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Research paper

Study of the synthesis of GAP-HTPB-GAP Liquid Copolymer

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Abstract: GAP and HTPB are polymers on which the copolymer obtained in our work is based. The following report indicates how to perform the polymerization reactions for these two polymers in order to obtain a copolymer that combines their individual positive physico-chemical properties. It demonstrates how the ratio of substrates and reaction conditions affect the polymer properties. It has been shown that increasing the amount of epichlorohydrin attached to HTPB significantly affects the copolymer viscosity. This has a later effect on polymer processing, as well as on the hydroxyl values being too low. This is important for the subsequent production of polyurethanes. Analysis of the results allows the reaction conditions to be designed so as to generate a polymer with the best properties. The reactions were carried out in two stages. The first stage was the connection of polyepichlorohydrin (PECH) to HTPB, and the second was azidation of the resultant PECH-HTPB-PECH copolymer. The influence of the amount of epichlorohydrin attached to HTPB on the copolymer properties (e.g. viscosity) was demonstrated. Analysis of the second stage, the preparation of the GAP-HTPB-GAP copolymer (by azidation of the PECH-HTPB-PECH copolymer), showed that the nitrogen content in the copolymer has a significant effect on the viscosity and heat of polymer combustion.

Keywords: HTPB, GAP, copolymerization, optimization, liquid energetic binder

1 Introduction

Both of the basic polymers, *i.e.* hydroxyl-terminated polybutadiene (HTPB) and glycidyl azide polymer (GAP), can be components of solid heterogeneous rocket propellants. However, each has its advantages and disadvantages. HTPB based polyurethanes have very good mechanical properties at low temperatures, but also a low oxygen balance. In contrast, GAP has a better oxygen balance and energetic groups but does not give as good mechanical properties as HTPB. Therefore, a combination of these two polymers should allow a binder with good mechanical and energy properties to be obtained.

Binders can be classified as being neutral (HTPB, Figure 1, with no explosophoric groups in its structure) or energetic (GAP, Figure 2, with explosophoric groups in the structure), depending on their capability to decompose with the generation of gases, as well as the activation energy of a given reaction. Presently, researchers in the field of rocket propellants strive to obtain more and more energetic polymers, whilst maintaining adequate mechanical properties [1]. Chemical modifications of known binders such as HTPB have also been carried out [2].

The inert polymer HTPB is a liquid polymer of outstanding physical properties, such as a low glass transition temperature ($-78\text{ }^{\circ}\text{C}$), low viscosity and low specific gravity (0.9 g/cm^3) [3, 4]. Depending on the route and method of preparation, the molecular weight (M_n) of commercial HTPB products ranges from 2000 to 4000 g/mol [5, 6]. The physico-chemical properties of the polymer have a large impact on the mechanical properties of polyurethanes produced from it [7, 8].

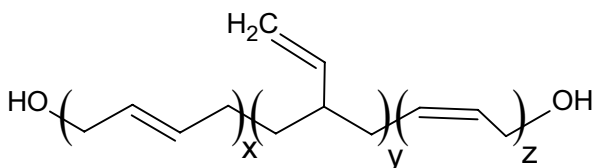
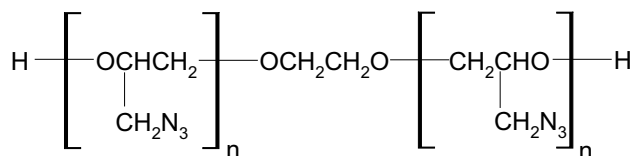


Figure 1. Hydroxyl-terminated polybutadiene (HTPB) [6]

The energetic polymer GAP possesses azide groups that ensure its highly energetic properties, the energy being generated by the decomposition of the azide groups to form nitrogen molecules. GAP is characterized by a high positive enthalpy of formation ($+957\text{ kJ/kg}$), and low sensitivity to thermal and mechanical effects. Its molecular weight is approximately 2000 g/mol, whereas the functionality (the number of reactive hydroxyl groups in a molecule)

is in the range of 1.6-3.1, depending on the type of initiator and catalyst used. GAP is characterized by a low glass transition temperature ($-45\text{ }^{\circ}\text{C}$), low viscosity and high density (1.3 g/cm^3), in comparison to other binders used in rocket fuels. In addition, GAP ensures an adequate level of compatibility with all energetic oxidizers [9, 10]. GAP-diols and GAP-triols are widely used in the production of polyurethanes, by reaction with di- and tri-isocyanates [11, 12].



GAP-DIOL

Figure 2. GAP [10]

GAP's energetic properties are determined by the location of the azide groups. Compounds where the azide group is substituted directly on the main chain, such as vinylpolyazide, do not demonstrate highly energetic polymer properties. This means that azidomethyl ($-\text{CH}_2\text{N}_3$) should be considered as the explosiveshoring group. Pure glycidyl azide polymer undergoes rapid decomposition leading to release of nitrogen gas from the side chain. The heat of decomposition is 957 kJ/kg [12].

2 Copolymerization of GAP and HTPB

Several descriptions of known HTPB and GAP copolymerization methods have been reported in the literature [15]. One involves a synthesis using macroinitiators (GAPMI) (free radical polymerization), whereas cationic ring-opening polymerization constitutes another method. Free radical polymerization can be used to synthesize cross-linked or grafted polymers. The technique always utilizes macro-azo initiators, such as polyesters and polyamides. Such macroinitiators are formed in high yield in the reaction of 4,4'-azobis(4-cyanovaleric acid) chloride (ACPC) with diols or diamines.

