BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 23, pp. 4515–4520, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/95/$10.00+0.00

Synthesis of poly(vinyl alcohol) core–polystyrene shell type microspheres

Reiko Saito*, Shin-ichi Okamura and Koji Ishizu
Department of Polymer Chemistry, Tokyo Institute of Technology, 2-12 Ookayama, Meguro-ku, Tokyo 152, Japan

(Received 6 December 1994; revised 22 February 1995)

Poly(vinyl alcohol-*g*-styrene) graft copolymers with various polystyrene contents (from 9 to 51 mol%) were synthesized. These graft copolymers formed poly(vinyl alcohol) (PVA) core–polystyrene (PS) corona micelles in tetrahydrofuran (THF)–dimethylsulfoxide mixtures when the THF content was from 66 to 69 vol%. The PVA cores of these micelles were crosslinked with terephthal aldehyde (TPA) in solution. When the TPA concentration in relation to vinyl alcohol groups was below 10 mol%, it was possible to hinder intermicelle crosslinking and PVA core–PS shell type microspheres were obtained. The minimum PS shell content of microspheres obtained in this work was 9 mol%.

(Keywords: core–shell morphology; microspheres; poly(vinyl alcohol-*g*-styrene))

INTRODUCTION

It is possible to synthesize monodisperse core-shell type microspheres by crosslinking the spherical microdomains of microphase-separated AB block copolymer films with sphere–matrix morphology[1–3]. In previous work, we reported that monodisperse poly(2-vinylpyridine) (P2VP) core–polystyrene (PS) shell type microspheres and monodisperse poly(4-vinylpyridine) (P4VP) core–polystyrene (PS) shell type microspheres could form well arranged two-dimensional and three-dimensional superstructures[4–6]. By adding poly(styrene-*b*-isoprene) diblock copolymers with a lamellar or polyisoprene spherical microdomain structure to these P4VP core–PS shell type microspheres, it was possible to lay out well ordered novel structures[7,8].

The microphase-separated morphologies of block or graft copolymers can be used as templates for the introduction of noble-metal nanoclusters. Control of the introduction of colloidal silver into the microphase of the polymer film is strongly desired from the viewpoint of the design of new materials such as semiconductors, nonlinear optical materials and carriers for catalysts. Cohen *et al.*[9–12] succeeded in controlling the introduction of colloidal metals into microphase-separated films by using poly[*rac*(diphenylphosphino)bicyclo[2.2.1]-heptene-*b*-methyltetracyclododecene] as a template.

We also found that colloidal silver could be introduced into the crosslinked P2VP microdomains of poly(styrene-*b*-2-vinylpyridine) (P(S-*b*-2VP) block copolymers by an ion-exchange method[13–15]. Especially, it was possible to synthesize P2VP core–PS shell type microspheres having colloidal silver in their P2VP cores. Microspheres containing colloidal silver in the core parts could be easily dispersed into solvents that were good for polystyrene. For the introduction of colloidal silver, there was an optimal swelling state of the P2VP core, which was governed by the crosslink density of the core. In contrast with the works of Cohen *et al.*, the poly(styrene-*b*-2-vinylpyridine) diblock copolymers, used as a template polymer in our work, were easy to synthesize. However, it is well known that colloidal silver forms a complex with the pyridine groups in poly(vinylpyridine)[16,17].

By changing the core from P2VP to poly(vinyl alcohol) (PVA), it will be possible to avoid complex formation between the colloidal silver and the functional groups in the core. The purpose of this paper is to synthesize PVA core–PS shell type microspheres with a thin polystyrene shell. The reason why a thinner shell is required for introducing colloidal silver is that a thinner shell makes it easy to swell with the silver solution deep into the crosslinked film.

