Arm-number effect of core–shell type polymer microsphere: 1. Control of arm-number of microsphere

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Poly[styrene(S)-*b*-2-vinyl pyridine (2VP)] diblock copolymer (SV1, $\overline{M_n} = 2.1 \times 10^4$, 2VP = 14.0 mol%) and poly[S-*b*-isoprene (IP)-*b*-2VP] triblock copolymer (SV2, $\overline{M_n} = 1.1 \times 10^4$, 2VP = 12.4 mol%, IP = 3.6 mol%) were synthesized by anionic addition polymerization. By blending SV1 and SV2 from benzene solution at 2 wt% polymer concentration, the co-micelled microphase separated film with P2VP spheres in a PS matrix was obtained. Monodispersed P2VP core–PS shell type polymer microspheres which had two types of PS arms owing to the PS sequences of SV1 and SV2 were synthesized by crosslinking the co-micellized films with 1,4-diiodobutane. Arm-numbers of the microsphere were between 440 and 540. PS arms owing to SV2 in the microsphere were cut off quantitatively from the microsphere by degradation of the PIP blocks of SV2 on the surface of the P2VP core with ozone. By changing the volume fraction of SV2 in the microsphere from 20 to 40 wt%, the arm-number of the microsphere could be controlled quantitatively in the range of 88–540.

(Keywords: block copolymer; blend; microsphere)

INTRODUCTION

It is well known that block and graft copolymers with incompatible sequences undergo microphase separation owing to the many interesting properties of the block and graft copolymers. We have proposed a novel synthetic method for obtaining a core–shell type polymer microsphere by crosslinking the segregated chains in spherical microdomains. Based on this concept, we have synthesized the following core–shell microspheres: poly[4-vinyl pyridine (4VP)] core–polystyrene (PS) shell type microsphere from poly[S-*b*-4VP][1–3], polyisoprene (PIP) core–PS shell type microsphere from poly(S-*b*-IP)[4], poly[2-vinyl pyridine (2VP)] core–PS shell type microsphere from poly(S-*b*-2VP)[5] and poly[methacrylic acid (MAA)] core–PS shell type microsphere from poly(S-*b*-MAA)[6]. In all cases, it was possible to synthesize monodispersed microspheres with a core–shell structure.

In the selective solvent which is good for the shell sequence and a non-solvent for the core, the core–shell microsphere is composed of a solid core with soluble shell chains (arms) grafted onto the core.

This core–shell structure is similar to that of the $(AB)_f$ type star block copolymer composed of an AB type block copolymer with *f*-arms. In fact, de la Cruz and Sanchez[7] calculated that the $(AB)_f$ type star block copolymer with large f (>100) formed a core–shell structure by itself in solution. The formation of a crystalline array of the star block copolymer near the overlap concentration is expected[8]. For the core–shell type microsphere which has a similar structure to the star polymer, formation of a crystalline array is also expected.

Based on this concept, the P4VP core–PS shell microspheres were cast on the carbon substrate from dilute benzene and tetrahydrofuran (THF) solutions. In some cases, a near ordered arrangement of the microspheres was observed on the carbon substrate[9]. However, microspheres with other characteristics did not align in an ordered arrangement[10].

According to Daoud and Cotton[11], the conformation of the arms, which affected the arrangement of the microspheres, could be predicted as a function of the arm-number (f), degree of polymerization of the arm (DP), excluded volume (v) and polymer concentration (c). In order to investigate the arrangement of the microspheres, these factors (f, DP, v and c) should be varied. However, it is very difficult to control the values of f and DP of the microsphere synthesized by this method. The morphology of the microphase-separated film of the block copolymer is determined using the composition of the block copolymer by Molau's rule.

In order to change f, removal of the arms from the microsphere is proposed in this paper. If the microsphere has both arms that can be removed and those that cannot, the arm-number of the shell can be reduced by cutting off the removable arms. By varying the ratio of removable arms in the microsphere, it will be possible to control f of the microsphere quantitatively. The purpose of this study is to control f of the microsphere by cutting off specific arms from the microsphere.

