



Synthesis of High-Energy Polymer – Glycidyl Azide Polymer (GAP)

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Abstract. Glycidyl Azide Polymer (glycidyl polyazide) (GAP) is one of the best known energetic binders, applicable as a component increasing a calorific value of rocket propellants. In this article, a synthesis of GAP is described allowing to obtain a polymer of different molecular masses. The change of a molecular mass can influence on properties of the obtained compounds. The synthesis was carried out according to an active monomer mechanism. The obtained products were characterized using such methods as FTIR, GPC, MALDI-ToF, TG, and NMR.

Keywords: high-energy materials, energetic binders, GAP

1. INTRODUCTION

Rocket propellants are chemical substances able to decompose with emission of large amount of heat and hot gases.

Currently used rocket fuels are divided into homogeneous and heterogeneous ones. Homogeneous fuels are uniform but heterogeneous fuels consist of oxidizer, binder, as well as of technological additives with significantly lower mass such as plasticizer, catalyst, curing agent, and the like. Binder in rocket fuel fulfils both, the role of fuel and of a structure-making factor that should ensure proper mechanical properties of the fuel. It amounts about 10% of the mass composition of the fuel [1]. The binder should have the following features:

- be compatible with other fuel components,
- to have high thermal stability and high heat of combustion, H ,
- to include a polymer matrix (skeleton) with the high C/H ratio,
- to have molecular masses (M_n and M_w) within the range from 2000 to 3500 g/mol,
- characterize with:
 - low viscosity for easier mixing all the components,
 - low glass transition temperature (T_g),
 - high chemical stability and low sensitivity to detonation,
 - low toxicity [2].

Modern polymer binders can be divided into neutral and energetic ones. Neutral polymers have a hydrocarbon chain in their structures. At present, the most popular neutral binder used in the rocket propellant is hydroxyl terminated polybutadiene (HTPB). It provides the product adequate mechanical properties but it has low oxygen balance what causes decrease in the energy of rocket propellant. Thus, more frequently the energetic binders are used. These are macromolecular compounds that have explosoforic groups, e.g., nitro group, nitrate group, and azide group, and the like, that cause a general change in the composition energy [3].

One of the best known energetic binders is glycidyl polyazide (GAP). The azide group ensures high-energy properties, the energy is emitted as a result of a nitrogen particle emission. GAP is an energetic polymer with the high positive heat generation (+ 957 kJ/kg), low sensitivity to thermal and mechanical stimuli, molecular mass from 500 g/mol even to 36 000 g/mol for branched polymers [3-5]. In dependence on the used initiator and catalyst, GAP can show different functionality (number of reactive hydroxyl groups in a particle) which amounts 1.6-3.1 GAP characterizes with low glass transition temperature, low viscosity, and high density in comparison to other binders used in rocket propellants.

Moreover, GAP is well compatible with all energetic oxidants. Due to the mentioned above properties, GAP is a high-energy binder widely used for increase in calorific value of rocket propellants [2, 4].

A lot of the methods describing GAP production are available in the literature. One of the simplest methods is a direct method in which the polymer can be obtained in a single step. Having epichlorohydrin (ECH) and adequate diol, the polymer of low molecular mass can be obtained (~500 g/mol) [5, 6]. The most known type of reactions of GAP production is substitution of a chlorine atom in polyepichlorohydrin (PECH) with an azide substituent. They are two-stage reactions.

The first stage is ECH polymerisation to PECH, the most frequently carried out at the presence of boron trifluoride etherate ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) and polyhydroxy alcohols that act as initiators. The polymerisation process proceeds according to the mechanism of the activated monomer (AMM) [7]. The second stage relies on the substitution of chlorine, that is in PECH, with the azide group. One of the solutions is typical reaction of bimolecular nucleophilic substitution ($\text{S}_{\text{N}}2$). The simplest reaction consists in addition, to dissolved, e.g. in N,N – dimethylformamide (DMF), the sodium azide polymer (EPCH) and mixing the total substance at 100°C. The alkaline metal azides (of potassium, lithium, sodium) are used [8, 9]. In dependence on the ratio of polyepichlorohydrin to the azide and on the used dissolvent, the reactions are carried out in various time.

