Synthesis and Characterization of glycidyl azide-*r*-(3,3-bis(azidomethyl)oxetane) copolymers

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Abstract: Glycidyl azide-*r*-(3,3-bis(azidomethyl)oxetane) copolymers were synthesized by cationic copolymerization of epichlorohydrin and 3,3-bis(bromomethyl)oxetane, using butane-1,4-diol as initiator and boron trifluoride etherate as catalyst, followed by azidation of the halogenated copolymer. The main objective of this work is the preparation of an amorphous polymer with energetic content higher than that of the well known glycidyl azide homopolymer. The effect of experimental conditions, like i.e. the rate of monomer feeding, on the final molecular weight and functionality of the copolymer has also been investigated. The obtained copolymers were extensively characterized to determine their composition and thermal stability. The heat of reaction for the polymerisation of the halogenated key precursors has also been measured.

Keywords: solid propellants, energetic binder, glycidyl azide polymer (GAP), 3,3-bis(azidomethyl)oxetane (BAMO), cationic polymerization, polyethers.

1- Introduction

Energetic binders are of growing importance in the formulation of cast-cured composite solid propellants. They are in the majority of the cases low molecular weight hydroxyl-terminated polyethers, carrying out azido or nitric groups, capable of holding together fuel and oxidizer compounds from the propellant. Usually, in the propellant mixture a hydroxyl terminated low molecular weight polymer is reacted with isocyanates to form a cross-linked polyurethanic matrix that binds together the solid propellant ingredients in a tough elastomeric three dimensional network structure capable of absorbing and dissipating energy. In addition to these “standard” specifications, energetic binders can give a significant contribution to the propellant impulse thanks to their content of azido or nitric groups. These binders can increase the burning rate and specific impulse in ammonium nitrate, ammonium dinitramide, nitramine and perchlorate propellant systems, due to their high heat of formation, plus capability of evolving gaseous decomposition products, thus leading to the development of a new generation of propellants with high energy content. Because of the high energy content the metal fuels, such as aluminium can be reduced or completely eliminated and the chlorine containing oxidizer ammonium perchlorate can be replaced by halogen-free oxidizers to get propellants with low signature.

Glycidyl azide polymer (GAP) is the most used energetic binder in this new class of propellants. It has a high positive heat of formation (+957 kJ/kg)[(1)], low detonation tendency and low glass-transition temperature (T_g=-48^{o}C). In addition, GAP has also good compatibility with high-energy oxidizers.

In a recent review[(2)] the synthesis of GAP/PolyBAMO has been mentioned but no properties of the copolymer are given. Due to the good capability of GAP to be used as binder and

plasticizer, this work has the aim to develop energetic binders also based on poly (glycidylazide-*r*-(3,3-bis(azidomethyl)oxetane) but fully characterised. This copolymer was developed to produce a binder with similar properties, but higher energy content than GAP. Since polyBAMO has a content of azido groups (49.98% by weight) higher than GAP (42.41%), but cannot be used as homopolymer due to its high crystallinity, the idea is to synthesize a random copolymer with an amount of PolyBAMO as high as possible, but keeping an amorphous morphology. In terms of processing castable rocket propellants, this copolymer should be liquid at room temperature, to facilitate the mixing with the other solid components and should have hydroxyl end groups, in order to allow the final cross-linking step with isocyanates.

Azido polyoxetanes, polyoxiranes and their respective copolymers can be prepared by two different synthetic strategies: i) synthesis of the azidated monomers and subsequent polymerization, or ii) direct azidation of a polyoxetanic/oxiranic substrate having suitable leaving groups [3-4]. The main limitation of the first synthetic route is related to safety, as it involves the handling and storage of azido monomers which are considerably more unstable and shock-sensitive than the corresponding polymers. Therefore, the second strategy, which is the one usually preferred to prepare GAP from poly (epichlorohydrin), was followed. The synthesis of the GAP/Poly BAMO binders was done by an initial cationic copolymerization of epichlorohydrin and 3,3-bis(bromomethyl)oxetane (BBrMO), using butane-1,4-diol (BDO) as initiator and boron trifluoride etherate (BF_3OEt_2) as catalyst, followed by azidation with sodium azide and dimethylsulfoxide as solvent (DMSO). While the second step is quantitative and does not directly affect the degree of polymerization and molecular weight distribution, a particular attention has been paid to investigate the effect of reaction conditions during the polymerization step, like i.e. the rate of monomer feeding, on the final properties of the copolymer. As BBrMO is not available on the market, it was synthesized from 2,2-bisbromomethyl-3-bromo-propan-1-ol.

2- Experimental

Solvents were purchased from Aldrich, Fluka or Merck according to their prices and availability.

Epichlorohydrin (ECH) was distilled at atmospheric pressure (116^{o}C), dichloromethane (DCM) was dried on P_2O_5 and distilled at atmospheric pressure (39°C); butane-1,4-diol (BDO) was distilled at 7mmHg, 103°C; boron trifluoride etherate (BTFE) was distilled at 20mmHg, 54°C. The other solvents were used as received.