To use core–shell type microspheres as the template for the introduction of colloidal silver, the interface between core and shell should be narrow and clear. The PVA core–PS shell type microspheres are synthesized by crosslinking the PVA core part of the spherical microstructure of poly(vinyl alcohol-*g*-styrene) (P(VA-*g*-S)) . For the synthesis of core–shell type microspheres with thinner PS shell, a P(VA-*g*-S) graft copolymer with lower content of PS is required. In the solid state, however, according to Molau's law[18], it is impossible to obtain a PVA sphere–PS matrix type microseparated structure with graft copolymer whose PS content is less than 65 vol%. In a solvent that is good for PS, P(VA-*g*-S) graft copolymers with various PS contents can form PVA core–PS corona type spherical polymer micelles. Thus, the crosslinking of PVA core sequences was carried out in a solvent in which P(VA-*g*-S) graft copolymers formed spherical P(VA) core–PS corona micelles. As described

---

*To whom correspondence should be addressed above, the swelling state of the core is an important factor for the introduction of colloidal silver. Thus, the effects of the polystyrene content in the graft copolymers and the crosslinking reagent concentration on the swelling behaviour of the PVA core are also examined in this paper.

EXPERIMENTAL

Synthesis of poly(vinyl alcohol-g-styrene)

Synthesis of carboxyl-ended polystyrene (PS macromonomer). First, 50 g of distilled styrene is polymerized with 1 g of 4,4′-azobis(4-cyanopentanoic acid) (V-501, Wako Pure Chemical Industries Ltd) for 96 h at 70°C under vacuum. The solvent was 200 ml of benzene/ethanol mixture (benzene, 66 vol%). Also, 4.3 g of allylmaloic acid diethyl ester was added as a degradative chain-transfer agent (telogen). After polymerization, the mixture was poured into methanol. Precipitated PS was collected by filtration and dried under vacuum. The PS was purified by reprecipitation with benzene and methanol three times. Then, the PS was fractionated from the benzene and methanol mixture. Molecular-weight distribution was limited to below 1.5.

Number-average molecular weight ($\overline{M}_n$) and molecular-weight distribution ($\overline{M}_w/\overline{M}_n$) of the PS were determined with a Tosoh HLC-8020 g.p.c. with tetrahydrofuran (THF) as eluent at 38°C. A TSK-gel GMHXL column was used and the flow rate was 1.0 ml min^{-1}. End functionality of the carboxyl group in the PS was estimated by neutralization titration with caesium hydroxide in water–THF mixture (water 9 vol%) with thymol blue as indicator.

PVA trunk polymer. Commercial PVA (poly(vinyl alcohol) No. 500, Kanto Chem) was used without any purification. Degree of polymerization (*DP*) and degree of saponification were 500 and 86.5–89.0%, respectively.

Synthesis of poly(vinyl alcohol-g-styrene). The PS macromonomer was grafted onto the PVA by esterification between the carboxyl groups in the PS macromonomer and the hydroxyl groups in the PVA. The PVA and the PS macromonomer were dissolved in a dimethyl sulfoxide (DMSO)–chloroform mixture (chloroform 40 vol%). *N,N*-Dicyclohexylcarbodiimide (DCC), a catalyst, was added to the solution ([DCC]/[–COOH]=3 (mol/mol)). The solution was stirred for 2 days at 40°C, and then the mixture was poured into ethanol. Precipitated gross polymer was collected by filtration and dried. Homopolymers of PS and PVA were extracted with benzene and water–methanol mixture (water 38 vol%), respectively. The insoluble polymer for both solvents was collected as P(VA-*g*-S). Styrene contents in the grafted copolymers were decided from u.v. absorption of phenyl groups in the polymer with a u.v. spectrophotometer (U-Best 35, JEOL) in DMSO–THF mixture (THF 50 vol%) at 269 nm. The conditions and the results of synthesis of graft copolymers are listed later in *Table 2*.

Morphological observation

The P(VA-*g*-S) graft copolymer or the crosslinked P(VA-*g*-S) was dissolved in DMSO–THF mixture (THF 50 vol%, polymer concentration 0.1 wt%). A drop of the sample was cast on a copper micro-grid coated with carbon. The polymer solution was dried gradually at room temperature. A specimen was annealed for 8 h at 110°C. The morphology of the microphase separation was observed with a transmission electron microscope (H-500, Hitachi) at 75 kV.

Turbidimetric titration

Micelle formation of the P(VA-*g*-S) graft copolymers in the solvent was estimated by turbidity titration. First, 0.5 g of the polymer was dissolved in 20 ml of DMSO. THF was then gradually added under vigorous stirring in a cylindrical pyrex cell at 25°C. At each step, the turbidity of the solution was measured with a single-beam u.v.-vis. spectrophotometer (Perkin–Elmer 139, Hitachi) at 600 nm.