In this paper, PS and P2VP were chosen as the shell and the core. 1,4-Polymerized PIP which could be

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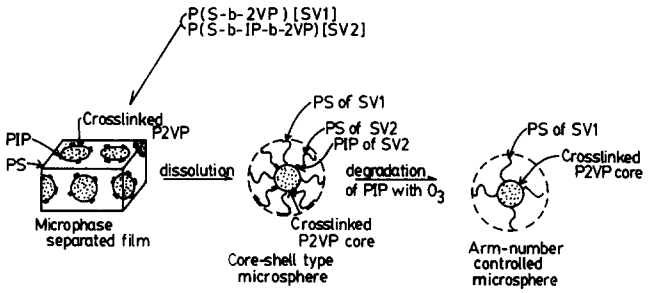

Figure 1 Schematic diagram illustrating the concept of controlling the arm-number by degradation of the PIP sequences in the microsphere

degraded by ozone[12] was used as the breakable junction of PS and P2VP sequences. P(S-*b*-2VP) diblock copolymer (SV1) and poly(S-*b*-IP-*b*-2VP) triblock copolymer (SV2) were synthesized as the stable and breakable block copolymers by ozone, respectively. Then, the microsphere with a P2VP core and PS shell arms from both SV1 and SV2 was synthesized by the crosslinking of a P2VP spherical microdomain formed with both SV1 and SV2.

In this paper, the co-micellization of SV1 and SV2 to form a P2VP spherical microdomain was also investigated. The change of the size and the shape of the microsphere by cutting off the arms formed with SV2 by ozone was investigated. A schematic diagram of the synthesis of the microsphere and the control of f is shown in *Figure 1*.

EXPERIMENTAL

Synthesis and characterization of block copolymers

P(S-*b*-2VP) diblock copolymer (SV1) and P(S-*b*-IP-*b*-2VP) triblock copolymer (SV2) were prepared by the usual sequential anionic addition polymerization procedure using n-butyllithium as an initiator. SV1 was synthesized in THF at −78°C . The P(S-*b*-IP) block of SV2 was synthesized in toluene at −78°C and living P(S-*b*-IP) was reacted with 2VP in a toluene–THF mixture (toluene 50 vol%) at −78°C.

The number-average molecular weights ($\overline{M}_n$) of precursor PS of SV1 and SV2 were determined with a Tosoh HLC-8020 g.p.c. with THF as an eluent at 38°C, a TSK-gel GMHXL column and a flow rate of 1.0 ml min^{-1}. The weight-average molecular weights ($\overline{M}_w$) of the block copolymers were determined by combining g.p.c. data and viscometric data in THF at 38°C. The 2VP contents of SV1 and SV2 and the IP content of SV2 were determined with a ^{1}H n.m.r. spectrometer (270 MHz, JEOL GX270 n.m.r. spectrometer).

Preparation and crosslinking of films

The microphase separated films (120 μm thick) of SV1, SV2 and their blends were cast from benzene (0.02 g ml^{-1}) solution on a Teflon sheet. The cast films were gradually dried for 4 days at room temperature. Crosslinking of segregated P2VP sequences in P2VP microdomains was carried out by quaternization with 1,4-diiodobutane (DIB) vapour. The degree of quaternization (DQ) and crosslink density of the P2VP sequence were measured by Volhard's titration with aqueous $AgNO_3$ and KCNS in benzene and benzene–triethylamine, respectively[5].

Degradation of polymer with ozone

Polymer was dissolved in chloroform at 0.2 wt% polymer concentration. Ozone was produced by passing an oxygen steam through an electric discharge. The flow rate of oxygen was monitored with a flow meter. Ozone was passed into the chloroform–polymer solution at 25°C. The concentration of ozone in the chloroform solution was measured by titration with aqueous KI and $Na_2S_2O_3$ with a small amount of starch solution as an indicator. After degradation, the chloroform solution was evaporated, and dried polymer was dissolved in benzene and freeze-dried. The degradation of block copolymer SV2 was measured by g.p.c. as described above.

