Introduction of colloidal silver into poly(2-vinyl pyridine) microdomains of microphase separated poly(styrene-*b*-2-vinyl pyridine) film: 3. Poly(2-vinyl pyridine) spherical microdomain

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Colloidal silver was introduced into the crosslinked spherical poly(2-vinyl pyridine) (P2VP) microdomains in microseparated poly(styrene-*b*-2-vinyl pyridine) diblock copolymer film by soaking the films in a $AgNO_3$/water/1,4-dioxane (DIOX) mixture, reducing the AgI and removing the unreacted AgI with $Na_2S_2O_3$. The amount of colloidal silver introduced per pyridine group, [Ag]/[Py], reached 0.45 mol mol^{-1} for M2–50 (the crosslink density of the film was 27.8 mol%, and the $AgNO_3$ concentration was 1.0×10^{-1} mol l^{-1} with DIOX = 50 vol%). From SEM and TEM observations, it was found that colloidal silver was introduced into the P2VP microdomains of M2–50 homogeneously. M2–50 became the P2VP core–PS shell microsphere containing the colloidal silver in the P2VP core by dispersing M2–50 in benzene.

(Keywords: colloidal silver; crosslinking; spherical microdomain)

INTRODUCTION

Polymer membranes[1–3], especially hydrophilic gels[4–7], have been studied as supporting materials for colloidal metals which are well known catalysts. To develop more functional colloidal metal–polymer materials, the localization of colloidal metal in the supporting material was controlled[8]. However, it was impossible to strictly control the shape and the size of the microscopic phases containing the colloidal metals.

When the hydrophilic gel phases are dispersed in the polymer matrix, it is possible to introduce the colloidal metals in just the hydrophilic gel phases. Based on this concept, we have introduced colloidal silver into the limited microdomains of the crosslinked poly(2-vinyl pyridine) (P2VP) (quaternized P2VP gel) phases in poly(styrene-*b*-2-vinyl pyridine) P(S-*b*-2VP) diblock copolymer film with lamellar morphology by using the microseparated structure of the film[9,10]. Application of the films with horizontal-oriented lamellar structure to electric isotropic materials was investigated[11].

For the film with lamellar morphology, it was easy to introduce colloidal silver into the film along the crosslinked P2VP phases, because this hydrophilic gel formed the continuous phases in the matrix. For the film with P2VP spherical morphology, the P2VP spherical microdomains are not continuous in the polystyrene (PS) matrix. Even though the crosslinked P2VP microdomains are isolated in the PS matrix, it is possible to introduce the colloidal silver into the crosslinked P2VP microdomains by swelling the matrix in solution.

The main purpose of this study is to introduce colloidal silver homogeneously into crosslinked spherical P2VP microdomains isolated in a PS matrix. This was done under varying conditions, e.g. Ag^+ ion concentration, volume fraction of 1,4-dioxane (DIOX) in the solution, the crosslink density and the degree of quaternization (*DQ*) of the film.

It was reported that the P2VP core–PS shell-type polymer microsphere could be synthesized by dispersing the film with crosslinked P2VP spheres in the PS matrix of P(S-*b*-2VP) diblock copolymer in good solvents for PS[12,13]. According to Brugger *et al.*[14], poly(4-vinyl pyridine) partially quaternized with bromohexadecane (with properties similar to the P2VP core of this study), was optimal for the protective colloid. If the P2VP core–PS shell microsphere containing colloidal silver in the P2VP core can be dispersed in the solvents, the crosslinked P2VP core as the supporting material is regarded as the more functional protective colloid for the colloidal silver than the polymer chains of the general protective colloid. The P2VP core–PS shell microsphere is expected to act as the stable polymer micelle which presents a reacting field in the solvent. We investigated the synthesis of the P2VP core–PS shell microsphere containing colloidal silver in the P2VP core by dispersing the film which introduced colloidal silver into the crosslinked P2VP spheres in the solvents.

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EXPERIMENTAL

Materials

P(S-*b*-2VP) diblock copolymer was synthesized by the usual sequential anionic polymerization using n-butyllithium as an initiator in tetrahydrofuran (THF) at −78°C[13,14].

The number-average molecular weight ($\overline{M_n}$) of the precursor PS (3.2×10^5) was determined with a Tosoh HLC-802A GPC using THF as eluent at 38°C, a TSK-gel GMH column and a flow rate of 0.9 ml min^{-1}. The weight-average molecular weight ($\overline{M_w} = 4.0 \times 10^5$) of the diblock copolymer was determined by combining g.p.c. data and viscometric data in THF at 38°C. The 2VP content in the diblock copolymer (19.9 mol%) was determined with a ^{1}H n.m.r. spectrometer (Hitachi, 24B).