After substitution of the groups at the level of 90%, decrease in the reaction rate can be observed, caused by formation of associates of dissolvent with metal ions what leads to limitation of the solubility and to double the reaction period [6]. Other method is a synthesis with the use of the melted salt without dissolvent application [10]. It eliminates the problems with solubility, described in the previous method. Time of reaction is two times shorter in comparison with the previous methods. Chlorine in monomers of the epichlorohydrin unit in PECH reacts with azide ion.

The used liquid or melted the quaternary ammonium azides can have the same or various aliphatic substituents with simple or branched or aromatic chains, while the melting temperature should be in the range from 80°C to 120°C. The basic method of GAP production is to mix the tetrabutylammonium azide (TBAB) with the hydrated polyepichlorohydrin at 100°C [11].

The next method, that is the most frequently used for GPA synthesis, is to substitute the chlorine in polyepichlorohydrin by the azide group using the phase transfer catalyst (PTC). It consists in conduction of the reaction in a system with two, not mixing phases, an organic liquid phase and a constant inorganic phase. The most important element is the presence of the phase transfer catalyst in the system. For anion reagents, usually quaternary ammonium salts are used.

A catalyst is used for anion transfer from the inorganic phase to the organic one, where the specific reaction proceeds. Advantages of the synthesis according to the mechanism of the phase transfer catalysis are: the possibility of carrying out different-type reactions, production of less amount of wastes, and achievement of synthesis efficiency even up to 90%.

2. EXPERIMENTAL PART

2.1. Materials

In the works, the following agents were used: ethylene glycol (pure POCH), dichloromethane (pure POCH) after distillation from the above the calcium hydride, boron trifluoride etherate (46%, Sigma-Aldrich), epichlorohydrin (pure Fluka), magnesium sulphate (VI) (pure 98%; POCH), sodium azide (pure 99%, Sigma-Aldrich), tetrabutylammonium bromide (pure 98%; Sigma-Aldrich), sodium hydroxide (pure for analysis 98%, POCH).

2.2. GAP synthesis

Epichlorohydrin polymerisation. Reaction of ECH polymerisation is carried-out in a flask situated in a thermostat. Ethylene glycol in the amount of 14.5 g (0.23 mol) and 0.58 ml (0.0047 mol) of the BF_3 complex with diethylene ether are put into the flask. After stabilisation of the temperature, at the value of 20°C, 385 ml (4.91 mol) of the epichlorohydrin is dropped into the flask by means of a peristaltic pump at the constant temperature for 48 hours. After addition of the whole amount of the epichlorohydrin, the solution is kept at the temperature of 20°C for 2 hours in order to complete the reaction. Next, the catalyst is deactivated through addition of 23.42 g (0.42 mol) of the calcium oxide. The calcium oxide (CaO) is removed from the solution due to the filtration process. The reaction can be carried out also at the presence of dissolvent – the dichloromethane was used for the investigations.

Substitution of chlorine in PECH with azide group. To obtain GAP, the following components are put in the flask: 27 g (0.42 mol) of the sodium azide, 1.5 g (0.023 mol) of TBAB (phase transfer catalyst), 0.75 g (0.019 mol) of the sodium hydroxide dissolved in 150 ml of water, and 15 g of the polyepichlorohydrin (PECH). All these components are mixed at the temperature of 100°C for 24 hours. When the reaction is completed, the dichloromethane is added. After separation of layers, an organic part is washed several times with water and next it is dehydrated with the magnesium sulphate (VI). After dissolvent evaporation, pale yellow oil is obtained.

2.3. Analytical methods

Spectroscopic analysis in IR (FTIR) was performed on the Nicolet 6700 Thermo Scientific spectrophotometer with the applied ATR attachment (Attenuated Total Reflectance method). The measurement resolution was of 4 cm^{-1} with an average number of scans of 32 at the room temperature.

The molecular masses (M_w and M_n) and the polydispersion coefficient (PDI) were determined using the Gel Permeation Chromatography (GPC). The investigations were carried out on the Aligent 1260 Infinity chromatograph with RID detector on the column filled with PL Gel $5\text{ }\mu\text{m}$ miniMix-C $250 \times 4.6\text{ mm}$, using the polystyrene pattern ($500 - 2 \times 10^6\text{ g/mol}$). A mobile phase was the tetrahydrofuran (THF), the flow was 0.3 ml/min and the furnace temperature 50°C .

