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Synthesis and Characterization of Poly BAMO Suitable for Binder Application

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Abstract: A new synthetic methodology has been developed for the synthesis of poly BAMO and poly BAMO-co-THF with controlled molecular weight and narrow molecular weight distribution. The synthesis of BCMO, the precursor of the BAMO monomer was accomplished using the reaction of Vilsmeir reagent with pentaerythritol. The BAMO monomer could be synthesized with an over all yield of 60% and polymerized using $BF_3 \cdot Et_2O$ as the initiator and 1,4-butane diol as the co-initiator. Computational evaluation of the energy releasing properties of the poly BAMO derivatives was performed using Gaussian algorithm. The theoretically calculated values agreed very well with the experimentally determined ones.

Key words: organic chemistry; poly BAMO; synthesis

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1 Introduction

Polymers synthesized from energetic oxetane derivatives have received a lot of attention in recent years, owing to their potential application as novel binders for rocket propellants[1-8]. For the said application, the synthesis of oxetane-based polymers are required to incorporate the properties of molecular weight control, low polydispersity, and introduction of energetic characteristics[4-8]. Novel living polymerization systems have been utilized in the synthesis of oxetane derivative-based polymers to control molecular weights and low polydispersity. Several initiating systems, such as boron trifluoride/epichlorohydrin, *p*-bis (dimethylchloromethyl) benzene/AgSbF6 and triflic etherate were employed[2,4]. However, the above systems are not favorable in the polymer synthesis, owing to the disadvantages of poor molecular weight distributions, failure in molecular weight control, difficulty in removal of impurity, and poor initiating efficiency.

In addition to the above, most of the researches on the energetic substituted oxetane, focused on the polymer synthesis. Yet the polymerization kinetics and mechanism, "living cationic" characteristics of the polymerization; and polymer characterization has not been investigated thoroughly. In the present work, an energetic oxetane derivative, 3,3-bis(azidomethyl) oxetane (BAMO), is used as the monomer in the polymerization. Good control of molecular weight and low molecular weight distribution were obtained. The $BF_3 \cdot Et_2O$ was found to be an initiator of choice for the polymerization of oxetane derivatives.

2 Experimental

2.1 Synthesis of BCMO

Pentaerythritol trichloride was prepared from pentaerythritol using thionyl chloride and dimethyl formamide. In a typical procedure, pentaerythritol (50 g) was added to a mixture of DMF (28.6 mL) and thionyl chloride (27 mL). During the addition the temperature was maintained at 55 ℃ for 1 h. The solution was slowly heated to 120 ℃ for 90 min. Thionyl chloride (58 mL) was added to the reaction mixture over 3h while the temperature was maintained at 120 ℃. The reaction mixture was stirred for a period of 6 h. The reaction mixture was subjected to vacuum fractional distillation . The fraction obtained at 80 ℃ at 1.33 kPa was predominantly the pentaerythritol trichloride. NaOH (125 mL, 1.2 mol/L) was added to the distillate and refluxed for 3 h. NaCl formed was separated and the organic part was extracted with ethanol. The fraction was concentrated and fractionated (80 ℃ at 1.33 kPa) to obtain BCMO in 60% yield.

2.2 Synthesis of BAMO

Sodium azide (12.7 g) was taken in 50% aqueous sodium hydroxide solution and BCMO (14 g) was added. Tetrabutyl ammonium bromide (0.63 g) was added and

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the biphasic mixture was heated to 100 ℃ for 24 h. The organic layer was washed with water and dried with magnesium sulphate for 1 h. The neat oil was passed through a column containing neutral alumina and the column was rinsed with methylene chloride. Yield, 13 g (85%).

2.3 Synthesis of Poly BAMO

Polymerization of BAMO was carried out using $BF_3 \cdot Et_2O$ as initiator and 1,4-butanediol as the co-initiator. In a typical procedure, 1,4-butanediol (0.15 g) was added to methylene chloride (15 mL). To this, 0.12 g of $BF_3 \cdot Et_2O$ was added and the reaction was allowed to continue for 1 h at room temperature. The reactor was cooled to −10 ℃ and BAMO (10 g) was added. The solution was allowed to come to room temperature and left to react for 24 h. The reaction was quenched by the addition of saturated brine solution (50 mL). The organic phase was separated and washed with 10% sodium bicarbonate solution and the solvent was removed by vacuum evaporation. The polymer was precipitated by the addition of methanol and dried under vacuum at 30 ℃. Yield, 8.63 g, 85%. By changing the ratio between the initiator and co-initiator, poly BAMO of varying molecular weights could be obtained.

