

Synthesis of Poly(vinyl alcohol) Core–Polystyrene Shell-type Flower Microgels

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ABSTRACT: Four types of poly(vinyl alcohol-*b*-styrene-*b*-vinyl alcohol) (P(VA-*b*-S-*b*-VA)) triblock copolymers were synthesized by hydrolysis of poly(vinyl acetate-*b*-styrene-*b*-vinyl acetate) triblock copolymers prepared by radical living polymerization. The polyvinyl alcohol (PVA) core–polystyrene corona-type flower micelles were formed with ASA-4 in benzene at 25°C. The PVA core part of the micelle was crosslinked with hexamethylene diisocyanate in solution. The monodispersed spherical products (microspheres) were synthesized by crosslinking. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 849–854, 1997

Key words: microsphere; core-shell; flower; polymer micelle

INTRODUCTION

It is well known that BAB-type triblock copolymers form polymer micelles in selective solvents which are good for one block and bad for another. When the solvent is good for end blocks and not for a middle block, the micelle formation of BAB-type triblock copolymers is similar to AB diblock copolymers.^{1–5} On the other hand, in solvent that is good for the middle block and not for the end blocks, the micelle formation of BAB triblock copolymers is complicated.^{6–11} At low polymer concentration, the block copolymers form isolated spherical micelles. As the polymer concentration increases, bridges between the polymer micelles appear; finally, the network (mesogel) is formed with the triblock copolymers. In these structures, the shell chains of the isolated spherical micelles form loops. These micelles are called “flower micelles.” For flower micelles, entanglement between the micelles will be neglected due to loop formation of the shell chains.

Previously, we have synthesized core–shell-type

polymer microspheres upon the crosslinking of the core part in the spherical polymer micelles formed with AB-type diblock copolymers in solvents.^{12–15} It will also be possible to synthesize core–shell-type polymer microspheres from flower polymer micelles composed with BAB-type triblock copolymers. Since all shell chains would be the loop, the interesting properties of the flower micelles (such as lower entanglement than the usual core–shell-type polymer microspheres) would be expected in the flower microgels. However, contrary to AB diblock copolymers, macrogelation will occur easily for the BAB triblock copolymer micelles.

The purpose of this work is to synthesize core–shell type flower microspheres upon crosslinking the core part of the flower micelles formed with BAB triblock copolymers. Poly(vinyl alcohol-*b*-styrene-*b*-vinyl alcohol) [P(VA-*b*-S-*b*-VA)] triblock copolymers and benzene were chosen as the BAB triblock copolymers and the selective solvent for the middle block, respectively. The triblock copolymers used in this paper were synthesized by radical living polymerization with iniferter.¹⁶ The micelle formation of the block copolymers was investigated by viscosity measurement and dynamic light scattering (DLS). The crosslinking of the polyvinyl alcohol (PVA) sequences was carried out with hexamethylene diiso-

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Table I Characteristics of the Iniferter Polystyrene

Sample Name ^a	$M_n^b \times 10^{-3}$	M_w/M_n^b	Yield (%)
PS	6.99	1.95	63.5
PS1	5.40	1.49	28.7
PS2	12.6	1.53	31.9

^a PS: iniferter polystyrene, PS1, and PS2 were fractionated polymers from PS.

^b M_n and M_w are number-average and weight-average molecular weights, respectively, determined with GPC.

cyanate (HDI). The size and the structures of the crosslinking products were analyzed with DLS and transmission electron microscopy (TEM).

EXPERIMENTAL

Synthesis of the P(VA-*b*-S-*b*-VA) Triblock Copolymers

Styrene and vinyl acetate monomers were purified by distillation under vacuum. Styrene, 90 g, was polymerized with 2.01 g of tetramethylthiuramdisulfide at 80°C for 8 h in the dark. Polystyrene (PS) was divided into two parts by fraction with benzene and methanol. Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured with a Tosoh H-8020 GPC with tetrahydrofuran as an eluent at 38°C, a TSK-gel GMHXL column and a flow rate of 1.0 ml/min.

