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Cationic Block Copolymerization of Tetrahydrofuran with 3,3-Bis(chloromethyl)oxacyclobutane

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ABSTRACT: Block copolymerization of tetrahydrofuran (THF) with 3,3-bis(chloromethyl)oxacyclobutane (BCMO) is reported. A cationic living polymer of THF was first prepared and the second polymerization was initiated by the cationic growing end of the living poly-THF. A mixture of BF_3 and epichlorohydrin was selected as the catalyst. Two types of block copolymers were prepared. One was an A–B type of block copolymer consisting of poly-THF (A) and poly-BCMO (B) blocks. The other was A–(AB)–B type of block copolymer in which two crystalline blocks of poly-THF (A) and poly-BCMO (B) are bound to each end of a central rubbery block of the THF–BCMO random copolymer (AB). The lengths of discrete blocks in the copolymers were calculated from the concentration of propagating species [P*] in polymerization. [P*] was determined by the "phenoxyl end-capping method" in which the propagating species was converted into the corresponding phenyl ether by treating the mixture with excess sodium phenoxide. The phenyl ether group at the polymer end was determined by uv spectroscopy. The A–(AB)–B type of block copolymer was thermoplastic and exhibited properties characteristic of vulcanized rubber at room temperature.

The present paper describes the cationic block copolymerization of tetrahydrofuran (THF) with 3,3-bis(chloromethyl)oxacyclobutane (BCMO). Two types of block copolymers were prepared. One was an A–B type of copolymer consisting of poly-THF (A) and poly-BCMO (B) blocks. The other was an A–(AB)–B type in which the central block of the THF–BCMO random copolymer (AB) connected the poly-THF (A) and poly-BCMO (B) blocks.

Several studies on the preparation of block copolymers by the cationic mechanism have been reported recently. Block copolymers consisting of polyether, polyacetal, and polyester blocks were prepared by cationic polymerization of cyclic acetals in the presence of polyacetal, polyether, or polyester,[1,2] and by the cationic reaction between these polymers having oxygen-containing backbones.[3] Polymers prepared by these methods, however, were mixtures of block copolymer and homopolymers, and the lengths of blocks could not be regulated.

In the present study, block copolymers of controlled block lengths were successfully prepared by cationic polymerization. The preparation of the A–B type of copolymer was performed by a procedure of two-stage polymerization. A cationic living polymerization of THF was first made and then the BCMO polymerization was initiated by the propagating chain end of a living poly-THF molecule. The concentration of propagating chains was determined by the phenoxyl end-capping method,[4] which was used for the calculation of the lengths of two blocks. The A–(AB)–B type of copolymer was prepared by a three-stage polymerization, *i.e.*, the living THF polymer was first made and the living end of poly-THF was used to initiate THF–BCMO random copolymerization, which was then followed by BCMO homopolymerization. In the A–(AB)–B type of block copolymer, the two crystalline blocks of poly-THF and poly-BCMO are bound to each end of the central rubbery block of the THF–BCMO random copolymer. This block copolymer exhibited the properties of a thermoplastic elastomer at room temperature.

Results and Discussion

Synthesis of an A–B Type of Block Copolymer. Figure 1 shows schematically the procedure for the preparation of the first block copolymer of the A–B type. The first stage of polymerization was the living THF polymerization, which was carried out in solution. The length of poly-THF could be controlled on the basis of the results of our previous kinetic studies.[5] BCMO was added to this living polymerization mixture and the system was cooled quickly to −50° in order to quench the reaction. Then the remaining THF was removed *in vacuo* and the system was warmed to

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(1) V. Jaacks and W. Kern, *Makromol. Chem.*, **83**, 71 (1965).

(2) St. Penczek, J. Fejgin, W. Sadowska, and M. Tomaszewicz, *ibid.*, **116**, 203 (1968).

(3) J. Fejgin and St. Penczek, *J. Polym. Sci., Part B*, **4**, 615 (1966).

