Preparation of core–shell type polymer microspheres from anionic block copolymers

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A well-defined poly[styrene (S)-*b*-2-vinylpyridine (2VP)] diblock copolymer was prepared by sequential anionic addition. The polystyrene (PS) block part of this diblock copolymer contained a small amount of isoprene (I) sequence units at the prescribed position. The crosslinking reaction of the block copolymer film with poly(2-vinylpyridine) (P2VP) spherical microdomains was carried out with 1,4-diiodobutane (DIB) vapour. Electron micrographs and particle size distribution of this crosslinking product showed the microstructure of core–shell type polymer microspheres. Cores and shells were formed by crosslinked P2VP blocks and PS branchings, respectively. Subsequently, ozonolysis of isoprene sequences on the core–shell type microspheres was performed in a chloroform solution. Through ozonolysis, the arm chains composed of PS blocks were cleaved at the 1,4-linkage of isoprene units. It was indicated from the dynamic light scattering that the shell thickness on the core–shell type microsphere decreased after ozonolysis. The arm length of PS branching was able to be controlled by ozonolysis at the position of the introduced isoprene units.

(Keywords: diblock copolymer; spherical microdomain; crosslinking reaction; core–shell type polymer microsphere; ozonolysis; arm length)

INTRODUCTION

Block copolymers composed of incompatible block segments generally form a microdomain structure in the solid state as a consequence of microphase separation of the constituent block chains. In previous work[1–6] we obtained monodisperse core–shell type polymer microspheres from the crosslinking of spherical microdomains of microphase-separated films with linking agents. The type of morphology adopted by the copolymer essentially depends on its composition[7]. The radius of the spherical cores can be controlled by changing the molecular weight of the diblock copolymers, because the aggregate number of micelles depends on the total molecular weight of the block copolymers. However, the shell acquires an intrinsic thickness through the microphase-separated domains.

In this article we suggest a new architecture for core–shell type polymer microspheres with well-defined sizes of core radius and shell thickness. The poly[styrene(S)-*b*-2-vinylpyridine(2VP)] diblock copolymers were prepared by sequential anionic addition. Polystyrene (PS) blocks contained a small amount of isoprene (I) sequence units at the prescribed position through three-stage addition of S, I and S monomers. The core–shell type polymer microspheres were obtained by the crosslinking reaction of block copolymer film having poly(2-vinylpyridine) (P2VP) spheres with 1,4-diiodobutane (DIB). Through ozonolysis of core–shell type microspheres, the arm chains composed of PS branchings were cleaved at the 1,4-linkage of isoprene units. Characteristics of the core–shell type microspheres were studied in detail before and after ozonolysis.

EXPERIMENTAL

Block copolymer synthesis and characterization

The well-defined poly(S_1-I-S_2-*b*-2VP) diblock copolymers used in this work were prepared by sequential anionic addition, like those used in preceding papers[4,8]. In brief, a polystyryl anion was prepared by anionic polymerization of the first styrene (S_1) using n-butyllithium (n-BuLi) as an initiator in benzene at 5°C in a sealed glass apparatus under a pressure of 10^{-6} mmHg. Next, isoprene was allowed to distill into PS_1 anion solution. After the orange colour of the polystyryl anion had turned to yellow (the characteristic colour of a PI anion), the reaction solution was stirred for 3 h at 30°C. An aliquot was taken from the solution to recover the polymer for characterization. Benzene solution of the second styrene (S_2) was added to the solution of PS_1 anion end-capped with isoprene at 5°C. The colour of the resulting mixture turned to orange again due to anionic propagation of styrene monomers. An aliquot of this solution was also taken to recover the polymer for characterization. After capping of poly(S_1-I-S_2) anion ends with 1,1-diphenyl ethylene, a tetrahydrofuran (THF) solution of 2VP was added. The product was purified three times by reprecipitation from THF solution with n-hexane.

The number-average molecular weight ($\bar{M}_n$) of PS precursors was determined by gel permeation chromatography (g.p.c.; Tosoh high-speed liquid chromatograph HLC-8020), with THF as eluent at 38°C, a TSK gel GMH_{XL} column and a flow rate of 1.0 ml min^{-1} using

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a calibration curve of standard PS. The $\bar{M}_n$ of poly(S_1-I-S_2-*b*-2VP) diblock copolymers was estimated from the $\bar{M}_n$ of the PS precursor and the block composition. The contents of the isoprene units and the block composition were determined by ^{1}H n.m.r. (270 MHz, JEOL GX 270 n.m.r. spectrometer) in $CDCl_3$. The polydispersity ($\bar{M}_w/\bar{M}_n$) was determined from g.p.c. distribution functions improved by the reshaping method[9] with a NEC personal computer PC-8801.

