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Preparation and Morphological Properties of a Triblock Copolymer of the ABC Type

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ABSTRACT: A styrene–(4-vinylbenzyl)dimethylamine–isoprene triblock copolymer of the ABC type with a fairly narrow molecular weight distribution was prepared by an anionic polymerization method with *sec*-butyllithium in benzene. The polymerization proceeded without appreciable side reactions. The morphology of the film specimen of the triblock copolymer was investigated with electron microscopy. A clear microphase separation structure from three components was observed.

The morphology of block copolymers has been studied by various methods, but electron microscopy using an osmium tetraoxide fixation technique is the most fully developed. For example, it is well-known that the block copolymers of styrene and dienes give typical microphase separation structures[1] and the structures change with compositions of the block segments,[2] molecular weights of the polymer components,[3] casting solvents,[4] etc. Domain structures in other block copolymers have been studied and similar structures observed. However, the study of the morphology of block copolymers has been restricted to two-component systems. Although there are a few papers[6,7] on the morphology of triblock copolymers of the ABC type, clear microphase separation structures have not been observed. It seems important for the further progress in the study of polymer morphology to study triblock copolymers of the ABC type. A main goal of this work was to establish whether or not different domains can clearly be distinguished.

Block copolymers with well-defined structures can be obtained by the use of anionic polymerization methods, especially, the sequential monomer addition technique. To prepare triblock copolymers of the ABC type with relatively narrow molecular weight distributions, the experimental techniques by which monodisperse polymers can be obtained from each monomer are indispensable. Furthermore, since fractionation of mixtures of various types of copolymers is very difficult, the polymerization conditions producing only the desired block copolymer must be employed.

Preceding work has shown the conditions of polymerization of the polar monomer (4-vinylbenzyl)dimethylamine (4-VBDMA, $CH_2{=}CHC_6H_4CH_2N(CH_3)_2$) with *sec*-butyllithium in benzene to satisfy the above proposal.[8] In this work, block copolymerizations are carried out using that monomer in addition to styrene and isoprene monomers. The preparations of two kinds of diblock copolymers of the AB type consisting of polystyrene and poly(4-VBDMA) and also of polyisoprene and poly(4-VBDMA) are first studied, followed by that of triblock copolymers of the ABC type containing these three monomers.

Experimental Section

Reagents. Styrene and 4-VBDMA monomers were first dried over calcium hydride under reduced pressure and then purified by benzophenone–sodium under a pressure of ca. 10^{-6} mmHg. Isoprene was dried over calcium hydride and sodium metal and then distilled in the presence of the dipotassium salt of α-methylstyrene tetramer. The initiator, *sec*-butyllithium, was synthesized by the reaction of *sec*-butyl chloride with lithium in *n*-hexane. The concentration of initiator was determined by titration with a standard hydrochloric acid of suitable concentration. The solvents used, i.e., benzene and *n*-hexane, were

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Table I
Polymerization of Diblock Copolymers of AB Type

sample code	amt of initiator $\times 10^4$, mol	amt of styrene or isoprene, g	amt of 4-VBDMA, g	vol of benzene soln, cm^3	% conversion	IE[a]	$10^{-4}M_n$ precursors	$10^{-4}M_n$ block copolymers
				(a) Styrene and 4-VBDMA				
SA-1	2.07	11.8	8.2	326	100	0.98 ± 0.05	5.8 (5.7)[b]	10.4 (10.3)
AS-1	2.26	11.8	9.4	344	99	0.99 ± 0.05	4.9 (4.2)	10.0 (9.9)
SA-2	1.26	13.4	11.0	364	92	1.0 ± 0.05	11.6 (10.8)	19.1 (20.3)
				(b) Isoprene and 4-VBDMA				
IA-1	2.28	9.9	12.4	415	97		5.1 (4.7)	10.0 (10.3)
AI-1	2.46	10.8	12.8	413	91	1.0 ± 0.05	5.8 (5.1)	8.8 (9.2)
IA-2	1.03	8.4	9.3	282	92		10.8 (9.6)	17.3 (19.1)
AI-2	0.79	9.9	9.7	265	96	1.0 ± 0.05	12.6 (11.8)	22.4 (23.5)

[a] Initiation efficiencies. [b] Parentheses show the molecular weights calculated from the amounts of monomers and initiator.

