

Novel Insensitive Energetic Nitrogen-rich Polymers Based on Tetrazoles

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Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

Nitrogen-rich polymers were synthesized by radical polymerization using the reaction of 5-aminotetrazole with methacryloyl chloride and acryloyl chloride, respectively. The nitrogen content of poly(methacrylamidotetrazole) and poly(acrylamidotetrazole), as well as the energetic character of these compounds was increased by nitration of the amido moiety. The products remained however insensitive and had a very good thermal stability. All substances were characterized by using vibrational spectroscopy (IR), mass spectrometry, elemental analysis, as well as multinuclear NMR spectroscopy. Additionally, the impact and friction sensitivities were determined by BAM standards, and also the sensitivity against electrostatic discharge was studied. The energetic properties were investigated by bomb-calorimetric measurements and calculations with the EXPLO5 software, and the thermal stability was investigated by differential scanning calorimetry. All compounds are thermally highly stable materials. The high stability of the polymers towards impact and friction and the good energetic character makes these polymers promising candidates for applications as environmentally friendly nitrogen-rich polymers.

Key words: Tetrazoles, Polymers, Energetic Performance, Thermal Properties

Introduction

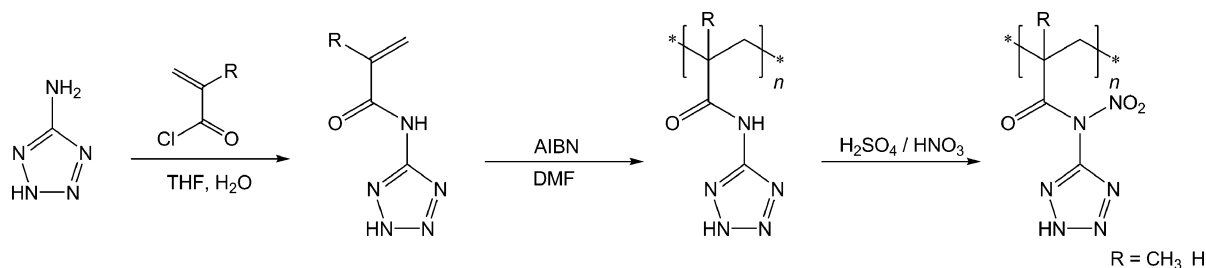
Nitrogen-rich energetic polymers are to date highly requested compounds for a wide range of applications. These applications vary from explosive binders and propellants in energetic compositions [1–3], to gas generating agents [4]. So far, commonly used polymers are nitrocellulose [5–7], azidocellulose nitrate [8] or glycidyl azide polymer (GAP) [9].

The disadvantages of these polymers are the energetic moieties. Azides [6] and nitro groups [7] are toxic and can be released into the environment by degradation of residues of unburned parts of the explosive composition. In order to replace these toxic substances, new energetic polymers, based on tetrazole rings in combination with groups that tend to polymerize easily are sought compounds. Therefore methacryl and acryl moieties were chosen [10]. These groups are known for their ability to easily polymerize. Another point of interest was the introduction of tetrazole moieties to these polymerizing systems. These heterocycles have

the advantage that the group itself possesses a nitrogen content of 79% in the case of 1*H*-tetrazole and therefore are promising candidates for environmentally friendly compounds [11]. This application is also supported by a combination of the high-energetic character with sufficient thermal stability [12] due to the aromatic ring system of the tetrazole moieties. These benefits could be useful for an application as an energetic polymer. The first known polymers based on tetrazoles were poly(1-vinyltetrazole) and poly(1-vinyl-5-aminotetrazole) [13]. But nevertheless, to date, within the wide range of applied nitrogen-rich polymers, compounds containing tetrazole moieties are rare.

Results and Discussion

Plenty of different techniques are known to polymerize various compounds. The polymerization of vinyl groups [10] is one of the most known and basic ways. Therefore 5-(methacrylamido)tetrazole (5-MAT, **1**) and 5-(acrylamido)tetrazole (5-AAT, **2**), showing an



Scheme 1. Synthesis of poly(methacrylnitramidotetrazole) and poly(acrylnitramidotetrazole).