(4) T. Saegusa and S. Matsumoto, *ibid.*, *Part A-1*, **6**, 1559 (1968).

(5) T. Saegusa and S. Matsumoto, *Macromolecules*, **1**, 442 (1968).

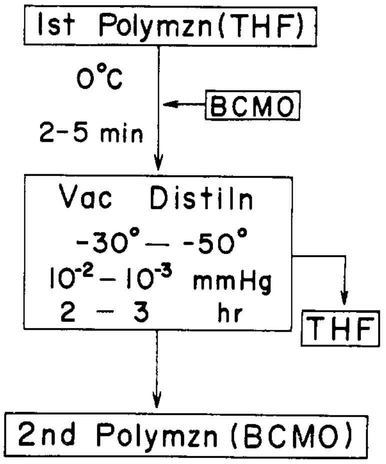

Figure 1. Scheme of two-stage block copolymerization.

the selected temperature, whereupon the second-stage polymerization of BCMO was carried out. In the process of THF removal, the solvent was also distilled out of the reaction system and therefore the second-stage polymerization apparently proceeded in the solid.

The selection of an initiator for the living polymerization of THF was essential. For this purpose, the change in concentration of propagating species [P*] during polymerization was examined by our "phenoxyl end-capping method."[4] In the THF polymerization by the BF_3-epichlorohydrin (ECH) system, it was shown that [P*] remained constant after the induction period.[5] In addition, data were obtained which indicate a linear relationship between the per cent conversion and the molecular weight of polymer made with the BF_3-ECH system.[6] On the basis of these facts, the BF_3-ECH system was shown to be one of the initiators of the living polymerization of THF. This initiator system was selected for our block copolymerization. An example of the two-stage polymerization is given in the Experimental Section.

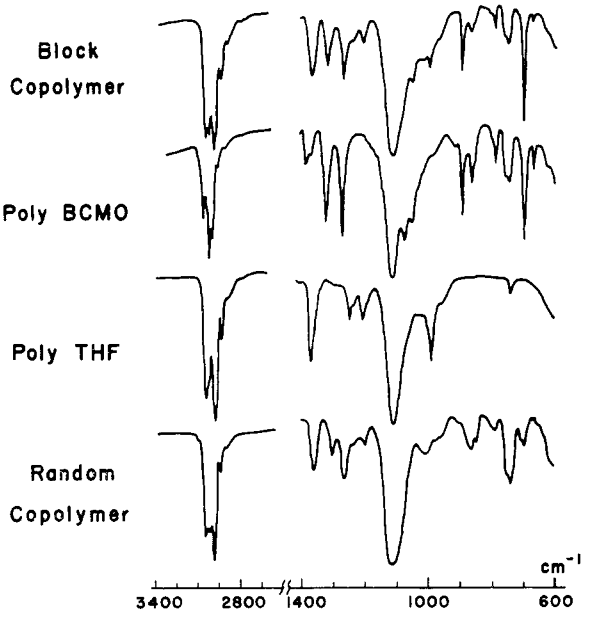

Figure 2. Comparison of infrared spectra of homopolymers and copolymers of THF and BCMO (film).

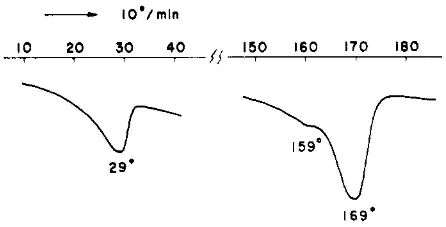

Figure 3. Dsc diagram of the block copolymer, (poly-THF)-(poly-BCMO), heating rate, 10°/min.

The product of two-stage block copolymerization was a resinous material shown by infrared and elemental analysis to contain both monomer units. The structure of the block copolymer was confirmed by the crystalline bands in the infrared spectrum and by the melting endotherm of dsc (differential scanning calorimetry) analysis as well as by the solubility behavior.

