# Introduction of colloidal silver into poly(2-vinyl pyridine) microdomains of microphase separated poly(styrene-*b*-2-vinyl pyridine) film:

# 2. Concentration effect

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

*(Received 9 March 1992)*

Colloidal silver was introduced into the crosslinked poly(2-vinyl pyridine) (P2VP) phases of microseparated poly(styrene-*b*-2-vinyl pyridine) (P(S-*b*-2VP)) film with lamellar morphology by soaking film in a mixture of AgAc/water/1,4-dioxane (10 and 0 vol% of 1,4-dioxane), varying the AgAc concentration ($8.5 \times 10^{-3}$ to $8.5 \times 10^{-2}$ $\mathrm{mol\,l^{-1}}$), reducing the AgI in the film with hydroquinone and removing the unreduced AgI from the film with $Na_2S_2O_3$. After soaking in $Na_2S_2O_3$ solution, the colloidal products appeared in the P2VP phases and were identified as silver by beam scattering electron (BSE) observation and energy dispersive X-ray analysis. It was possible to introduce colloidal silver into the depth of the film along the P2VP phases and to increase the total amount of colloidal silver introduced by increasing the AgAc concentration of the AgAc/water/1,4-dioxane solution.

**(Keywords: colloidal metal; microseparated film; block copolymer; polystyrene; poly(2-vinyl pyridine))**

## INTRODUCTION

Polymer membranes have been studied as supporting materials for colloidal metals, which are well known catalysts. Most of the work reported involves the use of homopolymers[1-3], random copolymers[4-6], ion-exchange resins and hydrophilic gels (hydrogels)[7-13]. The localization of colloidal metals producing Liesegang's ring in the matrix was observed in some cases[14]. However, it was impossible to design the position where the colloidal metal existed.

On the other hand, it is well known that poly(styrene-*b*-2-vinyl pyridine) (P(S-*b*-2VP)) diblock copolymer forms microseparated film[15], and it is possible to fix the microseparated structure by crosslinking the poly(2-vinyl pyridine) (P2VP) microdomain with diiodobutane (DIB)[16-18]. By crosslinking with DIB, the pyridine groups of P2VP sequences are quaternized to pyridinium ions, the counterion of the quaternized P2VP being the $I^-$ ions.

When the crosslinked film is swollen in water, $I^-$ ions exist in crosslinked P2VP phases. If the $Ag^+$ ion is added to crosslinked P(S-*b*-2VP) film swollen in water, AgI is formed only in the P2VP microdomains and the polystyrene (PS) phases do not contain AgI. It is possible to localize colloidal silver in the P2VP phases by photo and chemical reduction of AgI in P2VP phases. In other words, it is possible to design phases containing the colloidal silver by microseparated structure of the diblock copolymer.

Based on this concept, colloidal silver was introduced into the P2VP phase of microseparated P(S-*b*-2VP) diblock copolymer[19]; in order to introduce the colloidal silver to the depth of the film along the P2VP phase easily, microseparated film with lamellar morphology was chosen.

From the results of transmission electron microscopy (TEM), it was found that the colloidal silver existed only in P2VP phases, and the amount of colloidal silver introduced increased with an increase in AgAc concentration used for soaking the film. It was confirmed that the introduction of colloidal silver occurred from the surface of the film. However, the macroscopic state of the colloidal silver introduced was not examined previously[19].

The aim of this study is to clarify the AgAc concentration effect and the solvent composition effect of the 1,4-dioxane–water mixture on the localization of the colloidal silver in the film. In order to investigate the localization of the colloidal silver in the film, the cross-section of the film was analysed by scanning electron microscopy (SEM) and elemental analysis.

## EXPERIMENTAL

### *Materials*

P(S-*b*-2VP) diblock copolymer was synthesized by the usual sequential anionic addition polymerization[20] using

---

*To whom correspondence should be addressed

0032-3861/93/061183-06

n-butyllithium as an initiator in tetrahydrofuran (THF) at −78°C.

The number-average molecular weight ($\bar{M}_n$) of the precursor PS ($9.0 \times 10^4$) was determined with a Tosoh HLC-802A GPC with 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 ($\bar{M}_w$) of the diblock copolymer ($1.53 \times 10^5$) was determined by combining g.p.c. data and viscometric data in THF at 38°C. The 2VP content in the diblock copolymer (38 mol%) was determined with a $^1$H n.m.r. spectrometer (Hitachi R24B).

### *Crosslinking of the film*

The diblock copolymer film (60 $\mu$m thick) was cast from 1,1,2-trichloroethane (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 DIB vapour.