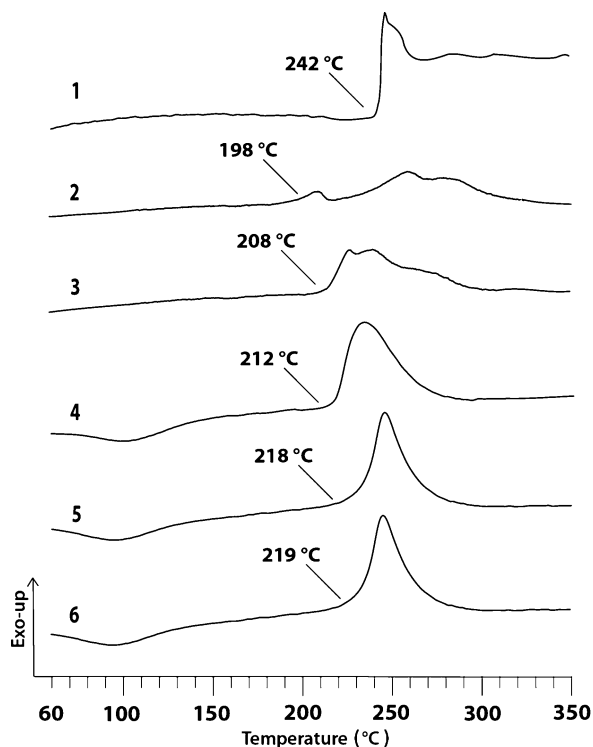
inherited vinyl group, were produced according to literature [14, 15].

To gain the polymers poly(methacrylamidotetrazole) (PMAT, **3**) and poly(acrylamidotetrazole) (PAAT, **4**) *via* the radical polymerization mechanism, azobisisobutyronitrile (AIBN) was used as initiator (Scheme 1).

Both products were analyzed by infrared spectroscopy, mass spectrometry and elemental analysis. Because all compounds were insoluble in common organic solvents, no NMR measurement could be performed.

Consequently the analytical methods for the characterization of solids were the confirmation techniques of choice. Mass spectrometry gave for both nitrated compounds **5** and **6** the molecular ion peak. Elemental analysis however showed small variations due to not nitrated molecules **3** and **4** as impurities diminishing the nitrogen content of the gained product, but also increasing the hydrogen and the carbon content. The fact that not all amido moieties are functionalized is a common problem in polymer chemistry, due to the sterical hindrance of the voluminous molecules.

Thermoplots of differential scanning calorimetry (DSC) measurements of **1–6** are depicted in Fig. 1. In order to determine the melting and decomposition temperatures, approximately 1 mg of each energetic material was measured in a pierced lid aluminum container. Whereas the compounds **1–3** show no melting point or range, the polymers PAAT (**4**), PMNT (**5**) and PANT (**6**) melt in the range of 70–110 °C. The monomers show rather diverse thermal stabilities. While **2** decomposes at 198 °C, 5-MAT (**1**) has a really good stability with a decomposition point of 242 °C. These desired properties are reflected in the polymers, most notably in the nitrated ones that are, with a decomposition temperature of 218 °C (**5**) and 219 °C (**6**), still more stable than GAP (200 °C) [16].

Fig. 1. DSC plots of 5-MAT (**1**), 5-AAT (**2**), PMAT (**3**), PAAT (**4**), PMNT (**5**), PANT (**6**).

The sensitivities of compounds **1–6** were investigated using the BAM (German Bundesanstalt für Materialforschung) drop hammer, [17] BAM friction tester [18] and an OZM electrostatic discharge device [19]. According to the UN recommendations on the transport of dangerous goods [20], compounds with greater impact sensitivity than 40 J and friction sensitivity of 360 N are classified as insensitive. Therefore, as all compounds (**1–6**) offer higher impact sensitivity than 40 J and friction sensitivity lower than 360 N, these products are insensitive, which is an out-

Table 1. Energetic properties and detonation parameters.

