Artificial Membranes from Multiblock Copolymers. 2. Molecular Characterization and Morphological Behavior of Pentablock Copolymers of the ISIAI Type

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ABSTRACT: Pentablock copolymers of the ISIAI type, poly(isoprene-*b*-styrene-*b*-isoprene-*b*-(4-vinylbenzyl)dimethylamine-*b*-isoprene), were prepared by sequential anionic polymerization with *sec*-butyllithium as the initiator and benzene as the solvent. They were characterized by GPC, ultracentrifugation, and osmometry. The morphologies of the films of these samples cast from benzene, dioxane, and cyclohexane solutions were studied by electron microscopy and viscoelastic spectrometry. The main results are as follows: (1) the morphologies are dependent on the kind of casting solvent employed; (2) three-layer lamellar structures are observed for the benzene- or dioxane-cast films of the samples with isoprene content of about 30–50% in weight if the molar weights of styrene block and amine block are nearly equal; (3) the samples in which the lengths of three isoprene blocks are equal or in which the length of the middle isoprene block is larger than those of two terminal isoprene blocks are favorable for lamellar structure.

Introduction

Multiblock copolymers in which microphase separation occurs are expected to be useful for preparing some functional membranes. However, the membranes are naturally required to be stable for chemical modifications. In preceding papers,[1,2] it was experimentally shown that films of the ISIAI-type pentablock copolymers may be tougher than those of the SIA-type triblock copolymers when S and A domains are chemically modified. The I domains can be used for maintaining the microphase structures of the membrane. The purpose of this work is to study the morphological behavior of the pentablock copolymers of the ISIAI type and to determine the experimental conditions for preparing membranes with three-layer lamellar structures.

Although extensive morphological studies have been done on diblock copolymers and the mechanism of microphase separation in diblock copolymers is now well elucidated,[3-5] few studies have been done on triblock copolymers of the ABC type[6-13] and only preliminary work[1,2] on pentablock copolymers of the ISIAI type has been reported by some of the present authors. To have well-defined microphase separation structures, it is necessary to have good homogeneity in both molecular weight and composition. Detailed molecular characterization of the pentablock copolymers is also a purpose of this work.

Experimental Section

Block Copolymers. All pentablock copolymers of the ISIAI type were prepared by a sequential anionic polymerization method,[1] in which isoprene, styrene, isoprene, (4-vinylbenzyl)dimethylamine (abbreviated as 4-VBDMA), and isoprene were added stepwise in this order. The polymerizations were carried out in benzene, using *sec*-butyllithium as initiator. Prior to the polymerization, these monomers and the solvent were purified by the methods described previously.[14] In Table I are listed the amounts of monomers added at each polymerization step, the amount of initiator used, the conversion of the polymerization, and the number-average molecular weights $\bar{M}_n$ of the final pentablock copolymers and their precursors. In this paper, styrene, 4-VBDMA, and isoprene are abbreviated by S, A, and I, respectively. That is, the designations IS, ISI, and ISIA mean block copolymers of isoprene and styrene, those of isoprene, styrene, and isoprene, and those of isoprene, styrene, isoprene, and 4-VBDMA, respectively. $\bar{M}_n$ of both precursors and final polymers were in good agreement with the kinetic molecular weights M_k calculated from the amounts of the monomers and initiator, assuming that the conversion was 100% in each polymerization.

The kinetic molecular weights M_k of each of the component blocks were calculated from the polymerization conditions and are shown in Table II, where I_1, I_3, and I_2 in parentheses denote the two terminal isoprene and the middle isoprene blocks, respectively. Samples TUN 1001, 1002, and 1003 were designed such that the M_k's of the S and A blocks are almost equal and also that the M_k's of the three I blocks are almost the same. The difference among three samples is in their ratios of the contents of S and A to that of I. In samples TUN 1008, 1009, and 1010, the M_k's of the S and A blocks and also the total I content are kept constant, but the ratio of M_k of the middle I block to those of the terminal I blocks is changed. That is, $M_k(I_1) = M_k(I_2) = M_k(I_3)$ in TUN 1008, $M_k(I_1) = M_k(I_3) < M_k(I_2)$ in TUN 1009, and $M_k(I_1) = M_k(I_3) > M_k(I_2)$ in TUN 1010.

