

Bis(azidomethyl) Oxetane/Hydroxyl-Terminated Polybutadiene/Bis(azidomethyl) Oxetane Triblock Copolymer: Synthesis and Characterization

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ABSTRACT: A copolymer consisting of bis(azidomethyl) oxetane and hydroxyl-terminated polybutadiene was synthesized with different monomer ratios via an activated monomer mechanism. The copolymer thus obtained was characterized with Fourier transform infrared, $^1\text{H-NMR}$, molecular weight, and polydispersity measurements. Rheological and thermal studies were also carried out. The mechanical properties of the gum stock obtained through curing with toluene diisocyanate and crosslinking with

pyrogallol at about 50°C were also determined. This was an attempt to combine the useful properties of hydroxyl-terminated polybutadiene (a nonenergetic binder providing excellent mechanical properties) and poly[bis(azidomethyl) oxetane] (an energetic binder). © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1885–1888, 2007

Key words: copolymerization; FT-IR; NMR; rheology; synthesis

INTRODUCTION

Recent advances in propellant research have been aimed at developing high-energy binders with better performance than the most common binder, hydroxyl-terminated polybutadiene (HTPB), and with compatibility with ecofriendly oxidizers such as ammonium dinitramide and hydrazinium nitroformate. Bis(azidomethyl) oxetane (BAMO) and its copolymers are very promising as alternate binders in solid propellants.^{1,2} The incorporation of these azido polymers into propellants results in increased burn rates because of the release of a large amount of energy on the propellant surface. Moreover, there is a gain in the energetics because of the high positive heat of formation, which results in a higher flame temperature.³ However, poly[bis(azidomethyl) oxetane], though energetic, because it is solid, cannot be directly used for binder applications, whereas HTPB is an ideal binder, notwithstanding its nonenergetic nature. To incorporate the merits of BAMO and HTPB into binders, a block copolymer approach has been applied in which energetic BAMO is chemically linked with rubbery polybutadiene to produce a copolymer, that is, hydroxyl-terminated polybutadiene-*co*-poly[bis(azidomethyl) oxetane] (HTPB-BAMO copolymer), similar to that reported by Subramaniam and coworkers.^{4,5} This copolymer imparts energetics and better mechanical

properties to the resulting binder. Therefore, an attempt has been made to synthesize an HTPB-BAMO copolymer of an appropriate monomer ratio and to characterize it before its evaluation as a binder in composite propellants.

EXPERIMENTAL

Materials

Pentaerythritol (98%), tetrahydrofuran (99%), sodium chloride, aluminum hydroxide, sodium hydroxide, and sodium azide (Qualigens, India) and *N,N*-dimethylformamide, dichloromethane, and sodium sulfate (anhydrous; S.D. Fine Chemical, Ltd., India) were used. Also, thionyl chloride (98%; Thomas Baker, India), boron trifluoride etherate (48%) and 1,4-butanediol (98%; Fluka, Germany) 1,1,1-tris(hydroxymethyl) propane (TCI, Japan), and HTPB (Anabond) with a number-average molecular weight (M_n) of 2800 were used as received.

Methods

IR spectra of the prepared monomer and polymer were recorded by the smear method with a Perkin-Elmer (Waltham, MA) model 1605 spectrophotometer. Differential scanning calorimetry experiments were carried out on a PerkinElmer Delta-Para series DSC 7 at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. The typical sample mass was 2 mg. Thermogravimetric analysis was performed on a Mettler-Toledo STAR instrument (Columbus, OH) in

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TABLE I
Quantities of the Ingredients

Batch	BAMO/HTPB molar ratio	BAMO (g)	HTPB (g)	DCE (mL)
1	5 : 1	3.4	11.2	40
2	10 : 1	6.8	11.2	40
3	17 : 1	56	56	140

DCE, dichloromethane.

a nitrogen atmosphere with a sample mass of 10 mg and a heating rate of 10°C/min. M_n was determined with a Knauer vapor pressure osmometer (Germany), and the weight-average molecular weight (M_w) along with the polydispersity was obtained by gel permeation chromatography. The rheology of the copolymers was studied on a Stress Tech rheometer supplied by M/s Chrome Line (Reologica, Sweden).

