# REACTION BETWEEN AZIDE MOLECULE WITH HYDROXYL TERMINATED POLYBUTADIENE

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## Abstract

*In previous work the compatibility between azide molecules and HTPB was discussed in terms of Gel Permeation Chromatography (GPC) and continuously recording Vacuum Stability Test (VST) results. Thus, the aim of this work is to evaluate the reaction between hydroxyl terminated polybutadiene (HTPB) and the energetic plasticizer ethylene glycol bis-(azidoacetate) (EGBAA). The mixture of HTPB with EGBAA was monitored by size exclusion chromatography (SEC) and the final product characterized by Attenuated total reflected Fourier transformed infrared spectroscopy (ATR/FT-IR). Strong increase in relative molar mass and the decreasing concentration of EGBAA in the eluted volume of the mixture showed that HTPB and EGBAA reacted to form branches in HTPB backbone. ATR/FT-IR spectrum indicates the formation of new Carbon-Nitrogen bonds assuming from the reaction between azide groups and double bonds of the HTPB.*

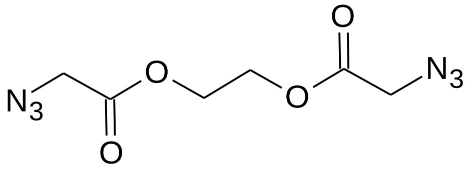
**Keywords**: *HTPB modification; Azido molecule; SEC/GP0043; ATR/FT-IR; Binder.*

## 1 Introduction

HTPB is a non-polar oligomer consisting of aliphatic chains containing double bonds in each repeat unit, whereby the configurations of these double bonds along the chains are amixture of cis, trans and 1,2-vinyl. When cured with isocyanates, it gives a polyurethane network with a good combination of stiffness, elongation and low glass-rubber transition temperature [1-5]. In general, HTPB-based polyurethanes fit the requirements to be demanded on binder of composite solid propellants. The formulation versatility is very useful for the intended materials and rocket scientists can design suitable propellant grains for space and tactical applications. However, despite all the advantages, the inert characteristic of HTPB is a drawback for the ballistic performance [6]. The insertion of highly energetic groups in the elastomer bulk is desirable, i.e. molecules containing chemical groups with high enthalpy of formation such as azides ($N_3$) and nitrate esters ($-O-NO_2$). These energetic groups can be inserted by reactions or grafted on the elastomer chains. Alternatively, those substances could be added to the HTPB elastomer binder formulation as additive substances, as energetic liquid fillers or as plasticizers [6-11]. But again the non-polarity of HTPB arises as a threshold for the compatibility with polar energetic molecules. Insertion of highly energetic chemical groups ($-N_3$ and $-O-NO_2$) in HTPB chains degrades mechanical properties in one way or another, and also can increase its sensitivity [12-24]. Nonetheless many authors have presented polymers and elastomer macromolecules based on HTPB containing azide groups, grafted in the chain or as additives, but with only some [23,24] describing the reaction between azide and the double bonds of the polybutadiene.

Therefore, this paper aims to present a chemical modification of HTPB by direct reaction between its double bonds and the azide group of an organic molecule. The azide containing energetic molecule investigated in this work is the organic azide ethylene glycol bis-(azidoacetate) (EGBAA; 228.17 g/mol) shown in Table 1.

**Table 1** – Organic azide used in this work: ethylene glycol bis-(azidoacetate) (EGBAA). Data of $\Delta H_0^f$ from ICT Thermochemical database.

| Name | Molecule | Molar mass | Enthalpy of formation $\Delta H_0^f$ |
|---|---|---|---|
| *Ethylene glycol bis-(azidoacetate)* (EGBAA) |  | 228.17 g/mol | -167 kJ/mol |

## 2 Experimental

### 2.1 Formulations and sample preparation

The mixture of polyol HTPB with EGBAA consisted of mass ratio 6:1. Liquid hydroxyl terminated polybutadiene (HTPB) of type R45 HTLO, from Sartomer, Polybd, Oakland, USA, handed by Fraunhofer ICT; was dried before use in a roto-evaporator under high vacuum and 60°C temperature. The antioxidant Vulkanox$^{TM}$ BKF was used to protect the polyol against oxidation effects. Ethylene glycol bis-(azidoacetate) – EGBAA, was synthesized following the literature [25].