The mixture of 30 ml of vinyl acetate (VAc), 9.0 g of the iniferter PS, and 30 ml of benzene was sealed in a glass ampule under vacuum. Then ultraviolet (UV) irradiation was carried out at room temperature for a certain time with a high-voltage mercury lamp (Ushio, 100 V, 300 W) without wavelength control. Gross polymer was precipitated in hexane. Homo polyvinyl acetate (PVAc) and homo PS were extracted with methanol and cyclohexane, respectively, at 35°C. The removal of PS and PVAc was confirmed with Fourier transform infrared spectroscopy (FTIR) (Shimadzu, FTIR-8500). PVAc content in poly(vinyl acetate-*b*-styrene-*b*-vinyl acetate) [P(VAc-*b*-S-*b*-VAc)] triblock copolymer was determined with FTIR. Then the hydrolysis of the PVAc block was carried out with lithium hydroxide in the benzene/methanol mixture. The characteristics of the iniferter PS and the triblock copolymers are shown in Tables I and II.

Micelle Formation of the Block Copolymers

The block copolymers were dissolved in benzene at room temperature. The solution was heated to 50°C, and the solution was gradually cooled to 25°C.

Crosslinking of the Core Part in the Micelle

The amount of 20 mol % of HDI to the hydroxyl group of the triblock copolymer was added to the polymer micelle solution and reacted for 48 h at 25°C.

Characteristics

Dynamic Light Scattering Measurement (DLS)

The diameter and its distribution of the micelle and crosslinked products were measured with DLS (Photal, DLS-7000) for the solutions at an angle of 90 degrees at 25°C.

Viscosity Measurement

The viscosity of the polymer solution was measured with an Ubbelohde viscometer at 25°C.

Morphological Observation by TEM

The solution of the crosslinked products was cast on the copper microgrid covered with carbon substrate. The solvent was evaporated quickly without heating. A sample specimen was stained with OsO₄ for 2 days at room temperature. Inner texture of the crosslinked products was observed with a transmission electron microscope (HITACHI, H-500) with 75 kV.

RESULTS AND DISCUSSION

Synthesis and Micelle Formation of Block Copolymers

The M_n and M_w/M_n of the PS iniferter are shown in Table I. The M_w/M_n was wide (1.95); therefore, the PS was divided into two (PS1 and PS2) by fraction with benzene and methanol. The M_w/M_n values of PS1 and PS2 were lower than 1.5. The PS1 and PS2 were then reacted with VAc by the irradiation of UV light. The conditions and the characteristics of the block copolymers are listed in Table II. According to Otsu and colleagues,¹⁶ the block copolymers of PS and PVAc synthesized by this method were the P(VAc-*b*-S-*b*-VAc) BAB triblock copolymers. In order to synthesize the polymer microspheres with thick shell, the PS

Table II Characteristics of P(VA-*b*-S-*b*-VA) Triblock Copolymers

Name ^a	Irradiation Time (h) ^b	Yield (%)	$M_n \times 10^{-3}$ ^c	S Content (mol %) ^d	Degree of Hydrolysis ^d
ASA-1	27	57.6	5.79	91.3	100
ASA-2	22	75.1	5.62	95.1	100
ASA-3	27	78.6	15.0	76.9	100
ASA-4	22	76.8	14.5	82.2	100

^a ASA-1, -2, and ASA-3, -4 polymers were synthesized from PS1 and PS2, respectively.

^b Irradiation time of UV light.

^c Determined with GPC.

^d Determined with FTIR.

contents in the block copolymers were set larger than 75 mol %.

These block copolymers were hydrolyzed with lithium hydroxide. In order to investigate the progress of the hydrolysis, FTIR measurement was carried out for the block copolymers. Figure 1 shows the FTIR spectra of the triblock copolymer of ASA-1 before and after hydrolysis. Since the specific absorption of carbonyl groups at 1730 cm^{-1} of the ASA-1 before hydrolysis vanished after hydrolysis, it was found that the VAc was completely hydrolyzed to VA. It was concluded that the P(VA-*b*-S-*b*-VA) triblock copolymers were synthesized.