The spectroscopic analysis of the magnetic nuclear resonance ^1H NMR was performed on the Varian NMR System 500 MHz using the internal pattern - tetrametylosilan (TMS). As a dissolvent, the deuterated chloroform (CDCl_3) was used. The measurements were made at the temperature of 25°C .

For observation of a decomposition profile of molecular masses of the obtained polymers, the mass spectrometry with sample ionisation and time measurement of ions time of flight was applied (MALDI-ToF – Matrix Assisted Laser Desorption/Ionization-Time-of-Flight). The analysis was performed on the ultrafleXtreme device of the Bruker Daltonics firm. As a matrix substance, the *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenyldiene]malononitrile (DCTB) was used.

The viscosity measurements of the obtained samples were carried out on the Brookfield DV2T viscometer with the attachment for small samples. The spindle type: SC4 - 13R(P). A vessel of a volume of 7.1 ml was used. The measurement was performed from low values of rotations to high values and in the reverse direction within the rage of temperatures $20^\circ\text{-}60^\circ\text{C}$.

The decomposition temperature and the loss of a sample mass were measured on the SDT Q600 Thermal Analysis Instruments thermogravimeter within the range from 100°C to 300°C . The measurement was made in the aluminium closed vessels with the heating rate of 5°C or 10°C per a minute.

3. RESULTS AND DISCUSSION

3.1. Polymerisation of epichlorohydrin

The paper presents the results related to the GAP prepared with two-stage method. The first discussed stage is the PECH receiving with application of the polymerisation according to the mechanism of the activated monomer.

In the carried-out reactions, there were used various amounts of the polymerisation initiator which was ethylene glycol in order to obtain the polymer of different molecular masses. The molar ratio of epichlorohydrin to initiator was changed within the range from 1 : 0.025 to 1 : 0.094. The amounts of the remaining reagents were not changed. In order to determine molecular masses of the obtained polymers, the GPC analysis was performed. Table 1 lists the amounts of reagents used for PECH synthesis and Table 2 lists approximated molecular masses of the obtained polymers.

Table 1. List of data of ECH polymerisation reaction

Synthesis	ECH/EG [mol/mol]	BF ₃ ·Et ₂ O [mol]	Yield [%]
I	1 : 0.094	0.047	80
II	1 : 0.047		76
III	1 : 0.025		74

Table 2. Results of GPC analysis for PECH

Synthesis	M _n [g/mol]	M _w [g/mol]	PDI
I	1000	1172	1.17
II	1718	2147	1.25
III	2287	3373	1.47

All the reactions have been carried-out at the presence of a dissolvent – the dichloromethane. Application of the dissolvent allows for easy filtration of the calcium oxide from the reaction mixture with no necessity of its heating. CaO filtration is difficult because of the high viscosity of the mixture at room temperature. On the basis of the obtained results, one can state that with increase in the ECH ratio to the initiator, the obtained polymer (PECH) has the higher molecular mass. The highest molecular mass of PECH was obtained for the molecular ratio of ECH/ ethylene glycol 1/0.025 which was 2200 g/mol.

The obtained PECHs of various molecular masses were subjected to the FTIR analysis that allows for determination of the presence of characteristic bands in the investigated compound. Images of FTIR spectra are the same for all obtained polymers, independently of the obtained molecular mass. Figure 1 presents the exemplary spectrum of PECH of the molecular mass 2200 g/mol.

At this spectrum one can observe the band originating from C-Cl bounds of a value 744 cm⁻¹ or ether bounds C-O 1100 cm⁻¹, the stretching band C-H, belonging to the methylene groups 2874 cm⁻¹. There are also present the stretching bands originating from O-H bonds in a hydroxyl group at 3401 cm⁻¹.