	1	2	3	4	5	6	GAP^a
Formula	C ₅ H ₇ N ₅ O	C ₄ H ₅ N ₅ O	C ₅ H ₇ N ₅ O	C ₄ H ₅ N ₅ O	C ₅ H ₆ N ₆ O	C ₄ H ₄ N ₆ O ₃	C ₃ H ₅ N ₃ O
Molecular mass, g mol ⁻¹	153.14	139.12	153.14	139.12	198.14	184.11	99.09
Impact sensitivity, J ^b	> 40	> 40	> 40	> 40	> 40	> 40	7
Friction sensitivity, N ^c	> 360	> 360	> 360	> 360	> 360	> 360	> 360
ESD test, J	0.6	0.6	1.5	0.7	0.7	1.1	–
N, % ^d	45.73	50.34	45.73	50.34	42.41	45.65	42.41
Ω, % ^e	–131	–109	–131	–109	–18	–61	–121
T _{dec.} , °C ^f	242	198	208	212	218	219	200
ρ, g cm ⁻³ g	1.6	1.6	1.4	1.5	1.6	1.7	1.3
Δ _f H _m ^o , kJ mol ⁻¹ h	614	–22	–18	38	479	459	–
Δ _f U ^o , kJ kg ⁻¹ i	4155	–21	30	410	2540	2606	–
EXPLO5 (version 5.05) values							
–Δ _E U _m ^o , kJ kg ⁻¹ j	5900	1997	2071	2406	5702	5697	4258
T _E , K ^k	3601	1831	1781	2065	4062	4436	2819
p _{C-J} , kbar ^l	87	41	44	46	86	91	71
V _{Det.} , m s ⁻¹ m	5459	3938	4074	4189	5461	5589	5047
Gas vol., L kg ⁻¹ n	710	678	678	682	738	745	739
I _{sp} , s	248	149	151	158	243	249	201

^a Values based on ref. [23] and the EXPLO5 database; ^b IS = impact sensitivity, BAM drop hammer, grain size (100–500 μm); ^c FS = friction sensitivity, BAM friction tester, grain size (100–500 μm); ^d nitrogen content; ^e oxygen balance [24]; ^f temperature of decomposition by DSC (β = 5 °C, onset values); ^g density obtained by pycnometer measurement; ^h molar enthalpy of formation; ⁱ energy of formation; ^j energy of explosion; ^k explosion temperature; ^l detonation pressure; ^m detonation velocity; ⁿ assuming only gaseous products.

standing advantage compared to GAP (impact sensitivity: 7 J). The energetic characteristics of the compounds were obtained by bomb calorimetric measurements along with calculations using the program package EXPLO5 utilizing version 5.05 [21, 22]. The input was made using the sum formula, energy of formation (bomb calorimetry) and the experimentally determined densities (pycnometer). The results of the detonation runs, together with the calculated energies of formation for the monomeric units (in case of the polymers) and the corresponding sensitivities are compiled in Table 1.

In a comparison of the values of Δ_EU_m^o (an indication of the work performed by the explosives during the detonation [25]) of the polymers, **5** and **6** show the highest energetic properties, even 25% higher than GAP (**5**: 5702 kJ kg⁻¹, **6**: 5697 kJ kg⁻¹, Table 1). Furthermore, the detonation velocity V_{Det.} of **5** and **6** exceeds that of GAP. A comparison of the values of polymers **5** and **6** shows that these polymers exceed the detonation velocity of GAP by 400 m s⁻¹ in case of **5** and by 500 m s⁻¹ in the case of **6**. The detonation velocity of the polymers **3** and **4** reside in a moderate area. The specific impulse, an indication of the qualification as propellant, is higher also for both nitrated polymers than the impulse of the com-

monly used polymer GAP. As a result, compounds **5** and **6** are suitable as environmentally friendly explosives or gas generators. Both compounds do not bear a toxic azide, but still possess very good explosive properties.

Conclusion

Four nitrogen-rich polymers were synthesized and characterized. Poly(methacrylamidotetrazole) (**3**) and poly(acrylamidotetrazole) (**4**) proved to be moderate explosives with good energetic properties that could be further improved by nitration, giving the compounds **5** and **6** with even better properties. The higher nitrogen content of 42% to 45% of these compounds, along with their outstanding insensitivity towards impact and friction, excellent energetic performance and good thermal stability, makes these polymers promising materials for the development of new gas-generating compositions and for an application as environmentally friendly nitrogen-rich materials for binder formulations.

