(16) Matsushita, Y.; Yamada, K.; Hattori, T.; Fujimoto, T.; Sawada, Y.; Nagasawa, M.; Matsui, C. *Macromolecules* **1983**, *16*, 10.
(17) Higo, Y.; Choshi, H.; Fujimoto, T.; Nagasawa, M. *Polym. J.* **1980**, *12*, 729.
(18) Fujimoto, T.; Nagasawa, M. *Polym. J.* **1975**, *7*, 397.
(19) Fujimoto, T.; Tani, S.; Takano, K.; Ogawa, M.; Nagasawa, M. *Macromolecules* **1978**, *11*, 673.
(20) Isono, Y.; Tanisugi, H.; Endo, K.; Fujimoto, T.; Hasegawa, H.; Hashimoto, T.; Kawai, H. *Macromolecules*, following paper in this issue.

Morphological and Mechanical Properties of Multiblock Copolymers

Yoshinobu Isono,[1a] Hideaki Tanisugi,[1a] Keiichi Endo,[1a] Teruo Fujimoto,*[1a] Hirokazu Hasegawa,[1b] Takeji Hashimoto,[1b] and Hiromichi Kawai[1b]

Department of Materials Science and Technology, Technological University of Nagaoka, Kamitomioka-cho, Nagaoka 949-54, Japan, and Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan. *Received January 26, 1982*

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

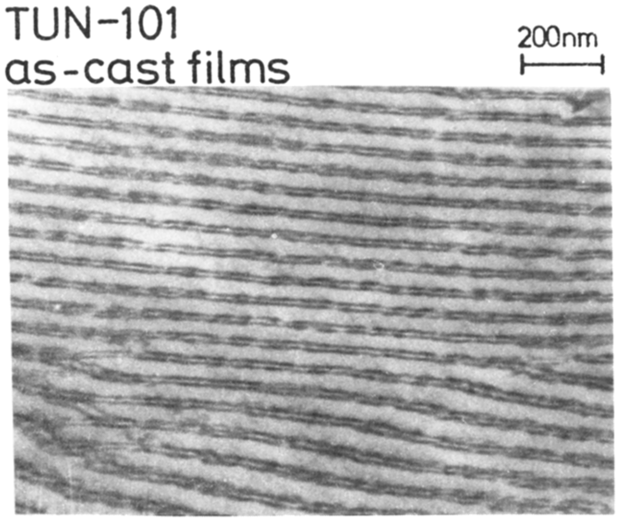
sample code	type	wt fraction, % S	I	A	$10^{-4}M_n$
TUN-101	SIA	34	28	38	16
TUN-1002	ISIAI	$36._5$	$32._2$	$31._3$	$29._1$

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.

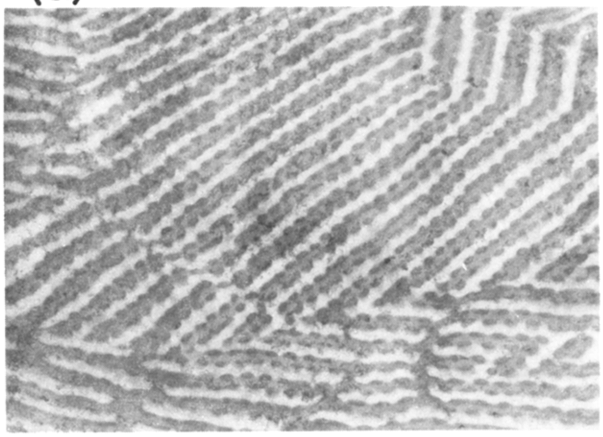
In order to examine the toughness of the cast films after chemical modification of multiblock copolymers, quaternization of the P(4-VBDMA) part was carried out by keeping the as-cast films in contact with a vapor of methyl iodide for about 2 days at room temperature.

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.

