Aggregation behaviour of core–shell type polymer microspheres

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The coalescence of core–shell type polymer microspheres was investigated through electron microscopy. The core and shell were formed by crosslinked poly(2-vinylpyridine) (P2VP) and polystyrene (PS) multi-branchings, respectively. The microspheres were dispersed in organic solvents. The arm length of PS branching was controlled by ozonolysis at the position of the introduced isoprene units. The aggregation of microspheres depended strongly on the volume fraction of shell portions. In microspheres with an extremely thin shell, coalescence between P2VP cores was caused by poor steric stabilizing of PS branchings in the dry film.

(Keywords: core–shell microspheres; arm length; aggregation)

INTRODUCTION

Core–shell type microspheres are stabilized even in a good solvent by multi-branchings.[1] These microspheres have interesting structural properties. That is to say, an ordered structure in solution[2] was observed close to the overlap concentration (C^*). A superlattice structure[3] was also observed in the solid state. More recently, Chevalier and coworkers[4] have reported similar results in the film formation of latex particles. These particles were made of a soft polymer core protected by a hydrophilic membrane, and they were dispersed in water. The process of film formation was viewed as a succession of four steps: (1) ordering of the particles as the dispersion is concentrated through evaporation, this step leading to colloidal crystals with a face-centred cubic (f.c.c.) structure; (2) contact between neighbouring particles; (3) coalescence, i.e. fusion of the particles; and (4) interpenetration of the cores of the particles. The volume fraction of shell or hydrophilic membrane of such particles seems to be one of the most important factors in clarifying the aggregation process.

In the preceding paper[5], we have established a novel architecture of core–shell type microspheres with well defined sizes of the core radius and shell thickness. There, poly(styrene-*b*-2-vinylpyridine) diblock copolymers were prepared by sequential anionic addition. The polystyrene (PS) blocks possessed a small amount of isoprene (I) units at a prescribed position, through three-stage addition of S_1, I and S_2 monomers. Core–shell type microspheres were synthesized by the crosslinking of block copolymer film having poly(2-vinylpyridine) (P2VP) spheres with 1,4-diiodobutane (DIB) vapour. Through ozonolysis of these core–shell type microspheres, the arm chains composed of PS branchings were cleaved at the 1,4-linkage of the isoprene units.

In this paper, we prepared core–shell type microspheres with various volume fractions of shell portions through ozonolysis. The dispersion and aggregation behaviours of these microspheres were investigated as a function of volume fraction of shell portion with the aid of electron microscopy, dynamic light scattering (d.l.s.) and turbidimetric measurements.

EXPERIMENTAL

Block copolymer and microsphere syntheses

Synthesis and characterization methods concerning diblock copolymers were given in the previous paper[5]. The characteristics of the diblock copolymers are listed in *Table 1*. Diblock copolymers B1–B3 showed the morphology of dispersed P2VP spheres in a PS matrix. The domain sizes of the P2VP spheres are also listed in *Table 1*.

Synthesis methods concerning core–shell type microspheres were also given in the previous paper[5]. Cleavage of the double bond of the isoprene units was performed by dispersing the core–shell type microspheres in chloroform (1 wt%) containing a 10-fold molar excess of ozone with respect to isoprene units at 25°C for 10 min[6]. Subsequently, precipitation fractionation was carried out in benzene/n-hexane to separate the cleaved PS_1 chains from the reaction products.

Dynamic light scattering and turbidimetric measurement

The particle size (hydrodynamic dimension) of core–shell type microspheres was determined by dynamic light scattering (Photal DLS-7000 dynamic light scattering spectrometer; He–Ne laser, scattering angle = 90°) in 0.1 wt% benzene at 25°C. The method of turbidimetric measurement was given in the previous paper[5].

