Introduction of colloidal silver into a poly(2-vinyl pyridine) microdomain of microphase separated poly(styrene-*b*-2-vinyl pyridine) film

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

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Colloidal silver was introduced into microphase separated poly(styrene-*b*-2-vinyl pyridine) diblock copolymer film by reduction of silver iodide. It was possible to localize silver in only poly(2-vinyl pyridine) phases in the microphase separated film. The polystyrene phases did not contain silver. The presence of silver in the film was confirmed by transmission electron microscopy.

(**Keywords: silver; colloidal metal; microphase separated 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, random copolymers[1–3], ion exchange resins[4–6] and hydrophilic gels (hydrogels)[7–12]. In general, the synthetic route to prepare these membranes consists of many complex processes. Kurokawa and Ueno[13] have synthesized a complex membrane of a hydrogel containing colloidal silver.

The localization of colloidal metals producing Liesegang's ring in the matrix was observed in some cases[14]. Strictly speaking, such a membrane contained colloidal metal-rich and metal-poor phases and the localization of colloidal metals was governed by non-linear diffusion equations[15].

On the other hand, it is well known that poly(styrene-*b*-2-vinyl pyridine) (P(S-*b*-2Vp)) diblock copolymer forms microphase separated film[16–18]. It is now possible to control the microphase separated structure of the film[19,20], and applications of the film as functional materials owing to its microphase separated structure have been studied[21]. For example, it is possible to fix the microphase separated structure of the film by crosslinking P2Vp sequences in P2Vp microdomains with diiodobutane (DIB)[17,18]. In this way, new functional materials, such as a P2Vp core–PS shell polymer microsphere, have been synthesized[22–24]. By crosslinking with DIB, the pyridine groups of P2Vp sequences are quaternized to pyridinium ions; the counter ion of quaternized P2Vp being the I$^-$ ion.

From these studies, it was found that the crosslinked films with lamellar morphology were not soluble but swollen in good solvents for PS and/or quaternized P2Vp[24]. Water was a good solvent for quaternized P2Vp. However, PS phases of microphase separated film did not swell in water. Therefore, it is suspected that the I$^-$ ion does not exist in the PS phase but in the crosslinked P2Vp phase of the crosslinked P(S-*b*-2Vp) film swollen in water.

If the Ag$^+$ ion is added to crosslinked P(S-*b*-2Vp) film swollen in water, AgI will be formed in the crosslinked P2Vp phases. The AgI will be localized in just the P2Vp microdomains and the PS phase will not contain any AgI. It is possible to reduce AgI in the P2Vp microdomains by photo and chemical reduction treatments[25]. Therefore, it is possible to localize colloidal silver just in the P2Vp phases in the microphase separated P(S-*b*-2Vp) film. The most important feature of this concept is that the shape of the phase (microdomain) containing silver is designed from the morphology of the microphase separated structure of the film.

The purpose of this study is to investigate whether or not silver can be introduced into the P2Vp microdomain of P(S-*b*-2Vp) microphase separated film. In this study, the microphase separated film of P(S-*b*-2Vp) was crosslinked with DIB vapour. Introduction of silver into the film was followed using transmission electron microscopy (TEM).

Experimental

Materials. P(S-*b*-2Vp) diblock copolymer was prepared by the usual sequential anionic addition polymerization using n-butyllithium as initiator in tetrahydrofuran (THF) at -78°C[16]. The number-average molecular weight ($\overline{M}_n$) of the precursor PS (9.0×10^4) 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 ($\overline{M}_v$) 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 was determined with a ^{1}H n.m.r. spectrometer (Hitachi, R-24B).

Crosslinking the film[18]. The diblock copolymer film (60 μm thick) was cast from 1,1,2-trichloroet (0.05 g ml^{-1}) solution on a Teflon sheet. The c[illegible]raction was gradually dried for 4 days at room tem

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Crosslinking of the segregated P2Vp sequences in the P2Vp microdomains was carried out by quaternization with DIB vapour.

The degree of quaternization of the P2Vp sequences 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 the swollen film to scission, the solution was exposed to ultrasonic irradiation (USH 3002-20S, 300 W, 19 Hz, Choonpa Kogyo Co. Ltd) for 15 min. Volhard's titration was then carried out with aqueous $AgNO_3$ and KCNS.

Morphological observation. 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.