Mixture were performed at Fraunhofer ICT in a planetary centrifugal vacuum mixer (from THINKY CORPORATION, Tokyo, Japan). Operational conditions were 1600 rpm rotation speed, 30 kPa vacuum during few minutes of mixing time and temperature of the mix was kept below 40°C. The batch of HTPB with EGBAA (6:1 mass ratio) was poured in vials with closed (but not gas tied) lid under inert (Ar) or air atmosphere, left reacting it in the oven cabinet at 40°C and 60°C and analyzed as a function of reaction time. Changes in molar mass distribution of HTPB were analyzed by size exclusion chromatography (SEC). As reference, pristine HTPB was also analyzed at same time intervals. The precursors, the reaction bulk freshly after mixing as well as the final product were characterized by Attenuated total reflected Fourier transformed infrared spectroscopy (ATR/FT-IR).

### 2.2 Characterization techniques

***Size exclusion chromatography (SEC)***

The SEC apparatus comprises units from the Agilent Series 1100: isocratic pump, injection block, auto-sampler, refractive index detector 1100-RID and column oven. Solvent degasser from company PSS, Mainz, Germany. The column set was compiled with SDV columns from company PSS, Mainz, Germany. SDV means modified styrene-divinylbenzene copolymer network. A pre-column for protecting the main column set was used: PSS precolumn SDV 5µ, in steel cylinder 8 mm in diameter and 50 mm long. The separation columns with particle size 5µm were in pore size 50 Å, 100 Å, 1000 Å and 100 000 Å. The dimensions of the separation columns were 8 mm in diameter and 300 mm long. Not stabilized tetrahydrofuran (THF) was used as solvent and eluent containing 0.2 mass-% TFA (trifluoroacetic acid). The eluent flow was 1.0 ml/min. The temperature of column oven and RID detection cell was set to 35°C. Typical sample concentration in THF was 0.5 to 3 mg/ml of the polymer and the injection volume was 100 µl. The calibration standards for the column set were polystyrene standards narrowly distributed with molar mass range from 162 to 1 210 000 g/mol (as peak molar mass Mp), obtained from company PSS, Mainz, Germany. All results on molar mass are relative to these standards. The data evaluation was performed by the SEC-software WinGPCUniChrom, from company PSS, Mainz, Germany.

The concentration of EGBAA in the mixture was followed by changes in peak intensity in the measured elugrams. For this, an analytical curve plotting peak intensity *versus* concentration was constructed by permeating different solutions with several known concentrations of EGBAA through the complete column set. Table 2 shows the concentration of these solutions and the corresponding peak intensity. A calibration curve is fitted through these points, and the resulted equation 1 of the fit line with a correlation coefficient equal to one is used to determine the effective EGBAA concentration in the sample (mixtures of HTPB with EGBAA).

**Table 2 –** Concentration of EGBAA in THF and the corresponding peak area in SEC.

| Peak area in SEC elugram (x) | 3.22 | 3.1 | 6.27 | 6.23 | 15.55 | 15.66 | 44.63 | 44.65 | 68.02 | 67.89 |
|---|---|---|---|---|---|---|---|---|---|---|
| Concentration of EGBAA (mg/ml) | 0.052 | 0.052 | 0.103 | 0.103 | 0.26 | 0.26 | 0.71 | 0.71 | 1.03 | 1.03 |

$$[EGBAA] = -3.10E\text{-}05x^2 + 0.0174x - 0.003874 \qquad \textbf{Equation (1)}$$

### *Attenuated total reflected Fourier transformed infrared spectroscopy (ATR/FT-IR)*

IR spectra were measured on a Thermo Scientific Nicolet 6700 (FTIR-Spectrometer) with Durascope diamond ATR accessory. Resolution of 4cm$^{-1}$, 16 scans per spectrum, using KBr crystal in the range of 4000-650 cm$^{-1}$.