2.4 Synthesis of BAMO-THF Copolymer

Copolymer of BAMO with THF (1.6 mol) was obtained using $BF_3 \cdot Et_2O$ (0.4 mol) and 1,4 butane diol (0.2 mol) and reaction was quenched by cooling the mixture to −5 ℃. BAMO (1.6 mol) was added to the above mixture and stirred for 18 h at room temperature. The polymerization reaction was terminated using sodium chloride and washed with sodium bicarbonate. The content was poured into methanol and the solvent was evaporated to get the pure polymer. Yield 80%.

2.5 Determination of Hydroxyl Group Functionality

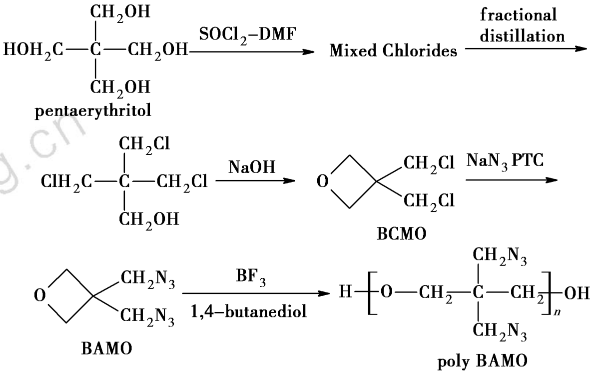
The hydroxyl value of the poly BAMO and BAMO-THF copolymer was determined by the usual acetylation method. Poly BAMO (1 g) was reacted with standard acetylating agent (2 mL) for 15 min at 95 ℃. Each analysis was compared with a blank by titrating with 0.1 N sodium hydroxide solution. Difference in the titrant value between the sample and the blank was used to calculate the hydroxyl value.

3 Results and Discussion

3.1 Synthesis and Characterization of Monomers and Polymers

Bischloromethyl oxetane (BCMO) was prepared by a new process, which involved the chlorination of pentaerythritol using Vilsmeir Reagent ($SOCl_2$ + DMF). The yield of BCMO based on pentaerythritol was 60%. BCMO was easily converted to BAMO by treatment with sodium azide in the presence of a phase transfer catalyst, tetrabutyl ammonium bromide. This reaction proceeded to 88% conversion. The two step process for the preparation of BAMO results in an overall yield of 60%.

Polymerization of BAMO was carried out in the presence of $BF_3 \cdot Et_2O$ as initiator and 1,4-butane diol as co-initiator. Depending up on the amount of the co-initiator taken, the molecular weight and chain morphology (linear or branched) of the poly BAMO could be controlled. Thus with a low co-initiator concentration, (0.75 equiv.), the molecular weight (M_n) could be limited to ~2000. But when the co-initiator concentration is above 1.5 equivalents, the molecular weight (M_n) could be ~5500. The properties of the poly BAMO prepared are presented in Table 1. The reaction scheme for the preparation of BCMO, BAMO and poly BAMO are given Scheme 1.



Scheme 1 Synthesis of BCMO, BAMO and poly BAMO

Copolymerization of BAMO with THF was carried out in the presence of $BF_3 \cdot Et_2O$ as initiator and 1,4-butanediol as co-initiator. The reaction procedure was same as that of poly-BAMO

3.2 Characterization of Monomers and Polymers

The monomers, BCMO, BAMO and the polymers were characterized by determination of physical constants, spectroscopic methods, molecular weight by GPC and thermal methods. The details are given in Table 1.

In the IR spectra (see in Fig. 1), BCMO shows C—H, C—O—C and C—Cl stretching bands at 2962, 1438, 1036, 979 and 738 cm^{-1} and BAMO shows apart from the C—H and C—O—C stretching, the additional band at 2102 cm^{-1} due to the azide groups and is devoid of C—Cl band. In the ^1H NMR of BAMO, signals are observed at δ 3.66 (s, 4H CH_2N_3) and 4.37 (s, 4H OCH_2). In the ^{13}C NMR spectra, signals are seen at δ 45.3 (bridge carbon), 54.1 (CH_2N_3) and 76.4 (OCH_2). Similarly ^1H NMR of poly BAMO shows a multiplet at δ 3.3 (CH_2N_3), and 3.6 (OCH_2). In the ^{13}C NMR spectra signal are seen at δ 51.6 (bridge carbon), 53.9 (CH_2N_3), and 70.1 (CH_2OH of BAMO).

