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Introduction of colloidal silver into the poly(2-vinylpyridine) microdomain of microphase-separated poly(styrene-*b*-2-vinylpyridine) film: 4. One-step method

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Silver nanoclusters in varying amounts were introduced into the poly(2-vinylpyridine) (P2VP) phases of three types of poly(styrene-*b*-2-vinylpyridine) block copolymers. Upon casting the block copolymer–silver nitrate–water–1,4-dioxane solutions and drying, the silver clusters selectively formed in the P2VP phases of the microphase-separated films. From wide angle X-ray scattering measurements and transmission electron microscopy it was found that microspheres composed of polystyrene shells and P2VP cores containing silver nanoclusters were formed by crosslinking of the P2VP phases and reduction of the silver compounds in the films. The content of silver nanoclusters in the microspheres could be controlled quantitatively by this method.

(Keywords: silver nanoclusters; diblock copolymer; microphase separation)

INTRODUCTION

Strict microscopic control of the amount and location of metal nanoclusters in the microphase-separated polymer films is very important in the design of the highly functional metal–polymer composite materials as semiconductors, optical materials and catalyst carriers. The placement of metal nanoclusters has been studied in the non-linear diffusion phenomena of metal compounds in hydrogel matrices[1-3]. Recently, stricter control of the location of introduced metal nanoclusters in polymers became possible through the use of microphase-separated structures of some specific block copolymers as templates. Cohen and coworkers have succeeded in the introduction of gold[4], silver[4,5], platinum[6], palladium[6], ZnS and CdS nanoclusters[7] into rubber films by using block copolymers in which complexes of these metals were attached to blocks of polycycloalkenes.

We have also succeeded in controlling the location and amount of silver nanoclusters in polymer films by using poly(styrene-*b*-2-vinylpyridine) diblock copolymers with lamellar[8,9] and spherical[10] crosslinked poly(2-vinylpyridine) (P2VP) phase morphologies and poly(vinyl alcohol-*g*-styrene) graft copolymers with a crosslinked spherical poly(vinyl alcohol) phase morphology[11]. The most important feature of our method is that the silver ions are introduced into the P2VP or poly(vinyl alcohol) (PVA) phase by ion exchange. In our method, iodide ions or hydroxide ions in the P2VP or PVA phase, respectively, are used as silver ion trappers. Another interesting feature is that the P2VP and PVA phases are each crosslinked. These template polymers with crosslinked spherical microdomains will dissolve in organic solvents such as benzene, THF and so on, because they form polystyrene (PS) shell-crosslinked P2VP core[12] or PS–PVA[13] shell-core polymer microspheres after dissolving. This suggests that silver nanoclusters can also be dispersed in these solvents. As an application of this method, we have succeeded in synthesizing an electrically anisotropic conductive polymer by using a horizontally oriented lamellar polymer[14].

Our method, however, has the serious disadvantage that the amount of introduced silver nanoclusters is governed by the crosslink density of the phases in which the nanoclusters are located[10], and it is difficult to control the amount of silver nanoclusters and the crosslink density of the film independently. This is because the dispersion of silver ions in the film is governed by the degree of swelling of not only the entire film but also both phases of the film.

The main purpose of the present work was to control the introduced amount of silver nanoclusters quantitatively. For comparison with new and previous methods, poly(styrene-*b*-2-vinylpyridine) (P(S-*b*-2VP)) diblock copolymers with various molecular weights and P2VP contents, one of which was the same block copolymer as used in previous studies[8-10], were chosen as templates. These polymers were cast from 1,4-dioxane–water mixtures containing silver nitrate. After casting the polymers with silver nitrate, the P2VP phases were crosslinked using 1,4-diiodobutane gas. Then, the silver compound was reduced to silver nanoclusters.

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Table 1 Characteristics of poly(styrene-*b*-2-vinylpyridine) diblock copolymers

Block	$10^{-5} M_n$		P2VP content[a]	D[b]
copolymer	Block	PS	(mol%)	(nm)
SV01	2.07	1.92	14	28
SV02	3.2	2.7	15.5	30.3
SV03	4.0	3.2	19.9	66

[a] Estimated by ^{1}H n.m.r.

