Oxidation polymerization of pyrrole on microphase-separated block copolymer films as template

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Poly(styrene-*b*-2-vinylpyridine) diblock copolymer films with horizontally oriented lamellar microdomains were obtained by the casting method. Poly(2-vinylpyridine) (P2VP) layers were not only quaternized but also crosslinked with 1,4-diiodobutane vapour with the intention of immobilizing the supermolecular structure. Cu^{2+} ions (oxidant) were introduced into P2VP layers by complexation based on the pyridine nitrogen interacting with the metal ions. Electrically conducting films were synthesized with such an oxidizing agent being added to a mixture of pyrrole and water vapour. The element distributions on a vertical section of the composite films were measured by energy dispersive X-ray spectrometry. These films showed conductivities of 10^{-1} S cm^{-1} parallel to the film plane and had high anisotropic conductivity.

(Keywords: diblock copolymer; lamellar microdomain; pyrrole)

INTRODUCTION

There have been reports of attempts to measure the electrical conductivity of diblock copolymers in which one of the blocks was poly(2-vinylpyridine) (P2VP)[1–3]. However, these materials have never shown electrical anisotropy with conductivity because the orientation of the microphase-separated structures formed by the block copolymers was uncontrolled.

We have previously indicated that the poly[styrene(S)-*b*-2-vinylpyridine (2VP)] diblock copolymer formed horizontally oriented lamellar microdomains by virtue of air–copolymer and substrate–copolymer interactions[4]. Subsequently, semiconducting materials were obtained by exposing the film to alkyl dihalide vapour[5]. The film had an anisotropic conductivity of about eight orders of magnitude (the ratio of conductivity parallel to the film plane to conductivity perpendicular to the film plane). Colloidal silver was also introduced into quaternized P2VP layers by reduction of silver iodide[6]. This film showed a 100-fold conductivity value (10^{-4} S cm^{-1}) parallel to the film plane, as compared with that observed in diblock copolymer films with quaternized P2VP layers. According to our results, high electrical anisotropy originates in the orientation of microphase-separated structures. On the other hand, Mohammadi *et al.*[7] have reported the synthesis of electrically conducting polymer composite films from the exposure of poly(4-vinylpyridine) (P4VP) complexed with an oxidizing agent such as cupric chloride ($CuCl_2$) or ferric chloride ($FeCl_3$) to a mixture of pyrrole and water vapour. The films produced by the template polymerization of pyrrole monomer into a matrix polymer of P4VP complexed with Cu^{2+} ions exhibited high electrical conductivity and good mechanical and environmental stability. By aligning the oxidant in P2VP layers of horizontally oriented lamellar microdomains, it may be possible to grow conducting polypyrrole on an ordered structure which may result in high electrical conductivity.

In this study, cast film exhibiting horizontally oriented PS/P2VP lamellar microdomains was prepared. P2VP layers were not only quaternized but also crosslinked with 1,4-diiodobutane (DIB) vapour with the intention of immobilizing the supermolecular structures. Cu^{2+} ions were introduced into P2VP layers by complexation based on the pyridine nitrogen interacting with metal ions. Electrically conducting composite films were synthesized from the exposure of diblock copolymer complexed with such an oxidizing agent being added to a mixture of pyrrole and water vapour. Morphological results were obtained by a transmission electron microscope on a vertical section of modified film. The element distributions on a vertical section of the films were measured by energy dispersive X-ray spectrometry (EDX). The anisotropic conductivity of these composite materials was studied in detail.

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Table 1 Characteristics and domain size of poly(S-*b*-2VP) diblock copolymer

Code	$\bar{M}_n$[a] ($\times 10^{-5}$)	PS block content (mol%)	$\bar{M}_w/\bar{M}_n$[a]	Domain size (nm)[b]	
				$\bar{D}_{PS}$	$\bar{D}_{P2VP}$
SV10	1.25	43.1	1.16	21.0	24.1

[a] Determined by g.p.c. using universal calibration

[b] $\bar{D}_{PS}$ ($\bar{D}_{P2VP}$), average domain distance of PS (P2VP) lamellae

EXPERIMENTAL

Polymer characterization and morphology

The well defined poly(S-*b*-2VP) diblock copolymers were prepared by the usual sequential anionic addition. The details concerning the synthesis and characterization of such block copolymers have been given elsewhere[4–6]. *Table 1* lists the characteristics of the 'monodisperse' diblock copolymers, which exhibited lamellar microdomain, and the microdomain sizes. The morphology of block copolymers depends strongly on the thermal history of the preparation process. In a previous study[4] we found that the SV (PS block, ~50 wt%) films, cast from $CHCl_3$/dioxane 6/4 (v/v) on a Teflon substrate, showed a microdomain structure of horizontally oriented lamellae. This mixture works as a non-selective solvent for both PS and P2VP components. The film was embedded in an epoxy resin and was cut perpendicular to the film surface into ultrathin sections (~70–100 nm thick) using an ultramicrotome (Reichert-Nissei Co., Ultracut N). Morphological results were obtained on a Hitachi H-500 at 75 kV.

