine(4VP)) diblock copolymer was prepared by sequential anionic addition. The crosslinking reaction of this block copolymer film having a poly(4-vinylpyridine) (P4VP) spherical structure was carried out with the vapour of 1,4-dibromobutane (DBB). Electron micrographs of multi-molecular micelles suggested the microstructure of core-shell type polymer microspheres in solution. The surface characterization of this restructural cast film from crosslinked product was carried out by X-ray photoelectron spectroscopy (X.p.s.). The X.p.s. results indicated that a very small amount of P4VP spheres at near the free surface was observed in film cast from 1,1,2-trichloroethane (TCE)/nitrobenzene mixture. Angular dependent X.p.s. studies (in sampling depths of ≈ 1 and ≈ 5 nm) showed that the concentration of P4VP spheres increased with increment of sampling depth.

(Keywords: block copolymer; crosslinking reaction; core-shell type polymer microsphere; X-ray photoelectron spectroscopy)

INTRODUCTION

Block copolymers with incompatible sequences exhibit characteristic morphological behaviour and interesting properties, owing to microdomain formation in the solid state. The thermodynamic approach to the problem of microdomain formation has been solved[1-5] by demonstrating that the morphology of the domain structure, such as equilibrium size, shape, and interfacial thickness, can be described in terms of a balance of physical factors. It has been established, especially by electron microscopy, small-angle X-ray scattering, and X-ray diffraction, that segregated microphases can be spheres, cylinders, or lamellae. The type of morphology adopted by the copolymer essentially depends on its composition[6]. We have recently synthesized well-defined AB type poly(S-b-4-vinylpyridine (4VP)) diblock copolymers by anionic techniques with the intention of preparing charge mosaic membranes with some chemical modifications (sulphonation, quaternization, and fixing of each domain by crosslinks)[7]. The microdomain structures of poly(S-b-4VP) block copolymer specimens cast from 1,1,2-trichloroethane (TCE) also showed the similar results depending on their compositions as those of poly(S-b-butadiene (Bu)) di- or triblock copolymers[8,9].

On the other hand, poly(S-b-Bu-b-S) block copolymer micelles with cores of PBu blocks in dilute solution were stabilized by crosslinking of the chains in the micellar cores by ultra-violet irradiation in the presence of a photoinitiator and fast electrons[10-12]. The irradiated, stabilized micelles, examined by light scattering, sedimentation, and gel permeation chromatography (g.p.c.), did not decompose upon heating or in good solvents for both blocks. More recently, we have carried out the crosslinking reaction between poly(S-b-4VP) diblock copolymer films with P4VP spherical structures and the vapour of 1,4-dibromobutane (DBB)[13]. *Figure 1* shows the schematic representation of the core-shell type polymer microspheres in solution prepared from poly(S-b-4VP) diblock copolymer films. The representation of the core-shell type polymer microspheres indicates the structure in which the P4VP chains in core are crosslinked in the state of maintaining spherical microdomains. These microspheres were stabilized even in good solvents.

In this paper, the aim is to reveal the surface composition and topography of the restructural cast film from crosslinked product by the application of X-ray photoelectron spectroscopy (X.p.s.) to the study of polymer surfaces. From the results of angular-dependent X.p.s. studies, the morphology of film surface was discussed considering surface changes by crosslinking of spherical microdomains.

EXPERIMENTAL

Polymer synthesis and characterization

The well-defined poly(S-b-4VP) diblock copolymer was prepared by the usual sequential anionic addition polymerization using n-butyllithium as an initiator in tetrahydrofuran at −78°C. The details concerning the synthesis, purification, and characterization of such block copolymer have been given elsewhere[13]. *Table 1* lists the characteristics of the 'monodisperse' diblock copolymer and the microdomain spacing of a speciman cast from TCE.

