Electrical anisotropy of horizontally oriented diblock copolymers

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Well defined poly(styrene-*block*-2-vinylpyridine) diblock copolymers were prepared by sequential anionic addition. Films were fabricated by casting diblock copolymer solutions on a Teflon sheet or flat glass dish by varying the casting conditions. Morphological results of these ultrathin sections were obtained using a transmission electron microscope. The surface characterization of diblock copolymer films was carried out by X-ray photoelectron microscopy. Both surface and bulk morphologies of these diblock copolymer films ($\sim$50 wt% polystyrene blocks) showed a tendency that alternating lamellar structures of two microphases were oriented with their interfaces parallel to the surface that has contact with air or the substrate. Semiconducting materials were obtained upon exposure of these diblock copolymer films to alkyl halide vapour. As a result, these materials showed electrical anisotropy with conductivity.

(Keywords: diblock copolymer; transmission electron microscopy; X-ray photoelectron microscopy; lamellar structure; electrical anisotropy)

INTRODUCTION

Many of the available conductive polymers possess undesirable characteristics, such as instability, poor processability or poor physical properties[1–4]. There have been reports of attempts to improve the physical properties of these conductive polymers by preparing block copolymers in which one of the blocks consists of a conducting polymer[5,6]. Such block copolymers composed of incompatible block segments generally form a microdomain structure in the solid state as a consequence of microphase separation of the constituent block chains. Thomas and O'Malley[7] have investigated the surface properties of block copolymers and, in particular, their surface composition and topography at the air–copolymer interface. They have shown that the surface and bulk were not identical because of significant differences in the solid state surface tension of each block. We have investigated the control of the microdomain structure of poly(styrene-*block*-isoprene) [poly(S-*b*-I)] diblock copolymers by means of the segment–segment interactions between one component of the diblock copolymer and the substrate film[8]. Even if [60 wt% polystyrene (PS) block] the thermal equilibrium morphology is polyisoprene (PI) cylinders in a PS matrix in the diblock copolymer specimen, some 10–100 layers of alternating lamellar structures of PI and PS microphases were oriented parallel near to the air–polymer interface or near the boundary surface of the substrate film. Subsequently, we have shown that poly(S-*b*-I) and poly(S-*b*-2-vinylpyridine (2VP)) diblock copolymers ($\sim$50 wt% PS blocks and relatively narrow molecular weight distribution) form horizontally oriented lamellar microdomains when they were cast from a non-selective solvent by means of air–polymer and Teflon substrate–polymer interactions[9].

More recently, there have been reports of attempts to measure the electrical conductivity of diblock copolymers (macroscopically oriented lamellae) in which one of the blocks consisted of poly(2-vinylpyridine) (P2VP)[10,11]. Semiconducting materials were obtained upon exposure of films of these block copolymers to iodine vapour. However, the materials prepared in these studies have never shown electrical anisotropy. Shimidzu *et al.*[12] reported the preparation of amphiphilic pyrrole Langmuir–Blodgett (LB) films from electropolymerization. They found that this LB film (200 layers) showed a highly anisotropic conductivity of $\sim$10 orders of magnitude (conductivity parallel to the multilayer, $\sigma_{\parallel} = 10^{-1}$ S cm^{-1}; conductivity in the perpendicular direction, $\sigma_{\perp} = 10^{-11}$ S cm^{-1}).

In this paper, well defined poly(S-*b*-2VP) diblock copolymer with $\sim$50 wt% PS blocks (this molecular weight is higher than that of the diblock copolymer prepared previously, because copolymer film having a low molecular weight does not possess toughness) was prepared by sequential anionic addition. The orientation on the surface and in the bulk microdomain structures of this diblock copolymer were defined by varying the

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casting conditions. Morphological results of these diblock copolymer films were obtained by transmission electron microscopy (TEM). The surface characterization of the film was carried out by X-ray photoelectron spectroscopy (X.p.s.). The horizontally oriented copolymer film, upon doping P2VP domains with alkyl halides, had anisotropic electrical properties with conductivities.

EXPERIMENTAL

Polymer synthesis and characterization

The well defined poly(S-*b*-2VP) diblock copolymers used were prepared by sequential anionic addition as for those used in our previous paper[9,13]. The monodisperse poly(S-*b*-2VP) diblock copolymers were prepared by anionic addition with n-butyllithium (n-BuLi) as initiator in tetrahydrofuran (THF) at −78°C.

