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Nitrogen-Rich Polymers Based on 5-Bromo-1-vinyl-1*H*-tetrazole

Thomas M. Klapötke*[a] **and Stefan M. Sproll**[a]

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Nitrogen-rich polymers with contents of nitrogen between 50 and 60 % were synthesized by radical polymerization using 1-(1-vinyl-1*H*-tetrazol-5-yl)hydrazine and 1-methyl-1-(1-vinyl-1*H*-tetrazol-5-yl)hydrazine. The monomers were obtained by substitution reactions of hydrazine derivatives and 5-bromo-1-vinyl-1*H*-tetrazole. Moreover, the poly-1-(1-vinyl-1*H*-tetrazol-5-yl)hydrazine was converted into the corresponding 5-azidotetrazolyl-containing polymer by the reaction with sodium nitrite. The polymers were characterized by measurements of the molecular weights, by vibrational spectroscopy (IR) and elemental analysis. The thermal stability was determined by differential scanning calorimetry and the sensitivity towards friction and impact were determined by BAM standards. The energetic properties were investigated by bomb calorimetric measurements and calculations with the EXPLO5 software. The high stability of the polymers towards impact and friction, along with their sufficient thermal stability (175–279 °C) and moderate energetic characters renders these polymers into promising compounds for an application as environmentally friendly nitrogen-rich polymers.

Introduction

Tetrazoles claim an outstanding place among the group of nitrogen-rich heterocycles. Their high content of nitrogen along with a high thermal stability predestined them as valuable building blocks for new energetic compounds.[1] Besides their usage for military or civil explosives,[2] they cover a wide field of applications ranging from pharmaceuticals[3] over biomedical applications[4] and membranes[5] to antifoggants in photographic materials.[6] Moreover, with a content of nitrogen of 79 % of 1*H*-tetrazole, these heterocycles are promising candidates for environmentally friendly propellants.[7]

Although tetrazoles are a well-investigated group of heterocycles, the number of polymers containing these heterocycles is small. The first polymers based on tetrazoles were 1-poly(vinyltetrazole) and 1-poly(vinyl-5-aminotetrazole).[8] Today, several approaches to synthesize 1-poly(vinyltetrazole) are known, either by radical polymerization of 1-poly(vinyltetrazole)[8] or by the conversion of polyvinylnitrile into the tetrazole moiety by a [2+3] cycloaddition reaction with hydrazoic acid.[9] The disadvantage of these polymers is their extremely low solubility in any solvent, preventing them from any application. Therefore, they are used as copolymers with polystyrene.[10]

In order to improve their solubility and thus the application of these polymers, the introduction of hydrazine moieties was investigated. 5-Bromo-1-vinyltetrazole (**1**) proved to be a versatile starting material. Since the intention of this work was the synthesis of nitrogen-rich polymers, only hydrazine and monomethylhydrazine were used.

To further improve the energetic characteristics, the conversion of polyvinyl tetrazolylhydrazine into the corresponding 5-azidotetrazole-containing polymer was investigated. The investigation of the physical stabilities of the small number of known alkylated 5-azidotetrazoles proves these energetic materials as very dangerous compounds (sensitivity towards friction: > 5 N, sensitivity towards impact: > 0.15 J).[11] Despite their high sensitivity towards physical stress, their thermal stability (up to 170 °C) turns these compounds into interesting building blocks for nitrogen-rich polymers. In the case of 5-azido-1*H*-tetrazole-containing polymer, the long carbon chains of the polyvinyl moiety could work as a protection against physical stress, turning this polymer into a very interesting nitrogen-containing polymer.

Results and Discussion

For the synthesis of 5-bromo-1-vinyl-1*H*-tetrazole (**1**), the corresponding 5-bromo-1-(2-hydroxyethyl)tetrazole (**2**), reported by Bayes,[12] proved to be a suitable starting material (Scheme 1).

In order to convert the hydroxyethyl group into the desired vinyl group, several approaches were investigated. The idea was the elimination of the hydroxy group, leading to the formation of the desired vinyl group. A conversion of the hydroxy group into the corresponding chlorinated compound, as reported in literature for 1-(2-hydroxyethyl)-5-amino-1*H*-tetrazole by Finnegan[13] and a subsequent elimi-

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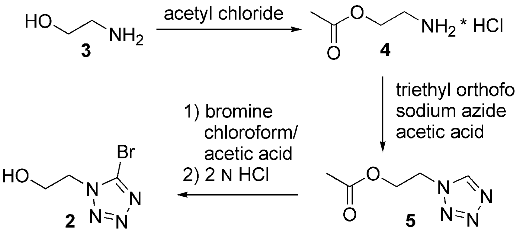
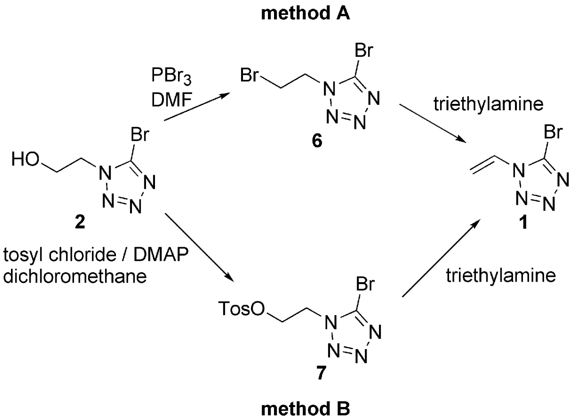
[a] Department of Chemistry and Biochemistry, University of Munich (LMU),
Butenandtstr. 5-13, 81377 München, Germany
Fax: +49-89-2180-77492
E-mail: tmk@cup.uni-muenchen.de