The solubility behavior confirmed that a copolymer, and not a mixture of homopolymers, had been formed. The block copolymer was insoluble in ethanol and soluble in hot chloroform. Since poly-BCMO is insoluble in hot chloroform and in ethanol, and poly-THF is soluble in these solvents, the solubility characteristics of the product indicated the formation of a copolymer.

In Figure 2, the infrared spectrum of the two-stage copolymer is compared with the spectra of poly-THF and poly-BCMO and with that of a random copolymer. The spectrum of the block copolymer as well as that of the random copolymer has absorptions due to the THF unit at 2935, 2850, and 1205 cm^{-1} and to those of the BCMO unit at 2900, 1320, and 1270 cm^{-1}. In addition to these bands, the spectrum of the block copolymer possesses the crystalline bands of poly-BCMO at 860 and 890 cm^{-1},[7] and the crystalline band of poly-THF at 1000 cm^{-1}.[8] These crystalline bands are not seen in the spectrum of the random copolymer. Furthermore, the spectrum of the block copolymer has no absorption at about 870 cm^{-1} which is characteristic for the THF–BCMO random copolymer.[9] Also the block copolymer was different from the random copolymer in the other regions of the spectrum.

A dsc diagram of the block copolymer is shown in Figure 3, which shows the presence of two endothermic peaks at 29 and 169° corresponding to the crystalline melting temperatures of poly-THF and poly-BCMO blocks, respectively. This finding, together with the infrared data, shows that the product is composed of poly-THF and poly-BCMO blocks.

On the basis of the P* value, the average lengths of the two blocks were calculated according to the equation

$$\bar{M}_n = (\text{grams of polymerized monomer})/P^* \qquad (1)$$

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[6] B. A. Rozenberg, O. M. Chekhuta, E. B. Ludwig, A. R. Gantmakher, and S. S. Medvedev, *Vysokomol. Soedin.*, **6**, 2030, 2035 (1964).

[7] G. Wasai, T. Saegusa, J. Furukawa, and H. Imai, *Kogyo Kagaku Zasshi*, **67**, 1428 (1964).

[8] G. Wasai, T. Saegusa, and J. Furukawa, unpublished results.

[9] T. Saegusa, H. Imai, and J. Furukawa, *Makromol. Chem.*, **56**, 55 (1962).

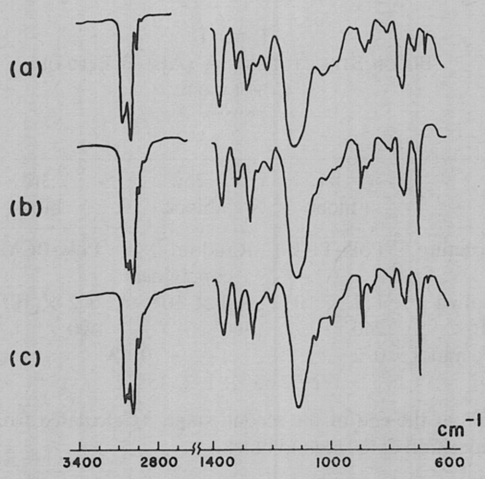

Figure 4. Infrared spectra of block copolymers (film): (a) (poly-THF)–(random copolymer); (b) A–(AB)–B type of block copolymer; (c) (poly-THF)–(poly-BCMO).

where $\bar{M}_n$ is the number average molecular weight of the corresponding block. The length of the poly-BCMO block was calculated from the P* value at the end of the first stage assuming that all the living ends initiated BCMO polymerization. This assumption was based on the fact that the final polymer was completely insoluble in ethanol, *i.e.*, no detectable quantity of the THF homopolymer was formed. The lengths of two blocks are shown in the Experimental Section.

In this case, chain transfer between the oxonium growing chain end and the ether linkage in the polymer molecule may occur. In a reference experiment, the BCMO polymerization was carried out in the presence of a dead polymer of THF. Examination of the product showed that the chain transfer between the BCMO growing end and the ether linkages of poly-THF occurred only to a very small extent. The above values have not been corrected for the occurrence of chain transfer. However, they are a sufficient approximation for the block copolymer.