Table II
Polymerization of Triblock Copolymers of ABC Type

sample code	amt of initiator $\times 10^4$, mol	amt of styrene, g	amt of 4-VBDMA, g	amt of isoprene, g	vol of benzene soln, cm^3	% conversion	IE[a]	$10^{-4}M_n$ first precursors	$10^{-4}M_n$ second precursors	$10^{-4}M_n$ final polymers
SAI-1	1.83	10.8	10.1	8.4	369	99	1.0 ± 0.05	6.0[b] (5.9)	12.4 (11.9)	16.4 (17.1)
ISA-1	1.56	10.3	10.7	8.0	363	98		5.1 (5.1)	12.9 (12.6)	19.1 (18.5)

[a] Initiation efficiencies. [b] The molecular weight of polystyrene in SAI-1 was determined from the elemental analysis of the second precursor.

purified with *n*-butyllithium after drying over calcium hydride.

Polymerization. Polymerizations were carried out in a sealed glass apparatus under a pressure of 10^{-6} mmHg. The cleaning of the glass apparatus and other techniques are almost the same as those employed for preparations of linear and star-shaped polymers having sharp molecular weight distributions.[9,10] Polymerization conditions of diblock copolymers of styrene and 4-VBDMA and also of isoprene and 4-VBDMA are shown in Table I. The polymerization of 4-VBDMA was carried out at concentrations lower than 3 wt %. It was previously confirmed[8] that the kinetics of polymerization of 4 -VBDMA with *sec*-butyllithium in benzene are first order and the molecular weight distribution of the polymer obtained is sharp, if the monomer concentration is as low as 3 wt %. If the monomer concentration is high (ca. 8–10 wt %), the polymerization rate deviates from first order and the molecular weight distribution of the polymer becomes broad. The reason for the phenomenon has not yet been clarified. Since the initiation reaction rate of isoprene may be slow,[11,12] isoprene was polymerized in two steps: a small amount of isoprene was first added to complete the initiation and then remaining monomer was added.

To study side reactions between the active chain end of the preceding polymer and succeeding monomer, two kinds of diblock copolymers initiated, for example, either from styrene or from 4-VBDMA (SA and AS), were simultaneously prepared under almost the same conditions. For characterization of each polymeric component in those block copolymers, precursors were sealed off before the second or third monomer was added. Polymerization conditions of triblock copolymers of the ABC type are listed in Table II. The initiation efficiency of the initiator was calculated from the ratio of the observed molecular weight of the polymer obtained to the expected molecular weight calculated from the amounts of monomer and initiator.

Characterization. The number-average molecular weights of block copolymers and their precursors thus obtained were determined by a Hewlett-Packard high-speed Type 502 membrane osmometer in toluene solution at 25 or 30 °C. Molecular weight distributions of these polymers were examined by sedimentation patterns of a Beckman Spinco Model E ultracentrifuge in cyclohexane at 35 °C. In addition, the fraction of 1,4 addition structure in polyisoprene was determined by proton NMR, while the fraction of trans structure in 1,4 addition was determined from ^{13}C NMR spectra.[13]

Morphology. The polymers thus characterized were cast into films of about 0.15-mm thickness on mercury by evaporating the solvent from dioxane solutions of 5–10 wt %. Dioxane is a good solvent for polystyrene and poly(4-VBDMA) but a Θ solvent for polyisoprene at 34 °C.[14] Polyisoprenes in the present molecular weight range ($(4\text{–}10) \times 10^4$) are soluble in dioxane at room temperature ($\simeq$25 °C). Moreover, the dioxane solutions of the block copolymers are always clear, and the films cast from the dioxane solutions are transparent. Considering the solvent power of dioxane, however, the polyisoprene part may be coiled in a compact form in the dioxane solutions. Benzene and tetrahydrofuran are common good solvents for the three components. However, the films cast from the solutions in these solvents are not so transparent as the films from dioxane solutions. The films obtained were completely dried under a vacuum of 10^{-4} mmHg for several days. The films stained with fixing reagents, osmium tetraoxide (OsO_4) and phosphotungstic acid ($P_2O_5{\cdot}24WO_3$, PTA), were embedded in a resin and were cut into ultrathin sections by an ultramicrotome. Some of the ultrathin sections were further fixed with the vapor of osmium tetraoxide.

Results and Discussion

Polymerization. Polymerization results of diblock copolymers are shown in Table I. The conversions are almost 100%, within experimental error, in all cases. The initiation efficiencies, that is, the ratios of calculated molecular weights to observed ones, are close to unity in all successful cases.