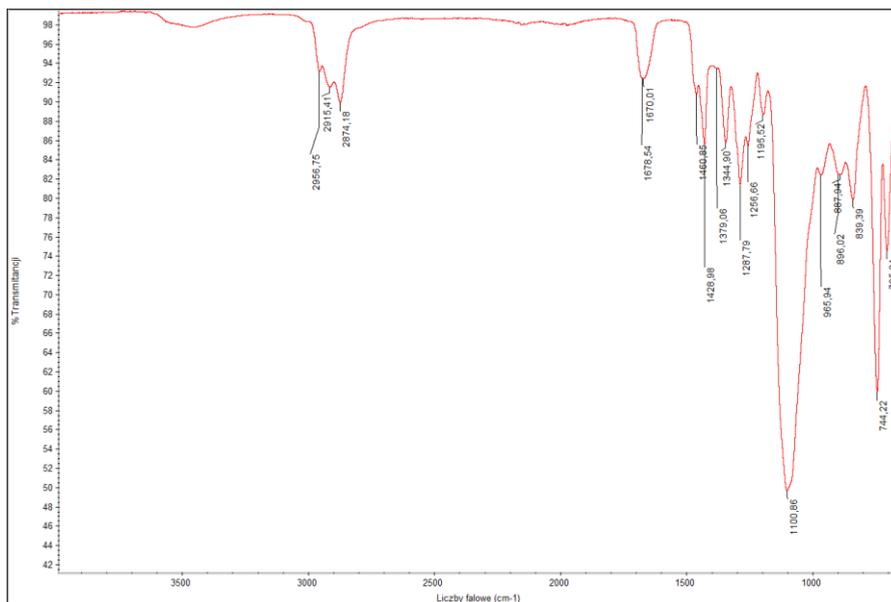


Fig. 1. FTIR PECH spectrum

In order to confirm the PECH structure, the MALDI-ToF analysis was made for the PECH sample obtained in the I-st synthesis. The measurements showed existence of five series. Below, in Table 3 and in Fig. 2, the obtained results of the analysis are presented.

Table 3. Results of MALDI-ToF analysis

Series	Final group	Repeating group	Adduct	M_n	M_w	PDI	% participation
S1	Ethylene glycol	ECH	K	2432	3002	1.23	32.85
S2	OH	ECH	K	2512	3140	1.25	33.48
S3	OH	ECH	Na	1868	2298	1.23	9.90
S4	Ethylene glycol	ECH	Na	2421	3075	1.27	12.64
S5	-	ECH	Na	2809	3528	1.20	11.13

The analysis confirms that the polymerisation reaction of epichlorohydrin has proceeded. Two series these are: ethylene glycol-terminated ECH with potassium and sodium adducts. Next two series: hydroxyl group-terminated ECH also with potassium and sodium adducts. In the last series, the epichlorohydrin can be seen. On the basis of the analysis one can also determine the average molecular mass that is about 2400 g/mol.

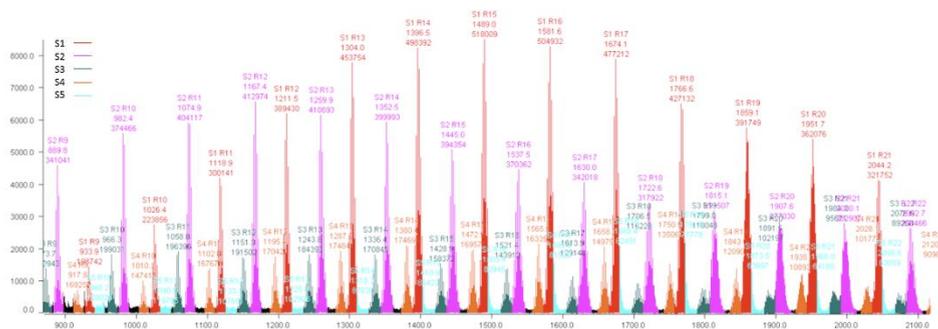
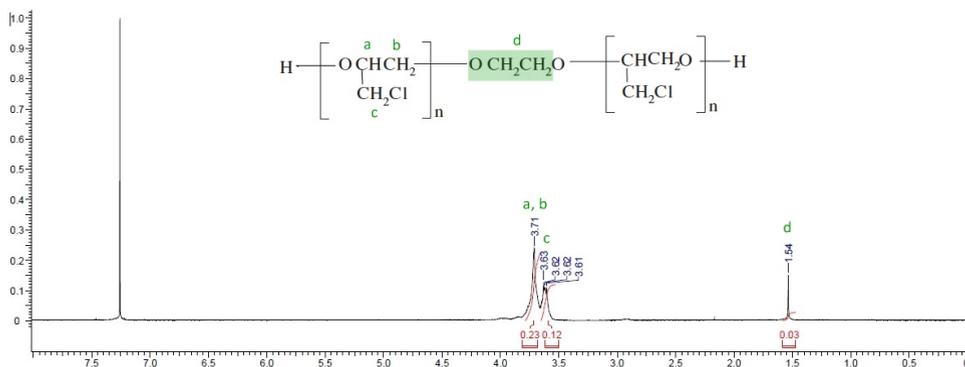


