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Preparation and Characterization of a Pentablock Copolymer of the ABACA Type

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ABSTRACT: SIA triblock copolymer and ISIAI pentablock copolymer were prepared from styrene (S), isoprene (I), and (4-vinylbenzyl)dimethylamine (A). Films of both copolymers cast from a common good solvent for the three components (benzene) have the same lamellar microphase separation structure. It is expected that the films of ISIAI will be tougher than those of SIA when the S and A parts are chemically modified.

Introduction

The synthesis, characterization, morphology, and properties of AB-, ABA-, and $(AB)_n$-type block copolymers, containing only two different polymer segments, have been studied extensively and are summarized in the literature.[2-4] Recently, ABC-type triblock copolymers have begun to attract much attention and have been reported.[5-12] The triblock copolymer poly[styrene-*b*-(4-vinylbenzyl)dimethylamine-*b*-isoprene] (abbreviated SAI) is one of them.[13] From recent work on these triblock copolymers,[13-16] it was concluded that they have a clear microphase separation structure of their three components if their films are cast from a common good solvent for the three components. The films are expected to be useful as functional membranes since the S and A parts can easily be modified. Films of such linear polymers, however, have the disadvantage that they may not be tough enough if one or two phases are chemically modified, though the film processing of linear polymers can easily be carried out.

Cross-linking may be a method for strengthening the films. Here, however, we propose another method in which the phases to be chemically modified are sandwiched by a supporting component (I in this case). That is, if we prepare the pentablock copolymer poly[isoprene-*b*-styrene-*b*-isoprene-*b*-(4-vinylbenzyl)dimethylamine-*b*-isoprene] (ISIAI), its films should have the same microphase separation structure as and would be tougher than the films of poly[styrene-*b*-isoprene-*b*-(4-vinylbenzyl)dimethylamine] (SIA). In previous work,[13] sequential anionic copolymerization could not be carried out in the order S–I–A but could only be carried out in the order S–A–I. In this work, it was found that the trouble was caused by impurities in the (4-vinylbenzyl)dimethylamine monomer (4-VBDMA). When the monomer was purified, it became possible to prepare multiblock copolymers having any sequential order of the three components. In this paper, we report details of the preparation and also the characterization, both molecular and material, of triblock (SIA) and pentablock (ISIAI) copolymers.

Experimental Section

Reagents. The initiator, *sec*-butyllithium (*sec*-BuLi), was prepared by the reaction of *sec*-butyl bromide with lithium in *n*-heptane. The concentration of initiator was determined by titration with a HCl solution.

Isoprene was dried over calcium hydride and also over sodium metal under reduced pressure and then purified by addition of *n*-BuLi. Styrene was first dried over calcium hydride under reduced pressure, then purified with benzophenone–sodium, and finally diluted to about 15% with purified benzene. The monomer 4-VBDMA, synthesized by the method of Higo et al.[17] and dried over calcium hydride under reduced pressure, was purified with benzophenone–sodium as in previous work.[13,17] However, it was thought that the purification was not very satisfactory. In the present work, therefore, the monomer was further purified by (triphenylmethyl)lithium [$(C_6H_5)_3CLi$] in the presence of excess lithium bromide (LiBr). The pure $(C_6H_5)_3CLi$ or an equimolar mixture of $(C_6H_5)_3CLi$ and LiBr initiates the polymerization of 4-VBDMA. In the presence of excess amounts of LiBr, however, $(C_6H_5)_3CLi$ does not initiate the polymerization but simply reacts with impurities in 4-VBDMA. $(C_6H_5)_3CLi$ was prepared by the reaction of triphenylmethyl bromide with lithium metal in tetrahydrofuran (THF) at 298 K. The additive LiBr, prepared by heating $LiBr{\cdot}H_2O$, was dissolved in a THF solution of $(C_6H_5)_3CLi$. 4-VBDMA thus purified was diluted to about 15% with purified benzene.

The benzene used for polymerization and the *n*-heptane used for the initiator solution were distilled, with the addition of *n*-BuLi after the usual purification. Benzene, toluene, and cyclohexane, which were used for the characterization of the polymer, were fractionally distilled over sodium metal wire after being washed with sulfuric acid. THF used for gel permeation chromatography was Nakarai Chemicals, Ltd., GR grade.

