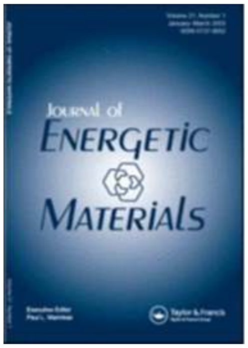

Synthesis of GAP and PAMMO homopolymers from mesylate polymeric precursors

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Synthesis of GAP and PAMMO homopolymers from mesylate polymeric precursors

Short title: **Azidic binders from mesylate precursors**

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Abstract

In azidic binders for solid propellants, the N_3 functionality is introduced by substitution of a halogen or tosyl group, but recently the mesyl group has been suggested as an alternative. The mesylate group has two advantages, mainly related to its small dimension and low cost. Poly(glycidyl azide) and poly 3-azidomethyl-3-methyl oxetane were prepared by using both tosylate and mesylate precursors. The azidation kinetics were studied at three different temperatures while keeping equal all the other operating parameters. The results confirmed the good potential of the mesylate precursors for the production of azidic binders.

1. Introduction

In solid propellant formulations, a reducer and an oxidizer in form of dry powder are mixed with a liquid pre-polymer that allows the formulation to be cast into large and irregular cases [1]. The polymer is then cross-linked to form an elastomeric network that provides mechanical integrity and safety during storage and transportation [2]. The most commonly used binder is hydroxy-terminated polybutadiene (HTPB), which, after cross-linking with isocyanates, provides optimal mechanical properties. However, HTPB do not contributes to the overall energy output and therefore the research is focused on alternative binders that could improve the propellant performance. During the last decades, several energetic binders have been developed and the interested reader may find detailed information in the reviews by Agrawal [3], Provatas [2], Badgujar et al. [4], Sikder and Sikder [5] and Gaur et al. [6]. Among the proposed binders, polyethers containing azidic functionalities are very promising and glycidyl azide polymer (GAP) is the most studied one. Several publications may be found concerning the synthesis as well as the thermal behavior and explosive properties of GAP [7-22]. The GAP synthesis was first described in a patent filed in 1972 by Vandenburg [23] who did azidation of polyepichlorohydrin (PECH) by using sodium azide in dimethylformamide. Twenty years later, Frankel et al. described a semi-industrial production of GAP in USA [24]. Other suggested polymeric azides are poly(3,3 bis(azidomethyl)oxetane-co-ε-caprolactone) [25], 3,3 bis(azidomethyl)oxetane-tetrahydrofuran [26, 27], polyglycidylazide-*b*-poly(azidoethyl methacrylate) [28] and polyoxetanes [6, 29-35], first synthesised by Manser [36-38], such as 3-nitratomethyl-3-methyl oxetane (NIMMO), 3,3-bis-(azidomethyl)oxetane (BAMO) and its analog monofunctional 3-azidomethyl-3-methyl oxetane (AMMO). In the first synthesis, the chlorinated or tosylate monomer was azidated and then subjected to cationic ring-opening polymerization by using a diol and a Lewis acid as catalyst. The approach is now changed, since the azidated ring-monomers are highly dangerous and may easily explode during processing and handling. Therefore, it is better if the azidation step follows the polymerization of non-energetic monomers [34]. This is a low technology, low-risk approach, but gives less opportunity to tailor the final properties of the polymer and suffers from the usual complications of modifying a macromolecule [39]. This means that azidation became the critical step: it may be time demanding and often does not proceed to complete substitution of the functional groups into azidic ones. Sodium azide is the preferred reagent for azidation, which has been performed in several organic solvents as well as in water [24, 40]. A procedure involving molten azidic salts has also been described [41]. In the first case, the reaction is much faster and proceeds in a homogeneous reaction medium, while in water, the use of a phase transfer catalyst is necessary.

The research in the synthesis of azidated polyethers is therefore mainly focused on both the tailoring of the binder properties and, in view of the industrial process, the optimization of the azidation step. The goal is to overcome the production difficulties and make the process competitive with that of HTPB, while keeping the advantages related to the higher energy input of the final product.

The thermodynamics and kinetics of the azidation reaction depend on two main factors: the chemical nature of the leaving group and the operating conditions. With regard to the first point, many different functionalities may be used as leving group to facilitate the introduction of the azidic group through a SN2 type mechanism. The most used ones are halogens, which however present a few disadvantages mainly related to the difficulty of obtaining their complete substitution that may require very long reaction times. Moreover, considering the well-known flame-retardant effect of halogens, it may be supposed that an incomplete substitution, could considerably limit the efficacy of the energetic binder. The tosyl group is an interesting alternative to halogens. This is a very good leaving group, but its steric hindrance may represent a problem. In other words, it may be difficult to remove the tosyl group from a polymeric chain. This is because, even if the macromolecules are dissolved in a solvent, the presence of many neighboring tosyl groups may considerably limit the access of N_3 groups to the reactive site and thus also the overall kinetic of azidation. This problem has been recently discussed by Cappello et al. [42] with respect to the synthesis of ether-HTPB-ether tri-block copolymers. Moreover, the steric hindrance may also play a role during polymerization and influence i.e. the molecular weight of the polymeric precursor.

With regard to the operating conditions, these include the appropriate choice of the solvent (or mixture of solvents) and temperature. The solvent must be a good one for monomers and the forming polymers and, of course, it has to solubilize at least partially the sodium azide. Another important aspect is the solvent boiling point. Higher boiling points allow higher reaction temperatures and thus shorter reaction times, but may complicate the purification of the final product. Moreover, too high temperatures may lead to partial decomposition of the azide groups [34]. Polymeric precursor and operating condition must be chosen in order to balance and optimize the above-mentioned factors. A partial list of azidation conditions described in the scientific and patent literature is reported in Table 1. DMF (dimethylformamide) and DMSO (dimethyl sulphoxide) are by far the preferred solvents.

To better understand the role of the leaving group in the synthesis of azidic binders, we prepared two different polyethers starting from tosylate and mesylate precursors. While the tosyl (Ts) group is well known and already adopted in the synthesis of energetic binders, the mesyl (Ms) one has not yet been used in this field. Therefore, on one side we have a bulky and heavy aromatic group, which is potentially one of the better leaving groups, while on the other one there is a smaller and lighter functional group, theoretically less suitable for azidation. The synthesized polymers are GAP and poly 3-azidomethyl-3-methyl oxetane (PAMMO). Thus, we compared tosyl and mesyl groups with both oxirane and oxetane starting monomers. This corresponds to four synthesis, as summarized in Figure 1. All the monomers, polymeric precursors and azidic binders were characterized by Fourier-Transform Infra-Red (FTIR) analysis and Nuclear Magnetic Resonance (NMR); the molecular weight of the polymers were evaluated by Gel Permeation Chromatography (GPC); their thermal behavior by Thermogravimetric Analysis (TGA). Moreover, the azidation reactions were performed at different temperatures, with time/conversion curves obtained by FTIR and used to evaluate the kinetic parameters.