Synthesis of BBrMO

BBrMO was synthesized from 2,2-bisbromomethyl-3-bromo-propan-1-ol (purchased from DSBG, Israel). A typical synthesis was as follow. A solution of 100 g of 2,2-bisbromomethyl-3-bromo-propan-1-ol, in 150 ml of ethanol was added to a 1L four-necked glass reactor, equipped with magnetic stirrer, condenser and an additional funnel. The funnel was charged with 200 ml alcoholic solution of NaOH (1.77 mol/L), which were quickly added to the reaction mixture. The reaction mixture was refluxed and left stirring for 1 hour, during which the formation of solid NaBr was observed. The reaction mixture was then cooled and the sodium bromide filtered off and washed twice with 100 ml of ethanol. Then ethanol was removed with 400 mL of distilled water. The organic layer was separated and the aqueous one was washed three times with DCM to recover the residual reaction product. All the organic layers were collected and the mixture was dried with $MgSO_4$ and concentrated at atmospheric pressure to remove DCM and the remaining ethanol. The residual viscous oil was distilled under vacuum (105-108°C, 16 mmHg) to give the purified BBrMO, with a total yield around 70%. The chemical structure of BBrMO was confirmed by infrared and ^{1}H-NMR analysis.

Copolymerization ECH/BBrMO

All copolymerizations were performed with a monomeric molar ratio ECH/BBrMO=75/25. A typical reaction procedure was as follow. A solution of BDO (1.80g) and $BF_3.Et_2O$ (5.76g) in anhydrous and freshly distilled methylene chloride (300 mL) was stirred at 25°C for 2 hours under argon in a reaction calorimeter to allow the formation of the complex $BF_3.Et_2O$-BDO whilst calibrating the instrument. Then, the reaction mixture was kept at 25°C and a solution of BBrMO (60.55g) and ECH (69.34g) in DCM (300 mL) was added drop by drop within a period of 2 (2.5 mL/min), 4 (1.26 mL/min), 6 (0.90 mL/min) or 96 (0.08 mLl/min) hours during which the heat of the reaction was measured. When the addition was complete, the reaction medium was left under stirring for an additional hour for the second calibration of the calorimeter and then left standing overnight at room temperature. Solvent was evaporated (vacuum/room temperature) and quenched with water. Then, the polymer was washed twice with 125mL of a water/methanol 50/50 v/v mixture, dissolved in DCM and dried with magnesium sulphate. Finally, the solvent was removed with a rotary evaporator and the copolymer dried under high vacuum at 70°C. The final product appeared as a clear highly viscous material.

Azidation of the copolymers

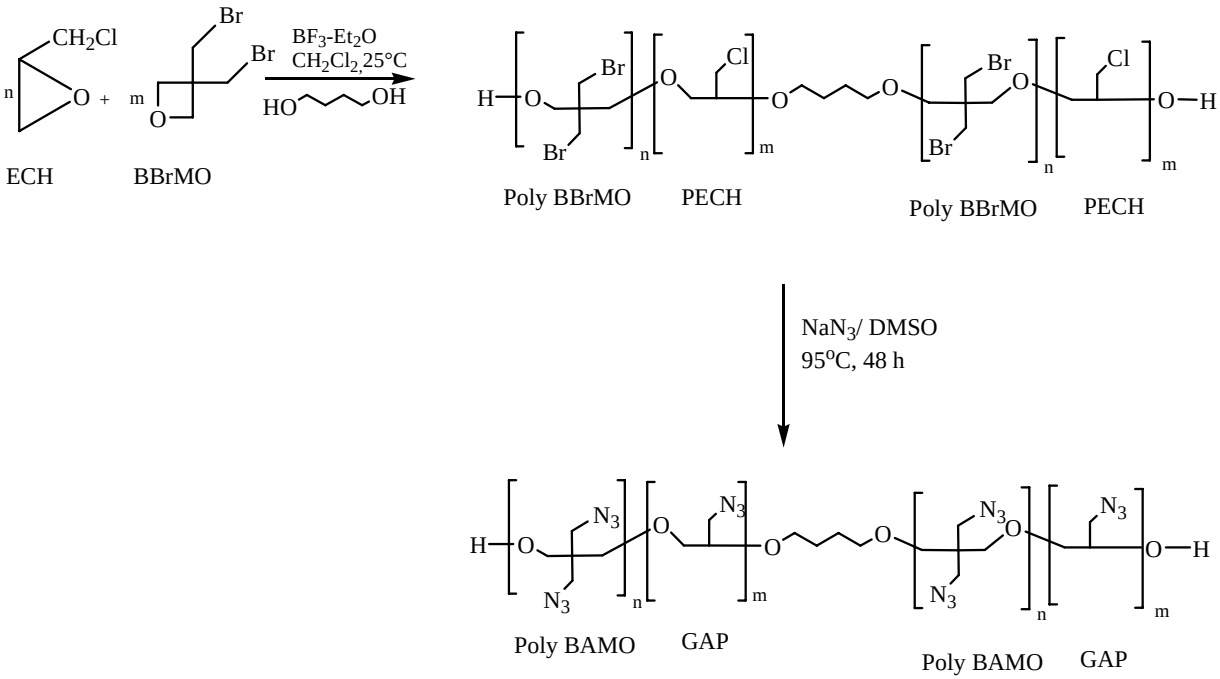
All azidations were performed with a molar ratio (bromine +chlorine)/NaN_3=1.1. A typical azidation procedure was as follow. The copolymer ECH/BBrMO (around 125 g) was added to a round bottom flask with 500 ml of DMSO and heated to 95°C. Then, sodium azide was added to this mixture and left under stirring for 48 hours after which the reaction mixture was cooled to room temperature and slowly added to 1.25 L of water at 0°C kept under stirring. The polymer was recovered, dissolved in about 100ml DCM and filtered to a clear solution free from the sodium salts. The final purification was done by re-precipitation in n-pentane (450 mL). The recovered polymer was finally dried under vacuum at 70°C to give a viscous, yellowish, semi-transparent compound.