[b] Number average diameter of poly(2-vinylpyridine) microdomains estimated by TEM

There are several problems in this method. First, we cannot be sure that the silver compound will be restricted to the P2VP phase. Second, it is uncertain that the P2VP microdomains can be crosslinked after silver compound introduction. Finally, it may be difficult for the amount of silver nanoclusters in the film to be controlled or, especially, increased. In the present work, the introduction of silver nanoclusters into polymer films was investigated with transmission electron microscopy (TEM) and wide angle X-ray scattering (WAXS).

EXPERIMENTAL

Materials

Block copolymers. The P(S-*b*-2VP) diblock copolymers were synthesized as described elsewhere[10,12,15] by anionic polymerization in THF with n-butyllithium as initiator at −78°C. The number average molecular weights, molecular weight distributions and contents of these block copolymers were measured as described elsewhere[10,12,15]. Some of these properties are listed in *Table 1*. The morphology of the phase separation of all polymers investigated was that of P2VP spheres in a PS matrix. The diameters of P2VP spheres are also listed in *Table 1*.

Introduction of silver nanoclusters into the block copolymer. The block copolymer was dissolved in a 1,4-dioxane–water mixture. The polymer concentration and the water content in the mixture were 4.5% and 3.2%, respectively. Silver nitrate was dissolved in the mixture. The solution was stirred overnight in the dark at room temperature. Then the solution was cast onto a flat Teflon sheet and allowed to dry gradually at room temperature. Each film was divided into two halves. One half of the film was crosslinked with 1,4-diiodobutane gas over a period of four days at room temperature. The other half of the film was soaked in a caesium hydroxide–water–1,4-dioxane mixture 2.5 wt% CsOH; 10 vol% 1,4-dioxane) for two hours at 20°C and then crosslinked with 1,4-diiodobutane gas over a period of four days at room temperature. The crosslinked film was exposed to light from a wolfram lamp (30 W, 100 V) without wavelength control for four hours. The exposed film was then soaked in a hydroquinone–water–1,4-dioxane mixture 2.5 wt% hydroquinone, 20 vol% 1,4-dioxane) for two hours at 20°C. The film was washed with water, dried and soaked in aqueous sodium bisulfite 2.5 wt% $Na_2S_2O_3$) for one hour at 20°C, then washed and dried. The content of silver nanoclusters was measured using a titration method reported elsewhere.

Characterization

Morphological observation. The solution of the sample (polymer concentration 1 wt%) was dropped onto a copper microgrid coated with carbon and allowed to dry gradually. For observation of the cross-section of the sample, an ultrathin film specimen was prepared by cutting the film with a microtome (Reichert–Nissei, Ultracut N). Morphological observations were made with a Hitachi H-500 transmission electron microscope at 75 kV.

Wide angle X-ray scattering. Wide angle X-ray scattering (WAXS) intensity distributions were measured with a rotating anode X-ray generator (Rigaku Denki Rotaflex RTP 300 RC) operating at 40 kV and 100 mA. The X-ray source was monochromatized to CuKα ($\lambda = 1.54$ Å) radiation. The WAXS patterns were recorded from a finely focused X-ray source on a flat plate camera (Rogaku Denki, RU-100).

RESULTS AND DISCUSSION

The most interesting feature of this method is that it uses the different affinities of aqueous silver nitrate for P2VP and PS sequences. The δ values for polystyrene[16] and water are $9.1\,\mathrm{cal}^{1/2}\,\mathrm{cm}^{-3/2}$ and $23.4\,\mathrm{cal}^{1/2}\,\mathrm{cm}^{-3/2}$ (1 cal = 4.2 J), respectively. According to the chemical structure of P2VP, the compatibility between water and P2VP is better than that between water and PS in spite of the fact that water is a non-solvent for both P2VP and PS. Silver nitrate dissolves in water rather than 1,4-dioxane. It is also known that silver ions can form complexes with pyridine groups[17]. It is therefore expected that silver nitrate should interact more strongly with P2VP than with PS. Thus, upon drying the P(S-*b*-2VP)–silver nitrate–water–1,4-dioxane mixture, the silver nitrate will stay in the P2VP phase.