Morphological observation

The morphology of the core–shell type microspheres was observed as follows. After dissolving the core–shell

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Table 1 Characteristics of poly(S_1-I-S_2-*b*-2VP) diblock copolymers and domain sizes

	$10^{-4}\bar{M}_n$				Content		
Specimen code	Poly(S_1-I)^a	Poly(S_1-I-S_2)^a	Block copolymer^b	$\bar{M}_w/\bar{M}_n$^{c}	Isoprene units^d (number/1-polymer)	P2VP blocks^d (mol%)	Domain size^e, $\bar{R}_{P2VP}$ (nm)
B1	4.2	5.4	6.9	1.08	16	22.2	9
B2	2.5	4.7	5.8	1.05	13	18.2	7
B3	2.6	3.9	4.5	1.10	9	12.9	5

^{a} Determined by gel permeation chromatography (g.p.c.)
^{b} Estimated from $\bar{M}_n$ of PS precursor and composition
^{c} Determined by g.p.c. distribution
^{d} Determined by ^{1}H n.m.r.
^{e} $\bar{R}_{P2VP}$, average domain radius of P2VP spheres

Table 2 Crosslinking conditions and results of B1 and B2 films having P2VP spherical domains with DIB vapour

No.	Reaction time (h)	Q_1^{a} (mol%)	Q_2^{b} (mol%)	Crosslink density^c (%)
B1-1M	12	59.2	61.0	57.4
B1-2M	30	41.3	62.6	20.0
B2-1M	12	34.9	42.0	27.8
B2-2M	30	34.1	60.4	7.8

^{a} The degree of quaternization of microspheres determined by Volhard's titration in benzene
^{b} The total degree of quaternization of microspheres and pendent I groups determined by Volhard's titration in benzene and triethylamine mixture

type microspheres in benzene, a 0.1 wt% solution was dropped onto a microscope mesh coated with carbon film for taking transmission electron micrographs (TEM). The quaternized P2VP cores were stained with osmium tetroxide (OsO_4) vapour. Microsphere particles were shadowed with platinum/palladium (60/40) at a low shadowing angle (15–20°) to provide contrast. Morphological results were obtained on a Hitachi H-500 TEM at 100 kV.

RESULTS AND DISCUSSION

The gel permeation chromatograph (g.p.c.) profiles showed that the diblock copolymers B1–B3 had unimodal and narrow molecular-weight distributions. The microstructure of polyisoprene (PI) units contained 50% 3,4- and 50% 1,4-structures (60% *cis*, 40% *trans*).

The segregated spherical P2VP domains were crosslinked using quaternization with DIB vapour at 50°C in the film state. We did not use diblock copolymer B3 for further crosslinking reaction, because the cast film was very brittle. *Table 2* lists the crosslinking conditions and the results for B1 and B2 films having P2VP spherical domains with DIB vapour, for varying reaction times. It is found from these results that effective crosslinkages of P2VP cores decrease with long reaction times (B1-2M and B2-2M).

The turbidity curves of the B1-M and B2-M series are shown in *Figures 1* and *2*, respectively. Both B1-1M and B1-2M precipitate in n-hexane fraction of low values (high-molecular-weight side) compared with the original B1 diblock copolymer. The precipitation behaviour of