As described in the INTRODUCTION, the flower micelle formation was carried out in benzene that was the good solvent for PS and not for PVA. It is well known that the change of the aggregation

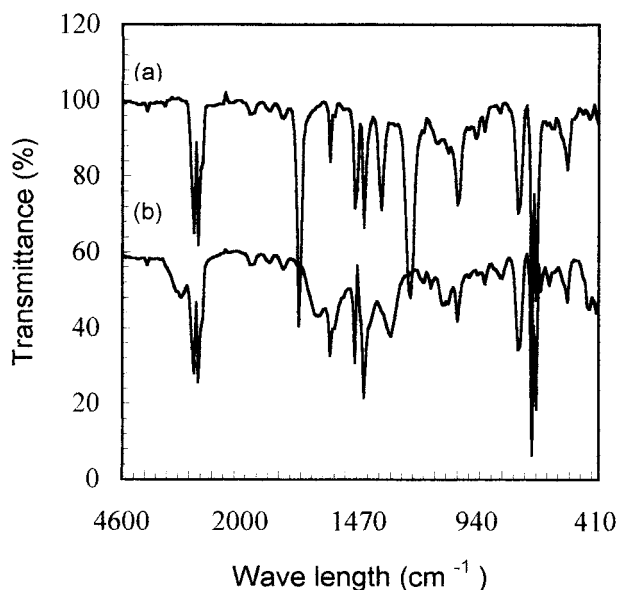


Figure 1 FTIR spectra of the triblock copolymer ASA-1, (a) before hydrolysis and (b) after hydrolysis.

state of the block copolymer can be observed from the viewpoint of the rheological change of the solution. Therefore, the viscosity of the triblock copolymer was measured. Figure 2 shows the reduced viscosity of ASA-3 and ASA-4 in benzene at 25°C . The gradient of the viscosity was changed at 0.65% and 1.09% for ASA-3 and ASA-4, respectively. In general, the change in the gradient of viscosity suggests the change in the aggregation state of the triblock copolymers. By increasing the polymer concentration, the viscosities of ASA-3 and ASA-4 increased drastically. Above 2% for ASA-3 and ASA-4, macrogelation of the system occurred. For the BAB-type triblock copolymer,

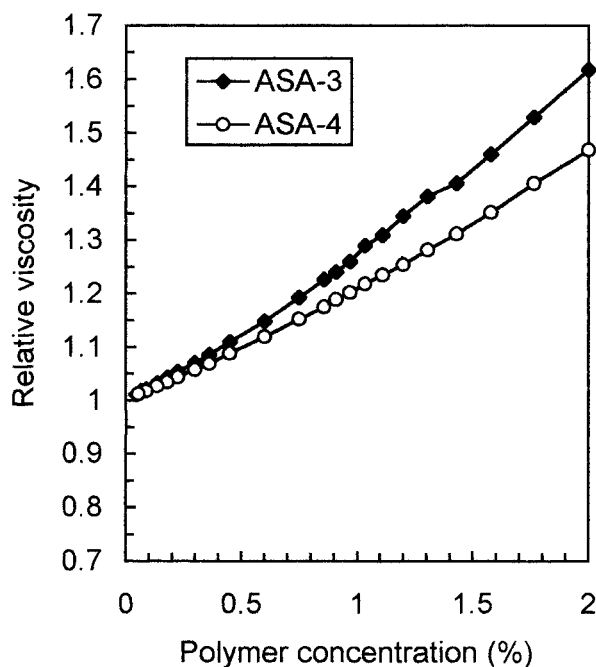


Figure 2 The polymer concentration effect on the relative viscosities of P(VA-*b*-S-*b*-VA) triblock copolymers in benzene at 25°C .

Table III The Hydrodynamic Diameters and Their Distribution of the Micelles and Crosslinked Products of ASA-4

Polymer Conc. (%)	Hydrodynamic Diameter (Dh) (nm)			
	Micelle		Crosslinked Products	
1.5	70.0	272.0	177.4	445.7 ^a
0.5	30.8	175.9	15.7	164.6
0.1	139.2		131.1	
0.01	121.9		—	

^a Diameters of the soluble part.

the network (mesogel) formation due to the increase of the bridges between micelles occurs in the condensed solution. Thus, the macrogelation of the systems suggests that the bridging between micelles occurred at high polymer concentrations. From these results, it was expected that bridges between micelles were formed above 0.65 and 1.09% for ASA-3 and ASA-4, respectively.

