

Characterization of Block Copolymers Based on Poly[3,3-Bis(ethoxymethyl)oxetane] and Other Novel Polyethers

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Synopsis

Diblock, triblock, and alternating block copolymers based on poly[3,3-bis(ethoxymethyl)oxetane] [poly(BEMO)] and a random copolymer center block poly(BMMO-co-THF) composed of poly[3,3-bis(methoxymethyl)oxetane] [poly(BMMO)], and poly(tetrahydrofuran) [poly(THF)] were synthesized and characterized with respect to molecular weight. Glass transition temperatures T_g and melting temperatures T_m were characterized via DSC, modulus-temperature, and dynamic mechanical spectroscopy (DMS). These polyethers had T_m between 70°C and 90°C, and T_g between -55°C and -30°C. The degree of crystallinity of poly(BEMO) was found to be 65% by X-ray powder diffraction.

Tensile properties of the triblock copolymer, poly(BEMO-block-BMMO-co-THF-block-BEMO) were also studied. A yield point was found at 4.1×10^7 dyn/cm² and 10% elongation and failure at 3.8×10^7 dyn/cm² and 760% elongation. Morphological features were examined by reflected light microscopy and the kinetics of crystallization were studied. Poly(BEMO) and its block copolymers were found to form spherulites of 2-10 μ m in diameter. Crystallization was complete after 2-5 min.

INTRODUCTION

Multiblock copolymers have become important as thermoplastic elastomers. The classic thermoplastic elastomers are the ABA triblock copolymers, in which the A blocks are of polystyrene while the B block is polybutadiene (SBS), polyisoprene (SIS), or their hydrogenated equivalents. The strength of these elastomers depends on the degree of phase separation. Thus, it remains desirable to have controlled but significant immiscibility between the two types of blocks, which is a function of their chemical structure and molecular weight. On the other hand, as the blocks become more immiscible, the melt viscosity increases, having a deleterious effect on the processibility of the material.¹

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There has been considerable interest recently in an alternative type of ABA triblock structure, where the end blocks are capable of crystallizing upon cooling, with the A and B blocks being mutually miscible in the melt.² With such a crystalline block copolymer, the melt viscosity decreases rapidly as the temperature rises above the melting point, and hence easier processing is possible. Furthermore, thermoplastic elastomers based on crystalline domains exhibit an advantageous resistance to solvents.³

Several crystalline block copolymers are already known. The work of Morton et al.^{1,2} and Mohajer et al.⁴ is based on hydrogenated polybutadiene, which forms a type of polyethylene. The work of Crystal et al.⁵ and Lotz and Kovacs⁶ provides much information about block copolymers based on amorphous polystyrene and crystallizable poly(ethylene oxide). Makowski and Lundberg⁷ describe novel plasticized thermoplastic semicrystalline copolymers based on polyethylene and polystyrene. Hirata et al.⁸ prepared diblock and triblock copolymers of poly(ethylene oxide) and polyisoprene. Another system of interest involves silicone rubber, where the crystallizable block is poly(diphenyl siloxane).⁹ The relationships among molecular structure, morphology, and mechanical behavior have been recently reviewed.¹⁰⁻¹³

The present study involves crystalline block copolymers based on poly[3,3-bis(ethoxymethyl)oxetane], [poly(BEMO)] and random copolymers based on other ether forming monomers. The objective of the work is to generate a block copolymer consisting of crystallizable polyether end blocks based on poly(BEMO) and an amorphous rubbery center block based on the polyether random copolymers. This paper will examine the interrelationships among glass and melting transition behavior, viscoelastic characteristics, tensile properties, and morphological features of these new block copolymers. The properties of the block copolymers will be compared with those of the homopolymer poly(BEMO).

EXPERIMENTAL

Materials and Synthesis

Burdick and Jackson UV grade THF and methylene chloride were dried and stored over molecular sieves. Commercial grade boron trifluoride etherate was freshly distilled in vacuo before use. 1,4-Butanediol was distilled from calcium hydride and stored over molecular sieves.

3,3-Bis(ethoxymethyl)oxetane (BEMO) monomer was prepared by the reaction of sodium ethoxide with 3,3-bis(chloromethyl)oxetane in refluxing ethanol.¹⁴ 3,3-Bis(methoxymethyl)oxetane (BMMO) monomer was likewise prepared by the reaction of sodium methoxide with 3,3-bis(chloromethyl)oxetane in refluxing methanol. Both monomers were freshly distilled from calcium hydride before use. All glassware was flame-dried and swept with nitrogen immediately preceding the introduction of reactants. During polymerization the reactants were maintained under a dry nitrogen atmosphere.

