

SYNTHESIS AND CHARACTERIZATION OF ENERGETIC ABA-TYPE THERMOPLASTIC ELASTOMERS FOR PROPELLANT FORMULATIONS

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Abstract

The main objective of these studies is the synthesis and characterization of energetic ABA-type thermoplastic elastomers for propellants formulations. Because the monomers (3-Azidomethyl-3-methyl oxetane (AMMO) and 3,3-Bis-azidomethyl oxetane (BAMO)) are not commercial available, they and their respective precursors, have also been synthesized. One object of this study was to find a safer method for synthesis of poly-AMMO and poly-BAMO in comparison to the published routes. Although all papers describe the polymerisation of energetic and sensitive azido-monomers AMMO and BAMO, we wanted to synthesize first the non-energetic halogeno-polymers and introduce only at the last step of synthesis the energetic azido groups, as it is done for the GAP synthesis. We could succeed in synthesis of these halogeno-polymers but the azidation step was not possible. The azidation reaction of poly-BrMMO to poly-AMMO was not quantitatively. In case of Bis-bromomethyl oxetane and Bis-chloromethyl oxetane the azidation step could not be done because of insolubility of both polymers. Although there are several papers published none of them give information about the friction and impact sensitivity of these azido-compounds. They were measured during this study and the monomers are comparable to nitrato compounds like nitro glycerine or other nitrato plasticizers which are commercially used by industry. The sensitivity is drastically reduced for the polymers poly-AMMO and poly-BAMO which are comparable with standard explosives like RDX (Hexogen).

For the synthesis of thermoplastic elastomers (TPE's), 2,4-toluene diisocyanate (TDI) has been used to link the block A (hard and mono-functional) to B (soft and di-functional). As hard A-block we used poly-BAMO and for soft B-block we used poly-AMMO.

Because the isocyanate group of 2,4-TDI at position 4 is more reactive than the one at the position 2, it is possible to end-cap poly-BAMO without any side reaction of adding two poly-

BAMO blocks on one TDI. The resulted polymer had a melting point about 75°C and was rubbery like granules. All the products have been characterised by IR- and (^1H , ^{13}C) NMR-spectroscopy, Differential Scanning Calorimetry (DSC) and sensitivity tests (friction, impact).

1- Introduction

Modern solid explosive compositions like propellants generally consist of particulate solids, such as fuel material (metal powders), oxidizers and explosives which are held together by a elastomeric binder matrix. In this binder matrix the energetic solid filler composition is embedded and immobilized to achieve defined combustion characteristics and also keep the propellant in fixed geometry. During combustion the binder acts as fuel but with the restriction that the energy output from the combustion of the binder is much lower in comparison to the energy output from combustion of metal powders. Therefore the use of binder materials that are energetic itself is one attempt to improve the performance of propellants. On the other hand with energetic binder systems the filler content can be reduced without any loss in performance but with the benefit of decreased signature that is caused from combustion products of the solid fillers (metal powders, halogenated oxidizers). Another benefit from reduced filler content might be reduction of sensitivity.

Conventional binder systems consist of liquid pre-polymers that are cross-linked by chemical curing agents. These systems have to be cast within a short time frame after addition of the curative, which gives some restriction for the industrial processing. Additionally the once cured binder material can not be reused or recycled because the curing reaction is irreversible. Energetic thermoplastic elastomers (E-TPE) are one possibility to overcome all these disadvantages. E-TPE's are copolymers with rubber-like elasticity and they do not require any curing agents. For processing in principle they are heated above their melting point and the solid fillers and additives are added and homogenized. For solidifying the composition is allowed to cool down below the melting point. Another technique is the use of solvents for processing. In this case the E-TPE's are dissolved and mixed with the solid fillers. After evaporation of the solvent the composition returns to its solid but elastic mode.