2. Materials and methods

2.1. Materials

All the chemicals, unless differently stated, were purchased from Sigma Aldrich. Toluene (99,8%), dimethylformamide (DMF) (99.8%), methanol (99.9%), sodium azide (>99.5%), boron trifluoride tetrahydrofuranate (BTF·THF), triethylamine (TEA) (≥99%), 3-hydroxy-methyl-3-methyloxetane (HMMO) (98%), glycidol (G) (96%), toluene-4-sulfonyl chloride (TsCl) (≥99%), methanesulfonyl chloride (MsCl) (>99.7), sodium chloride (>99%), sodium hydroxide (>98%), sodium carbonate anhydrous (>99.7), magnesium sulfate (>99.5), phosphorous pentoxide, hydrochloric acid, potassium hydroxide were used as received. Diethyl-ether and dichloromethane (DCM) were dried with P_2O_5 and distilled at 1 atm. Epichlorohydrin (ECH) and butanediol (99.9%) (BDO) were distilled under the reduced pressure.

2.2. Synthesis of the monomers

2.2.1. Glycidyl tosylate (GT)

The synthesis was performed according to a procedure described by Nakabayashi et al [46]. A 250 mL two-necked round bottom flask, fitted with a nitrogen inlet and a mechanical stirrer set at 180 rpm was fed with 50 mL of anhydrous toluene and 4.2 mL of TEA (corresponding to a G/TEA=1/1 molar ratio). In a beaker a solution of 5.42 g TsCl (corresponding to a TsCl/G=0.95/1.0 molar ratio) in 12 mL of toluene was also prepared. The round bottom flask and the beaker were then conditioned at -15°C for 1.5 h. At the end of conditioning time, the round bottom flask was fed with 2 mL of distilled G (also cooled to -15°C) and then drop-wise with the TsCl solution while maintaining the system under gentle stirring. At the end of the TsCl feeding, the stirrer was stopped and the system maintained at -15 °C for 24 h. Then, the solution was filtered under vacuum to remove the solid TEA·HCl complex and distilled at 65 °C and 2000 Pa to remove the toluene. The remaining liquid was dropped slowly into cold petroleum-ether (containing a few GT crystals previously prepared with the same procedure, in order to favor the crystallization process) thus forming a white suspension that crystallizes while cooled at -15°C. The petroleum ether was finally removed by distillation under vacuum. The GT was obtained with a 98.6% yield, as white anhydrous crystals.

2.2.2. Glycidyl mesylate (GM)

The synthesis was performed according to a procedure described by Nakabayashi et al [46]. A 500 mL two-necked round bottom flask, fitted with a nitrogen inlet and a mechanical stirrer set at 180 rpm was fed with 100 mL of anhydrous toluene and 22.2 mL of TEA. In a 250 mL beaker a solution of 11.7 mL MsCl in 20 mL of toluene was also prepared. The round bottom flask and the beaker were then conditioned at -15°C for 1.5 h. At the end of conditioning time, the round bottom flask was fed with 11 mL of distilled G (also cooled to -15°C) and then drop-wise with the MsCl solution while maintaining the system under gentle stirring. At the end of the MsCl feeding, the stirrer was stopped and the system maintained at -15 °C for 24 h. Then, the solution was filtered under vacuum and distilled at 65 °C and 2000 Pa to remove the toluene and obtain GM as a yellowish liquid with a 84% yield.

2.2.3. 3-tosyloxymethyl-3-methyl oxetane (TMMO)

The synthesis was performed in the solid state, according to a procedure described by Kazemi et al [47]. A mortar was fed with 31.8 g of anhydrous Na_2CO_3, 10.2 g of HMMO (Na_2CO_3/HMMO=3/1 molar ratio) and manually milled with a pestle for about 7 min. Then 28.7 g of TsCl (TsCl/HMMO=1.5/1 molar ratio) where added and milled for further 23 min. Finally, 28.05 g of KOH were added (KOH/HMMO=5/1 molar ratio) and milled for about 50 min to remove the unreacted TsCl. The whole reaction was conducted in a glove box under nitrogen atmosphere. The obtained solid was added to 200 mL of diethyl-ether and filtered several times. The obtained clear liquid phase was finally subjected to distillation at 48°C and 8500 Pa thus inducing the crystallization of TMMO that was obtained with a 40 % yield.

2.2.4 3-mesyloxymethyl-3-methyl oxetane (MMMO)

The synthesis was performed according to a procedure described by Nakabayashi et al [46]. A 500 mL two-necked round bottom flask, fitted with a nitrogen inlet and a mechanical stirrer set at 180 rpm was fed with 150 mL of anhydrous toluene and 13.7 mL of TEA. In a 250 mL beaker, a solution of 7.22 mL MsCl in 30 mL of toluene was also prepared. The round bottom flask and the beaker were then conditioned at -15°C for 1.5 h. At the end of conditioning time, the round bottom flask was fed with 10 mL of distilled HMMO (also cooled to -15°C) and then drop-wise with the MsCl solution while maintaining the system under gentle stirring. At the end of the MsCl feeding, the stirrer was stopped and the system maintained at 4 °C for 24 h and distilled at 65 °C and 2000 Pa to remove the toluene. The remaining liquid was then placed in a fridge to crystallize and recover the MMMO.