Experimental Section

General Procedures. All chemical reagents and solvents of analytical grade were obtained from Sigma-Aldrich Inc.,

Fluka or Acros Organics and were used as supplied without further purification. ^1H and ^{13}C NMR spectra were recorded in $[\text{D}_6]\text{DMSO}$ using a Jeol Eclipse 400 instrument at 25 °C. The chemical shifts (δ) are given in ppm relative to tetramethylsilane (^1H , ^{13}C) as external standard. Coupling constants (J) are given in Hertz (Hz). Infrared (IR) spectra were recorded at room temperature using a Perkin Elmer Spectrum BX FT-IR-System equipped with an ATR unit. Transmittance values are qualitatively described as “very strong” (vs), “strong” (s), “medium” (m), “weak” (w) and “very weak” (vw). Mass spectra of the described compounds were measured using a Jeol MStation JMS 700 spectrometer. To record elemental analyses (CHNO), a Netsch Simultaneous Thermal Analyzer STA 429 was used. Melting and decomposition points were determined by differential scanning calorimetry (Linseis DSC PT-10 instrument, calibrated with pure indium and zinc as standards). Measurements were performed at a heating rate of 5 °C min^{-1} in closed aluminum containers with a hole (1 μm) in the lid for gas release to avoid an unsafe increase in pressure under a nitrogen flow of 5 mL min^{-1} . The reference sample was a closed aluminum container. The sensitivity data were performed using a BAM drop hammer and a BAM friction tester. The electrostatic sensitivity tests were carried out using an Electric Spark Tester ESD 2010 EN (OZM Research).

CAUTION! Tetrazoles are highly energetic compounds with sensitivity towards heat and impact. Although we had no problems in the syntheses, proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar[®] gloves and ear plugs) should be used when undertaking work involving these compounds.

Synthesis of 5-methacrylamidotetrazole (5-MAT, 1) [14]

Compound **1** was prepared according to a literature procedure using 5.00 g (48.52 mmol) 5-aminotetrazole monohydrate yielding a colorless solid (2.98 g, 40% yield). – IR (cm^{-1}): (intensity) $\tilde{\nu}$ = 3193 (s), 1667 (s), 1618 (s), 1596 (vs), 1444 (m), 1390 (s), 1231 (m), 1186 (m), 1036 (s), 738 (m). – ^1H NMR (270.2 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): δ = 1.96 (s, 3 H, CH_3), 5.73 (d, 1H, 3J = 1.47 Hz, = CH), 6.10 (s, 1H, = CH), 11.95 (s, 1H, CONH), 15.9 (s, 1H, tetrazole-NH). – ^{13}C NMR (67.9 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): δ = 18.8 (CH_3), 124.4 (CH_2), 138.2 (C_q), 150.8 (C_q -tetrazole), 167.2 ($\text{C}_q=\text{O}$). – MS ((+)-DEI): m/z = 41.08 [C_3H_5] $^+$, 69.03 [$\text{C}_4\text{H}_5\text{O}$] $^+$, 153.09 [M] $^+$. – EA ($\text{C}_5\text{H}_7\text{N}_5\text{O}$, 153.14): calcd. C 39.21, H 4.61, N 45.73; found 38.90, H 4.48, N 44.71 %.

Synthesis of 5-acrylamidotetrazole (5-AAT, 2) [14]

Acryloyl chloride (2.8 g, 2.5 mL, 31 mmol) was added dropwise to a suspension of 5-amino-1H-[1,2,4]tetrazole monohydrate (3.00 g, 29.2 mmol) in 50 mL THF and 3 mL water. The solution was stirred over night. Most