## 3 Results and discussion

### *Size Exclusion Chromatography (SEC)*

The molar mass distribution of the HTPB alone aged in 60°C as reference for the measurements of the mixtures is shown in Figure 1. The aging of the HTPB in contact with air and under inert atmosphere has not caused any significant changes.

In the Figure 2 (a) the molar mass distributions (MMD) is shown of the mixture HTPB:EGBAA aged at 40°C, and in Figure 2 (b) the MMDs of the samples aged at 60°C, in air or argon (Ar) atmosphere. After only 24 hours of breeding at 60°C the results showed that the mixture presented already a slightly broader molar mass distribution, with tailing towards higher molar mass values.

After 120 h at 60°C there were already measured macromolecules outside of the upper exclusion limit with up to 1000 times greater molar mass values. Considering that HTPB alone had not presented such behaviour, thus it is a clear indication of reactions between the precursors. The mixtures under argon atmosphere and in contact with air presented both nearly the same molar mass distribution after 120 hours at 60°C. The molar mass distribution of the samples aged at 40°C did not show such strong molar mass increase. However, after 168 hours of breeding at this low temperature the reaction was also verified by a tailing up to higher molar mass.

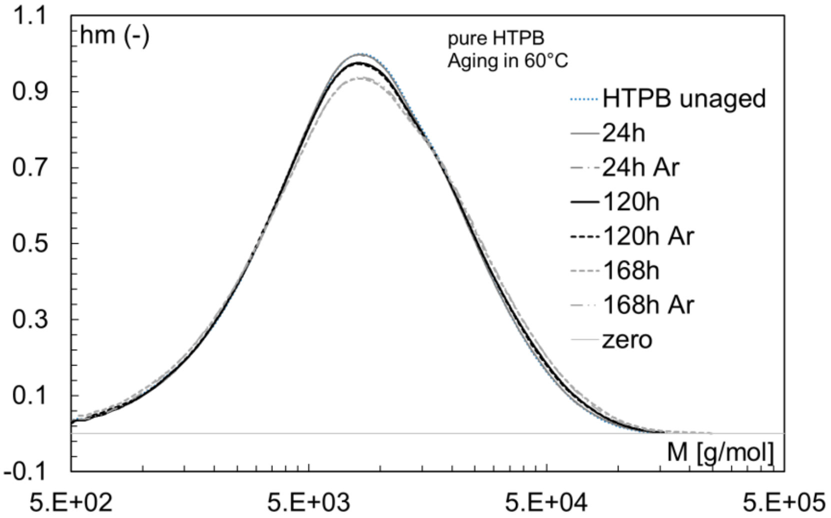


**Figure 1** – Molar mass distribution hm of HTPB relative to polystyrene standards, aged at 60°C over several time periods, see the insert in figure.