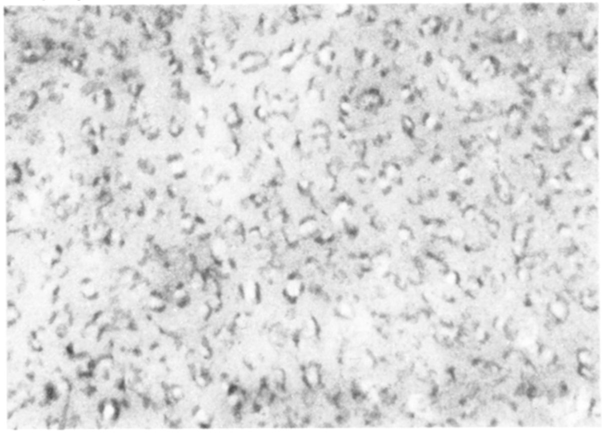
0024-9297/83/2216-0005$01.50/0



(a) Benzene



(b) Dioxane



(c) Cyclohexane

Figure 1. Transmission electron micrographs of TUN-101 triblock copolymer films cast from (a) benzene, (b) dioxane, and (c) cyclohexane solutions.

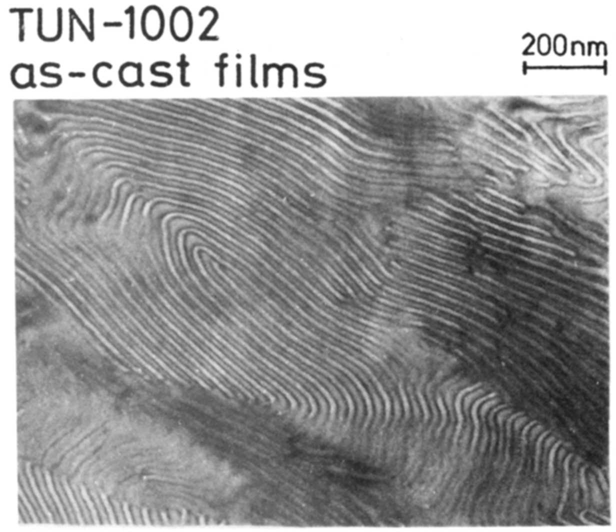
Mechanical Properties. The storage (E') and loss (E'') moduli were measured with a VES-S (Iwamoto Seisakusho) viscoelastic spectrometer. The measuring frequency was 10 Hz. The temperature was varied from 173 to 433 K and the heating rate was about 1 K·min^{-1}.

Results and Discussion

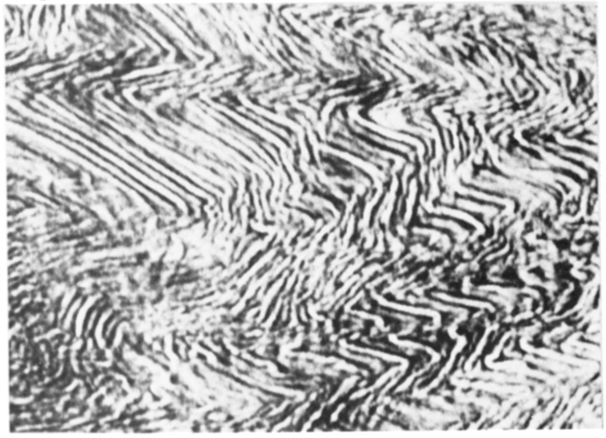
Morphology. Figures 1a–c show electron micrographs of the triblock copolymer TUN-101 cast from benzene, dioxane, and cyclohexane solution, respectively. Figure 1a is reproduced from the preceding paper[2] for the sake of comparison. It shows a clear three-layer-lamellar –ISIAI– structure with the three components in the same order as in the SIA molecule (Figure 1a). This is the characteristic structure for the triblock copolymer films with nearly comparable fractional compositions cast from common good solvents for three components.[3,4,6] If TUN-101 films are cast from a solvent that is poor for any of the components, their domain structures change from that of Figure 1a. The dioxane-cast film has a lamellar structure of PS and P(4-VBDMA) between which spherical islands of PI are aligned as shown in Figure 1b. In cyclohexane-cast film, PS spherical islands partly surrounded by PI spheres are dispersed in the matrix of P(4-VBDMA) as shown in Figure 1c. These domain structures are reasonable because dioxane is a poor solvent for PI and cyclohexane is a poor solvent for PS. However, the sequential order of the three components in the molecule is found to be retained and the domain structures seem to be as clear as in Figure 1a.