Synthesis of core–shell type polymer microspheres

The block copolymer film (50 μm thick) was cast from 1,1,2-trichloroethane (TCE, 0.03 g ml^{-1}) solution on a Teflon sheet. The cast film was dried under vacuum for 24 h at room temperature. Crosslinking of the segregated P2VP chains in spheres was carried out using quaternization with DIB vapour at 50°C for 6 h under reduced pressure. The product was purified twice by reprecipitation from THF solution with n-hexane.

Ozonolysis of PS arms

Cleavage of the double bond of isoprene units was performed by dispersing the core–shell type microspheres in chloroform (1 wt%) containing a 10-fold molar excess of ozone compared to isoprene units at 25°C for 10 min[10]. The resulting mixture was precipitated with n-hexane.

In order to separate the cleaved PS chains from the reaction products, the precipitation fractionations were carried out in the benzene–n-hexane system (benzene fraction = 0.33) at 20°C, where the turbidity of poly(S_1-I) was measured beforehand. The composition of the fractionated core–shell type microspheres was determined by Fourier transform infra-red (*FT*i.r.) spectroscopy (Shimadzu FTIR-8500 spectrophotometer) by absorptions at 1495 cm^{-1} (benzene ring) and 1475 cm^{-1} (2VP ring).

Morphological observation

An ultra-thin film specimen of the starting diblock copolymer was prepared for electron microscopy by placing a droplet of a 1 wt% TCE solution on a microscope mesh coated with a carbon film, and then evaporating the solvent as slowly as possible at 25°C. This specimen was then exposed to osmium tetroxide (OsO_4) vapour for 24 h at room temperature.

The morphology of the core–shell type microspheres was observed as follows. After dissolving the core–shell type microsphere in benzene, a 0.1 wt% solution was dropped onto a microscope mesh coated with carbon film. The specimen was stained with OsO_4 vapour. Morphological results were obtained on a Hitachi H-500 transmission electron microscope (TEM) at 100 kV.

Dynamic light scattering (DLS)

The particle size of core–shell type microspheres was determined by a submicron-particle analyser (Coulter model N4: He–Ne laser, scattering angle = 90°) in 0.5 wt% benzene at 25°C.

Turbidimetric measurement

The turbidimetric measurements of the polymer microsphere and corresponding diblock copolymer were carried out at a wavelength of 500 nm. Ten milligrams of each polymer sample were dissolved in THF (70 ml), then n-hexane was added stepwise with vigorous stirring in the cell (Pyrex cylinder, 150 ml) for turbidimetric measurements at 20°C (Hitachi Perkin–Elmer 139 UV-VIS spectrometer).

RESULTS AND DISCUSSION

Dai and White[11] have reported that the microstructure of polyisoprene (PI) contained more than 95% of the 1,4-addition with a relatively small amount of the 3,4-addition isomer under the living polymerization of isoprene initiated by n-BuLi in toluene. Therefore we first attempted to synthesize poly(S_1-I-S_2-*b*-2VP) diblock copolymers initiated by n-BuLi in toluene at −78°C. However, the resulting diblock copolymers showed a bimodal pattern on the g.p.c. profile after the addition of THF solution of 2VP monomer. Then we used the benzene as a polymerization solvent for the synthesis of the poly(S_1-I-S_2) precursor. *Figure 1* shows typical sets of g.p.c. profiles of PS precursors and poly(S_1-I-S_2-*b*-2VP) diblock copolymer SISV1. The g.p.c. elution peak of SISV1 shifts to the side of high molecular weight, as compared with its precursor poly(S_1-I-S_2). The g.p.c. profiles show that both PS precursors and the diblock copolymer have a single and narrow molecular weight distribution. The microstructure of PI obtained from the above method contains 50% 3,4- and 50% 1,4-structures (60% *cis*, 40% *trans*)[12]. The ^{1}H n.m.r. spectrum of the poly(S_1-I) precursor shows the characteristic resonances of the 1,4-structure (δ5.2 ppm) and 3,4-structure (4.7 ppm). The microstructure of the isoprene units was also found to be 50% of the 1,4-structure from this spectrum. *Table 1* lists the characteristics and the domain size of a poly(S_1-I-S_2-*b*-2VP) diblock copolymer.