Crosslinking of the film

The diblock copolymer film (60 μm thick) was cast from benzene (0.05 g ml^{-1}) solution on a Teflon sheet. The cast film was gradually dried for 4 days at room temperature. Crosslinking of the segregated P2VP sequences in the P2VP microdomains was carried out by quaternization with 1,3-diiodobutane (DIB) vapour[12]. The film and DIB liquid were put into a 500 ml separating flask. The flask was cooled to 0°C, the air in the system was extracted under vacuum and the system was closed. The flask was then heated to 25°C, and the crosslinking was carried out. The conditions for the crosslinking are listed in *Table 1*.

Introduction of colloidal silver into the film

Crosslinked film (0.05 g) was soaked in a silver nitrate ($AgNO_3$)/water/DIOX solution (10 ml) for 5 days in the dark. The film was washed with water and soaked in a hydroquinone/water/DIOX mixture (hydroquinone, 2.5 wt%) for 2 h at 20°C. The film was washed with water and then soaked in a sodium bisulphate/water/DIOX mixture ($Na_2S_2O_3$, 2.5 wt%) for 1 h at 20°C, washed and dried. The conditions are listed in *Tables 2* and *3*.

Characterization

Crosslink density and degree of quaternization. The *DQ* of the 2VP sequences was measured by Volhard's titration as follows: crosslinked film (0.01 g) was dissolved in benzene (20 ml) for 2 days at room temperature. Volhard's titration was then carried out with aqueous $AgNO_3$ and KCNS. The sum of the *DQ* of 2VP sequences and pendant I (DQ_{TEA}) was measured by Volhard's titration in benzene and triethylamine (TEA) mixture with aqueous $AgNO_3$ and KCNS. The crosslink density (c.d.) was calculated from $2DQ - DQ_{TEA}$.

To determine the degree of swelling of crosslinked film, the film (0.05 g) was swollen in a water/DIOX mixture for 5 days at 20°C. The weights of the film before and after swelling, Q_0 and Q_w, respectively, were measured and the degree of swelling, Q_w/Q_0, was calculated.

Table 1 Crosslinking of the diblock polymer film

Film no.	Reaction time (h)	Crosslink density (mol%)[a]	*DQ* (mol%)[a]
M1	3.8	19.6	35.5
M2	7.5	27.8	43.2
M3	15.0	37.6	47.6

[a] Determined by Volhard's titration

Measurement of the Ag^+ ion concentration in the solution. While the film was soaked in the $AgNO_3$ solution, 0.1 ml of the solution was sampled and dissolved in 50 ml water, 5.0 ml of ionic strength adjusting agent (TISAB-01, TOA Electronics) was added, and then the Ag^+ ion concentration was measured with a potentiometer (HM-30S, TOA Electronics), equipped with an Ag^+ ion electrode and reference electrode (Ag-125 and HS305DS, TOA Electronics, respectively).

Measurement of the amount of colloidal silver in the film. Film (0.01 g) after introduction of colloidal silver was swollen and dispersed in 20 ml of benzene for 1 day and broken with ultrasonic irradiation (USH 3002-20S, 300 W, 19 Hz, Choompa kogyo Co. Ltd) for 15 min. Then, concentrated (3 ml) of HNO_3 and water (20 ml) were added, and the Ag^+ ion was titrated with aqueous KCNS with aqueous iron alum as an indicator.

Morphological observation

The ultra-thin film specimens of the starting diblock copolymer and modified products were prepared for TEM observation by placing a drop of benzene solution on a copper grid coated with carbon substrate, and then evaporating the solvent as gradually as possible at room temperature. The diblock copolymer specimen was stained with methyl iodide vapour for 4 days at room temperature. The ultra-thin film specimen was prepared for TEM by cutting the film with a microtome (Reichert-Nissei Co., Ultracut-N) to give a cross-section of the film. The morphological result was obtained with a Hitachi H-500 TEM at 75 kV.

A cross-section of the film was obtained by breaking the film in liquid nitrogen. The cross-section of the film was observed with a SEM (JSM-T220, Jeol). Elements of Ag, I and S on the cross-section of the film were analysed by energy dispersive X-ray spectrometry (EDX; EDAXPV9900lL, Phillips).

