Synthesis and Characterization of Energetic Oxetane-Oxirane-Polymers for use in Thermoplastic Elastomer Binder Systems

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1- Introduction

Conventional solid Composite Propellants binders utilize cross-linked elastomers in which prepolymers are cross-linked by chemical curing agents. However there are some disadvantages of using these prepolymers as cross-linked elastomers as it must be cast within a short period of time after addition of the curative, which time period is known as the "pot life". Additionally the use of nonenergetic binders also gives lower performance (1,2).

In view of the inherent disadvantages associated with the use of cross-linked elastomeric polymers as binder materials, there has been considerable interest in developing energetic thermoplastic elastomers (E-TPE) suitable as binders for solid, high energy compositions.

Thermoplastic elastomers are block copolymers that exhibit rubber-like elasticity without requiring chemical cross-linking. Block copolymers that behave as thermoplastic elastomers are copolymers of ABA, AB, or (AB)n structure, where A and B are the hard and the soft segments respectively. 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 (3,4,5,6).

Therefore as an advantage of thermoplastic elastomers over the conventional binders is that they do not need to be cured, so there is no possibility of missed batches.

In Solid Rocket Propellant the E-TPE's and their synthesis should present the following properties (7):

- Molecular weight control
- Reproducible molecular weight
- Low dispersity
- Low glassy transition temperature
- Good and easy handle processibility
- Energetic characteristics
- Low sensitivity against mechanical stimulus and shock wave impact
- Good thermal stability
- Good compatibility with other propellant ingredients

It has being desirable that a thermoplastic elastomer polymer for use as binder in high energy system have a melting point temperature of between about 60°C to 120°C. The 120°C is determined by the instability of many components which ordinarily used in propellant compositions, particularly oxidizers, explosives and energetic plasticizers (8).

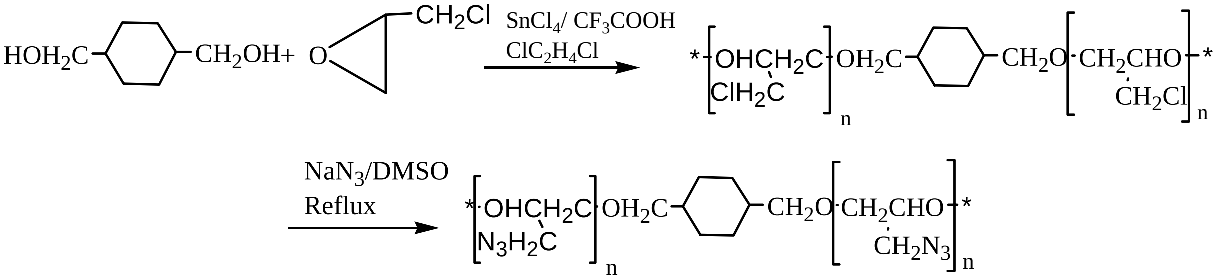
An attractive approach to high energy and low sensitivity propellants involves the use of energetic oxetane prepolymers with N_3 groups . Therefore polymers like GAP, Poly-AMMO, Poly-BAMO has been the target compounds of our studies.

2- Results and Discussion

This paper presents the synthesis the monomer precursors of Poly-AMMO and Poly-BAMO. GAP has also been synthesised. Although GAP is commercially available, it has also been synthesized due to the fact that for the synthesis of TPE´s it is necessary to have access to GAP with adjustable molecular weights and the commercial ones are available only in a few different molecular weights.

2.1- Synthesis of GAP

GAP was prepared following the literature procedure (9a,b,c), as it is shown in Scheme 1:



Scheme 1- Synthesis of GAP

Initially epichlorohydrin is polymerized to poly-epichlorohydrine (PECH) in the presence of 1,4-bis(hydroxymethyl)cyclohexane (BHMC) as initiator and $SnCl_4$ as catalyst. Then the reaction followed with the azidation in aprotic polar solvents which gave the product in 87 - 96% yield. The solvents used for the azidation were dimethylsulfoxide (DMSO), dimethylformamide (DMF) or dimethylacetamide (DMA).

2.1.1- Reproducibility of PECH synthesis:

In order to check the reproducibility of the polymerisation reaction of PECH, the synthesis was performed in 03 different runs and the molecular weights were measured by gelpermeation chromatography (GPC). The GPC analysis was done in comparison to the calibration samples (polystyrene (PS) and polypropyleneglycol (PPG)). The table 1 and 2 shows the results:

Table 1 – Molecular weights of PECH by GPC relative to Polypropyleneglycol (PPG):

Sample	Mw (D)	D	Mn (D)	Mp (D)
PECH 1	2243	1,272	1764	2560
PECH 2	2067	1,171	1766	2245
PECH 3	2366	1,189	1991	2560

Table 2 – Molecular weights of PECH by GPC relative to Polystyrene (PS):

Probe	Mw (D)	D	Mn (D)	Mp (D)
PECH 1	3363	1,345	2483	3746
PECH 2	3010	1,221	2466	3193
PECH 3	3565	1,260	2829	3746

Mw	Molecular weight (average weight)
Mn	Molecular weight (average number)
D	Polydispersity (dispersion broadness): Mw/Mn
MP	Molecular weight at peak maximum

The molecular weights of PECH 1 and PECH 2 are nearly identical and only PECH 3 showed a different value. If it is taken into account that all 03 synthesis runs were performed on small scale of about 100g the reproducibility of PECH synthesis is considered as very good.

The 03 PECH lots were combined into one common lot for further azidation reaction.