Morphology

Ultra-thin specimens were prepared by cutting the films with a microtome (Reinhert-Nissei Co., Ultracut N) and stained with OsO_4. TEM specimens of crosslinked products and degraded products were prepared by using a drop of 0.05 wt% benzene solution, and drying and staining with OsO_4. To observe the external shape of the crosslinked products and degraded products, the specimens cast from 0.05 wt% benzene solution were shadowed with chromium at an angle of 30° or 20°. The morphological results were obtained using a Hitachi H-500 TEM at 75 kV.

Turbidimetric behaviour

A sample of polymer (0.05 g) was dissolved in THF (20 ml) and then n-hexane was added stepwise with vigorous stirring in a cell at 25°C. At each step, the turbidity of the solution was measured with a single beam ultraviolet-visible spectrophotometer (Hitachi, u.v.-vis. spectrophotometer 139) at 600 nm.

RESULTS AND DISCUSSION

Synthesis of block copolymers

The characteristics of the block copolymers are given in *Table 1*. The molecular weight distributions of SV1 and SV2 were narrow and the 2VP contents (~14 mol%) were <30 mol%.

For breakable SV2, 1,4-polymerized PIP was required for degradation with ozone. The polymerization of P(S-*b*-IP) was carried out in toluene[13] and the polymerization of the P2VP block sequence was carried out in THF, respectively.

The IP content in SV2 was small (4 mol%). This was due to the decrease of the effect of IP on the microphase separated structure of P(S-*b*-IP-*b*-2VP) film. *Figure 2* shows the ^{1}H n.m.r. spectrum of SV2. The peak corresponding to C=C of PIP was observed at 4.7 ppm (1,4-type), but the peak corresponding to 1,2-type PIP could not be observed. Therefore the structure of the PIP sequence was that of the 1,4-polymer.

Table 1 Characteristics of block copolymers SV1 and SV2

No.	$\overline{M}_n$[a] of (×10^{-5}) block	$\overline{M}_n$[a] of (×10^{-5}) precursor PS	$\overline{M}_w/\overline{M}_n$[a] of block	Composition[b] (mol%) S	2VP	IP
SV1	2.07	1.92	1.11	86	14	0
SV2	1.16	0.80	1.04	84	12.4	3.6

[a] Determined by g.p.c.
[b] Determined by ^{1}H n.m.r.

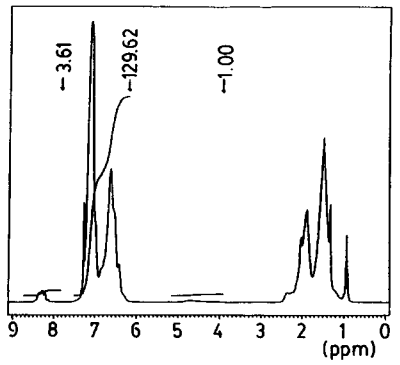

Figure 2 ^{1}H n.m.r. spectrum of triblock copolymer SV2

Co-micellization of SV1 and SV2

In order to co-micellize the SV1 and SV2 in the film, a blend film of SV1 and SV2 was prepared. The conditions are listed in *Table 2*.

Figure 3 shows TEM micrographs of cross-sections of SV1, SV2 and their blend containing 40 wt% SV1 (F40). The dark regions are the selectively stained 2VP chains. The microphase separated structures of these films were P2VP spheres in a PS matrix. The number-average diameters ($\overline{D_n}$) of the P2VP microdomain were 28.1 and 40.0 nm for SV1 and SV2, respectively. The P2VP diameter of the blend of SV1 and SV2 was 56.4 nm. The diameter distributions ($\overline{D_w}/\overline{D_n}$) of the P2VP spherical microdomain in all films were narrow (<1.1). In *Figures 3b* and *c*, no microdomain of the PIP sequence owing to SV2 was observed clearly, because the *DP* of the PIP sequences was small (25). Thus, the effect of the PIP sequence on the microphase separation was neglected. From the architecture of SV2, P(S-*b*-IP-*b*-2VP), it was considered that the PIP sequences existed at the interface of P2VP and PS.