RESULTS AND DISCUSSION

*Crosslinking of the P(S-*b*-2VP) film*

The P2VP content of the P(S-*b*-2VP) determined with ^{1}H n.m.r. was 19.9 mol%. According to the Molau's rule[15], the microphase separated structure of this diblock copolymer would be a P2VP sphere in a PS matrix.

Figure 1a shows the TEM micrograph of P(S-*b*-2VP). The black region in the figure is the segregated P2VP chains selectively stained with methyl iodide. The microseparated structure of the P(S-*b*-2VP) was the P2VP sphere in the PS matrix. The number-average diameter of the P2VP spherical microdomains was 68 nm.

The crosslinking of the P2VP chains in the P2VP microdomains was carried out with DIB. The conditions and the results (the *DQ* and the c.d.) are listed in *Table 1*. By varying the reaction time from 3.8 to 15 h, three types of crosslinked films, M1, M2 and M3, with different c.d. and *DQ* were obtained. After crosslinking, all films were dissolved freely in benzene, toluene and THF.

Figure 1b shows the TEM micrograph of the crosslinked product M2 cast from a benzene solution at a polymer concentration of 0.01 wt%. For P(S-*b*-2VP), the microseparated structure was not formed from a benzene

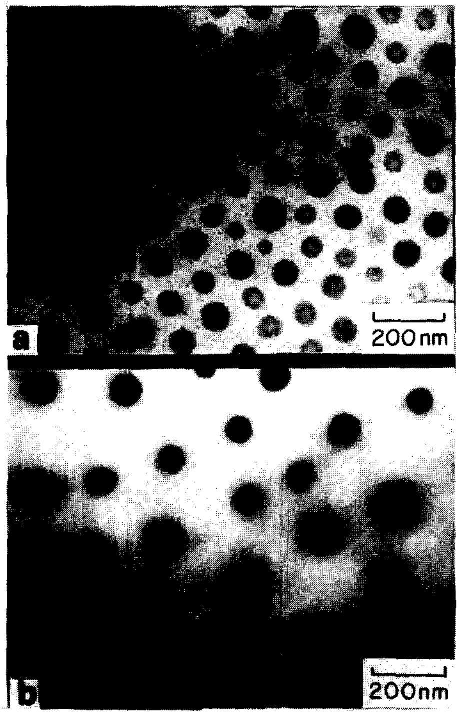

Figure 1 TEM micrographs of P(S-*b*-2VP) film cast from benzene and stained with methyl iodide: (a) before and (b) after crosslinking

solution at a polymer concentration of 0.01 wt%, because of the isolation of the polymer chain on a carbon substrate. After crosslinking, it was observed that the black spheres were dispersed and isolated on the carbon substrate. The diameter of P2VP domains after crosslinking (66 nm) agreed well with that before crosslinking (68 nm). Therefore it was concluded that the P2VP microdomain of the microseparated P(S-*b*-2VP) film was fixed by crosslinking and did not change its shape and size by dissolving in the good solvents. Subsequently, the crosslinked products became P2VP core–PS shell polymer microspheres by dissolving in the solvent.

Swelling behaviour of the crosslinked film

Before the introduction of the colloidal silver into the film, the basic conditions were determined. The most important feature for the introduction of colloidal silver into the film is to penetrate the Ag^+ ion into the film. Compared to the film with lamellar structure, it was difficult to penetrate the Ag^+ ion into the film with the P2VP sphere. This was because the P2VP microdomains were isolated in the PS matrix, and water was a non-solvent for the continuous PS phase. Thus, the PS phases in the film were swollen by adding DIOX to the water.

Figure 2 shows the swelling behaviour of M1 in the water/DIOX mixture. In the range 30–70 vol% DIOX, the M1 was swollen and the Q_w/Q_0 increased in the volume fraction of DIOX. At 80 vol%, the Q_w/Q_0 decreased. The film swollen in the solution with 80 vol% DIOX was dried. The film weight was decreased from 0.05 to 0.046 g. This shows that the film dissolved partially in the solution. It was decided that the introduction of the colloidal silver was carried out in the solution with 30–70 vol% DIOX.