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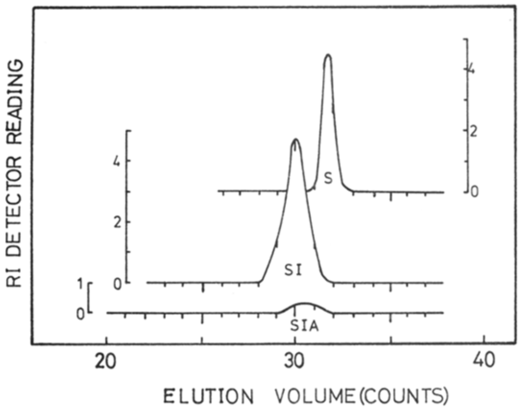

Figure 1. GPC chromatograms of TUN-101 and its precursors, S and SI. Carrier is THF at 308 K. Flow rate, 1.6 mL/min; concentration, 0.1 g/dL.

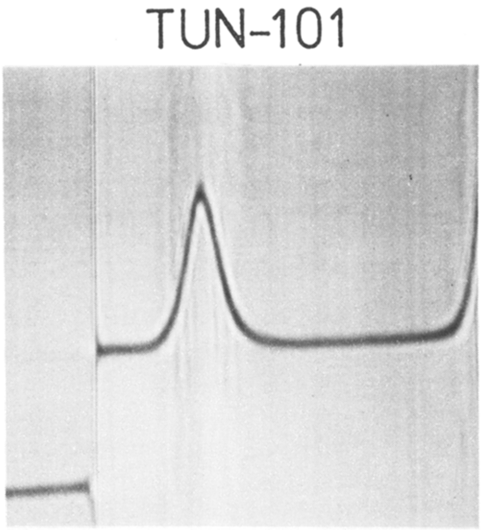

Figure 2. Sedimentation pattern of TUN-101. Solvent, THF; temperature, 298 K; speed of rotation, 59 780 rpm; angle, 75°; concentration, 0.7 g/dL; time, 118 min.

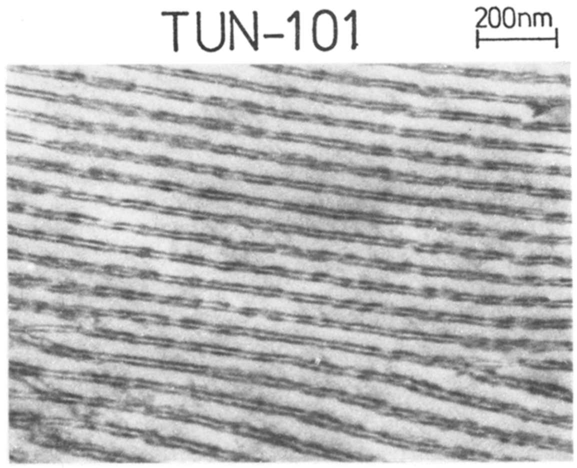

Figure 3. Electron micrograph of TUN-101 film stained with OsO_4. Cast from 5 wt % benzene solution. Light band, S phase; gray band, A phase; dark band, I phase.

Polymerization. Poly(4-VBDMA), triblock copolymer SIA, and pentablock copolymer ISIAI were prepared by a living anionic polymerization technique. Polymerizations were carried out in a sealed glass apparatus under a pressure of 10^{-6} torr. The polymerization techniques are almost the same as those employed in previous work.[13,18,19] The anionic polymerization of the triblock copolymer SIA was carried out by a three-stage sequential addition of styrene, isoprene, and 4-VBDMA in benzene, using *sec*-BuLi as the initiator. The triblock copolymer polymerization in the order of SIA was not successful in previous work[13] but could successfully be carried out in this work, probably because 4-VBDMA was better purified. The anionic polymerization of pentablock copolymer (ISIAI) was also carried out by a five-stage sequential addition.

For characterization of each component in those block copolymers, precursors were sealed off before the next monomer was added. That is, S and SI precursors were sealed off in the preparation of the triblock copolymer SIA, and also IS and ISIA precursors in the preparation of the pentablock copolymer ISIAI.

