Journal of Aerospace Technology and Management

ISSN: 1948-9648

secretary@jatm.com.br

Instituto de Aeronáutica e Espaço

Brasil

Kawamoto, Aparecida M.; Oliveira, José Irineu S.; de Cássia L. Dutra, Rita; Rezende, Luis Claudio; Keicher, Thomas; Krause, Horst

Synthesis and characterization of energetic thermoplastic elastomers for propellant formulations

Journal of Aerospace Technology and Management, vol. 1, núm. 1, enero-junio, 2009, pp. 35-42

Instituto de Aeronáutica e Espaço

São Paulo, Brasil

Aparecida M. Kawamoto*
Institute of Aeronautics and Space
São José dos Campos - Brazil
cidak@iae.cta.br

José Irineu S.Oliveira
Institute of Aeronautics and Space
São José dos Campos - Brazil
jirineu@iae.cta.br

Rita de Cássia L. Dutra
Institute of Aeronautics and Space
São José dos Campos - Brazil
chefia.aqi@iae.cta.br

Luis Claudio Rezende
Institute of Aeronautics and Space
São José dos Campos - Brazil
lcrezende@iae.cta.br

Thomas Keicher
Institut Chemische Technologie
Pfinztal - Germany
thomas.keicher@ict.fhg.de

Horst Krause
Institut Chemische Technologie
Pfinztal - Germany
kr@ict.fhg.de

* author for correspondence

Synthesis and characterization of energetic thermoplastic elastomers for propellant formulations

Abstract: *Synthesis and characterization of energetic ABA-type thermoplastic elastomers for propellant formulations has been carried out. Following the working plan elaborated, the synthesis and characterization of Poly 3-bromomethyl-3-methyl oxetane (PolyBrMMO), Poly 3- azidomethyl-3-methyl oxetane (PolyAMMO), Poly 3,3-bis-azidomethyl oxetane (PolyBAMO) and Copolymer PolyBAMO/AMMO (by TDI end capping) has been successfully performed. The thermoplastic elastomers (TPEs) were synthesized using the chain elongation process PolyAMMO, GAP and PolyBAMO by diisocyanates. In this method 2.4-toluene diisocyanate (TDI) is used to link block A (hard and mono-functional)) to B (soft and di-functional). For the hard A-block we used PolyBAMO and for the soft B-block we used PolyAMMO or GAP.This is a joint project set up, some years ago, between the Chemistry Division of the Institute of Aeronautics and Space (IAE) - subordinated to the Brazilian Ministry of Defense - and the Fraunhofer Institut Chemische Technologie (ICT), in Germany. The products were characterized by different techniques as IR- and (^{1}H,^{13}C)NMR spectroscopies, elemental and thermal analyses. New methodologies based on FT-IR analysis have been developed as an alternative for the determination of the molecular weight and CHNO content of the energetic polymers.*

Key words: *Energetic thermoplastic elastomers, PolyAMMO, PolyBAMO, Copolymer PolyBAMO/AMMO, Propellants.*

LIST OF SYMBOLS

AMMO	3-Azidomethyl-3-methyl oxetane
BA	Benzyl Alcohol
BAMO	3,3-Bis-azidomethyl oxetane
BDO	Butanediol
BrMMO	3-Bromomethyl-3-methyl oxetane
CHN	Elemental analysis
CsI	Cesium Iodide
DSC	Differential scanning calorimetry
E-TPE	Energetic thermoplastic elastomer
FT-IR	Fourier transform infrared spectroscopy
GAP	Glycidyl azido polymer
GPC	Gel permeation chromatography
IR	Infrared spectroscopy
KBr	Potassium bromide
M_w	Molecular weight (average weight)
M_n	Molecular weight (average number)
NMR	Nuclear magnetic resonance
N_3	Azide
PolyAMMO	Polymer of 3-azidomethyl-3-methyl oxetane
PolyBAMO	Polymer of 3,3-bis-azidomethyl oxetane
PolyBBrMO	Polymer of 3- bromomethyl-3-methyl oxetane
ppm	Parts per million
TDI	Toluene di-isocyanate
THF	Tetrahydrofuran
δ	Chemical shift

Received: 14/04/09
Accepted: 07/05/09

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 an elastomeric binder matrix. In this binder matrix the energetic solid filler composition is embedded and immobilized to achieve defined combustion characteristics and also to keep the propellant in a 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 the combustion of metal powders. Therefore, the use of binder materials, which are energetic itself, is an 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 caused from the combustion products of the solid fillers (metal powders, halogenated oxidizers). Another benefit in

the reduced filler content might be sensitivity reduction.