Reaction time

To determine the reaction time (the soaking time) of the film in the Ag^+ ion solution, the penetrating time of the Ag^+ ion into the film was measured. *Figure 3* shows the change of the Ag^+ ion concentration of the solution (50 vol% DIOX, initial Ag^+ ion concentration, 1.59×10^{-3} mol l^{-1}) for M2. The molar amounts of Ag^+ ion and I^- ion in the initial solution were 3.18×10^{-5} and 1.03×10^{-5} mol, respectively. The amount of Ag^+ ion in solution decreased rapidly for the first 4 h. It then became constant at 2.09×10^{-5} mol. The decreased amount of Ag^+ ion in solution (1.07×10^{-5} mol) agreed well with the initial amount of I^- ion in the film (1.03×10^{-5} mol). It was concluded that the penetration of the Ag^+ ion into the film was complete after 4 h. Previously[10], it was considered that the penetration of the Ag^+ ion into the film occurred in the first stage and then the penetrated Ag^+ ion reacted with the I^- ion in the film. In light of previous results, the reaction time (the soaking time in the Ag^+ ion solution) was set up for 5 days.

Effects of Ag^+ concentration and the volume fraction of DIOX

In a previous paper[10], it was found that the amount of colloidal silver introduced into the film increased with increase in Ag^+ ion concentration in the solution. Thus, the effect of Ag^+ ion concentration on the introduction

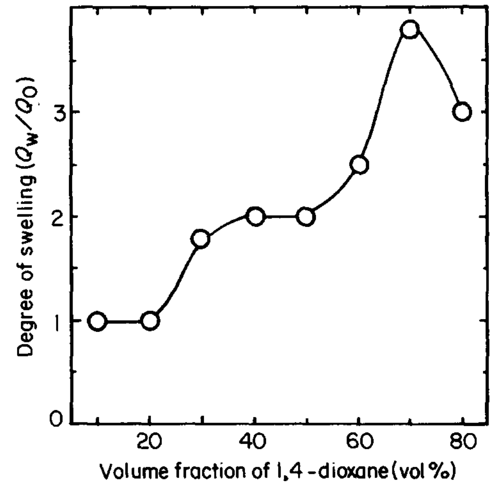

Figure 2 Swelling behaviour of M1 in the water/DIOX system

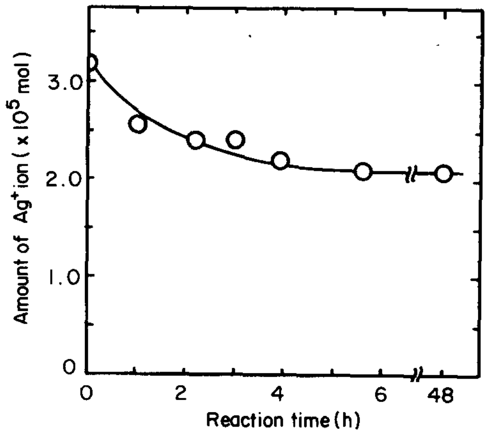

Figure 3 Change in the molar amount of Ag^+ ion in the solution in which M2 was soaked

Table 2 Introduction of colloidal silver into M2[a]

Run no.	DIOX content (vol%)	Ag^+/I^- (mol/mol)[b]	$[Ag^+]/[Py^+]$ (mol/mol)[c]	$[Ag]/[Py^+]$ (mol/mol)[d]	[Ag]/[Py] (mol/mol)[e]
M20-40	40	11	0.65	0.27	0.12
M20-50	50	11	1.30	0.42	0.18
M20-60	60	9	1.02	0.72	0.31
M20-70	70	10	0.59	0.28	0.12
M2-40	40	205	0.0	0.0	0.0
M2-50	50	71	1.26	1.04	0.45
M2-60	60	85	1.43	0.53	0.23
M2-70	70	66	1.13	0.42	0.18

[a] M2: crosslink density, 27.8 mol%; degree of quaternization, 43.2 mol%. M20 series: $AgNO_3$, 0.98×10^{-2} mol l^{-1}. M2 series: $AgNO_3$, 1.0×10^{-1} mol l^{-1}

[b] Initial molar ratio of the Ag^+ ion to the I^- ion in the system

[c] Molar ratio of introduced Ag^+ ion to the Py^+ ion in the film

[d] Molar ratio of the colloidal silver to the Py^+ ion in the film

[e] Molar ratio of the colloidal silver to the pyridine group in the film

of colloidal silver into M2 with P2VP spherical morphology was investigated. In this study, $AgNO_3$ and not silver acetate was used for preparing the Ag^+ ion solution, because the silver acetate did not dissolve in the water/DIOX mixture at room temperature when the volume fraction of DIOX was above 10 vol%.

The conditions and results are listed in *Table 2*. The Ag^+ ion concentrations of the solutions were 0.98×10^{-3} mol l^{-1} (M20 series) and 1.0×10^{-1} mol l^{-1} (M2 series). For sample M2-40, the volume fraction of DIOX in solution corresponded to 40 vol%.

