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Dedication ((optional))

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Abstract: New energetic polymers were synthesized from monomers featuring the *trans*-2-tetrazene unit. In contrast to traditional binders, such as the inert hydroxytelechelic polybutadiene or the glycidyl azide polymers – where the energetic features are on the side chains –, the energetic groups in the polytetrazenes are incorporated directly in the polymer backbone. Thermal analyses evidenced that decomposition occurs at ~130 °C, regardless of the polymer structure. Glass transition temperatures range from –34.2 to 0.2°C, and they could be lowered further (to –61°C) with the help of a new diazido tetrazene energetic plasticizer. Interestingly, hexafluoro isopropanol (HFIP) enables a complete, room temperature depolymerization within one week. This should enable the recycling of the unused pyrotechnic compositions based on these new binders.

Today's rockets are equipped with solid-fuel boosters, which deliver most of the take-off thrust. The latter are loaded with a composite propellant composed of a metallic fuel, an oxidant, plasticizers and a binding polymer, which in most cases is hydroxytelechelic polybutadiene (HTPB).[1]

The quest for more energetic charges to include in solid boosters and enhance thrust performances, or explosives, has been a staple of pyrotechnic chemistry for decades.[2-4] However, any increase of the energy density of the energetic charges implies a likely higher sensitivity to impact, friction or electrostatic discharge. The hazard that results generates extra protection costs for their preparation and handling (when it does not simply forbid the latter). Gains in the performance of the boosters could instead be achieved by replacing the non-energetic HTPB with binders including energetic functions. The overall energy stored can thus be higher, while the sensitivity is kept below the acceptable threshold.

Numerous energetic polymers for binders bearing various energetic groups such as nitric esters, tetrazoles or azides have been synthesized over the years (Figure 1).[5,6] In these polymers, the energetic moieties are installed as side-chains of an otherwise inert backbone. Energetic phosphazenes are the latest entry in that family. They have good density and glass transition temperatures, but the main energetic content is again on the side-chains.[7,8]

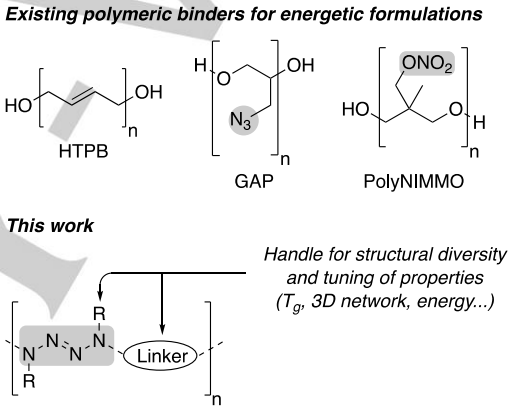
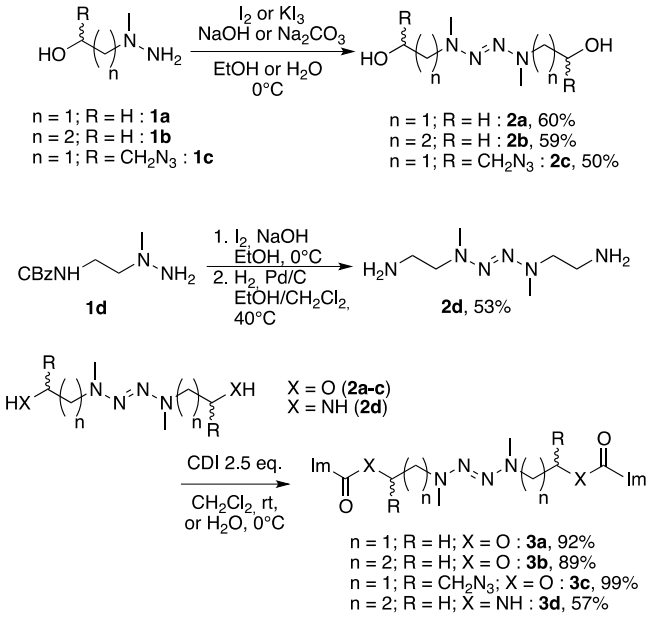


Figure 1. Structures of current binders and new tetrazenic polymers.

