



## Synthesis and Characterization of Polyethylene Glycol Dinitrates

Robert MATYÁŠ\*, Jakub ŠELEŠOVSKÝ, Zdeněk JALOVÝ  
and Jana ROHÁČOVÁ

*Institute of Energetic Materials, Faculty of Chemical Technology,  
University of Pardubice,  
Studentska 95, CZ-532 10 Pardubice, Czech Republic  
\*E-mail: robert.matyas@upce.cz*

**Abstract:** Polyethylene glycol dinitrates (PEGN) with molecular weights between 400 and 20 000 g·mol<sup>-1</sup> were prepared from polyethylene glycols by esterification with nitric acid/sulfuric acid in dichloromethane. The products were characterized by gel permeation chromatography. The yield of PEGN increases with increasing reaction temperature (0-40 °C) however large liberation of nitrogen oxides was observed at 40 °C. No influence of reaction temperature (0-40 °C) on the cleavage of the polyethylene glycol chain during esterification was observed. The dependence of melting point on the molecular weight of PEGN was determined. Polyethylene glycol dinitrates with molecular weights  $M_n$  above 454 are not sensitive to impact. Heat of combustion of PEGN increases with increasing molecular weight. All samples tested decompose in a similar way during thermal exposition.

**Keywords:** Polyethylene glycol dinitrate, synthesis, properties, decomposition, kinetic of decomposition

## Introduction

Nitrate esters, among them ethylene glycol dinitrates (Figure 1), are powerful explosives, and have been produced on an industrial scale for a long time [1]. Only the first three ethylene glycol dinitrates are extensively used in energetic materials compositions. Ethylene glycol dinitrate (Figure 1,  $n = 1$ ) has been widely used as a component of gelatinous industrial explosives for almost hundred years [2, 3]. Diethylene glycol dinitrate (Figure 1,  $n = 2$ ) has been used as a component

of double base propellants and rocket propellants. Triethylene glycol dinitrate (Figure 1,  $n = 3$ ) has lower volatility than diethylene glycol dinitrate and has many uses in explosive compositions [4, 5], e.g. for low calorific double base propellants [6]. Triethylene glycol dinitrate has very important properties, such as good chemical stability, low impact sensitivity and the ability to gelatinize nitrocellulose [6].



**Figure 1.** Structure of ethylene glycol dinitrates.

The explosive properties of ethylene glycol dinitrates decrease with the length of their chain due to the proportionally lower content of the energetic nitroxy groups in the molecule. Nevertheless, these less energetic ethylene glycol dinitrates were expected to be useful for low calorific double base propellants or as a deterrent for the surface layer of smokeless powders. But relatively high solubility of polyethylene glycol dinitrates (molecular weight between 400 and 20 000  $\text{g}\cdot\text{mol}^{-1}$ ) in water disqualifies these compounds from this application [7]. However, these esters can be utilized as easily synthesised intermediates for other derivatives of polyethylene glycols (e.g. polyethylene glycol diazides) [8].

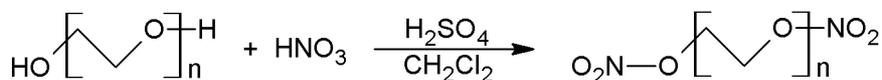
Although the higher ethylene glycol dinitrates ( $n > 3$  in Figure 1) have been known for many years [9], they have not been studied as extensively as the first three members. Aubertein [10] studied the properties of ethylene glycol dinitrates – from monoethylene glycol dinitrate through to heptaethylene glycol dinitrate. He prepared these esters by the esterification of the relevant ethylene glycol using a mixture of nitric acid/sulfuric acid. Wilson and Frankel [8] prepared some higher ethylene glycol dinitrates from polyethylene glycols of molecular weight from 200 to 400  $\text{g}\cdot\text{cm}^{-3}$ . The polyethylene glycol dinitrates thus prepared were not studied in detail, but they were used as intermediates for the preparation of polyethylene glycol diazides.

The purpose of this study is to determine the important properties of polyethylene glycol dinitrates for their use in practical applications.

## Experimental

**Materials.** Starting polyethylene glycols were purchased from the Aldrich company except for polyethylene glycol 6 000 (Merck) and polyethylene glycol 20 000 (Fluka).