Figure 2 shows the TEM micrograph of a diblock copolymer SISV1 specimen cast from TCE. The dark areas indicate the selectively stained P2VP blocks. The

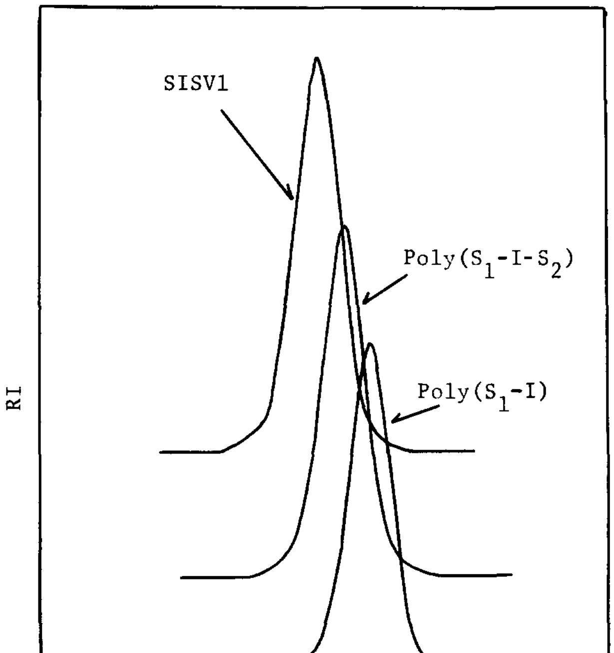

Figure 1 G.p.c. profiles of SISV1 diblock copolymer and poly(S_1-I-S_2) and poly(S_1-I) precursors

Table 1 Characteristics of poly(S_1-I-S_2-*b*-2VP) diblock copolymer and microdomain size

Specimen code	$10^{-4}\bar{M}_n$			$\bar{M}_w/\bar{M}_n$[c]	Content		Domain size (nm)[e]
	Poly(S_1-I)[a]	Poly(S_1-I-S_2)[a]	Block[b] copolymer		Isoprene[d] units (number/1-polymer)	P2VP[d] blocks (mol%)	$\bar{R}_{P2VP}$
SISV1	4.2	5.4	6.9	1.08	16	22.2	9

[a] Determined by 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

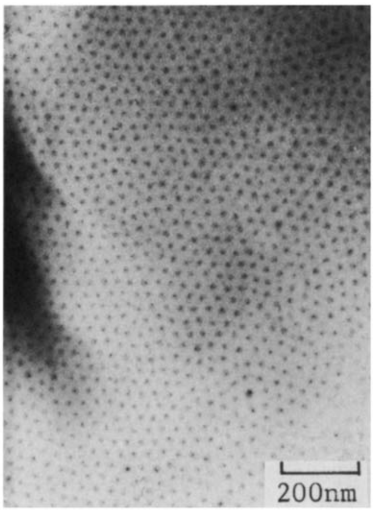

Figure 2 TEM micrograph of SISV1 diblock copolymer cast from TCE

microdomain structure in the SISV1 specimen shows the texture of discrete P2VP spheres in a PS matrix. The absolute value of the radius of the P2VP spheres ($\bar{R}_{P2VP}$) is 9 nm.

The segregated spherical P2VP domains were crosslinked using quaternization with DIB vapour in the film state. Under these reaction conditions, the crosslink density of P2VP domains was 57.4%. Thus, P2VP spheres seem to be tightly crosslinked.

The molecular weight of segregated P2VP cores ($M_{w(c)}$) is given by:

$$M_{w(c)}=(4\pi/3)R^3_{P2VP}\rho_{P2VP}N_A \tag{1}$$

where R_{P2VP}, ρ_{P2VP} and N_A are the radius of the P2VP core, the density of P2VP (11.4×10^3 mol m^{-3})[13] and Avogadro's number (6.023×10^{-23} mol^{-1}), respectively. The aggregation number N of P2VP cores is given by:

$$N=M_{w(c)}/\bar{M}_{P2VP} \tag{2}$$

where $\bar{M}_{P2VP}$ is the molecular weight of the P2VP block in the diblock copolymer SISV1. As the value of R_{P2VP} is equal to 9 nm, the aggregation number, N, can be calculated to be 300 using equations (1) and (2).