The number-average molecular weight ($\bar{M}_n$) of PS prepolymers was determined with a Tosoh high-speed liquid chromatograph HLC-802A, with THF as eluent at 38°C, a TSK gel GMH column and a flow rate of $1.0\ \mathrm{ml\ min^{-1}}$. The $\bar{M}_n$ of the diblock copolymers was determined by means of a Mechrolab model 501 membrane osmometer in benzene at 37°C. The molecular weight distribution ($\bar{M}_w/\bar{M}_n$) of the diblock copolymers was determined by gel permeation chromatography (g.p.c.) distributions after improvement by the reshaping method[14]. *Table 1* lists the characteristics and the domain size of poly(S-*b*-2VP) diblock copolymer.

Morphology of diblock copolymer films

The morphology of block copolymers depends strongly on the thermal history in the preparation process. In a previous work[9], we have found that a $CHCl_3$/1,4-dioxane 6/4 (v/v) mixture is a non-selective solvent for both PS and P2VP components. Consequently, poly(S-*b*-2VP) film (40 μm thick) was cast from a $0.03\ \mathrm{g\ ml^{-1}}$ $CHCl_3$/dioxane solution on a Teflon sheet ($0.11\ \mathrm{ml\ cm^{2}}$) or flat glass dish as a substrate. The casting solvent was evaporated as gradually as possible under saturated vapour. Annealing treatment was not carried out for these films. Next, the films were embedded in an epoxy resin and cut perpendicularly to the film interfaces into ultrathin sections (~700–1000 Å thick) using an ultramicrotome (Hitachi UM-3 ultramicrotome). This specimen was exposed to osmium tetraoxide (OsO_4) vapour for 24 h. Morphological results were obtained with an Hitachi H-600A transmission electron microscope.

Sample preparation and instrumentation

The cast film of poly(S-*b*-2VP) (40 μm thick) was dried under vacuum for 2 days at room temperature. The sample film ($7 \times 20\ \mathrm{mm^2}$) was coated on a copper sample holder with double-sided adhesive tape and copper wire, and was dried in an argon atmosphere at ambient temperature.

Spectra were recorded on a Spectoros XSAM 800 apparatus using Al Kα exciting radiation. Typical operating conditions were: X-ray gun, 14 kV and 20 mA; pressure in the analysis chamber, 6.7 mPa. Owing to the rather long analysis times required for the angular-dependent studies, a liquid nitrogen cooled sample holder was used. A value of 285.0 eV was used for the C_{1s} core level of the hydrocarbon. Overlapping peaks were resolved into their individual components using a DEC PDP11/03L curve resolver. These studies have shown that the lineshapes are approximately Gaussian for individual components.

The angular-dependent X.p.s. studies were carried out as follows. The sample was rotated relative to the fixed energy analyser by an angle θ, which is the angle between the normal to the sample and the slits in the analyser. Spectra were recorded at two different polar angles ($\theta = 0$ and 80°) with respect to the sample surface, to achieve effective sampling depths of ~5 and ~1 nm, respectively, where the mean free length (λ) is dependent on the 1/2 power of the kinetic energy. The average values for λ as a function of kinetic energy for the polymer systems are ~14, ~22, ~23 and ~29 Å for kinetic energies of ~969, ~1170, ~1202 and ~1403 eV, respectively[15].

Conductivity of modified samples

Diblock copolymer films (40 μm thick) cast on Teflon sheet were dried for 3 days under a high vacuum. Doping of P2VP microdomains was carried out by alkyl halide compounds. At first, the film was exposed to diiodobutane vapour at 40°C under a reduced pressure. This reagent leads to not only quaternization but also crosslinking of P2VP microdomains. Subsequently, the unreacted P2VP parts of the lamellar domains were quaternized with methyl iodide vapour at room temperature for 3 days. The degree of quaternization was determined by Volhard's titration[16].

The schematic representation of conductivity measurements for modified samples is shown in *Figure 1*. The sample behaved as a two-dimensional conductor (conductivity parallel to the film plane $\sigma_{\parallel}$: x and y axes) due to horizontally oriented lamellae. Rectangular samples, with approximate dimensions of 0.8×0.6 mm (x and y axes), were mounted on the conductivity measurement cell with colloidal graphite in methyl ethyl ketone. Electrical conductivity was measured using a Takeda Riken TR-8651 electrometer in dry nitrogen atmosphere. Electrical conductivity in the direction perpendicular to the film plane $\sigma_{\perp}$ (z axis) was measured by sandwiching a modified film between two platinum plates.