Introduction of oxidant in P2VP phases

The diblock copolymer films with PS/P2VP lamellae were exposed to DIB vapour at 70°C under reduced pressure for 6 h. This reagent leads to not only quaternization, but also to the crosslinking of P2VP microdomains. Subsequently, this film was quaternized with methyl iodide vapour at room temperature for 24 h. The degree of quaternization (Q_1) was determined by Volhard's titration. The pendent I group content (Q_2) of the P2VP phases can be estimated from quaternization with triethylamine (Et_3N). The crosslink density can be calculated from $2Q_1 - Q_2$.

It is known that the Cu^{2+} ion is a stronger oxidant than the Fe^{3+} ion[8,9]. So, the introduction of an ionic complex to P2VP layers was performed as follows. Crosslinked films (~20–45 mg) were soaked in a water or dioxane/water (1/10 v/v) mixture (15 ml) of $CuCl_2$ for 8 h. The film was washed with water and was dried at 30°C. The Cu^{2+} ion content introduced was determined by the following titration[10]. After soaking the film, the residual $CuCl_2$ solution was reacted with an excess amount of potassium iodide (KI). The I_2 produced was titrated with aqueous sodium thiosulfate ($Na_2S_2O_3$) solution using 0.2 wt% of starch as an indicator. In this work, the same method for introducing an ionic complex was carried out in the film samples after treating block copolymer films with hydrochloric acid (the P2VP·HCl salts were converted to hydrophilic segments). The element (Cl, I and Cu atoms) distributions on a vertical section of the ionic complex films were measured by EDX (Philips EDAX 9900I). The K intensity was fitted with a Zn atom ($K_\alpha = 8.628$ and $L_\alpha = 1.019$ keV). The mass concentration of the elements was estimated using a ZAF correction [stopping power, absorption and fluorescence corrections: RT-11 SJ(S) V5.01C] on a computer (LSI-11/23). The ultrathin vertical sections were observed directly on a transmission electron microscope without the staining treatment.

Oxidation polymerization of pyrrole

The reaction vessel was a 200 ml flask with a flat flange, lid and stopcock (*Figure 1*). The ionic complex films were mounted on a glass plate with double-sided adhesive tape around the walls inside the reaction vessel. The mixture of pyrrole/water (1/1 v/v) was charged into the bottom of the reaction vessel. The vessel was reduced by a vacuum pump at −78°C and was held in thermostatically controlled baths at 60°C.

In order to determine whether or not polypyrrole was formed in the P2VP layer phases, ultrathin vertical sections were observed on a transmission electron microscope after staining with osmium tetraoxide (OsO_4) vapour. The amount of polymerization of polypyrrole on the ionic complex films was estimated by the element analysis.

The composite film was broken in liquid nitrogen and the morphology of a vertical section of the polypyrrole formed was observed directly on a scanning electron microscope (JEOL-T220).

Conductivity of composite films

The sample behaved as a two-dimensional conductor (conductivity parallel to the film plane, $\sigma_{/\!/}$ and conductivity perpendicular to the film plane, $\sigma_\perp$), due to the horizontally oriented lamellae. The method and instrument used to measure conductivities have been given in a previous report[5].

RESULTS AND DISCUSSION

Morphology of diblock copolymer films

Figure 2 shows a cross-sectional TEM micrograph of the SV10 film cast from $CHCl_3$/dioxane (6/4 v/v) mixture. The dark portions are the P2VP blocks selectively stained with OsO_4. It was noted in previous work that the