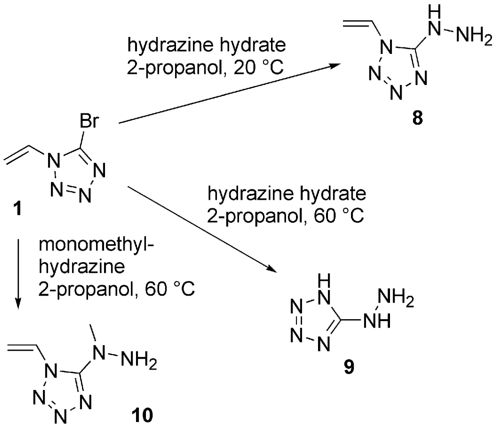
Scheme 1. Synthesis of **2**.

nation by potassium hydroxide proved not to be efficient, due to a halogen exchange at the 5-position of **2** along with side products, resulting in alkaline hydrolyses of the bromine atom. Taking these results into account, two methods for the preparation of **1** were developed. **Method A** (Scheme 2) avoids the halogen exchange at the 5-position by a bromination instead of the chlorination of the hydroxy group by using PBr_3 in dimethylformamide.[14] The following elimination of the bromine atom was undertaken by triethylamine with a yield of 50%. In order to improve the resulting overall yield of 21%, the hydroxy group was converted into the corresponding tosylate by the reaction of tosylchloride with **2** in dichloromethane[15] (**method B**, Scheme 2). The yield of the tosylation with 80% exceeded the yield of the bromination of the hydroxy group by 40%. The elimination of the tosyl group of **7** by triethylamine at 100 °C gave higher yields (57%) than the elimination of the bromine (Scheme 2). The overall yield of **method A** (21%) could be improved to 46% in the case of **method B**.



Scheme 2. Synthesis of 5-bromo-1-vinyl-1*H*-tetrazole (**1**).

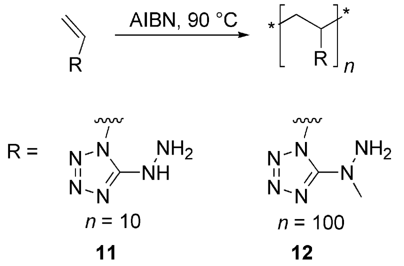
In order to increase the nitrogen content of the monomer, the bromine atom was substituted by hydrazine and methylhydrazine.[12b] The experiments showed that the formation of the products **8** and **10** is dependent on the reaction conditions. In contrast to the formation of **10**, which was performed at 60 °C, the formation of **8** was only possible at ambient temperature. Applying the same conditions as for the synthesis of **10** resulted in a loss of the vinyl group and only yielded 5-tetrazolylhydrazine **9**. Moreover, the purification of **8** was difficult, because of its high solubility in water, along with a hygroscopic character. Beside the impurities of water and hydrazine, **8** was more likely to form the corresponding bromide by the reaction of **8** with hydrobromic acid formed during the substitution reaction, than compound **10** (Scheme 3).



Scheme 3. Synthesis of the nitrogen-rich monomers **8** and **10**.

Besides the polymerization of the tetrazolylhydrazine, another method for the synthesis of nitrogen-rich polymers based on **1** would be a polymerization of **1** and a subsequent substitution of the bromine atom by a polymer analogue reaction. Trials to polymerize **1** by using AIBN in bulk at 80 °C resulted in a deflagration of **1** after 5 to 10 min in three of four experiments. Beside the radical polymerization in bulk, a radical polymerization in different solvents and anionic and cationic polymerization in solution were carried out, but only yielded starting material.

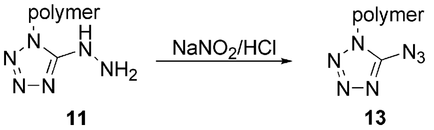
The polymerization of **8** and **10** was carried out in bulk by using AIBN. A polymerization in solution only yielded starting materials, like the experiments of the polymerization of **1** in solution. Therefore, the polymerization had to be performed in bulk at 90 °C. The AIBN had to be added carefully in several steps over 15 min, because an addition of more than 60 mg of AIBN resulted in a rise of temperature and a subsequent deflagration of **8** or **10**. One problem of the polymerization turned out to be the hydrazine moiety. The hydrogen atoms act as radical interceptors, leading to short chains along with starting material. To obtain a complete conversion, several portions of AIBN had to be added over 15 min (Scheme 4). Nevertheless, the yield of the polymerization of **8** (25%–30%) was much lower than the yield of the polymerization of **10** (85%). An explanation could be the loss of the vinyl moiety at higher temperatures along with a decomposition initiated by the AIBN.



Scheme 4. Polymerization of **8** and **10**.

The investigation of the average molecular masses (M_n) of **11** and **12** showed the expected difference. Whereas the polymer formed by the polymerization of **8** possessed a value for M_n corresponding to 10 molecular formulas in one chain, the polymer of **10** was much longer (about 100 molecular formulas per chain). This effect can be explained by the acidic NH-proton of **8** acting more efficiently as a radical interceptor of the NH_2-protons. Moreover the shorter chains can also be explained by impurities of water or hydrazine, being always present in the samples of **8** along with the slow decomposition of **8** at increased temperature.

In order to further increase the nitrogen content of the polymer, the hydrazine moiety was converted into an azide group. The conversion of **11** to the corresponding 5-azido-1*H*-tetrazole-containing polymer (**13**) was carried out by the reaction of sodium nitrite and the hydrazine moiety in 2N HCl. Being not soluble in aqueous media, a suspension of **11** in the hydrochloric acid was used. To ensure a complete conversion, an excess of sodium nitrite was applied (Scheme 5).