2.1.2- Reproducibility of GAP synthesis:

According to the literature (9a,b,c), the best solvents that are recommended for the azidation process are dimethylsulfoxide (DMSO), dimethylformamide (DMF) or dimethylacetamide (DMA). Therefore an azidation reaction was run for each solvent in order to establish the best one. For the reactions an amount of 50 g of the unified PECH were used with the necessary amount of NaN_3 at the different solvents, but using identical reaction conditions and work up procedure. The yields and analysis of GAP synthesis are shown at tables 3, 4 and 5:

Table 3 – Analysis of GAP

Synthesis Run No.	Solvent for Azidation	Beilstein Test	Yield [%]
GAP 1	DMSO	negative	96.4
GAP 2	DMF	negative	87.4
GAP 3	DMA	trace of Cl	90.0

All the solvents gave good yields but in the case of DMA the chlorine substitution was not complete and some traces were left in the GAP even after 36 h reaction time. The best result, from point of yield and azide replacement, was given by DMSO, which will be the solvent to be used at the synthesis of GAP in our studies.

Table 4 – Molecular weights of GAP by GPC relative to polystyrene (PS):

Sample	Mw (D)	D	Mn (D)	Mp (D)
GAP 1 (DMSO)	4106	1,31	3133	4160
GAP 2 (DMF)	3857	1,28	3004	4126
GAP 3 (DMA)	3540	1,23	2890	3992

Table 5 – Molecular weights of GAP by GPC relative to polypropyleneglycol (PPG):

Sample	Mw (D)	D	Mn (D)	Mp (D)
GAP 1 (DMSO)	2402	1,19	2,015	2474
GAP 2 (DMF)	2298	1,18	1946	2474
GAP 3 (DMA)	2161	1,15	1882	2426

Mw	Molecular weight (average weight)
Mn	Molecular weight (average number)
D	Polydispersity (dispersion broadness): Mw/Mn
MP	Molecular weight at peak maximum

The GPC analysis shows clearly the good reproducibility of the GAP synthesis. The molecular weights did not change very much between the 03 runs. The different calibration standards deliver different molecular weights whereas the PS standard always gives higher values. From chemical nature the PPG ones is more comparable to GAP because both are polyether. So the data delivered from PPG is considered more precise. The measuring curves from GPC analysis are shown in figure 1.