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

Specimen code	$10^{-4}\bar{M}_n$ PS[a]	$10^{-4}\bar{M}_n$ Block[b] copolymer	Content of PS block (wt%)	$\bar{M}_w/\bar{M}_n$[a]	Shape	Domain size (nm)[c] $\bar{D}_{PS}$	Domain size (nm)[c] $\bar{D}_{P2VP}$
SV	4.7	10.0	47.0	1.13	Lamellae	25	27

[a] Determined by g.p.c.
[b] Determined by osmometry
[c] $\bar{D}_{PS}$ ($\bar{D}_{P2VP}$), average domain distance of PS (P2VP) lamellae

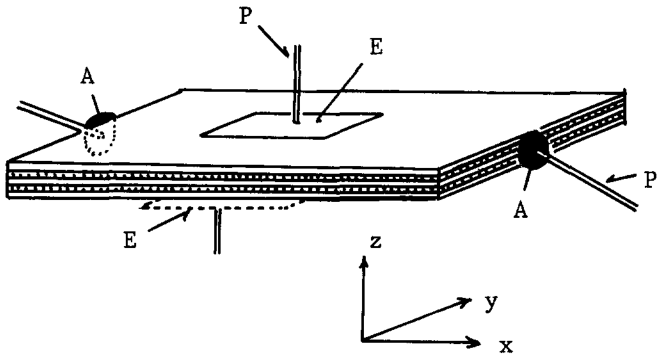

Figure 1 Schematic presentation of conductivity measurements for horizontally oriented SV film: (A) graphite; (P) platinum wire; (E) platinum plate

RESULTS AND DISCUSSION

The SV diblock copolymer prepared by anionic addition has a single and relatively narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.13$) from the g.p.c. analysis (*Table 1*). Solvent-cast film of this diblock copolymer possesses toughness.

Figure 2 shows a cross-section of the SV film cast from $CHCl_3$/dioxane 6/4 (v/v) mixture near the air–polymer interface (*Figure 2a*), in bulk and near the substrate (Teflon)–polymer interface (*Figure 2c*). The upper and lower arrows indicate the free surface of the film and the surface that has contact with the Teflon substrate, respectively. *Figure 2b* is an enlarged micrograph of the boxed section in *Figure 2c*. The dark portions are the selectively stained P2VP blocks. The thermal equilibrium morphology of SV film (47 wt% PS blocks) is alternating lamellar structures of P2VP and PS microphases. The distribution of P2VP and PS domain sizes is very uniform owing to the monodispersity ($\bar{M}_w/\bar{M}_n = 1.13$) of SV diblock copolymer. It is found from these micrographs that the alternating lamellar structures of PS and P2VP microphases are oriented with their interfaces parallel to the surface that contacts air not only near the free surface but also in bulk. These results are the same as those obtained in a previous work[9] using poly(S-*b*-2VP) diblock copolymer ($\bar{M}_n = 2.1 \times 10^4$; 54 wt% PS blocks). The surface tension of PS is 36×10^{-3} N m^{-1} (ref. 17). On the other hand, the surface tension of P2VP is estimated to be $>40 \times 10^{-3}$ N m^{-1} from the relationship between the parachor and molar volume. Therefore, the PS domains having lower solid state surface tension are considered to accumulate at the air interface.

X.p.s. on the cast film is one of the best ways to inspect the orientation on microdomains near both surfaces. *Figure 3* shows C_{1s} and N_{1s} core level spectra of X.p.s. near the free surface and the boundary surface of Teflon substrate at a sampling depth of ~1 nm. The core level spectra near the free surface at a sampling depth of ~1 nm (*Figure 3a*) show the presence of carbon alone. This result supports the surface morphology in which the cast film SV is covered with a thin PS layer at the free surface, as shown in *Figure 2a*. It is indicated however from these core level spectra that a small amount of nitrogen (0.2%) is detected near the boundary surface of the Teflon substrate at a sampling depth of ~1 nm. In the TEM micrographs, the PS layers correspond to the white regions because the staining reagent is OsO_4. It is very difficult to judge whether the outermost layer is covered with PS microphases. The Hildebrand solubility parameters (δ_{PS}, δ_{P2PVP} and δ_{PTFE}) for PS, P2VP and Teflon[poly(tetrafluoroethylene): PFTE] are 9.10[13], 10.5[13] and 6.2[18] cal$^{1/2}$ cm$^{-3/2}$, respectively. Hence, the PS layer seems to be absorbed predominantly on the boundary surface of the Teflon substrate by segment–segment interactions. In *Figure 2c*, the lower surfaces of the specimen are damaged sporadically. The presence of nitrogen may be due to the breakdown of the film surface.