**Synthesis.** All polyethylene glycol dinitrates were prepared by the method used by Wilson and Frankel [8]. Polyethylene glycols were esterified using nitric acid/sulfuric acid in the presence of dichloromethane (Figure 2). The reaction was carried out at 5-10 °C. The amount of dichloromethane in the reaction mixture was increased in comparison to the published value [8] in order to reduce the viscosity of the dichloromethane phase, especially in the case of polyethylene glycols with higher molecular weights. After the esterification was completed, the aqueous phase was extracted with fresh dichloromethane. Collected organic phases were washed with water, aqueous sodium bicarbonate and finally with water again to obtain a neutral pH. The time required for water/dichloromethane separation phases increased with increasing molecular weight of the polyethylene glycol dinitrates. The product was isolated by evaporation of dichloromethane *in vacuo*.



**Figure 2.** Synthesis of polyethylene glycol dinitrates.

The influence of reaction temperature on PEGN yield and on the potential fragmentation of the molecule chain was studied for polyethylene glycol dinitrate prepared from polyethylene glycol 1500. Esterification was carried out at reaction temperatures of 10, 20, 30 and 40 °C.

**Gel permeation chromatography.** The molecular weights of the starting polyethylene glycols and resulting polyethylene glycol dinitrates were determined by gel permeation chromatography. An Alliance 2695 system with 2414 refractive detector (both from Waters) was used. Two PLgel Mixed-E x 7.5 (Waters) columns were used for separation, with tetrahydrofuran as a mobile phase with a flow rate of 1 mL·min<sup>-1</sup>. The concentration of measured samples was 0.3%, the injection volume was 100 µL. Ten polyethylene glycols standards (Polymer Laboratories) with molecular weights in the range 106-22 000 g·mol<sup>-1</sup> were used for calibration.

**Impact sensitivity.** The BAM fallhammer apparatus, produced by Reichel and Partner was used for determination of impact sensitivity using a 10 kg hammer. Both piston and cylinders were produced by OZM Research. Only the samples prepared from polyethylene glycol 400 and 950-1050 were subjected to the impact sensitivity test.

**Heat of combustion.** Heat of combustion of the prepared PEGN was measured using an MS-10A combustion calorimeter (Laget) in an oxygen atmosphere (pressure of oxygen was 2 MPa, sample mass was approx. 0.6 g). The

calorimeter was calibrated using benzoic acid (heat of combustion 26 434 J·g<sup>-1</sup>).

**Kinetics of decomposition.** The kinetics of the decomposition reaction of polyethylene glycols dinitrates was determined using the modified vacuum stability test. The samples were placed into test tubes, evacuated (below 1 kPa) and heated. The pressure of decomposition gases was monitored at one minute intervals. Several isothermal runs were carried out for each sample; temperatures were in the range 150-175 °C. Decomposition of end nitrogroups was assumed and the sample mass was varied to have the end pressure in a suitable range (70-130 kPa). Activation energies and preexponential factors were determined by the isoconversional method.

## Results and Discussion

**Synthesis.** The yields of polyethylene glycol dinitrates (PEGN) were in the range 58-88% (see Table 1). Significant losses of product occurred during the washing process due to the high solubility of all polyethylene glycol dinitrates in water. The influence of reaction temperature (0, 10, 20, 30 and 40 °C) on PEGN yield was investigated for PEGN prepared from polyethylene glycol 1500. The yield of PEGN increases with increasing reaction temperature (Table 2). However large liberation of nitrogen oxides was observed at 40 °C.

