Dissertation zur Erlangung des Doktorgrades
der Fakultät für Chemie und Pharmazie
der Ludwig-Maximilians-Universität München

Investigation of Nitrogen-Rich Polymers based on Cellulose, Tetrazoles and Triazoles

Franziska Maria Betzler
aus
München

2012

Erklärung

Diese Dissertation wurde im Sinne von § 7 der Promotionsordnung vom 28. November 2011 von Herrn Prof. Dr. Thomas M. Klapötke betreut.

Eidesstattliche Versicherung

Diese Dissertation wurde eigenständig und ohne unerlaubte Hilfe erarbeitet.

München, den 17.12.2012

(Franziska Maria Betzler)

Dissertation eingereicht am:	17.12.2012
1. Gutachter:	Prof. Dr. Thomas M. Klapötke
2. Gutachter:	Prof. Dr. Konstantin Karaghiosoff
Mündliche Prüfung	24.01.2013

„Du musst noch sehr viel lernen, mein junger Padawan.“

(Obi-Wan Kenobi in Star Wars)

Danksagung

Mein besonderer Dank gilt Prof. Dr. Thomas M. Klapötke, der mich mit einem interessanten und vielseitigen Thema ausgestattet hat, sowie mir eine gute Betreuung hat zukommen lassen. Ich konnte mich zu jeder Zeit mit allen Fragen an ihn wenden.

Herrn Prof. Dr. Karaghiosoff möchte ich für die Übernahme des Zweitgutachtens danken, als auch für die vielen netten Gelegenheiten sich nett zusammenzusetzen und zu ratschen.

Herrn Akad. ORat Dr. Burkhard Krumm danke ich für seine Unterstützung und Hilfe bei zahlreichen NMR Problemen.

Herrn Akad. Rat Dr. Jörg Stierstorfer danke ich für das Korrekturlesen dieser Arbeit, sowie für die Beantwortung meiner Fragen.

Frau Irene S. Scheckenbach möchte ich für ihre Freundlichkeit, als auch für ihre Unterstützung in organisatorischen Dingen und allen möglichen anderen Problemen danken.

Der Firma Diehl BGT Defence GmbH & Co. KG, im speziellen Herrn Pham-Schönwetter und Herrn Dr. A. Hahma, danke ich für die Zusammenarbeit und für die Durchführung zahlreicher Messungen.

Natürlich möchte ich mich auch bei dem gesamten Arbeitskreis Klapötke, wie auch dem Arbeitskreis Karaghiosoff für die überaus angenehme Arbeitsatmosphäre, die sich ein ums andere Mal auch in die späteren Abendstunden hinziehen konnte, bedanken. Danke für die schöne Zeit!

Allen voran möchte ich meinen lieben Laborkollegen für die schöne Zeit danken: dem „Rest vom Labor“, Alexander Dippold, für vielerlei technische Unterstützung, die musikalische Untermalung des Laboralltags (so viel Bayern 1 hab ich schon lang nicht mehr gehört) und allerlei leckere Verköstigungen, sowie das Messen von meinen „zahlreichen“ Kristallen, wenn sie denn mal messbar waren… Niko Fischer für seine jahrelange Begleitung meines Laboralltags und das Versorgen mit vielerlei kulinarischen Köstlichkeiten wie auch immer wieder für das Bereitstellen einer Laborhalbe, sowie Dennis Fischer und Davin Piercey für die angenehme Zusammenarbeit.

Meinem Nachbarlabor danke ich dafür dass es immer wieder als Zufluchtsort fungiert durfte, wenn ich mal wieder von meinem Labor das Weite suchen musste.

Meiner Teerunde danke ich für die nachmittäglichen Pausen, die stets geholfen haben mich kurz zu erholen um anschließend wieder mit neuen Kräften in die Arbeit zu stürzen:

Vera Hartdegen, meiner „Polymerschwester“, für zahlreiche Aufmunterungen, für den chemischen und nicht chemischen Austausch während des Laboralltags, als auch für das mühevolle Korrekturlesen dieser Arbeit.

Steffi Schönberger dafür dass sie mir eine gute Freundin geworden ist, immer wieder versucht hat mich aufzumuntern, aber natürlich auch für die Versorgung mit Keksen und Tee, was wohl ein großer Teil der Aufmunterungstaktik war.

Anian Nieder für die Beantwortung und Hilfe vielerlei chemischer Probleme die leider immer wieder auftauchten, sowie das stetige Versorgen mit Antworten zu allen möglichen gestellten und nicht gestellten Fragen.

Camilla Evangelisti für das Messen von Bombenpresslingen und das Durchführen von Rechnungen, aber vor allem für ihre Essensverpflegung mit leckeren italienischen Keksen und anderen Köstlichkeiten von Evangelisti Feinkost.

Caro Pflüger für ihre nette Begleitung bei kulturellen Veranstaltungen und ihre immerzu gute Laune

Richard Moll danke ich für die jahrelange Begleitung meines Laboralltags, die ja schon in den Kinderschuhen meines Chemiestudiums angefangen hat, sowie für viele gelöste Computerprobleme.

Bei Susanne Scheutzow möchte ich mich vor allem für den regen Informationsfluss am Ende meiner Doktorarbeit bedanken, die mir hier viele Fragen beantworten konnte.

Stefan Huber möchte ich für das Messen von Bombenpresslingen, sowie Schlag- und Reibeempfindlichkeiten meiner Substanzen, als auch für das Bestellen meiner Chemikalien danken.

Meinen Praktikanten Ruth Boller, Adriana Grossmann, Stefan Scherpe und Sebastian Böck danke ich dafür dass sie mich während meiner praktischen Arbeit tatkräftig unterstützt haben.

Zu guter Letzt gilt ein ganz besonderer Dank natürlich meinen Eltern und meiner Familie für die jahrelange Unterstützung, sowie Nikolaus Naredi-Rainer der das große Vergnügen hat sich mein Gejammer anzuhören, mich aufzubauen, anzutreiben und immer wieder zum Lachen zu bringen, sowie mein Leben besser zu machen.

Abstract

The aim of this thesis is the investigation and development of new nitrogen-rich energetic polymers based on various groups like cellulose, tetrazoles and triazoles, respectively. This definition implicates furthermore the synthesis and development of energetic materials related with these polymers, like precursor. The requirement of the new designed polymers was the suitability as energetic binders. Therefore these compounds should possess a positive influence on safety and performance, by inheriting a high thermal and physical stability, in order to stabilize the energetic filler, along with moderate to good explosive properties and the absence of toxicity. A good chemical and physical compatibility with all ingredients is mandatory to prevent reactions between the polymer and the energetic filler.

This thesis can be divided into four parts. The first chapter deals with energetic materials based on cellulose, as continuation of my master thesis[1]. The advantage of cellulose as a polymer is the easy and cheap availability, as well as the high amount of oxygen of the free hydroxyl groups that can be additionally used to link the polymer to small nitrogen rich molecules, like a methylamine group. This group offers the facility to be nitrated to further increase the oxygen content as well as the energetic character of the molecule. This compound, methylnitraminocellulose, has outstanding energetic properties and convinces with its insensitivity and its long term stability that exceeds that of nitrocellulose, a commonly used binder.

In the second part energetic polymers based on glycidyl azide polymer (GAP) are examined. A general high yielding synthesis of a polymer was developed by reacting GAP with ethyl cyanoformate. The nitrogen-rich polymer possesses a nitrogen content of 28 %, due to the contained tetrazole ring and the unreacted azide groups of the original starting polymer. Based on these heterocyclic moieties this compound is also characterized by its insensitivity towards outer stimuli, which is a great advantage compared to GAP, although the energetic performance is slightly diminished. Moreover GAP was reacted to form a 1,2,3-1*H*-triazole to improve the synthesis of (4,5-di(azidomethyl)-1*H*-1,2,3-triazol-1-yl)glycidyl polymer by S. SPROLL[2].

The third part deals with polymers generated by the diazotation of 1,2,4-1*H*-triazoles. The high nitrogen content of these compounds along with their physical and thermal stability, makes them desirable molecules. Unfortunately most of the compounds could not successfully be converted into suitable polymers or precursor.

The last part of this thesis highlights the examination of polymers created by the reaction of various tetrazoles and triazoles with methacryloyl and acryloyl chloride and their polymerization. These acid chlorides where chosen due to their similarity to vinyl groups and thus their ability to easily polymerize by radical polymerization. The reaction of 5-aminotetrazole with these moieties was the most promising one of the numerous syntheses. The nitrogen content of the formed polymers, poly(methacrylamidotetrazole) and poly(acrylamidotetrazole) could be further increased by a nitration of the amido moiety to yield molecules with an increased energetic character, even better than GAP. The gained substances remained nevertheless insensitive and had good thermal stabilities with a decomposition points around 220 °C.

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1. Introduction

1.1 Energetic Materials

Energetic materials are metastable substances that discharge big amounts of energy as well as huge amounts of gas, to some extent, while decomposing. These substances are stable under normal conditions (pressure, temperature) and are partly manageable, however react highly exothermic under certain conditions. [3]

1.2 Classification of Energetic Materials

Energetic materials can be roughly classified in four different categories, as depicted in figure 1: primary and secondary explosives, propellants and pyrotechnics. Secondary explosives can be further divided in a military and civil field of application and propellants into propelling charges for ammunition and rocket propellants.[4]

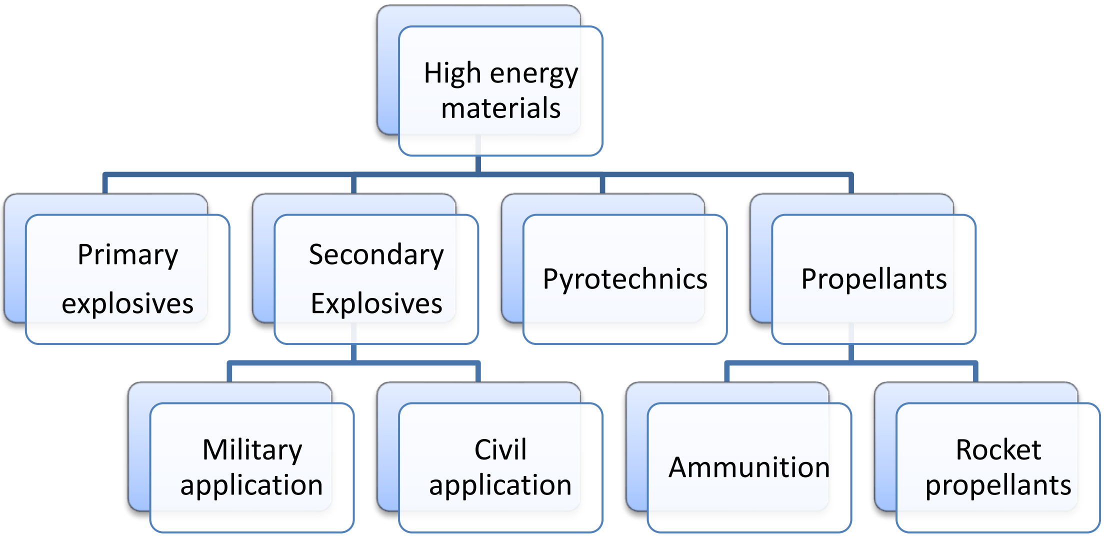
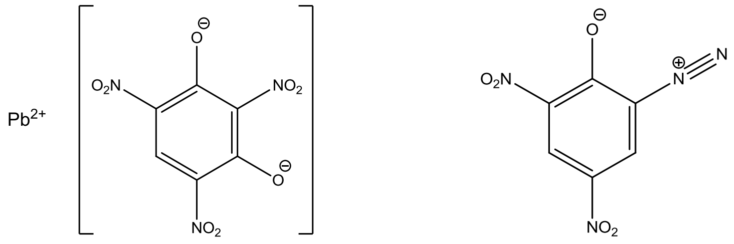


Figure 1. Classification of energetic materials.

1.2.1 Primary Explosives

Primary explosives[5,6] are highly sensitive explosives that can be initiated by a spark, impact, friction or heat. Contrary to secondary explosives, they undergo a rapid transition from combustion (or deflagration) to detonation[4] and therefore release an amount of energy ranging from 400 to 600 kcal kg^{-1} in a short period of time (µs – ms). The detonation velocity only ranges from 3000 – 6000 m s^{-1} and is therefore much slower than that of secondary explosives. A selection of commonly used primary explosives is depicted in figure 2.

$Pb(N_3)_2$

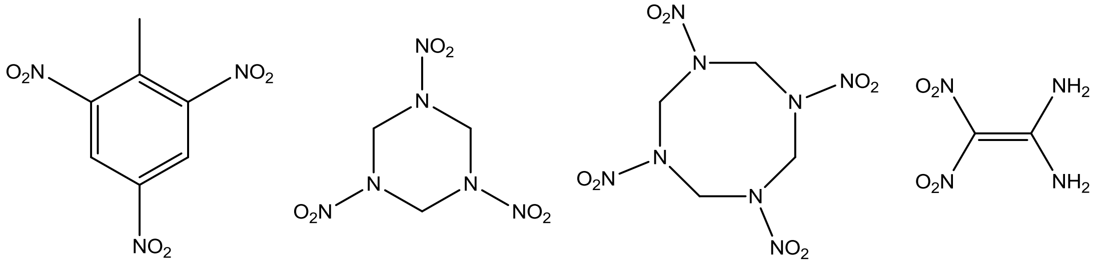


lead azide **lead styphnate** **diazodinitrophenol**

Figure 2. Molecular structure of primary explosives.

1.2.2 Secondary Explosives

During the detonation process of a primary explosive, a shock wave is formed, which is able to initiate secondary explosives. This group is also known as "high explosives" (HE). The main difference between secondary and primary explosives is the higher detonation velocity (3500 - 9000 m s^{-1}) along with the high thermal and physical stability of secondary explosives. On basis of this property it is difficult to initiate secondary explosives by friction, impact, spark or heat. Common secondary explosives are TNT, RDX, HMX and FOX-7 (figure 3).



TNT **RDX** **HMX** **FOX-7**

Figure 3. Molecular structure of secondary explosives.

Whereas RDX and HMX are mainly used in military explosives, cheaper formulations possessing less power, like ANFO (ammonium nitrate fuel oil), are used in civil applications (mining, tunnel construction etc.). New compounds are sought after to increase the performance and lower the sensitivity as well as the toxicity of the explosives, their biological degradation products and the detonation products. [4] A good performance is mainly characterized by the heat of explosion *Q*, the detonation velocity *D* and the detonation pressure *P*.

$$P_{C-J} = K\rho_0^2\Phi \qquad (1)$$

$$D = A\Phi^2(1 + B\rho_0) \qquad (2)$$

$$\Phi = N\sqrt{M}\sqrt{Q}$$

Equation 1 and 2. ρ_{C-J} is given in [kbar] and D in [mm μs^{-1}]. K, A and B are constants with the values of 15.88, 1.01 and 1.30. N is the molar quantity of released gases per gram explosive, M the mass of gases [g] per mol gas and Q is the heat of explosion.

Therefore compounds offering a high heat of explosion along with a high density are in demand.

1.2.3 Propellants

Propellants, or low explosives, are combustible materials. They are, contrary to primary and secondary explosives, intended to deflagrate instead of detonate and function by producing gas.[7]

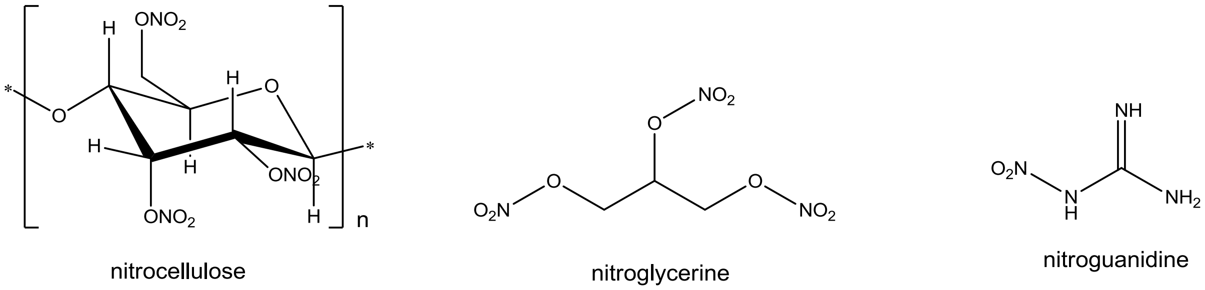
The various fields of applications for these compounds demand different properties. Propellants used in propelling charges for ammunition need decomposition products that do not contain corrosive gases, together with low burning temperatures, as high temperatures would lead to severe erosion of the gun barrel (formation of iron carbide from the reaction of iron with carbon). The desired low burning temperature complicates the development of good performing propellants, because the specific impulse of the compounds depends on the burning temperature (equation 3). The specific impulse I_{sp} describes the efficiency of rocket and jet engines and is therefore one of the most important characteristic of mono- and bipropellants.

$$I_{sp} = \sqrt{\frac{2\gamma RT_c}{(\gamma-1)M}} \qquad (3)$$

Equation 3. Specific impulse I_{sp}. γ: ratio of the specific heat capacity of the gas mixture; R: ideal gas constant; T_c: temperature in the burning chamber [K]; M: average molecular weight [mol kg^{--1}].

The first propellant used for ammunition was black powder (75 % KNO_3, 10 % sulfur and 15 % charcoal dust). Due to the huge amount of corrosive gases evolved during the decomposition (NO_x and SO_x), black powder is not in use in contemporary ammunition or propellant charges any more.[2]

A commonly used propellant in ammunition is nitrocellulose (NC), a single-base propellant. Due to the advantageous ratio of oxygen to carbon, this compound leads to a residue free burning and is therefore often referred to as “smokeless” powder[4]. This is the reason why it is used in weapons ranging from pistols to artillery weapons. To improve the specific impulse, double-based propellants were developed, based on NC and nitroglycerine (NG) that are utilized in pistols or mortars. Double based propellants possess an enhanced performance, unfortunately accompanied by a higher erosion of the gun barrel, due to the high explosion temperature. To decrease this property, triple-based propellants, consisting of NC, NG and nitro guanidine (NQ), were developed, mostly for use in large tanks and naval artillery ammunition.[4]



nitrocellulose nitroglycerine nitroguanidine

Figure 3. Molecular structure of propellants.

The preferred properties of rocket propellants are similar to the before discussed ammunition propellants, as they combust in a controlled manner and do not detonate. However, in contrast to guns or cannons, rockets are usually only fired once, therefore the erosion of rocket engines can be neglected. Instead, compounds with a high specific impulse are desired materials.

Rocket propellants can be divided into solid and liquid propellants. Solid propellants contain double based propellants (nitrocellulose and nitroglycerine) or a mixture of ammonium perchlorate and aluminum, stabilized by a binder (composite propellants). Liquid propellants are hydrazine or mixtures of an oxidizer and fuel (nitric acid and hydrazine / methyl hydrazine).

1.2.4 Pyrotechnics

Pyrotechnics can be classified into three areas: heat generating, smoke generating and light emitting pyrotechnics. Whereas heat generating pyrotechnics are used for priming charges, detonators, incendiary and matches, smoke generating pyrotechnics are used for camouflage and signaling purposes. The light emitting pyrotechnics are used either for illumination (visible and infrared), fireworks or decoy flares.

The pyrotechnical combustibles, like carbon, are oxidized in presence of a catalyst. Factors like temperature, pressure and particle size have a big influence on the combustion behavior of pyrotechnics. Sometimes the type of ignition has an influence on the combustion of the pyrotechnics as well.[8]

The first pyrotechnics were made of gunpowder, a mixture of potassium nitrate (75 %), carbon (15 %) and sulfur (10 %).[9] Constituents of strontium nitrate and barium nitrate were used for 100 years as the typical red and green color. Copper (II) salts cover the blue and green spectrum of pyrotechnics.[10]

The components of pyrotechnics can be divided in three different types: combustibles, oxidizer and additional substances. Oxidizers guarantee the supply of the pyrotechnic with oxygen independent of the air oxygen. The reaction obtains the required oxygen by means of oxygen-rich substances like KNO_3.[11] The constituents of the additional substances are catalysts, colorants and binders, like nitrocellulose.[12]

1.3 Energetic Polymers

Energetic polymers have contributed considerably to the advancements in the technological field of both, propellants and explosives. In addition to the use of NC in explosive fills, applications of polymers have been more and more applied in binders and plasticizers.[13] Over the years, with the use of composite propellants and polymer bonded explosive (PBX) technology, diverse classes of polymers have been developed for binder applications, in order to meet the dual objectives of insensitivity and high performance.[14]

Commonly used energetic polymers contain either nitro groups, nitric esters or azide groups.

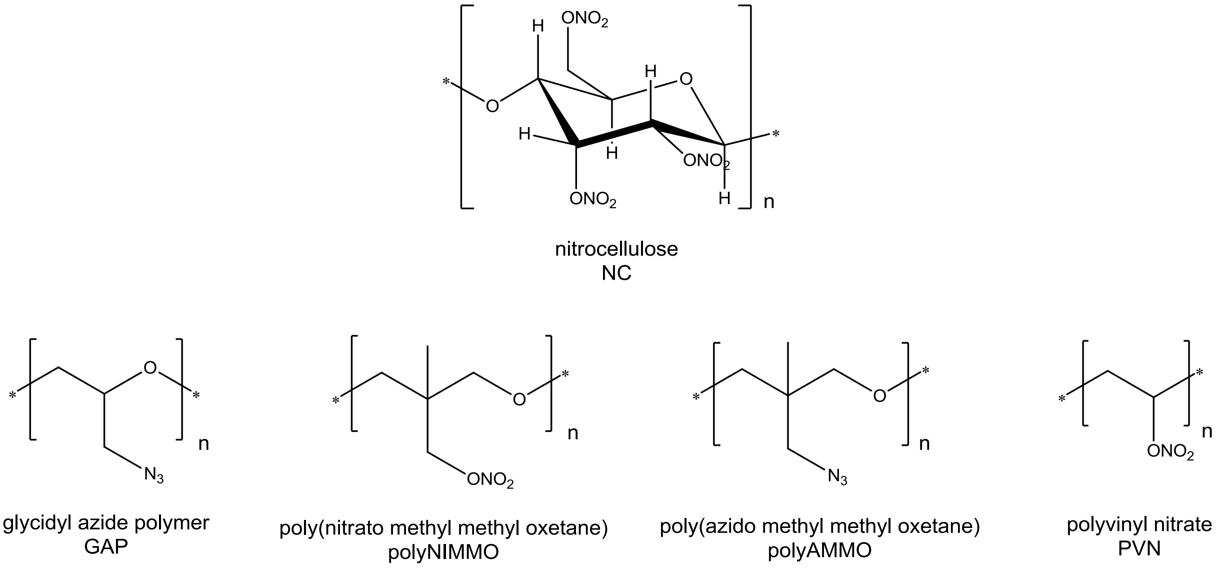


Figure 4. Selected energetic polymers.

1.3.1 Energetic Polymers based on Cellulose

The primary choice of an energetic polymer was nitrocellulose (NC). This compound was discovered 1846 by SCHÖNBEIN[15], whilst examining the effect of a mixture of nitric and sulfuric acid on various inorganic and organic materials, like cotton or sugar.

Completely nitrated cellulose, cellulose nitrate, has the elemental formula $[C_6H_7O_2(ONO_2)_3]_n$ and a nitrogen content of 14.15 %. For the applications, that normally take cotton as purest natural cellulose, there are two types of different qualities: the highly nitrated one with 12 to 14 % nitrogen and the 2/3 nitrated collodion with 10 to 12 % nitrogen[9]. Purification of the nitrocellulose has been an important problem, as the long term stability rises with the purity, as experiments showed.

The physical stability of NC with an impact sensitivity >3 J and a friction sensitivity >353 N[5] along with a thermal stability of only 160 °C and a poor long term stability, is compensated by the extreme low costs of production.

The application of NC as a binder was exploited when it was used for propulsion purposes in homogenous propellants, with the invention of the smokeless powder, Poudre B, by Paul VIEILLE in 1884.[16] It was made by treating a mixture of soluble and insoluble NC with a 2 : 1 ether-alcohol mixture, kneading it to form a thick jelly, and rolling into thin sheets. The NC binder provided the necessary structural integrity for the propellant, which could be molded to conform to a wide range of motor geometries and can be used to deliver long duration thrust.

To date, only few efforts are made to develop new energetic materials based on cellulose. Some of the better investigated energetic compounds are azidocellulose or azido cellulose nitrate.[17,18] Thereby it is possible to substitute either only the primary hydroxyl group[19-21] or the primary and secondary hydroxyl groups[22], as well.

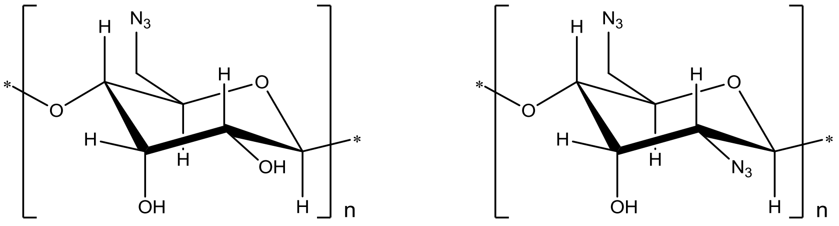


Figure 5. Derivatives of azidocellulose

1.3.2 Energetic Polymers based on Azide Moieties

Glycidyl azide polymer (GAP) is, besides NC, a common energetic binder. The synthesis of GAP is carried out by polymerization of epichlorohydrin with a subsequent substitution of the chlorine atom with sodium azide.

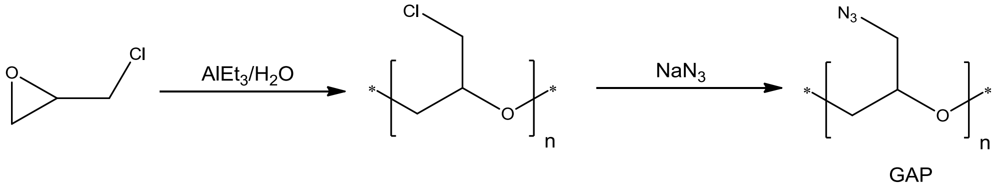


Figure 6. Synthesis of GAP

Glycidyl azide polymer (GAP) has been one of the most top-rated candidates for the next generation fuel-binder of composite propellant and hybrid rocket fuel due to its high density[23,24] and its sufficient thermal stability for propellant formulations.[25] Based on those properties it is a unique high-density polymer with a positive heat of formation, equal to +490.7 kJ mol^{-1}.[14] At present GAP is the most readily available energetic polymer due to the low cost of the synthetic route and its excellent binder properties.[26]

The friction and impact sensitivity of GAP (M_n = 2000 g mol^{-1}) are determined to be >360 N and 7 J [5]. The high stability against friction can be explained by the oily consistency of the polymer, reducing friction forces. The thermal decomposition point was found to be 216 °C[5]. Based on the honey like consistency a explosive composition containing GAP has to be further mixed with a curing agent, which cross-links the different chains of GAP.

Common methods use the hydroxyl terminated GAP for the linking reactions with diisocyanates.[27]

On the basis of its already polymerized structure and the azide group, various functionalization possibilities, like cycloadditions, are available. Due to these facts the syntheses of nitrogen rich compounds based on GAP were performed in this thesis.

Other azide containing polymers derived from oxetane monomers, 3,3-bis(azidomethyl)oxetane (BAMO) and 3-azidomethyl 3-methyl oxetane (AMMO), were also sought for binder applications, because of their low viscosity and good mechanical properties after cross linking. They are synthesized by the cationic ring opening polymerization of the respective monomers using borontrifluoride etherate catalyst.[28,29]

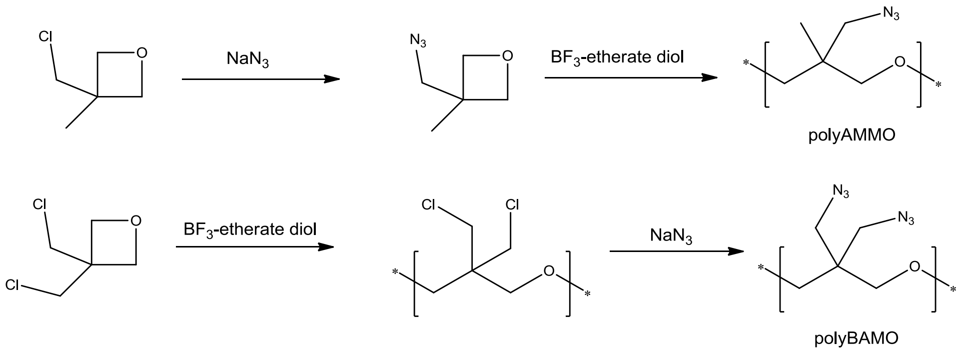


Figure 6. Synthesis of polyAMMO and polyBAMO.

PolyAMMO and polyBAMO are solids at ambient temperature. This is in comparison with GAP a great advantage as these compounds need no curing agent.[30,31] Comparing the friction and impact sensitivity of polyBAMO (>288 N and >5 J)[5] with GAP, reveals the higher stability of GAP. This fact arises from the solid character of polyBAMO compared to the oily consistency of GAP. The thermal stabilities of both polymers are in a comparable range (polyBAMO: 203 °C).[32]

1.3.3 Energetic Polymers based on Nitric Esters

Commonly known energetic polymers containing nitric esters are poly(nitrato methyl methyl oxetane) (polyNIMMO) or polyvinyl nitrate (PVN). The downside of these polymers compared to the compounds based on azide is the thermal stability. The decomposition point of PVN with 175 °C is about 40 °C lower than that of GAP. However the physical stability (friction >196 N, impact >10 J) is comparable to polyBAMO[5]. The advantage of PVN is its high density, resulting in a good performance as explosive. As for PVN and other common nitric esters, the decomposition point of polyNIMMO is found at 170 °C[5].

The critical aspects of the preparation of energetic polyoxetanes are the ease of preparation and purity of monomers. The nitrato alkyl oxetane monomer, NIMMO, was first prepared by the nitration of 3-hydroxy methyl-3-methyl oxetane (HMMO) with acetyl nitrate.[28] However due to the hazardous nature of the reaction, the synthesis was modified by selective nitration of HMMO using dinitrogen pentoxide as nitrating agent in a flow nitration system[14]. Therefore polyNIMMO gained popularity due to its scalable and safe procedure of preparation.[33] The disadvantages of polyNIMMO are that it is like GAP a viscous liquid that needs curing to harden the explosive composition, as well as its instability towards energetic radiation. Experiments showed that gamma radiation results in a change of the structure.[3]

1.3.4 Energetic Polymers based on Tetrazoles

Research interests in tetrazole polymers are especially based on the high nitrogen content, as the tetrazole group itself possesses a nitrogen content of 79 % in the case of 1*H*-tetrazole and therefore are promising candidates for environmentally friendly compounds.[34] Furthermore, they possess considerable energetic performance and the high thermal stability of the tetrazole heterocycle. Such polymers are considered to be prospective energetic binders for propellant and explosive formulations due to their high heats of formation. The tetrazole group is similar to the azido groups and releases comparable amounts of energy upon combustion. It is more stable and versatile than the azide group.[14]

One of the first known polymers based on tetrazole was poly(vinyl tetrazole) (PVT)[35,36]. It is an important candidate among the tetrazole polymers used in energetic material applications.[37]

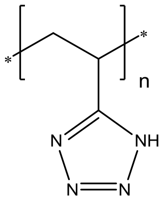


Figure 6. Synthesis of poly(vinyl tetrazole).

Nevertheless, to date, within the wide range of applied nitrogen rich polymers, compounds containing tetrazole moieties are rare.

1.4 Energetic Polymers as Binders

Over the last years there has been an increasing emphasis on reducing the response of munitions to outer stimuli such as fire, impact, shock waves, etc. without any degradation in performance. This strategy of using insensitive munitions[38] has resulted in a move away from the use of nitrocellulose based propellants and melt case (TNT based) explosive, which tend to be brittle materials, to composite type formulations consisting of energetic solids bound together by polymeric binder.[13] The most commonly used polymer binder in propellants and explosives is hydroxyl-terminated polybutadiene (HTPB). This formulation has outstanding mechanical properties, hydrolytic stability, ageing stability, and desirable viscosity and solids loading. The polymer binder acts by wetting the solid filler to provide a void-free matrix which gives enhanced mechanical and safety properties and also allows the formulation to be cast into large and irregular cases.

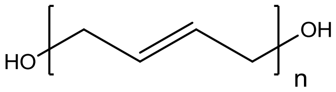


Figure 4. Molecular structure of HTPB.

HTPB is, however, non energetic and thus the performance of the composition is limited unless there is a high solids loading. At very high solids loadings there can be processing problems, which might limit the range of possible manufacturing methods, as well as cause problems with the vulnerability. Reduction of the solid loading would reduce the vulnerability to stimuli since the solid is the sensitive component. Therefore, to reduce the sensitivity without lowering the performance, energy can be added by utilizing energetic binder, enabling a lower solids loading, or, alternatively, maintaining the solids loading whilst using an energetic binder should lead to increased performance.

All in all, with the addition of non-energetic or inert binders into formulations, a high level of energetic solids loading is required to meet the given performance requirements, as the explosive energy is diluted. This should be avoided by enhancing the performance by the use of energetic binders instead of inert ones.

