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ARTICLE

Evaluating the Bis-isoxazole Core for Energetic Heterocyclic-Based Oligomers

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Development of energetic polymers is at the forefront of the energetics research enterprise. Formulations having high energy density as well as robust safety are goals that can be realized with implementation of new energetic polymers that target performance and mechanical properties. Presented herein are a series of oligomers synthesized from the small molecule BIDO (**1**) as our group's first attempt at making heterocyclic based energetic polymers absent sensitive explosophores. Crystallographic investigation of the BIDO core with surrogate addends demonstrated the significant stacking ability of the BIDO core. Synthesis of four unique oligomers (**3**⍰**6**) are presented and characterized by spectroscopic and thermochemical measurements. Polymerization of **6** was demonstrated and tested for Tg and thermal sensitivity by way of DSC measurements. The polymer **7** exhibits a Tg value (−18 °C), close to operating range of other energetic materials and thermally decomposes at 320 °C.

Introduction

The design of new explosive and propellant formulations, in compliance with insensitive munitions (IM) directives, require that performance be increased, while concurrently increasing stability and safety. Additional requirements include higher density, reduced environmental impact, improved mechanical properties, and extended service life. These metrics often contradict each other in that additional performance generally comes at the cost of safety and stability. The combination of high explosives (HE) with modest quantities of polymer delivered a way to desensitize explosive material to external stimuli (impact, friction, spark, heat, shock). The dilution of the HE, however, limits performance of the formulation to the percent solids loading of the HE.[1] The research of energetic polymers began upon realization of this problem, and the development of materials that increase safety but also provide energy to the system – to maintain a minimum threshold, or to increase performance – have been extensively researched henceforth.[2, 3]

Conventional hydrocarbon-based binders like hydroxy-terminated polybutadiene (HTPB), cellulose acetate butyrate (CAB), Estane®, and a variety of halogenated polymers were incorporated for their inertness, density and excellent mechanical properties, yet lacked any energetic prowess.[4] Energetic pre-polymers such as glycidyl azide polymer (GAP), polyGLYN (PGN), polyNIMMO and others (Figure 1) have been researched extensively in efforts to bolster performance of formulations.[4-13] Materials like GAP, polyAMMO, and polyBAMO, exhibit azido (–N_3) explosophores from the backbone. The pendant azide group provides nitrogen content and exceptional energy release (~685 kJ/mol) by scission of the azide moiety (N_3) to molecular nitrogen (N_2) leaving behind a nitrile group (CN) on the backbone.[1, 14] Furthermore, oxygen in the backbone of these polymers provides added density and oxygen balance (OB), both beneficial for maximizing performance. Other established energetic polymers such as polyNIMMO and PGN have nitrate ester groups in the repeat monomer. These have excellent miscibility with high energy oxidizers[10] but have poor mechanical properties and higher (less negative) T_g values than that of corresponding azido materials.[15]

A commonality between these materials is crosslinking to a final polymer via urethane linkage. Polymerization of polyols into polyurethanes with polyfunctional isocyanates is robust, well established commercial chemistry that produces durable materials spanning every major market. Polyurethanes find usage in clothing, automobiles, construction, and medicine, to name a few, and since their incorporation into polymer bonded explosives (PBX's), they have been a staple in the energetics industry as well.[16]

Some drawbacks of the current azide/nitrate ester-based energetic polymers are the thermal and chemical stability of the explosophores. Azides have excellent stored energy (~685 kJ/mol), but add no oxygen to the system, and are noted for their sensitivity to external insults.[17] Nitrate esters provide better oxygen content than azides, but generally require stabilizers to scavenge the NO_x products that catalyze further exothermic decomposition and off-gassing that can lead to unpredictable and delayed but violent reactions.[18, 19]

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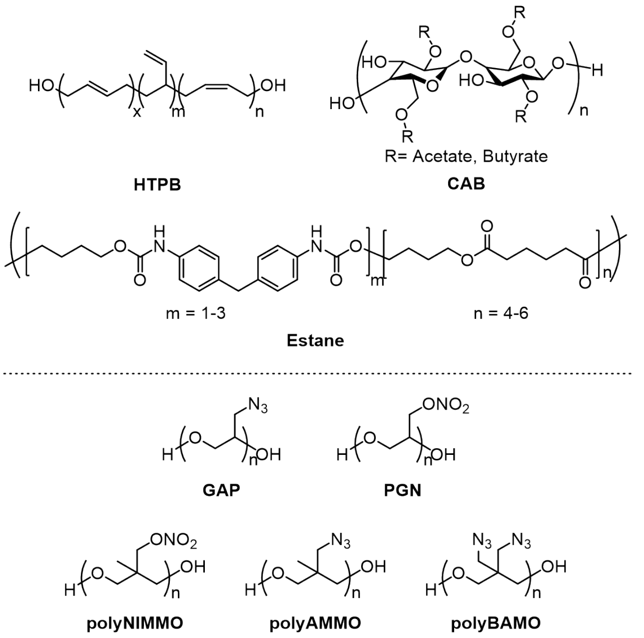


Figure 1. Repeating units of common inert prepolymers (top) and energetic pre-polymers (bottom).