If we compare these results for SIA-type triblock copolymer with those for SAI-type triblock copolymer,[3-5] it is explicitly confirmed that the characteristics of the morphology of the ABC-type triblock copolymers are based on the high restraint in the middle B chain, which has been already implied by Shibayama et al.[4] or Matsushita et al.[5] It is, however, to be noted that a subtle difference exists between the morphology of the SIA type and that of the SAI type. The SIA-type TUN-101 sample used in this work has a clear lamellar structure in benzene-cast film, while the SAI-1 sample used by Matsushita et al.,[5] which has almost the same molecular weight ($M_n = 1.64 \times 10^5$) and fractional compositions ($\Phi_{PS}:\Phi_{PI}:\Phi_{P(4\text{-VBDMA})} = 0.37:0.24:0.39$) as TUN-101, has a complicated structure composed of hexagonal packing of PS rods and PI rods in benzene-cast films. In our morphological observation with TUN-101 film specimens, rods or a rodlike domain could not be observed. It is unknown what causes such a difference in morphology.

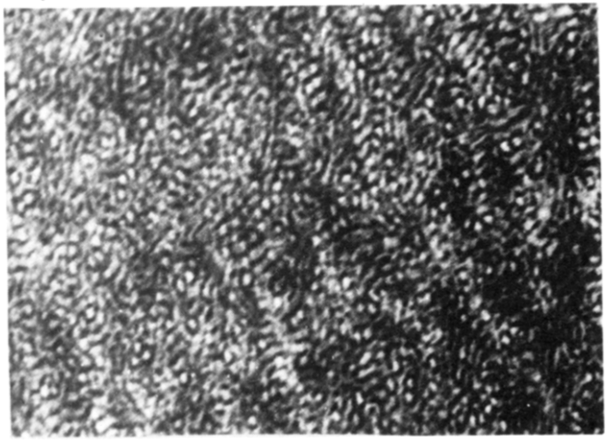
Electron micrographs of TUN-1002 cast from various solvents are shown in Figure 2. Figures 2a and 2c are reproduced from the preceding paper[2] for comparison. It is found that the domain structures in Figures 2a (benzene-cast film) and 2c (cyclohexane-cast film) are similar to those in Figures 1a and 1c, respectively, as already mentioned in the preceding paper.[2] That is, in Figure 2a, the lamellar domains are arranged in the sequential order of –ISIAI– just as expected from the molecular architecture, and in Figure 2c, the islands of the PS phase are dispersed in the matrix of PI and P(4-VBDMA). The difference in morphology between the benzene-cast film and the dioxane-cast film seems to be small (see Figure 2a and 2b). Thus the effect of casting solvent on the morphology of pentablock copolymer films seems to be somewhat less than that of the corresponding triblock copolymer films. Furthermore, if we compare Figure 2 with Figure 1, there seems to be little difference in morphology between films of TUN-101 and those of TUN-1002. However, there appears to be a clear difference between them in the way of spatial arrangement of block chains in the domains, as schematically illustrated for the lamellar structure in Figure 3. That is, in Figure 3a for TUN-101, P(4-VBDMA) chains or PS chains having one end free merely mingle in the P(4-VBDMA) phase or PS phase, respectively. In Figure 3b for TUN-1002, ends of the P(4-VBDMA) chain (or PS chain) are anchored to the adjacent PI phases at both sides, respectively, though both



(a) Benzene



(b) Dioxane



(c) Cyclohexane

Figure 2. Transmission electron micrographs of TUN-1002 pentablock copolymer films cast from (a) benzene, (b) dioxane, and (c) cyclohexane solutions.

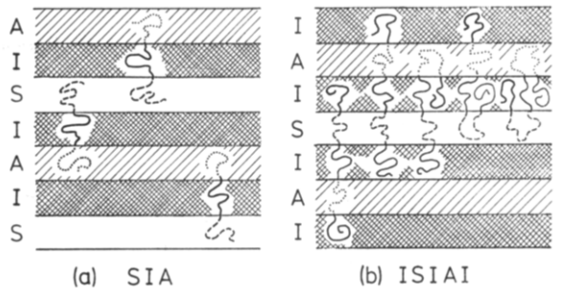
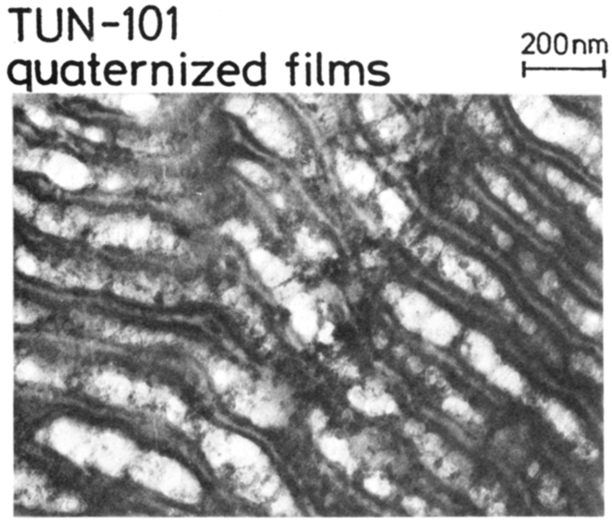