2.3. Polymerizations

The polymerization may proceed either by: the Active Chain End (ACE) mechanism, or the Activated Monomer Mechanism (AMM). The first one involves protonation of the oxetane and subsequent propagation until the chain is terminated either with water or alcohol to give the hydroxy-terminated polymer. ACE allows a reasonable molecular weight control, but may lead to the formation of cyclic oligomers [39]. In AMM, which has considerable similarities with the living polymerization, the growing chain is OH terminated and the “active” role is played by the monomer. In this case the side reactions, including cyclization, should be minimized [6]. However, it must be underlined that it is not easy to drive the reaction toward the desired mechanism and often both mechanisms may be present at the same time [31, 35]. For our synthesis, the catalyst and operating conditions were set in order to favor the AMM. BTF·THF and butanediol were used to initiate the polymerization and the quantities were chosen to have a molar ratio between BTF·THF and OH functionalities equal to 2/1, while the molar ratio between monomers and OH functionalities was equal to 50/1. The polymerization procedure was as follows. A 1L three-necked round bottom flask , fitted with a reflux condenser, a nitrogen inlet and a mechanical stirrer set at 120 rpm was fed with 80 ml of DCM, 0.15 mL of BTF·THF, about 0.031 g of BDO and maintained for 2 h under stirring at room temperature. Then, the reactor was covered with aluminum foil, immersed in a water bath at 20±0.5 °C and the monomer (0.0345 mole), previously dissolved in 30 mL of DCM, was added drop-wise to the reactor through a dropping funnel. From the end of the monomer feeding, the reaction mixture was kept in the same conditions for 20 or 120 h (mesylate or tosylate monomers respectively) and then hydrolyzed with 400 mL of an aqueous solution of NaCl (10% w). The mixture was maintained under vigorous stirring for further 2 h and then the organic and aqueous phase were separated. The aqueous phase was washed with DCM, subsequently recovered and added to the organic phase. The organic phase was washed once with a water/methanol = 50/50 v/v solution to remove unreacted monomers and catalyst, then again several times with the aqueous solution of NaCl, dried with $MgSO_4$, filtered and distilled at 45 °C, under vacuum (6500 Pa) in order to remove all the DCM.

2.4 Azidation

The azidation is a second-order reaction with SN2 type mechanism performed using sodium azide in DMF. As already underlined (see Table 1) these azidation conditions are well known and have been already used by our research group [30, 31, 33-35].

A typical azidation procedure was as follows. About 2 g of polymeric precursor were dissolved in 100 ml of DMF and fed in a 250 mL three-necked round bottom flask, fitted with a reflux condenser, a nitrogen inlet and a magnetic stirrer. The flask was immersed in an oil bath set at 85±1 °C and conditioned for 30 minutes. Then, NaN_3 was added in 20% molar excess with respect to the stoichiometric quantity and the temperature of the bath raised to the desired temperature while maintaining the system under constant stirring. Periodically, samples were taken from the reactor and subjected to FTIR analysis to evaluate the degree of azidation. Once the IR spectra were stationary, the reaction medium was filtered under vacuum in order to remove the formed sodium salts and the unreacted sodium azide.

The solution was then washed several times with an aqueous solution of NaCl (10 % w) in order to complete the salts removal. The aqueous phases resulting from the washings were mixed together and washed with DCM to remove possible traces of polymer, while the organic phase was dried with $MgSO_4$, filtered again and distilled at 45 °C, under vacuum (1000 Pa) in order to remove all the organic solvents.

The structure and purity of all synthesized polymers (before and after azidation) were checked by FTIR and NMR, while their thermal properties were determined by TGA.

2.5. Characterization of the monomers and polymers

Fourier-transform infrared spectroscopy was performed on a Bruker Tensor 27 and nuclear magnetic resonance (^{1}H-NMR, ^{13}C-NMR) on a VXR300 and INOVA600 instruments. Thermogravimetric analysis was done by using a TA Q500 apparatus, under nitrogen atmosphere, with a heating rate of 10°C/min until 600 °C and using samples of about 5 mg. The molecular weight of the polymers was measured from solution in $CHCl_3$ (2 mg/mL) by using a Gel Permeation Chromatography (GPC) apparatus Jasco PU-1580, equipped with PL Mesopore column, calibrated with low polydispersity polystyrene standards.

3. Results and discussion

3.1. Chemical characterization (IR – NMR)

The FTIR spectra of all monomers and polymers are reported in Figure 2. The main peaks corresponding to the tosyl, mesyl and azidic functionalities are: 1174-1176 cm^{-1} = υ_s SO_2, 1280 cm^{-1} = υ_s N_3, 1350-1360 cm^{-1} = υ_{as} SO_2, 1600 cm^{-1} = υ C=C aromatic ring, 2100 cm^{-1} = υ_{as} N_3. Some of these peaks have been chosen for the kinetics study, as reported in section 3.3.

For the sake of brevity, the NMR spectra are reported only for the mesylate compounds (Figure 3), which are not common in the binder literature. Nevertheless, all the NMR spectra were recorded and confirmed the chemical composition and high purity of the synthesized compounds. Moreover, the NMR spectra were useful to confirm the absence of tosyl or mesyl groups in the energetic polymers, so that a final conversion equal to 1 was assumed for the azidation reactions.

3.2. Molecular weights

The GPC analysis was performed on the polymeric precursors. As an example, Figure 4 shows the spectrum of PGT (a) and the corresponding fit after deconvolution into two separate peaks (b). The spectra of the other polymeric precursors are qualitatively similar and in all cases showed a small peak corresponding to the formation of oligomers. A deconvolution procedure was then used to calculate separately the mean average molecular weights of polymer and oligomers.

Table 2 reports the number (Mn) and weight (Mw) average molecular weights, the average degree of polymerization (Xn=Mn/Mo, where Mo is the molecular weight of the repeating unit) as well as the polymer dispersion (PD=Mw/Mn) and the Xn and weight fraction of the oligomers. A first observation was that the molecular weights were relatively low. The higher Xn was found for the case of PMMO and it is about half that of the HTPB used as binder for propellants. However, it should be emphasized that the operating conditions were fixed a priori and then applied to all polymerizations. The molecular weight optimization was not an objective of this work and may be modulated by changing many operating parameters as temperature, BDO concentration, catalyst, solvent etc. Nevertheless, these values are comparable with previous results reported for energetic binders (see e.g. [30]). Another interesting point is that in both cases the mesylate monomers gave longer polymeric chains. Since the four polymerization reactors were fed with the same monomer/initiator ratio and molar concentrations, in case of similar yield the polymers should also have similar Xn. Therefore, the Xn values can be somehow read as an indicator of the reaction yield.

3.3. Azidation kinetics

In order to quantify the azidation kinetics of the four polymeric precursors, the time-conversion curves were obtained at three different temperatures. For each precursor, the temperatures were chosen in order to obtain reasonable reaction times. A too fast reaction strongly complicates the sampling procedure and may induce errors in the estimation of the time-conversion curve. A too slow reaction is not advisable for future potentially large scale productions. As described in section 2.4., samples were taken from the reaction medium at different times and their IR spectra recorded and analyzed. Of course, the peaks available to follow the azidation are those corresponding to both the incoming N_3 and the leaving tosyl or mesyl groups. The N_3 asymmetric stretching at 2100 cm^{-1} was chosen among the N_3 peaks because it falls on a clean zone (for both azidated polymers), where it can be easily detected and integrated. This peak has the disadvantage that it tends to increase in intensity at low conversion and broaden at high conversions. This may lead to a partial superposition with the CO_2 peak, which never completely disappears even though the base line was recorded and subtracted each time. As a consequence, the integration was a bit noisy at high conversions. With regard to the tosyl and mesyl groups, the symmetric stretching of SO_2 at 1174-1176 cm^{-1} was chosen. In this case the disadvantage is that the peaks are in the fingerprint region, where 1) the superposition with neighbor peaks may happen and 2) it may be difficult to recognize the base line.