The solution polymerization of poly(BEMO) or poly(BMMO) proceeds as follows¹⁴: 100 g of calcium hydride dried methylene chloride is charged into

a flame-dried 500 cm³ resin flask which is maintained under a nitrogen atmosphere. To this flask, the calculated quantity of freshly distilled 1,4-butanediol is then added, followed by the calculated amount of boron trifluoride etherate in the mole ratio of 1:2. This solution is allowed to react for 1 h at room temperature. The reactor is then cooled to -10°C and after 30 min a solution of monomer is added dropwise in methylene chloride (25% w/w concentration). The time of addition usually ranges from 20 min to 2 h. After a conversion of 90% is reached, the contents of the flask are quenched with 50 cm³ of saturated brine solution. The organic phase is separated off, washed with 10% sodium bicarbonate solution, dried over magnesium sulfate, and evaporated to dryness at room temperature. The resultant polymer is purified by precipitation from cold methanol. The homopolymers used in this study, their structures and abbreviations are shown in Table I.

The random copolymer, poly(BMMO-co-THF), is prepared by bulk polymerization as follows. Into a 500-cm³ flame-dried resin flask, which is maintained under a nitrogen atmosphere, a calculated amount of freshly distilled THF is charged. While maintaining the flask at room temperature, a calculated amount of freshly distilled 1,4-butanediol is added, followed by a calculated amount of boron trifluoride etherate. The flask is then cooled to 0°C, and after 60 min the calculated amount of BMMO monomer is added in bulk. The rate of addition is governed by the reactivity ratio of the monomer pair. The polymerization is allowed to achieve 90% conversion, and is then quenched, first by addition of 100 cm³ of methylene chloride, followed by the addition of 50 cm³ of saturated brine solution. The organic layer is then separated, washed with a 100 cm³ sodium bicarbonate solution, dried over magnesium sulfate, and then evaporated to dryness. THF polymers are readily purified by precipitation from cold methanol.

The homopolymers were linked together using the bischloroformate technique.¹⁵ Into a 500-cm³ flame-dried resin flask is added a solution of the soft block (BMMO-co-THF) in dried solvent (benzene, dichloromethane, or tetrachloroethane); the amount of polymer is governed by the equivalent

TABLE I
Polyether Structures

Name	Abbreviation	Structure
Poly [3,3-bis (ethoxymethyl) oxetane]	Poly(BEMO)	$\left(\text{O} - \text{CH}_2 - \underset{\begin{array}{c} \text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_3 \\ \\ \text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_3 \end{array}}{\text{C}} - \text{CH}_2 \right)_m$
Poly [3,3-bis (methoxymethyl) oxetane]	Poly (BMMO)	$\left(\text{O} - \text{CH}_2 - \underset{\begin{array}{c} \text{CH}_2 - \text{O} - \text{CH}_3 \\ \\ \text{CH}_2 - \text{O} - \text{CH}_3 \end{array}}{\text{C}} - \text{CH}_2 \right)_m$
Polytetrahydrofuran	Poly (THF)	$\left(\text{O} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \right)$

weight of the polymer. A five times excess of phosgene is then added while maintaining the flask at 25°C. The normal precautions regarding phosgene should be carefully followed, including placing a KOH trap at the end of the gas/flask train. The formation of the bischloroformate is allowed to continue for 2 h at which time the excess phosgene is removed by passing a stream of dry nitrogen through the flask at slightly elevated temperatures. To this solution is quickly added a solution of BEMO end block at an amount required to end cap the center block. The addition of HCl scavenger (pyridine, piperazine, triethylamine) is normally required for good reaction. At this time, the flask is heated to 60°C and an immediate rise in viscosity will be noted. The heating is usually continued overnight. After this time the block copolymer can be isolated by precipitation from methanol or water. The final polymer may be reprecipitated from methanol.

Instrumental

The molecular weights of various poly(BEMO)-polyether block copolymers were estimated by intrinsic viscosity using an Ubbelohde viscometer with tetrahydrofuran as solvent. All measurements were made near room temperature, 20°C. The molecular weights were also estimated by gel permeation chromatography (GPC) using a Waters GPC calibrated with polypropylene glycol standards of various molecular weights.