Determination of the critical micelle concentration of poly(vinyl alcohol-g-styrene)

The P(VA-*g*-S) graft copolymers were dissolved in DMSO–THF mixture. The polymer concentration was set at 1.5 wt%. These solutions were gradually diluted with the solvent till the polymer concentration of the solution became 0.2 wt%. The viscosity of the solution was measured at each step with an Ubbelohde viscometer at 35°C.

Synthesis of poly(vinyl alcohol) core–polystyrene shell microspheres

The P(VA-*g*-S) graft copolymer was dissolved in DMSO–THF mixture. Polymer concentration was 1.0 wt%. Terephthal aldehyde (TPA) and dilute HCl, as the crosslink reagent and catalyst, respectively, were added to the solution. The molar ratio of HCl to hydroxyl group in PVA ([HCl]/[–OH]) was 0.24. The reaction was carried out for 2 days at 35°C. The THF contents in the solvents and the molar ratio of the crosslinking reagent to the hydroxyl groups ([TPA]/[–OH]) are listed later in *Table 3*. After crosslinking, the solutions were neutralized with aqueous ammonia, and then poured into ethanol. The precipitate, crosslinked P(VA-*g*-S), was dried under vacuum.

Characteristics of microspheres

A drop of benzene solution of crosslinked P(VA-*g*-S) with 0.1 wt% of polymer concentration was cast on carbon-coated glass and dried at room temperature. The sample was sputtered with gold and observed with a scanning electron microscope (JSM-T200, JEOL).

RESULTS AND DISCUSSION

There are several methods to synthesize the P(VA-*g*-S) graft copolymer, such as graft polymerization of styrene monomer onto a PVA trunk, grafting of PS onto PVA, etc. In order to obtain PVA core–PS shell type microspheres with homogeneous structure, homogeneous P(VA-*g*-S) graft copolymers are required. However, it is difficult to synthesize monodisperse graft polymer by the graft copolymerization of styrene onto a PVA trunk. Thus, carboxyl-terminated PS macromonomer was synthesized and it was grafted onto PVA by esterification between the carboxyl group on one end of PS and the hydroxyl group in PVA.

Synthesis of polystyrene macromonomer

The carboxyl-ended PS (PS macromonomer) can be synthesized by the following methods: (a) by initiation with radical initiator containing carboxyl groups of the radical polymerization of styrene; (b) by termination with radical transfer reagents containing carboxyl groups of the radical polymerization of styrene; (c) by termination of the living end of anionic living polystyrene with carbon dioxide. In this work, a large amount of PS macromonomer is needed. Thus, the PS macromonomer was synthesized by radical polymerization with an indicator, V-501, containing the carboxyl group. Allylmalonic acid diethyl ester was added as the degradative radical transfer agent to control the polydispersity of the molecular weight. As usual in radical polymerization, the molecular-weight distribution of PS macromonomer without fractionation was wide (2.00). In order to synthesize monodisperse microspheres, a PS macromonomer with narrow molecular-weight distribution of graft copolymer is required. Thus, the PS was fractionated with benzene and methanol.

The molecular weights, the molecular-weight distributions and the functionality, as the carboxyl group, of the fractionated PS homopolymers (PS macromonomers) are listed in *Table 1*. From these results, it was found that these PS macromonomers are suitable for grafting onto PVA, because one end of the PS homopolymers was terminated with a carboxyl group and their molecular-weight distributions were limited to below 1.5.

*Poly(vinyl alcohol-*g*-styrene)*

The P(VA-*g*-S) graft copolymers were synthesized by esterification between the carboxyl groups in the PS macromonomers and the hydroxyl groups in PVA. To accelerate the reaction, *N*, *N*-dicyclohexylcarbodiimide was added. *Figure 1* shows the schematic grafting process. *Table 2* shows the conditions and results of grafting PS macromonomers onto PVA.

In order to control the PS content in the graft copolymers, the feed amount of the PS macromonomers was varied. Graft copolymers with various PS contents in the range from 9 to 51 mol% were obtained by changing the feed amount of PS from 16 to 50 mol%. The yield of the graft copolymers was decreased by increasing PS macromonomer in the feed. The grafting in this work was a chemical reaction between polymer and polymer; in particular, the hydroxyl group in PVA has to be reacted with only one end of PS. The lower yield in the higher feed of PS macromonomer was due to the higher viscosity of the solution, which caused a reduction in the reactivity of grafting. The poly(vinyl alcohol-*g*-styrene) graft copolymers were dissolved in DMSO–THF and the DMSO–benzene at specific compositions.