The anionic polymerization of 4-VBDMA was carried out at concentrations lower than 3 wt %. It was previously confirmed that the molecular weight distribution of poly(4-VBDMA) obtained is sharp if the monomer concentration is as low as 3 wt %.[17]

Molecular Characterization. Number-average molecular weights, M_n, of the block copolymers and their precursors were determined by osmometry in toluene at 303 K with a Hewlett-Packard Type 502 high-speed membrane osmometer. Molecular heterogeneities of the triblock copolymer SIA and the precursors were tested by gel permeation chromatography in THF at 308 K using a Toyo Soda Ltd. HLC Type 827 having high-resolution columns (GMH6 × 2) and also by ultracentrifugation in THF at 298 K using a Beckman Spinco Model E analytical ultracentrifuge.

Material Characterization (Morphology). The triblock copolymer SIA and the pentablock copolymer ISIAI were cast from 5 wt % benzene or 5 wt % cyclohexane solutions, all into thin films of about 0.2 mm thickness on mercury by evaporating the solvents gradually at 303 K. Benzene is a common good solvent for the three components. Cyclohexane is a good solvent for both poly(4-VBDMA) and polyisoprene but a Θ solvent for polystyrene at 307 K. The films obtained were completely dried under a reduced pressure of 10^{-4} torr for 3 days at 313 K. The films, stained with the fixing reagent osmium tetraoxide (OsO_4), were embedded in a resin and cut into ultrathin sections by an ultramicrotome. Some ultrathin sections were further fixed with the vapor of OsO_4. The morphology of these sections was examined by a Hitachi Type HU-12 transmission electron microscope.

Results and Discussion

Poly(4-VBDMA) Having High Molecular Weight. The poly(4-VBDMA) polymerization results are shown in Table I. The molecular weight is much higher than in previous work.[17] The conversion is 100%, within experimental error. The molecular weight observed is close to the value expected from the amounts of monomer and initiator used. Thus it is certain that 4-VBDMA was satisfactorily purified with $(C_6H_5)_3CLi$ in the presence of excess LiBr.

Triblock Copolymer SIA. Polymerization results of the triblock copolymer SIA are also shown in Table I. The conversion is 100%. The molecular weights of the precursors and also the final triblock copolymer agree well with the values predicted from the amounts of monomers and initiator. The GPC chromatograms of S and SI precursors and also of the final triblock copolymer TUN-101 are shown in Figure 1. Figure 1 shows that the two precursors have a single and narrow molecular weight distribution, as expected. However, the chromatogram of the final triblock copolymer was abnormal because of the its adsorption on the GPC gel. Therefore, the final triblock copolymer was examined by the sedimentation pattern in Figure 2. TUN-101 has a single and narrow molecular weight distribution.

An electron micrograph of the triblock copolymer TUN-101 specimen cast from benzene solution and stained with OsO_4 is shown in Figure 3. Both polyisoprene and poly(4-VBDMA) phases can be fixed with OsO_4. However, the former is darker than the latter, as reported in the previous paper.[13] That is, the white band corresponds to the polystyrene phase, the gray band to the poly(4-

Table I
Preparation of Poly(4-VBDMA) and SIA-Type Triblock Copolymer[a]

sample code	amt of initiator $\times 10^4$, mol	amt of styrene, g	amt of isoprene, g	amt of 4-VBDMA, g	vol of benzene, cm^3	conversion, %	$10^{-4}M_n$ precursors S		final polymer SIA
							S	SI	
poly-(4-VBDMA)	0.32			9.0	280	100			28.1 (28.2)
TUN-101	2.15	12.4	9.7	13.3	373	100	5.4 (5.8)	9.9 (10.3)	16.4 (16.5)

[a] The values in parentheses show the molecular weights calculated from the amounts of monomer and initiator.