Table 2 Conditions and results for silver nanocluster introduction

	Feed conditions		Results			
Sample name	Polymer type	$[Ag^+]/[Py]$	$[Ag]/[Py]$	Yield[a] (%)	Cluster size[b] (nm)	Q_{obs}[c] (mol%)
SV01-2	SV01	2.0	1.82	91	7	36.3
SV02-2	SV02	2.0	2.27	100	8	30.2
SV03-2OH	SV03	2.0	1.43	71	10	16.9
SV02-0.2	SV02	0.2	0.19	96	8	62.7
SV03-0.5	SV03	0.5	0.52	100	10	11.7

[a] $[Ag]/[Ag^+]$ measured by Volhard titration

[b] Estimated from TEM results

[c] Measured by Volhard titration

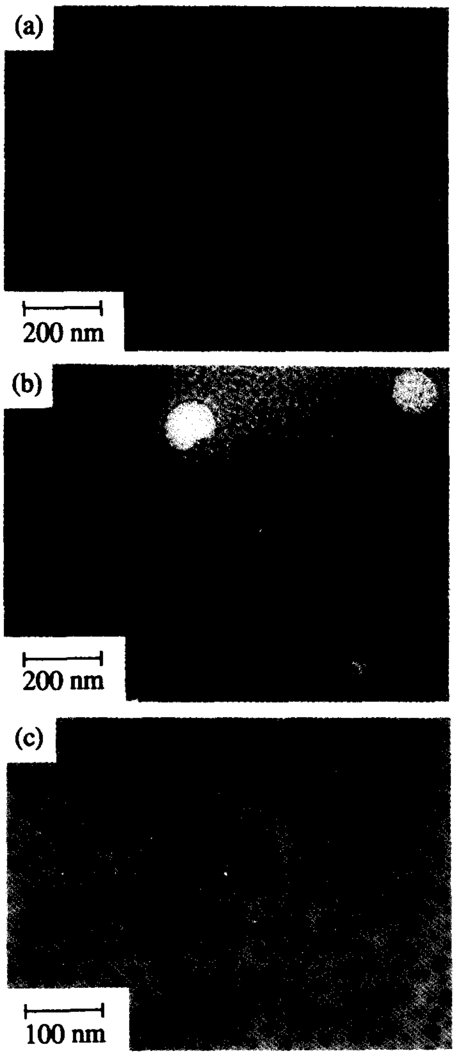

Figure 1 Transmission electron micrographs of cross-sections of SV01-2 films: (a) as-cast film; (b) crosslinked film; (c) microspheres cast from THF solution at 0.1 wt% polymer concentration

The conditions for sample preparation are listed in *Table 2.* First, the P(S-*b*-2VP) block copolymers were dissolved in 1,4-dioxane, which is a good solvent for these block copolymers. The 1,4-dioxane solutions of these polymers were clear. Aqueous silver nitrate was then added to these solutions. The mixture became turbid immediately. The maximum tolerable amount of aqueous silver nitrate in these 1,4-dioxane solutions was 3.2wt%. Above 3.2wt%, the P(S-*b*-2VP) diblock copolymers were precipitated.

After continuous stirring overnight, all mixtures became clear again. The molar ratio of silver ions to pyridine groups ($[Ag^+]/[Py]$) was varied from 0.2 to 2.0. The mixtures were cast onto Teflon dishes with smooth surfaces and dried. Films of the SV03 series and SV02-02 became transparent and brown after complete drying, and SV02-2 was a colourless transparent film. No macroscopic crystals were observed in these films.

Location of silver

Figure 1 shows the transmission electron micrographs of films of a block copolymer prepared with $[Ag^+]/[Py] = 2.0$ (SV01-2). For the as-cast film with silver nitrate (*Figure 1a*), neither PS nor P2VP was stained with a specific reagent. However, a clear morphology of microphase separation for this SV01 block copolymer can be seen. The dark particles are aggregated and form spherical microdomains 25 nm in diameter in a white matrix. The average diameter of microdomains in *Figure 1a* (25 nm) agrees well with the diameter of P2VP microdomains in SV01 without silver nitrate (28 nm). Thus, the dark microdomains in *Figure 1a* are P2VP microdomains. Only silver clusters have a high enough electron density to be observed as dark areas by TEM in this specimen. Thus we can say that the silver compounds are held selectively in the P2VP microdomains.