Fig. 2. MALDI-ToF PECH spectrum

In the mixture, cyclic compounds were not detected, thus it means that polymerisation reaction has occurred according to the active monomer mechanism. The obtained results, to some extent, differ from GPC results of analysis (they are higher) what can be caused by a selection of a calibrant for GPC analysis. Improper selection of the calibrant can cause decrease in GPC analysis results. The adequate calibrant have to be, at the highest degree, similar to the analysed sample. For the obtained polymers, also the $^1\text{HNMR}$ analysis was made. The spectrum received from the spectroscopic analysis of the magnetic nuclear resonance $^1\text{HNMR}$ confirms the PECH getting. The results of analysis are shown in Fig. 3.

Fig. 3. $^1\text{HNMR}$ spectrum of PECH

The signals, visible at 3.62 ppm, originate from the protons of CH_2Cl group (c – in Fig. 3), the signals at 3.71 ppm, originate from the protons of CH_2 and CH groups (a, b – in Fig. 3). The signal 1.54 ppm originates from the ethylene glycol group $\text{CH}_2\text{-CH}_2\text{-O}$ (d – in Fig. 3).

For each the PECH sample, the viscosity measurements were made and the results and the values of temperature of the measurement are given in Table 4.

Table 4. The results of viscosity measurement for PECH

Synthesis	Viscosity [mPas]				
	20°C	30°C	40°C	50°C	60°C
I	21533	6994	2606	1100	-
II	85665	25409	8629	3418	1592
III	256960	48543	17304	6806	3066

For the synthesis I, the measurement at 60°C was not performed, because the sample showed the lower viscosity than the other samples viscosities, and the measuring range exceeded the possibility of the available apparatus. Figure 4 presents the chart of the viscosity dependence on temperature of the investigated sample.

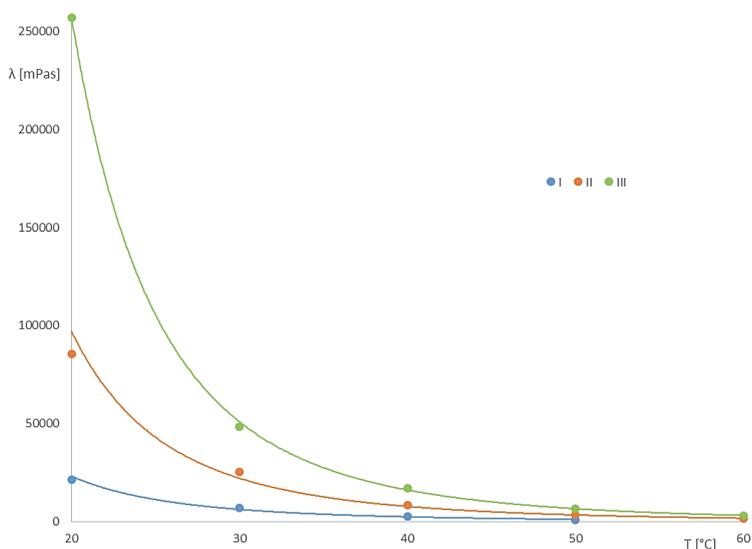


Fig. 4. Dependence of PECH viscosity on temperature

The PECH viscosity shows very high dependence on the temperature change. The highest viscosity has the sample III of the highest molecular mass of polymer but the lowest viscosity has the sample I of the lowest molecular mass. These values correlate with the determined molecular masses of the obtained polymers.