We introduce herein a new family of energetic materials, where more highly energetic moieties are part of the polymer main chain. We selected the *trans*-2-tetrazene function because of its high enthalpy of formation. Indeed, *trans* 1,1,4,4-tetramethyltetrazene (TMTZ) has a measured $\Delta H_f°$ of 214 kJ.mol^{-1}, or 1843 kJ.kg^{-1} if one factors in the density of the liquid.[9] Also, the external nitrogen atoms offer valuable handles for installing substituents, therefore enabling the tuning of mechanical and energetic properties of the polymer (Figure 1). We decided to target polyurethanes (PUs), because PUs offer a wide variety of properties, and therefore are widely employed in industry (construction, furniture, the automotive industry, etc.), as their low glass transition temperature (T_g) and high structural cohesion due to effective H-bonding, make them highly suitable as surface coatings, flexible or rigid foams, sealants, adhesives, etc.[10,11]

• *Synthesis*. To prepare our target polymers, we initially decided to rely on the AA-BB type polyaddition of tetrazene-containing diols to bis-isocyanates. To this purpose, we prepared the desired diols (**2a-c**) by oxidative dimerization of hydrazines **1a-c** (Scheme 1).[12]

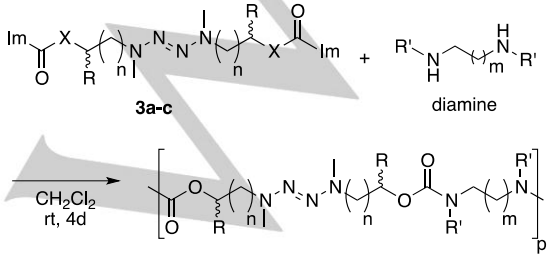


Scheme 1. Preparation of the energetic monomers.

Hexamethylene diisocyanate (HDI) was selected as co-monomer to access structures both flexible enough to be binders and with an acceptable C/H content to secure energy density. However, all the materials resulting from the polyadditions were hard solids with poor solubilities in all the common organic solvents. We therefore switched our focus to the polycondensation of diisocyanate surrogates **3a-d** with organic diols or diamines.

We first attempted to react carbamate **3d** with alcohols, to no avail, as the test addition of benzyl alcohol to **3d** led to no reaction. We therefore switched the functionalization and decided to add the more nucleophilic amines on tetrazenic diols activated as imidazolyl-carbamates. In a standard procedure for the phosgenation we activated diols **2a-c** with carbonyl diimidazole in anhydrous dichloromethane at room temperature. The corresponding activated monomers **3a-c** were obtained in excellent yields (92, 89 and 99%, respectively, Scheme 1). Interestingly, the yields for the preparation of carbamates **3a-c** were much higher that the yield of urea **3d** (which was prepared in water).

• *Polymerization by polycondensation.* Too many carbons in the materials are detrimental because they require more oxidant to react and dilute the energetic charge. To keep their number, we used the shortest possible co-condensation monomers (Scheme 2).



Scheme 2. Polymerization of activated diols with diamines.

A strictly controlled equimolar amount of ethylenediamine was first added to tetrazene **3b** in dichloromethane (1 g.mL^{-1}) at room temperature for 4 days. Concentration of the reaction mixture delivered a hard, insoluble and unprocessable polymer. For this reason, we replaced the diamine with N-N'-dimethylethylenediamine (DMEDA) and 1,3-diaminopropane (DAP). They are commercially available, inexpensive, and easy-to-handle diamines. The polycondensations were all carried out by mixing equimolar amounts of both co-monomers in dry dichloromethane over 4 days (Table 1).

Table 1. Tetrazene-based polymers isolated

Entry[a]	Tetrazene (R, n)	Diamine (R', m)	Polymer, Yield (%)[b]	M_n (g.mol^{-1}), $Đ$
1	**3a** (H, 1)	DAP (H, 2)	**A**, 86	5200, 2.0
2	**3b** (H, 2)	DAP (H, 2)	**B**, 96	5800, 2.0
3[c]	**3b** (H, 2)	DMEDA (Me, 1)	**C**, 85	3500, 2.0
4	**3c** (CH_2N_3, 1)	DAP (H, 2)	**D**, 87	3400, 2.0
5	**3c** (CH_2N_3, 1)	DMEDA (Me, 1)	**E**, 92	3500, 1.9

[a] Conditions: Diamine (1 equiv.), diol (1 equiv.) in anhydrous dichloromethane (1 g.mL^{-1}). The mixture was left at room temperature for 4 days. [b] All yields were determined after aqueous washings of the organic phase. The observed yields are slightly less than quantitative, which is normally expected for a polycondensation reaction. It is likely that some lower molar mass-oligomers were removed from the bulk of the polymer during the washing step; [c] This polycondensation was scaled up at the multigram scale.

