

4-Amino-1-Butyl-1,2,4-Triazolium Nitrate – Synthesis and Characterization

Uwe Schaller,^{*[a]} Thomas Keicher,^[a] Volker Weiser,^[a] and Jürgen Hürttlen^[a]

Abstract: An improved synthesis of the energetic ionic liquid 4-amino-1-butyl-1,2,4-triazolium nitrate (C4 N) is presented via a one-step metal-free route using butyl nitrate. C4 N offers promising properties like very low vapour pressure combined with good insensitivity. In addition, long-term and thermal stability were investigated. The potential

use as an energetic additive to improve the rheological properties of GAP-based energetic polymers was studied resulting in an almost four times lower viscosity at 15 wt.-% C4 N content. As an additive to a nitromethane-based monopropellant C4 N works as burning rate modifier which additionally reduces the propellant sensitivity.

Keywords: Energetic Ionic Liquids · Characterization · Triazolium · Nitrate · Additive

1 Introduction

Ionic liquids are in the focus of current research and are used in more and more areas of life. The spectrum of applications includes novel reaction media [1], electrolyte in batteries [2], media for electrodeposition of metals [3], solar cells [4], gas storing media [5], lubricants [6] and additives in polymer systems [7], to mention only a small excerpt of the investigated and in-use applications.

Studies on ionic liquids are documented for the first time back to the 19th century [8]. More detailed investigations on the phenomenon of low-melting salts were carried out in 1888 with ethanolammonium nitrate (T_m 52–54 °C), an energetic protic ionic liquid synthesized and characterized by Gabriel [9] and ethylammonium nitrate (T_m 13–14 °C, Paul Walden 1914 [10]). However, the new class of ionic liquids only became subject of interest in the late 1990s, where the publications on ionic liquids started growing significantly [1].

In the field of energetic materials and their processing, ionic liquids receive serious interest [11]. The energetic ionic liquids (EILs) can be divided into three different categories as shown in Figure 1.

For Melt Cast EILs, melting points (T_m) above 80 °C are crucial to replace the toxic trinitrotoluene (TNT), which furthermore shows poor Insensitive Munition (IM) properties [13]. The developments in this area has begun at the beginning of the 20th century in search of castable explosive mixtures of energetic salts with low melting points (e.g. dimethylammonium nitrate or hydrazinium nitrate) [14].

A theoretical explanation for the low melting or glass transition points of ionic liquids is based on the Gibbs energy of fusion. The liquid state in ionic liquids is thermodynamically favourable, because of the size and conformational flexibility of the ions involved, resulting in small lattice enthalpies and large entropy changes that favour

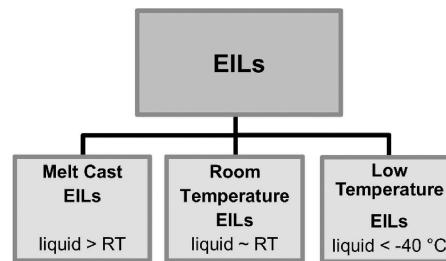


Figure 1. Classification of EILs by temperature range [12].

melting [15]. Among the most studied IL cations are asymmetrical imidazolium cations like 1-ethyl-3-methylimidazolium and 1-butyl-3-methyl-imidazolium which tend to hamper an efficient crystal packing. The same principle shows up in C4 N with an asymmetrical triazolium cation and the symmetrical nitrate anion. In C4 N, 4-amino-1,2,4-triazole (nitrogen content: 66.6%) instead of 1-methylimidazole (nitrogen content: 34.1 %) is used as an educt resulting in a significantly higher nitrogen content. C4 N was first published by Greg W. Drake et al. [16] using the corresponding bromide salt and the silver route. Even with small residues of silver cations and bromide anions compat-

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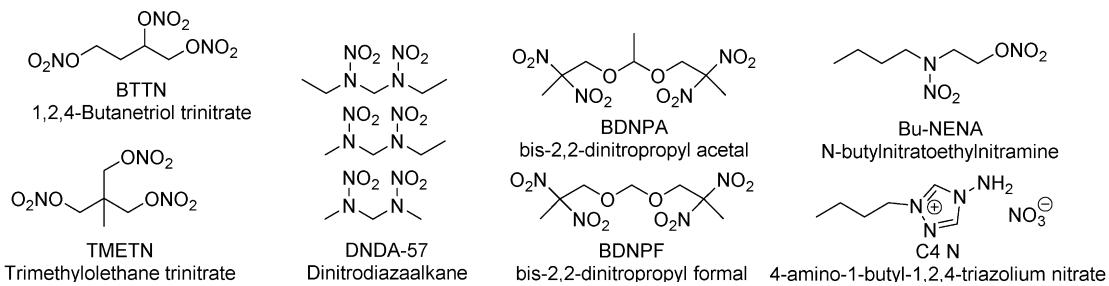


Figure 2. Structural formulas of modern energetic plasticizer and C4 N.