The degree of quaternization of the 2VP sequence was measured by Volhard's titration as follows. Crosslinked film (0.01 g) was swollen in benzene (20 ml) for 2 days at room temperature. In order to cause scission of the swollen film, the solution was exposed to ultrasonic irradiation (USH 3002-20S, 300W 19 Hz, Choompa Kogyo Co. Ltd) for 15 min. Volhard's titration was then carried out with aqueous $AgNO_3$ and KCNS. The characteristics of the crosslinked film are listed in *Table 1*.

### *Morphological observations*

An ultra-thin film specimen was prepared by cutting the film with a microtome (Reichert-Nissei Co., Ultracut N) for TEM observation. The morphological result was obtained with a Hitachi H-500 TEM at 75 kV.

The cross-section of the film, obtained by breaking the film in liquid nitrogen, was observed by SEM (Jeol JSM-T220). Ag, I and S in the cross-section of the film were analysed by energy dispersive X-ray (EDX) (Philips EDAXPV9900IL).

**Table 1** Characteristics of the crosslinked P(S-*b*-2VP) film

| Run no. | Reaction time (h) | DQ[a] (mol%) | Crosslink density[b] (mol) |
|---|---|---|---|
| L1 | 6.0 | 25.4 | 24.8 |
| L2 | 17.0 | 40.7 | 28.0 |

[a] Degree of quaternization measured by Volhard's titration
[b] Crosslink density measured by Volhard's titration in benzene/water mixture

### *Introduction of silver into the film*

Crosslinked films (0.05 g) were soaked in silver acetate solution (10 ml AgAc/water/1,4-dioxane mixture) in the dark. The film was washed with water and dried at 30°C in the dark. After drying, the film was exposed to light for 4 h using a wolfram lamp (30 W, 100 V) without wavelength control. The exposed film was soaked in hydroquinone/water/1,4-dioxane mixture (2.5 wt% hydroquinone, 10 vol% 1,4-dioxane) for 2 h at 20°C. After washing the film with water, the film was soaked in aqueous sodium bisulfate (10 ml, 2.5 wt% $Na_2S_2O_3$) for 1 h at 20°C and washed with water for 10 min and dried. The conditions are listed in *Table 2*.

The amount of colloidal silver introduced into the film was measured as follows: 0.01 g of the film with introduced colloidal silver was swollen in 20 ml benzene for 1 day and broken by ultrasonic irradiation for 15 min. Then, 3 ml concentrated $HNO_3$ and 20 ml water were added, and $Ag^+$ ion was titrated with aqueous KCNS with aqueous iron alum as an indicator.

## RESULTS AND DISCUSSION

### *Introduction of colloidal silver into the film*

The characteristics of the crosslinked P(S-*b*-2VP) films L1 and L2 are listed in *Table 1*. The crosslink densities of L1 and L2 were 24.8 and 28.0 mol%, respectively. For L1, the crosslink density (24.8 mol%) was close to the degree of quaternization (25.4 mol%). Thus, it was found that the pendant I group did not exist in L1.

For L2, the degree of quaternization (40.7 mol%) was larger than the crosslink density (28.0 mol%). From these values it was concluded that the pendant I group in L2 was 12.7 mol%, and the ratio of the element I to the pyridinium ion was 53.4 mol%.

*Figure 1a* shows the TEM micrograph of L1. The dark area is the segregated P2VP sequences crosslinked and stained with DIB. The morphology of L1 was completely lamellar; number-average thickness of the P2VP phase ($L_{\mathrm{P2VP}}$) was 35 nm and that of PS ($L_{\mathrm{PS}}$) was 30 nm. The lamellar morphology was preferable for this study because the $Ag^+$ ion could reach the depth of the film along the P2VP lamellar phase easily. The L1 and L2 films did not dissolve in either water or benzene.

Then, the introduction of the silver into the L1 was carried out. The conditions of the introduction are listed in *Table 2*. In order to form AgI in the P2VP phase, L1 was soaked in the AgAc/water/1,4-dioxane mixture (10 vol% 1,4-dioxane). The 1,4-dioxane was included in

**Table 2** Conditions and results of the introduction of colloidal silver into the film L1

| Run no. | [AgAc] ($\times 10^{-2}$ mol l$^{-1}$) | Film weight[a] (mg): after AgAc addition | Film weight[a] (mg): final | $[Ag^+]/[Py^+]$[b] | $[Ag]/[Py^+]$[c] |
|---|---|---|---|---|---|
| L1-1 | 8.5 | 74.4 | 66.0 | 1.30 | 1.18 |
| L1-2 | 7.2 | 88.6 | 75.3 | 1.94 | 0.88 |
| L1-3 | 4.3 | 80.6 | 68.2 | 0.81 | 0.42 |
| L1-4 | 2.1 | 93.0 | 69.8 | 1.13 | 0.10 |
| L1-5 | 0.9 | 82.7 | 58.6 | 2.16 | 0.09 |

