in the schematic model of Figure 3b.

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Registry No. Isoprene–styrene–(4-vinylbenzyl)dimethylamine copolymer, 74418-57-8.

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Modification of Poly(styrene-*b*-4-vinylpyridine) and Morphology of Polyelectrolytes

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ABSTRACT: A well-defined poly(styrene (ST)-*b*-4-vinylpyridine (4VP)) was prepared by anionic polymerization in tetrahydrofuran (THF) at −78 °C. Sulfonation of PST blocks was carried out with sulfuric anhydride as a sulfonating reagent in a mixture of chloroform–tetrachloromethane at 0 °C. Casting poly(sulfonated ST (SST)-*b*-4VP) from triethylamine (Et$_3$N)–1,2-dichloroethane (DCE) gave a specimen with a lamellar-like morphology, using methyl iodide as a fixing reagent. These results are discussed in some detail.

Introduction

In a previous paper,[1] a well-defined poly(ST-*b*-4VP) was prepared by anionic polymerization and there it was made clear that casting poly(ST-*b*-4VP) from 1,1,2-trichloroethane (TCE), DCE, and chloroform gave specimens with three morphologies: P4VP particles in a PST matrix, lamellae, and PST particles in a P4VP matrix, depending on the volume fractions of the phases. Quaternization of the P4VP blocks and sulfonation of the PST blocks for the films having lamellar structures were carried out in that order under various reaction conditions. As a result, a charge mosaic membrane having both cationic and anionic domains was prepared by these routes. The theoretical performance of such a membrane, which contains alternating regions of positive and negative charges, has been calculated.[2] A crude model of such a membrane has been prepared and indeed exhibited piezodialysis to give a salt-enriched permeate.[3] Kurihara et al.[4] and Chapiro et al.[5] have also reported the preparation of mosaic membranes, but good results could not be obtained.

In this work, we investigated another route for the modification of poly(ST-*b*-4VP). Previously, sulfonation of PST blocks was carried out with sulfuric anhydride as a sulfonating reagent. We reported details of the studies on the morphological properties of these poly(SST-*b*-4VP) cast from several solvents. Quaternization of the P4VP blocks of poly(SST-*b*-4VP) film was carried out with tetramethylene bromide (TMB) vapor. We tried to prepare a charge mosaic membrane by the route described above.

Experimental Section

Polymer Synthesis and Characterization. The poly(ST-*b*-4VP) was prepared by the usual sequential anionic addition using *n*-butyllithium as an initiator in THF at −78 °C. The cleaning of the glass apparatus and other techniques are the same as those employed for preparation of an AB poly(ST-*b*-4VP) having a sharp molecular weight distribution.[1,6] The samples used in this work were prepared from block copolymers prepared in the previous report.[1] The number-average molecular weights (M_n) of the block copolymers were determined by means of a Mechrolab Model 501 membrane osmometer in TCE at 37 °C. The M_n of the PST precursors was determined with a Toyo Soda high-speed liquid chromatograph HLC-801A, with THF as eluent at 40 °C, a GMH column, and a flow rate of 1.4 mL/min. The PST:P4VP block composition ratio was measured in the infrared (IR) (Hitachi grating infrared spectrophotometer 285) by the absorptions at 1030 cm^{-1} (benzene ring) and 980 cm^{-1} (pyridine ring). The compositions of the P4VP blocks determined this way were in agreement with those calculated from feed monomers. Their characterizations are shown in Table I. Casting the block copolymers shown in Table I from DCE or TCE gave specimens with lamellar structures.[1]

Table I
Characterization of Poly(ST-*b*-4VP)

	$10^{-4}M_n$		composition of P4VP blocks, mol %	
sample	PST precursor	block copolymer	from IR[b]	calcd
BP4	5.7 (5.6)[a]	11.9 (11.8)[a]	54	52
BP6	23.0 (22.6)	49.1 (48.6)	51	53
BP7	7.0 (6.7)	16.8 (17.3)	60	61
BP8	2.8 (2.8)	8.5 (8.3)	65	66

[a] Parentheses show M_n calculated from the ratio of monomer to initiator. [b] By the absorptions at 1030 cm^{-1} (benzene ring) and 980 cm^{-1} (pyridine ring).

Sulfonation of PST Blocks. Roth[7,8] investigated in detail the sulfonation of PST. According to his results, insoluble or water-swellable products due to sulfone links were obtained during

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Table II
Reaction Conditions of Sulfonation and Solubility of Poly(SST-*b*-4VP) Salts

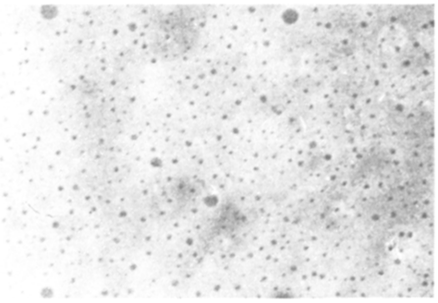
sample[a]	feed of BP series, g	solvent $CHCl_3/CCl_4$, mL/mL	reaction time, h	DS,[b] %	counterion	solubility[c] water	TCE	DCE
BP4S-1	0.309	20/40	4	100	Na	○	×	×
BP4S-2	0.198	20/40	0.5	25	Et_3N	×	○	○
BP6S-1	0.313	40/20	3	90	Na	△	×	×
BP6S-2	0.202	40/20	0.5	21	Et_3N	×	○	○
BP7S-1	0.307	10/50	3	100	Na	△	×	×
BP7S-2	0.215	10/50	0.5	15	Et_3N	×	○	○
BP8S-1	0.218	30/30	3	100	Na	△	×	×
BP8S-2	0.201	30/30	0.5	25	Et_3N	×	○	○

[a] For example, BP4S means sulfonation sample BP4. [b] Degree of sulfonation. [c] (○) soluble; (△) swelling; (×) insoluble.