The $\overline{D_n}$, $\overline{D_w}/\overline{D_n}$ and M_{2VP}, molecular weight of P2VP in the system averaged with the values of SV1 and SV2, are listed in *Table 2*. For all films, $\overline{D_n}$ increased with increase in M_{P2VP} between the range of $\overline{D_n}$ values of SV1 and SV2. The diameter distributions of all films were narrow. This suggested that the blended polymers obeyed a mixed micelle theory[14] and SV1 and SV2 were co-micellized in a P2VP microdomain homogeneously in the film. In other words, each P2VP microdomain was formed with both SV1 and SV2 at the feed blend ratio. For example, the P2VP microdomain in F40 was formed with 40% SV1 and 60% SV2. Then, the P2VP microdomains of blend films were crosslinked with DIB.

Microsphere synthesis

The conditions and results for crosslinking are given in *Table 3*. The M series in *Table 3* indicates the crosslinked products or microspheres. The crosslink densities of all films were >13 mol%. These values indicated that they were sufficient to fix the microdomain structure in the good solvent.

In order to examine the shape and size of the crosslinked products, TEM observation of the crosslinked products obtained by casting and quickly drying the dilute solution (polymer concentration 0.05 wt%) was carried out. It is impossible to obtain the microphase separated film of block copolymer under these conditions. *Figure 4* shows the TEM micrographs of M40 shadowed at an angle of 20° (*Figure 4a*) and P2VP chains stained

Table 2 Characteristics of blend films of SV1 and SV2

No.	SV1 (wt%)	SV2 (wt%)	M_{2VP}[a] ($\times 10^{-4}$)	$\overline{D_n}$[b] of 2VP (nm)	$\overline{D_w}/\overline{D_n}$[b]	f[c]
SV1	100	0	1.50	28.1	1.09	552
SV2	0	100	3.60	40.0	1.07	670
F20	20	80	1.90	36.0	1.03	229
F30	30	70	2.10	64.7	1.31	5090
F40	40	60	2.34	56.4	1.07	2890
F50	50	50	2.55	109.0	1.07	24020

[a] $\overline{M_n}$ of P2VP averaged with $\overline{M_n}$ of SV1 and SV2
[b] Determined by TEM data
[c] Arm-number calculated from the diameter of the P2VP microdomain

Table 3 Conditions and results of crosslinking of films

No.	Film	DC[a] (mol%)	DQ[b] (mol%)	f[c]	Diameter (nm)[d] External	Core
M20	F20	13.3	54.6	440	47 (1.00)	28 (1.06)
M30	F30	25.6	38.4	540	82 (1.01)	31 (1.16)
M40	F40	15.8	18.8	530	41 (1.00)	32 (1.03)
M50	F50	42.9	55.7	540	47 (1.05)	33 (1.02)

[a] Crosslink density measured by Volhard's titration
[b] Degree of quaternization measured by Volhard's titration
[c] Arm-number calculated from the diameter of the P2VP core
[d] Number-average diameter measured by TEM. Values in parentheses indicate size distribution