Table 1 Characteristics of polystyrene macromonomers

Polymer	$\overline{M_n}^a$	$\overline{M_w}/\overline{M_n}^a$	Functionality^b
PS1	1.1×10^4	1.46	1.08
PS2	2.2×10^4	1.45	1.02

[a] Determined by g.p.c.

[b] The number of carboxyl groups per PS chain

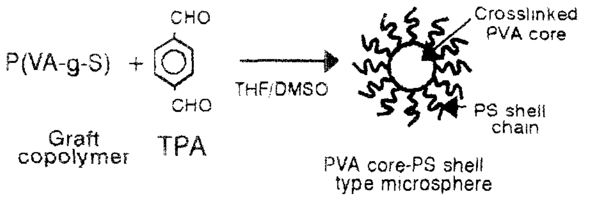

Figure 1 The scheme of the synthesis of microsphere

Table 2 Conditions and results of the synthesis of poly(vinyl alcohol-*g*-styrene) copolymers

Run No.	Feed PVA (g)^a	Feed PS (g)	Feed PS (mol%)	Graft copolymer Yield (%)	Graft copolymer PS (mol%)^b	Graft copolymer N^c
G1	8.0	3.5^d	16.0	88.8	9.0	0.5
G2	6.0	4.7^d	25.0	76.0	16.7	0.9
G3	4.0	6.3^d	40.0	57.5	23.0	1.4
G4	5.5	13.0^e	50.0	50.0	51.4	2.5

[a] Poly(vinyl alcohol) $\overline{M_n} = 2.2 \times 10^4$

[b] Polystyrene content determined by u.v. adsorption at 269 nm in THF–DMSO mixture (THF 50 vol%)

[c] Branch number per polymer

[d] PS1

[e] PS2

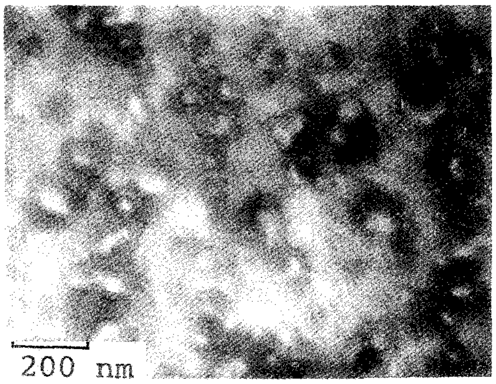

Figure 2 Transmission electron micrograph of G1 stained with OsO_4

Figure 2 shows an electron micrograph of the graft copolymer G1 cast from THF–DMSO mixture. The dark portions in the micrograph are segregated PVA stained with OsO_4. The PS content in G1 was 9 mol%. Based on Molau's law[18], the PS formed spherical microdomains with 40 nm diameter in a PVA matrix. If PVA and PS homopolymers remained in the system, 'macrophase' separation of the PS and the PVA would be observed. The microphase separation observed in this micrograph indicates that the polymer obtained in this work was P(VA-*g*-S) and the homopolymers were removed by purification.

PVA core–PS corona type micelle formation

In this work, as described in 'Introduction', core–shell type microspheres are synthesized by crosslinking the core part of the polymer micelle. In order to obtain PVA core type microspheres, first, PVA core–PS corona type polymer micelles should be formed in the solvent.

Here, the DMSO–THF mixture was chosen for micelle formation. The micelle formation of graft copolymers in the DMSO–THF mixture was investigated by turbidimetric titration. For all graft copolymers, the mixtures were opaque when the THF content in the mixture was from 0 to 28 vol%. Between 30 and 60 vol% of the THF content, the solutions of all graft copolymers were transparent due to the dissolution of