3.2. Glycidyl polyazide

At the second stage of synthesis, the polyepichlorohydrin was subjected to azidation to get the GAP. The reaction was carried out in a heterogenic two-phase system using TBAB as a phase transfer catalyst.

The reactions were conducted with application of the same molecular ratio of the reagents and similar capacities of the syntheses were obtained (of about 90%). The reactions were monitored by means of FTIR spectroscopy. During the reactions, the decay of the band, originating from the C-Cl (743 cm^{-1}) bond and increase in characteristic bands for the azide group at 2092 cm^{-1} were observed. After 24 hours since the moment of the reaction beginning, the changes in signals intensity were not observed. Figure 5 shows the comparison of the PECH spectrum (red line) and the GAP spectrum (blue line).

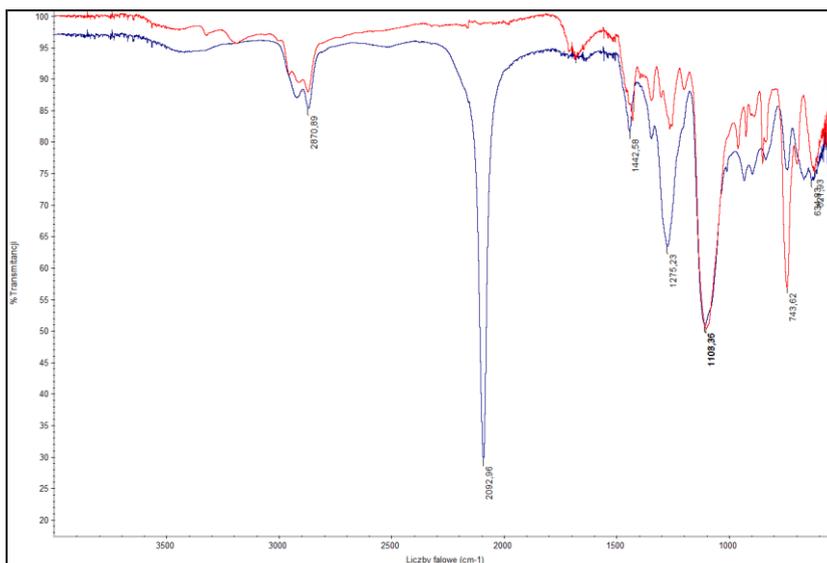


Fig. 5. Comparison of FTIR spectra of PECH and GAP

The obtained GAP was subjected to the analysis. The spectrum from the spectroscopic analysis of the ^1H NMR magnetic nuclear resonance confirmed the GAP production. The analysis results are shown in Fig. 6.

For the azide, characteristic signals of the protons of CH_2N_3 group (c – Fig. 6) can be seen for the shifts within the range of 3.34-3.40 ppm but the protons' signals at ether bounds $-\text{O}-\text{CH}_2-\text{CH}-$ (d – Fig. 6.) can be seen for the value of 1.54 ppm.

The signal, appearing at the value of 5.30 ppm, can suggest the esterification process of II order hydroxyl group (existing at the carbon atom denoted as “a” – Fig. 6) in the polymer chain.

For the obtained azides, also the thermogravimetric analysis was made allowing for determination of the decomposition temperature of the obtained samples. Despite various molecular masses of the obtained polymers, the decomposition curves were similar for all GAP samples.

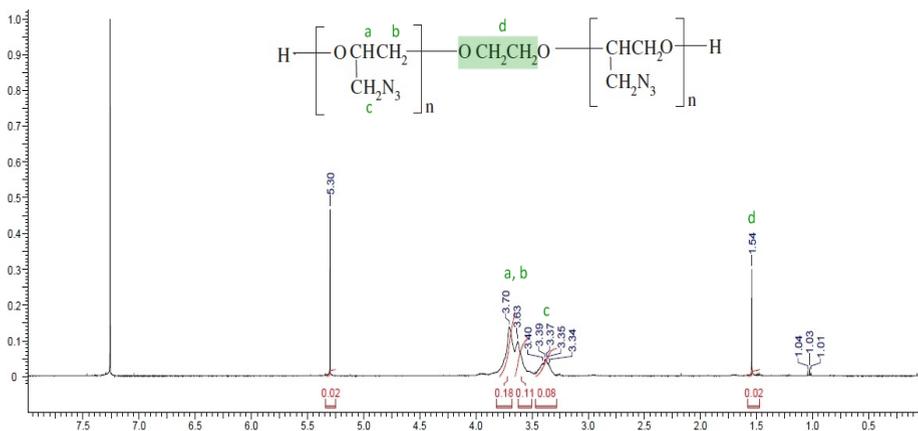

 Fig. 6. ¹H NMR spectrum of GAP

Figure 7 presents exemplary TG and DTG curves for the GAP of the molecular mass of 2200 g/mol.