Analysis

The heat of reaction was evaluated by carrying out all polymerizations in a RC1 calorimeter from Mettler Toledo. ^{1}H-NMR and ^{13}C-NMR were conducted on a 300 MHz Bruker MSL-300 spectrometer. Infrared spectroscopy was done on a Nicolet SX 5 spectrometer. Gel Permeation Chromatography (GPC) was conducted on a Water's gel permeation chromatography equipped with four ultrastyragel columns (100 Å, 500 Å, 1000 Å and 10000 Å), a refractive index detector and a Datamodule 730. Tetrahydrofuran was used as the mobile phase and polystyrene standards were used for calibration. Differential scanning calorimetry (DSC) was done by a TA instruments Q 1000 using aluminium pans. Scans were carried out on each sample, at scan rates of 5°C/min, under argon flux, in the 40-450 °C range. Thermogravimetric analysis (TGA) was done by a TA Q500 apparatus, with a scan rate of 10°C/min, under nitrogen flux, in the 30-530 °C range. OH group titration was done by standard ASTM procedure [(5)]. The friction and impact sensitivity was measured on a BAM impact machine and friction apparatus according to NATO STANAG 4487 and NATO STANAG 4489.

3- Results and Discussion

As stated above, the synthesis of the GAP/Poly BAMO copolymer was done by cationic polymerization of halogenated monomers using butane-1,4-diol as initiator and boron trifluoride etherate (BF_3OEt_2) as catalyst, followed by azidation with sodium azide in dimethylsulfoxide (DMSO) medium. The reaction steps are outlined in Scheme 1.



Scheme 1 – Synthesis of GAP/BAMO copolymer.

Under the conditions described in the experimental part, the polymerization reaction is expected to proceed mainly by an activated monomer mechanism (AMM) involving successive additions of the protonated (activated) monomer to the terminal hydroxyl groups of the growing macromolecules [6-7]. In theory, this polymerization produces polymers of narrow polydispersity since all the chains at the reaction mixture are expected to grow at approximately the same rate. However, in practice, the control of the growing chain is not that simple and a large molecular weight distribution and the presence of cyclic oligomers can occur during the polymerization process. In fact, formation of cyclic oligomers is a feature of the cationic ring-opening polymerization of cyclic ethers [8] and in some case cyclic oligomers can even be the predominant product. In case of ECH polymerized with BF_3OEt_2, generally there is about 5-20% by weight of cyclic oligomers [9] which constitute an undesirable compound as they contain no functionality and therefore do not participate in the cross-linking step and their low molecular weight may interfere in the desirable mechanical properties of the final product.

In order to favor the AMM mechanism and thus limit the appearance of these cyclic oligomers it is very important to keep the monomer concentration as low as possible during the polymerization [10-14]. Therefore, all synthesis were performed by slowly dropping the ECH and BBrMO monomers mixture, and different feeding rates (total feeding time equal to 2, 4, 6 and 96 hours respectively) have been compared in order to verify the influence of this parameter on the molecular structure of the resulting polymers (referred as cop02, cop04, cop06 and cop96, respectively). A better understanding of the effect of this parameter would be obtained by preparing also a copolymer by instantaneous addition of all the monomers (a so called “cop00”). However, since this reaction is exothermic the control of temperature might not be possible. In fact, the 2 hours dropping time was the minimum that guaranteed very precise isothermal conditions during all the reaction time.