In the copolymerization of styrene and 4-VBDMA, molecular weight distributions of SA, which were polymerized from styrene, are clearly narrower than that of AS, which was polymerized from 4-VBDMA, as shown in Figure 1. Even in the case of AS, however, no tailing can be observed on both higher and lower molecular weight sides in the sedimentation pattern. Combining these facts, we speculate that the broader molecular weight distribution of AS than that of SA is not due to side reactions but due to the slow initiation in the polymerization of styrene monomer by poly[(4-vinylbenzyl)dimethylaminyl] anion.

In the block copolymerization of isoprene and 4-VBDMA, on the contrary, the desirable samples are obtained when the polymerization is initiated from 4-VBDMA (AI). The block copolymer IA show a sedimentation pattern of double peaks, as shown in Figure 2. In

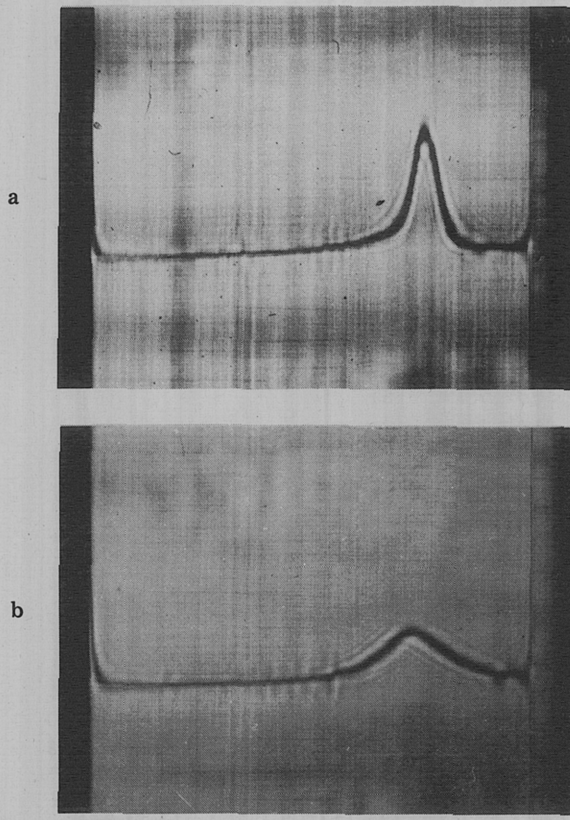

Figure 1. Sedimentation patterns of samples (a) SA-2 and (b) AS-1. Solvent, cyclohexane; temperature, 35 °C; speed of rotation, 59 780 rpm; angle, 70°; concentration, (a) 0.5, (b) 0.4 g/dL; time, (a) 37, (b) 39 min.

Table III
Microstructures of Polyisoprene

sample code	% cis 1,4	% trans 1,4	% 1,2 or 3,4
PI[a]	74	15	11
AI-2	33	7	60
SAI-1	32	9	59

[a] Isoprene homopolymer, $M_n = 10.7 \times 10^4$.

the copolymer AI, the microstructures of the polyisoprene part are very much different from that of isoprene homopolymer, as shown in Table III. That is, the fraction of 1,2 and 3,4 structures in AI-2 is much larger than that in polyisoprene (PI). The reason for this difference may be due to the elevation of the dielectric constant of solution by addition of polar 4-VBDMA.

Thus, it can be predicted from the above two polymerization results of SA and AI that a triblock copolymer of the ABC type can be prepared if the polymerization is carried out in the order of styrene, 4-VBDMA, and isoprene (SAI-1) or of isoprene, styrene, and 4-VBDMA (ISA-1). The polymerization results of these block copolymers are shown in Table II. It is clear that the copolymerization reaction proceeded satisfactorily in SAI-1. The conversion of SAI-1 is almost 100% and the molecular weights obtained in each step agree well with the values predicted from the amounts of each monomer and initiator. The molecular weight of the final triblock copolymer also agrees with the value expected. Figure 3 shows that the triblock copolymer SAI-1 shows a single and narrow molecular weight distribution of the sample, as is expected. In the case of ISA-1, on the other hand, it is clear from the sedimentation pattern in Figure 3b that the polyisoprene–polystyrene diblock copolymer was obtained in addition to the triblock copolymer. It was confirmed that the IS precursor in ISA-1 shows a single sedimentation peak. Since all the monomers used in the copolymerization of SAI-1 and ISA-1 are the same, the presence of impurities in 4-VBDMA is not the reason for the unsatisfactory in-