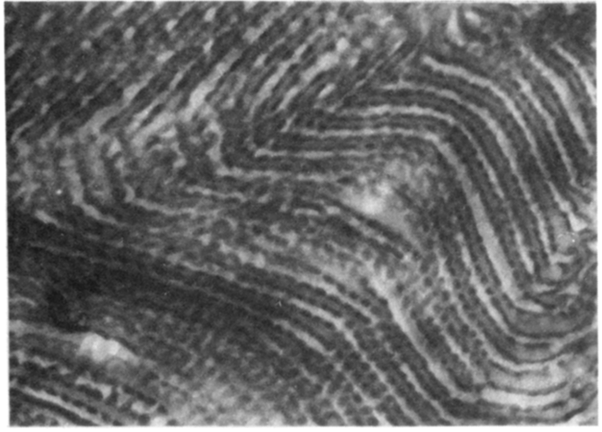
Figure 3. Schematic illustrations of the molecular arrangement in the three-layer-lamellar structure for (a) triblock copolymer of the SIA type and (b) pentablock copolymer of the ISIAI type.

ends of some P(4-VBDMA) chains (or PS chains) are anchored to the same adjacent PI phase as a result of a turning back of the P(4-VBDMA) chain (or PS chain). It would be expected that such a difference has an effect when the multiblock copolymers are chemically modified. For example, if the P(4-VBDMA) domain is not strong enough, it is possible that the domain structure of the triblock copolymer whose P(4-VBDMA) part is quaternized with methyl iodide (CH_3I) fails in water because of the hydrophilicity of quaternized P(4-VBDMA) (poly[(4-vinylbenzyl)trimethylammonium iodide]).[7] This idea on structural weakness of triblock copolymer films was examined by the transmission electron microscopic observation of the multiblock copolymer films treated with CH_3I and then with water. Thus chemically modified TUN-101 and TUN-1002 samples are abbreviated as TUN-101-Q and TUN-1002-Q, respectively. Figures 4 and 5 show electron micrographs of TUN-101-Q and TUN-1002-Q films cast from various solvents, respectively. A clear difference can be found between Figures 4a and 5a. In Figure 5a, the three-layer-lamellar structure is observed as well as in Figure 2a. However, the domain structure in Figure 4a changes undoubtedly from that in Figure 1a. In this figure, the gray portions, which correspond to the quaternized P(4-VBDMA) domain, cannot be detected although the ISI lamellar subunit can be clearly detected. This would imply that the quaternized P(4-VBDMA) in the TUN-101-Q film cast from benzene solution dissolves in water and the domain structure of the film is broken as expected. Therefore, in Figure 4a, the large white portions seem to correspond not to the PS phase but to holes created in quaternized P(4-VBDMA) domains. A similar feature can be found in the quaternized films cast from cyclohexane solutions (see Figures 4c and 5c). In Figure 4b, broken portions are not observed. This reason is unknown at this stage. In any case, the anchoring chains of the quaternized P(4-VBDMA) clearly prevent the formation of the holes. It is clearly confirmed from these facts that films of ABC-type triblock copolymers are weakened by chemical modification in comparison with those of ABACA-type pentablock copolymers. Furthermore, it is to be noted that the PI phase changes from the lamellar domain into the spherical domain through quaternization (see Figures 2a and 5a). Such a remarkable change is not found in films cast from other solvents as shown in Figures 5b and 5c, but even in these figures, contrast among white, gray, and dark portions appear to be clear in comparison with Figures 2b and 2c. Such a change may imply that the segregation between PI and P(4-VBDMA) components proceeds during quaternization.