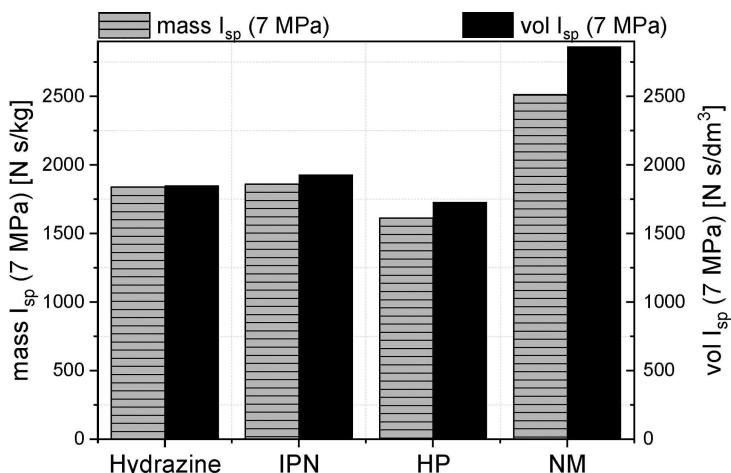


Figure 3. Mass-specific (mass I_{sp}) and volume-specific impulse (vol I_{sp}) of hydrazine, isopropyl nitrate (IPN), hydrogen peroxide (HP) and nitromethane (NM) at an expansion ratio of 70:1 calculated with ICT Thermodynamic Code (frozen equilibrium) [26].

ibility and long-term stability problems can arise. We developed and published a method for synthesizing C4 N without the use of heavy metal cations using 4-amino-1-butyl-1,2,4-triazolium chloride (C4 Cl) and ammonium nitrate for anion metathesis [17]. Now we present a direct method which is metal and halogen-free, shows an advanced atom economy and is a direct one-step method starting from 4-amino-1,2,4-triazole and n-butyl nitrate. Alkylation with nitrate ester was used over 120 years ago [18] and already during this time nitrate esters were used to synthesize the corresponding alkylated organic nitrate salts [19] but is rarely mentioned or used nowadays [20]. Through advanced micro-reaction techniques, organic nitrate esters, which have broad applications as plasticizers, are easily accessible on a safe and reliable method in multigram to kilogram scale [21]. In the field of energetic plasticizer, the most common modern plasticizers are shown in Figure 2 with C4 N.

Although these energetic plasticizers have already proven their suitability and reliability, new plasticizers with improved properties are still being under research to enable new applications [22]. For example, non-volatile plasticizers are required especially for additive manufacturing using the FDM (Fused Deposition Modelling) process, in which the

entire polymer formulation is heated/melted twice, once during filament production and subsequently during the additive manufacturing process.

Another area that has been researched for at least as long as energetic plasticizers are liquid or gelled monopropellants for ground-based systems. One very intensively studied candidate is nitromethane (CH_3NO_2 , NM), the simplest nitroalkane which is available. The use of nitromethane in combustion processes especially as monopropellant is under investigation for more than 70 years [23]. It is still in focus of nowadays gelled propellant research with its oxygen balance of -39% and is, therefore, able to burn without additional oxidizers [24].

In comparison to other monopropellants such as hydrazine, isopropyl nitrate, and hydrogen peroxide [25], nitromethane has a higher theoretical specific impulse as shown in Figure 3.

As NM shows favourable performance data in its use as a monopropellant, sensitivity towards impact and detonation is critical to fulfil modern IM requirements. NM shows a mechanical sensitivity towards impact, according to BAM test procedure for liquid samples [27]. The results can vary significantly depending on the sample position. If placed in the correct sample position for liquids between

steel guide ring and steel cylinder an impact sensitivity of above 5 N·m is measured [28], whereas an impact sensitivity of 25–30 N·m is measured, if NM is placed in the centre, the sample position for solids or gels [28]. Few percent of gelling agent enable the gelation of NM [29] and therefore, a different sample position has to be chosen according to BAM procedure [27]. The obtained impact sensitivity values are better than with pure liquid NM and give the impression of increased safety. However, this effect cannot be attributed mainly to the gelation but more likely to the modified test position within the BAM drop hammer test. Therefore, additives for NM to increase insensitivity and not strongly reducing performance are still under research and EILs are under consideration.

2 Experimental Section

2.1 General

Safety precautions for the handling of energetic materials must be applied. All laboratory chemicals used were sourced from Aldrich, Merck, abcr or Carl Roth. Nitromethane (purity 99.9%) has been purchased from LD Sportsline 2000 GmbH. For NMR spectroscopy deuterated solvents ($\text{DMSO}-d_6$) were stored via molecular sieve (3 Å). Most of the energetic plasticizers used for the comparison were synthesized at ICT (EGDN, BTTN, and TMETN). DNDA-57 was received from Zelinsky Institute in Moscow and BuNENA, BDNPA/F from Chemring Nobel. GAP-DIOL (06 S12) was supplied from Eurelco. All solvents used for anion metathesis had p. A. quality and were dried via conventional techniques. The ethanol used was denatured with dichloromethane. Amberlyst® A-26 was purified and loaded with nitrate as described in Ref. [30] and used for further purification of C4 N via anion metathesis.