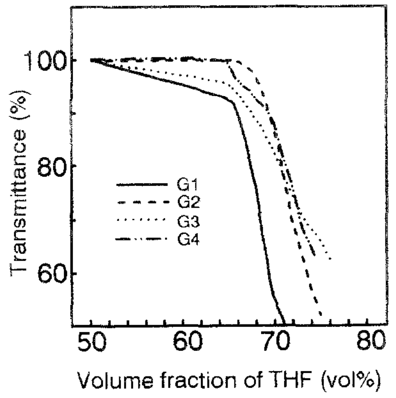

Figure 3 Dissolution behaviours of graft copolymers in THF–DMSO mixtures

both sequences of the graft copolymers in the mixture. *Figure 3* shows the transmittance changes of the graft copolymers/DMSO–THF mixtures. Above 65 vol% of the THF content, the transmittance of the solutions decreased. Above 60 vol% of THF content, the polystyrene macromonomer dissolved in the mixture. Moreover, the bluish tint, which was one of the specific properties of the micelle solution, appeared for all graft copolymer mixtures when the transmittance of the mixture decreased to 90%. From these results, the formation of the PVA core–PS corona type polymer micelles was suggested. Thus, the poly(vinyl alcohol) core–polystyrene shell type microspheres are expected to be synthesized by crosslinking PVA sequences in these mixtures. The THF contents of the mixtures whose transmittance was 90% are listed in *Table 3*. These THF contents were slightly increased with the PS content of the graft copolymers.

For polymer micelle formation, the polymer concentration of graft copolymer is also one of the important features. Below the critical micelle concentration (c.m.c.), the graft copolymer does not form micelles[19]. Above the c.m.c., increasing the concentration increases the polydispersity of the polymer micelle size[20]. Therefore, the c.m.c. values of the graft copolymers were estimated by viscometric measurement in the DMSO–THF mixture with the specific THF content described above. The maximum c.m.c. in all graft copolymers was 0.7 wt% for G1. Thus, crosslinking was carried out at 1 wt% of the polymer concentration for all cases.

Crosslinking of PVA core of the polymer micelle

Other crosslinking conditions are listed in *Table 3*. To change the crosslink density of the microspheres, the molar concentration ratio of terephthal aldehyde (TPA) to hydroxyl group was set at 1, 5 and 10 mol%.

The crosslinked products of G1 and G2 with lower PS content graft copolymer were aggregated with 10 mol% of PTA. For G3 and G4, no aggregated products were observed. This was due to the fact that PS contents of G1 and G2 were too low to hinder intermicelle crosslinking (aggregation). When the TPA concentration was lower than 10 mol%, no aggregated products were obtained.

The synthesis of microsphere was confirmed by SEM and TEM observations. *Figure 4a* shows the specific SEM micrograph of G4-1, which was crosslinked G4 with 1 mol% of TPA. The crosslinked products were spheres with 200 nm diameter and narrow size distribution. The inner texture of the microsphere can be observed by TEM (*Figure 4b*). The dark portions on *Figure 4b* are segregated PVA domains selectively stained with OsO_4. The PVA sequences formed a spherical microdomain with 96 nm diameter in each microsphere. The diameter of PVA microdomain was smaller than the external diameter of the microsphere. The diameter

Table 3 The conditions and results of crosslinking of micelles

Run No.	Crosslinking conditions			Results			
				Domain size (nm)		Degree of swelling	
	PS content[a] (mol%)	THF fraction[b] (vol%)	TPA/VA[c] (mol%)	Core[d]	Shell[e]	Film[f]	PVA core[g]
G1–1	9.0	66	1.0	120	18	2.93	3.51
G1–5	9.0	66	5.0	106	57	1.25	1.50
G1–10	9.0	66	10.0	158	aggrgtd	–	–
G2–1	16.7	68	1.0	110	49	1.57	2.20
G2–5	16.7	68	5.0	96	73	1.27	1.78
G2–10	16.7	68	10.0	142	aggrgtd	–	–
G3–1	23.0	68	1.0	110	49	1.41	2.25
G3–5	23.0	68	5.0	88	61	1.07	1.71
G3–10	23.0	68	10.0	87	56	–	–
G4–1	51.4	69	1.0	96	52	1.34	4.17
G4–5	51.4	69	5.0	90	90	1.11	3.46
G4–10	51.4	69	10.0	80	67	1.11	3.46

[a] Polystyrene content in graft copolymer
[b] In THF–DMSO mixture
[c] Feed amount of TPA
[d] Diameter of PVA core
[e] Thickness of polystyrene shell
[f] Weight degree of swelling of the entire film
[g] Calculated degree of swelling of PVA core