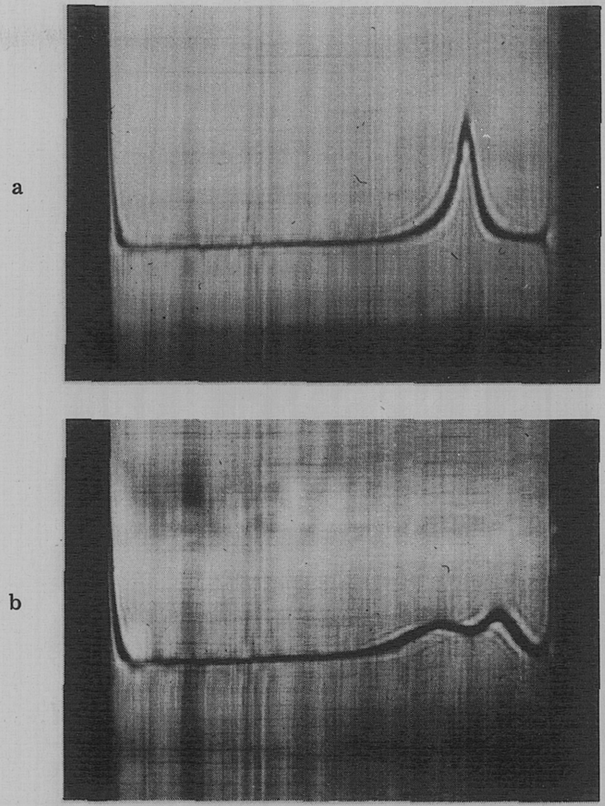

Figure 2. Sedimentation patterns of samples (a) AI-2 and (b) IA-2. Concentration, 0.5 g/dL; time, (a) 68, (b) 70 min. Other experimental conditions are the same as those in Figure 1.

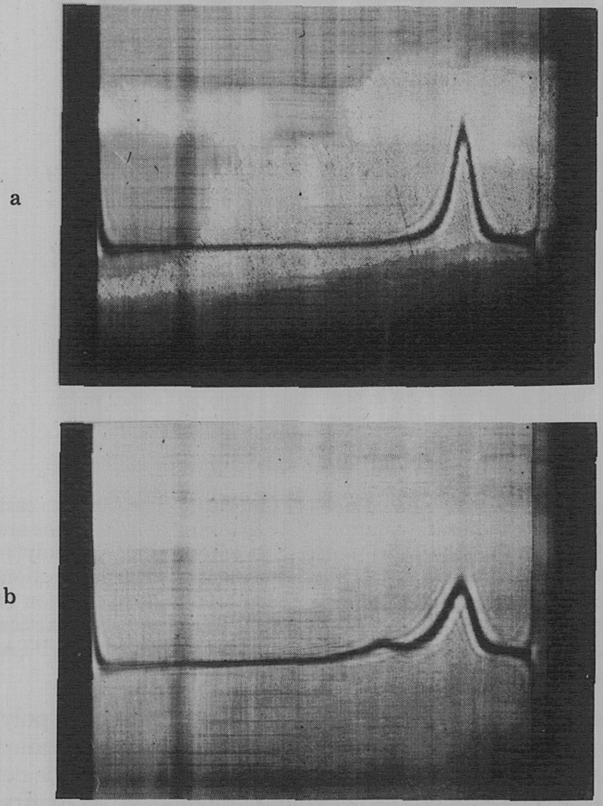

Figure 3. Sedimentation patterns of samples (a) SAI-1 and (b) ISA-1. Concentration, 0.5 g/dL; time, (a) 44, (b) 43 min. Other experimental conditions are the same as those in Figure 1.