^1H -NMR and ^{13}C -NMR spectra were collected on a 400 MHz Bruker AV-400 spectrometer in $\text{DMSO}-d_6$. Differential scanning calorimetry (DSC) was done on TA instruments Q 1000 using pierced aluminium pans. Scans were carried out on each sample, at heating rates of 5 K/min, under nitrogen flux (25 mL/min). Glass transition points were measured from the 2nd heating cycle after cooling to –90 °C. Reported values are inflection point temperatures. Thermogravimetric analysis (TGA) was done on a TA Q500 apparatus with a heating rate of 10 K/min in a platinum 100 μL pan under nitrogen flux (25 mL/min). Reported values are the central points, according to DIN EN ISO 11358. Infrared spectroscopy was done on a Nicolet SX 5 spectrometer. Impact sensitivity and friction sensitivity tests were determined according to NATO STANAG 4487 and NATO STANAG 4489 procedures with the BAM-Impact sensitivity tester and the BAM-Friction sensitivity tester made by the former company Julius Peter (Berlin). The samples used were bubble-free and filled between steel guide ring and steel cylinder. Aluminium tubes (wall thickness 1.5 mm) and

aluminium witness plates (thickness 4 mm) were used with a diameter to length ratio of 1:6. Seismoplast (Eurodyn) was used as booster charge – for 10 mm 2.2 g, 13 mm 3.7 g, 15 mm 4.9 g. Rheological measurements were done with a Rheometer Physica MCR 501. Performance data were calculated with ICT Thermodynamic Code [26], impulses are calculated with frozen equilibrium at a chamber pressure of 7 MPa and an expansion pressure of 0.1 MPa. Heat flow calorimetry was performed on TAM III by TA Instruments, USA, using stainless steel ampoules with glass inlets under normal atmospheric conditions. ARC was conducted on an ARC® instrument from Thermal Hazard Technology using a sample mass between 300–500 mg to obtain same Φ factor. SET Test was performed with a heating rate of 5 °C/min and 0.2 g of sample mass. GAP-based energetic thermoplastic elastomers (ETPE) was used produced out of 74 wt.-% GAP-Diol, 5.5 wt.-% ethylene glycol and 20.5 wt.-% hexamethylene-1,6-diisocyanate as described in Ref. [31] with other chain extenders.

To measure burning rates the liquids were filled into glass test tubes (Ø 8 mm, length 70 mm) and burnt under nitrogen in an optical bomb, which is a high-pressure autoclave equipped with glass windows allowing the application of non-intrusive combustion measurement techniques as in this case of a colour high-speed camera (Redlake MotionPro X3) and an emission spectrometer (ZEISS MCS 611 NIR 2.2). The experimental setup is described in detail in Ref. [32]. The burning rates are derived from video records with image post-processing [33]. NIR-emission spectra of the water bands between 1 and 2 μm were used to determine the flame temperature applying the ICT-BAM method described in Ref. [32].

2.2 Synthesis

The microwave-assisted synthesis of the triazolium salts was performed with a CEM Discovery microwave using fibre-optic temperature sensors for temperature control. The evaporation of solvent mixtures and C4 N was performed using a modified remote-controlled rotary evaporator based on a Heidolph Hei-VAP™ Precision. Drying was performed in an oven at 60 °C for 48 hours in a diaphragm pump vacuum and continued with a turbopump (Pfeiffer HiCube™ 80) for 24 hours. C4 N was handled via Schlenk technique or in a glove box (GSconcept from GS GLOVEBOX Systemtechnik GmbH) using argon (5.0). The increase of C4 N concentration in the reaction mixture of butyl nitrate and 4-amino-1,2,4-triazole at different temperatures was determined by ^1H -NMR after removing the non-reacted butyl nitrate in a vacuum without further isolation.

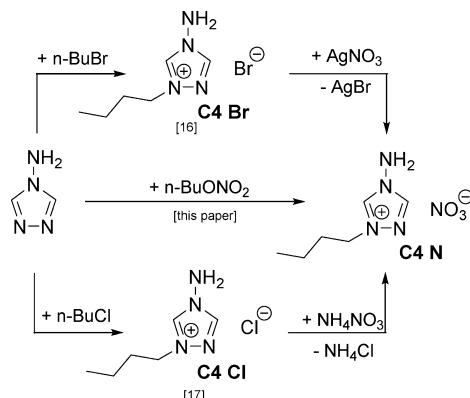


Figure 4. Published synthesis route to C4 N (top, bottom) and selected routes presented in this paper.

2.3 4-Amino-1-butyl-1,2,4-triazolium nitrate (C4 N)

A stirred suspension consisting of 4-amino-1,2,4-triazole (14.28 mmol, 1.20 g) and butyl nitrate (17.86 mmol, 2.13 g) in methanol (28.57 mmol, 0.92 g) and acetonitrile (57.14 mmol, 2.34 g) was stirred for 4 h at 100 °C yielding C4 N (2.55 g, 12.57 mmol, 88%) after pouring on acetonitrile/ethyl acetate (1:2), phase separation and drying.