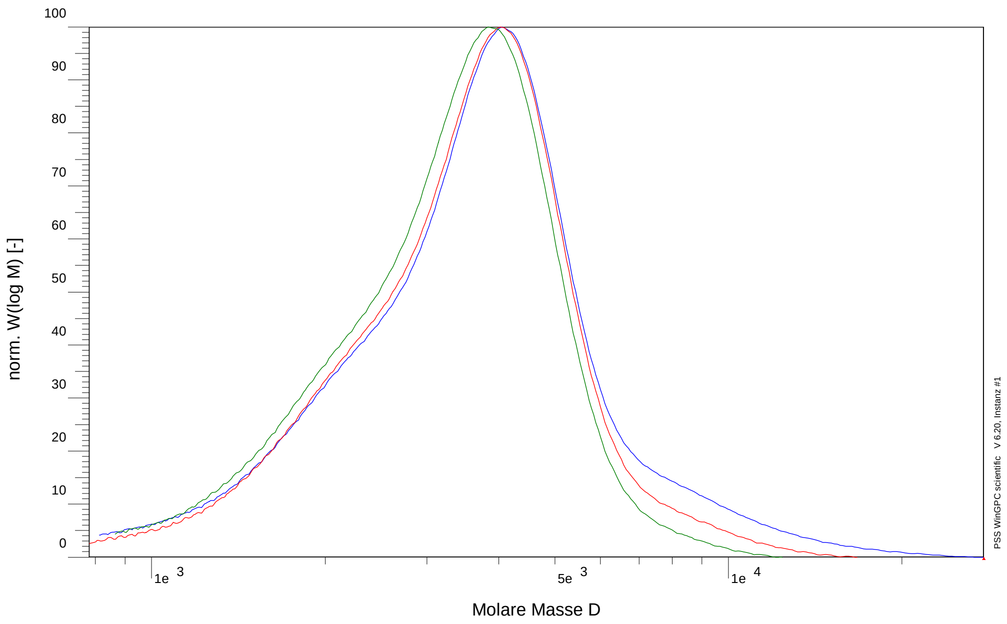


Figure 1 – GPC measuring curves of GAP 1, GAP 2, GAP 3

2.1.3- Spectra and thermal analysis of PECH and GAP

IR spectra

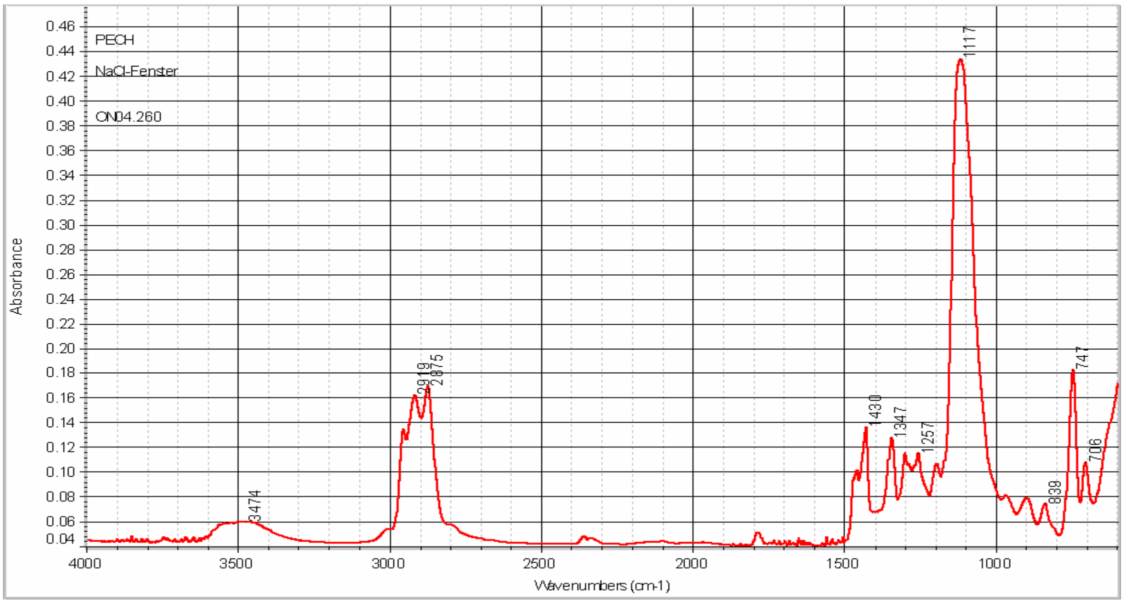


Figure 2.1- IR spectrum of PECH

The formation of glycidyl azide polymers was confirmed from the characteristic peaks obtained in IR spectra (Figure 2.1 for PECH and Figure 2.2 for GAP). The IR spectra presented in Fig.2.2 for GAP shows the main characteristic peaks at 1280 and 2080 cm^{-1}, corresponding to formation of the azide group in the polymer chain and with the total disappearance of the CH_2Cl peak at 746 cm^{-1} (10). The presence of the strong prominent peaks corresponding to CH_2N_3 groups and complete disappearance of the CH_2Cl and also the absence of green flame at Beilstein Test indicates that all the chlorine atoms in the PECH were replaced by the azide groups in the azidation reactions.

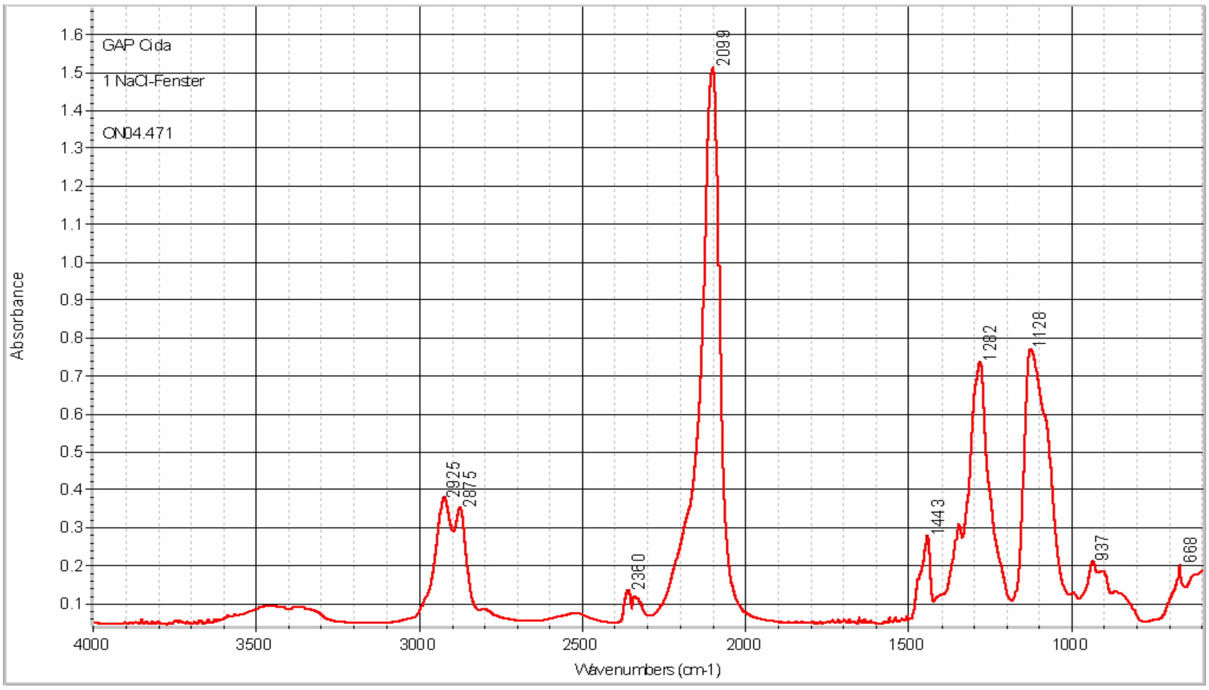


Figure 2.2- IR spectrum of GAP

NMR spectra

^{1}H-NMR for PECH and GAP are presented at Fig 3.1 and 3.2 respectively. ^{1}H-NMR at Fig 3.2, for GAP, the peaks observed around 3.8 ppm refers to CH_2 and CH protons of the main polyether and at 3.4 ppm it refers to the CH_2N_3 protons of the azide pendant group. Comparison of the protons signal intensities of the protons in GAP and BHMC segments at ^{1}H-NMR on the polymer reveals the presence of 19 repeated units of GAP. The ratio of the signal protons intensity of BHMC at approximately 4.0 ppm that belongs to one of the CH_2O-groups (2H) related to protons of repeated units of GAP polymer (5H) is 2mm:94mm. Since the ratio of protons is 2:5 this means that the repeated unit of GAP is contributing with approximately 19mm per H. Therefore the ratio of molecules of repeated unit to monomer is 19:1, or for every initiator there are attached 19 repeated units. This will then give a polymer with a molecular weight of approximately 1881 which is in accordance with the one that has been measured by GPC.