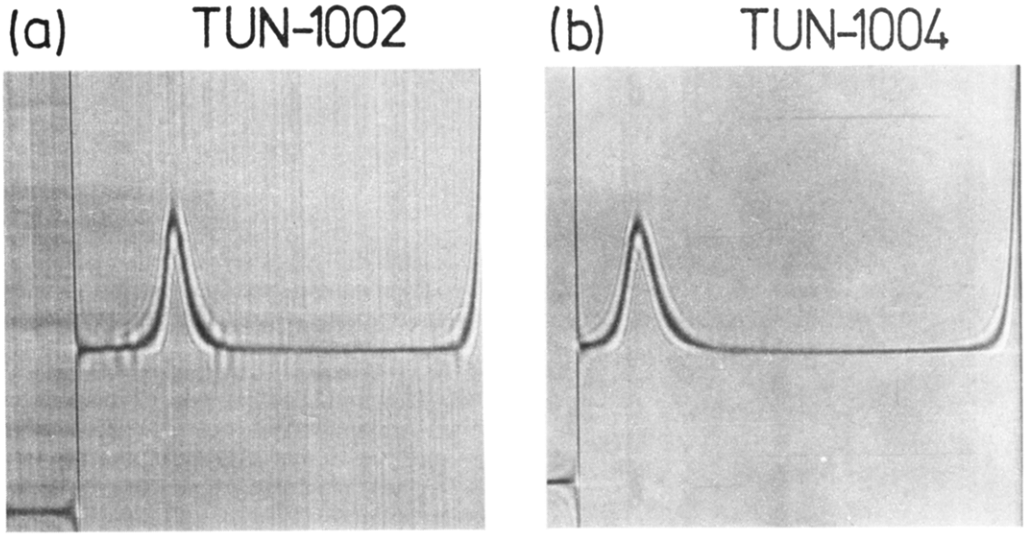

Figure 4. Sedimentation patterns of pentablock copolymers TUN-1002 (a) and TUN-1004 (b). Concentration, 0.5 g/dL; time, (a) 99 and (b) 110 min. Other experimental conditions are the same as in Figure 2.

VBDMA) phase, and the dark band to the polyisoprene phase. It can be concluded from Figure 3 that the lamellar structure is –I–S–I–A–I–.

Pentablock Copolymer ISIAI. Polymerization results of the pentablock copolymers ISIAI are shown in Table II. The conversions of two samples, TUN-1002 and TUN-1004, are almost 100% and their molecular weights agree well with the values calculated. Sedimentation patterns of TUN-1002 and TUN-1004 as shown in Figures 4a and 4b, respectively, show that both samples have single peaks and narrow molecular weight distributions. An electron micrograph of the TUN-1002 specimen cast from benzene solution and stained with OsO_4 is shown in Figure 5a, while that of a film cast from a cyclohexane solution is shown in Figure 5b. A clear lamellar structure is observed in Figure 5a. The lamellar structure is the same as that of the triblock copolymer SIA in Figure 3, that is, –I–S–I–A–I–. In Figure 5b, the islands of the polystyrene phase are dispersed in the mixed matrix of polyisoprene and poly(4-VBDMA).

Figure 6a shows an electron micrograph of a TUN-1004 specimen cast from benzene solution. Its microphase separation structure is three-component lamellar but the structure is not very clear, probably because of the short chain length of the polystyrene part. Figure 6b shows an electron micrograph of a TUN-1004 specimen cast from cyclohexane solution. Its microphase separation structure is the same as that of TUN-1002 in Figure 5b.

Thus it can be concluded that if the films are cast from benzene solutions, both the triblock copolymer of the SIA type and the pentablock copolymer of the ISIAI type give the same lamellar microphase structure. Moreover, we point out that the film of ISIAI is tougher than the films of SIA when the S or A part is sulfonated or quaternized