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 adding the curative, which sets some restriction for the industrial processing. Additionally, the once cured binder material cannot be reused or recycled because the curing reaction is irreversible (Archibald et al., 1997, Wardle et al., 1996).

Energetic thermoplastic elastomers (E-TPE) are one possibility to overcome all these disadvantages. Thermoplastic elastomers are block copolymers that exhibit rubber-like elasticity without requiring chemical cross-linking, which present 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 behavior, whereas the soft segment (rubbery at room temperature) gives the elastomeric behavior. The thermoplastic behavior results from the formation of rigid domains by chain association due to reversible interaction such as dipole-dipole interactions, hydrogen bonding, etc. The soft segments are incompatible with the hard segments, hence leading to a microphase separation. Therefore, a thermoplastic elastomer behaves like a rubber because it is cross-linked in the same manner as a conventional elastomer, but with reversible physical cross-links instead of chemical ones. For processing, the E-TPE can be heated above the transition temperature to melt it or it can be dissolved in a solvent, then mixed with other components of a formulation, and processed. Cooling the E-TPE or evaporating the solvent allows the broken physical cross-links to re-form and the elastomeric properties are recovered. Depending on the processing technique used to prepare a Gun or Rocket Propellant, or a High Explosive formulation, steps such as cooling or evaporating the solvent can allow the E-TPE physical bonds to re-form and give the final material. This also means that a formulation containing E-TPE, when obsolete, could be heated above the transition temperature or dissolved, allowing for the recovery of the ingredients that could be separated. Therefore, the use of E-TPE will lead to recyclable energetic materials (Sanderson and Edwards, 2000, Manser and Miller, 1993, Manser et al., 1996, Saegusa et al., 1970).

Energetic Thermoplastic Elastomers (E-TPEs), have exhibited their wide value application in the research development of novel binders for Solid Rocket Propellants. They are considered as crosslinked polymers that provide a matrix which binds the explosive ingredients together with particulate particle oxidizer, burning rate catalyst, plasticizers and so forth, resulting in a tough elastomeric three-dimensional network structure capable of absorbing and dissipating energy from hazardous stimuli. They represent the next generation of energetic binders. Since they mimic the elastomeric behavior of conventional binders, they can lead to insensitive munitions and increase the energy of the formulations. They can also be recuperated, which leads to recyclable munitions (Murali et al., 2004).

Another 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. They are reusable and are reprocessed a number of times, and can also be solvated by organic solvents, so surplus material can be recuperated, cleaned and used again

As for the use in Solid Rocket Propellant the E-TPE's and their synthesis should present the following properties (Provatas, 2000).

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

However, many non energetic commercially available Thermoplastic Elastomers fail to meet the aforementioned important requirements expected in propellant formulations, particularly that of being processible below approximately 120°C. It has been desirable that a Thermoplastic Elastomer polymer for use as binder in a high energy system should have a melting point temperature of between 60°C to 120°C. The 60°C is related to the fact that the propellant composition may be subject to somewhat elevated temperatures during storage and use, and it is undesirable that significant softening of the propellant composition occurs. The 120°C is determined by the instability of many components ordinarily used in propellant compositions, particularly oxidizers, explosives and energetic plasticizers (Hsiue et al., 1994).

An attractive approach to high energy and low sensitivity propellants involves the use of energetic oxetane prepolymers (Wardle, 1989). These binders act as energy partitioning agents by allowing an energetic formulation to maintain a constant energy level at lower solid percentages. Partitioning a portion of the formulation energy into the binder phase is predicted to result in significant improvements in the formulation. The lower solid is

predicted to result in improved processing mechanical properties, and reduced friability (Wardle, 1989).