A Gehman torsion stiffness tester^{16,17} was used to measure the 10-s shear modulus, 3G(10), as a function of temperature. The glass transition and melting temperatures were obtained. For temperatures below 20°C, a liquid-nitrogen-cooled methanol bath was used, and silicone oil was used for temperatures above 20°C. The heating rate was 1°C/min throughout. Glass transition and melting temperatures were also obtained using a Perkin-Elmer DSC 1-B.¹⁸

Spherulite microphotographs were taken by reflected light using an Olympus BH-2 microscope equipped with an Olympus PM-10AD automatic exposure control 35 mm photomicrographic camera. As appropriate, polarizing and color filters were used to enhance the image. Kodacolor VR ISO1000 and Kodak Tri-X ISO400 films were used. Polymer samples were prepared by placing the sample on a microscope slide, which was heated until the sample melted. The slide was then allowed to cool to ambient temperature on the microscope stage. The kinetics of spherulite growth was determined by allowing polymer samples to cool from the melt on the microscope stage while taking photographs at timed intervals. The increases in spherulite sizes were determined from direct measurements of at least 10 representative spherulites in each case.

Dynamic mechanical spectroscopy (DMS) studies employed a Rheometrics Dynamic Spectrometer to obtain the storage shear modulus G' and the loss tangent, $\tan \delta$. The heating rate was adjusted to 1°C/min and the frequency was set at 110 Hz.

Stress-strain measurements were conducted on an Instron Universal tester according to ASTM D638.^{19,20} A crosshead speed of 0.6 in./min was used.

Wide angle X-ray powder diffraction studies employed a Phillips APD 3600 automated X-ray powdered diffractometer with a copper target and a

Phillips XRG 3100 X-ray generating unit. A nickel filter was used to isolate the $\text{CuK}\alpha$ line, $\lambda = 1.542 \text{ \AA}$. The scan rate was $2.0^\circ/\text{min}$ by increments of 0.03° .

RESULTS

Molecular Weight Determination

The molecular weight of various poly(BEMO)-polyether block copolymers was estimated by intrinsic viscosity and GPC.

The Mark-Houwink equation for intrinsic viscosity was used to calculate the molecular weight of the individual polymers:

$$[\eta] = K'M_v^a \quad (1)$$

Since the constants K' and a are unknown for poly(BEMO) and the other novel polyethers, the values $K' = 21.9 \times 10^{-3}$ and $a = 0.78$ were taken from the polymer polyoxytrimethylene, which is the polyether corresponding to poly(BEMO) without the disubstituents in the gamma positions.²¹ Results are presented in Table II. Also presented in Table II are the GPC results, which are somewhat higher than the viscosity average results. The discrepancy between the GPC and viscosity results probably arise from the difference in calibration systems. The actual molecular weights are more likely closer to the gel permeation chromatography results. If the intrinsic viscosity molecular weights are multiplied by the ratio of the mer molecular weights of poly(BEMO) over polyoxytrimethylene, to correct for the presence of side groups, numerical agreement is much better.

The number of blocks in the block copolymer was estimated using the intrinsic viscosity results. For an alternating block copolymer of the type $\text{---}(\text{---AB---})_n\text{---}$, the relation between molecular weight and the number of repeat units, n , is

$$M\text{---}(\text{---AB---})_n\text{---} = n(M_A + M_B) \quad (2)$$

Substituting the Mark-Houwink equation [eq. (1)] and assuming that K' is nearly constant, the relation becomes

$$([\eta]_{\text{---}(\text{---AB---})_n\text{---}})^{1/a} = n([\eta]_A^{1/a} + [\eta]_B^{1/a}) \quad (3)$$

This assumes a certain degree of independence of the A and B blocks in dilute solution. The quantity a is unknown for the blocks. As a varies between 0.5 and 0.9, the number of repeat units estimated from viscosity results varies between 1 and 2 (two-four block units). From these results, it was concluded that the AB and ABAB block copolymers had been successfully synthesized. A similar approach was used to estimate if the triblock had been formed. Equation (3) must include two units of A block rather than one. It was found that the value of n was equal to approximately 1; therefore, the triblock (ABA) was also successfully synthesized.