In order to investigate the triblock copolymers in detail, the hydrodynamic diameters (Dh) of the polymer micelles of ASA-3 and ASA-4 in benzene were measured by DLS. Table III lists the Dh and the distribution of Dh (Dh_w/Dh_n). As the typical results, the distribution of the Dh of aggregates of ASA-4 are shown in Figure 3. As described above, for the ASA-4 series the bridge formation between micelles was expected above 1.09%. From the DLS results, it was found that two types of aggregates existed in 1.5% solution [Fig. 3(a)], with Dh values of 70 and 272 nm. If the observed aggregate is a flower micelle with one core, the Dh of the polymer micelle should be limited. The maximum diameter of the flower micelle of ASA-4 is calculated as 152.3 nm under the fully stretched conditions by using the M_n and M_w/M_n values of ASA-4. Since the Dh of the large aggregate (272 nm) is much larger than the calculated maximum diameter, the large aggregate was identified as the bridged micelles. A similar distribution pattern was obtained for the 1% solution.

Two peaks were still observed for the 0.5 and 0.1% solutions, although they were more dilute solutions than 1.09%. However, in the 0.1% solution the peaks became one under ultrasonic irradiation [Figs. 3(b) and 3(c)]. After the ultrasonic irradiation, the polymer solution was stable more than 1 month. The peak pattern of the solution over 0.5% did not change with ultrasonic irradiation.

These results indicate that the bridges between the micelles had already formed at 0.5%, which was much lower than the 1.09% estimated from the viscosity measurement. We also found that the bridging between micelles in the 0.1% solution was weak and could not be formed again after ultrasonic irradiation. For the 0.01% solution, since the peak pattern was similar to the 0.1% solution after ultrasonic irradiation, the flower micelle formation in the 0.1–0.01% solutions was expected.

Crosslinking of Polymer Micelles

In order to synthesize the flower microgels, the crosslinking of the PVA core part of the micelles with HDI was carried out. The molar ratios of isocyanate to hydroxyl groups were 0.58 for 1.5–0.5% solutions and 0.7 for solutions lower than 0.1%. After the crosslinking no visible changes were observed for all solutions, except for the 1.5% solution of ASA-4. In the 1.5% solution of ASA-4, the white precipitant (macrogel) appeared after crosslinking.

In order to investigate the size of the crosslinked products, DLS measurements were carried

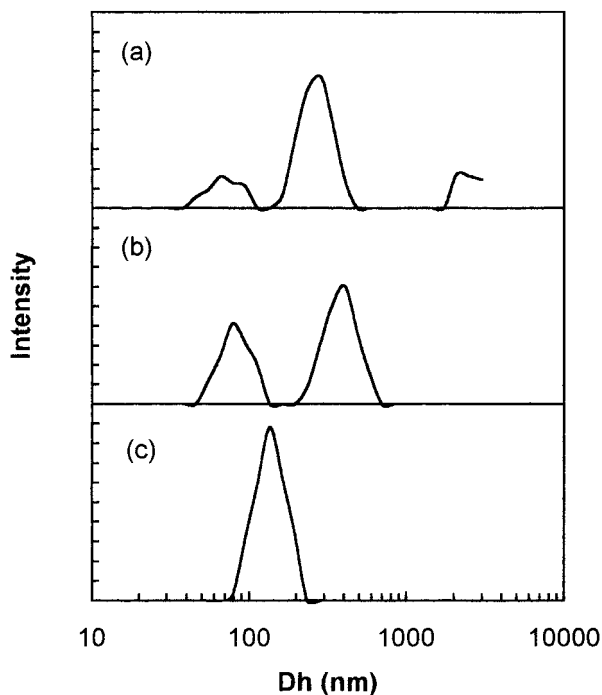


Figure 3 The hydrodynamic diameter distribution of ASA-4 in benzene at 25°C, (a) at 1.5%, (b) at 0.1% without ultrasonic irradiation, and (c) at 0.1% with ultrasonic irradiation.