Scheme 5. Synthesis of **13**.

The analysis of **13** showed a partial decomposition of the tetrazolylhydrazine moieties. The determination of the average molecular weight M_n was undertaken by GPC. One problem was the insolubility even in DMF. The determination of M_n was carried out with the soluble parts of the polymer whereas the insoluble parts were dismissed (insoluble parts: ca. 15%). Using an IR and UV 275 nm detector the average M_n was determined to be 1400 g/mol, corresponding to ten monomers in a chain. The elemental analysis (different charges of the polymer varied only little), along with the average molecular weight, allowed an estimated formula of $C_{37}H_{56}N_{51}O_{10}$. The calculated formula for a chain of ten monomers ($C_{30}H_{30}N_{70}$) differs significantly from the experimentally obtained one. The main differences are the reduced content of nitrogen and the increased content of oxygen. The reduced content of nitrogen can be explained with a partial decomposition of the hydrazine and tetrazole moiety yielding amine-containing parts. Taking this assumption into account, the oxygen content can be explained by a nitration of the formed amines, yielding primary or secondary nitramines, besides other impurities. The nitro groups can be detected in the IR spectra of **13**. Beside the strong vibration of the azide group around 2100 cm^{-1}, the commonly known vibrations of the nitro group around 1600–1500 cm^{-1} and at 800 cm^{-1} can be inevitably assigned.[16] The brown color of the polymer can be ascribed to the big amount of decomposition products, results of the diazotization of the hydrazine moiety.

Compound **7** crystallizes in the monoclinic space group $P2_1/c$ with four molecular formulas per unit cell (Figure 1). The arrangement of the molecules in the crystal structure is zig-zag-like along the *y*-axis. The structure is stabilized by an intermolecular interaction of the bromine atom with one oxygen atom of the tosyl moiety (Figure 2). The distance between the bromine atom and the oxygen atom O2 is found to be 3.0006(14) Å. The distance between a bromine atom and an oxygen atom without any interactions is reported as 3.37 Å.[17] The distance found in the crystal structure is by 12% shorter than the distance without interaction, allowing the assumption of an intermolecular bromine–oxygen interaction.

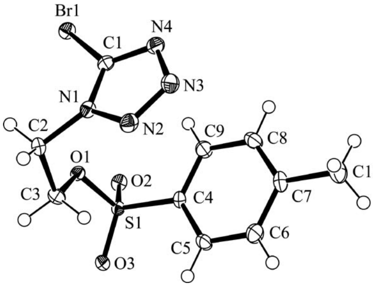


Figure 1. Molecular structure of **7**. Thermal ellipsoids are drawn at the 50% probability level.

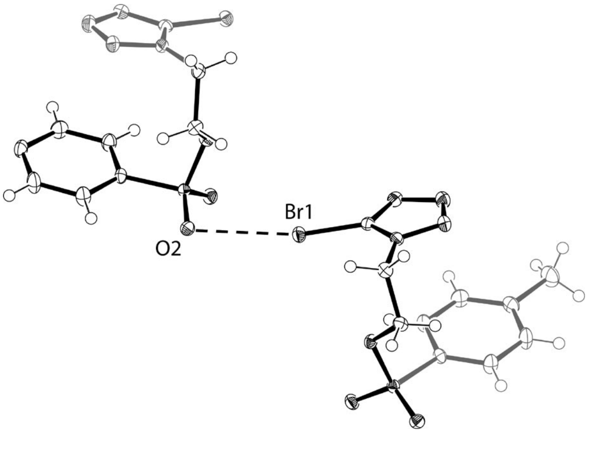


Figure 2. Intermolecular interaction of the bromine atom with the oxygen atom O2.

Compound **1** crystallizes in the orthorhombic space group *Pnma* with four molecular formulas per unit cell (Figure 3). The geometry of the molecule is planar, allowing the assumption, that the π-system is delocalized over the whole molecule. The molecules form zig-zag chains along the x-axis, caused by intermolecular interactions of the bromine atom and N4 of the tetrazole moiety (Figure 4). The distance between Br1 and N4 in the crystal structure is found to be 2.999(2) Å. The distance between a bromine atom and a nitrogen atom without interactions is reported to be 3.4 Å.[17] Due to the planar geometry of **1**, the chains form layers. Between these layers, no intermolecular interactions can be observed.

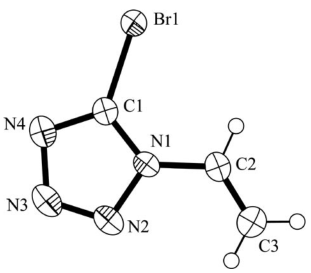


Figure 3. Molecular structure of **1**. Thermal ellipsoids are drawn at the 50% probability level.

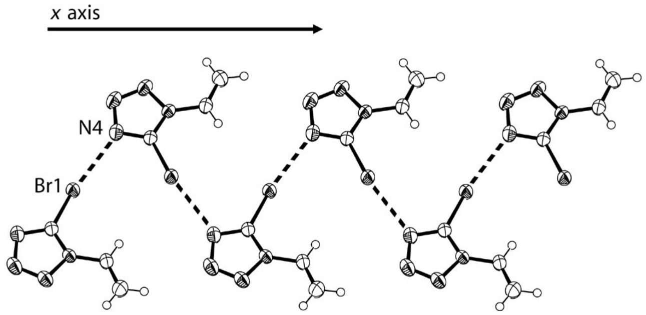


Figure 4. Intermolecular interactions of the bromine with N4 along the *x*-axis.