Copolymers are generally advantageous relative to homopolymers because of the presence of an additional oxetane or other monomer unit(s), even in small amounts, which substantially reduces chain regularity. Homopolymers with a high degree of chain regularity exhibit substantial chain folding, resulting in a compact structure which tends to be crystalline or highly viscous (Sanderson and Edwards, 2000).

A high energy binder based on block copolymers of ABA, AB, or (AB)n structure of cylic ethers and oxetanes and derivatives, will be examined to determine whether the postulated improvements for the binder will be possible in solid rocket propellants. Attention has been particularly focused on polymers that contain the energetic azido group.

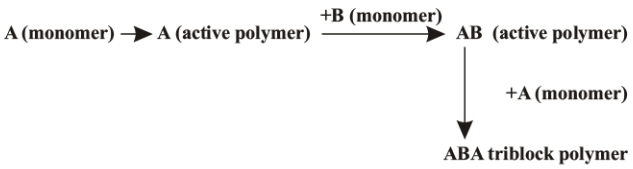
The monomer or combination of monomers of the A block are selected to prove a crystalline structure at usual ambient temperature, whereas the monomer or combination of monomer of the B block are selected to ensure an amorphous structure at usual ambient temperature.

The A and B blocks of such polymers are mutually miscible in a polymer melt. The melt viscosities of such a TPE decrease rapidly as the temperature is raised above the melting point of the crystalline A blocks, contributing to its processibility.

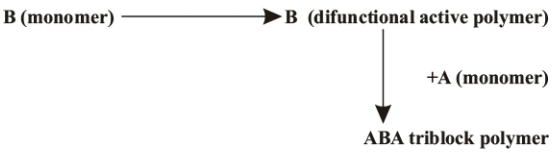
Furthermore, a thermoplastic elastomer based on crystalline domains exhibits advantageous solvent-resistance and minimal setup shrinkage. Such a TPE can be formulated to have a melting temperature which falls within a desirable 60°C to 120°C range.

Two methods can be used to prepare these TPEs. One method to get the ABA triblock or (AB)n polymers may be to join them together through a block linkage technique in which a linking moiety, such as isocyanate, is reacted with both ends of the middle (B) block and the end (A) blocks are subsequently reacted with the linking group (x). Generally the reaction is:

The other method is when the ABA copolymer is formed by systematic monomer addition. For example, the A monomer may be reacted with an initiating adduct to form an A block by cationic polymerization and the reaction is allowed to proceed until monomer A is substantially exhausted. Then, the monomers of block B are added and polymerization proceeds from the active end of block A. When the monomers of block B are substantially exhausted, additional monomers of block A are added, and polymerization proceeds for the active end of block B. The reaction is represented by the equation:



Alternatively, a difunctional initiator could be used to initiate the polymerization of the B block. When the A block is added, the polymerization would proceed from both active ends of the B block. The reaction is represented by the equation:



By selecting the appropriate block functionality or by repetition of steps, these methods are also proposed as suitable for producing (AB)n polymers.

Both of these methods to produce TPEs have been proven to be satisfactory. Joining blocks A and B is found to be much better, as described by Wardle et al. (1996).

According to Wardle (1989), a three stage method is provided for forming thermoplastics that have polyether crystalline A blocks and B blocks that are individually synthesized. The A blocks and B blocks are each separately end-capped with a diisocyanate, in which one isocyanate is substantially more reactive with active groups on the blocks than is the other isocyanate group.

Finally, the end-capped blocks are mixed and reacted with a difunctional linking chemical, in which each function on the linking chemical is isocyanate reactive and sufficiently unhindered to react with a free isocyanate group in a capped block. However, to link difunctional A and B bocks and form exclusively ABA elastomers by controlling the blocks' stoichiometry is statistically unrealistic.

Therefore the same author in another patent (Wardle et al., 1996) developed a novel one pot method for the synthesis of the copolymer. After individual synthesis of monofunctional A blocks and di functional B blocks, the monofunctional crystalline A block is end-capped with a difunctional isocyanate that has one of the isocyanate groups more reactive than the other one. Therefore the more reactive isocyanate group reacts to the functional group of A block, leaving the less reactive isocyanate group free and unreacted. Thereafter, adding the difunctional B blocks to the end-capped A blocks at approximately the stoichiometric ratios that they are intended to be present in the Thermoplastic Elastomer, the free and unreacted

isocyanate group on the end-capped monofunctional A block reacts with a functional group of the B blocks to produce ABA Thermoplastic Elastomers.