TABLE II
Molecular Weight Characterization of Polyethers

No.	Sample	Description	$[\eta]^a$ (mL/g)	M_v , $[\eta]$ (g/mol)	M_n (GPC) (g/mol)
1	Poly(BEMO)		23.2	7550	9200
2	Poly(BMIMO-co-THF)		29.0	10,050	15,300
3	Poly(BMIMO-co-THF)		30.0	10,500	17,600
4	Poly(BMIMO-co-THF)		33.0	12,000	26,800
5	Poly[BEMO-block-BMIMO-co-THF] _n		52.5	21,550	—
6	Poly[BEMO-block-BMIMO-co-THF] _n		63.9	28,000	—
7	Poly[BEMO-block-BMIMO-co-THF] _n		51.3	20,600	—
8	Poly[BEMO-block-BMIMO-co-THF-block-BEMO]		61.1	26,150	—
9	Poly[BEMO-block-BMIMO-co-THF-block-BEMO]		41.9	16,100	—

^a All intrinsic viscosity measurements done at 20°C.

^b Reprecipitated sample.

Viscoelastic Behavior

Three times the 10-s shear modulus, $3G(10)$, vs. temperature curves for poly(BEMO) and poly[BEMO-block-BMMO-co-THF-block-BEMO] as determined on the Gehman are shown in Figure 1. The lower temperature decrease in the modulus corresponds to the glass transition temperature and the upper decrease in the modulus corresponds to the melting temperature. The homopolymer BEMO has a glass transition temperature of -30°C and melts at 85°C . The triblock copolymer has a glass transition of -45°C , softens at approximately 65°C , and melts at 72°C .

Several points should be emphasized here. Both the T_g and T_m are governed by the soft block in significant measure. There seems to be a certain degree of mixing between the hard block poly(BEMO) and the center block poly(BMMO-co-THF) in the triblock copolymer, as shown by the shifting of the poly(BEMO) transitions to lower temperatures. The rubbery plateau of the modulus-temperature curve is governed by the hard block. A typical value of the plateau for soft elastomers is 1×10^7 dyn/cm², whereas in this case the value of the modulus is 1×10^8 – 1×10^9 dyn/cm², indicating stiff rubbery to leathery behavior. There is a direct correlation between the morphology and the plateau level. The crystallinity adds a degree of stiffness to the material, increasing the modulus above the typical value for ordinary soft elastomers. Yet as Figure 1 depicts, the center block of the triblock copolymer causes the material to behave elastomerically lowering the modulus of the plateau.

Physical Properties

Various block copolymers studied by modulus-temperature (Gehman) show glass transition temperatures in the range of -30 – 55°C , characteristic of this type of polyether, and melting temperatures in the range of 65 – 80°C (Table III). The last two compounds listed in Table III are a series of block copolymers differing in the composition of the random copolymer. The first has the largest ratio of tetrahydrofuran (THF) to BMMO: 75 mol

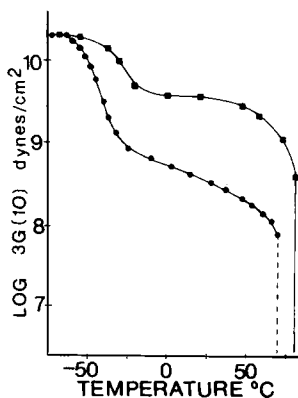


Fig. 1. Modulus-temperature shift for poly(BEMO) (■), sample no. 1, and poly(BEMO-block-BMMO-co-THF-block-BEMO) (●), sample no. 8, by Gehman instrumentation. The lower transition corresponds to T_g and the upper transition corresponds to T_m .

TABLE III
Glass Transition and Melting Temperatures of Polyethers by Gehman and DSC (°C)

No.	Sample	Gehman, T_g	Gehman, T_m	DSC, T_g^a	DSC, T_m^b
1	Poly(BEMO)	-30	85	-35	79
8	Poly[BEMO-block-BMMO-co-THF-block-BEMO]	-45	72	-50	68
5	Poly[BEMO-block-BMMO-co-THF-]n	-55	78	—	—
7	Poly[BEMO-block-BMMO-co-THF-]n	-40	—	—	—

^a Scan speed 5°C/min.

^b Scan speed 20°C/min.

% THF/25 mol % BMMO. The later compound has a random copolymer ratio of 50 mol % THF/50 mol % BMMO. The THF lowers the glass transition temperature significantly due to its T_g of approximately -80°C . This allows the properties of the polymer to be changed by changing the composition of the soft block. The transitions were confirmed for a few of the compounds of DSC (Table III).