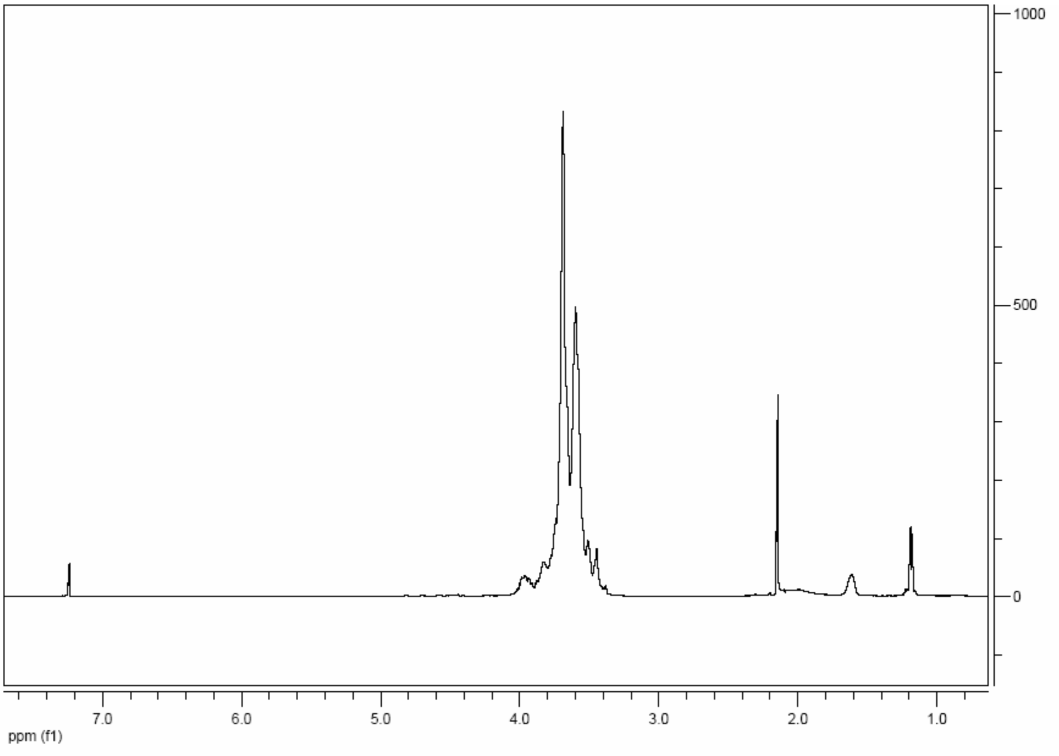


Figure 3.1- ^{1}H-NMR for PECH

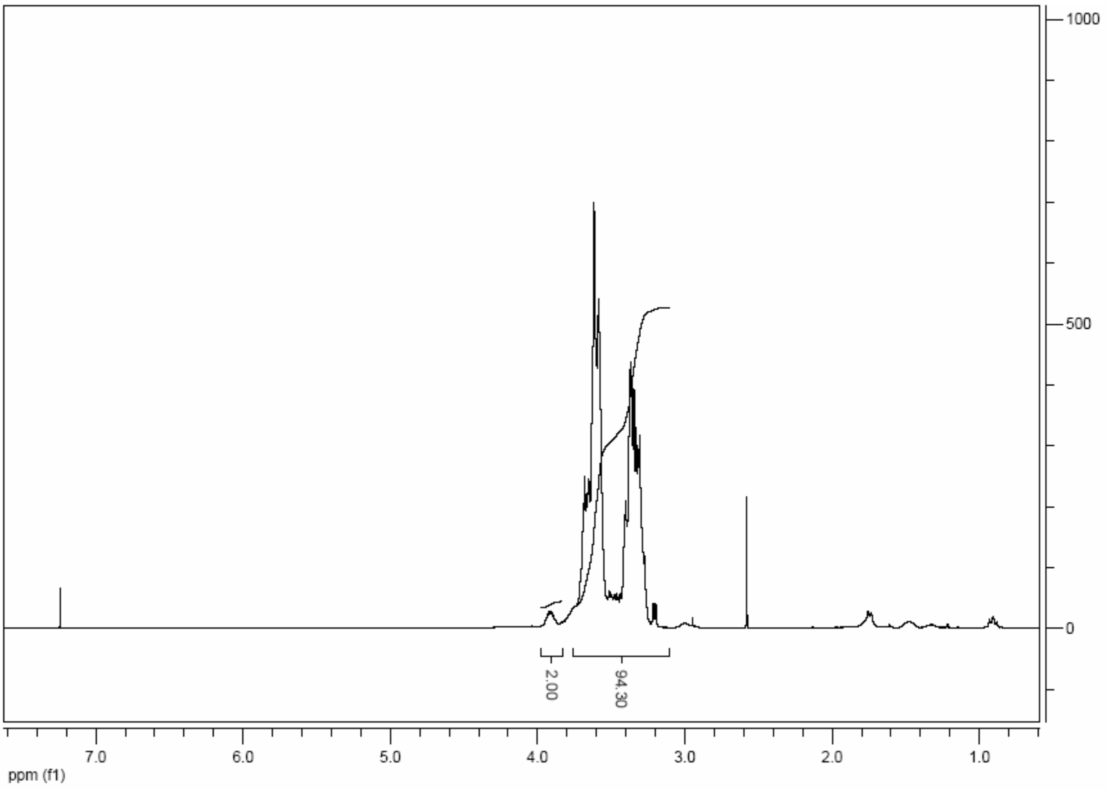
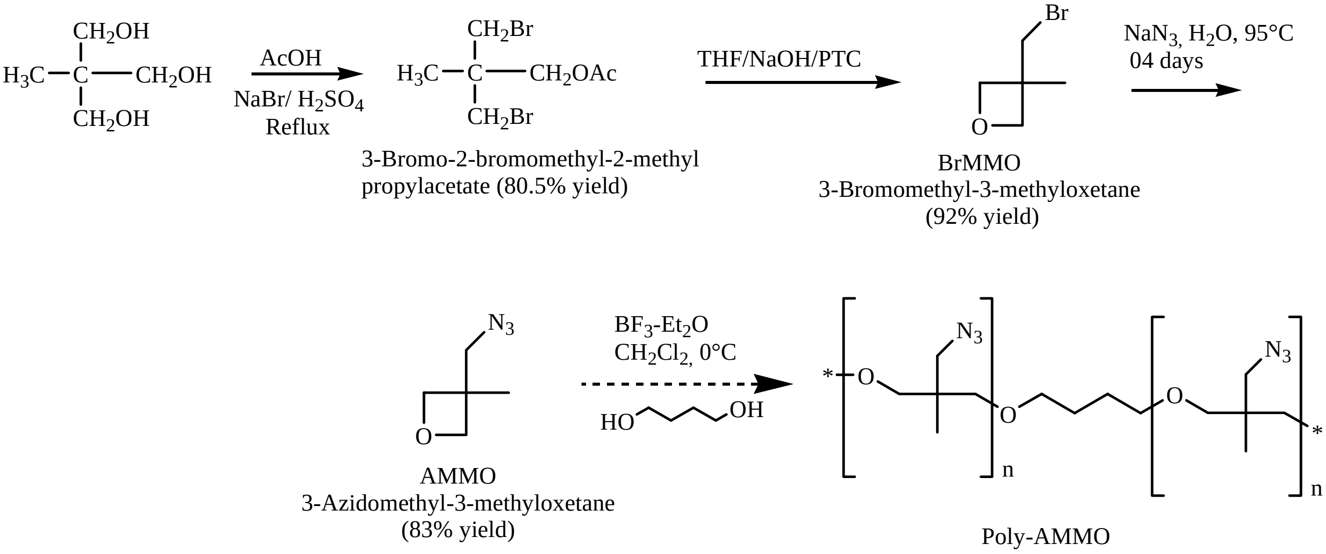