**Table 1.** Yields and melting temperatures of polyethylene glycol dinitrates

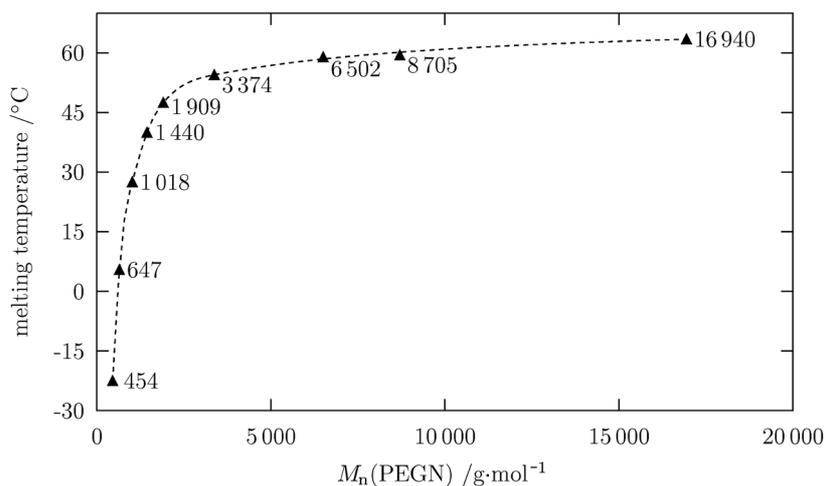
Trade name of starting polyethylene glycol	Yield [%]	Melting temperature [°C]
Polyethylene glycol 400	88	-23 to -22
Polyethylene glycol 600	85	5 - 6
Polyethylene glycol 950-1050	74	27 - 28
Polyethylene glycol 1500	68	39 - 41
Polyethylene glycol 2000	58	47 - 48
Polyethylene glycol 3400	73	54 - 55
Polyethylene glycol 6000	81	58 - 60
Polyethylene glycol 10 000	85	59 - 60
Polyethylene glycol 20 000	80	63 - 64

**Table 2.** Influence of reaction temperature on the molar weight of PEGN.  $M_n$  is number average molar weight,  $M_w$  is weight average molar weight

Temperature [°C]	$M_n$ (PEGN) [g·mol <sup>-1</sup> ]	$M_w$ (PEGN) [g·mol <sup>-1</sup> ]	Yield [%]
0	1443	1480	56
10	1440	1477	58
20	1426	1463	59
30	1417	1457	64
40	1420	1458	72

An emulsion in the form of white, dense foams are formed during washing PEGN in dichloromethane solution with water. The separation of the water and dichloromethane layers is slow; it takes from several minutes to several weeks. Generally, the separation time increases with increasing molecular weight of the PEGN. The addition of sodium chloride or potassium sulfate was effective only in some cases.

Lower polyethylene glycol dinitrates are oily liquids (PEGN 454 and PEGN 647) or waxy materials (PEGN 1018 – PEGN 3374); higher dinitrates are solids. The dependence of melting temperature on molecular weight is shown in Figure 3. As expected, the melting temperature increases with increasing molecular weight of the PEGN.



**Figure 3.** The dependence of melting temperature on the molecular weight of PEGN samples.

**Gel permeation chromatography.** Molecular weights of polyethylene glycols (PEG) and polyethylene glycol dinitrates (PEGN) determined using gel permeation chromatography are shown in Table 3. The fragmentation of the PEG molecular chain during esterification was observed in the case of PEGN prepared from polyethylene glycols 10 000 and 20 000.

**Table 3.** Molecular weights of polyethylene glycols (PEG) and polyethylene glycol dinitrates (PEGN) determined on gel permeation chromatography

Trade name of starting	PEG		PEGN	
	$M_n$ [g·mol <sup>-1</sup> ]	$M_w$ [g·mol <sup>-1</sup> ]	$M_n$ [g·mol <sup>-1</sup> ]	$M_w$ [g·mol <sup>-1</sup> ]
Polyethylene glycol				
Polyethylene glycol 400	400	427	454	480
Polyethylene glycol 600	590	624	647	678
Polyethylene glycol 950-1 050	967	1010	1018	1057
Polyethylene glycol 1500	1374	1413	1440	1477
Polyethylene glycol 2000	1839	1883	1909	1956
Polyethylene glycol 3400	3238	3350	3374	3519
Polyethylene glycol 6000	6493	6690	6502	6759
Polyethylene glycol 10 000	10 386	10 798	8705	9904
Polyethylene glycol 20 000	18 188	19 079	16 940	18 758

The theoretical elemental composition was calculated based on the averaged molar weights from the GPC measurements of PEGN. The results of experimental determination correspond to the calculated values, as can be seen in Table 4.

The molecular weight of those PEGN prepared decreases only very slightly with increasing reaction temperature (Table 2). This indicates that increasing the reaction temperature does not cause significant fragmentation of the PEG molecular chain.

