



Research paper / Praca doświadczalna

Analysis of glycidyl nitrate polymerization reaction Badanie reakcji polimeryzacji azotanu glicydylu

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Abstract: Poly(glycidyl nitrate) (PGN) is a high-energetic polymer whose properties are determined by the presence of an $-ONO_2$ explosophoric group. PGN can be obtained by polymerization of glycidyl nitrate (GN) monomers. The preferred polymerization route is via the activated monomer mechanism, due to its two main advantages: narrow molecular mass distribution of the obtained polymer and ability to control the heat generated during the reaction. The study allowed the GN monomer to be obtained as a product of nitration of epichlorohydrin. A series of GN polymerization reactions was conducted under different conditions (temperature, time and reactant amounts). The analysis showed that the lower the catalyst to initiator ratio, the higher the molecular mass of the obtained polymer (PGN). A temperature between 0-10 °C is the optimum temperature for GN polymerization. The longer the GN polymerization time the higher the molecular mass of the PGN. The GN polymerization reaction was scaled up without affecting the molecular mass or other properties of the obtained polymers. The following tests were carried out to determine the basic properties of PGN: GPC, 1H NMR, FTIR, DSC, TG, calorific value, viscosity, sensitivity to friction and impact.

Streszczenie: Poli(azotan glicydylu) (PGN) to wysoce energetyczny polimer, który posiada swoje właściwości dzięki obecności grupy eksplozoforowej $-ONO_2$. PGN otrzymuje się w wyniku polimeryzacji monomeru – azotanu glicydylu (GN). Preferowaną techniką polimeryzacji jest polimeryzacja według mechanizmu aktywowanego monomeru, ze względu na dwie główne zalety: wąski rozkład masy cząsteczkowej otrzymanego polimeru oraz kontrolę wydzielanego ciepła podczas reakcji. W trakcie pracy otrzymano monomer GN w wyniku reakcji nitrowania epichlorohydryny. Następnie wykonano szereg polimeryzacji GN zmieniając temperaturę, czas oraz ilości dozowanych substratów. Podczas badań stwierdzono między innymi, że im mniejszy jest stosunek katalizatora w stosunku do inicjatora tym ciężar cząsteczkowy otrzymanego polimeru (PGN) jest większy. Optymalną temperaturą prowadzenia reakcji polimeryzacji GN jest temperatura z zakresu 0-10 °C. Im dłuższy czas prowadzenia reakcji polimeryzacji GN tym otrzymany PGN ma większy ciężar cząsteczkowy. W trakcie badań zwiększono skalę prowadzonej polimeryzacji GN bez wpływu na ciężary cząsteczkowe otrzymanych polimerów i ich właściwości. W celu poznania podstawowych właściwości otrzymanego PGN wykonano szereg badań: GPC, 1H NMR, FTIR, DSC, TG, pomiar ciepła spalania, pomiar lepkości. Zbadano również wrażliwość uzyskanego polimeru na tarcie i uderzenie.

Keywords: poly(glycidyl nitrate), PGN, glycidyl nitrate, polymerization

Słowa kluczowe: poli(azotan glicydylu), PGN, azotan glicydylu, polimeryzacja

1. Introduction

1.1. High-energy polymers

Cellulose nitrate (nitrocellulose, NC) was the first polymer analysed in detail and qualified as a high-energy polymer. NC had been synthesized between 1845 and 1847 by Christian Friedrich Schonbein and Rudolf Christian Bottger. Since then, new high-energy polymers have significantly contributed to the development of explosive and rocket propellant technology. High-energy polymers are types of polymer characterized by significantly higher calorific value compared to other polymers. The characteristic feature of high-energy polymers is the presence of an explosophoric group in the polymer structure. The main explosophoric groups usually introduced into the polymer structure, often as a side chain, include: nitro group ($-\text{NO}_2$), nitrate group ($-\text{ONO}_2$), halide amine group ($-\text{NF}_2$) and azide group ($-\text{N}_3$) [1].

Poly(glycidyl nitrate) (PGN) was the first energetic pre-polymer studied for use as a binding agent in solid heterogenous rocket propellants. The first studies on PGN were carried out at the Naval Surface Warfare Center (NSWC) in the 1950s. The development of studies on this polymer was delayed due to hazardous monomer synthesis, refining and polymerization processes, however, some studies are still being conducted.

PGN is a high-energy polymer whose properties are determined by the presence of $-\text{ONO}_2$ explosophoric group (nitrate group). PGN is a linear polymer with terminal hydroxyl groups which can be cross-linked with diisocyanates to obtain materials with natural rubber properties. PGN can be obtained by polymerization of glycidyl nitrate (GN) monomers. At room temperature, GN is a yellow liquid with explosive properties [2]. Figures 1 and 2 show the constitutional formulae of PGN and GN, respectively.

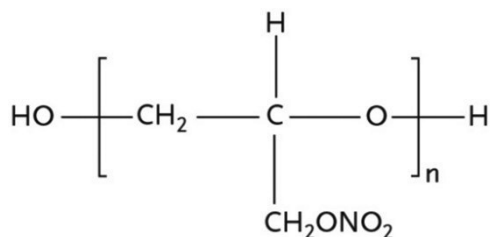


Figure 1. Constitutional formula of PGN

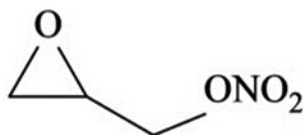


Figure 2. Constitutional formula of GN

1.2. Synthesis of GN

The first developed and the most dangerous method of obtaining GN is esterification of glycerine with nitric acid (HNO_3) to obtain 1,2,3-propanetriol, 1,2-dinitrate (dinitroglycerin), and epoxy ring closure with a strong base. The reaction is highly exothermic, takes 8 h with an 80% yield and a purity of 50%. In the first dinitroglycerin synthesis stage, a 1,3-dinitrooxypropan-2-yl nitrate (trinitroglycerine) by-product, which contaminates the main product, is also formed. The second reaction stage can be implemented in two ways: with the intermediate product (dinitroglycerine) or without the intermediate product [3].