Synthesis of the BAMO–HTPB copolymer

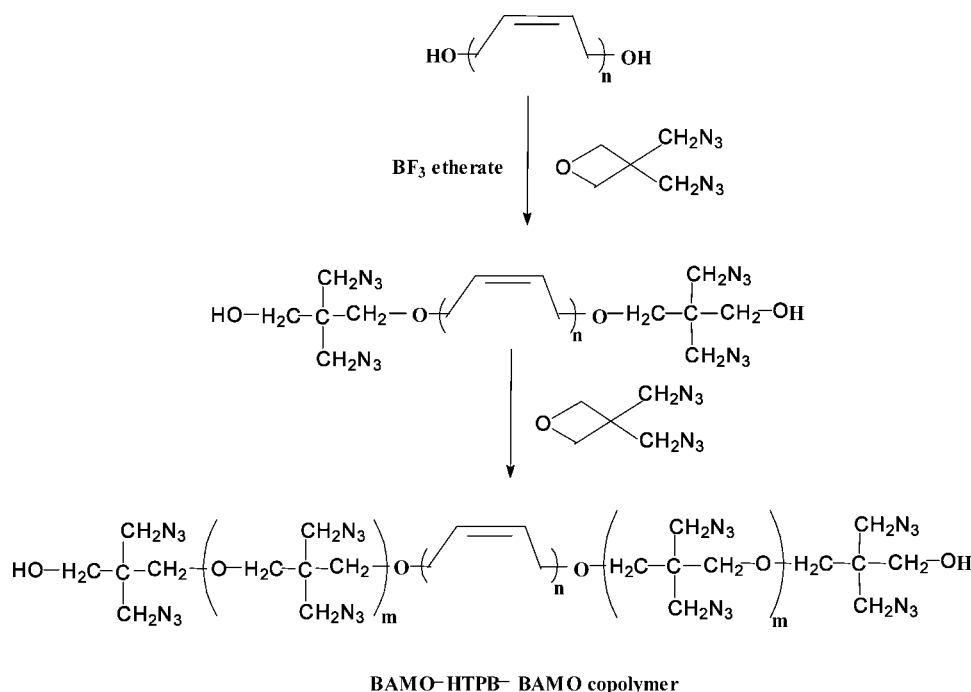
BAMO was synthesized according to a procedure reported earlier.⁶ HTPB, obtained from Anabond, was used after deaeration. The synthesis of the BAMO–HTPB copolymer was carried out with dichloromethane as an inert solvent and boron trifluoride etherate as a catalyst under a nitrogen atmosphere. A typical procedure was carried out in a 1-L, four-necked, round-bottom flask fitted with a mechanical stirrer, a thermowell, a nitrogen inlet tube, and a funnel for the addition of the monomer

BAMO. HTPB (56 g, 0.02 mol) in 60 mL of dichloromethane was cooled to 10°C. Boron trifluoride etherate (4 mL) in 25 mL of dichloromethane was added over a period of 1 h. BAMO (56 g) in 50 mL of dichloromethane was added at 25°C over a period of 1 h. After the addition was complete, the mixture was stirred for 4.5 h. The reaction was terminated with a saturated solution of sodium chloride. Subsequently, the reaction mixture was washed with distilled water and dried by passage through anhydrous sodium sulfate. The solvent was then removed *n vacuo*, and the polymer was precipitated in methanol, vacuum-dried, and characterized. Different batches were made with different molar proportions of BAMO and HTPB (Table I).

RESULTS AND DISCUSSION

BAMO–HTPB copolymers of various ratios were synthesized successfully. The reaction proceeded via an activated monomer mechanism in which hydroxyl-terminated butadiene acted as a bifunctional diol initiator and boron trifluoride etherate acted as a Lewis acid catalyst. The monomer BAMO was added on both sides of the diol initiator, leading to the formation of a triblock copolymer (BAMO–HTPB–BAMO copolymer). The reaction is presented in Scheme 1.

Because we were looking for a copolymer with a flowable nature and a maximum BAMO content, we limited our studies to a BAMO–HTPB copolymer with a monomer ratio of 17 : 1. When the BAMO



Scheme 1 Synthesis of the BAMO–HTPB–BAMO copolymer.

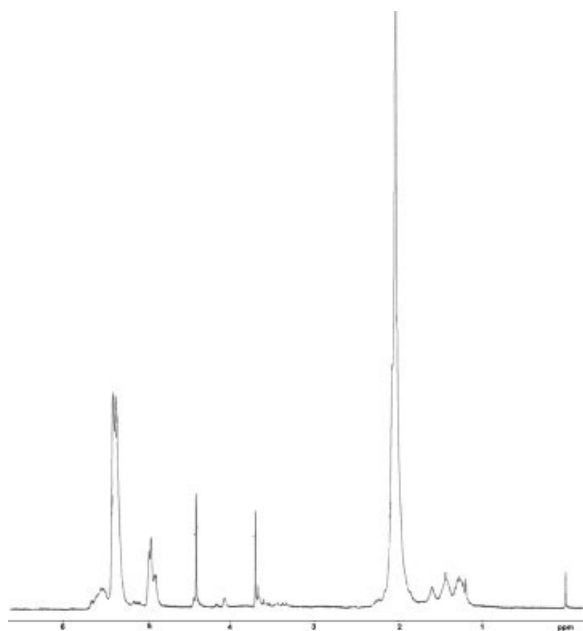


Figure 1 $^1\text{H-NMR}$ spectrum of the BAMO-HTPB copolymer.

concentration was increased above 17, the copolymer was solid. The copolymer was characterized with spectroscopic methods as well as thermal methods.