In a typical polymerization, **3a** was mixed with of DAP in dichloromethane at rt (1 equiv. each, 1 g.mL^{-1} concentration). After 4 days, the reaction mixture was diluted in dichloromethane (approx. 20 volumes). The organic phase was washed three times with water, dried, filtered and concentrated. Polymer **A** was isolated as a viscous oil, as expected for a polymer with a T_g below room temperature (Table 1, Entry 1). The only side-product of the polycondensation is imidazole. We removed it during the work-up to determine accurately the decomposition energies of our materials. This is however not necessary on a larger scale, since imidazole has a N/C ratio high enough to avoid large detrimental effects on the energetic applications. The molar masses of **A** were assessed by size exclusion chromatography (SEC) using THF as eluent and polymethyl methacrylate standards. The M_n for **A** was estimated at 5200 g.mol^{-1} with a dispersity $Đ$ of 2, as expected from polycondensation theory.[13] Polymer **B** was obtained similarly from tetrazene **3b** (M_n = 5800 g.mol^{-1}, $Đ$ = 2, entry 2). The bis-secondary diamine led to **C** when polymerized with **3b**, with a slightly shorter chain (3500 g.mol^{-1}, entry 3). The even more energetic tetrazene **3c** (featuring two azide substituents) led to polymers **D** with DAP (entry 4) and **E** with DMEDA (entry 5). In both cases the molar masses obtained were ~3500 g.mol^{-1} with a dispersity again very close to 2.[14]

• *Energetic Properties*. Thermal analyses were performed by differential scanning calorimetry (DSC) on all polymers to

determine any potential glass transition (T_g) and decomposition temperatures (T_d, Table 2).

Table 2. Thermal properties of the polytetrazenes

Entry[a]	Polymer	T_g (°C)	T_d (°C)	E_c (J.g^{-1})
1	**A**	0.2	120	750
2	**B**	–12.6	124	880
3	**C**	–34.2	136	500
4	**D**	–1.8	129	1340
5	**E**	–8.3	123	1790

[a] Glass transition midpoints were measured at 10 °C.min^{-1} heating rate. Decomposition temperatures and energies were measured at 2 °C.min^{-1} heating rate.

The glass-transition temperatures were measured in pierced lid aluminum crucibles at a 10 °C.min^{-1} heating rate under a 150 mL.min^{-1} air flow. The first observation is that all five polymers exhibit a marked glass transition. Polymers **C** and **E** exhibited much lower T_g's compared to their DAP-derived analogues **B** and **D** (compare entries 2&4 to 3&5). We attribute this to the strong influence of the H-bond network – present in **B** and **D**, but not in **C** and **E** – which increases the T_g in polymers **B** and **D** (and **A**). A 12°C gap was observed between polymers **A** and **B** (entries 1-2), which have similar molar masses. This might be due to the higher number of carbons present on monomer **3b**, which likely allows a higher degree of flexibility in the polymer. Increasing the carbon content further might be beneficial to lower the T_g (see below), but that would result in a dramatic loss of the energetic properties and was therefore not attempted.

Several syntheses of polymers **A**, **B** and **E** were performed at various co-monomer ratios (here with **3a**, **3b** or **3c** in excess), to map the relationship between molar mass and glass transition temperature. Deviation from stoichiometry is a common strategy used in polycondensation to lower the molar masses and control the end groups. A linear M_n/T_g correlation was observed for polymers **B** and **E** prepared at various non-stoichiometric ratios (see Figure S4). Such a behavior is typical for oligomers, which means that the products isolated have chain lengths that remain below the critical mass required for full entanglement. This is not an issue for a potential application as energetic binder, since only oligomers or prepolymers are needed, which are crosslinked during the formulation.[15]

The decomposition temperatures were determined in the same conditions as the T_g determination, but with a heating rate fixed at a 2 °C.min^{-1}, to get more accurate values for the integrals and onset temperatures. Conversely, decomposition of the polymers always occurred between 120°C and 130 °C (with the exception of **C**, whose decomposition is slightly higher, compare entries 1-2, 4-5 to entry 3). This suggests that the polymer structure has only a weak influence and therefore that the decomposition is governed by the tetrazene unit (and not by the azide, in the case of **D-E**). This temperature is suitable for further energetic applications.