Another method of obtaining GN is based on nitration of epichlorohydrin and consists of two stages. The first stage involves forming an epoxy ring by nitration of epichlorohydrin and substituting chlorine with a nitrate group. In the second stage, the ring is closed with a strong base. The yield of the first stage

is low when using dilute HNO_3 only, and can be improved by adding 5-aminotetrazole nitrate. The authors [4] explain the effects of 5-aminotetrazole nitrate as a catalyst and a co-nitrating agent in obtaining GN in moderate conditions and with good yield. A mechanism of the reaction is also suggested in this article. The method allows GN to be obtained with 96% purity and an 81% yield [4].

Another method of obtaining GN is a two-stage synthesis of glycidol using a tosyl derivative. Glycidyl tosylate is obtained at the first stage in the reaction of glycidyl with *p*-tosyl chloride and triethylamine (base). The reaction is conducted at 30 °C, and the yield at this stage is 90%. At the second stage, the tosyl group is substituted by the nitrate group from sodium nitrate. The reaction is conducted at 85 °C in a polar solvent – acetonitrile and in the presence of a phase-transfer catalyst (PTC) – tetrabutylammonium nitrate. The phase-transfer catalyst is required due to the low solubility of sodium nitrate in acetonitrile. The yield of this reaction is 76% [5].

Another method of synthesizing GN is a direct esterification of glycidol with dinitrogen pentoxide in dichloromethane. The reaction involves side reactions yielding different products and is a continuous reaction conducted in a suitable flow reactor. The reactor improves the process safety, yield and purity of the product. The reaction is conducted at –10 °C and the yield is 97% [6].

GN can be polymerized using two methods:

- cationic polymerization following the activated monomer mechanism (AMM), and
- cationic polymerisation following the active chain end (ACE) mechanism.

The preferred polymerization route is via the activated monomer mechanism due to its two main advantages: narrow molecular mass distribution of the obtained polymer and ability to control the heat generated during the reaction.

The activated monomer mechanism has its name from a protonated monomer which reacts after each propagation stage with the growing polymer chain. The monomer is activated after each chain propagation stage. A fragment of the initiator – 1,4-butanediol for PGN synthesis – is at the centre of the polymer chain. The obtained polymer is terminated with hydroxyl groups, which can be used to cross-link the polymer with diisocyanates. The mechanism of the activated monomer is presented in [7].

Two key factors in the AMM mechanism include maintaining at least 10-fold excess of hydroxyl groups in relation to the catalyst and slowly adding the monomer solution for 16 to 40 h. The first factor ensures that the protonated monomer reacts with the excess hydroxyl groups. The second factor – slow adding the monomer solution – additionally suppresses the propagation following the ACE mechanism, since the monomer is fed with a rate which does not allow the activated monomer to react with a non-protonated monomer. In other words, the monomer feeding rate must be lower than the monomer protonation rate and the rate of its reaction with the hydroxyl group of the formed polymer chain.

As a result, linear PGN chains terminated with hydroxyl groups are formed. There are also some disadvantages to this method. Firstly, the method mostly yields secondary hydroxyl groups as a result of an electrophilic attack of an oxygen atom on a hydroxyl group of the existing chain. Secondly, achieving a molecular mass greater than 3500 (M_n) is very difficult, probably due to impurities in the monomer, alcohol or catalyst or accidental moisture in the reactor. Thirdly, the polymerization reaction yield is approximately 80%.

The ACE mechanism can be used to polymerize GN, but it is not recommended. The polymerization using this mechanism shows a very low yield of product with varying molecular mass. In the ACE mechanism, the active chain end of the formed polymer reacts with the monomer in the reaction system. Side reactions may occur during the main reaction and result with termination thereby ending the polymerization. An additional disadvantage of GN polymerization using the ACE mechanism is the lack of control over the generated heat which, in case of epoxy compounds, may lead to explosion.

Most often, GN polymerization proceeds in nitrogen at 10–25 °C with a catalyst (Lewis acid) and 1,4-butanediol as an initiator. A cationic polymerization uses a suitable organic solvent, *e.g.* methylene chloride or chloroform. The end product is a yellow, viscous liquid. The yield is approximately 80% [7].

The purpose of the study was the optimization of the reaction of glycidyl nitrate, GN, polymerization and analysis of the basic properties of PGN, obtained under determined optimum conditions.