Crosslinking of block copolymer films

The block copolymer film 50 μm thick was cast from 0.03 $\mathrm{g\,ml^{-1}}$ TCE solution on a Teflon sheet. The cast film was dried under vacuum for 2 days at room temperature. Crosslinking of the segregated P4VP chains in sphere was carried out by using quaternization with the vapour of DBB at 110°C under dry nitrogen atmosphere for 24 h. In the infra-red spectrum of crosslinked product, the absorption of the pyridine ring at 820 and 980 $\mathrm{cm^{-1}}$ disappeared

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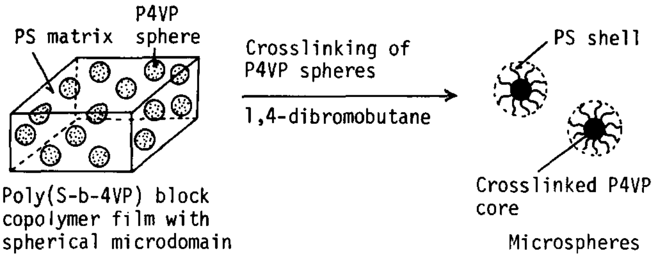

Figure 1 Schematic representation of core-shell type polymer microspheres prepared from poly(S-b-4VP) diblock copolymer film with P4VP spherical microdomains

Table 1 Characteristics of poly(styrene-b-4-vinylpyridine) diblock copolymer and domain spacing

	$\bar{M}_N \times 10^{-4}$				
Specimen code	Block copolymer[a]	P4VP block[b]	P4VP block[c] (wt%)	Shape of P4VP domain	Domain radius, $\bar{R}_{P4VP}$[d]
SV1	11.2	2.7	24	sphere	17

[a] Measured by osmometry in TCE at 37°C
[b] Estimated from the $\bar{M}_n$ data of the diblock copolymer and PS precursor
[c] Determined from infra-red spectra
[d] Determined by means of electron microscopy of specimen cast from TCE. $\bar{R}_{P4VP}$ = average radius of P4VP sphere structure

completely, and the appearance of the quaternized pyridine absorption at 840 and 1640 cm^{-1} was observed[13]. Therefore, the P4VP chains in a sphere were almost quantitatively quaternized with DBB in a reaction time of 24 h. It was made clear from previous results[14] that films with both P4VP spherical and lamellar shapes, which consist of continuous PS segment phases, were quantitatively quaternized with DBB vapour. Thus, the diffusion-controlled reaction of poly(S-b-4VP) with DBB became more conspicuous in the reaction systems of different microphase-separated structures.

Morphological observation

Ultra-thin film specimen of starting diblock copolymer was prepared for electron microscopy by placing a drop of a 1 wt% TCE solution on a microscopy mesh coated with carbon film, and then evaporating the solvent as gradually as possible at 25°C. This specimen was exposed to osmium tetraoxide vapour for 24 h at room temperature. The morphology of the crosslinked product was observed as follows. After dissolving block copolymer films quaternized with DBB in TCE/nitrobenzene = 10/1 (v/v), their 1.0 and 0.1 wt% solutions were dropped on a microscopy mesh coated with carbon film, respectively. This specimen was exposed to osmium tetraoxide. Both crosslinked and quaternized P4VP domains in a sphere were stained by this method. Morphological results were obtained on a Jeol JEM-100CX transmission electron microscope (TEM).

X.p.s. sample preparation and instrumentation

The starting block copolymer film and restructural cast film from crosslinked product 50 μm thick were cast from 0.03 g ml^{-1} TCE and TCE/nitrobenzene = 10/1 (v/v) solutions, respectively, on a Teflon sheet. The cast film was dried under vacuum for 2 days at room temperature. The sample film (7 × 20 mm) was coated on a copper sample holder with double-faced adhesive tape and copper wire, and was dried in an argon atmosphere at ambient temperature.