As mentioned before, the ratio of the monomers was selected taking in consideration that the binder must be completely non-crystalline in order to be used in propellant formulations. Based on preliminary investigations using different molar ratios of the halogenated monomers, all polymerizations were carried out with the following molar ratios:

ECH/BBrMO=75/25 (corresponding to a theoretical nitrogen content equal to 45.14% by weight); (ECH+BBrMO)/BF_3OEt_2=25/1 and BF_3OEt_2/BDO=2/1.
The IR spectra gave a first confirmation of the copolymer structure. In Figure 1 the spectra of the unreacted monomers mixture, of the halogenated copolymer and of the azido copolymers are reported. The comparison between the first two spectra shows that the C-O-C symmetrical stretching is shifted from 987 cm^{-1} to 1125 cm^{-1}, due to the opening of the heterocyclic rings of the monomers. The two peaks at 1277 cm^{-1} and 2108 cm^{-1}, corresponding to the symmetrical and the asymmetrical stretching of N_3 groups respectively, show the presence of the azido group in the third spectrum. The quantitative substitution of chlorine groups is confirmed by the complete disappearance of the CH_2Cl peak at 746 cm^{-1}, while the same cannot be done for bromine groups because the signal at 605 cm^{-1}, corresponding to the C-Br bond, is not detectable even in the spectrum before azidation.

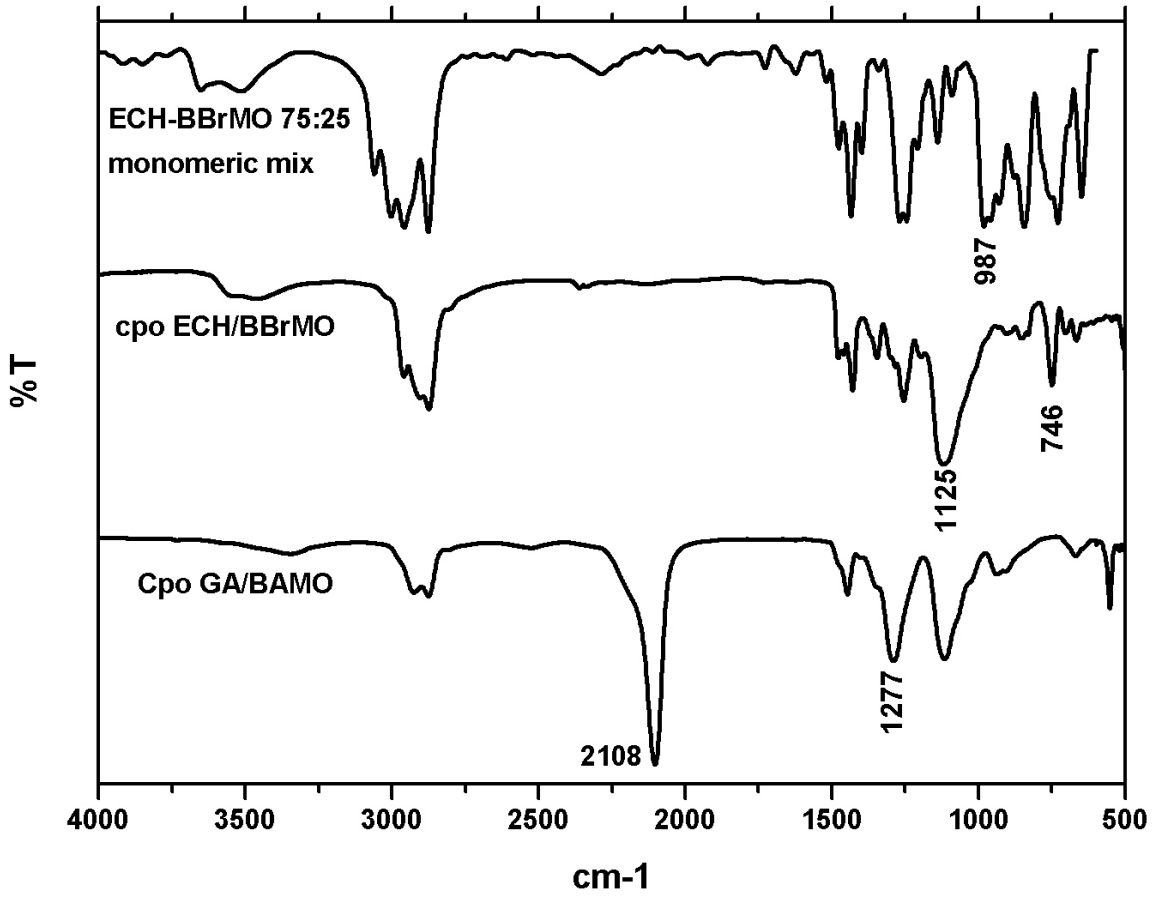


Figure 1 – Infrared spectra of ECH/BBrMO=75/25, molar ratio, mixture of unreacted monomers, and of the corresponding copolymer before and after azidation.