Figure 2 shows the fusion endotherm for poly(BEMO). The temperature of the maximum in the DSC trace is the melting temperature T_m at approximately 79°C . The upper portion of the curve shows the decomposition temperature of poly(BEMO), at approximately 330°C . Thermal decomposition of poly(BEMO) and related polyethers is the subject of another paper.²² From the DSC trace (Fig. 2), a heat of fusion of 1.70 kcal/mol was obtained from the area under the curve. This technique measures both the amorphous and the crystalline portions combined.

Figure 3 shows a wide angle X-ray powder diffractometer scan of poly(BEMO) with the crystalline reflections, the amorphous peaks, and the background indicated. Total amounts of crystalline and amorphous scattering were measured as the sum of the areas underneath all the crystalline peaks and amorphous peaks, respectively. The degree of crystallinity was taken as the ratio of crystalline to total scattering minus background and was found to be 65% for poly(BEMO). Based on 65% crystallinity, the heat of fusion of the crystalline portion of poly(BEMO) is estimated to be 2.60 kcal/mol.

Morphology and Kinetics of Crystallization

Reflected light microphotographs of poly(BEMO), poly(BEMO-block-BMMO-co-THF-block-BEMO), and poly(BEMO-block-BMMO-co-THF)_n are shown in Figure 4. Spherulites which have grown below the polymer surface show a spherical shape, while those that have grown at the surface appear as a cross section with the slightly visible characteristic maltese cross pattern. As can be seen from the photomicrographs, there is a significant difference in the size of the spherulites of the three polymers.

Table IV presents mean spherulite diameters calculated from at least 10

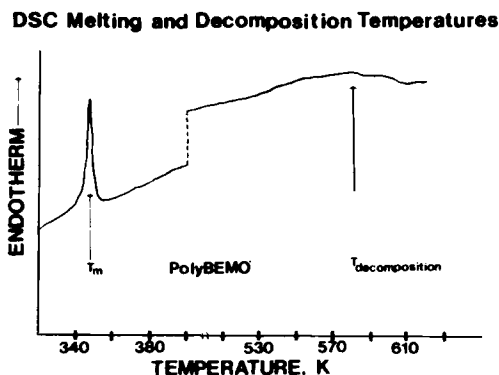


Fig. 2. The determination of the melting temperature and heat of fusion by differential scanning calorimetry, DSC, for poly(BEMO), Sample No. 1. The area under the curve at T_m yields the heat of fusion. At higher temperatures, the decomposition temperature is shown.

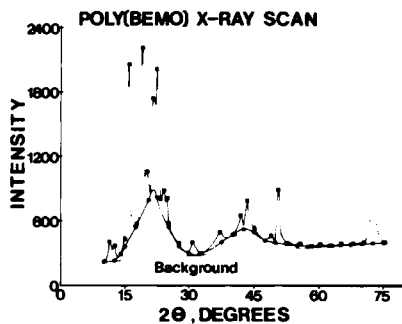


Fig. 3. Wide angle X-ray powder diffractometer scan of poly(BEMO), sample no. 1; units of intensity are arbitrary: (●) amorphous; (■) crystalline.

representative spherulites in each case. The spherulite sizes of the polyether block copolymers are more than an order of magnitude smaller than the size of poly(ethylene oxide) spherulites, which have been extensively studied by transmitted light microscopy.⁵ The mean spherulite diameters depend on the composition of the blocks. The poly(BEMO) blocks become increasingly restricted in the ability to form spherulites and hence, spherulite sizes decrease as the ratio of rubbery to crystalline molecular weights increases. As the concentration of tetrahydrofuran increases in the alternating block copolymers listed in Table IV, the spherulite size decreases.