For the synthesis of TPEs, first it is necessary to synthesize the polymer that will serve as the A block, which is crystalline in nature and with a relatively elevated melting point, i.e., between about 60°C and 120°C, preferably near 80°C and then the synthesis of a polymer, which is to serve as the B block, which is amorphous in structure, with a glass transition temperature (T_g) below about -20°C and preferably below -40°C.

The property of the block polymer depends on the molecular weights of the individual blocks and the total molecular weights. Typically the A blocks have molecular weights ranging from about 3000 to about 12500, whereas the B blocks have molecular weights ranging from about 5000 to about 50.000. Preferably, the A blocks are shorter than B blocks, the total molecular weight of the A blocks typically range from about ½ to 1 times the molecular weight of the B blocks in an ABA triblock copolymer.

The decomposition and combustion products of polyBAMO contain relatively high concentrations of fuel fragments such as C(s), H_2, and CO. Thus, the addition of oxidizers in combination with azide polymers enables the propellant a better performance, such as high specific impulse.

In 2004, a joint project was set up between the Chemistry Division of the Institute of Aeronautics and Space (IAE) - subordinated to the Brazilian Ministry of Defense - and the Fraunhofer Institut Chemische Technologie (ICT), in Germany, with the goal to synthesize some energetic binders that could have several applications, including their use in propellants. Therefore the compounds Poly 3-bromomethyl-3-methyl oxetane (PolyBrMMO), Poly 3-azidomethyl-3-methyl oxetane (PolyAMMO), Poly 3,3-bis-azidomethyl oxetane (PolyBAMO) and Copolymer PolyBAMO/AMMO (by TDI end capping) have been synthesized and characterized by different techniques. The appropriate characterization of these energetic polymers is the key point for selecting the best thermoplastic elastomer for propellant applications and also to verify the effects of its structure on the propellant properties, comparable to ordinary binders.

EXPERIMENTAL

^{1}H-NMR, ^{13}C-NMR analysis were conducted using a 300 MHz Bruker MSL-300 spectrometer. The proton and carbon chemical shifts are recorded in ppm and calibrated on the solvents as internal standard. Infrared spectroscopy was recorded by a Spectrum 2000 PERKINELMER FT-IR spectrometer, in the spectral region of 6500 to 250 cm^{-1}, gain 1, resolution of 4 cm^{-1} and 40 scans. Liquid samples were analyzed as liquid film in CsI cells separated in 0.025 cm of space. Solid samples were analyzed in KBr pellets (0.8:400mg). GPC (Gel Permeation Chromatography 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. THF was used as the mobile phase. It was calibrated with a set of well characterized (i.e., M_n, M_w are well known) polystyrene and polypropylene standards (Narrow Standards), and thus the number average molecular weight (M_n) and weight average molecular weight (M_w) are reported relative to polystyrene and polypropylene. The solvents were purchased from Aldrich, Fluka or Merck according to the purity required, price and availability. Butanediol was purified by distillation prior to use.

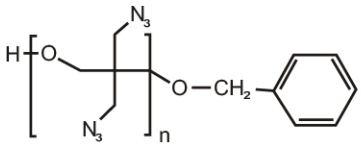
Synthesis of polymers and copolymers was performed according to the literature (Kawamoto et al., 2005, Kawamoto et al., 2006) and was fully characterized as it has also been the object of other studies at our laboratory (Oliveira et al., 2006, Oliveira et al., 2007).

The synthesis of polyAMMO, polyBAMO and of the copolymer polyBAMO/AMMO were performed in accordance to a previous paper (Kawamoto et al., 2006). The ABA-type copolymer was synthesized by using 2,4-toluene diisocyanate (TDI) as chain extender, with polyAMMO as soft block and polyBAMO as hard block.