Spectra were recorded on a Spectoros XSAM 800 apparatus using Al Kα exciting radiation. Typical operating conditions were: X-ray gun, 14 kV, 20 mA; pressure in the analysis chamber: 5×10^{-8} Torr. Due to the rather long analysis times required for the angular-dependent studies, a liquid-nitrogen-cooled sample holder was used throughout the experiments. A value of 285.0 eV was used for the C_{1s} core level of the hydrocarbon. Overlapping peaks were resolved into their individual components by use of a DEC PDP11/03L curve resolver. These studies have shown that the line shapes are approximately Gaussian for individual components. The angular-dependent X.p.s. studies were carried out as follows. The sample was rotated relative to the fixed energy analyser by angle θ, which is the angle between the normal to the sample and the slits in the analyser. Spectra were recorded at two different polar angles (θ), $\theta = 0$ and 80° with respect to the sample surface, to achieve effective sampling depths of ≈ 5 and ≈ 1 nm, respectively, where the mean free length (λ) is dependent on the 0.5th power of kinetic energy. The average values for λ as a function of kinetic energy for the polymer systems are ≈ 14, ≈ 22, ≈ 23, and ≈ 29 Å for kinetic energies of ≈ 969, ≈ 1170, ≈ 1202, and 1403 eV, respectively[15].

RESULTS AND DISCUSSION

Figure 2 shows an electron micrograph of a diblock copolymer SV1 specimen cast from TCE. The dark portions are the selectively stained P4VP blocks. The microdomain structure in SV1 specimen (24 wt% P4VP) shows the texture of discrete P4VP spheres in a PS matrix. The absolute value of the radius of the P4VP spheres, $\bar{R}_{P4VP}$ is far below the theoretical value (32 nm)[16]. The TCE used is a good solvent for PS, and a somewhat poor one for P4VP blocks, judging from the Hildebrand parameter. This morphology is considered to demonstrate the non-equilibrium state of the spherical domain system.

These segregated P4VP chains in a sphere were crosslinked by using quaternization with DBB vapour in the solid state. The morphological results of the crosslinked product SV1-M are shown in *Figure 3*. *Figures 3a* and *b* indicate TEM micrographs of SV1-M cast from 1.0 and 0.1 wt% TCE/nitrobenzene: 10/1 (v/v) solutions, respectively. The textures shown in *Figure 3a* are almost the same as those of the SV1 film specimen (*Figure 2*). That is to

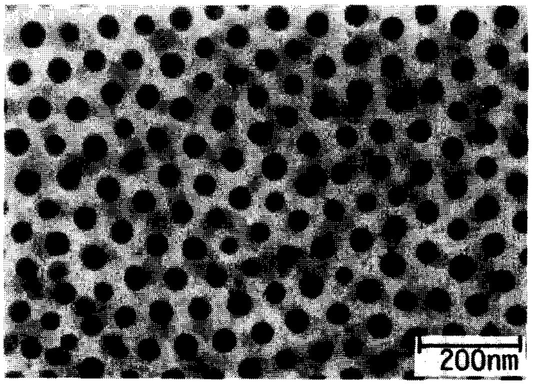

Figure 2 TEM micrograph of SV1 diblock copolymer specimen cast from TCE

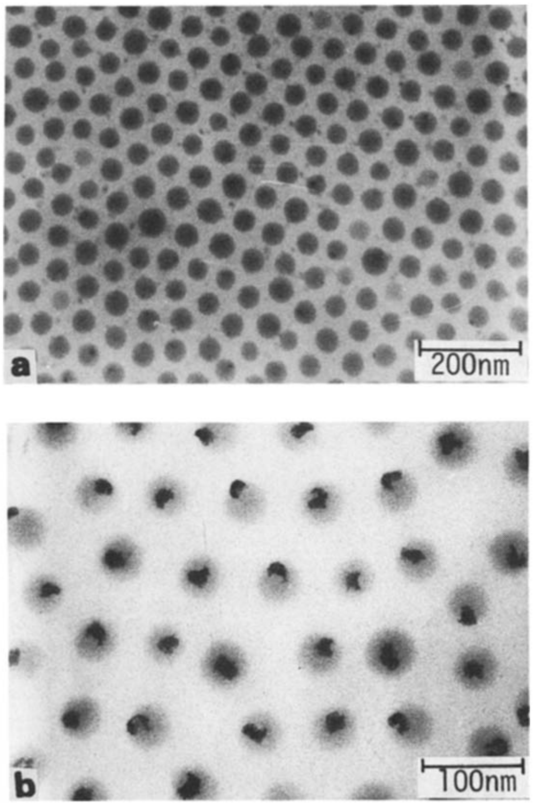

Figure 3 TEM micrographs of restructural cast film from crosslinked product SV1-M, varying the concentration of casting solutions