Binders are typically cross linked polymers providing a matrix to bind the solids together with a plasticizer (usually not more than 50 % of the total binder system) to ease processing of the uncured mix and to modify the mechanical properties of the final composition.[26]

These energetic polymers are usually obtained by the substitution of energetic material functional groups, such as azido and nitrato moieties, as associated groups to the polymer backbone. The presence of energetic functional groups on the polymer allows the composition to have comparatively less explosive filler, thereby rendering the formulation less sensitive to external stimuli.[14]

1.5 Energetic Polymers as Plasticizers

The mechanical properties of the binder are altered by the addition of a plasticiser, which imparts the rubbery characteristic that is required for insensitive munitions, reduces the viscosity for ease of casting and enables higher solids loading. The primary role of energetic plasticizers in energetic material formulations is to modify the mechanical properties of the charge to improve safety characteristics. This is achieved by softening the polymer matrix and making it more flexible.

Certain characteristics a plasticizer should obtain are a positive influence on safety and performance, chemical and physical compatibility with all ingredients, chemical stability and absence of toxicity, low environmental impact and of course availability and affordability. These compounds are also used to alter the glass transition temperature, the temperature at which the binder changes from rubbery to brittle.[39]

Plasticizers are typically oligomeric materials with an average molecular weight ranging from 200 to 2000. Compounds with a molecular weight above 2000 tend to be viscous, having properties more like a polymer matrix. Those with molecular weights lower 200 may be more effective in reducing the glass transition temperature, but they are highly volatile and tend to migrate out of the formulation. An average molecular weight of plasticizers between 400 to 1000 are considered to give an optimum plasticizing effect.[26]

In general plasticizers can be divided in non energetic and energetic ones.[40]

Non energetic plasticizers are effective in improving mechanical properties, but degrade the output of the formulation. Examples include triacetin, diethyl phthalate and dioctyl adipate (figure 4).

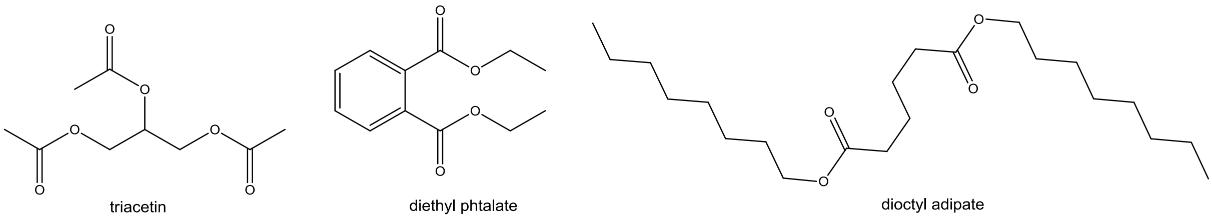


Figure 4. Non energetic plasticizers.

Similar improvements in mechanical properties are desired of energetic plasticizer, but with a contribution to the oxygen balance and the energy of the formulation. Energetic plasticisers are typically nitro compounds or nitrate esters (figure 5).

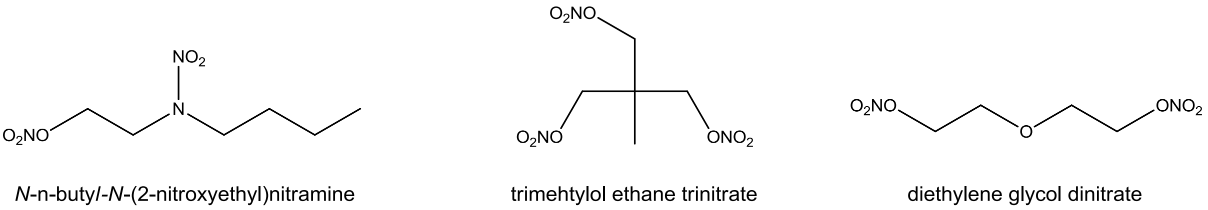


Figure 5. Energetic plasticizers.

The difficult part arises in polymerizing the monomer in a controlled manner, to give polymeric products that are well characterized and reproducible, as well as introducing the energetic groups in a controlled and reproducible way.

However, the mechanical properties of an explosive formulation are easily altered by varying the proportion of plasticizer, binder and solids. A good formulation should give a viscous mix which is castable and cures to a rubbery composite without the settling of solids and without migration of the plasticizer. The particle size of solids also affects the viscosity of the polymer bond explosives (PBX). The amount of solid that can be added to the mix while maintaining the desired viscosity is dependant upon the density, shape and size of the ingredients, although the viscosity of the formulation can then be optimized by altering the binder content.[39]

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2. Concepts and Aim

Over the years, a variety of polymer binders have been developed and used in energetic material applications. However despite the existence of several energetic polymers suitable or in use, new polymers as energetic binders are still desired to cope with the demand for insensitive and high performance propellant and explosive formulations. Therefore, contributing to this research, polymers containing new energetic groups, or the functionalization of traditional used systems, was investigated.

The low thermal stability of polymers containing nitric esters along with the low adhesive properties of the thermally stable azide polymers, further justifies this development. Although tetrazole and triazoles compounds have a minor demand in this field of application, the high thermal stability, due to the aromatic ring system of these compounds, along with their energetic character and high nitrogen content, turns these moieties into promising candidates.

The environmental compatibility is another important point, as, despite the detonation of the explosive composition, a certain amount of unreacted or decomposed material will remain and widespread in the surrounding area. In order to replace toxic substances and obtain environmentally friendly or at least less toxic materials, polymers based on cellulose were investigated. As cellulose itself is a biological product it is perfectly biological degradable. However tetrazoles and triazoles have the advantage of containing high nitrogen content and therefore releasing no or less toxic gases, as their decomposition products are only molecular nitrogen and carbon monoxide and carbon dioxide, respectively. For this reason compounds containing these moieties can be considered a “green” alternative to some commonly used binders.

Taking all this into considerations, investigations of nitrogen-rich polymers based on tetrazoles, triazoles and cellulose for binder applications were accomplished. Special interest was put to improve the energetic properties along with the thermal and physical stability, of commonly known polymers.

3. Energetic Polymers based on Cellulose

3.1 Introduction

Nitrogen-rich polymers are to date used as binders in energetic compositions [1] and as gas generating agents[2]. So far, commonly used polymers are nitrocellulose[3-5], azidocellulose nitrate[6], or glycidyl azide polymer (GAP)[7]. The disadvantages of these polymers are the energetic azide moieties[8,9] and nitro groups[10]. These compounds are toxic and can be released into the environment by degradation of residues of unburned parts of the explosive composition[11]. In order to replace these toxic substances, new energetic polymers have to be developed.

The advantage of cellulose as a polymer is the easy and cheap availability, as well as the high amount of contained oxygen [12,13]. This can be improved by nitration, or addition of nitrogen rich compounds, generating desired decomposition products. Due to these facts, nitrocellulose [14] has been successfully established as a binder and propellant.

The free hydroxyl groups of cellulose can be used to link the polymer to small, nitrogen rich molecules. But the applications of nitrocellulose are limited, because no further modifications are possible. Therefore, the search for molecules that can be linked to cellulose and that offer more possibilities than nitrocellulose, could lead to a new group of energetic polymers. Nevertheless, these molecules should contain a high amount of oxygen and nitrogen by themselves, because when used as explosive binder or propellant, they should not decrease the efficiency of the compound.

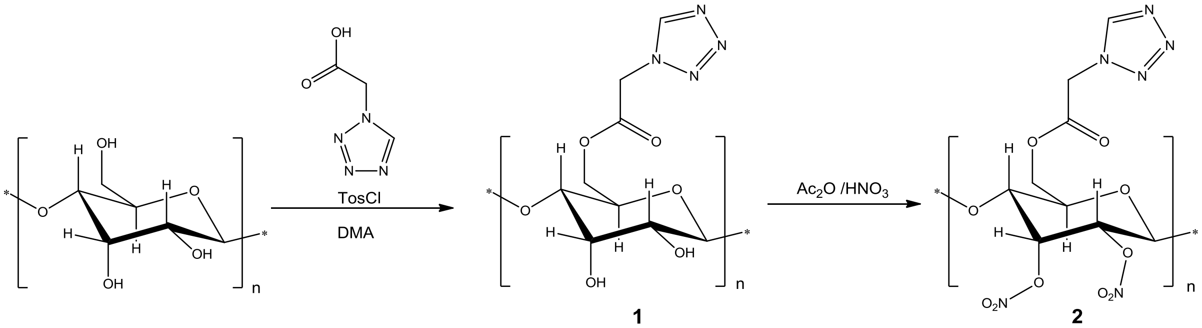
To date, only few efforts have been made to develop new energetic materials based on cellulose. However, tetrazole and nitramine moieties can be applied to cellulose to form energetic polymers that can be more energetic as well as offer more thermal and physical stability compared to nitrocellulose.

3.2 Results and Discussion

3.2.1 Polymers based on Cellulose containing Tetrazole Moieties

Tetrazoles are nitrogen rich compounds, covering a wide range of applications. Amongst others they are used as pharmaceuticals [15-18], membranes [19], or as energetic materials [20,21]. The advantages of tetrazoles include that the tetrazole moiety itself possesses a nitrogen content of 80 % along with a combination of high-energetic character with sufficient thermal stability[22]. Therefore, they are often used in gas generators, but can also be useful for an application as energetic polymers. Still, within the wide range of applied nitrogen rich polymers, compounds containing tetrazole moieties are rare. Hence these groups were applied to obtain polymers based on cellulose with a high content of nitrogen.

As already published[23], 1-(1*H*-tetrazol-1-yl) acetic acid was introduced to cellulose to obtain 1-cellulose-2-(1*H*-tetrazol-1-yl)acetate (CTA, **1**), presuming its high nitrogen content and its high thermal stability. A further advantage of this molecule is the possibility of increasing the nitrogen content even more by nitration, giving 1-nitrocellulose-2-(1H-tetrazol-1-yl)acetate (NCTA, **2**).



Scheme 1. Synthesis of **1** and **2**.

1 was obtained in high yields (97 %). The degree of substitution was estimated by elemental analysis. Comparing different degrees of substitution, **1** gave the highest conformance with a degree of substitution of 1.2 tetrazole moieties per glucose unit. An explanation of this effect is the higher availability of the methylene hydroxyl group, compared to the hydroxyl groups of the ring system. The comparison of different degrees of substitution, according to the elemental analysis of **2**, depicted that the carbon and hydrogen content of this compound suited better to a degree of substitution of one nitro group per free hydroxyl group, whereas the nitrogen content fitted better when two hydroxyl groups where substituted by nitrogen groups. This means that the product still contains *N*,*N*-dimethylacetamide, HNO_3 or NO_2, respectively.

To analyze the degree of conversion, vibrational spectroscopy is a useful analytical method. For this reason, the comparison of the infrared spectra of **1** and **2** showed that both spectra still contain unoccupied hydroxyl groups, which can be seen at the OH-vibration at about 3400 cm^{-1}. Furthermore the C=O vibration at 1629 cm^{-1} demonstrates the ester linkage between the cellulose and the tetrazole moiety is formed in **1** and is still present at 1750 cm^{-1} in **2**. The infrared spectrum of **2** shows the expected appearance of vibrations of the nitro groups at 1630 cm^{-1} and 1342 cm^{-1}, indicating a successful nitration [24].

In accordance with the expected results, the thermal stability of **2**, shown in figure 2 was lower than that of **1**. The melting area of **2** starts at 40 °C and ends with the point of decomposition at 200 °C. However it has two decomposition points, the first decomposition point at about 175 °C is the decomposition of the nitrate ester, whereas the second one at about 200 °C is the decomposition of the tetrazole ring, which is comparable to that of **1**. This compound has a melting area ranging from 40 °C to 185 °C, whereas the point of decomposition of **1** is at 215 °C.

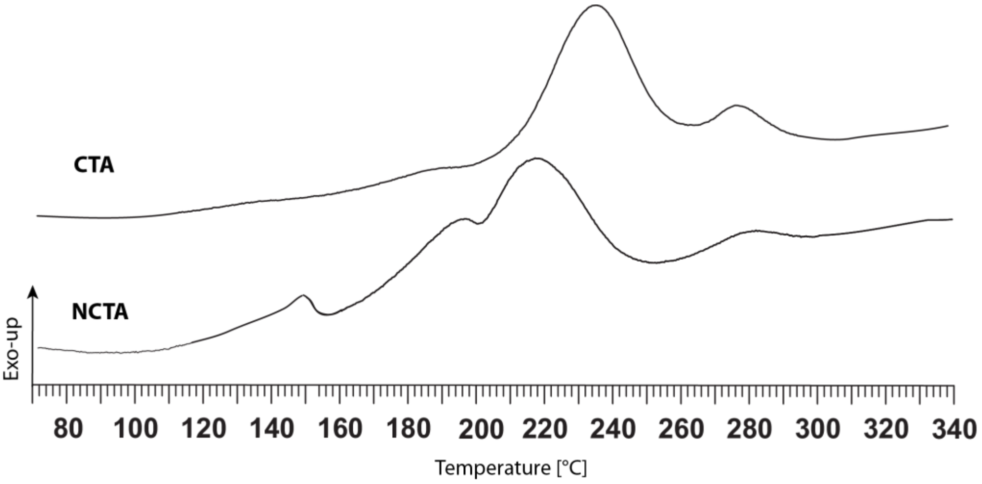


Figure 1. DSC data of **1** and **2**.

The sensitivity data was obtained using a BAM[25] drophammer and friction tester. These methods obtained that **1** and **2** are insensitive against impact of 40 J and friction of 360 N and can therefore be regarded as insensitive. Besides compared to commonly used nitrocellulose (impact sensitivity: 3 J, friction sensitivity: > 353 N)[26], it has a better response to impact and friction, which can be regarded as a clear advantage in terms of safety.

The energetic values of the energy of explosion, the explosion temperature, the detonation pressure, the detonation velocity and the gas volume have been calculated using the enthalpies of formation and the EXPLO5 5.04 program [27,28]**.** This program also contains the corresponding data of nitrocellulose which has a practical maximum value of nitrogen content of approximately 13.4 % [26] and is therefore calculated with a nitrogen content of 13.5 %.

Given that the nitration of the polymer destroyed the cellulose chains, and the right length of the polymer can not be stated, the calculation was done by calculating with the monomers of the cellulose derivatives.

Table 1. Energetic properties of **2**.

	2	**Nitrocellulose (13.5 %)[p]**
Formula	$C_{9.00}H_{10.00}N_{6.00}O_{10.00}$	$C_{6.00}H_{7.26}N_{2.74}O_{10.48}$
Molecular mass [g mol^{-1}]	362.21	285.43
Impact sensitivity [J][a]	40	3
Friction sensitivity [N][b]	360	353
N [%][c]	23.20	13.5
Ω [%][d]	-49	-33
T_{dec} [°C][e]	175	192[29]
ρ (g cm^{-3})[f]	1.5	1.7
$-\Delta_f H_m$(kJ mol^{-1})[g]	1237	-
$-\Delta_f U_m$(kJ kg^{-1})[h]	3504	-
Values calculated by Explo5 V5.04		
$-\Delta_E U_m°$ (kJ kg)[i]	3930	4890
T_E(K)[j]	3216	3933
$p_{C\text{-}J}$ (kbar)[k]	66	81
D (m s^{-1})[l]	4851	5279
Gas vol. (L kg^{-1})[m]	725	744
I_s (s)[n]	187	232
I_s (s) (70 % ADN)[o]	242	236

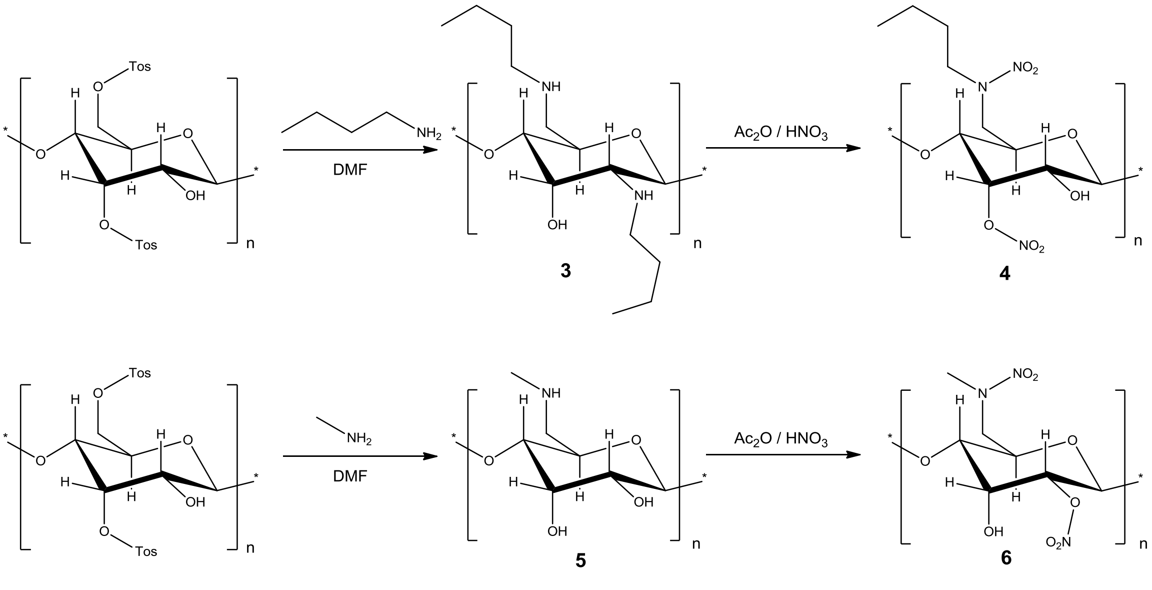
[a] BAM drop hammer; [b] BAM friction tester; [c] Nitrogen content; [d] Oxygen balance; [e] Temperature of decomposition by DSC (*β* = 5 °C, Onset values); [f] derived from pycnometer measurement; [g] Molar enthalpy of formation; [h] Energy of formation; [i] Energy of Explosion; [j] Explosion temperature; [k] Detonation pressure; [l] Detonation velocity; [m] Assuming only gaseous products; [n]

specific impulse (isobaric combustion, chamber pressure 60 bar, frozen equilibrium), [o] specific impulse of a mixture containing 70 % ammonium dinitramide as oxidizer; [p] values based on Ref. [30] and the EXPLO5.5 database.

According to the calculated values, the temperature of explosion of NCTA is lower than that of nitrocellulose. Therefore, it diminishes the erosion when applied. The detonation pressure and the detonation velocity of NCTA are slightly lower, too. However, by addition of an oxidizer, like ammonium dinitramide (ADN), the specific impulse is higher than that of nitrocellulose and hence predicts a good performance.

3.2.2 Polymers based on Cellulose containing Nitramine Moieties

Butylamine was introduced to cellulose to increase the nitrogen content of the derivative. Additionaly this product offers the possibility of being oxidized to butylnitraminocellulose (BNAC, **4**), which has higher nitrogen content than butylaminecellulose (BAC, **3**) and should be more stable and more energetic than nitrocellulose. To further increase the nitrogen content, methylamine was introduced to cellulose, to achieve methylnitraminocellulose (MNAC,**6**) by further nitration of methylaminecellulose (MAC, **5**) and therefore obtaining a highly energetic and nitrogen rich polymer.



Scheme 2. Synthesis of **3-6**.

Infrared spectroscopy was performed as a valuable instrument to analyze the degree of conversion during the synthesis. The comparison of the infrared spectra of **4** and **6** shows the expected appearance of the vibrations of nitro groups at roughly 1600 cm^{-1} (A) and nitramino groups at about 1200 cm^{-1} (B). The OH-vibration at 3400 cm^{-1} (C) of both spectra indicates that not all hydroxy groups of cellulose were nitrated[24].

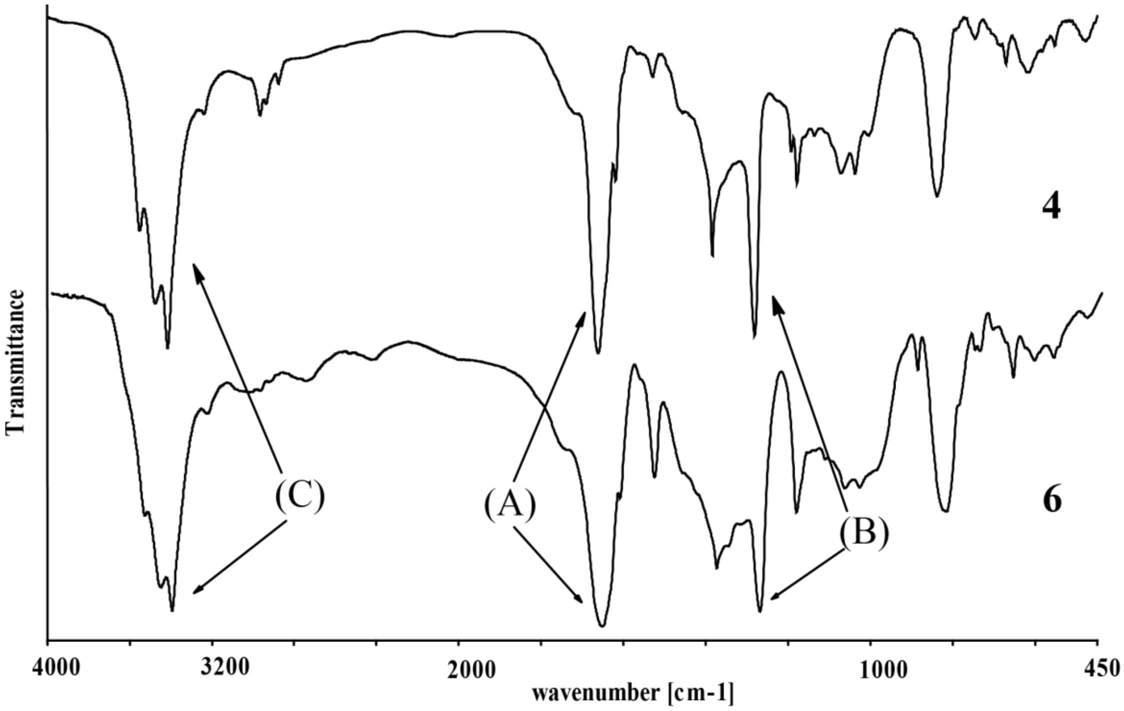


Figure 2. Infrared spectra of **4** and **6**.

The gained product was also analyzed by elemental analysis. The comparison of different degrees of substitution had the best agreement for **4** with a degree of substitution of one nitramino and one nitro group per glucose unit. An explanation of this effect is, according to **1** and **2**, the higher availability of the methylene hydroxyl group, compared to the hydroxyl groups of the ring system. However, one butylamine group was probably split of and substituted by a hydroxyl group, whereas the hydroxyl group at the 3C was nitrated, giving a nitramine group. The elemental analysis of **6** gave the greatest convenience with one nitramine and one nitric ester formed per unit cell. It also verifies the fact, already indicated by infrared spectroscopy, that not all hydroxyl groups were nitrated [24].

To analyze the energetic properties of **4** and **6**, the energy of combustion (ΔU_c) was measured using bomb calorimetry. Using these values, the enthalpy of formation was calculated by applying the Hess thermochemical cycle, as reported in literature [31]. The heats of formation of H_2O (l) and CO_2 (g) -286 kJ mol^{-1} and -394 kJ mol^{-1} were obtained from literature [32,33] and the combustion reaction of BNAC is given in figure 3.

$$C_{10}H_{17}N_3O_8 + 10.25\ O_2 \rightarrow 10\ CO_2 + 8.5\ H_2O + 1.5\ N_2$$

Figure 3: Combustion reaction of **4**.

These measurements produced the following data of **4** and **6** that are specified in table 2 and are herein compared to nitrocellulose, containing a nitrogen content of 13.5 %.

Table 2. Energetic properties of **4** and **6**.

	4	**6**	**Nitrocellulose**[p]
Formula (monomer)	$C_{10}H_{17}N_3O_8$	$C_7H_{11}N_3O_8$	$C_6H_{7.26}N_{2.74}O_{10.48}$
Molecular Mass [g mol^{-1}]	307.10	265.05	285.43
Impact sensitivity [J][a]	35	10	3
Friction sensitivity[b]	360	120	353
N [%][c]	14.68	15.85	13.50
Ω [%][d]	-107	-69	-33
$T_{dec.}$ [°C][e]	151	176	192[29]
ρ (g cm^{-3})[f]	1.5	1.5	1.7
$-\Delta_f H_m°$ [kJ mol^{-1}][g]	849	454	-
$-\Delta_f U_m°$ [kJ kg^{-1}][h]	2650	1608	-
Values calculated by Explo5 V5.05			
$-\Delta_E U_m°$ [kJ kg^{-1}][i]	3477	4668	4889
T_E [K][j]	2432	3331	3935
$p_{C\text{-}J}$ [kbar][k]	54	73	81
D [m s^{-1}][l]	4472	5100	5280
Gas vol. [L kg^{-1}][m]	739	769	744
I_s [s][n]	170	200	232
I_s [s] (70 % ADN)[o]	245	249	236

[a] BAM drop hammer; [b] BAM friction tester; [c] Nitrogen content; [d] Oxygen balance; [e] Temperature of decomposition by DSC (β = 5 °C, Onset values); [f] derived from pycnometer measurement (4); [g] Molar enthalpy of formation; [h] Energy of formation; [i] Energy of Explosion; [j] Explosion temperature; [k] Detonation pressure; [l] Detonation velocity; [m] Assuming only gaseous products; [n] specific impulse (isobaric combustion, chamber pressure 60 bar, frozen equilibrium), [o] specific impulse of a mixture containing 70 % ammonium dinitramide as oxidizer; [p] values based on Ref. [30] and the EXPLO5.5 database.

Compared to nitrocellulose, the temperatures of explosion of **4** and **6** are lower, thus they diminish the erosion when applied. The detonation pressure and the detonation velocity of **4** are slightly lower, whereas the detonation pressure of **6** is comparable with nitrocellulose. However, the specific impulse of **4** and **6** is a bit lower than that of nitrocellulose, whereas by addition of an oxidizer, like ammonium dinitramide (ADN), both compounds exceed the value of nitrocellulose.

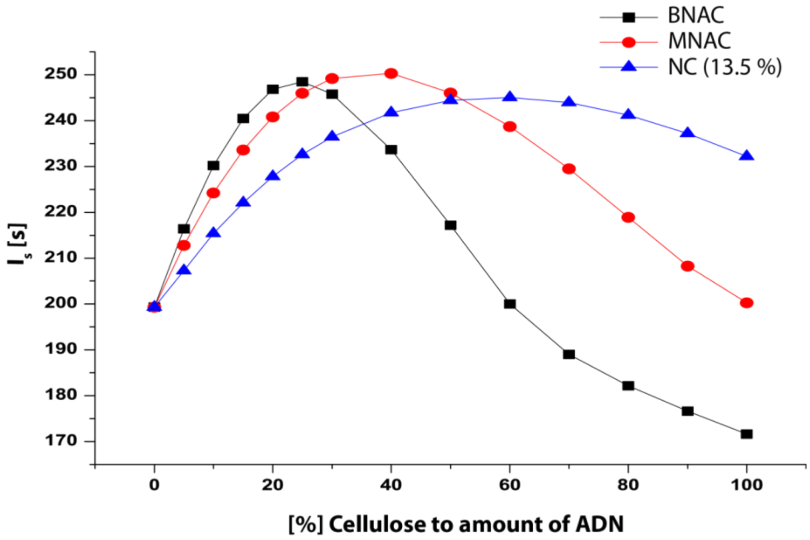


Figure 4. Comparison of the specific impulse of **4** and **6** with nitrocellulose (13.5 % nitrated) by the addition of ADN, calculated by EXPLO5 V5.04.

The comparison of the different mixing ratios of **4**, **6** and nitrocellulose (13.5 % nitrated) with ADN as an oxidizer, depicts that by the addition of smaller amounts of the cellulose derivatives, those compounds have a better performance than nitrocellulose, which is generally used in amounts of 12 to 14 % nitrogen.

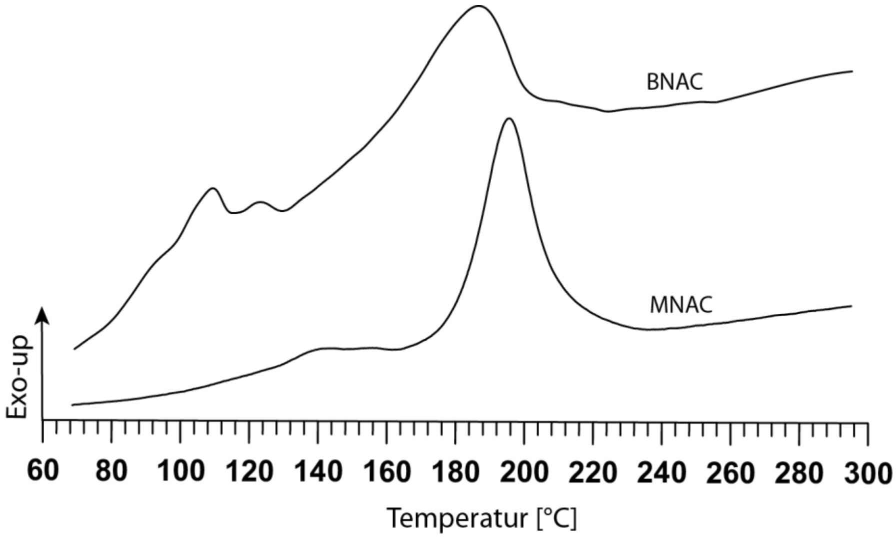


Figure 5. DSC spectrum of **4** and **6**.

The melting area of **4** starts at 107 °C and ends with the point of decomposition at 151 °C, as proven by DSC measurements. **6** has a better thermal stability, as suggested by its decomposition point of 176 °C, which is also the end of the melting area that starts at 141 °C.

Sensitivity tests of the compounds using standard BAM tests [34], revealed an impact sensitivity of 10 J as well as a friction sensitivity of 120 N for **6**, whereas **4** displayed an impact sensitivity of 35 J and a friction sensitivity of 360 N. As a result **4** can be regarded as less sensitive in terms of impact and insensitive in terms of friction according to literature [25]. Whereas **6** should be considered as sensitive, although compared to commonly used nitrocellulose (impact = 3 J, friction > 353 N) [26] it has a better response to impact, which is a clear advantage in terms of safety.

3.2.3 Application of MNAC in Impulse Cartridges

In some ignition mixtures that are used in serial production, the binder of the pyrotechnic is made of nitrocellulose. Due to bad chemical stability of the compound and the addiction to autocatalytic decomposition, the storage stability and warranty of the pyrotechnic is limited. In the course of a survey for nitrocellulose-free ignition mixtures, the ignition mixture AZM 421a, which is already established in mass production, was modified. This work was carried out in cooperation with Diehl BGT Defence[35], and tested in the ignition caps DM 82 versus the original mixture. The ignition mixture AZM 421a was produced in 10 g mixtures. It is usually used in the production of the impulse cartridge DM 82 and consists of barium chromate, potassium perchlorate, titanium, zirconium and nitrocellulose. According to the identical work instruction, the ignition mixture AZM 421a mod LMU was produced. Here, nitrocellulose was replaced by MNAC (**6**).

3.2.3.1 Construction of the impulse cartridge DM 82

To perform the comparative measurements twelve DM 82 impulse cartridges for both varied compositions were produced. The ignition mixture AZM 421 of the impulse cartridge DM 82 (Figure 6) is electrically ignited by a bridge wire (Figure 7). In the next step the ignition mixture ignites the propellant that affects the impulse and the pressure. The pressure and the impulse are commonly used to discharge mechanical parts out of the bullet casing.

Figure 6. Impulse cartridge DM 82.

Figure 7. Contacts and bridge wire of the impulse cartridge.

Figure 8. Side of connection.

Figure 9. Electronic rotary disc loader.

Figure 10. DM 82 burnt down and new.

3.2.3.2 Measurement of the ignition parameters

The impulse cartridges DM 82 were ignited in a pressure bomb and the ignition delay, the time of pressure increase, maximum pressure and the power drop were measured with an ignition contact. These parameters are the crucial factor for the discharge. The power drop has to take place as fast as possible, because the pilot would otherwise get an error indication over the software system.

In the first instance six DM 82 with the original ignition mixture and nine DM 82 with the modified ignition mixtures were measured. The remaining impulse cartridges were artificially altered for 14 days at 80 °C and measured. This correlates to an aging process of 856 days under normal conditions.

Figure 11. Pressure bomb open .. and connected.

Unfortunately the measurements without aging were not provided by Diehl at the time of this thesis.

3.2.3.3 Results of the measurements after aging

In the following tables the results of the measurements that were received with the different ignition mixtures are displayed.

Table 3 depicts the results of the measurement with the ignition mixture AZM 421a by Diehl, whereas table 5 illustrates the results that were achieved by the AZM 421a of the modified LMU ignition mixture (AZM 421a mod LMU).

Table 3. Results of measurement with AZM 421a.

Ifd.Nr **AZM 421a original**	Resistance R_i (**Ω**)	Ignition delay t_1 (until wire break)	Ignition delay t_1 (until 10 % p_{max})	Ignition increase t_2 (10–90 % p_{max})	Ignition delay t_3 (10-90 % p_{max})	Max. pressure increase	Max. gas pressure
	0.8-1.3	**2–6 ms**		**< 20 ms**	**< 50 ms**	**< 6.9 bar/ms**	**34-50 bar**
1	0.90	3.94	9.06	13.24	22.31	2.68	44.3
2	0.90	4.33	9.96	13.49	23.45	2.62	43.5
3	0.90	3.99	9.01	13.47	22.48	2.73	44.7
4	0.90	3.94	8.06	13.08	21.13	2.65	44.5
5	0.90	4.03	8.92	13.43	22.35	2.64	44.1
6	0.90	4.29	9.39	13.78	23.15	2.65	44.4

Table 2. Results of the measurement with AZM 421a mod LMU

Ifd.Nr **AZM 421a mod LMU**	Resistance R_i (Ohm)	Ignition delay t_1 (until wire break)	Ignition delay t_1 (until 10 % p_{max})	Ignition increase t_2 (10–90 % p_{max})	Ignition delay t_3 (10-90 % p_{max})	Max. pressure increase	Max. gas pressure
	0.8-1.3	**2–6 ms**		**< 20 ms**	**< 50 ms**	**< 6.9 bar/ms**	**34-50 bar**
1	0.90	4.33	8.21	13.44	21.66	2.67	44.6
2	0.90	4.49	7.78	13.04	20.82	2.63	43.5
3	0.90	3.91	7.40	13.56	20.97	2.64	44.3

The given data is also displayed for better understanding in the following figures (figure 12 – 17).