$T_g = -59.0^\circ\text{C}$. $T_d = 248.9^\circ\text{C}$. $\text{TGA} = 239.4^\circ\text{C}$. Density = 1.245 g/cm³. $^1\text{H-NMR}$ (DMSO-d₆, 400 MHz): δ (ppm) = 0.89 (3H, t, C10), 1.27 (2H, m, C9), 1.81 (2H, d, C8), 4.34 (2H, m, C7), 6.99 (2H, s, NH₂), 9.19 (1H, s, C3), 10.23 (1H, s, C5). $^{13}\text{C-NMR}$ (DMSO-d₆, 101 MHz): δ (ppm) = 13.5 (C10), 18.9 (C9), 30.3 (C8), 51.7 (C7), 143.0 (C3), 145.5 (C5). FT-IR (ATR, cm⁻¹) = 3275 (w), 3123 (w), 2962 (w), 2876 (w), 1638 (w), 1564 (w), 1319 (s), 1165 (m), 1075 (w), 988 (m), 882 (w), 828 (w), 755 (w). FT-RAMAN (cm⁻¹) = 3153 (w), 2917 (m), 2875 (m), 2737 (w), 1566 (w), 1526 (w), 1445 (m), 1412 (m), 1312 (w), 1115 (w), 1076 (m), 1043 (s), 991 (w), 825 (w), 711 (w), 605 (w). **Impact sensitivity** = > 50 Nm. **Friction sensitivity** = > 360 N. Data correspond to the published results in Ref. [17].

3 Results and Discussion

3.1 Synthesis

The published synthesis route for C4 N proceeds via alkylation at the triazole nitrogen atom in position 1 using n-bromobutane (n-BuBr) and subsequent anion metathesis using silver nitrate [16] (Figure 4 top).

When using a metal-free nitrate source for the anion metathesis, bromide and iodide salts as starting materials cannot be used. The corresponding salts, which are usually removed from the product by precipitation, are too soluble in organic solvents. Starting from 4-amino-1,2,4-triazole and n-chlorobutane (n-BuCl) leads to C4 Cl which opens the route to C4 N via the metal free metathesis reaction with

ammonium nitrate. However, the reaction time for the alkylation step is significantly increased compared to the use of n-BuBr as we have shown in Ref. [17] (Figure 4 bottom).

The one-step method for C4 N (Figure 4 middle), which is more atom efficient and free of foreign ion impurities especially halogen ions, can be used for all conventional nitrate based alkylated EILs. However, the alkylation strength decreases significantly from methyl nitrate to butyl nitrate comparable to the corresponding chloroalkyl compounds. While methyl nitrate can react with 4-amino-1,2,4-triazole at RT within 4 weeks nearly quantitatively, for alkylation with butyl nitrate, high temperatures have to be applied. Although the heating of n-butyl nitrate and 4-amino-1,2,4-triazole was done remotely, safety investigations were conducted via measuring the adiabatic self-heating rates of the reaction mixtures at different concentrations of the nitrate ester (identical molar ratio – 1:1.25). A reaction mixture containing 30 wt.-% of n-butyl nitrate does not show any thermal runaway reactions and no sharp increase in the self-heating rate (Figure 5 left).

After 1920 min at 100 °C, an only slightly yellowish reaction mixture was obtained showing a conversion of >99% from 4-amino-1,2,4-triazole into C4 N as measured by $^1\text{H-NMR}$. At a reaction temperature of 110 °C under otherwise identical conditions, red coloration of the reaction solution is already visible after 240 min (Figure 5 – picture right) due to decomposition reactions. After 240 min at 110 °C reaction temperature, a decrease of the product in the reaction mixture was recognized and further investigations were stopped.

3.2 Characterization

An overview of the properties of C4 N in comparison to conventional energetic plasticizers is shown in Table 1. C4 N offers a wide operating temperature range with a very low mechanical sensitivity and still has a high gas volume yield at decomposition conditions. The heat of explosion is the lowest in the overview due to the strong negative oxygen balance but could be improved by creating eutectic mixtures with the corresponding methyl (~65%) or ethyl (~87%) analogues of C4 N.

To investigate the long-term stability a TAM measurement of C4 N at 80 °C for 40 days revealed no significant generation of heat as shown in Figure 6 (left). An ARC measurement of C4 N is shown in Figure 6 right showing the peak maximum slightly above the measured self-ignition temperature (SET) of 246 °C. These results indicate a good long-term and thermal stability of C4 N.