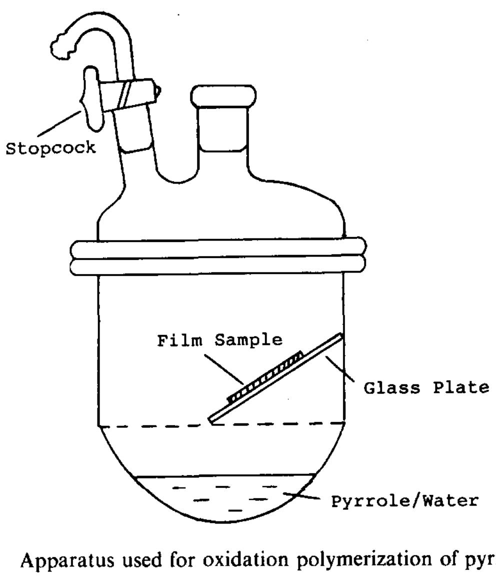

Figure 1 Apparatus used for oxidation polymerization of pyrrole

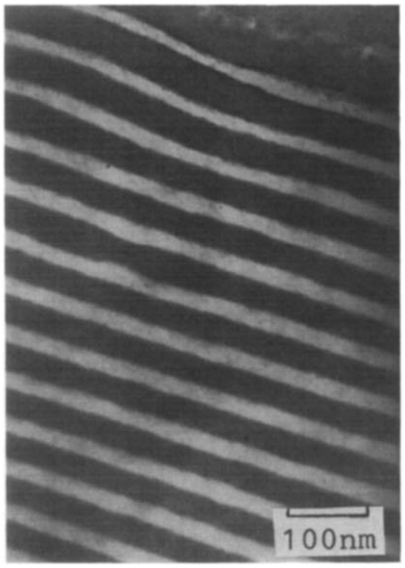

Figure 2 Cross-sectional TEM micrograph of a diblock copolymer film

Table 2 Reaction conditions and results of introducing Cu^{2+} ions into P2VP phases

Expt no.	Film weight (mg)	Solvent	$[CuCl_2]$ (mol l^{-1})	$Cu^{2+}/2VP^a$ (mol mol^{-1})
SV10-C1	29.6	H_2O	0.05	0.16
SV10-C2	31.8	H_2O	0.10	0.24
SV10-C3	30.8	H_2O	0.40	0.33
SV10-C4	25.0	H_2O/dioxane	0.05	0.13
SV10-C5	22.9	H_2O/dioxane	0.10	0.21
SV10-N1	28.0	H_2O	0.05	0.02
SV10-N2	27.0	H_2O	0.10	0.16
SV10-N3	25.5	H_2O	0.20	0.21

[a] Determined by oxidation–reduction titration

alternating lamellar structures of the PS and the P2VP phases (SV diblock copolymers) were oriented with their interfaces parallel, not only to the surface in contact with air, but also to the Teflon substrate. It was also recognized from X-ray photoelectron spectroscopy (X.p.s.) studies[4,5] that the outermost layer consisted of a single layer of PS block chains with a lower solid-state surface tension. In addition, the PS layer was also aligned with its interface parallel to the surface that was in contact with the Teflon substrate.

Introduction of Cu^{2+} ions to P2VP phases

P2VP domains of the SV10 film were not only quaternized but also crosslinked with DIB and methyl iodide (Q_1, 40 mol%; crosslink density, 7 mol%). It was mentioned in previous reports[5,6] that the morphological structure of diblock copolymer films was not disturbed before or after the quaternization reaction.

Table 2 lists the reaction conditions and the results of introducing Cu^{2+} ions into P2VP phases. The abbreviations SV-C and SV-N indicate diblock copolymer films composed of partially quaternized P2VP and P2VP·HCl phases, respectively. *Figure 3* shows the relationship between the ratio of the introduced ionic complex to 2VP units ($Cu^{2+}/2VP$) and $CuCl_2$ concentration. It is found from these curves that the ionic complex increases with an increase in $CuCl_2$ concentration. The amount of introduced ionic complex to the crosslinked films (SV-C) is larger than that to SV-N films. It seems that the hydrophilic and network characters of P2VP layers are advantageous for the incorporation of Cu^{2+} ions. The diffusion effect of $CuCl_2$ in the swollen state of PS layers is scarcely observed in the reaction systems (SV10-C4 and SV10-C5) using H_2O/dioxane mixture as solvent.

We observed directly the cross-sectional TEM micrograph of the SV10-C2 specimen (*Figure 4*). In this micrograph, the TEM image is constructed by electrons scattered from Cu atoms. This texture is the same as that shown in *Figure 2*. It is found that Cu^{2+} ions distribute only in the quaternized P2VP layers.