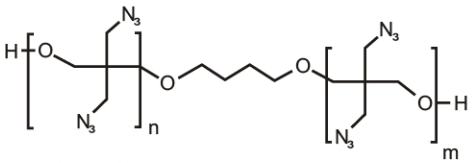
The molecular weight (MW) of PolyAmmo, PolyBamo and their copolymer PolyAmmo/Bamo was performed by means of infrared spectroscopy (IR). This method was developed at the Chemistry Division (IAE/Brazil) as an alternative for the determination of the number average molecular weight of polyAMMO, polyBAMO and their copolymer polyAMMO/BAMO. The measurement is based on the azide absorption (FT-IR) band at 2100 cm^{-1}, having as reference the MW determined by NMR analysis of a certain azide polymer. However, as the NMR technique did not work for the copolymers, due to the overlapping of the bands of both polymer segments, the MW of the copolymers was measured by GPC. The band intensity plotted versus the inverse of MW provides a fitting of type $Y = a + bX$, enabling a simple way of measuring the MW of these kind of polymers.

RESULTS AND DISCUSSION

PolyBAMO (Fig. 1) and PolyAMMO (Fig. 1) were synthesized by cationic polymerization and the copolymers PolyAMMO/BAMO (Fig. 1) were synthesized by TDI endcapping. AMMO was polymerized using butane diol (BDO) as initiator, and BAMO with benzyl alcohol (BA). The molecular weights of the products were measured by GPC (standard Poly-Styrene) and by ^{1}H-NMR spectroscopy. At the NMR method the molecular weights were calculated from the correlation between integrals of BDO protons and -CH_2N_3-, -CH2O- or CH_3-groups.



PolyAMMO



Poly BAMO

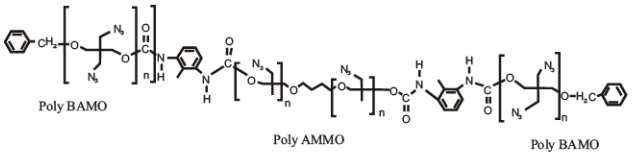


Figure 1: Structures of PolyAMMO, PolyBAMO and Poly AMMO/BAMO.

PolyBAMO is a yellow solid with the melting point between 65 to 75°C. The molecular weight calculated from NMR spectra was based on the integrals of BA-ring protons and BAMO-azidomethyl protons. ^{1}H-NMR of polyBAMO exhibited two major peaks close to one another, corresponding to the methylene protons of the azidomethyl group (δ = 3.33ppm) and to the methylene groups of the backbone (δ= 3.32 ppm). The aromatic protons of benzyl alcohol give a multiplett at 7.26-7.37 ppm.

The infrared spectrum of polyBAMO shows the opening of the oxetane ring with the formation of the C-O bond, leading to the disappearance of the band related to the oxetane ring at 980 cm^{-1} (ring stretching) and the appearance of new bands related to the formation of C-O (1000-1100 cm^{-1}) and OH (3400 cm^{-1}), the latter at the end of the polymeric chain. The dominating band is the azide group at around 2110 cm^{-1}.

The DSC analysis of all poly BAMO showed the endothermic melting peaks (Tab. 1) and exothermic decomposition peaks with onset temperatures at around 246C, which is typical for organic azide compounds.

PolyAMMO is a highly viscous to waxy material depending on the molecular weight. Because polyAMMO is the soft block in the E-TPEs and is located mostly at the centers of the thermoplastic polymer sequences, it was synthesized only as di-functional. This difunctionality allows the later chain elongation on both ends of the molecule. The molecular weight is mainly influenced by the monomer/initiator ratio. The lower the initiator concentration, the lower the number of growing chains that consumes the added monomer, leading to a higher molecular weight. ^{1}H-NMR of polyAMMO exhibited three major peaks. At = 3.32 ppm the singlet related to the methylene protons of azidomethyl groups, the splitting at 3.24 ppm refers to CH_2O protons of the backbone, and the singlet at 0.98 ppm to the protons of the methyl groups. The small multiplet peak at 1.68-1.69 ppm belongs to the protons of butanediol. The integrals of methylene protons from butane diol and the methyl groups were used for calculating the molecular weights.