2. Materials and analytical methods

Analytical grade substances were used in the study. The distribution of molecular mass was analysed using an Agilent 1260 Infinity LC system with an RID detector. A PL Gel 3 μ m miniMix-E 250 \times 4.6 mm packed column for molecular mass between 500-20,000 g/mol, THF – 0.3 cm³/min as a solvent and 50 °C thermostat temperature, were used. Fourier-transform infrared spectroscopy (FTIR) was carried out at room temperature using a Nicolet 6700 Thermo Scientific spectrometer with an ATR accessory. ¹H NMR spectra were recorded using a Varian Gemini 400 with deuterated chloroform (CDCl₃) as a solvent. The density was measured using a Micromeritics Accu Pyc II 1340 Series Pycnometer with an accuracy of 0.01 g/cm³. The thermogravimetric analysis was carried out with a SDT Q600 (TA Instruments) in an inert gas (nitrogen) atmosphere. The end temperature was 550 °C at a 10 °C/min increase rate. The DSC analysis was carried out using a Q2000 at temperatures from –160 to 100 °C. The mass of specimen for glass transition temperature measurements was approximately 2.5 mg, and the mass for decomposition temperature measurement was 5 mg. The rate of temperature increase was 10 °C/min. The friction sensitivity of the specimen was tested on a Julis Peters type device. The sensitivity was defined as a lower limit of sensitivity – a maximum height at which a single explosion occurred (one in six test). The impact sensitivity tests were carried out using a Kast drop-hammer and a 2 kg weight. The sensitivity was defined as a lower limit of sensitivity – a maximum height at which a single explosion occurred (one in six tests). The calorific value was measured using a KL-12Mn2 calorimeter. The specimen was combusted in a pure oxygen atmosphere. The viscosity was measured using a Brookfield DV2T viscometer with a small specimen attachment, spindle type: SC4-13R (P), 7.1 cm³ vessel. The measurement was made from low to high speed at 25 and 50 °C.

3. Synthetic preparation of GN

The reaction system includes a 1000 cm³ three-neck flask, a magnetic stirrer, a dropper and a thermometer. 11.1 g of 5-aminotetrazole nitrate was added to the flask. 180 cm³ 45% HNO₃ solution was prepared in a beaker and transferred to the flask. The dropper was filled with 138 g epichlorohydrin and the solution was introduced over 60 min at 20 \pm 2 °C, into the flask. After addition of the epichlorohydrin, the solution was stirred for 140 min and then cooled to 0 °C. 120 g NaOH in 150 cm³ water was added to the dropper and introduced over 45 min at a temperature not exceeding 15 °C. The solution was stirred for 1 h. The mixture was transferred to a separator where the organic phase was separated from the aqueous phase. The product from the aqueous phase was extracted 3 times with methylene chloride. From the combined organic phases, the solvent was evaporated in a vacuum evaporator to obtain GN, a colourless liquid, as a residue.

GN was obtained using a safe and simple nitration of epichlorohydrin. The method involves two stages, first – opening the epoxy ring by nitration of epichlorohydrin and second – closing the ring with a strong base. All the reactants are commonly available in the chemical industry and are relatively cheap. The reaction progresses under moderate conditions, and the temperature does not exceed 20 °C. The purity of the obtained GN is satisfactory at 96%. The nitrate does not require further refinement, and the reaction time is short.

4. GN polymerization and PGN refining

The reaction system included a three-neck 1000 cm³ flask, a mechanical stirrer and a peristaltic pump. The reaction mixture was kept at a fixed temperature of 10 °C. 1484 μ l of 1,4-butanediol dissolved in 12.7 cm³ of dried chloroform and 508 μ l catalyst – boron trifluoride etherate (BF₃·Et₂O) were added to the flask. The mixture was stirred for 10 min. 102 g GN and 305 g dried chloroform were added to the flask. The GN solution was introduced into the chloroform for 35 h (at a 10 cm³/h flow rate). After addition, the mixture was stirred for 2 more days. After polymerization, 300 cm³ of saturated sodium bicarbonate was prepared and added to the reaction flask. The mixture was stirred for 30 min, and the solution was added to the separator to separate the organic phase and dried over magnesium sulphate (MgSO₄). The solvent was partially distilled in the vacuum

evaporator to 100 cm³. A mixture of 300 cm³ methanol and 100 cm³ water was prepared in a 2000 cm³ beaker. The magnetic stirrer was placed inside the beaker and the mixture was stirred. A partially distilled PGN and chloroform mixture was introduced into the solution. Methanol with water was decanted from the polymer and the refined polymer was dried over MgSO₄. The remaining solvent was distilled in the vacuum evaporator. A colourless, viscous liquid was obtained.

To optimize the polymerization of GN, a series of reactions was carried out by changing not only the amount of reacting substances but also the polymerization times and temperature.

5. Results and discussion

5.1. Synthetic preparation of GN

¹H NMR analysis was carried out for the obtained GN. Figure 3 shows the results of the analysis. The spectrum shows a double peak from the hydrogen atom in the -CH₂ONO₂ group at $\delta = 4.3$ and 4.7 ppm. The signal at $\delta = 3.2$ ppm is from a hydrogen atom in the C-H group in the ring, and a multiplet within $\delta = 2.7$ -2.9 ppm is from the hydrogen atoms in CH₂ group in the ring. The signal at $\delta = 3.5$ ppm is from the contaminants. ¹H NMR analysis shows that the obtained substance is in fact GN.