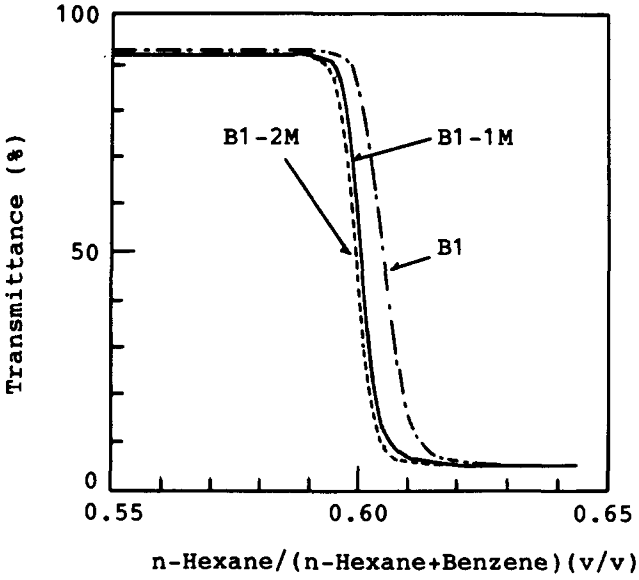

Figure 1 Turbidity curves of B1-1M and B1-2M crosslinked products

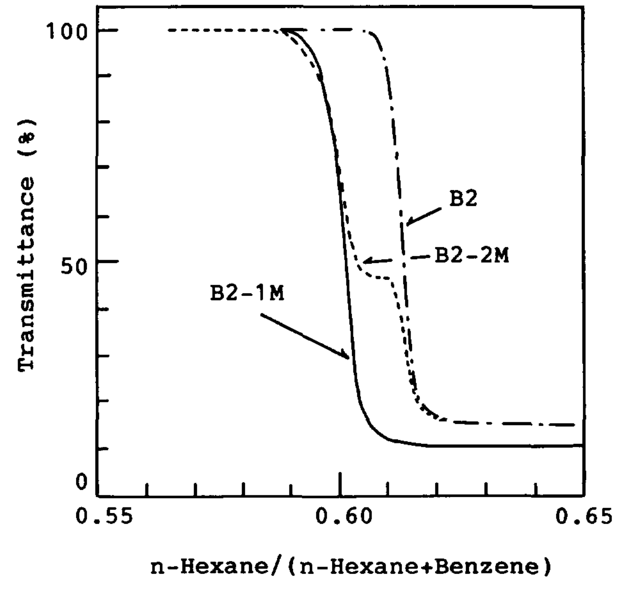

Figure 2 Turbidity curves of B2-1M and B2-2M crosslinked products

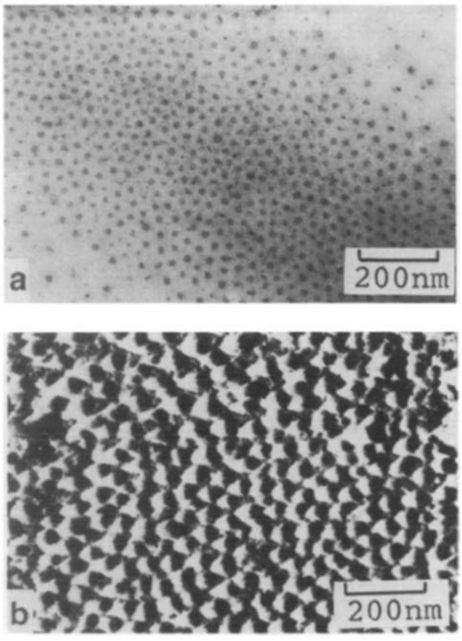

Figure 3 TEM micrographs of B1-1M microspheres cast from 0.1 wt% benzene solution: (a) stained with OsO_4; (b) shadowed with Pt/Pd

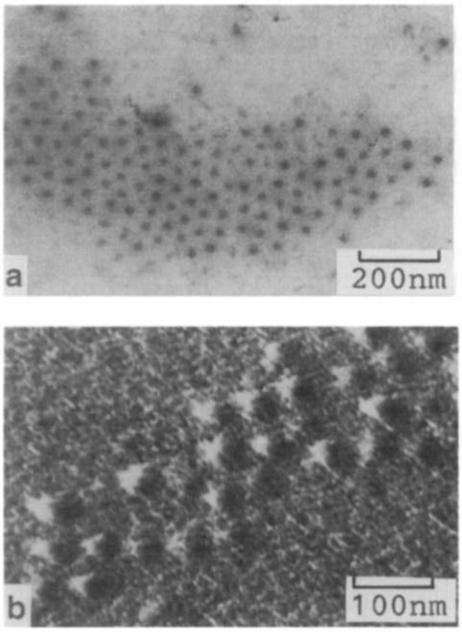

Figure 4 TEM micrographs of B2-1M microspheres cast from 0.1 wt% benzene solution: (a) stained with OsO_4; (b) shadowed with Pt/Pd

B2-1M also shows a similar result to the crosslinked products of the B1-M series. It is therefore suggested that B1-1M, B1-2M and B2-1M are core–shell type microspheres in which P2VP chains in the core are completely immobilized. However, the turbidity curve of B2-2M shows a plateau at a fraction of 0.61 and subsequent turbidity overlaps with that of B2 diblock copolymer. So, the B2-2M product is a mixture of core–shell type microspheres and unimmobilized B2 diblock copolymer owing to the low crosslink density (7.8%) of P2VP chains in the core. This sample was not employed in the following work.