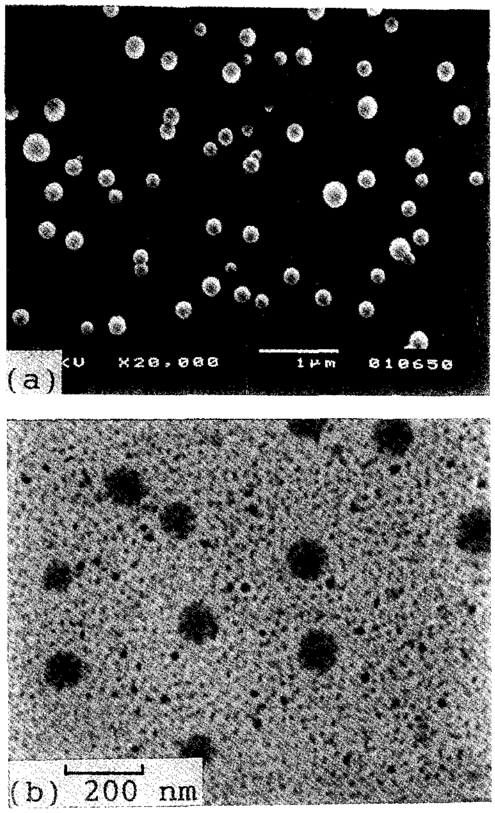

Figure 4 Electron micrographs of the G4–1 microspheres: (a) observed with a scanning electron microscope; (b) stained with OsO_4 and observed with a transmission electron microscope

distribution of PVA spherical microdomains was narrow. By combining the SEM and TEM results, it was found that the crosslinked product, G4-1, was a PVA core–PS shell type microsphere with 96 nm core size and 52 nm shell thickness. The diameters of PVA cores and the thickness of PS shell of other microspheres are listed in *Table 3*.

Next, the change of the diameter of the microspheres with the TPA concentration was examined. If the core part in the polymer micelle is ideally crosslinked, the external diameter of the microsphere and the PVA core diameter depend not on the TPA concentration but on the polymer type of the graft copolymers. The concentration of TPA should affect only the crosslink density of the core. As we expected, the diameters of the microspheres were specific for each graft copolymer and independent of the TPA concentration, except for G1 and G2 at 10% of TPA. This indicates that the PVA core parts of the polymer micelles were crosslinked ideally. It should be noted that the PS content in G1 was only 9 mol%. From the volume fraction of PS and PVA in G1, the ratio of shell thickness to the entire radius of the microsphere is calculated as 3% at the solid state. Consequently, we succeeded in the synthesis of PVA core–PS shell microspheres with very thin PS shell. It was suggested that the crosslink densities of the microspheres were different as the TPA concentration was changed. However, the ideal values of the crosslink densities could not be obtained in this work.

Swelling behaviour of core–shell type microspheres

In order to estimate the crosslink state of the core, the swelling behaviour of the microspheres was investigated. As each microsphere was too small to measure its swelling behaviour by the usual measurement methods, the microspheres were cast into films. The films were swollen in water at 35°C for 2 days. The degrees of swelling (*DS*) of the films are listed in *Table 3*. Since the PS matrix in films cannot be swollen in water, *DS* values of the PVA cores are calculated by combining the *DS* of the film and the volume fractions of PS and PVA. The calculated *DS* values of the PVA cores are also listed in *Table 3*.

For all graft copolymers, the calculated *DS* values of PVA cores with 5% of TPA were smaller than those with 1% of TPA. Thus, the crosslinking of the microspheres with 5% of TPA was tighter than that with 1% of TPA. Especially, the *DS* values of G1, G2 and G3 crosslinked with 5% of TPA were very close (about 1.7). This indicates that the crosslink states of their PVA cores were almost the same. At 5% of TPA concentration, the *DS* value of G4 was larger than for other graft copolymer products. It is found that the crosslinking of the G4 cores was looser than for microspheres of other graft copolymers. This was due to the lower dispersity of TPA into the polymer micelle of G4 with thick PS shell. For G4-5 and G4-10, the calculated *DP* values were the same, and thus their crosslink densities would be very similar.

