Research Article

Propellants,
Explosives,
Pyrotechnics

doi.org/10.1002/prep.202100368

pep.wiley-vch.de

Energetic Polymers: A Chance for Lightweight Reactive Structure Materials?

Max Born,[a] Jakob Plank,[a] and Thomas M. Klapötke*[a]

Abstract: Today's ammunition still consists of about 70 wt% structure-providing materials such as metals providing no energetic contribution. Therefore, reactive structure materials (RSMs) offer tremendous room for improvement. While current research focuses on rather heavy, metal-based materials (e.g., alloys, thermites), energetic polymers appear as an under-recognized opportunity for very lightweight RSMs. Unfortunately, suitable polymers are unavailable as energetic polymer research has almost exclusively focused on elastic binders with the least possible glass transition temperature. An application as RSM, however, requires rigid polymers with a glass transition above operational temperatures. Accordingly, monomers with fundamentally different structures are required. The first step in this particular direction is 3-(2,4,6-trinitrophenoxy)oxetane (TNPO). Herein, we report the synthesis of its homopolymer and investigate its polymerization behavior by copolymerization with prior art energetic oxetanes. All polymers were intensively studied by vibrational and multinuclear (^{1}H, ^{13}C, ^{14}N) NMR spectroscopy, elemental analysis, gel permeation chromatography, and differential scanning calorimetry (DSC). Hereby, DSC revealed the high effect of the TNPO repeating unit on the glass transition temperature. The performance of all polymers was calculated using the EXPLO5 code to evaluate the potential performance range of polymeric RSMs. Further, their shock and friction sensitivity was determined by BAM standard procedures.

Keywords: Energetic polymers · Energetic oxetanes · Reactive structure material · 2,4,6-trinitrophenoxyoxetane · TNPO

1 Introduction

Modern ammunitions and effector systems contain only about 30 weight percent of energetic fillers like secondary explosives, while the predominant mass fraction is constituted by structure-providing materials such as metals (e.g., steel, aluminum) that offer no energetic contribution [1]. A potential solution to reduce deadweight is provided by reactive structural materials (RSM), which serve as structural elements and store chemical energy which is released upon a suitable stimulus [1]. Although the first RSMs were composites of polytetrafluoroethylene and aluminum [2,3] which could be viewed as predecessors of polymer-based RSMs, research has almost exclusively focused on metal-based materials such as thermites or alloys, which provide additional energy through redox reactions [1]. However, the underlying chemical reactions are often too slow and require the presence of gaseous oxidizers such as atmospheric oxygen, thereby limiting the scope of application [1]. Therefore, energetic polymers with sufficient performance and mechanical properties appear far more promising as they require no oxidizer, react much faster (deflagration or detonation), and can drastically reduce the effector systems weight due to their lower density compared to metal-based materials. Hence, polymeric RSMs may contribute to a high weight reduction and thereby an increased operational range [4]. Conceptual applications range from structure-providing casings to combustible single components. For this purpose, thermoplastic polymers of low sensitivity, high performance, mechanical strength, and thermostability together with processability by conventional techniques (e.g., extrusion, 3D printing), appear to be most suitable [4]. However, to provide the necessary stiffness and mechanical strength for the envisioned use, polymeric RSMs ought to be employed below their glass transition temperature (T_G) – similar to technically relevant everyday polymers like polycarbonates (PC), polystyrene (PS), or acrylonitrile-butadiene-styrene (ABS) terpolymers. This is very problematic, as energetic polymer research has focused almost exclusively on binders that are elastic at operational temperatures to absorb mechanical forces acting upon an energetic formulation, thereby reducing the overall sensitivity toward friction and impact [5,6]. Therefore, binder polymers are re-

---

[a] *M. Born, J. Plank, T. M. Klapötke*
Department of Chemistry and Biochemistry, Energetic Materials Research, Ludwig-Maximilian University, Butenandtstr. 5–13 (D), 81377 Munich, Germany
**e-mail: tmk@cup.uni-muenchen.de*

Supporting information for this article is available on the WWW under https://doi.org/10.1002/prep.202100368

quired to exhibit a T_G as low as possible (e.g., glycidyl azide polymer (GAP): −46 °C) [5,6]. As the glass transition temperature correlates with a polymer's chain flexibility, high chain rigidity is needed to achieve high glass transition temperatures [7]. In the case of polyoxetanes, this can be implemented, for instance, by bulky side-groups which impose rigidity to the polymer chains by their steric demand or through interlocking and intermolecular interactions [7]. For example, aromatic or heteroaromatic structures could be employed. Hence, 3-(2,4,6-trinitrophenoxy)oxetane (TNPO), which was first described by *Born et al.* in 2019, represents the first monomer of a potentially suitable structure. It is formally a picric acid derivative and can be obtained by a one-pot reaction between picryl chloride and lithium oxetan-3-olate formed *in situ* from lithium hydride and commercially available oxetan-3-ol in THF [8]. Moreover, it combines very low sensitivity with sufficient thermostability and performance comparable to TNT. Herein, we report the preparation of its homopolymer by cationic ring-opening polymerization (CROP) using the well-known boron trifluoride etherate/diol initiator system. In addition, TNPO was copolymerized with various, energetic state-of-the-art oxetanes. As these are known to polymerize readily, conclusions about TNPO's polymerization behavior and any adverse effects caused by its steric demand or the relatively low basicity of the oxetane oxygen atom were possible. Besides, copolymerization allowed an evaluation of the glass transition temperature increase caused by a rigid motif like TNPO by comparison with the corresponding parent homopolymers. Next to the thermal behavior, we assessed the heat of formation of all polymers, calculated their energetic performance, and determined their sensitivity towards impact and friction. Although a true polymeric RSM seems currently unfeasible based on the state of research, we hope to give a first impression regarding the general feasibility, as well as the possible advantages and applications of such materials. Beyond, the achievable performance range of energetic polymers – even under non-optimized conditions, was demonstrated.

2 Experimental Section

The sensitivities of all described monomers and polymers toward impact and friction were assessed using a BAM (Bundesanstalt für Materialforschung) drop hammer according to STANAG 4489 modified instruction [9] and a BAM friction tester according to STANAG 4487 modified instruction [10].

2.1 Monomer Synthesis

Next to TNPO (**1**), several well-known energetic oxetanes have been synthesized to prepare copolymers. These can be subdivided in two groups – organic azides including 3-azidooxetane (3AO, **2**), 3-azidomethyl-3-methyloxetane (AMMO, **3**) as well as 3,3-bis(azidomethyl)oxetane (BAMO, **4**) and organic nitrates which include 3-nitratomethyl-3-methyloxetane (NIMMO, **5**) and 3-azidomethyl-3-nitratomethyloxetane (AMNMO, **6**). Due to the extend, the synthetic procedures and assessed data for monomers **1**–**6** can be found in the Supporting Information (SI).