The Fourier transform infrared spectrum of the copolymer shows absorption at 2104 and 1100 cm^{-1} due to C–N₃ and C–O–C stretching vibrations of BAMO along with those of HTPB vibrations.

The $^1\text{H-NMR}$ spectrum of the BAMO-HTPB-BAMO copolymer is shown in Figure 1. It shows signals at $\delta = 3.67$ (s, 4H, CH₂N₃) and $\delta = 4.4$ (s, 4H, OCH₂) for BAMO and at $\delta = 2.02$ (CH₂) and $\delta = 5.39$ (CH=CH) for HTPB.

The azide content, estimated by iodometric titration, is 37% (theoretical value = 38%), indicating that the BAMO/HTPB ratio of the copolymer is 17 : 1.

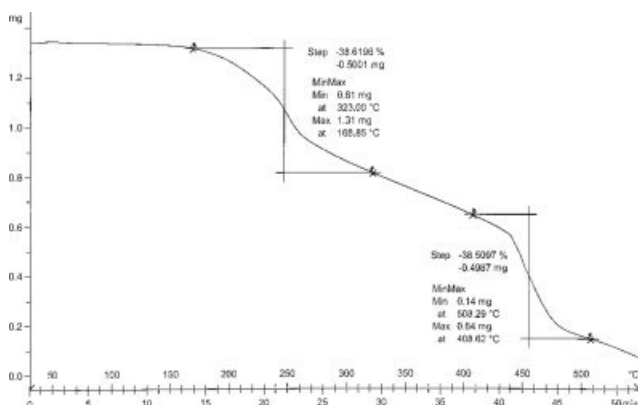


Figure 2 Thermogravimetric analysis of the BAMO-HTPB copolymer.

TABLE II
Properties of the Copolymers

Batch	M_n	M_w	Polydispersity	Hydroxyl value (mg of KOH/g of sample)
1	6,717	30,050	4.47	16.70
2	6,913	42,707	4.84	16.23
3	8,023	40,917	5.10	13.98

A thermogravimetric analysis curve of the BAMO-HTPB copolymer is shown in Figure 2. It shows two-stage decomposition. The first stage of decomposition occurs around 223°C and corresponds to the decomposition of the methyl azide group of BAMO, and the second stage occurs at 375°C because of the decomposition of HTPB and the polymer backbone of BAMO.

The M_n , M_w , hydroxyl, and polydispersity values of the copolymers are shown in Table II.

Rheological studies

The rheological curves (i.e., flow curves in Fig. 3) at 40°C show initially non-Newtonian behavior up to approximately 300 Pa of stress, but afterwards, it becomes almost constant; as the stress increases, the

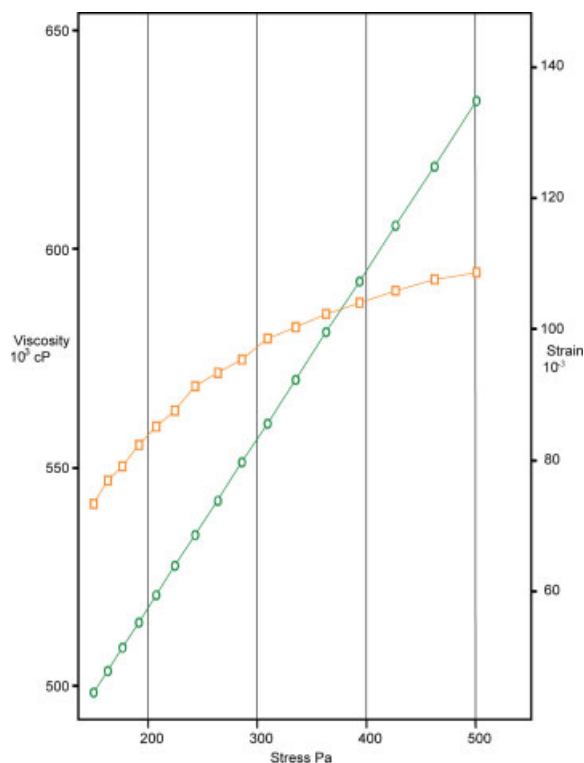


Figure 3 Variation of the flow behavior of BAMO-HTPB with the stress. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