**Impact Sensitivity.** Sensitivities to impact of the lowest PEGN 454 and the first solid PEGN 1018 were examined by the drop hammer method. As expected, both PEGN samples were not sensitive to impact. The highest applied energy of the drop hammer was 98 J without producing any reaction.

**Table 4.** Results of elemental analysis of polyethylene glycol dinitrates (PEGN)

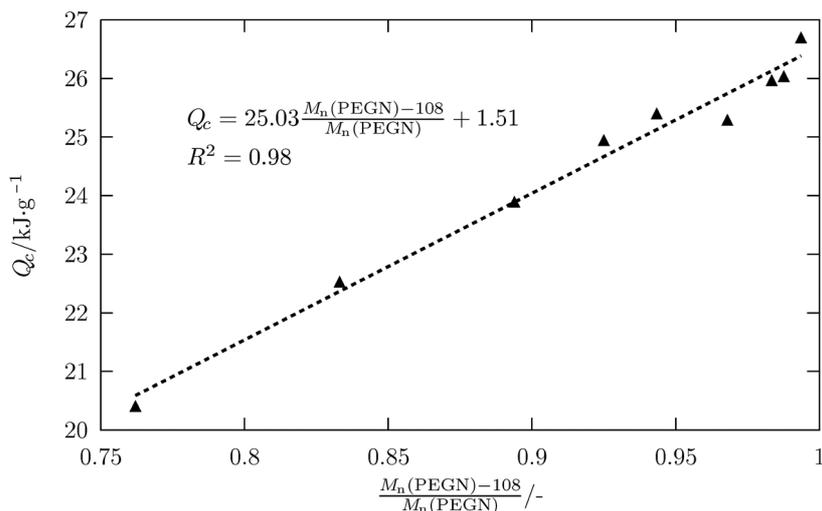
$M_n$ (PEGN) [ $\text{g}\cdot\text{mol}^{-1}$ ]		C	H	N
454	Calc.	41.55	6.98	6.17
	Found	42.55	7.30	5.43
647	Calc.	45.42	7.62	4.33
	Found	43.57	7.72	3.93
1018	Calc.	48.74	7.62	2.75
	Found	49.05	8.21	2.22
1440	Calc.	50.43	8.47	1.95
	Found	51.21	8.88	1.58
1909	Calc.	51.44	8.63	1.47
	Found	51.35	8.84	0.97
3374	Calc.	52.78	8.86	0.83
	Found	54.30	8.98	0.80
6502	Calc.	53.62	9.00	0.43
	Found	53.71	9.18	0.43
8705	Calc.	53.85	9.04	0.32
	Found	53.36	8.86	0.52
16 940	Calc.	54.18	9.09	0.17
	Found	54.05	9.25	0.24

**Table 5.** Heat of combustion of PEGN samples

$M_n$ (PEGN) [ $\text{g}\cdot\text{mol}^{-1}$ ]	$Q_c$ [ $\text{J}\cdot\text{g}^{-1}$ ]
454	20 401
647	22 524
1018	23 890
1440	24 911
1909	25 394
3374	25 286
6502	25 963
8705	26 034
16 940	26 692

**Heat of combustion.** The measured heats of combustion are stated in Table 5. The values of heat are expressed as a change of internal energy; the measurements were carried out in a constant volume. Heat of combustion increases with increasing molar mass. This trend was expected because increasing