Molecular Characterization. Heterogeneities in molecular weights of pentablock copolymers and their precursors were tested by gel permeation chromatography (GPC), where a high-speed liquid chromatograph (HLC 803D, Toyo Soda Mfg. Co., Ltd., equipped with a 60-cm GMH_6 column) was used. For precise observation of the GPC elution patterns in the region of lower molecular weights, the column was replaced by a 60-cm $G4000H_8$ column. Both columns were packed with cross-linked polystyrene gels (TSK-GEL). The detector system consisted of a low-angle laser light scattering (LALLS) photometer (LS-8), Toyo Soda Mfg. Co., Ltd.) and a differential refractometer (RI-8, Toyo Soda Mfg. Co., Ltd.) connected in series. The initial concentration of polymer was 0.03–0.07 wt %, a 0.5-cm^3 sample was used, and the flow rate was 1 cm^3/min.

We observed serious adsorption of our pentablock copolymers onto the above columns if tetrahydrofuran (THF) was used as the eluent. The same phenomenon was reported by Arai et al.[11] when a triblock copolymer of styrene, butadiene, and 4-vinylpyridine was analyzed with G4000H columns in chloroform. The amine groups of these polymers may interact with a very small amount of residual carboxy groups on the gels. In order to prevent such an interaction, a small amount of *N,N*-dimethylbenzylamine (DMBA) (5% in volume) was added to THF. The molecular weight vs. elution time relationship determined with a series of Toyo Soda's standard polystyrene samples was almost unchanged by the addition of DMBA, as shown in Figure 1.

Molecular heterogeneities of the pentablock copolymers were also tested by ultracentrifugation of THF solutions at 298 K, using an analytical ultracentrifuge, Beckman Spinco Model E.

Number-average molecular weights, $\bar{M}_n$, of the pentablock copolymers and their precursors were determined by osmometry in toluene at 303 K with a Hewlet-Packard high-speed membrane osmometer, Type 502.

Film Preparation. Films of about 50-μm thickness were cast on mercury from 5 wt % solutions of pentablock copolymers, using benzene, dioxane, and cyclohexane as solvents. Benzene is a good solvent for the three components: polystyrene, poly[(4-vinyl-

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

sample code	amt of initiator × 10^4/mol	amt of monomer/g: I	S	I	4-VBDMA	I	convrsn/%	$\bar{M}_n/10^5$ precursors: IS	ISI	ISIA	final polymers: ISIAI
TUN 1001	1.16	7.6	11.4	7.5	11.2	7.6	96	1.6_2 (1.64)	— (2.28)	3.2_0 (3.25)	3.9_0 (3.91)
TUN 1002	1.92	6.8	17.4	6.8	17.0	6.1	98	1.2_1 (1.26)	— (1.61)	2.3_8 (2.50)	2.9_1 (2.82)
TUN 1003	2.63	4.5	19.5	3.7	19.3	4.3	97	0.84 (0.91)	— (1.05)	1.8_1 (1.79)	1.9_4 (1.95)
TUN 1008	1.08	6.5	9.6	6.5	13.9	6.2	97	1.4_3 (1.49)	2.1_2 (2.09)	3.2_4 (3.38)	3.8_2 (3.95)
TUN 1009	1.34	4.1	10.6	13.5	16.6	4.1	97	1.0_7 (1.10)	2.0_9 (2.10)	3.2_4 (3.34)	3.4_0 (3.65)
TUN 1010	1.34	8.9	11.1	3.1	16.4	8.9	98	1.4_1 (1.49)	1.6_4 (1.72)	3.0_4 (2.95)	3.5_6 (3.61)

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

Table II
Kinetic Molecular Weights M_k of the Five Component Blocks of the Pentablock Copolymers

sample code	$M_k/10^4$: $M_k(I_1)$	$M_k(S)$	$M_k(I_2)$	$M_k(A)$	$M_k(I_3)$
TUN 1001	6.6	9.8	6.5	9.7	6.6
TUN 1002	3.5	9.1	3.5	8.9	3.2
TUN 1003	1.7	7.4	1.4	7.3	1.6
TUN 1008	6.0	8.9	6.0	12.9	5.7
TUN 1009	3.1	7.9	10.1	12.4	3.1
TUN 1010	6.6	8.3	2.3	12.2	6.6