The FT-IR analysis of polyAMMO showed that polymerization of the corresponding monomer leads to a broadening of most of the vibration modes. The C-O-C stretch of the oxetane ring at 980 cm^{-1} is replaced by an intense absorption at 1111 cm^{-1} which refers to C-O-C stretch of the polymer. The OH stretch (broad band around 3300 cm^{-1}) is also present, which is attributed to 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 spectrum.

The DSC analysis of polyAMMO shows only an exothermic peak from decomposition of the azide groups at the expected onset temperature around 256C.

The ^{1}H-NMR analysis of the copolymer showed the main peaks of the corresponding polymers (polyAMMO and polyBAMO) and also from TDI (small peaks). From polyAMMO peaks were observed 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 athe zidomethyl groups. From polyBAMO at 3.30-3.32 a broad singlet can be observed that corresponds to 4H of -CH_2O- and 4H of -CH_2N_3. The small multiplet peak at 1.55-162 ppm belongs to the protons of butanediol and at 2.13 and 2.19 singlets of the 3H of -CH_3 can be observed from the TDI isomers.

The FT-IR spectra of polyAMMO/BAMO showed that the addition reaction was quantitative because of the 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 the urethane groups.

The DSC analysis of the copolymer shows an endothermic melting peak at 74 °C and an exothermic peak at 248 C. For the starting polymers polyBAMO and polyAMMO, the exothermic peaks are at 246 C and 256 C, respectively. It is seen that the decomposition peak temperature of the copolymer is very close to that of polyBAMO, indicating that AMMO units do not significantly affect the thermal decomposition of the copolymer. Therefore, the thermochemical characteristics of the copolymer polyBAMO/AMMO are similar to polyBAMO.

Table 1 shows the molecular weight values of polyAMMO, polyBAMO and of copolymer polyAMMO/BAMO, measured by NMR and GPC, together with the absorbance of the azide group at 2100 cm^{-1}. This refers to the N_3 group that was measured to use the measuring method of the molecular weight (Mw) of polyAMMO, polyBAMO and their copolymer polyAMMO/BAMO by means of infrared spectroscopy (IR).

Table 1: Properties of polymers and copolymers.

Polymers/Copolymers	Mw by NMR	Mw by GPC	IR absorbance (azide group)
AK 80 Poly AMMO	9779	-	2.626
AK 96 Poly AMMO	6350	-	2.773
AK 113 Poly AMMO	15875	-	2.354
AK 97 Poly BAMO	4200	-	2.693
AK 81 Poly BAMO	4368	-	2.623
AK 110 Poly BAMO	9744	-	2.260
AK 116 Poly BAMO	4872	-	3.116
AK 133 Poly BAMO	1680	-	5.927
AK 98 Poly AMMO/BAMO	-	5358	2.604
AK 109 Poly AMMO/BAMO	-	2332	2.513
AK 120 Poly AMMO/BAMO	-	3076	2.405

The molecular weight of the aforementioned polyBAMO was calculated by correlating the NMR spectra integrals of benzyl alcohol (BA)-ring protons and BAMO-azidomethyl protons. The molecular weight of polyAMMO was calculated by correlating the NMR spectra integrals of butanediol (BDO) protons and $-CH_2N_3-$, $-CH_2O-$ or CH_3- groups. The Mw of the copolymer was measured by GPC.

With these results it was possible to build four curves that relate the intensity of the IR band of the azide group with the inverse of molecular weight of PolyAMMO (Fig. 2), Poly BAMO (Fig. 3), PolyAMMO/BAMO (Fig. 4) and all of them together in only one curve (Fig. 5).

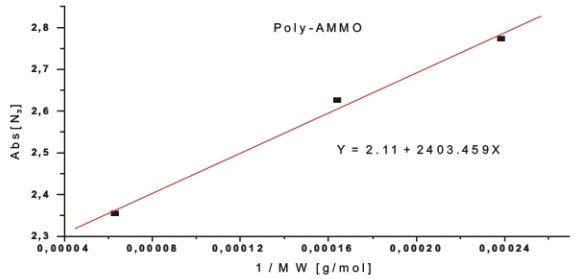


Figure 2: Intensity of azide band vs. inverse of molecular weight for PolyAMMO.