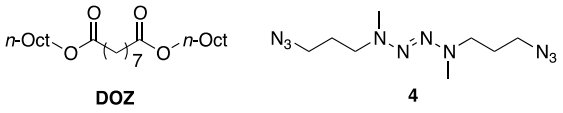
Gratifyingly, the decomposition energy density of the polymers was high.[16] The simple polytetrazenes **A** and **B** exhibit a decomposition energy of ~800 J.g^{-1} (entries 1-2). Interestingly, the addition of the energetic azide group as substituent nearly doubled the energy density of **D**, relative to **B**, and more than tripled that of **E**, relative to **C**. Clearly, tetrazenes are very promising as they allow to pack more energy in the polymer main chain, while retaining the possibility to install energetic substituents on the side-chains as well.

Thermo Gravimetric Analyses (TGA) were then carried out. Polymer **A** decomposed in a single step, corresponding to a 95% mass loss. The other four polymers decomposed in two steps, a first one (approx. 120-220°C) with a 20-30% mass loss, immediately followed by the degradation of the remaining material (overall > 95% mass loss, see SI).

Given its thermal sensitivity profile, one could expect the tetrazene moiety to be the first to decompose.[17,18] Therefore, the tetrazene motif could act as a weak link, that ruptures at a moderately high temperature, thus enhancing the performance of the decomposition. TGA obviously does not provide an accurate representation of the phenomena happening inside a rocket booster. However, a lower combustion residue implies that the polymers decomposes easily and more fully (< 5 wt% residue at 1000 °C), which is desirable in a booster binder.

• *Plasticization*. If one wants to use the polytetrazenes in propellant formulations, they need to withstand harsh environmental conditions. In particular, this means that their T_g should be as low as possible to keep the mechanical properties in the cold. Plasticizing our polytetrazenes appeared to us as a highly suitable method to reach lower T_g's.

Polymers **C** and **E** were selected for this study because **C** has a promisingly low T_g and **E** has the highest energy content of the five materials we prepared. As the plasticizer, we initially chose dioctyl azelate (DOZ, Figure 2) as it is a common plasticizer. However, DOZ proved ineffective at reducing the T_g of **C** at any weight ratio, likely because of its incompatibility with the polymer matrix. Indeed, demixing was observed macroscopically above 9.0% weight ratio. Besides, DOZ is also inert from an energy standpoint, thus any amount of it would cut into the overall energy stored.



DOZ **4**

Figure 2. Plasticizers used in this work.

We therefore thought that an acceptable plasticizer should also include the tetrazene moiety. This is why we turned our attention to the use of **4**, which is easily obtained in one step from **1b**, via direct azidation with diphenylphosphoryl azide (DPPA) in toluene at 70°C (see SI). The insertion of the azide groups on **4** further enhances its energetic potential (decomposition energy of 950 J.g^{-1} at 131°C).[19,20]

The addition of **4** to polymers **C** and **E** resulted in substantial T_g decreases, up to ~30°C (Table 3). The lowest T_g measured was –61°C at 30 wt% of **4** (Entry 6). Nevertheless, the more realistic formulations with 18 wt% of **5** allowed us to reach a T_g of –50°C for formulated polymer **C** and –36°C for formulated polymer **E** (entry 5).

This shows that **4** is an efficient energetic plasticizer. Most of the energetic plasticizers used today are nitric esters, such as nitroglycerine, 1,2,4-butanetriol trinitrate or triethylene glycol

dinitrate, which can react with the binder over time, leading to stability issues which can cause accidents.[21] From that point of view, having an azido-based plasticizer should be of interest for pyrotechnic applications.

Table 3. Glass transition temperatures of copolymers **C** and **E** with tetrazene **4** at various weight ratios.

Entry	**4** (wt%)	**C**: T_g (°C)	**E**: T_g (°C)
1	0	–28	–7
2	5	–33	–13
3	9	–39	–21
4	14	–42	–29
5	18	–50	–36
6	30	–61	n.d.

• *Depolymerization*. During our SEC optimization, we observed that the dissolution of the polytetrazenes in HFIP led to their partial degradation. We decided to investigate this further. Polymer **C** was left in HFIP for a week at room temperature. The ^{1}H-NMR of the crude product revealed a shielding of the signal attributed to the methyl of the tetrazene, from 2.74 to 2.41 ppm. We suspected that HFIP reacted with the tetrazene via H-bond activation, triggering a reaction leading to the release of N_2. Besides, the SEC showed that the average molar masses decreased almost ten-fold to a single narrow distribution, reminiscent of a discrete organic molecule, albeit a slight shouldering of the signal remains visible. This suggests that the polymer is converted to almost a single product (Figure 3, see NMR in SI).