The P2VP microdomains were then crosslinked with 1,4-diiodobutane gas. All the block copolymer films turned yellow owing to the presence of iodide. Upon crosslinking, the P2VP domains were stained grey with iodide. TEM results (*Figure 1b*) indicate that the silver compound turned from grey to black after crosslinking. However, these small black particles of silver compound still appeared only in the P2VP microdomains. The particle sizes of the black particles did not change after crosslinking.

After crosslinking, the block copolymers turned to P2VP core–PS shell microspheres since the P2VP spherical microdomains were fixed chemically. These microspheres dissolved freely in THF, in spite of the gelation of the P2VP spherical microdomains, because of the high solubility of the uncrosslinked PS shell chains. The silver compound present in the P2VP spherical microdomains was retained in the crosslinked P2VP cores. *Figure 1c* shows the final products from SV01-2 namely P2VP core–PS shell microspheres containing silver nanoclusters in the P2VP cores. For TEM observation, the specimen was recast from the THF solution at 0.1 wt% polymer concentration without staining. As expected, the spherical polymer products, i.e. the polymer microspheres, were dispersed on the carbon substrate. Each spherical product was composed of a white PS shell and a grey P2VP core containing a black particle of silver compound. As described later, the silver was in the form of nanoclusters. The average diameter of the silver nanoclusters was 7 nm. The diameters of the P2VP cores of SV01-2 were constant (ca. 25 nm) throughout crosslinking, reduction and removal of unreacted silver iodide. In *Table 2*, the average diameters of the silver nanoclusters are listed.

The existence of silver nanoclusters in the P2VP cores caused an increase in the average P2VP core diameter of only ca. 5%. It is concluded that P2VP core–PS shell microspheres with silver nanoclusters in the P2VP cores can be readily synthesized by this method.

Silver compounds in the film in each step

In order to characterize the silver compounds in the film in each step, WAXS measurement were carried out. The WAXS intensity distributions of films of SV02-2 are shown in *Figure 2.* For the as-cast film of SV02 with silver nitrate, major peaks appeared clearly at angles of 22.6°, 23.95°, 32.4° and 34.7°. These peaks came from silver nitrate crystals. We can deduce that silver–pyridine complexes were not formed in the film because no WAXS peaks for such complexes were apparent.

After crosslinking, all the peaks from silver nitrate crystals vanished and new peaks appeared at different angles. The new peaks indicated the presence of cubic

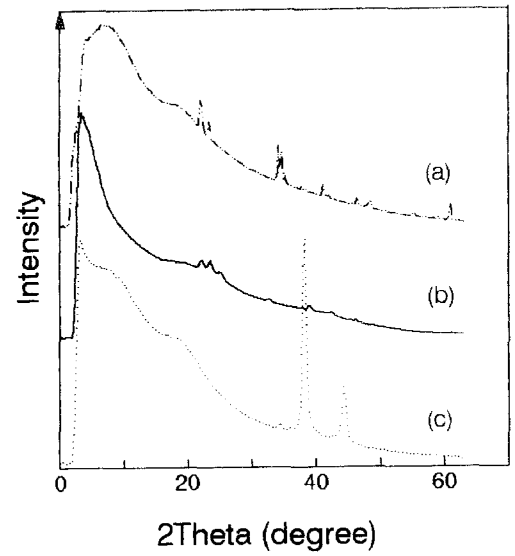

Figure 2 WAXS intensity distributions of SV02-2 films: (a) as-cast film; (b) crosslinked film; (c) reduced film