The relationship between the azide band intensity and the inverse of molecular weight for PolyAMMO shown in Fig. 2 enabled to observe a linear tendency relationship with a coefficient of 0.997, which can be represented by the following equation:

$$Y = 2.11 + 2403.459\ X$$

Where:
Y = medium value of N_3 absorbance (A_{2100})
X = inverse of molecular weight for PolyAMMO

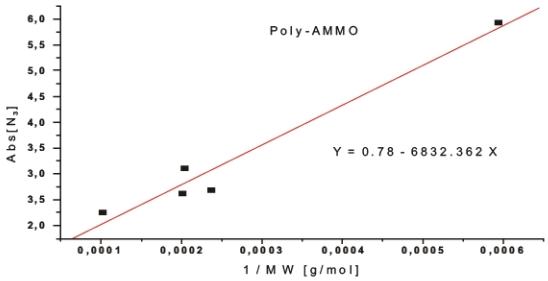


Figure 3: Intensity of azide band vs. inverse of molecular weight for PolyBAMO.

The relationship between the azide band intensity and the inverse of molecular weight for PolyBAMO shown in Fig. 3 enabled to observe a linear relation with a coefficient of 0.981. A good linear relationship was obtained (R= 0.981) and it is represented by the following equation:

$$Y = 0.78 - 6832.362\ X$$

Where:
Y = medium value of N_3 absorbance (A_{2100})
X = inverse of molecular weight for PolyBAMO

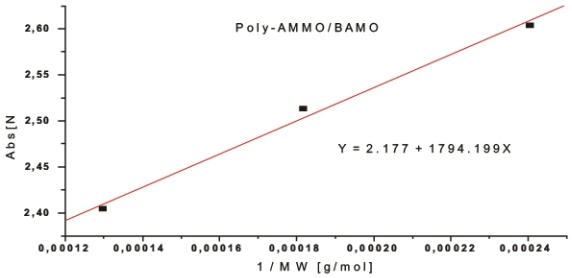


Figure 4: Intensity of azide band vs. inverse of molecular weight for PolyAMMO/BAMO.

The relationship between the azide band intensity and the inverse of molecular weight for PolyAMMO/BAMO shown in Fig. 4 enabled to observe a linear tendency relationship with a coefficient of 0.996 which can be

represented by the following equation:

$$Y = 2.177 + 1794.199\,X$$

Where:
Y = medium value of N3 absorbance (A2100)
X= inverse of molecular weight for PolyAMMO/BAMO

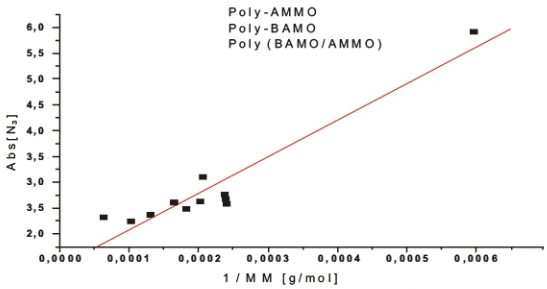


Figure 5: Intensity of azide band vs. inverse of molecular weight for PolAMMO, PolyBAMO and PolyAMMO/BAMO.

The relationship between the azide band intensity and the inverse of molecular weight for PolyAMMO, PolyBAMO and PolyAMMO/BAMO shown in Fig. 5 also enabled to observe a linear relationship with a coefficient of 0.950. A good linear relation was obtained (R= 0.950) and it is represented by the following equation:

$$Y = 1.388 + 7041.963\,X$$

Where:
Y = medium value of N3 absorbance (A2100)
X= inverse of molecular weight for PolyAMMO/BAMO
The linear relationship in this case is not very precise as it is for single compounds, given that the points in the curves are not precisely distributed and also a curve could fit to join the points. Therefore the method for predicting a molecular weight from the intensity of azide band of the polymers or copolymers is better estimated using curves for only a specific compound.

CONCLUSION

PolyAMMO and polyBAMO has been successfully synthesized by cationic polymerization, and the thermoplastic elastomers (TPEs) were synthesized using the chain elongation method of PolyAMMO, GAP and PolyBAMO by diisocyanates. 2.4-Toluene diisocyanate (TDI) was used to link block A (hard and mono-functional)) to B (soft and di-functional). For the hard A-block we used PolyBAMO and for soft B-block we used PolyAMMO or GAP. This copolymer will be included in future research program to be tested in formulations of solid rocket propellants.