2.2 Polymer Synthesis

To ensure comparability, all polymers were prepared under the same conditions according to the following, general procedure. Experimental details, yields, and the assessed data can be found in the Supporting Information.

General Procedure:

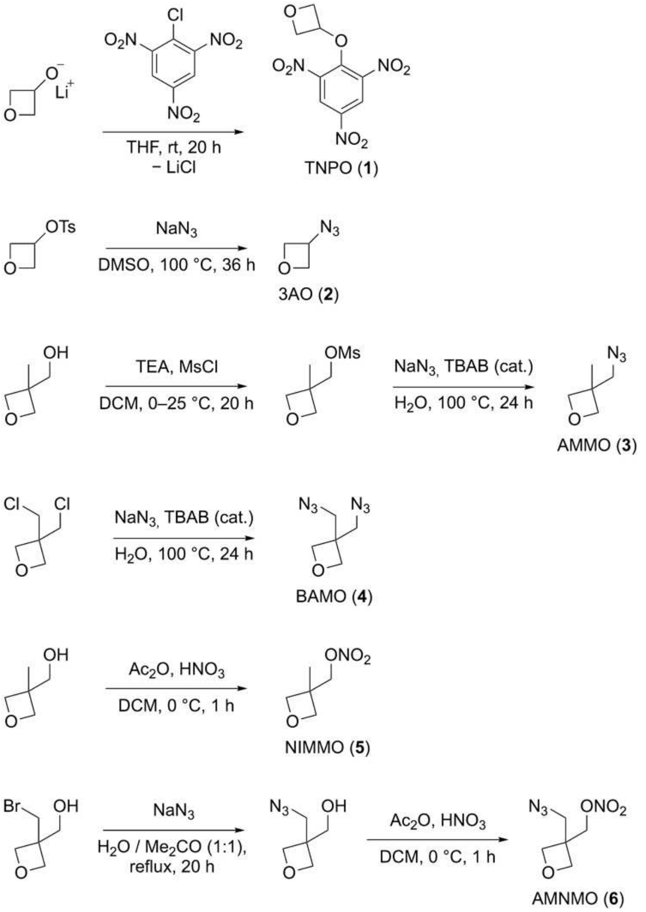
A *Schlenk* round bottom flask (25 mL) was closed with a silicone rubber septum and thoroughly dried under a protective atmosphere (argon). An initiating mixture was prepared by the addition of butane-1,4-diol and boron trifluoride etherate (molar ratio 1:2) using a 100 μL Hamilton syringe. The mixture was stirred for 15 minutes and 30 % of the total solvent volume (sulfolane-DCM (dry), 9:1) required to achieve a final monomer concentration of 2 $\text{mol}\,\text{L}^{-1}$ was added. The residual volume (70 %) was used to prepare a solution of TNPO (homopolymer) or an equimolar solution of the respective comonomers. Subsequently, the monomer solution was added using a syringe pump at different feed rates (see SI). The reaction mixture was then stirred for 48 hours at 250 rpm before quenching the polymerization reaction with water (1 mL). The resulting emulsion was vigorously stirred for five minutes and an excess of methanol (~20 mL) was added to precipitate the crude polymer which was allowed to settle. Afterward, the supernatant was decanted and the polymer was dissolved in a minimal amount of acetone and precipitated again using methanol (~20 mL). The polymer was then collected by centrifugation (20 min, 6000 rpm) and the supernatant was removed using a pipette. The purified polymer was transferred to a round bottom flask using acetone and all volatiles were removed by rotary evaporation. Afterward, the polymer was thoroughly dried under high vacuum conditions (0,1 Pa, 24 h) at 70 °C to afford yellow to orange, brittle solids.

2.3 Poly(AMNMO)

Since poly(AMNMO) was needed as a reference but is insufficiently described in the literature [11], it was prepared by a modified procedure and characterized in detail.

A Schlenk round bottom flask was closed with a silicone rubber septum and thoroughly dried under a protective atmosphere (argon). Boron trifluoride etherate (98.4 μL, 797 μmol, 0.1 equiv.) and butane-1,4-diol (35.2 μL, 398 μmol, 0.05 equiv.) were added using a 100 μL Hamilton syringe and the mixture was stirred for 15 minutes before the addition of dry dichloromethane (1.12 mL). Afterward, a solution of 3-azidomethyl-3-nitratomethyloxetane (1.50 g, 7.97 mmol) in dry dichloromethane (2.87 mL) was added over three hours using a syringe pump. The colorless reaction mixture was subsequently stirred for 48 hours at 250 rpm. The reaction was then quenched by the addition of water (0.5 mL) and vigorously stirred for five minutes. Afterward, methanol (15 mL) was added to precipitate the crude polymer which settled at the bottom of the flask as a colorless oil. The supernatant was removed using a pipette and the polymer dissolved in a minimal amount of acetone followed by the addition of methanol (15 mL) to precipitate the purified polymer. The supernatant was again removed and the polymer dried under high vacuum conditions (1 Pa, 25 °C, 2 d) to give 0.96 g (64 %) of poly(AMNMO) as colorless (opaque) resin-like material.

^{1}H NMR (400 MHz, Acetone-d_6, 25 °C): $\delta = 4.70$–4.54 (m, 2H, CH_2ONO_2), 3.70–3.39 (m, 6H, polymer backbone, CH_2N_3). **^{13}C{^{1}H} NMR** (101 MHz, Acetone-d_6, 25 °C): $\delta = 73.1$, 70.7, 52.1, 45.3. **^{14}N NMR** (29 MHz, Acetone-d_6, 25 °C): $\delta = -43.3$, -133.2. **FT-IR** (ATR, cm^{-1}): $\tilde{\nu} = 3292$ (vw), 3140 (vw), 2890 (w), 2102 (s), 1830 (vw), 1630 (vs), 1456 (m), 1272 (vs), 1100 (vs), 992 (s), 854 (vs), 752 (m), 702 (m), 646 (m), 552 (w). **Raman** (1075 nm, 1000 mW, cm^{-1}): $\tilde{\nu} = 2967$ (96), 2938 (91), 2880 (100), 2834 (26), 2811 (26), 2109 (39), 1486 (35), 1465 (43), 1453 (43), 1279 (78), 1239 (52), 1044 (22), 942 (26), 928 (22), 869 (52), 653 (22), 622 (22), 614 (22), 604 (22). **EA** calcd. for $C_5H_8N_4O_4$ (188.1430 g mol^{-1}): C 31.92, H 4.29, N 29.78. Found: C 33.08, H 4.14, N 27.96. **DSC** (5 °C min^{-1}): -31.0 °C (glass transition), 186.4 °C (dec). **M_n** (calculated, MW (188 g mol^{-1})·[M]/[I]): 3762 g mol^{-1}. **IS**: 7 J. **FS**: >360 N.