This property is achieved because the copolymer structure is composed from hard blocks and soft blocks. The hard segment (glassy or semi crystalline at room temperature) gives its thermoplastic behaviour, whereas the soft segment (rubbery at room temperature) gives the elastomeric behaviour. At room temperature the polymer chains of the hard blocks built inflexible hard domains by reversible interaction such as dipole-dipole interactions, hydrogen bonding, etc. Heating above the melting temperature or dissolving in a solvent the interactions

of the hard blocks are overcome and the binder gets liquid for processing operations. This mechanism of melting/dissolving and re-forming of physical cross-links is reversible and therefore when a TPE containing formulation is obsolete the ingredients can be recovered by melting or dissolving. During production there is also no more danger of missed batches because the material could be reused and reprocessed several times.

The ideal melting temperature for E-TPE's is in the range of 80 to 110°C. The lower temperature is determined by the use and storage conditions which should not be able to soften the propellant compositions at elevated temperatures. The upper temperature border attributes to the fact that many components which are ordinarily used in propellant compositions are unstable at higher temperatures.

The open literature ⁽¹⁻¹²⁾ contains several systems for E-TPE's which most of them describe poly-oxetanes with energetic azide groups.

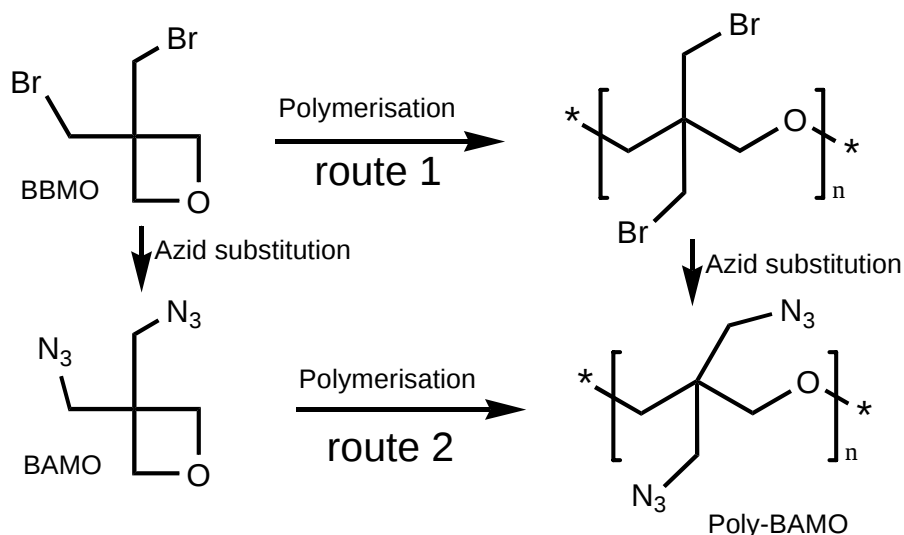
2- Results and Discussion

This paper presents the synthesis of Poly-AMMO, Poly-BAMO and TPE's from ABA type of AMMO/BAMO via chain elongation of Poly-AMMO and Poly-BAMO with Isocyanate. In our case, we used poly-AMMO as soft block and poly-BAMO as hard block.

2.1. Synthesis of poly-BAMO and poly-AMMO

In theory there should be two main routes possible for the synthesis of poly-BAMO or poly-AMMO. One starts from synthesis of halogenomethyl-oxetane followed by the polymerisation and then substitution of the halogen groups for azido substituents (route 1 at scheme 1). This route should be safer as it avoids the handling of highly sensitive azido-monomers BAMO or AMMO. In case of bis-chloromethyl-oxetane (BCMO) and bis-bromomethyl-oxetane (BBMO) the products from polymerisation were all insoluble in common organic solvents. Therefore the final reaction step for introducing the energetic azido-groups could not be performed. The AMMO synthesis via the azidation of poly-bromomethylmethyl-oxetane also failed because the azidation reaction was not complete. The substitution level reached only 90% after 03 days reaction time at 95°C in DMSO. Therefore the route 2 was the successful alternative which leads to the desired compound.

These experiments also delivered the explanation that all published synthesis routes for poly-BAMO and poly-AMMO has been proceed via energetic azido-monomer BAMO or AMMO (route 2 at scheme 1).