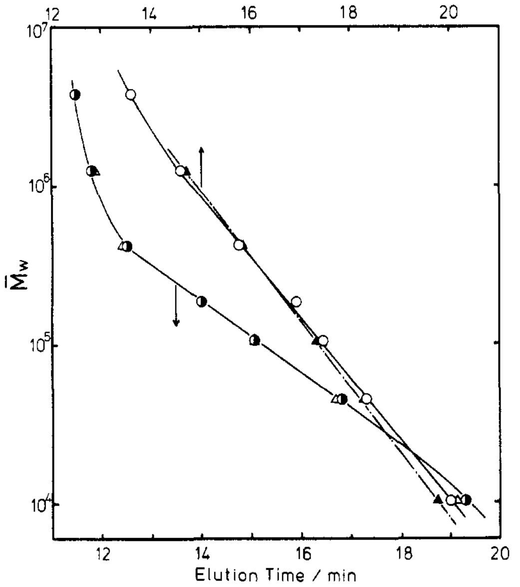

Figure 1. Molecular weight vs. elution time relationships of the GPC systems determined by the usual peak method with Toyo Soda's standard polystyrene samples: (▲) GMH_6 column and THF; (○) GMH_6 column and THF containing DMBA; (△) $G4000H_8$ column and THF; (◑) $G4000H_8$ column and THF containing DMBA.

benzyl)dimethylamine] [poly(4-VBDMA)], and polyisoprene. Cyclohexane is a good solvent for both poly(4-VBDMA) and polyisoprene but a poor solvent for polystyrene. Dioxane is a good solvent for both poly(4-VBDMA) and polystyrene but a poor solvent for polyisoprene. The solvents were evaporated slowly at 25 °C over a period of 4–7 days under an atmosphere of dry air. The cast films were then dried in vacuo for about 5 days at room temperature.

Quaternization of the A part was performed by keeping the as-cast films in contact with methyl iodide vapor for about 2 days at room temperature. The films were further dried in vacuo for 2 days at 40 °C.

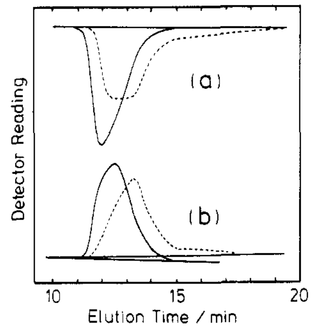

Figure 2. GPC chromatographs of sample TUN 1008 measured with $G4000H_8$ column: (a) detected by LS-8; (b) detected by RI-8. The full curves were measured with THF containing 5 vol % DMBA and the dotted curves were measured with pure THF.

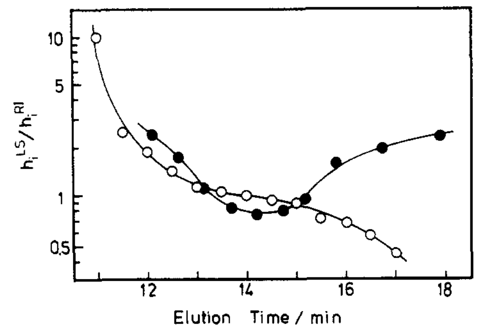

Figure 3. Ratio h_i^{LS}/h_i^{RI} calculated from the chromatograms of TUN 1008, shown in Figure 2. h_i^{LS} and h_i^{RI} are the heights of an ith cut of the chromatograms detected by LS-8 and RI-8, respectively. (●) THF; (○) THF + DMBA.

Observation by Electron Microscopy. The as-cast and quaternized films were exposed to a 1% aqueous solution of osmium tetraoxide (OsO_4), which stains the I domain more heavily than the A domain but does not stain the S domain at all. The films were then cut into ultrathin sections and observed by transmission electron microscopy using Model HO-12 (Hitachi Seisakusho) and Model JEM-100U (Nihon Denshi) electron microscopes.

Viscoelastic Measurements. Measurements of the storage and loss moduli (E' and E'', respectively) were made with a VES-S viscoelastic spectrometer (Iwamoto Seisakusho), where the temperature was increased from 173 to 433 K at a rate of 1 K/min at a fixed frequency of 10 Hz.

Results and Discussion

Molecular Characterization. GPC chromatograms of sample TUN 1008 detected with the LS-8 detectors are shown in Figure 2, where the curves measured by using

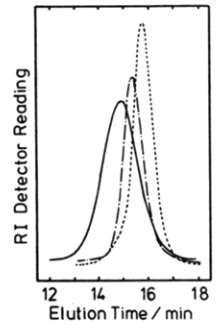

Figure 4. GPC chromatograms of sample TUN 1008 and its IS and ISI precursors measured with GMH$_6$ and THF containing DMBA as the column and eluent, respectively, and detected by RI-8: fulll curve, pentablock copolymer TUN 1008; dotted curve, IS precursor; dot–dash curve, ISI precursor.