Figure 3a shows a TEM micrograph of the crosslinked product SISV1–M, cast from 0.1 wt% benzene solution. The dark areas indicate the crosslinked P2VP cores. However, in this micrograph it is difficult to distinguish the shell of PS branchings from the carbon support. The radius of these P2VP cores is the same as that of segregated P2VP spherical domains shown in the SISV1 diblock copolymer specimen. The crosslinked P2VP cores are aligned in a near-ordered arrangement on the carbon mesh.

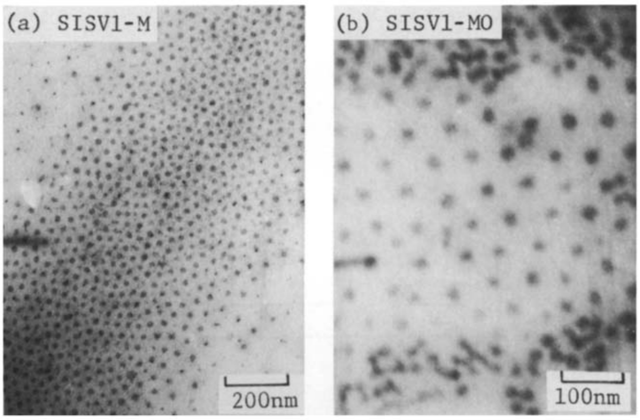

Figure 3 TEM micrographs of core–shell type polymer microspheres, cast from 0.1 wt% benzene solution: (a) SISV1–M; (b) SISV1–MO

Figure 4a shows the typical particle size distribution of the crosslinked product SISV1–M in benzene by means of DLS. The SISV1–M has a unimodal pattern of particle species (weight-average particle size $\bar{D}_w=55.3$ nm, size distribution $\bar{D}_w/\bar{D}_n=1.12$). The DLS data show that the crosslinked product SISV1–M is the core–shell type microsphere in which P2VP chains in the core are completely immobilized. Moreover, this microsphere has a narrow particle size distribution. The core and shell are formed by the crosslinked P2VP and PS branchings, respectively.

Through ozonolysis, it is anticipated that the PS arm chains composed of the shell are cleaved at the 1,4-linkage of isoprene units to form a PS_1 homopolymer. The arm chains have enough content of 1,4-linkage of isoprene units (eight molecules per one arm chain) to be cleaved. *Figure 4b* shows the particle size distribution of the reaction product SISV1–MO after ozonolysis. The SISV1–MO has two kinds of particle species ($\bar{D}_w=11.5$ and 39.7 nm). The DLS data indicate that the SISV1–MO is a mixture of the cleaved PS_1 and the core–shell type microsphere. The SISV1–MO microsphere with a narrow distribution ($\bar{D}_w/\bar{D}_n=1.16$) shows a smaller average particle size ($\bar{D}_w=39.7$ nm) than that of the SISV1–M microsphere.

Figure 3b shows a TEM micrograph of the SISV1–MO microsphere, cast from 0.1 wt% benzene solution. The dark areas indicate the crosslinked P2VP cores. The radius of these P2VP cores is constant before and after

