Polyurethanes based on 2,2-dinitropropane-1,3-diol and 2,2-bis(azidomethyl)propane-1,3-diol as potential energetic binders

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ABSTRACT: On the base of 2,2-bis(azidomethyl)propane-1,3-diol (BAMP) and 2,2-dinitropropane-1,3-diol (DNPD) four different polyurethanes were synthesized in a polyaddition reaction using hexamethylene diisocyanate (HMDI) and diisocyanato ethane (DIE). The obtained prepolymers were mainly characterized using vibrational spectroscopy (IR) and elemental analysis. For determination of low and high temperature behavior, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used. Investigations concerning friction and impact sensitivities were carried out using a BAM drop hammer and friction tester. The energetic properties of the polymers were determined using bomb calorimetric measurements and calculated with the EXPLO5 V6.02 computer code. The obtained values were compared with the glycidyl azide polymer (GAP). The compounds turned out to be insensitive toward friction (>360 N) and less sensitive toward impact (40 J). The good physical stabilities, along with their sufficient thermal stability (170–210 °C) and moderate energetic properties renders these polymers into potential compounds for applications as binders in energetic formul;ations. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43991.

INTRODUCTION

Energetic formulations, like in use for propelling charges, blasting agents or pyrotechnics are usually composed of several energetic ingredients, for example, oxidizer, fuel, explosive and so on. Over the decades, the use of energetic materials increased and the demand for more safety and better handling properties of those materials grew even more. This involved a reduction of the sensitivity toward outer stimuli like heat, impact, shockand so on, without decreasing the energetic performance of the system. Consequently, insensitive munitions,[1] composite propellants[2] and polymer-bonded explosives (PBX)[3] were developed amongst others. Here, the crystalline or liquid energetic components are embedded in a matrix of cross-linked polymers. Thus, a better and easier handling of the mixtures is achieved, also by reducing the formulations sensitivity toward external stimuli.[4,5] In that context, the use of inert polymers, such as hydroxyl-terminated polybutadiene (HTPB), or terpolymers based on butadiene, acrylonitrile and acrylic acid (PBAN) is widely reported.[6] Although these polymers are well suited as binders, due to their properties (chemically inert, low glass transition temperature, thermally stable...), they have major issue of being non-energetic. If used as binder in energetic systems the loss of the energetic performance of the overall system is reduced by the amount of non-energetic material. Therefore a replacement by energetic polymers, which can even contribute to the energetic performance, is of great interest. During the past decades, various energetic polymers were reported.[5,7–10] One of the most promising energetic polymers so far is the glycidyl azide polymer (GAP), which is depicted in Figure 1.

Like other liquid energetic polymers, GAP has to be cured after the mixing process with the energetic ingredients. In case of available terminal hydroxyl groups, this is achieved with the formation of polyurethane linkages using di- or polyfunctionalized isocyanates. As an example, the reaction of GAP with the curing agent diphenylmethane-4,4′-diisocyanate (MDI) is shown in Scheme 1.[11]

Because of their good mechanical properties and the fast and easy reaction, the formation of polyurethanes is a standard curing procedure for energetic formulations.[12,13] In today's literature some new developments concerning energetic polyurethanes and related polymers are described.[14–16]

Due to their overall positive properties, their versatility, chemical and thermal stability[3] and good mechanical properties, as
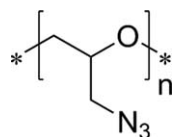
Figure 1. Repeating unit of GAP.

well as increased oxygen balance, polyurethanes seemed to be promising compounds for the application as energetic binders. Furthermore, carbamate moieties can form hydrogen bridges to the energetic filler and therefore lead to increased adhesion forces. And, especially for nitramine containing energetic fillers, these carbamate-based compounds may be particularly qualified as energetic binder, since these moieties are structurally similar to the amide group, which turned out to form good interactions with nitro groups.[17] In this work we report the synthesis and characterization of polyurethanes containing the energetic functional groups $-NO_2$ and $-N_3$. The structural analysis and energetic behavior, as well the high and low temperature behavior of each compound was determined. The properties of these compounds are discussed with respect to their potential use as energetic binders.

EXPERIMENTAL

CAUTION! *All azide containing compounds, especially acyl azides, are potentially explosive energetic materials, although no hazards were observed during preparation and handling of these compounds. Nevertheless, this necessitates additional meticulous safety precautions, while handling these compounds (grounded equipment, Kevlar® gloves, Kevlar® sleeves, face shield, leather coat, ear plugs, and safety shield, during reactions).*

General: All chemical reagents and solvents of analytical grade were obtained from Sigma-Aldrich, Arcos Organics or ABCR and used without further purification. Polyaddition reactions were carried out in previously dried glass ware under nitrogen using standard Schlenk techniques. Syringes used to transfer anhydrous solvents and reagents were flushed three times with nitrogen. ^{1}H, ^{13}C NMR spectra were recorded with a JEOL 400 or a Bruker 400 (TR) instrument. The spectra were measured at 25 °C. The chemical shifts are given relative to tetramethylsilane as external standards. Coupling constants (J) are given in Hertz (Hz). Infrared spectra were measured with a Perkin–Elmer Spectrum BX–FTIR spectrometer equipped with a Smiths DuraSamplIR II ATR device. All spectra were recorded at ambient temperature. Mass spectra were recorded on a Thermo Finnigan MAT 95 or a Jeol MStation sector field mass spectrometer.