Figure 3.2- ^{1}H-NMR for GAP

The DSC thermogram of GAP shows a main single exothermic peak between 240°C and 250°C which is attributed to the elimination of nitrogen by the scission of the azide bonds from the azide pendent groups (10,11).

2.2- Synthesis of AMMO



Scheme 2- Synthetic route for AMMO

The retro-synthesis has gone as far as the ready and commercial available non expensive starting compound 1,1,1-tris(hydroxymethyl) ethane (Scheme 2). Therefore the first step for the synthesis of AMMO is the reaction of 1,1,1-tris(hydroxymethyl) ethane with acetic acid, sulphuric acid and sodium bromide under reflux affording 3-bromo-2-bromomethyl-2-methyl propylacetate in 80.5% yield (12). Then it was followed by a ring closure reaction with NaOH in THF to give the 3-bromomethyl-3-methyloxetane (BrMMO) in 92% yield. AMMO was then obtained in 83% yield by the reaction of BrMMO with NaN_3 in water at 95°C (13). The ring closure reaction of BrMMO described in this report is improved in comparison to the method recommended in the literature (12) where the ring closure reaction is performed by use of phase transfer catalyst in CCl_4 as solvent. The improvement achieved concerns to the changing the solvent from CCl_4 to the halogen free and less hazardous THF.

The product has been characterized by IR, NMR, CHN analysis, DSC, TGA and sensitivity tests (drop hammer and friction). Also Beilstein Test with the absence of green flame indicated that all the bromine has been successfully replaced by azide group.

AMMO as monomer is a yellowish viscous liquid with quite high sensitivity comparable to nitroglycerin. The sensitivity data of AMMO and nitroglycerin, which is not yet published in the open literature, is shown in Table 8.

Table 8 – Sensitivity data for AMMO and Nitroglycerine

Date: 19.01.2005		Department: EM		Climate Data:		Room Temperature: 20°C		Air Humidity: 51%	
Sample	Sample Cond.	Drop Hammer Weight [Kg]	Falling Height [m]	Impact Sensi-tivity [Nm]	Reaction	Results Pos / Neg	Friction Sensi-tivity [N]	Reaction	Results Pos / Neg
AMMO (Monomer)	Liquid	1	0,10	1,0	Very Weak Bang	1 of 6 POS	40	Tiny Flames	2 of 6 POS
Nitro Glycerine	Liquid	1	0,10	< 1,0*	Strong Bang	6 of 6 POS	112	Tiny Flames	1 of 6 POS
* Impact Sensitivity for Nitro Glycerine at Literature is 0,2 Nm, but the lowest detectable value at ICT apparatus is 1,0 Nm									

The infrared spectrum shows the specific absorption of the oxetane ring at 981 cm^{-1} and the absorption of the azide group at 2102 cm^{-1} (Fig. 5).