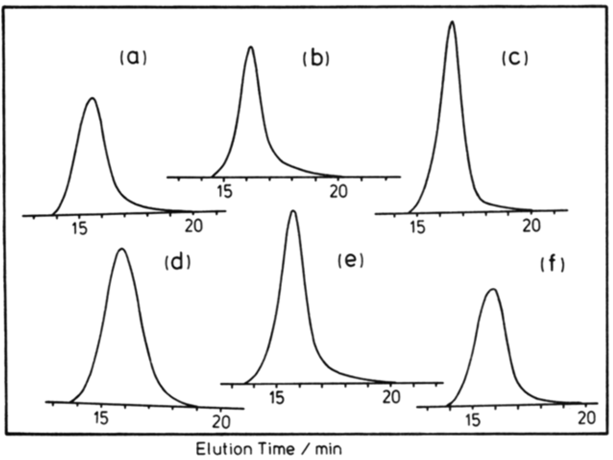

Figure 5. GPC chromatograms of the pentablock copolymers measured with G4000H$_8$ and THF containing DMBA as the column and eluent, respectively, and detected by RI-8: (a) TUN 1001; (b) TUN 1002; (c) TUN 1003; (d) TUN 1008; (e) TUN 1009; (f) TUN 1010.

tetrahydrofuran containing 5 vol % *N*,*N*-dimethylbenzylamine as the eluent are compared with those measured by using pure tetrahydrofuran. More pronounced tailing of the chromatographic peaks was observed for the latter than for the former eluent. In Figure 3, the ratio $h_i^{\rm LS}/h_i^{\rm RI}$ calculated from the chromatograms in Figure 2 is plotted against elution time, where $h_i^{\rm LS}$ and $h_i^{\rm RI}$ are the heights of an *i*th cut of the chromatograms detected by LS-8 and RI-8, respectively. The value of $h_i^{\rm LS}/h_i^{\rm RI}$ is approximately proportional to the molecular weight of the *i*th cut. Although the ratio may be influenced by the composition,[15,16] the upswing in the region of late elution time in the curve with pure tetrahydrofuran suggests that relatively high molecular weight components were eluted late. This fact indicates the presence of adsorption of the sample onto the GPC column. On the other hand, the curve obtained with tetrahydrofuran containing *N*,*N*-dimethylbenzylamine shows a monotonic decrease in $h_i^{\rm LS}/h_i^{\rm RI}$ with time, indicating the absence of such adsorption.

Figure 4 shows GPC chromatograms of sample TUN 1008 together with those of its IS and ISI precursors, all of which were measured with amine-containing tetrahydrofuran. It can be seen that the chromatographic peak is shifted to the direction of higher molecular weight as the polymerization proceeds, and the final product TUN 1008 has a fairly narrow molecular weight distribution. The GPC chromatograms of the other samples used in this study are shown in Figure 5 together with that of TUN 1008. They display sharp peaks comparable to that of TUN 1008.

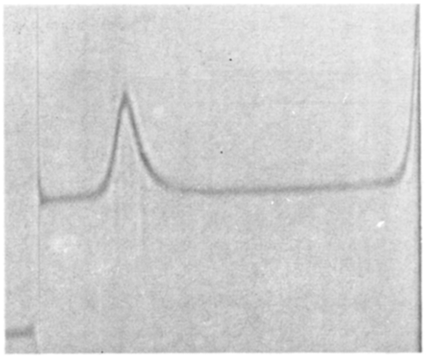

Figure 6. Schlieren sedimentation-boundary pattern of a 0.5 wt % solution of sample TUN 1008 taken after 100-min centrifugation at 59 800 rpm.