Elemental analyses (C/H/N) were performed with an Elementar Vario EL or Vario Micro Analyzer. Decomposition temperatures were determined by differential scanning calorimetry (DSC)

with a Linseis DSC PT10 calibrated by standard pure indium and zinc, using a heating rate of 5 °C min^{-1} in covered Al-containers, with a hole in the lid and a nitrogen flow of 20 mL min^{-1}. Glass transition temperatures were also determined by DSC with a NETZSCH 204 Phoenix in closed Al-containers, using a heating rate of 5 °C min^{-1}. Thermogravimetric analyses (TGA) were measured in a platinum pan (100 µL) in a nitrogen atmosphere on a TA TGA Q5000 instrument, using a heating rate of 5 °C min^{-1}. The molecular weights were measured at Fraunhofer-Institut für Chemische Technologie ICT, Pfinztal, Germany, using an Agilent Series 1100 HPLC System with a flow rate of 1.0 mL min^{-1} and an injection volume of 100 µL of the polymer sample dissolved in THF (2 mg mL^{-1}). THF containing 0.2% trifluoroacidic acid was used as solvent and eluent. As detector an Agilent Series 1100 refractive index detector was used. The analysis was done using the PSS WinGPCU-niChrom software. As column a SDV column set was used, consisting of precolumn PSS SDV 5 µ, PSS SDV 5 µ 50 Å, PSS SDV 5 µ 100 Å, PSS SDV 5 µ 1000 Å, PSS SDV 5 µ 10^5 Å, with 8.0 mm inner diameter and 300 mm length. The calibration was done using a narrowly distributed polystyrene standard from Fa. PSS, Mainz, within the molecular mass range of 1.210.000 g mol^{-1} to 162 g mol^{-1}.

Bomb Calorimetry was undertaken using a Parr 6200 isoperibol bomb calorimeter equipped with static bomb. For the analysis three samples of 0.1 g of the substance were covered with 0.5 to 0.6 g of paraffin oil. Pycnometric measurements were carried out with a Quantachrome Ultrapyc 1200e pycnometer. Impact and friction sensitivity tests were carried out according to STA-NAG 4489[18] and STANAG 4487[19] modified instructions[20,21] using a BAM (Bundesanstalt für Materialforschung) drop hammer and friction tester.[22] The classification of the tested compounds results from the "UN Recommendations on the Transport of Dangerous Goods." Electrostatic sensitivities were measured with a OZM small scale electrostatic discharge tester.[23]

General Procedure 1 (GP1), Preparation of the HMDI-based Polyurethanes
A solution of the respective diol in dry THF was degassed for 30 min. Hexamethylene diisocyanate (HMDI) and dibutyltin dilaurate (DBTDL; 0.01 mL, 18 µmol) were added in a nitrogen countercurrent and the solution was stirred for 24 h at 50 °C (in a nitrogen atmosphere, with drying tube). The reaction mixture was then slowly poured in H$_2$O (300 mL) and stirred over night at room temperature. The solvent was decanted and the remaining precipitate was dried *in vacuo*.

General Procedure 2 (GP2), Preparation of the DIE-based Polyurethanes
To a freshly prepared solution of diisocyanato ethane in benzene under inert atmosphere, the corresponding diol and DBTDL
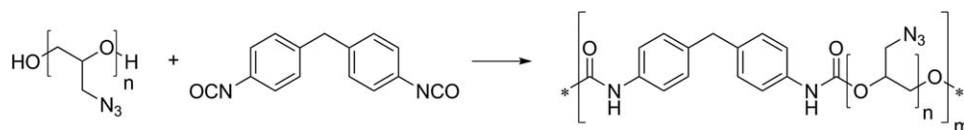
Scheme 1. Curing of hydroxyl-terminated GAP using MDI.

(0.01mL, 18 μmol) were added in a nitrogen countercurrent under vigorous stirring. The reaction mixture was stirred at 50 °C for 24 h (in a nitrogen atmosphere, with drying tube) and then slowly poured in H_2O (200 mL). After stirring over night the solvent was decanted, the remaining product was washed with hot water and dried *in vacuo*.

Succinyl Hydrazide, 3

The reaction was carried out according to standard procedures.[24] A solution of hydrazine hydrate (6.8 mL, 7.0 g, 140 mmol) and dimethyl succinate (**4**) (3.6 mL, 4.0 g, 27.4 mmol) in methanol (100 mL) was heated to reflux for 2 h. The mixture was then stirred over night at room temperature. The resulting precipitate was filtered off. The colorless solid was washed using methanol and diethyl ether and dried *in vacuo*, yielding 3.80 g (95%) of a colorless crystalline solid.

^{1}H NMR (400 MHz, DMSO-*d6*, δ): 8.96 (s, 2H, N*H*), 4.13 (s, 4H, N*H*$_2$), 2.24 (s, 4H, C*H*$_2$) ppm. ^{13}C NMR (100 MHz, DMSO-*d6*, δ): 170.7 (C_q), 28.9 (*C*H$_2$); Anal. calcd. for $C_4H_{10}N_4O_2$: C 32.87, H 6.90, N 38.34; found C 32.92, H 6.87, N 38.25.

2,2-Dinitropropane-1,3-Diol (DNPD, 6a)

The reaction was carried out in accordance to literature procedures.[25–27] A solution of nitromethane (0.88 mL, 1.00 g, and 16.4 mmol) and formaldehyde (2.90 mL, 2.66 g, and 31.9 mmol) in H_2O (2.5 mL) was cooled to 0 °C. Afterward a mixture of sodium hydroxide (0.75 g, 18.8 mmol) in H_2O (2 mL) was added dropwise. The temperature was kept below 40 °C during addition. After stirring at 0 °C for 90 min, sodium nitrite (1.13 g, 16.4 mmol) was added. This mixture was added slowly to a solution of silver nitrate (5.57 g, 32.8 mmol) in H_2O (7.2 mL), while the temperature was kept below 25 °C. After stirring for another 2 h the precipitated silver was filtered off and the product was extracted using diethyl ether (3 × 15 mL). The extract was concentrated *in vacuo* and the resulting solid was purified by recrystallization using dichloromethane, yielding 8.93 g (66%) of **1a** as a colorless crystalline solid.