[a] Weight of film before crosslinking, 50.0 mg; after crosslinking, 62.0 mg
[b] Molar ratio of introduced $Ag^+$ ion into the film to the pyridinium ion in the film
[c] Molar ratio of introduced colloidal silver into the film to the pyridinium ion in the film measured by Volhard's titration in the benzene/nitric acid mixture

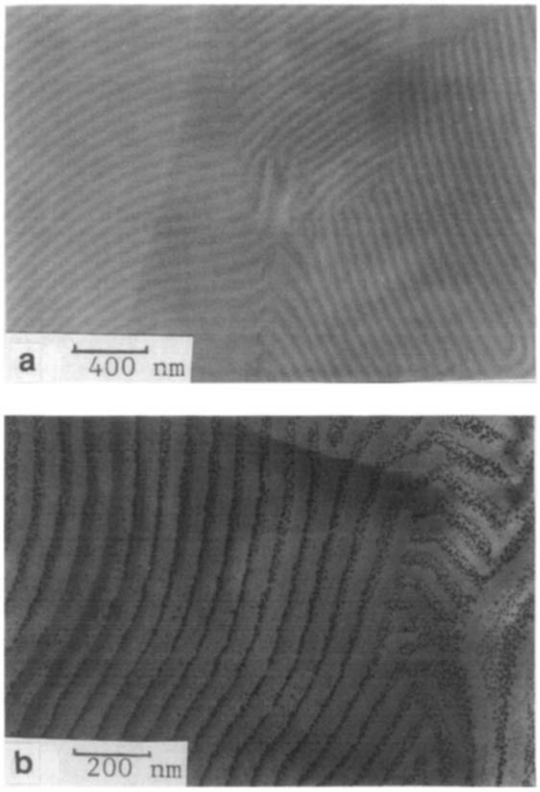
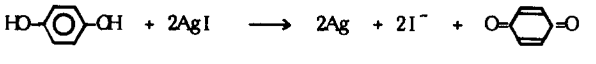


**Figure 1** TEM micrographs of the cross-sections of the films before and after the introduction of the colloidal silver: (a) L1; (b) L1-3

the system to increase the penetrability of the $Ag^+$ ion into the film by swelling the film, because the L1 was not swollen in the water owing to the existence of excess hydrophobic PS phases in the film.

After soaking in the AgAc solution, the weights of all films increased from 62 mg. From the increasing weight of the film, the amount of $Ag^+$ ion introduced to the film was calculated as the ratio of $Ag^+$ ion to pyridinium ion ($[Ag^+]/[Py^+]$) in the film. The amount of the pyridinium ion $[Py^+]$ was equal to the amount of the initial $I^-$ ion. The amount of the $I^-$ ion was varied with the onset of the reaction, thus, the value of $[Py^+]$ was constant. If the $I^-$ ion reacted with $Ag^+$ ion quantitatively, $[Ag^+]/[Py^+]$ should be unity. However, the ratio $[Ag^+]/[Py^+]$ of the film exceeded unity, for example, 1.94 for L1-3. This indicates that the $Ag^+$ ion was introduced to the film not only as AgI but also as AgAc.

Then, the chemical reduction of the introduced AgI in the P2VP phases was carried out with hydroquinone. The chemical reduction of AgI with hydroquinone is as follows:



(1)

After chemical reduction, the film was soaked in $Na_2S_2O_3$ solution to remove unreacted AgI from the film. *Figure 1b* shows the TEM micrograph of the cross-section of L1-3 near the surface. After soaking in $Na_2S_2O_3$ solution, the morphology of the film did not change and the black colloidal products (~10 nm in diameter) were observed along the P2VP phases. Thus, it was confirmed that the microseparated structure of the film was not changed by the introduction of the colloidal products.

In order to identify the colloidal products, elemental analysis was carried out on the cross-section of L1-2 by BSE observation and EDX analysis.

*Figures 2* and *3* show the BSE image on the cross-section of the final products of the film L1-2 and the profile of the elemental analysis of the film near its surface, respectively. From the BSE image, Ag is seen to exist homogeneously in the film. Thus, it was found that silver was introduced into the film. Near the surface, the molar ratio of I = 3%, Ag = 40% and S = 57% (*Figure 3*). It was found that after soaking L1-2 in the $Na_2S_2O_3$ solution, the element I did not remain in the film. The black colloidal products observed in *Figure 1b* were identified as silver.