Compound **10** crystallizes in the monoclinic space group $P2_1/n$ with four molecular forumulas per unit cell (Figure 5). The planar coordination geometry of N5 (the three angles are 120° and the N6–N5–C1–N4 torsion angle is found to be 177°) showing the sp^2-hybridisation of the N5 nitrogen, with the free electron pair being part of the delocalized π-electron system of the molecule. The free electron pair of N6 directly points towards the proton at C3 of the vinyl groups. This finding leads to the assumption that N6 forms an intramolecular hydrogen bridge to the proton at C3 [D···A: 2.957(3) Å; <DHA: 124.9(17)°]. In addition to the intramolecular hydrogen bridge, two other hydrogen bridges are found. The first is formed by the first proton of N6 to N4 and the second by the second proton of N6 to N2 [D···A: 3.070(2) Å, 3.270(3) Å; <DHA: 158(2)°, 150(2)°; Figure 6]. The arrangement of the molecules leads to a zig-zag pattern along the *y*-axis.

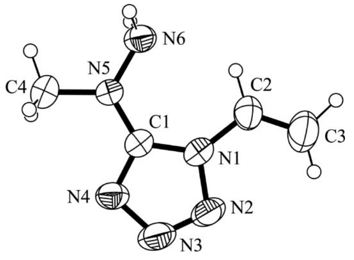


Figure 5. Molecular structure of **7**. Thermal ellipsoids are drawn at the 50% probability level.

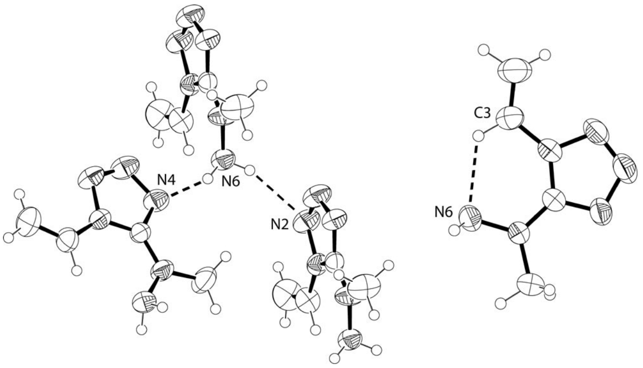


Figure 6. Inter- and intramolecular hydrogen bridges of **7**. Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Energetic properties of **11**, **12** and **13**.

	11	**12**	**13**	**GAP**[j]
Molecular formula	$C_{31}N_{56}H_{65}O_2$	$C_{413}N_{575}H_{760}O_{14}$	$C_{37}N_{51}H_{56}O_{10}$	$(C_3N_3H_5O)_{20}$
T_{dec} [°C]	203	276	174	216
M_n [g mol^{-1}]	1254	13990	1375	2000
Density [g cm^{-3}][a]	1.45	1.45	1.45	1.3
Sensitivity towards friction [N]	360	360	160	360
Sensitivity towards impact [J]	35	45	7	7
$-\Delta U_{comb.}$ [cal g^{-1}][b]	4460	4650	4464	–
$-\Delta H_{comb}$ [kJ mol^{-1}][c]	23384	272630	25656	–
$\Delta_f H_m$ [kJ mol^{-1}][d]	1754	–30	2962	–
Values calculated by EXPLO5 V5.02				
$-\Delta_E U_m°$ [kJ kg^{-1}][e]	2621	1160	4324	4444
T_E [K][f]	2015	1249	2957	2860
p_{C-J} [kbar][g]	154	100	173	135
D [m s^{-1}][h]	7074	6005	7205	6629
Gas vol. [L kg^{-1}][i]	792	764	721	738
I_s [s][k]	166	126	200	195
I_s [s][l]	243	234	247	248

[a] Estimated from a structure determination. [b] Experimental (constant volume) combustion energy. [c] Experimental molar enthalpy of combustion. [d] Molar enthalpy of formation. [e] Energy of explosion. [f] Explosion temperature. [g] Detonation pressure. [h] Detonation velocity. [i] Assuming only gaseous products. [j] Obtained from the database of EXPLO5 V5.02. [k] Specific impulse (isobaric combustion, chamber pressure 60 bar, frozen expansion). [l] Specific impulse of a mixture containing 75% ammonium dinitramide as oxidizer.

Comparing the values of $\Delta_E U_m^\circ$ (an indication of the work performed by the explosive) of the polymers, **13** showes the highest energetic properties, due to the 5-azidotetrazole moieties (**11**: –2621 kJ kg^{-1}, **12**: –1160 kJ kg^{-1} and **13**: –4324 kJ kg^{-1}; Table 1). As expected, polymer **12** possesses the lowest energetic properties, due to the methyl moiety stabilizing the tetrazolylhydrazine ($\Delta_E U_m^\circ$ only 25% of $\Delta_E U_m^\circ$ of **13**). The energetic character of polymer **11** lies between the $\Delta_E U_m^\circ$ values of **12** and **13**. The value of $\Delta_E U_m^\circ$ is in the case of **13** almost equal to that of glycidyl azide polymer (GAP, a common energetic binder). Another important value for the evaluation of energetic characteristics is the detonation velocity *D*. A comparison of these values of polymers **11** to **13** shows, that polymer **11** and **13** exceed the detonation velocity of GAP by 400 m s^{-1} in case of **11** and 600 m s^{-1} in the case of **13**. The specific impulse, an indication of the qualification as propellant, is only in the case of **13** comparable with the value of GAP.