Figure 4 shows C_{1s} and N_{1s} core level spectra of X.p.s. near the free surface and the boundary surface of the Teflon substrate at a sampling depth of ~5 nm. These core level spectra show the presence of a small amount of nitrogen near both the free surface (0.5%) and boundary surface of the Teflon substrate (0.1%). According to the explanation by Hasegawa and Hashimoto[19] the outermost layer must consist of a single layer of PS block chains since the PS chain ends connected by the chemical junctions to P2VP chains cannot emerge from the air interface, while the inner layer is composed of bimolecular layers. The thickness of the outermost PS layer is judged to be ~12 nm. Confirmation of the presence of nitrogen at a sampling depth of ~5 nm was not obtained. A single layer of PS block chains may be disturbed randomly at both outermost surfaces.

Figure 5 shows a cross-section of the SV film cast from $CHCl_3$/dioxane 6/4 (v/v) mixture near the air–polymer interface (*Figure 5a*), in bulk and near the glass

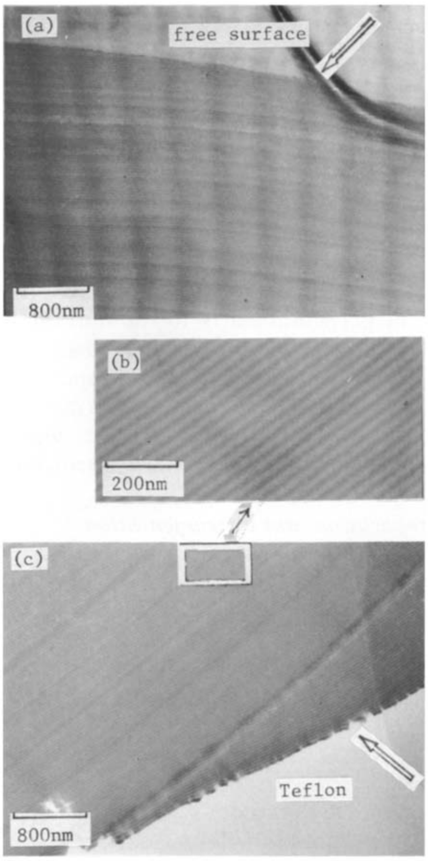

Figure 2 Cross-sectional TEM micrographs of the SV film cast from $CHCl_3$/dioxane 6/4 (v/v) mixture on the Teflon substrate: (a) near the air–polymer interface; (b) enlarged micrograph of the boxed section in (c); (c) near the substrate–polymer interface