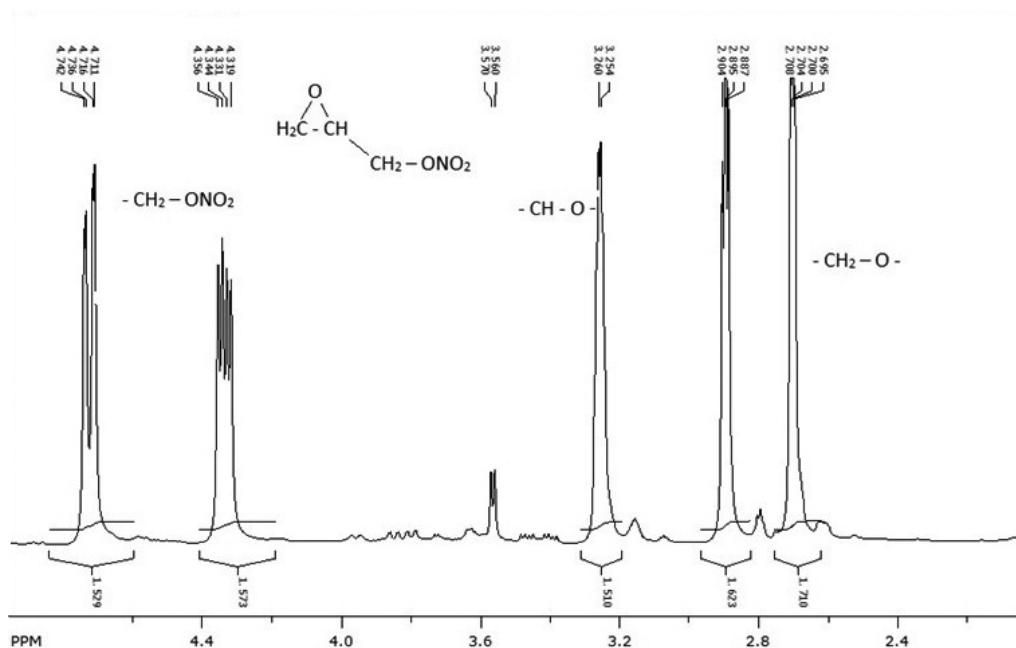


Figure 3. ¹H NMR spectrum of the obtained GN

HPLC analysis (Figure 4) and FTIR analysis (Figure 5) were also carried out on the obtained GN. HPLC shows a GN retention time of 2.53 min. The monomer purity was 96%. The FTIR spectrum shows clear bands at 1627 and 1278 cm⁻¹ indicating the presence of a nitrate group. A band at 966 cm⁻¹ from the stretching vibrations in the C-O bond can also be observed. A strong stretching vibration signal for the O-N bond can also be observed at 849 cm⁻¹. A band with an average band intensity at 757 cm⁻¹ corresponds to the deformation vibrations of a -ONO₂ group.