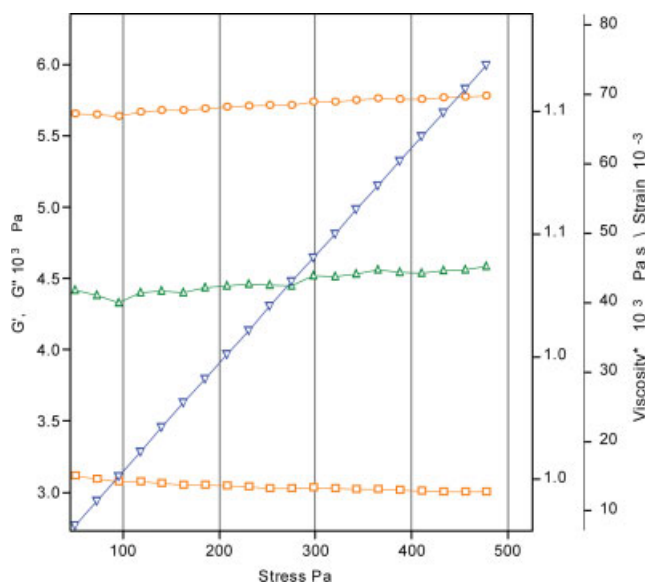


Figure 4 Flow curve of the BAMO-HTPB copolymer at 30°C (G' is the storage modulus, and G'' is the loss modulus). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

viscosity remains constant around 600 Pa s (a linear viscoelastic region). The viscosity (Fig. 4) can be interpreted as approximately 1.08×10^3 at 30°C Pa s. Figure 5 shows the crossover of the loss modulus and storage modulus at a frequency of about 42 Hz when the phase differences between these parameters become equal. In other words, the contribution of each modulus is 50%. Initially, the loss modulus is higher than the storage modulus, and this indicates that selected BAMO-HTPB resins initially act as viscous liquids and subsequently show solidlike behavior at a higher frequency or at a higher stress, that is, dilatancy. This may occur because at a higher frequency or shear rate, the polymer structure might be disintegrated, and pendent $\text{CH}_2\text{-N}_3$ groups of BAMO may be responsible for the higher viscosity (the hard-core part of BAMO present in the polymer is also very high). This polymer can be used as a binder, and the frequency of oscillation, that is, linear motion, of the blade/mixer has to be kept at a lower rate so that the binder acts as a viscous liquid (not an elastic one) for better mixing of the solid ingredients of the propellant.

CONCLUSIONS

A triblock BAMO-HTPB-BAMO copolymer was successfully synthesized with various BAMO concentra-

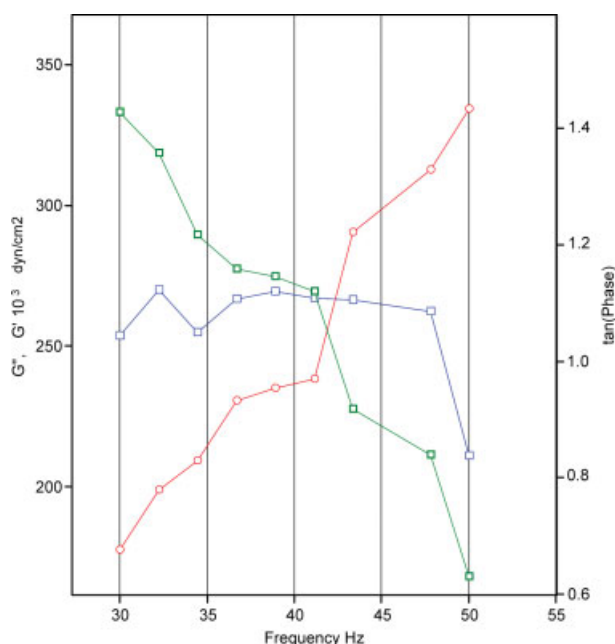


Figure 5 Crossover curve of the BAMO-HTPB copolymer (G' is the storage modulus, and G'' is the loss modulus). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tions. It was characterized spectroscopically and thermally. The rheological properties of the copolymer were also studied and indicated that this polymer has potential use as an energetic binder, showing dilatancy at a high frequency or shear rate. Also, it is more viscous than elastic and shows solidlike behavior at a lower shear rate.

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References

- Cheum, Y. G.; Kim, J. S.; Jo, B. W. Proceedings of the 25th International Conference of the Institute of Chemical Technology, Karlsruhe, Germany, June 28 to July 1, 1994; p 71.1.
- Ou, Y.; Chen, H.; Yan, H.; Jia, J.; Dong, S. J Propulsion Power 1995, 11, 838.
- Oyumi, Y. Propellants Explos Pyrotech 1992, 17, 226.
- Subramaniam, K. Eur Polym J 1999, 35, 1403.
- Vasudevan, V.; Sunderarajan, G. Propellants Explos Pyrotech 1999, 24, 295.
- Nair, J. K.; Satpute, R. S.; Mukundan, T.; Asthana, S. N.; Singh, H. Defence Sci J 2002, 52, 147.