The kinetics of spherulite formation for poly(BEMO) and poly(BEMO-block-BMMO-co-THF-block-BEMO) are shown in Figure 5. The poly(BEMO) begins spherulite formation after 5–10 s while the triblock copolymer went through an induction period of 70–75 s. Once initiated, spherulite formation

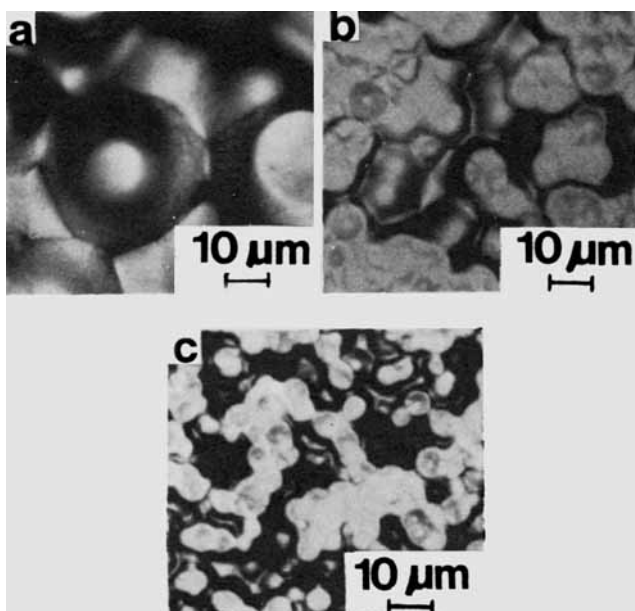


Fig. 4. Reflected light microphotographs of spherulites. (a) poly(BEMO), sample no. 1, 13.8-s exposure; (b) poly(BEMO-block-BMMO-co-THF-block-BEMO), sample no. 8, 15-s exposure; (c) poly(BEMO-block-BMMO-co-THF)_n, sample no. 5, 12-s exposure.

TABLE IV
Mean Spherulite Diameters (μm)

Poly(ethylene oxide)	800-1000
Poly(BEMO)—sample no. 1	22.8
Poly(BEMO-block-50%BMMO-co-50%THF-block-BEMO)—sample no. 8	12.3
Poly(BEMO-block-50%BMMO-co-50%THF) _n —sample no. 7	7.2
Poly(BEMO-block-25%BMMO-co-75%THF) _n —sample no. 5	2.0

occurred more rapidly and led to considerably larger spherulites for poly(BEMO). The poly(BEMO) formed spherulites of approximately $25 \mu\text{m}$ while the poly(BEMO-block-BMMO-co-THF-block-BEMO) formed spherulites of only $12 \mu\text{m}$ (Table IV). The induction period probably occurs in the triblock because the intervening noncrystalline rubbery center block restricts the motions of the chains during spherulite formation.

The relatively uncontrolled conditions under which the kinetics experiments were conducted allow only a qualitative comparison of the kinetics of spherulite growth of the two polymers studied. A similar constant rate of diameter growth was predicted in a series of papers by Keith and Padden.²³ Further studies are planned using a controlled temperature microscope stage.

Dynamic Mechanical Spectroscopy (DMS)

Figure 6 depicts the storage (shear modulus) G' the loss (shear modulus) G'' , and the loss tangent, $\tan \delta$, as a function of temperature for the triblock copolymer, poly(BEMO-block-BMMO-co-THF-block-BEMO). The storage modulus is a measure of energy elastically stored during deformation and is closely related to Young's modulus numerically. The loss modulus is a measure of energy lost as heat during the experiment.

Dynamic mechanical spectroscopy is a sensitive indicator of the extent of molecular mixing. The advantage of the dynamic method (DMS) over the static tests (Gehman 10-s modulus) is that the loss modulus is obtained. Some materials show important transitions with DMS that are missed with the static test. In both the static and dynamic tests for the triblock copolymer a single sharp glass transition occurs (Figs. 1 and 6), which implies

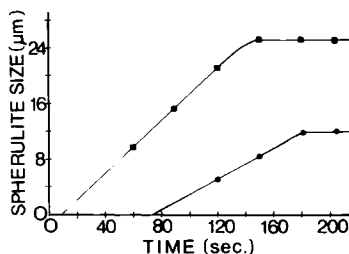


Fig. 5. Kinetics of spherulite formation for poly(BEMO) (■), sample no. 1, and poly[BEMO-block-BMMO-co-THF-block-BEMO] (●), sample no. 8.

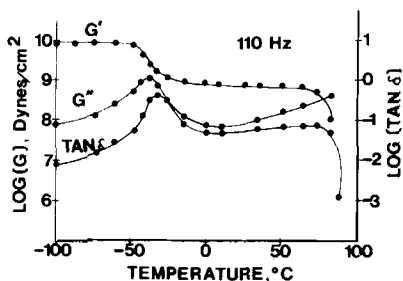


Fig. 6. Dynamic mechanical spectroscopy of poly[BEMO-block-BMMO-co-THF-block-BEMO], sample no. 8, 110 Hz.

complete mixing between the amorphous portions of the polymer. In Figure 6, the glass transition temperature of poly[BEMO-block-BMMO-co-THF-block-BEMO] is taken as the maximum of the loss modulus curve at -40°C . If the amorphous portions of the polymers are totally miscible, the glass transition temperature occurs at a temperature controlled by the weight fractions of the components.