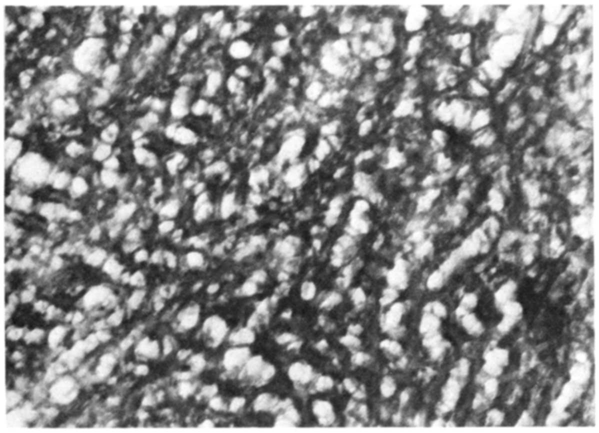
Mechanical Properties. The temperature dependencies of the storage modulus E' and loss modulus E'' of triblock copolymer TUN-101 cast from various solvents are shown by circles in Figure 6. Although the experimental results are not shown in this paper, it was ascertained in preliminary experiments that the PI homopolymer, which is composed of 95% 1,4 structures and 5% 3,4 (or 1,2) structures, and the PS homopolymer showed primary temperature dispersions at about 203 and about 370 K, respectively. Furthermore, it was found that the temperature dispersion of P(4-VBDMA) appeared at about 328 K. There are only two main peaks of E'' observed in Figure 6, though TUN-101 films have a three-phase structure. The lowest temperature transition appears at



(a) Benzene

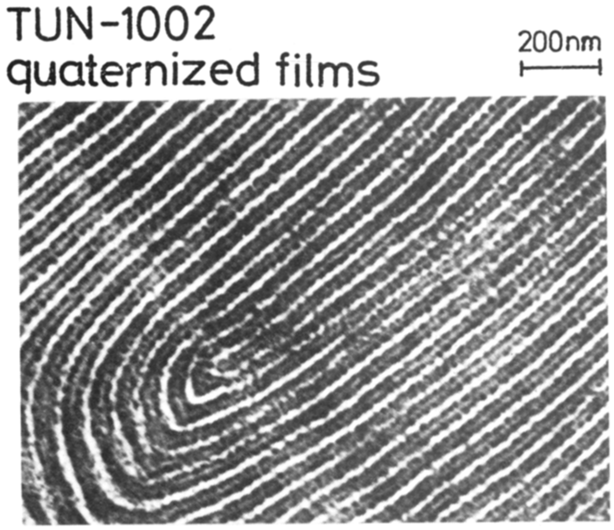


(b) Dioxane

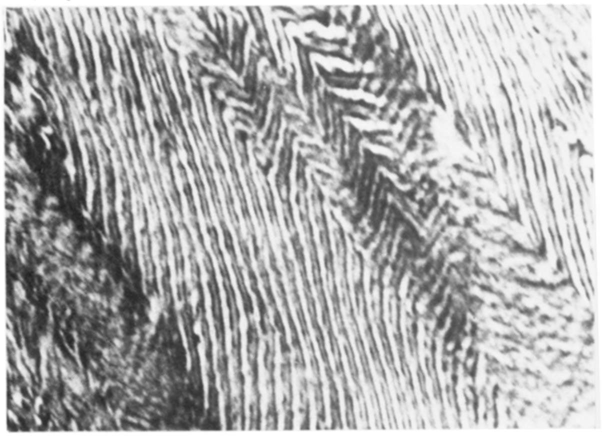


(c) Cyclohexane

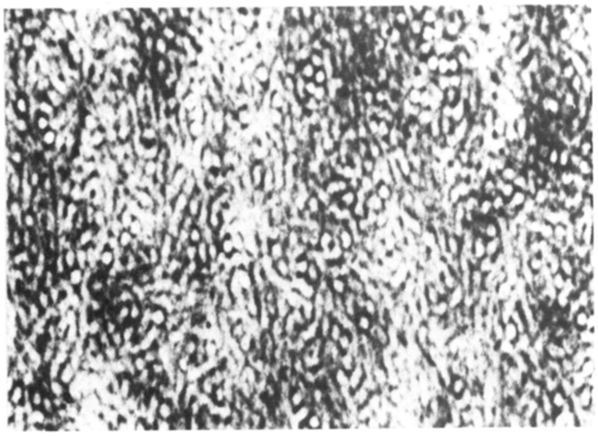
Figure 4. Transmission electron micrographs of TUN-101 triblock copolymer films cast from (a) benzene, (b) dioxane, and (c) cyclohexane solutions treated with methyl iodide and later with water.