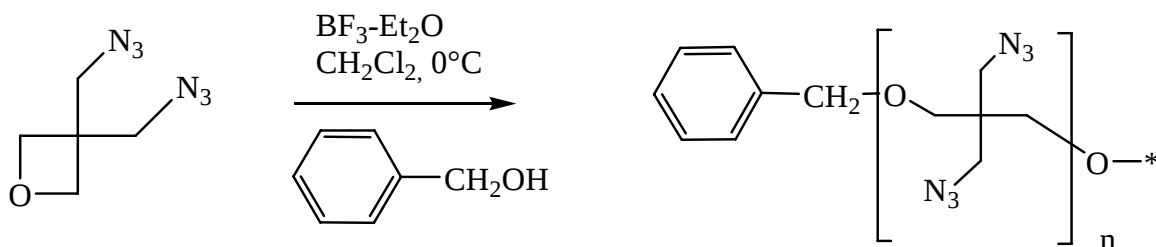
Scheme 1: Synthesis of poly-BAMO; conventional and planned route

2.1.1. Synthesis of poly-BAMO mono-functional

In following we describe the synthesis of poly-BAMO mono-functional from polymerisation of BAMO. The defined functionality of poly-BAMO is essential for the later crosslinking reaction with poly-AMMO to built thermoplastic elastomers of type (ABA)_n structure. To deliver mono-functional poly-BAMO the initiator benzyl alcohol has been used together with the catalyst BF₃·Et₂O in cationic polymerisation.

We followed the published synthesis route shown at scheme 2 ^(13, 14, 15).

The products have been characterized by IR, NMR, CHN analysis, DSC, TGA and sensitivity tests (drop hammer and friction). Poly-BAMO is a yellow solid with melting point between 65 to 75°C. The following table gives an overview to the performed synthesis.



Scheme 2: Synthesis of poly-BAMO mono-functional

Table 1: BAMO homo polymerization initiated by benzyl alcohol (BA) and BF₃OEt₂ (as catalyst) in CH₂Cl₂.

Experiment	Initiator	Ratio BAMO/BA	Repeated units (Calc. by NMR)	MW (NMR calc.)	Melting point by DSC (°C)	Catalyst	Ratio Catalyst/Initiator
1	BA	3	13	2184	74,3	BF ₃ .Et ₂ O	2
2	BA	6	25	4200	65.78	BF ₃ .Et ₂ O	2
3	BA	6	29	4872	72,0	BF ₃ .Et ₂ O	2
4	BA	30	58	9744	78.24	BF ₃ .Et ₂ O	2

Table 1 shows the achieved molecular weights and their corresponding melting points in dependence to the amounts of BA and BF₃.Et₂O. It was expected that the melting point of poly-BAMO shows a strong correlation to the molecular weight. Indeed the measured data support the expectation that higher molecular weights should have higher melting points but the dependence seems to be not very strong. All the melting points are around 70°C. An obviously increase in melting point might be achieved only by much higher molecular weights.

The molecular weights were calculated from NMR spectra integrals of BA-ring protons and BAMO-azidomethyl protons. ¹H-NMR of poly-BAMO exhibited two major peaks close together corresponding to methylene protons which belongs to azidomethyl group ($\delta = 3.33$ ppm) and to methylene groups of the backbone ($\delta = 3.32$ ppm). The aromatic protons of benzyl alcohol give a multiplett at 7.26-7.37 ppm.