The topography of the vertical section (SV10-C2 fragment) and concentration distributions of Cu and I atoms (EDX data) are shown in *Figure 5a*, where the concentration of Cu and I atoms on the white scanning line is superimposed on the backscattered electron image. It is found from the Cu atom distribution that the introduction of Cu^{2+} ions to P2VP domains was

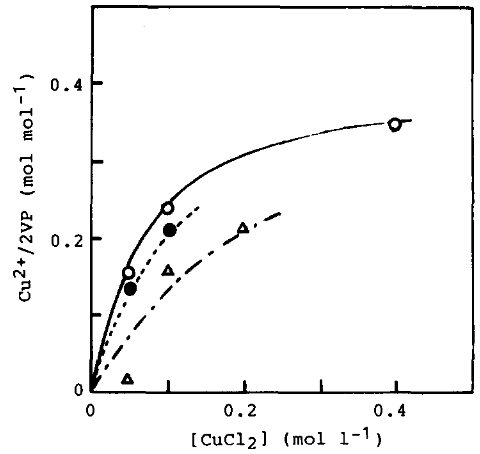

Figure 3 Relationship between the amount of Cu^{2+} ions introduced and $CuCl_2$ concentration: (○) SV-C series in water; (●) SV-C series in H_2O/dioxane (10/1 v/v) mixture; (△) SV-N series in water

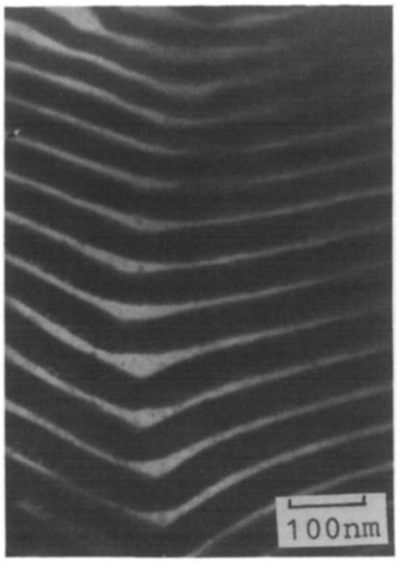

Figure 4 Cross-sectional TEM micrograph of the ionic complex composite film SV10-C2

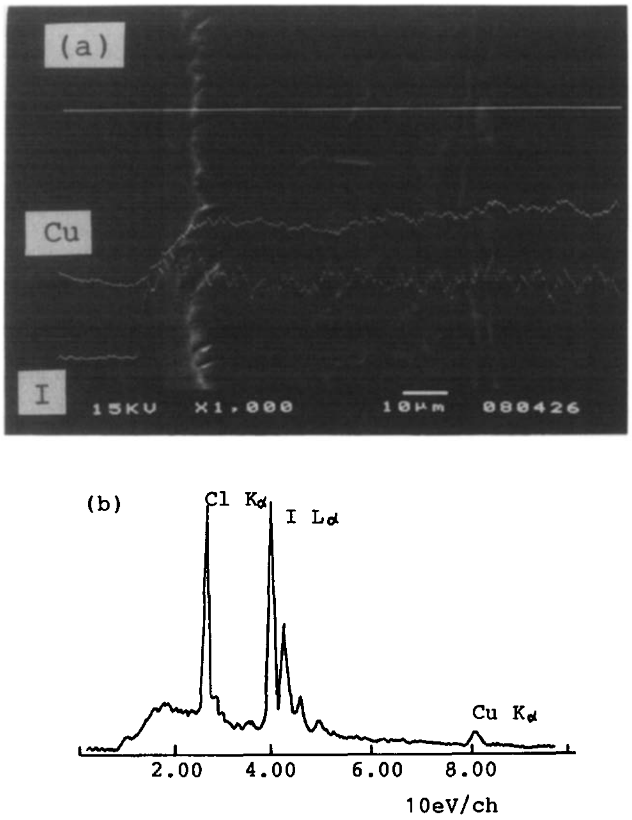

Figure 5 EDX data of SV10-C2 fragment: (a) b.s.c. image and concentration distribution of Cu and I atoms; (b) spot analysis of the centre

Table 3 Spot analysis of SV10-C2 and SV10-C5 films by means of EDX

		Element (at%)		
Code	Position	Cu	I	Cl
SV10-C2	Left	11.69	47.27	41.05
	Right	10.69	44.78	44.53
	Centre	9.47	46.89	43.64
SV10-C5	Left	7.25	58.38	34.38
	Right	7.84	56.89	35.27
	Centre	7.02	56.51	36.46

performed homogeneously on the white scanning line in the vertical section. *Figure 5b* shows the spot analyses of Cu, I, and Cl atoms at the centre. *Table 3* summarizes the results of spot analyses on SV10-C2 and SV10-C5 composite films. It is found from these results that the observed values of Cu at the centre are almost the same as those at both edges for SV10-C2 and SV10-C5 fragments. Moreover, the amount of ionic complex introduced for SV10-C2 increases in comparison with that for SV10-C5 film. This supports the result obtained from oxidation–reduction titration (*Figure 3*).