^{1}H NMR (400 MHz, acetone-*d6*, δ): 5.34 (t, $^3J_{HH}$ = 6 Hz, 2H, O*H*), 4.51 (d, $^3J_{HH}$ = 6 Hz, 4H, C*H*$_2$); ^{13}C NMR (100 MHz, acetone-*d6*, δ): 119.7 (C_q), 61.7 (*C*H$_2$); Anal. calcd. for $C_3H_6N_2O_6$: C 32.87, H 6.90, N 38.34; found C 32.92, H 6.87, N 38.25.

2,2-Bis(azidomethyl)propane-1,3-Diol (BAMP, 6b)

The reaction was carried out in accordance to a literature procedure.[28] Sodium azide (1.74 g, 28.8 mmol) and 2,2-bis(bromomethyl)propane-1,3-diol (2.8 g, 10.7 mmol) were dissolved in 20 mL DMSO and heated to 100 °C for 48 h. Then H_2O (15 mL) and brine (15 mL) were added. The solution was extracted using ethyl acetate (3 × 20 mL). The combined organic phases were washed with brine (2 × 20 mL) and dried over sodium sulfate. After filtration *n*-heptane (25 mL) was added to the crude liquid and the solvents were removed under reduced pressure. Drying *in vacuo*, yielded 1.85 g (9.94 mmol, 93%) of **1b** as a yellowish liquid.

^{1}H NMR (400 MHz, DMSO-*d6*, δ): 4.74 (t, J = 5 Hz, 2H, O*H*), 3.29 (s, 4H, C*H*$_2$—N$_3$), 3.27 (d, J = 5 Hz, 4H, C*H*$_2$—OH); ^{13}C

NMR (100 MHz, DMSO-*d6*, δ) 59.8 (*C*H$_2$), 51.2 (C_q), 45.5 (*C*H$_2$); ^{14}N NMR (DMSO-*d6*, δ): −129 (N_β), −170 (N_γ), −310 (N_α); Anal. calcd. for $C_5H_{10}N_6O_2$: C 32.26, H 5.41, N 45.14; found C 32.13, H 5.68, N 42.61.

Diisocyanato Ethane (DIE, 5)

The slightly modified reaction was carried out, according to a literature procedure.[29] Concentrated hydrochloric acid was added dropwise to a solution of **3** (1.00 g, 6.84 mmol), sodium nitrite (1.1 g, 16 mmol) and ice (2 g) in CCl_4 (15 mL) at 0 °C, maintaining the temperature below 10 °C. After the addition was completed the mixture was stirred for 2 h and allowed to warm to room temperature. The phases were separated and the aqueous phase was extracted, using benzene (3 × 10 mL). The combined organic phases were dried over sodium sulfate and filtrated into a preheated, nitrogen flushed flask. The completion of the transformation into the acyl azide (**4**) was observed *via* TLC and IR measurements. Due to its instability, **4** was not further concentrated, but directly processed to the diisocyanate **5**. The solution was therefore heated from room temperature to 80 °C in 5 °C steps and then stirred for 4 h in a nitrogen atmosphere (with drying tube). The completion of the rearrangement was monitored *via* TLC and IR measurements. The obtained diisocyanate solution was directly used for the polyaddition step.

Poly[hexamethylene(2,2-dinitropropylene)carbamate] (HMDI-DNPD, 7a)

HMDI-DNPD was synthesized from DNPD (1.0 g, 6,0 mmol) in THF (40 mL) with 1 eq. of HMDI (0.97 mL, 6.0 mmol) and DBTDL, applying **GP1**. The reaction gave 1.92 g (5.74 mmol, 96%) of **2a** as orange, elastic foil.

T_{Dec} = 165 °C; ^{1}H NMR (400 MHz, DMSO-*d6*, δ): 7.58 (br, 2H, N*H*), 5.00 (br, 4H, C*H*$_2$—O), 2.95 (br, 4H, C*H*$_2$—NH), 1.35 (br, 4H, C*H*$_2$—CH$_2$—NH), 1.21 (br, 4H, C*H*$_2$—CH$_2$CH$_2$); ^{13}C NMR (100 MHz, DMSO-*d6*, δ): 153.9 (*C*=O), 115.6 (C_q), 60.9 (*C*H$_2$—O), 30.4 (*C*H$_2$—N), 29.0 (*C*H$_2$—CH$_2$—NH), 25.8 (*C*H$_2$—CH$_2$CH$_2$); IR (ATR): ṽ = 3330 (m, ν(NH)), 2934 (m), 2860 (w), 1712 [vs, ν(C=O, amide I)], 1570 [vs, ν$_{as}$(NO$_2$)], 1527 [vs, δ(NH, amide II)], 1457 (m), 1408 (m), 1322 [m, ν$_s$(NO$_2$)], 1235 [vs, δ$_{as}$(C—O)], 1130 (s), 1047 (s), 960 (w), 848 (m), 766 (m), 729 (w) cm^{-1}; Anal. calcd. for $C_{11}H_{18}N_4O_8$ * 0.25 THF * 0.5 H_2O: C 39.89, H 5.86, N 15.51; found C 39.81, H 5.92, N 15.55.

Poly[Ethylene(2,2-Dinitropropylene)Carbamate] (DIE-DNPD, 8a)

DIE-DNPD was synthesized from a solution of DIE in benzene and DNPD (1.0 g, 6.0 mmol), applying **GP2**. The reaction gave 0.95 g (3.42 mmol, 57%) of **3a** as reddish, glutinous solid.