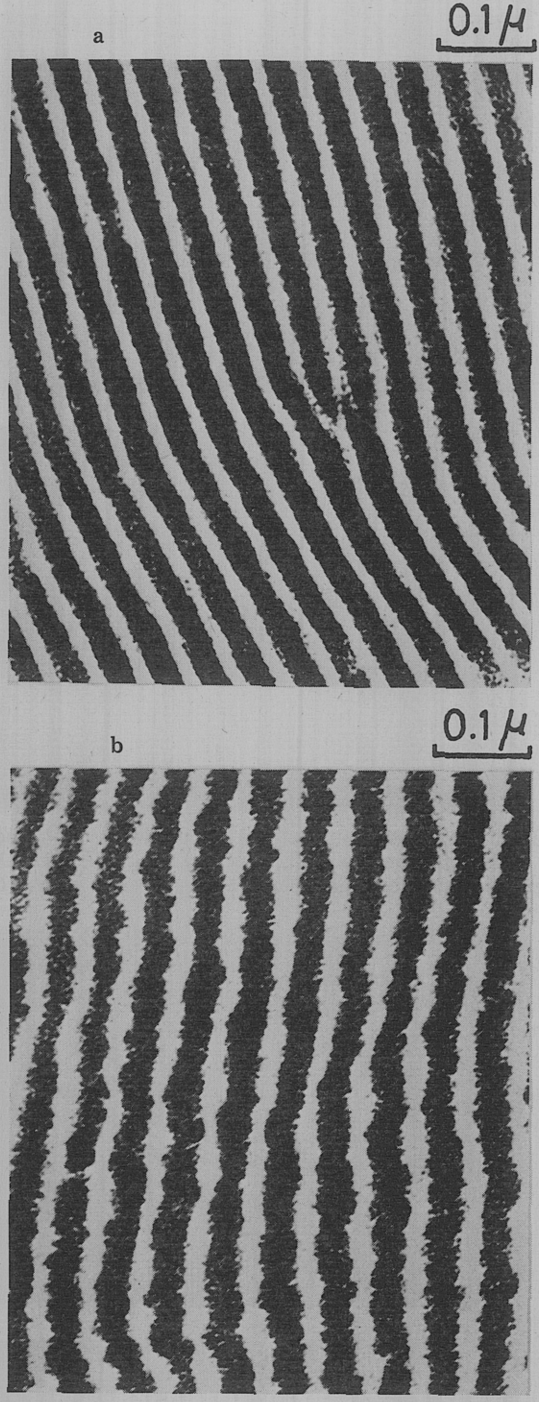

Figure 4. Electron micrographs of film SA-1. The film was cast from 10 wt % dioxane solution. The following abbreviations are used in the figures in this paper: S = polystyrene, A = poly(4-VBDMA), I = polyisoprene. (a) Stained with OsO_4: dark region, A phase; light region, S phase. Calculated volume fraction of polystyrene phase (V_F), calcd(S) = 0.55. Observed area fraction of polystyrene phase (A_F), obsd(S) = 0.38. (b) Stained with PTA: V_F, calcd(S) = 0.55; A_F, obsd(S) = 0.46.