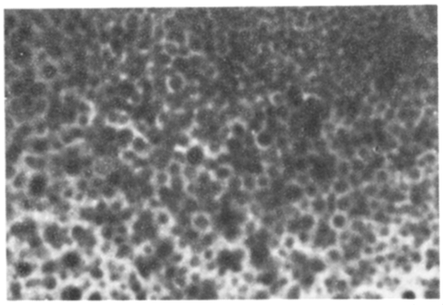
sulfonation under various conditions of time, temperature, concentration, and kind of sulfonating reagent. In this work, we employed sulfuric anhydride as a sulfonating reagent in order to obtain water-soluble products and avoid the formation of sulfone links. The block copolymer was dissolved in chloroform, and tetrachloromethane was added to this solution until micelle formation (the solution showed turbidity). Sulfuric anhydride was bubbled into the resultant solution with stirring at 0 °C for 0.5–4.0 h under a nitrogen atmosphere. The white precipitate product was washed with methyl ethyl ether and then dried under vacuum. The degree of sulfonation was determined by pH titration of residual aqueous NaOH after sulfonated product was exposed to a large excess of aqueous NaOH. In the low-conversion sulfonation (reaction time 0.5 h), a precipitate was not observed in the reaction solution. In the latter case, the solution was poured into *n*-hexane and the precipitate was dried under vacuum. The resultant sulfonic acid groups (SO_3H) of poly(SST-*b*-4VP) were converted into sulfonic acid salts (sodium or Et_3N salts) using the following procedures. (1) High-conversion solfonation: The poly(SST-*b*-4VP) was added to a small amount of water (pH ca. 3). This aqueous polymer was neutralized with aqueous NaOH and refluxed for 1 h. The water was evaporated from the product. The resultant mixture was washed with *N,N*-dimethylformamide and methyl ethyl ether and dried under vacuum. (2) Low-conversion sulfonation: The poly(SST-*b*-4VP) was dissolved in TCE. The solution showed a little turbidity due to micelle formation. This turbidity disappeared after a small amount of Et_3N was added. The resultant mixture was precipitated in *n*-hexane and dried under vacuum.

Electron Microscopy. A small amount of 1% (w/v) poly(SST-*b*-4VP) solution was dropped on the mesh plate vaporized carbon film and the solvent was allowed to evaporate slowly at room temperature. This specimen was exposed to methyl iodide (fixing and quaternization reagent) for 48 h at room temperature. The solvents were water–propanol, 8:2 (v/v) 1% aqueous Et_3N–propanol, and 1:9 (v/v) Et_3N–DCE. Morphological observations were measured with a Japan Electron Optics Laboratory (JEOL Model 7) electron microscope.

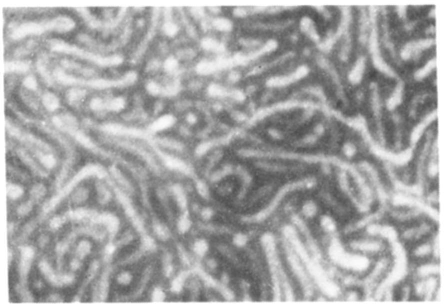
Quaternization of P4VP Blocks. Sulfonation of poly(ST-*b*-4VP) was carried out under the conditions described in Sulfonation of PST Blocks. Usually, 0.03–0.2-mm films were cast from 0.05–0.15 g/mL solutions. The solvent was 1:9 (v/v) Et_3N–DCE. The solution was cast on a Teflon seat, and the solvent was allowed to evaporate at room temperature. This cast film was soaked in 1% aqueous NaOH, washed with water, and dried under vacuum. Quaternization of the P4VP blocks was carried out with TMB vapor as a quaternization reagent. This dihalide was a very useful reagent for fixing the quaternized P4VP domain having microphase-separated structures. The resultant film was soaked in acetone for several hours and then dried under vacuum.



a) BP4S-1; 8:2 1%aq Et_3N/Propanol (v/v)



b) BP7S-2; 1:9 Et_3N/DCE (v/v)



c) BP8S-2; 1:9 Et_3N/DCE (v/v)

Figure 1. Electron micrographs of BPS series specimens cast from 1% aqueous Et_3N–propanol and Et_3N–DCE.

