

Energetic ABA and (AB)_n Thermoplastic Elastomers

BAOPEI XU, Y. G. LIN, and JAMES C. W. CHIEN*

Department of Polymer Science and Engineering, Department of Chemical Engineering,
University of Massachusetts, Amherst, Massachusetts 01003

SYNOPSIS

Linear ABA triblock and (AB)_n segmented block copolymers of energetic monomers have been synthesized. The rigid and soft blocks are prepared from 3,3-bis(azidomethyl)oxetane (BAMO) and 3-nitratomethyl-3-methyloxetane (NMMO), respectively. Polymerization of BAMO initiated by triethyloxonium tetrafluoroborate and by spiro (benzoxasilole)/propanediol produced α -monohydroxy-PBAMO (**3**) and α,ω -dihydroxy-PBAMO (**4**) of \bar{M}_n 16,000 and 2,000, respectively, and α,ω -dihydroxy-PNMMO (**5**) of $\bar{M}_n = 13,000$ was synthesized by the latter method. The block copolymers were prepared from the appropriate telechelic polymers and toluene diisocyanate. The PBAMO-PNMMO-PBAMO copolymer **6** has $T_m = 82^\circ\text{C}$, $T_g = -3^\circ\text{C}$, and is strongly phase separated even in the melt. It decomposes sharply within 1°C at 224°C evolving 0.69 kJ/g of heat. Copolymer **6** has excellent mechanical properties with elongation of 683% at break, 5.25 MPa stress, and 82% recovery. The (PBAMO-PNMMO)_n copolymer **7** has similar thermal properties and spectroscopic characteristic, but is inferior to copolymer **6** in all rheological and mechanical properties.

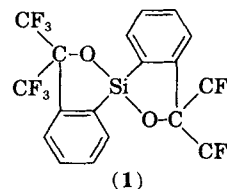
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INTRODUCTION

Thermoplastic elastomers (TPE) are useful materials.¹ They can be prepared from any combination of low T_g building block with high T_g or crystalline ones. Segmented TPE is prepared by coupling the appropriate telechelic prepolymer in equal molar ratio. Linear ABA triblock copolymer can be elegantly synthesized by sequential polymerization if living propagation of all the constituent monomers can be achieved. It is more readily prepared by coupling telechelic low T_g prepolymer with monofunctional high T_g /crystalline prepolymer as the terminal hard blocks. The synthesis of these functional prepolymers are prerequisite for this route. TPE containing energetic groups have been considered to be binder for propellant. The central purpose of this research is to synthesize both segmented and ABA TPE's from energetic monomers.

It has been reported that 3,3,3',3'-tetrakis-

(trifluoromethyl)-1,1'-(3H, 3H')-spirobis(2,1-benzoxasilole) (**1**) is a catalyst for living polymerization of oxetane derivative.^{2,†} This catalyst was employed by us to polymerize four oxetane monomers⁴:



Though living polymerization was not achieved for these oxetanes, α,ω -dihydroxypolymer was obtained with **1**/propanediol. Furthermore, α -monohydroxypolyoxetanes was synthesized using either the **1**/benzyl alcohol catalyst or the $\text{Et}_3\text{O}^+\text{BF}_4^-$ initiator. We present here the synthesis of TPE from these prepolymers and their properties.

* To whom correspondence should be addressed.

† Sogah³ reported that **1** and benzyl alcohol initiates living polymerization of 3-methyl-3-trimethylsiloxydimethyl oxetane to yield polymers having $\bar{M}_n = g$ monomer/mol benzyl alcohol up to $\bar{M}_n = 150,000$.

EXPERIMENTAL

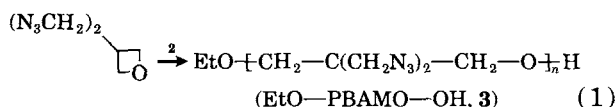
Materials

3,3-Bis(azidomethyl)oxetane (BAMO) and 3-nitratomethyl-3-methyl oxetane (NMMO) were obtained from G. Manser of Aerojet Solid Propulsion Co. All the other chemicals were from Aldrich. Spiro(benzoxosilole) (**1**) was synthesized according to the procedure described by Perozzi et al.⁵ Triethyloxonium tetrafluoroborate (**2**) (1M solution in dichloromethane) and dibutyltindilaurate (DBTDL) were used as received. Toluene-2,4-diisocyanate (TDI) was purified by vacuum distillation. Chloroform was distilled from CaH₂. 1,3-Propanediol and 1,4-butanediol were dried over molecular sieve and distilled.

Polymerizations

 α -Monohydroxy Poly(BAMO) (**3**)

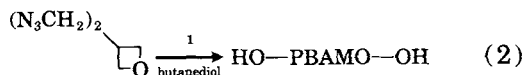
Polymerization and block coupling reactions were performed using dry argon purged Schlenk type apparatus. The crystalline block **3** was synthesized by



BAMO, catalyst **2**, and methylene chloride in the desired ratios were mixed and stirred at 25°C. The polymerization was quenched with water and the white powdery polymer **3** was precipitated with tenfold excess of aqueous NH₃ in methanol. It exhibits ¹H-NMR (300 MHz, CDCl₃), σ 3.44 ppm (4H, S), 3.35 ppm (4H, S), and IR absorption at 2110 cm⁻¹ for the N₃ groups.