### *Effect of AgAc concentration*

In order to investigate the effect of [AgAc] on the introduction of colloidal silver into the film, the concentration of the $Ag^+$ ion in the AgAc solution was varied from $8.5 \times 10^{-3}$ to $8.5 \times 10^{-2}$ $mol^{-1}$ (*Table 2*). As described above, the element I did not exist in the film at the final stage. Thus, the amount of colloidal silver in the film could be measured quantitatively by the titration with KCNS in benzene/nitric acid mixture.

In the previous paper[19], the amount of colloidal silver was estimated from the film weight. However, those

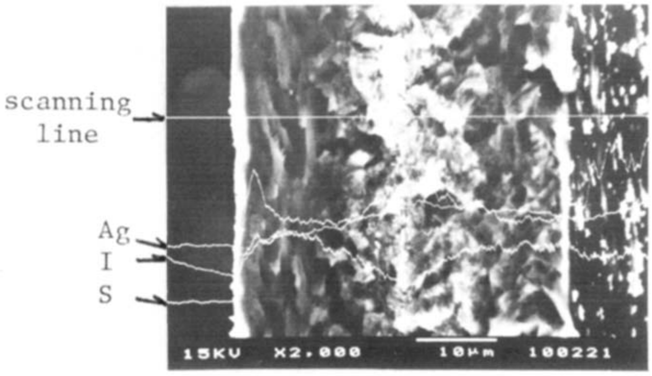


**Figure 2** BSE image of the cross-section of L1-2

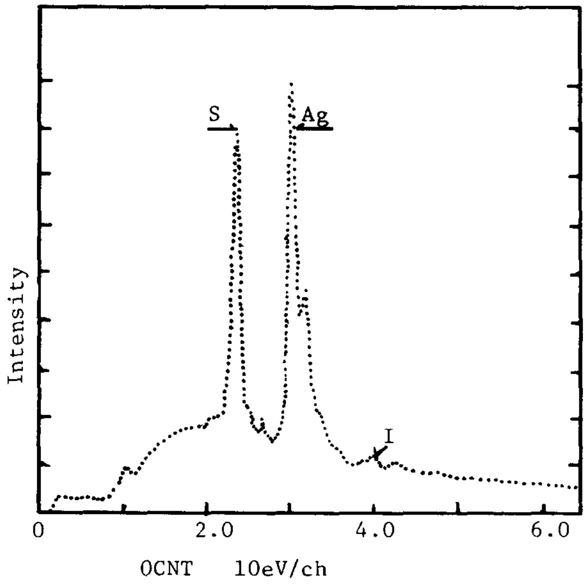


**Figure 3** EDX profile near the surface of the cross-section of L1-2

values were incorrect because it was impossible to determine accurately the counterion to the pyridinium ion. Therefore, the molar ratio of the colloidal silver to the pyridinium ion in the film, $[Ag]/[Py^+]$, was recalculated from the data of the titration and is shown in *Figure 4*. The $[Ag]/[Py^+]$ obtained in this paper is more accurate than that in previous work[19].

The $[Ag]/[Py^+]$ was increased drastically with the increase in [AgAc]. At $[AgAc] = 8.5 \times 10^{-2}\,mol\,l^{-1}$, the $[Ag]/[Py^+]$ reached unity. It seemed that the amount of the colloidal silver was governed by the AgAc concentration of the solution although $[Ag^+]/[Py^+]$ was greater than unity for all cases.

In this paper, the conditions of the chemical reduction with hydroquinone and the removal of unreacted AgI with $Na_2S_2O_3$ were constant. So the degree of the chemical reduction of AgI must be constant for any sample. It was supposed that the amount of AgI in the film of this study was less than our expectation ($[AgI]/[Py^+] = 1$). It is noted that the ionic reaction in the gel is generally slower than that in the solution, so that it is supposed that the formation of AgI with $I^-$ ion and $Ag^+$ ion introduced into the film has not finished. It was impossible to obtain the ratio of AgI and AgAc in the film from the film weight. Before completion of the reaction, however, the amount of the products can be calculated by kinetics.

