

# Conducting Diblock Copolymers with Ionic Complex/Insulator Lamellar Microdomains

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## SYNOPSIS

Poly(styrene-*b*-2-vinylpyridine) diblock copolymer films with horizontally oriented lamellar microdomains were obtained by the casting method. Poly(2-vinylpyridine) (P2VP) microdomains were not only quaternized, but were also crosslinked with 1,4-diiodobutane vapor. Subsequently, ionic complex phases were constructed by an ion-exchange reaction of quaternized P2VP phases with lithium perchlorate. The element (chlorine and iodine atoms) distributions on the vertical section of the modified films were measured by means of an energy dispersive X-ray spectrometer. These materials had highly anisotropic conductivity with approximately 6 orders of magnitude. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

There have been reports of attempts to measure the electrical conductivity of diblock copolymers in which one of the blocks consisted of poly(2-vinylpyridine) (P2VP).<sup>1-3</sup> However, these materials have never shown electrical anisotropy with conductivities, because the orientation of microphase-separated structures, formed by block copolymers, was not controlled.

We have subsequently shown that poly[styrene(*S*)-*b*-2-vinylpyridine(2VP)] diblock copolymer formed horizontally oriented lamellar microdomains, by means of the air-copolymer and the substrate-copolymer interactions.<sup>4</sup> Following this, semiconducting materials were obtained upon the exposure of film with alkyl dihalide vapor.<sup>5</sup> The quaternized P2VP domains exhibited the nature of ionic conduction. This film had an anisotropic conductivity with about 8 orders of magnitude (conductivity parallel to the film plane  $\sigma_{\parallel} = 10^{-6}$  and conductivity perpendicular to the film plane  $\sigma_{\perp} = 10^{-14}$  s/cm). Colloidal silver was also introduced into quaternized P2VP layers by reduction of silver iodine.<sup>6</sup> This film showed the 100-fold  $\sigma_{\parallel}$  value, as compared with that observed in diblock copolymer

films with the quaternized P2VP layers. According to our results, high electrical anisotropy originates in the orientation of microphase-separated structures. Thus, it is important that the morphological structure of diblock copolymer films is not disturbed during the modification process.

In this article, the ionic complex was introduced into the quaternized P2VP layers by an ion-exchange reaction with lithium perchlorate (LiClO<sub>4</sub>) in various reaction conditions. The element (chlorine and iodine) distributions, on the vertical section of the modified films, were measured by means of an energy dispersive X-ray spectrometer (EDX). We studied the anisotropic conductivity of these materials.

## 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.<sup>4-6</sup> Table I lists the characteristics of "monodisperse" diblock copolymers, which exhibited lamellar microdomains, and the microdomain size of a specimen cast from 1,1,2-trichloroethane (TCE). The morphology of block copolymers

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**Table I** Characteristics and Domain Size of the Poly(*S-b*-2VP) Diblock Copolymer

Specimen Code	$10^{-5} \times M_n^a$	Content of PS Block (wt %)	$\bar{M}_w/\bar{M}_n^a$	Casting Solvent	Shape	Domain Size (nm) <sup>b</sup>	
						$\bar{D}_{PS}$	$\bar{D}_{P2VP}$
SV2	2.0	32.8	1.13	TCE	Lamellae	53	37

<sup>a</sup> Determined by gel permeation chromatography using universal calibration.

<sup>b</sup>  $\bar{D}_{PS}$  ( $\bar{D}_{P2VP}$ ), average domain distance of PS (P2VP) lamellae.

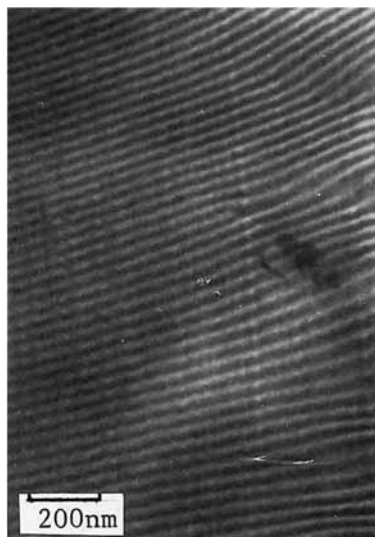
depends strongly on the thermal history of the preparation process. In a previous work,<sup>6</sup> we have found that the SV2 film, cast from a TCE solution on a Teflon substrate, showed the microdomain structure of horizontally oriented lamellae. The TCE seems to work poorly for the P2VP component. The film was embedded in an epoxy resin and was cut perpendicular to the film interfaces into ultrathin sections (about 70–100 nm thick) using an ultramicrotome (Reichert-Nissei Co., Ultracut N). Morphological results were obtained on a Hitachi H-500 transmission electron microscopy (TEM) at 75 kV.