Synthesis of A–(AB)–B Type of Block Copolymer. The A–(AB)–B type of block copolymer was prepared by a three-stage polymerization, *i.e.*, the living polymerization of THF was followed by THF–BCMO random copolymerization (the second stage) and then BCMO homopolymerization (the third stage). The first and second stages of polymerization were carried out in methylcyclohexane as solvent. After the first stage of the polymerization of THF was carried out at 0°, BCMO was added to the mixture and then the second stage of the THF–BCMO random copolymerization was performed. The amount of THF in the second stage was the THF remaining from the first stage. After the second stage, THF was evaporated *in vacuo* at −50 to −30° and the third stage of the polymerization of BCMO was carried out at 0°. An example of the three stages of polymerization is given in the Experimental Section.

The product of the three-stage block copolymerization was an elastic material which was soluble in hot chloroform and in hot THF but insoluble in ethanol. In Figure 4, the infrared spectrum of the A–(AB)–B polymer (spectrum b) is compared with the spectra of the A–(AB) block copolymer (spectrum a) consisting of a poly-THF block and a block of THF–BCMO random copolymer, and with an A–B block copolymer (spectrum c) of poly-THF and poly-BCMO blocks. In the spectrum of the A–(AB)–B type of block copolymer, there is a crystalline band of poly-BCMO at 890 cm^{-1} as well as a band at 870 cm^{-1} characteristic of the random copolymer. In addition, spectrum b has a strong band at 700 cm^{-1} which is characteristic of the poly-BCMO block as indicated in spectrum c. The presence of the crystalline blocks of poly-THF and of poly-BCMO was further demonstrated by X-ray diffraction analysis. Figure 5 shows the X-ray fiber diagram of a highly stretched sample (about 700% elongation) of the A–(AB)–B block copolymer. Besides the strong crystalline reflections of the poly-BCMO (α form),[7] the diagram has reflections of crystalline poly-THF (A_1, A_2). Furthermore, the diagram shows that both crystalline blocks are highly oriented.

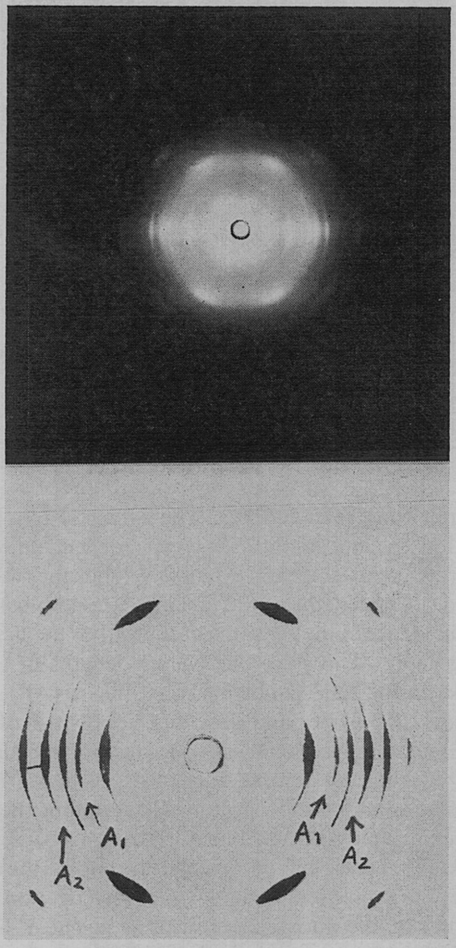

Figure 5. X-Ray fiber diagram of the A–(AB)–B type of THF–BCMO block copolymer: fiber at maximum elongation (*ca.* 700%); exposure time 1 hr (35 kV, 40 mA).

The above findings as well as the mechanical properties described below support the essential conclusion that this copolymer has the structure (poly-THF)–(THF–BCMO random copolymer)–(poly-BCMO).