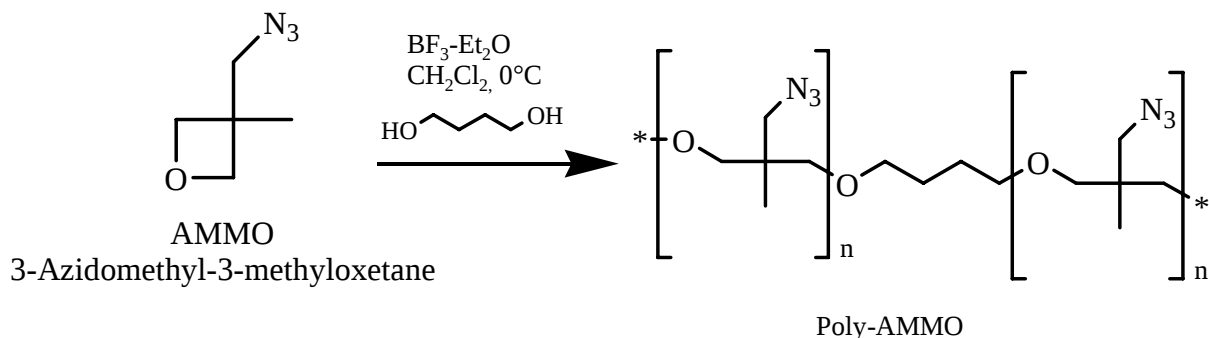
The infrared spectra of poly-BAMO's show the opening of the oxetane ring with the formation of the C-O bond which results in the disappearance of the band related to the ring at 980 cm⁻¹ (ring stretching) and the appearance of the new bands for C-O (1000-1100. cm⁻¹- ν C-O), and OH (3400 cm⁻¹ - ν OH) for the end termination of the polymer. The dominating band is at about 2110 cm⁻¹ caused by the azido-groups.

The DSC analysis of all poly-BAMO's showed the endothermic melting peaks (table 1) and exothermic decomposition peaks with onset temperatures of around 220°C which is typical for organic azide compounds.

2.1.1. Synthesis of poly-AMMO

Because poly-AMMO is the soft block in the ETPE's and the soft blocks are mostly at the centres of thermoplastic polymer sequences we synthesised it only di-functional. This di-

functionality allows the later chain elongation on both chain ends.



Scheme 3: Synthesis of poly-AMMO

AMMO is polymerised by cationic polymerisation with the catalyst BF₃·Et₂O and the initiator butanediol. We followed the published synthesis route shown at scheme3^(13, 14, 16, 17). The products have been characterized by IR, NMR, CHN analysis, DSC, TGA and sensitivity tests (drop hammer and friction). Poly-AMMO is a highly viscous to waxy material depending on the molecular weight. The following table gives an overview to the performed synthesis.

Table 2: Polymerization of AMMO – Influence of Monomer/Initiator Ratio on Molecular Weight

Polymer	Monomer/ Initiator AMMO/BDO	Initiator BDO [mmol]	Monomer/ Catalyst AMMO/ BF ₃ ·Et ₂ O	Catalyst BF ₃ ·Et ₂ O [mmol]	Molecular Weight (measured by NMR)
5	5	15,73	2,5	31,46	5965
6	10	7,86	5	15,73	6350
7	20	11,80	10	23,60	9779
8	35	1,10	17,5	2,20	15875

Table 2 shows the expected result of higher molecular weights with increasing monomer/initiator ratios. At this series the molar amount of catalyst BF₃·Et₂O to initiator BDO was 2:1.

The molecular weight is mainly influenced by the ratio of monomer/initiator. Less initiator results in less number of growing chains that consume the added monomer and this creates higher molecular weight (see table 2).

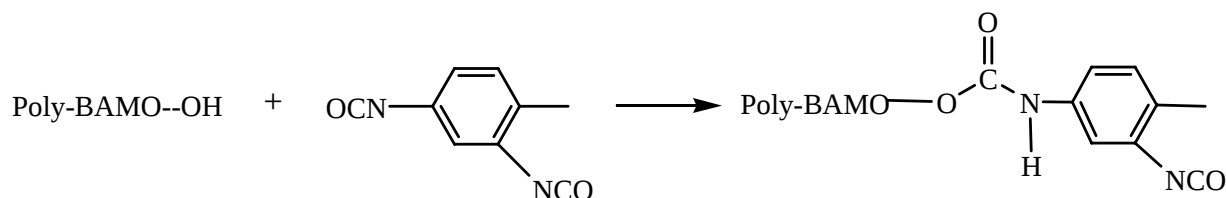
$^1\text{H-NMR}$ of poly-AMMO exhibited three major peaks. At $\delta = 3.32$ ppm the singlet correspond to methylene protons of azidomethyl groups, the AB system at 3.24 ppm refers to CH_2O protons of the backbone, and the singlet at 0.98 ppm to the CH_3 protons of methyl groups. The small multiplet peak at 1.68-1.69 ppm belongs to the protons of butane diol. The integrals of methylene protons from butane diol and the methyl groups were used for calculating the molecular weights.