Figure 12 illustrates the ignition delay until wire break. Both compounds, AZM 421a – the original of Diehl - and AZM 421a mod LMU - that one of the LMU - are in the target area and therefore fulfill the given parameters perfectly.

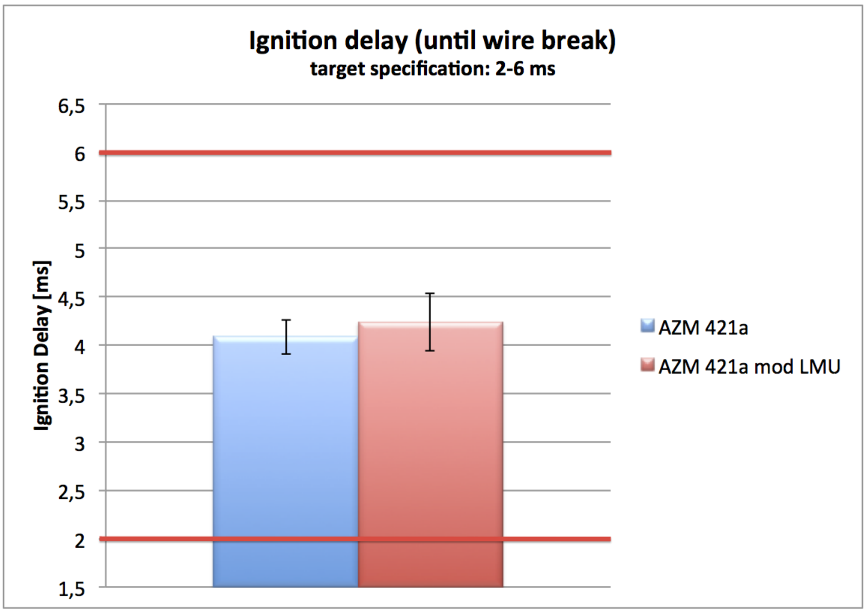


Figure 12. Ignition delay t_1 until wire break.

This is also the case for both compounds for the ignition delay t_1, up to 10 % maximum pressure, depicted in figure 13, the time of pressure increase t_2 of 10 % to 90 % maximum pressure (figure 14), the ignition delay t_3 up to 90 % maximum pressure (figure 15), the maximum pressure increase (figure 16) and the maximum gas pressure (figure 17). The resistance is for all measurements identical with a value of 0.9 Ω, which also fits perfectly into the specified parameters.

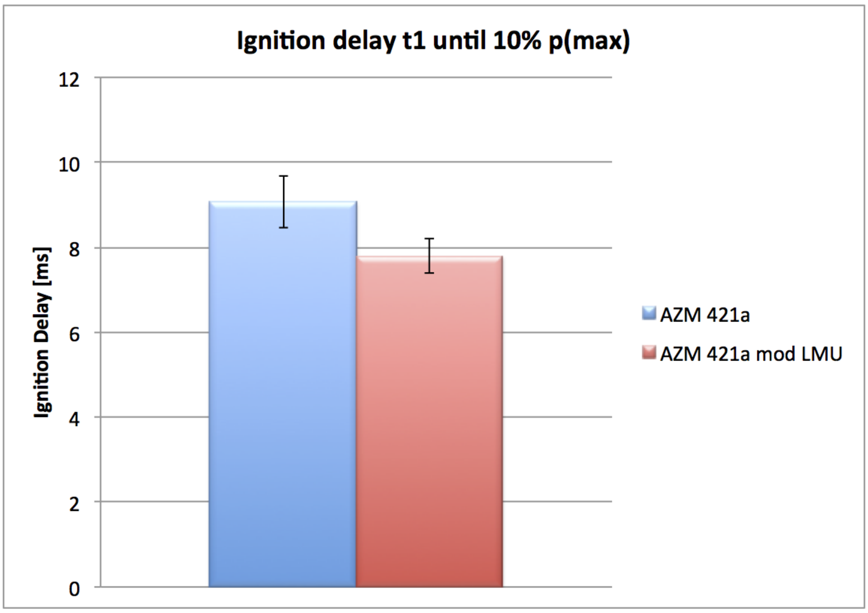


Figure 13. Ignition delay t_1 up to 10 % maximum pressure.

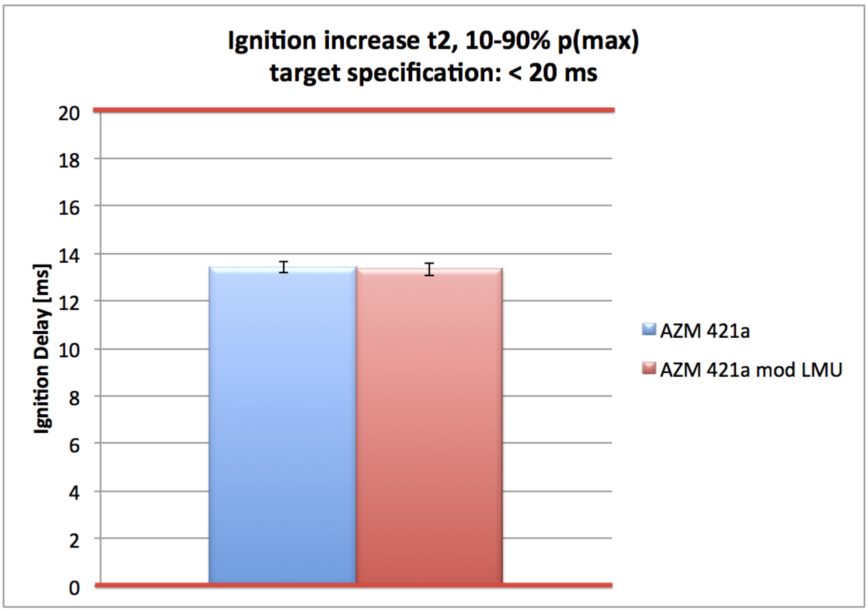


Figure 14. Pressure increase 10 % to 90 % maximum pressure.

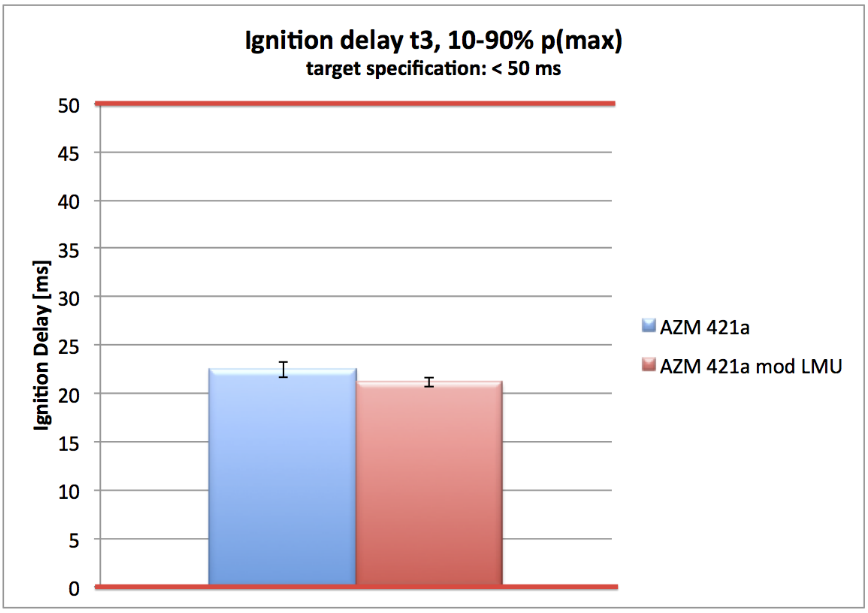


Figure 15. Ignition delay to 90 % maximum pressure.

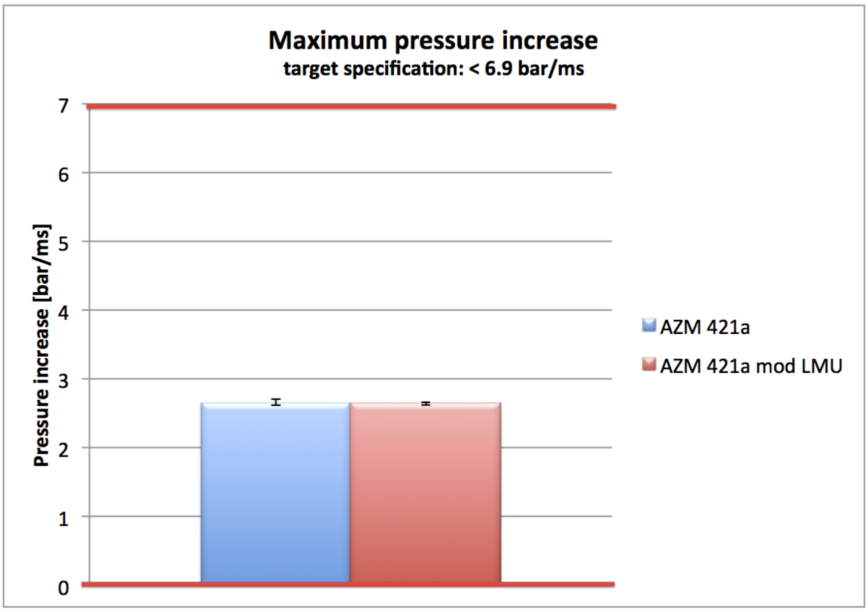


Figure 16. Maximum pressure increase.

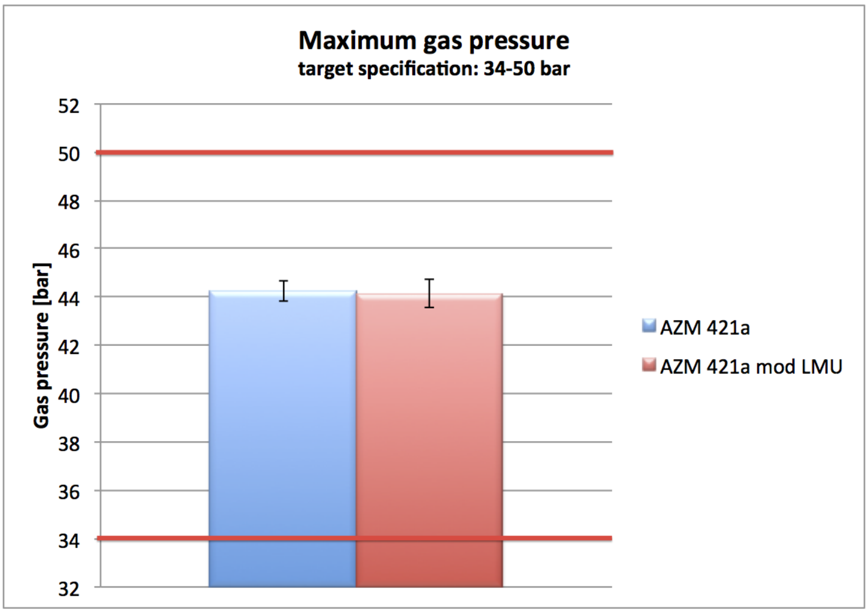


Figure 17. Maximum gas pressure.

The modified ignition mixture AZM 421a mod LMU revealed in the impulse cartridge, after the artificial aging, a constant performance within the target area in the claimed parameters according to TL1375-1115, Ausg. 4 “ignition delay time until wire break”, “pressure increase to 90 % maximum pressure”, “maximum pressure increase” and “maximum gas pressure”. Hence this examination is passed according to the technical delivery instruction and the ignition mixture is qualified for an application in the impulse cartridge DM 82. The binder replacement of nitrocellulose to methylnitraminocellulose was therefore successful and had no negative influences on the combustion behavior of the pyrotechnic in the impulse cartridge. We can successfully conclude that on the basis of the methylnitramino moiety the binder has better long term stability as common nitrocellulose.

3.3 Conclusion

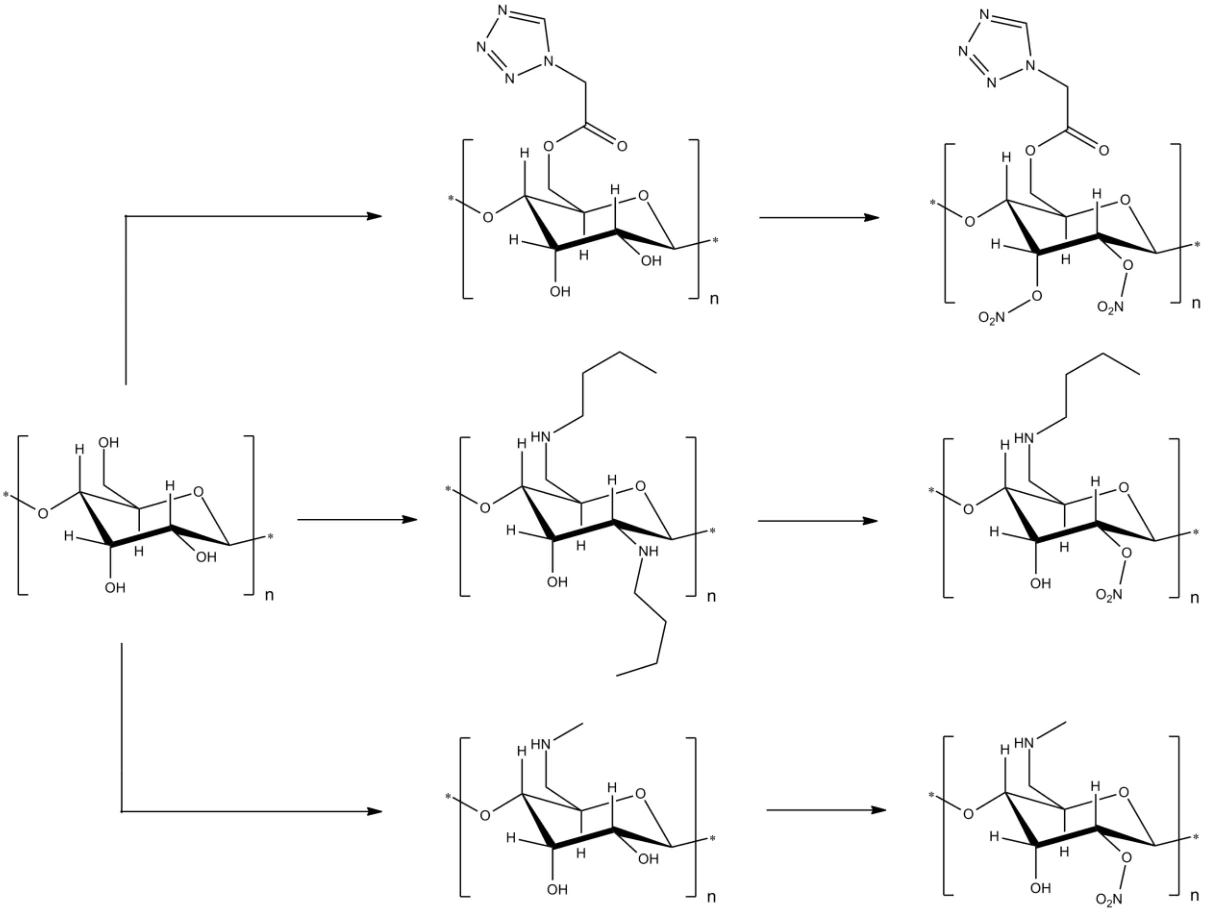


Figure 6. Overview of the polymers based on cellulose that were gained.

In this work, several approaches were presented to synthesize nitrogen rich polymers that are equally or even more energetic than nitrocellulose. The goal was to fully exploit the possibilities that a natural polymer like cellulose offers, with all its advantages of biocompatibility, low cost acquirement, economical friendliness and moreover the possibility of a biological degradation, which arise from the fact, that cellulose itself is a biological product.

Finally, some of the materials described in this work hold promise for an application. The low detonation temperature of MNAC and BNAC renders these polymers a valuable alternative to nitrocellulose, as they also reach higher performances than nitrocellulose by adding an oxidizer, like ammonium dinitramide. Hence, both MNAC that additionally offers a good thermal stability, and BNAC, should perform better as a propellant than nitrocellulose, which has been established as propellant and binder in pyrotechnical and explosive compositions. Furthermore, due to the bad chemical stability of nitrocellulose and its addiction to autocatalytic decomposition, MNAC proved itself superior to nitrocellulose in application of ignition mixtures, which was performed in collaboration with Diehl BGT Defense. Therefore MNAC is definitely worth of being applied as binder in ignition mixtures.

One should additionally keep in mind that NCTA has a detonation velocity only slightly lower than nitrocellulose and a better response to impact and friction, thus making it interesting as well for various applications.

3.4 Experimental Part

A determining problem of performing experiments with cellulose is the insolubility of this material in any common solvent, because of the supra-molecular structure[12]. The dissolution of cellulose destroys the highly organized hydrogen-bonding system surrounding the single polyglucan chain. The system *N*,*N*-dimethylacetamide (DMA) / LiCl as solvent, shows an enormous potential for the analysis of cellulose and for the preparation of a wide variety of derivatives. Its usefulness in analysis derives from the fact that the solvent is colorless and dissolution succeeds without or at least with negligible degradation, even in case of high molecular weight polysaccharides.

Consequently, the first step in doing reactions with cellulose is its dissolution. This was performed by the procedure of K. RAHN *et al* [36] gaining a solution containing 4.3 wt. % cellulose.

Therefore, dried cellulose (Avicel PH 101) was suspended in *N*,*N*-dimethylacetamide, kept at 160 °C for one hour and stirred. In order to replace water bound to cellulose, a small amount of *N*,*N*-dimethylacetamide was removed by heating the solution. After the slurry had been cooled down to 100 °C, anhydrous lithium chloride was added. By cooling to room temperature and stirring, the cellulose dissolved completely within some hours, resulting in a yellowish solution of 4.3 wt. % cellulose.

3.4.1 Synthesis of Polymers based on Cellulose containing Tetrazole Moieties

3.4.1.1 1-Cellulose-2-(1*H*-tetrazol-1-yl) acetate (1)

2-(1*H*-Tetrazol-1-yl) acetic acid (0.5 g, 3.9 mmol) and a cellulose solution (4.3 wt. %, 3.7 g, 1.02 mmol) were refluxed with 4-toluenesulfonyl chloride (0.75 g, 3.9 mmol) in 5 mL *N*,*N*-dimethylacetamide at 60 °C. After 24 hours the resulting suspension was emptied into water. The product was filtered off, washed with acetonitrile and the remaining solvent was removed under reduced pressure. The polymer was obtained as brown solid. (0.24 g, 96 %).

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3260 (s), 2963 (m), 2918 (m), 2252 (w), 2128 (w), 1753 (s), 1629 (m), 1552 (m), 1420 (m), 1325 (m), 1261 (m), 1166 (m), 1166 (s), 1102 (s), 1054 (s), 925 (w), 800 (w), 657 (w), 570 (w).

EA ($C_9H_{12}N_4O_6$, 272.22): calculated: C 37.22 %, H 3.90 %, N 21.70 %; found: C 39.02 %, H 4.41 %, N 21.30 %.

3.4.1.2 1-Nitrocellulose-2-(1*H*-tetrazol-1-yl) acetate (2)

1-Cellulose-2-(1*H*-tetrazol-1-yl) acetate (1 g, 3.03 mmol) was dissolved in 3 mL acetic anhydride as well as 1.5 mL nitric acid and stirred at room temperature. After two hours the liquid was emptied into ice water and the product was filtered off. It was obtained as pale yellow glasslike solid. (0.77 g, 65 %).

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3436 (s), 3148 (w), 2963 (w), 1767 (m), 1708 (m), 1645 (m), 1485 (m), 1436 (m), 1384 (m), 1285 (m), 1262 (m), 1230 (m) 1176 (m), 1101 (m), 1063 (m), 1020 (m), 826 (m), 796 (m), 745 (w), 700 (w), 654 (w), 571 (w), 531 (w).

EA ($C_9H_{10}N_6O_8$, 330.21): calculated: C 35.89 %, H 3.68 %, N 23.25 %; found: C 35.36 %, H 3.25 %, N 24.14 %.

3.4.2 Synthesis of Polymers based on Cellulose containing Nitramine Moieties

3.4.2.1 Butylaminecellulose (3)

To a solution of tosylcellulose[36] (1 g, 3.16 mmol) in 30 mL *N*,*N*-dimethylformamide, butylamine (1.87 mL, 18.97 mmol) was slowly added. The suspension was refluxed for three days at 100 °C.

The resulting solution was emptied in water. Because no precipitate was formed, the solvent was removed under reduced pressure and the product was obtained as brown oil. (3.46 g, 94 %).

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3292 (m), 3040 (m), 2957 (m), 2931 (m), 2873 (m), 1627 (vs), 1549 (m), 1496 (m), 1458 (m), 1397 (m), 1264 (m), 1220 (m), 1175 (s), 1121 (s), 1033 (s), 1013 (vs), 816 (m), 740 (w), 711 (w), 680 (vs).

EA ($C_{14}H_{28}N_2O_3$, 272.39): calculated: C 61.73 %, H 10.36 %, N 10.28 %; found: C 53.19 %, H 9.46 %, N 10.59 %.

3.4.2.2 Butylnitraminocellulose (4)

Butylaminecellulose (1 g, 3.67 mmol) was dissolved in 4 mL acetic anhydride as well as 2 mL nitric acid and stirred at room temperature. After two hours the liquid was emptied in water and the product was filtered off. The product was obtained as yellowish solid. (0.84 g, 63 %).

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3552 (s), 3477 (vs), 3416 (vs), 2966 (m), 2940 (m), 1721 (m), 1662 (vs), 1619 (m), 1529 (w), 1384 (s), 1281 (s), 1192 (m), 1178 (m), 1072 (m), 1037 (m), 839 (m), 746 (w), 672 (w), 621 (w), 477 (w).

EA ($C_{10}H_{18}N_2O_6$, 262.26): calculated: C 45.80 %, H 6.92 %, N 10.68 %; found: C 39.09 %, H 5.12 %, N 11.49 %.

3.4.2.3 Methylaminecellulose (5)

To a solution of tosylcellulose[36] (5.00 g, 12.71 mmol) in 250 mL *N*,*N*-dimethylacetamide, methylamine (40 % in H_2O, 37.48 mL, 535.77 mmol) was added. The suspension was refluxed for 48 hours at 60 °C. The resulting solution was emptied in 1L isopropyl alcohol. The formed precipitate was filtered and washed with water. The product was obtained as colorless solid (1.17 g, 49 %).

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3341 (m), 2897 (m), 2361 (m), 2337 (m), 2159 (w), 1986 (w), 1623 (s), 1498 (m), 1415 (m), 1398 (m), 1358 (m), 1266 (w), 1187 (m), 1173 (m), 1058 (vs), 1037 (vs), 1011 (vs), 816 (m).

EA ($C_7H_{13}NO_4$, 175.18): calculated: C 47.99 %, H 7.48 %, N 8.00 %; found C 47.62 %, H 7.60 %, N 8.09 %.

3.4.2.4 Methylnitraminocellulose (6)

Methylaminecellulose (1 g, 5.71 mmol) was dissolved in 4 mL acetic anhydride as well as 2 mL nitric acid and stirred at room temperature. After two hours the liquid was emptied in water and the product was filtered off. The product was obtained as yellowish solid (0.92 g, 59 %).

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3553 (s), 3477 (vs), 3415 (vs), 2927 (w), 2031 (w), 638 (m), 1618 (m), 1385 (w), 1277 (w), 1177 (w), 1110 (w), 829 (w), 710 (w), 617 (m), 479 (w).

EA ($C_7H_{11}N_3O_8$, 265.18): calculated: C 31.71 %, H 4.18 %, N 15.85 %; found C 29.02 %, H 3.33 %, N 15.17 %.

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4. Energetic Polymers based on Glycidyl Azide Polymer (GAP)

4.1 Introduction

To date, energetic nitrogen-rich polymers are mainly used as binders[1,2] in energetic compositions, plasicisers for explosive formulations[3] and as gas generating agents[4]. The low thermal stability of polymers bearing nitric esters along with the low adhesive properties of the thermally stable azide polymers, which is a severe drawback, justifies the development of new energetic polymers.[5] Accordingly, there is still a need for novel binders to enhance the energetic properties of the already available compounds to increase the performance, despite the fact that several polymers are already successfully in use in energetic compositions. [6]

Although heterocyclic compounds do not play an important role in binder systems of energetic compositions so far, special attention should be drawn to their application due to the outstanding properties of tetrazoles and triazoles that often combine high nitrogen contents and a highly positive heat of formation with good thermal stabilities and sensitivities owing to their aromatic ring systems. [7] In order to synthesize environmentally friendly compounds, these materials have the advantage of inheriting a high nitrogen content and therefore releasing non or less toxic gases, like molecular nitrogen and CO/CO_2.

4.2 Results and Discussion

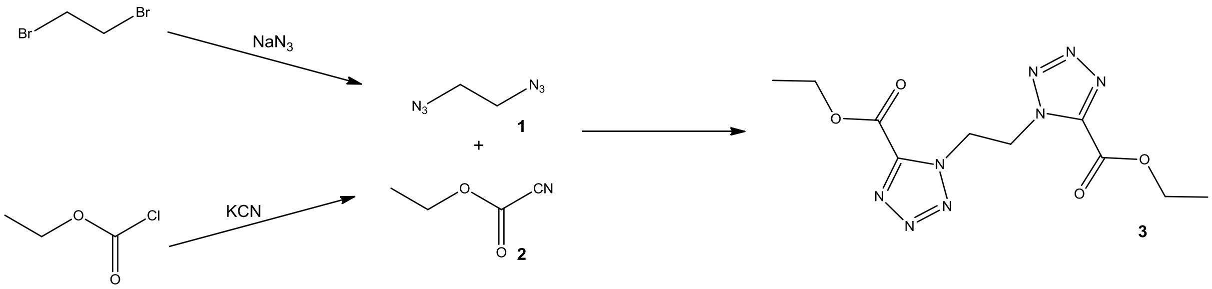
4.2.1 Glycidyl-5-(carboxyethyl-1*H*-tetrazol)polymer and 1,2-Bis-(5-carboxyethyl-1*H*-tetrazolyl)ethane as Polymeric Precursor

An excellent technique to attach a tetrazole group to a polymer backbone is a cycloaddition of an azide to a cyanide moiety[8]. The preferred polymer for this synthesis is glycidyl azide polymer (GAP)[9], a commercially available polymer inheriting an azide group. Here we present the synthesis of an energetic nitrogen-rich polymer via cycloaddition of ethyl cyanoformate to the azide moiety of GAP, as well as the synthesis of a comparable polymer precursor.

In order to evaluate the potential properties of the corresponding polymer, the analogue ethyl-bridged bistetrazole was prepared and characterized. Therefore the reaction of ethyl cyanoformate was undertaken with 1,2-diazidoethane (**1**) having two azide moieties, before reacting it with glycidyl azide polymer (GAP), having an azide functionality as well.

The synthesis is carried out with the products of two different reactions. One is the reaction of ethyl chloroformate with sodium cyanide to obtain ethyl cyanoformate (**2**)[10], which is reacted with 1,2-diazidoethane (**1**).

Compound 1 is obtained by a nucleophilic substitution of sodium azide at 1,2-dibromoethane (Scheme 1)[11]. These two products are the starting materials in the synthesis leading to **3**. To achieve a complete conversion of the starting materials, a reaction time of two days is mandatory to gain the product.



Scheme 1. Synthesis of 1,2-bis-(5-carboxyethyl-1*H*-tetrazolyl)ethane (**3**).

A single crystal diffraction measurement was accomplished for compound **3**. 1,2-Bis(5-carboxyethyl-1*H*-tetrazolyl)ethane (**3**) crystallizes in the monoclinic space group P2_1/*n* with a cell volume of 713.69(5) Å^3 and two molecular formulas per unit cell. The calculated density at 173 K is 1.444 g cm^{-3}. The asymmetric unit of **3**, together with the atom labels is presented in Figure 1.

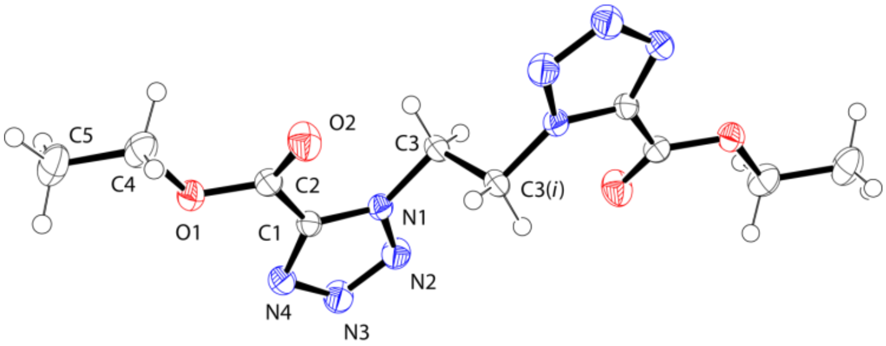


Figure 1. Asymmetric unit of **3**. Thermal ellipsoids are set to 50 % probability. Symmetry operators: (i) = -x, 1-y, 1-z. Selected bond lengths /Å = O1-C2 1.3214(15), O1-C4 1.4717(16), N1-N2 1.3411(14), N1-C1 1.3457(15), N1-C3 1.4670(16), N2-N3 1.3011(15), O2-C2 1.2079(15), C1-N4 1.3180(16), C1-C2 1.4877(17), N4-N3 1.3641(16), C4-C5 1.500(2); selected bond angles /°: C2-O1-C4 115.15(10), N2-N1-C1 108.16(10), N2-N1-C3 119.65(10), C1-N1-C3 119.65(10), N3-N2-N1 106.65(10), N4-C1-N1 109.03(11), N4-C1-C2 127.11(11), N1-C1-C2 127.11(11), O2-C2-O1 126.46(12), O2-C2-C1 122.06(11), O1-C2-C1 111.48(10), C1-N4-N3 105.39(10), N2-N3-N4 110.77(10), O1-C4-C5 106.91(12).

A closer look at the bond lengths and angles within the crystal structure of the compound reveals no evident differences relative to those for other heterocyclic ring systems.[12]

The molecular structure is stabilized by several electrostatic interactions that keep the molecules in plane, forming a chain along the the *a* axis, by connecting the molecules with short contacts of 3.237(2) Å between the C4 and O2(*i*) as well as O2 and C4(*i*), respectively (H4a-O2(*i*): 2.8144(184) Å; H4b-O2(*ii*): 2.9188(145)) that are similar to the van der Waals radii of oxygen and carbon [$r_w(O) + r_w(C) = 3.22$ Å] and oxygen and hydrogen [$r_w(O) + r_w(H) = 2.72$ Å], respectively.[13] The formation of the chain is shown in Figure 2, as well as the intermolecular interactions as dotted lines.

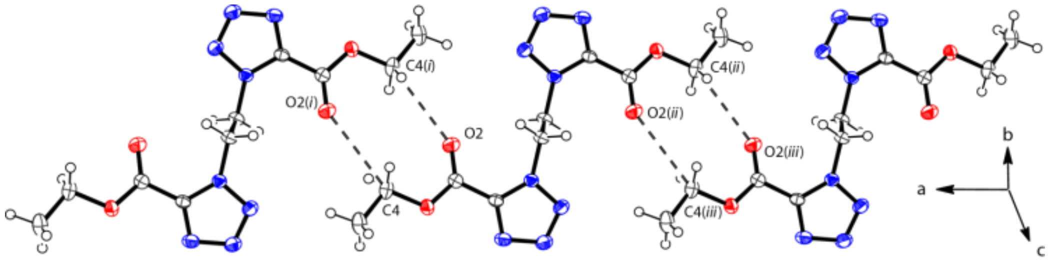


Figure 2. Short contact scheme within the band structures of 3. Thermal ellipsoids represent the 50 % probability level. Symmetry operators: (i) = 1-x, 1-y, 1-z; (ii) = -x, 1-y, 1-z; (iii) = -1+x, y, z.

The chains elongate along the *a* axis and are stacked above one another. The connected chains are attached by short N-CH_2 contacts, N4···H3a(*ii*), where the contact is with 2.82(1) Å analog to the sum of the van der Waals radii of nitrogen and hydrogen [$r_w(N) + r_w(H) = 2.75$ Å].[13] The stacking is displayed in Figure 3 together with the short contacts between the connected chains as dotted lines.