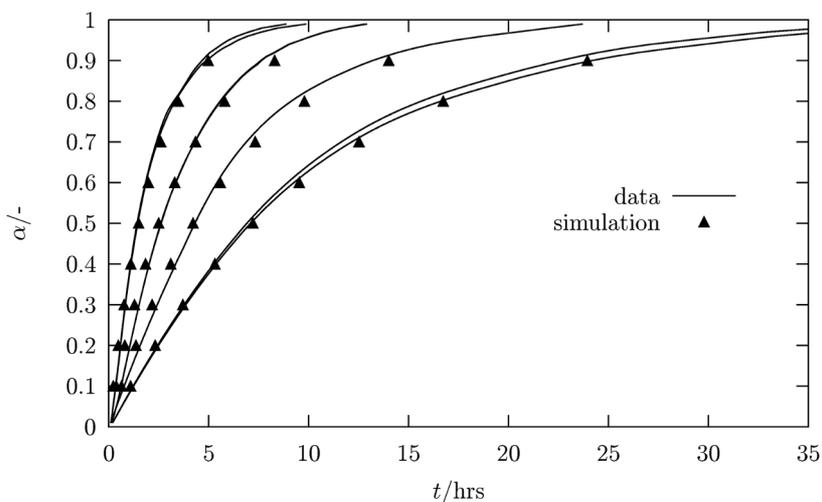
molar mass is caused by adding the  $-\text{CH}_2-\text{CH}_2-\text{O}-$  groups, which carry the fuel to be combusted. This idea is demonstrated in Figure 4, where is plotted the linear relationship between the heat of combustion and the relative amount of  $-\text{CH}_2-\text{CH}_2-\text{O}-$  groups in PEGN molecule, expressed as a ratio of  $M_n(\text{PEGN})$  decreased by 108 (molar weight of both ending groups  $-\text{NO}_2$  and  $-\text{O}-\text{NO}_2$ ) and  $M_n(\text{PEGN})$ .



**Figure 4.** The relationship between the heat of combustion and the relative amount of the  $[-\text{CH}_2-\text{CH}_2-\text{O}-]$  groups in the molecule of PEGN.

**Kinetics of decomposition.** The thermal decomposition of the first two samples (PEGN 454 and PEGN 647) was not analyzed. These samples evaporate during evacuation and therefore they cannot be measured using the vacuum stability test. The last sample (PEGN 16 940) was also not measured.

The calculated activation energies ( $E$ ) and preexponential factors ( $A$ ) are similar for all measured samples, as can be seen from Table 3. The decomposition reaction obeys the first order reaction model. A comparison of measured decomposition data and the calculated values is presented in Figure 5. The calculated data agree well with the experiments in the full  $\alpha$  range. The agreement for the other explored samples is similar.



**Figure 5.** Decomposition of PEGN 1018. Solid lines represent the vacuum stability test measurements (they corresponds to the temperatures 150, 155, 160 and 165 °C from left to right) and the points are the reaction progresses calculated for  $E = 161.50 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $A = 2.31 \times 10^{15} \text{ s}^{-1}$  and  $f(\alpha) = 1 - \alpha$  (values from Table 6).

The observed decomposition reaction corresponds probably to the decomposition of end nitroxy groups. The mass of the sample used for the kinetic measurements had to be increased for the samples with higher molecular mass. The mass of the sample was adjusted to have the whole pressure of decomposition gases in the range of 70-130 kPa. The total content of nitroxy groups was approximately the same for all samples. Nevertheless, the kinetic parameters obtained are very similar for all samples. This also indicates that the decomposition reaction is the same.

**Table 6.** Kinetic parameters of PEGN decomposition

$M_n$ (PEGN) [g·mol <sup>-1</sup> ]	Sample mass [g]	Temp. range [°C]	$E$ [kJ·mol <sup>-1</sup> ]	$A$ [s <sup>-1</sup> ]
1018	0.70	150-165	161.50	$2.31 \times 10^{15}$
1440	1.00	150-165	162.88	$2.95 \times 10^{15}$
1909	1.00	150-175	155.14	$3.18 \times 10^{14}$
3374	1.00	150-175	156.19	$4.12 \times 10^{14}$
6502	2.00	160-175	149.24	$6.51 \times 10^{13}$
8705	4.00	160-175	159.21	$1.34 \times 10^{15}$

## Conclusions

Synthesis and characterization of nine polyethylene glycol dinitrates (with molecular weight  $M_n$  from 454 to 16 940) are reported. Polyethylene glycol dinitrates were prepared by esterification of polyethylene glycols by nitric/sulfuric acid in dichloromethane. The yield of PEGN increases with increasing reaction temperature (0-40 °C) however large liberation of nitrogen oxides was observed at 40 °C. No influence of reaction temperature (0-40 °C) on the cleavage of the polyethylene glycol chain during esterification was observed. Polyethylene glycol dinitrates with molecular weight above 454 are not sensitive to impact. Heat of combustion increases with increasing molecular weight. Thermal decomposition of PEGN starts with the first order decomposition of the ending  $-O-NO_2$  groups. The kinetic parameters obtained ( $E$ ,  $A$ ) are similar for all samples.

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