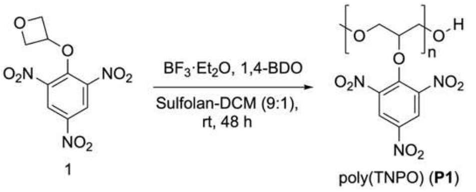
Scheme 1. Preparation of monomers **1**–**6**.

3 Results and Discussion

3.1 Monomer Synthesis

All monomers were prepared according to literature, modified literature procedures, or common synthetic strategies (NIMMO) as depicted in Scheme 1.

The key monomer, TNPO (**1**), was prepared by the reaction of lithium oxetan-3-olate (formed *in situ)* with picryl chloride in THF to afford TNPO as yellow solid in 70 % yield. If necessary, the crude product can be purified by recrystallization from hot chloroform [8]. Azidation of 3-tosyloxyoxetane using sodium azide in dry DMSO according to our recently published procedure gave 3-azidooxetane (**2**) as yellowish liquid [12]. To achieve purity suitable for polymerization, the crude product was distilled under reduced pressure to afford colorless 3AO in 60 % yield. To prepare AMMO (**3**), 3-hydroxymethyl-3-methyloxetane was first mesylated in DCM using mesyl chloride and triethylamine as a base. After liquid-liquid-extraction, the crude product was azidated analogous to literature using sodium azide in water under reflux conditions and tetrabutylammonium bromide (TBAB) as catalyst [13]. To achieve sufficient purity, the crude compound was subject to vacuum distillation to afford 58 % of colorless AMMO. The same reaction conditions were applied for the literature-analogous [13] azidation of 3,3-bis(chloromethyl)oxetane (BCMO) to afford crude BAMO (**4**) in 81 % yield as yellow liquid. As before, the monomer was purified by vacuum distillation to give colorless BAMO with an overall yield of 70 %. The organic nitrate NIMMO (**5**) was prepared by nitration of the corresponding alcohol in DCM using acetyl nitrate as a mild, cost-efficient nitrating agent. After liquid-liquid extraction, traces of acid and acetyl nitrate were fully removed using sodium bicarbonate solution to allow a safe purification by vacuum distillation to afford NIMMO as a colorless liquid in 52 % yield. AMNMO (**6**) was obtained in a two-step process according to patent literature [11]. First, 3-bromomethyl-3-hydroxymethyloxetane (BMHMO) was azidated under reflux conditions using sodium azide and a 1 : 1 mixture of water and acetone to provide 3-azidomethyl-3-hydroxymethyloxetane as a yellow liquid. Subsequently, the crude compound was nitrated using acetyl nitrate in DCM. Again, sodium bicarbonate solution was used to ensure that the product is free of acid and acetyl nitrate after liquid-liquid extraction and before vacuum distillation. Ultimately, colorless AMNMO was obtained in 42% yield. Of all monomers purified by distillation, the purifying effect was the lowest in the case of AMNMO. We assume that the compound partially decomposes during vacuum distillation. Hence, the compound may be purified by column chromatography if a higher purity is required.



Scheme 2. Preparation of poly(TNPO) by cationic ring-opening polymerization.

3.2 Polymer Synthesis

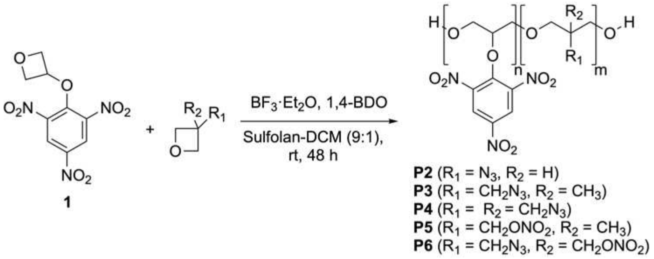
A boron trifluoride etherate polyol (butane-1,4-diol) initiating system was used to prepare all polymers by cationic ring-opening polymerization (CROP). This initiator is advantageous, as it allows chain propagation via the activated monomer mechanism (AMM) and thereby lowers the participation of the undesired activated chain end mechanism (ACE). In general, a high AMM participation significantly reduces side reactions such as backbiting or ring elimination. This in turn decreases the proportion of cyclic species to offer an improved end group functionality. Further, the AMM is known to provide improved molecular weight control and polydispersity [14, 15].

Apart from the initiator system, the choice of solvent turned out to be problematic, as TNPO is sparingly soluble in typical, inert solvents for CROP such as dichloromethane or chlorobenzene. With these solvents, the desired monomer concentration of 2 $mol\,L^{-1}$ was only achieved by slight heating and application of ultrasound before dosing of the monomer solution. Unfortunately, TNPO showed a high tendency to precipitate partially and thus clogged the feeding needle. As sulfolane is reported to have a rate accelerating effect on the CROP of 2-oxazolines [16], dissolves TNPO well, and may show similar effects in the case of oxetanes, it was chosen as an alternative. As the solvent dryness is of utmost importance for a successful CROP, sulfolane was dried in the molten state (30 °C) using calcium hydride under a protective atmosphere (argon). Afterward, it was distilled under high vacuum conditions (110 °C, 0,1 Pa) onto a mole sieve using a protective atmosphere (argon). As sulfolane itself tends to solidify at room temperature, 10 vol% of dry dichloromethane was added. To ensure comparability of the reactions and to evaluate TNPO's polymerization behavior, its homopolymer and all copolymers were prepared under the same conditions (see 2.2, SI). Unfortunately, electron-withdrawing substituents as in the case of TNPO lower the basicity of the oxetane oxygen atom which is crucial for a successful polymerization [17]. Further, we assumed steric hindrance during chain propagation due to the bulky, nitroaromatic motif. Hence, a quite low monomer to initiator ratio ($[M]/[I] = 20$) was used to ensure proper initiation, and a rather long reaction time of 48 hours was applied.

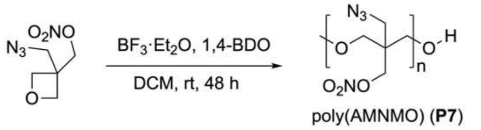
In the case of poly(TNPO) (Scheme 2), an initiator solution was prepared under dry conditions and a protective atmosphere according to the stated general procedure. Then, the intense yellow monomer solution was dosed uniformly using a syringe pump.