In order to examine the amount of AgI in the film, the kinetics of AgI formation was considered. The reaction rate of AgI is given as:

$$d[AgI]/dt = k[Ag^+][I^-]$$

where $k$ is the rate constant. At time $t$, the [AgI] ($x$) can be calculated as follows:

$$\ln\frac{b(a-x)}{a(b-x)} = \frac{kt}{a-b} \qquad (2)$$

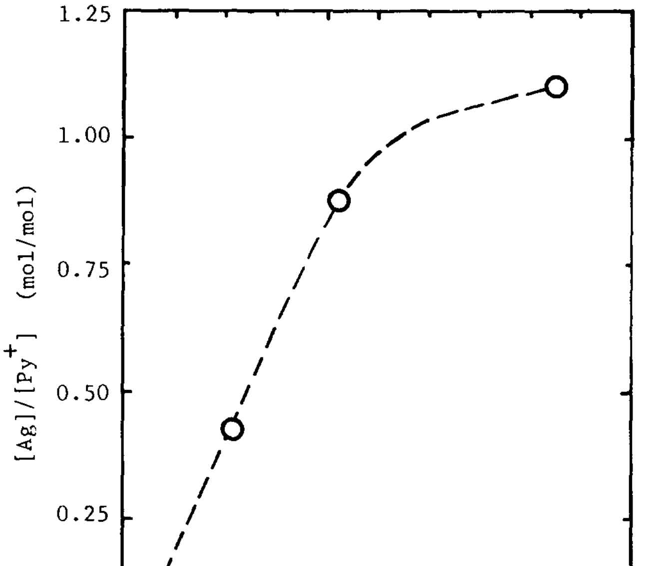


**Figure 4** Amount of colloidal silver introduced into L1

where $a$ and $b$ are the initial concentrations of the $Ag^+$ ion and the $I^-$ ion in the system, respectively. At time $t$, $\ln[b(a-x)/a(b-x)]$ is directly proportional to $1/(a-b)$.

In this study, the degree of chemical reduction of AgI can be assumed constant, because of the constant conditions during chemical reduction. Thus, the amount of colloidal Ag ($[Ag]/[Py^+] = c$) can be regarded as $x$. The reaction time of this study was constant (5 days). If the formation of AgI in the film has not finished at 5 days, the amount of AgI is determined by [AgAc], and equation (1) holds.

*Figure 5* shows a plot of $1/(a-b)$ *versus* $\ln[b(a-x)/a(b-x)]$. In order to simplify, $a$ and $b$ are assumed to be the molecular ratio of AgAc to $I^-$ in the initial solution, and unity, respectively, because the amount of $I^-$ ion in the solution was constant. The data follow a straight line. It was found that the amount of colloidal silver obtained followed equation (1) with [AgAc]. It was considered that the amount of AgI formed in the film was determined by [AgAc].

Consequently, it was suggested that the AgI formation in this study was not completed, and the dependence of $[Ag]/[Py^+]$ on [AgAc] was due to the amount of AgI formed slowly in the film governed by [AgAc].

Next, the effect of [AgAc] on the localization of the colloidal silver in the film was investigated. *Figures 6* and *7* show the TEM micrographs and the secondary electron profiles of the cross sections of L1-3 and L1-1 observed by BSE with EDX. In the TEM micrographs, the white area corresponds to PS and the black area to colloidal silver. In the BSE images, the white area shows the products reflecting the secondary electron and the white lines indicate the distribution of the elements Ag, I and S.

For *Figure 6*, at $[AgAc] = 2.1 \times 10^{-2}\,mol\,l^{-1}$ (L1-3), the TEM micrograph and the BSE image showed the same results. The depth of the black lines, which indicated the existence of the colloidal silver in the TEM micrograph, was about 3.5 μm from the surface (*Figure 6a*) and [Ag] detected by BSE was high near the surface and low deeper in the film (*Figure 6b*). From these figures, it was concluded that the colloidal silver was introduced only near the surface for L1-3.