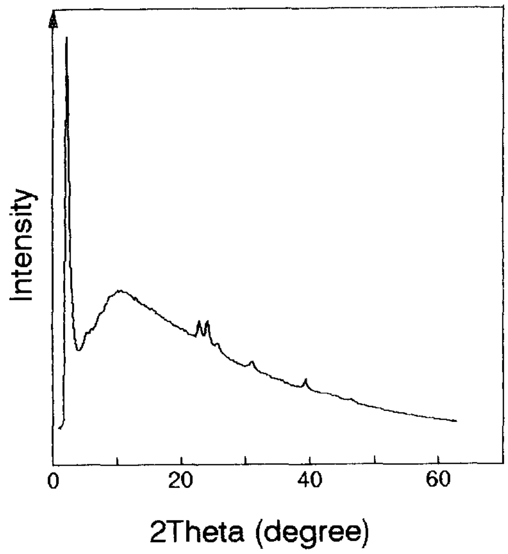

Figure 3 WAXS intensity distribution of reduced SV02-2 film recast from THF solution

and hexagonal crystals of silver iodide. The crosslinking of the P2VP chans with 1,4-diiodobutane involved quaternization of the pyridine groups. Upon crosslinking, iodide ions were produced in the P2VP microdomains. Silver iodide was formed from silver nitrate and the iodide ions produced upon crosslinking. After reduction of the silver iodide crystals with hydroquinone, all peaks corresponding to silver iodide vanished and new peaks appeared at 38.1° and 44°. These two peaks correspond to crystals of pure silver. Therefore, it is concluded that the silver iodide was reduced to silver. Again, from these results it is concluded that the black particles observed in the TEM micrograph in *Figure 1c* are silver nanoclusters.

In general, the surfaces of silver nanoclusters are highly reactive. At this stage, the iodide ions were still in the film. There was the possibility that the silver would form silver iodide by reacting with the remaining iodide ions in the film. To investigate this point, the film was subjected to conditions under which the silver nanoclusters and iodide ions might react. For this purpose, the mobility of the iodide ions in the polymer matrix was increased by dissolving the film in THF, and the solution was stirred overnight. When the film was dissolved in THF, the solution was colourless and had a bluish tint specific to the presence of microspheres in the solvent. Two hours later, the solution had turned green-yellow with a bluish tint. This solution was cast onto a Teflon dish and dried to obtain a film for the WAXS measurement. The WAXS intensity distribution of the recast film is shown in *Figure 3*. Since the WAXS profiles for the films before reduction (*Figure 2b*) and after recasting from THF solution are the same, it can be concluded that the silver in the film was active and silver iodide was easily re-formed in the film from silver and iodide ions. Thus, it was found that the iodide ions must be removed from the film after the reduction step to prevent the re-formation of silver iodide.

According to our previous results[9,10], the iodide ions in the film could be removed completely by soaking the film in $Na_2S_2O_3$ solutions. Thus all reduced films were soaked in $Na_2S_2O_3$ solution and the iodide ions were completely removed.

The crosslinking density of the microsphere is one of the most important features of core–shell microspheres, and the introduced amount of the silver in the core–shell microspheres depends on the crosslink density[10]. In previous papers[8–10,12,15], the crosslink densities were calculated by combining the concentrations of pendent iodide and iodide ions produced by quaternization (crosslinking) in the film. However, some iodide ions produced by crosslinking react with silver nitrate, making unclear the crosslink density of the film. The amount of iodide that reacts with silver nitrate is unknown at this stage. If a silver compound that cannot react with iodide ions is formed in the film before crosslinking, the side reaction between iodide ions and the silver compound will be prevented; consequently, it will be possible to determine the crosslink density of the microspheres.

Based on this consideration, the as-cast film of SVO3-2 was soaked in aqueous caesium hydroxide (giving SV03-2OH) to form silver oxide in the film. Silver oxide is insoluble in water; moreover, it is a convenient precursor for the synthesis of silver nanoclusters by reduction[1]. Upon soaking the as-cast film of SVO3-2 in caesium hydroxide solution, the film turned black. *Figure 4* shows the WAXS intensity distributions of the SV03-2OH films. The distribution for freshly prepared SVO3-2OH (*Figure 4a*) showed peaks at angles of 33.7° and 38.4° for silver oxide. As the peak for silver nitrate could still be seen at an angle of 28.5°, it was concluded that not all of the silver nitrate in the film reacted with caesium hydroxide. After crosslinking (*Figure 4b*), peaks were found for silver hydroxide and, unfortunately, silver iodide (22.9° and 38.4° for silver iodide), although the peaks for silver oxide at angles of 33.7° and 38.4° did not change. Thus it was impossible to prevent silver iodide formation in the film by formation of silver oxide.