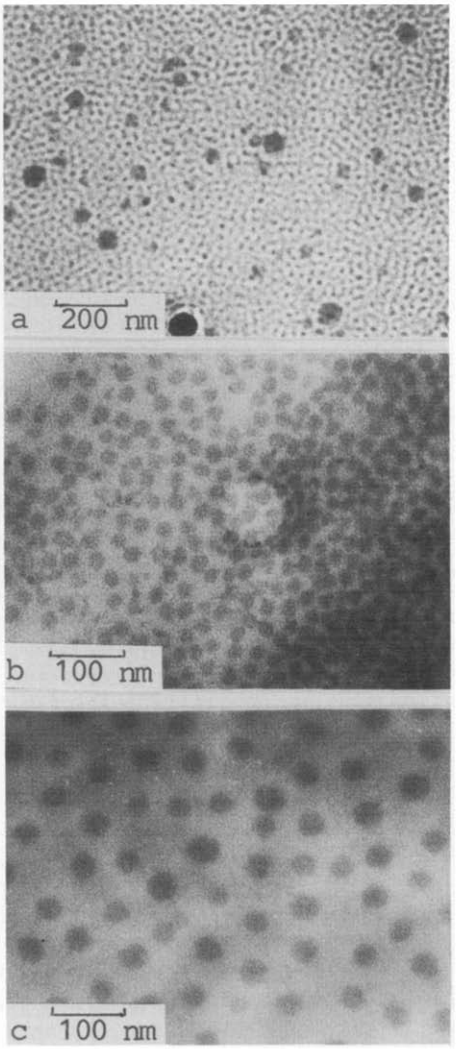

Figure 3 TEM micrographs of SV1 and SV2 cast from benzene solution and stained with OsO_4: (a) SV1; (b) SV2; (c) F40

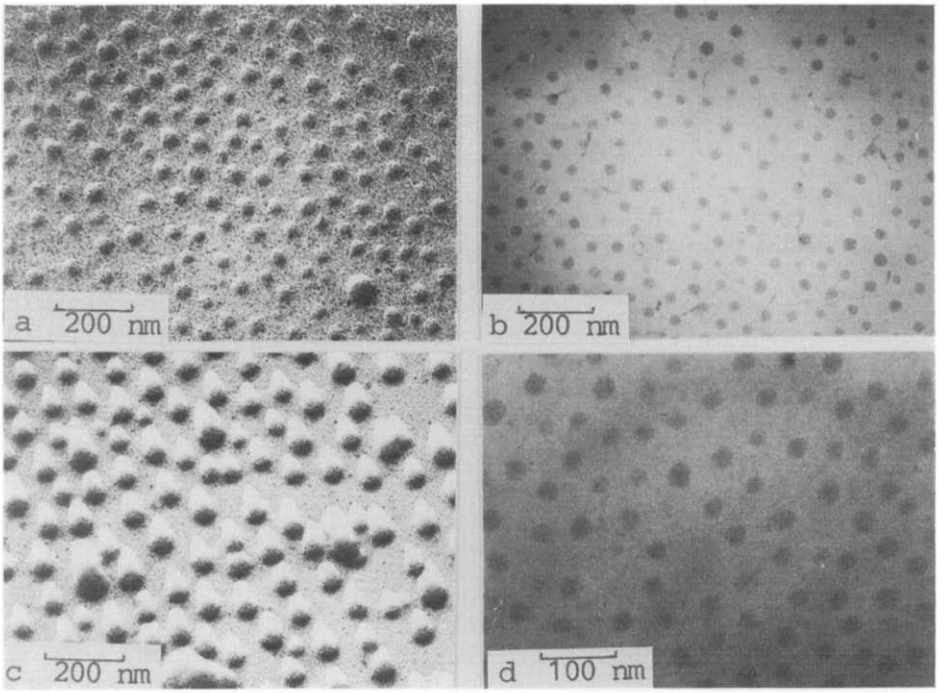

Figure 4 TEM micrographs of microspheres: (a) M40 shadowed at an angle of 20°; (b) M40 stained with OsO_4; (c) O40 shadowed at an angle of 20°; (d) O40 stained with OsO_4

with OsO_4 (*Figure 4b*). From the observation of the external shape (*Figure 4a*), the isolated spherical products ($\overline{D_n}$ = 41 nm; $\overline{D_w}/\overline{D_n}$ = 1.00) were dispersed on the carbon substrate.

For M40, the diameter of the P2VP microdomain (the dark region in *Figure 4b*) was 32 nm and its distribution was narrow. As in *Figure 3*, no PIP microdomain was observed in *Figure 4b*.

As the external diameter of the microsphere (41 nm) was larger than that of the P2VP core (32 nm) and the diameter distribution was very narrow, it was concluded that one type of monodispersed P2VP core–PS shell microsphere was synthesized. The P2VP size and external size for all crosslinked products are listed in *Table 3*.