 α,ω -Dihydroxy Poly(BAMO) (**4**)

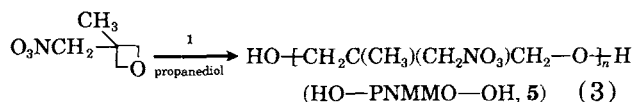
The telechelic crystalline block **4** was obtained with catalyst **1**/butanediol. BAMO (5 g, 30 mmol), butanediol (0.2 g, 2.2 mmol), and



1 (0.31 g, 0.6 mmol) was charged into a Schlenk reactor and stirred for 8 days. The thick reaction mixture was first thinned with 5 mL of Me₂Cl₂; then 50 mL of methanol was added to precipitate **4** (yield = 56%). The waxy prepolymer has $\bar{M}_n = 2000$ and $\bar{M}_w/\bar{M}_n = 2.38$.

 α,ω -Dihydroxy Poly(NMMO) (**5**)

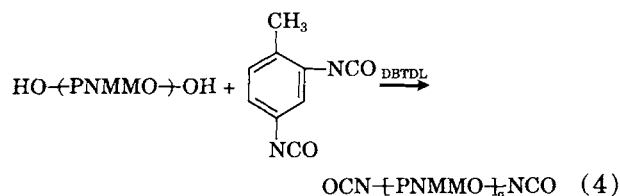
The telechelic amorphous block **5** was also prepared using catalyst **1** and propanediol:



NMMO (9.9 g, 67 mmol), propanediol (0.5 g, 7 mmol), and **1** (0.3 g, 0.59 mmol) were combined and reacted for 3 days. The product was washed with an equal volume of aqueous methanol three times, then dissolved in 5 mL CH₂Cl₂, and dried with molecular sieve. After removal of CH₂Cl₂, the oily product **5** was dried at 70°C/1 torr for 4 h for a yield of 88.5%. It has $\bar{M}_n = 1010$ and $\bar{M}_w/\bar{M}_n = 1.85$ by GPC.

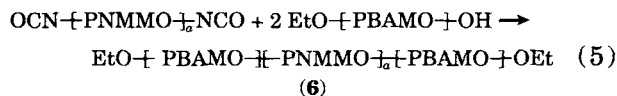
Synthesis of PBAMO-PNMMO-PBAMO TPE (**6**)

Into a 150-mL three-necked flask, equipped with mechanical stirrer, condenser, thermometer, and argon inlet and outlet, was charged **5** (5.5 g, 3.9 mmol), 2,4-TDI (0.73 g, 4.2 mmol), and 15 mL dried dioxane. After 15 min of stirring 0.1 mL of DBTDL was added. The reaction mixture was maintained at 60–65°C for 16.5 h. During this time chain extension of **5** took place:



where $a \sim 12$ –13, which is the number of molecules of prepolymer **5** coupled by TDI.

For the second stage of synthesis, the above mixture was heated to 90°C and prepolymer **3** (2.5 g) was introduced. Reaction to linear triblock TPE was prepared by reaction at 90–95°C for 30 h:



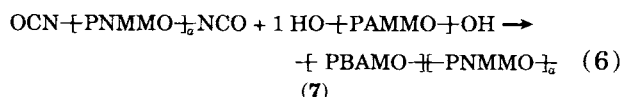
The polymerization was quenched by pouring the mixture into 180 mL methanol with vigorous stirring. The brown gummy polymer was washed twice with methanol and dried at 50°C/1 torr for 6 h to produce 7.5 g of **6**.

Table I Et₃OBF₄-Initiated Polymerization of BAMO^a

Run No.	[Et ₃ OBF ₄] (mM)	[BAMO] (M)	t _p ^b (h)	Yield (%)	GPC			
					$\bar{M}_n \times 10^{-4}$	PD ^c	$\bar{M}_{eq} \times 10^{-4}$	f ^d
1	130	2.6	1	91.8	1.35	1.9	1.58	0.88
2	90	2.7	1	91.1	1.56	1.8	1.59	0.99
3	6.8	2.7	1	88.0	1.71	2.0	1.73	0.97
4	2.9	2.9	4	74.6	1.46	1.6	1.24	1.18

^a Polymerization at 25°C in CH₂Cl₂ solvent.^b t_p = time of polymerization.^c PD = \bar{M}_w/\bar{M}_n .^d f = functionality = \bar{M}_n/\bar{M}_{eq} .**Synthesis of Segmented (PBAMO-PNMMO) TPE (7)**

In the above described reactor was charged **5** (5.1 g, 3.6 mmol), TDI (0.72 g, 4.1 mmol), dioxane (10 mL), and DBTDL (0.1 mL) and reacted for 10 h at 50°C [eq. (4)]. Then prepolymer **4** (2.1 g, 1.05 mmol) in 5 mL dioxane was added and reacted for 24 h at 80–85°C:



This reaction produced, after workup as above, 5.3 g of **7** with $\alpha \sim 7$ –8.

Methods

A Varian XL-300 MHz spectrometer was used to record ¹H-NMR spectra of CDCl₃ solution of polymers. TMS served as the external standard. A Perkin-Elmer 1420 ratio IR spectrophotometer was used to record IR spectra. Gel permeation chromatographic measurements were made with a Waters GPC with three μ-styrogel columns (10⁵, 10⁴, 10³ Å) operating at a tetrahydrofuran flow rate of 10 mL/min. Peak MW estimate was based on a calibration curve derived from seven narrow dispersity polystyrene standards obtained from Polysciences. All DSC measurements were made on a Perkin-Elmer DSC-4 differential scanning calorimeter at a heating rate of either 20 or 10°C/min. The temperature at the midpoint of the increment in ΔC_p is taken to be the T_g. A Perkin-Elmer TGS-2 thermogravimetric analyzer was used to record the TGA curve in nitrogen. Dynamic mechanical measurements were made on a Rheometrics mechanical spectrometer (RMS-800), the heating and cooling rate was 0.3°C/min, and frequency ω = 1 rad/s. Stress-strain data were obtained on an Instron

Model TTBN universal testing instrument at an extension rate of 20 mm/min. Specimens were die-cut from a sheet of the TPE 0.5 mm thick; the gage length was about 5 mm.