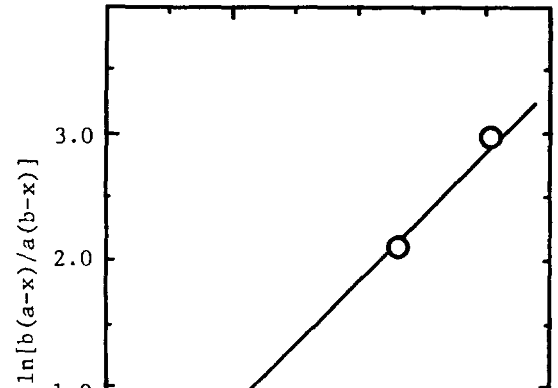


**Figure 5** Calculated amount of AgI formed in L1 after 5 days

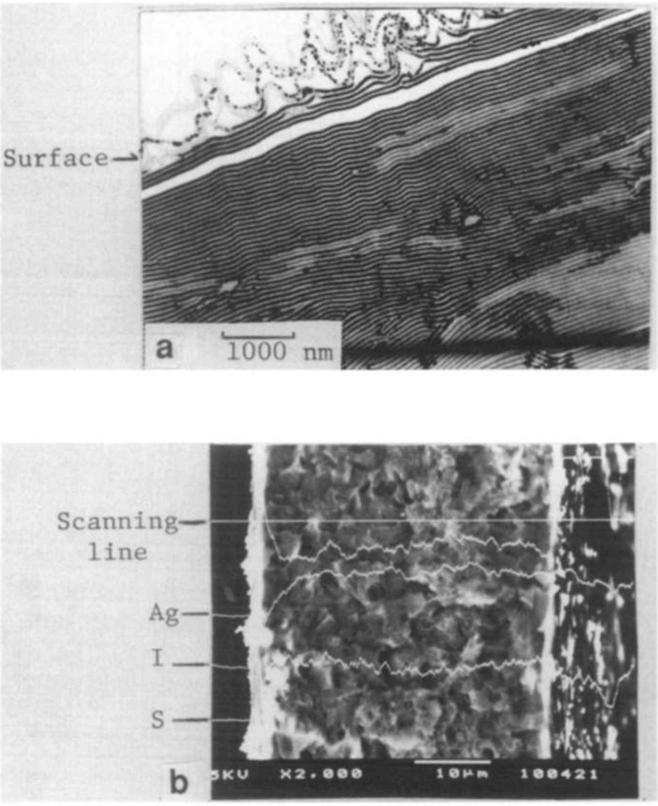


**Figure 6** (a) TEM micrograph and (b) BSE image of the cross-section of L1-3

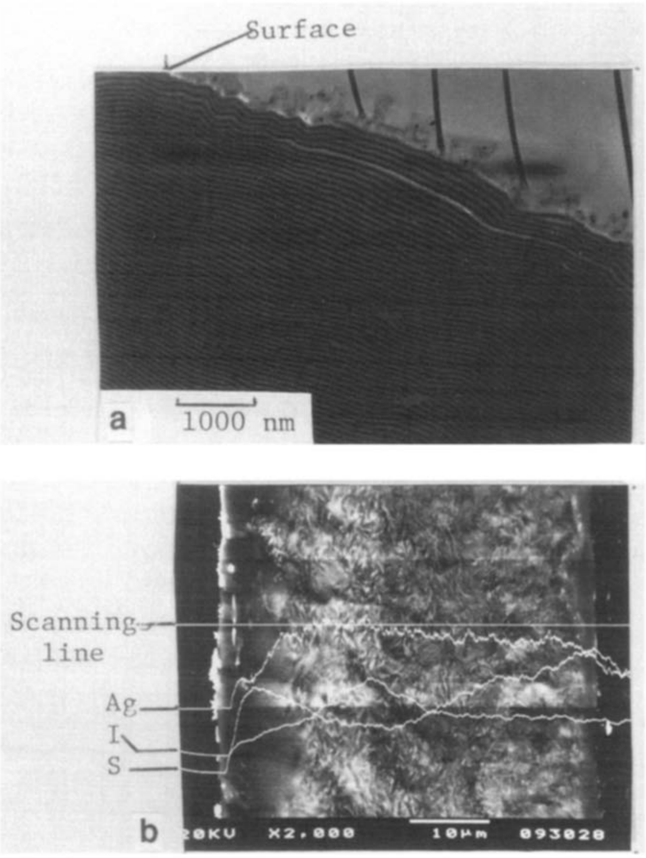


**Figure 7** (a) TEM micrograph and (b) BSE image of the cross-section of L1-1

On the other hand, at [AgAc] = $8.5 \times 10^{-2}$ mol l$^{-1}$ (L1-1, *Figure 7*), the Ag seemed to be introduced homogeneously. The content of S decreased at the centre of the film. At any place in the L1-1, [Ag] was much higher than [S] and [I], because the values of the molar ratio between the elements Ag/I/S were 88/3/14 and 66/3/31 at the centre of the film and near the surface, respectively. The total amount of silver introduced, [Ag]/[Py$^+$], into L1-1 was increased to 1.18 from that of L1-3 (0.42) with the increase in [AgAc]. Consequently, it was concluded that the colloidal silver was introduced from the surface to the depth of the film and it was possible to introduce the colloidal silver into the film homogeneously by increasing [AgAc].

*Effect of 1,4-dioxane in the solution*

By careful observation of *Figure 7a*, it was found that [Ag] in the film was slightly decreased near the surface. It was concluded above that the colloidal silver was introduced from the surface. It was supposed that the colloidal silver near the surface escaped from the film, because the film was slightly swollen with 1,4-dioxane added in the solutions used for this study.