After several hours, a continuous color change from yellow to orange was observed. After 48 hours, the solution had turned deep red. The polymerization was quenched with water, vigorously stirred for five minutes and the crude polymer was precipitated by the addition of excess methanol. Hereby, the polymer was obtained as a deep orange slurry at the bottom of the flask. The supernatant was removed and the crude polymer dried under high vacuum conditions (70 °C, 0,1 Pa, 24 h). Unfortunately, NMR spectroscopy (^1H) revealed larger traces of sulfolane, butane-1,4-diol (BDO), and TNPO. For further purification, the polymer was dissolved in the minimal amount of hot acetone and precipitated again with a large excess of methanol. A yellow to orange, homogeneous suspension was obtained and the polymer was collected by centrifugation (6000 rpm, 20 min). The supernatant was removed (pipette) and drying under high vacuum conditions (70 °C, 0,1 Pa, 24 h), gave poly(TNPO) (**P1**) as brittle, yellow solid with a satisfying yield of 70%. The copolymers **P2**–**P6** were obtained by copolymerization of TNPO with the azido comonomers 3AO (**P2**), AMMO (**P3**), BAMO (**P4**) as well as the organic nitrates NIMMO (**P5**) and AMNMO (**P6**) using identical conditions and a similar scale (Scheme 3).

The respective comonomers were used in equimolar amounts to examine whether the stoichiometry is ultimately mirrored by the copolymers as deviations would indicate significantly different monomer reactivities. As in the case of **P1**, a notable color change from initially yellow over dark orange to dark red was observed during the polymerization. After quenching with water and the addition of ex-



Scheme 3. Preparation of copolymers **P2**–**P6** using TNPO and prior art energetic oxetanes as comonomers.



Scheme 4. Preparation of poly(AMNMO) using modified literature conditions.

cess methanol, copolymers **P2–P6** were obtained as dark orange slurries, which settled at the bottom of the flask. In each case, the supernatant was removed (pipette) and the crude polymer was analyzed by ^{1}H NMR spectroscopy. Again, an impurification with sulfolane, BDO, and larger quantities of TNPO was found. The latter can be explained by the fact that TNPO partially precipitates together with the polymer, while all other monomers represent liquids that easily migrate into the organic phase for their removal. For this reason, **P2–P6** were further purified as performed in the case of **P1**. After centrifugation and removal of the supernatant, the copolymers were transferred to another flask using acetone. Subsequently, the solvent was removed by rotary evaporation, and **P2–P6** were dried (70 °C, 0,1 Pa, 24 h) to give essentially orange, brittle solids with yields in the range of 46–83 %.

Since we intended to study the influence of the TNPO repeating unit on the glass transition temperature of these copolymers, it was necessary to know the glass transition temperatures of the parent homopolymers. Unfortunately, the corresponding T_G is not literature-known in the case of **P6** as poly(AMNMO) (**P7**) has only been incompletely described in a patent [11]. As the stated polymerization conditions seemed inappropriate regarding monomer feeding and reaction time, we prepared **P7** using modified conditions (Scheme 4).

Here, the monomer feeding duration, as well as the reaction time, was increased from 10 minutes and 17 hours to 3 hours and 48 hours, respectively. A monomer concentration of 2 $mol\,L^{-1}$ instead of roughly 2.7 $mol\,L^{-1}$was employed, but the monomer to initiator ratio [M]/[I] of 20 was kept as well as the solvent which dissolves both monomer and polymer well [11]. Contrary to the information disclosed, the polymer was not obtained as colorless oil but rather as an opaque, colorless, and resin-like material with a yield of 64 %, which is slightly below the claimed yield of 75 %.

3.3 Polymer Characterization

3.3.1 Gel Permeation Chromatography

The molecular weight distribution of all polymers was assessed by gel permeation chromatography (GPC) using polystyrene standards and a HITACHI L-2350 instrument equipped with a RI and UV detector and a "PSS SDV combination low" column (100–60.000 Da). THF was employed as solvent at a flow rate of 1 $mL\,min^{-1}$. The evaluation was performed using the PSS WinGPC software. Subsequently, the experimentally determined average molecular weight M_n was compared to the theoretical average molecular weight (M_n (th.)). The latter was calculated based on the monomer to initiator ratio (20), the molecular weight of the repeating unit (MW_R), and the assumption that BDO ($MW = 90.1\ g\,mol^{-1}$) acts as an initiator to become incorporated into the polymer chain ($M_n\ (th.) = 20 \cdot MW_R + 90.1\ g\,mol^{-1}$). The values of M_n, M_n (th.), the weighted average molecular weight $M_{W,}$ and the corresponding polydispersities Đ for polymers **P1–P6** are summarized in Table 1.

Surprisingly, the actual molecular weights are far below expectation and unfortunately reveal the predominant formation of oligomers. Further, the polydispersities are rather high and linked to broad molecular weight distributions as can be seen in the corresponding GPC plots of **P1–P6** (Figure 1). These findings contradict a "living character" of the polymerization reactions and further indicate a high contribution of the ACE mechanism. These results can be largely explained by a very slow polymerization initiation. In this case, the monomers are added considerably faster than

Table 1. GPC results in comparison to calculated average molecular weights for polymers **P1–P6**.

Polymer	M_n(th.)[a]	M_n[b]	M_W[c]	Đ[d]
P1	5703	2008	4548	2.27
P2	7685	1995	4071	2.04
P3	8246	1352	4356	3.22
P4	9066	1768	4388	2.48
P5	8646	1586	2630	1.66
P6	9466	1530	4939	3.23

[a] Theoretical average molecular weight ([M]/[I] + 90.1); [b] Average molecular weight by GPC; [c] Weight average molecular weight by GPC; [d] Polydispersity (M_W/M_n).

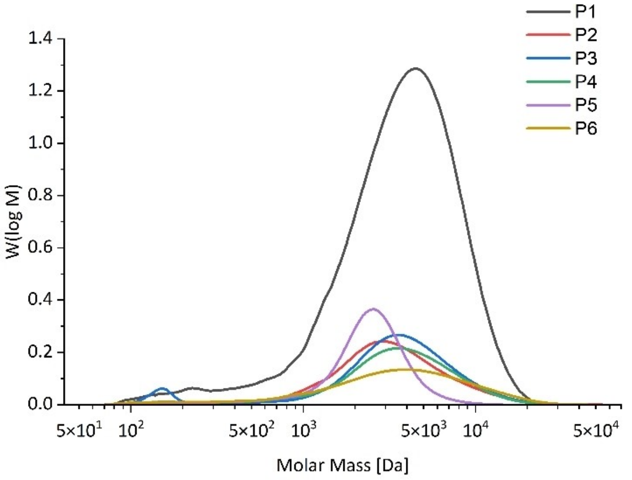


Figure 1. GPC analysis of poly(TNPO) (**P1**) and copolymers **P2–P6**.

they are initiated to result in a propagating chain. Due to overdosing, the monomers are initiated when present in high concentration and cause a large number of chains to grow in parallel. This results in correspondingly short chains and high polydispersities as observed. This assumption was further supported by a brief screening experiment. As the highest molecular weight deviation and polydispersity was observed for **P6**, we dosed the monomer solution at three different feed rates according to Table 2.