RESULTS AND DISCUSSION**Telechelic Polymers of Oxetane Derivatives**

Two general types of telechelic oxetane polymers were synthesized. They are mono- and dihydroxy-terminated polymers; their synthesis are illustrated below.

α-Monohydroxy terminated polymers were synthesized using triethyloxonium ion initiator (**2**). It initiates the polymerization of oxetane monomer (**M**) by alkylation of the most nucleophilic site.^{6,7} α-Terminal hydroxyl group was introduced by quenching the polymerization with water. The results of four polymerizations are summarized in Table I. The polymers have narrow molecular weight distributions. The polydispersity index (PD = \bar{M}_w/\bar{M}_n) is slightly smaller than the most probable value.

The equivalent molecular weight (\bar{M}_{eq}) is the mass per hydroxyl group. Hexafluoroacetone was used to react with the alcohol to form hemiacetal.

Table II Spirobenzoxasilole-Catalyzed Polymerization of NMMO^a

Run No.	T _p (h)	Conv. (%)	$\bar{M}_n \times 10^{-4}$	PD
5	3	24.8	0.87	1.3
6	5.5	44.2	1.2	1.7
7	7.0	50.7	1.3	1.8
8	24	83.6	1.5	1.8

^a Polymerization conditions are [NMMO]₀ = 4.3 M, [1] = 0.44 mM, T_p = 10°C, solvent = CH₂Cl₂.

Table III Block Copolymer Composition

Copolymer	Analysis			Content (mol %)		
	C	H	N	PBAMO	PNMMO	TDI
	(%)	(%)	(%)			
6	40.82	5.59	21.53	29.2	63.8	7.0
7	41.56	5.53	20.04	25.0	65.5	9.5

Quantitative ^{19}F -NMR measurement of this adduct afforded the \bar{M}_{eq} value⁸; the functionality is $f = \bar{M}_n / \bar{M}_{\text{eq}}$. The PBAMO of runs 2 and 3 of Table I can be considered as monofunctional. The polymers of run 1 and 4 have respectively slightly lower and higher functionality than unity. We hasten to point out that f is the average functionality and that there are PBAMOs with two hydroxyl terminal groups and others without any. Lowering of the initiator concentration had the effect of raising \bar{M}_n ; $\bar{M}_n \sim (165 [\text{M}]) / [\text{I}]$ in run 4. These polymerization behaviors can be attributed to $k_i \ll k_p^0$ and chain transfers.⁹

α, ω -Dihydroxy terminated polymers were synthesized using the spiro(benzoxasilole) catalyst (**1**).⁴ The molecular weight of the polymer could be calculated by the amount of diol used as coinitiator. Table II illustrates the method for the synthesis of α, ω -dihydroxy PNMMO (**5**). There was steady increase of conversion with t_p , but both \bar{M}_n and PD increase to plateau values after 5 h of polymerization.

The ^{19}F -NMR method for the determination of \bar{M}_{eq}^0 (*vide supra*) could not be used on HO-

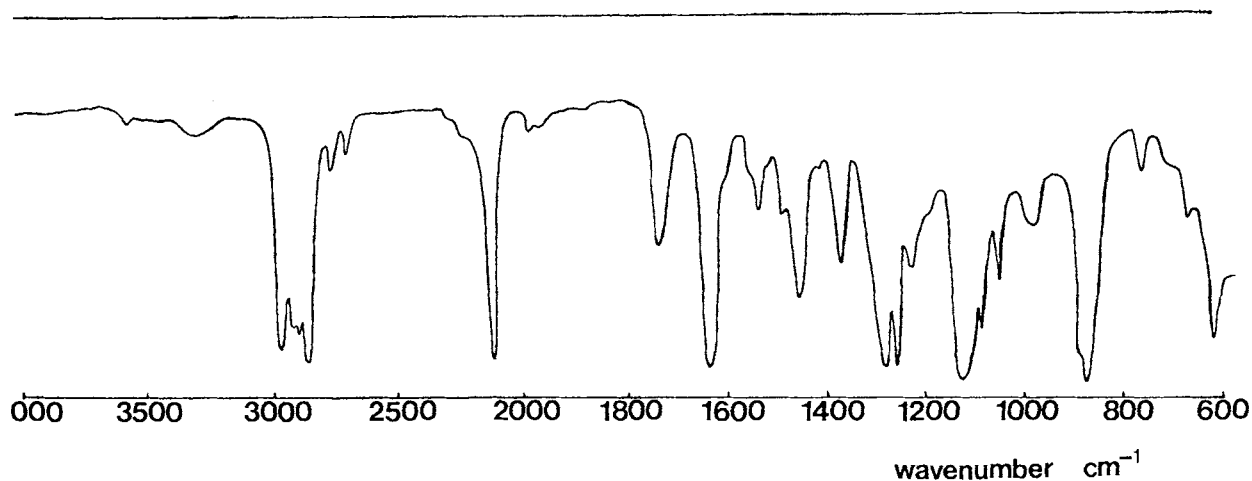
(PNMMO)OH because of reactions between the nitrate group and hexafluoroacetone. Another method for the estimation of f , which is also at once practically useful is the titration of **5** with TDI monitored with IR. The end point corresponds to the appearance of the characteristic asymmetric stretching band of NCO at 2260 cm^{-1} .