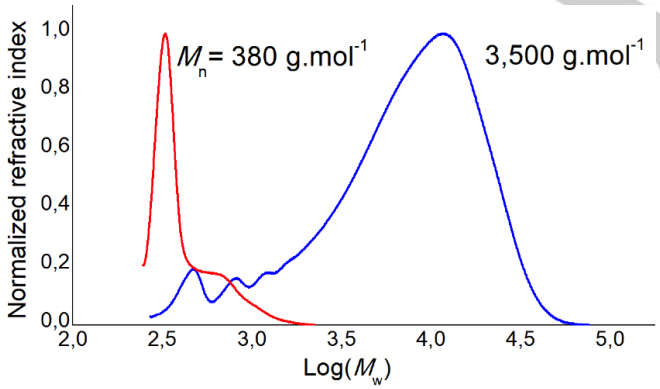


Figure 3. SEC profile of Polymer **C** before (blue) and after (red) treatment by HFIP.

We identified this product as **5** by mass spectrometry thanks to its molecular peaks and fragments (mostly, the deaminated ions (Figure 4). It very likely comes from the radical cleavage of the tetrazenes, leading to the release of nitrogen and the formation of aminyl radicals, that abstract a hydrogen atom from somewhere on the polymer chain. Tetrazenes are known to decompose into (among other molecules) aminyl radicals under acidic conditions.[22-24] While there is no acid in the HFIP solution of **C**, the polarized OH bond of HFIP can play the same role as an actual proton. Step by step, the polymer chains are cleaved in small pieces, with **5** being the smallest (and major) one observed.

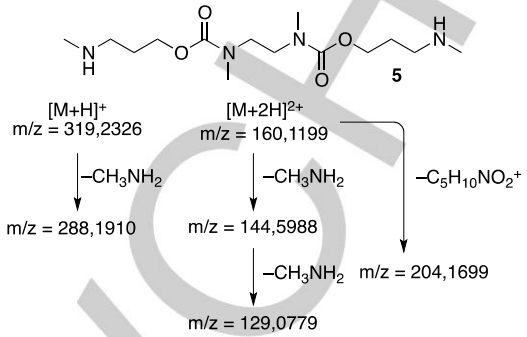


Figure 4. Diamine **5** obtained from the depolymerization of **C** and its main fragments observed in ESI-MS.

We believe this depolymerization to be of interest. Indeed, most out-of-date pyrotechnic compositions containing inert binders are disposed of by fire. The environmental impact of this method is a growing concern, and research is being made to improve the recycling process.[25] The HFIP-mediated easy depolymerization of the binding polymer could therefore prove beneficial for the dismantling of obsolete ordnance.[26]

To conclude, a new class of energetic polymers based on tetrazene motifs embedded in their main chain and with decomposition energies up to 1790 J.g^{-1} was synthesized via the polycondensation of tetrazene-based monomers and diamines. The T_g values of the polytetrazenes ranged from 0°C to –34°C. They could be significantly lowered upon plasticization with a tetrazene-based energetic plasticizer. Also, all decompositions left little residue at 1000 °C. Finally, HFIP is able to depolymerize the polytetrazenes, a first step toward industrial recycling. Future work will focus on the downstream requirements for the production of boosters, ie compatibility of the polymers towards charges and cross-linking to propergols.

Acknowledgements

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Keywords: Nitrogen • Azo Compounds • Polymers • Energetic Materials • Depolymerization

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[14] The yields were determined after aqueous work-up. The observed values were inferior to the quantitative yield expected for a polycondensation. It is likely that oligomeric chains of lower average molar masses were separated from the bulk of the polymer during this washing step.

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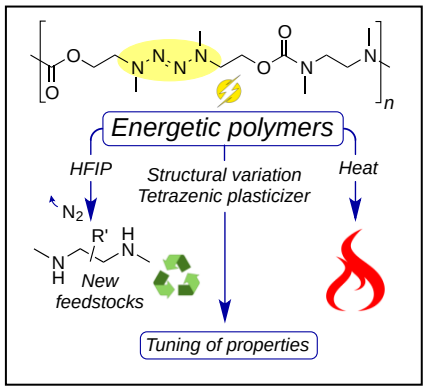

Polytetrazenes are energetic polymers with main-chain energetic moieties, obtained by polycondensation of tetrazene monomers and diamines. They decompose thermally at ~130 °C and release up to 1790 $J.g^{-1}$; their glass-transition temperatures range from –61 to 0°C, depending on the nature of the monomers and the presence of a diazido-tetrazene plasticizer. HFIP enables depolymerization of the chains, in a reaction that releases nitrogen.

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