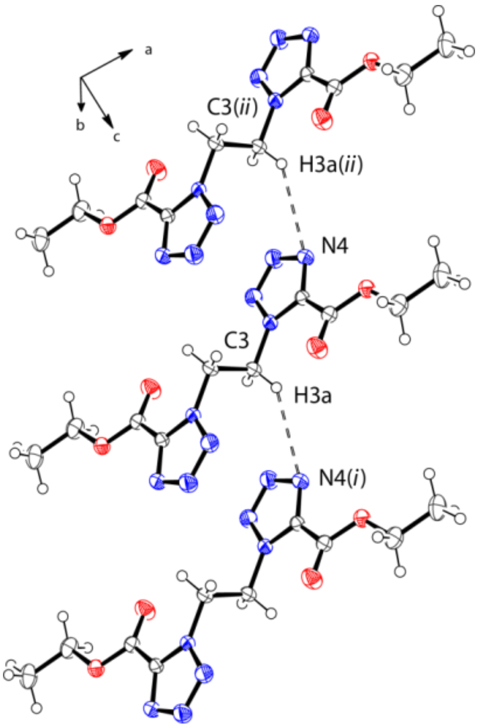


Figure 3. Connected chains of **3** along the *a* axis. Thermal ellipsoids represent the 50 % probability level. Symmetry operators: (i) = x, 1+y, z; (ii) = x, -1+y, z.

The calculations regarding the energy of formation of **3** were carried out using the Gaussian G09W Version 7.0 program package.[14] Since very detailed descriptions of the calculation process have been published earlier[15] and can be found in specialized books,[16] only a short summary of computational methods will be given. The enthalpies (*H*) and Gibbs free energies (*G*) were calculated using the complete basis set method (CBS) of Petersson *et al.* in order to obtain very accurate energies. In this contribution, we used the modified CBS-4M method with M referring to the use of minimal population localization, which is a re-parameterized version of the original CBS-4 computational method and also includes additional empirical calculations.[17,18] The enthalpies of formation for the gas phase species were computed according to the atomization energy method, using NIST[19] values as standardized values for the atoms standard heats of formation ($\Delta_f H^0$) according to equation 1.[20-22]

$$\Delta_f H^0{}_{\text{(g, Molecule, 298)}} = H_{\text{(Molecule)}} - \sum H^0{}_{\text{(Atoms)}} + \sum \Delta_f H^0{}_{\text{(Atoms, NIST)}} \qquad (1)$$

The solid state enthalpy of formation for neutral compounds is estimated from the computational results using TROUTONS rule,[23] where T_m was taken equal to the decomposition temperatures.

$$\Delta H_m = \Delta_f H^0{}_{\text{(g, Molecule, 298)}} - \Delta H_{sub} = \Delta_f H^0{}_{\text{(g, Molecule, 298)}} - (188\ [\text{J mol}^{-1}\text{K}^{-1}] * T_m)$$

The solid state enthalpies of formation for the ionic compounds are derived from the calculation of the corresponding lattice energies (U_L) and lattice enthalpies (H_L), calculated from the corresponding molecular volumes, using the equations provided by Jenkins *et al.*[24,25]. The derived molar standard enthalpies of formation for the solid state (ΔH_m) were used to calculate the solid state energies of formation (ΔU_m) according to equation (3), with Δn being the change of moles of gaseous components.[16]

$$\Delta U_m = \Delta H_m - \Delta n RT \qquad (3)$$

The calculated standard energies of formation were used to perform predictions of the detonation parameters with the program package EXPLO5, Version 5.05.[26] The program is based on the chemical equilibrium, steady state model of detonation. It uses Becker-Kistiakowsky-Wilsons equation of state (BKW EOS) for gaseous detonation products together with Cowan-Ficketts equation of state for solid carbon.[27-29] The calculation of the equilibrium composition of the detonation products is performed by applying modified White, Johnson and Dantzigs free energy minimization technique. The program was designed to enable calculations of detonation parameter at the Chapman-Jouguet point. The BKW equation as implemented in the EXPLO5 program was used with the BKW-G set of parameters (α, β, κ, θ) as stated below the equation, with X_i being the mol fraction of the i-th gaseous detonation product while k_i is the molar co-volume of the i-th gaseous detonation product[26-29].

$$pV / RT = 1 + xe^{\beta x} \quad (4) \qquad \text{with} \quad x = (\kappa \Sigma X_i k_i) / [V (T + \theta)]^{\alpha}$$

$$\alpha = 0.5,\ \beta = 0.096,\ \kappa = 17.56,\ \theta = 4950$$

The results of the detonation runs, together with the calculated energies of formation and the corresponding sensitivities in comparison to GAP, are compiled in table 1.

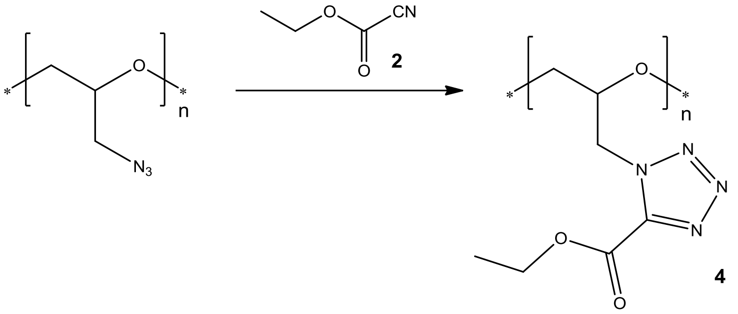
Table 1. Energetic properties and detonation parameters of **3** and **4**.

	3	**4**	**GAP**[p]
Formula	$C_{10}H_{14}N_8O_4$	$C_{55}H_{80}N_{34}O_{23}$	$C_3H_5N_3O$
Molecular Mass [g mol^{-1}]	310.27	1585.44	99.09
Impact sensitivity [J][a]	>40	>40	7
Friction sensitivity [N][b]	>360	>360	>360
ESD–test [J]	1.5	-	-
N [%][c]	34.55	30.04	42.41
Ω [%][d]	-119	-128	-121
$T_{\text{dec.}}$ [°C][e]	212	208	200
ρ [g cm^{-3}][f]	1.4	1.3	1.3
$-\Delta_f H_m°$ [kJ mol^{-1}][g]	141	3653	-142
$-\Delta_f U°$ [kJ kg^{-1}][h]	557	2197	-1545
EXPLO5 values: V5.05			
$-\Delta_E U°$ [kJ kg^{-1}][i]	2748	1605	4258
T_E [K][j]	2140	1486	2819
$p_{C\text{-}J}$ [kbar][k]	49	34	71
$V_{\text{Det.}}$ [m s^{-1}][l]	4279	3683	5047
Gas vol. [L kg^{-1}][m]	695	679	739
I_{sp}(s)[n]	160	135	201
I_{sp}(s) (70 % ADN)[o]	241	230	251

[a] BAM drop hammer; [b] BAM friction tester; [c] Nitrogen content; [d] Oxygen balance; [e] Temperature of decomposition by DSC (β = 5 °C, Onset values); [f] derived from X-ray structure (3) and pycnometer measurement (4); [g] Molar enthalpy of formation; [h] Energy of formation; [i] Energy of Explosion; [j] Explosion temperature; [k] Detonation pressure; [l] Detonation velocity; [m] Assuming only gaseous products; [n] specific impulse (isobaric combustion, chamber pressure 60 bar, frozen equilibrium), [o] specific impulse of a mixture containing 70 % ammonium dinitramide as oxidizer; [p] values based on Ref. [30] and the EXPLO5.5 database.

As proven by DSC measurement, compound **3** has a melting point at 108 °C. Furthermore it is a very stable and insensitive compound according to its decomposition point of 212 °C, which is even higher compared to commercially used GAP (200 °C) and its insensitivity towards impact and friction (IS > 40 J; FS > 360 N), which is also an advantage related to GAP (IS = 7). Although the detonation velocity is lower, **3** convinces with a lower temperature of explosion which diminishes the erosion in applications. Furthermore the specific impulse I_{sp} that describes the efficiency of rocket and jet engines, is rather good and can be further improved by the addition of ammonium dinitramide as an oxidizer. A mixture of 70 % ADN and 30 % of compound **3** even enhances the performance of pure ADN (I_{sp} (100 % ADN) = 199 s; values based on the EXPLO5 database).

To avoid the known difficulities of polymerizing monomers - the fact that energetic moieties can rather easy be lost during the polymerization step - an already formed polymer structure equipped with an azide functionality, commonly known as GAP, was chosen for this synthesis. This compound was reacted with ethyl cyanoformate to give glycidyl-5-(carboxyethyl-1*H*-tetrazolyl)polymer (**4**) (Scheme 2).



Scheme 2. Synthesis of Glycidyl-5-(carboxyethyl-1*H*-tetrazolyl)polymer (**4**).

The verification of the results of this synthesis implied some difficulites, due to the fact that **4** is hardly soluble in any commonly known solvent, except DMSO and DMF. Therefore an NMR spectroscopy measurement was performed in DMSO. However because of the overlap of the various polymer chains, both intermolecular and intramolecular, one gets rather broad signals that are hard to assign to the various functional groups of the compound. On the other hand mass spectrometry was the confirmation technique of choice, resulting in specific molecule peaks that can be ascribed to the desired molecule and some of its derivatives, having still some additional unreacted GAP monomers present. This fact can be ascribed to a further problem of polymers: oftentimes not all functional groups are included in the reaction, due to conformation issues. Consequently, not all azide groups of GAP got attacked by ethyl cyanoformate and by the end of the reaction some azide groups were still left over.This is also confirmed by infrared spectroscopy, which shows a strong vibration at 2100 cm^{-1} [31] due to the azide moiety.

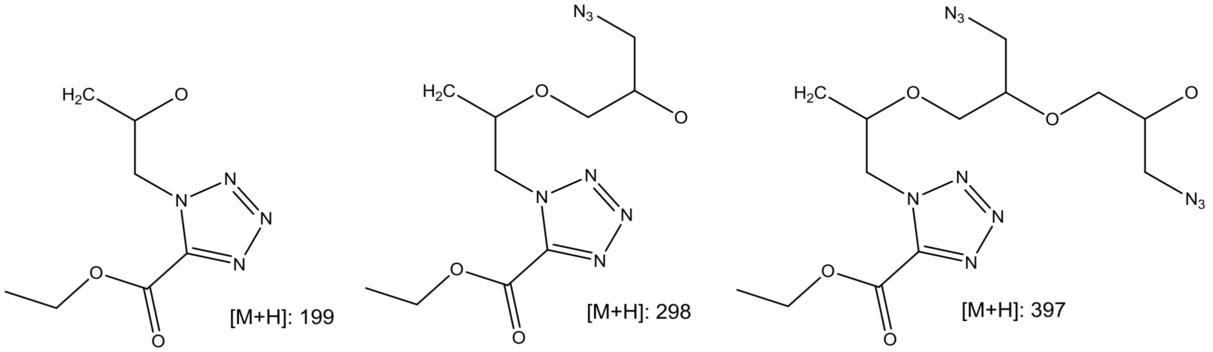
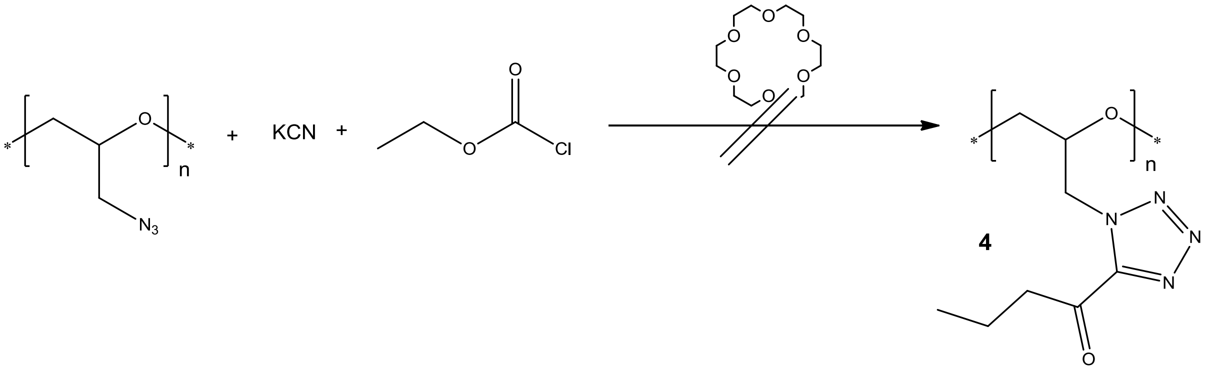


Figure 4. Molecule fragments corresponding to mass spectrometry peaks.

Also, the higher nitrogen content of the product, referring to the elemental analysis, points to the fact that there are still some monomeric GAP units present in the product. This analysis agrees best, when on average every 3.5 monomeric unit has the azide group of the monomeric GAP unit. Therefore the product has a high nitrogen content of 30.04 % and an oxygen balance of -128 %. Based on these values the detonation parameters determined by the Explo5 program package [26], were calculated. The standard energies of formation were ascertained by bomb calorimetric measurements. The results of the detonation runs, together with the corresponding sensitivities and the decompostion temperature are outlined in Table 1.

Although some GAP units are still present in the molecule, this compound is characterized as a highly stable and insensitive molecule with a decomposition point of 208 °C, which exceeds that of GAP, and its insensitivity towards impact and friction (IS > 40 J; FS > 360 N). However, due to the raised carbon content of compound **4**, caused by the carboxyethyl group, the performance is a bit decreased in comparison to GAP. This influences the detonation velocity that is 27 % lower than that of GAP, but it also affects the temperature of explosion and lowers it by 52 %, which is, as already mentioned, an advantage due to erosion problems. Although the specific impulse of **4** is rather low it can be highly influenced and improved by the addition of an oxidizer like ADN.

To further optimize this method by reducing the contamination by self-made ethyl cyanoformate, a one-pot synthesis was performed. Therefore ethyl chloroformate, potassium cyanide, GAP and 18-crown-6 as phase transfer catalyst were mixed togeher in one reaction and refluxed for 2 days in toluene.

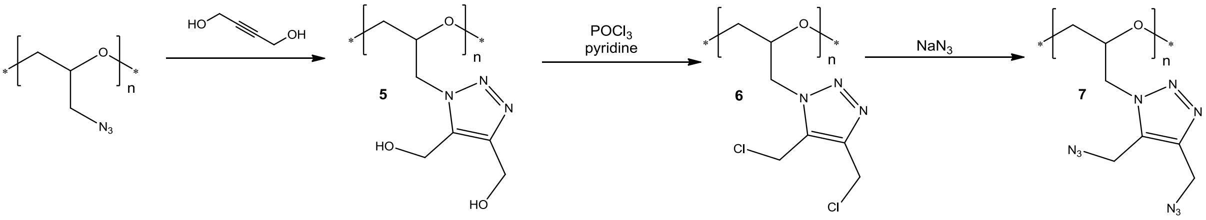


Scheme 3. One pot synthesis of **4**.

By means of this synthesis route the product could unfortunately not be obtained in a pure way, but was contaminated by educts.

4.2.2 (4,5-Di(azidomethyl)-1*H*-1,2,3-triazol-1-yl)glycidyl polymer

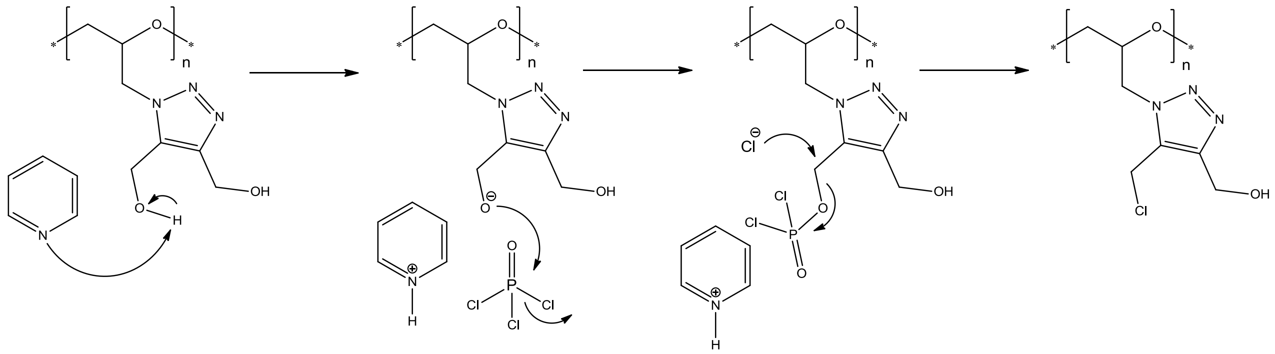
For the preparation of 1,2,3-triazoles several methods are known. A rather comfortable way is the [2+3] cycloaddition using azide and a derivative of acetylene. [32,33] Another way of preparation uses polymer bound azide for the synthesis of 5-(hydroxymethyl)-1*H*-1,2,3-triazole. [34] Therefore (4,5-di(azidomethyl)-1*H*-1,2,3-1-yl)glycidyl polymer (DATGP, **7**) was synthesized. Although the synthesis of **7** is already outlined in a previous work by S. SPROLL[5], due to the need for further improvements of the synthesis conditions, this reaction was performed again.



Scheme 4. Synthesis of **7**.

The triazole polymer (4,5-di(hydroxymethyl)-1*H*-1,2,3-triazol-1-yl)glycidyl polymer (DHTGP, **5**) is obtained by the reaction of GAP with 1.5 equivalents of 2-butyne-1,4-diol in toluene. In order to achieve suitable releasing groups to get the azide derivative, the hydroxyl groups were chlorinated to obtain (4,5-di(chloromethyl)-1*H*-1,2,3-triazol-1-yl) glycidyl polymer (DCTGP, **6**).

The chlorination was carried out by refluxing DHTGP in phosphorous oxychloride with one equivalent of pyridine per hydroxyl group. The reaction gave 85 % conversion of the hydroxyl groups into chlorine atoms.



Scheme 5. Chlorination of **5**.

The following conversion of the chlorine atoms into azide groups to obtain **7** was carried out in a mixture of water and acetonitrile providing an excess of 17 equivalents of azide groups per chlorine atom.

In Figure 5 the conversion of **5** to **7** is illustrated by the IR spectra of DHTGP and DATGP. The spectrum of **5** shows the appearance of the hydroxyl groups at about 3400 cm^{-1} (A)[31], whereas the small peak at 2100 cm^{-1} (B)[31] indicates that some azide groups of GAP were not substituted by 2-butyne-1,4-diol. The infrared spectrum of **7** on the other hand depicts the degree of conversion of the chlorine atoms of **6** into azide groups. The vibration at 2100 cm^{-1} (B)[31] indicates the appearance of the azide groups, whereas the small band at 3400 cm^{-1} (A)[31] highlights the presence of still existent hydroxyl groups of **5**.

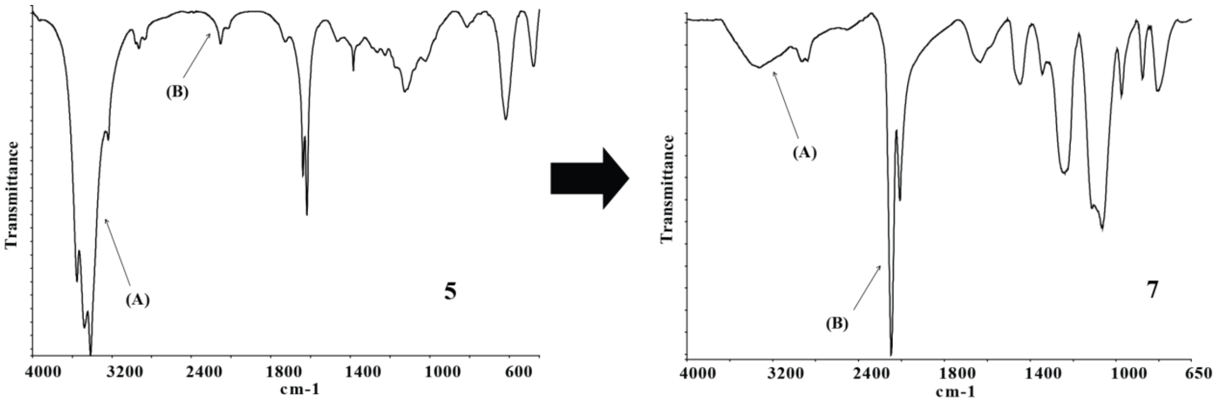


Figure 5. Infrared spectra of **5** and **7**.

The great advantage of **7** is the high thermal stability of up to 205 C. The comparison between the energetic performance of DATGP and GAP shows, that **7** possesses a higher detonation velocity than GAP, whereas the specific impuls is in the same range. Another advantage of **7** is however that it is solid. Additionally it is soluble in acetone and can therefore be applied as binder without further curing.

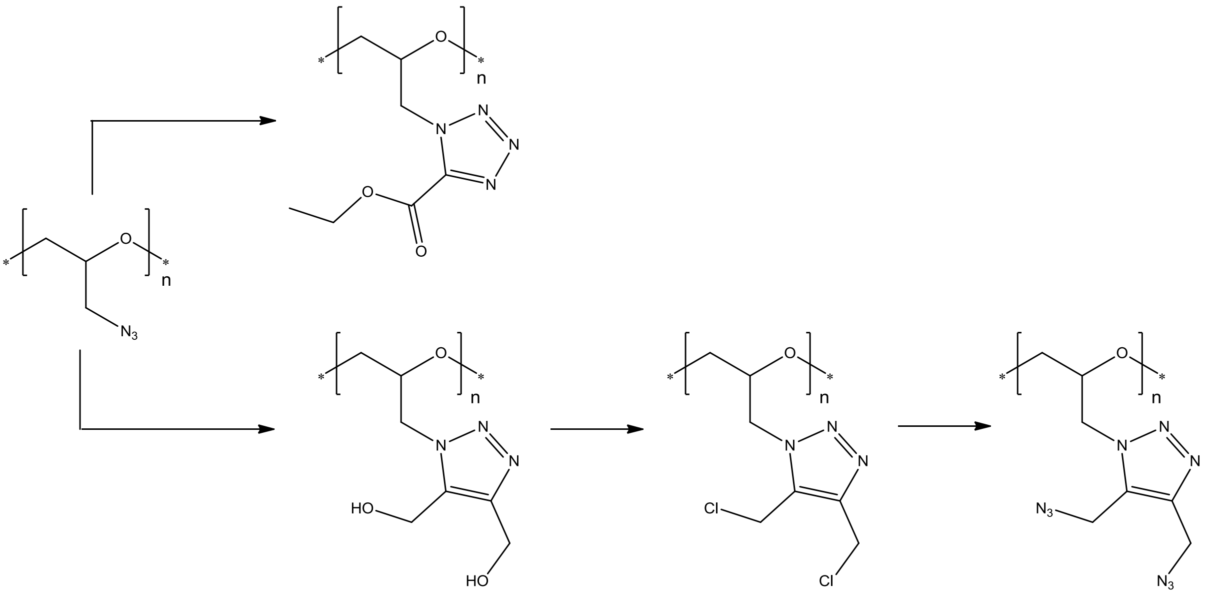
Table 2. Energetic properties and detonation parameters of **7**.

	7	**GAP**[p]
Formula	$C_7H_9N_9O$	$C_3H_5N_3O$
Molecular Mass [g mol^{-1}]	235.21	99.09
Impact sensitivity [J][a]	6	7
Friction sensitivity [N][b]	>360	>360
N [%][c]	53.60	42.41
Ω [%][d]	-11	-121
$T_{\text{dec.}}$ [°C][e]	205	200
ρ [g cm^{-3}][f]	1.7	1.3
$\Delta_f H_m°$ [kJ mol^{-1}][g]	7339	142
$\Delta_f U°$ [kJ kg^{-1}][h]	-557	1545
EXPLO5 values: V5.05		
$-\Delta_E U°$ [kJ kg^{-1}][i]	3917	4258
T_{E} [K][j]	2716	2819
$p_{C\text{-}J}$ [kbar][k]	219	71
$V_{\text{Det.}}$ [m s^{-1}][l]	7744	5047
Gas vol. [L kg^{-1}][m]	686	739
I_{sp}(s)[n]	187	201
I_{sp}(s) (70 % ADN)[o]	243	251

[a] BAM drop hammer; [b] BAM friction tester; [c] Nitrogen content; [d] Oxygen balance; [e] Temperature of decomposition by DSC (β = 5 °C, Onset values); [f] derived from pycnometer measurement; [g] Molar enthalpy of formation; [h] Energy of formation; [i] Energy of Explosion; [j] Explosion temperature; [k] Detonation pressure; [l] Detonation velocity; [m] Assuming only gaseous products; [n] specific impulse (isobaric combustion, chamber pressure 60 bar, frozen equilibrium), [o] specific impulse of a mixture containing 70 % ammonium dinitramide as oxidizer; [p] values based on Ref. [30] and the EXPLO5.5 database.

By modifying the varying parameters, like increasing the temperature of the chlorination or the reaction time, unfortunately no substantial improvement could be achieved, therefore this issue was made subject of the master thesis of Vera HARTDEGEN[35] who examined this matter more intensly.

4.3 Conclusion



Scheme 8. Overview of the polymers that were gained based on GAP.

A highly thermally stable molecule, including two ethyl bridged tetrazole rings, was produced as a polymer precursor. Furthermore a general high yielding synthesis of a polymer was developed by reacting ethyl cyanoformate with 1,2-diazidoethane. This nitrogen-rich polymer possesses a nitrogen content of 30 %, due to the inherited tetrazole ring and the unreacted azide groups of the original starting polymer. Based on these moieties this compound also is characterized by a high thermal stability and its insensitivity towards outer stimuli, which is a great advantage in comparison to GAP, although its energetic performance is slightly diminished. However these characteristics suggest an application as a binder, particularly when combining it with ammonium dinitramide.

Furthermore the remaining azide groups of **4** can be reduced to amine moieties by means of a Staudinger Reaction[36], increasing on the one side the thermal stability of this compound and on the other hand establishing a position where a nitramine group can be gained as well, to further increase the energetic character of the molecule.

The improvement of the synthesis of **7** to gain this compound both in better yields and more reproducible was further pursued by V. HARTDEGEN[35].

4.4 Experimental Part

CAUTION: Tetrazoles and triazoles, as well as small organic azides, are highly energetic compounds with sensitivity towards heat and impact. Although we had no problem in synthesis, 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.

4.4.1 Synthesis of Glycidyl-5-(carboxyethyl-1*H*-tetrazol)polymer and 1,2-Bis-(5-carboxyethyl-1*H*-tetrazolyl)ethane as Polymeric Precursor

4.4.1.1 1,2-Diazidoethane (1)

To a solution of sodium azide (26.0 g, 400 mmol) in 100 mL water, 1,2-dibromoethane (3.4 mL, 39.9 mmol) was added dropwise at room temperature. The solution was refluxed at 80 °C for 24 hours and extracted with diethylether (2 x 75 mL), dried with magnesium sulfate and the organic solvent was evaporated to yield 3.21 g (72 %) of a slightly yellowish liquid.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 2978 (vw), 2912 (vw), 2868 (vw), 2515 (vw), 2083 (s), 1443 (w), 1343 (w), 1281 (m), 1142 (vw), 1114 (w), 1077 (vw), 1013 (vw), 908 (vw), 847 (w), 824 (w), 649 (w).

^{1}H NMR ([D_6]-DMSO): $\delta = 3.52$ (s, 2H, CH_2) ppm.

^{13}C NMR ([D_6]-DMSO): $\delta = 50.6$ (CH_2) ppm.

4.4.1.2 Ethyl cyanoformate (2)[10]

Compound **2** was prepared according to Nii *et al.*[10] by cooling ethyl chloroformate (50.0 mL, 520 mmol) to 0 °C and adding sodium cyanide (27.0 g, 550 mmol), as well as the phase transfer catalyst tetra-*n*-butyl ammonium bromide (1 mol%) and dichloromethane (DCM, 180 mL). After the slow addition of water (150 mL), the mixture was stirred for one hour at 0 °C. The layers were separated and the DCM phase was washed with water and vice versa. The organic phase was dried over sodium sulfate, the solvent was evaporated and the suspension was distilled (300 mbar, 70 °C) giving 27.0 g (52 %) of a colorless liquid.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 2992 (vw), 2946 (vw), 2912 (vw), 2246 (w), 1744 (s), 1471 (w), 1449 (w), 1391 (w), 1369 (w), 1300 (w), 1235 (vs), 1173 (w), 1151 (w), 1113 (w), 1097 (w), 1006 (m), 910 (w), 852 (m), 793 (w), 745 (m), 691 (w).

^{1}H NMR ([D$_6$]-DMSO): δ = 1.53 (t, ^{3}J = 7.15 Hz, CH_3), 4.55 (q, ^{3}J = 7.15 Hz, 2H, CH_2) ppm.

^{13}C NMR ([D$_6$]-DMSO): δ = 13.8 (CH$_3$), 65.5 (C ppm.

4.4.1.3 1,2-Bis-(5-carboxyethyl-1*H*-tetrazolyl)ethane (3)

Ethylcyanoformate (20.1 g, 202.3 mmol) was dissolved in 40 mL of toluene and 1,2-diazidoethane (2.3 g, 20.2 mmol) was added. The suspension was refluxed at 100 °C for two days yielding in 2.5 g (39 %) of colorless crystals.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3453 (w), 3001 (w), 2107 (w), 1738 (s), 1642 (vw), 1578 (vw), 1518 (m), 1469 (m), 1452 (m), 1393 (w), 1371 (w), 1333 (m), 1322 (m), 1286 (s), 1185 (s), 113 (w), 1058 (w), 1017 (w), 992 (w), 861 (w), 850 (w), 791 (w), 716 (w), 669 (w), 515 (vw).

^{1}H NMR ([D$_6$]-DMSO): δ = 1.33 (t, ^{3}J = 7.12 Hz, 3 H, CH_3), 4.40 (q, ^{3}J = 7.12 Hz, 2 H, CH_2), 5.27 (s, 2 H, CH_2) ppm.

^{13}C NMR ([D$_6$]-DMSO): δ = 14.3 (CH$_3$), 48.9 (CH$_2$), 63.7 (CH$_2$-O), 147.2 (C_q), 156.3 (C=O) ppm.

MS (DEI+): *m/z* (%) = 311.2 (14) [M + H], 266.1 (21), 237.1 (21), 210.1 (32), 209.1 (13), 156.1 (67), 143.1 (41), 115.1 (10), 83.1 (12), 55.1 (54), 29.1 (100).

EA ($C_{10}H_{14}N_8O_4$, 310.27): calc.: C 38.71 %, H 4.55 %, N 36.11 %; found: C 38.76 %, H 4.49 %, N 36.37 %.

4.4.1.4 Glycidyl-5-(carboxyethyl-1*H*-tetrazol)polymer (4)

Glycidyl azide polymer (2.0 g) was mixed with ethylcyanoformate (20.0 g, 202 mmol) in toluene (75 mL) and refluxed for two days at 90 °C. The suspension was cooled to room temperature and the solvent evaporated giving 3.1 g (78 %) of a colorless viscous liquid.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3441 (m), 2988 (w), 2929 (w), 2880 (w), 2103 (s), 1743 (m), 1630 (w), 1513 (w), 1449 (m), 1370 (w), 1279 (m), 1188 (m), 1120 (m), 1013 (w), 938 (vw), 854 (vw), 791 (vw), 673 (vw), 558 (vw).

^{1}H NMR ([D$_6$]-DMSO): δ = 1.09 (t, ^3J = 6.98 Hz, 3 H, C*H*$_3$), 3.34-3.49 (m, -C*H*$_2$-CH(-O-)-C*H*$_2$), 3,63 (quin., ^{3}J = 6.53 Hz, 1 H, C*H*), 4.43 (q, ^3J = 6.23 Hz, 2 H, C*H*$_2$) ppm.

^{13}C NMR ([D$_6$]-DMSO): δ = 14.3 (*C*H$_3$), 51.6 (*C*H$_2$N), 63.5 (*C*H$_2$O), 69.2 (*C*H$_2$), 78.6 (*C*H), 147.3 (*C*$_q$), 156.6 (*C*O) ppm.

MS (DCI+): *m/z* (%) = 397.3 (4), 369.3 (6), 341.3 (8), 326.3 (2), 316.3 (2), 298.3 (7), 269.3 (9), 244.3 (4), 242.3 (3), 199.2 (11) [monomeric unit + H], 188.2 (15), 171.2 (100), 143.2 (5), 128.2 (8), 99.1 (60), 81.1 (22), 72.1 (7).

EA ($C_7H_{10}N_4O_3$, 198.18): calc.: C 42.42 %, H 5.09 %, N 28.27 %; found: C 43.98 %, H 5.47 %, N 30.16 %.

4.4.2 Synthesis of (4,5-Di(azidomethyl)-1*H*-1,2,3-1-yl)glycidyl polymer

4.4.2.1 Synthesis of (4,5-di(hydroxymethyl)-1*H*-1,2,3-1-yl)glycidyl polymer (6)

GAP (4.5 g) was dissolved in toluene and but-2-yne-1,4-diol (17.1 g, 200 mmol) was added. The reaction mixture was refluxed for 24 hours at 80 °C. After cooling to room temperature, the toluene was decanted and the residue was washed with methylene chloride, acetone and methanol. After drying, DHTGP was obtained as 4.8 g (67 %) of a colorless, hygroscopic solid.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3552 (s), 3477 (s), 3415 (vs), 3241 (m), 2961 (vw), 2927 (w), 2871 (vw), 2104 (w), 2026 (vw), 1725 (w), 1638 (m), 1618 (m), 1463 (w), 1385 (w), 1267 (w), 1228 (w), 1126 (w), 1022 (w), 813 (vw), 619 (m), 480 (w).

EA ($C_7H_{11}N_3O_3$, 185.18): calc.: C 45.40 %, H 5.99 %, N 22.69 %; found: C 45.23 %, H 5.62 %, N 29.05 %.