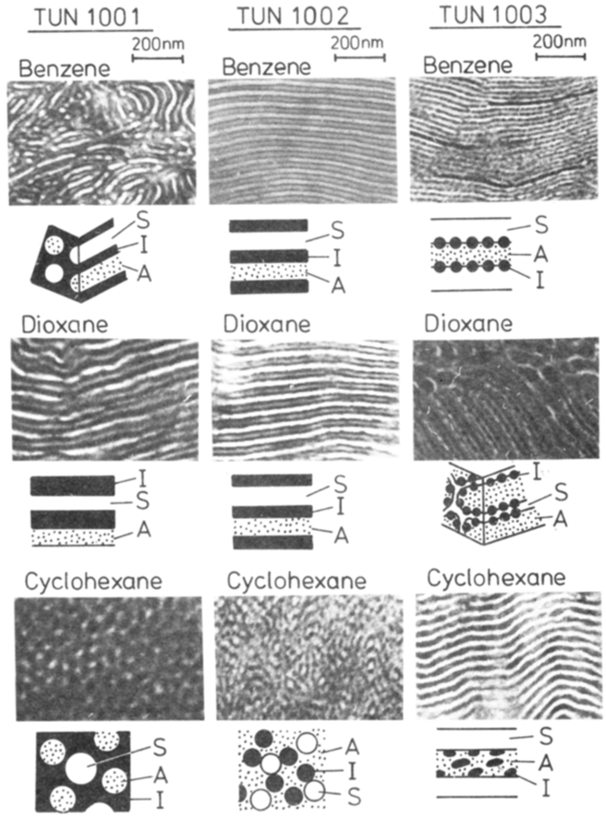

Figure 7. Electron micrographs of the as-cast films of samples TUN 1001, 1002, and 1003 cast from benzene, dioxane, and cyclohexane solutions and schematic illustrations of their microphase separation modes: S, polystyrene domain; I, polyisoprene domain; A, poly(4-VBDMA) domain.

Narrow molecular weight distributions of the pentablock copolymers were also confirmed by ultracentrifugation. Figure 6 shows a typical example of a schlieren sedimentation-boundary pattern of a 0.5 wt % solution of sample TUN 1008, which was taken after 100-min centrifugation at 59 800 rpm. It shows no undesirable shoulder indicative of heterogeneities in the sample. The sedimentation patterns for the other samples were almost the same as that for TUN 1008.

Electron Microscopy. Figure 7 shows electron micrographs of the as-cast films of pentablock copolymers TUN 1001, 1002, and 1003, together with schematic illustrations of their microphase separation modes. First, we compare the microphase structures of the films cast from benzene solutions. The micrograph of sample TUN 1001, which has the highest isoprene content among the samples, shows a chaos of small domains. But careful

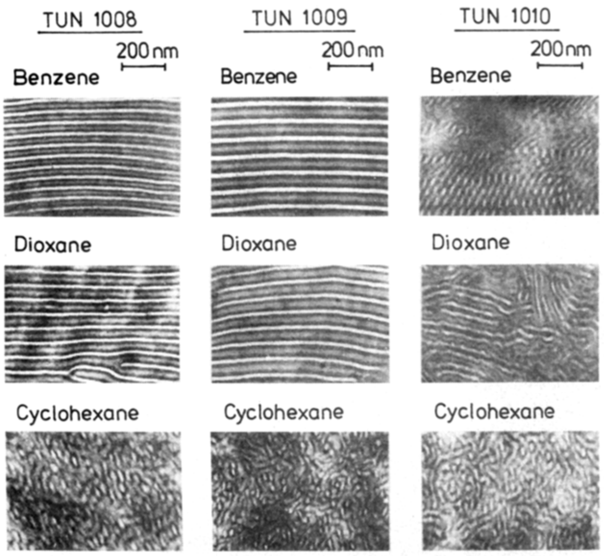

Figure 8. Electron micrographs of the as-cast films of samples TUN 1008, 1009, and 1010 cast from benzene, dioxane, and cyclohexane solutions.

observation can reveal that some parts in the micrograph show parallel arrays of three phases of S, I, and A, respectively, in the order of –I–S–I–A– and the other parts show spherical S and A domains in an I matrix. It is likely that sample TUN 1001 has a structure of irregularly winding rods of S and A in an I matrix. On the other hand, sample TUN 1002, which has a lower isoprene content than TUN 1001, shows a flat three-layer lamellar structure of the repeating unit –I–S–I–A–. In the micrograph of TUN 1003, which has the lowest isoprene content, we can find spherical domains of I dispersed at the phase boundaries of S and A lamellae. It thus can be said that in the case of benzene-cast films of samples in which $M_k(I_1) = M_k(I_2) = M_k(I_3)$ and $M_k(S) = M_k(A)$, the isoprene content must be at least in the range 25–50% in weight to have regularly arranged lamellae of S, A, and I.

The micrographs of the films cast from dioxane solutions in Figure 7 show fairly regular arrays of S, A, and I lamellae in the order –I–S–I–A– in samples TUN 1001 and 1002, though discontinuous (spherical) domains of I, partly discontinuous and partly continuous domains of A, and continuous domains of S can be observed in TUN 1003. In sample TUN 1003, the continuous domains of S seem to surround rodlike domains of A and the small spherical domains of I are dispersed at the boundaries of the S and A domains. It thus appears that when dioxane, a poor solvent of polyisoprene, is used for the film preparation, a lamellar structure can be formed only with higher isoprene contents than when benzene, a good solvent of the three components, is used.