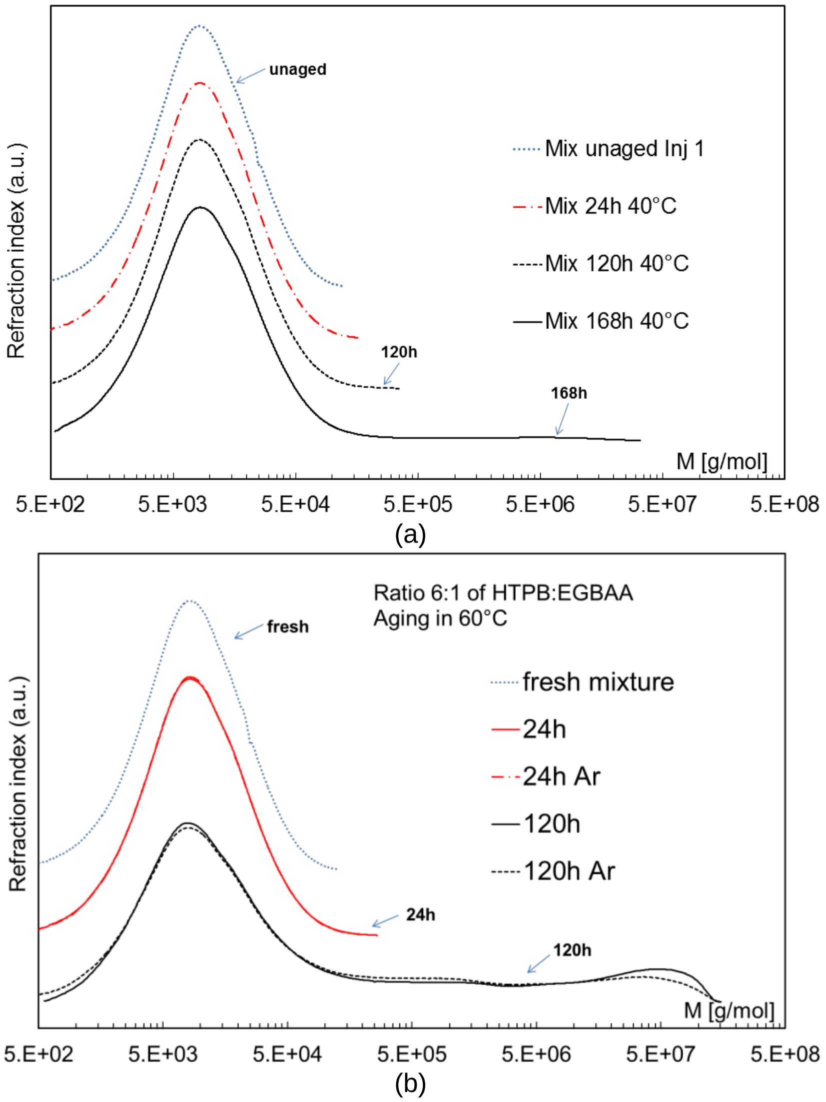


**Figure 2** - Molar mass distribution of HTPB relative to polystyrene standards in the mixture (ratio 6:1) with EGBAA after aging over several times at 40°C (a); and at 60°C (b) in air and argon atmosphere.

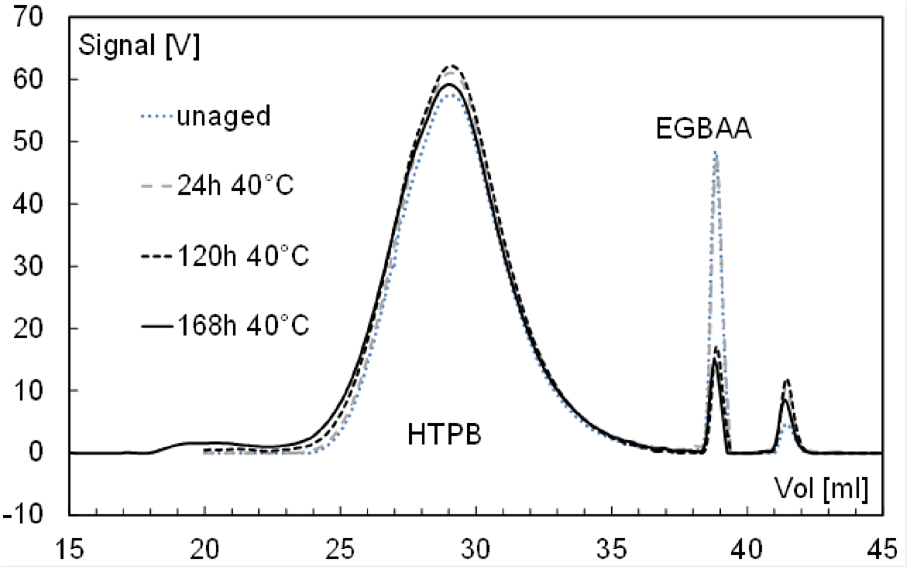
The complete elugrams of the mixture at 40°C and 60°C are shown in Figure 3 (a) and 3 (b). A longer molecule such as the HTPB leaves the separation column set earlier than small molecules like EGGBA. In principle the SEC separates the molecule by its hydrodynamic volume (based on size exclusion), so molecules with larger hydrodynamic volume permeate faster through the column because they are less trapped inside the column pores, as a consequence they are detected first, means at smaller elution volumes. Before the first signals related to longer molecules only the solvent (movable phase in the column) is eluted, means it constitutes the baseline.