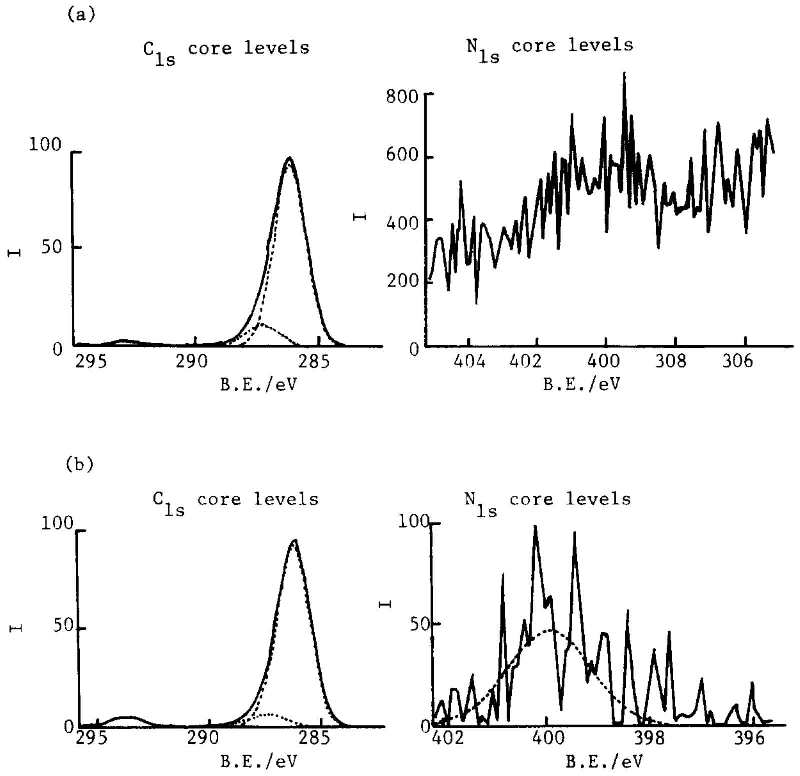

Figure 3 C_{1s} and N_{1s} core level spectra of the SV film at a sampling depth of ~1 nm: (a) near the free surface; (b) near the boundary surface of the Teflon substrate

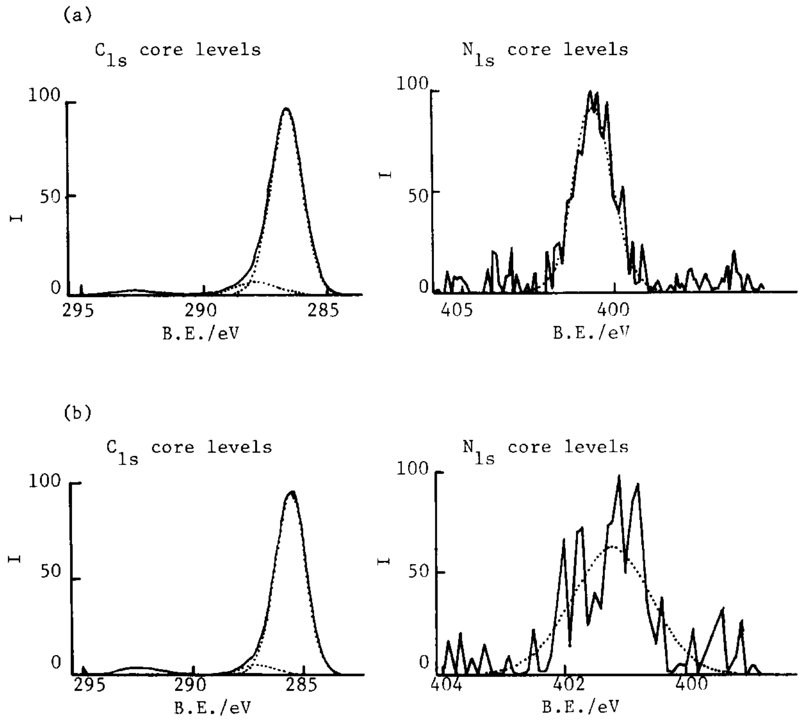

Figure 4 C_{1s} and N_{1s} core level spectra of the SV film at a sampling depth of ~5 nm: (a) near the free surface; (b) near the boundary surface of the Teflon substrate

substrate–polymer interface (*Figure 5b*). The upper and lower arrows indicate the free surface of the film and the surface that makes contact with the glass substrate, respectively. It is also found from these micrographs that the alternating lamellar structures of PS and P2VP microphases are oriented with their interfaces parallel to the surface that has contact with air near both the free surface and in bulk. At the boundary surface of the glass substrate, a thin P2VP layer seems to be aligned with its interface parallel to the lower surface of the film. *Figures 6a* and *b* show C_{1s} and N_{1s} core level spectra of X.p.s. near the boundary surface of the glass substrate at sampling depths of ~1 and ~5 nm, respectively. *Table 2* lists the surface chemical composition of SV film near the boundary surface of the glass substrate as a function of sampling depth. At sampling depths of ~1 and ~5 nm, the SV film has almost the same chemical composition. Theoretical carbon and nitrogen atomic percentages of P2VP are 80.0 and 13.3 wt%, respectively. Therefore, the outermost lower surface of the SV film is almost covered by P2VP layers. As the glass plate has a hydrophilic surface, the P2VP layer seems to be absorbed on the boundary surface of the glass substrate by segment–segment interactions.