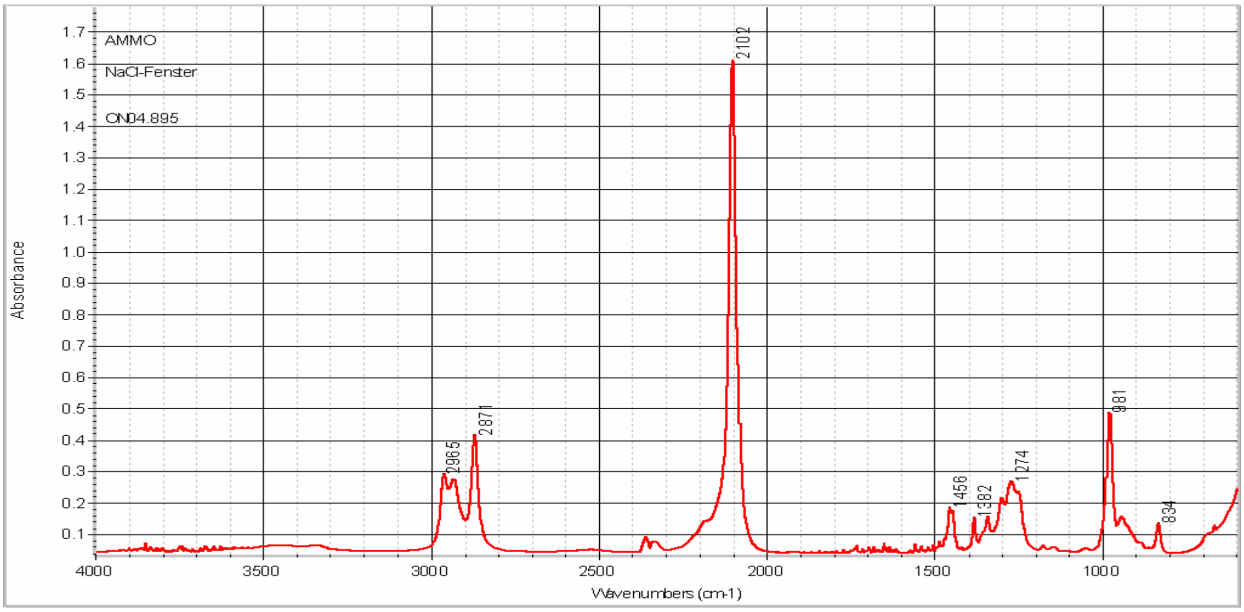


Figure 5- IR spectrum of AMMO

^{1}H-NMR (Fig. 6) of AMMO exhibited two singlet peaks at 1.29 and 3.50 ppm corresponding to methyl and methlylene protons belonging to azidomethyl group respectively and one AB system at 4.33-4.41 ppm corresponding to the protons of OCH_2C oxetane ring.

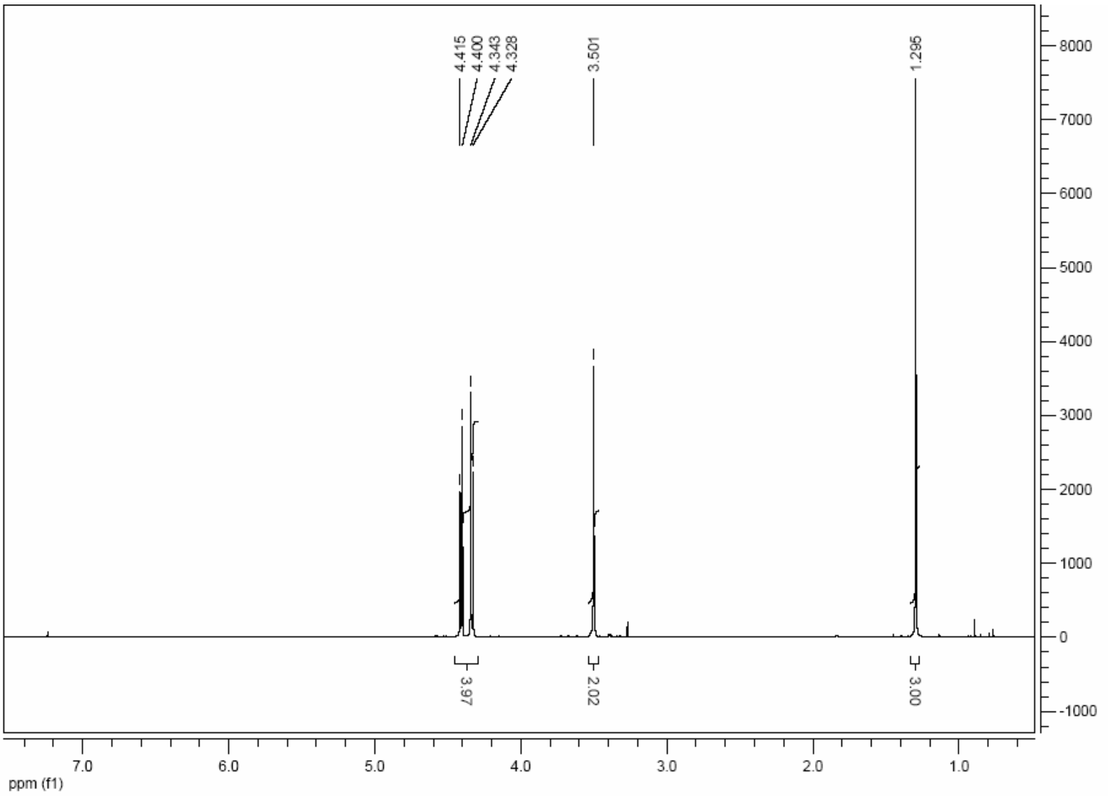
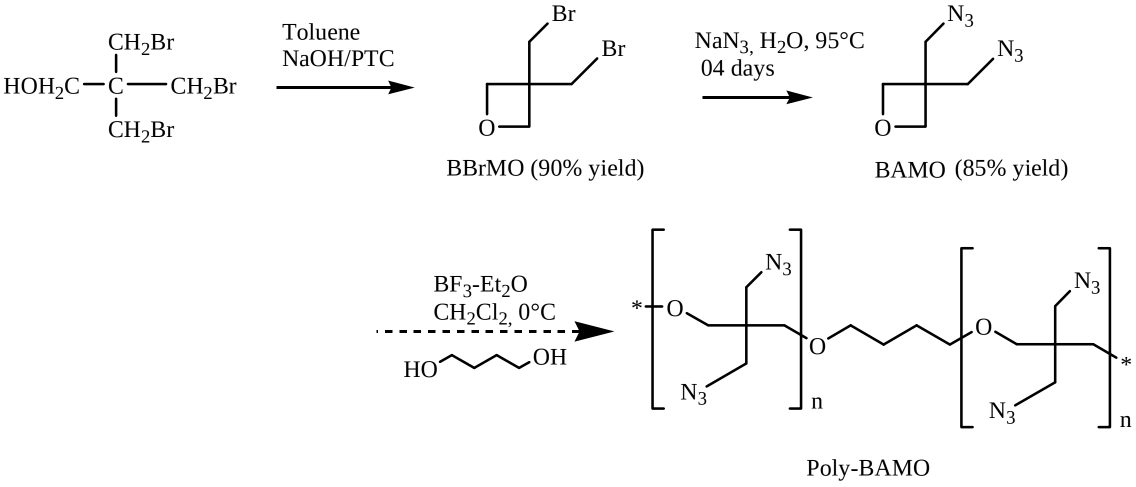