Block Copolymers

Both ABA triblock type copolymer **6** and segmental copolymer **7** were synthesized. Their analysis and compositions are shown in Table III.

Spectroscopic Features

The IR and ^1H -NMR spectra of ABA copolymer **6** are shown in Figures 1 and 2, respectively. The IR spectrum is characterized by asymmetric stretch for azido and nitrate groups at 2110 and 1630 – 1650 cm^{-1} , respectively. The NH and C=O stretching bands are located at 3200 – 3450 and 1650 – 1750 cm^{-1} , respectively. The spectrum of (AB)_n copolymer **7** is essentially the same as above.

Figure 1 IR spectrum of ABA copolymer **6**.

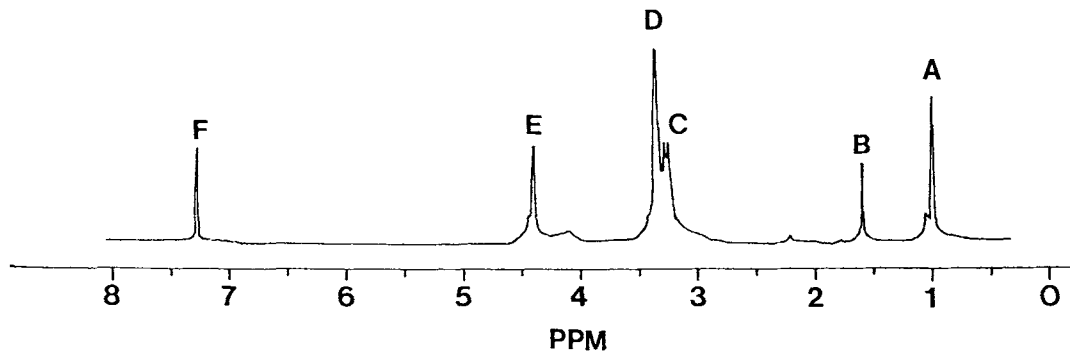


Figure 2 $^1\text{H-NMR}$ spectrum of ABA copolymer **6**.

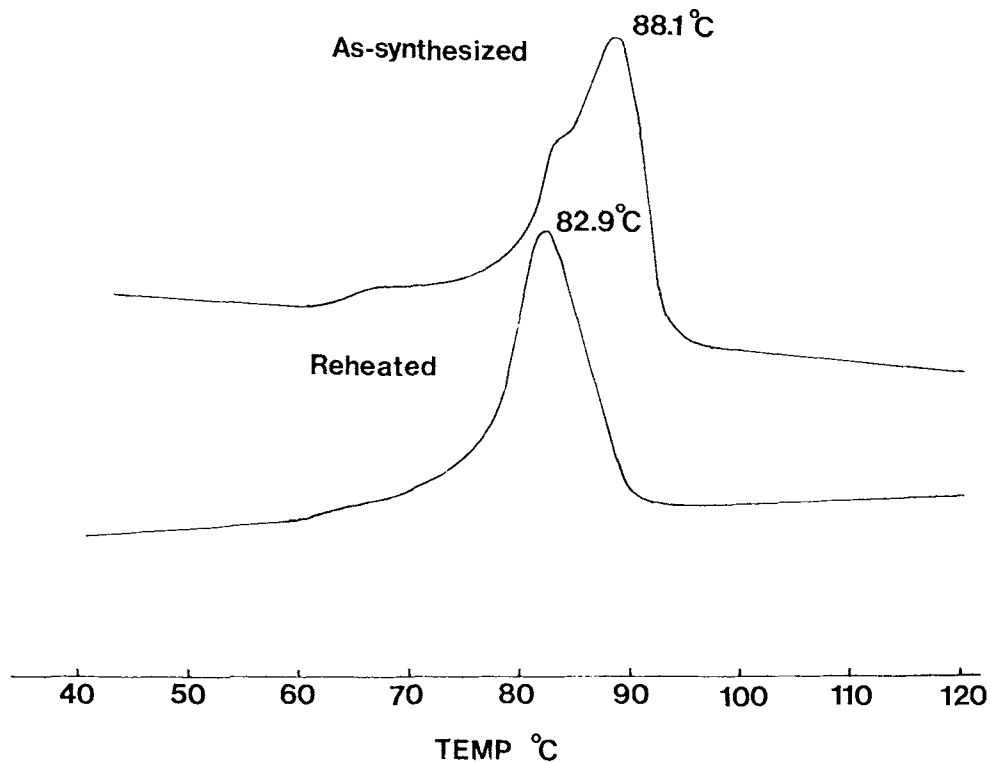


Figure 3 DSC curves for EtO(PBAMO)OH: (top) as synthesized, $20^\circ\text{C}/\text{min}$ heating rate; (bottom) cooled and reheated at $10^\circ\text{C}/\text{min}$ heating rate.