In order to find the best way to evaluate the peak area, we compared the data obtained with or without a deconvolution analysis of the peaks and we did not found significant differences between the two procedures. The presence of the above-mentioned uncertainties (peak overlapping, ambiguous base line) is the reason why the time-conversion curves were evaluated by using both N_3 and tosyl (mesyl) peaks: since the azidic one substituted the tosyl (mesyl) groups, the two conversions are supposed to coincide and can be used to crosscheck one each other. As the reference peak, the CH_2 scissoring at 1456 cm^{-1} was chosen (see Figure 2).

As an example, Figure 5 show the time dependence of the FT-IR spectra during azidation of PGM at 85 °C.

Since the NMR analysis of the final products in all cases indicated a complete azidation, the conversions were evaluated as:

$$x_{N(t)} = \frac{A_N(t)}{A_R(t)} \Big/ \frac{A_N(t_f)}{A_R(t_f)} \tag{1}$$

$$x_{T(t)} = 1 - \frac{A_T(t)}{A_R(t)} \Big/ \frac{A_T(t_0)}{A_R(t_0)} \tag{2}$$

$$x_{M(t)} = 1 - \frac{A_M(t)}{A_R(t)} \Big/ \frac{A_M(t_0)}{A_R(t_0)} \tag{3}$$

where the N, R, T, M subscripts indicate azide, reference, tosyl and mesyl groups respectively, *t* is time, t_0 and t_f are start and end of the reaction and A indicates the area of the peak (evaluated in absorbance and expressed in arbitrary units).

All azidations were performed with a starting quantity of sodium azide corresponding to a 20% excess with respect to the stoichiometry. In the chosen operating conditions, the sodium azide fed to the reactor corresponds to a quantity lower than its solubility limits. Assuming that the substitution is an elementary reaction, we have a second order kinetic law. Moreover, if we disregard volume changes, the following kinetic expression can be written [34]:

$$v = \frac{d[N_3]}{dt} = -\frac{d[T]}{dt} = -k[N_3][T] \tag{4}$$

where *v* is the reaction rate, $[T]$ and $[N_3]$ are the concentrations of unreacted tosyl and azido groups, respectively, *t* is the time and *k* the kinetic constant. Of course, equation (4) is valid also for the mesyl precursor, simply substituting [T] with [M] = concentration of the mesyl groups. Since:

$$[N_3]_0 - [N_3]_t = [T]_t - [T]_0 \qquad (5)$$

where the subscripts refer to time. Equation (5) has solution:

$$[T] = \frac{(r-1)[T]_0}{r\, exp[kt[T]_0(r-1)]-1} \qquad (6)$$

where $r = [N_3]_0/[T]_0$=1.2. Equation (6) can be also written as:

$$x_T = \frac{\exp[kt[T]_0(r-1)]-1}{\exp[kt[T]_0(r-1)]-1/r} \qquad (7)$$

Again, the same equation applies to the azidic and mesyl functionalities, therefore equation (7) can be “generalized” simply including the initial concentration in the kinetic constant: $k' = k[T]_0$:

$$x = x_T = x_N = x_M = \frac{\exp[k\prime t(r-1)]-1}{\exp[k\prime t(r-1)]-1/r} \qquad (8)$$

Equation (8) can be used to fit the experimental data of x_T, x_S and x_N and obtain an estimation of k’.

As already underlined, the experimental time-conversion curves were obtained for each reaction by using both the azide and mesyl (or tosyl) signals from the FTIR spectra. These values should theoretically coincide, but of course the inevitable uncertainties correlated with the use of IR spectra for quantitative analysis lead to small discrepancies. As an example, the comparison of conversion obtained with azide and mesyl signals in the case of PGM at 85°C is reported in Figure 6. The image clearly shows that x_N has an irregular trend between 30 and 60 minutes, while x_M gives a more reliable and smooth behavior. Nevertheless, the two sets of data are in good accordance and the reported example was chosen because it is the one where the noise in x_N is more pronounced.

As a second example, the PMMMO azidation kinetics at different temperatures, obtained from the mesyl peaks, are reported in Figure 7, together with the best fit obtained from equation (8) with *k'* as unique fitting parameter. The whole list of estimated *k'* values for the four polymers is reported in Table 3, together with the activation energy (Ea) and the pre-exponential factor (A) evaluated by a linear fit in the plot of the logarithmic *k'* values against the inverse of temperature, expressed in Kelvin degrees.

Independently on the use of mesyl or tosyl groups, the azidation reaction was faster for GAP than for PAMMO. This is why in the first case the adopted temperatures were 75, 85, and 95 °C, while they were raised to 85, 105 and 125 for PAMMO. As expected, in both cases the temperature strongly influences the rate of reaction and the time needed for a quantitative azidation may vary from approximately one week to about one day while comparing the lower and higher tested temperatures. The *k'* values reported in Table 3 confirms that the tosyl group is a better leaving group in the case of GAP precursors. In contrast, in the case of PAMMO the difference between the two precursors is less pronounced and the mesyl group is the one with the highest azidation kinetic. Moreover, it is interesting to observe that for both polymers the azidation reaction from the mesylate precursors has a higher activation energy (thus indicating a higher dependence on temperature) and a higher pre-exponential factor (thus indicating a higher frequency of collisions between reactant molecules).A simple theoretical calculation indicates that in the case of GAP the azidation kinetics from the two different precursors should coincide at about 110 °C which is still in a feasible range of operating temperature (even lower than those already adopted for PAMMO in the present study).

Finally, it is interesting to report the thermogravimetric analysis of the polymers and corresponding precursors (Figure 8). As it has been already observed and discussed in many other works, the azidic polymers shows a two-step decomposition behaviour [7, 11, 16, 21, 48]. The nitrogen release from the N_3 group is responsible for the first step, while during the second step the main chain decomposition occurs. It is not the aim of this work to discuss this well-known behaviour, which has been already showed for both GAP and PAMMO polymers. The curves presented here because they allow the comparison between behavior of polymers prepared from tosyl and mesyl precursors. It can be clearly seen that the thermal behaviour of the azidated polymers are almost identical, with the differences comparable to the experimental uncertainty always present while observing fast and uncontrollable decomposition phenomena.