From a detailed observation, the diameter of the P2VP core decreased from 56 to 32 nm. The decrease of the core diameter by crosslinking has been observed previously[5]. As in the previous case, this phenomenon can be explained in terms of the escape of uncrosslinked (unfixed) block copolymer from the microdomains. It is noticed that in spite of such an escape, the microsphere is monodispersed.

In order to investigate turbidimetric behaviour, the precipitating behaviour of SV1, SV2 and the microsphere in THF/n-hexane was measured (*Figure 5*). For SV1 and SV2, the volume fractions of n-hexane were 75 and 32 vol%, respectively. F20, the blend film, shows two steps for turbidity. The solvent compositions at each step agreed well with the precipitant for SV2 and SV1.

On the other hand, M20 precipitated suddenly at 70 vol% n-hexane. This indicates that the precipitating property of M20 is uniform. If the products owing to the crosslinking of microdomains formed with SV1 and/or SV2 were formed, a few steps precipitation behaviour or gradual turbidimetric behaviour would be observed during the turbidimetric titration. Hence, the co-micellization of SV1 and SV2 and crosslinking of the co-micelled microdomain were successful.

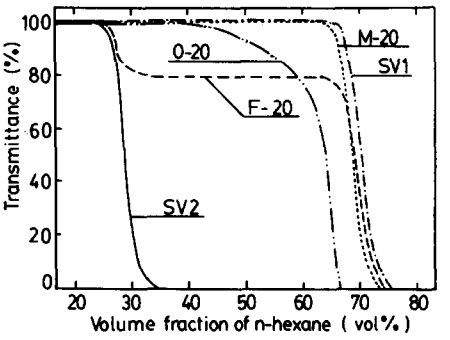

Figure 5 Turbidimetric behaviours of SV1, SV2, F20, M20 (crosslinked F20) and O20 in THF/n-hexane

Consequently, it was concluded that the P2VP core–PS shell type microsphere containing both SV1 and SV2 was synthesized, and the composition of SV1 and SV2 in the microsphere was uniform. In other words, the F20 microsphere, which was synthesized from the blend film of 20% SV1, was composed of 20% SV1. This conclusion supports the results for the relationship between $\overline{D_n}$ and M_{2VP} in *Table 2*.

From the volume of the P2VP core, the aggregation number (arm-number), f, of the microsphere was calculated by using the following equation:

$$f=(4\pi/3)R_{2VP}^3\rho_{2VP}N_A/DP_{2VP} \quad (1)$$

where R_{2VP}, ρ_{2VP}, N_A and DP_{2VP} are the radius of the P2VP core, the density of P2VP, the Avogadro number (6.02×10^{23} mol^{-1}) and the average degree of polymerization of the P2VP block in the blend, respectively. In this study, the density of P2VP[15] is 11.4×10^3 mol m^{-3}. The f values calculated are listed in *Table 3*. The f values of the microspheres synthesized in this study were between 440 and 540.

Table 4 Degradation of block copolymer SV2 in chloroform at 25°C

No.	O_3/IP (mol/mol)	Yield[a] (%)
1	0.062	29.3
2	0.124	30.3
3	0.393	100
4	0.497	100
5	0.994	100

[a] Fraction of block copolymer cut off determined by g.p.c. data

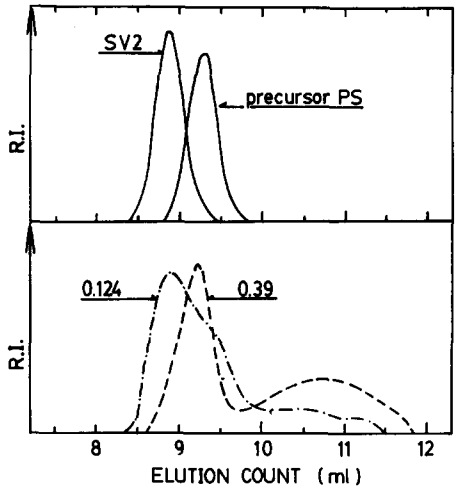

Figure 6 G.p.c. profiles of degraded SV2

Cutting off specific arms

In order to determine the degradation condition, SV2 was degraded by varying the conditions. The conditions and results are given in *Table 4*. *Figure 6* shows typical g.p.c. profiles of degraded SV2. When the molar ratio of ozone to isoprene (O_3/IP) was 0.12, the SV2 peak (8.8 ml) decreased and new peaks appeared at 9.6 and 11.3 ml. From the areas of these peaks, the degradation yield was found to be 30.3 mol%.