Figure 4c shows the WAXS profile for SV03-2OH film after reduction with hydroquionone. The peaks at 33.7° and 38.4° were replaced by two new peaks for pure silver at 38.1° and 44.4°. However, weak peaks for silver iodide at 22.9° and 38.4° could still be seen. These results

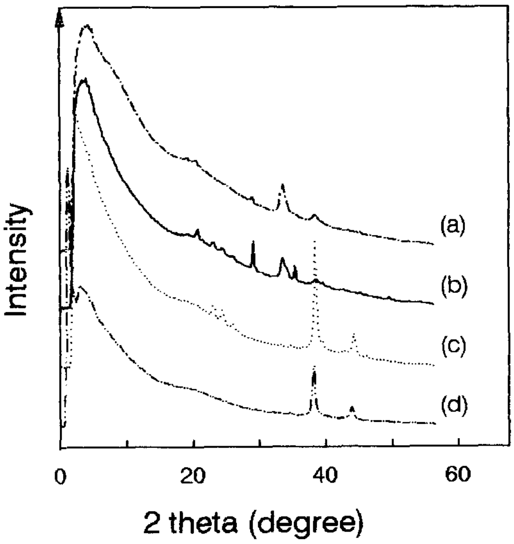

Figure 4 WAXS intensity distributions of SV03-2OH films: (a) SV03-2 film after soaking in aqueous caesium hydroxide; (b) crosslinked film; (c) reduced film; (d) film after soaking in aqueous $Na_2S_2O_3$

indicate that the reduction to pure silver was not complete in this film. The concentration of silver nitrate in this film was the largest in this study. Therefore it was supposed that the reduction conditions were not sufficient for this film. For complete reduction of the silver compounds in this film, more severe reduction conditions such as, among others, a higher hydroquinone concentration in the solution and a longer soaking time would be required.

To remove any silver iodide not reduced by hydroquinone and stray iodide ions produced by crosslinking, the film of SV03-2OH was soaked in aqueous $Na_2S_2O_3$. However, the silver might be contaminated with ions other than iodide by this treatment. The WAXS intensity distribution of the film after soaking in $Na_2S_2O_3$ solution *Figure 4d* showed almost the same pattern as for the film before such treatment (*Figure 4c*). The peaks for silver did not change after soaking the film in $Na_2S_2O_3$ solution. However, the peaks for silver iodide were no longer present.

Comparison of methods of introducing silver

The silver nanocluster contents in the films are listed in *Table 2*. The degrees of quaternization were also measured for the films before reduction. As described above, the exact values of the crosslink density and degree of quaternization could not be measured. However, degree of quaternization measurement was carried out using an earlier method with the guidance of the crosslink density of the microspheres. The observed degrees of quaternization (Q_{obs}) are shown in *Table 2*.

As the earlier method used iodide ions produced by quaternization of pyridine groups, the amount of introduced silver nanoclusters was determined from the degree of quaternization. Theoretically, the maximum value of [Ag]/[Py] should be 1 for this method. In fact, the maximum experimental value obtained for this method was 0.45 for SV03 microspheres with optimum crosslink density. The molar ratio of introduced silver nanoclusters to pyridine groups ([Ag]/[Py]) was varied in the range 0.19–2.27. The range of values for Q_{obs} was 11.7–62.7 mol% for pyridine groups in the film. It was found that the amount of silver nanoclusters introduced by this method was independent of the degree of quaternization. This suggests that the amount of introduced silver nanoclusters and the crosslink density of the microspheres were independent.