We employed the solvent-cast SV film on the Teflon substrate for electrical conductivity measurements. Both outermost surfaces are composed of thin PS layers (insulator). Morphological changes on the SV film during doping with alkyl halides were not observed from TEM micrographs, The conductivities of pure P2VP and PS are ~10^{-15} and 10^{-17} S cm^{-1}, respectively[20]. *Figure 7* shows the relationship between conductivity of the

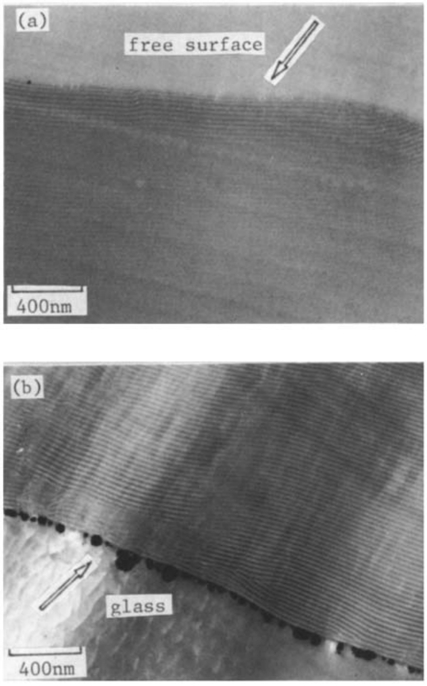

Figure 5 Cross-sectional TEM micrographs of the SV film cast from $CHCl_3$/dioxane 6/4 (v/v) mixture on the glass substrate: (a) near the air–polymer interface; (b) near the substrate–polymer interface

Table 2 Surface chemical composition of SV film near the boundary surface of the glass substrate as a function of sampling depth

Sampling depth (nm)	C_{1s} (%)	N_{1s} (%)
~1	70	5
~5	73	6

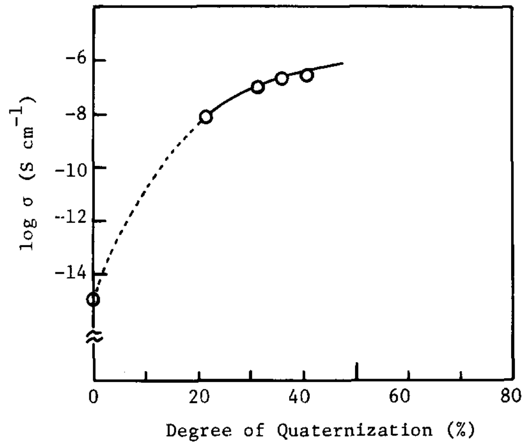

Figure 7 Relationship between conductivity (σ) of the quaternized P2VP and the degree of quaternization

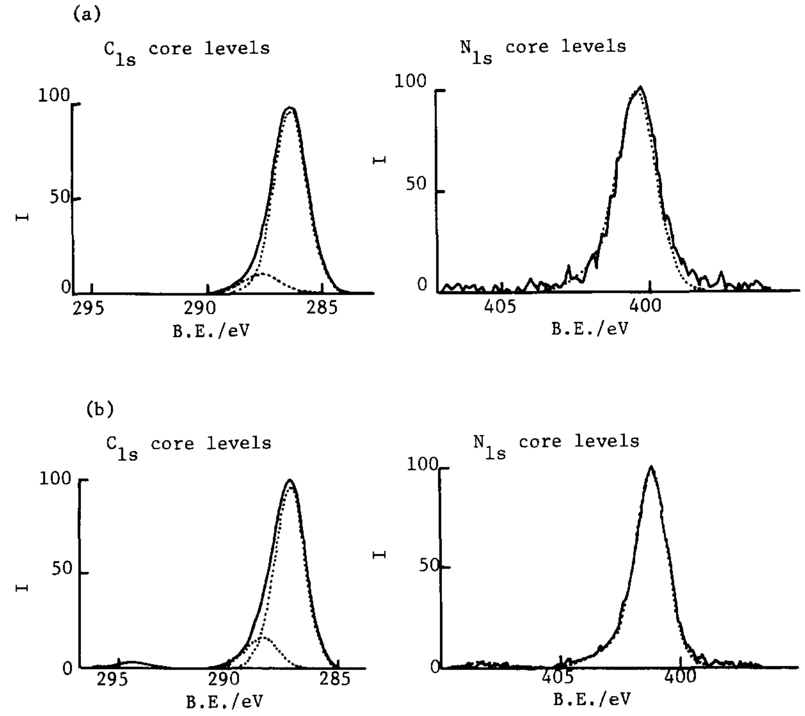

Figure 6 C_{1s} and N_{1s} core level spectra of the SV film near the boundary surface of the glass substrate: (a) sampling depth of ~1 nm; (b) sampling depth of ~5 nm