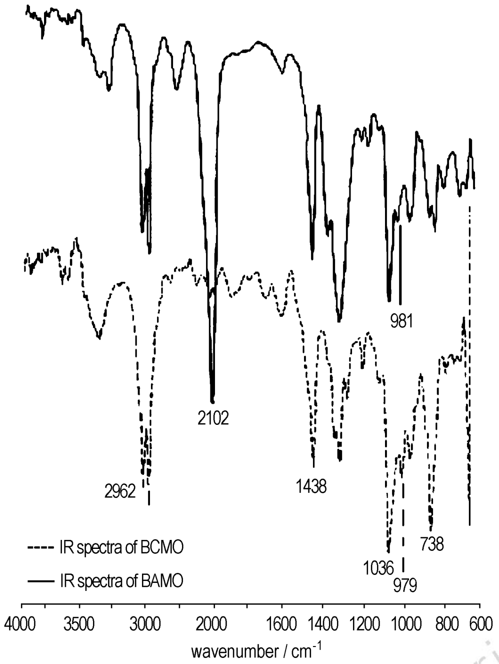


Fig. 1　IR spectra of BCMO and BAMO

The BAMO-THF copolymer shows singlet at δ 1.68 (CH_2 in THF), multiplet at δ 3.35 (CH_2N_3) and ^{13}C-NMR spectra of copolymers show peaks at δ 26.00 (CH_2 of BD), δ 44.89 (CH_2 of THF), δ 51.55 (bridge carbon), δ 53.83 (CH_2N_3), δ 62.36 (CH_2OH of BD) and δ 70.67 (CH_2OH of BAMO).

Thermogravimetry (T_G) and Differential Scanning Calorimetry (DSC) were carried out at a heating rate of 100 ℃/min (see in Figs. 2,3). The TG curve of Poly BAMO shows initiation of decomposition temperature (T_i) at 202 ℃ and peak temperature (T_{max}) at 237 ℃, whereas in case of copolymer the T_i is at 210 ℃ and T_{max} at 240 ℃. The TGA of polyBAMO showed one step weight lose at 237 ℃. This is Due to the decomposition of methyl azide group. The TGA of BAMO-THF copolymer also showed a one step weight loss beginning at 241 ℃. The glass transition temperature was obtained from DSC curve.

Table 1　Characterization of monomers and polymers

properties	BCMO	BAMO	poly BAMO		poly BAMO-THF
			M_n = 2200	M_n = 5500	M_n = 1900
IR/cm^{-1}	1438 C—H 1036 C—O—C 738 C—Cl	1446 C—H 1104 C—O—C 2102 N_3	2100 N_3 3440 OH	2100 N_3 3450 OH	2100 N_3 3450 OH
T_g/℃			−42	−30	−50
functionality			2	2	2
density /g·cm^{-3}	1.1	1.2	1.3	1.5	1.1
B.P/M.P	80 ℃ at 1.33 kPa	68 ℃ at 1.33 kPa	76 ℃	83 ℃	72 ℃