T_{Dec} = 168 °C; ^{1}H NMR (400 MHz, DMSO-*d6*, δ): 7.62 (br, 2H, N*H*), 5.01 (br, 4H, C*H*$_2$–O), 3.02 (br, 4H, C*H*$_2$–N); ^{13}C NMR (100 MHz, DMSO-*d6*, δ): 154.1 (*C*=O), 115.4 (C_q), 61.1 (*C*H$_2$—O), 29.0 (*C*H$_2$—NH); IR (ATR): ṽ = 3333 [w, ν(NH)], 2957 (w), 2886 (w), 1714 [vs, ν(C=O, amide I)], 1562 [vs, ν$_{as}$(NO$_2$)], 1520 [s, δ(NH, amide II)], 1438 (m), 1322 [m, ν$_s$(NO$_2$)], 1230 [vs, δ$_{as}$(C—O)], 1143 (s), 1116 (s), 1043 (s), 963 (w), 863 (w), 845 (m), 764 (m), 673 (w) cm^{-1}; Anal. calcd.

for $C_7H_{10}N_4O_8$ * 0.5 H_2O * 0.3 C_6H_6: C 34.40, H 4.49, N 17.83; found C 34.32, H 4.52, N 18.23.

Poly[hexamethylene(2,2-bis(azidomethyl)propylene)carbamate] (HMDI-BAMP, 7b)

HMDI-BAMP was synthesized from BAMP (1.11 g, 5.95 mmol) in THF (40 mL) with 1 eq. of HMDI (0.96 mL, 5.95 mmol) and DBTDL, applying **GP1**. The reaction gave 1.91 g (5.39 mmol, 91%) of **2b** as yellowish highly viscous liquid.

T_{Dec} = 205 °C; ^{1}H NMR (400 MHz, DMSO-$d6$, δ): 7.13 (br, 1.7H, NH trans conformer), 6.89 (br, 0.3H, NH cis conformer), 3.87 (br, 4H, CH_2—O), 3.40 (br, 4H, CH_2—N_3) 2.96 (br, 4H, CH_2—NH), 1.37 (br, 4H, CH_2—CH_2—NH), 1.23 (br, 4H, CH_2—CH_2CH_2); ^{13}C NMR (100 MHz, DMSO-$d6$, δ): 155.7 (C=O), 62.4 (CH_2—O), 51.3 (CH_2—N_3), 43.2 (C_q), 40.2 (CH_2—NH), 29.3 (CH_2—CH_2—NH), 25.9 (CH_2—CH_2CH_2); IR (ATR): $\tilde{v}$ = 3324 [w, v(NH)], 2929 (m), 2857 (w), 2097 [vs, v(N_3)], 1694 [vs, v(C=O, amide I)], 1525 [s, δ(NH, amide II)], 1449 (m), 1412 (w), 1359 (w), 1235 [vs, δ_{as}(C—O)], 1136 (s), 1035 (s), 900 (w), 805 (w), 772 (m), 729 (w), 666 (w) cm^{-1}. DCIMS [m/z (%)]: 355.4 (9) [monomeric unit + H]$^+$, 201.4 (5), 187.3 (41), 86.2 (11), 57.2 (100), 43.2 (17); Anal. calcd. for $C_{13}H_{22}N_8O_4$ * 0.3 THF * 0.1 H_2O (377.80): C 45.15, H 6.56, N 29.66; found C 45.17, H 6.71, N 29.57.

Poly[ethylene(2,2-bis(azidomethyl)propylene)carbamate] (DIE-BAMP, 8b)

DIE-BAMP was synthesized from a solution of DIE in benzene and BAMP (1.12 g, 6.00 mmol), applying **GP2**. The reaction gave 0.93 g (3.12 mmol, 52%) of **3b** as yellow, viscous liquid.

T_{Dec} = 210 °C; ^{1}H NMR (400 MHz, DMSO-$d6$, δ): 7.19 (br, 2H, NH), 3.83 (br, 4H, CH_2—O), 3.29 (br, CH_2—N_3), 3.02 (br, 4H, CH_2—NH); ^{13}C NMR (100 MHz, DMSO-$d6$, δ) 154.9 (C=O), 58.6 (CH_2—O), 50.0 (CH_2—N_3), 43.2 (C_q), 39.3 (CH_2—NH); IR (ATR): $\tilde{v}$ = 3328 [w, v(NH)], 2938 (w), 2875 (w), 2360 (w), 2094 [vs, v(N_3)], 1697 [s, v(C=O, amide I)], 1524 [m, δ(NH, amide II)], 1447 (m), 1404 (w), 1359 (w), 1253 [vs, δ_{as}(C—O)], 1142 (s), 1042 (s), 950 (m), 896 (w), 772 (w), 700 (w), 667 (w) cm^{-1}; DEIMS [m/z (%)] = 597.7 (0.1) [dimeric unit + H]$^+$, 387.5 (2), 299.4 (2) [monomeric unit + H]$^+$, 273.4 (6), 131.2 (56), 113.2 (39), 86.2 (80), 81.2 (24), 72.2 (19), 69.2 (36), 57.2 (44), 54.2 (47), 43.1 (82), 30.1 (64), 28.1 (100); Anal. calcd. for $C_9H_{14}N_8O_4$ * 0.1 H_2O: C 36.02, H 4.77, N 37.34; found C 35.75, H 4.91, N 37.58.

RESULTS AND DISCUSSION

Syntheses

The syntheses of the required diols 2,2-dinitropropane-1,3-diol[25–27] (DNPD) and 2,2-bis(azidomethyl)propane-1,3-diol[28] were carried out according to literature known procedures. Hexamethylene diisocyanate (HMDI, **1**) and diisocyanato ethane (DIE, **5**) were either purchased (HMDI) or synthesized (slightly modified) according to established procedures[29] (Scheme 2).