The thermal stability was determined by DSC measurements. Polymer **12** possesses the highest thermal stability of 276 °C. Polymers **11** and **13** are in the range of GAP (203 °C and 174 °C), whereas the decomposition point of **13** is about 30 °C lower than that of **11**. The sensitivity towards impact and friction was determined by BAM methods.[18] Polymers **11** and **12** proved to be insensitive towards friction and less sensitive towards impact. Polymer **13** was sensitive towards friction and sensitive towards impact. The physical stability of polymers **11** and **12** is much higher than that of GAP, whereas the values of **13** are in the same range. The difference of the sensitivity towards friction of **13** and GAP can be explained by the consistency of the polymers (solid in the case of **13**, viscous oil in the case of GAP).

The advantage of polymer **13** is its comparable value of $\Delta_E U_m^\circ$ with the value of GAP, along with a much higher detonation velocity. Moreover, **13** is a solid, in contrast to GAP, which has to be cured if applied as binder.

Conclusions

Three nitrogen-rich polymers were synthesized and characterized. Poly-1-vinyl(5-hydrazinyl)-1*H*-tetrazole (**11**), poly-1-vinyl(5–1-methylhydrazinyl)-1*H*-tetrazole (**12**) and the 5-azido-1*H*-tetrazole-containing polymer (**13**) proved to be moderate to good explosives along with sufficient thermal and physical stabilities. Their content of nitrogen is located between 50 and 60%, turning them into promising materials for the development of new gas generating compositions. The synthesis of **11**, **12** and **13** was carried out using 5-bromo-1-vinyltetrazole **1** as starting material. The polymers were investigated by vibrational spectroscopy (IR) and the energetic properties were determined by bomb calorimetric measurements. The polymers **11** and **12** are soluble in DMSO and in acids.

Experimental Section

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

General: All chemical reagents and solvents of analytical grade were obtained from Sigma–Aldrich or Acros Organics and used as supplied. All chemical reagents and solvents of analytical grade were obtained from Sigma–Aldrich or Acros Organics and used as supplied. 2-(5-Bromo-1*H*-tetrazol-1-yl)ethanol (**2**) was prepared according to Bayes.[12] ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded using a JEOL Eclipse 400 instrument. The spectra were measured in [D$_6$]DMSO, $CDCl_3$ or D_2O. The chemical shifts are given relative to tetramethylsilane (^{1}H, ^{13}C) or nitromethane (^{15}N) as external standards. Coupling constants (J) are given in Hertz (Hz). Infrared (IR) spectra were recorded using a Perkin–Elmer Spectrum One FT-IR instrument and KBr pellets or NaCl plates at room temperature. Raman spectra were recorded using Perkin–Elmer Spectrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm). The intensities are reported in percentages relative to the most intense peak and are given in parentheses. Elemental analyses were performed with a Netsch Simultaneous Thermal Analyzer STA 429. Melting points were determined using differential scanning calorimetry (Linseis DSC PT-10 instrument). Measurements were performed at a heating rate of 5 °C min^{-1} in closed aluminium containers with a hole (1 µm) on the top for gas release with a nitrogen flow of 5 mL min^{-1}. The reference sample was a closed aluminium container. The molecular weights were measured by Fa. PSS, Mainz using a TSP P1000 HPLC pump with 1.0 mL min^{-1} flow, a TSP AS3000 injection system with 50 µL volume of injection and a Showdex Differentialrefractometer RI 71 as detector. The analysis was done using PSS-WinGPC Unity Version 7.2. As column were used PSS-GRAM, 10 µm 30 Å, ID 8.0 mm × 50 mm, PSS-GRAM, 10 µm 30 Å, ID 8.0 mm × 300 mm, PSS-GRAM, 10 µm 100 Å, ID 8.0 mm × 300 mm and -GRAM, 10 µm 3000 Å, ID 8.0 mm × 300 mm. DMF containing 0.01 M $LiNO_3$ or DMSO containing 5 g L^{-1} was used as eluent. The calibration was done using a polystyrene standard.

2-(5-Bromo-1*H*-tetrazol-1-yl)ethyl 4-Methylbenzenesulfonate (7): *p*-Toluenesulfonyl chloride (18.0 g, 94 mmol), triethylamine (9.8 g, 98 mmol) and 4-(dimethylamino)pyridine (5.7 g, 47 mmol) were added to a solution of 2-(5-bromo-1*H*-tetrazol-1-yl)ethanol (18.0 g, 94 mmol) in dichloromethane at 0 °C. After stirring for 3 h at ambient temperature, the reaction mixture was washed three times with saturated ammonium chloride solution. The organic phase was dried with sodium sulfate and the solvent was removed under reduced pressure. The product was obtained as brownish solid (25.7 g, 74.3 mmol, 79%). m.p. 91 °C. IR (KBr): $\tilde{\nu}$ = 3977 (vw), 2975 (vw), 2973 (vw), 1597 (w), 1454 (m), 1436 (m), 1412 (m), 1395 (m), 1355 (vs), 1293 (w), 1241 (w), 1190 (vs), 1177 (vs), 1135 (m), 1094 (m), 1052 (m), 1005 (s), 906 (s), 809 (m), 776 (m), 776 (s), 664 (s), 578 (m), 554 (s), 489 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.42 (s, 3 H, C*H*$_3$), 4.46 (t, ^3J = 4.95 Hz, 2 H, C*H*$_2$), 4.63 (t, ^3J = 4.95 Hz, 2 H, C*H*$_2$), 7.29 (d, ^3J = 7.97 Hz, 2 H, C*H*), 7.61 (d, ^3J = 8.25 Hz, 2 H, C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.8 (*C*H$_3$), 47.3 (*C*H$_2$), 66.1 (*C*H$_2$), 127.8 (*C*H), 130.3 (*C*H), 141.7 (C_q), 145.9 ($C_{qtetrazol}$) ppm. *m*/*z* (DCI$^+$): 348.0 (10), 346.0 (10) (M), 284.1 (22), 282.1 (22), 240.1 (5), 238.1 (5), 198.1 (7), 175.2 (12), 171.1 (4), 155.1 (36), 131.2 (7), 91.1 (100), 90.2 (24), 89.2 (7), 65.2 (23), 63.2 (5), 39.1 (5). $C_{10}H_{11}BrN_4O_3S$ (347.19): calcd. : C 34.59, H 3.19; N 16.14; found C 34.73, H 3.03, N 16.26: Friction sensitivity: >360 N; impact sensitivity: >100 J.