The resulting cross-linked polymer was characterized by two glass transition temperatures, -73.03 and $-35.84\text{ }^{\circ}\text{C}$, which was caused by the absence of compatibility between the HTPB and GAP chains in the copolymer. Crosslinking has also been found to occur between flexible HTPB segments and rigid GAP segments, to form a copolymer with very good mechanical properties, containing

highly energetic groups [13, 14]. Phase separation at a lower temperature leads to the formation of a grafted polymer, whilst increased temperature causes the formation of a cross-linked polymer with a homogeneous structure and higher potential as a binder [15].

The second method, cationic polymerization, is used to synthesize the GAP-HTPB-GAP three-block copolymer in two stages (Figure 3). The reaction is carried out in the same way as a GAP synthesis. A diol, HTPPB, is used as the initiator. *i.e.*:

- stage 1 (BF_3 etherate ($\text{BF}_3 \cdot \text{OEt}_2$) and organic solvent) cationic ring-opening polymerization of epichlorohydrin (ECH). In the first stage, a PECH-HTPB-PECH copolymer, where PECH means polyepichlorohydrin, is obtained.
- stage 2 (sodium azide (NaN_3) and organic solvent or water) the azidation reaction of that copolymer occurs to generate the final GAP-HTPB-GAP copolymer [16].

The overall yield amounts to 80%.

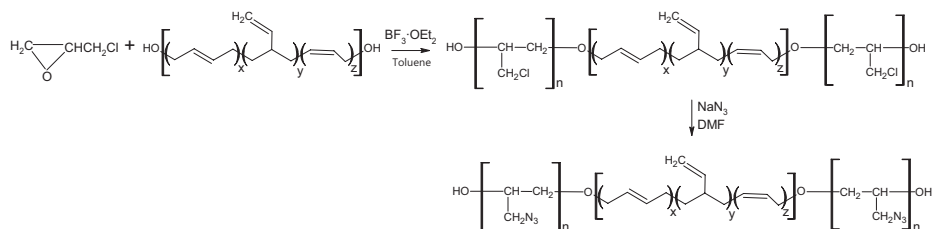


Figure 3. GAP-HTPB-GAP synthesis – cationic ring-opening polymerization and azidation reaction [16]

Considering the copolymer properties required for the production of solid rocket fuels, the second method of copolymerization was chosen for further analysis. In this reaction, the amount of PECH attached to HTPB is extremely important. Our own research on the synthesis and copolymerization of HTPB (not yet published) demonstrated that a too high molecular weight of the polymer prevents it from being used in rocket fuels. Furthermore, excessive viscosity of the polymer impedes the process of fuel mixing and affects its rheology [17].

Previous studies only reported on the possibility of synthesizing such a copolymer, whilst failing to describe the effect the amount of GAP attached to HTPB has on the properties of the copolymer. Likewise, studies on the azidation of the PECH-HTPB-PECH copolymer and the effect of the reaction parameters on the nitrogen content of the copolymer are not available. Previous work stated that the copolymer was obtained, but did not mention how it could be obtained,

and that it had properties like other known binders, that the resulting polymer was a liquid and had a suitable viscosity. The research presented below proves that it is not as obvious as has been described so far in work describing this copolymer. In the experimental section below, the method for obtaining a liquid GAP-HTPB-GAP copolymer that can be used in solid rocket fuels is presented. The influence of individual parameters at every synthesis stage on the properties of resulting polymers is described.

The present study was aimed at verification of the possibility of combining the physical properties of HTPB and the energetic characteristics of GAP by a copolymerization reaction. In this study, a cationic ring-opening polymerization method was chosen for the synthesis of GAP-HTPB-GAP copolymers. This method was chosen with consideration of the economic factors, *i.e.* the general availability and low-cost of the raw materials (ECH, and the polymerization catalyst). The potential extension of the synthesis scale was also taken into account (these raw materials are used extensively in the civil industry, are widely available and relatively cheap).

3 Experimental

3.1 Materials and test methods

The following raw materials were used for the synthesis:

- HTPB R45HTLO: – Cray Valley, – hydroxyl number, $L_{OH} = 48$ mg KOH/g, – viscosity at 30 °C = 5100 mPa, – $M_n = 2800$ g/mol, and
- Epichlorohydrin, C_3H_5ClO (Sigma-Aldrich, $\geq 99\%$), CH_2Cl_2 , (Avantor, 99,8%), $BF_3 \cdot OEt_2$ (Sigma Aldrich, for synthesis 46-51%) and DMF (Avantor, p.a.).

GPC: Analysis by gel permeation chromatography (SEC) was performed on an Agilent 1260 Infinity liquid chromatograph equipped with a RID detector using a PLgel MiniMIX-E 250×4.6 mm column (Agilent), thermostated at 50 °C.

FTIR: infrared analysis of the polymers was performed on an FT-IR NICOLET 6700 spectrophotometer using the ATR technique. Infrared spectra were obtained at 600-4000 cm^{-1} .

Polymer viscosity tests were carried out using a Brookfield HB DV2T viscometer with a small volume sample adapter. Each sample was thermostated in the measuring chamber. Viscosity tests were carried out in the temperature range from 25 to 60 °C. During the measurements, an SC4-21 type spindle was used.