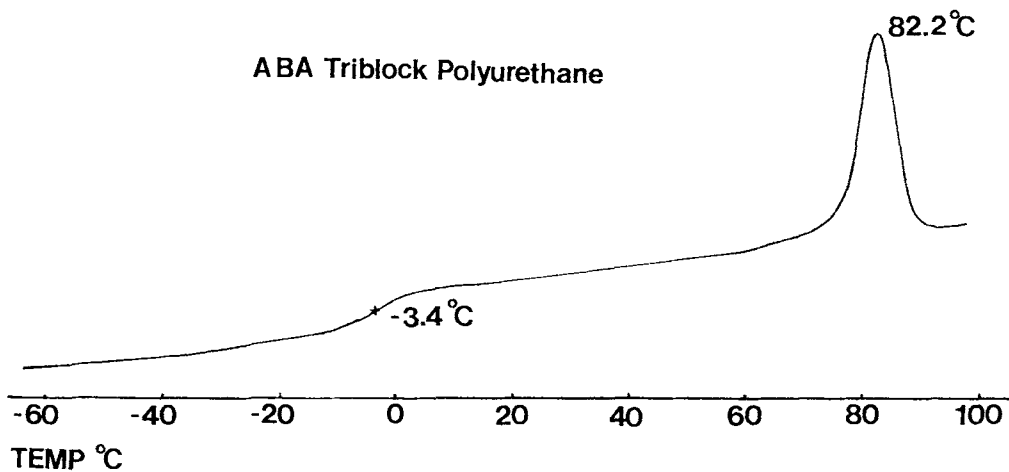


Figure 4 DSC curve for ABA copolymer **6**.

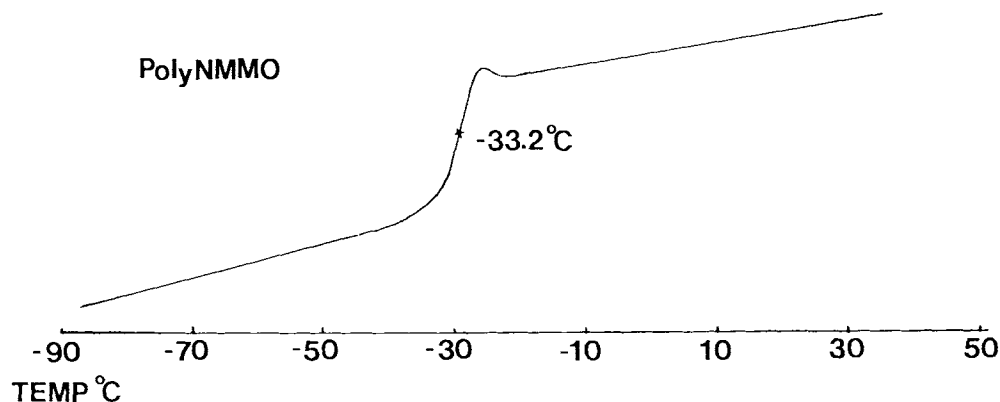
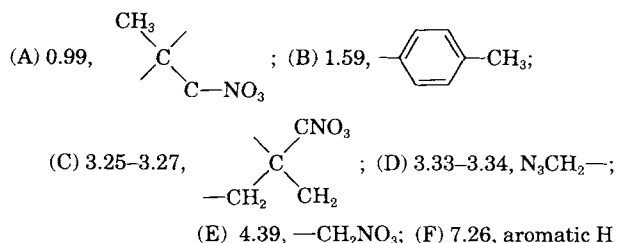


Figure 5 DSC curve for PNMMO 5.

The $^1\text{H-NMR}$ spectra of **6** and **7** also showed close resemblance. The assigned resonances are



Thermal Properties

Figure 3 contains the DSC curves for PBAMO **4**. There are three endotherms with the highest one at 88.1°C. Upon cooling and reheating at 10°C/min, the DSC was simplified to a single endotherm at 82.9°C. The results indicate heterogeneity of crystallite size in the as-synthesized polymer, and this broad size distribution is narrowed upon reheating. The DSC curve of ABA copolymer **6** in Figure 4 also exhibits this melting endotherm at 82.2°C. The ΔH_f