quaternized P2VP and its degree of quaternization. The quaternized P2VPs (degree of quaternization = 40–50 mol%) show an electrical conductivity of $\sim 10^{-7}$ S cm^{-1}. On the other hand, the quaternized SV film (degree of quaternization = 69.6 mol%) showed conductivities: $\sigma_{\parallel} = 1.7 \times 10^{-6}$ S cm^{-1} and $\sigma_{\perp} = 5.6 \times 10^{-14}$ S cm^{-1}. This film has a highly anisotropic conductivity of about eight orders of magnitude. The conductivity parallel to the film plane is a reasonable value judging from the relation shown in *Figure 7*. This result also supports that good horizontal orientation has been achieved in SV diblock copolymer film on casting. Alkyl halides are compatible reagents for PS blocks but incompatible for P2VP blocks in the quaternization reaction. The quaternization is controlled by the diffusion of alkyl halide from the film surface. The SV film with lamellar shape was quaternized with a relatively high degree of quaternization, because the lamellar shape consists of continuous PS segments. However, the value obtained does not reach that characteristic of semiconductors ($> 10^{-5}$ S cm^{-1}). We are investigating the preparation of highly electrical anisotropic block copolymer films by varying the kinds of dopants used. The results will be reported shortly.

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REFERENCES

1 Chance, R. R., Schacklette, L. W., Miller, G. G., Ivory, D. M., Sowa, J. M., Elsenbaumer, R. L. and Baughman, R. H. *Chem. Commun.* 1980, 348
2 Chien, J. C. W. 'Polyacetylene Chemistry, Physics and Material Science', Academic Press, New York, 1984
3 Wneck, G. E., Chien, J. C. W., Karasz, F. E. and Lilya, C. P. *Polymer* 1979, **20**, 1441
4 Gibson, H. W., Bailey, F. C., Epstein, A. J., Rommelmann, H. and Pochaw, J. M. *Chem. Commun.* 1980, 426
5 Lee, K. I. and Jopson, H. *Polym. Bull.* 1983, **10**, 105
6 Ikeno, S., Yokoyama, M. and Mikawa, H. *Polym. J.* 1978, **10**, 123
7 Thomas, H. R. and O'Malley, J. J. *Macromolecules* 1979, **12**, 323
8 Ishizu, K. and Fukutomi, T. *Macromolecules* 1989, **22**, 244
9 Ishizu, K., Yamada, Y. and Fukutomi, Y. *Polymer* 1990, **31**, 2047
10 Möller, M. and Lenz, R. W. *Makromol. Chem.* 1989, **190**, 1153
11 Stanković, R. I., Lenz, R. W. and Karasz, F. E. *Eur. Polym. J.* 1990, **26**, 359
12 Shimidzu, T., Iyoda, T., Ando, M., Ohtani, A., Kaneko, T. and Honda, K. *Thin Solid Films* 1988, **160**, 67
13 Ishizu, K., Inagaki, K., Bessho, K. and Fukutomi, T. *Makromol. Chem.* 1984, **185**, 1169
14 Pierce, P. E. and Armonas, J. E. *J. Polym. Sci. C* 1968, **21**, 23
15 Clark, T. and Thomas, H. R. *J. Polym. Sci., Polym. Chem. Edn* 1977, **15**, 2843
16 Iwasaki, G. 'Bunseki Kagaku Gaisetzu (Introduction to Quantitative Analysis)', Gakujutzutosho, Tokyo, 1963, p. 276
17 Lee, L. H. *Adv. Chem. Ser.* 1968, **87**, 106
18 Tobolsky, A. V. 'Properties and Structure of Polymers', Wiley, New York, 1960, p. 66
19 Hasegawa, H. and Hashimoto, T. *Macromolecules* 1985, **18**, 589
20 Brandrup, J. and Immergut, E. H. (Eds) 'Polymer Handbook', Plenum Press, New York, 1975