Heat of combustion was determined using a KL-14 calorimeter of the company Precyzja-Bit (Poland).

Elemental analysis was performed using an Elementar CHNS analyzer model Vario EL III. The percentage content of C, N, H in the polymer samples obtained was determined.

Thermal analysis: Differential Scanning Calorimetric (DSC) analyses were carried out with a TA Instruments Q2000 calorimeter. Measurements were performed with airtight aluminum pans with a nitrogen flow of $50 \text{ mL} \cdot \text{min}^{-1}$. Thermogravimetric analyses (TG) were carried out with a TA Instruments SDT Q600 device. These measurements were performed in aluminum pans with a nitrogen flow of $100 \text{ mL} \cdot \text{min}^{-1}$. DSC and TG studies were performed with a temperature increase rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ in the temperature range: $30\text{-}550 \text{ }^\circ\text{C}$.

3.2 Synthesis of GAP-HTPB-GAP copolymer

The synthesis consisted of two stages. PECH-HTPB-PECH copolymer was synthesized in the first step (Figure 4). In order to obtain the PECH-HTPB-PECH copolymer, methylene chloride was used as a solvent, ECH was added into the reactor by means of a dosing pump at 16 mL/h . The reaction was carried out in a 1 L jacketed vessel with a temperature controller. HTPB (200 g) was used as the initiator and BF_3 etherate (0.56 mL) as the catalyst. The reaction was run at $10 \text{ }^\circ\text{C}$. Two copolymer synthesis reactions were performed, with different amounts of ECH in each reaction. After a certain time (2.5 and 7.5 h) of polymerization, distilled water (100 mL) was added to the reaction mixture. Subsequently, the organic phase was purified on an evaporator. The solvent and unreacted ECH were distilled off and two polymers, P1 and P2, with different properties were obtained (Table 1). The reaction conditions are the result of the authors' work on ECH polymerization (not yet published). The yield is given as % conversion of ECH.

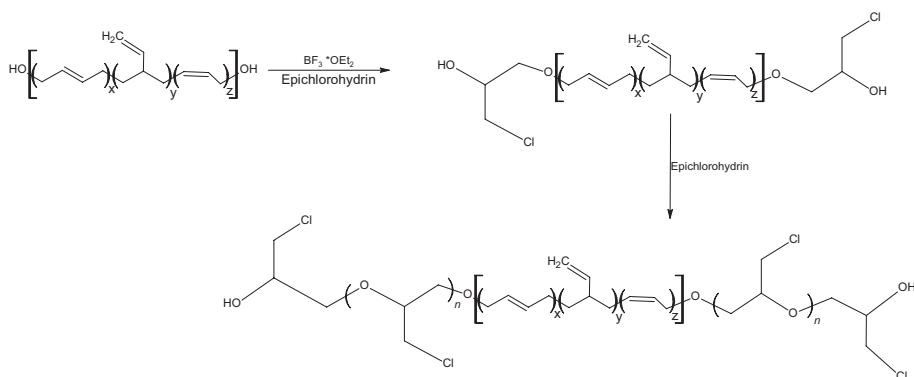


Figure 4. Copolymerization of ECH with HTPB

Table 1. Reaction conditions for the preparation of the PECH-HTPB-PECH copolymer

Parameter	Copolymer	
	P1	P2
HTPB [g]	200	
Toluene [mL]	200	
Reaction temperature [°C]	10	
ECH [mL]	40	120
Polymerization time [h]	2.5	7.5
Reaction yield [%]	95	92

The PECH-HTPB-PECH copolymer obtained in the first stage was then subjected to the azidation reaction (second stage). The azidation reaction (Figure 5) was performed under the following conditions: temperature: 95 °C, DMF solvent (30 mL), reaction time: 4 h, PECH-HTPB-PECH amount: 30 g. Reactions were conducted using different NaN_3 /copolymer ratios (Table 2). The same reactions were carried out for the two copolymer types (P1 and P2). For the A4P1 and A4P2 copolymers, the ratio of the number of $-\text{Cl}$ groups to the theoretical number of $-\text{N}_3$ groups was 1:1. These reactions resulted in the formation of 8 different liquid GAP-HTPB-GAP copolymers. FTIR, viscosity, TG/DSC, nitrogen content and heat of combustion were determined for all of these polymers.

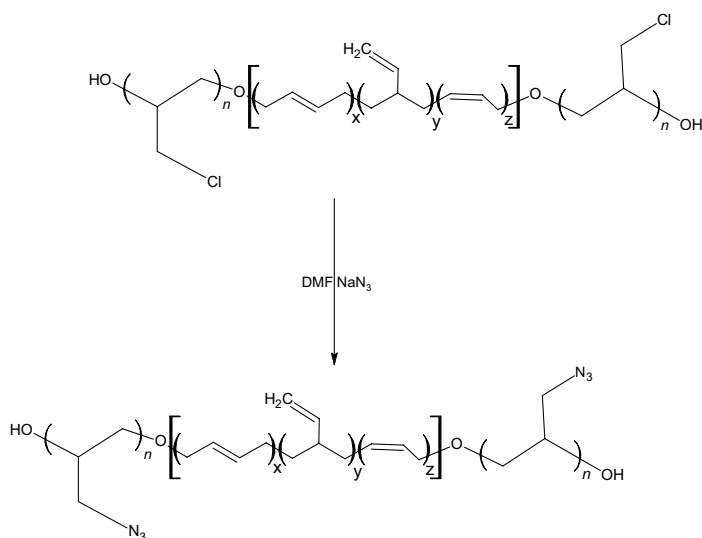
**Figure 5.** Azidation reaction of the PECH-HTPB-PECH copolymer