Due to its instability, the succinyl azide (**4**) was not further concentrated after purification, but directly converted into the diisocyanate (**5**). After the completion of the reaction, DIE, with regard to its high reactivity, was as well directly used for the
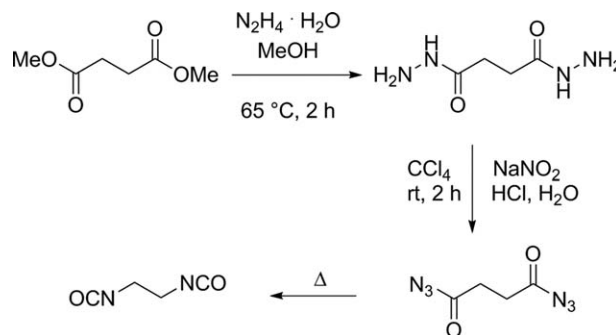
Scheme 2. Synthesis of diisocyanato ethane (DIE, **5**).

polyaddition reaction. The successful formation of the desired diisocyanate (**5**) was confirmed by TLC and IR measurements. Here, the acyl azide vibration at 2140 cm^{-1} vanished and instead the isocyanate vibration occurred at 2280 cm^{-1}.[30]

The polyaddition reactions were carried out using dibutyltin dilaurate (DBTDL) as catalyst over two different synthetic routes (Scheme 3). The obtained BAMP-based polyurethanes HMDI-BAMP (**7b**) and DIE-BAMP (**8b**) were yellowish viscous liquids with yields of 91% and 52%. In case of the DNPD-based polyurethanes HMDI-DNPD (**7a**) and DIE-DNPD (**8a**) the products were either an orange elastic foil or a red ductile solid with yields of 96% and 57%.

Characterization

NMR measurements were performed in DMSO-$d6$. As example, the recorded ^{1}H and ^{13}C NMR spectra of HMDI-BAMP (**7b**) are depicted in Figure 2. In the proton NMR spectrum the trans and the cis conformers of the carbamate N—H group are visible at 7.13 ppm and 6.89 ppm.[31] The signals of the methylene groups of the diol fragment appear at 3.87 ppm (CH_2—O) and 3.40 ppm (CH_2—N_3). The methylene groups of the HMDI corresponding carbon chain show signals at 2.96 ppm (CH_2—NH), 1.37 ppm and 1.23 ppm. The ^{13}C NMR spectrum shows a similar signal pattern as the ^{1}H NMR spectrum. The signals of the carbon atoms corresponding to the diol fragment occur at 62.4 ppm (CH_2—O), 51.3 ppm (CH_2—N_3) and 43.2 ppm (C_q). The signals appearing at 40.2 ppm (CH_2—NH), 29.3 ppm and 25.9 ppm can be assigned to the carbon atoms of the HMDI chain. At 156.7 ppm the signal of the carboxyl carbon of the carbamate group is visible.

The other compounds (**7a**, and **8a, b**) show similar values for the specific fragment CH_2—NH—CO—O—CH_2—. In the ^{1}H NMR spectra, the DNPD-based compounds HMDI-DNPD (**7a**) and DIE-DNPD (**8a**) show signals around 7.60 ppm for the N—H group and 5.01 ppm for the CH_2—O fragment. Whereas the signals of DIE-BAMP (**8b**) are shifted to higher field compared with the signals of **7a** and **8a** with 7.19 and 3.83 ppm, respectively. The chemical shift of the signal for the CH_2—NH group depends on the respective diisocyanate unit. The compound based on HMDI (**7a**) shows the signal at 2.95 ppm (just like the above mentioned **7b**), while the signal of the DIE-based **8a** and **8b** occurs at 3.02 ppm.

The ^{13}C NMR spectra of compounds HMDI-DNPD (**7a**), DIE-DNPD (**8a**) and DIE-BAMP (**8b**) also confirm the successful
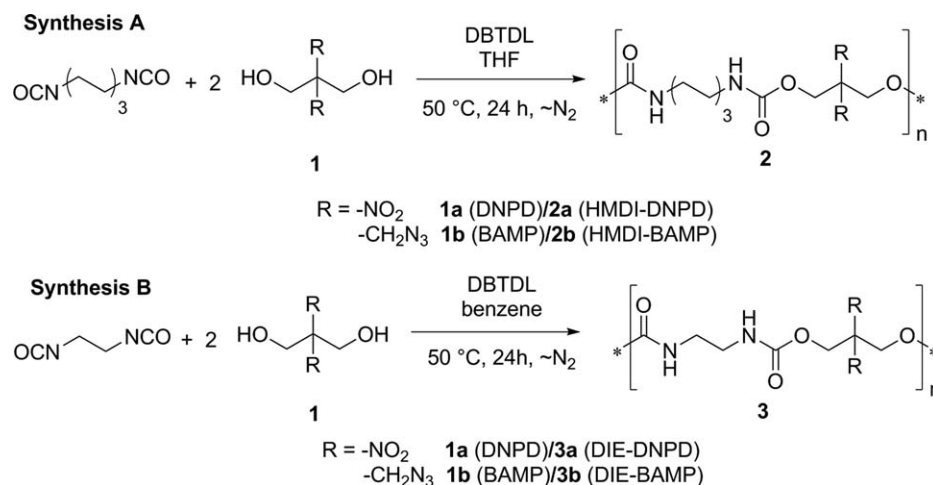
Scheme 3. Synthetic routes toward energetic polyurethanes **7-8**.

formation of the polyurethanes. The signal of the quaternary C atom of the carboxyl group occurs around 154 ppm, the carbon atom of the CH$_2$—O fragment shows signals in the range of 58.6–61.1 ppm. For the CH$_2$—NH carbon atom the DNPD-based **7a** and **8a** show signals around 30 ppm, while the signal for DIE-BAMP (**8b**) occurs at 39.3 ppm, which is in the range of the corresponding signal of HMDI-BAMP (**7b**).

Elemental analysis revealed some remaining inclusions of water and organic solvent in the synthesized polymers.