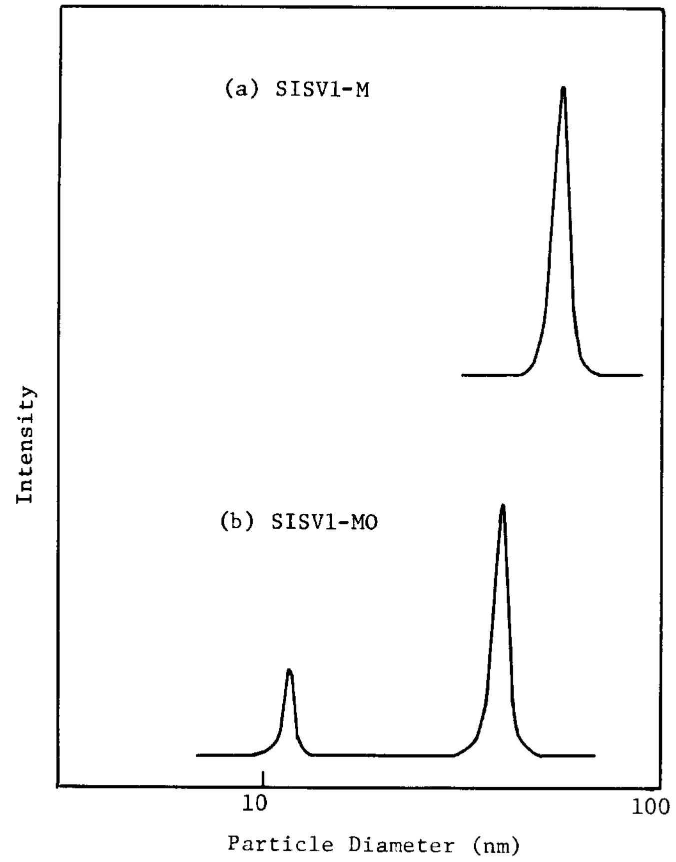

Figure 4 Particle size distributions of core–shell type polymer microspheres in benzene: (a) SISV1—M; (b) SISV1–MO

ozonolysis. Therefore, the DLS data suggest that the PS arm lengths composed of the shell parts decrease after ozonolysis due to cleavage of the isoprene units. It is also noted from *Figure 3b* that several P2VP cores fuse with each other. In a recent study[14] we have made clear that in a solution of the core–shell type polymer microspheres the macrocrystalline order appeared near the overlap concentration. Daoud and Cotton[15] were the first to study the conformation and dimensions of star polymers using scaling concepts. A star polymer consists of three regions: a central core, a shell with a semi-dilute segment density in which the arms have their unperturbed chain conformation and an outer shell in which the arms of the star assume a self-avoiding conformation. The solution (TCE, benzene and THF) of core–shell type polymer microsphere SISV1–M had a bluish tint (the characteristic colour of micelles). After crosslinking, the quaternized P2VP chains in the core became insoluble in hydrophobic solvents. All the solvents (e.g. TCE, benzene and THF) are good for PS segments. Consequently, the cores are dispersed in these solvents by a stabilizing layer of PS branching. Thus the crosslinked P2VP cores are aligned in a near-ordered arrangement on the carbon mesh as shown in *Figure 3a*. The solubility of these core–shell type microspheres depends strongly on that of the stabilizing shell segments. The primary structures of SISV1–M and SISV1–MO are composed of the same size of crosslinked P2VP core (core radius = 9 nm in the solid state) with the same branch number of 300, but with long ($\bar{M}_n = 5.4 \times 10^4$) and short arm lengths ($\bar{M}_n = 1.2 \times 10^4$), respectively. The shell of SISV1–MO is thinner than that of the SISV1–M microsphere. The phenomenon of fusion among P2VP cores may be caused by the poor steric stabilization due to the thin shell parts.

The turbidity curves of SISV1–M and SISV1–MO microspheres. SISV1 diblock copolymer and poly(S_1-I) precursor are shown in *Figure 5*. In a n-hexane fraction of about 0.59, the SISV1–M microsphere suddenly precipitates and the SISV1 diblock copolymer precipitates in the n-hexane fraction of 0.60. On the other hand, the SISV1–MO microsphere precipitates in the fraction of 0.64 in spite of a higher molecular weight compared with the SISV1 diblock copolymer. Subsequently, the turbidity curve of SISV1-MO is flat with an intrinsic value beyond the n-hexane fraction of 0.67. Fundamentally, this curve should overlap with that of poly(S_1-I) at the fraction position of 0.71. The solubility of the core–shell type microsphere SISV1–M with long arm lengths is very similar to that of PS. However, the shell of the SISV1-MO microsphere is extremely thin. Therefore the above solubility behaviour seems to be caused by the ionic strength of quaternized P2VP cores.