In contrast to conventional plasticizers like nitrate esters, BDNPA/F and DNDA-57, C4 N does not evaporate upon heating in nitrogen flux up to 120 °C due to its ionic nature (see Figure 7). And as the investigated traditional energetic plasticizer showing a mass loss of 3–15 wt.-%, no mass loss for C4 N under the same conditions was observed. Heating

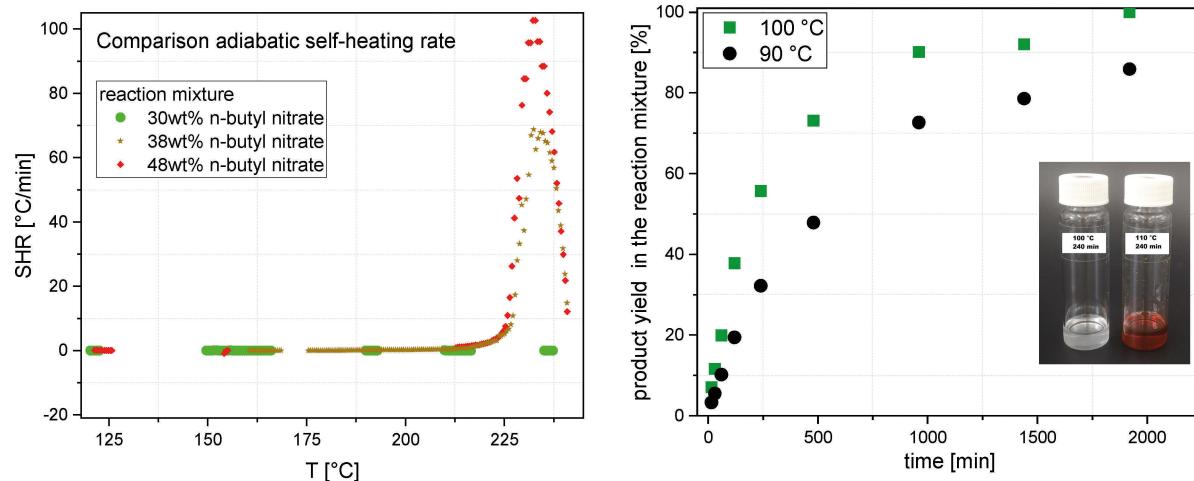


Figure 5. Accelerating rate calorimeter (ARC) measurements for reaction mixture of n-butyl nitrate and 4-amino-1,2,4-triazole (left) and increase of C4 N in the reaction mixture at 90 °C and 100 °C (right) with a picture of the reaction mixture after 240 min at 100 °C and 110 °C.

Table 1. Comparison of conventional energetic plasticizers to C4 N [12, 17].

	Glass transition temperature (DSC) [°C]	Decomposition temperature (TGA) [°C]	Impact sensitivity [Nm]	Heat of explosion ^[a] [J/g]	Oxygen balance [%]	Nitrogen content [%]	Gas volume ^[b] [cm ³ /g]
BTTN	-65	156	1	6022	-16.6	17.4	634
TMETN	-62	155	1	5053	-34.5	16.5	794
DNDA57	-52	159	3	3848	-72.3	30.9	1078
BDNPAF	-67	182	3	3469	-57.6	17.6	957
Bu-NENA	-82	152	6	3573	-104.3	20.3	1045
C4 N	-59	239	> 50	2708	-122.0	34.5	1057

^[a] calculated by ICT-Thermodynamic code (water liquid), ^[b] without H₂O at 25 °C.

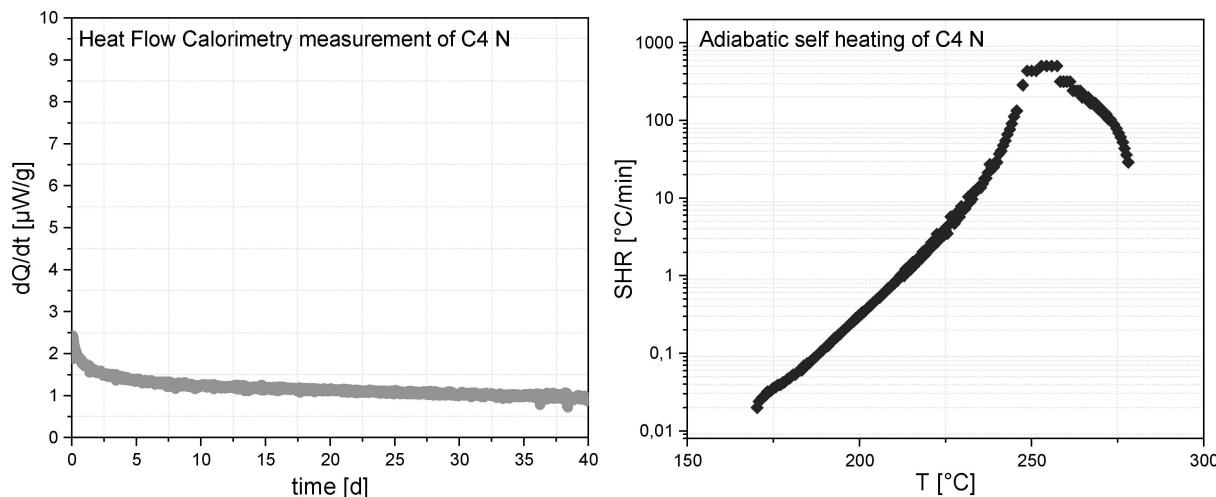


Figure 6. Heat Flow Calorimetry measurement of C4 N in a Thermal Activity Monitor calorimeter at 80 °C for 40 days (left) and adiabatic self-heating of C4 N (right).