The measured IR spectra of the compounds **7-8** clearly show the characteristic vibrations for monosubstituted carbamates (Figure 3). At about 3330 cm^{-1} the N—H valence vibration (A) is visible, the valence vibration of the C=O group (amide I

occurs around 1700 cm^{-1} (B), as well as the amide II vibration (N—H bending) and the asymmetric C—O bending vibration at about 1525 cm^{-1} (C) and 1235 cm^{-1} (D), respectively.[30] The asymmetric and symmetric valence vibrations of the NO$_2$ groups in HMDI-DNPD (**7a**) and DIE-DNPD (**8a**) appear at about 1565 cm^{-1} (overlapping signal with the amide II vibration) and 1320 cm^{-1} (E).[30] Besides this, the characteristically strong azide vibration is visible at 2100 cm^{-1} (F) in case of the BAMP-based HMDI-BAMP (**7b**) and DIE-BAMP (**8b**). These results, together with the determined values of the elemental analysis and NMR measurements prove the successful synthesis of compounds **7-8**.

The molecular weights of the polymers were determined by GPC measurements. The average molecular masses (M_n) of HMDI-BAMP (**7b**), DIE-DNPD (**8a**) and DIE-BAMP (**8b**) are determined to be 3100 g mol^{-1} (for **7b**) and 850 g mol^{-1} (for **8a** and **8b**) corresponding to approximately 10 and 3 molecular formulas in one chain. Although HMDI-DNPD (**7a**) was soluble in THF, no significant separation could be obtained, most likely due to reprecipitation of the compound on the column.

Thermal Properties

An important factor for energetic binders is their thermal stability and in case of liquid materials a preferably low glass transition temperature T_g.[32] The determination of the low and high temperature behavior of the polyurethanes was carried out *via* differential scanning calorimetry (DSC). Figure 4 shows the decomposition temperatures of **7-8**.

As expected, the compounds based on the same diol show decomposition temperatures in the same temperature range. HMDI-DNPD (**7a**) and DIE-DNPD (**8a**) decompose around 170 °C, which is initiated by the geminal nitro groups. HMDI-BAMP (**7b**) and DIE-BAMP (**8b**) are stable up to higher temperatures (around 210 °C), which is in accordance with the thermal stability of aliphatic azides.[33,34] Due to their liquid character additional low temperature DSC measurements were done with the BAMP-based compounds **7b** and **8b** to determine their glass transition temperature (T_g). The obtained plots are depicted in Figure 5.
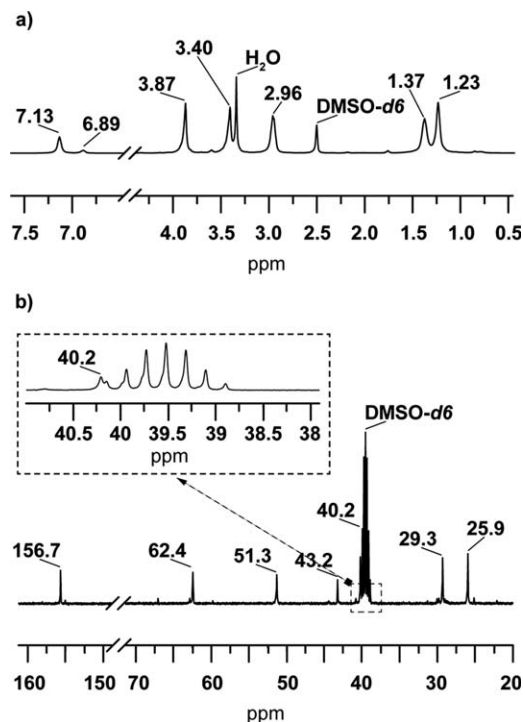
**Figure 2.** (a) ^{1}H and (b) ^{13}C NMR spectrum of HMDI-BAMP (**7b**).
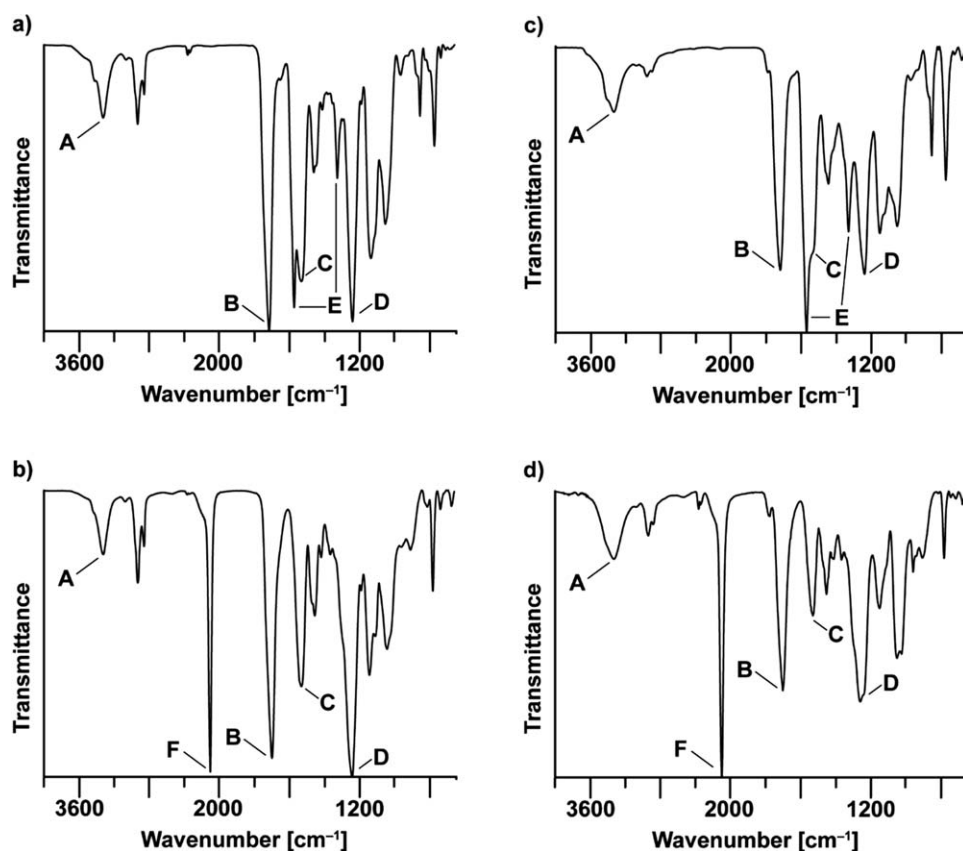
Figure 3. IR spectra of (a) HMDI-DNPD (**7a**), (b) HMDI-BAMP (**7b**), (c) DIE-DNPD (**8a**), and (d) DIE-BAMP (**8b**).