(a) Benzene



(b) Dioxane



(c) Cyclohexane

Figure 5. Transmission electron micrographs of TUN-1002 pentablock copolymer films cast from (a) benzene, (b) dioxane, and (c) cyclohexane solutions treated with methyl iodide and later with water.

about 233 K, irrespective of the kind of casting solvent. This temperature is different from the transition temperature of any component polymers in TUN-101. In considering why this transition appears at this temperature, it is necessary to take into account the microstructure of the PI part and/or the molecular compatibility of the component polymers. It is well-known that the glass transition temperature for PI increases with an increase in the content of 3,4 structure. The content of the 3,4 structure of the PI part in TUN-101 is about 15% and is higher than in the PI homopolymer. However, the glass transition temperature for PI having such a content of 3,4 structure is at most about 207 K.[8] Therefore, the transition at about 233 K is not because of the increase in 3,4 structure. On the other hand, the following facts are well-known. The primary transition temperatures in a two-component blend system composed of highly com-

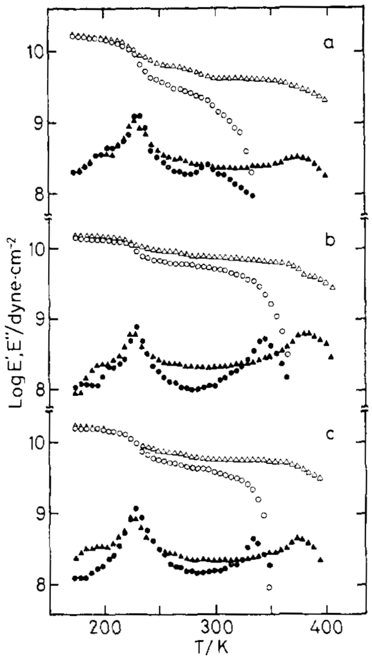


Figure 6. Temperature dependencies of E' (open symbols) and E'' (filled symbols) at 10 Hz of TUN-101 triblock copolymer films cast from (a) benzene, (b) dioxane, and (c) cyclohexane solutions. Circles denote the data for as-cast films, while triangles denote the data for films treated with methyl iodide.

patible polymers approach one another or unite to a limiting value of the corresponding random copolymer. It is presumed that P(4-VBDMA) is considerably compatible with PI.[3,5] Therefore we may consider that the glass transition temperature for the PI component shifted from about 203 K to about 233 K because of the compatibility of the PI component with the P(4-VBDMA) component. Small shoulders of E'' at about 203 K in Figure 6 may correspond to the transition of the pure PI component. It may be considered that the glass transition temperature, T_g, for the P(4-VBDMA) component shifts from 328 K to the low-temperature side, contrary to that for the PI component. The T_g for the PS component may also shift to the low-temperature side because the PS chain is connected to the PI chain. In fact, the second transition temperature in the higher temperature region is different from that for P(4-VBDMA) or PS homopolymers. In this work, it may be negligible that the P(4-VBDA) chains come in contact with the PS chains because of the sequential order of components in the molecule and the morphology in Figure 1. In Figures 6b and 6c, therefore, the temperature transition for P(4-VBDMA) may overlap with that for PS. In Figure 6a, the E'' peak at about 293 K presumably corresponds to T_g for P(4-VBDMA) and the temperature transition for PS may not be observed in the measured range of moduli.

Similar plots for pentablock copolymer TUN-1002 cast from various solvents are shown by circles in Figure 7. The lowest temperature transition appears at about 233 K as in the case of TUN-101. This indicates that the molecular environment of the PI chain in the PI-rich domain in TUN-1002 film is the same as in TUN-101 film. However, the transition temperatures in the higher temperature region in Figure 7 are different from those in Figure 6. That is, the second transition in Figure 7a shifts slightly to the high-temperature side in comparison with that in Figure 6a. In Figure 7a, moreover, the third transition, which is considered to correspond to PS, is observed at about 350 K. Similar features are found in Figure 7c, though the third transition becomes minor. In Figure 7b, the temperature transition for P(4-VBDMA) appears to overlap with that for PS, as well as in Figure 6b. However, this transition shifts slightly to the high-temperature side in comparison with that in Figure 6b. These are probably because the molecular motion of the P(4-VBDMA) chain or the PS chain in TUN-1002 is fairly restricted, since both sides of that chain are connected to PI chains. The effect of casting solvent on the mechanical properties of pentablock copolymer TUN-1002 is smaller than that of triblock copolymer TUN-101. This is presumably because the P(4-VBDMA) chain and the PS chain in the former copolymer are under greater constraint than those in the latter copolymer.