While a one-hour addition led to an extreme discrepancy of number and weight average molecular weight associated with a broad distribution, it was possible to reduce the polydispersity from 20.2 to 4.3 by doubling the addition time (2 hours). Further, the sixfold addition time (6 hours) resulted in improved convergence of M_n and M_W – but the additional decrease of polydispersity is rather limited. Overall, the data reveals a strong dependence of polydispersity and molecular weight control on the monomer feeding duration. This behavior further proves the initial assumption and can be explained by the existence of a so-called induction period leading to an undesired accumulation of monomers [14]. The effect was described by *Kim et al.* and is linked to the aggregation of BDO with boron trifluoride at the start of the monomer addition [14,18]. Aggregated initiators are thought to be less reactive [18,19] and can cause an uncontrolled favoring of the ACE mechanism to result in the formation of cyclic oligomers, a high polydispersity, and decreased hydroxyl group functionality [14]. The fact that a considerably increased addition time only resulted in a slight improvement (Table 2) is consistent with the assumption of an induction period due to a reduced initiator activity. Ultimately, high participation of the ACE mechanism was confirmed by NMR spectroscopy (^{1}H, ^{13}C). In case of propagation through the AMM, BDO is incorporated into the polymer providing a distinctive signal in the proton spectrum (1.4–1.7 ppm) [20] and the carbon spectrum (~15 ppm). As these signals were not observed (see SI), chain propagation through the ACE mechanism is strongly indicated. However, improved results may be obtained by further adjustment of the polymerization conditions or the use of other initiators.

Table 2. Dependence of molecular weight distribution and polydispersity on monomer addition time (**P6**).

Feed duration [h]	M_n[a]	M_W[b]	Đ[c]
1	972	19591	20.2
2	517	2209	4.28
6	1530	4939	3.23

[a] Average molecular weight by GPC; [b] Weight average molecular weight by GPC; [c] Polydispersity (M_W/M_n)

3.3.2 Polymer Constitution

If two monomers M_1 and M_2 shall form a copolymer (**P2–P6**), the chain sequence depends on their reactivity described by the corresponding reactivity ratios r_1 and r_2. Several important limiting cases can occur, first described by Mayo and Lewis [21]. If both reactivity ratios (r_1, r_2) are significantly larger than 1, both monomers solely react with themselves to form homopolymers. If both ratios are slightly larger than 1, homopolymerization is preferred (M_1 adds to M_1, M_2 adds to M_2), resulting in a block copolymer. If r_1 is significantly larger than 1, while r_2 is significantly below 1, M_1 adds faster to growing chains already terminated by M_1 to cause an increased M_1 content in the final polymer (composition drift). If r_1 and r_2 are close to 0, M_1 adds M_2 and vice versa to give a perfectly alternating chain. If both ratios are close to 1, a statistical copolymer is formed. Therefore, we analyzed the composition of the copolymers **P2–P6** to allow first conclusions to be drawn about the polymerization behavior of TNPO and the reactivity ratio. In this context, the composition was mainly studied via ^{1}H NMR spectroscopy as TNPO provides a very distinctive signal in the aromatic region (~9 ppm) which does not overlap with other signals. Here, the obtained integrals indicated very equal proportions of both monomers in each case with exception of **P5**. Here, the methyl group of NIMMO provided a distinctive signal (0.73–1.66 ppm) with an integral of only 2 indicating a slight composition toward an increased TNPO content. In addition, the copolymers were subject to elemental analysis. Here, the found contents for hydrogen, carbon, and nitrogen essentially matched the calculated compositions for 1:1 copolymers. However, it must be considered that polymers, in general, show higher deviations than monomers, thereby reducing the overall significance of the elemental analysis. Thermal analysis by DSC revealed only one glass transition temperature for **P2–P6** contradicting block copolymers. As both NMR spectroscopy (^{1}H) and elemental analysis revealed slight deviations from the ideal comonomer ratio (1:1), statistical copolymers are strongly indicated. Nevertheless, we can conclude that the polymerization behavior of TNPO is very comparable to the literature-known energetic oxetanes. Based on the obtained polymer constitutions, reactivity ratios close to 1 can be anticipated for all employed monomers.

3.3.3 Thermal Analysis

The thermal behavior of all polymers was assessed by differential scanning calorimetry at a heating rate of 5 °C min^{-1}. Before the measurement, these were stored at room temperature for three weeks to ensure the same thermal history. The highest decomposition temperature was found for poly(TNPO) which decomposes surprisingly early at 205 °C in comparison to the monomer which decomposes 253 °C. As expected, rather low decomposition temperatures were found for copolymers containing nitrato groups. Here, polymer **P5** decomposes at 185 °C, while **P6** decomposes even earlier at 183 °C. Unfortunately, equally low decomposition temperatures below 200 °C were assessed in the case of the azido-copolymers **P2**–**P4**. The lowest decomposition temperature was observed for **P2** (178 °C), followed by **P3** (184 °C) and **P4** (190 °C). Here, it is notable that **P5** and **P6** decompose at a marginally higher temperature than the corresponding comonomers NIMMO and AMNMO. Contrary to this, the decomposition temperatures of **P2**–**P4** are significantly lower than those of the corresponding comonomers 3AO, AMMO, and BAMO (see SI). Since the decomposition temperature is lowered by more than 4 °C compared to the respective azido-comonomers, a polymer-internal incompatibility of the azido motifs with the nitroaromatic TNPO motif is likely [22]. Further, all polymers have a stepwise, non-uniform decomposition with overlapping exothermic signals in common, while none of the polymers showed an exothermic signal attributable to a crystallization process. Therefore, all polymers are fully amorphous.

Most importantly, the influence of the TNPO repeating unit on the glass transition temperatures (T_G) of copolymers **P2**–**P6** was examined by comparing these with the glass transition temperatures of the corresponding parent polymers [5,12,23,24].

Here, the TNPO repeating unit showed a very dominating effect on the T_G and caused a drastic increase in all cases as desired (Table 3). The smallest shift of +43 °C was observed for poly(TNPO-*stat*-AMMO) (**P3**), while a tremendous shift of +80 °C was observed for poly(TNPO-*stat*-3AO) (**P2**). Very surprisingly, poly(TNPO) itself only shows a T_G of 63 °C, further emphasizing the considerable effect of the slightly bulky TNPO motif on the glass transition in the case of **P2**–**P6**.