4.4.2.2 Synthesis of (4,5-di(chloromethyl)-1*H*-1,2,3-1-yl)glycidyl polymer (7)

Pyridine (1.89 mL, 23mmol) was added dropwise to phosphoroxychloride (58.8 g, 383 mmol). Then DHTGP (2.20 g, 12 mmol) was added. The reaction mixture was heated 3 hours to 120 °C under stirring. After cooling to room temperature, the mixture was quenched by 800 mL of ice/water-mixture and stirred over night. The brown solid was filtrated and washed with 2M NaOH, hot acetone and hot dichloromethane to give 2.51 g (95 %) of a brownish solid.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3639 (vw), 2963 (w), 2934 (w), 2875 (w), 2101 (w), 1720 (w), 1662 (m), 1528 (w), 1462 (w), 1440 (w), 1384 (m), 1352 (w), 1280 (s), 1192 (w), 1177 (w), 1091 (m), 1070 (m), 1042 (m), 839 (w), 748 (w), 714 (w), 673 (w), 554 (vw).

EA ($C_7H_9Cl_2N_3O$, 222.07): calc.: C 37.86 %, H 4.08 %, N 18.92 %; found: C 37.15 %, H 4.31 %, N 19.53 %.

4.4.2.3 Synthesis of (4,5-di(azidomethyl)-1*H*-1,2,3-1-yl)glycidyl polymer (8)

DCTGP (2.31 g, 10 mmol) and sodium azide (11.55 g, 178 mmol) were heated in a water / acetonitrile mixture (39mL/ 155mL) at 90°C for 24 hours. The acetonitrile was removed by rotary evaporation and the resulting (water insoluble) solid was suction filtered. The solid product was washed with acetone and dried, yielding in 2.23 g (91 %) of a colorless solid.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3324 (w), 2926 (w), 2098 (s), 1010 (m), 1631 (w), 1448 (w), 1343 (w), 1239 (m), 1110 (m), 1062 (m), 975 (w), 877 (w), 811 (w).

EA ($C_7H_9N_9O$, 235.21): calc.: C 35.75 %, H 3.86 %, N 53.60 %; found: C 35.49 %, H 4.01 %, N 48.45 %.

4.5 Crystal Section

Structure Analysis: The single X-ray diffraction data of **3** was collected using an Oxford Xcalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD area detector with graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The data collection was undertaken using the CrysAlis CCD software[37] while the data reduction was performed with the CrysAlis RED software[38]. The structure was solved with Sir-92[39] and refined with Shelxl-97[40] implemented in the program package WinGX[41] and finally checked using Platon[42]. CCDC-892844 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.cdc.cam.ac.uk/data_request/cif. Selected crystal data for **3** is summarized in Table 1.

Table 1. Selected crystal data for **3**.

	3
Chemical formula	$C_{10}H_{14}N_8O_4$
Molecular weight [g mol^{-1}]	310.27
Color, habit	Colorless block
Size [mm]	0.3 x 0.2 x 0.15
Crystal system	Monoclinic
Space group	$P2_1/n$
a [Å]	10.3257(5)
b [Å]	6.5382(2)
c [Å]	11.2029(5)
α [°]	90
β [°]	109.330(5)
γ [°]	90
V [Å^3]	713.69(5)
Z	2
$\rho_{\text{calcd.}}$ [g cm^{-3}]	1.444
μ [mm^{-1}]	0.115
Irradiation	MoK_α 0.71073
F(000)	324
Θ-Range	4.53-25.99
T [K]	173
Index range	$-12 \leq h \leq 12$ $-8 \leq k \leq 8$ $-13 \leq l \leq 13$
Reflections coll.	6825
Independent refl.	1387
Observed refl.	1174
Parameters	128
$R_{\text{int.}}$	0.307
GOOF	1.058
R_1/wR_2 [I>2σ(I)]]	0.0308, 0.0676
R_1/wR_2 (all data)	0.0395, 0.0726
Weighting scheme	0.0280, 0.1818
Remaining density	-0.213, 0.180
Device type	Oxford XCalibur3
Adsorption corr.	Multi scan

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5. Energetic Polymers based on 1,2,4-Triazoles

5.1 Introduction

A prominent family of energetic materials are triazole compounds, as they show a perfect balance between thermal stability and high positive heats of formation. Even though the heats of formation are larger for tetrazoles (ΔH_f^0 = + 237.2 kJ mol^{-1})[1] as well as 1,2,3-triazoles (ΔH_f^0 = + 272 kJ mol^{-1}), [2] 1,2,4-triazoles (ΔH_f^0 = + 109 kJ mol^{-1})[2] are better suited for the development of energetic materials, since they have less catenated nitrogen molecules in one chain, which generally makes them more stable to outer stimuli. [3]

Many energetic compounds combining the triazole backbone with energetic moieties such as nitro groups have been synthesized over the last decades. Examples for these kind of molecules are 5-amino-3-nitro-1,2,4-triazole (ANTA) [4,5] or 3-nitro-5-triazolone (NTO)[6]. The thermal stability of these materials is remarkably high with decomposition taking place well above 200 °C together with low sensitivity values. [3]

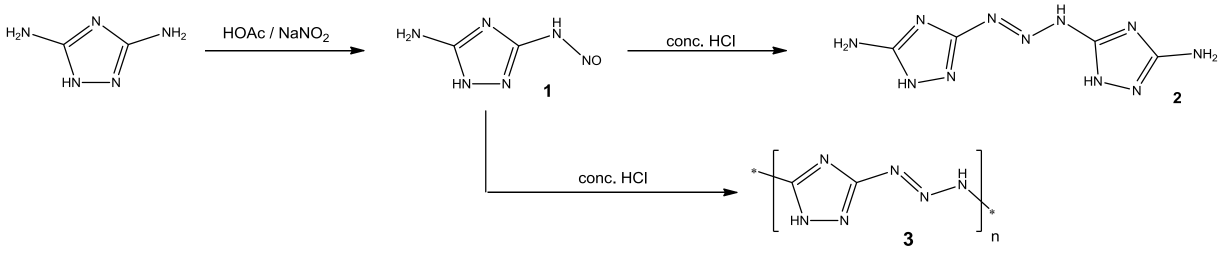
For this reason 1,2,4-triazoles were used to develop new energetic polymers for the applications as binder.

5.2 Results and Discussion

5.2.1 Poly(3-diazoamino-1,2,4-triazole)

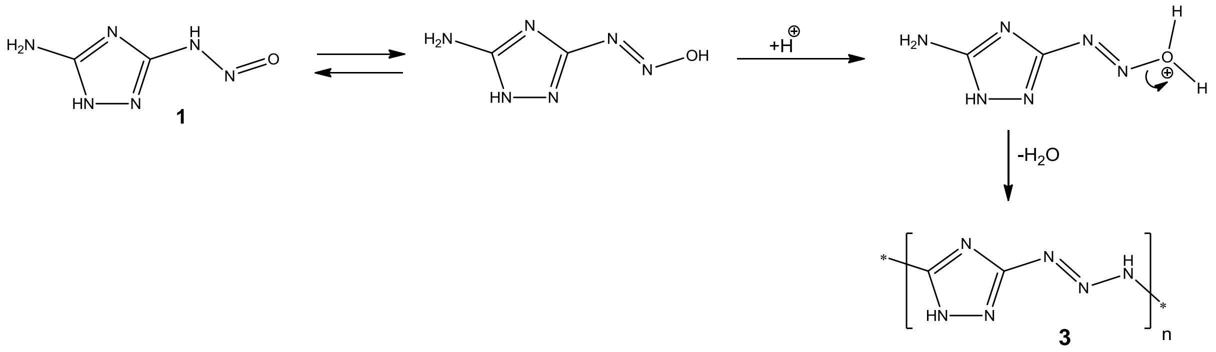
Various methods for the functionalization of 1,2,4-triazoles are known. One possibility is the diazotation of 3,5-diamino-1,2,4-triazole to gain 3-amino-5-nitrosamino-1,2,4-triazole **1**. This compound can easily be polymerized to obtain poly (3-diazoamino-1,2,4-triazole) **3**.

This polymer has the advantage of a high nitrogen content (75.65 %) and with the NH of the triazole ring a spot where the compound can still be functionalized.



Scheme 1. Synthesis of **1-3**.

According to HAUSER *et al.* [7] **3** should be easily obtained by reacting **1** with concentrated hydrochloric acid. However to estimate the characteristics of the compound at first the dimer 1,3-bis(3-(5-amino-1,2,4-triazoyl))triazene **2** should be synthesized by the addition of hydrochloric acid to **1**, that was obtained by the diazotation of 3,5-diamino-1,2,4-triazole.[8] Whilst by the synthesis of **2** 3,4-diamino-1,2,4-triazole is added after the diazotation to stop the polymerization and to get dimer **2**, the polymer **3** is obtained by reacting hydrochloric acid with **1** and neutralizing this mixture with sodium hydroxide.



Scheme 2. Mechanism to obtain **3** by protonating **1**.

Unfortunately **2** could only be obtained containing impurities of the polymer **3** and could not be further purified by recrystallization as described in the literature[7].

The nitrogen rich polymer **3** that was synthesized by protonating **1** was analyzed by infrared spectroscopy depicting the vibration modes of the triazole ring in the range of 1300 - 1500 cm^{-1}[9], as well as the azo group at 1573 cm^{-1}[9]. The elemental analysis gave a rather good convenience with the calculated one, although the nitrogen content of the experimental data is a bit lower, indicating the presence of unreacted compounds.

The compounds **1** – **3** were decomposing under gas emission of nitrogen when adding DMSO-*d6* whilst preparing the samples for NMR experiments. Unfortunately they were not soluble in any other solvent. Therefore analytics by NMR were neglected.

DSC measurements depict a decomposition point at 170 °C for **3**.

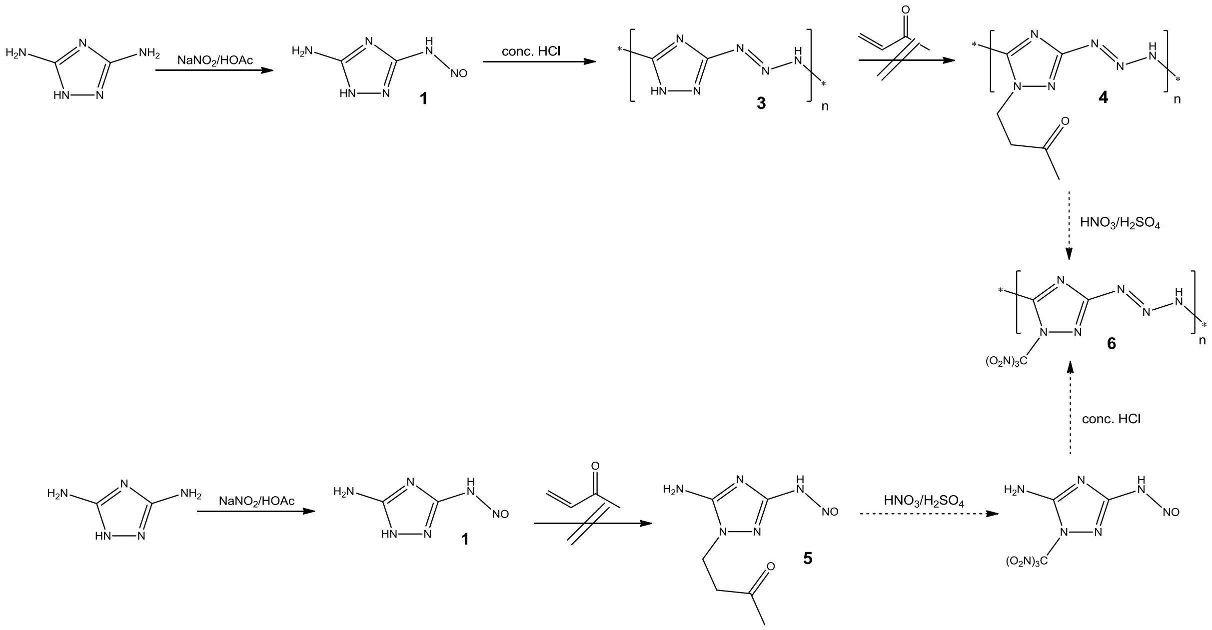
5.2.2 Poly (3-diazoamino-1-trinitromethyl-1,2,4-triazole)

KOFMAN *et al.*[10] are claiming that by oxidizing a 2-oxobutyl group of a 3,5-substituted triazole ring with a mixture of sulfuric and nitric acid a trinitromethyl group is obtained.

Therefore this knowledge should be implemented at the polymer **3** by introducing the 2-oxobutyl group by means of methyl vinyl keton to the NH position of the triazole ring included in the polymer and oxidizing it to the trinitromethyl group to obtain poly(3-diazoamino-1-trinitromethyl-1,2,4-triazole) **6**, a compound with a high nitrogen content of 48.65 % and a great oxygen balance of −3.09 %.

This compound can be achieved by two different main methods. One is synthesizing polymer **3**, and functionalizing it by introducing the methyl vinyl group[11,12] to obtain poly(1-(3-diazoamino-2-oxobutyl-1,2,4-triazole) **4** and oxidizing this compound to get **6**. The other method is functionalizing at first the monomer and polymerizing it in the last step.

The challenge in obtaining the desired compound **6** is that there are manifold ways how it can be obtained. There are at least four steps from the starting material, 3,5-diamino-1,2,4-triazole, to the product that can be arranged in various ways. Consequently those which might have a chance to achieve the aim were pursued.

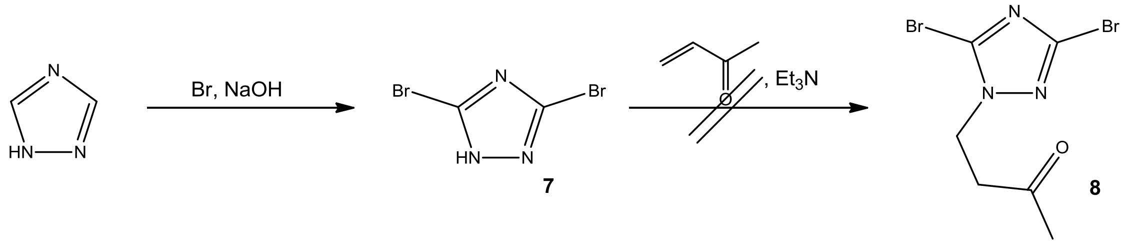


Scheme 3. Synthesis of **6**.

Unfortunately the first method did not work because the methyl vinyl ketone group could not be introduced to the polymer **3** and therefore this compound could not be functionalized any further. On this account the second route was tried by functionalizing the monomers. However here the introduction of the methyl vinyl group did neither work with the 5-amino-3-nitrosamino-1,2,4-triazole **1** to get 5-amino-3-nitrosamino-1-(2-oxobutyl)-1,2,4-triazole **5**.

Therefore different substitutents were given a chance. According to the literature[10] mostly substituents with a high electron density were used. Therefore we tried to introduce the methyl vinyl ketone to a triazole ring containing these groups and then functionalizing them.

Accordingly 3,5-dibromo-1,2,4-triazole (**7**) was synthesized[13], having with the two bromine substituents groups with a high electron density, whereas in the before used moieties, like the amine group, the electron density is considerably lower. Nevertheless the introduction of the methyl vinyl ketone group was not successful and 3,5-dibromo-1-(2-oxobutyl)-1,2,4-triazole (**8**) could not be obtained.

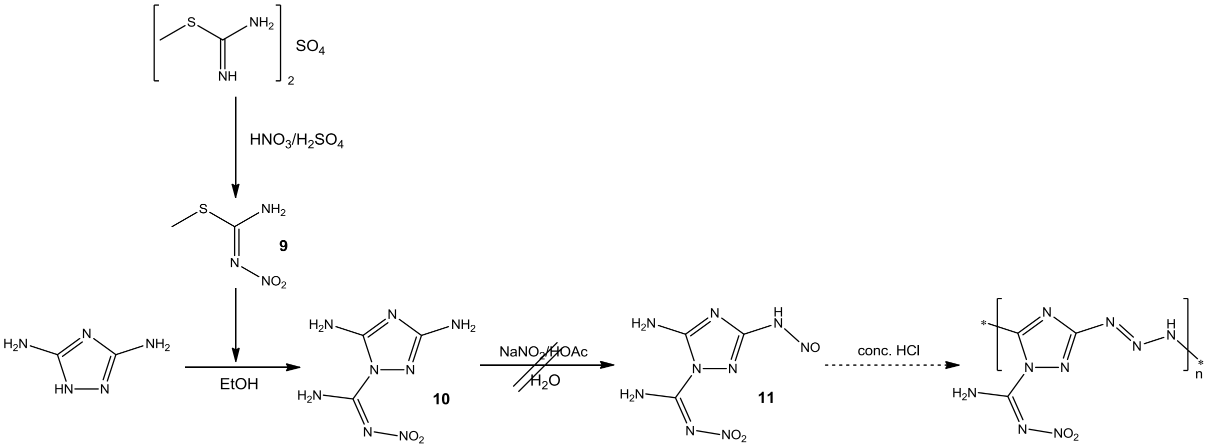


Scheme 4. Synthesis of **8**.

As all of these various attempts did not gain the desired compound **6,** this topic was abandoned and another molecule analog to this system was investigated.

5.2.3 Poly(3-diazoamino-1-nitroamidino-1,2,4-triazole)

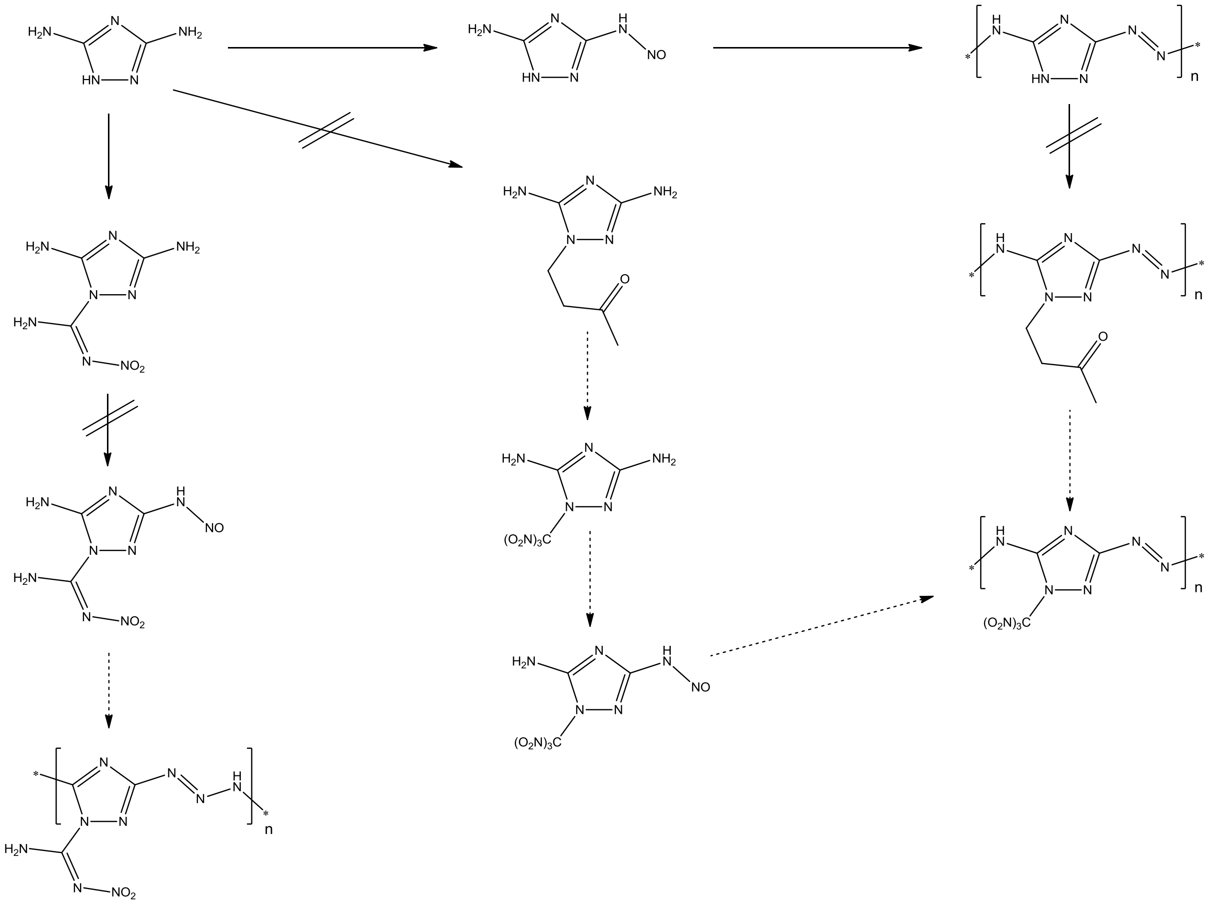
A different approach by means of synthesizing a nitrogen rich polymer based on 1,2,4-triazoles, was the synthesis of 3,5-diamino-1-nitroamidino-1,2,4-triazole (**15**). This compound has a high nitrogen content of 60.20 % and with its two amino groups good possibilities for functionalizing *via* diazotation.



Scheme 5. Attempt to synthesize poly(3-diazoamino-1-nitroamidino-1,2,4-triazole).

Therefore 2-methyl-1-nitroisothiourea (**9**), that was synthesized with the help of 2-methyl-2-thiopseudouroniumsulfate[15], was reacted with 3,5-diamino-1,2,4-triazole to obtain **10** according to ASTAKHOV *et al.*.[16] Unfortunately the diazotation of **10** by means of the before mentioned technique did not work as several analytical techniques revealed. 5-Amino-3-nitrosamino-1-nitroamidino-1,2,4-triazole (**11**) could not be obtained, probably due to the various moieties that could also been react during the diazotation, resulting in many different products, that could not be separated to obtain the pure product.

5.3 Conclusion



Scheme 6. Overview of the various synthesis ways to obtain polymers based on 3,5-diamino-1,2,4-triazole.

The polymerization of triazoles offers various advantages. On the one hand these compounds have a good nitrogen content and are less sensitive towards outer stimuli than tetrazoles. Furthermore they have three spots that can be further functionalized.

The possibility of polymerizing 3,5-diamino-1,2,4-triazoles by diazotation as depicted by HAUSER *et al.* [7] is even more a great alternative to other energetic binder. Poly (3-diazoamino-1,2,4-triazole, offers the chance to be a compound with high potential regarding its nitrogen content of 76.35 % and the facility of further functionalization at the NH position of the triazole ring.

Unfortunately some problems occurred during the functionalization as well for the monomer as for the polymer, probably due to the fragility of the compound. Especially the diazoamino moiety is quite sensitive and reacts effortless with other reagents. On account of this, the molecule decomposes easily and generates besides the desired compounds also various impurities.

For this reason functionalizing poly(3-diazoamino-1,2,4-triazole) was abandoned and the search for energetic nitrogen rich polymers that can be applied as binder was turned towards other systems.

5.4 Experimental Part

CAUTION! Although all presented triazoles are rather stable against outer stimuli, proper safety precautions should be taken, when handling the dry materials. Lab personnel and the equipment should be properly grounded and protective equipment like earthed shoes, leather coat, Kevlar® gloves, ear protection and face shield is recommended.

5.4.1 Synthesis of Poly(3-diazoamino-1,2,4-triazole)

5.4.1.1 5-Amino-3-nitroso-1*H*-1,2,4-triazole[8] (1)

To a solution of 3,5-diamino-1*H*-1,2,4-triazole (1.00 g, 10.09 mmol) in 20 mL water, sodium nitrite (0.60 g, 8.70 mmol) in 3.30 mL water and ice cooled acetic acid (15.0 mL, 3 M) was added while cooling in ice water and stirred for 30 minutes. The precipitate was filtered off and washed with ice cooled water and ethanol giving 0.72 g (65 %) of a yellow solid.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3452 (m), 3340 (s), 3178 (m), 3090 (m), 2925 (m), 2770 (m), 1696 (m), 1619 (vs), 1575 (s), 1521 (w), 1475 (m), 1434 (m), 1383 (m), 1317 (m), 1207 (w), 1137 (w), 1101 (w), 1038 (w), 850 (vw), 801 (vw), 746 (w), 688 (vw).

EA ($C_2H_4N_6O$, 128.09): calc.: C 18.75 %, H 3.15 %, N 65.61 %; found: C 21.15 %, H 3.75 %, N 66.83 %.

5.4.1.2 Poly(3-diazoamino-1*H*-1,2,4-triazole)[7] (3)

A mixture of 5-amino-3-nitroso-1*H*-1,2,4-triazole (2.00 g, 15.62 mmol) and 50 mL concentrated hydrochloric acid was stirred for 1 hour at room temperature, then cooled to 10 °C and neutralized with 5 N sodium hydroxide solution. The resulting precipitate was filtered, washed with boiling water and dried to give 0.88 g (51 %) of a dark red solid.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3447 (m), 3336 (vs), 3178 (s), 2868 (m), 2765 (m), 1690 (m), 1615 (vs), 1573 (s), 1420 (m), 1473 (m), 1430 (m), 1378 (m), 1314 (m), 1207 (m), 1137 (m), 1098 (m), 1037 (m), 848 (w), 799 (w), 746 (w), 688 (w).

EA ($C_2H_2N_6$, 110.08): calc.: C 21.82 %, H 1.83 %, N 76.35 %; found: C 19.57 %, H 4.28 %, N 61.13 %.

5.4.2 Synthesis of Poly(3-diazoamino-1-trinitromethyl-1,2,4-triazole)

5.4.2.1 3,5-Dibromo-1,2,4-triazole[13] (7)

1,2,4-Triazole (1.00 g, 14.48 mmol) was dissolved in water and cooled with an ice bath. Bromine (4.70 g, 1.52 mL, 68.05 mmol) in 1.45 mL dichloro methane and sodium hydroxide (3.48 g, 87 mmol) were added drop wise simultaneously. During this procedure the temperature should not exceed 15 to 20 °C. After the end of the addition the mixture was stirred over night at room temperature. The solution was acidified with concentrated hydrochloric acid, the precipitate was filtered to give 2.92 g (89 %) of colorless needles that were dried *in vacuo*.

^{1}H NMR (270 MHz, DMSO-*d6*, 25 °C) $\delta = 8.56$ (s, 1H, N*H*) ppm.

^{13}C{^{1}H} NMR (270 MHz, DMSO-*d6*, 25 °C) $\delta = 146.8$ (C_q) ppm.

EA ($C_2HBr_2N_3$, 226.86): calc.: C 10.59 %, H 0.44 %, N 18.52 %; found: C 10.66 %, H 0.52 %, N 18.55 %.

5.4.3 Synthesis of Poly(3-diazoamino-1-nitroamidino-1,2,4-triazole)

5.4.3.1 2-Methyl-1-nitroisothiourea[15] (9)

Fuming nitric acid (20.0 mL) and concentrated sulfuric acid (60.0 mL) were cooled to −10 °C. During 10 minutes the first half of *S*-methyl-2-thiopseudouroniumsulfat (20.00 g, 0.11 mol) was added. Then the flask was letting warmed up to 5 °C and the second half was added. The solution was cooled to 0 °C and emptied on ice. The precipitate was filtered off, washed with ice water, recrystallized in a water-ethanol-mixture (2:1) and dried giving 14.31 g (96 %) of colorless crystals.

^{1}H NMR (400 MHz, DMSO-*d6*, 25 °C) $\delta = 2.39$ (s, 3H, CH_3), 0.14 (s, 2H, NH_2) ppm.

^{13}C{^{1}H} NMR (400 MHz, DMSO-*d6*, 25 °C) $\delta = 13.7$ (CH_3), 172.6 (C_q) ppm.

MS (DEI$^+$) m/z: 135 [$C_2H_5N_3O_2S^+$].

EA ($C_2H_5N_3O_2S$, 135.14) calculated: C 17.77 %, H 3.73 %, N 31.09 %, S 23.73 %; found: C 17.72 %, H 3.67 %, N 31.00 %, S 23.84 %.

5.4.3.2 3,5-Diamino-1-nitroamidino-1,2,4-triazole[16] (10)

2-Methyl-1-nitroisothiourea (1.00 g, 7.40 mmol) was added to a solution of 3,5-diaminotriazole (1.00 g, 10.09 mmol) was dissolved in 15 mL and refluxed for 5 hours. The precipitate was filtered off, washed with water and dried on air giving 1.37 g (73 %) of a yellowish solid.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3447 (m), 3396 (m), 3345 (m), 3091 (m), 1681 (m), 1613 (s), 1564 (s), 1492 (m), 1408 (s), 1266 (s), 1202 (s), 1156 (m), 1104 (m), 1047 (m), 952 (w), 851 (vw), 781 (vw), 757 (vw), 729 (vw), 689 (w), 623 (w).

^{1}H NMR (270 MHz, DMSO-*d6*, 25 °C) δ = 5.91 (s, 4H, triazole-NH_2), 7.57 (s, 2H, NH_2) ppm.

^{13}C{^{1}H} NMR (270 MHz, DMSO-*d6*, 25 °C) δ = 153.7 (C_q-NH_2), 156.2 (5C_{triazole}), 163.1 (3C_{triazole}) ppm.

EA ($C_3H_6N_8O_2$, 186.13) calculated: C 19.36 %, H 3.25 %, N 60.20 %,; found: C 19.36 %, H 3.25 %, N 60.20 %.

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6. Energetic Polymers based on Methacrylic and Acrylic Moieties

6.1 Introduction

Nitrogen-rich energetic polymers are to date highly requested compounds, having a wide range of applications. These applications vary from explosive binder 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, because of their double bond and thus their similarity to vinyl groups[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 high-energetic character with sufficient thermal stability[12] due to the aromatic ring system. These benefits could be useful for an application as an energetic polymer. The first known polymers based on tetrazoles were 1-poly(vinyltetrazole) and 1-poly(vinyl-5-aminotetrazole)[13]. But nevertheless, to date, within the wide range of applied nitrogen-rich polymers, compounds containing tetrazole moieties are rare.

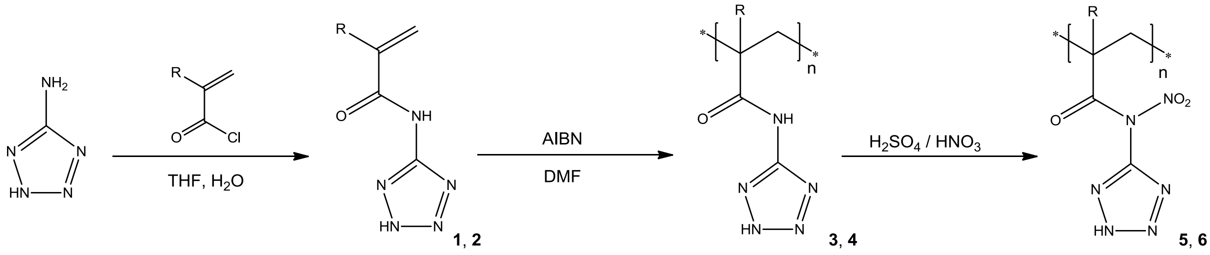
6.2 Results and Discussion

6.2.1 Tetrazole based Compounds

In order to gain substances inheriting the two desired properties, on the one side tetrazole moieties, to increase the nitrogen content and the energetic performance and on the other side methacryl and acryl groups to simplify the polymerization, various compounds were investigated.

6.2.1.1 Synthesis of Poly(methacrylnitramidotetrazole) and Poly(acrylnitramidotetrazole)

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**), offer an inherited vinyl alike group, were produced according to literature[14,15]. To gain the polymers poly(methacrylamidotetrazole) (PMAT, **3**) and poly(acrylamidotetrazole) (PAAT, **4**) via radical polymerization mechanism azobisisobutyronitrile (AIBN) was used as initiator.



R = CH_3 (**1**, **3**, **5**), H (**2**, **4**, **6**)

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

Both compounds were analyzed by common methods, like infrared spectroscopy, mass spectrometry and elemental analysis. In the case of PMAT a NMR measurement could be performed due to its little solubility in DMSO. Unfortunately compound **4** was not soluble in any solvent. The insolubility of polymers is oftentimes a problem. This fact complicated doing NMR, for the nitrated compounds, the poly(methacrylnitramidotetrazole) (PMNT, **5**) and the poly(acrylnitramidotetrazole) (PANT, **6**), due to their insolubility in any known solvent, as well.

The nitration of the compounds was attempted with monomers **1** and **2** as well as with polymers **3** and **4**. In both cases two different nitration mixtures were used (Ac_2O : HNO_3 and H_2SO_4 : HNO_3) and also various mixing ratios (1:1 and 1:2).

The monomers decomposed during the treatment in all cases, as the carbon content as well as the nitrogen content is always much smaller than the calculated value, as can be seen in table 1.

Table 1. Elemental analysis of the nitration of **1**.

Ratio of the acids	**C (%)**	**H (%)**	**N (%)**
2:1 / Ac_2O : HNO_3	23.23	4.04	11.47
1:1 / Ac_2O : HNO_3	22.44	3.48	16.30
2:1 / H_2SO_4 : HNO_3	14.12	4.52	24.43
1:1 / H_2SO_4 : HNO_3	21.77	3.45	38.53
Calculated values	**26.09**	**2.19**	**45.65**

Therefore the nitration was also performed with the polymers. Here is the problem that due to the sterical hindrance of the polymeric structure it is more complicated to reach every amino group that should be nitrated, but on the other side the compounds should not decompose as the monomers did.

As can be seen in table 2 the values of the different reactions agree much better with the calculated values than the ones that were listed in table 1. Also there is not much difference in the varying mixing compositions, whereas the 1:1 mixtures give better data. However due to the still existing small aberration of the found values to the calculated ones one can see that not all spots that should get nitrated were nitrated.

Table 2. Elemental analysis of the nitration of **3**.