Oxidation polymerization of pyrrole

In the oxidation polymerization of pyrrole, the SV-C film was employed as an ionic complex composite film (soaked in 0.4 mol l^{-1} of aqueous $CuCl_2$ solution for 8 h). The preparation of polypyrrole composite films (SV10-P series) was carried out in the reaction vessel shown in *Figure 1*. The dark colour of the ionic complex composite film changed to black on exposure to pyrrole vapour. Fourier transform infra-red studies were carried out on SV10-P films. The spectra obtained showed bands near 1539, 1167, 941 and 768 cm^{-1} which were characteristic of polypyrrole[7].

Experiments were carried out to investigate the effect of the polymerization time of exposure to pyrrole/water vapour on the amount of polypyrrole formed (*Figure 6*). The amounts of polypyrrole formed on P2VP phases (PPy/SV10-P) were estimated using the data from element analyses. The growth of polypyrrole film proceeds at a fast rate in the initial stage of polymerization and a 5 h exposure time is enough for complete diffusion of pyrrole vapour through the matrix polymer. *Figure 7* shows a cross-sectional TEM micrograph of SV10-P film after exposure for 5 h. This specimen was stained with OsO_4. Consequently, the dark portions correspond not only to polypyrrole but also to P2VP phases. From this micrograph it can be seen that the growth of polypyrrole proceeds within the P2VP phases as a template. However, the domain size of the PS lamellar layers seems to be narrow compared with

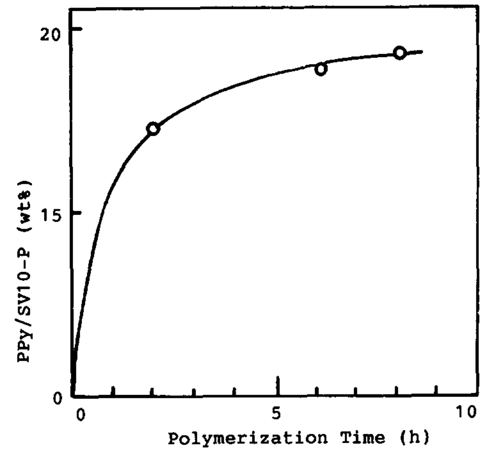

Figure 6 Relationship between the feed amount of polypyrrole and polymerization time of exposure to pyrrole/water vapour

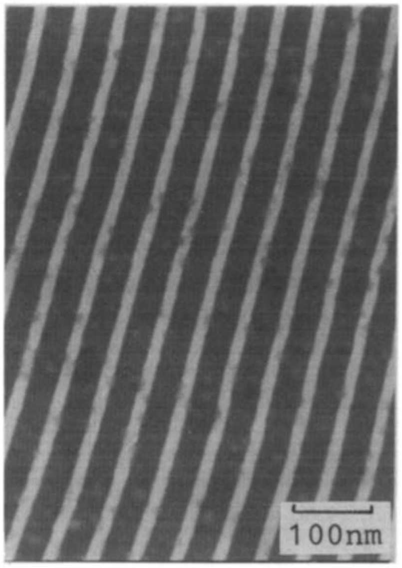

Figure 7 Cross-sectional TEM micrograph of SV10-P film

Table 4 Conductivities of composite films[a]

Code	$[CuCl_2]$ (mol l^{-1})	Water treatment[b]	Conductivities (S cm^{-1}) $\sigma_{/\!/}$	Conductivities (S cm^{-1}) $\sigma_{\perp}$	Anisotropy, $\sigma_{/\!/}/\sigma_{\perp}$
SV10-P1	0.4	No	0.158	5.4×10^{-8}	3×10^6
SV10-P2	1.0	Yes	6.2×10^{-7}	8.7×10^{-12}	7×10^4
SV10-P3[c]	0.4	No	7.2×10^{-7}	3.6×10^{-11}	2×10^4
P2VP/PPy[d]	–	No	0.235	–	–
SV10-C	0.2	Yes	6.6×10^{-8}	5.0×10^{-13}	1×10^5