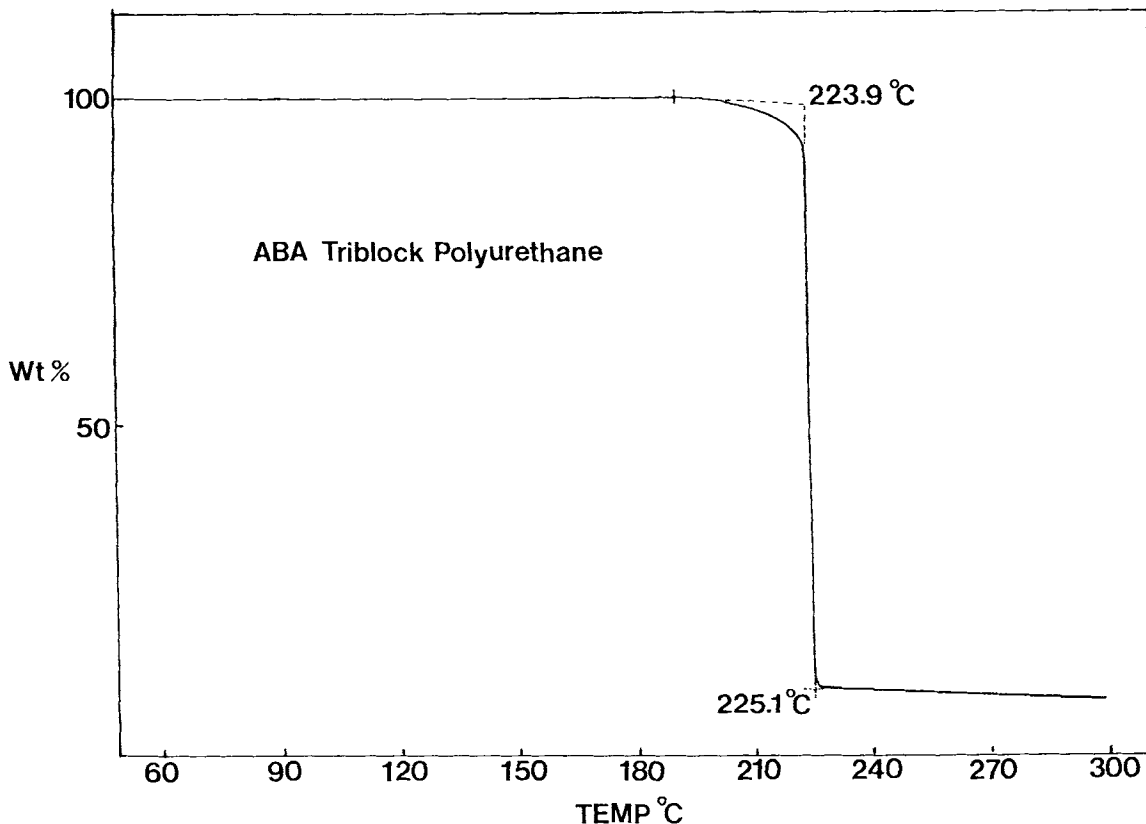


Figure 6 TGA curve for ABA copolymer 6.

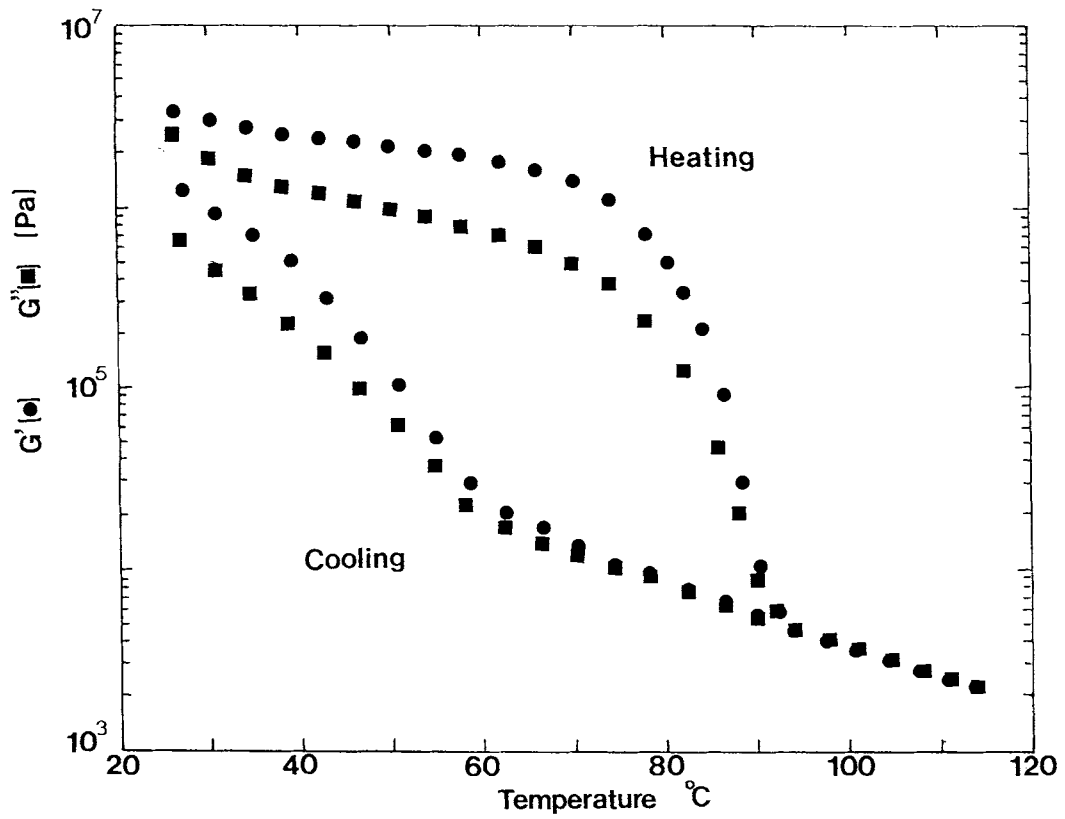


Figure 7 Storage modulus (G') and loss modulus (G'') of ABA copolymer 6 measured at 1 rad/s and during $1^{\circ}\text{C}/\text{min}$ heating.