However, both the presence of bromine groups and their complete displacement after azidation has been confirmed by ^{13}C-NMR analysis (disappearance of the peak at 36 ppm from the spectra of the halogenated copolymers). The NMR analysis was used to determine the real composition of the synthesized copolymers. As an example, the ^{13}C-NMR spectrum of cop96 is shown in Figure 2 with some peaks assignment: 44.3 ppm is attributed to the quaternary carbon atom of poly-BAMO units (**a**), 51.8-49.5 and 53.2-52.5 ppm to CH_2N_3 of poly-BAMO and GAP units (**b**), 71.75 and 67.44 ppm to CH_2O (**c**) and 77.65 ppm to CHO of GAP units (**d**).

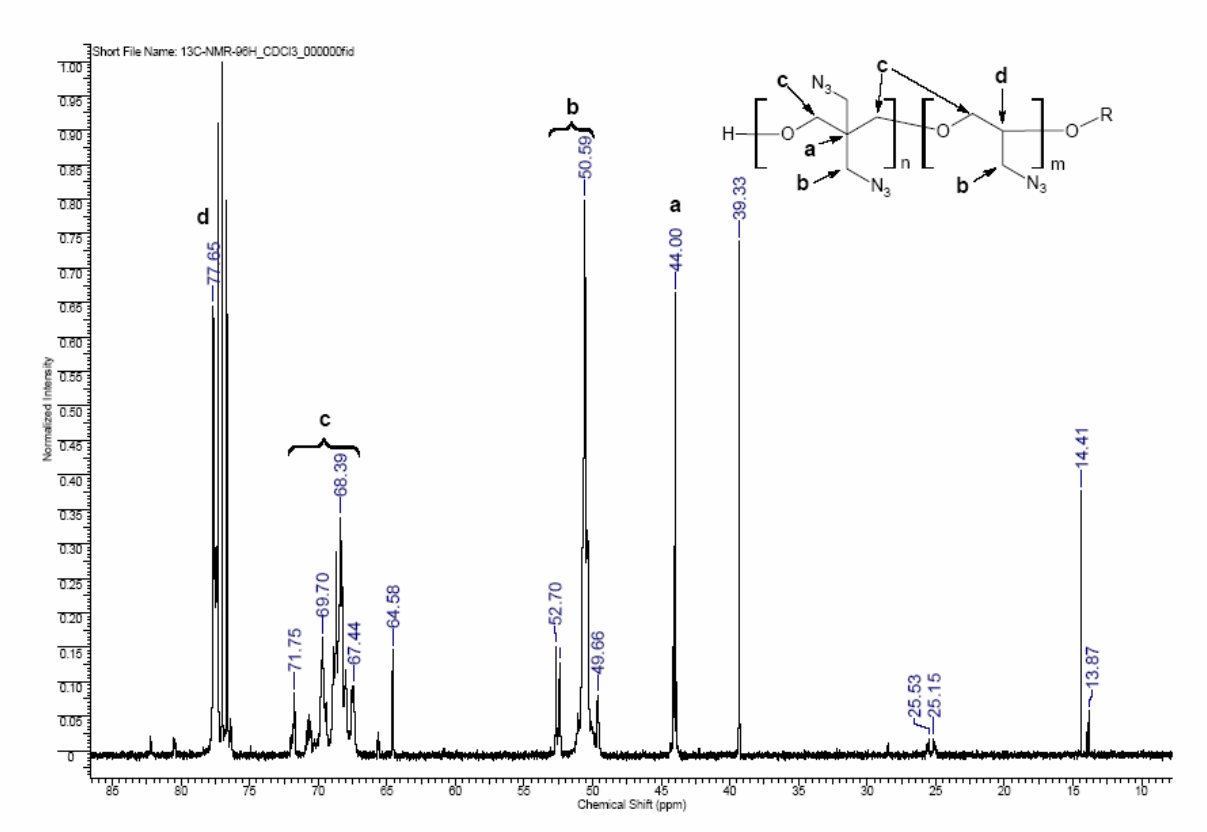


Figure 2 - ^{13}C NMR spectrum for cop96.

The relative amount of the monomers can be calculated using peaks (**a**) and (**b**) or (**a**) and (**c**). In both cases similar results are obtained (Table 1) and the composition of the copolymer just slightly differs from the theoretical calculated value, which shows a reactivity ratio for the two monomers close to one.

Sample	BAMO/GAP Molar ratio[1]	BAMO/GAP Molar ratio[2]
Cop02	21.9/78.1	19.6/80.4
Cop04	23.6/76.4	21.2/78.8
Cop06	24.9/75.1	24.0/76.0
Cop96	18.9/81.1	19.6/80.4

1. calculated using peaks (**a**) and (**b**)
2. calculated using peaks (**a**) and (**c**)

Table 1 - Composition of azido-copolymers from ^{13}C-NMR

The ^{13}C-NMR technique was used also to evaluate the chain-end groups. For this purpose, the hydroxyl end groups were converted into ester ones by reaction with acetyl chloride. As an example, the spectra of acetylated and not-acetylated Cop 04 are shown in Figure 3.