Figure 3a shows the TEM micrograph of B1-1M microspheres cast from 0.1 wt% benzene solution. The dark portions indicate the crosslinked P2VP cores. *Figure 3b* shows the TEM micrograph of B1-1M microspheres shadowed with Pt/Pd. It is clear that particles of core–shell type microspheres are immobilized on the carbon substrate and that these particles have a narrow size distribution. The microsphere particles are aligned in a nearly ordered arrangement on the carbon mesh. *Figures 4a* and *4b* show the TEM micrographs of B2-1M microspheres stained with OsO_4 and shadowed with Pt/Pd, respectively (cast from 0.1 wt% benzene solution). The morphological behaviour of B2-1M is quite similar to that of B1-1M microspheres. The aggregation numbers of B1-1M (B1-2M) and B2-1M microspheres can be calculated to be 100 and 98, respectively, using $\bar{R}_{P2VP}$ and the density of P2VP ($11.4 \times 10^3\ \mathrm{mol\,m^{-3}}$)[7]. *Figure 5* shows typical TEM micrographs of the dry film of B1-1M microspheres cast from 1.0 wt% benzene solution. The P2VP cores seem to be aligned in a hexagonal array. According to three-dimensional TEM observation for this film[3], the packing structure of microspheres was concluded to be an f.c.c. lattice. The domain sizes of microspheres and the average domain distance ($\bar{L}_n$) of P2VP cores for the dry films are listed in *Table 3*. The crosslinked P2VP cores do not interpenetrate with each other and the microspheres are compatible with only the portion of PS shells.

The core–shell type microspheres after ozonolysis were separated by precipitation fractionation. *Figures 6* and *7* show the TEM micrographs of ozonolysis products of B1-2M microspheres (B1-2MD) and B2-1MD, respectively. *Figures 6a* and *7a* indicate the TEM samples shadowed with Pt/Pd (cast from 0.1 wt% benzene solution), and *Figures 6b* and *7b* indicate the TEM specimens of the dry films stained with OsO_4

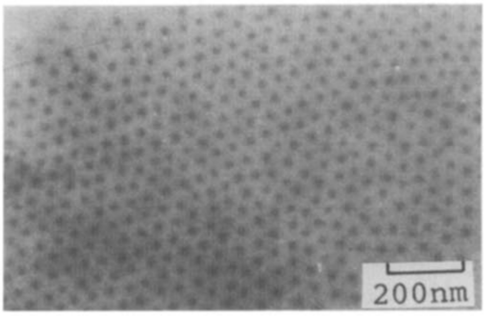

Figure 5 TEM micrograph of the dry film of B1-1M microspheres

Table 3 Domain sizes of microspheres and domain distance of P2VP cores for the dry films

	Microsphere			Dry film	
Specimen code	$\bar{R}_{P2VP}$[a] (nm)	$\bar{D}_n$[b] (nm)	$\bar{D}_w/\bar{D}_n$[c]	$\bar{L}_n$[d] (nm)	$\bar{L}_w/\bar{L}_n$[e]
B1-1M (B1-2M)	9	45	1.03	46	1.01
B2-1M	7	40	1.01	43	1.01

[a] Radius of P2VP cores
[b] Particle diameter of microspheres in the solid state
[c] Distribution of particle diameter
[d] The average domain distance of P2VP cores
[e] Distribution of domain distance of P2VP cores

