preparation of the electron micrographs, especially of the TUN-1002 films.

Registry No. TUN-101, 74418-57-8; TUN-1002, 83615-67-2.

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Morphologies of ABC-Type Triblock Copolymers with Different Compositions

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ABSTRACT: The morphologies of three triblock copolymers composed of polystyrene (PS), poly[(4-vinylbenzyl)dimethylamine] (PA), and polyisoprene (PI) with almost equal chain lengths of PS and PA but with different chain lengths of PI were investigated by electron microscopy. The effect of the casting solvent on the morphologies is minor if the solvent is a good solvent for all three components. However, remarkable differences exist between morphologies of different polymer samples cast from the same solvent. Very complicated but highly ordered structures were observed.

Introduction

Several triblock copolymers of the ABC type have been prepared to study their microphase separation morphologies.[2–6] In a previous paper,[4] we reported a method for preparation of a triblock copolymer composed of polystyrene (PS), poly[(4-vinylbenzyl)dimethylamine] (PA), and polyisoprene (PI) having a well-defined structure. The morphologies of films cast from dioxane, benzene, and THF were studied by electron microscopy[4,5] and by a small-angle X-ray scattering method.[5] It was concluded that the PS and PA phases formed a lamellar structure and that PI islands were dispersed in the PA phase. In the present work, two samples with compositions different from the former one were prepared, and the morphologies of the microphase structures of these three samples were compared.

Experimental Section

Preparation and Characterization of Polymers. The details of the preparation and characterization methods were reported in a previous paper.[4] The number-average molecular weights of the first and second precursors and also of the final block copolymers were determined by osmometry. The number-average molecular weights of the three component blocks were calculated by taking differences between them. The microstructure of PI in the samples was determined with Varian XL-100 ^{13}C and Varian XL-100-15 ^{1}H NMR spectrometers.

Morphology. The film specimens were prepared by casting from various solvents: from benzene or THF, which are good solvents for the three components, from dioxane, which is a good solvent for both PS and PA but a poor solvent for ordinary PI (the Θ temperature is 34 °C),[7] and from cyclohexane, which is a good solvent for both PA and PI but a poor solvent for PS (the Θ temperature is 35 °C). The casting solutions and the films obtained were all transparent. The morphologies of the block copolymer films were observed by electron microscopy. Only osmium tetraoxide was used for staining of the sample films. The domains of PS, PA, and PI can be clearly distinguished as white, gray, and dark regions, respectively.[4]

Table I[a]
Number-Average Molecular Weights of the Three Components in the Triblock Copolymers

	$10^{-4}M_n$			
sample	S	A	I	SAI
SAI-3	6.1 (6.2)	4.4 (4.3)	9.3 (10.6)	19.8 (21.1)
SAI-1	6.0 (5.9)	6.4 (6.0)	4.0 (5.2)	16.4 (17.1)
SAI-4	5.3 (5.5)	5.8 (6.0)	2.0 (1.7)	13.1 (13.2)

[a] The values in parentheses are the values calculated from the amounts of monomers and initiator.

Table II
Microstructure of the Polyisoprene Sequence in the Triblock Copolymers

sample	cis 1,4, %	trans 1,4, %	3,4, %
SAI-3	46	13	41
SAI-1	32	9	59
SAI-4	46	10	44
PI	82	13	5

Results

Preparation of Block Copolymers. The three samples prepared have different PI chain lengths, that is, different weight percents of isoprene content, with the chain lengths of the other two component blocks designed to be roughly equal in the three samples. The number-average molecular weights of the three component blocks determined experimentally are compared with the values (in parentheses) calculated from the amounts of each monomer and the initiator (*sec*-butyllithium) in Table I. The agreement between the observed and calculated values is within experimental error. Moreover, it was confirmed from their sedimentation patterns that the molecular weight distributions of the triblock copolymers are narrow