isotherm in nitrogen flux at 120 °C for 120 minutes caused for all conventional investigated energetic plasticizers a weight loss between 49.9–99.8 wt.-%. However, under same

conditions C4 N showed only 3.0 wt.-% weight loss. Because of the very low vapour pressure of C4 N, a significantly reduced environmental risk and better handling

plasticizer	mass loss 120 °C [wt.-%]	mass loss 120 °C / 2 h [wt.-%]
BTTN	11.0	99.6
TMETN	10.7	99.6
DNDA57	8.4	99.8
Bu-NENA	15.0	97.5
BDNPFA/F	2.5	49.9
C4 N	0.0	3.0

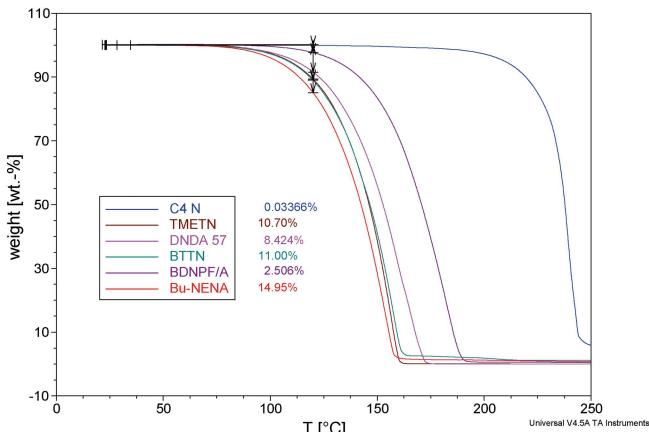


Figure 7. Mass loss of different energetic plasticizers during heating in a nitrogen stream (TGA).

properties are expected. This aspect is important especially for additive manufacturing of energetic material formulation via the FDM (Fused Deposition Modelling) method.

In our former work, C4 N was already investigated as a mixture with the methyl analogue of C4 N (50:50 wt.-%) in polyester-based polyurethane elastomers and showed an increased strain capability combined with higher maximum tensile strength [34]. As an example of an energetic polymer for additive manufacturing, a GAP-based ETPE was used to investigate the viscosity decrease by the addition of C4 N. At a typical processing temperature of 110 °C the viscosity was measured with 5, 10 and 15 wt.-% addition of C4 N (Figure 8). To measure pure ETPE in rotation mode the ETPE had to be measured at 120 °C. At a shear rate of 1 s⁻¹, the viscosity of the ETPE/C4 N (15 wt.-%) mixtures was almost four times lower than that of pure ETPE ($1.4 \cdot 10^7$ mPa·s vs $3.6 \cdot 10^6$ mPa·s). So C4 N can significantly reduce processing viscosities during the production of energetic for-

mulations and due to its high thermal stability combined with its low vapour pressure, processing operations at elevated temperatures can be performed much safer. Furthermore, it provides the possibility to increase the energetic crystalline filler content, like RDX or HMX, in energetic filament formulations.

Safety issues have to be considered if an energetic filament is processed via the FDM method and pressed through a heated nozzle. Therefore, the adiabatic self-heating of a GAP-based ETPE alone and with increasing C4 N content in an ARC has been measured and is shown in Figure 9. Pure ETPE showed the earliest and steepest increase of the self-heating rate (SHR) over the temperatures showing the thermal runaway safety is improved by C4 N.

Another important property for energetic materials is their glass transition temperature. The improvement of the glass transition temperature was only marginally by C4 N in the investigated GAP-based ETPE (1 °C). Modified side chains of the triazolium cation might be necessary to ach-

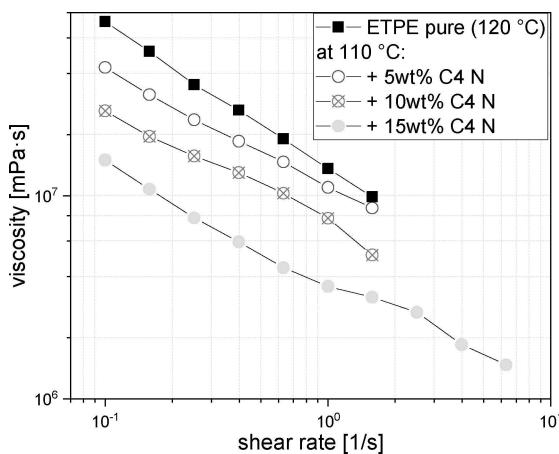


Figure 8. Viscosity of GAP-based ETPE with increasing C4 N content at different shear rates.