say, the crosslinked P4VP domains in a sphere are not able to interpenetrate with each other and the polymer microspheres are compatible with only the portion of PS shells. The P4VP spheres of SV1 film are fixed almost same size by crosslinking reaction. It seems from this micrograph that P4VP chains are fixed by quaternization in the spherical microdomain portion. On the other hand, the micrograph shown in *Figure 3b* indicates a multi-molecular micelle. In the preparation conditions of this cast specimen, the multi-molecular micelles are frozen with a structure like the core-shell type polymer microspheres. The dark, grey, and white portions indicate the crosslinked P4VP cores, shell of PS chains, and carbon support, respectively. This micrograph shows clearly the structure of the core-shell type polymer microspheres. It is clear that these microsphere particles have only a narrow size distribution. In the multi-molecular micelle of polymer microspheres however, the crosslinked P4VP core seems to be located on the position far from the centre of the microsphere particles. From the TEM micrograph shown in *Figure 3b*, the average radius of the microsphere particles is 24 nm. The weight fraction of P4VP spheres of SV1 diblock copolymer is 0.24 (*Table 1*) and its volume fraction is estimated to be 0.217 by using densities (ρ) of PS and P4VP segments ($\rho_{PS} = 10.1 \times 10^3$, $\rho_{P4VP} = 11.4 \times 10^3\,\mathrm{mol\,m^{-3}}$)[16]. We make the assumption that the core and shell of the polymer microsphere are constructed of simple body-centred cubic structures. According to the volume fractions of PS and P4VP segements, the theoretical radius of the polymer microsphere is estimated to be 28 nm. The observed value for the polymer microsphere is about the same as the theoretical value.

In previous studies[13,17], we investigated the solution behaviour of core-shell type polymer microspheres. In turbidimetric measurement of microspheres, the solubility depended strongly on that of shell segments. In the nuclear magnetic resonance spectrum, peaks due to the shell segments appeared and peaks due to the core segments disappeared. These results indicate that the micelle of the core-shell type polymer microsphere moves like a suspension in solution. It can be speculated from the above solubility behaviour that the P4VP chains are fixed in the spherical portion, and the crosslinked P4VP chains do not interpenetrate in the shell of PS chains.

According to these results, the cross-sectional structure of the restructural cast film from the crosslinked product seems to be depicted by an imaginary model A in bulk and model B near the free surface (*Figure 4*). Region II constitutes a spherical domain, while the matrix of region I formed by compatible PS chains surrounds the sphere.

The X.p.s. measurement on restructural cast films is one of the best for the inspection of imaginary models. *Figure 5* shows the X.p.s. survey scan (Al Kα; sampling depth: ≈ 5 nm) of the restructural cast film SV1-M. Theoretical atomic percentages of SV1-M are as follows: C, 75.9%; H, 6.9%; N; 2.6; Br, 14.6%. This corresponds to the surface analysis of the composition of the TEM sample film shown in *Figure 3a*. This spectrum shows the presence of surface oxygen (O_{1s}) and silicon (Si_{2s} and Si_{2p}). Confirmation of the presence of surface silicon was not obtained, and in this study we neglect the presence of this element.

Figure 6 shows typical C_{1s}, N_{1s}, and Br_{3d} core level spectra from angular-dependent X.p.s. studies (Al Kα: in *Figure 6a*) sampling depth ≈ 1 nm; (*Figure 6b* sampling depth ≈ 5 nm) on the film SV1-M, where band areas were reproducible to within $\pm 0.4\%$. *Table 2* shows the surface chemical composition of SV1-M at sampling depths of ≈ 1 and ≈ 5 nm calculated from the X.p.s. core level data. The surface characterization of starting diblock copolymer SV1 film as a standard material was also carried out by angular-dependent X.p.s. studies. Theoretical atomic percentages of diblock copolymer SV1 are as follows: C, 89.2%; H, 7.6%; N, 3.2%. This X.p.s. survey scan also shows the presence of surface oxygen and silicon. *Table 3* gives the surface chemical composition of poly(S-b-4VP) diblock copolymer SV1 film at sampling depths of ≈ 1 and ≈ 5 nm calculated from the X.p.s. core