Table 2. Amounts of azide used in the reaction to prepare the GAP-HTPB-GAP copolymer

P1	NaN ₃ [g]	P2	NaN ₃ [g]
A4P1	6	A4P2	11.25
A5P1	3	A5P2	7.5
A6P1	1	A6P2	2.25
A7P1	0.5	A7P2	0.75

4 Results

The copolymer (PECH-HTPB-PECH) was subjected to analysis in terms of its properties:

- P1 copolymer: $M_n = 3800$ g/mol, PDI = 1.92, $L_{OH} = 43$ mgKOH/g,
- P2 copolymer: $M_n = 7500$ g/mol, PDI = 1.96, $L_{OH} = 35$ mgKOH/g.

A three-fold increase in the amount of ECH used in the copolymerization reaction resulted in an increase in the molecular weight from 3800 to 7500 g/mol.

The viscosity versus temperature function of the copolymers obtained was also analysed. The P1 copolymer had a viscosity at room temperature only one third that of the P2 copolymer of higher molecular weight. The viscosity of the tested copolymers decreased proportionally as the temperature was increased. At 60 °C, the viscosity of both copolymers was at the same level. The graph shows that the viscosity of the copolymers is much higher than that of the HTPB polymer.

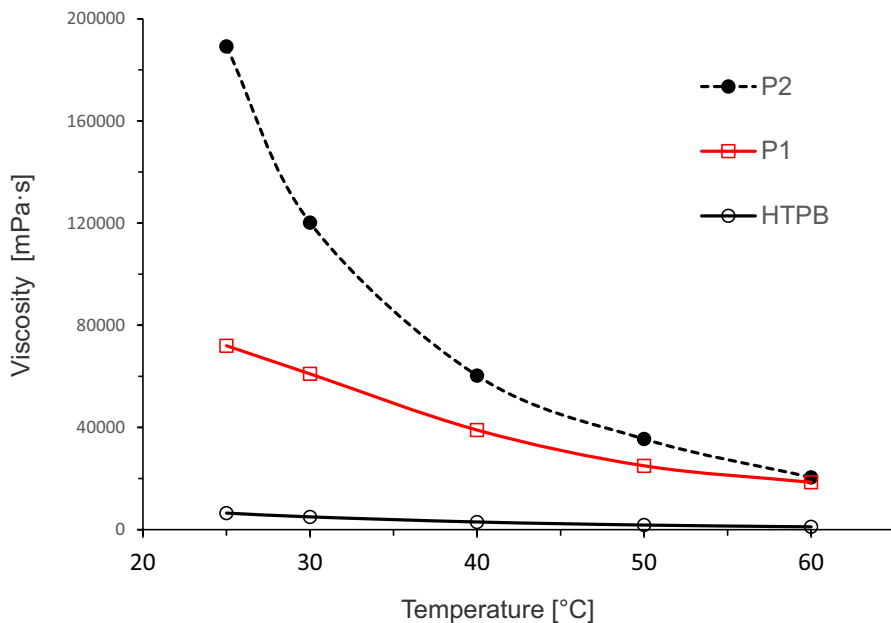


Figure 6. Dependence of the product viscosity value on temperature for the copolymers obtained

FTIR analysis confirmed the chain structure of the copolymer. The overlapped HTPB and PECH spectra are presented in Figure 6. The P1 and P2 spectra represent the two polymers obtained.

FTIR analysis confirmed the formation of PECH attached to the polybutadiene chain. Two characteristic peaks can be seen in the PECH spectrum: 744 cm^{-1} , corresponding to C–Cl bonds and 1100 cm^{-1} , which corresponds to C–O bonds. Peaks corresponding to 1,4-*cis*, 1,2-*cis* and 1,4-*trans* HTPB units are present in the HTPB spectrum at approximately 740 , 910 and 960 cm^{-1} , respectively. Additionally, a peak at 1639 cm^{-1} corresponding to C=C double bonds was also observed. FTIR analysis of the P1 and P2 polymers demonstrated the presence of a $-\text{CH}_2\text{Cl}$ group specific peak at approximately 740 , 1109 for the C–O–C group and 2843 cm^{-1} for methylene groups.

The analysis of the synthesized polymer samples confirmed the possibility of obtaining the PECH-HTPB-PECH copolymer by this method. The ECH dosing rate and the amount of ECH being attached to the polybutadiene chain should be controlled. An excessive amount of ECH attached will cause a rapid increase in the viscosity and molecular weight of the copolymer, as well as a decreased hydroxyl value, which would affect the subsequent processing of this polymer.