Ratio of the acids	**C (%)**	**H (%)**	**N (%)**
2:1 / Ac_2O : HNO_3	30.50	4.61	37.82
1:1 / Ac_2O : HNO_3	29.91	4.64	42.20
2:1 / H_2SO_4 : HNO_3	27.29	4.47	38.54
1:1 / H_2SO_4 : HNO_3	29.79	4.53	42.16
Calculated values	**26.09**	**2.19**	**45.65**

Thermoplots of differential scanning calorimetry (DSC) measurements of **1-6** are depicted in Figure 3. In order to determine the melting - and decomposition temperatures approximately 1 mg of each energetic material was measured in a pierced lid Al-container with a nitrogen flow of 5 mL min^{-1} with a Linseis PT10 DSC. Calibration was done with standard pure indium and zinc at a heating rate of 5 K min^{-1}. Whereas the compounds **1-3** show no melting point or area, the polymers PAAT (**4**), PMNT (**5**) and PANT (**6**) have a melting area 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 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 remarkably higher than that of GAP (200 °C).

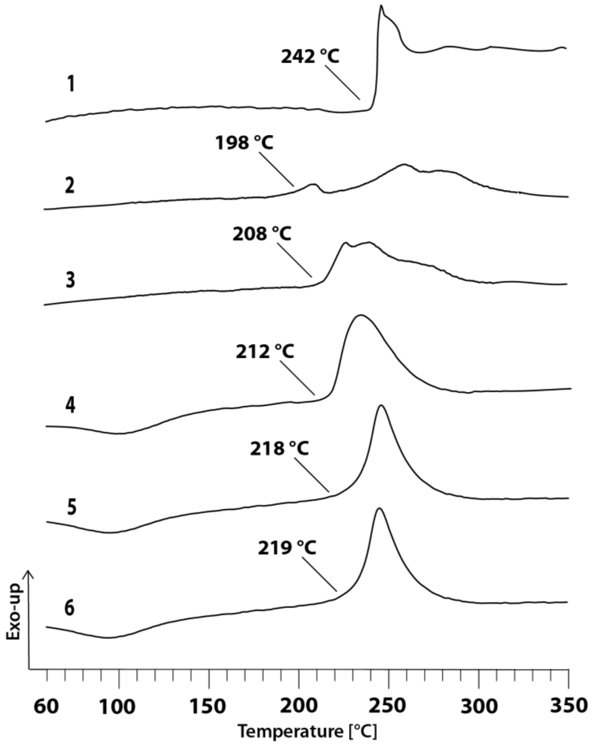


Figure 2. DSC plots of 5-MAT (**1**), 5-AAT (**2**), PMAT (**3**), PAAT (**4**), PMNT (**5**), PANT (**6**).

The sensitivities of compounds **1-6** were investigated using the BAM (German Bundesanstalt für Materialforschung) drop hammer[16], BAM friction tester [17] and a OZM electrostatic discharge device [18]. According to the UN recommendations on the transport of dangerous goods [19], compounds bearing a greater impact sensitivity than 40 J and friction sensitivity of 360 N are classified as insensitive. Therefore, as all compounds (**1-6**) offer a higher impact sensitivity than 40 J and friction sensitivity than 360 N, these molecules are insensitive, which is a outstanding 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 the program package EXPLO5 in the 5.05[20] version. 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 3.

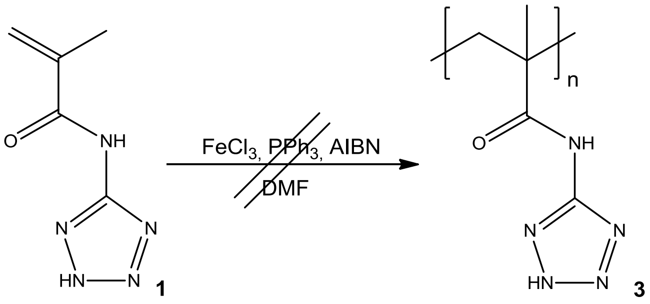
Table 3. Energetic properties and detonation parameters.

	1	**2**	**3**	**4**	**5**	**6**	**GAP**[a]
Formula	$C_5H_7N_5O$	$C_4H_5N_5O$	$C_5H_7N_5O$	$C_4H_5N_5O$	$C_5H_6N_6O$	$C_4H_4N_6O_3$	$C_3H_5N_3O$
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
$T_{\text{dec.}}$ [°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
$\Delta_f H_m°$ [kJ mol^{-1}][h]	614	−22	−18	38	479	459	-
$\Delta_f U°$ [kJ kg^{-1}][i]	4155	−21	30	410	2540	2606	-
EXPLO5 values: V5.05							
$-\Delta_E U_m°$ [kJ kg^{-1}][j]	5900	1997	2071	2406	5702	5697	4258
T_E [K][k]	3601	1831	1781	2065	4062	4436	2819
$p_{C\text{-}J}$ [kbar][l]	87	41	44	46	86	91	71
$V_{\text{Det.}}$ [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][o]	248	149	151	158	243	249	201

[a] Values based on Ref.[21] 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.[22] [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. [o] Specific impulse (isobaric combustion, chamber pressure 60 bar, frozen equilibrium).

Comparing the values of $\Delta_E U_m^o$ (an indication of the work performed by the explosives during the detonation[23]) of the polymers, **5** and **6** show the highest energetic properties, even 25 % higher than that value of GAP (**5**: 5702 kJ kg^{-1}, **6**: 5697 kJ kg^{-1}, Table 1). Furthermore the detonation velocity D of **5** and **6** exceed 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 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 also for both nitrated polymers higher than the impulse of the commonly used polymer GAP. As a result, compounds **5** and **6** are suitable as environment friendly explosives or gas generators. Both compounds bear no toxic azide, but still possess very good explosive properties.

Another approach to improve the polymerization step of this synthesis was by utilizing a catalyst. For this purpose iron trichloride as a catalyst and triphenylphosphine as ligand were stirred with compound 1 for 96 hours at room temperature, analogue to MOINEAU *et al.* [24].

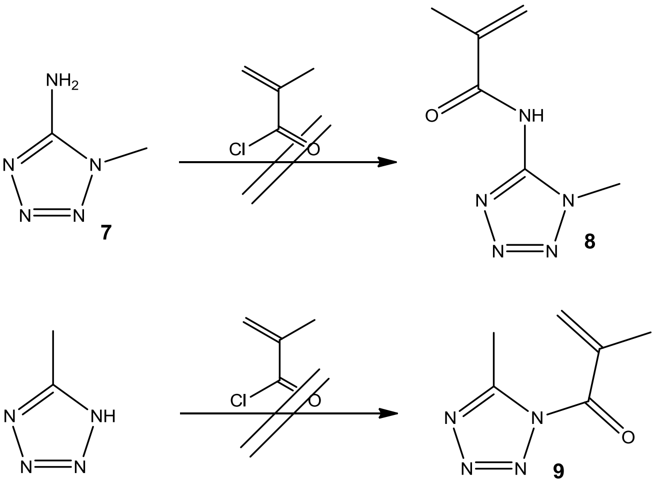


Scheme 2. Polymerization of **1** by using a catalyst.

The precipitated colorless solid was analyzed by mass spectrometry, due to its very low solubility in any solvent which is equal to **3**. The mass spectrum depicted the molecule peak of the monomer, but it also illustrated quite well that no polymer was formed. Even by heating the mixture or elongating the reaction time, compound **3** was not formed. Therefore attempts to improve the polymerization of **1** and **2** by using catalysts were dropped.

6.2.1.2 Attempts to synthesize 5-Methacrylamido-1-methyltetrazole and 1-Methacryl-5-methyltetrazole

Analogue to 5-aminotetrazole, other tetrazoles with varying moieties were chosen to synthesize methacryl tetrazoles. 5-Amino-1-methyltetrazole and 5-methyltetrazole were treated with methacryloyl chloride according to the synthesis of 5-MAT, as shown in scheme 3.



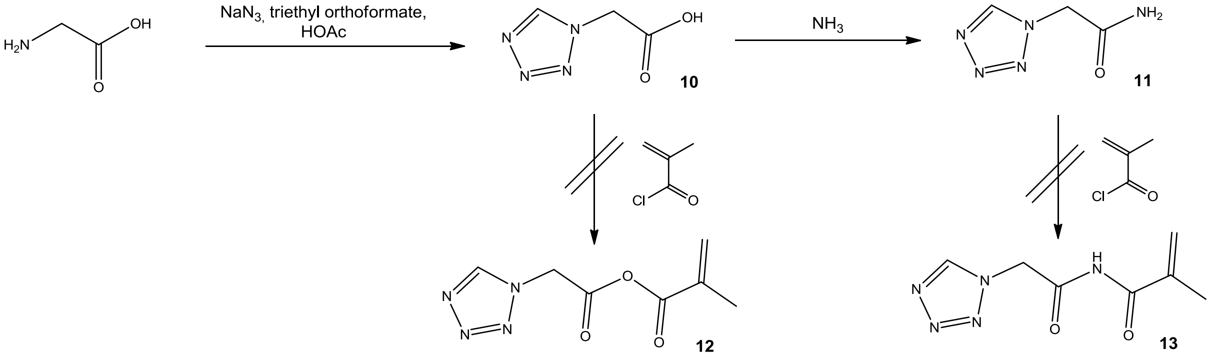
Scheme 3. Synthesis of **8** and **9**.

5-Amino-1-methyltetrazole was provided by F. MARTIN, who provided it according to KLAPÖTKE *et al.*. [25]

Both reactions were performed several times with varying parameters, like an increase in time and/or temperature. Nevertheless no product could be obtained, neither the 5-methacrylamido-1-methyltetrazole (**8**) nor the 1-methacryl-5-methyltetrazole (**9**), as was confirmed by spectroscopic data.

6.2.1.3 Attempts to synthesize 2-(1*H*-Tetrazol-1-yl) acetic acid methacryl anhydride and 2-(1*H*-Tetrazol-1-yl)methacrylacetamide

In order to expand this route of synthesis to other systems, tetrazole rings with other functional groups were synthesized.



Scheme 4. Synthesis of **10-13**.

According to literature [26] 2-(1*H*-tetrazol-1-yl) acetic acid (**10**) was obtained out of glycin, sodium azide, acetic acid and triethyl orthoformate.

It is known that various amine containing substances react with ortho carbon acids to iminoether. [27,28] During the reaction sodium azide turns in the acidic medium to hydrazoic azid that condenses with the imino ether, whilst eliminating water, to **10**. The imino ether is mostly obtained in low yields and is also rather unstable. [28] To avoid this step and to give the imino ether the chance to react instantly, sodium azide is added in this reaction at the beginning. Nevertheless the yield could not be improved (40.6 %, Lit.[26]: 67.2 %).

The analysis shows that compound **10** is gained all clean. This conclusion is confirmed by NMR spectroscopy. The ^{1}H spectrum shows the CH group of the tetrazole ring at 9.22 ppm, as well as the CH_2 group at 5.37 ppm.. IR spectroscopy and mass spectrometry also emphasize that 2-(1*H*-tetrazol-1-yl)acetic acid was obtained.

To further enhance the nitrogen content of compound **10** and to gain a position where a nitro group can attack the system, to further increase the energetic properties and to improve the oxygen balance, an amino moiety was introduced. According to literature [29] compound **7** was reacted with concentrated ammonia by means of an addition-elimination-mechanism, to gain 2-(1*H*-tetrazol-1-yl)acetamide (**11**). Generally is it hard to gain amides out of carbon acids by reacting it with ammonia, because ammonia reacts besides the already mentioned mechanism also as typical inorganic base in a acid-base-reaction with **10**, giving also a salt[30], that was also detected by analytical methods. Consequently a competitive reaction to the desired amid formation takes place, which diminishes the yield. This is confirmed in this experiment with a yield of 55 %. Nevertheless the product could be clearly identified by several analytical methods.

An improved yield can possibly be achieved by thermodynamic control (higher temperatures and longer reaction time). Through this the equilibrium should be shifted towards the desired amide.

To introduce the methacryloyl group to achieve a better polymerizability **10** was reacted with this group analogue to the literature of HUANG *et al.* [31] that synthesizes 2-(1*H*-tetrazol-1-yl)acetic pivalic anhydride. Instead of pivaloyl chloride methacryloyl chloride was used. This change should actually not influence the reaction process, because both compounds should have comparable reactivity since both the ester of the pivalic acid and the ester of the methacrylic acid are verifiable thermally stable. [32] 2-(1*H*-Tetrazol-1-yl)acetic acid methacryl anhydride (**12**) was obtained as expected and confirmed by several spectroscopic methods, but only in traces. Primarily the educt **10** could be found in the various spectra.

The related reaction of the amine, **11**, with methacryloyl chloride to synthesize 2-(1*H*-tetrazol-1-yl)methacrylacetamide (**13**) to achieve a better nitrogen content and to create a spot that can be nitrated, was tried to perform analogue to the method of TADEN *et al.* [14].

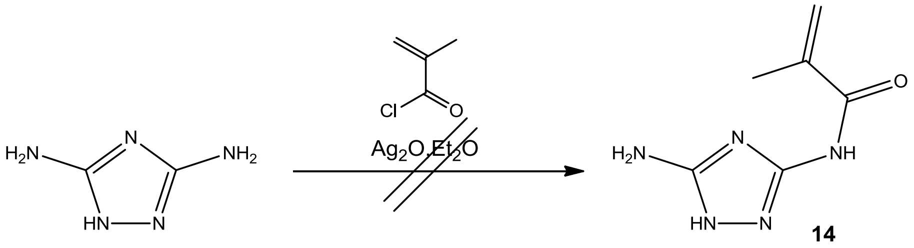
Mass spectrometry shows as main product the educt **11** (m/z = 128 (M^+H)). However, product **13** can be detected, first by a peak in the mass spectrum, although with very small intensity (0.30 %) and also by ^1H NMR spectroscopy.

Consequently, both compound **12** and **13** were obtained, but in very bad yields and both still contained lots of impurities, mainly by not converted educt. Therefore both compounds could not be utilized any further for polymerizations.

6.2.2 1*H*-1,2,4-Triazole based Compounds

6.2.2.1 Attempt to synthesize 5-Amino-3-methacrylamido-1*H*-1,2,4-triazole

In order to increase both the thermal stability and the stability towards impact and friction of the compounds, the tetrazole moieties were exchanged by triazole moieties.



Scheme 5. Synthesis of **14**.

Therefore 3,5-diamino-1*H*-1,2,4-triazole should be reacted with methacryloyl chloride analogue to literature [33] (Scheme 5) in presence of silver oxide to precipitate the chlorine ions.

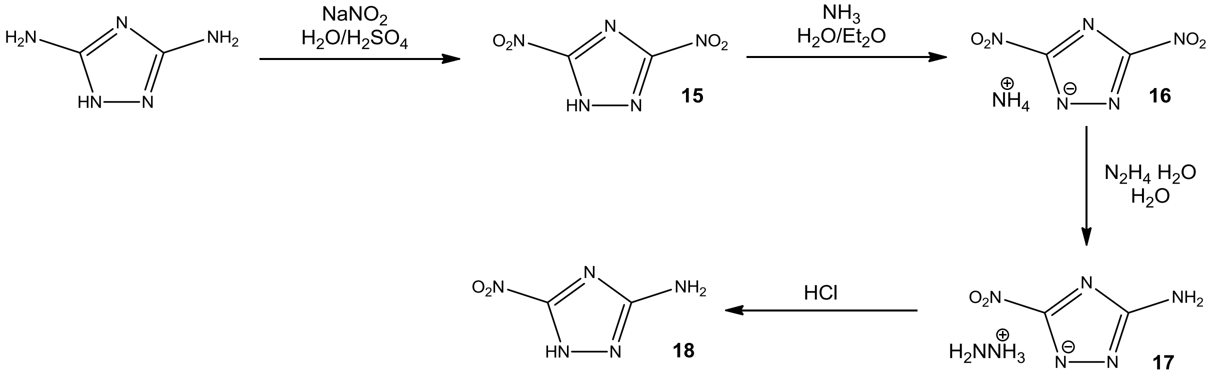
5-Amino-3-methacrylamido-1*H*-1,2,4-triazol (**14**) could not be obtained experimentally as pure compound. Varying various parameters, amongst others an elongation of the reaction time, did not improve that result. Anyhow **14** could be identified in the mass spectrum but with a very small intensity.

6.2.2.2 Attempt to synthesize 3-Methacrylamido-5-nitro-1*H*-1,2,4-triazole

A different approach was to introduce on the one side an amine moiety that can react with the methacryloyl chloride and on the other side a nitro group that increases the nitrogen content as well as the oxygen balance of the compound.

Therefore 3-amino-5-nitro-1*H*-1,2,4-triazole (ANTA, **18**) was synthesized as starting material [34,35].

According to SIMPSON *et al.*[35] and LEE *et al.*[34] ANTA was synthesized having 3,5-diamino-1*H*-1,2,4-triazole as a starting material and 3,5-dinitro-1*H*-1,2,4-triazole (**15**), as well as ammonium 3,5-dinitro-1*H*-1,2,4-triazolate (ADNT, **16**) and the hydrazinium salt of 3-amino-5-nitro-1*H*-1,2,4-triazole (HANTA, **17**) as an intermediate.



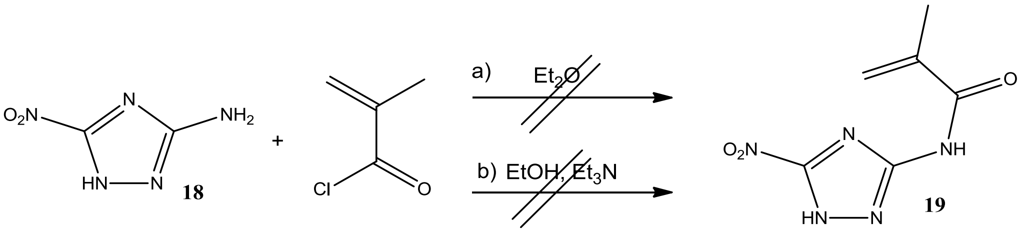
Scheme 6. Synthesis of ANTA **15**.

The compounds **15** and **16** were obtained pure and in good yields.

16 is needed to synthesize ANTA (Scheme 5). The reaction of ADNT with hydrazine hydrate is carried out at 80 °C and results at first in the hydrazinium salt HANTA (**17**). Hydrazine hydrate acts in this reaction as reduction agent that reduces the nitro group to a primary amine and is oxidized to nitrogen. Compound **18** is then gained by acidification by hydrochloric acid that protonates the triazole ring to convert it into its neutral form.

The overall yield of the reaction starting with 3,5-diamino-1*H*-1,2,4-triazole to achieve 3-amino-5-nitro-1*H*-1,2,4-triazole (**18**) is rather low (25% yield), but could be improved if not every intermediate is isolated.

To achieve an easy polymerazibility compound **18** was reacted with methacryloyl chloride. This synthesis was performed by two different methods (Scheme 7).



Scheme 7. Two methods to synthesize **19**.

Method **a** was carried out analogue to the prescription used for compound **14**.[33] Besides 3-methacrylamido-5-nitro-1*H*-1,2,4-triazol (**19**) was extracted with ethyl acetate, instead of ethanol, because of its better solubility in that solvent.

The other method **b** was a modified version in which **18** was reacted with methacryloyl chloride in presence of a base, triethylamine, in ethanol.

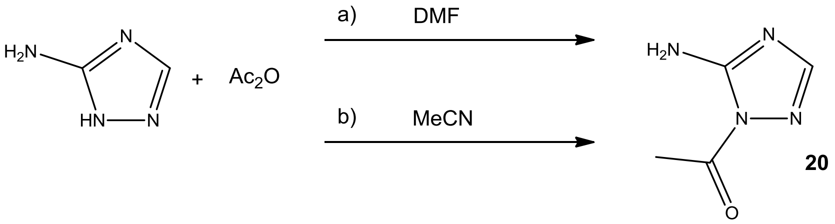
By means of method **a** hardly any educt was reacted. Consequently the ^{1}H NMR of **19a** only reveals the two protons of the NH_2 group (6.77 ppm) and the NH group at the triazole ring (13.10 ppm). Also the mass spectrum only displayed traces of **19a**.

Method **b** just as well reveals no different result, as the mass spectrum only shows a small peak for the compound. The obtained substance can mainly be regarded as the used triethylamine. This conclusion is also supported by NMR spectroscopy.

6.2.2.3 Attempt to synthesize 3-Methacrylamido-1*H*-1,2,4-triazole and 3-Acrylamido-1*H*-1,2,4-triazole

To avoid a competing reaction of other groups, like the nitro group in ANTA or the second amino moiety in 3,5-diamino-1*H*-1,2,4-triazole, 5-amino-1*H*-1,2,4-triazole was used instead. Nevertheless the N1 position of the triazole ring had to be protected at first by an acetic moiety to avoid an attack at the ring nitrogen atoms.

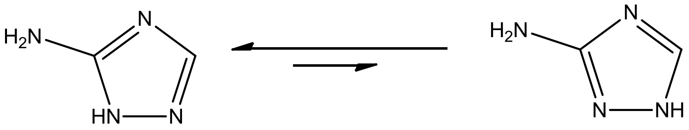
The synthesis of 1-acetyl-5-amino-1*H*-1,2,4-triazole (**20**) was performed according to DZYGIEL *et al.* [36] in two different methods.



Scheme 8. Two methods to synthesize **20**.

The first method **a** used DMF as a solvent, and stirred the solution for 1 hour, whereas the second method **b** used acetonitrile as a solvent and stirred this solution for 1 hour at 65 °C. Both methods gave the product as pure material which was confirmed by NMR and IR spectroscopy. However method **a** had the advantage of a higher yield (71 %) compared to method **b** (57 %). Therefore this technique was used for the following procedures.

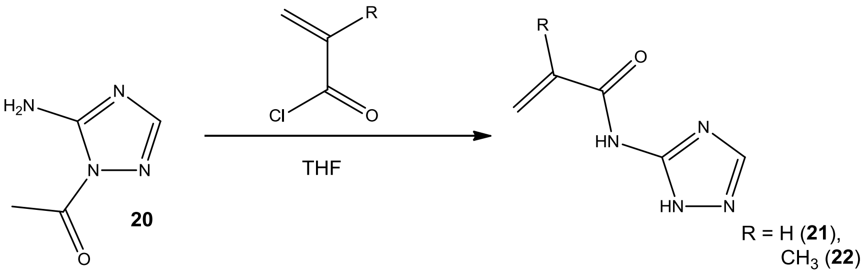
The characteristic carbonyl valence vibration appears in the IR spectrum 1639 cm^{-1}. However the very small signal at 1752 cm^{-1} is a sign of 1-acetyl-3-amino-1*H*-1,2,4-triazole. This compound is formed in small amounts due to the tautomeric equilibrium between 3-amino-1*H*-1,2,4-triazole and 5-amino-1*H*-1,2,4-triazole (scheme 8), though the main part is on the side of the 5-amino-1*H*-1,2,4-triazole. [36]



Scheme 9. Equilibrium between 5-amino-1*H*-1,2,4-triazole and 3-amino-1*H*-1,2,4-triazole.

All determined values (NMR and IR), are in accordance with the literature[36]. Also the melting point of **20** of 156 °C is in the range of the in the literature reported value of 158 °C:

In 1982 BAUER *et al* published a synthesis procedure to achieve 3-acryloylamido-1*H*-1,2,4-triazole **21** and 3-methacryloylamido-1*H*-1,2,4-triazole **22**. According to the prescription the reaction of **20** with the particular acid chloride takes place in aqueous THF, whereas the reduction agent hydroquinone catalyses the S_N2 reaction. The protection group is removed by a selective hydrolysis, because of the weaker acetamide bond.



Scheme 10. Synthesis of **21**/ **22**.

The reaction of acryloyl chloride with **20** was performed with four different reaction conditions:

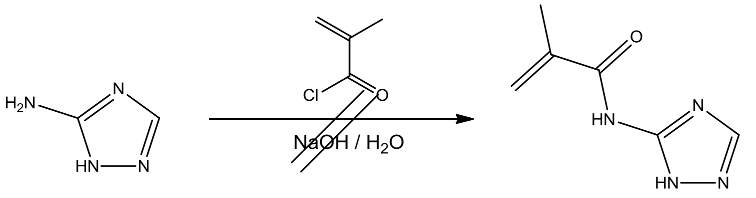
a) Over night at room temperature
b) Over night at 40 °C
c) Three days at room temperature. During this time THF evaporates completely. Afterwards the solid is dissolved in water.
d) Over night at room temperature and argon-inert gas

Only with method **c** the product could be verified in the mass spectrum (mass peak at m/z = 138), however with small intensity. Furthermore the spectrum also shows the 5-amino-1*H*-1,2,4-triazole (m/z = 84) with high intensity. The existence of this byproduct nevertheless reveals that the deprotection by hydrolysis takes place.

The products of reactions **a** and **b** could not be identified clearly. However due to various evidences one can act on the assumption that **21** was not formed. In the ^{1}H NMR of method **a** and **b** the characteristic signals of the CH_2=CH group is missing. Furthermore the mass spectra do not depict a mass peak of **22**. But there is a peak of the amide group (CHON) (m/z = 43) so there had to be a reaction between **20** and acryloyl chloride.

Elemental analysis supports the conclusion that **22** was not synthesized, although some signals in the ^{1}H NMR could be assigned to the molecule. Mass spectrometry also depicts the mass peak of the favored product, but only with very small intensity, whereas the methacryloyl chloride gives a big signal. Consequently this method was not a successful way to obtain compound **22**.

A different technique was performed without previous protection with acetic anhydride. According to literature [37] methacryloyl chloride and 5-amino-1*H*-1,2,4-triazole were mixed in aqueous NaOH.



22a

Scheme 11. Second way to synthesize **22**.

The product of this reaction (scheme 11) could only be identified by crystallographic analysis. Although LYNN *et al.* claim to obtain this product by means of this synthesis, the crystal structure could only be assigned to 6-chlorido-2,5-dimethyl-*N*-(1*H*-1,2,4-triazol-5-yl)-3,4-dihydro-2*H*-pyran-2-carboxamid (**23**).

Compound **23** crystallizes in the monoclinic space group C2/c with a density of 1.44 g cm^{-3} and one molecular formula per unit cell.

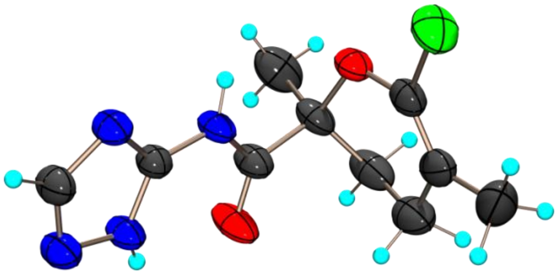
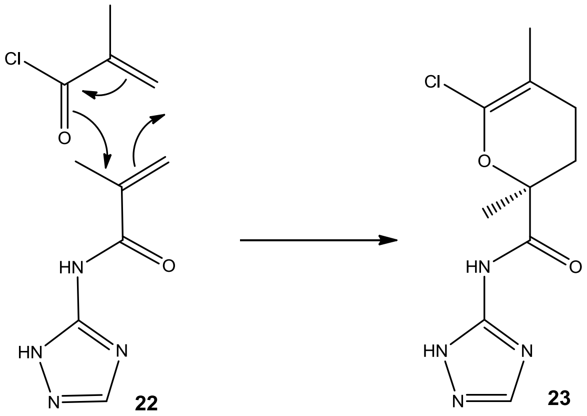


Figure 3. Crystal structure of **23**. Thermal ellipsoids are set to 50 % probability.

The reaction mechanism of this synthesis (scheme 12) is a [4+2] cyclo addition. The acid chloride acts as a electron rich donor and the 3-methacrylamido-1*H*-1,2,4-triazole as an acceptor.

This result is also supported by elemental analysis that is in good conformance with the calculated values. The molecule peak is also depicted in the mass spectrum, as well as the fragment $C_{10}H_{13}O_2N_4$ (m/z = 221) which is formed by the elimination of the Cl-atom.

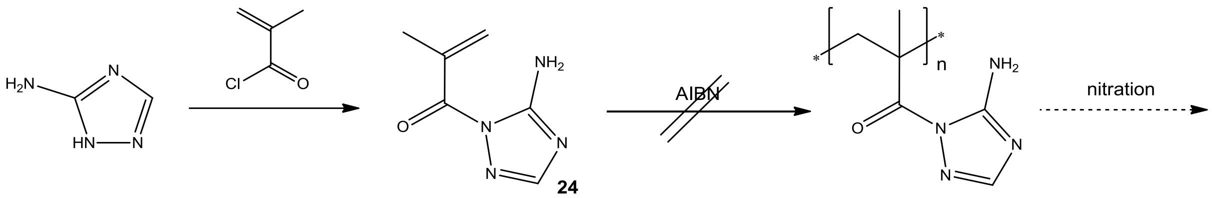


Scheme 12. Reaction mechanism of the electrocyclic reaction.

Instead of the favored molecule **22a** 6-chlorido-2,5-dimethyl-*N*-(1*H*-1,2,4-triazol-5-yl)-3,4-dihydro-2*H*-pyran-2-carboxamide (**23**) was synthesized, by the reaction of two molecules of the acid chloride with 3-amino-1*H*-1,2,4-triazole. Although the minimal excess was diminished and in a further reaction only a 1:1 ratio of acid chloride to triazole was used, **22a** could not be obtained.

6.2.2.4 Synthesis of 5-Amino-1-methacryl-1,2,4-triazole

Another attempt to react 5-amino-1*H*-1,2,4-triazole with methacryloyl chloride worked quite well. According to BAUER *et al*. methacryloyl chloride was added to 5-amino-1*H*-1,2,4-triazole and stirred for 20 hours under normal reaction conditions in THF (scheme 12). The triazole ring got attacked in the N1 position and gave 5-amino-1-methacryl-1,2,4-triazole (**24**) that has a melting point of 106 °C and a point of decomposition at 117 °C.



Scheme 13. Synthesis of **24**.

Unfortunately some problems in polymerization occurred and could not be solved so far. Therefore the intention to further nitrate the molecule at the amine group could not be followed anymore as well. Nevertheless the energetic character of the monomer was determined. The standard enthalpy of formation was calculated at the CBS-4M level of theory[38-43] and the sublimation enthalpy was calculated by Troutons's rule (ΔH_{sub} [kJ mol] = 188 · T_m[K])[44]. With these values and the experimental density, several detonation parameters such as detonation pressure and velocity were computed using the EXPLO5 code[45].

Table 4. Energetic properties and detonation parameters of **24**.

	24
Formula	$C_6H_8N_4O$
Molecular Mass [g mol^{-1}]	152.15
Impact sensitivity [J]^{a}	>40
Friction sensitivity [N]^{b}	>360
ESD–test [J]	>1.5
N [%]^{c}	36.82
Ω [%]^{d}	−158
$T_{\mathrm{dec.}}$ [°C]^{e}	117
ρ [g cm^{-3}]^{f}	1.35
$\Delta_f H_m°$ [kJ mol^{-1}]^{g}	−11
$\Delta_f U°$ [kJ kg^{-1}]^{h}	34
EXPLO5 values: V5.04	
$-\Delta_E U°$ [kJ kg^{-1}]^{i}	2196
T_{E} [K]^{j}	1728
$p_{C\text{-}J}$ [kbar]^{k}	42
$V_{\mathrm{Det.}}$ [m s^{-1}]^{l}	4068
Gas vol. [L kg^{-1}]^{m}	649

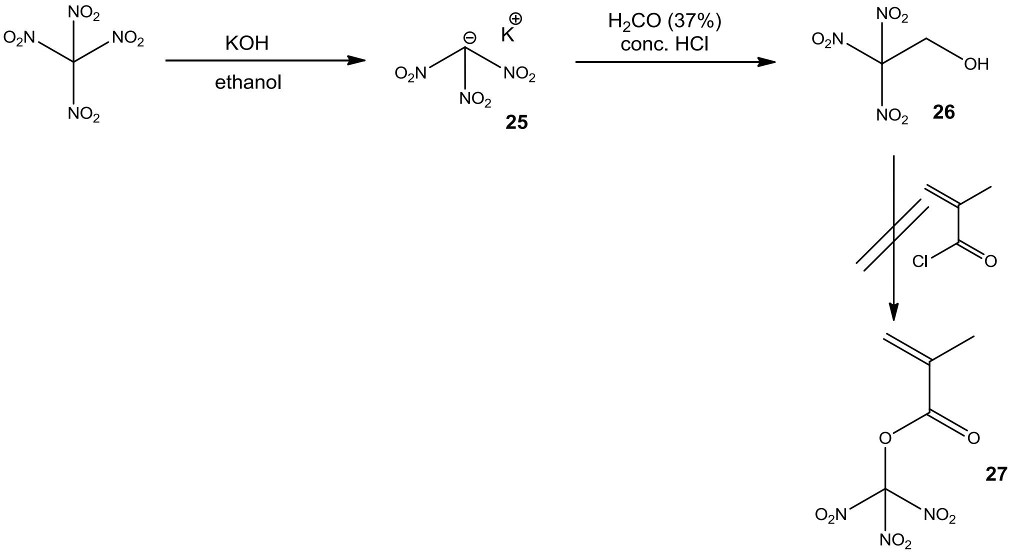
[a] BAM drop hammer; [b] BAM friction tester; [c] Nitrogen content; [d] Oxygen balance; [e] Temperature of decomposition by DSC (β = 5 °C, Onset values); [f] derived from X-ray structure; [g] Molar enthalpy of formation; [h] Energy of formation; [i] Energy of Explosion; [j] Explosion temperature; [k] Detonation pressure; [l] Detonation velocity; [m] Assuming only gaseous products.

Compound **24** is a insensitive compound according to its sensitivity towards impact and friction (IS > 40 J, FS > 360 N) that is a great property. Unfortunately it is thermally not very stable, with its decomposition temperature of 117 °C. Furthermore its detonation parameters, like detonation velocity, are not very convincing. However its low temperature of explosion of 1728 K could be seen as an advantage, because it diminishes the erosion in gun barrels when applied.