The micrographs of the cyclohexane-cast films in Figure 7 show that S, A, and I block chains segregate into respective island-like microdomains in sample TUN 1001, while spherical domains of S and I are dispersed in an A matrix in sample TUN 1002, as was reported in the preceding paper.[2,3] In sample TUN 1003, on the other hand, A lamellae, in which spherical I domains are dispersed, and S lamellae are alternatively arranged in space. Accordingly, if cyclohexane, a poor solvent of polystyrene, is used, a sample of relatively low isoprene content likely will form a lamellar structure. However, a three-layer lamellar structure was not observed here.

In Figure 8 are shown the morphologies of a series of samples TUN 1008, 1009, and 1010, where the ratio of $M_k(I_2)$ to $M_k(I_1)$ or $M_k(I_3)$ was changed under the condition that the overall isoprene content was fixed at about 45% in weight, the degrees of polymerization of the A and S blocks are almost equal, and $M_k(I_1) = M_k(I_3)$. It is seen that the films of sample TUN 1008 cast from benzene and dioxane solutions show three-layer lamellar structures of –I–S–I–A–, while the film cast from cyclohexane solution does not show such a regular structure but shows a chaotic structure of S, A, and I domains, in which spherical S domains seem to be dispersed in the matrix of A and I domains. The morphologies of the films of TUN 1009 are not distinguishable from the corresponding ones of TUN 1008, in spite of the difference in molecular architecture. On the other hand, a regular array of lamellae is not observed in the films of TUN 1010 with any casting solvent. Thus, if $M_k(I_1) = M_k(I_2) = M_k(I_3)$ or $M_k(I_1) = M_5(I_3) < M_k(I_2)$, a three-layer lamellar array may be formed more easily than if $M_k(I_1) = M_k(I_3) > M_k(I_2)$.

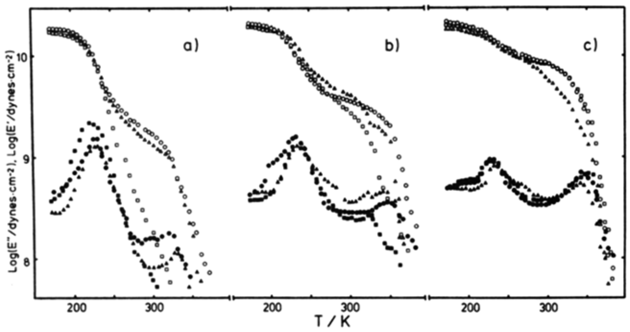

Figure 9. Temperature dependences of the dynamic Young's modulus E' and the loss modulus E'' of the specimens of TUN 1001, 1002, and 1003: (a) TUN 1001; (b) TUN 1002; (c) TUN 1003. Unfilled circles, triangles, and squares denote the Young's modulus E' and filled circles, triangles and squares denote the loss modulus E''. Triangles, cast from benzene solutions; circles, cast from dioxane solutions; squares, cast from cyclohexane solutions.

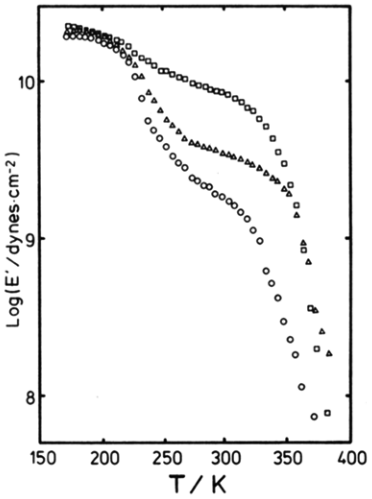

Figure 10. Temperature dependences of the dynamic Young's modulus E' of the specimens cast from dioxane solutions: circles, TUN 1001; triangles, TUN 1002; squares, TUN 1003.

Mechanical Properties. The composition and morphology of a block copolymer should influence its viscoelastic properties. In order to confirm the morphologies assumed from observation by transmission electron microscopy for our pentablock copolymers, we show the temperature dependences of the dynamic Young's modulus E' and the loss modulus E'' of the films of TUN 1001, 1002, and 1003 cast from benzene, dioxane, and cyclohexane solutions in Figures 9 and 10. Although the data of TUN 1002 were shown elsewhere, they are again shown here for comparison. In Figure 9, two or three E'' peaks are ob-

Table III
Transition Temperatures of ISIAI-Type Pentablock Copolymers

	transition temp/K		
sample code	benzene	dioxane	cyclohexane
TUN 1001	231, 333	230, 325	227
TUN 1002	238, 323, 343	233, 349	233, 325, 353
TUN 1003	233, 343	229, 346	232, 353

served for each specimen, except for the cyclohexane-cast film of TUN 1001, which shows only one peak. Their peak temperatures are listed in Table III. The E'' peaks which appear at 227–238 K may be assigned to the transitions of I domains as described in the preceding paper.[2] The peaks in the region of higher temperature, which appear at 325–353 K, should be related to the transitions of A and S domains, but unambiguous assignments are difficult. The peaks are located between the glass transition temperatures of poly[(4-vinylbenzyl)dimethylamine] and polystyrene.