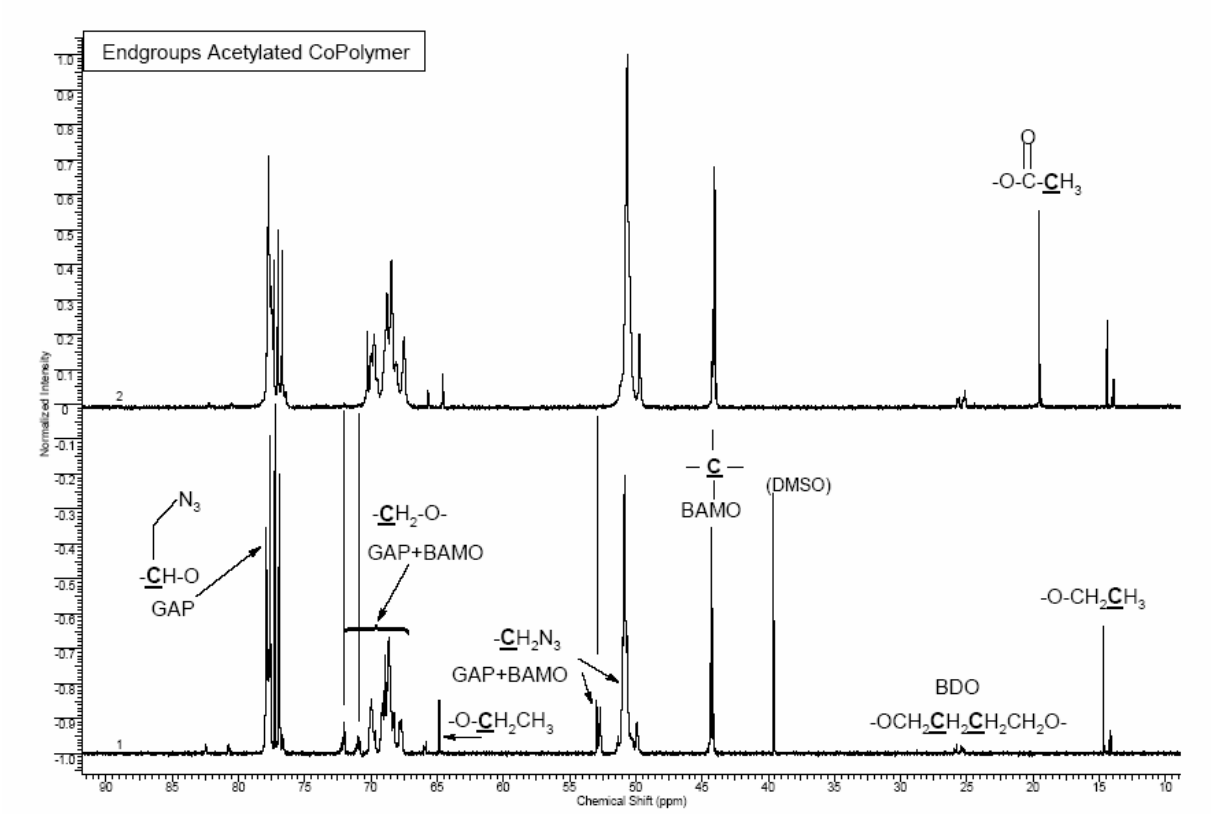


Figure 3 - ^{13}C-NMR spectra for Cop 04 before (lower spectra) and after acetylation (upper spectra)

After acetylation, the peak of the methylic carbon of O(C=O)***C***H_3 appears at 19.51 ppm and that from carbonyl carbon of O(***C***=O)CH_3 appears at 168.84 ppm while the weak peaks at 52.5-52.2 ppm and 72.5-70.6 ppm are shifted upper field and overlapped with their respective main signals. Since the end-groups affect the position of the latter peaks [15], these carbon signals have been assigned at the last monomeric units in the chains. In particular, the signal at 52.5-52.2 ppm belongs to ***C***H_2N_3 of terminal GAP units and that at 72.5-70.6 ppm belongs to ***C***H_2O of terminal BAMO units.

The comparison between the areas of these peaks and those of the signals at 26.4-25.1 ppm, generated by the two central carbons of BDO, show that the total amount of diol is lower then the value expected from the AMM mechanism which should lead to one BDO molecule per chain. Therefore, the presence of a mechanism of propagation alternative and contemporary to the AMM, must be hypothesized. This is reasonable, also considering that the chosen starting ratio BF_3OEt_2/BDO is 2/1 and a chain transfer reaction with unreacted ether groups of BF_3OEt_2, leading to O-CH_2CH_3 end-groups may occur. This is compatible with the weak signals at 65.5-64.6 ppm and 14.4-13.9 ppm, assigned to O-***C***H_2CH_3 and O-CH_2***C***H_3, respectively.

Assuming that OH and OCH_2CH_3 are the only existing end groups in the co-polymer, their relative amount was quantified to be around 74% of OH and 26% of OCH_2CH_3 for all the copolymers.