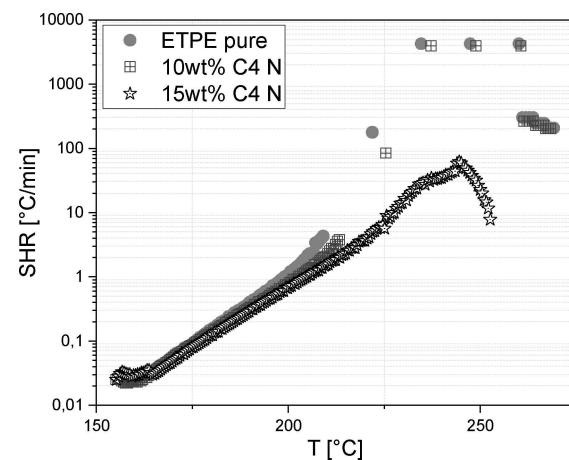


Figure 9. Adiabatic self-heating of GAP-based ETPE pure and with C4 N (10 wt.-%, 15 wt.-%).

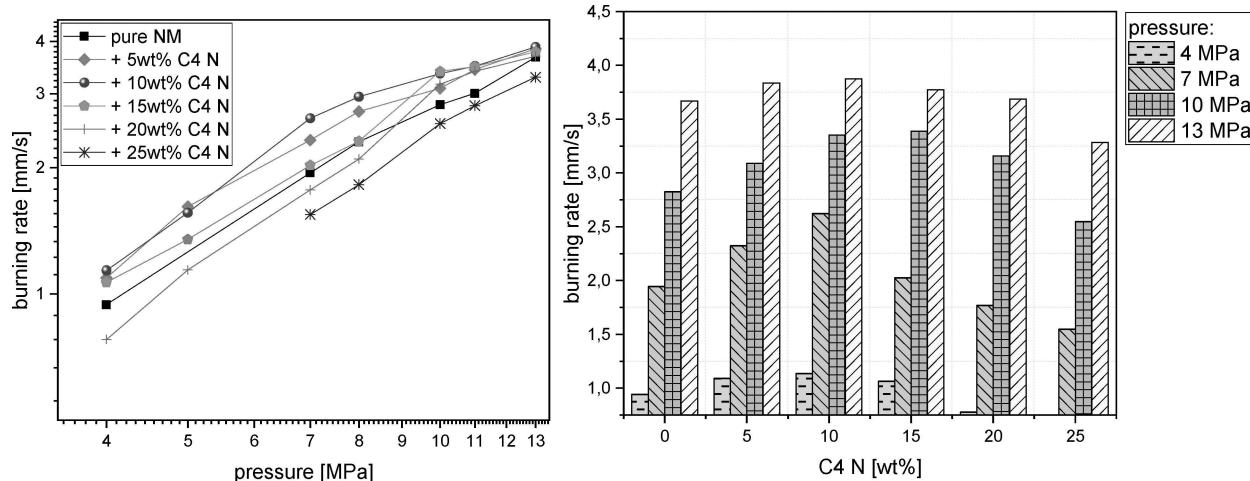


Figure 10. Burning rate of NM and NM/C4 N mixtures at different pressures.

ieve a better interaction between the polymer chain of the polyether GAP and the EIL. Another approach would be synthesizing GAP-based ETPE using a more polar isocyanate instead of the nonpolar hexamethylene diisocyanate or more suited chain extender.

In this context, C4 N can be more considered as a processing additive for ETPE than as an effective plasticizer for GAP-based ETPE systems and as a starting point for new task-specific EILs.

Besides as additive in ETPEs, we were interested to evaluate possible benefits from C4 N with its good insensitivity as an additive in liquid propellants. The potential of C4 N as a component in NM-based monopropellant mixtures was investigated by testing mixtures of NM/C4 N in an optical bomb. Burning rates of the combustion of pure NM and NM/C4 N mixtures are shown in Figure 10. Upon adding C4 N to NM, the burning rate increases reaching a maximum of 3.9 mm/s at 13 MPa and 10 wt.-% and then subsequently dropping down with increasing C4 N content.

Figure 11 summarizes measured maximum temperatures of each test as function of pressure. The temperature maxima are usually found close above the condensed surface. The temperature of pure NM increases from about 2070 K at 4 MPa to 2150 K at 13 MPa. With added C4 N, a temperature maximum at 7 MPa is observed. At higher pressure, the flame temperature decreases. The temperatures of NM/C4 N mixtures are lower than of pure NM and decreasing with C4 N content.

Performance data of the mixtures calculated using ICT-Thermodynamic Code [26] are shown in Figure 12. The specific impulse (frozen equilibrium 70:1), adiabatic combustion temperature and oxygen balance decrease with addition of C4 N. At an addition of 10 wt.-% C4 N, the specific impulse is lowered by 4% whereas the adiabatic temperature drops by 10% to 2210 K and at 18 wt.-% C4 N the adiabatic combustion temperature reaches 2000 K. Low combustion temperatures are advantageous because they

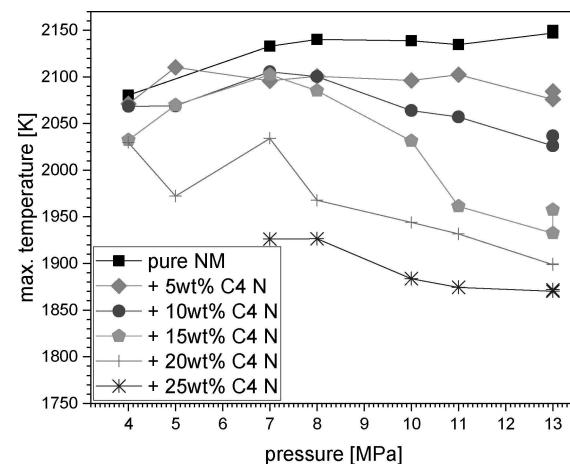


Figure 11. Maximum measured temperature of NM and NM/C4 N mixtures at different pressures.

significantly reduce the demands on a non-regenerative cooled combustion chamber.