All things considered, compound **24** might be useful in applications for binder if the energetic properties could be improved by nitration of the amino moiety. However for the purpose of an application as binder a suitable way of polymerization has to be explored as well.

6.2.3 2,2,2-Trinitroethanol based Compound

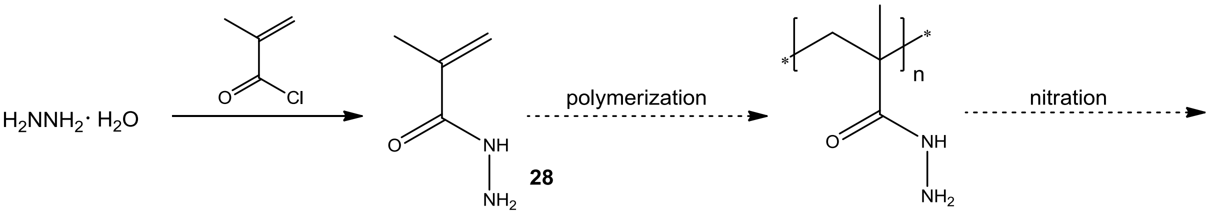
2,2,2-Trinitroethanol (**26**) was synthesized by reacting potassium nitroformate (**25**) with paraformaldehyde in hydrochloric acid at ambient temperature. Similar preparation methods were described numerous times [46-50], whereas for safety reasons a slightly modified and thus a more convenient synthesis route with no heating and no distillation was performed. Furthermore, high purity was achieved by sublimation of the crude product in vacuum. **26** was reacted with methacryloyl chloride analogue to FEUER *et al.* [51] (scheme 14). But contrary to the published results **27** could not be obtained. The recrystallization out of petroleum ether did not work as the product was not soluble in this solvent and the analysis of the gained compound just gave a mixture of various compounds that could not be assigned.



Scheme 14. Synthesis route to synthesize **27**.

6.2.4 Hydrazine based Compound

According to KOLB *et al.* [52] methacryloyl chloride was reacted with hydrazine hydrate, to get methacrylhydrazid (**28**).



Scheme 15. Synthesis of **28**.

This reaction was quite successful as the crystal structure (figure 4) proves. Compound **28** crystallizes in the monoclinic space group $P2_1$ with a density of 1.26 g cm^{-3} and two molecular formulas per unit cell.

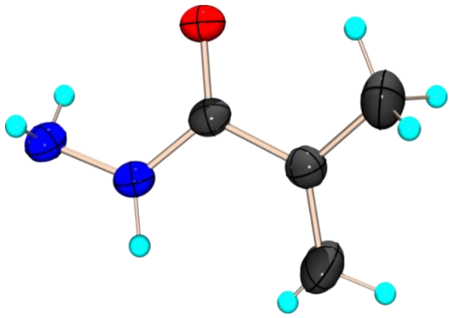


Figure 4. Crystal structure of **28**. Thermal ellipsoids are set to 50 % probability.

To examine the energetic properties of **28** the standard enthalpy of formation was calculated at the CBS-4M level of theory[38-43] and the sublimation enthalpy was calculated by Troutons's rule (ΔH_{sub} [kJ mol] = 188 · T_m[K])[44]. With these values and the experimental density the detonation parameters were computed using the EXPLO5 code[45].

Table 5. Energetic properties and detonation parameters of **28**.

	28
Formula	$C_4H_8N_2O$
Molecular Mass [g mol^{-1}]	100.12
Impact sensitivity [J]^{a}	>40
Friction sensitivity [N]^{b}	>360
ESD–test [J]	>1.5
N [%]^{c}	27.98
Ω [%]^{d}	−175.77
$T_{\text{dec.}}$ [°C]^{e}	95
ρ [g cm^{-3}]^{f}	1.26
$\Delta_f H_m°$ [kJ mol^{-1}]^{g}	−127
$\Delta_f U°$ [kJ kg^{-1}]^{h}	−1132
EXPLO5 values: V5.04	
$-\Delta_E U°$ [kJ kg^{-1}]^{i}	2204
T_E [K]^{j}	1616
$p_{C\text{-}J}$ [kbar]^{k}	51
$V_{\text{Det.}}$ [m s^{-1}]^{l}	4485
Gas vol. [L kg^{-1}]^{m}	744

[a] BAM drop hammer; [b] BAM friction tester; [c] Nitrogen content; [d] Oxygen balance; [e] Temperature of decomposition by DSC (β = 5 °C, Onset values); [f] derived from X-ray structure; [g] Molar enthalpy of formation; [h] Energy of formation; [i] Energy of Explosion; [j] Explosion temperature; [k] Detonation pressure; [l] Detonation velocity; [m] Assuming only gaseous products.

The molecule is completely insensitive towards impact and friction. Its moderate detonation parameters and the low thermal stability disqualifies the compound as a good energetic precursor or monomer that should be polymerized. Due to these disadvantages and the competition with compounds based on triazole and tetrazole moieties, that generally perform better, further syntheses with **28** were not followed any more.

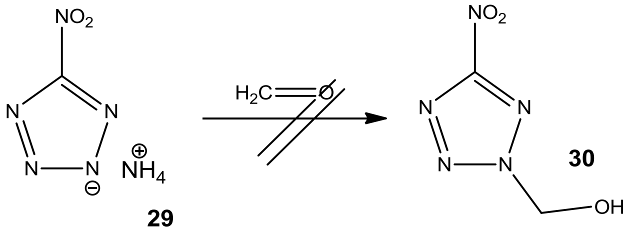
6.2.5 Tetrazole based Compounds containing Spacers

As the reaction of the methacryloyl and the acryloyl chloride with a tetrazole or triazole moiety did just work out in some cases, spacers were introduced to the system to simplify the attack of these acid chlorides by giving the system some degree of freedom.

6.2.5.1 Attempt to synthesize 2-(2-Hydroxymethyl)-5-nitrotetrazole

At first we started with a shorter carbon chain of one methylene between the tetrazole moiety and the hydroxyl group that should be reacting by a nucleophilic attack.

The synthesis of 2-(2-hydroxymethyl)-5-nitrotetrazole (**30**) was performed as described in literature [53] (scheme 16) out of ammonium 5-nitrotetrazole (**29**).



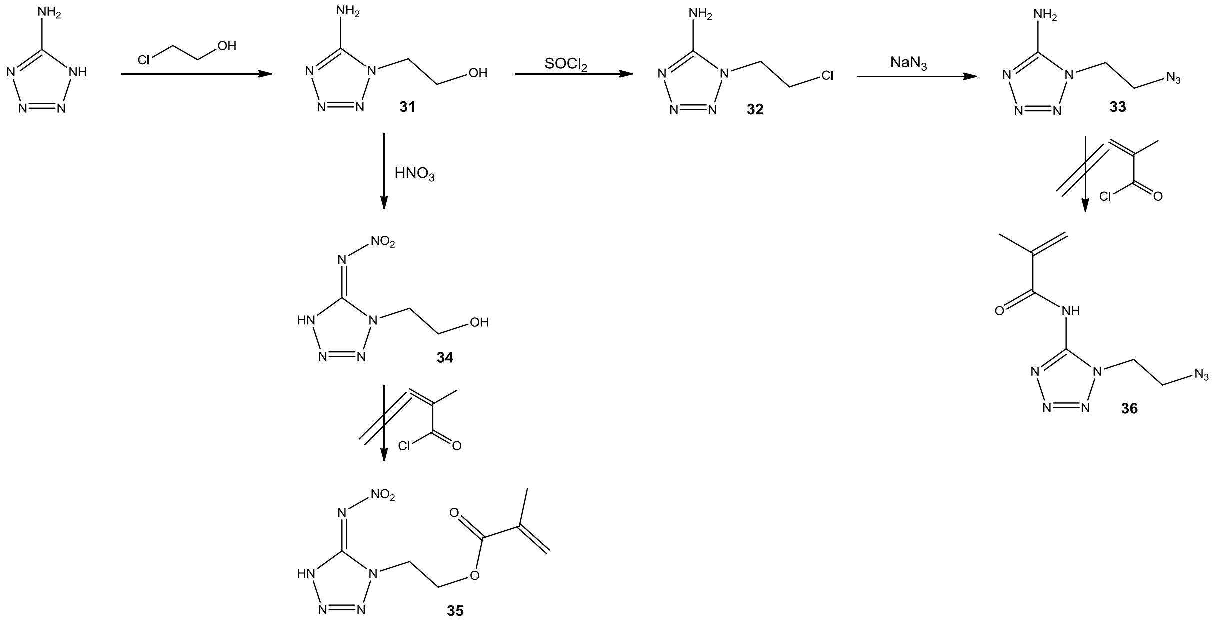
Scheme 15. Synthesis of **30**.

Unfortunately the product could not be obtained, although a yellow solid was achieved, but it apparently decomposed due to stability issues.

6.2.5.2 Attempt to synthesize 1-(2-Methacryl-ethoxy)-5-nitriminotetrazole and 1-(2-Azidoethyl)-5-methacrylamidotetrazole

The carbon chain was then elongated by reacting 5-aminotetrazole with 2-chloroethanol to give 1-(2-hydroxyethyl)-5-aminotetrazole (**31**). The advantage of this molecule is that one the one side it can be chlorinated at the hydroxyl group to give 1-(2-chloroethyl)-5-aminotetrazole (**32**) having an area where an azide group can attack to give 1-(2-azidoethyl)5-aminotetrazole (**33**), which still has an area with its amino group where an methacryloyl moiety can attack. On the other side **31** can be reacted with nitric acid to give 1-(2-hydroxyethyl)-5-nitriminotetrazole (**34**) that can be attacked at the hydroxyl group with the methacryloyl chloride. Therefore we got two different compounds (**33** and **34**) that inherit with its azide and nitrimino group energetic molecules, but they still possess a spot that can be attacked by the acid chloride.

The synthesis of the molecules **31** to **34** were performed according to STIERSTORFER *et al.* [54] (scheme 15) and were gained as pure compounds only **34** had minor impurities.



Scheme 15. Synthesis of **31-36**.

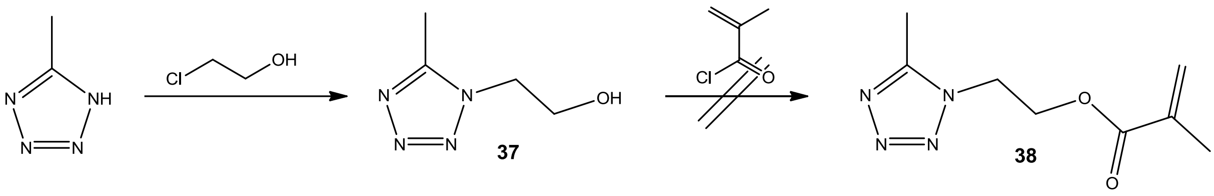
The gained product **34** was treated with methacryloyl chloride to actually give 1-(2-methacryl-ethoxy)-5-nitriminotetrazole (**35**). However the obtained semi-solid product decomposed under the development of gas.

To synthesize 1-(2-azidoethyl)5-methacrylamido)tetrazole (**36**), **33** was reacted with methacryloyl chloride but the analytic showed that the acid chloride could not attack the amine group, probably due to sterical hindrance. Consequently **36** could not be obtained.

6.2.5.3 Attempt to synthesize 1-(2-Methacrylethyl)-5-methyltetrazole

5-Methyltetrazole was reacted, similar to **31** with 2-chloroethanol (scheme 16) to give 1-(2-hydroxyethyl)-5-methyltetrazole (**37**). After the reaction the product was dried yielding a liquid colorless product that appears to exist in two diastereomers (1-(2-hydroxyethyl)-5-methyltetrazole and 2-(2-hydroxyethyl)-5-methyltetrazole), according to the ^{1}H NMR spectrum in which the CH_3 and the two CH_2 groups appear twice, as well as in the ^{13}C NMR spectrum. The signals are approximately equivalent.

After treating this mixture with THF, a colorless powder was gained, that unfortunately still possessed the double signals in the NMR spectra, but in a different ratio. Presumably 1-(2-hydroxyethyl)-5-methyltetrazole was gained in excess, because of the lower chemical shift of the CH_2 group signal.



Scheme 16. Synthesis of **37.**

37 was then mixed with methacryloyl chloride in order to synthesize 1-(2-methacrylethyl)-5-methyltetrazole **38**, but no product could be obtained by filtration and when the solvent was evaporated, the residue was identified as the educt. Therefore the desired nucleophilic attack did not take place.

6.3 Conclusion

Various 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 poly(methacrylnitramidotetrazole) (**5**) and poly(acrylnitramidotetrazole) (**6**) with even better properties. The high 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, turns these polymers into promising materials for the development of new gas generating compositions and an application as environmental friendly nitrogen rich polymer in binder formulations.

In order to further improve these properties by means of other compounds, further approaches to obtain high energetic polymers were undertaken. Although some attempts getting them based on tetrazoles, even by introducing spacer to reduce the sterical hindrance of the molecules and simplify the polymerization mechanism by the use of catalysts, failed. However some molecules were obtained in quite good yield, like the 5-amino-1-methacryl-1,2,4-triazole (**24**), but they could not reach the outstanding properties of compounds **5** and **6**.

6.4 Experimental Part

CAUTION! Tetrazoles can be highly energetic compounds with sensitivity towards heat, friction and impact. Although we had no problems in synthesis, 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.

6.4.1 Synthesis of Tetrazole based Compounds

6.4.1.1 5-Methacrylamidotetrazole (5-MAT)[14] (1)

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 $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3193 (s), 1667 (s), 1618 (s), 1596 (vs), 1444 (m), 1390 (s), 1231 (m), 1186 (m), 1036 (s), 738 (m).

^{1}H NMR (400 MHz, DMSO-*d6*, 25°C) δ = 1.92-1.93 (m, 3H, CH_3), 5.69-5.70 (m, 1H, $=CH_{cis}$), 6.04 (s, 1H, $=CH_{trans}$), 11.91 (s, 1H, CON*H*), 15.9 (s, 1H, tetrazole-N*H*) ppm.

^{13}C{^{1}H} NMR (67.9 MHz, DMSO-*d6*, 25°C) δ = 18.8 (CH_3), 124.4 (CH_2), 138.2 (C_q), 150.8 (C_q-tetrazol), 167.2 (C_q=O) ppm.

MS (DEI+) m/z: 41 [$C_3H_5^+$], 69 [$C_4H_5O^+$], 153 [M^+].

EA ($C_5H_7N_5O$, 153.14): calculated: C 39.21 %, H 4.61 %, N 45.73 %; found: C 38.90 %, H 4.48 %, N 44.71 %.

6.4.1.2 5-Acrylamidotetrazole (5-AAT)[14] (2)

Acryloyl chloride (2.8 g, 2.5 mL, 31 mmol) was added dropwise to a suspension of 5-amino-1*H*-[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 $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 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).

^{1}H NMR (400 MHz, DMSO-*d6*, 25 °C) δ = 5.93 (dd, 1H, $^{3}J_{\text{H-H (trans)}}$ = 9.62 Hz, $^{3}J_{\text{H-H (cis)}}$ = 2.20 Hz; RC*H*=CH$_2$), 6.40 (dd, 1H, $^{3}J_{\text{H-H (trans)}}$ = 17.04 Hz, $^{3}J_{\text{H-H (cis)}}$ = 2.20 Hz, RCH=CH_{cis}H), 6.48 (dd, 1H, $^{3}J_{\text{H-H (trans)}}$ = 17.18 Hz, $^{3}J_{\text{H-H (cis)}}$ = 9.48 Hz, RCH=CHH_{trans}), 12.20 (s, 1H, CON*H*) ppm;

^{13}C{1H} NMR (400 MHz, DMSO-*d6*, 25 °C) δ = 129.8 (*C*H), 130.9 (*C*H$_2$), 150.1 (*ipso-C*), 163.8 (*C*=O) ppm.

MS (DEI+) m/z: 27 [$C_2H_3^+$], 55 [$C_3H_3O^+$], 139 [M$^+$].

EA ($C_4H_5N_5O$, 139.12): calculated: C 34.54 %, H 3.62 %, N 50.35 %; found: C 34.71%, H 3.49 %, N 49.80 %.

6.4.1.3 Poly(methacrylamidotetrazole) (PMAT)[14] (3)

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 overnight 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 colorless solid.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 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 [2M$^+$].

EA ($C_5H_8N_5O$, 154.15): calculated: C 38.96 %, H 5.23 %, N 45.43 %; Found: C 45.14 %, H 38.13 %, N 45.61 %.

6.4.1.4 Poly(acrylamidotetrazole) (PAAT) (4)

5-AAT (1.50 g, 10.8 mmol) and AIBN (11.5 mg, 0.07 mmol) in 12 mL DMF were degassed and stirred overnight at 65 °C. The suspension was then added dropwise to 250 mL methanol and 5 mL concentrated hydrochloric acid. The precipitate was collected by filtration and washed with methanol, giving 1.40 g (94 %) of a colorless solid.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 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 ($C_4H_5N_5O$, 139.12): calculated: C 34.54 %, H 3.62 %, N 50.35 %; found: C 29.58 %, H 5.91 %, N 33.08 %.

6.4.1.5 Poly(methacrylnitramidotetrazole) (PMNT) (5)

PMAT (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 stirred. After two hours the liquid was quenched with ice and the product was filtered off. It was obtained as colorless solid (0.42 g, 65 %).

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 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 ($C_5H_6N_6O_3$, 198.14): calculated: C 30.31 %, H 3.05 %, N 42.41 %; found: C 31.30 %, H 5.54 %, N 35.59 %.

6.4.1.6 Poly(acrylnitramidotetrazole) (PANT) (6)

PAAT (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 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 $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 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 ($C_4H_4N_6O_3$, 184.11): calculated: C 26.09 %, H 2.19 %, N 45.65 %; found: C 29.79 %, H 4.53 %, N 42.16 %.

6.4.1.7 2-(1*H*-Tetrazol-1-yl)acetic acid[26] (10)

Glycin (3.75 g, 50.0 mmol), sodium azide (3.90 g, 60.0 mmol) and triethyl orthoformate (8.00 g, 54.0 mmol) was heated for 2 hours at 80 °C in 25 mL acetic acid and further acidified with 5 mL conc. hydrochloric acid. The solvent was evaporated and the recidue was extracted with warm ethyl acetate (4 x 20 mL). The solvent of the united ethyl acetate layers was evaporated and the yellowish brown residue was recrystallized with 2-propanol to give 2.60 g (41 %).

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3151 (m), 1998 (w), 2962 (w), 2728 (w), 2603 (w), 2552 (w), 2362 (w), 1732 (s), 1713 (s), 1494 (w), 1485 (w), 1439 (w), 1429 (w), 1411 (w), 1347 (m), 1304 (w), 1269 (w), 1240 (s), 1211 (s), 1179 (s), 1153 (m), 1120 (m), 1097 (s), 1049 (w), 1022 (w), 995 (m), 982 (m), 927 (w), 894 (s), 794 (s), 721 (w), 675 (m).

^{1}H NMR (270 MHz, DMSO-*d6*, 25 °C) δ = 5.43 (s, 2H, CH_2), 9.38 (s, 1H, C*H*) ppm.

^{13}C{^{1}H} NMR (270 MHz, DMSO-*d6*, 25 °C) δ = 49.1 (*C*H_2), 145.5 (*C*H), 168.5 (*C*=O) ppm.

MS (DCI^+) m/z: 129 [M^+H], 100 [$C_3H_4N_2O_2^+$], 83 [$C_2H_3N_4^+$].

EA ($C_3H_4N_4O_3$, 128.09) calculated: C 28.13 %, H 3.15 %, N 43.74 %; found: C 28.81 %, H 3.28 %, N 41.82 %.

6.4.1.8 2-(1*H*-Tetrazol-1-yl)acetamide (11)

2-(1*H*-Tetrazol-1-yl)acetic acid (2.50 g, 19.5 mmol) and 37.3 mL concentrated ammonia was stirred for 3 hours at room temperature. The solvent was evaporated and the residue was recrystallized with ethanol giving 1.35 g (55 %) of a yellowish powder.

^{1}H NMR (400 MHz, DMSO-*d6*, 25 °C) δ = 4.74 (s, 2H, CH_2), 7.33 (br. s, 2H, NH_2), 9.16 (s, 1H, C*H*) ppm.

$^{13}C\{^1H\}$ NMR (400 MHz, DMSO-*d6*, 25 °C) δ = 51.8 (CH_2), 145.0 (CH), 167,5 (CO) ppm.

MS (DEI$^+$) m/z: 128 [M^+H], 111 [$C_3H_3N_4O^+$], 100 [$C_3H_5N_3O^+H$], 72 [$C_2H_4N_2O^+$], 83 [$C_2H_3N_4^+$].

EA ($C_3H_5N_5O$, 127.10) calculated: C 28.35 %, H 3.96 %, N 55.10 %; found: C 25.11 %, H 4.60 %, N 47.75 %.

6.4.2 Synthesis of 1*H*-1,2,4-Triazole based Compounds

6.4.2.1 3,5-Dinitro-1*H*-1,2,4-triazole[35] (15)

3,5-Diamino-1*H*-1,2,4-triazole (1.00 g, 10.09 mmol) was dissolved in sulfuric acid (0.68 M, 36.8 mL). Under ice cooling a solution containing sodium nitrite (6.70 g, 97.0 mmol) in 6.9 mL water was added drop wise and stirred for 1 hour at 65 °C. The reaction mixture is than cooled by means of an ice salt bath and a mixture of concentrated sulfuric acid and water (1: 2) was added drop wise until no more gas evolved. Urea was added until the solution did not foam anymore and was then extracted with ethyl acetate (6 x 200 mL), dried with magnesium sulfate and the ether was evaporated under reduced pressure to obtain 1.28 g (80 %) of an orange solid.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 1715 (s), 1652 (w), 1580 (s), 1559 (vs), 1516 (s), 1465 (w), 1441 (w), 1428 (m), 1394 (s), 1315 (vs), 1293 (m), 1242 (m), 1185 (w), 1174 (s), 1120 (m), 1063 (w), 1009 (m), 868 (s), 840 (m), 830 (vs), 762 (m), 752 (m), 707 (s).

6.4.2.2 Ammonium 3,5-dinitro-1*H*-1,2,4-triazolate[35] (16)

14 (5.21 g, 32.8 mmol) was dissolved in 5 mL water and by means of ammonia (6.7 M) a pH value of 8 was adjusted. Most of the water was removed by evaporation under reduced pressure, the residue was covered with a layer of ether and stored over night in the refrigerator. The precipitated red crystals were filtered off and dried, giving 5.12 g (89 %) of **12**.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3438 (m), 3325 (m), 3233 (m), 3166 (m), 3028 (m), 2969 (m), 2714 (w), 1738 (s), 1635 (m), 1534 (m), 1506 (vs), 1492 (m), 1445 (m), 1396 (m), 1365 (m), 1309 (m), 1388 (s), 1229 (m), 1217 (m), 1099 (w), 1035 (s), 1014 (m), 971 (w), 845 (m), 768 (vw), 735 (m).

^{1}**H NMR** (400 MHz, DMSO-*d6*, 25 °C) $\delta = 6.69$ (br, s, 4H, NH_4) ppm.

^{13}**C{^{1}H} NMR** (400 MHz, DMSO-*d6*, 25 °C) $\delta = 156.1$ (*C*-NO_2) ppm.

MS (FAB$^-$) m/z = 158 [$C_2N_5O_4^-$], 113 [$C_2N_5O_4^-$], 317 [$C_4N_{10}O_8^-$].

6.4.2.3 3-Amino-5-nitro-1*H*-1,2,4-triazole (18)

Hydrazine hydrate (5.97 mL, 122.8 mmol) was added to **15** (4.69 g, 26.6 mmol) at room temperature. After the compound dissolved, the solution was heated to 80 °C for 2 hours. The cooled solution was diluted with 7 mL of water and acidified with 10 % hydrochloric acid until an pH value of 4 was achieved. The precipitate was filtered and dried to give 1.93 g (56 %) of a yellow powder.

^{1}**H NMR** (270 MHz, DMSO-*d6*, 25 °C) $\delta = 6.80$ (s, 2H, NH_2), 13.13 (s, 1H, N*H*) ppm.

^{13}**C{^{1}H} NMR** (270 MHz, DMSO-*d6*, 25 °C) $\delta = 157.9$ (*C*-NH_2), 161.4 (*C*-NO_2) ppm.

^{15}**N{^{1}H} NMR** (400 MHz, DMSO-*d6*, 25 °C) $\delta = 50.2$ (NO_2), 177.2 (N2), 198.1 (N3), 269.9 (N1), 353.6 (NH_2) ppm.

MS (FAB$^-$) m/z = 128 [M-H].

EA ($C_2H_3N_5O_2$, 129.08) calculated: C 18.61 %, H 2.34 %, N 54.26 %; found: C 17.35 %, H 2.88 %, N 50.20 %.

6.4.2.4 1-Acetyl-5-amino-1*H*-1,2,4-triazole (20)

Method a

3-Amino-1*H*-1,2,4-triazole (0.84 g, 10 mmol) was dissolved in 10 mL DMF. Acetic anhydride (1.38 mL, 15 mmol) was added and the solution was stirred for 1 hour at room temperature. The solvent was evaporated and the residue crystallized out of 10 mL ethanol to give colorless needles (0.89 g, 71 %).

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3404 (w), 3284 (m), 3258 (m), 3107 (w), 2969 (w), 1736 (m), 1683 (s), 1613 (vs), 1556 (m), 1499 (m), 1426 (w), 1375 (s), 1332 (w), 1294 (s), 1264 (vs), 1230 (w), 1217 (w), 1196 (vs), 1152 (w), 1059 (vs), 1005 (w), 978 (w), 946 (s), 918 (vs), 879 (m), 804 (w), 746 (w), 659 (s).

^{1}H NMR (270 MHz, DMSO-*d6*, 25 °C) δ = 2.52 (s, 3H, CH_3), 7.47 (br. s, 2H, NH_2) ppm.

^{13}C{^{1}H} NMR (270 MHz, DMSO-*d6*, 25 °C) δ = 23.6 (CH_3), 151.5 (N-*C*H), 157.3 (*ipso*-*C*), 172.1 (*C*=O) ppm.

MS (FAB^+) m/z = 127.1 [M^+H], 85 [$C_3H_4N_2O^+H$], 43 [$C_2H_3O^+$].

EA ($C_4H_6N_4O$, 126.12) calculated: C 38.09 %, H 4.80 %, N 44.42 %; found: C 38.17 %, H 4.61 %, N 44.17 %.

Method b

Acetic anhydride (1.38 mL, 15 mmol) was added to 5-amino-1*H*-1,2,4-triazole (0.84 g, 10 mmol) in 20 mL acetonitrile. The suspension was stirred for 1 hour at 65 °C to yield 1.07 g (57 %) of a colorless solid.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3404 (w), 3284 (m), 3258 (m), 3107 (w), 2969 (w), 1736 (m), 1683 (s), 1613 (vs), 1556 (m), 1499 (m), 1426 (w), 1375 (s), 1332 (w), 1294 (s), 1264 (vs), 1230 (w), 1217 (w), 1196 (vs), 1152 (w), 1059 (vs), 1005 (w), 978 (w), 946 (s), 918 (vs), 879 (m), 804 (w), 746 (w), 659 (s).

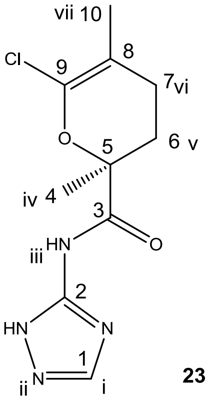
MS (DEI^+) m/z = 126.1 [M^+], 111 [$C_4H_5N_3O^+$], 84 [$C_3H_4N_2O^+$], 57 [$C_2H_3NO^+$], 43 [$C_2H_3O^+$].

EA ($C_4H_6N_4O$, 126.12) calculated: C 38.09 %, H 4.80 %, N 44.42 %; found: C 38.09 %, H 4.61 %, N 43.77 %.

6.4.2.5 6-Chlorido-2,5-dimethyl-*N*-(1*H*-1,2,4-triazol-5-yl)-3,4-dihydrido-2*H*-pyran-2-carboxamide (23)

Methacryloyl chloride (2.62 mL, 27.1 mmol) was added drop wise to a solution of sodium hydroxide (1.90 g, 47.6 mmol) and 3-amino-1*H*-1,2,4-triazole (2.00 g, 23.8 mmol) in 9.5 mL water at 0 °C. After warming up to room temperature and recrystallization with ethanol, colorless crystals (0.16 g, 2.5 %) were formed.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3308 (m), 3183 (vw), 3096 (vw), 2980 (w), 2942 (w), 2916 (w), 2861 (vw), 2848 (vw), 2766 (vw), 2350 (w), 2282 (vw), 1780 (w), 1676 (s), 1580 (vs), 1531 (m), 1484 (s), 1445 (m), 1434 (w), 1385 (w), 1375 (w), 1349 (w), 1288 (w), 1268 (m), 1259 (m), 1247 (m), 1226 (w), 1212 (w), 1200 (w), 1188 (m), 1140 (m), 1116 (s), 1080 (m), 1047 (m), 1036 (s), 1027 (vs), 967 (s), 954 (w), 930 (m), 911 (m), 892 (m), 854 (w), 817 (m), 753 (s), 712 (m), 694 (m).



23

^{1}H NMR (270 MHz, DMSO-*d6*, 25 °C) δ = 1.51 (s, 3H, CH_3, iv), 1.63 (s, 3H, CH_3, vii), 1.73-1.86 (mult., 2H, CH_2, vi), 2.02 (t, ^{3}J = 6.23 Hz, 2H, CH_2, v), 7.75 (s, 1H, C*H*, i), 11.40 (s, 1H, N*H*, iii), 13.52 (s, 1H, N*H*, ii) ppm.

^{13}C{^{1}H} NMR (270 MHz, DMSO-*d6*, 25 °C) δ = 18.5 (*C*H$_3$, 10), 24.0 (*C*H$_2$, 7), 25.2 (*C*H$_3$, 4), 29.7 (*C*H$_3$, 6), 82.3 (C_q, 5), 104.2 (C_q, 8), 135.6 (C_q, 9), 148.6 (*C*H, 1), 149.4 (C_q, 2), 167.1 (C_q, 3) ppm.

MS (DEI$^+$) m/z: 41 [C_3H_5], 43 [CHON], 69 [C_4H_5O], 84 [$C_2H_4N_4$], 111 [$C_3H_3ON_4$], 152 [$C_6H_7ON_4$], 221 [$C_{10}H_{13}O_2N_4$], 256 [M$^+$].

EA ($C_{10}H_{13}ClN_4O_2$, 256.69) calculated: C 46.79 %, H 5.10 %, Cl 13.81 %, N 21.83 %; found: C 46.75 %, H 4.98 %, Cl 13.93 %, N 21.95 %.

6.4.2.6 5-Amino-1-methacryl-1,2,4-triazole (24)

A suspension of 5-amino-1*H*-1,2,4-triazole (5.00 g, 59.00 mmol) and methacryloyl chloride (2.91 mL, 29.5 mmol) in 114 mL THF was stirred over night at room temperature. The precipitate was filtered of and the solvent was removed *in vacuo*. The residue was recrystallized in benzene to give 1.66 g (37 %)of a colorless solid.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3403 (w), 3283 (w), 3210 (w), 3119 (m), 2979 (m), 2936 (m), 1693 (s), 1630 (s), 1589 (s), 1542 (vs), 1479 (m), 1455 (m), 1387 (s), 1345 (s), 1297 (m), 1244 (m), 1201 (s), 1082 (m), 1032 (m), 977 (m), 938 (m), 744 (m), 730 (m), 680 (s).

^{1}H NMR (400 MHz, DMSO-*d6*, 25 °C) δ = 2.00 (m, 3H, CH_3), 5.75-5.76 (m, 1H, =CH_{trans}), 6.00 (s, 1H, =CH_{cis}), 7.53 (s, 1H, CH), 7.54 (s, 2H, NH_2) ppm.

^{13}C{^{1}H} NMR (270 MHz, DMSO-*d6*, 25 °C) δ = 19.9 (CH_3), 127.0 (=CH_2), 138.3 (C_q), 151.7 (CH), 158.5 (C_q-triazole), 169.4 (C=O) ppm.

MS (DEI$^+$) m/z = 41 [$C_3H_5^+$], 69.1 [$C_4H_5O^+$], 84.1 [$C_2H_4N_4^+$], 152.1 [M$^+$].

EA ($C_6H_8N_4O$, 152.15) calculated: C 47.36 %, H 5.30 %, N 36.82 %; found: C 46.42 %, H 5.30 %, N 32.58 %.

6.4.3 Synthesis of Trinitroethanol based Compounds

6.4.3.1 Potassium nitroformate (25)

The synthesis was performed analogue to the literature of Göbel *et al.* [55]. Therefore tetranitromethane (18.50 g, 94.4 mmol) was added to potassium hydroxide (5.37 g, 95.6 mmol) in 180 mL ethanol. After the addition, the mixture was stirred at 0 °C for 20 minutes, then the ice bath was removed and the mixture was allowed to warm up to room temperature. The precipitates was filtered off and washed two times with 75 mL ethanol and three times with 25 mL of diethyl ether, yielding a yellowish powder (14.12 g, 78 %).

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 1508 (s), 1494 (s), 1419 (s), 1262 (vs), 1166 (s), 871 (w), 792 (s), 732 (vs).

$^{13}C\{^1H\}$ NMR (400 MHz, Acetone-*d6*, 25 °C) δ = 151.4 (*C*(NO_2)$_3$) ppm.