For all cases, the amount of Ag^+ ion exceeded the initial amount of I^- ion in the whole system. The amount of I^- ion decreased with the onset of the reaction. Therefore, the amount of pyridinium ion (Py^+) which was equal to the initial amount of I^- ion was used as the constant value.

First, the amount of Ag^+ ion which had penetrated into the film was obtained from the increased weight of the film. *Figure 4* shows the $[Ag^+]/[Py^+]$ values, the molar ratios of the penetrated Ag^+ ion to the Py^+ ion in the film. At both Ag^+ ion concentrations, the $[Ag^+]/[Py^+]$ values showed similar behaviour. The maximal point of $[Ag^+]/[Py^+]$ was obtained with a volume fraction of DIOX in the region of 50-60 vol%. From these two curves, it was considered that the amount of penetrated Ag^+ ion did not depend on the Ag^+ ion concentration but the volume fraction of DIOX resulting in the swelling of the film. As described above, the amount of Ag^+ ion fed into the system exceeded the film. Therefore, the penetration of Ag^+ ion was governed by just the swelling state of the film.

The effect of the volume fraction of DIOX on the penetration of the Ag^+ ion was explained as follows. When the volume fraction of DIOX was 40 vol%, the degree of swelling of the film was too small for the Ag^+ ion to penetrate into the film. The penetration of the Ag^+ ion into the film occurred because of the swelling of the film due to the increase in the volume fraction of DIOX. When the volume fraction of DIOX was above 60 vol%, the film was too swollen to retain the I^- ion and AgI in the film. Subsequently, $[Ag^+]/[Py^+]$ decreased when the volume fraction of DIOX was above 60 vol%. It was concluded that there was an optimal swelling state for the penetration of the Ag^+ ion into the film.

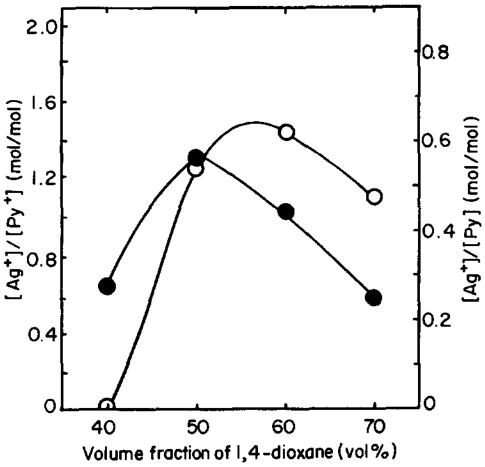

Figure 4 Amount of Ag^+ ion penetrated into the film: (●) M20 series; (○) M2 series

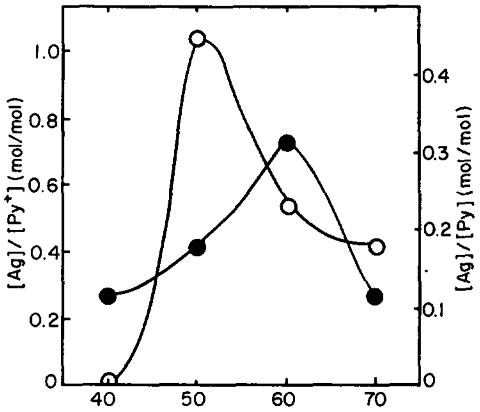

Figure 5 Amount of colloidal silver introduced into the film: (●) M20 series; (○) M2 series

The chemical reduction of the AgI formed in the film to colloidal silver was then carried out. The molar ratios of the colloidal silver to the Py^+ ion in the film, $[Ag]/[Py^+]$, were measured by titration with HNO_3 and KCNS, and are shown in *Figure 5*.

Similar to *Figure 4*, the maximal amounts of the colloidal silver introduced were observed when the volume fraction of DIOX was 50 and 60 vol% for the

M2 series (Ag^+, 1.0×10^{-1} mol l^{-1}) and M20 series (Ag^+, 0.98×10^{-3} mol l^{-1}), respectively.

Much of the colloidal silver was introduced into the solution at an Ag^+ ion concentration of 1.0×10^{-1} mol l^{-1} rather than at 0.98×10^{-3} mol l^{-1}. It was found that the amount of colloidal silver introduced increased with increase in Ag^+ ion concentration. This result was consistent with the result of the lamellar film investigated previously[9,10]. From these results, it was concluded that for the introduction of colloidal silver into the spherical P2VP microdomains, the most important factor was the swelling state of the film due to the volume fraction of DIOX. It was possible to increase the amount of colloidal silver introduced by increasing the Ag^+ ion concentration.