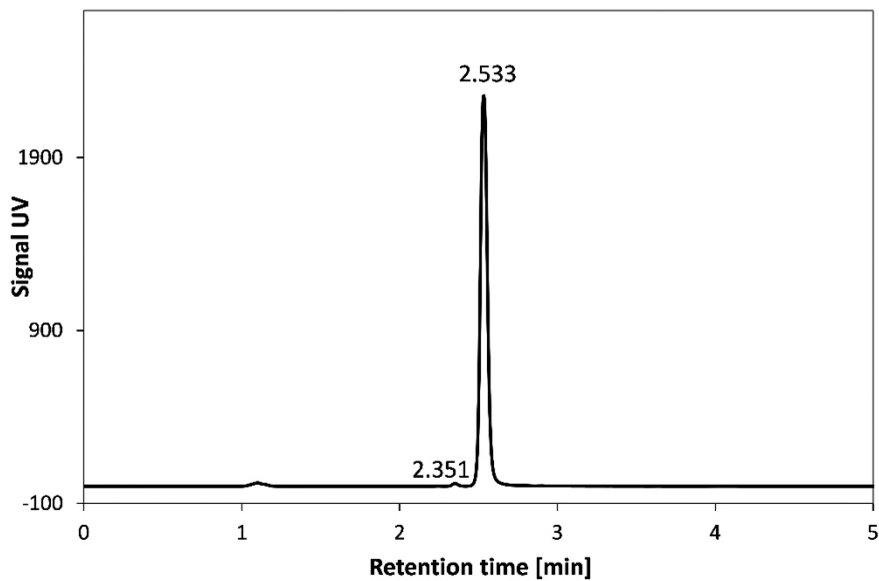


Figure 4. HPLC chromatogram for GN

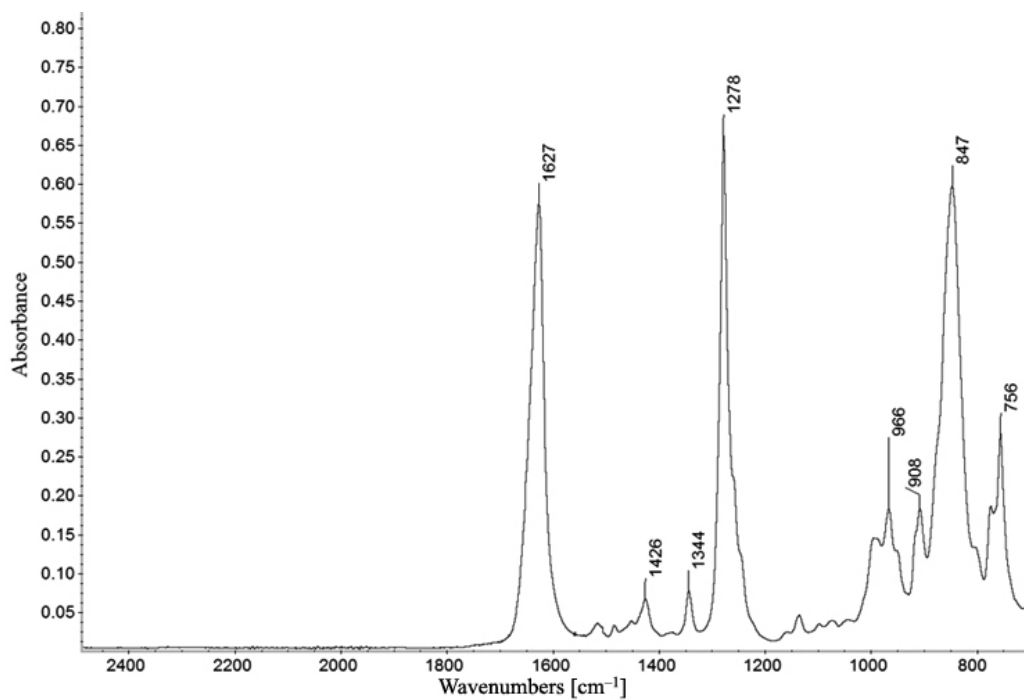


Figure 5. FTIR spectrum for GN

5.2. Polymerization of GN

5.2.1. Effect of catalyst amount and initiator type on molecular mass of PGN

The effect of catalyst amount ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) and initiator type on the molecular mass of obtained PGN, was analysed. The reactions were carried out at the same temperature (0°C) for 4 days, with the monomer addition time of approximately 6 h. The other reacting substances were added in the same amounts for all reactions. The effect of change in catalyst amount was evaluated for two initiator types: 1,4-butanediol and ethylene glycol. Table 1 shows the results.

Table 1. The effect of changes in catalyst amount and initiator type on the molecular mass of obtained PGN

Catalyst amount [μl]	Initiator type	Yield of reaction [%]	Mole ratio GN:catalyst:initiator	M_n [g/mol]	M_w [g/mol]	D
100	1,4-butanediol	82.2	1:0.02:0.02	749	1520	2.03
	ethylene glycol	88.6		786	1513	1.92
50	1,4-butanediol	88.0	1:0.01:0.02	1101	1784	1.62
	ethylene glycol	85.0		856	1803	2.11
25	1,4-butanediol	78.8	1:0.005:0.02	823	2068	2.51
	ethylene glycol	86.6		1020	2079	2.04

M_n – number-average molecular mass, M_w – weight-average molecular mass, D – polydispersity factor

The polymers with a number-average molecular mass M_n from 749 to 1101 g/mol and weight-average molecular mass M_w from 1513 to 2079 g/mol were obtained as a result of polymerization under the conditions specified above. The polydispersity factor was from 1.62 to 2.51. The highest molecular mass was obtained for the polymerization at the mole ratio of GN:catalyst:initiator of 1:0.005:0.02 both for 1,4-butanediol and ethylene glycol used as the initiator.

The results show that the lower the catalyst amount compared to the initiator amount, the higher the molecular mass of obtained polymer (PGN). This relationship is valid both for 1,4-butanediol and ethylene glycol used as the initiator. The initiator type does not affect the polymerization of GN.

The polydispersity factors are close to 2 indicating high distribution of molecular masses in obtained polymers and do not depend on the catalyst amount and the initiator type.

The yields are between 78-88%. No relationship between the amount and type of catalyst and the yield of reaction can be observed. The differences may result from the apparatus preparation procedures, moisture content in reactants and losses in polymer processing.

5.2.2. Effect of initiator amount on molecular mass of PGN

To analyse the effect of initiator amount on the molecular mass of PGN, three reactions with three different initiator amounts were conducted. 1,4-butanediol was used as the initiator. The reactions were conducted with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as a catalyst at the same temperature (0°C). The monomer addition time was approximately 6 h. The catalyst to GN ratio was the same for all reactions. Table 2 shows the test results.

Table 2. The effect of initiator amount on the molecular mass of PGN

Initiator amount [μl]	Mole ratio GN:catalyst:initiator	Yield of reaction [%]	M_n [g/mol]	M_w [g/mol]	D
146	1:0.005:0.02	89.1	851	2044	2.40
73	1:0.005:0.01	82.0	514	1086	2.11
36.5	1:0.005:0.005	85.8	574	1308	2.28

M_n – number-average molecular mass, M_w – weight-average molecular mass, D – polydispersity factor

The polymers with a number-average molecular mass M_n from 514 to 851 g/mol and weight-average molecular mass M_w from 1086 to 2044 g/mol were obtained as a result of polymerization under the conditions specified above. The polydispersity factor was from 2.11 to 2.40. The highest molecular mass was obtained during polymerization with the largest amount of initiator used. Mole ratio GN:catalyst:initiator was 1:0.005:0.02. At lower amounts of initiator, a polymer with a significantly lower average molecular mass was obtained. Similar results were obtained at catalyst to initiator mole ratios of 0.005:0.01 and 0.005:0.005. The difference in molecular masses of the obtained polymers may have different causes, *e.g.* moisture content in the reactor. Analysis of the results shows that the highest yield and the highest molecular mass were obtained in reaction with the highest excess of initiator, compared to the amount of catalyst. Under those conditions, GN polymerization mainly follows the AMM mechanism corresponding to data available in the literature [7]. The study validates the need to use a large excess of the initiator compared to the catalyst.

5.2.3. Effect of polymerization temperature on molecular mass of PGN

The effect of temperature on the yield and the molecular mass of the product, was analysed in the reactions shown in Table 3. GN polymerization temperature was changed from -20 to 20 °C. 1,4-butanediol was used as an initiator. The reactions were conducted with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as a catalyst. GN to catalyst and initiator ratio was identical for all reactions at 1:0.005:0.02. The polymerization took 4 days to complete.