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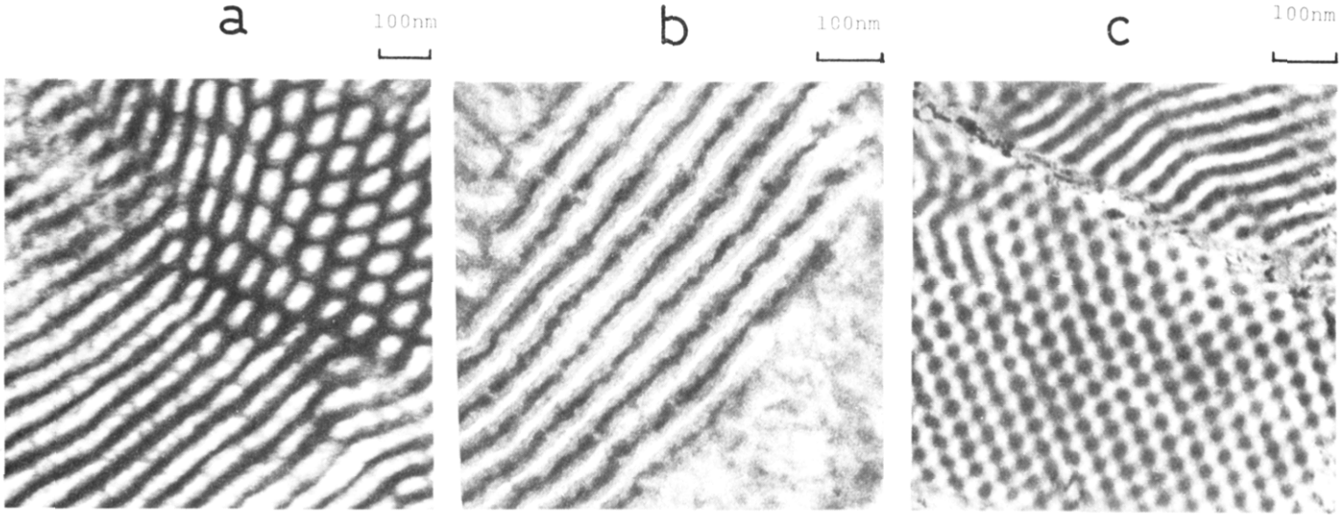

Figure 1. Electron micrographs of three triblock copolymer films cast from dioxane: (a) SAI-3; (b) SAI-1; (c) SAI-4.

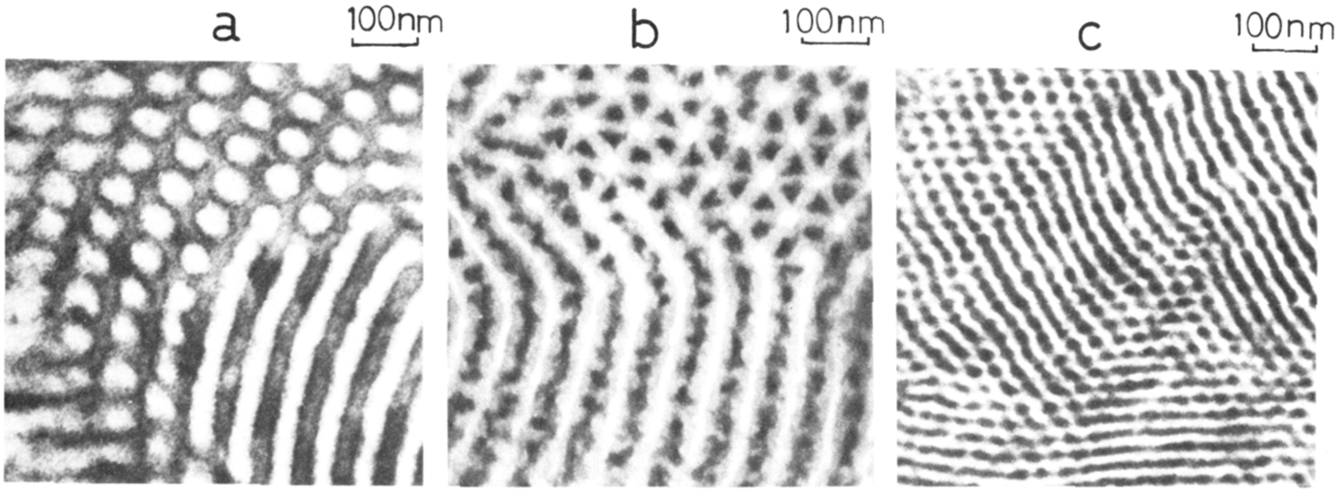

Figure 2. Electron micrographs of three triblock copolymer films cast from benzene: (a) SAI-3; (b) SAI-1; (c) SAI-4.

and that the samples do not contain their precursors. Their sedimentation patterns are similar to those in Figure 3a in the previous paper.[4] Thus it can be concluded that polymerization of the samples proceeded satisfactorily, as before.

The microstructures of the PI chains in the block copolymers are shown in Table II, together with that of the isoprene homopolymer, which was prepared with *sec*-butyllithium in benzene. The amount of the 3,4 structure in the block copolymers is higher than that in an isoprene homopolymer, as was previously pointed out.[4] The Θ temperature in dioxane is 34 °C for the isoprene homopolymer.[7,8] However, as the content of the 3,4 structure in PI increases, the Θ temperature decreases. On the other hand, the Θ temperature in dioxane is 47.7 °C if the PI has an all-trans 1,4 structure.[9] Therefore dioxane may not necessarily be a poor solvent for PI with 3,4 structure of about 40% or more.