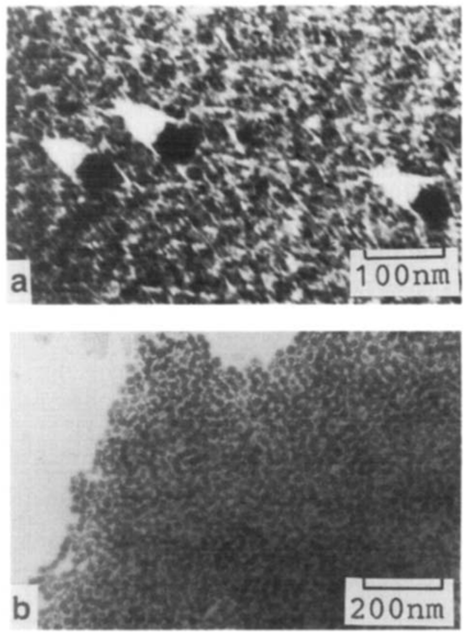

Figure 6 TEM micrographs of B1-2MD specimens: (a) microsphere shadowed with Pt/Pd; (b) dry film stained with OsO_4

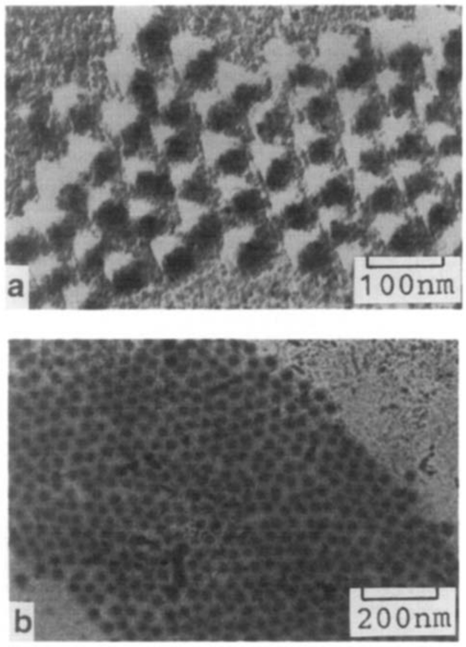

Figure 7 TEM micrographs of B2-1MD specimens: (a) microsphere shadowed with Pt/Pd; (b) dry film stained with OsO_4

(cast from 1.0 wt% benzene solution). It is found from *Figures 6a* and *7a* that both particle diameters of B1-2MD and B2-1MD decrease compared with those of B1-2M and B2-1M, respectively. The B2-1MD microsphere particles are aligned in a nearly ordered arrangement on the carbon mesh. It is found also from *Figure 7b* that the crosslinked P2VP cores do not interpenetrate with each other, though the domain distance ($\bar{L}_n$) of P2VP cores decreases compared with that of the dry film B2-1M. However, it is found from *Figure 6b* that coalescence between P2VP cores is caused by the poor steric stabilizing of PS shell in the dry film B1-2MD. The shell thickness of B1-2MD is thinner than that of B2-1MD microspheres. *Table 4* lists the particle sizes of microspheres B1-2MD and B2-1MD and domain distance of P2VP cores for the dry films.

Figure 8 shows typical particle size distributions of the B1-2M and B1-2MD microspheres in benzene by means of d.l.s. Both microspheres have a unimodal pattern of particle species. The d.l.s. data support the idea that B1-2MD is a core–shell type microsphere in which the quaternized P2VP chains in the core are completely immobilized. *Table 5* lists the particle sizes and their distributions of microspheres before and after ozonolysis in benzene.