As the glass transition temperatures of poly(TNPO) (T_{G2}) and the parent homopolymers of **P2**–**P6** (T_{G1}) are known, the T_G of copolymers with different compositions can be calculated using the Gordon-Taylor equation [25]:

$$T_{G\,copolymer} = \frac{w_1 T_{G1} + k w_2 T_{G2}}{w_1 + k w_2}$$

Here, w_1 and w_2 represent the mass fractions of the associated parent homopolymers. To determine the dimensionless Gordon-Taylor constant k, the equation was rearranged:

$$k = \frac{w_1(T_G - T_{G1})}{w_2(T_{G2} - T_G)} = \frac{MW_1(T_G - T_{G1})}{MW_2(T_{G2} - T_G)}$$

As equimolar monomer amounts were employed in the case of **P2**–**P6**, the mass fraction w_1/w_2 can be replaced by the monomer's molecular weight fraction (MW_1/MW_2). For instance, with k = 0.73, poly(TNPO-*stat*-3AO) comprising 0.05 mass fractions TNPO (w_2) and 0.95 mass fractions of 3AO (w_1) would roughly show a T_G of −51 °C.

Apart from calculations, our results indicate the feasibility of glass transition temperatures suitable for the envisioned purpose and bulky, energetic side groups will surely take a key role. Therefore, other bulky motifs that impose rigidity to the polymer chains like energetic heterocycles (e.g., tetrazoles, pyrazoles), are a promising starting point for the development of suitable oxetane monomers. Beyond, an adjustable crosslinking of the chains should be implemented through functional side groups to allow tailoring of both T_G and mechanical properties.

Table 3. Glass transition temperature of the parent homopolymers (T_{G1}) versus T_G of the copolymers and calculated Gordon-Taylor-constants k.

Homopolymer	T_{G1} [°C]	T_G copolymer	ΔT_G	k
Poly(3AO)	−55 [12]	25	80	0.73
Poly(AMMO)	−42 [5]	1	43	0.31
Poly(BAMO)	−41 [23]	23	64	0.94
Poly(NIMMO)	−25 [24]	36	61	1.17
Poly(AMNMO)	−31	42	73	2.29

3.4 Physicochemical and Energetic Properties

To consider energetic polymers as RSM, a performance at least equal to known, metal-based RSMs is required. Unfortunately, the performance of known energetic polyoxetanes (e.g., poly(AMMO), poly(NIMMO), poly(BAMO)) is very low. Foremost, this is attributed to their low density (1.17–1.25 g cm^{-3}) [26] on which detonation velocity and detonation pressure strongly depend [6]. As polymer densities roughly match the monomer densities, TNPO offers a considerable energetic contribution to copolymers **P2**–**P6** with a high density of 1.70 g cm^{-3}. The polymer densities were determined by helium pycnometry on a Micromeritics AccuPyc II 1345 device. As expected, poly(TNPO) offers the highest density (1.62 g cm^{-3}), while the lowest was found for **P3** (1.46 g cm^{-3}). All other polymer densities range between 1.50 and 1.54 g cm^{-3}. Thereby, all densities are notably higher than in the case of the aforementioned polyoxetanes.

To calculate the performance of **P1**–**P6** using the EXPLO5V 6.04 code, the heats of formation were determined by bomb calorimetry using literature methods [14,27]. A Parr 6200 Isoperibol bomb calorimeter was employed and calibrated using benzoic acid (combustion enthalpy 26432 ± 32.7 J g^{-1}) [28]. Nitric acid formation was directly factored by the device. Tablets were prepared by dissolving the respective polymer and benzoic acid (ratio 3:10 by mass) in acetone followed by careful rotary evaporation. The obtained solid was dried (drying cabinet, 48 h, 50 °C) and then ground until homogeneous. Subsequently, tablets were pressed (5 s, 3 tons) and again dried under the aforementioned conditions. Afterward, each tablet was burned in a pure oxygen atmosphere (3,5 MPa) on a platinum crucible. According to Hess' law, the heat of formation (HOF) is obtained as the difference between the HOF of the combustion products (CP) and the measured heat of combustion H_C:

$$\Delta H_f^0(polymer) = \Delta H_f^0(CP) - \Delta H_C(polymer)$$

The heat of formation of carbon dioxide and water is $-393.52\ \mathrm{kJ\,mol^{-1}}$ and $-241.83\ \mathrm{kJ\,mol^{-1}}$, respectively [29]. Table 4 summarizes the obtained average values for H_C and the calculated heats of formation for **P1**–**P6**. Further details can be found in the Supporting Information.

For all polymers, a positive heat of formation was found. As expected, the lowest HOF was found for **P5**, as it exhibits the least nitrogen content and additional carbon-hydrogen ballast is introduced by the NIMMO monomer. As the nitrato group of **P5** is formally replaced by an azido group, **P3** shows a significantly higher heat of formation ($241.2\ \mathrm{kJ\,mol^{-1}}$), closely followed by poly(TNPO) ($281.2\ \mathrm{kJ\,mol^{-1}}$). The HOF further increases in accordance with expectation from **P2** ($426.7\ \mathrm{kJ\,mol^{-1}}$) to **P6** ($703.5\ \mathrm{kJ\,mol^{-1}}$) and culminates with a value of $906.4\ \mathrm{kJ\,mol^{-1}}$ in case of **P4**, as it represents the by far most nitrogen-rich azido-polymer.

Table 4. Heat of combustion as determined by bomb calorimetry and calculated heat of formation for polymers **P1**–**P6**.

Polymer	$-H_C$ [kJ mol^{-1}]	HOF [kJ mol^{-1}]
P1	4669.3	281.2
P2	6599.9	426.7
P3	7685.1	241.2
P4	8229.4	906.4
P5	7452.1	8.2
P6	8026.5	703.5

Ultimately, we calculated the performance of **P1**–**P6** based on the assessed densities and heats of formation. Due to its comparatively low density and HOF, **P3** shows the lowest performance with a detonation velocity of only $6620\ \mathrm{ms^{-1}}$ and a detonation pressure of 17.5 GPa. With the most advantageous combination of HOF and density, **P2** and **P6** show the highest performances with detonation velocities of $7417\ \mathrm{ms^{-1}}$ and $7498\ \mathrm{ms^{-1}}$ next to detonation pressures of 23.5 GPa and 20.2 GPa, respectively.

Therefore, with exception of **P3**, all polymers show a calculated performance comparable to (**P5**) or above TNT (EXPLO5 V6.04: $p_{C\text{-}J}$ 18.7 GPa, $D_{C\text{-}J}$ 6809 $\mathrm{ms^{-1}}$) as a secondary explosive (Table 5). Hence, energetic polymers can indeed provide considerable performance and may offer a significant energetic contribution when employed as RSM.

The potential applicability of such materials is further supported by the found sensitivities towards mechanical stimuli such as impact and friction. These are rather low – even when TNPO was copolymerized with very sensitive monomers like BAMO or 3AO. According to the "UN recommendations on the transport of dangerous goods" [30], all polymers are "insensitive" toward friction (FS > 360 N) with exception of **P2** which is "sensitive" (FS < 360 N). Regarding impact sensitivity, poly(TNPO) (**P1**) can be classified as "insensitive", while polymers **P2**, **P3**, **P5**, and **P6** show impact sensitivities between 25 J and 30 J. Thus, they fall slightly

Table 5. Important physicochemical and energetic properties of homopolymer **P1** and copolymers **P2**–**P6**.