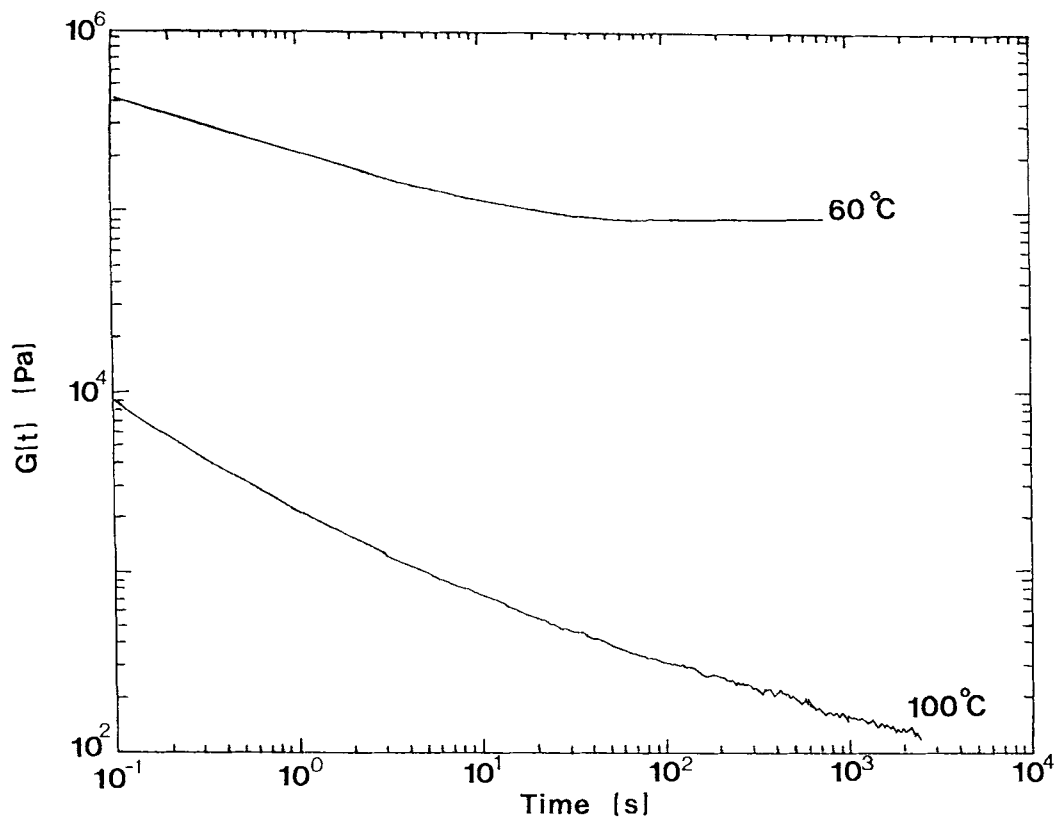


Figure 8 Transient modulus curves of ABA copolymer 6 after a step shear at the indicated temperature.

of the PBAMO blocks in **6** is 17.4 J/g, which is about one third of the ΔH_f (48.7 J/g) of PBAMO **3**. This corresponds to about 30 wt % of BAMO in **6**. In addition to the T_m , there is also a T_g at -3.4°C .

Figure 5 is the DSC curve of PNMMO **5**, the T_g in this sample is situated at a much lower temperature of -33.2°C . The ΔC_p is 0.57 J/g K as compared to a $\Delta C_p = 0.31$ J/g K for the copolymer **6**.

Figure 6 is the TGA curve for polymer **6**. It has an onset decomposition temperature of 200°C . Most of polymer was pyrolyzed within about 1°C between 223.9 and 225.1°C . This sharp decomposition is consistent with the high energy content of the polymer due to the N_3- and NO_3- groups. The exothermicity is 0.69 kJ/g. The segmented polymer **7** decomposes just as sharply between 220.7 and 221.9°C .

Rheological and Mechanical Properties

In dynamic mechanical temperature sweep (Fig. 7), ABA triblock copolymer **6** melts at about 82°C , as indicated by a decay of both storage and loss moduli (G' and G'') over 2 orders of magnitude. Below the melting temperature, the ABA copolymer behaves as a crosslinked polymer; its storage modulus is al-

ways higher than the loss modulus. Even above the T_m the storage modulus remains very close to the loss modulus. This implies a microphase separation in the melt of polymer **6**.

In a step shear strain experiment at 60°C (Fig. 8), ABA copolymer **6** shows a gradual stress relaxation within the first 100 s; then the transient modulus levels off to a equilibrium value at 90,000 Pa. According to rubber elasticity theory, this equilibrium modulus is roughly corresponding to a soft chain weight average molecular weight of about 27,000 g/mol in excellent agreement with the GPC value of $\bar{M}_w = 27,000$ (Table II, run no. 8). This equilibrium modulus ceased to be an observable phenomenon at 100°C due to the melting of the crystalline region which served as crosslinks.

The segmented $(\text{AB})_n$ copolymer **7** exhibits higher solid moduli and lower melt viscosity than the ABA copolymer **6** (Fig. 9). This suggests that for a multiblock thermoplastic elastomer, reducing the molecular weight of the soft segments would increase the crosslinking density in the solid state and would reduce the phenomenon of microphase separation in the melted state.