The lengths of the three blocks were estimated from the P* values of the first and the second stages. Unfortunately, the THF–BCMO random copolymerization in the second stage was not a perfect living polymerization, and some termination occurred. The product contained a block copolymer consisting of poly-THF and

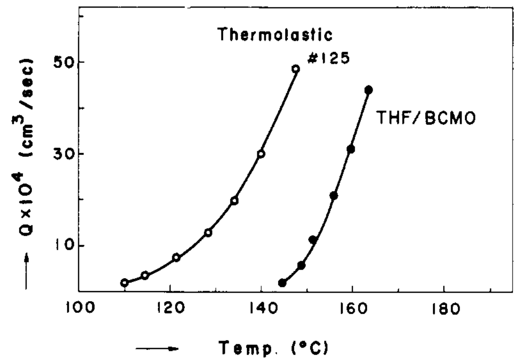

Figure 6. Thermoplasticity of block copolymers: heating rate, 3°/min; Q, flow rate.

random copolymer blocks. The extent of termination reaction in the second stage was dependent on the nature of the solvent. Methylcyclohexane was preferred. The lengths of the first and second blocks were calculated from the P* value at the end of the first stage using eq 1. This gave the average lengths of the two blocks in the total copolymer, *i.e.*, the A-(AB)-B type of block copolymer and the block copolymer of (poly-THF)-(random copolymer). Because of the decrease of P* during the second stage, these values are to be taken as approximate. In the calculation of the length of the third poly-BCMO block in the A-(AB)-B type of block copolymer, the P* value at the end of the second stage was employed in eq 1. Characterization of the product of the above experiment is given in Table I. From the chlorine content of the block copolymer and the lengths of three blocks, the average composition of the second block was calculated to be THF/BCMO = 54/46 (molar ratio).

Exploration of a better catalyst system which does not cause termination in the second and the third stages is now underway in our laboratory.

Mechanical Properties of the A-(AB)-B Type of Block Copolymer. Some mechanical properties of the A-(AB)-B type of block copolymer were examined. Measurements were made on the copolymer sample which is characterized in Table I.

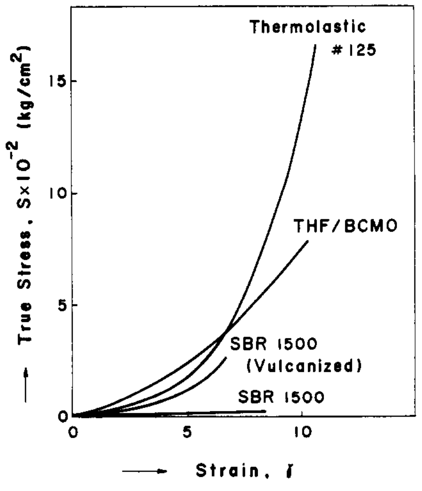

Figure 7. Stress-strain curves of various rubbers: at room temperature; 50 cm/min.

Table I

Block Structure of A-(AB)-B Type of Copolymer

1 2 3

	1st block	2nd block	3rd block
Structure	Poly-THF	Random copolymer	Poly-BCMO
Mol wt	1.7×10^4	$\sim 4 \times 10^4$	6.2×10^4
DP	240	360[b]	400
P*, mmol	0.2	0.13[a]	
	1-2-3, 65%; 1-2, 35%		

[a] P* at the end of the second stage. [b] Calculated from the composition of the second block.

In Figure 6, the thermoplasticity of the A-(AB)-B type of block copolymer of the present study is compared with that of Shell's "Thermolastic No. 125," [10] which is an A-B-A block copolymer based on polystyrene (A) and polybutadiene (B). The thermoplasticizing temperature of the THF-BCMO A-(AB)-B block copolymer is about 20° higher than that of the butadiene-styrene A-B-A polymer. These data clearly indicate that the copolymer is not chemically cross-linked.