The glass transition temperatures of **7b** and **8b** are with -38 and $-27\,°C$ in a good temperature range for application. Nevertheless, if applied as binder (especially in propellant formula-

tions), a plasticizer additive will be needed to reduce T_g below the requested minimum working range (usually $-55\,°C$).[32]

To determine the weight loss during the heating process thermogravimetric analysis (TGA) was used (Figure 6).

As already observed in the DSC plots (Figure 4) the compounds based on the same energetic diol show similar behavior. DIE-DNPD (**8a**) shows a beginning weight loss at $100\,°C$, which can be assigned to the loss of H_2O and organic solvent during the heating process. The second step (recognizable by the small dent in the curve at approximately 95 wt %), starting around
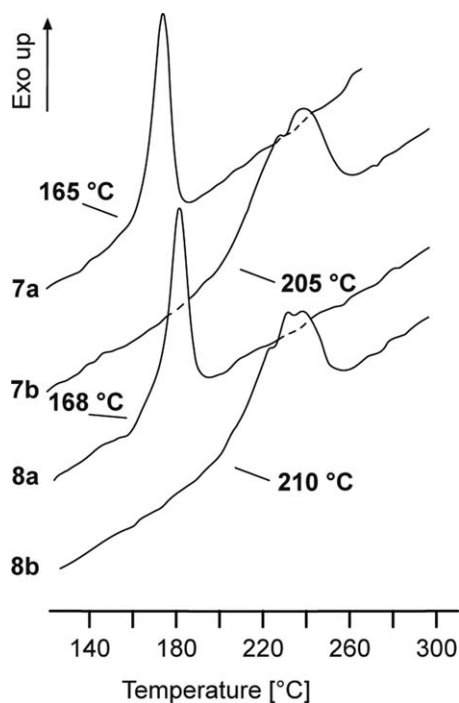
Figure 4. DSC plots of decomposition temperatures of **7-8** (onset temperatures).
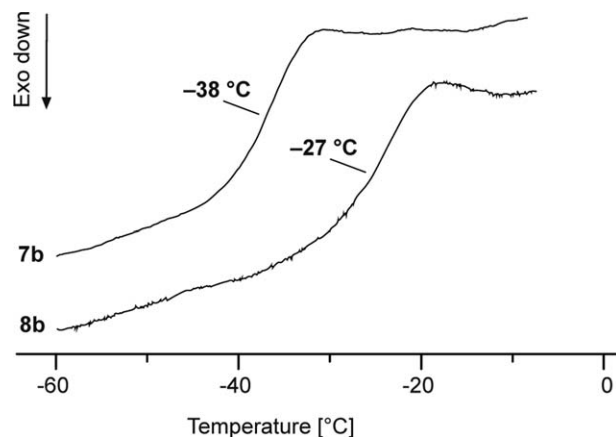
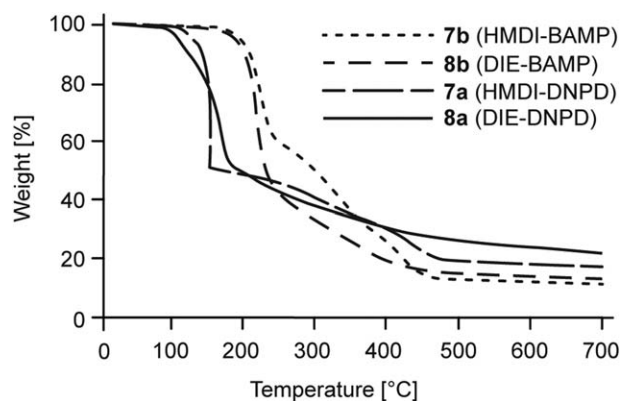**Figure 5.** DSC plots of glass transition temperatures of HMDI-BAMP (**7b**) and DIE-BAMP (**8b**) (T_{gMid}).

Figure 6. TGA plots of compounds **7-8**.

170 °C is the beginning decomposition of the polyurethane, starting with the geminal nitro groups. The following steps of weight losses are assignable to the decomposition of the remain-ing polyurethane backbone, including the carbamate group and the aliphatic chain. Similar observations can be made for the other three compounds. The decomposition of the compounds is initiated by the decomposition of the energetic functional groups, around 165 °C for HMDI-DNPD (**7a**) (after solvent loss, recognizable by the dent in the curve at about 97 wt %) or 200 °C for HMDI-BAMP (**7b**) and DIE-BAMP (**8b**) and is fol-lowed by a stepwise decomposition of the polymeric backbone. At the end temperature of 700 °C the compounds have reached an overall weight loss of 90% (**7b**) to (not fully completed) 80% (**8a**).

Energetic Properties

Sensitivity data concerning impact and friction sensitivity were obtained using a BAM drop hammer and friction tester.[21] These methods revealed that compounds **7-8** are insensitive toward friction (>360 N) and less sensitive toward impact (40 J).