[a] Composite films ($\sim 100\,\mu m$ thick) exposed to pyrrole/water vapour for 4 h

[b] Ionic complex composite film soaked in water for 24 h (yes) or washed with a small amount of water (no)

[c] Exposed to pyrrole/methanol vapour

[d] After dissolving P2VP (80 mg) and $CuCl_2 \cdot 2H_2O$ (50 mg) in water (5 ml) and some drops of concentrated HCl, the solutions were cast on glass slides

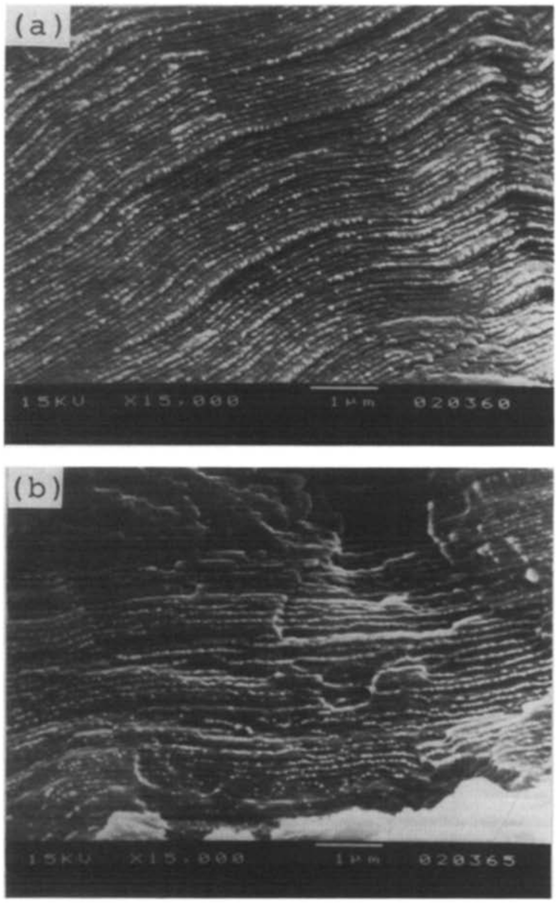

Figure 8 Cross-sectional SEM micrographs of: (a) SV10-P1; (b) SV10-P2

that of the original SV10 film. The growing polypyrrole chains seem to percolate a little into the PS phases.

Conductivity of composite films

Electrical conductivity measurements were carried out for the SV10-P composite films (*Table 4*). The conductivity of pure PS is $\sim 10^{-17}$ S cm^{-1} (see ref. 11). From *Table 4*, P2VP/PPy indicates that P2VP/pyrrole composite film is a model sample. The SV10-P1 film shows almost the same $\sigma_{/\!/}$ value as that of P2VP/PPy. However, the observed $\sigma_{/\!/}$ value of SV10-P2 is extremely small compared with that of SV10-P1. We carried out water treatment on ionic complex composite films with the intention of removing free Cu^{2+} ions, because the Cu^{2+} ions were introduced into the P2VP layers by complexation based on their interaction with the pyridine nitrogen. In previous work[5], we fabricated semiconducting materials composed of poly(S-*b*-quaternized 2VP) diblock copolymer films with lamellar microdomains. The quaternized P2VP domains (counter ion, I^-) showed ionic conduction ($\sigma_{/\!/} \sim 10^{-6}$ S cm^{-1}). Both the SV10-P2 and SV10-C films showed $\sigma_{/\!/}$ values with similar orders of magnitude.

We obtained directly SEM micrographs of vertical sections of SV10-P1 and SV10-P2 films (*Figure 8*). The white portions correspond to polypyrrole phases. It is found from these micrographs that the supermolecular structure of the horizontally oriented lamellar microdomains is maintained in the SV10-P1 film but is destroyed in the SV10-P2 film. Therefore, soaking an ionic complex composite film in water for a long time seems to lead to the destruction of microdomains. As a result, the SV10-P2 composite film shows a low $\sigma_{/\!/}$ value regardless of the growth of polypyrrole. The SV10-P1 composite film possesses a high conductivity (anisotropy, $\sigma_{/\!/}/\sigma_{\perp} = 10^6$) owing to the continuous polypyrrole layers. More recently, examination of the morphological structures observed in doped polypyrrole reveals that the films are either of an aggregated granular or dendritic appearance[12,13], fibrillar[14,15] or fractal[16,17]. It is necessary to investigate such morphological structures in the SV/PPy composite films. The results will be reported shortly.

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