Morphological Properties. Sample SAI-3 has a higher content of PI than SAI-1, while SAI-4 has a lower content. The morphologies of the SAI-3, SAI-1, and SAI-4 films cast from dioxane and benzene are compared in Figures 1 and 2, respectively. Practically no effect of solvent is observed, particularly in the SAI-3 and SAI-4 films, though a difference can be observed between SAI-1 films cast from dioxane and from benzene (Figures 1b and 2b). Although the photographs of the films cast from THF are not shown here, their domain structures are practically the same as those of the films cast from benzene. Thus the effect of casting solvent on the morphology of these triblock copolymer films is minor if the solvent is a good solvent for three components.

Much larger differences are found between the films of different polymer samples. If the isoprene content is high, PS rods are coaxially surrounded by a gray PA phase and the coaxial rods run in the matrix of dark-stained PI (see Figures 1a and 2a). The domain structures of SAI-1 in Figures 1b and 2b are quite different from those of SAI-3. From the cross section, which is observed in Figure 2b, it is clear that the structure is a highly ordered one with an array of PS rods and PI islands in a PA matrix. PS rods are hexagonally arranged and PI islands are located with high regularity at the vertices of a hexagon whose center is occupied by a PS rod. The cross sections in Figures 1a and 2b are enlarged in Figures 3a and 3b, respectively. Their structures are schematically illustrated below the photographs.

The domain structure of the SAI-1 film cast from dioxane in Figure 1b is practically the same as that reported previously.[4] This is, the film has a lamellar structure of PS and PA, with PI islands dispersed in the PA phase. Despite careful examination of the electron micrographs, we did not observe the cross section of rods in the structure of SAI-1 films cast from dioxane, thus indicating the lamellar morphology.

If the isoprene content is very low (Figures 1c and 2c), the PS phase forms a matrix with embedded fused rods of PI and PA. It was previously reported[4] that PA may

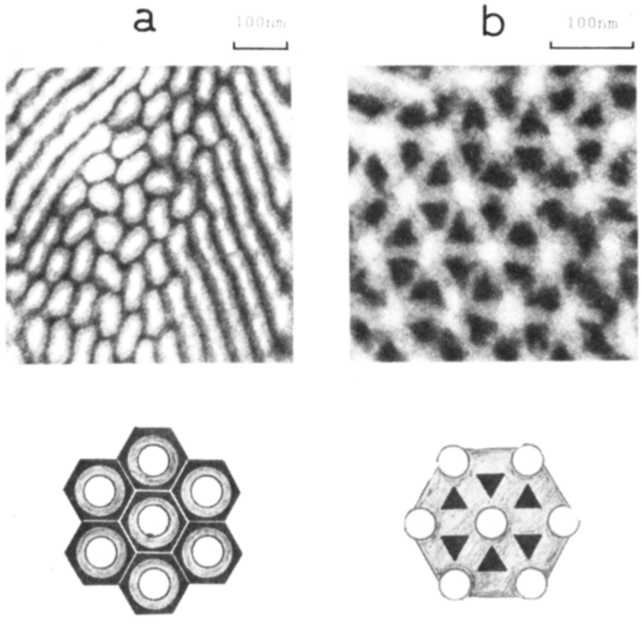

Figure 3. Detailed structures of the cross sections in Figures 1a and 2b and their schematic representations: (a) SAI-3 film cast from dioxane; (b) SAI-1 film cast from benzene.

be compatible, to some extent, with PI. The microphase separation was not complete in a diblock copolymer of PI and PA with molecular weights of 3.0×10^4 and 5.8×10^4, respectively. Moreover, as will be reported elsewhere, the mechanical dispersions of PI and PS in these triblock copolymers occur at positions considerably different from those in the diblock copolymers of PI and PS.

Cyclohexane, which is different from the other three casting solvents in being a poor solvent for PS, has a large effect on the morphology of the triblock copolymers. The electron micrographs of three sample films cast from cyclohexane are shown in Figure 4. In Figures 4a and 4b, PA and PI form a wormlike matrix in which isolated islands of PS are dispersed. The morphology of SAI-4 in Figure 4c resembles a lamellar structure but the domain boundary is not clear.

The domain size changes with the molecular weights of the three samples. The thickness of the quasi-lamellar spacing or the distances between the nearest-neighboring rods determined from the electron micrographs are listed in Table III. The values are comparable to the unperturbed root-mean-square of the end-to-end distances of the three samples, as was discussed by Shibayama et al.[5] The theory of microphase separation of diblock copolymers has extensively been developed by Meier, Helfand, and others.[10-13] The theories, however, are not applicable because of the complicated structures of the present systems.