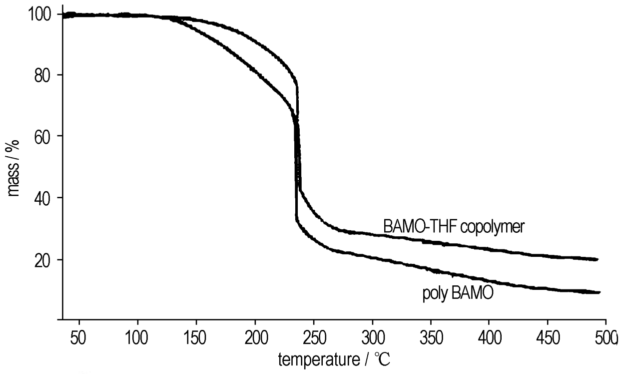


Fig. 2 TGA curves of poly BAMO and BAMO-THF copolymer

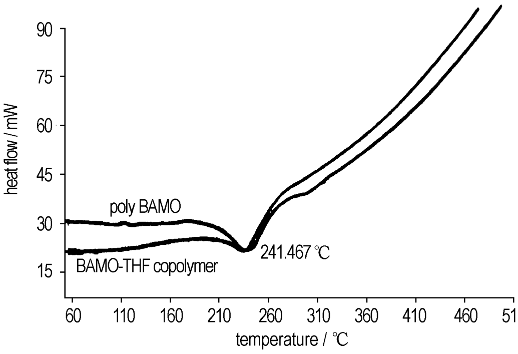


Fig. 3 DSC curves of poly BAMO and BAMO-THF copolymer

4　Computational Evaluation of Energy Releasing Property of Poly BAMO Derivatives

Compared to typical C—H—N—O explosives, BAMO is a small energetic molecule. It is a four membered heterocyclic molecule with very high stability. Its high ground state energy and the four membered ring structure are the attractive features of this system for theoretical studies, particularly as a prototype for modeling the complex physics and chemistry associated with initiation and growth of reactions to detonation in solid energetic materials. Since we can easily model the geometry, stereochemistry and the ground state energies of the ring systems, these systems can be easily modified with the help of theory and carry out the synthesis of only the potential candidates in the laboratory. Such studies can be used to identify and characterize phenomena that contribute to explosive sensitivity, thereby creating a theoretical means with which to screen energetic materials for Insensitive Munitions (IM) applications. In this way, theoretical simulations serve to reduce the risk associated with time-consuming and repetitive testing of these hazardous materials.

A natural starting point for theoretical studies of the initiation of the molecules is to investigate chemical decomposition at the molecular scale. For this purpose, ab-initio (first principles) quantum chemical calculations provide the most accurate and detailed description of the reaction chemistry in the absence of empirical data. Energetic binders made from polyoxetanes have been investigated for use in gun propellants and in other applications where, an energetic binderwould be useful. In order to predict the performance of an energetic material, it is important to have accurate, experimentally determined values for the material's heat (enthalpy) of formation (HF).

The main aim of this work was to calculate the heat of formation of the BAMO and its polymers so as to predict the more useful propellants polymeric network. Different types of polymers (Block and Alternating) have been designed and the HF of these polymeric chains was calculated using ab-initio methods. The results provide a good idea about the propellant efficiency. By this method we can predict the method of effective polymerization to get an effective energetic material. Also vibrational frequency calculations (static) of polymers with semi empirical method give an idea about the thermal stability and / or decompositions of these systems.

4.1 Computational Methods

The molecules considered in this study are shown in Scheme 2. All the molecules have been optimized using restricted Hartree Fock formalism in using doubly diffused and doubly polarized 6-31G basis set available in the Gaussian algorithm to get the maximum sensitivity to the optimized geometry in the prediction because of high sensitivity of frequency values to geometry. The optimized geometries were used to compute the SCF MO energies and heat of formation (HF). The static vibrational frequencies of molecules have been studied with semi-empirical AM1 level of theory available in the Gaussian codes. The studies were restricted to AM1 level to overcome the high computational cost of ab-initio calculation for frequency predictions.

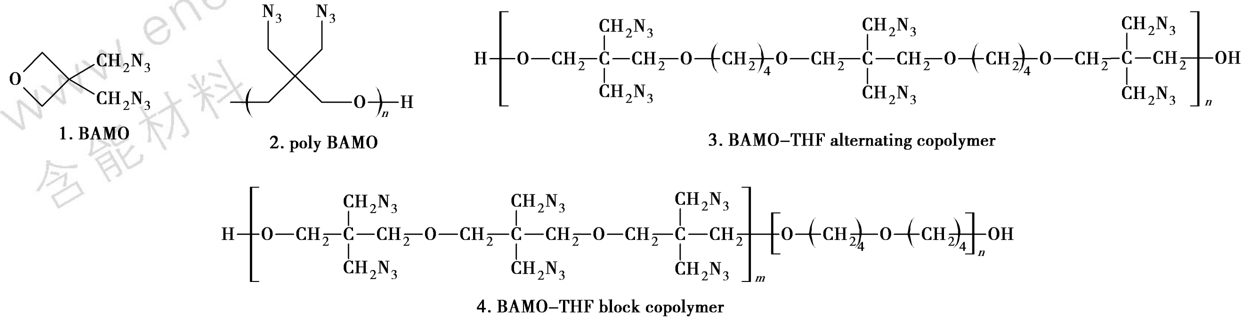
4.2 Geometry Optimization

The optimized geometries of the polymers using HF/ $6\text{-}31++G^{**}$ basis set are given in Figure 4.