The molecular weight measurements by GPC and NMR and the IR absorbance of N_3 band intensity of PolyAMMO, Poly BAMO and Poly AMMO/BAMO have been measured and the curves of the N_3 band intensity were plotted vs. the inverse of MW, hence providing a type Y= a + bX curve, which will allow a simple analysis of the same type of MW polymer/copolymer.

The curves suggest that the methodology developed in our laboratory and described herein are very useful as a practical and fast alternative to determine a molecular weight of a known polymer that needs to be synthesized routinely and also for scaling up purposes.

REFERENCES

Archibald, T. G., Carlson, R. P., Malik, A. A., Manser, G. E., 1997, "Preparation and Polymerization of Initiators Containing Multiple Oxetane Rings: New Routes for Star Polymers", US Patent 5,663,289.

Hsiue G. H., Liu Y. L. and Chiu Y. S., 1994, "Triblock Copolymers Based on Cyclic Ethers: Preparation and Properties of Tetrahydrofuran and 3,3-bis (Azidomethyl) Oxetanetriblock Copolymers", Journal of Polymer Science, Part A: Polymer Chemistry, Vol. 32, pp. 2155-2159.

Kawamoto A. M. et al., 2005, "Synthesis and Characterization of Energetic Oxetane-Oxirane-Polymers for use in Thermoplastic Elastomer Binder Systems", Proceedings of the 36th International Annual Conference &32th International Pyrotechnics Seminar of ICT, Karlshure, Germany.

Kawamoto A. M., et al., 2006, "Synthesis and Characterization of Energetic ABA-Type Thermoplastic Elastomers for Propellants Formulations", Proceedings of the 37th International Annual Conference of ICT, Karlshure, Germany.

Manser, G. E., Miller, R. S., 1993, "Thermoplastic Elastomers Having Alternate Crystalline Structure For Us as High Energy Binders", US Patent 5,210,153.

Manser, G. E., Malik, A. A., Archibald, T. G., 1996, "3-Azídation-3-Nitratomethyloxetane", US Patent 5,489.

Murali M. Y., Padmanabha R. M., and Mohana R. K., 2004, "Synthesis, Spectral and DSC Analysis of Glycidyl Azide Polymers Containing Different Initiating Diol Unit", Journal of Applied Polymer Science, Vol. 93, pp. 2157-2163.

Oliveira, J. I. S., et al., 2006, "Characterization MIR/NIR/FIR of Energetic Binders used in Solid Propellants", Propellants, Explosives, Pyrotechnics, Vol. 32, pp. 395.

Oliveira, J. I. S., et al., 2007, "Determination of CHN Content in Energetic Binder by MIR Analysis", Polímeros: Ciência e Tecnologia, Vol. 17, pp. 46.

Provatas, A., "Energetic Polymers and Plasticizers for Explosive Formulations-A Review of Recent Advances", Defense Science & Technologie Organization, DSTO-TR-0966.

Saegusa T., Matsumoto S., and Hashimoto Y., 1970, "Cationic Block Copolymerization of Tetrahydrofuran with 3,3-Bis(Chloromethyl) Oxacyclobutane", Macromolecules, Vol. 3, pp. 377.

Sanderson, A. J., Edwards, W., 2000, "Method for the Synthesis of Energetic Thermoplastic Elastomers in Inon-Halogenated Solvents", WO 00/34353, (PCT)/US99/24013".

"Synthesis of energetic thermoplastic elastomers containing oligomeric urethane linkages", 2000, WO 00/34350 A3 (PCT).

Wardle, R. B., Edwards, W. W., Hinshaw, J. C., 1996, "Method of Producing Thermoplastic Elastomers Having Alternate Crystalline Structure Such as Polyoxetane ABA or Star Block Copolymers by a Block Linking Process", US Patent 5,516,854.

Wardle, R. B., 1989, "Method of Producing Thermoplastic Elastomers Having Alternate Crystalline Structure for Use as Binders in High-Energy Compositions", US Patent 4.