4. Conclusions

Azidic binders are probably the most interesting and promising alternative to HTPB and the scientific research was focused on their synthesis for many years. Usually, the N_3 functionality is added to a polymeric precursor by SN2 type substitution of a halogen or tosyl group. The use of chlorine and bromine, as groups have some disadvantages, mainly related to the possibility of incomplete substitution during azidation. The residual halogen atoms may impart a sort of anti-flame character to the binder and significantly reduce its efficiency. Analogously, the tosyl group has disadvantages related to its very high molecular weight, which strongly increases the weight of reagents and by-product to be processed. This is negligible on the lab scale, but may represent a problem to scale up the process for industrial production. Moreover, the introduction of several tosyl groups in a polymeric chain may result in a steric hindrance that can limit both the molecular weight of the polymer and its reactivity during azidation. This is the reason why the methane-sulfonyl chloride has been suggested as a potential alternative to halogen and tosyl groups. On a theoretical basis, the mesyl group should be comparable to the tosyl one in leaving the polymeric chain during azidation. However, there are also some potential advantages connected with the use of such molecule. First of all, it is convenient from an economic point of view, since it is a low cost compound that can be easily introduced in the oxetane and oxirane monomers. Secondly, the reduced dimension, when compared to the tosyl group, allows a greater mobility of the polymeric chains. The synthesis and azidation of GAP and PAMMO starting from tosyl and mesyl precursors confirmed the high potential of the latter. The mesylate precursors were prepared in form of oxetanic and oxiranic monomers, subsequently polymerized and azidated. From the operating point of view, all the synthetic steps were comparable with those adopted for the case of conventional precursors. The azidation reaction led to fully substituted polymers, with final properties almost identical to those prepared by using the tosyl groups. Finally, the kinetic of azidation at high temperatures showed to be perfectly comparable with that of the other precursors. This is not surprising if we consider that: 1) the tosyl functionality, as a better (more stable) leaving group, simply lowers the transition state energy, relative to that of the mesyl analogue; 2) the higher mobility of the mesyl groups leads to a pre-exponential factor two or three order of magnitude higher that of the tosylated reactant. We can thus conclude that methane-sulfonyl (mesyl) group is a good candidate for the production of azidic binders for solid rocket propellants.

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Figure captions

Figure 1 - Synthesis and azidation of GAP and PAMMO.

Figure 2 – FTIR spectra of monomers, precursors and azidated polymers.

Figure 3 – H-NMR spectra of the mesylate monomers and polymers.

Figure 4 – GPC curve of PGT (a) and the resultant fitting obtained by deconvolution into two peaks corresponding to polymer and oligomers (b).

Figure 5 – FT-IR spectra of PGM during azidation at 85 °C.

Figure 6 - Comparison between x_N and x_M for PGM azidation at 85 °C.

Figure 7 – x_M for PTMMO azidation at different temperatures: ○ 85 °C; □ 105 °C; ◊ 125 °C. Solid lines represent the curves calculated with eq. (8).

Figure 8 – TGA curves of the synthesized polymers.

Table 1. Azidation reactions of polyether precursors: exiting group, reaction medium and operating temperatures, as reported in literature.

Exiting group	medium	Temperature (°C)	reference
Tosyl, Br	DMSO, DMF	95, 120, 150	[34]
Cl, Br	DMF	90-95	[30]
Cl	DMF	120	[29]
Cl, Br	DMSO	95	[31]
Tosyl, Br	DMSO	120	[35]
Cl, Br	DMSO	120	[33]
Cl	DMSO	100	[8]
Cl	DMF	100	[11]
Cl	DMSO	105	[25]
Cl	DMF	120	[28]
Cl	DMSO	100	[13]
Cl	DMSO	90-95	[24]
Cl	Water	95	[40]
Cl	tetrabutyl ammonium azide (molten salt)	105	[41]
NO_2	DMSO	100	[43]
Cl	DMSO	105	[44]
Cl	Water	95-100	[45]

Table 2 – Molecular weights of the polymeric precursors calculated by GPC analysis.

Polymer	Mn	Mw	PD	Xn	Oligomer Xn	Oligomer content (w%)
PGT	2300	3200	1.4	14	683	10
PGM	2150	3380	1.6	22	500	3
PTMMO	2400	6650	2.8	26	450	6
PMMMO	3000	5900	2.0	33	700	9

Table 3 - Comparison between the kinetic constants evaluated by using the azide (N), tosyl (Ts) and mesyl (Ms) signals in the FT-IR spectra.

polymer	T	PGM		PGT		T	PMMMO		PTMMO	
group	(°C)	N	Ms	N	Ts	(°C)	N	Ms	N	Ts
k' (s^{-1})	75	0.041	0.0457	0.1168	0.1334	85	0.0313	0.03321	0.046	0.0445
	85	0.118	0.1064	0.1807	0.1933	105	0.17445	0.14741	0.15097	0.14771
	95	0.172	0.1747	0.2727	0.3288	125	0.49413	0.41202	0.31482	0.35203
A (s^{-1})		$2.4*10^8$	$4.3*10^7$	$3.4*10^4$	$1.1*10^4$		$5.2*10^8$	$4.7*10^7$	$1.8*10^5$	$6.8*10^5$
Ea (KJ/mol K)		76.6	71.5	47.9	45.1		82.0	74.8	57.1	61.4