of the solvent was removed *in vacuo*, and the colorless solid (0.41 g, 10%) that precipitated was collected by filtration. – IR (cm^{-1}): (intensity) $\tilde{\nu}$ = 3454 (w), 3162 (m), 3016 (m), 2970 (s), 2948 (m), 2889 (m), 2143 (w), 1984 (w), 1738 (vs), 1678 (s), 1623 (m), 1593 (m), 1546 (m), 1455 (w), 1420 (s), 1365 (s), 1228 (s), 1308 (w), 1271 (w), 1229 (vs), 1217 (vs), 1112 (m), 1074 (m), 1057 (m), 1036 (s), 991 (s), 976 (s), 932 (w), 900 (w), 821 (m), 806 (m), 788 (vs), 737 (s), 690 (s), 657 (m). – ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): δ = 5.93 (dd, 1H, $^3J_{\text{H-H}(\text{trans})}$ = 9.62 Hz, $^3J_{\text{H-H}(\text{cis})}$ = 2.20 Hz; $\text{RCH}=\text{CH}_2$), 6.40 (dd, 1H, $^3J_{\text{H-H}(\text{trans})}$ = 17.04 Hz, $^3J_{\text{H-H}(\text{cis})}$ = 2.20 Hz, $\text{RCH}=\text{CH}_{\text{cis}}\text{H}$), 6.48 (dd, 1H, $^3J_{\text{H-H}(\text{trans})}$ = 17.18 Hz, $^3J_{\text{H-H}(\text{cis})}$ = 9.48 Hz, $\text{RCH}=\text{CH}_{\text{trans}}\text{H}$), 12.20 (s, 1H, CONH). – ^{13}C NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): δ = 129.8 (CH), 130.9 (CH_2), 150.1 (*ipso*-C), 163.8 (C=O). – MS ((+)-DEI): m/z = 139 [M] $^+$. – EA ($\text{C}_4\text{H}_5\text{N}_5\text{O}$, 139.12): calcd. C 34.54, H 3.62, N 50.35; found C 34.71, H 3.49, N 49.80 %.

Synthesis of poly(methacrylamidotetrazole) (PMAT, 3) [14]

A solution of **1** (2.35 g, 15.35 mmol) and azobisisobutyronitrile (AIBN, 24 mg, 0.14 mmol) in 20 mL dimethylformamide (DMF) was degassed for an hour and stirred over night at 65 °C. The reaction mixture was added dropwise to 250 mL methanol and 5 mL concentrated hydrochloric acid. The colorless solid was collected by filtration, washed with methanol and dried to give 2.05 g (87%) of a colorless solid. – IR (cm^{-1}): (intensity) $\tilde{\nu}$ = 3168 (m), 3000 (m), 2780 (m), 2455 (w), 1695 (m), 1651 (vs), 1574 (vs), 1586 (m), 1468 (m), 1439 (m), 1411 (m), 1385 (m), 1253 (w), 1157 (w), 1101 (m), 1036 (m), 995 (w), 894 (vw), 817 (vw), 739 (vw), 698 (vw), 663 (vw). – MS ((+)-DEI): m/z = 153 [M] $^+$, 306 [$\text{M}+\text{M}$] $^+$. – EA ($\text{C}_5\text{H}_8\text{N}_5\text{O}$, 154.15): calcd. C 38.96, H 5.23, N 45.43; found C 45.14, H 38.13, N 45.61 %.

Synthesis of poly(acrylamidotetrazole) (PAAT, 4)

A mixture of **2** (1.50 g, 10.8 mmol) and AIBN (11.5 mg, 0.07 mmol) in 12 mL DMF was degassed and stirred over night at 65 °C. The suspension was then added dropwise to 250 mL of methanol and 5 mL of concentrated hydrochloric acid. The precipitate was collected by filtration and washed with methanol, giving 1.40 g (94%) of a colorless solid. – IR (cm^{-1}): (intensity) $\tilde{\nu}$ = 3538 (w), 3016 (m), 2970 (m), 2942 (m), 2365 (w), 2337 (w), 2134 (w), 1738 (s), 1584 (s), 1448 (m), 1414 (m), 1365 (s), 1229 (s), 1217 (s), 1205 (s), 1116 (w), 1091 (w), 1043 (m), 1003 (m), 895 (w), 740 (s), 668 (s). – MS ((+)-DEI): m/z = 139 [M] $^+$. – EA ($\text{C}_4\text{H}_5\text{N}_5\text{O}$, 139.12): calcd. C 34.54, H 3.62, N 50.35; found C 29.58, H 5.91, N 33.08 %.

Synthesis of poly(methacrylnitramidotetrazole) (PMNT, 5)

Tetrazole **3** (0.5 g, 3.28 mmol) was dissolved in 1.5 mL acetic anhydride and 0.5 mL nitric acid, whilst cooling with ice, and the mixture stirred. After two hours the liquid was quenched with ice, and the product was filtered off. It was obtained as a colorless solid (0.42 g, 65%). – IR (cm^{-1}): (intensity) $\tilde{\nu} = 3217$ (w), 2361 (w), 1700 (vs), 1653 (m), 1576 (vs), 1457 (m), 1391 (m), 1165 (s), 1024 (s). – MS ((+)-DEI): $m/z = 199$ [M+H]⁺. – EA (C₅H₆N₆O₃, 198.14): calcd. C 30.31, H 3.05, N 42.41; found C 32.47, H 5.32, N 37.31%.