In the present work, the maximum value of $[Ag^+]/[Py]$ was 2.27 for the film of SV02 cast with silver nitrate – much larger than the theoretical maximum of 1 for the earlier method. Thus it was possible to introduce silver nanoclusters to an [Ag]/[Py] ratio greater than 1 by this method. Moreover, the yield, i.e. the molar ratio of introduced silver nanoclusters to silver ions in the feed ($[Ag]/[Ag^+]$), was very close to 100% for all except SV03-2OH. The molecular weight of the block copolymer was independent of the presence of silver nanoclusters. Also the silver nitrate introduced into the film by casting could be almost completely converted to silver nanoclusters. These results indicate that the amount of introduced silver nanoclusters could be controlled easily by changing the amount of silver nitrate in the feed.

CONCLUSIONS

By using the better compatibility of poly(2-vinylpyridine) and aqueous silver nitrate as compared to polystyrene and aqueous silver nitrate, silver nitrate was introduced into the spherical poly(2-vinylpyridine) microdomains in microphase-separated films of poly(styrene-*b*-2-vinylpyridine) diblock copolymers. The poly(2-vinylpyridine) microdomains were crosslinked and the silver nitrate was converted to silver iodide and reduced to pure silver with hydroquinone. The silver compounds in each step were characterized from the viewpoints of their location and character by transmission electron microscopy and wide angle X-ray scattering, respectively. From these results, it was found that the silver nanoclusters were held in the crosslinked poly(2-vinylpyridine) cores of poly(2-vinylpyridine) core–polystyrene shell microspheres. Compared to an earlier method, the method for introducing silver nanoclusters described herein showed the following advantages:

1. the amount of introduced silver nanoclusters could be controlled quantitatively by changing the amount of silver nitrate in the feed;
2. the silver nanoclusters could be introduced to an [Ag]/[Py] ratio greater than 1; and
3. the amount of introduced silver nanoclusters was independent of the degree of quaternization of the poly(2-vinylpyridine) microdomains.

However, this new method had the disadvantage that the crosslink density of the microspheres was unclear. In order to clarify this issue, a film was soaked in aqueous caesium hydroxide in order to form silver oxide, which does not react with iodide ions in the film during crosslinking. However, the silver nitrate did not react completely with caesium hydroxide and silver iodide was still formed in the film during crosslinking. Thus the exact crosslink density was not obtained in this work.

REFERENCES

1 Korokawa, Y. and Ueno, K. *J. Appl. Polym. Sci.* 1982, **27**, 621
2 Mueller, K. F. *Science* 1984, **225**, 1021

3 Holba, V. *Colloid Polym. Sci.* 1986, **267,** 456
4 Cheang Chan, Y. Ng., Schrock, R. R. and Cohen, R. E. *Chem. Mater.* 1992, **4,** 24
5 Cheang Chan, Y. Ng., Schrock, R. R. and Cohen, R. E. *J. Am. Chem. Soc.* 1992, **114,** 7295
6 Cheang Chan, Y. Ng., Craig, G. S. W., Schrock, R.R. and Cohen, R. E. *Chem. Mater.* 1992, **4,** 885
7 Cummins, C. C., Cheang Chan, Y. Ng., Schrock, R. R. and Cohen, R. E. *Chem. Mater.* 1992, **4,** 27
8 Saito, R., Okamura, S. and Ishizu, K. *Polymer* 1992, **33,** 1099
9 Saito, R., Okamura, S. and Ishizu, K. *Polymer* 1993, **34,** 1183
10 Saito, R., Okamura, S. and Ishizu, K. *Polymer* 1993, **34,** 1189
11 Saito, R., Okamura, S. and Ishizu, K. *Polymer* in press
12 Saito, R., Kotsubo, H. and Ishizu, K. *Polymer* 1992, **33,** 1073
13 Saito, R., Okamura, S. and Ishizu, K. *Polymer* in press
14 Ishizu, K., Yamada, Y., Saito, R., Kanbara, T. and Yamamoto, T. *Polymer* 1993, **34,** 2256
15 Saito, R., Kawachi, N. and Ishizu, K. *Polymer* 1994, **35,** 866
16 Mangaraj, D., Bhatnager, S. K. and Rath, S. B. *Makromol. Chem.* 1963, **67,** 75
17 Bjerrum, J. *Chem. Rev.* 1950, **46,** 381