EGBAA has less molar mass then HTPB and is trapped longer throughout the column set, thus it takes longer to elute. The signal peak around 38 ml is caused by EGBAA molecules. Measurements of samples loaded at both temperatures indicated a decrease of the peak signal related to EGBAA with time, and therefore decrease of its concentration in the mixture. It is also important to highlight that after 24 and 120 hours at 60°C more molecules with smaller hydrodynamic volume then EGBAA are formed and eluted through the column afterwards (around 40 and 42 ml). At time it is not possible to infer, which molecules these are but certainly they are either products of decomposition of EGBAA or of the reaction between HTPB and EGBAA.

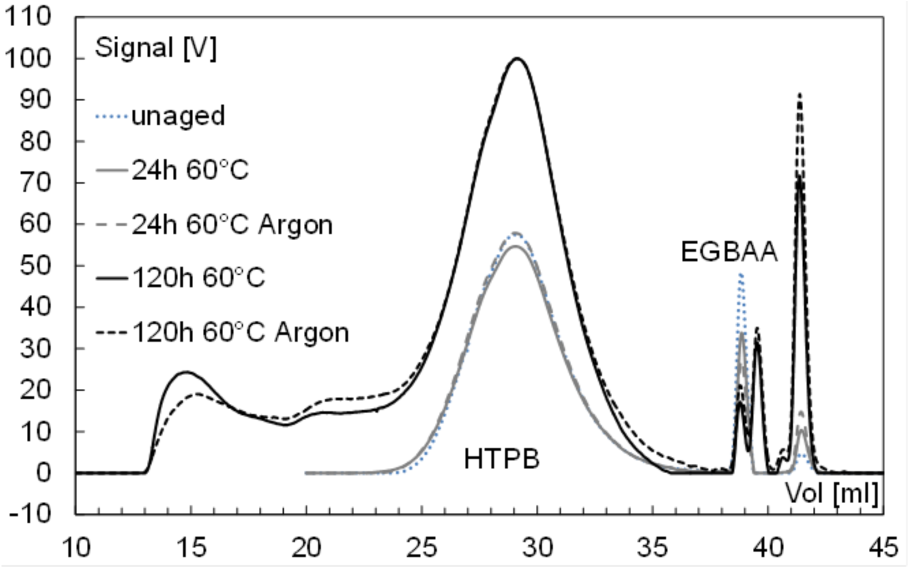
By calculating the areas of the elugram peak corresponding to the EGBAA elution and using the Equation 1, it is possible to estimate the concentration of this plasticizer in the sample. Results are listed in Table 3.

**Table 3 -** Results of EGBAA concentrations (in mg/ml) in the mixture 6:1 HTPB : EGBAA aged at different times at 40°C and 60°C, under air or Argon atmosphere. The abbreviation nd means not determinable.

| | 40°C,air | 60°C, air | 60°C Argon |
|---|---|---|---|
| Time (h) | mg/ml | | |
| 0 | 0.384 | 0.384 | 0.384 |
| 24 | 0.381 | 0.274 | 0.217 |
| 120 | 0.136 | 0.052 | 0.062 |
| 168 | 0.119 | nd | nd |



(a)



(b)

**Figure 3 -** Complete elugrams from GPC of the mixture 6:1 of HTPB : EGBAA aged at different times at 40°C (a) and 60°C, under air or Argon atmosphere (b).