	P1	**P2**	**P3**	**P4**	**P5**	**P6**
Formula	$C_9H_7N_3O_8$	$C_{12}H_{12}N_6O_9$	$C_{14}H_{16}N_6O_9$	$C_{14}H_{15}N_9O_9$	$C_{14}H_{16}N_4O_{12}$	$C_{14}H_{15}N_7O_{12}$
FW [g·mol^{-1}]	285.17	384.26	412.31	453.33	432.29	473.31
IS[a] [J]	40	25	25	> 7	30	30
FS[b] [N]	> 360	324	> 360	> 360	> 360	> 360
N, O[c] [%]	14.7, 44.9	21.9, 37.5	20.4, 34.9	27.8, 31.8	12.9, 44.4	20.7, 40.6
Ω[d] [%]	−75.7	−28.5	−104.8	−93.5	−88.8	−79.4
T_G[e]/ T_{dec}[f] [°C]	63.0, 204.6	25.2, 177.6	0.7, 183.6	23.4, 190.0	36.0, 185.1	42.4, 183.0
ρ[g] [g·cm^{-3}]	1.62	1.54	1.46	1.50	1.51	1.54
ΔH_f°[h] [kJ·mol^{-1}]	281.2	426.7	241.1	906.4	8.1	703.5
EXPLO5V6.04						
$-\Delta_E U^{\circ}$[i] [kJ·kg^{-1}]	5794	4686	4713	5555	5168	6091
$T_{C\text{-}J}$[j] [K]	3907	3373	3147	3607	3362	3800
$p_{C\text{-}J}$[k] [GPa]	22.0	23.5	17.5	19.4	18.4	20.2
$D_{C\text{-}J}$[l] [m·s^{-1}]	7197	7417	6620	7056	6817	7498
V_0[m] [dm^3·kg^{-1}]	658	704	701	720	706	728

[a] Impact sensitivity (BAM drop hammer, method 1 of 6). [b] Friction sensitivity (BAM friction apparatus, method 1 of 6). [c] Nitrogen and oxygen content. [d] Oxygen balance based on CO formation. [e] Glass transition temperature (DSC, $\beta = 5\ ^{\circ}\mathrm{C\cdot min^{-1}}$). [f] Decomposition temperature (DSC, $\beta = 5\ ^{\circ}\mathrm{C\cdot min^{-1}}$). [g] Density at 298 K (helium pycnometry). [h] Standard molar enthalpy of formation. [i] Detonation energy. [j] Detonation temperature. [k] Detonation pressure. [l] Detonation velocity. [m] Volume of detonation gases at standard temperature and pressure.

short of the classification as "less sensitive" ($\mathrm{IS} \geq 35$ J) and have to be declared as "sensitive" ($\mathrm{IS} \geq 4$ J) despite their overall low impact sensitivity. According to expectation, copolymer **P4** shows the highest impact sensitivity (>7 J) owing to the BAMO repeating unit and needs to be classified as "sensitive". With exception of **P4**, the overall sensitivity of the copolymers seems predominantly influenced by the high insensitivity of the TNPO monomer. This raises hope that a particularly insensitive but still high-performing monomer like TNPO can be copolymerized in high proportions with more performant, maybe more sensitive monomers to only cause a minor sensitivity increase.

4 Conclusion

As energetic binder research has mainly focused on elastic polymers with the lowest possible glass transition temperature, the development of polymers suitable as RSM is likely to be a long path with major obstacles. This can be attributed to the lack of suitable monomers and not least to the requirements for a viable polymer such as high thermostability and performance, low sensitivity, high glass transition temperature, mechanical strength, and processability by common polymer techniques. Of course, copolymerization of TNPO with prior art monomers unsuitable for the intended purpose cannot meet these requirements. Nevertheless, our results allow interesting conclusions to be drawn. For instance, simple but slightly bulky motifs like TNPO already provide notably high glass transition temperatures. Especially, the equimolar copolymerization of TNPO with prior art monomers designed to provide binders of low glass transition temperature revealed its dominant effect. In the case of **P2**, a tremendous shift of $+80\,^{\circ}\mathrm{C}$ was observed in comparison to the parent homopolymer poly(3-azidooxetane). Thus, it can be assumed that bulky monomers similar to TNPO can easily provide the desired, high glass transition temperatures. In particular, energetic heterocycles (e.g., pyrazoles, tetrazoles) may offer a valuable contribution. At first glance, the fact that we only obtained oligomers with also high polydispersity seems very disadvantageous. However, a reduced initiator activity was identified as the main cause. The basic phenomenon is known to literature and improved results are likely using other polymerization initiators. Nevertheless, as all copolymers essentially reflect the intended 1:1 comonomer ratio, no indication is given that sterically more demanding motifs such as TNPO suffer from a reduced polymerizability. Apart from this, the performance of the investigated polymers appears very promising for the envisioned use of such materials as RSM. In this context, performances in the range of TNT were obtained even under non-optimized conditions. Thus, energetic polymers as reactive structure materials could provide a significant energetic contribution to increasing the blast effect of various ammunitions and effector systems. In addition, the rather high performance was linked to very acceptable sensitivities. Copolymerization of the insensitive TNPO monomer with more sensitive but also more performant monomers led to an almost negligible increase of the friction sensitivity, while the increase in shock sensitivity was found to be more pronounced. Overall, polymer-based RSMs may provide a favorable balance between performance and sensitivity – especially when insensitive but rather powerful monomers such as TNPO partially compensate for the higher sensitivity of higher-performing comonomers. Nevertheless, to achieve any substantial progress in the intended direction, the development of new, suitable monomers is of utmost importance. These should be designed to allow the formation of rigid polymer chains and semi-crystalline polymers. Exhibiting a melting point would allow processing techniques from injection molding to 3D printing. Even though the development of viable polymers appears challenging, we consider their development as reasonable, given the manifold advantages. Among others, these include a high weight reduction compared to metal-based RSMs, a high performance, independence from atmospheric oxygen, broad applicability, and the possibility to obtain energetic, technical components by common processing techniques. Therefore, we hope that the concept will find sufficient appeal to provide an impetus for more focused research in this area.

5 Abbreviations

DCM	dichloromethane
DMSO	dimethyl sulfoxide
TEA	trimethylamine
THF	Tetrahydrofuran
TNT	2,4,6-trinitrotoluene

Acknowledgements

Financial support by the Ludwig Maximilian University of Munich (LMU), the Office of Naval Research (ONR) under grant no. ONR N00014-19-1-2078 and the Strategic Environmental Research and Development Program (SERDP) under contract no. W912HQ19C0033 is gratefully acknowledged. Beyond, we want to thank Stefan Huber for the sensitivity testing and Elena Reinhardt for her great efforts regarding bomb calorimetry. Open Access funding enabled and organized by Projekt DEAL.