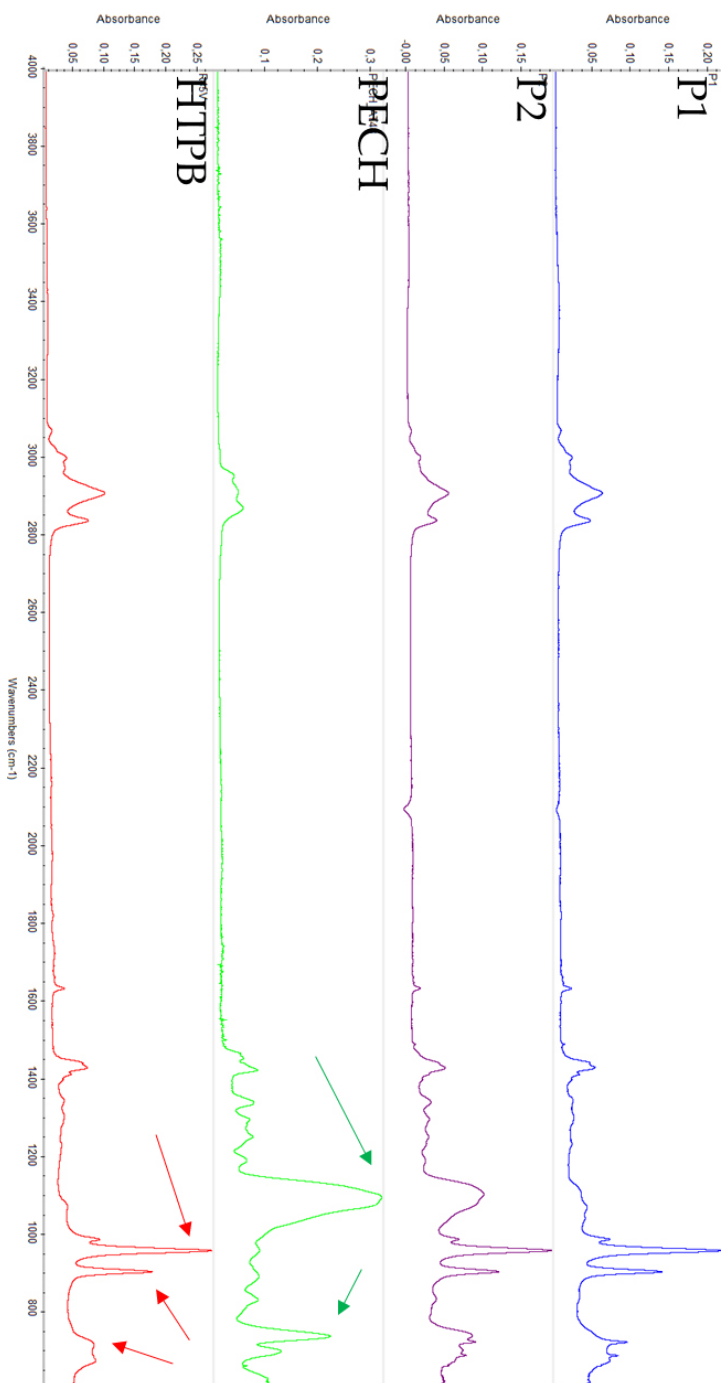


Figure 7. FTIR analysis of the synthesised PECH-HTPB-PECH copolymers

The GAP-HTPB-GAP copolymers obtained in the second stage were carefully analysed. The nitrogen content in the copolymers was determined by elemental analysis. The level of nitrogen in the final product increased proportionally with an increase in the sodium azide to PECH-HTPB-PECH copolymer ratio. A low nitrogen content was obtained for the copolymer based on P1 as the starting polymer. A higher nitrogen content was obtained by azidation of the P2 copolymer. For the A4P2 polymer, where the ratio of –Cl group number in the copolymer to the introduced –N₃ groups amounted theoretically to 1:1, a nitrogen content of 16.8% was observed. The theoretical level of nitrogen in pure GAP is about 40%. Our previous research (not published) had demonstrated that the use of excess NaN₃ (20% excess) in proportion to the number of –Cl groups in the copolymer, generated a solid copolymer. In this form, the copolymer is not suitable for use as a binder.

Table 3. Nitrogen content of the individual synthesised GAP-HTBP-GAP copolymers

P1	N [%]	P2	N [%]
A4P1	2.7	A4P2	16.8
A5P1	1.5	A5P2	13.6
A6P1	0.41	A6P2	5.45
A7P1	0.2	A7P2	3.9

As in the synthesis of pure GAP, the polymer viscosity decreased after the azidation reaction. Own research of GAP synthesis showed GAP viscosity at 25°C:

- 18% N: 28600 mPa·s,
- 27% N: 10300 mPa·s,
- 39% N: 6000 mPa·s.

The viscosity decreased with an increased content of azide groups in the polymer. The substitution of chlorine with the azide group reduces the viscosity of the copolymers obtained. The viscosity of the final copolymers was measured at various temperatures (from 25 to 60 °C). As the temperature was increased, the viscosity of the copolymers decreased. The same relationships were observed in the cases of copolymers obtained from P1 and P2. As with the PECH-HTPB-PECH copolymer, the viscosity value is higher for copolymers obtained from the P2 polymer.