Table III
Domain Sizes Determined from the Electron Micrographs

	casting solvent		
sample	dioxane	benzene	THF
SAI-3	55–65	55–68	56–78
SAI-1	51–65	53–67 (63–75)[a]	46–62
SAI-4	33–38	35–42	34–40

[a] The values in parentheses are the distances between the nearest-neighboring rods.

Discussion

The microphase separation structures of SAI-3 and SAI-1 in Figures 1 and 2 give us an idea of their basic structures. If the isoprene content is high (SAI-3), the basic structure may be a PS rod surrounded by PA and embedded in a PI matrix, as schematically shown in Figure 3a. It is clear that the domain structure of SAI-3 in Figure 1a, 2a, or 3a is an assembly of these basic rods.

If the isoprene content is not high enough to embed the coaxial rods of PS and PA, the basic structure may be the coaxial rod of PS and PA around which PI grains are attached. If these basic rods aggregate to form a structure, PI cannot be the matrix, and the coaxial rods of PS and PA must touch each other. Then PI would be distributed at their interstices. This model appears to represent the structure of SAI-1 films cast from benzene in Figure 2b or 3b. Moreover, the cross sections of the PI phases in Figure 3b are clearly triangular. This means that the hexagonal frame of PS and PA was first formed in the structure. Because of the presence of triangular PI islands, it appears that PS rods are connected by bridges of PA.

Such a highly ordered cross section as in Figure 3b is not observed in Figure 1b. The domain structure in Figure 1b was regarded as a lamellar structure in previous works.[4,5] However, the difference between the domain structures in Figures 1b and 2b may be minor. The structure in Figure 2b may also be regarded as a quasi-lamellar structure if only the bottom part of the figure is observed. Moreover, we have the quasi-lamellar structure of Figure 1b if the separation between PS rods by PA is not complete

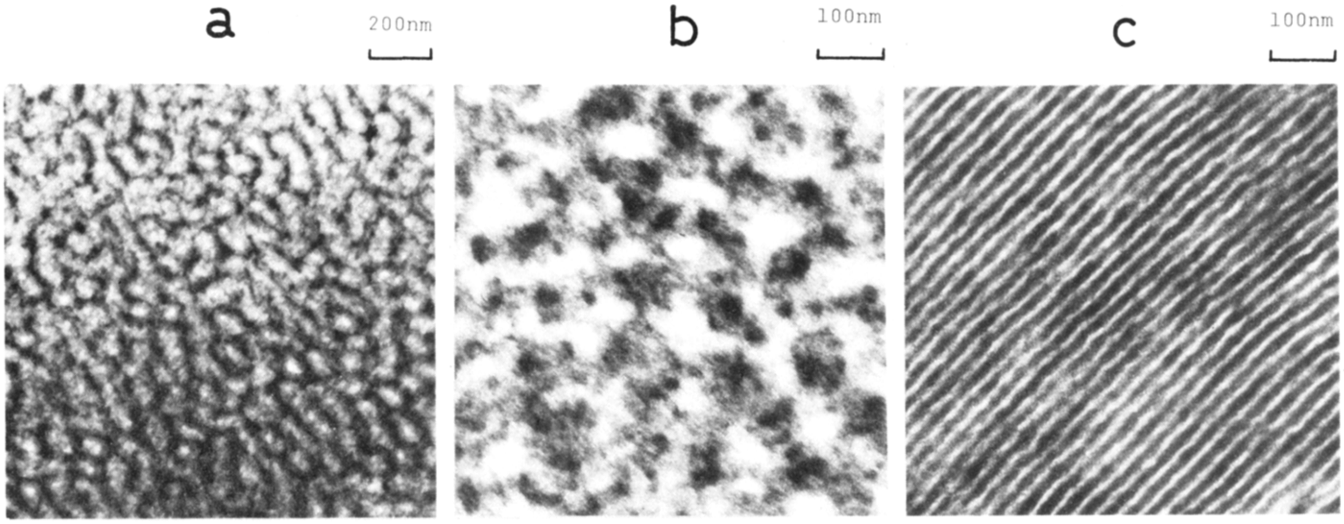

Figure 4. Electron micrographs of three triblock copolymer films cast from cyclohexane: (a) SAI-3; (b) SAI-1; (c) SAI-4.

in the schematic model of Figure 3b.

Acknowledgment. We thank the Ministry of Education, Science and Culture for support through a Grant in Aid for Scientific Research (Grant 547087).

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_3N)–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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