To investigate the distribution of silver in the film, the beam-scattering electron (BSE) image and an elemental analysis of Ag, I and S on the cross-section of the film were carried out by SEM and EDX. Elemental I was removed completely from the film. The molar fraction of elemental I to Ag+I+S was less than 10% at any place in all films.

Figure 6 shows the BSE images of M2–50, M2–60 and M2–70. For M2–50, with the maximal [Ag]/[Py^+], elemental Ag existed homogeneously in the film, and the internal structure of the film was not destroyed. For M2–60, it was found that the concentration of elemental Ag was high near the surface. For M2–70, it was introduced homogeneously, but the distribution curve of Ag was low. The most clear feature of M2–70 was the existence of voids with diameters of a few micrometres. M2–70 was highly swollen three times in the solution with a volume fraction of DIOX of 70 vol%. Consequently, where there was weak crosslinking, the structure could not be maintained through these chemical modifications. From these results, it was concluded that the [Ag]/[Py^+] ratio increased by the homogeneous introduction of colloidal silver into the film.

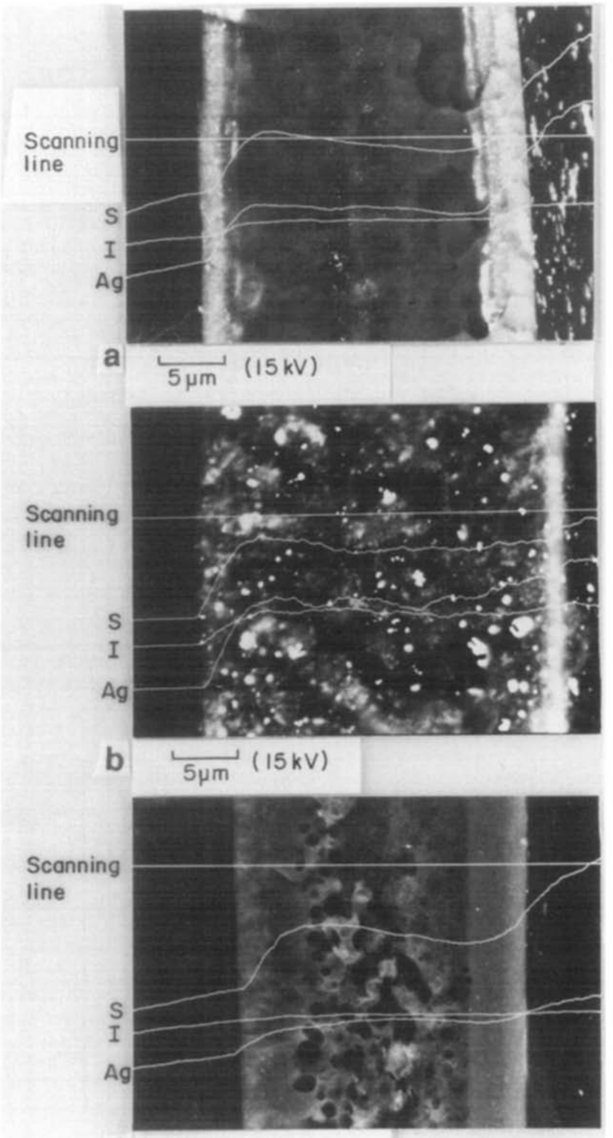

Figure 6 BSE images of the cross-section of the M2 series observed by SEM: (a) M2–50; (b) M2–60; (c) M2–70