In the graphs for TUN 1001 in Figure 9, E' of the cyclohexane-cast specimen falls rapidly as compared to those of the other specimens after the first transition appears. As is well-known, E' of a specimen having a multiphase structure is strongly dependent on the properties of the continuous phases.[17,18] Such a viscoelastic behavior of TUN 1001 is consistent with the morphology described above; in the specimen cast from cyclohexene solution, the S and A block chains are segregated into respective discontinuous spherical domains (hard domains) dispersed in the soft I matrix, while in the specimens cast from benzene and dioxane, they are segregated into respective continuous rods or lamellae. Also in the case of TUN 1002, E' of the specimen cast from cyclohexane solution decreases more rapidly than the other specimens, although not as remarkably as in the case of TUN 1001. This feature of E' in the cyclohexane-cast specimen of TUN 1002 can be attributed to its morphology, in which the continous phase is not I, but A. A different situation is encountered in the E' curves for TUN 1003, in which the value of E' for the cyclohexane-cast specimen is not lower than those for the other specimens but higher than that for the benzene-cast one and comparable to that for the dioxane-cast one in the temperature region between the first and second transitions. This elevated E' value of the cyclohexane-cast specimen can be ascribed to the continuity of the S domain.

The values of E' for TUN 1001, 1002, and 1003 are replotted in Figure 10. In the temperature region below the first transition, every specimen shows almost the same value, while, in the region between the first and second transitions, TUN 1001 and 1002 show a more rapid decrease with increasing temperature than does TUN 1003. This is mainly attributable to the morphological difference between the I domains of these specimens; those of TUN 1001 and 1002 are lamellar but those of TUN 1003 are spherical.

Molecular Packing in Lamellae. When each block chain in the pentablock copolymers segregates into the lamellar domains arranged in the sequential order –I–S–I–A–, five spatial arrangements are possible, as shown in Figure 11. In the type a and b arrangements, the molecular chains are extended so that two ends of an A block are anchored to the adjacent I phases, respectively, as also are the two ends of an S block. In types c and e, on the other hand, an A block chain is turned back and both ends of the A block are anchored to the same I phase. In types d and e, the same arrangements are observed for the S block chains.

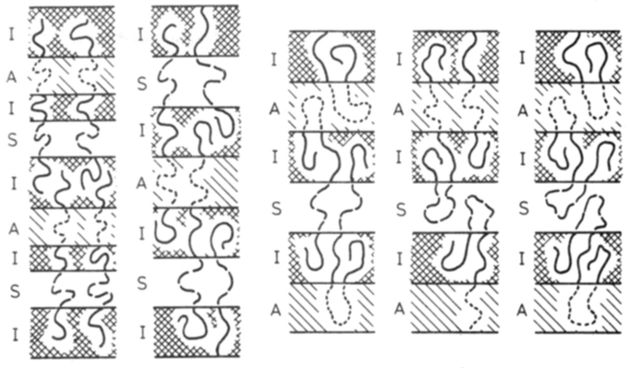

Figure 11. Spatial arrangements of the pentablock copolymers of the ISIAI type: I, polyisoprene domain; S. polystyrene domain; A, poly(4-VBDMA) domain.

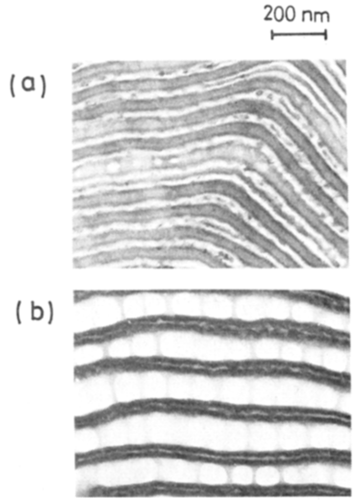

Figure 12. Electron micrographs of the quaternized films of samples TUN 1008 and 1009 prepared by treating the films cast from their dioxane solutions with methyl iodide vapor: (a) TUN 1008; (b) TUN 1009.

Samples TUN 1001, 1002, and 1008 have a composition of $M_k(I_1) = M_k(I_2) = M_k(I_3)$. If they have a molecular packing structure of type a, two I lamellae which are different in width by a factor of 2 should appear alternatively. However, the electron micrographs (Figures 7 and 8) show that this is not the case. The molecular arrangements in these samples should be one of the types b–e or their mixture.