^{14}N NMR (400 MHz, Acetone-*d6*, 25 °C) δ = -29.2 (*N*O_2) ppm.

MS (FAB^+) m/z: 39 [K^+].

MS (FAB^-) m/z = 46 [NO_2], 62 [NO_3^-] 150 [$M-K^+$].

EA (CKN_3O_6, 198.13) calculated: C 6.35 %, N 22.22 %; found: C 6.08 %, N 21.00 %.

6.4.3.2 2,2,2-Trinitroethanol (26)

Potassium nitroformate (14.07 g, 74.4 mmol), formaldehyde (37 %, 6.33 g, 77.9 mmol) and 25 mL conc. hydrochloric acid were stirred for 15 minutes at 0 °C and then for 17 hours at room temperature. The reaction mixture was extracted with 200 mL dichloromethane. The organic phase was washed with a saturated NaCl-solution, dried with magnesium sulfate and the solvent was evaporated *in vacuo* giving 10.60 g (78 %) of colorless crystals.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3419 (s), 3013 (w), 2960 (w), 2897 (w), 2657 (w), 2615 (w), 2362 (w), 2335 (w), 1586 (vs), 1440 (w), 1407 (w), 1373 (w), 1350 (w), 1308 (s), 1297 (s), 1243 (m), 1121 (w), 1089 (s), 1059 (m), 1005 (w), 881 (w), 856 (w), 802 (s), 780 (m), 712 (w), 658 (w), 640 (w).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 4.87 (s, 2H, CH_2), 3.39 (s, 1H, OH) ppm.

^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$, 25 °C) δ = 125.4 ($C(NO_2)_3$), 63.3 (CH_2) ppm.

^{14}N NMR (400 MHz, $CDCl_3$, 25 °C) δ = -32.8 (NO_2) ppm.

MS (DEI^{+}) m/z = 72 [M^{+}-OH-2NO_2], 89 [M^{+}-2NO_2], 118 [M^{+}-OH-NO_2], 164 [M^{+}-OH], 182 [M^{+}].

EA ($C_2H_3N_3O_7$, 181.06) calculated: C 13.27 %, H 1.67 %, N 23.21 %; found: C 13.51 %, H 1.75 %, N 22.54 %.

6.4.4 Synthesis of Hydrazine based Compounds

6.4.4.1 Methacrylhydrazid[52] (28)

Hydrazine hydrate (9 mL, 185.54 mmol) in 31 mL chloroform was cooled to -10 °C to 0 °C and stirred firmly. Methacryloyl chloride (6 m, 61.42 mmol) was added drop wise in 10 mL chloroform. The chloroform and the water layer were separated, the suspension was cleared by filtration and the chloroform was evaporated. The residue was recrystallized with ethyl acetate to give colorless crystals (2.64 g, 43 %).

^{1}H NMR (400 MHz, DMSO-*d6*, 25 °C) δ = 1.83-1.84 (m, 3H, CH_3), 1.87 (s, 2H, NH_2), 5.27-5.28 (m, 1H, =CH_{trans}), 5.61 (s, 1H, =CH_{cis}), 9.21 (s, 1H, N*H*) ppm.

^{13}C{^{1}H} NMR (400 MHz, DMSO-*d6*, 25 °C) δ = 19.0 (CH_3), 119.5 (CH_2), 139.1 (C_q), 167.6 (C=O) ppm.

6.4.5 Synthesis of Tetrazole based Compounds containing Spacers

6.4.5.1 Ammonium 5-nitrotetrazolate [56] (29)

Copper (II) sulfate pentahydrate (11.53 g, 46 mmol) and sodium nitrite (20.72 g, 304 mmol) were dissolved in 60 mL distilled water in a 500 mL plastic beaker. This solution was cooled to 0 to 5 °C by means of an ice bath.

Meanwhile a solution of 5-amino-1*H*-tetrazol (8.63 g, 101 mmol) and a spatula point of copper (II) sulfate pentahydrate in 140 mL distilled water and concentrated sulfuric acid (5.6 mL, 105 mmol) was prepared. This solution was added to the previous one by means of a dropping-funnel.

This suspension was stirred at room temperature for about ten minutes and sodium hydroxide (8.04 g, 200 mmol) were added in a water bath at 70 °C and stirred for 1.5 hours in order to convert the blue copper (II) hydroxide into black copper (II) oxide.

The copper (II) oxide was filtered hot through previously washed celite, yielding a pale yellow solution.

Concentrated sulfuric acid (3.2 mL, 60 mmol) were added to this solution and stirred with about two spatula points of charcoal for about ten minutes while still warm. The greenish solution was filtered into an extraction funnel and acidified with further concentrated sulfuric acid (3.2 mL, 60 mmol).

The aqueous solution was extracted with ethyl acetate (8 x 75 mL). The organic phase was dried with magnesium sulphate and reduced in volume using a rotator evaporator to about 100 mL and placed in a wash bottle. Ammonia gas was carefully bubbled through the solution resulting in a precipitation of a yellowish powder. The compound was filtered off, washed with ethylacetate and left to air dry, yielding in a yellowish powder. (3.1 g, 24 %).

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3417 (m), 3268 (m), 3165 (m), 3010 (s), 2848 (m), 2464 (w), 2220 (w), 2205 (w), 2140 (w), 2084 (w), 1860 (w), 1704 (m), 1683 (m), 1554 (s), 1507 (m), 1462 (s), 1448 (s), 1417 (s), 1317 (s), 1181 (m), 1166 (m), 1062 (m), 1037 (m), 834 (s), 773 (w), 732 (w), 671 (m), 664 (m), 539 (w).

6.4.5.2 5-Amino-1-(2-hydroxyethyl)tetrazole[54] (31)

5-Aminotetrazole (10.0 g, 118 mmol) was dissolved in 24 mL water and treated with sodium hydroxide (4.8 g, 120 mmol) and 2-chloroethanol (9.4 mL, 10.4 g, 129 mmol). The mixture was heated to reflux for six hours, extracted with boiling acetone (2 x 12 mL) and boiling ethanol (2 x 12 mL). The organic solutions were evaporated *in vacuo* and the solid product was recrystallized from boiling ethanol to give a colorless crystalline product (4.07 g, 27 %).

^{1}H NMR (400 MHz, DMSO-*d6*, 25 °C) δ = 3.71 (t, ^3J = 5.5 Hz, 2H, CH_2), 4.14 (t, ^3J = 5.6 Hz, 2H, CH_2), 6.57 (s, 2H, NH_2) ppm.

^{13}C{^{1}H} NMR (400 MHz, DMSO-*d6*, 25 °C) δ = 47.8 (CH$_2$), 59.5 (CH$_2$), 156.4 (*ipso*-*C*) ppm.

MS (DEI$^+$) m/z = 28 [$C_2H_4^+$], 43 [$C_2H_3O^+$], 86 [$CH_4N_5^+$], 98 [$C_2H_4N_5^+$], 129 [M^+].

EA ($C_3H_7N_5O$, 129.12) calculated: C 27.91 %, H 5.46 %, N 54.24 %; found: C 27.84 %, H 5.25 %, N 54.12 %.

6.4.5.3 5-Amino-1-(2-chloroethyl)tetrazole[54] (32)

31 (0.84 g, 6.5 mmol) was added slowly into an ice cooled flask, filled with thionyl chloride (2.8 mL, 4.6 g, 39.0 mmol). The solution was heated for 4 hours at reflux and then the solvent was evaporated. The residue was treated with ethanol (1 mL) and water (1 mL) and dried *in vacuo*. The colorless solid product was recrystallized from boiling water and filtered after cooling to give 0.35 g (36 %).

^{1}H NMR (270 MHz, DMSO-*d6*, 25 °C) δ = 3.96 (t, ^3J = 5.86 Hz, 2H, CH_2), 4.47 (t, ^3J = 5.86 Hz, 2H, CH_2), 6.79 (s, 2H, NH_2) ppm.

^{13}C{^{1}H} NMR (270 MHz, DMSO-*d6*, 25 °C) δ = 42.5 (CH$_2$), 46.6 (CH$_2$), 156.3 (*ipso*-*C*) ppm.

MS (DEI$^+$) m/z = 28 [$C_2H_4^+$], 43 [$C_2H_2NH^+$], 63 [$C_2H_4Cl^+$], 98 [$C_2H_4N_5^+$], 147 [M^+].

EA ($C_3H_6N_5Cl$, 147.57) calculated: C 24.42 %, H 4.10 %, N 47.46 %; found: C 24.55 %, H 3.94 %, N 47.16 %.

6.4.5.4 5-Amino-1-(2-azidoethyl)tetrazole[54] (33)

32 (0.76 g, 5.15 mmol) was dissolved in 12 mL DMF and treated with sodium azide (0.4 g, 6.15 mmol) dissolved in 12 mL DMF. The mixture was heated for 4 hours at reflux, dried *in vacuo* and recrystallized from water to give 0.45 g (57 %) of colorless crystals.

^{1}H NMR (400 MHz, DMSO-*d6*, 25 °C) δ = 3.68 (t, ^3J = 5.76 Hz, 2H, CH_2), 4.28 (t, ^3J = 5.66 Hz, 2H, CH_2), 6.77 (s, 2H, NH_2) ppm.

^{13}C{^{1}H} NMR (400 MHz, DMSO-*d6*, 25 °C) δ = 44.6 (*C*H$_2$), 49.4 (*C*H$_2$), 156.2 (*ipso-C*) ppm.

MS (DEI$^+$) m/z = 28 [$C_2H_4^+$], 43 [$C_2H_2NH^+$], 69 [CHN_4^+], 99 [$C_2H_5N_5^+$], 154 [M^+].

EA ($C_3H_6N_8$, 154.13) calculated: C 23.38 %, H 3.92 %, N 72.70 %; found: C 23.64 %, H 3.95 %, N 72.41 %.

6.4.5.5 1-(2-Hydroxyethyl)-5-nitriminotetrazole[54] (34)

31 (1.4 g, 11.0 mmol) was added slowly and under stirring to nitric acid (2 mL, 49 mmol) that was cooled by means of an ice bath. The solution was then stirred for another 2 hours at 0 °C and over night at room temperature. Afterwards the solution was poured on ice, stirred until the ice melted and the solvent was removed *in vacuo* to yield in 4.07 g, (27 %) of a colorless solid.

IR $\tilde{\nu}$ (cm^{-1}) (rel. int.) = 3357 (w), 3160 (w), 1688 (vs), 1639 (vs), 1368 (s), 1278 (vs), 998 (m), 843 (s).

^{1}H NMR (400 MHz, DMSO-*d6*, 25 °C) δ = 4.51 (t, ^3J = 4.97 Hz, 2H, CH_2), 4.85 (t, ^3J = 4.98 Hz, 2H, CH_2), 8.17 (s, 1H, O*H*) ppm.

^{13}C{^{1}H} NMR (400 MHz, DMSO-*d6*, 25 °C) δ = 59.2 (CH_2), 70.8 (CH_2), 155.6 (*ipso-C*) ppm.

MS (DEI$^+$) m/z = 28 [$C_2H_4^+$], 43 [$C_2H_3O^+$], 70 [$CH_2N_4^+$], 98 [$C_3H_6N_4^+$], 129 [$CHN_6O_2^+$], 174 [M^+].

EA ($C_3H_6N_6O_3$, 174.12) calculated: C 20.69 %, H 3.47 %, N 48.27 %; found: C 15.22 %, H 3.37 %, N 38.57 %.

6.5 Crystal Section

Structure Analysis: The single X-ray diffraction data of **3** was collected using an Oxford Xcalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD area detector with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The data collection was undertaken using the CrysAlis CCD software[57] while the data reduction was performed with the CrysAlis RED software[58]. The structure was solved with Sir-92[59] and refined with Shelxl-97[60] implemented in the program package WinGX[61] and finally checked using Platon[62].

Table 6. Selected crystal data of **23** and **28**.

	23	**28**
Chemical formula	$C_{10}H_{13}ClN_4O_2$	$C_4H_8N_2O$
Molecular weight [g mol^{-1}]	256.69	100.12
Color, habit	Colorless plate	Colorless needles
Size [mm]	0.42 x 0.31 x 0.02	0.84 x 0.23 x 0.05
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	$P2_1$
a [Å]	24.271(4)	6.2163(10)
b [Å]	9.9406(15)	3.8949(7)
c [Å]	9.818(2)	10.995(2)
α [°]	90	90
β [°]	95.164(19)	96.068(17)
γ [°]	90	90
V [Å^3]	2359.2(7)	264.72(8)
Z	1	2
$\rho_{calcd.}$ [g cm^{-3}]	1.440	1.256
μ [mm^{-1}]	0.320	0.093
Irradiation	MoK$_\alpha$ 0.71073	MoK$_\alpha$ 0.71073
F(000)	1064	108
Θ-Bereich	4.35-26.50	4.6998-33.4778
T [K]	239(2)	173(2)
Index range	$-30 \le h \le 30$	$-7 \le h \le 7$
	$-12 \le k \le 11$	$-4 \le k \le 4$
	$-11 \le l \le 12$	$-7 \le l \le 13$
Reflections coll.	6137	1411
Independent refl.	2449	1071
Observed refl.	1741	973
Parameters	206	84
R$_{int.}$	0.044	0.0140
GOOF	1.035	1.074
R_1/wR_2 [I>2σ(I)]]	0.0472, 0.1057	0.0571, 0.1549
R_1/wR_2 (all data)	0.0764, 0.1241	0.0630, 0.1631
Weighting scheme	0.0510, 1.3224	0.1058, 0.0519
Remaining density	-0.433, 0.296	-0.377, 0.423
Device type	Oxford XCalibur3	Oxford XCalibur3
Adsorption corr.	Multi scan	Multi scan

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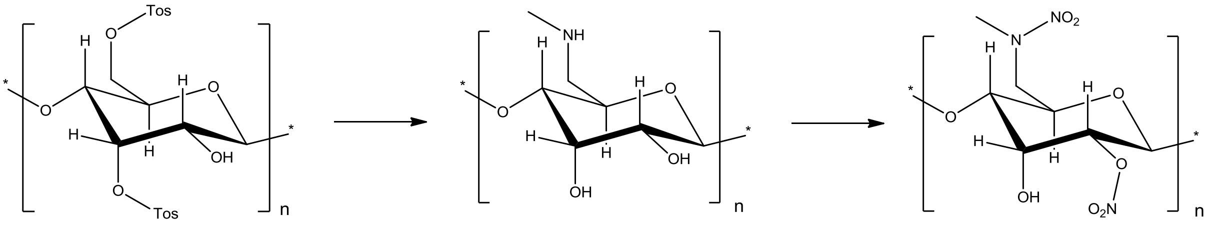
7. Summary

This thesis concerns the investigation and development of new nitrogen-rich energetic polymers based on various moities like cellulose, tetrazoles and triazoles and their polymeric precursor.

One intensely studied topic was the examination of polymers based on cellulose. Here, various energetic groups like tetrazoles and nitramines were introduced to this β-*D*-polyglucose by linking them to the polymers hydroxy groups. The most promising compound was methylnitraminocellulose (MNAC, scheme 1). This molecule convinces with its easy availability, biocompatibility and reproducibility, along with its great performance and its good stability in terms of thermal and physical stimuli. Due to the bad chemical stability of nitrocellulose and its addiction to autocatalytic decomposition, MNAC proved itself superior to nitrocellulose in the application in ignition mixtures. This was performed in collaboration with Diehl BGT Defense.



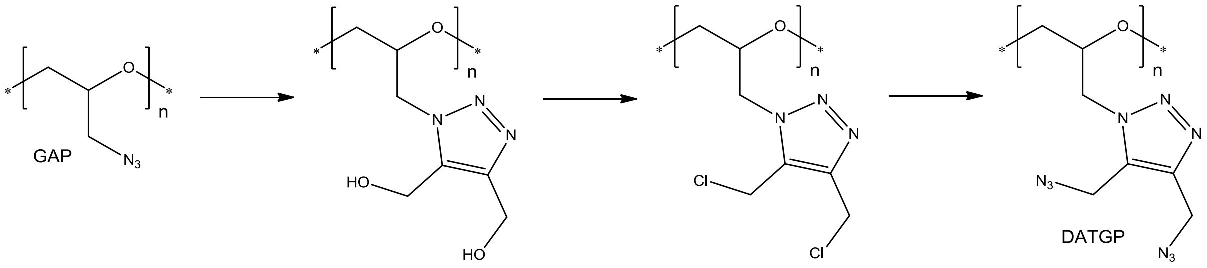
MNAC

Scheme 1. Synthesis of MNAC.

In the application in the impulse cartridge DM 82 (figure 1), MNAC not only convinced with a very good performance, but even exceeded that of the commonly used nitrocellulose in terms of long-term stability. Therefore this compound and its synthesis was handed in as patent for a future use as binder.

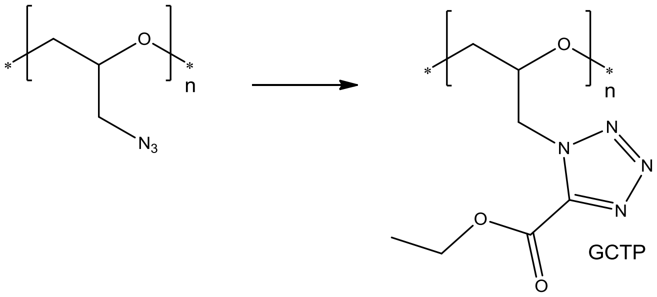
Figure 1. Impulse cartridge DM 82.

The second polymer class was prepared by functionalizing an already existing polymer, glycidyl azido polymer (GAP). The contained azido group of this compound simplifies the formation of a cycloaddition to create tetrazole and triazole moieties. For this reason GAP was reacted to form (4,5-di(azidomethyl)-1*H*-1,2,3-triazol-1-yl)glycidyl polymer (DATGP, scheme 2). Due to the two contained azide moieties this molecule has a very good performance, not surprisingly exceeding that of GAP. However in terms of safety it does not improve the moderate sensitivity of GAP towards impact sensitivity, but it is insensitive to friction. A further advantage, additional to the better performance, is the solid character. It can therefore be applied without further curing. A drawback however is the reproducibility. Due to this fact the topic was further attended to by V. HARTDEGEN.



Scheme 2. Synthesis of DATGP.

The introduction of ethyl cyanoformate, yielding a tetrazole containing polymer, glycidyl-5-(carboxyethyl-1*H*-tetrazolyl) polymer (GCTP, scheme 3), was more successful in terms of reproducibility. This molecule is thermally and physically stable, with a decomposition point of 208 °C, which exceeds that of GAP (200 °C). It is also insensitive towards impact and friction (IS > 40 J, FS > 360 N). This can be regarded as great advantage in terms of safety. This polymer moreover convinces with its nitrogen content of 30 % due to the tetrazole ring and the unreacted azide groups of the original starting material. These unreacted groups occur due to the molecular structure of the polymer. Because of the sterical hindrance of the voluminous compound not all azide groups of the educt could react with the ethyl cyanoformate. Therefore some unreacted azide groups are left over. The energetic performance of GCTP is excellent, although it is slightly diminished compared to the commonly used GAP, but simultaneously the compound is insensitive as a result of the ethyl carboxylate group.



Scheme 3. Synthesis of GCTP.

In the course of this synthesis a further highly thermally stable molecule, including two ethyl bridged tetrazole rings, 1,2-bis(5-carboxyethyl-1*H*-tetrazolyl)ethane (figure 2) was produced as polymeric precursor of GCTP.

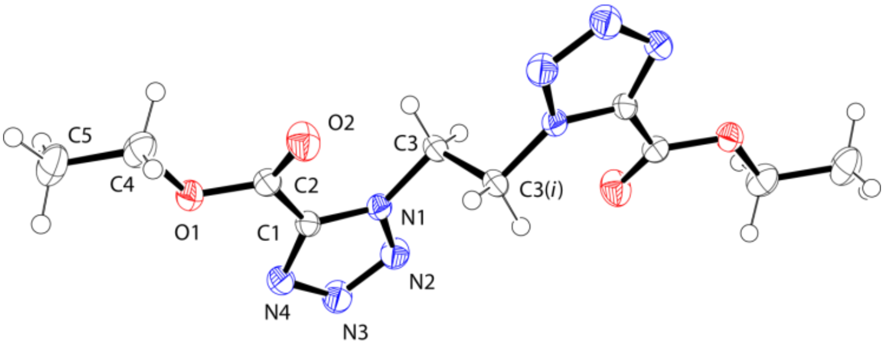
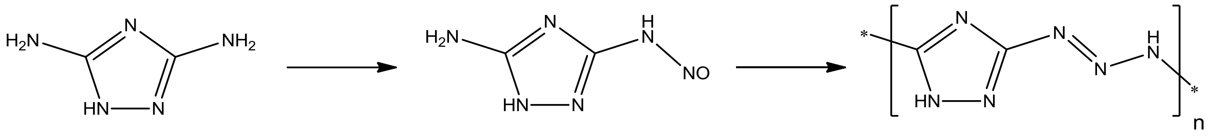


Figure 2. Asymmetric unit of 1,2-bis(5-carboxyethyl-1*H*-tetrazolyl)ethane in the crystalline solid state. Thermal ellipsoids are set to 50 % probability.

This compound complies not only with the requirements due to its thermal stability (decomposition point: 212 °C), but also with its insensitivity towards impact and friction (IS > 40 J; FS > 360 N). Although the detonation velocity is lower than that of GAP, the lower temperature of explosion is an important advantage since this property is directly responsible for the erosion in gun barrels, when it comes to applications. Furthermore, the specific impulse I_{sp} that describes the efficiency of rocket and jet engines is rather good and can be further improved by the addition of ammonium dinitramide as an oxidizer.

The polymerization of triazoles offers various advantages. These compounds feature good nitrogen content and are less sensitive towards outer stimuli as tetrazoles. Consequently the third topic of this work is dealing with the polymerization of triazoles. The possibility of polymerizing 3,5-diamino-1,2,4-triazoles by diazotation offers a great alternative to other energetic binders, as this molecule, poly(3-diazoamino-1,2,4-triazole), has high potential regarding its nitrogen content of 76 % and the facility of further functionalization.



Scheme 4. Synthesis of poly(3-diazoamino-1,2,4-triazole).

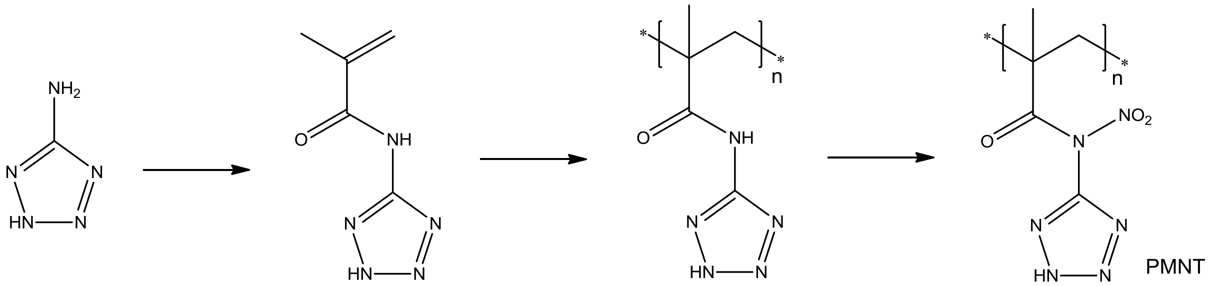
Unfortunately several difficulties occurred during this functionalization, probably due to the fragility of the compound, especially the diazoamino moiety. This group is rather sensitive and reacts effortless with other reagents. On account of this, the molecule decomposes easily and generates not only the desired compound, but also various impurities.

For this reason the functionalizing of poly(3-diazoamino-1,2,4-triazole) was abandoned and the search for energetic nitrogen-rich polymers as binder was turned towards other systems.

The last topic covers the reactions of tetrazole and triazole moieties with methacryloyl chloride and acryloyl chloride. In order to gain substances inheriting two desired properties, on the one side energetic groups, like tetrazoles and triazoles, to increase the nitrogen content and the energetic performance of the molecule and on the other side methacryl and acryl groups to simplify the polymerization process, various compounds were investigated.

To obtain energetic properties achieving or even exceeding those of GAP manifold approaches were undertaken. Regrettably some attempts of introducing tetrazole moieties, even by utilizing a spacer to reduce the sterical hindrance of the molecule and simplifying the polymerization mechanism by the use of catalyst, failed. However some compounds with prospective properties were obtained.

The most promising compound turned out to be the poly(methacrylnitramidotetrazole) (PMNT, scheme 5). The functionalization of 5-aminotetrazole by the methacryloyl chloride and the following nitration of the amido moiety yielding a compound with outstanding properties.



Scheme 5. Synthesis of PMNT.

The high nitrogen content of 42 % of this compound, along with its extraordinary insensitivity towards impact and friction (IS > 40 J; FS > 360 N), excellent energetic performance and good thermal stability, due to its decomposition point of 218 °C, turns this polymer into a promising candidate for the development of new gas generating compositions and an application as environmental friendly nitrogen-rich polymer in binder systems.

Unfortunately the polymeric distribution of the obtained compounds could not be investigated properly as the only gel permeation chromatographs we have access to are run with either water or THF. Due to the insolubility of all gained molecules in these solvents the molcular lengths of the synthesized products could not be determined.

Although during this work some problems occured that arise from dealing with polymers, several of the mentioned molecules were already published or submitted, respectively, to notable journals or even handed in as patent due to ther great performance, insensitivity and utility.

8. Materials and Methods

8.1 Chemicals

All chemical reagents and solvents of analytical grade were obtained from Sigma-Aldrich, Acros Organics, ABCR or as found in the labaroatory and used without further purification. GAP was ordered with an average molecular weight of 2000 g mol^{-1}.

8.2 General Methods

Infrared spectroscopy

Infrared (IR) spectra were recorded using a *Perkin Elmer Spectrum BX FT-IR System* instrument equipped with an ATR unit at room temperature. The intensities are reported in parentheses, distinguishing between very weak (vw), weak (w), medium (m), strong (s) and very strong (vs).

NMR spectroscopy

The NMR spectra were recorded using a *JEOL Eclipse 400* or *JEL Eclipse 270* instrument. ^{1}H, ^{13}C and ^{15}N NMR spectra were measured in [*d6*] DMSO, if not stated different in the experimental section. 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).

Mass spectrometry

Mass spectrometry was performed on a *JEOL MStation JMS-700*. The different ionization methods (EI, DEI, DCI and FAB) are indicated in the experimental section.

Elemental analysis

Elemental analyses were performed with a *Netsch Simultaneous Thermal Analyzer STA 429*.

DSC measurements

DSC measurements were performed by a Linseis DSC PT-10 instrument at a heating rate of 5 °C min^{-1} in a closed aluminum container with a hole (1 µm) on top for gas release with a nitrogen flow of 5 mL min^{-1}. The reference sample was a closed aluminum container. If a volatile compound was measured, a closed aluminum container without hole on top was used.

Melting point

Melting points were either determined using the DSC data or by using a *Büchi Melting point B-540*.

Density

The density of the compounds was either obtained from the crystal structure or was measured by Quantachrome instruments *Ultrapyc 1200e* using the amorphous compound.

Bomb calorimetric measurements

Bomb Calorimetry was undertaken using a *Parr 1356 Isoperibol Bomb calorimeter* with a *Parr 1108CL oxygen bomb*. For the analysis of the solid compounds, 100 mg to 150 mg of the energetic substance was mixed with 950 mg to 1100 mg of benzoic acid. The mixture was converted into a pellet which was used for the measurement.

Crystal structures

The single X-ray diffraction data of **3** was collected using an Oxford Xcalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD area detector with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The data collection was undertaken using the CRYSALIS CCD software[1] while the data reduction was performed with the CRYSALIS RED software[2]. The structure was solved with SIR-92[3] and refined with SHELXL-97[4] implemented in the program package WinGX[5] and finally checked using PLATON[6]. All non-hydrogen atoms were refined anisotropically. Ortep plots are showing thermal ellipsoids with 50 % probability for the non-hydrogen atoms.

Impact and friction sensitivity

The impact and friction sensitivity was determined using a BAM drophammer and a BAM friction tester[7]. The sensitivities of the compounds are indicated according to the UN

Recommendations on the Transport of Dangerous Goods: impact: insensitive > 40 J, less sensitive > 35 J, sensitive > 4 J, very sensitive < 4 J; friction: insensitive > 360 N, less sensitive = 360 N, 360 N > sensitive > 80 N; very sensitive < 80 N, extreme sensitive < 10 N.

8.3 Calculations

Energetic calculations

The energetic properties of the compounds were determined by bomb calorimetric measurements and the density along with calculations using the EXPLO5 software. [8]

Calculations of the enthalpy of formation:

The calculations were performed by Camilla Evangelisti and Sebastian Rest, respectively. The enthalpy of formation was calculated using CBS-4M. [9-14] In the case of the neutral compounds, their calculated sublimation enthalphie was calculated by the Troutons' rule (ΔH_{sub} [kJ mol] = 188 · T_m [K]).[15]

8.4 References

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9. Appendix

9.1 Curriculum Vitae

Franziska Maria Betzler
Geboren am 19. Dezember 1983 in München

PROMOTIONSSTUDIUM

Seit 2009	Promotion im Fachbereich Anorganische Chemie unter der Anleitung von Prof. Dr. Thomas M. Klapötke Ludwig-Maximilians-Universität München

STUDIUM

2007 - 2009	Studium der Chemie, Master of Science (M.Sc.) Ludwig-Maximilians-Universität München
2003 – 2007	Studium der Chemie, Bachelor of Science (B.Sc.) Ludwig-Maximilians-Universität München

BERUFSERFAHRUNG

2008 – 2009	Seminarleiter für Vorlesung der anorganischenChemie an der Ludwig-Maximilians-Universität München
2007 – 2008	Zusammenarbeit mit der Firma Huntsman, Belgien, während eines Auslandspraktikum an der University of Glasgow, UK
2009 – 2010	Studentische Hilfskraft im AK Klapötke, Ludwig-Maximilians Universität
2010 – 2011	Ausbildung von drei Chemielaboranten
ab 2012	Mitarbeiter in der LPU (Labor für Pharma- und Umweltanalytik), Martinsried

9.2 Full List of Publications

9.2.1 Articles

1. . Betz, F. Betzler, P. Kluefers, *Acta Cryst. E*, rac-2-Hydroxy-2-(2-nitrophenyl)acetic acid, **2007**, *E63(10)*, o4184.
2. R. Betz, F. Betzler, P. Kluefers, *Acta Cryst. E*, 2-Bromobenzaldehyde cyanohydrin, **2008**, *E64(1)*, o55.
3. F. M. Betzler, T. M. Klapoetke, *Central European Journal of Energetic Materials*, Energetic nitrogen-rich polymers based on cellulose, **2011**, *8 (3)*, 157-171.
4. J. Callison, F. Betzler, K. de Cuba, W. van der Borden, K. van der Velde, R. H. Carr, H. Senn, L. J. Farrugia, J. M. Winfield, D. Lennon, *Industrial and Engineering Chemistry Research*, Origin of impurities formed in a polyurethane production chain. Part 2: A route to the formation of coloured impurities, **2012**, *51* (34), 1021-11030.
5. F. M. Betzler, T. M. Klapoetke, S. M. Sproll, *European Journal of Organic Chemistry*, Synthesis of 1,2-Bis-(5-carboxyethyl-1*H*-tetrazolyl)ethane as Polymeric Precursor, **2013**, 509-514.
6. F. M. Betzler, R. Boller, A. Grossmann, T. M. Klapötke, *Z. Naturforsch.*, Novel Insensitive Energetic Nitrogen-Rich Polymers based on Tetrazoles, *submitted*.

9.2.2 Poster Presentation

1. F. Betzler, T. M. Klapoetke, S. Sproll, *New Trends in Research of Energetic Materials*, *Proceedings of the Seminar*, *12th*, New energetic polymers based on cellulose, Pardubice, Czech Republic **2009**, 451-454.
2. F. Betzler, T. M. Klapoetke, *New Trends in Research of Energetic Materials*, *Proceedings of the Seminar*, *13th*, New energetic nitrogen-rich polymers, Pardubice, Czech Republic **2010**, 408-412.

3. F. Betzler, T. M. Klapoetke, *New Trends in Research of Energetic Materials, Proceedings of the Seminar, 14*th, New energetic nitrogen-rich polymers, Pardubice, Czech Republic **2011**, 485-489.

9.2.3 Patent

1. F. Betzler, A. Hahma, O. Pham, T. M. Klapötke, Nitraminocellulose als Binder in Pyrotechnik und Treibstoffen, *submitted*.

9.1 List of Abbreviations

Abbreviation	Meaning	Abbreviation	Meaning
a.u.	atomic units (Hartree)	NMR	nuclear magnetic
calcd.	calculated	ppm	parts per million
D	detonation velocity	$p_{C\text{-}J}$	detonation pressure
dec.	decomposition	q	quartet
DMF	dimethylformamide	RT	room temperature
DMSO	dimethylsulfoxide	s (NMR)	singlet
DSC	differencial scanning	s	solid phase
EI	electron ionization	s (IR)	strong
g	gas phase	T	temperature
h	hours	t (NMR)	triplet
Int.	intensity	vs (IR)	very strong
IR	Infrared	vw (IR)	very weak
$\boldsymbol{I_{sp}}$	specific impulse	w (IR)	weak
J	coupling constant	Å	Angström (10^{-10} m)
l	liquid phase	δ	chemical shift
m (IR)	medium	ρ	density
m (NMR)	multiplet	Ω	oxygen balance
min	minutes	ν	frequency
m.p.	melting point		

Further abbreviations are explained within the thesis.