When the O_3/IP ratio was between 0.39 and 0.99, the SV2 peak at 8.8 ml vanished completely and two peaks appeared clearly at 9.6 ml ($\overline{M}_n = 8.0 \times 10^4$) and 11.3 ml ($\overline{M}_n = 7.0 \times 10^3$). The yield of degradation was 100 mol%. The molecular weights of the new peaks agreed well with the molecular weights of PS ($\overline{M}_n = 8.0 \times 10^4$) and P2VP ($\overline{M}_n = 3.6 \times 10^4$) of SV2. Similar to the results of Smith and Meier[16], the PS and P2VP sequences were not degraded with ozone. Consequently, it was decided that the degradation of PS arms in the microsphere was carried out at an O_3/IP ratio of 0.66 in chloroform at 25°C.

Next, the PS arms from SV2 in the microsphere were cut off by degrading PIP sequences by ozone. The conditions and results are listed in *Table 5*. The O series indicates the degraded products with ozone. The PS arms cut off from the microsphere were removed by reprecipitation using a THF/n-hexane mixture (n-hexane 80 vol%), which was a good solvent for precursor PS and a non-solvent for the microsphere. This process was carried out three times.

In order to investigate the effect of degradation on the core–shell structure of the products, TEM observation of the microspheres degraded with ozone was carried out.

Figures 4c and *4d* show TEM micrographs of O40 cast from dilute solution (polymer concentration 0.05 wt%) shadowed with chromium at an angle of 20° (*Figure 4c*) and the P2VP core stained with OsO_4 (*Figure 4d*), respectively. After degradation, the product was spherical and the diameter of the P2VP core (33 nm) was unchanged. Subsequently, it was concluded that the core–shell morphology of the microsphere was stable during the degradation of PIP with ozone.

The PS content in the degraded microspheres was measured by i.r. absorptions at 1500 cm^{-1} (styryl group) and 1470 cm^{-1} (pyridyl group). The PS content measured in the degraded microsphere is listed in *Table 5*. In all cases, the measured values were in good agreement with the calculated values. The degradation yield was >99% for all films. This suggests that the PS arms owing to SV2 were cut off by degradation of PIP with ozone quantitatively and that all the arms cut off were completely removed.

The arm-number in the degraded microspheres was calculated from the PS content in the microsphere and the P2VP diameter (*Table 5*). The arm-number decreased from 440 to 88 and from 530 to 212 in O20 and O40, respectively. It was concluded that f of the shell of a core–shell type microsphere was controlled quantitatively by this method.

In order to investigate the effect of the reduction of PS arms on the properties of the microsphere, TEM observation of the microsphere film and turbidimetric titration of the microsphere were carried out. *Figure 7*

Table 5 Degradation of core–shell type microsphere

No.	Film no.	PS content[a] (mol%)	Yield[b] (%)	f[c]
O20	M20	62.5	94.8	88
O30	M30	67.7	98.9	162
O40	M40	74.2	100	212

[a] PS content determined by i.r. absorption at 1500 and 1470 cm^{-1}
[b] Calculated from PS content
[c] Calculated from PS content and the diameter of the P2VP core