In any type of packing from b to e, if $M_k(I_1) = M_k(I_2) = M_k(I_3)$, the middle I chain ($I_2$) will be more expanded than the terminal I chains (I_1 and I_3). If $M_k(I_1) = M_k(I_3) > M_k(I_2)$ such as in sample TUN 1010, the packing of I_2 chains in lamellar structures will be exceedingly unfavorable. If $M_k(I_1) = M_k(I_3) < M_k(I_2)$ such as in sample TUN 1009, the molecular chains can be easily packed without any expansion. In practice, TUN 1010 did not show a regular array of lamellae. And there was no distinguishable difference between the electron micrographs of TUN 1009 and 1008.

A difference between TUN 1009 and the other samples with $M_k(I_1) = M_k(I_2) = M_k(I_3)$ was found when their A domains were quaternized with methyl iodide. Figure 12 shows the electron micrographs of the quaternized films of samples TUN 1008 and 1009. A three-layer lamellar structure is observed for sample TUN 1008 just as in the case of its as-cast film. It was also the case for sample TUN 1002 as was reported in the preceding paper.[2] On the other hand, large holes were created in the quaternized

A domains of TUN 1009. These are considered to be caused by partial dissolution of the A domains during the treatment with aqueous solution of OsO_4. The same phenomenon was observed for the quaternized film of a triblock copolymer of the SIA-type.[2] In this connection, it can be pointed out that the molecular arrangement of type e in Figure 11 is equivalent to that of triblock copolymers as shown in Figure 3a of ref 3, in which adjacent I domains are not chemically bound by A or S block chains. This may become the reason for the film weaknesses to swelling by water of quaternized films of such molecular arrangements.

Thus type b or d is probably the dominant molecular arrangement of samples with $M_k(I_1) = M_k(I_2) = M_k(I_3)$ and type c or e is that of samples with $M_k(I_1) = M_k(I_3) < M_k(I_2)$ when they give three-layer lamellar structures of the type -I-S-I-A-.

It can be concluded that an ISIAI-type pentablock copolymer with isoprene content of about 30-50% in weight, $M_k(S) \approx M_k(A)$, and $M_k(I_1) \approx M_k(I_2) \approx M_k(I_3)$, is required in order to obtain a film with the three-layer lamellar structure of -I-S-I-A-, which is stable to chemical modifications. The preparation of a charge-mosaic membrane from such a pentablock copolymer and its performance will be reported in a subsequent paper.

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Chelating Copolymers Containing Photosensitive Functionalities

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ABSTRACT: A series of azoaromatic polyureas was synthesized with incorporated pyridine moieties as polymeric ligands. The activation energies for cis-trans thermal isomerization of these polyureas suggest similar energy barriers to low molecular weight analogues, as well as to polymers with different molecular weights and chain segments. An increase in E_a values was observed upon complexation with cobalt and nickel. The photodecrease in viscosity was more pronounced in the (PU-MDI-DAP)-Co complex than in the PU-MDI-DAP. The viscosity of the solution increased after complexation. Preirradiated polymer solutions showed a greater increase in viscosity and slightly larger incorporation of metal ion compared to its behavior in the dark. This observation is attributed to conformational rearrangement of the macromolecular ligand prior to complexation.

Introduction

The combination of a chelating agent and a readily isomerizable group in a synthetic macromolecule, the physical and mechanical properties of which can be controlled, presents the possibility of a structurally modifiable photosensitive ion switch. Though many have studied the photochemistry and cis-trans isomerization of azobenzene and its derivatives[1] and several groups have studied the effect of this isomerization process on the stereochemistry and properties of macromolecules,[2-5] there are no examples of conformational changes induced by the absorption of a specific wavelength light quantum which have been used to drive a macromolecule's ability to complex metal ions of specific shape and stereochemical requirements.

This program was designed to establish the possibility of, and ground rules for, photochemically induced processes in macromolecules whose very change altered the metal ion chelation capabilities of an associated functionality.[6] Under the ideal circumstances, the goal would be to find a synthetic macromolecule whose conformational state at equilibrium absorbed a metal ion completely but which released that metal ion in its isomeric state, the latter being produced by a photochemical isomerization process.

Azobenzenes undergo a reversible photochemical isomerization reaction. Depending upon the associated conjugated functional groups, the photostationery state, i.e., the state at photochemical equilibrium, ranges from 70% to 100% cis isomer under conditions where the trans iso-