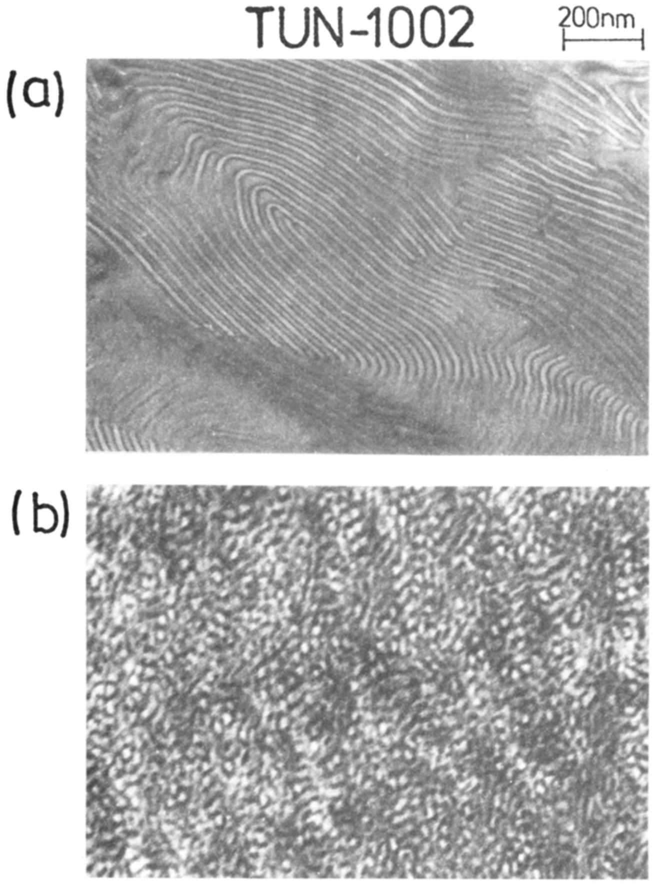

Figure 5. Electron micrographs of TUN-1002 film stained with OsO_4: (a) cast from 5 wt % benzene solution; (b) cast from 5 wt % cyclohexane solution.

Table II
Preparation of ISIAI-Type Pentablock Copolymers[a]

sample code	amt of initiator × 10^4, mol	amt of isoprene, g	amt of styrene, g	amt of isoprene, g	amt of 4-VBDMA, g	amt of isoprene, g	vol of benzene, cm³	conversion, %	$10^{-4}M_n$ precursors I	precursors IS	precursors ISI	precursors ISIA	final polymers ISIAI
TUN-1002	1.92	6.8	17.4	6.8	17.0	6.1	780	98		12.1		23.8	29.1
									(3.5)	(12.6)	(16.1)	(25.0)	(28.2)
TUN-1004	3.43	7.3	14.4	7.1	25.0	6.9	773	99		6.6		16.7	17.8
									(2.1)	(6.3)	(8.4)	(15.7)	(17.7)

[a] The values in parentheses show the molecular weights calculated from the amounts of monomer and initiator.

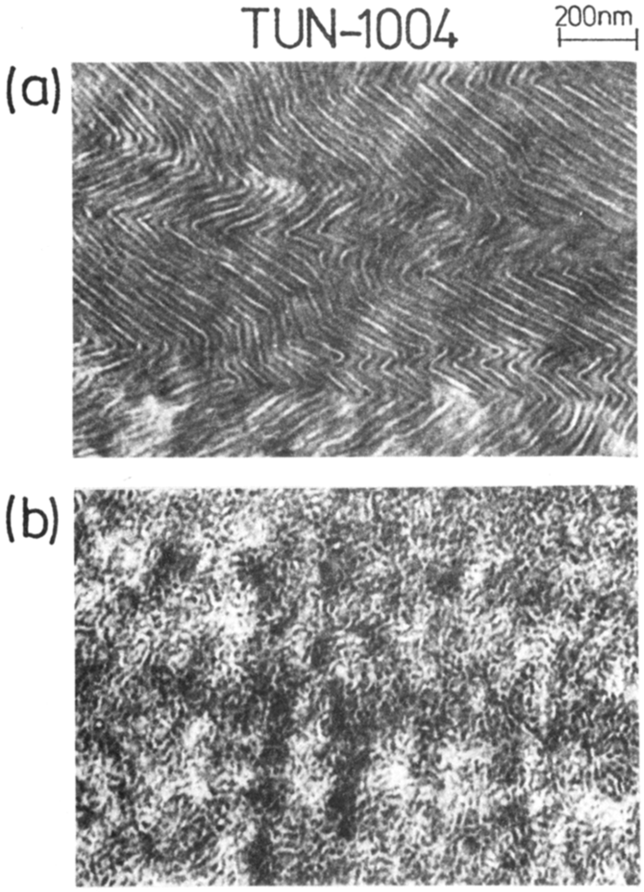

Figure 6. Electron micrographs of TUN-1004 film stained with OsO_4: (a) cast from 5 wt % benzene solution; (b) cast from 5 wt % cyclohexane solution.

(the experimental results are reported in the following paper[20]).