#### Introduction of Ionic Complex to P2VP Phases

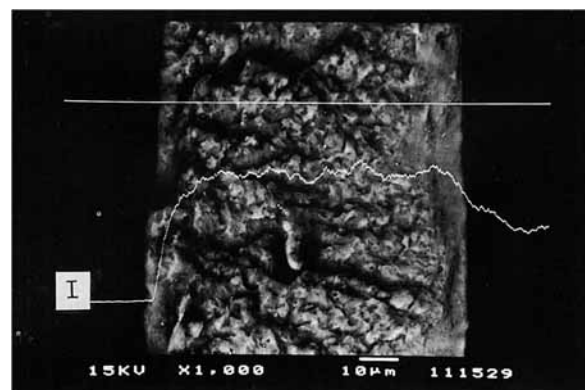
Diblock copolymer films (110–190  $\mu\text{m}$  thick), cast on a Teflon sheet, were dried for 3 days under high vacuum. This film was exposed to 1,4-diiodobutane (DIB) vapor at 60°C under reduced pressure. This

reagent leads to not only quaternization, but also to the crosslinking of P2VP microdomains. Subsequently, the unreacted P2VP parts of the lamellar domains were quaternized with methyl iodide vapor at room temperature for 3 days. The degree of quaternization ( $Q_1$ ) was determined by Volhard's titration. The content of the pendant I-groups ( $Q_2$ ) of P2VP phases can be estimated from the quaternization with triethylamine. The crosslinking density can be calculated from  $2Q_1 - Q_2$ .

The introduction of an ionic complex to P2VP layers was performed as follows. Crosslinked films (*ca.* 60 mg) were soaked in an ethanol/water mixture (15 mL) of  $\text{LiClO}_4$  (0.19 mol/L) for 24 h. The film was washed with water and was dried at 30°C. The equilibrium swelling degree ( $SQ$ ) of the crosslinked films depended strongly on the composition of the mixed solvent. The  $SQ$  is expressed by  $(M_s - M_d)/M_d$  (%), where  $M_d$  and  $M_s$  are the weights of the sample in the dry and in the swollen states, in ethanol/water mixtures, respectively. The content of the perchlorate ion ( $\text{ClO}_4^-$ ), introduced into the P2VP layers, was measured by the oxidation-reduction titration as follows. The modified film was



**Figure 1** Cross-sectional TEM micrograph of an SV2 specimen cast from TCE.



**Figure 2** EDX data (BSE image and concentration distribution of I atoms) of SV2-M fragments.

**Table II** Reaction Condition and Results of the Introduction of the Ionic Complex into SV2-M Film<sup>a</sup>

Run No.	Solvent: Ethanol/Water (v/v)	SQ of Films <sup>b</sup> (%)	Dopant <sup>c</sup> [LiClO <sub>4</sub> ]/[QPy] (mol/mol)	Ionic Complex <sup>d</sup> [ClO <sub>4</sub> <sup>-</sup> ]/[QPy] (mol/mol)
SV2-M1	2/8	108	12.1	0.40
SV2-M2	4/6	116	12.3	0.52
SV2-M3	6/4	122	11.1	—
SV2-M4	8/2	128	11.2	0.73
SV2-M5	10/0	121	10.8	0.60

<sup>a</sup> SV2-M,  $Q_1 = 47.1$  mol %, crosslinking density = 35.2%.

<sup>b</sup> (SQ) equilibrium swelling degree.

<sup>c</sup> Films were soaked in a 0.1 mol/L of LiClO<sub>4</sub> solution for 5 days [QPy], pyridinium units of SV2-M. <sup>d</sup> Determined by oxidation-reduction titration.

soaked in an excess of aqueous solution of sodium oxalate and the unreacted sodium oxalate was titrated with an aqueous solution of potassium permanganate.

The element (chlorine and iodine atoms) distributions on a vertical section of the modified 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 computer).

### Conductivity of Modified Films

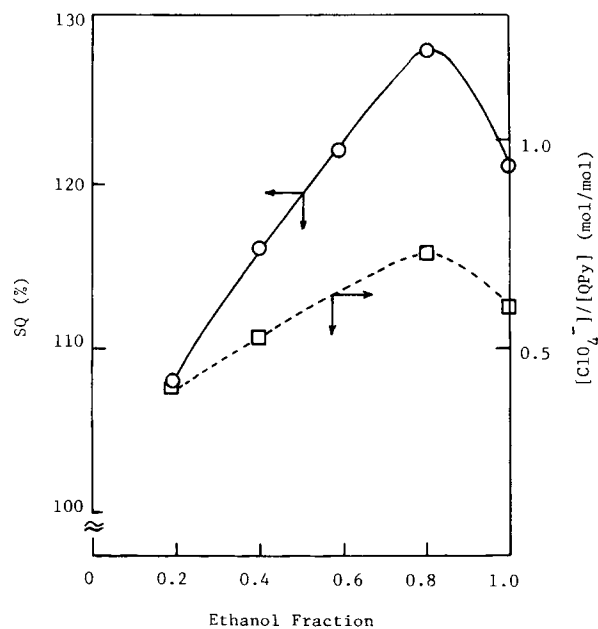
The sample would behave as a two dimensional conductor (conductivity parallel to the film plane,  $\sigma_{\parallel}$ , and conductivity perpendicular to the film plane,  $\sigma_{\perp}$ ), due to the horizontally oriented lamellae. The measurement method and instrument for conductivities were given in a previous report.<sup>5</sup>