Finally, the solubilities of the microspheres in benzene were investigated. The crosslinked G4 film is dissolved in benzene freely. Other films, however, were insoluble in benzene after swelling and drying, whereas they were all soluble in benzene before swelling measurements. The following two reasons are proposed: (a) the remaining poly(vinyl alcohol) chains seeped out into the polystyrene shell part during swelling, and these chains connected the poly(vinyl alcohol) cores; (b) inter-core crosslinking occurred by the pendent –CHO functional groups in the core due to the thinner shell and the higher swelling of the core.

CONCLUSIONS

PS macromonomers with one end capped with a carboxyl group were synthesized by using radical polymerization initiated with V-501, which contains carboxyl groups. Four P(VA-*g*-S) graft copolymers with various PS contents were synthesized by esterification between the carboxyl end-groups in PS macromonomers and the hydroxyl groups in the PVA. By changing the feed amount of PS, the content of PS in the graft copolymers could be controlled from 9 to 51 mol%. These graft copolymers could dissolve in THF–DMSO mixture. In THF, these graft copolymers formed PS core–PVA corona type polymer micelles. By adding DMSO to the THF polymer solution, they completely dissolved in the mixture, and then formed the PVA core–PS corona type polymer micelles.

By crosslinking PVA core parts of the PVA core–PS corona type polymer micelles with terephthal aldehyde (TPA), PVA core–PS shell type microspheres were obtained. Their shape and size were estimated by using a scanning electron microscope and a transmission electron microscope. When TPA concentration with respect to PVA was lower than 10 mol%, the cores of the polymer micelles of all graft copolymers could be crosslinked ideally, even when the PS shell fraction was only 9 mol%. Increasing the TPA concentration led to intermicelle crosslinking for the graft copolymers with polystyrene content less than 16.7 mol%. When the polystyrene content was larger than 23 mol%, the TPA concentration affected not the size and shape of the microspheres but the crosslinking density of the core.

REFERENCES

1 Ishizu, K. *Polym. Commun.* 1989, **30**, 209
2 Saito, R., Kotsubo, H. and Ishizu, K. *Polymer* 1992, **33**, 1073
3 Saito, R., Kotsubo, H. and Ishizu, K. *Eur. Polym. J.* 1991, **27**, 1153
4 Ishizu, K. *J. Colloid Interface Sci.* 1993, **156**, 299
5 Saito, R., Kotsubo, H. and Ishizu, K. *Polymer* 1994, **35**, 1747
6 Ishizu, K., Sugita, M., Kotsubo, H. and Saito, R. *J. Colloid Interface Sci.* 1995, **169**, 456
7 Saito, R., Kotsubo, H. and Ishizu, K. *Polymer* 1994, **35**, 1581
8 Saito, R., Kotsubo, H. and Ishizu, K. *Polymer* 1994, **35**, 2296
9 Ng Cheong Chan, Y., Schrock, R. R. and Cohen, R. E. *Chem. Mater.* 1992, **4**, 24
10 Cummins, C. C., Schrock, R. R. and Cohen, R. E. *Chem. Mater.* 1992, **4**, 27
11 Ng Cheong Chan, Y., Schrock, R. R. and Cohen, R. E. *J. Am. Chem. Soc.* 1992, **114**, 7295
12 Ng Cheong Chan, Y., Craig, G. S. W., Schrock, R. R. and Cohen, R. E. *Chem. Mater.* 1992, **4**, 885
13 Saito, R., Okamura, S. and Ishizu, K. *Polym. Commun.* 1992, **33**, 1099
14 Saito, R., Okamura, S. and Ishizu, K. *Polymer* 1993, **34**, 1183
15 Saito, R., Okamura, S. and Ishizu, K. *Polymer* 1993, **34**, 1189
16 Bjerrum, J. *Chem. Rev.* 1950, **46**, 381
17 Kurokawa, Y. and Ueno, K. *J. Appl. Polym. Sci.* 1992, **27**, 621
18 Molau, G. E. 'Block Copolymer' (Ed. S. L. Aggrawal), Plenum Press, New York, 1970
19 Israelachvili, J. N., Matchell, D. J. and Ninham, B. W. *J. Chem. Soc. Faraday Trans. (I)* 1976, **72**, 1525
20 Israelachvili, J. N. 'Intermolecular and Surface Forces', Academic Press, London, 1985