Thus core and shell are formed by crosslinked P2VP (hydrophilic) and PS (hydrophobic) multi-branchings, respectively. The solubility of core–shell type microspheres with long length of branchings depends strongly on that

Table 4 Particle sizes of microspheres after ozonolysis and domain distance of P2VP cores for the dry films

	Microsphere		Dry film	
Specimen code	$\bar{D}_n$[a] (nm)	$\bar{D}_w/\bar{D}_n$[b]	$\bar{L}_n$[c] (nm)	$\bar{L}_w/\bar{L}_n$[d]
B1-2MD	30	1.01	–	–
B2-1MD	35	1.02	36	1.03

[a] Particle diameter of microspheres in the solid state
[b] Distribution of particle diameter
[c] The average domain distance of P2VP cores
[d] Distribution of domain distance of P2VP cores

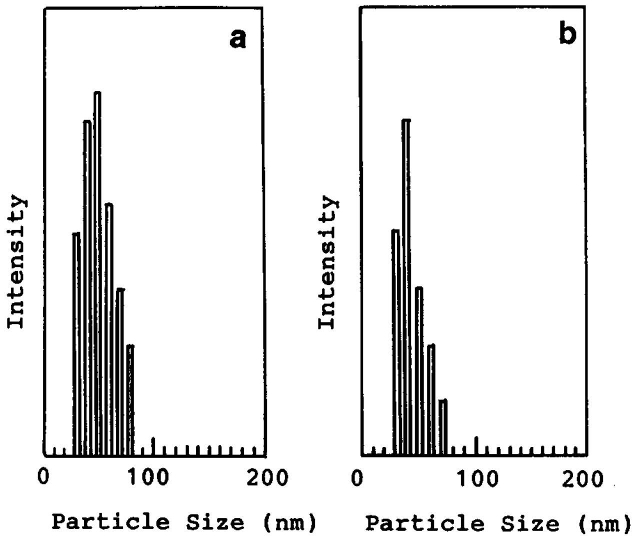

Figure 8 Particle size distributions of the B1-2M and B1-2MD microspheres in benzene: (a) B1-2M; (b) B1-2MD

Table 5 Particle sizes and their distributions of microspheres before and after ozonolysis in benzene

Sample	$\bar{D}_w$[a] (nm)	$\bar{D}_w/\bar{D}_n$[b]
B1-2M	55.3	1.3
B1-2MD	39.7	1.1
B2-M	50.0	1.2
B2-1MD	40.3	1.1

[a] Weight-average particle size
[b] Distribution of particle size

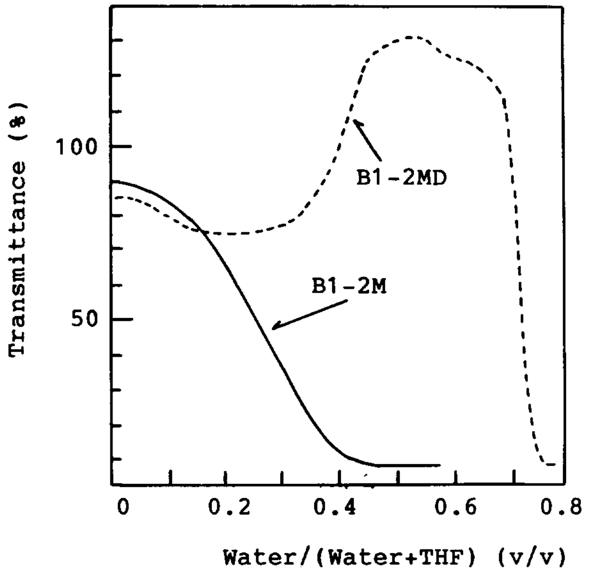

Figure 9 Turbidity curves of B1-2M and B1-2MD in water/tetrahydrofuran solvent system

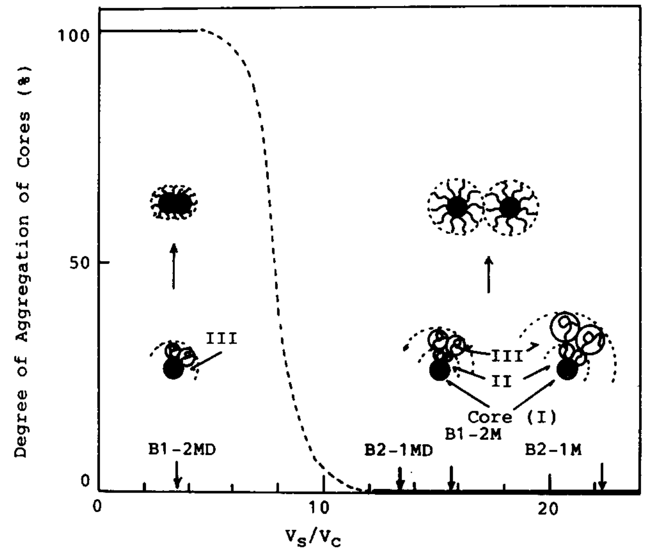

Figure 10 Schematic representation of aggregation process for core–shell type microspheres as a parameter of V_s/V_c