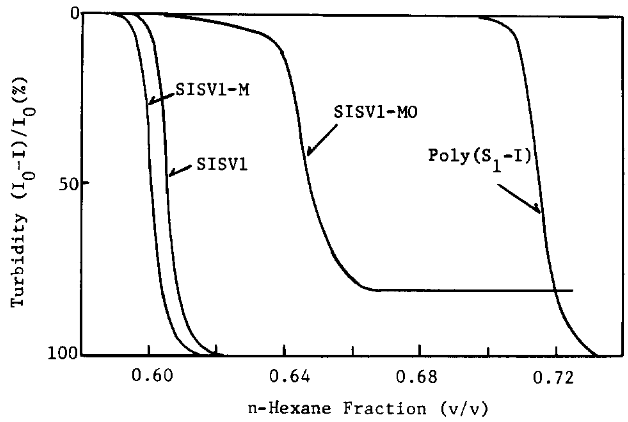

Figure 5 Turbidity curves of SISV1–M and SISV1–MO microspheres, SISV1 diblock copolymer, and poly(S_1-I) precursor

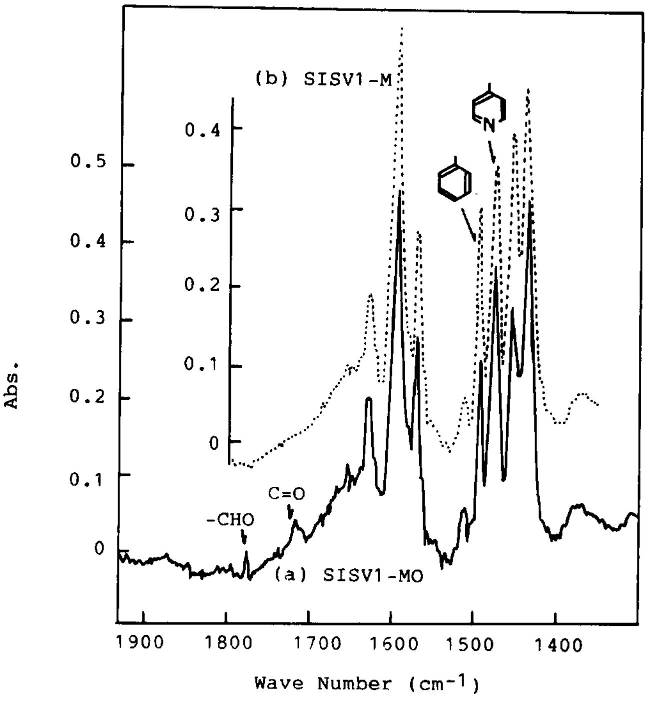

Figure 6 *FT*i.r. spectra of the fractionated SISV1–MO (a) and SISV1–M (b) microspheres

To support the mechanism proposed above, we performed a spectroscopic analysis of microspheres as follows. In order to separate the cleaved PS_1 chains from SISV1–MO microspheres we carried out first, precipitation fractionation in the THF–n-hexane system and dried the fractionated microsphere in high vacuum, but this microsphere did not dissolve in benzene or THF. Subsequently, we adopted the benzene–n-hexane system as the fractionation solvent. The fractionated SISV1–MO was purified by a freezing–drying method using benzene. The SISV1–MO microsphere obtained dissolved in benzene. *Figure 6* shows *FT*i.r. spectra of the fractionated SISV1–MO and SISV1–M microspheres. In spectrum (b) (SISV1–M) the characteristic absorptions due to the styryl and 2VP groups are observed at 1495 and 1475 cm^{-1}, respectively. The bands are observed at 1640 and 1600 cm^{-1}, attributable to the quaternized P2VP core and overlapping of styryl and 2VP groups, respectively. After ozonolysis (in spectrum (a) – SISV1–MO), the strong absorption bands of styryl groups at 1600 and 1495 cm^{-1} decrease in intensity. Moreover, weak bands are observed at 1770 and 1728 cm^{-1}, attributable to aldehyde and ketone groups, respectively, which are presumably attached to PS branching ends due to oxidative cleavage. The composition of the fractionated SISV1–MO microsphere is estimated to be 44.7 mol% PS from the absorptions at 1495 (styryl group) and 1475 cm^{-1} (2VP group). If the PS arm chains of the shell are cleaved quantitatively at the 1,4-linkage of isoprene units, the calculated composition of SISV1–MO is 44.6 mol% PS. The experimental value is in good agreement with the calculated one. The mechanism proposed through ozonolysis is also confirmed from spectroscopic analysis of the fractionated SISV1–MO microsphere.

We are investigating the stability of core–shell type polymer microspheres, varying the arm lengths of shell parts. The results will be reported in the near future.

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