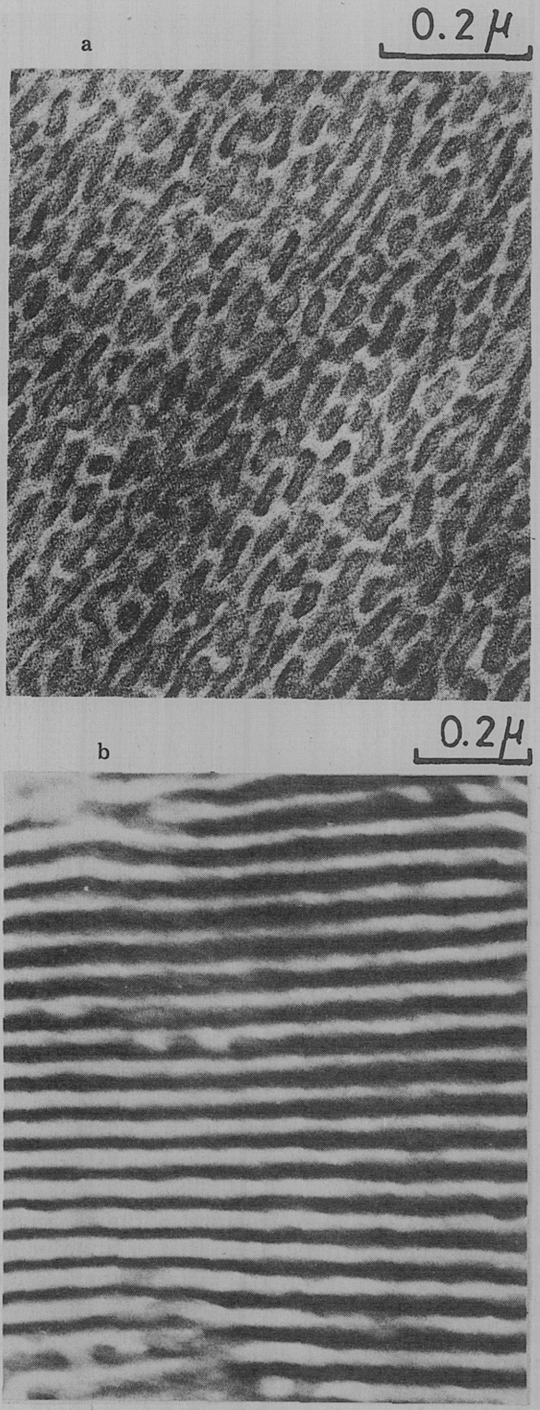

Figure 5. Electron micrographs of film AI-2 stained with OsO_4. (a) Cast from 5 wt % dioxane solution: dark region, I phase; light region, A phase. V_F, calcd(I) = 0.54; A_F, obsd(I) = 0.38. (b) Cast from 5 wt % benzene solution. V_F, calcd(I) = 0.54; A_F, obsd(I) = 0.62.

itiation of 4-VBDMA. It appears that not only poly-*isoprenyl anion but also polyisoprene–polystyryl anion* cannot initiate 4-VBDMA satisfactorily. The reason is not clear at present and further studies are required to confirm the phenomena and clarify the reason. Thus, it can be concluded that if we polymerize styrene, 4-VBDMA, and isoprene in that order, we can obtain a triblock copolymer of the ABC type without impurities.

Morphology. By staining a SA-1 film with OsO_4 and PTA separately, it was found that both reagents can fix the 4-VBDMA phase only. The typical alternating lamellar structure of the polystyrene and poly(4-VBDMA) phases was observed, as shown in Figure 4. In the AI block copolymers, both polyisoprene and poly(4-VBDMA) phases can be fixed by OsO_4 but the polyisoprene phase is darker than the poly(4-VBDMA) phase, so that each phase can be clearly distinguished, as shown in Figure 5a. In this case, the film cast from dioxane showed the morphology of the sphere or rodlike domain of polyisoprene in the matrix of poly(4-VBDMA).

If the copolymer SAI-1 is fixed with OsO_4 aqueous solution, a lamellar structure similar to that of SA-1 is observed, except that the ratio of the black band to the white band in SAI-1 is larger than that in SA-1. In the case of

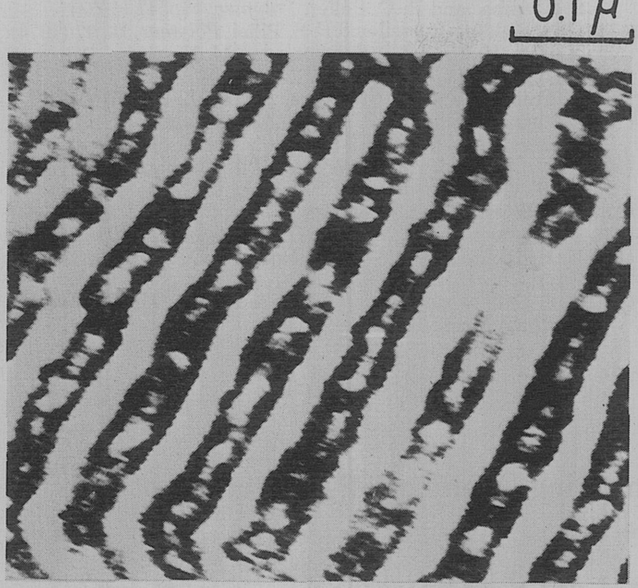

Figure 6. Electron micrograph of SAI-1 stained with PTA. Cast from 8 wt % dioxane solution: light band, S phase; dark region, A phase; light island, I phase. V_F, calcd(S) = 0.35; A_F, obsd(S) = 0.41. V_F, calcd(A) = 0.39; A_F, obsd(A) = 0.37. V_F, calcd(I) = 0.27; A_F, obsd(I) = 0.22.

PTA fixation of SAI-1, a lamellar structure is also observed and, moreover, the white portions can be seen inside the dark poly(4-VBDMA) phase, as shown in Figure 6. If a subsequent fixation with OsO_4 vapor is given to the ultrathin sections of SAI-1 treated by PTA, the white portions become darker than the gray strips (see Figure 7a). Therefore, the darker domain is believed to be the polyisoprene phase. Thus we can assign each colored phase as follows: the white band corresponds to the polystyrene phase, the gray matrix to the poly(4-VBDMA) phase, and the dark portion to the polyisoprene phase. Furthermore, if we choose suitable conditions for fixation, three components can be distinguished only with OsO_4, as shown in Figure 7b.