The calculated adiabatic temperatures widely correlate with the measured ones in Figure 11. The difference of about 200 K is characteristic and can be explained due to heat loss. Even at 25 wt.-% C4 N, the calculated mass and volume specific impulse (2130 N s/kg, 2479 N s/dm³) is higher than that of all conventional monopropellants shown in Figure 3.

One important parameter for liquid propellants is their viscosity. The viscosity increases by adding C4 N to NM from 0.61 mPa·s for pure NM to 0.73 mPa·s (10 wt.-% C4 N) and 1.10 mPa·s (20 wt.-% C4 N). This increase of viscosity can be considered only marginal and will not limit the application of C4 N as liquid propellant additive. For the handling of a propellant, the sensitivity toward impact is essential. A mixture of NM with 10 wt.-% C4 N showed impact sensitivity above 50 Nm (pure NM 6–30 Nm [28], own meas-

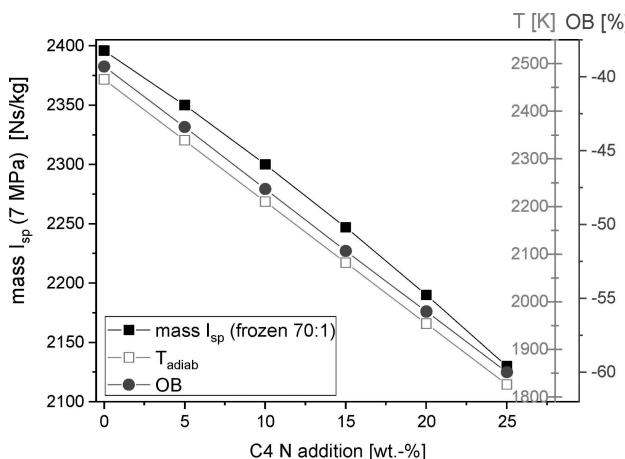


Figure 12. Calculated mass specific impulse (I_{sp}), adiabatic combustion temperature (T_{adia}) and oxygen balance (OB) of the investigated NM/C4 N mixtures at an expansion ratio of 70:1.

urements 30 Nm). The BAM drop hammer test has been performed three times resulting each time 0 of 6 positive tests. However, for liquids, the impact sensitivity measurements using a drop hammer should not be overestimated regarding insensitivity. Therefore, we conducted detonation tests in aluminium tubes to verify the increased insensitivity. Pure NM did not detonate in 10 mm (0/3) but detonated in 13 mm diameter in this test conditions (Figure 13), which is in good agreement with published results [35]. NM/C4 N mixture containing 10 wt.-% of C4 N did not detonate in 13 mm (0/3) and therefore showing an increased insensitivity towards shock waves. However, in 15 mm diameter, the next tested diameter, a full detonation was already achieved as shown in Figure 13 (bottom).

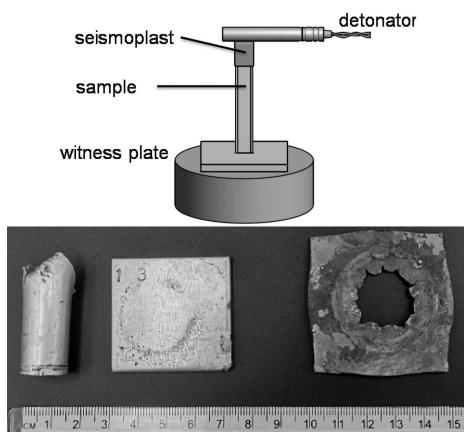


Figure 13. Test setup for the critical diameter of NM and NM/C4 N mixture and results of NM/C4 N 10 wt.-% mixture in aluminium tubes with an inner diameter of 13 mm and 15 mm.

4 Conclusion

A new synthesis route (metal-free and halogen-free) for the synthesis of the nitrate-based EIL C4 N was established and successfully performed in multigram scale. C4 N offers promising properties like very low vapour pressure combined with good insensitivity (> 50 Nm) and a wide potential operation temperature range. With its good thermal and long-term stability, it may find application as a processing additive in GAP-based ETPE compositions to enable additive manufacturing via FDM process, however, without decreasing the glass transition temperature. Another promising application for C4 N is its use as an additive in NM-based monopropellants to improve the insensitivity by reducing the sensitivity to mechanical stimuli and shock waves while simultaneously increasing the burning rate and slightly reducing the specific impulse. Based on these results, C4 N prepares the pathway for new task-specific EILs and systems with improved properties.

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