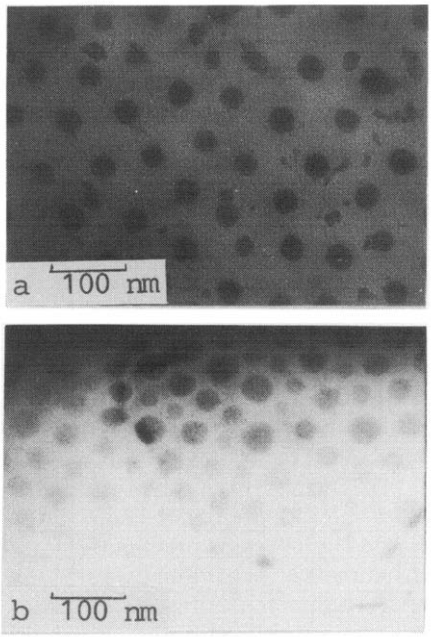

Figure 7 TEM micrographs of (a) M40 and (b) O40 stained with OsO_4

shows the TEM micrographs of M40 and O40. The microspheres M40 and O40 were cast from a condensed benzene solution at a polymer concentration of 2.0 wt% and dried gradually. The distance between the centres of the P2VP cores was decreased from 80 to 60 nm by degradation. From these micrographs, the area of the core in the micrograph increased from 16 to 28% by reduction of f. These values agree well with the P2VP contents in the films determined by i.r. (before degradation, 15.5 mol%; after degradation, 25.8 mol%). This indicates that the number of PS arms in the microsphere was reduced by cutting off the PS arms owing to the SV2 removed from the microsphere.

The change of precipitating behaviour of O20 is shown in *Figure 5*. The volume fraction of n-hexane in the precipitant decreased from 73 to 66 vol% with the decrease in f from 440 to 88. This was due to the reduction of PS content in the microsphere. Additionally, O20 gradually precipitated from 40 to 66 vol% n-hexane. As described above, the microsphere M20 precipitated suddenly. Thus, the gradual precipitation of O20 was not due to the dispersion of the composition of the microspheres. This precipitation behaviour suggests a gradual change in conformation of the PS arms during the precipitation.

CONCLUSIONS

P(S-*b*-2VP) diblock copolymer (SV1) and P(S-*b*-IP-*b*-2VP) triblock copolymer (SV2) were synthesized by anionic addition polymerization. In order to co-micellize SV1 and SV2, in other words, to form a spherical microdomain of P2VP with both SV1 and SV2, blend films were prepared from a benzene mixture of SV1 and SV2. From TEM results, the diameter distribution of the P2VP spherical microdomain was narrow, and it was found that SV1 and SV2 were co-micellized in the film.

In order to fix the P2VP microdomains, the P2VP chains in the P2VP microdomain of blend films were crosslinked with DIB. The crosslink densities of the P2VP microdomains in the blend films were >13.3 mol%. From the results of TEM and precipitation behaviour, it was confirmed that only one type of crosslinked product was synthesized for each blend film, and all the crosslinked products were spheres with a P2VP core–PS shell morphology and a narrow size distribution. Thus, it was concluded that P2VP core–PS shell type polymer microspheres composed of both SV1 and SV2 were synthesized.

Then the PIP of SV2 was degraded with ozone. To determine the degradation conditions with ozone, SV2 was degraded with ozone in chloroform at 25°C. When the O_3/IP ratio was between 0.39 and 0.99, SV2 was completely cut off from PS and P2VP and other side reactions did not occur. Thus, the cutting off of PS arms owing to SV2 was carried out in chloroform solution at a polymer concentration of 0.2 wt% and at an O_3/IP ratio above 0.39. After degradation and purification, the PS shell contents were decreased and their values agreed well with the calculated values from the blend ratio of SV1 and SV2. From TEM observation, it was found that the structure of the microsphere (P2VP core–PS shell morphology) and P2VP core size did not change and the distance between the centres of the P2VP core of the microsphere was reduced by cutting off the PS arms of SV2 from the microsphere. Consequently, PS arms of SV2 in the microsphere were cut off completely by degradation of the PIP blocks of SV2 with ozone in the microspheres. By changing the volume fraction of SV2 in the blend film, the arm-number of the microsphere could be quantitatively controlled in the region from 88 to 540.

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