## RESULTS AND DISCUSSION

Figure 1 shows a cross-sectional TEM micrograph, cast from TCE on the Teflon substrate. The dark portions are the selectively stained P2VP blocks with osmium tetroxide (OsO<sub>4</sub>). The distribution of P2VP and PS domain sizes is uniform, due to the monodispersity ( $\bar{M}_w/\bar{M}_n = 1.13$ ) of the SV2 diblock copolymer. It was mentioned in a previous article<sup>4</sup> that the alternating lamellar structures of the PS and the P2VP phases were oriented with their interfaces parallel, not only to the surface that contacted air, but also to the Teflon substrate. It was also recognized, from X-ray photoelectron spec-

troscopy (X.p.s.) studies,<sup>4,5</sup> that the outermost layer consisted of a single layer of PS block chains having lower solid-state surface tension. In addition, the PS layer was also aligned with its interface parallel to the surface that contacted the Teflon substrate.

P2VP microdomains of the SV2 film were not only quaternized but also were crosslinked with DIB and methyl iodide (SV2-M:  $Q_1 = 47.1$  mol %, crosslinking density = 35.2%). It was mentioned in previous reports<sup>5,6</sup> that the morphological structure of diblock copolymer films was not disturbed before nor after the quaternization reaction. The topography of the vertical section and concentration dis-



**Figure 3** Plots of an ethanol fraction against the equilibrium swelling degree (SQ) and the ratio of the introduced ionic complex to pyridinium units [ClO<sub>4</sub><sup>-</sup>]/[QPy].

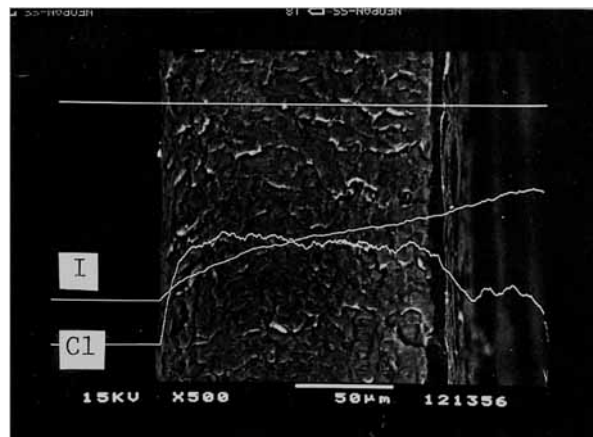


Figure 4 EDX data of SV2-*M4* fragments.

tribution of I atoms (EDX data) for the SV2-*M* fragment are shown in Figure 2, where the concentration of I atoms on the white scanning line is superimposed in the backscattered electron (BSE) images. In this micrograph, the left and right edges of the SV2-*M* fragment corresponded to the free surface and the surface that contacted the Teflon substrate, respectively. It was found from this micrograph that the concentration gradient of I atom in quaternized P2VP layers was almost constant even in bulk.

Table II lists the reaction conditions and results of the introduction of the ionic complex into the SV2-*M* film. The ionic complex was introduced into the quaternized P2VP layers, changing the equilibrium swelling degree (*SQ*) of the SV2-*M* film. Figure 3 shows the plots of the ethanol fraction against the *SQ* and the ratio of the introduced ionic complex to pyridinium units  $[\text{ClO}_4^-]/[\text{QPy}]$ . Both curves showed similar tendencies. That is, the value of the  $[\text{ClO}_4^-]/[\text{QPy}]$  increases with an increment of the *SQ* of films. The  $\text{LiClO}_4$  salts are able to permeate

into the bulk with a large diffusion rate in the swollen state of the films. Figure 4 shows the EDX data of the SV2-*M4* fragments ( $[\text{ClO}_4^-]/[\text{QPy}] = 0.73$  (mol/mol)), where the concentration distributions of the Cl and I atoms on the white scanning line are superimposed in the backscattered electron (BSE) image. This result shows that  $\text{ClO}_4^-$  ions are introduced homogeneously in quaternized P2VP layers during the ion-exchange reaction. The  $\text{I}_2$  concentration, however, is not nonuniform. It is not clear, within the limits of this experiment, that the  $\text{I}_2$  concentration has gradient through the vertical section of the film. It can be speculated that the  $\text{I}^-$  ions may be excluded from the film during the ion-exchange reaction with the  $\text{ClO}_4^-$  ions.