5-Bromo-1-vinyl-1*H*-tetrazole (1): Benzenesulfonate **7** (10.3 g, 29.3 mmol) was suspended in 20 mL of triethylamine and refluxed for 4 h. After addition of 200 mL of 2N HCl, the aqueous phase was then extracted 3 times with ethyl ether. The combined organic phases were then extracted with 80 mL of 2N HCl, saturated sodium carbonate solution and 100 mL of brine. After removal of the solvent in slightly reduced vacuum, the product was recovered by sublimation from the dark brown residue and obtained as colorless crystals (2.9 g, 17 mmol, 57%). m.p. 57 °C, dec. 136 °C. IR (KBr): $\tilde{\nu}$ = 3128 (vw), 3100 (vw), 2944 (vw), 1734 (vw), 1638 (s), 1424 (s), 1401 (s), 1373 (s), 1259 (w), 1227 (m), 1200 (w), 1108 (vs), 1053 (m), 1017 (m), 962 (w), 944 (m), 962 (m), 802 (w), 720 (vw), 669 (m), 637 (w), 550 (vw), 532 (vw) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 5.50 (d, ^1J = 1.92, $^3J_{cis}$ = 8.79 Hz, 1 H, CH_2), 6.19 (d, ^1J = 1.92, $^3J_{trans}$ = 15.39 Hz, 1 H, CH_2), 7.92 (dd, $^3J_{trans}$ = 15.39, $^3J_{cis}$ = 8.79 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 111.8 (CH_2), 125.1 (CH), 131.9 (C_q) ppm. *m/z* (DCI^+): 175.0 [M + H], 69. $C_3H_3BrN_4$ (174.99): calcd. C 20.59, H 1.73, N 32.02; found N 31.82, C 20.92, H 1.91. Friction sensitivity: >120 N; impact sensitivity: >35 J.

1-(1-Vinyl-1*H*-tetrazol-5-yl)hydrazine (8): Tetrazole **1** (2.0 g, 11.6 mmol) was dissolved in 20 mL of 2-propanol. Hydrazine monohydrate (2.3 g, 46.4 mmol) was added and the reaction mixture stirred for 12 h. The formed hydrazinium hydrobromide was filtered off and the solvent removed under reduced pressure. The product was obtained as slightly impure oil, which solidified over several hours (0.4 g, 3.2 mmol, 27%). m.p. 70 °C, dec. 207 °C. IR (KBr): $\tilde{\nu}$ = 3426 (vs), 2956 (m), 2918 (m), 2853 (w), 1645 (m), 1580 (m), 1393 (w), 1312 (vw), 1260 (w), 1168 (w), 1099 (m), 1017 (w), 972 (m), 800 (m), 735 (w) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 4.55 (br. s, 2 H, NH_2), 5.16 (d, $^3J_{cis}$ = 8.91 Hz, 1 H, CH_2), 5.70 (d, $^3J_{trans}$ = 15.73 Hz, 1 H, CH_2), 7.30 (dd, $^3J_{trans}$ = 15.73, $^3J_{cis}$ = 8.91 Hz, 1 H, CH), 8.44 (s, 1 H, NH) ppm. ^{13}C NMR ([D_6]DMSO): δ = 105.6 (CH_2), 126.6 (CH), 157.2 (C_q) ppm. *m/z* (DEI^+): 126.2 [M] (18), 99.2 (43), 91.2 (9), 84.2 (18), 82.1 (11), 80.1 (11), 69.2 (10), 68.2 (15), 57.2 (17), 44.1 (15), 43.2 (100), 42.2 (53), 41.2 (18), 39.2 (11), 30.2 (11), 29.1 (24), 28.2 (76), 27.1 (17). $C_3H_6N_6\cdot 0.2HBr$ (126.12): calcd. C 25.32, H 4.39, N 59.06; found C 24.94, H 4.70, N 59.37. Friction sensitivity: >360 N; impact sensitivity: >50 J.