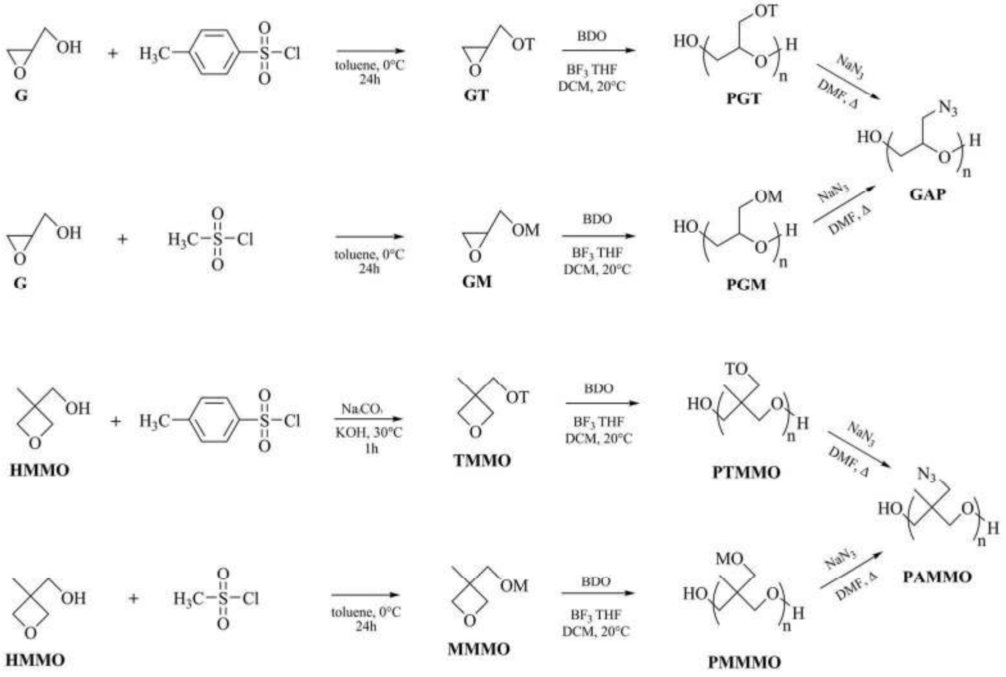

Figure 1 - Synthesis and azidation of GAP and PAMMO.
136x92mm (300 x 300 DPI)

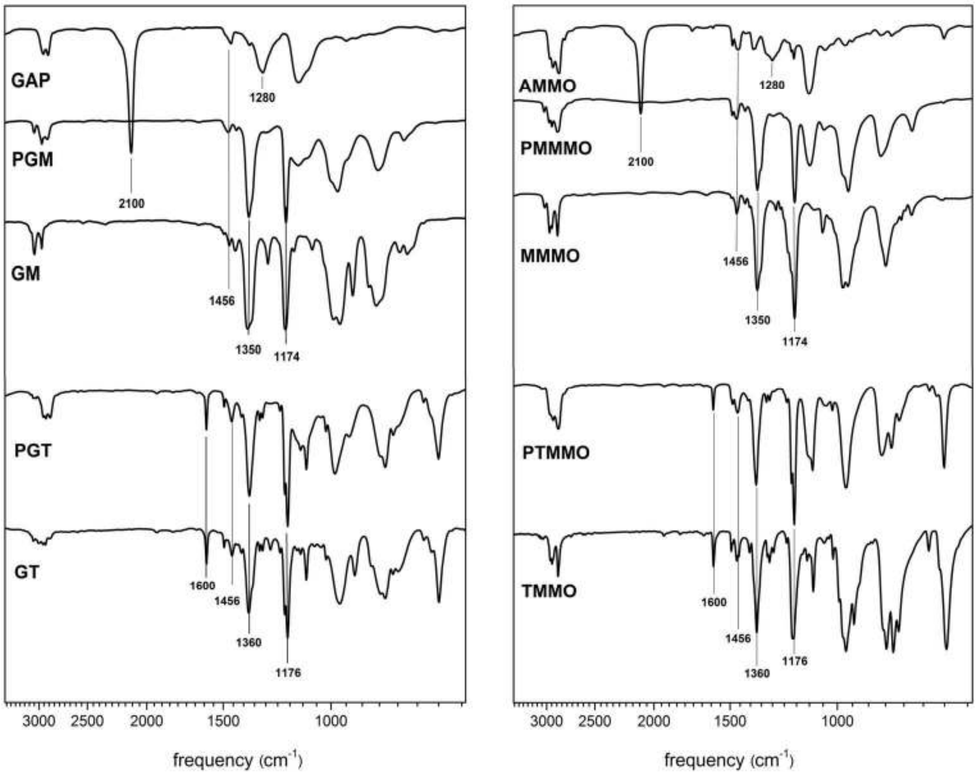

Figure 2 – FTIR spectra of monomers, precursors and azidated polymers.
151x121mm (300 x 300 DPI)

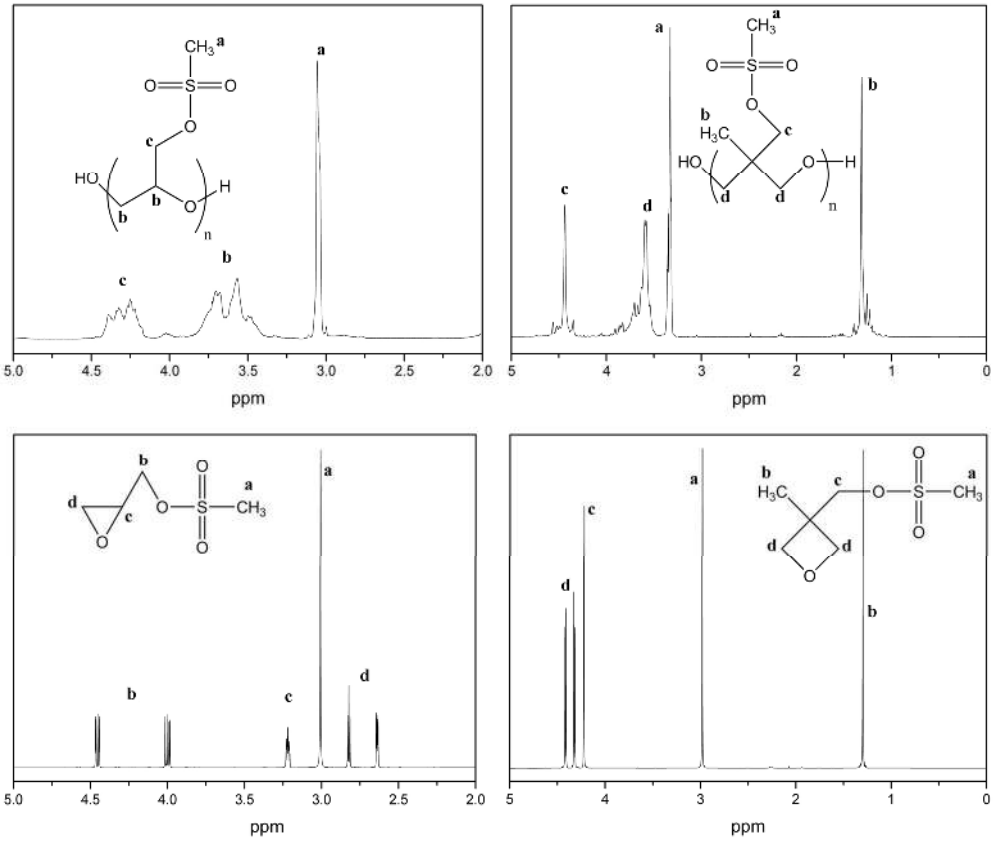

Figure 3 – H-NMR spectra of the mesylate monomers and polymers.
165x142mm (300 x 300 DPI)