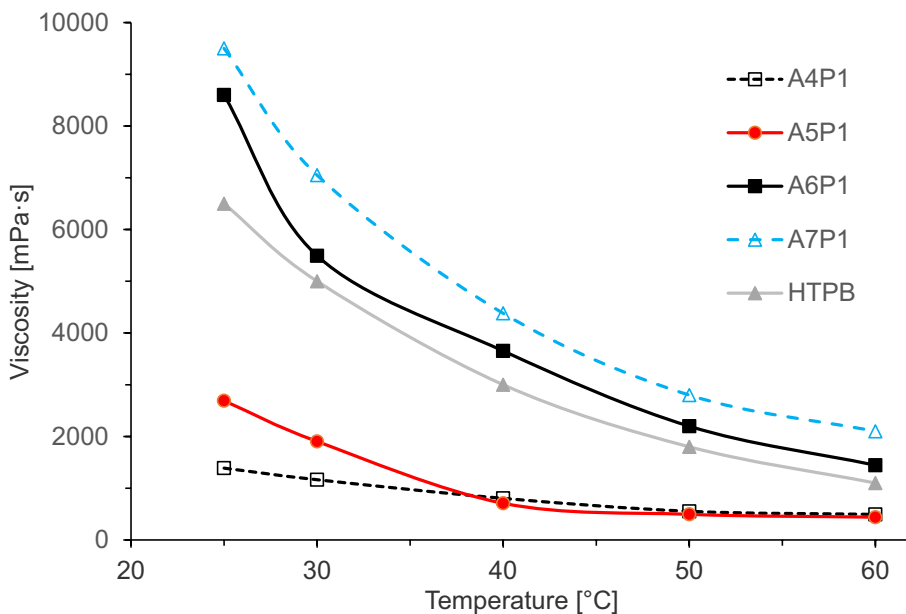


Figure 8. Viscosity dependence on temperature for the copolymers obtained by reaction of P1 with azide at various weight ratios

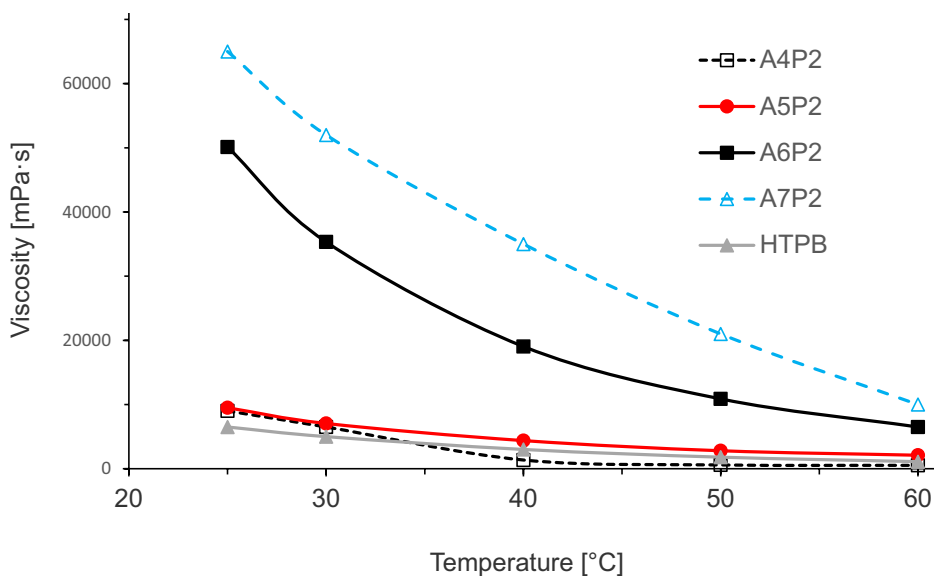


Figure 9. Viscosity dependence on temperature for the copolymers obtained by reaction of P2 with azide at various weight ratios