The IR spectra of poly-AMMO showed that polymerization of the corresponding monomer broaden most of the vibration modes. The C-O-C stretch of the oxetane ring at 980 cm^{-1} is replaced by an intense absorption in the 1111 cm^{-1} which refers to C-O-C stretch of the polymer. The OH stretch (broad band at approximately 3300 cm^{-1}) is also present, which is originated from the end group of the polymer chain. The azide group appears at approximately 2100 cm^{-1} and does not have a significant change in comparison to AMMO spectra.

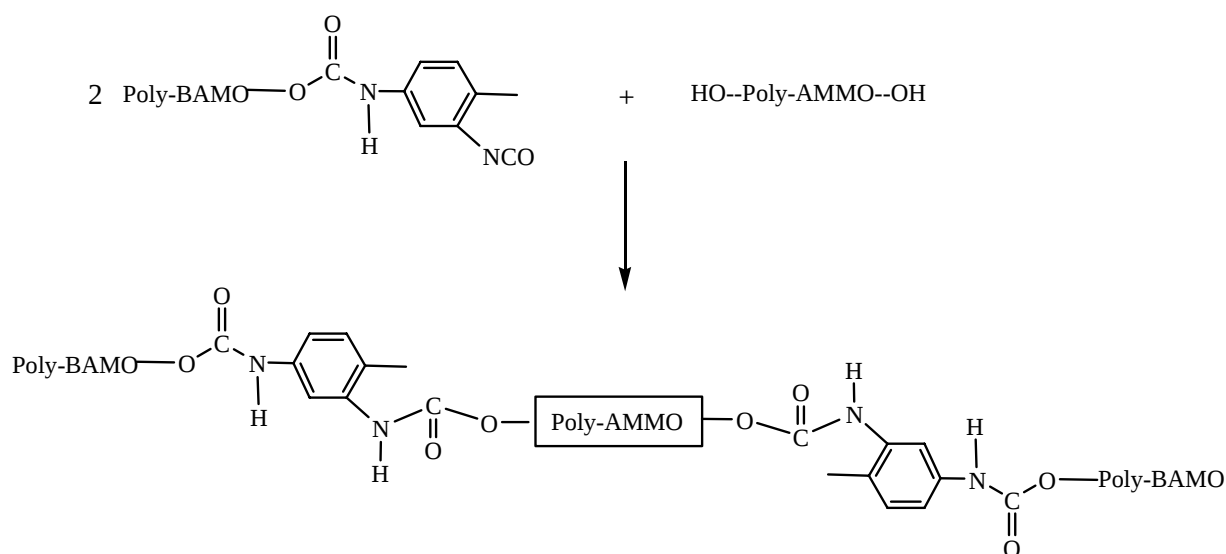
The DSC analysis of poly-AMMO shows only an exothermic peak from decomposition of the azide groups at the expected range of around 220°C onset temperature.

2.2. Copolymers- Synthesis of E-TPE's

2,4-Toluene diisocyanate (TDI) has been used to link the hard blocks (A) from poly-BAMO with the soft blocks from poly-AMMO (B). Because the isocyanate group of 2,4-TDI at position 4 is more reactive than the one at the position 2 it is possible to end-cap poly-BAMO without side reaction of adding two poly-BAMO blocks on one TDI. . The resulting isocyanate-terminated polymer is then reacted with the di-functional soft block poly-AMMO^(13, 14). Generally the reaction sequence is:



Scheme 4: Synthesis of isocyanate capped poly-BAMO



Scheme 5: Synthesis of ABA-type E-TPE by joining isocyanate capped poly-BAMO with di-functional hydroxyl terminated poly-AMMO

The reaction was done without isolation of the end-capped poly-BAMO in a one-pot procedure by adding sequentially the components to a CH_2Cl_2 -solution. After the reaction was finished the solvent was evaporated and the solid product washed by methanol.