Figure 6- ^{1}H-NMR for AMMO

2.3- Synthesis of BAMO

The synthetic route for BAMO is shown below in Scheme 3:



Scheme 3- Synthetic route for BAMO

The synthetic process started from the available tribromo-neopentyl alcohol supplied as free sample from the American Brom, Inc. of New York Company. Tribromo-neopentyl alcohol was then converted into the corresponding bisbromomethyl oxetane (BBrMO) in a reaction with toluene and sodium hydroxide described in the literature (13) which uses tetrabutyl-ammonium bromide as phase transfer catalyst for the synthesis.

Then BBrMO was converted into BAMO. Initially the reaction was carried out following the method described by Sanderson *et al* at the patent WO 00/343450 A3 (13) which used a mixture of water and Toluene as solvent and phase transfer catalyst. However it was possible to convert BBrMO into BAMO following the same method described for AMMO at the same literature (13). Therefore the method for AMMO has been successfully adopted for BAMO synthesis.

So the use of water as solvent has turned the method much more competitive by reducing costs with higher yield and better environmental conditions.

The BAMO has been characterized by IR, NMR, CHN analysis, DSC, TGA and sensitivity tests (drop hammer and friction). Also Beilstein test with the absence of green flame indicated that all the bromine has been successfully replaced by azide group.

Table 9 – Sensitivity data for BAMO and Nitroglycerine

Date: **19.01.2005**		**Department:** **EM**		**Climate Data:**		**Room Temperature:** **20°C**		**Air Humidity:** **51%**	
Sample	**Sample Cond.**	**Drop Hammer Weight [Kg]**	**Falling Height [m]**	**Impact Sensi-tivity [Nm]**	**Reaction**	**Results Pos / Neg**	**Friction Sensi-tivity [N]**	**Reaction**	**Results Pos / Neg**
BAMO (Monomer)	**Liquid**	**1**	**0,10**	**1,0**	**Very Weak Bang**	**2 of 6 POS**	**60**	**Tiny Flames**	**1 of 6 POS**
Nitro Glycerine	**Liquid**	**1**	**0,10**	**< 1,0***	**Strong Bang**	**6 of 6 POS**	**112**	**Tiny Flames**	**1 of 6 POS**
*** Impact Sensitivity for Nitro Glycerine at Literature is 0,2 Nm, but the lowest detectable value at ICT apparatus is 1,0 Nm**									

BAMO is a liquid monomer having a high degree of explosive character. It behaves similarly to nitroglycerin with slightly lower sensitivity against impact but higher sensitivity for friction (Tab. 9).