1-Methyl-1-(1-vinyl-1*H*-tetrazol-5-yl)hydrazine (10): Tetrazole **1** (2.0 g, 11.6 mmol) was dissolved in 30 mL of 2-propanol. Monomethylhydrazine (1.1 g, 23.2 mmol) was added and the reaction mixture was refluxed for 12 h. The solvent was removed under reduced pressure and the residue was washed with dichloromethane. The residue was extracted using acetonitrile. After removal of the solvent, the product was obtained as colorless solid (1.4 g, 9.9 mmol, 85%). m.p. 56 °C, dec. 203 °C. IR (KBr): $\tilde{\nu}$ = 3430 (s), 3341 (s), 300 (w), 2964 (m), 2927 (m), 2870 (w), 2801 (vw), 1646 (vs), 1554 (w), 1441 (m), 1421 (s), 1412 (s), 1323 (w), 1261 (m), 1216 (m), 1159 (m), 1099 (m), 1040 (m), 988 (w), 909 (m), 802 (m), 735 (m), 693 (vw), 661 (vw), 617 (vw) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 3.19 (s, 3 H, CH_3), 5.03 (s, 2 H, NH_2), 5.05 (d, $^3J_{cis}$ = 8.91 Hz, 1 H, CH_2), 5.63 (d, $^3J_{trans}$ = 15.73 Hz, 1 H, CH_2), 7.92 (dd, $^3J_{trans}$ = 15.73, $^3J_{cis}$ = 8.91 Hz, 1 H, CH) ppm. ^{13}C NMR ([D_6]DMSO): δ = 44.3 (NCH_3), 104.9 (CH_2), 129.6 (CH), 157.2 (C_q) ppm. *m/z* (DCI^+): 141.2 [M], 87.1, 75. $C_4H_8N_6$ (140.14): calcd. C 34.28, H 5.75, N 59.97; found C 34.41, H 5.80, N 59.76. Friction sensitivity: >360 N; impact sensitivity: >100 J.

Poly-1-vinyl(5-hydrazinyl)-1*H*-tetrazole (11): Hydrazine derivative **8** (700 mg, 5.5 mmol) was molten at 85 °C and AIBN (15 mg) was added carefully. Additional 15 mg of AIBN was added two times over 20 min. After 4 h, the polymer was cooled to ambient temperature and washed with 20 mL of water. The polymer was obtained as colorless solid after filtration (130 mg, 19%); dec. 203 °C. IR (KBr): $\tilde{\nu}$ = 3431 (m), 3250 (m), 3086 (m), 2978 (m), 2926 (m), 1608 (vs), 1520 (m), 1434 (m), 1402 (m), 1374 (m), 1337 (m), 1314 (w), 1262 (w), 1082 (m), 948 (vw), 879 (vw), 821 (vw), 804 (vw), 733 (vw), 697 (vw), 660 (vw). 553 (vw) cm^{-1}. ($[C_3H_6N_6]_x$) calcd. C 28.57, H 4.80, N 66.64; found C 27.20, H 5.03, N 61.35. Friction sensitivity: >360 N; impact sensitivity: >35 J.

Poly-1-vinyl(5–1-methylhydrazinyl)-1*H*-tetrazole (12): Hydrazine derivative **10** (300 mg, 2.1 mmol) was molten at 78 °C and AIBN (15 mg) was added carefully. Additional 15 mg of AIBN was added two times over 20 min. After 4 h, the polymer was cooled to ambient temperature and washed with hot dichloromethane and 20 mL of water. The polymer was obtained as colorless solid (260 mg, 87%); dec. 276 °C. IR (KBr): $\tilde{\nu}$ = 3430 (vs), 3341 (vs), 3225 (m), 3010 (m), 2964 (m), 2927 (m), 2873 (w), 2801 (vw), 1646 (vw), 1554 (vw), 1412 (m), 1382 (m), 1323 (w), 1261 (m), 1216 (m), 1099 (m), 1040 (m), 987 (w), 909 (m), 802 (w), 735 (w), 693 (vw), 658 (vw), 617 (vw) cm^{-1}. $[C_4H_8N_6]_x$ (1254.23): calcd. C 34.28, H 5.75, N 59.97; found C 35.44, H 5.45, N 57.49. Friction sensitivity: >360 N; impact sensitivity: >45 J.

5-Azido-1*H*-tetrazole-Containing Polymer (13): Poly-1-vinyl(5-hydrazinyl)-1*H*-tetrazole (**11**) (200 mg) was suspended in 15 mL of 2 N HCl. Saturated sodium nitrite solution was added dropwise at 0 °C over 10 min, until the formation of NO_2 was observed. After 10 min, the solid was filtered off and washed with 200 mL of water. The polymer was obtained as brown solid (120 mg, 60%); dec. 174 °C. IR (KBr): $\tilde{\nu}$ = 3432 (vs), 2963 (w), 2929 (w), 2851 (vw), 2164 (m), 1697 (w), 1625 (m), 1531 (s), 1442 (w), 1384 (w), 1261 (w), 1177 (w), 1093 (m), 1020 (w), 803 (w), 721 (vw), 581 (vw), 523 (vw) cm^{-1}. $C_{37}H_{56}N_{51}O_{10}$ (1375.19): calcd. C 32.32, H 4.10, N 51.95; found C 31.46, H 3.99, N 50.53. Friction sensitivity: >160 N; impact sensitivity: >7 J.

Table 2. Selected crystal data for **1**, **7** and **10**.

	1	**7**	**10**
Formula	$C_3H_3BrN_4$	$C_{10}H_{11}BrN_4O_3S$	$C_4H_8N_6$
M_r [$g mol^{-1}$]	175.00	347.20	140.16
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	*Pnma*	$P2_1/c$	$P2_1/n$
a [Å]	7.4368(2)	6.9438(2)	7.1943(3)
b [Å]	6.4442(3)	26.6687(5)	12.6152(5)
c [Å]	11.8738(3)	7.6877(2)	7.8085(3)
α [°]	90	90	90
β [°]	90	113.713(3)	91.199(3)
γ [°]	90	90	90
V [$Å^3$]	569.04(3)	1303.43(6)	708.53(5)
Z	4	4	4
F(000)	336	696	296
$\rho_{calcd.}$ [$g cm^{-3}$]	2.043	1.769	1.314
μ [mm^{-1}]	7.11	3.323	0.13
2θ [°]	53.99	54.00	52.00
Index range	$-9 \leq h \leq 9$	$-8 \leq h \leq 8$	$-8 \leq h \leq 8$
	$-8 \leq k \leq 8$	$-34 \leq k \leq 34$	$-15 \leq k \leq 15$
	$-15 \leq l \leq 15$	$-9 \leq l \leq 9$	$-9 \leq l \leq 9$
λ	0.71073	0.71073	0.71073
T [K]	200(2)	200(2)	200(2)
Reflections collected	7395	14131	5187
Unique reflections	678	2829	1391
Parameter	58	216	111
S	1.154	1.054	0.978
R_{int}	0.0494	0.0312	0.0286
R_1/wR_2 [$I > 2\sigma(I)$]	0.0197/ 0.0457	0.0347/0.0538	0.0731/0.1321
R_1/wR_2	0.0249/0.0516	0.0224/0.0496	0.0441/0.1160