The molecular weights of the copolymers were evaluated by GPC analysis and the hydroxyl terminal functionalities, responsible for the peak around 3400 cm^{-1} in Figure 1 were measured by titration. As an example, GPC of cop02 is shown in Figure 4. The curve is bimodal and the left peak, corresponding to lower molecular weights, should belong to cyclic oligomers or H_3CH_2CO-terminated oligomers while the right one to the desired linear chains. From the curves the content of the oligomers was estimated to be in the range of 6-11% by weight (Table 2). Combining the GPC analysis and the OH group titration, the degree of functionality

relative to the linear chains could be estimated. However it should emphasized that the GPC was calibrated with polystyrene standards (since a copolymer standard was not available) and this can lead to significant errors in the absolute values. Nevertheless, despite this possible source of error, the GPC analysis offers a good possibility to compare the properties of the different copolymers.

copolymer	Oligomers [g/mol]		Linear chains (LC) [g/mol]		Mw/Mn	Oligomers [%w]	Equivalent Weight [g/mol –OH]	Functionality [Mn (LC)/Equivalent Weight]
	Mn	Mw	Mn	Mw				
Cop02	548	563	1382	1684	1.22	11.7	922	1.50
Cop04	560	575	1461	1762	1.21	6.8	864	1.69
Cop06	554	568	1347	1581	1.17	10.3	877	1.54
Cop96	488	515	1382	1696	1.23	6.1	935	1.48

Table 2- Properties of the copolymers

From the data reported in Table 2 it can be seen that the influence of the rate of addition on the equivalent weight and molecular weight of the polymer is not very significant. This is reasonable since the rate of monomer additions was considerably slow even for cop 02 (2.5 mL/min) when compared with the rate of reaction. So for all the reactions a comparable and very low monomer concentration is probably kept during the reaction time. Due to the fact that some of the chains grow with a mechanism different from that of activated monomer, this leads to the production of copolymer chains with a degree of OH functionality close to 1.5 and lower than the desired value of two. This value is in good accordance with the percentage of OH end-groups (75%) measured by ^{13}C-NMR analysis.
The reasonably low value of the polydispersity suggests AMM mechanism as the prevailing one for this polymerisation reaction.

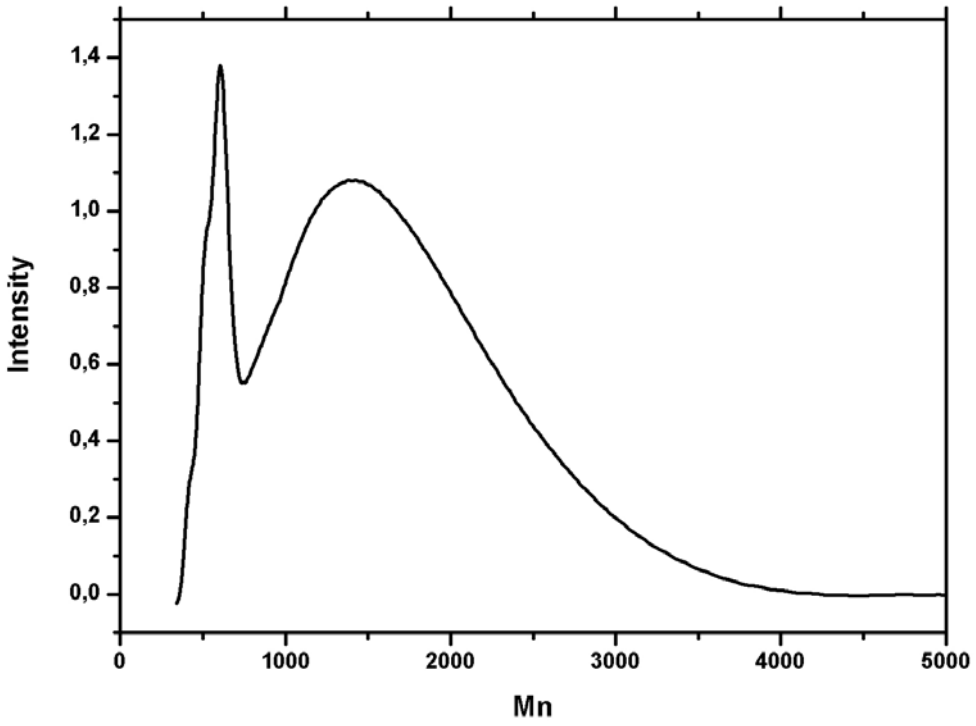


Figure 4 – GPC analysis of cop02.

The measurement of the heat of the reaction was possible only for cop02 and cop04 because for lower addition rates, the heat generation per unit of time was too small for the sensitivity of the equipment. The obtained values were equal to 78 and 80 KJ/mole of monomer respectively, being this small difference reasonably within the range of experimental error.
Since thermal decomposition of the propellant binders is a very important and crucial parameter for the combustion of the composite solid propellant, DSC and TGA analysis were performed for all the copolymers. At DSC, all the curves presented a main single exothermic peak between 244-245^{o}C that can be associated to the decomposition of the azide groups to give nitrogen molecules. Considering that the same peak for GAP homopolymer correspond to an energy release of 2240 J/g, the values obtained for the copolymers can be compared with those expected based on the composition estimated with NMR (Table 3).