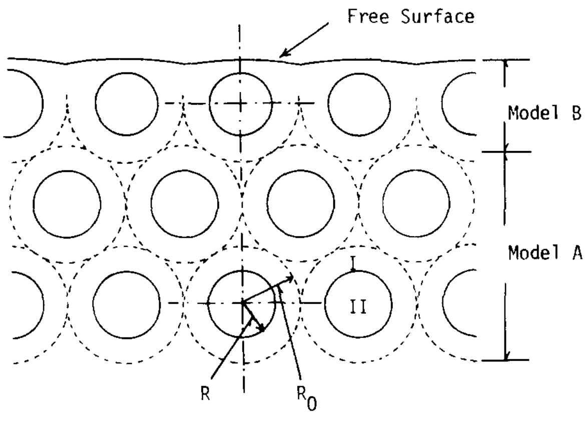

Figure 4 Cross-sectional representation of imaginary models for aggregation film of core-shell type multi-molecular micelles. *R*, radius of a spherical domain II; R_0, radius of an imaginary spherical region containing both matrix I and sphere II

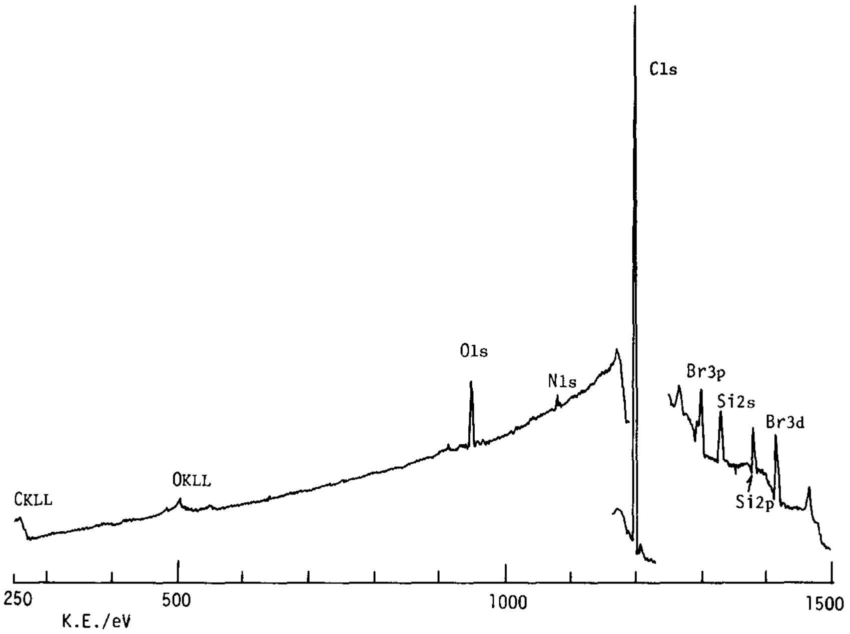

Figure 5 X.p.s. survey-scan of restrucural cast film SV1-M (X-ray Al Kα; sampling depth $\approx$5 nm). KE, kinetic energy