Crystal Structure Analysis: The crystallographic data were collected using an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a Kappa CCD area detector with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97)[19] and refined using SHELXL-97.[20] All non-hydrogen atoms were refined anisotropically. ORTEP plots showing thermal ellipsoids with 50% probability for the non-hydrogen atoms (Table 2).

CCDC-742853 (for **1**), -742852 (for **7**) and -742851 (for **10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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[1] a) G. M. Nazin, V. G. Prokudin, G. B. Manelis, *Russ. Chem. Bull.* **2000**, *49*, 234–237; b) T. M. Klapötke, C. M. Sabate, J. Stierstorfer, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1867–1874.

[2] a) J. Köhler, R. Mayer, *Explosivstoffe*, VCH Verlagsgesellschaft, Weinheim, 9th vol., **1998**, p. 1; b) R. P. Singh, R. D. Verma, D. T. Meshri, J. M. Shreeve, *Angew. Chem. Int. Ed.* **2006**, *45*, 3584–3601; c) T. M. Klapötke, *Structure and Bonding: High Energy Density Compounds*, vol. 125, Springer, Berlin, Heidelberg, **2007**.

[3] a) E. Makino, N. Iwasaki, N. Yagi, H. Kato, Y. Ito, H. Azuma, *Chem. Pharm. Bull.* **1990**, *38*, 201–207; b) C. V. Reddy, C. J. Rao, E. Rajanarendar, A. K. Murthy, *Indian J. Chem., Sect. B* **1990**, *29*, 386–389; c) C. T. Alabaster, *J. Med. Chem.* **1989**, *32*, 575–583; d) M. Uchida, M. Komatsu, S. Morita, T. Kanbe, K. Nagakawa, *Chem. Pharm. Bull.* **1989**, *37*, 322–326.

[4] a) K. Matyjaszewski, B. S. Sumerlin, N. Tsarevsky, J. Spanswick, J. *Int. Patent 2005087818*, **2005**; b) F. Mwale, P.-L. Girard-Lauriault, H. T. Wang, S. Lerouge, J. Antoniou, M. R. Wertheimer, *Tissue Eng.* **2006**, *12*, 2639–2647; c) F. Truica-Marasescu, M. R. Wertheimer, *Plasma Processes Polym.* **2008**, *5*, 44–57.

[5] P. N. Gaponik, O. A. Ivashkevich, V. P. Karavai, A. Lesnikovich, N. Chernavina, G. T. Sukhanov, G. A. Gareev, *Angew. Makromol. Chem.* **1994**, *219*, 77–88.

[6] R. C. Tuites, T. E. Whiteley, L. M. Minsk, *US Patent 1,245,614*, **1971**.

[7] T. M. Klapoetke, C. M. Sabate, *Chem. Mater.* **2008**, *20*, 3629–3637.

[8] a) W. G. Finnegan, R. A. Henry, S. Skolnik, *US Patent 3004959*, **1961**; b) W. G. Finnegan, R. A. Henry, S. Skolnik, *US Patent 3055911*, **1962**.

[9] C. G. Miller, G. K. Williams, *U. S. Patents 264982*, **2007**.

[10] N. V. Tsarevsky, K. V. Bernaerts, B. Dufour, F. E. Du Prez, K. Matyjaszewski, *Macromolecules* **2004**, *37*, 9308–9313.

[11] T. M. Klapötke, S. M. Sproll, *Eur. J. Org. Chem.* **2009**, *25*, 4284–4289.

[12] a) D. E. Bayes, *Eu. Patent EP011736 8A1*, **1982**; b) J. Heppekausen, T. M. Klapötke, S. M. Sproll, *J. Org. Chem.* **2009**, *74*, 2460–2466.

[13] W. G. Finnegan, R. A. Henry, *J. Org. Chem.* **1959**, *24*, 1565.

[14] R. M. Coates, P. D. Senter, W. R. Baker, *J. Org. Chem.* **1982**, *47*, 3597–3607.

[15] E. Pinot, A. Guy, A. Fournial, L. Balas, J.-C. Rossi, T. Durand, *J. Org. Chem.* **2008**, *73*, 3063–3069.

[16] M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der organischen Chemie*, 6th edition, Thieme, Stuttgart, New York, **2002**, p. 48, 55.

[17] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

[18] a) M. Suceska, *Test Methods for Explosives*, Springer, New York, **1995**, p. 21 (impact), p. 27 (friction); b) http://www.bam.de/; c) impact: insensitive > 40 J, less sensitive > 35 J, sensitive > 4, very sensitive > 3 J; friction: insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N >80 N, very sensitive < 80 N, extremely sensitive < 10 N; according to the UN Recommendations on the Transport of Dangerous Goods (+) indicates: not safe for transport.

[19] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany), **1997**.

[20] G. M. Sheldrick, SHELXS-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany), **1997**.

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