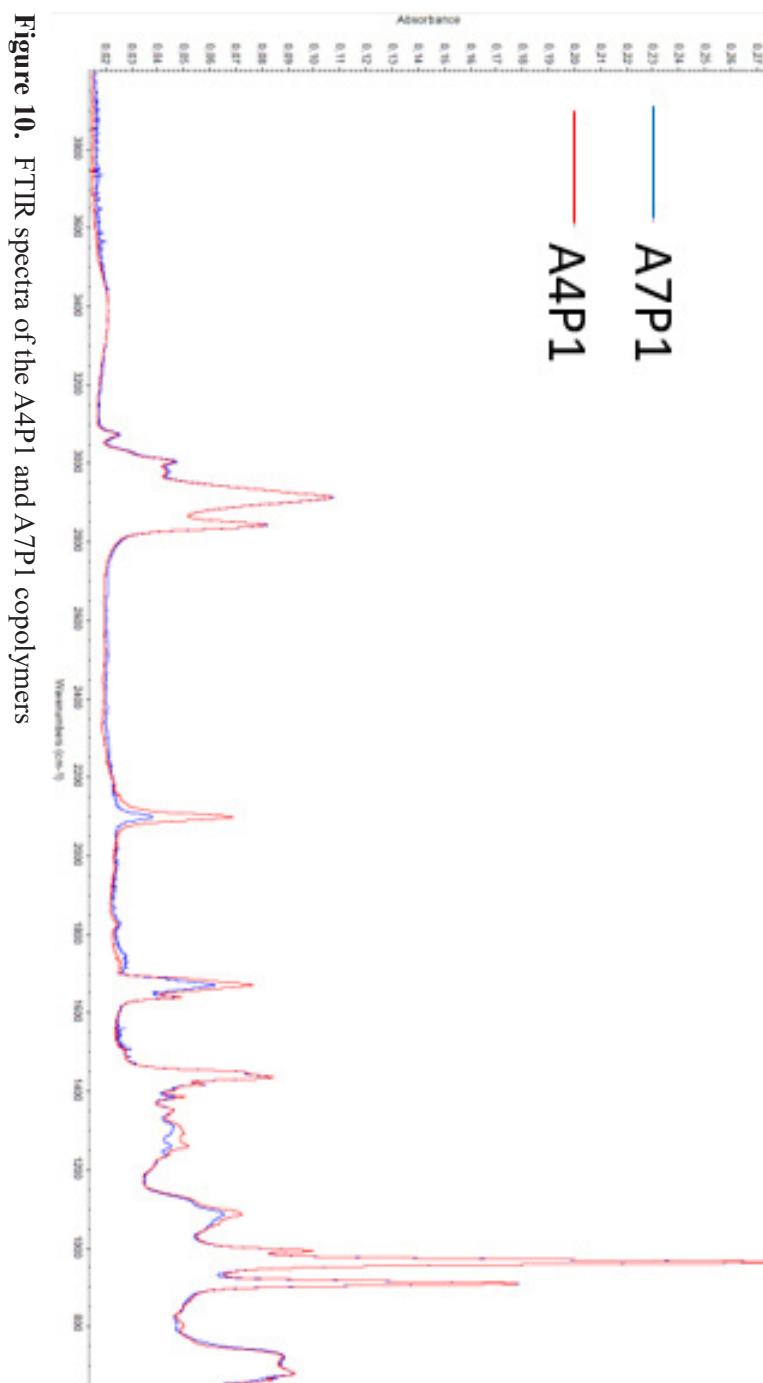


Figure 10. FTIR spectra of the A4P1 and A7P1 copolymers

The copolymers of lowest viscosity were obtained at the highest sodium azide to copolymer ratios, for PECH-HTPB-PECH obtained from smaller and larger amounts of ECH. As the temperature was increased, a decrease in viscosity was observed for all of the copolymers obtained. Figures 8 and 9 show the effect of the amount of the energetic part (GAP) on the viscosity of the copolymer relative to the HTPB polymer. The copolymer produced with a nitrogen content of over 16% exhibited properties that would allow it to be used as a binder in solid heterogeneous rocket fuels. FTIR analysis was performed for the GAP-HTPB-GAP copolymers obtained. A comparison of the spectra for samples with extreme nitrogen content, for A4P1 and A7P1, as well as for A4P2 and A7P2 copolymers, is presented in Figures 10 and 11, respectively.

The infrared analysis demonstrated the presence of peaks specific for the azide group $-N_3$ at approximately 2100 and 1300 cm^{-1} and the disappearance of the $-CH_2Cl$ group peak at 748 cm^{-1} . A visible difference in the peak intensity at 2100 cm^{-1} between products obtained at lower and higher azide to copolymer ratios, was noted. In both cases, the spectrum of the polymer with a higher nitrogen content had a more intense signal originating from the $-N_3$ groups. Higher reaction yield (degree of substitution) is connected with a higher amount of sodium azide being added.

A calorimeter was used to measure the heat of combustion in oxygen of the copolymers obtained, as well as HTPB and GAP basic polymers (Table 4). The highest heat of combustion value was obtained for HTPB, whereas the lowest value was for pure GAP. The longer the PECH chain attached to HTPB, the lower the heat of combustion value in the PECH-HTPB-PECH copolymer was observed. Substitution of chlorine atoms with azide groups in these copolymers resulted in a reduction in the heat of combustion. As in the case of the nitrogen content or the viscosity of the copolymers obtained, the heat of combustion values are between the values of basic polymers.