The thermogravimetric analysis shows that there exist two stages of polymer decomposition. The first stage with the mass loss of about 45% can be connected with exothermic distribution of the N₃ groups. The second stage it is slow decomposition of the remaining chains of the polymer. One can observe that this decomposition is not complete.

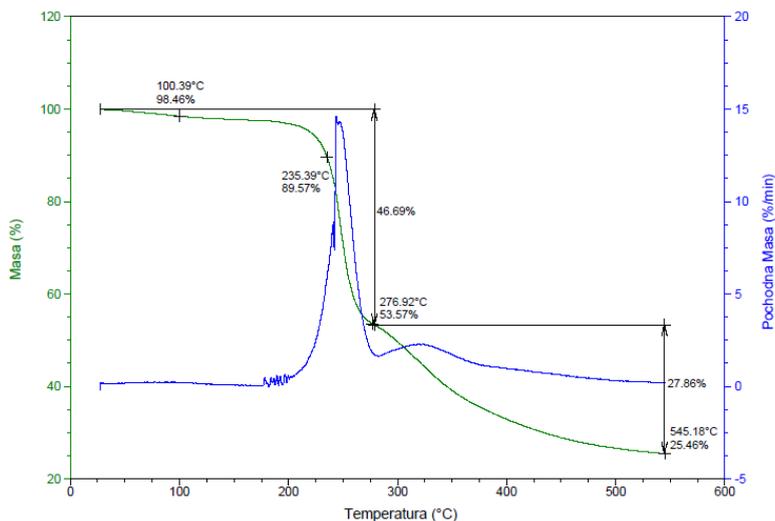


Fig. 7. TG and DTG curves for GAP – 2200 g/mol

It was stated for all the analyses that rapid decomposition of the sample started above the temperature 200°C and the disturbance at the DTG curve, close to this temperature, results from the release of small-molecule components being present in a sample during the measurement.

4. SUMMARY

During the carried-out investigations, the GAPs of various molecular masses were obtained. On the basis of the investigations it was determined that:

- analysis in IR is fast and simple method allowing for checking the course of the ECH azidation process, however, it does not allow for differentiation of the polymers of various molecular masses,
- MALDI-ToF analysis showed lack of cyclic compounds in the product what suggest that reaction of polymerisation has proceeded according to the required mechanism,
- PECH shows high dependence of viscosity on temperature. The higher temperature, the lower value of viscosity,
- the value of viscosity is also dependent on the molecular mass of the ECH polymer. The viscosity increases with the increase in molecular mass of the polymer
- thermogravimetric analysis showed that the GAP decomposition is a multi-stage one. It is supposed that the stage, at which the mass loss is the highest, is connected with the decomposition of N₃ groups,
- GAP is a polymer, the rapid decomposition of which starts above 200°C.

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Synteza wysokoenergetycznego polimeru – poliazydku glicydylu (GAP)

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Streszczenie. Poliazydek glicydylu (GAP) jest jednym z najbardziej znanych lepiszczy energetycznych, znajdujących zastosowanie jako składnik zwiększający kaloryczność paliw raketowych. W artykule opisano syntezę GAP-u pozwalającą na uzyskanie polimeru o różnych masach cząsteczkowych. Zmiana masy cząsteczkowej może wpływać na właściwości otrzymanych związków. Syntezę prowadzono według mechanizmu aktywnego monomeru. Otrzymane produkty scharakteryzowano z wykorzystaniem takich technik, jak: FTIR, GPC, MALDI-ToF, TG i NMR.

Słowa kluczowe: materiały wysokoenergetyczne, energetyczne lepiszcza, GAP