4.3 Heat of Formation

Since the efficiency of the energetic materials as gun propellants mainly dependent on their heat of formation (HF), HF was calculated with high degree of accuracy using doubly diffused and doubly polarized basis sets using Hartree Fock formalism. The results are given in Table 2.

The calculated value of heat of formation of BAMO is in good agreement with the literature experimental values (BAMO: 479 kJ · mol^{-1}). These data prove the accuracy of the theoretical calculation using the ab-initio methods.



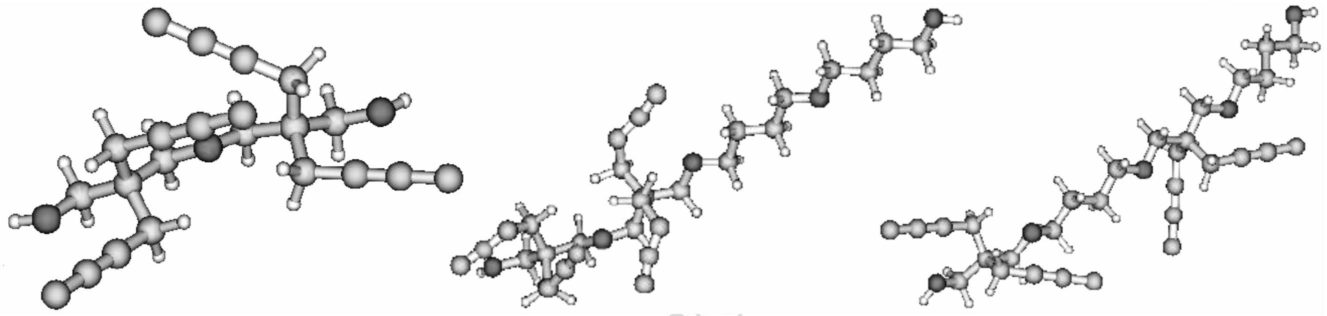
1. BAMO

2. poly BAMO

3. BAMO–THF alternating copolymer

4. BAMO–THF block copolymer

Scheme 2 BAMO and its polymers



optimized structure of PolyBAMO　optimized structure of BAMO-THF Block polyme　optimized structure of BAMO-THF Alternating polymer

Fig. 4　Optimized structures of polymers (2 repeating units)

Table 2　Heat of formation for molecules

molecule	HF /kJ · mol^{-1}
BAMO	446.88
Poly BAMO	988.92
BAMO-THF(BD) alternating copolymer	833.94
BAMO-THF(BD) block copolymer	85.36

From Table 2 it is clear that, as a high energy material releasing high energy, BAMO is a potential candidate. Comparing the different types of polymers synthesized based on different polymerizing technique, the alternating copolymer of BAMO and THF (or BD) is ten times better in releasing energy than its block copolymer. This provides the idea about the synthetic pathway as well the structural organization of the polymers.

4.4　Frequency Calculations

Vibrational frequencies of polymers are calculated using semi-empirical AM1 method. Since the normal modes tend to be a combination of several types of bond motions (*e. g.* stretching or bending), identification of mode type is limited to a description of the most significant displacements. Of particular interest are the stretching modes of terminal C—H, N—N, and C—O bonds. The frequencies of these vibrations are the clear indications of thermal stability and /or decompositions of these systems. The low frequencies of the modes indicate that they will be activated at low temperatures, and may play an active role in the thermal decomposition of the energetic molecules. The results are given in Table 3.

The heats of formation (HF) and IR absorption frequencies of polymers have been calculated using ab-initio and semi empirical methods respectively. These data help to get a good idea about the thermal decomposition and performance of high energy material based on poly BAMO derivatives.

Table 3　IR Frequencies of polymers

polymer	stretching modes (wave number)		
	C—H	N—N	C—O
Poly BAMO	1065.21	1524.18	2024.34
BAMO-THF(BD) Block polymer	1178.54	1743.09	2315.90
BAMO-THF(BD) Alternating polymer	1270.13	1824.15	2528.43

5　Conclusion

In conclusion, we have achieved the synthesis of the BAMO monomer through a new and more efficient synthetic route and could synthesize poly BAMO with controlled molecular weight for use as binder as well as plasticizer, just by adjusting the feed ratios. Quantum chemical determination of the heats of formation and spectroscopic properties showed good correlation of theory and experiments and they revealed that poly BAMO derivatives could be used effectively as binder materials.

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