The microphase separation structure of SAI-1 in Figure 7 is understandable if we combine the domain structure of SA (Figure 4) and AI (Figure 5a). That is, the domain structure of SAI-1 is the combination of two kinds of phase separation structures: an alternating lamellar structure of polystyrene and poly(4-VBDMA) and continual islands of polyisoprene in the matrix of poly(4-VBDMA).

The following problems remain, however. First, the area fractions of the micrograph are fairly different from the calculated volume fractions of the components. By stereology,[15] the area fraction (A_F) is roughly equal to the volume fraction (V_F). The values of A_F determined from the figures are noted in Figures 4–7 in comparison with the values of V_F calculated from the molecular weights. A few reasons are conceivable for this difference between observed A_F and calculated V_F. (1) The extent of staining with the two reagents (OsO_4 and PTA) is not the same. The two pictures in Figure 4 show the microphase separation structure of the same part of the sample. Nevertheless, the ratios of the two phases in the two pictures differ considerably. (2) The compatibility of poly(4-VBDMA) with the other components has not been studied. It may be possible that the boundary regions between poly(4-VBDMA) and the other components are fairly broad.

Secondly, the domain sizes differ considerably with the sampling place in the film. This may mean that equilibrium conditions were not attained in casting films in the present work. These effects are not discussed in this paper.

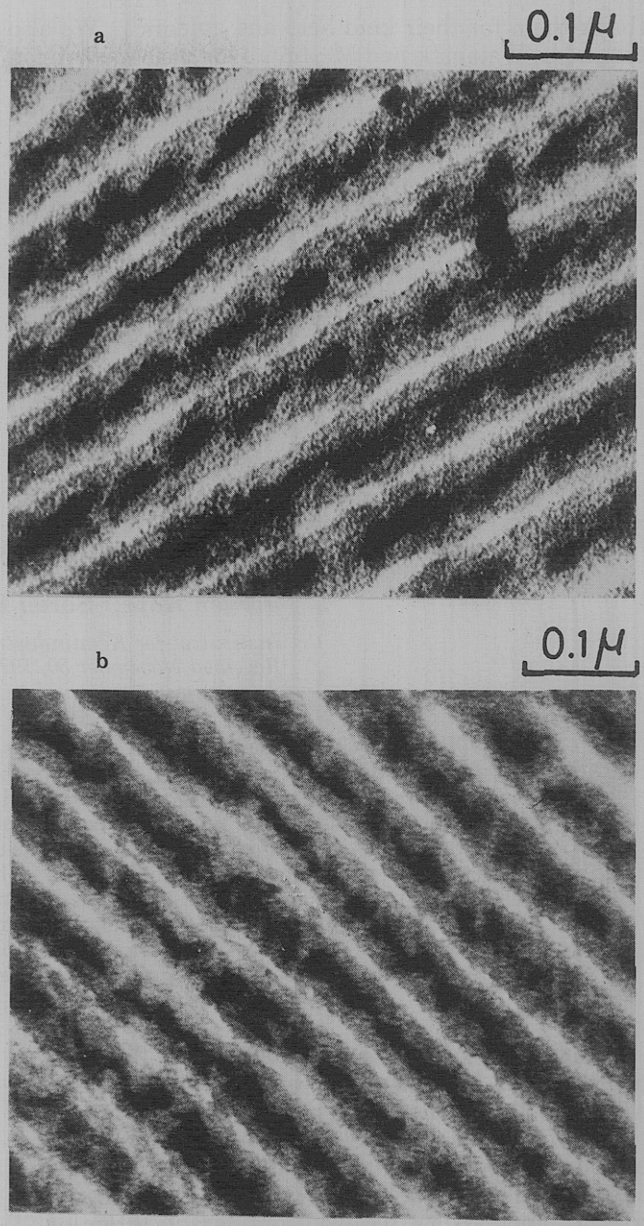

Figure 7. Electron micrographs of SAI-1. Cast from 8 wt % dioxane solution. (a) Stained with PTA and OsO_4: light region, S phase; gray region, A phase; dark region, I phase. V_F, calcd(S) = 0.35; A_F, obsd(S) = 0.19. V_F, calcd(A) = 0.39; A_F, obsd(A) = 0.46. V_F, calcd(I) = 0.27; A_F, obsd(I) = 0.35. (b) Stained with OsO_4. A_F: obsd(S) = 0.25, obsd(A) = 0.51, obsd(I) = 0.24.