Synthesis of poly(acrylnitramidotetrazole) (PANT, 6)

Tetrazole **4** (0.5 g, 3.28 mmol) was dissolved in 1.5 mL acetic anhydride and 0.5 mL nitric acid, whilst cooling with ice, and the mixture stirred. After two hours the liquid was quenched with ice. The product was filtered off and gave a colorless solid (0.42 g, 65%). – IR (cm^{-1}): (intensity) $\tilde{\nu} = 3212$ (w), 3045 (w), 2914 (w), 2052 (vw), 1992 (vw), 1698 (m), 1583 (vs), 1540 (vw), 1447 (w), 1406 (m), 1330 (m), 1247 (m), 1169 (m), 1117 (w), 1040 (s), 1000 (w), 942 (w), 868 (w), 796 (w), 737 (m), 657 (w). – MS ((+)-DEI):

$m/z = 184$ [M]⁺. – EA (C₄H₄N₆O₃, 184.11): calcd. C 26.09, H 2.19, N 45.65; found C 29.79, H 4.53, N 42.16%.

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- [1] I. B. Mishra, L. J. Vande Kieft, US 4875949, **1989**.
 [2] F. J. Einberg, US 4013596, **1977**.
 [3] D. A. Merran, DSTO-GD-0492, **2006**.
 [4] C. G. Miller, G. K. Williams, US 2005272873, **2005**.
 [5] W. E. Thomas, T. E. Martin, US 3963545, **1976**.
 [6] W. E. Baumgartner, P. G. Butts, US 3861970, **1975**.
 [7] I. I. A. Wallace, P. C. Braithwaite, J. B. Neidert, US 5468313, **1995**.
 [8] E. E. Gilbert, *J. Energ. Mater.* **1985**, *3*, 319.
 [9] J. K. Nair, R. R. Soman, N. T. Agawane, R. S. Satpute, T. Mukundan, S. D. Kakade, M. Gupta, S. N. Asthana, *J. Polym. Mater.* **2005**, *22*, 87.
 [10] H. Nulwala, D. J. Burke, A. Khan, A. Serrano, C. J. Hawker, *Macromolecules* **2010**, *43*, 5474.
 [11] T. M. Klapötke, C. M. Sabaté, *Chem. Mater.* **2008**, *20*, 3629.
 [12] P. N. Gaponik, O. A. Ivashkevich, N. I. Chernavina, A. I. Lesnikovich, G. T. Sukhanov, G. A. Gareev, *Angew. Makromol. Chem.* **1994**, *219*, 89.
 [13] W. G. Finnegan, R. A. Henry, S. Skolnik, US 3004959, **1961**.
 [14] A. Taden, A. H. Tait, A. Kraft, *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 4333.
 [15] S. Samanta, Dissertation, Georgia Institute of Technology, Atlanta, Georgia (USA), **2007**.
 [16] R. Meyer, J. Köhler, A. Homburg *Explosives*, 6th ed., Wiley-VCH, Weinheim, **2007**.
 [17] *NATO standardization agreement (STANAG) on explosives, impact sensitivity tests*, no. 4489, 1st ed., **1999**.
 [18] *NATO standardization agreement (STANAG) on explosive, friction sensitivity tests*, no. 4487, 1st ed., **2002**.
 [19] *NATO standardization agreement (STANAG) on explosives, electrostatic discharge sensitivity tests*, no.4490, 1st ed., **2001**.
 [20] *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*; 4th ed., United Nations, New York, **2004**.
 [21] M. Sueska, EXPLO5 (version 5.5), Zagreb (Croatia) **2010**.
 [22] M. Sueska, *Mat. Sci. For.* **2004**, 465–466, 325.
 [23] R. Meyer, J. Köhler, A. Homburg, *Explosives*, 5th ed., Wiley-VCH, Weinheim, **2002**.
 [24] www.bam.de/en/index.htm (accessed February 15, 2013).
 [25] T. M. Klapötke, S. M. Sproll, *Eur. J. Org. Chem.* **2010**, *2010*, 1169.