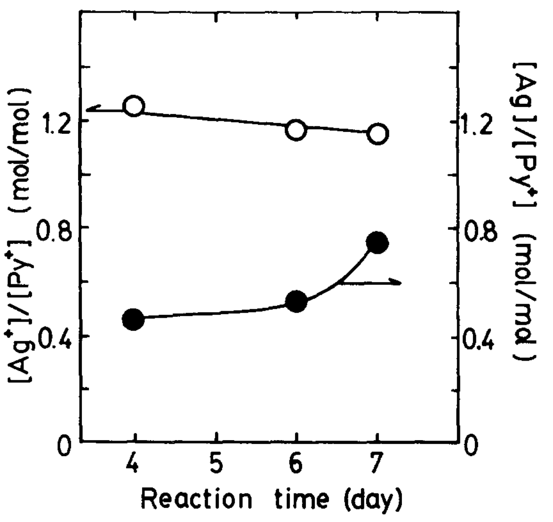


**Figure 8** Time dependence of amount of colloidal silver introduced into L2 in the system with 1,4-dioxane: ○, [Ag$^+$]/[Py$^+$]; ●, [Ag]/[Py]

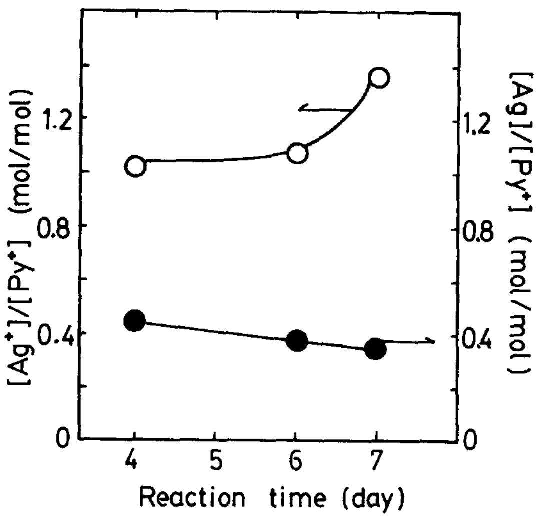


**Figure 9** Time dependence of amount of colloidal silver introduced into L2 in the system without 1,4-dioxane: ○, [Ag$^+$]/[Py$^+$]; ●, [Ag]/[Py]

**Table 3** Conditions and results of introduction of colloidal silver into the film L2

| Run no. | Reaction time (day) | 1,4-dioxane (vol%) | $[Ag^+]/[Py^+]^a$ | $[Ag]/[Py^+]^b$ |
|---|---|---|---|---|
| L2-1[c] | 4 | 9 | 1.02 | 0.45 |
| L2-2[c] | 6 | 9 | 1.08 | 0.38 |
| L2-3[c] | 7 | 9 | 1.36 | 0.35 |
| L2-4[d] | 4 | 0 | 1.25 | 0.45 |
| L2-5[d] | 6 | 0 | 1.16 | 0.53 |
| L2-6[d] | 7 | 0 | 1.11 | 0.75 |

[a] Molar ratio of introduced $Ag^+$ ion into the film to the pyridinium ion in the film

[b] Molar ratio of introduced colloidal silver into the film to the pyridinium ion in the film measured by Volhard's titration in the benzene/nitric acid mixture

[c] $[AgAc] = 9.3 \times 10^{-2}$ mol $l^{-1}$

[d] $[AgAc] = 8.5 \times 10^{-2}$ mol $l^{-1}$

In order to investigate the escape of products from the film, the introduction of the colloidal silver into the film L2 was carried out varying the reaction time from 4 to 7 days. The conditions and results are listed in *Table 3* and plotted in *Figure 8*.

For 4–7 days, all values of $[Ag^+]/[Py^+]$ exceeded unity. The film continued to swell because $[Ag^+]/[Py^+]$ increased to 1.2 at 7 days. Contrary to the increase of $[Ag^+]/[Py^+]$, $[Ag]/[Py^+]$ decreased with increasing time. The amount of AgI formed in the whole system never decreased with increasing time, because AgI was insoluble in the water and 1,4-dioxane. Thus, it was concluded that the escape of the products occurred with the increase in the reaction time and consequently $[Ag]/[Py^+]$ decreased with increase in time.

In order to hinder the escape of the products from the film L2, the introduction of colloidal silver into the film was carried out without 1,4-dioxane in the system. The conditions and the results are shown in *Table 3* and the results are plotted in *Figure 9*.