Tensile Properties

Figure 7 shows the stress-strain behavior of the triblock copolymer poly(BEMO-block-BMMO-co-THF-block-BEMO). This figure is characteristic of the successive stages in elongation of a spherulitic polymer.²⁴ A yield point is reached at 10% elongation, where large inelastic deformation begins. The yield stress was 4.1×10^7 dyn/cm² at 10% elongation. After 10% elongation, a neck appeared and grew until failure. The tensile strength was 3.8×10^7 dyn/cm² at 760% elongation.

The modulus of elasticity (Young's modulus) E was determined from the initial slope of the stress-strain curve. The modulus was found to be 3.5×10^8 dyn/cm² indicating leathery behavior. Agreement was found between this result and the modulus obtained by static measurements (Gehman) at 25°C (Fig. 1). Using the approximation $E \cong 3G(10)$, the value for E from Figure 1 was 3.2×10^8 dyn/cm². The energy to break was calculated from the area under the stress-strain curve and found to be approximately 2.5×10^8 ergs/cm³ (25 MJ/m³).

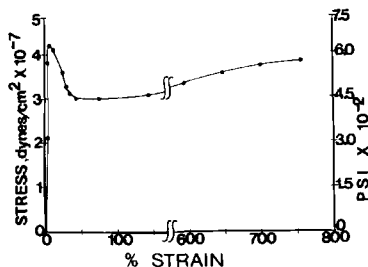


Fig. 7. Stress-strain curve for poly[BEMO-block-BMMO-co-THF-block-BEMO], sample no. 8, at 75°F .

DISCUSSION

The concept of the thermoplastic elastomer as a rubbery material without the need of vulcanization, which flows on heating and sets on cooling, has resulted in several different materials. The first and most famous was the SBS triblock copolymer known as Kraton.²⁵ Later, the center block was hydrogenated for environmental resistance.²⁶ The concept was further broadened, as people discovered that combinations of crystalline and cross-linked polymers such as polypropylene and EPDM yielded similar properties.²⁷⁻³⁰

Problems associated with the amorphous block copolymers such as the SBS and the hydrogenated SEBS system reside in their high viscosity and relatively broad softening range. The high viscosity is caused by the high molecular weights necessary to ensure proper phase separations, while the broad softening range to flow of 20–50°C is a consequence of the molecular nature of the glass transition.

Crystalline block copolymers may be miscible in the melt, permitting lower molecular weights and concomitant lower melt viscosities. Since polymer melting is a sharper transition than the glass transition, the change over from a semicrystalline solid to the melt is about 10°C. Thus, the particular polyether block copolymers characterized herein, melt in the range of 70–80°C (Table III), and are easily processible in the range of 90–100°C.

Although this paper does not examine the organization of the crystalline-amorphous regions within the spherulites, the data obtained are consistent with the notion of folded chain lamellae sandwiched by rubbery amorphous portions.³¹ As the rubbery center block increases in length relative to the crystalline end blocks, the amorphous portion increases and the modulus decreases.

CONCLUSIONS

A series of novel polyether block copolymers were synthesized and characterized. Diblock, triblock, and alternating block copolymers with two repeat units, of poly(BEMO) and poly(BMMO-co-THF), were prepared. The glass transition temperatures of these materials were in the range of –30––55°C while the melting temperatures were between +70°C and +90°C. A single glass transition temperature was found for the block copolymers, suggesting complete mixing between the amorphous portions of the polymer. The triblock copolymer exhibited stiff rubbery to leathery viscoelastic behavior. All of the polyether block copolymers showed a spherulitic morphology due to the crystalline end blocks. Spherulite size was dependent on the composition of the blocks. Crystallization was complete after approximately 2–5 min, with more rapid spherulite formation for the homopolymer poly(BEMO). Stress-strain behavior was found to be characteristic of spherulitic polymers with a yield point followed by necking and final failure after extreme elongation. These block copolymers exhibit encouraging properties in the synthesis of novel thermoplastic elastomers.

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