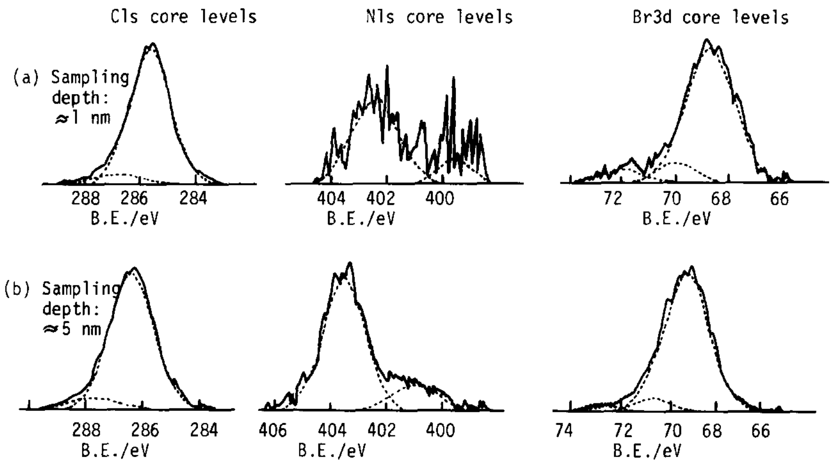

Figure 6 Typical C_{1s}, N_{1s}, and Br_{3d} core level spectra of restructural cast film SV1-M in angular-dependent X.p.s. studies (X-ray Al Kα; (a) sampling depth $\approx$1 nm, (b) sampling depth $\approx$5 nm). BE, binding energy

Table 2 Surface chemical composition of SV1-M restructural cast film

	C_{1s}	O_{1s}	N_{1s}	Br_{3d}	Si_{2p}	Total
Sampling depth: $\approx$1 nm						
Binding energy (eV)[a]	285.0	532.5	401.7	67.9	–	
Peak area (counts)[b]	1.54×10^5	2.77×10^4	834	2.28×10^3	–	
Corrected peak area	1.54×10^5	1.83×10^4	616	523	–	1.75×10^5
factor)[c]	(1.00)	(0.660)	(0.740)	(0.229)	–	
Atom content (wt%)	89	11	(0.4)	(0.3)	–	100
Sampling depth: $\approx$5 nm						
Binding energy (eV)[a]	285.0	532.6	402.1	68.1	102.6	
Peak area (counts)[b]	5.91×10^5	4.01×10^4	7.15×10^3	2.30×10^4	1.23×10^4	
Corrected peak area	5.91×10^5	2.64×10^4	5.29×10^3	5.26×10^3	1.03×10^4	6.38×10^5
(factor)[c]	(1.00)	(0.660)	(0.740)	(0.229)	(0.838)	
Atom content (wt%)	93	4	1 (0.8)	1 (0.8)	2	101

[a] The C_{1s} level at 285.0 eV is used for binding energy calibration

[b] Peak areas are nomalized for DWELL × SWEEP = 1

[c] Correction factors are calculated as follows:

$$\text{factor} = \frac{1}{\sigma}\left(\sqrt{\frac{1203}{\text{KE}}}\right)\frac{0.726195701}{t}$$

where σ = cross-section according to Scofield[18], KE = kinetic energy, and t = transmission

Table 3 Surface chemical composition of SV1 diblock copolymer

	C_{1s}	O_{1s}	N_{1s}	Si_{2p}	Total
Sampling depth: ≈1 nm					
Binding energy (eV)[a]	285.0	532.5	399.4	–	
Peak area (counts)[b]	1.71×10^5	2.31×10^4	2.35×10^3	–	
Corrected peak area	1.71×10^5	1.52×10^4	1.74×10^3	–	1.88×10^5
(factor)[c]	(1.00)	(0.660)	(0.740)	–	
Atom content (wt%)	91	8	1 (0.9)	–	100
Sampling depth: ≈5 nm					
Binding energy (eV)[a]	285.0	532.6	399.4	102.5	
Peak area (counts)[b]	5.58×10^5	2.86×10^4	1.25×10^4	8.07×10^3	
Corrected peak area	5.58×10^5	1.89×10^4	9.25×10^3	6.76×10^3	5.93×10^5
(factor)[c]	(1.00)	(0.660)	(0.740)	(0.838)	
Atom content (wt%)	94	3	2 (1.6)	1	100

[a–c] Cf. *Table 2*

Table 4 N_{1s}/C_{1s} and Br_{3d}/C_{1s} atomicity ratios of diblock copolymer SV1 and restructural cast film SV1-M as a function of sampling depth