out at 0.001%. Since clear intensity was not obtained in the 0.001% solution of the triblock copolymers, the Dh of the crosslinked products could be estimated. For the 1.5% solution of ASA-4, DLS measurement was carried out for the soluble part. The Dh values of the crosslinked products and their original micelles are listed in Table III. Above 0.5%, two types of the crosslinked products were observed. For the 1.5% solution, the Dh values of the soluble polymers increased with crosslinking. The Dh values of the crosslinked products of the 0.5% solution show fair agreement with the original values. From previous investigation of the crosslinking of polymer micelles of AB diblock copolymers,¹³ it was found that the strong interactions between polymer micelles were due to the macrogelation of the system even for the AB diblock copolymers. According to theoretical calculations,¹⁷ the number fraction of the bridges, which are very strong interactions between the micelles, increases linearly with the polymer concentration. Therefore the macrogelation appeared drastically above 0.5 in this study. For the 0.01 and 0.1% solutions of ASA-4, the Dh values did not change with crosslinking; their distributions were still very close to 1. Therefore it was found that the micelle structures in the 0.01 and 0.1% solutions were fixed upon crosslinking. Again, the flower micelle formation was expected for these solutions from the viscosity measurements.

In order to investigate the inner texture of the crosslinked products, TEM observation was carried out for the ASA-4 series (Fig. 4). Since the specimen was prepared by casting the very diluted solution (0.001%), all products were isolated on the carbon substrate. In Figure 4, the black regions are the PVA and the gray regions are PS. For the ASA-4 solution crosslinked at 0.5% (Fig. 4a), the multi-core products were observed. For the solution of ASA-4 crosslinked at 0.1%, all products were PS spheres with 100 nm of diameter and only one PVA core existed in each sphere. The number-average diameter of the PVA core was 10 nm. Consequently, it was concluded that the crosslinked products lower than 0.1% were PVA core-PS shell-type flower microgels. The aggregation number of the ASA-4 in these microgels was calculated as 550 by using the M_n of PVA block and the density of PVA.

CONCLUSIONS

The P(VAc-*b*-S-*b*-VAc) triblock copolymers were synthesized by radical living polymerization and

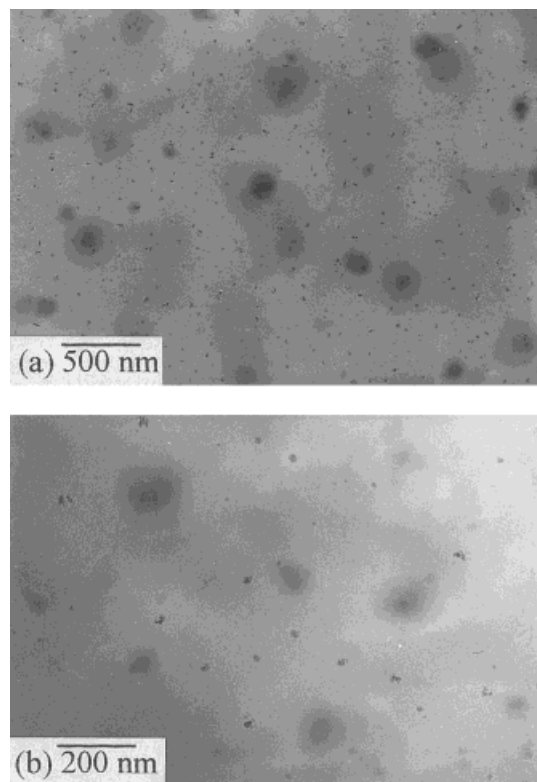


Figure 4 The transmission electron micrographs of crosslinked products of the ASA-4 series cast at 0.0001% and stained with OsO_4 , (a) crosslinked at 0.5% and (b) crosslinked at 0.1%.

converted to P(VA-*b*-S-*b*-VA) triblock copolymers by hydrolysis. The micelle formation of these triblock copolymers in benzene was investigated by viscosity measurement and DLS measurement. It was found that the bridges between micelles were formed at lower polymer concentrations than the values expected from the viscosity measurements. Upon crosslinking of the 0.1 and 0.01% solutions, only one type of crosslinked product with monodispersed diameter was synthesized. By TEM observation, the crosslinked products of the 0.1 and 0.01% were found to be PVA core-PS shell-type flower microgels.

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