Table 3. The effect of polymerization temperature on the molecular mass of PGN

Temperature [°C]	Yield [%]	M_n [g/mol]	M_w [g/mol]	D
-20	No reaction			
0	89.1	851	2044	2.40
10	86.9	1246	2018	1.62
20	79.0	578	1009	1.74

M_n – number-average molecular mass, M_w – weight-average molecular mass, D – polydispersity factor

Polymers with a number-average molecular mass M_n from 578 to 1246 g/mol and weight-average molecular mass M_w from 1009 to 2044 g/mol were obtained as a result of polymerization under the conditions specified above. The polydispersity factor was from 1.62 to 2.40. Polymerization did not proceed at -20 °C, and the product only contained an unreacted monomer. The analysis showed that depending on the GN polymerization temperature, the polymers show different polydispersity factors. The changes are not linear, but rather random, being affected by factors other than temperature. The higher the polydispersity factor, the higher the distribution of molecular mass of the obtained polymer, *i.e.* long chains and short chains are present. Side reactions may occur during the main reaction and result in termination and ending of the polymerization. This might be caused by impurities in the monomer, initiator or catalyst, moisture in the reactor and side ring formation reactions.

The analysis showed that changes in temperature significantly affect polymerization of GN. At low temperatures, the reaction does not occur, and at high temperatures, the average molecular mass of the polymer is reduced which indicates that short polymer chains are formed. A temperature of between 0-10 °C is optimum for GN polymerization.

5.2.4. Effect of polymerization time on molecular mass of PGN

In subsequent polymerization reactions, the effect of polymerization time on the yield of reaction and the molecular mass of the product were analysed. The reactions were conducted at 0 °C with 1,4-butanediol as an initiator. The reactions were carried out with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as a catalyst. GN to catalyst and initiator ratio was identical for all reactions at 1:0.005:0.02. Table 4 shows the results.

Table 4. The effect of polymerization time on the molecular mass of PGN

Polymerization time [days]	Yield of reaction [%]	M_n [g/mol]	M_w [g/mol]	D
4	92.5	829	1961	2.36
2	88.5	760	1846	2.43
1	78.7	633	1490	2.35

M_n – number-average molecular mass, M_w – weight-average molecular mass, D – polydispersity factor

Polymers with a number-average molecular mass M_n from 633 to 829 g/mol and weight-average molecular mass M_w from 1490 to 1961 g/mol, were obtained as a result of polymerization under the conditions specified. The polydispersity factor was from 2.35 to 2.43. The highest molecular mass was obtained as a result of polymerization lasting 4 days. Analysis of the results shows that the longer the GN polymerization time, the higher the molecular mass of PGN. The polydispersity factors of 2.3-2.4 indicate a high distribution of molecular masses in the obtained polymers which is not dependent on the reaction time.

5.2.5. Scaling up

After determining the optimum polymerization conditions, the reaction of GN polymerization was scaled up. Table 5 shows the effect of scaling up the reaction of GN polymerization on the yield and molecular mass of the polymer. The reactions were conducted at 0 °C with 1,4-butanediol as an initiator using the determined optimum parameters. The reactions were conducted with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as a catalyst. GN to catalyst and initiator ratio was identical for all reactions at 1:0.005:0.02. The reaction was completed after 4 days.

Table 5. The effects of scaling up the reaction of GN polymerization

GN mass [g]	Yield of reaction [%]	M_n [g/mol]	M_w [g/mol]	D
5	78.8	823	2068	2.51
10	92.5	829	1961	2.36
100	76.9	1246	2018	1.62

M_n – number-average molecular mass, M_w – weight-average molecular mass, D – polydispersity factor

Polymers with a number-average molecular mass M_n from 823 to 1246 g/mol and weight-average molecular mass M_w from 1961 to 2068 g/mol, were obtained as a result of polymerization under the conditions specified. The polydispersity factor was from 1.62 to 2.51. PGN obtained at a 100 g scale was refined and contained a smaller number of short chains as indicated by the lower polydispersity factor compared to the polymers obtained at a smaller scale without refining. The procedure is detailed in the experimental section. The refining method used, allowed a polymer with a number-average molecular mass M_n of 1246 g/mol and a polydispersity factor of 1.62, to be obtained.

The experiment verified that the obtained polymers show similar weight-average molecular masses. Changing the scale does not affect the molecular masses of the obtained polymers. Further scaling up should not affect the quality of polymerization.

5.3. Analysing the properties of obtained PGN

PGN obtained at a 100 g scale after refining, was further analysed. Table 6 shows the main properties of PGN obtained under the determined optimum conditions.

Table 6. The main properties of PGN obtained in the optimum conditions

Properties	PGN
Molecular mass M_w [g/mol]	2018
Dispersion D	1.62
Glass transition temperature [°C]	-32.3
Decomposition onset temperature [°C]	194.8
Maximum decomposition temperature [°C]	211.5
Decomposition enthalpy (DSC) [J/g]	2846
Calorific value [J/g]	14458
Viscosity at 25 °C [cP]	12100
Viscosity at 50 °C [cP]	860
Sensitivity to friction (lower sensitivity limit) [N]	110.4
Sensitivity to impact (lower sensitivity limit) [J]	20.6

The PGN specimen was also analysed using ^1H NMR (Figure 6) and FTIR (Figure 7) techniques. Figure 6 shows the ^1H NMR spectrum of PGN obtained under the determined optimum conditions. The signal from the hydrogen atoms in the $-\text{CH}_2\text{ONO}_2$ group in the side chain can be observed at $\delta = 4.45\text{--}4.66$ ppm. The signals $\delta = 3.44\text{--}3.83$ ppm are from the hydrogen atoms in the $-\text{CH}_2\text{CHO}-$ groups in the main polymer chain. The signals $\delta = 1.15\text{--}1.62$ ppm are from the hydrogen atoms of alkyl groups in the middle of the chain from 1,4-butanediol (initiator). Figure 7 shows the FTIR spectrum of PGN obtained under the determined optimum conditions. The PGN spectrum shows intensive bands at 1622 and 1257 cm^{-1} indicating the presence of a nitrate group.