Polymer code	Sampling depth	N_{1s}/C_{1s}	Br_{3d}/C_{1s}
Block copolymer SV1	≈1 nm	1.0×10^{-2}	–
	≈5 nm	1.7×10^{-2}	–
(Theoretical ratio of bulk composition)		(3.1×10^{-2})	
Polymer microsphere SV1-M	≈1 nm	4.0×10^{-3}	3.4×10^{-3}
	≈5 nm	9.0×10^{-3}	8.9×10^{-3}
(Theoretical ratio of bulk composition)		(2.9×10^{-2})	(2.9×10^{-2})

level data. It is found from the surface chemical compositions shown in *Tables 2* and *3* that the surface nitrogen content is higher at a sampling depth of ≈5 nm than at a sampling depth of ≈1 nm for both diblock copolymer and restructural cast film. Theoretical nitrogen atomic percentages of SV1 and SV1-M are 3.2 and 2.6 wt%, respectively. Both SV1 and SV1-M films show the rich presence of surface PS chains, and the outermost surface of restructural cast film is almost covered by PS matrix. The surface nitrogen contents (sampling depths of ≈1 and ≈5 nm) of restructural cast films are lower than those of diblock copolymer film. The crosslinked P4VP spheres are considered to be located in a deeper position far from the free surface compared with that of P4VP spheres dispersed in the diblock copolymer film.

In order to distinguish the topographical structure of the restructural cast film from crosslinked product near the free surface, the N_{1s}/C_{1s} and Br_{3d}/C_{1s} atomic ratios are calculated from the X.p.s. spectral data (*Table 4*). The values of N_{1s}/C_{1s} and Br_{3d}/C_{1s} for restructural cast film are almost the same at both the sampling depths (≈1 and ≈5 nm). This fact supports that P4VP chains of the diblock copolymer SV1 film were quantitatively quaternized with DBB. More importantly, if the topographical structure of restructural cast film near the free surface can be represented with model A shown in *Figure 4*, the thickness of the PS matrix from the free surface to the crosslinked P4VP sphere is estimated to be 7 nm ($R_0 - R$). In this case, N_{1s} and Br_{3d} core levels of SV1-M ought not to be detected in angular-dependent X.p.s. spectra at sampling depths of ≈1 and ≈5 nm. Therefore, the results of angular-dependent X.p.s. spectra indicate that the crosslinked P4VP chains in the sphere are accumulated near the free surface, probably due to the deformation of the PS matrix during the aggregation of multi-molecular micelles.

Two models for the topography of the restructural cast film from crosslinked product are presented from experimental results as follows: (1) in the bulk of polymer film, the crosslinked P4VP domains in sphere are not able to interpenetrate and multi-molecular micelles are compatible with only the portion of PS shells. The bulk of restructural cast film then has an ordered structure as shown by model A (*Figure 4*). The texture of the micrograph shown in *Figure 3a* corresponds to this ordered microstructure; (2) in the surface of the polymer film, the portions of PS matrix which contact with air are reduced to deformation, such as model B. Subsequently, the crosslinked P4VP spheres are accumulated near the free surface.

Finally, the topography of multi-molecular micelles is shown by the micrograph given in *Figure 3b*. From this micrograph it is found that the shape of the crosslinked P4VP core is not a spherical structure, and the shell and core of the polymer microsphere are not simple body-centred cubic structures. The crosslinked P4VP core is located at a position far from the centre of microsphere particle. When the multi-molecular micelles are cast on a carbon support, the PS shell will be reduced by deformation. Subsequently the spherical structure of the core will change due to the deformation stress of the PS shell. On the other hand, Okano *et al.*[19] reported that in the 2-hydroxyethyl methacrylate(HEMA)-S-HEMA triblock copolymer, the hydrophilic domains (PHEMA) were accumulated near the free surface compared with in the bulk. This result corresponded to the remarkable increase in wettability. The polymer microsphere used in this work is a hydrophilic core (quaternized P4VP) with a hydrophobic shell (PS). This wettability effect may also appear in the topography of the core-shell type multi-molecular micelle through the solvent evaporation process. In the surface of polymer film, the crosslinked P4VP portions may have other structures, differing from model B in *Figure 4*. To explain this contradiction, it will be necessary to try another characterization of restructural cast film from crosslinked product, for example, the TEM study of a ultrathin cross-section of restructural cast film.

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