Table 6 Characteristics of core–shell type polymer microspheres in the solid state

Sample	$\bar{R}_{\mathrm{P2VP}}$[a] (nm)	T[b] (nm)	V_s/V_c[c]
B1-2M	9	13.5	15.7
B1-2MD	9	6.0	3.6
B2-1M	7	13.0	22.3
B2-1MD	7	10.5	13.3

[a] The average radius of P2VP cores
[b] Thickness of PS shell portions
[c] V_s and V_c indicate volume fractions of shell and core portions, respectively

of the stabilizing shell segments. Such solubility of microspheres is expected to change after ozonolysis. *Figure 9* shows the turbidity curves of B1-2M and B1-2MD in water/tetrahydrofuran solvent system. The B1-2M microspheres precipitate with addition of water. However, the B1-2MD microspheres precipitate until a water fraction of 0.20, but the turbidity decreases suddenly beyond this fraction value. The shell thickness of B1-2MD microspheres is extremely thin, so the hydrophilic nature of quaternized P2VP cores is reflected in the solubility. The solubility of B2-1M and B2-1MD microspheres is very similar to that of B1-2M microspheres.

Daoud and Cotton[8] were the first to study the conformation and dimensions of star polymers in a solvent of low molecular weight by means of scaling ideas. According to them, each arm can be seen as a succession of growing spherical 'blobs'. The picture presented for a star polymer consists of three regions, a central core (region I), a shell with semidilute segment density in which the arms have their unperturbed chain conformation (region II), and an outer shell in which the arms of the star assume a self-avoiding conformation (region III). More recently, Fredrickson and coworkers[9] have investigated the static behaviour of star polymers in high-molecular-weight solvents. The conformation of core–shell type microspheres employed in this study is very similar to that of a star polymer. In a core–shell microsphere, the crosslinked P2VP microgel can be regarded as the central core of region I. The PS arm of the shell can be seen as a succession of growing blobs in regions II and III. As mentioned in the former results, the coalescence of core–shell microspheres in film formation depends on the volume fraction of the shell portion. *Table 6* lists the characteristics of core–shell microspheres in the solid state; V_s/V_c indicates the volume fraction ratio of shell to core.

Figure 10 shows the schematic representation of the aggregation process for core–shell type microspheres as a function of V_s/V_c. In B2-1MD, B1-2M and B2-1M microspheres, the cores (region I) are dispersed in solvent by a stabilizing layer of PS arms (regions II and III). Within one blob, an arm behaves like an ideal chain. The ordering of these microspheres may appear close to the concentration C^*. The crosslinked P2VP cores do not interpenetrate with each other and the core–shell microspheres are compatible with their PS shells during solvent evaporation. As a result, a packing structure such as an f.c.c. lattice appears in the dry film. On the other hand, in the B1-2MD microspheres with extremely thin shell, the cores are dispersed in solvent by the layer of PS arms (region III). The next step leads to direct contact between the P2VP cores of neighbouring particles owing to the poor steric stabilizing of PS arms, and subsequently leads to coalescence of the microspheres.

CONCLUSION

Core–shell type polymer microspheres with various volume fractions were prepared through ozonolysis of PS arms. In microspheres with high volume fraction of PS shell, the cores were dispersed in solvent by a stabilizing layer of PS arms. A packing structure such as an f.c.c. lattice appeared in the dry film. In microspheres with extremely low volume fraction of PS shell, coalescence of the microspheres occurred in the dry film.

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