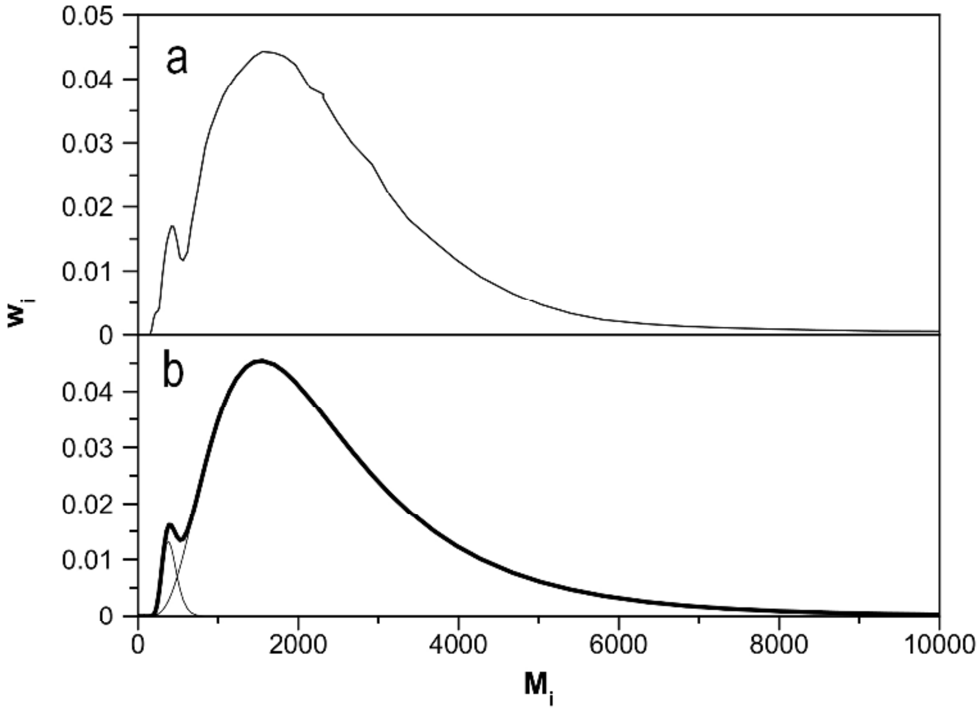

Figure 4 – GPC curve of PGT (a) and the resultant fitting obtained by deconvolution into two peaks corresponding to polymer and oligomers (b).
666x499mm (72 x 72 DPI)

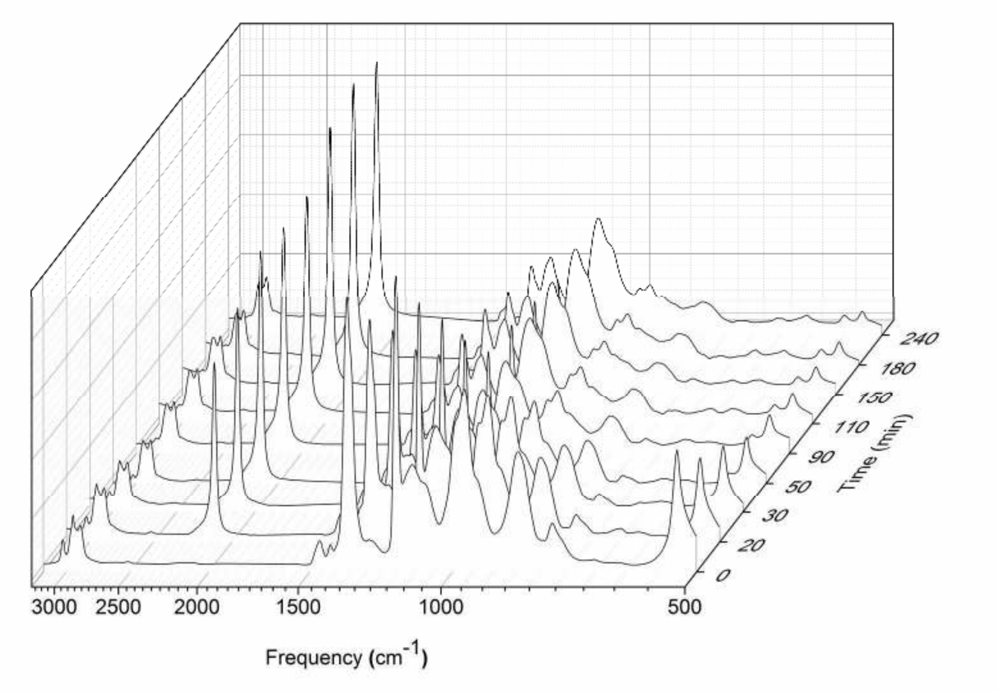

Figure 5 – FT-IR spectra of PGM during azidation at 85 °C.
199x139mm (300 x 300 DPI)

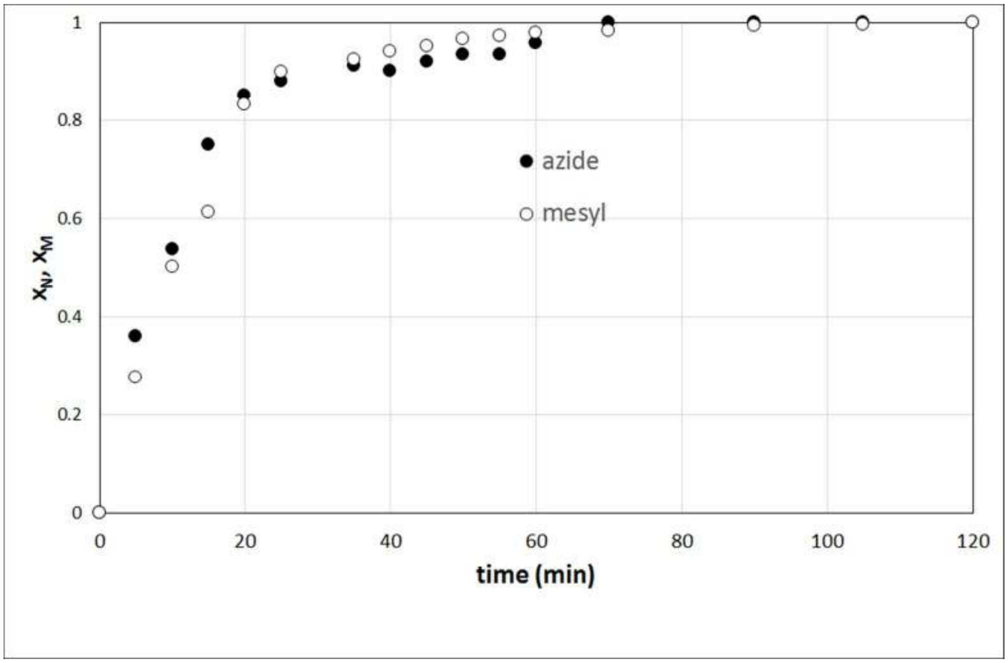

Figure 6 - Comparison between xN and xM for PGM azidation at 85 °C.