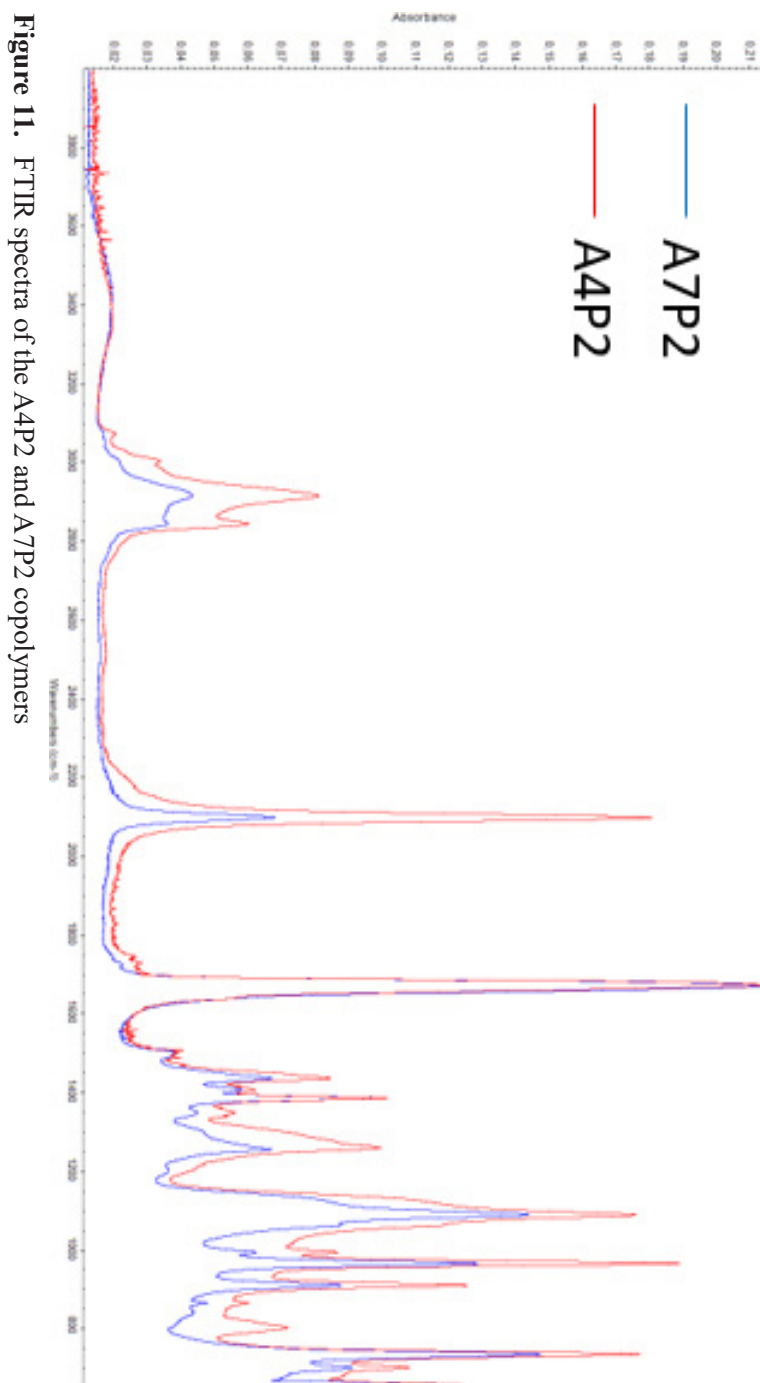
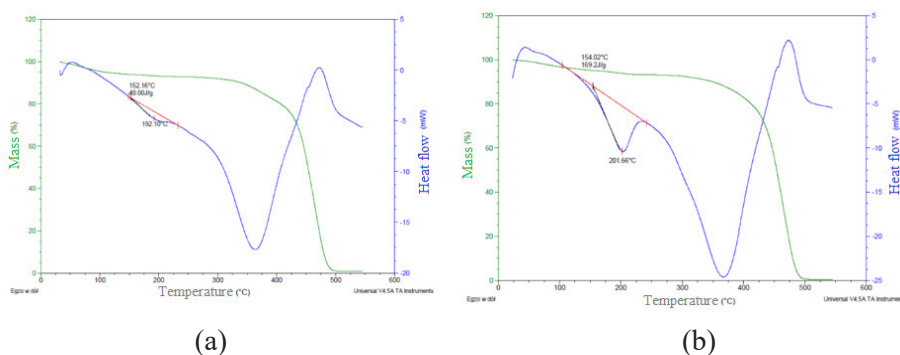


Figure 11. FTIR spectra of the A4P2 and A7P2 copolymers

Table 4. Values of the heat of combustion of the tested polymers

Polymer	Heat of combustion Q_s [kJ/g]
HTPB	45.75 \pm 0.25
GAP	21.25 \pm 0.20
P1	43.40 \pm 0.15
P2	37.50 \pm 0.15
A4P1	41.20 \pm 0.17
A5P1	41.60 \pm 0.17
A6P1	41.80 \pm 0.17
A7P1	42.30 \pm 0.17
A4P2	31.80 \pm 0.17
A5P2	32.30 \pm 0.17
A6P2	33.20 \pm 0.17
A7P2	33.80 \pm 0.17

Selected copolymers were subject to thermo-gravimetric analysis. The analytical curves are shown in Figure 12. In each instance, two peaks indicating mass loss were observed, which correspond to exothermic reactions, at about 200 °C the azide groups from the GAP segment of the copolymer, and at approximately 350 °C the HTPB segment of the copolymer, respectively. The peak intensity of the GAP segment depends on the length of polychlorohydrin chain and the degree of substitution of chlorine in the chain. Peaks corresponding to the decomposition of the HTPB parts are characterized by a comparable intensity.

**Figure 12.** Thermograms of A7P1 (a) and A4P1 (b)

The glass transition temperature of selected synthesized copolymers was determined by DSC. According to previous assumptions, the copolymer temperature (-65 °C) was intermediate between the glass transition temperatures

of the basic polymers, GAP ($-45\text{ }^{\circ}\text{C}$) and HTPB ($-78\text{ }^{\circ}\text{C}$). No two separate signals from the glass transition temperatures were observed.

5 Summary and Conclusions

A two-step synthesis of the GAP-HTPB-GAP copolymer resulted in the formation of liquid polymers. A maximum of 16.8% nitrogen content was achieved. The extension of the chain attached to HTPB by reaction with epichlorohydrin may result in a deterioration in the processing properties of the copolymer (viscosity significantly increased). The second step, *i.e.* azidation of the PECH-HTPB-PECH copolymer, results in a decrease in polymer viscosity. The higher the nitrogen content in the final copolymer, the lower the viscosity. Excess azide in relation to PECH-HTPB-PECH copolymer leads to the formation of insoluble solid GAP-HTPB-GAP polymers. According to the assumption, all key properties of the copolymers (viscosity, heat of combustion, glass transition temperature, *etc.*) have values intermediate between the properties of HTPB and GAP. Copolymers synthesized under these conditions exhibit properties that would allow their use as binders in solid heterogeneous propellants.

Based on the results of the analysis of the copolymer obtained, it can be assumed that another solution would be to use a low molecular weight (and lower viscosity) HTPB ($M_n < 2000\text{ g/mol}$). Then the more energetic parts (GAP-type) could be introduced while maintaining good mechanical and processing properties.

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