Results indicated that the reaction is finished nearly after 120 hours at 60°C. After this time the samples cured to solids which could not be dissolved in THF to permeate through the column and no results could be obtained. Even the samples aged for 120h were not completely dissolvable in THF. Filtering the solvent for SEC measurement decreased the total concentration of sample. Thus such measurement is not completely elusive.

The possible reaction is between azide groups and the double bonds of HTPB which can proceed by a defined mechanism at such temperature, schematically shown in Figure 4: by [3+2] cycloaddition forming as an intermediary compound a 1,2,3-triazol hetero cycle, which is unstable and decomposes by releasing nitrogen [26-29]. Decomposition of azides to give nitrene (releasing nitrogen gas) is also a path to bond EGBAA into HTPB backbone if temperature or energy is high enough, say around 100°C [30,31].

Substantial increase in molar mass is explained by the crosslinking of HTPB chains promoted by such reaction with EGBAA, which has two terminal azide groups and is being consumed over reaction time. Such outcome is to be proven with the FTIR results to be presented here.

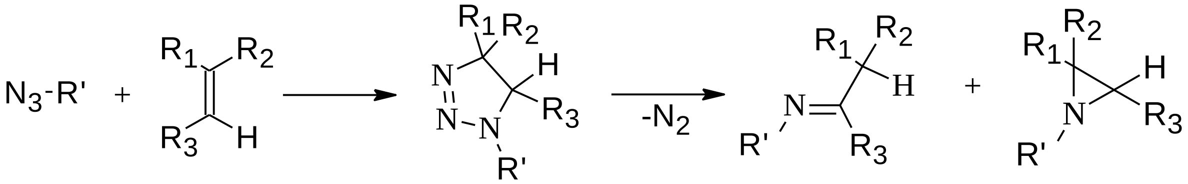


**Figure 4** – Possible reaction path scheme, considering the reaction between double bonds of HTPB and azide groups of the energetic plasticizer.

### *Attenuated total reflected Fourier transformed infrared (ATR/FT-IR)*

So far the results show clearly that mixing the HTPB with azide containing molecules leads to reaction between both with releasing gaseous products ($N_2$). This fact is an important result, because many authors in the literature have presented molecules/composites/binders derived from HTPB as potential energetic binder for propellants, which consider the existence of available azide groups in an elastomer bulk containing HTPB and its double bonds.

Results of ATR/FT-IR spectroscopy were used to identify possible IR absorption of formation of new bonds resulting from the reaction between HTPB and EGBAA. Also the disappearance or intensity reduction of peaks relative to consumed precursor groups are of great interest. In Figure 5**Erro! Fonte de referência não encontrada.** are plotted together the ATR/FT-IR experiment results of HTPB along with pure EGBAA, its fresh mixture and after 120 hours at 60°C.