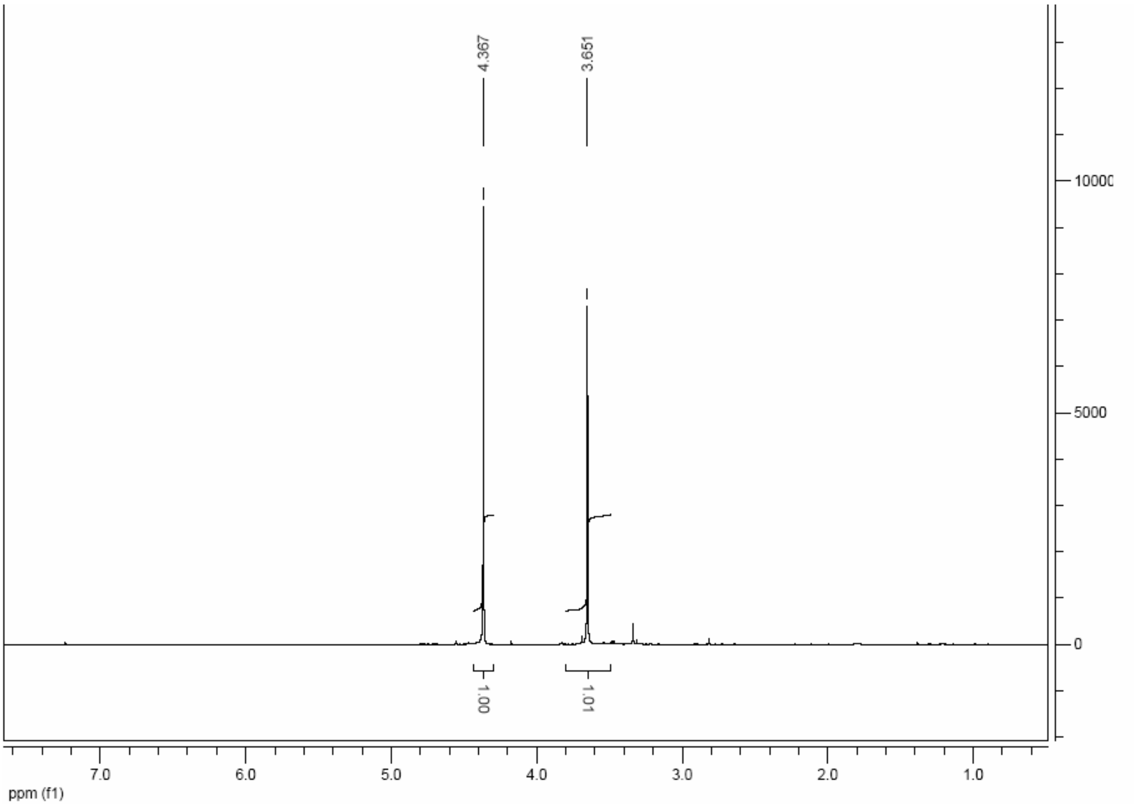


Figure 7- ^{1}H-NMR for BAMO

^{1}H-NMR (Fig. 7) of BAMO exhibited two peaks corresponding to methylene protons which belongs to azidomethyl group ($\delta = 3.7$) and to oxetane ring (($\delta = 4.4$). The infrared spectrum shows the specific absorption of the oxetane ring at 983 cm^{-1} and the absorption of the azide group at 2100 cm^{-1} (Fig. 8). DSC analysis shows an exothermic peak at 239.62^{o}C which is result of the decomposition of the azide groups. This high temperature of decomposition indicates that the compound has rather sufficient thermal stability.

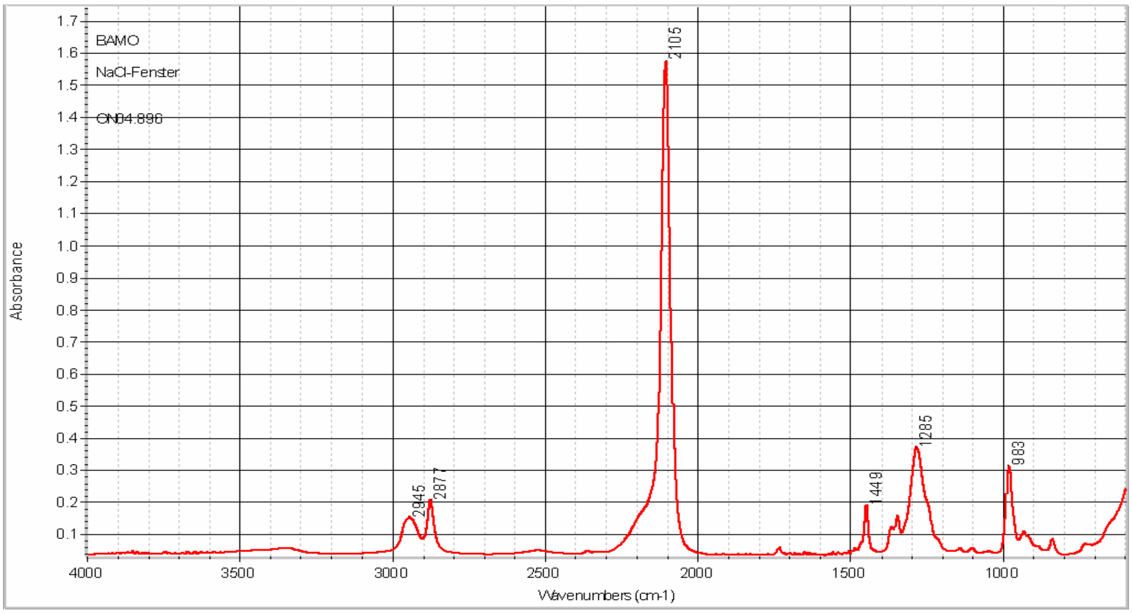


Figure 8- IR spectrum of BAMO

4- References:

1. United States Patent 5,663,289, Sep. 2, 1997, Preparation and polymerization of initiators containing multiple oxetane rings: new routes for star polymers.
2. United States Patent 5,516,854, May 14, 1996, Method of producing thermoplastic elastomers having alternate crystalline structure such as polyoxetane ABA or star block copolymers by a block linking process.
3. WO 00/34353, (PCT)/US99/24013, Method for the synthesis of energetic thermoplastic elastomers in non-halogenated solvents.
4. United States Patent 5,210,153, May 11, 1993, Thermoplastic elastomers having alternate crystalline structure for us as high energy binders.
5. United States Patent 5,489,700, Feb. 6, 1996, 3-Azídation-3-Nitratomethyloxetane.
6. Cationic block copolymerization of tetrahydrofuran with 3,3-Bis(chloromethyl) oxacyclobutane, Macromolecules, 3, 4, 377, 1970, T. Saegusa, S. Matsumoto, and Y. Hashimoto.
7. Energetic polymers and plasticisers for explosive formulations – A review of recent advances, Arthur Provatas, Defense Science & Technologie Organization, DSTO-TR-0966.
8. Triblock copolymers based on cyclic ethers: Preparation and properties of tetrahydrofuran and 3,3-bis (azidomethyl)oxetane triblock copolymers, Journal of

Polymer Science, Part A: Polymer Chemistry, vol. 32, 2155-2159, 1994, Ging-Ho Hsiue, Ying-Ling Liu and Yie-Shun Chiu.

9. (a) Process for obtaining hydroxy finished glydidyl azide polymer, European Patent Application 0 526 381 A2, 1992, (b) Process for the preparation of alkyl azide-substituted hydroxyl-terminated polyethers, European Patent Application 0 274 213 A1, 1987, (c) Branched energetic polyether elastomers, United States Patent 5,130,381, Jul. 14, 1992.
10. Synthesis Spectral and DSC Analysis of Glycidyl Azide Polymers Containing Different Initiating Diol Unit, Journal of Applied Polymer Science, vol. 93, 2157-2163, 2004, Y. Murali Mohan, M. Padmanabha Raju, and K. Mohana Raju.
11. Kubota N.; Brill T. B., Propel Exlos. Pyrotech. 1988, 75, 172.
12. United States Patent 5,650,483, Jul. 22, 1997, Preparation of Mono-substituted fluorineated oxetane prepolymers.
13. WO 00/34350 A3 (PCT), 15 June 2000, Synthesis of energetic thermoplastic elastomers containing oligomeric urethane linkages.