The ABA triblock copolymer has good mechanical

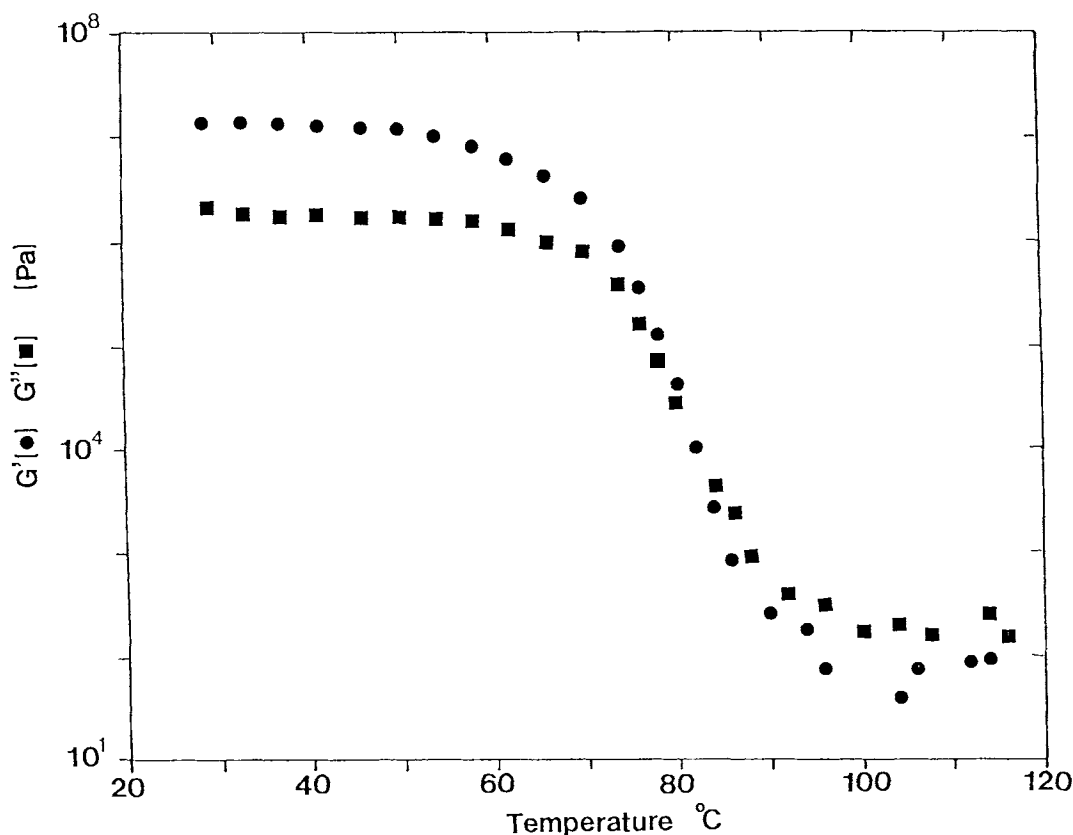


Figure 9 Storage modulus (G') and loss modulus (G'') measured at 1 rad/s and during $1^\circ\text{C}/\text{min}$ heating.

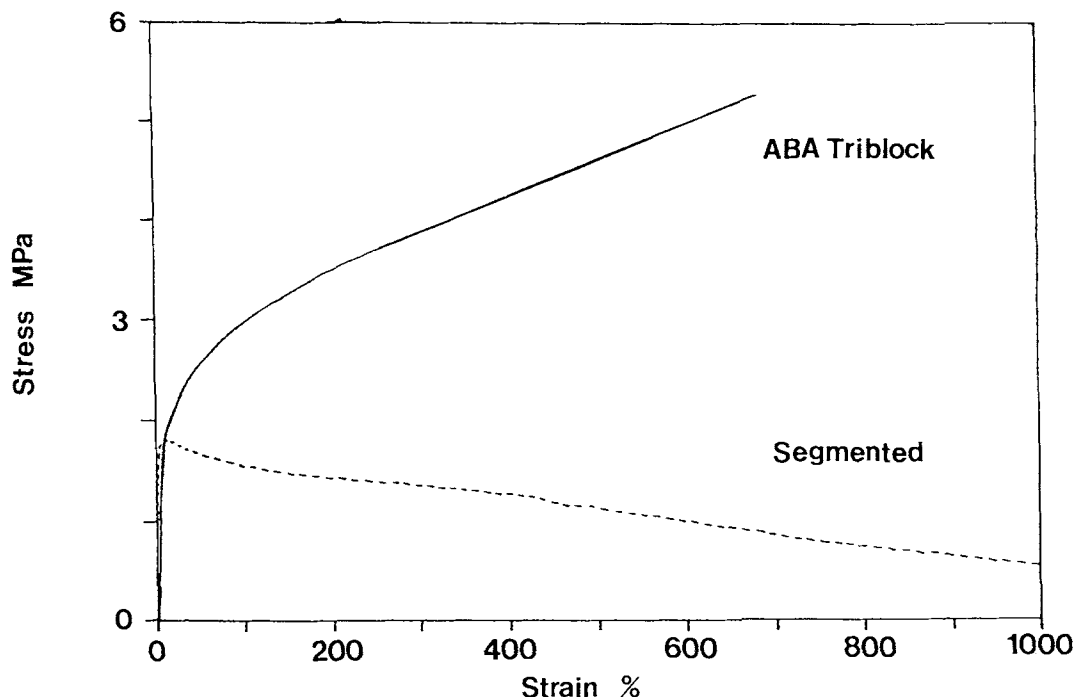


Figure 10 Stress-strain curves for (—) ABA copolymer 6 and (· · ·) (AB)_n copolymer 7 at a strain rate of 100%/min.

properties (Table IV). The tensile stress curve does not show a yield point, as typical for a crosslinked rubber (Fig. 10). The elongation at break is 683%. The segmented copolymer 7 has relatively weak mechanical properties in comparison. After showing a yield point at 16% strain with a stress 160 MPa, the tensile stress keeps decaying until an elongation to break over 2000%. This suggests that in the segmented copolymer the short hard segments cannot form effective crosslinks due to the low strength of the crystalline regions.

CONCLUSION

Both ABA and (AB)_n thermoplastic elastomers have been synthesized from crystalline PBAMO and amorphous PNMMO building blocks. These materials have good mechanical and elastic properties. Because the building blocks have high energy con-

tents, these thermoplastic elastomers can be valuable propellant binders.

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Table IV Stress-Strain Properties of Triblock Copolymer 6

Strain (%)	Stress (MPa)	Recovery (%)
100	2.96	90
200	3.49	88
300	3.91	85
683	5.25	82