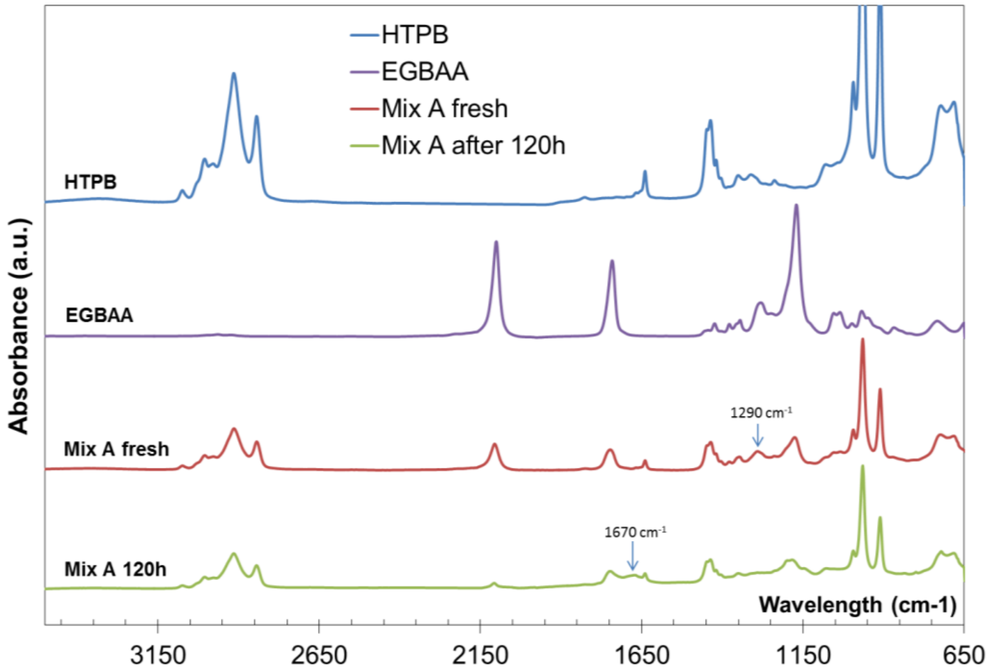


**Figure 5 -** ATR/FT-IR spectrum of the sample of HTPB pure and of the mix (ratio of 6:1 by mass with EGBAA), shortly after mixing (fresh) and after 120h hours in 60°C.

In the mixture the weak band in the region around 1290 $cm^{-1}$ and the peak in region 2170-2080 cm-1 have nearly disappeared. The first peak is related to symmetric stretching of azide group (1345-1175 $cm^{-1}$) whereas the second is characteristic from the asymmetric stretching vibration of the $N_3$ groups [32,33]. Thus, it is the indication that $N_3$ groups have been consumed.

The formation of new peak around 1670$cm^{-1}$ is indicative of a new aliphatic imines (-C=N) bond formation, which have such weak band in the region of 1690-1640 cm-1. Medium to weak bands in the region of 1675-1660 $cm^{-1}$ can be related to C=N stretching vibration in R-CH=N-R groups [32,33]. However, closeness of these bands to those related to C=C stretching vibrations (from double bonds of HTPB backbone) impart difficulties in the analysis.

According to literature, reactions between alkenes (such as the HTPB) and azide containing molecules are sources of nitrogen-carbon bond containing molecules [26-29]. As already demonstrated by ATR-FT-IR results, C=N bonds are forming, probably according to the reaction schemes demonstrated in Figure 4.

However, aziridines is also expected to be formed by such reaction. Aziridinyl compounds have medium to strong signals in the region of 3100-3060 $cm^{-1}$ (asymmetric stretching of $CH_2$); 1465-1425 $cm^{-1}$ (deformation vibration of $CH_2$) and 1260-1160 $cm^{-1}$ (torsional vibration of $CH_2$). None signals have been detected here either by the absence, or by the very low concentration of aziridine in the final products. Aziridine formation or its stabilization in the bulk may not be favored by the reaction conditions chosen here.

Presence of aziridine groups could be very useful to improve interface bonding between filler and binder in a composite propellant [34]. In future work further efforts shall be employed in order to shift the equilibrium to stabilize this chemical group.

## 4 Conclusion

Chemically modified hydroxyl terminated polybutadiene was successfully produced by a bulk reaction of HTPB with EGBAA. The outcome of molecules with high molar mass in the polyol bulk characterized by Size Exclusion Chromatography is seen as indication of such reactions. Solid elastomers were produced by crosslinking HTPB chains with a di-azide terminated molecule such as EGBAA. Infrared spectroscopy results showed the decomposition of the azide group. Possible reaction mechanisms is by the formation of 1,2,3-triazol ring which decomposes to release $N_2$.

## Acknowledgements

The authors would like to thank the chemical group of the Fraunhofer ICT for the synthesis of EGBAA used here; and W. Schweikert for IR spectroscopic measurements.

## Abbreviations

| | |
|---|---|
| HTPB | hydroxyl terminated polybutadiene |
| EGBAA | ethylene glycol bis-(azidoacetate) |
| THF | tetrahydrofuran |
| GPC | gel permeation chromatography |
| SEC | size exclusion chromatography |
| ATR-FT-IR | attenuated total reflected Fourier transformed infrared |

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