Copolymer	Energy of decomposition (J/g)	
	Measured	Expected [(a)]
Cop02	2477	2369-2357
Cop04	2423	2378-2365
Cop06	2347	2384-2371
Cop96	2367	2357-2353

(a) - From data reported in Table 1

Table 3- Energy decomposition of the copolymers

In fact, the experimental values are a little bit higher (except for cop06) but quite close to the expected ones. This small difference can be explained by the TGA analysis (Figure 5) that in correspondence of the same phenomena shows a sharp weight loss of around 40-45% with respect to the total. Again, this value is higher than that corresponding to nitrogen release alone, but at those temperatures the phenomenon is superposed to an incipient degradation of the polymer chains as it can be seen from the TGA curve that after the sharp step do not level, but instead shows a gradual weight loss. In any case, both DSC and TGA confirm that the copolymers start to decompose/degrade at high temperatures, thus showing a satisfactory thermal stability.

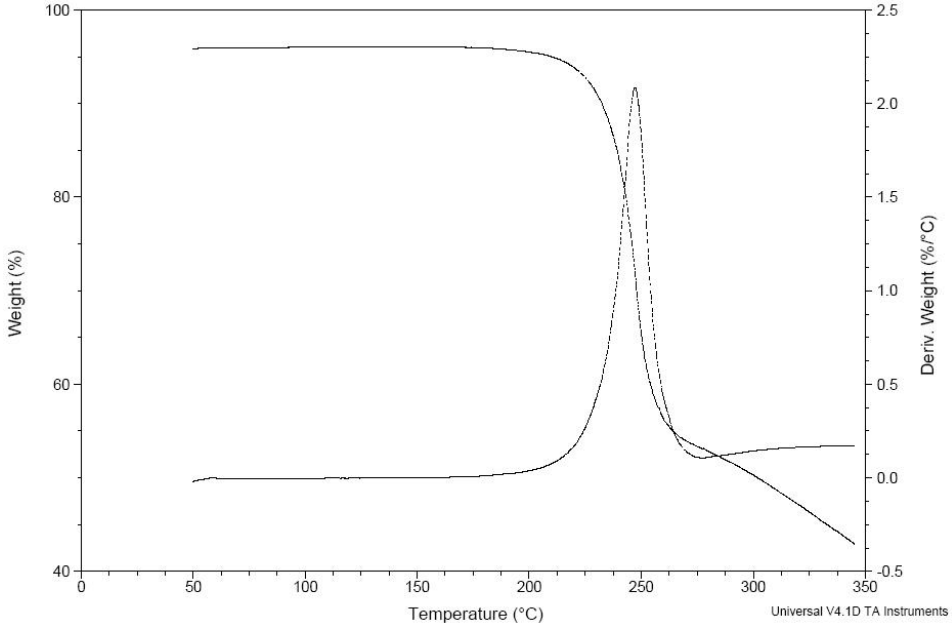


Figure 5 – Thermogravimetric curve and its derivative with respect to temperature for cop96.

For safe handling of the copolymers, the sensitivity of the copolymers against mechanical stress was measured. In comparison to GAP homopolymer the sensitivity is increased which is affected by the increased amount of azido groups. The impact sensitivity is only marginal higher than for GAP but the friction sensitivity is clearly increased (Table 4). Nevertheless the copolymers show sensitivity data that are in the typical range of secondary explosive material and can be handled with the common safety precautions.

Polymer	Impact Sensitivity [Nm]	Friction Sensitivity [N]
Cop04	7.5	288
Cop96	7.5	324
GAP	7.9	> 360

Table 4- Impact and friction sensitivity of the copolymers in comparison to GAP

4- Conclusions

Random copolymers GAP/Poly BAMO with nominal composition 75/25 were synthesized to produce a material for potential application as energetic binder for solid rocket propellant. The synthetic route started with the synthesis of the halogenated polymeric precursor and then by azidation of the same. The introduction of Poly BAMO units in the GAP chain has the advantage of an increasing number in the azide groups and consequently in the energetic content of the material, but to a limited value that preserves the amorphous morphology of the polymer. The operating conditions and the catalytic system were chosen in order to favor a living character of the polymerization and the formation of hydroxyl-terminated chains. However, the characterization of the final product showed that the addition of monomeric units followed also some alternative way which led to the formation of oligomers and chains not hydroxy terminated. Although the measurements of GPC have been done without an appropriate standard, the calculated average number of OH groups for each chain resulted coherent with some preliminary curing experiments of these copolymers performed with poly-isocyanates.

The results of these curing tests were elastomeric rubbers with promising good mechanical properties which will be presented in a future paper.

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