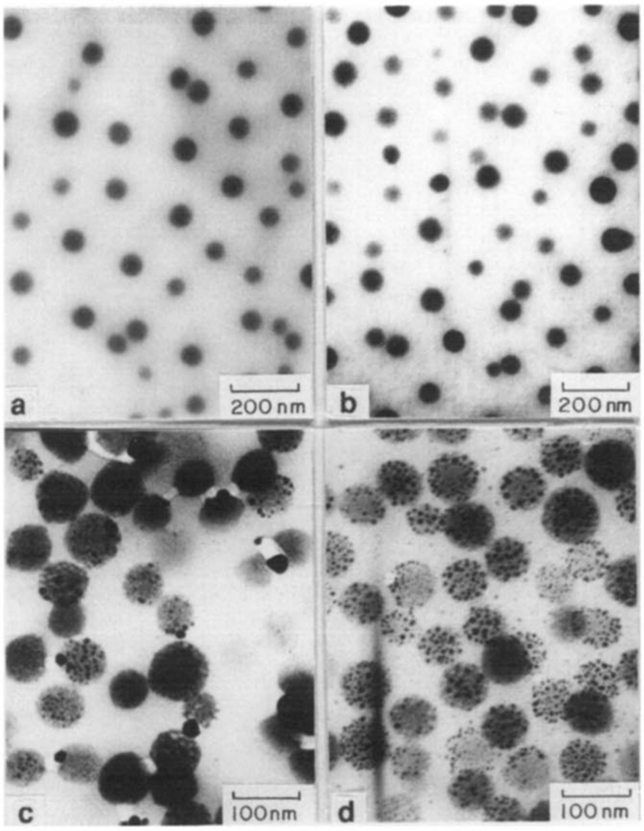

Figure 7 TEM micrographs of M2–50: (a) before soaking in the Ag^+ ion solution; (b) after soaking in the Ag^+ ion solution; (c) after chemical reduction; (d) after removing AgI with $Na_2S_2O_3$

To determine where the colloidal silver existed on a microscopic level, TEM was carried out. *Figure 7* shows the TEM micrographs of M2–50 with Ag introduced homogeneously with maximal [Ag]/[Py^+] at each stage. Before and after soaking the film in the Ag^+ ion solution, the inner textures of the P2VP microdomains (the dark regions) did not change. The small black particles (diameter 5–40 nm) appeared in and near the P2VP microdomains after chemical reduction. After removing the unreacted AgI with $Na_2S_2O_3$ solution, the small black particles with a diameter of 40 nm vanished; the small black particles (the colloidal silver) with narrow size distribution (number-average diameter, 11 nm) remained in the P2VP microdomains. The size of the colloidal silver obtained in this study agreed well with the size of the colloidal silver synthesized on the ion exchange resins ($\approx$14 nm)[16]. It was concluded that the colloidal silver was only introduced in the spherical P2VP microdomains.

Table 3 Introduction of colloidal silver into the films[a]

Run no.	DIOX content (vol%)	Ag^+/I^- (mol/mol)[b]	$[Ag^+]/[Py^+]$ (mol/mol)[c]	$[Ag]/[Py^+]$ (mol/mol)[d]	[Ag]/[Py] (mol/mol)[e]
M1-30	30	208	0.26	0.07	0.00
M1-40	40	323	0.35	0.20	0.07
M1-50	50	124	1.75	0.24	0.09
M1-60	60	188	1.62	0.16	0.06
M2-40	40	205	0.0	0.0	0.0
M2-50	50	71	1.26	1.04	0.45
M2-60	60	85	1.43	0.53	0.23
M2-70	70	66	1.13	0.42	0.18
M3-30	30	190	0.35	0.07	0.03
M3-40	40	88	0.29	0.11	0.05
M3-50	50	108	0.64	0.27	0.13
M3-60	30	92	1.07	0.26	0.12

[a] $AgNO_3$, 1.0×10^{-1} mol l^{-1}. M1: crosslink density, 19.6 mol%; degree of quaternization, 35.5 mol%. M2: crosslink density, 27.8 mol%; degree of quaternization, 43.2 mol%. M3: crosslink density, 37.6 mol%; degree of quaternization, 47.6 mol%

[b] Initial molar ratio of the Ag^+ ion to the I^- ion in the system

[c] Molar ratio of introduced Ag^+ ion to the Py^+ ion in the film

[d] Molar ratio of the colloidal silver to the Py^+ ion in the film

[e] Molar ratio of the colloidal silver to the pyridine group in the film

All films of the M2 and M20 series were dissolved freely in benzene, toluene and THF. No precipitation was observed for any of the solutions. It was considered that the solubility of the crosslinked film did not change through these chemical modifications and it was possible to synthesize the P2VP core–PS shell microsphere containing the colloidal silver in the P2VP core.

Crosslink density effect

As described above, it was concluded that the most important factor for the introduction of colloidal silver was the swelling state of the film. The swelling behaviour of the film can be controlled by changing not only the solvent composition but also the c.d. of the gel. Thus, the introduction of colloidal silver was carried out by varying the c.d. of the film. A solution with Ag^+ ion concentration of 1.0×10^{-1} mol l^{-1} was used. The conditions and results of the introduction of colloidal silver are listed in *Table 3*. For M1, M2 and M3 not only c.d. but also *DQ* were different. To compare these three series, the pyridine group content in the diblock copolymer, [Py], was used as the common value.