Introduction of silver into the film. Crosslinked films (0.05 g) were soaked in silver acetate (AgAc, 10 ml) water–dioxane mixture (dioxane 10 vol%) for 1 day 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) with no wavelength control. The exposed film was soaked in hydroquinone water–dioxane mixture (hydroquinone 2.5 wt%, dioxane 10 vol%) for 2 h at 20°C.

The film was washed with water, soaked in aqueous sodium bisulphite ($Na_2S_2O_3$, 10 ml, 2.5 wt%) for 1 h at 20°C and washed with water for 10 min and dried.

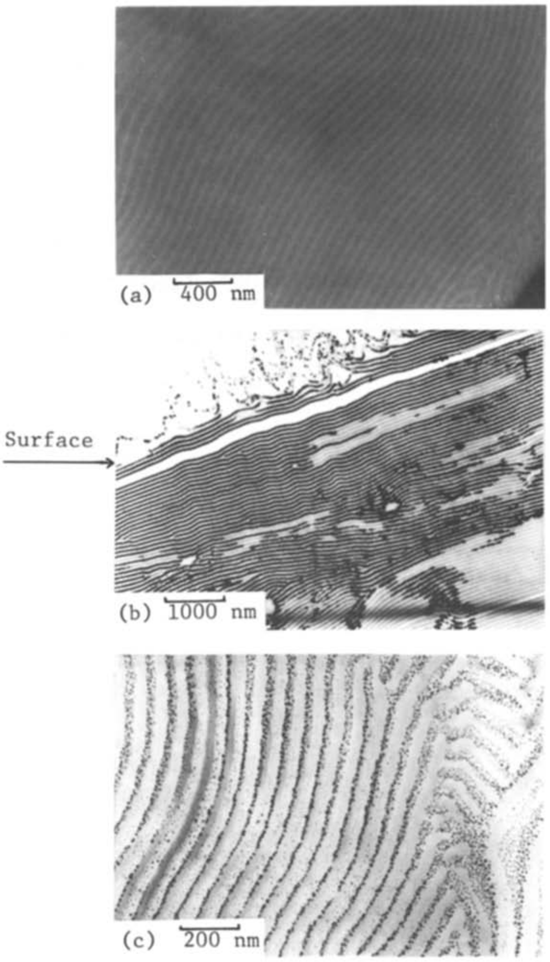

Figure 1 TEM micrographs of P(S-*b*-2Vp) films: (a) after crosslinking with DIB; (b) after soaking in aqueous $Na_2S_2O_3$; (c) after soaking in aqueous $Na_2S_2O_3$

Table 1 Conditions and results of the introduction of colloidal silver into the film

Run no.	Conc. of aqueous AgAc $\times 10^2$ ($mol\,l^{-1}$)	Weight of film (mg)[a] after soaking in		$[Ag^+]$[b]	$[Ag]$[c]
		AgAc	$Na_2S_2O_3$	$[I^-]$	$[I^-]$
1	8.5	74.4	66.0	1.30	0.613
2	7.2	88.6	75.3	2.78	0.555
3	4.3	80.6	68.2	1.94	0.459
4	2.1	93.0	69.8	3.24	0.144
5	0.85	82.7	58.6	2.16	0.059

[a] Weight of film: before crosslinking, 50.0 mg; after crosslinking, 62.0 mg

[b] Ratio of introduced Ag^+ ion into the film to initial I^- ion in the film

[c] Yield of colloidal silver per initial I^- ion in the film

Results and discussion

The characteristics of the crosslinked P(S-*b*-2Vp) film are as follows: $\bar{M}_n = 1.53 \times 10^5$; 2Vp content = 38 mol%; the degree of quaternization of the P2Vp in the film = 29.3 mol%. The crosslinked film was clear pale yellow. *Figure 1a* shows the TEM micrograph of crosslinked P(S-*b*-2Vp) film. The dark area of the figure is segregated P2Vp sequences crosslinked and stained with DIB. The morphology of the microphase separated structure of the film was completely lamellar. The number-average thickness of the P2Vp phase was 35 nm and the domain spacing of the lamellar phase was 65 nm. The lamellar morphology of microphase separated film was preferable for this study, because the Ag^+ ion could reach the depth of the film along the P2Vp lamellar phase easily. After crosslinking, the film was fixed physically, since it was not dissolved but swollen in benzene which was a good solvent for PS.

The introduction of silver into the film was then carried out (*Table 1*). A water–dioxane mixture (dioxane = 10 vol%), in which the PS phase could swell, was used as the solvent. (The crosslinked film was not swollen in water owing to the existence of excess hydrophobic PS phases in the film.) AgAc was used to prepare the Ag^+ ion solution. The concentration of Ag^+ ion was varied from 8.5×10^{-3} to $8.5 \times 10^{-2}\,mol\,l^{-1}$.