Without 1,4-dioxane in the system, the introduction of $Ag^+$ ion into the film was finished after 4 days and the amount of the introduced $Ag^+$ ion into the film was sufficient to form AgI because $[Ag^+]/[Py^+]$ was constant ($\sim 1.2$) and exceeded unity in this period. On the other hand, the amount of colloidal silver, $[Ag]/[Py^+]$, increased from 0.45 to 0.75 between days 4 and 7. As $[Ag]/[Py^+]$ reflected the amount of AgI, it was considered that the formation of AgI was continued at 7 days and the escape of the products could be neglected in this system. Thus, it was concluded that it was possible to hinder the escape of the colloidal silver without the addition of 1,4-dioxane, and it was possible to increase the amount of colloidal silver in the film by increasing the reaction time. From these data it was found that the formation of AgI was slow and was not completed at 7 days. This supports the kinetic treatment given above.

## CONCLUSION

The P(S-*b*-2VP) diblock copolymer ($M_n = 1.53 \times 10^5$, 19.9 mol% 2VP) was synthesized by anionic polymerization. The microseparated morphology of the P(S-*b*-2VP) cast from trichloroethane was completely lamellar. Crosslinking of the P2VP phases was carried out with DIB. The crosslink densities of the crosslinked film L1 and L2 were 24.8 and 28.0 mol%, respectively.

Colloidal silver was introduced into the crosslinked P2VP phases of the film and identified by BSE observation and EDX analysis. It was possible to introduce the colloidal silver into the depth of the film along the P2VP phases and to increase the total amount of colloidal silver introduced by increasing the AgAc concentration of the AgAc/water/1,4-dioxane solution.

By the detailed observation of the BSE image of the cross-section of the film and the reaction time dependence on the amount of colloidal silver introduced, the escape of colloidal silver was detected for the system with 1,4-dioxane. It was possible to hinder the escape of colloidal silver from the film by omitting 1,4-dioxane from the system, and the total amount of colloidal silver introduced into the film could be increased by increasing the reaction time.

## REFERENCES

1 Burner, H. and Bailar, J. C. Jr *Inorg. Chem.* 1973, **12**, 1465
2 Holy, N. L. and Shelton, S. R. *Tetrahedron* 1981, **39**, 25
3 Ning, Y. P., Tang, M. Y., Jiang, C. Y. and Mark, J. E. *J. Appl. Polym. Sci.* 1984, **29**, 3209
4 Pineri, M., Jesior, J. C. and Coey, J. M. P. *J. Membr. Sci.* 1985, **24**, 325
5 Sakai, T., Takenaka, H. and Torikai, E. *J. Membr. Sci.* 1987, **31**, 727
6 Nakao, Y. and Kaeriyama, K. *J. Colloid Interface Sci.* 1989, **131**, 186
7 Chanda, M., O'Driscoll, K. F. and Rempel, G. L. *J. Catal.* 1980, **61**, 533
8 Chanda, M., O'Driscoll, K. F. and Rempel, G. L. *J. Mol. Catal.* 1980, **7**, 389
9 Chanda, M., O'Driscoll, K. F. and Rempel, G. L. *J. Mol. Catal.* 1980, **8**, 339
10 Chanda, M., O'Driscoll, K. F. and Rempel, G. L. *J. Mol. Catal.* 1981, **12**, 197
11 Hines, L., O'Driscoll, K. F. and Rempel, G. L. *J. Catal.* 1975, **38**, 435
12 Tong, S. B., O'Driscoll, K. F. and Rempel, G. L. *Can. J. Chem. Eng.* 1978, **36**, 340
13 Kurokawa, Y. and Ueno, K., *J. Appl. Polym. Sci.* 1982, **27**, 621
14 Mueller, K. F. *Science* 1984, **225**, 1021
15 Ishizu, K., Inagaki, K., Bessho, K. and Fukutomi, T. *Makromol. Chem.* 1984, **185**, 1169
16 Saito, R., Kotsubo, H. and Ishizu, K. *Polymer* 1992, **33**, 1073
17 Saito, R., Kotsubo, H. and Ishizu, K. *Polymer* submitted
18 Ishizu, K., Yamada, Y., Saito, R., Yamamoto, T. and Kanbara, T. *Polymer* 1992, **33**, 1816
19 Saito, R., Okamura, S. and Ishizu, K. *Polymer* 1992, **33**, 1099
20 Scindler, A. and Williams, J. L. *Am. Chem. Soc., Div. Polym. Chem. Polym. Prepr.* 1969, **10**, 832