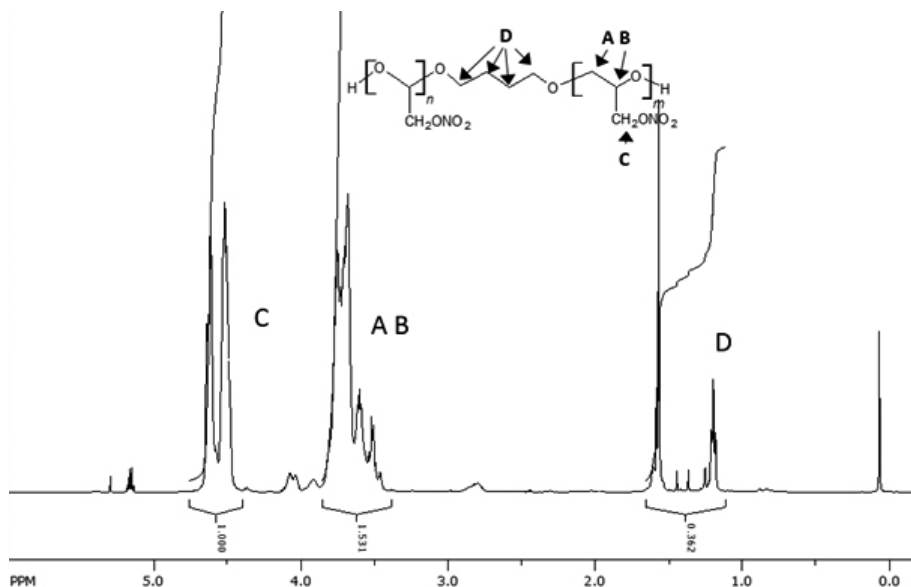


Figure 6. ^1H NMR spectrum of obtained PGN

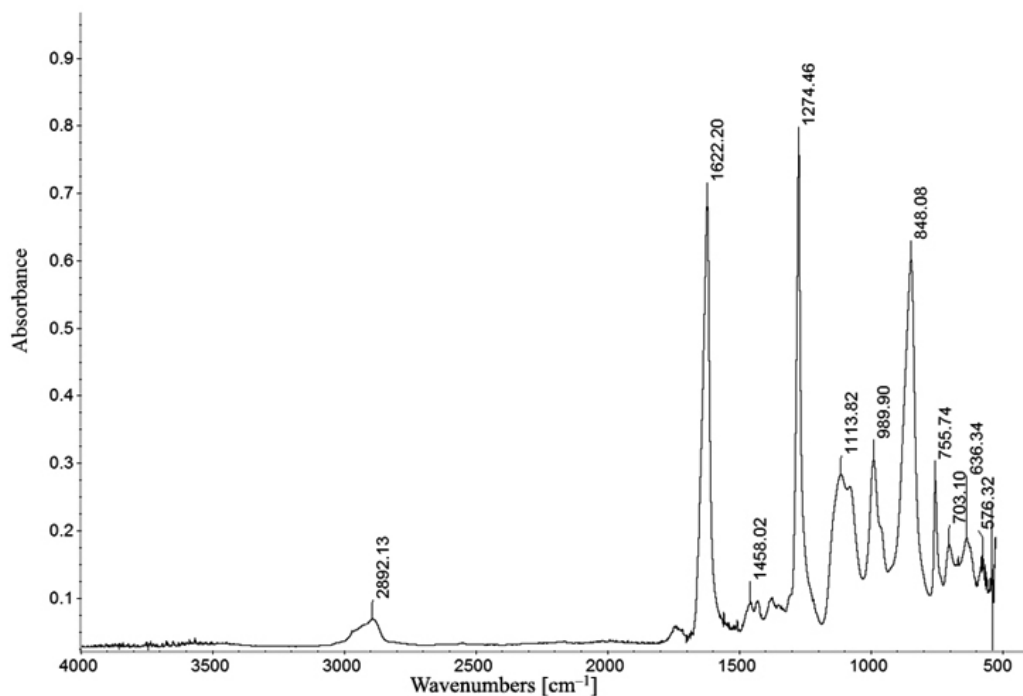


Figure 7. FTIR spectra of obtained PGN

DSC and DSC-TGA analyses were also conducted to determine the glass transition temperature and decomposition temperature of PGN. Figure 8 shows the DSC curve. The glass transition temperature of the PGN sample is -32.3 °C. The analysed PGN shows a single glass transition temperature indicating that the obtained PGN is homogenous, *i.e.* with a single polymer structure present. Figure 9 shows the thermogravimetric analysis conducted to determine the decomposition temperature and the enthalpy of the PGN sample decomposition. The curve T_g for the PGN sample shows a single-stage mass loss. The mass loss is 80%, and the remaining part does not decompose up to 500 °C. Based on the DSC curve, the decomposition is exothermic and is a single-stage process. The maximum decomposition temperature is 211 °C, and the decomposition enthalpy is 2646 J/g.