In Figure 7 the room temperature stress-strain behavior of the THF-BCMO block copolymer is compared with Thermolastic No. 125, and vulcanized and unvulcanized SBR. Both block copolymers behave like a vulcanized rubber. However, the THF-BCMO block copolymer shows a considerable hysteresis loss, particularly in the first cycle of stretching, as shown in Figure 8. In addition, a yield point is observed in the first cycle. As the cycle is repeated, however, the hysteresis loss becomes quite small and the yield point disappears. This behavior is characteristic of a physically cross-linked block copolymer. In the third cycle, the behavior of the THF-BCMO block copolymer is similar to that of vulcanized SBR.

Figure 9 shows the plot of the strain at break (γ_b) *vs.* temperature. The thermal behavior of the THF-BCMO block copolymer was compared with that of "Thermolastic No. 125." The figure shows that γ_b of the THF-BCMO block copolymer falls quite sharply at

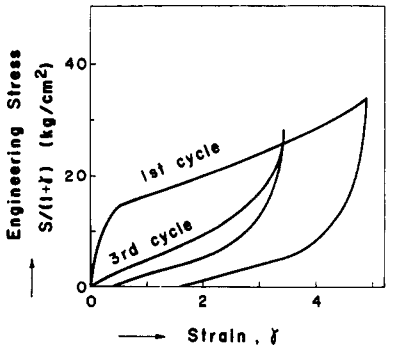

Figure 8. Hysteresis curves of the A-(AB)-B type of THF-BCMO block copolymer in the first and the subsequent cycles of stretching, at room temperature.

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(10) G. Holden and R. Milkovich, U. S. Patent 3,231,635 (1966); Belgian Patent 627,652 (1963).

about 40°. The critical temperature corresponds to the crystalline melting temperature of poly-THF. This finding indicates that poly-THF blocks are responsible for the so-called "cross-linking by crystallization" at room temperature.

All these data are taken as supporting the A–(AB)–B type of structure of the block copolymer, *i.e.*, (poly-THF)–(THF–BCMO random copolymer)–(poly-BCMO).

Experimental Section

Materials. THF, ECH, and Methylene Dichloride. Commercial reagents were purified as described in our previous papers.[5,11]

BCMO. Commercial reagent was purified and dried by repeated distillation over calcium hydride under reduced nitrogen pressure, bp 79° (10 mm).

***n*-Heptane and Methylcyclohexane.** Commercial reagents were treated with concentrated sulfuric acid for 1 day, washed successively with an aqueous solution of sodium hydroxide and with water, dried by calcium chloride, and distilled repeatedly under a nitrogen atmosphere over sodium–potassium alloy, bp 98 and 101°, respectively.

Catalyst. BF_3–THF complex was prepared from BF_3 and THF, and purified by distillation under reduced nitrogen pressure, bp 70° (4 mm).[5]

Block Copolymerization. Reactions were carried out in a flask directly attached to a vacuum system with magnetic stirring under an atmosphere of dry nitrogen. Reagents were transferred by means of a syringe which had been thoroughly dried and kept in a nitrogen-filled container.

An example of the two-stage polymerization was as follows. In 7 ml of *n*-heptane, 3 ml (37 mmol) of THF was polymerized by a mixture of 0.2 mmol of BF_3 and 0.1 mmol of ECH for 18 hr at 0°. Then 5 mmol (0.6 ml) of BCMO was added to the living THF polymerization system. On the addition of BCMO, the precipitated living poly-THF was dissolved. The homogeneous mixture was cooled immediately to −50°, and excess THF and *n*-heptane were removed by distillation at 10^{-2} mm for 2.5 hr. Then the second stage of polymerization was carried out at −30° for 3 hr. The polymeric product was purified by reprecipitation using chloroform–ethanol as a solvent–precipitant pair. The yield of polymer was 1.02 g, and the chlorine content was 20.7%. The absolute value of P* at the end of the first stage of polymerization was 3.3×10^{-2} mmol. The P* determination is described in the following section. The lengths of poly-THF and poly-BCMO blocks were DP = 260 (mol wt 1.9×10^4) and 75 (mol wt 1.2×10^4), respectively.