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Morphological and Mechanical Properties of Multiblock Copolymers

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ABSTRACT: The morphologies and the mechanical properties of two multiblock copolymers, a triblock copolymer of the SIA type and a pentablock copolymer of the ISIAI type with almost equal fractional compositions, were studied by electron microscopic methods and dynamic viscoelasticity investigations. Films of both types of multiblock copolymers have the same three-phase microdomain structures for a given casting solvent. In dynamic viscoelastic behavior, a new temperature transition is observed at about 233 K in both copolymers, but the temperature dependencies in the SIA type in the higher temperature region are different from those in the ISIAI type. Moreover, the latter films are stronger than the former. The difference in strength between them becomes remarkable when they are chemically modified. It is confirmed that films of ISIAI are tougher than those of SAI even through chemical modification.

Introduction

It was reported in a series of works on the ABC-type triblock copolymer poly[styrene-*b*-(4-vinylbenzyl)dimethylamine-*b*-isoprene] (abbreviated SAI) that various three-phase structures were observed, depending on the kind of casting solvent and/or the fractional compositions.[3-5] Moreover, it was confirmed in the previous paper[5] that the microphase-separated structure of SAI is as expected from the order of the three components in the molecule. Films of these copolymers are expected to be useful as functional membranes, since the S and A parts can easily be modified. From such a practical viewpoint, however, it would be presumed that SIA (poly[styrene-*b*-isoprene-*b*-(4-vinylbenzyl)dimethylamine]) or ISIAI (poly[isoprene-*b*-styrene-*b*-isoprene-*b*-(4-vinylbenzyl)dimethylamine-*b*-isoprene]) is more desirable than SAI. In a preceding paper,[2] multiblock copolymers SIA and ISIAI were prepared and it was reported that if the films are cast from benzene solutions, both triblock copolymer SIA and pentablock copolymer ISIAI give the same lamellar microphase structure. Moreover, it was pointed out that the film of ISIAI would be tougher than that of SIA when the S or A part is chemically modified. In this work, the morphological behavior and mechanical properties of multiblock copolymers of the SIA and ISIAI types prepared in the preceding work[2] are investigated as a function of casting solvent. Furthermore, those of the quaternized SIA and ISIAI are also studied.

Experimental Section

Samples. Triblock copolymer of the SIA type and pentablock copolymer of the ISIAI type having fairly narrow molecular weight distributions were prepared by the sequential anionic polymerization method of the previous work.[2] These polymers have nearly equal fractional compositions, but the isoprene part in the latter sample is divided into three equal parts. The molecular weights and the fractional compositions of these samples are listed in Table I. These values were determined by osmometry in the previous work.[2]

Table I
Molecular Characteristics of Multiblock Copolymers

sample code	type	wt fraction, % S	I	A	$10^{-4}M_n$
TUN-101	SIA	34	28	38	16
TUN-1002	ISIAI	$36._5$	$32._2$	$31._3$	$29._1$

Film Preparation. The films used for observation of morphology and measurements of dynamic mechanical properties were prepared by a solvent casting method. That is, the solutions of the multiblock copolymers were cast into thin films of about 0.2-mm thickness on mercury by evaporating the solvent gradually from benzene, cyclohexane, or dioxane solution of about 5 wt % for about 5 days at 30 °C. The films thus formed were further dried in a vacuum oven for about 3 days. Benzene is a common good solvent for the three components. Cyclohexane is a good solvent for both polyisoprene (abbreviated as PI) and poly[(4-vinylbenzyl)dimethylamine] [P(4-VBDMA)] but a Θ solvent for polystyrene (PS) at 34 °C. Dioxane is a good solvent for both P(4-VBDMA) and PS but a Θ solvent for PI at 35 °C. All the films cast from these solvents were quite transparent and tough.

In order to examine the toughness of the cast films after chemical modification of multiblock copolymers, quaternization of the P(4-VBDMA) part was carried out by keeping the as-cast films in contact with a vapor of methyl iodide for about 2 days at room temperature.

Morphology. The thin films thus obtained were stained with osmium tetraoxide (OsO_4). OsO_4 is a selective staining reagent for the PI and P(4-VBDMA) components, but the PI domains are stained more heavily than P(4-VBDMA).[3,4] Stained films were embedded in epoxy resin and cut into ultrathin sections by an ultramicrotome. The ultrathin sections of the films were floated on 10% ethanol aqueous solution, subsequently dried, and subjected to electron microscopic observations. Some of the ultrathin sections were further stained with OsO_4 vapor. A Model HU-12 (Hitachi Seisakusho) transmission electron microscope and a Model JEM-100U (Nihon Denshi) were used for morphological observation.

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