References

[1] D. L. Hastings, E. L. Dreizin, Reactive Structural Materials: Preparation and Characterization, *Adv. Eng. Mater.* **2018**, *20*, 1700631.

[2] R. J. Lee, W. Mock, J. R. Carney, W. H. Holt, G. I. Pangilinan, R. M. Gamache, J. M. Boteler, D. G. Bohl, J. Drotar, G. W. Lawrence, Reactive Materials Studies, *AIP Conference Proceedings* **2006**, American Institute of Physics, *845*, 169–174.

[3] Z. Bogdan, Explosive Properties of the Mg–Al/PTFE Composition, *Chin. J. Energet. Mater.* **2007**, *15*, 592–596.

[4] M. Born, D. Dosch, *Energetische Polymere als reaktive Strukturmaterialien zur Verwendung für Waffensysteme*, DE102011118462B4, Germany **2011**.

[5] H. G. Ang, S. Pisharath, *Energetic Polymers: Binders and Plasticizers for Enhancing Performance*, Wiley-VCH, Weinheim **2012**.

[6] T. M. Klapötke, *Chemistry of High-Energy Materials*, 5th ed., De Gruyter, Berlin, Boston, **2019**.

[7] R.-M. Wang, S.-R. Zheng, Y.-P. Zheng, *Polymer Matrix Composites and Technology*, Woodhead Publishing, Sawston (UK) **2011**.

[8] M. Born, M. Voggenreiter, New energetic oxetane monomers based on nitroaromatic scaffolds, *New Trends in Research of Energetic Materials (NTREM)*, **2019**, Pardubice, Czech Republic.

[9] NATO Standardization Office, NATO STANAG 4489: Explosives. Impact Sensitivity Tests, **1999**.

[10] NATO Standardization Office, NATO STANAG 4487: Explosives. Friction Sensitivity Tests, **2002**.

[11] T. G. Archibald, A. A. Malik, G. E. Manser, 3-Azidomethyl-3-Nitratomethyloxetane, US Patent 5,489,700, Aerojet-General Corporation, Sacramento, CA, USA, **1996**.

[12] M. Born, K. Karaghiosoff, T. M. Klapötke, A GAP Replacement: Improved Synthesis of 3-Azidooxetane and Its Homopolymer Based on Sulfonic Acid Esters of Oxetan-3-ol, *J. Org. Chem.* **2021**, *86*, 12607–12614.

[13] T. I. Mukhametshin, A. I. Petrov, N. V. Kuznetsova, V. A. Petrov, N. V. Averianova, I. K. Garaev, A. V. Kostochko, A. T. Gubaidullin, D. B. Vinogradov, P. V. Bulatov, Synthesis and copolymerization of azidomethyl-substituted oxetanes: the morphology of statistical block copolymers, *Chem. Heterocycl. Compd.* **2017**, *53*, 811.

[14] S. Hafner, Internal plasticized glycidyl azide copolymers for energetic solid propellant binders, Ph.D. Dissertation, LMU Munich, Munich, **2019**.

[15] S. Penczek, Cationic ring-opening polymerization (CROP) major mechanistic phenomena, *J. Polym. Sci.* **2000**, *38*, 1919–1933.

[16] M. Vergaelen, B. Verbraeken, B. D. Monnery, R. Hoogenboom, Sulfolane as Common Rate Accelerating Solvent for the Cationic Ring-Opening Polymerization of 2-Oxazolines, *ACS Macro Lett.* **2015**, *4*, 825–828.

[17] M. P. Dreyfuss, P. Dreyfuss, Oxetane Polymers, in *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, Hoboken, New Jersey, **2011**.

[18] J. S. Kim, J. O. Kweon, S. T. Noh, Online monitoring of reaction temperature during cationic ring-opening polymerization of epichlorohydrin in presence of BF3 and 1,4-butanediol, *J. Appl. Polym. Sci.* **2014**, *131*.

[19] J. S. Kim, D. K. Kim, J. O. Kweon, J. M. Lee, S. T. Noh, S. Y. Kim, The influence of initiator Diol-BF3 complex solubility and other factors on the induction period in BF3 catalyzed cationic ring-opening polymerization of epichlorohydrin, *Macromol. Res.* **2014**, *22*, 436–444.

[20] U. Barbieri, T. Keicher, G. Polacco, Homo- and copolymers of 3-tosyloxymethyl-3-methyl oxetane (TMMO) as precursors to energetic azido polymers, *e-Polym.* **2009**, *9, 046*.

[21] F. M. Lewis, F. R. Mayo, Copolymerization. I. A Basis for Comparing the Behavior of Monomers in Copolymerization; The Copolymerization of Styrene and Methyl Methacrylate, *J. Am. Chem. Soc.* **1944**, *66*, 1594–1601.

[22] NATO Standardization Office, NATO STANAG 4147: Chemical compatibility of ammunition components with explosives (non-nuclear applications), **2001**.

[23] H. Cheradame, J. P. Andreolety, E. Rousset, Synthesis of polymers containing pseudohalide groups by cationic polymerization, 1. Homopolymerization of 3,3-bis(azidomethyl)oxetane and its copolymerization with 3-chloromethyl-3-(2,5,8-trioxadecyl)oxetane. *Makromol. Chem.* **1991**, *192*, 901–918.

[24] M. E. Colclough, H. Desai, R. W. Millar, N. C. Paul, M. J. Stewart, P. Golding, Energetic polymers as binders in composite propellants and explosives. *Polym. Adv. Technol.* **1994**, *5*, 554–560.

[25] M. Gordon, J. S. Taylor, Ideal copolymers and the second-order transitions of synthetic rubbers. i. non-crystalline copolymers, *J. Appl. Chem.* **1952**, *2*, 493–500.

[26] A. Homburg, J. Köhler, R. Meyer, *Explosives*, 6th ed., Wiley-VCH, Weinheim **2007**.

[27] Q. J. Axthammer, C. Evangelisti, T. M. Klapötke, Characterization, bomb calorimetric measurements and quantum chemical calculations of high energetic dense oxidizers (HEDO), *44th International Annual Conference of ICT*, Energetic Materials – Past, Present, and Future, 2013, Karlsruhe, Germany, 88/1-88/15.

[28] P. J. Linstrom and W. G. Mallard, Eds., NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg MD; https://webbook.nist.gov (accessed 2021–10-01).

[29] M. W. Chase, NIST-JANAF Thermochemical Tables, 4th ed., *J. Phys. Chem. Ref. Data Monogr.* **1998**, 1–1951.

[30] United Nations (UN), UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, **2009**.

Manuscript received: December 20, 2021
Revised manuscript received: January 31, 2022
Version of record online: February 21, 2022