Table 3: E-TPE from poly-BAMO and poly-AMMO via linking with TDI

Experiment	poly-BAMO [mmol]/MW	TDI [mmol]	poly-AMMO [mmol]/MW	MP [$^{\circ}\text{C}$]
9	0.441 / 4536	0.46	0.2205 / 5588	73.9

The product was characterized by IR, NMR, CHN analysis, DSC, TGA and sensitivity tests (drop hammer and friction). The product has lower sensitivity when comparable to the original monomers and starting polymers

At ^1H -NMR of the copolymer it can be observed the main peaks of the corresponding polymers poly-AMMO, poly-BAMO and also from TDI (small peaks). From poly-AMMO it can be observed peaks at 0.92 ppm (singlet) corresponding to the CH_3 protons, a multiplet at 3.16 – 3.21 ppm of the CH_2O protons of the chain backbone and another singlet at 3.24 ppm of the methylene protons of azidomethyl group. From poly-BAMO it can be observed at 3.30-3.32 a broad singlet that correspond to 4H of $-\text{CH}_2\text{O}-$ and 4H of $-\text{CH}_2\text{N}_3$. A small multiplet peak at 1.55-1.62 ppm belongs to the protons of butanediol and at 2.13 and 2.19 it can be observed singlets of the 3H of $-\text{CH}_3$ from TDI isomers.

The IR spectra of poly-AMMO/BAMO shows that the addition reaction was quantitatively because of absence of the isocyanate band at 1700 cm^{-1} . The strongest band is caused by the azido groups at 2106 cm^{-1} and from the C-O-C stretch vibration of the polymer backbone (1102 cm^{-1}). A broad band at 3364 cm^{-1} comes from the N-H-vibration of urethane groups.

The DSC of the copolymer shows an exothermic peak at 248.11°C . For the starting polymers poly-BAMO and poly-AMMO, the exothermic peaks are at 246.08°C and 256.17°C respectively. The decomposition peak temperature of the copolymer is only slightly higher than poly-BAMO, which indicates that AMMO units do not affect in a significant way the thermal decomposition of the copolymer. Therefore the thermochemical characteristics of the copolymer poly-BAMO/AMMO are similar to poly-BAMO. At 73.89°C the endothermic melting peak can be seen.

2.3. Sensitivity data for AMMO, BAMO, poly-AMMO, poly-BAMO and poly-AMMO/BAMO in comparison to Nitroglycerine

The sensitivity data of the monomers and the polymers which is not yet published in the open literature is shown in Table 4. It can be clearly seen that the final product has much lower sensitivity against mechanical stimulus like impact or friction than the starting materials. The friction sensitivity of the ETPE is even out of the measure region of the friction apparatus.

Table 4: Sensitivity data for PolyAMMO, AMMO and Nitroglycerine

Sample	Drop Hammer mass [kg]	Falling Height [m]	Impact Sensitivity [Nm]	Reaction	Friction Sensitivity [N]	Reaction
AMMO	1	0.10	1.0	very weak bang	40	tiny flames
poly- AMMO	5	0.15	7.5	very weak bang	160	very weak crackling
BAMO	1	0.10	1.0	very weak bang	60	tiny flames
poly-BAMO	5	0.20	10.0	very weak bang	192	very weak crackling
Copolymer poly- AMMO/ BAMO	5	0.40	20.0	weak bang	>360	none
Nitro glycerine	1	0.10	< 1.0*	strong bang	112	tiny flames
* Impact Sensitivity for Nitroglycerine in literature is 0.2 Nm, but the lowest detectable value at ICT apparatus is 1.0 Nm						

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