After soaking in AgAc solution, the films turned ash-coloured and the weights of all the films increased. The increased film weight indicated that AgAc had been introduced into the film. The formation of AgI in the solvent did not occur because the AgAc solution was clear. It was suggested that AgI was formed in the film.

The amount of introduced Ag^+ ion was calculated from the increased weight of the film. The ratio of the amount of Ag^+ and I^- ions introduced into the film, $[Ag^+]/[I^-]$, was >1 for all films. This showed that the Ag^+ ion was introduced into film not only as AgI but also as AgAc.

After drying the film, the film was exposed to light and reduction with hydroquinone was carried out. The film turned black due to reduction with hydroquinone and the removal of AgI and I_2 with $Na_2S_2O_3$. Complete removal of I_2 and unreacted AgI from the film with $Na_2S_2O_3$ solution was confirmed by u.v. absorption of I_2 in chloroform solution used for eluting the film.

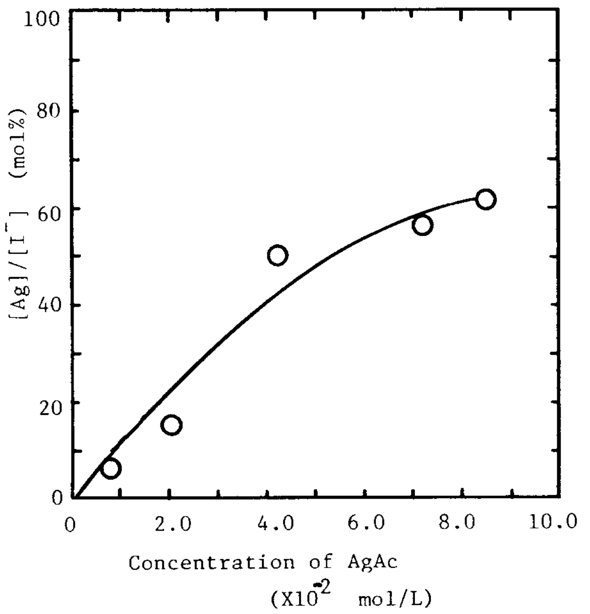

Figure 2 Yield of colloidal silver to initial I^- ion in the film

The morphological observation of reacted film was carried out. *Figures 1b* and *c* show TEM micrographs of the film after soaking in $Na_2S_2O_3$ solution and drying. The grey areas of the micrographs are segregated P2Vp sequences crosslinked with DIB, the white areas are PS phases and the black areas are colloidal silver. The black microdomains which indicated the existence of silver, were continued for a few micrometres along the P2Vp phases. The black microdomains did not cross the PS phase and did not protrude from the P2Vp phases. The introduced silver particles had diameters between 10 nm and 20 nm (*Figure 1c*). It was concluded that it was possible to localize colloidal silver in microphase separated P2Vp phases.

It was noticed that a lot of colloidal silver was observed in the P2Vp phases nearer the surface; the depth of the P2Vp phases containing colloidal silver was 3.5 μm. It was also suggested that Ag^+ ions were introduced from the surface and that the reduction of AgI occurred at the surface of the film. A similar phenomenon was observed by Kraeutler and Bard[25] who reduced a platinum salt by light reduction.

The yield of colloidal silver from the initial I^- ion in the film, $[Ag]/[I^-]$, was calculated from the final weights of the films (*Table 1* and *Figure 2*). When the concentration of the AgAc solution used for soaking the film was 8.5×10^{-2} mol l^{-1}, the yield was 61.3 mol%. The yield of colloidal silver decreased with decrease in concentration of AgAc solution. The size of the colloidal metal formed in the gel was governed by the concentration of the solution used to introduce the metal and the crosslinking density of the gel[13]. The colloidal metal was eluted from the supporting gel matrix when the colloidal metal size was too small to compare with the crosslinking density of the gel. Therefore, it was suggested that the decrease in the yield of colloidal silver with the concentration of AgAc solution was due to the decrease of the size of the colloidal silver in the gels.

We succeeded in introducing colloidal silver into the P2Vp microdomain of microphase separated P(S-*b*-2Vp) film. Further investigation is necessary to clarify the amount and state of colloidal silver in the film. We are continuing our studies and intend to study the applications of these membranes.

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