Finally, it is important to note that the microphase separation structures in Figures 4, 5a, 6, and 7 are observed in the film cast from dioxane solutions, in which polyisoprene may be in an unexpanded form. The nonlamellar structure of sample AI-2 (Figure 5a), in spite of its approximate 50:50 composition, is likely due to this reason. If the film of AI-2 is cast from benzene (a common good solvent for both components) solution, the film has a lamellar structure, as shown in Figure 5b. The solvent effect on the morphology of the present sample will be reported by Professor H. Kawai and co-workers of Kyoto University in a separate paper.

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Structural Aspects of the Ring-Opening Polymerization of 2-Methyloxacyclobutane

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ABSTRACT: ^{13}C NMR measurements on polymers of 2-methyloxacyclobutane prepared at −78 to 0 °C have revealed that the number of structural irregularities of the head-to-head type increases with the polymerization temperature. By comparison with results expected on the basis of influence from the neighboring carbons on the chemical shifts for particular carbons in various triad configurations, stereochemical effects are clearly observable. The meso and racemic configurations in head-to-head units are noticeable as are longer range effects. The signal from the methine carbon in head-to-tail units is influenced by the chirality of the corresponding carbon four bond distances removed in the adjoining units. Iso-, syndio-, and heterotactic triads are observed roughly in the ratio 1:1:2, indicating random incorporation of the enantiomeric monomers. The methyl carbons in the same triad are, however, outside the range of influence and appear as a singlet. Stereochemical effects are also noticeable for the irregular sequences.

Oxacyclobutane (oxetane), as well as the 2-methyl, 3-methyl, and 3,3-dimethyl derivatives, will easily undergo cationic polymerization by a ring-opening reaction.[1–4] In the last few years the kinetics of polymerization of these compounds have been studied in detail,[5,6] and recently the oligomer formation accompanying the polymerization of these compounds has received considerable attention.[7–9] The structural aspects have generally not been considered, although, in principle, tacticity is possible in the polymers of the 2-methyl- and 3-methyloxacyclobutanes.[10] It has been pointed out that the amorphous structure of poly(2-methyloxacyclobutane) may be connected with irregularities due to the unsymmetrical monomer.[2] In the case of copolymerization of oxacyclobutane and 3,3-dimethyloxacyclobutane the microstructure with respect to the *distribution of the two comonomers has recently* been investigated by means of 300-MHz ^{1}H NMR.[11] In the present investigation the structural features related to head-to-head and tail-to-tail irregularities as well as to the presence of asymmetric carbons in poly(2-methyloxacyclobutane) have been studied by ^{13}C NMR and related to polymerization conditions.

Results and Discussion

The polymerization results are summarized in Table I. Two initiators were used, PF_5 and Et_3OPF_6, and experiments were carried out in bulk as well as in CH_2Cl_2 solution. The oxonium salt appears to yield polymers with higher molecular weights than those obtained with PF_5. When the polymerization temperature is lowered, the molecular weights become higher for the polymers prepared with both initiators. After workup of the polymers, no significant amounts of oligomers were present, as indicated by GPC analysis. A detailed polymerization study has not been carried out at this point; the objective of the present investigation has been to detect if any gross changes in the polymer structure occur as a result of changing the polymerization conditions, particularly the temperature.

A typical 22.63-MHz ^{13}C NMR spectrum of a polymer prepared at −50 °C is shown in Figure 1. More signals appear than correspond to the four different carbons in the regular head-to-tail structural units. The additional signals originate first of all from head-to-head and tail-to-tail configurations. It should be expected that the head-to-tail structure would predominate, and this assumption has been verified by evaluating the chemical shifts on the basis of structural parameters and model studies. In the following, the methyl carbon is labeled C-1, the methine carbon is indicated C-2, and the methylene carbons are labeled C-3 and C-4.

The influence of structure on the ^{13}C NMR chemical shifts is known to be predictable by a scheme based on the effects of the carbons in α, β, γ, δ, and ϵ positions relative to the observed carbon.[12,13] Generally a deshielding is observed except for the γ effect, which causes an upfield shift. The effect of the neighboring carbons diminishes with distance and the ϵ effect is very small. This attenuation has also been observed in the case of the configurational splittings in diastereomeric alkanes.[14] In the case of polymers containing heteroatoms in the main chain it was recently pointed out by Ivin[15] that since chemical shifts for carbons in such polymers are sensitive to substitution at a distance only up to four bonds, triad configurational

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