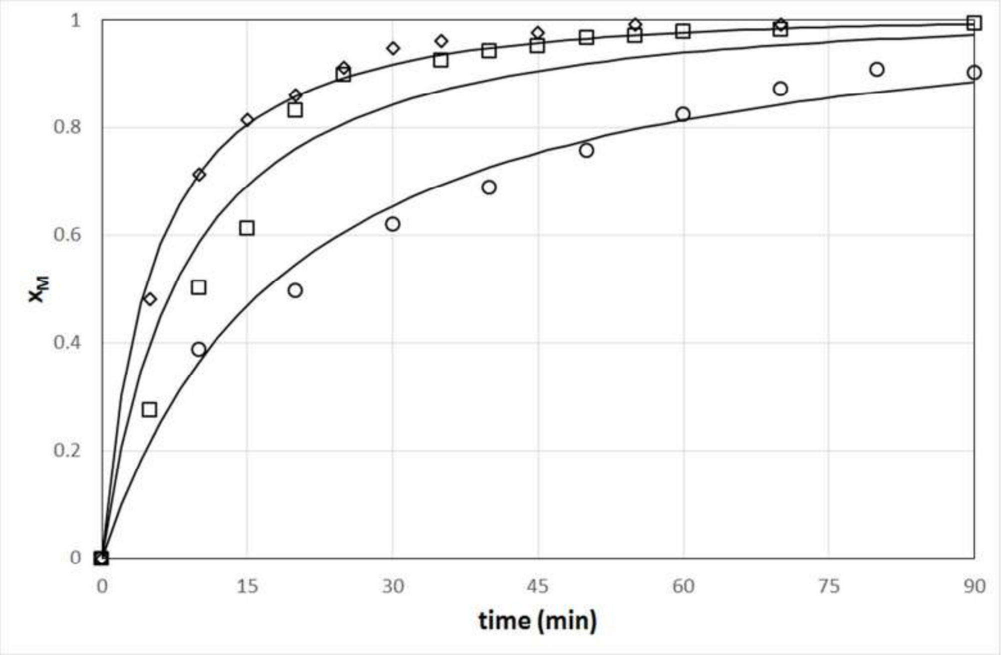

Figure 7 - xT for PTMMO azidation at different temperatures: ○ 85 °C; □ 105 °C; ◇ 125 °C. Solid lines represent the curves calculated with eq. (8).

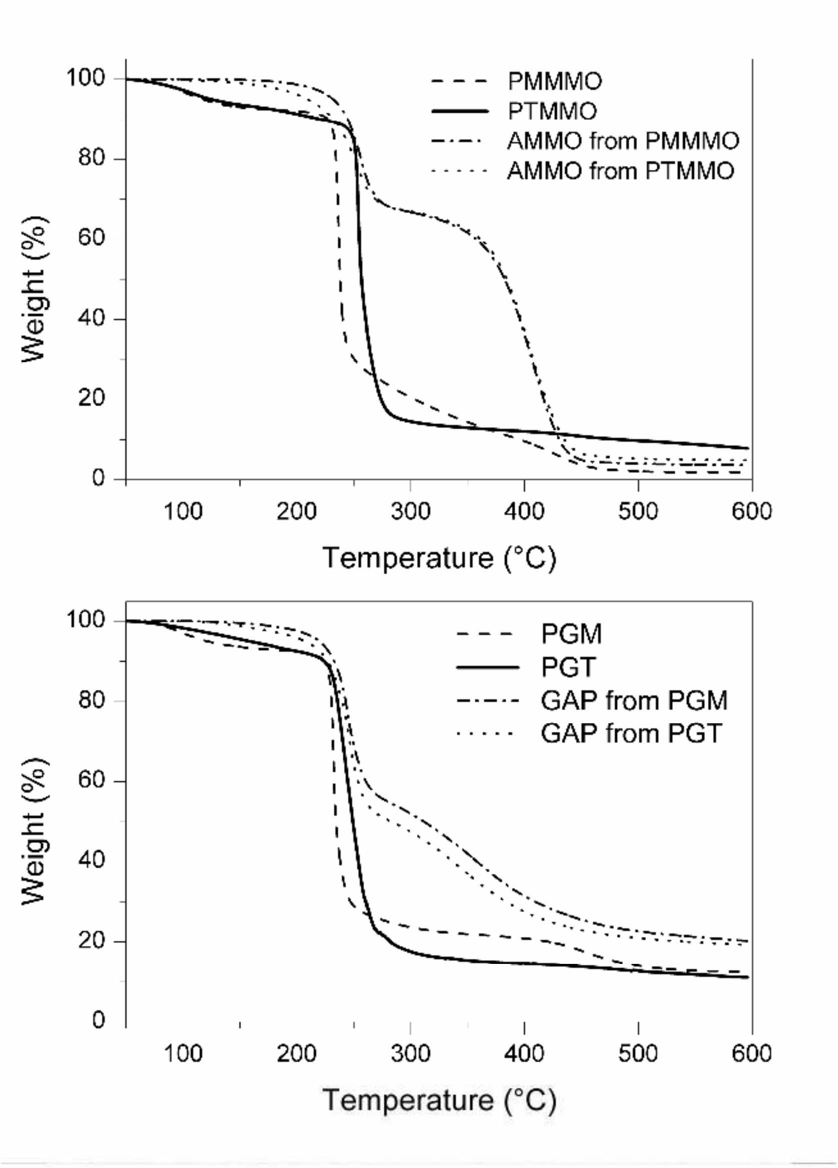

Figure 8 – TGA curves of the synthesized polymers.
426x612mm (300 x 300 DPI)