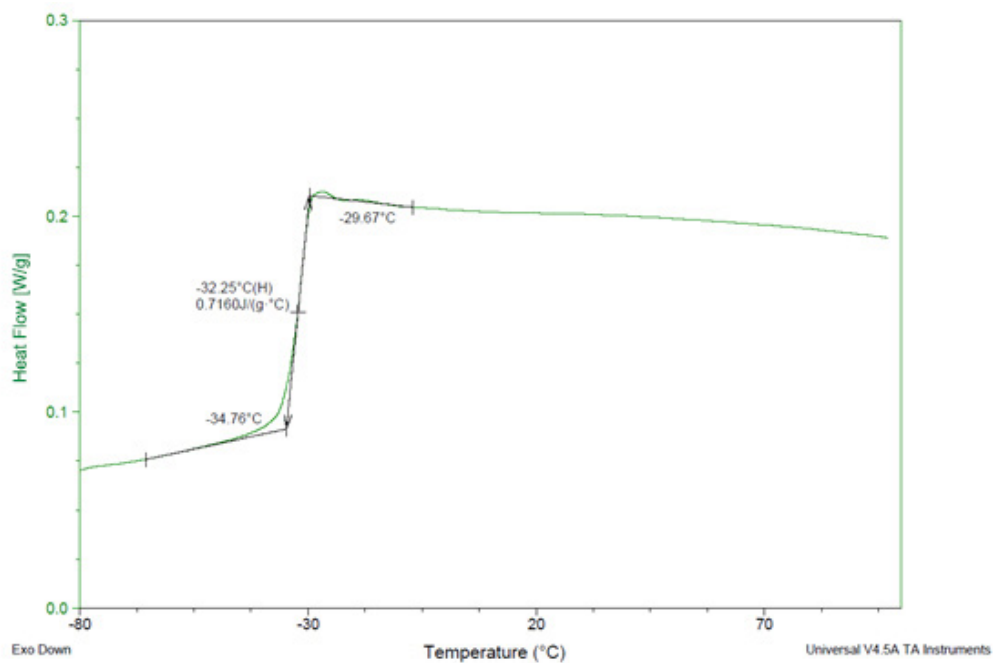


Figure 8. The DSC curve of obtained PGN

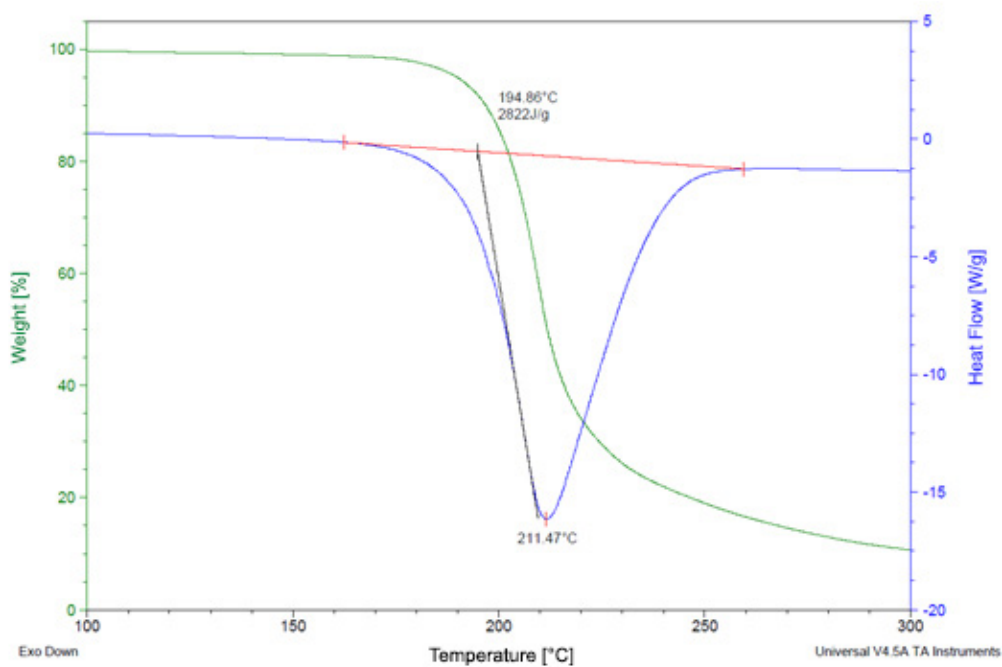


Figure 9. The results of thermogravimetric analysis of obtained PGN

6. Summary

The first stage of the analysis involved obtaining a monomer in a two-stage nitration of epichlorohydrin. FTIR and ^1H NMR analysis has verified the structure of the obtained glycidyl nitrate. A series of GN polymerization reactions was carried out. Polymerization temperature and time, and the amount of reacting substances were changed. The highest yield of reaction and the highest molecular mass were obtained during polymerization with the largest excess of initiator compared to the catalyst. A temperature between 0-10 °C is optimum for GN polymerization. Both higher and lower polymerization temperatures affect the molecular mass of PGN. The longer the GN polymerization time, the higher the molecular mass of PGN. Scaling the GN polymerization from 5 to 100 g does not affect the molecular masses of obtained polymers. Further scaling up should not affect the polymerization process.

PGN is one of the most promising energetic binding agents for rocket propellants and explosive compositions. A comparison of PGN with other known high-energy polymer (poly(glycidyl azide), GAP) shows its higher sensitivity to thermal and mechanical stimuli and higher energetic properties.

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