Results and Discussion

Sulfonation of PST Blocks. The reaction conditions of sulfonation and solubility of poly(SST-*b*-4VP) salts are shown in Table II. It was found from these results that a degree of sulfonation (DS) of 100% was possible and that DS could be controlled by varying the reaction time. In the field of organic chemistry, the sulfonation of pyridine groups has been reported. For example, 4-methylpyridine-3-sulfonic acid was obtained from the sulfonation of 4-methylpyridine.[9] $C_6H_5N{\cdot}SO_3$ and $C_6H_5N{\cdot}HCl$ salts were produced from the reaction of pyridine with chlorosulfonic acid.[10] Therefore, some side reactions of P4VP blocks are also considered to occur in the sulfonation of poly(ST-*b*-4VP). The poly(SST-*b*-4VP) obtained was insoluble in water, TCE, and DCE. The main reason is considered to be due to salt formation between SO_3H groups and pyridine rings. By converting the SO_3H groups to sulfonic acid salts, however, BP4S-1 (DS = 100%) is soluble in water, and polyelectrolytes having Et_3N salts (DS = 15–25%) are also soluble in TCE and DCE.

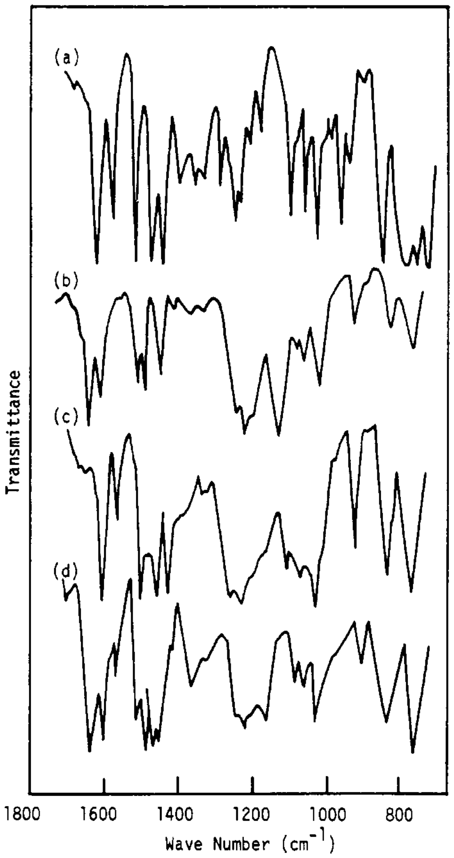


Figure 2. IR spectra of poly(SST-*b*-4VP) and its quaternized film: (a) BP8; (b) BP8S-2; (c) film cast from Et_3N–DCE; (d) quaternized film of (c) with TMB.

Morphology. We examined the morphologies of the poly(SST-*b*-4VP) specimens cast from several solvents. No films (DS = 100%) cast from water–propanol showed the microphase separation structures. Figure 1 shows electron micrographs of the BPS series specimens cast from 8:2 (v/v) 1% aqueous Et_3N–propanol and 1:9 (v/v) Et_3N–DCE. The dark portions are the selectively stained P4VP blocks. The BP4S-1 film (a) (DS = 100%) cast from 8:2 (v/v) 1% aqueous Et_3N–propanol shows quaternized P4VP particles in a PSST matrix. The micrograph of 54 mol % P4VP blocks has spherical domains with very little surface area, so evidently a large number of pyridine groups have not reacted with methyl iodide. Methyl iodide was reacted quantitatively with the P4VP blocks of poly(ST-*b*-4VP) under these reaction conditions.[1] This main reason is considered to be due to some side reactions in the sulfonation of pyridine groups. On the other hand, the BP8S-2 film (c) (DS = 25%) cast from 1:9 (v/v) Et_3N–DCE shows a lamellar-like structure. This film can be converted to the charge mosaic membrane by further sulfonation of residual PST blocks. The poly(SST-*b*-4VP) does not clearly show the microphase separation structures, when compared with poly(ST-*b*-4VP). In order to obtain the lamellar structure of poly(SST-*b*-4VP), it is necessary to control the sulfonation (DS = 15–25%) of poly(ST-*b*-4VP) (composition of P4VP blocks, 50–65 mol %) and cast from a good solvent with basic compounds such as Et_3N present.

Quaternization of P4VP Blocks. Figure 2 shows IR spectra of poly(SST-*b*-4VP) and its quaternized film (BP8S-2 series). After sulfonation of the film of (a) with sulfuric anhydride as a sulfonating reagent, the SO_3H absorptions[11] at 1200, 1040, and 1010 cm^{-1} appeared (see (b)). However, the pyridine absorptions[4] at 1420 and 980 cm^{-1} decreased compared with (a), and new absorptions at 1630 and 1470 cm^{-1} (pyridinium salts) appeared. The appearance of pyridinium salts in the IR spectrum indicates the sulfuric anhydride neutralized the pyridine in addition to interpolymer neutralization. In the film of (c), cast from Et_3N–DCE, the pyridinium salt absorptions disappeared and pyridine ring absorptions reappeared. These facts also support intramolecular salt formation between SO_3H groups and pyridine rings. In the film of (d), which was the film of (c) quaternized with TMB, both quaternized pyridine and sulfonic acid salt absorptions appeared.

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