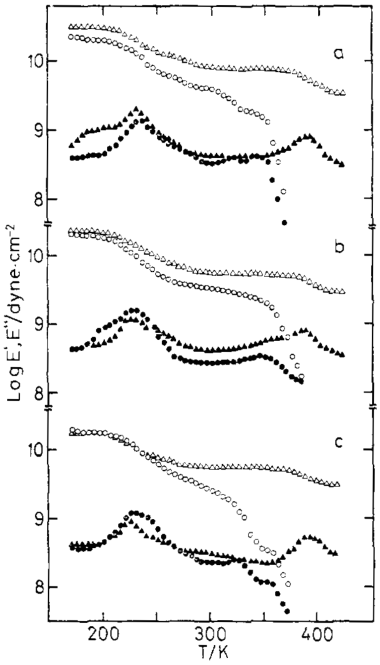


Figure 7. Temperature dependencies of E' and E'' at 10 Hz of TUN-1002 pentablock copolymer films cast from (a) benzene, (b) dioxane, and (c) cyclohexane solutions. Symbols are the same as in Figure 6.

Chemical modification exerts a more serious effect on the mechanical properties than casting solvents do. Similar plots for quaternized TUN-101 and TUN-1002 are shown by triangles in Figures 6 and 7, respectively. It is to be noted that the transition temperatures in the higher temperature region shift strongly to the high-temperature side. Moreover, Figure 7 implies the existence of the third transition at a temperature higher than 430 K. Presumably, this transition corresponds to T_g for quaternized P(4-VBDMA). This high value of T_g for the quaternized P(4-VBDMA) would cause the T_g for the PI component to shift from 233 K to the high-temperature side since the PI component is considered to be compatible with the quaternized P(4-VBDMA). While it was already mentioned that segregation between the PI and P(4-VBDMA) components may proceed during quaternization, if so, this would cause the T_g for the PI component to shift to the low-temperature side. Because of the balance of these two effects, the T_g for the PI component in quaternized films may appear at about 233 K by chance as shown in Figures 6 and 7. Moreover, T_g for the PS component appears around that for PS homopolymer. This may also be due to the high value of T_g for the quaternized P(4-VBDMA).

Acknowledgment. We are deeply indebted to Mr. T. Ofuka, Dr. M. Fukuda, and Dr. Y. Miyaki, the Planning Research Institute, Toyo Soda Manufacturing Co., Ltd., Sinnanyo, Yamaguchi-ken, Japan, for kindly arranging for

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

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

References and Notes

(1) (a) Technological University of Nagaoka. (b) Kyoto University.

(2) Funabashi, H.; Miyamoto, Y.; Isono, Y.; Fujimoto, T.; Matsushita, Y.; Nagasawa, M. *Macromolecules*, preceding paper in this issue.

(3) Matsushita, Y.; Choshi, H.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1980**, *13*, 1053.

(4) Shibayama, M.; Hasegawa, H.; Hashimoto, T.; Kawai, H. *Macromolecules* **1982**, *15*, 274.

(5) Matsushita, Y.; Yamada, K.; Hattori, T.; Fujimoto, T.; Sawada, Y.; Nagasawa, M.; Matsui, C. *Macromolecules* **1983**, *16*, 10.

(6) Arai, K.; Kotaka, T.; Kitano, Y.; Yoshimura, K. *Macromolecules* **1980**, *13*, 1670.

(7) Higo, Y.; Choshi, H.; Fujimoto, T.; Nagasawa, M. *Polym. J.* **1980**, *12*, 729.

(8) Widmaier, J. M.; Meuer, G. C. *Macromolecules* **1981**, *14*, 450.

Morphologies of ABC-Type Triblock Copolymers with Different Compositions

Yuhshu Matsushita,* Katsuya Yamada, Toshihiro Hattori, Teruo Fujimoto,[1a]
Yasuhide Sawada,[1a] Mitsuru Nagasawa, and Chiaki Matsui[1b]

Department of Synthetic Chemistry, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya, 464 Japan.

Received November 12, 1981

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

0024-9297/83/2216-0010$01.50/0