The three-stage block copolymerization is exemplified by the following procedure. In 35 ml of methylcyclohexane. 15 ml (185 mmol) of THF was polymerized at 0° for 13 hr by an initiator system of 1.0 mmol of a $BF_3 \cdot$THF complex and 0.6 mmol of ECH. The value of P* at the first stage of polymerization was 0.20 mmol, and the quantity of living poly-THF was 3.3 g (per cent conversion 25.0%). To the mixture of the first stage of polymerization, 11 ml (92 mmol) of BCMO was added, and the second stage of polymerization (THF–BCMO random copolymerization) was carried out at 0° for 1.5 hr. At the end of the second stage of copolymerization, P* was 0.13 mmol (the procedure is given in the following section) and the polymer yield was 10.6 g. Then, excess THF was removed at −50 to −30° (10^{-2} mm) for 3 hr. The third stage of polymerization (BCMO polymerization) was made at 0° for 2 hr. The yield of the final block polymer was 18.3 g and the chlorine content was 30.3%.

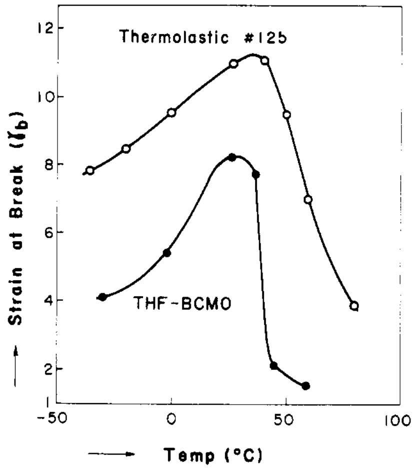

Figure 9. Thermomechanical properties of block copolymers.

Determination of [P*]. The [P*] values and polymer yields in the first and second stages were determined in reference runs carried out under entirely identical conditions. The reproducibility of the polymerization was within 5%. The [P*] determination of the THF polymerization by the phenoxyl end-capping method was carried out as described previously.[4,5]

The determination of [P*] in the THF–BCMO random copolymerization (second stage in the A–(AB)–B block copolymerization) was performed as follows. The polymerization system was treated with excess sodium phenoxide solution and the mixture poured into a large amount of methanolic sodium hydroxide solution. The precipitated polymer was collected by filtration, washed repeatedly with methanol, redissolved in CH_2Cl_2, and the phenoxyl end group was determined by ultraviolet analysis. A reference experiment showed that no polymer phenyl ether group was lost during these operations.

Characterization of Block Copolymer. The infrared spectra of the copolymer films were taken at room temperature. X-Ray diffraction analysis was made by a Rigaku Denki Rotaunit (Rigaku Denki, Japan) at room temperature. Dsc measurements were done by a Perkin-Elmer DSC-IB calorimeter with a heating rate of 10°/min. Mechanical properties of the A–(AB)–B block copolymer were measured on a copolymer sample containing 0.3% phenyl-β-naphthylamine as an antioxidant. The thermoplasticity was measured by a Shimadzu Koka flow tester (Shimadzu Seisakusho, Japan) with a constant heating rate of 3°/min. For stress–strain measurements, a ring-shaped specimen was cut out from a sheet of 1 mm thickness that had been molded at 150°. Measurements were made by means of a Shimadzu autograph, Model IM-500 (Shimadzu Seisakusho), with a cross-head speed of 50 cm/min.

Acknowledgment. The authors are indebted to Dr. S. Kusamizu (Japan Synthetic Rubber Co., Japan) for the mechanical property measurements and to Mr. H. Ishihara (Toyobo Co., Japan) for the X-ray characterization of our polymers.

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(11) H. Imai, T. Saegusa, S. Matsumoto, T. Tadasa, and J. Furukawa, *Makromol. Chem.*, **102**, 222 (1967).