We carried out electrical conductivity measurements for diblock copolymer films possessing an ionic complex (Table III). Figure 5 shows the plot of conductivity, parallel to the film plane  $\sigma_{\parallel}$ , against the ratio of the introduced ionic complex to pyridinium units  $[\text{ClO}_4^-]/[\text{QPy}]$ . The  $\sigma_{\parallel}$  values increase rapidly with an increment of  $[\text{ClO}_4^-]/[\text{QPy}]$ . The observed  $\sigma_{\parallel}$  ( $10^{-7}$  s/cm) is the same order of magnitude as that reported in quaternized P2VP-perchlorate complexes.<sup>7</sup> The  $\sigma_{\perp}$  values are approximately  $10^{-14}$  s/cm and correspond to the conductivity of *PS*. These films have anisotropic conductivities ( $\sigma_{\parallel}/\sigma_{\perp}$ ) of 4–6 orders of magnitude. Thus, these films have the laminated structure of *PS* (insulator)/ionic complex (ion conduction) alternating lamellae.

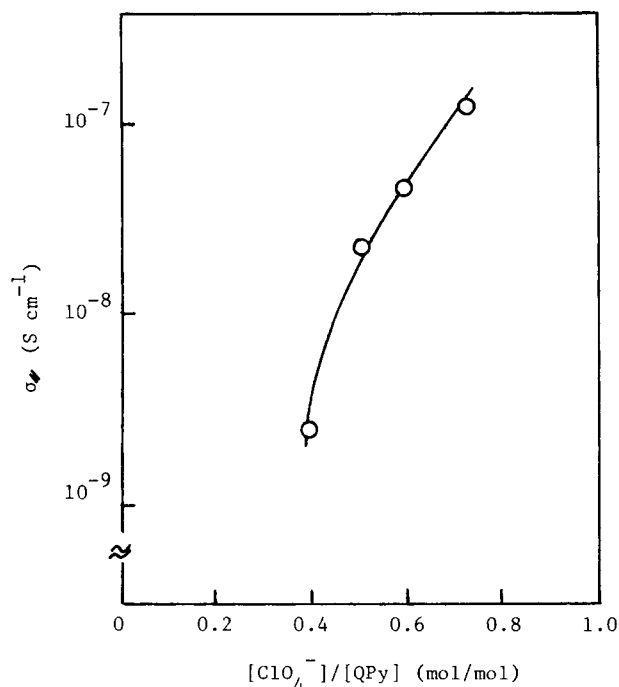
## CONCLUSIONS

The alternating lamellar structures of *PS* and P2VP microdomains were oriented with parallel interfaces, not only to the surface that contacted air, but also to the Teflon substrate. The  $\text{ClO}_4^-$  ions were introduced homogeneously in quaternized P2VP layers

Table III Conductivities of Diblock Copolymer Films Possessing the Ionic Complex

Film Code	Thickness of Film ( $\mu\text{m}$ )	Conductivity (s/cm) <sup>a</sup>		
		$10^8 \times \sigma_{\parallel}$	$10^{14} \times \sigma_{\perp}$	$10^{-6} (\sigma_{\parallel}/\sigma_{\perp})$
SV2- <i>M1</i>	113	0.43	5.58	0.08
SV2- <i>M2</i>	165	3.90	6.40	0.06
SV2- <i>M3</i>	185	6.12	6.11	1.00
SV2- <i>M4</i>	158	10.8	3.89	2.78
SV2- <i>M5</i>	190	6.71	4.26	1.58

<sup>a</sup> ( $\sigma_{\perp}$ ) conductivity perpendicular to the film plane, ( $\sigma_{\parallel}$ ) conductivity parallel to the film plane.



**Figure 5** Plot of conductivity, parallel to the film plane  $\sigma_{\parallel}$ , against  $[\text{ClO}_4^-]/[\text{QPy}]$ .

under the swollen state of the film during the ion-exchange reaction. These films had an anisotropic conductivities ( $\sigma_{\parallel}/\sigma_{\perp}$ ) of 4–6 orders of magnitude, because the films had the laminated structure of the

PS (insulator)/ionic complex (ion conduction) alternating lamellae. We are investigating the introduction of a charge transfer complex (tetracyanoquinodimethane: TCNQ) to quaternized P2VP phases of diblock copolymer films. The results will be reported.

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