Table I. Energetic Data of Compounds **7-8** Compared with GAP

	7a	7b	8a	8b	GAP[q]
Formula	$C_{11}H_{18}N_4O_8$	$C_{13}H_{22}N_8O_4$	$C_7H_{10}N_4O_8$	$C_9H_{14}N_8O_4$	$C_3H_5N_3O$
FW (monomer) (g mol^{-1})	334.28	354.36	278.18	298.26	99.09
IS (J)[a]	40	40	40	40	7
FS (N)[b]	>360	>360	>360	>360	>360
ESD (J)[c]	1.5	—	1.5	—	—
Ω (%)[d]	−110	−149	−63	−113	−121
T_{Dec} (°C)[e]	165	205	168	210	216
T_g (°C)[f]	—	−38	—	−25	
ρ (g cm^{-3})[g]	1.5	1.3	1.5	1.3	1.3
$-\Delta U_{comb}$ (cal g^{-1})[h]	4626	4969	3291	4324	—
$-\Delta H_{comb}$ (kJ mo^{-1})[i]	6466	7366	3822	5390	—
$\Delta_f H_m°$ (kJ mol^{-1})[j]	−435	−894	−362	−153	142
Explo5 V6.02 values					
$-\Delta_E U°$ (kJ kg^{-1})[k]	4545	967	4805	3051	4307
T_E (K)[l]	2742	1061	3234	2179	2677
p_{CJ} (kbar)[m]	156	64	176	98	129
V_{Det} (m s^{-1})[n]	6873	5065	6986	5885	6638
Gas vol. (L kg^{-1})[o]	787	774	771	793	822
I_s [s][p]	199	122	210	177	207

GAP, glycidylazidepolymer.
[a] BAM drop hammer (1 of 6).
[b] BAM friction tester (1 of 6).
[c] Electrostatic discharge.
[d] Oxygen balance.
[e] temperature of decomposition by DSC (β = 5 °C, onset values).
[f] Glass transition temperature (T_{mid}).
[g] density derived from pycnometer measurements.
[h] experimental combustion energy (constant volume).
[i] experimental molar enthalpy of combustion.
[j] molar enthalpy of formation.
[k] energy of explosion.
[l] explosion temperature.
[m] detonation pressure.
[n] detonation velocity.
[o] assuming only gaseous products.
[p] specific impulse (isobaric combustion, chamber pressure 70 bar, equilibrium expansion).
[q] values obtained from the EXPLO5 V6.02 database and Reference [40].

Compared with GAP (IS: 8 J, FS: > 360 N)[35] this can be regarded as clear advantage in terms of safety.

For analyzing the energetic properties of **7-8**, the energy of combustion (ΔU_c) was determined *via* bomb calorimetry. The enthalpy of formation could be calculated from the obtained values applying the HESS thermochemical cycle, as reported in literature.[36]

All calculations concerning the detonation parameters were carried out using the program package EXPLO5 (version 6.02)[37,38] and were based on the calculated heats of formation and attributed to the corresponding densities, determined *via* pycnometer. The obtained data of compounds **7-8** are given in Table I and compared with the energetic values of GAP.

As expected, the DIE-based compounds DIE-DNPD (**8a**) and DIE-BAMP (**8b**) show better energetic properties (regarding their energy of explosion $-\Delta_E U°$, detonation velocity V_{Det} and detonation pressure p_{CJ}, which are important values for the overall energetic performance of the system), due to their lower carbon content, than their corresponding HMDI-based derivatives HMDI-DNPD (**7a**) and HMDI-BAMP (**7b**), respectively. Whereas the DNPD-based compounds **7a** and **8a**, in accordance with their higher oxygen balance Ω, show in total better energetic values,[39] than the azide containing **7b** and **8b**. Compared with GAP, HMDI-DNPD (**7a**) and DIE-DNPD (**8a**) show a 6 to 12% higher energy of explosion $-\Delta_E U°$, which is an indication for the performed work of an explosive. Other important values for the evaluation of the energetic character of a compound are the detonation velocity V_{Det} and detonation pressure p_{CJ}. A comparison of these values shows, that compound **7a** and **8a** exceed the detonation velocity of GAP by 250 and 350 m s^{-1}, respectively. In case of the detonation pressure, the values of **7a** and **8a** are about 30 kbar to 50 kbar higher. The specific impulse I_s of **7a** and **8a**, an indication for the qualification as propellant, is in the same range like GAP. All in all, the calculations showed moderate energetic properties for the synthesized polyurethanes **7-8**, which establishes those compounds as interesting substances for further investigations concerning their suitability as binder in energetic formulations.

CONCLUSIONS

Four new polyurethanes were synthesized *via* two differing polyaddition reaction methods and were based on the diols 2,2-dinitropropane-1,3-diol (DNPD) and 2,2-bis(azidomethyl)propane-1,3-diol (BAMP) and the diisocyanates hexamethylene diisocyanate (HMDI) and diisocyanato ethane (DIE). Dependent on the respective diol, the obtained compounds possessed different consistencies, varying from elastic solids (DNPD based) to viscous liquids (BAMP based). The successful syntheses were proven by elemental analysis, ^{1}H, ^{13}C NMR and infrared spectroscopy. Compared with already established energetic polymers like the glycidyl azide polymer (GAP) or poly(glycidyl nitrate) (polyGLYN) the herein synthesized polyurethanes stand out due to their high mechanical stability (IS 40 J, FS >360 N; vs. IS 8 J, FS >360 N(GAP)[40]; IS 10 J FS 112 N (polyGLYN)[41]), which is a clear advantage in terms of safety. Besides the mechanical

stability, the synthesized polyurethanes also possess a moderate to good thermal stability with decomposition temperatures of 170 °C up to 210 °C, which are in the range of polyGLYN (170 °C)[5] or GAP (216 °C).[40]

The calculations of the energetic properties, based on bomb calorimetric measurements and the computer program EXPLO5 (version 6.02), showed moderate energetic properties for the compounds. The DNPD-based polyurethanes showed even better detonation parameters than GAP. These facts, along with glass transition temperatures as low as −38 °C (in case of the liquid BAMP-based compounds) mark the synthesized polyurethanes promising compounds for applications as new energetic binders in energetic formulations.

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