Figure 8 shows the amount of penetrated Ag^+ ion, $[Ag^+]/[Py]$, for M1, M2 and M3. For M1 and M2, $[Ag^+]/[Py]$ increased drastically, reached a maximum and then decreased with increase in the volume fraction of DIOX. For M1 and M2, the volume fraction of DIOX of the maximum point was increased with increase in the c.d. For M3, $[Ag^+]/[Py]$ did not seem to reach a maximum in the region studied. It was considered that the optimal swelling state for the penetration of the Ag^+ ion occurred at a higher volume fraction of DIOX, when the c.d. of the film was increased.

Figure 9 shows the amount of introduced colloidal silver, [Ag]/[Py], for M1, M2 and M3. For any series, the maximum point of the colloidal silver introduced was obtained at 50 vol% DIOX, and the most colloidal silver was introduced for the M2 series. For these three series, the most effective factor was not the *DQ* but the c.d., because the *DQ* values of M2 and M3 were similar (43.2

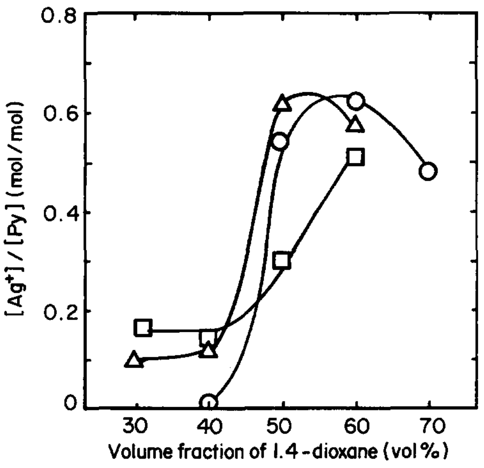

Figure 8 Amount of Ag^+ ion penetrated into the film: (△) M1 series; (○) M2 series; (□) M3 series

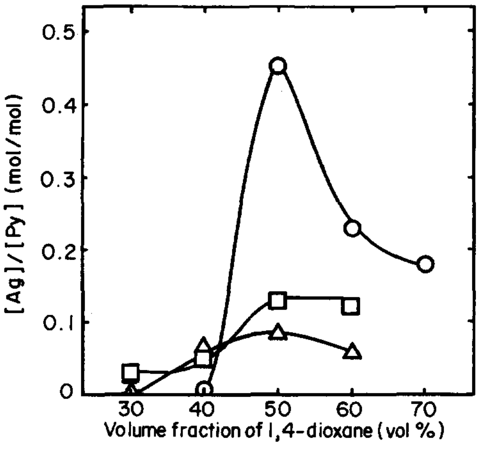

Figure 9 Amount of colloidal silver introduced into the film: (△) M1 series; (○) M2 series; (□) M3 series

and 47.6 mol%, respectively). Thus, the optimum c.d. for introducing colloidal silver was found.

The relation between the c.d. and the amount of colloidal silver introduced was explained from the viewpoint of the swelling behaviour of the gel as follows. When the c.d. of the film was low (M1 series), removal of colloidal silver from the highly swollen film occurred easily. When the film was highly crosslinked, it was difficult to penetrate the Ag^+ ion into the film (see *Figure 8*). Subsequently, the amount of colloidal silver introduced was lower for the M1 and M3 series.

From the results of the effects of the volume fraction of DIOX and the c.d., it was concluded that for the introduction of colloidal silver there was an optimum swelling state which was governed by both the volume fraction of DIOX and the c.d.

CONCLUSIONS

The introduction of colloidal silver into the spherical P2VP microdomains crosslinked with DIB in the PS matrix was carried out by varying the Ag^+ ion concentration, the volume fraction of DIOX, the *DQ* and the c.d. of the film. It was found that to introduce colloidal silver there was an optimum volume fraction of DIOX and c.d. This was explained from the viewpoint of the swelling behaviour of the film. When the film was very swollen at the optimum level of the volume fraction of DIOX and/or c.d., then the colloidal silver detached easily from the film. When the film was less swollen at a less than optimum level of the volume fraction of DIOX and/or c.d., it was difficult to penetrate the Ag^+ ion into the film. For both cases the amount of colloidal silver introduced was decreased.

The identification of the colloidal silver and the determination of the microscopic place where the colloidal silver existed were carried out by BSE and EDX with SEM, and by TEM, respectively. From these results it was concluded that the colloidal silver with a diameter of 11 nm existed just in the P2VP microdomains. It was possible to form the P2VP core–PS shell microsphere containing the colloidal silver in the P2VP core by dispersing the film in benzene, toluene and THF.

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