A noted exception to the rule is that of PETN, one of the most useful nitrate ester explosives. PETN is used without typically added stabilizers with minimal issue, so other useful nitrate esters are probable. Aside from the sensitivity of the functional groups; GAP, PGN, and other energetic pre-polymers described above have thermal degradation temperatures between 195⍰230 °C (Table 1), which are significantly lower than that of HTPB or Estane® which decompose at temperatures greater than 375 °C. The GAP pre-polymers exhibit T_g values of approximately –40 °C, values close to the acceptable lower-bound of the operational temperature window, but could still cause aging problems.[3, 8] As PGN is cured, degradation of the material is often observed from the terminal nitrate ester.[2, 20] Efforts to end modify the material (EM-PGN) to slow or stop the degradation were seemingly unsuccessful,[21] yet there is still significant interest in EM-PGN for its energetic and mechanical qualities.[22-24] PolyNIMMO has exhibited off-gassing in the curing process requiring stabilizer in the final product,[1] and PolyBAMO is a solid material with a high melting point limiting its use as a homopolymer in most formulations. It is instead commonly used as a copolymer with polyNIMMO or other liquid materials.[11] Thus, an opportunity presents itself to bridge the gap between energetics and inerts – in both thermal and mechanical regimes – by use of HE precursor CHNO compounds that have exceptional energetic properties, high oxygen balance, and avoid sensitive explosophores like azides and nitrate esters.

To understand which properties of novel explosives have the greatest effect on performance the equations from Kamlet and Jacobs classic text "Simple Method for Calculating Detonation Properties of CHNO Explosives"[25] is still very relevant and enlightening. The equation for detonation pressure (*P*) is shown in Equation 1, and the equation for detonation velocity (*D*) is shown in Equation 2.

$$P = K\rho_0^2 N\sqrt{M}\sqrt{Q} \qquad \textit{Eq. 1}$$

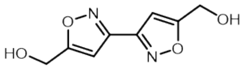
Where: P = pressure (kbars), K = 15.58, ρ_0 = initial density, N = mol of product gas/gram explosive, M = Avg molecular weight of product gases, Q = chemical energy of detonation waves

$$D = A\sqrt{(N\sqrt{M}\sqrt{Q})}\,(1 + B\rho_0) \qquad \textit{Eq. 2}$$

Where: D = detonation velocity (mm/μs), A = 1.01, B = 1.30, ρ_0 = initial density, N = mol of product gas/gram explosive, M = Avg molecular weight of product gases, Q = chemical energy of detonation waves

From equations 1 and 2 it is shown that *P* is related to ρ_0^2, *N*, $M^{1/2}$, and $Q^{1/2}$ and that *D* is related to ρ_0, $N^{1/2}$, $M^{1/4}$, and $Q^{1/4}$. Following Kamlet and Jacobs the chemical properties that should maximize performance increases over inert polymers would be to maximize ρ_0, and *N*, while increases in *M* and *Q*, will have diminishing returns, although they should not be ignored.[26] A well-documented way to increase density and molar product gases is to incorporate heterocycles with minimal hydrogen.[26-30] Heterocycles have higher density over their carbocycle equivalents, and reducing hydrogen further increases density. Furthermore, reduced hydrogen increases oxygen balance driving the products more towards gaseous CO and CO_2. Finally, nitrogen rich heterocycles also tend to have increased heats of reaction.[26, 29, 30]

The current work seeks to incorporate heterocyclic materials into a polymeric network differing from previously reported pendant heterocycle[2, 31] and energetic salt polymer works[32] and to investigate the thermal and mechanical properties as they pertain to their utility in explosives. The isoxazole heterocycle is an attractive target as it has high heat of formation, and reduced carbon and hydrogen content.[33] Bis-isoxazole molecular precursors first reported by Quilico *et al.,*[34] were further developed by Wingard *et al.*,[35] at the 25 g scale and have shown excellent reaction with isocyanates in our studies. BIDO was oligomerized with various di-isocyanates to investigate physical state and thermal properties, furthermore, one of the oligomers (**6**) was polymerized and crosslinked with the commercially available toluene-2,4-diisocyanate terminated poly(propylene glycol) and CAPA 8025E, a commercially available polycaprolactone-based triol. The synthesis, thermal, properties and insights into using BIDO as a building block for new energetic polymers are discussed as well as the viability for polymers of this type as it pertains to the energetics enterprise to develop safer, higher performing materials.



BIDO

Figure 2. Depiction of [3,3'-biisoxazole]-5,5'-diyldimethanol (BIDO, **1**) discussed in the current work.

Experimental

General Considerations

Deuterated solvents were purchased from Cambridge Isotopes and used without further purification. The starting materials: glyoxal, hydroxylamine, N-chlorosuccinimide, 1,4-phenylene diisocyanate (Aldrich), propargyl alcohol, phenyl isocyanate (Alfa Aesar), hexamethylene diisocyanate, isophorone diisocyanate, 1,3-bis(isocyanatomethyl) cyclohexane (TCI) were all purchased and used without further purification. Additionally, toluene-2,4-diisocyanate terminated poly(propylene glycol) (Sigma) was used without further purification. Furthermore, BIDO (**1**) was prepared via previously reported procedures.[35]

Physical Measurements

Nuclear magnetic resonance (^1H and ^{13}C) spectra were collected on an Agilent 500 MHz spectrometer, chemical shifts (δ, ppm) were referenced to remaining protic species in the respective solvents. Infrared spectra were measured under ambient conditions on a Bruker Alpha Fourier transform infrared (FTIR) spectrometer equipped with a zinc selenide (ZnSe) ATR crystal. Crystallographic data were obtained on a Bruker three-circle platform diffractometer equipped with a PHOTON II CPAD detector utilizing Montel optics and a 1 µs microfocus CuKα source (λ = 1.54178 Å). Bomb Calorimetry were performed on a Parr 6300 Calorimeter. DSC measurements were carried out on a TA Instruments DSC Q2000 and analyzed with TA instruments SoftwareV24.11 Build 124. Density measurements were taken at room temperature on an Accupyc 1330 v3.03 from Micromeritics. Shore Hardness was measured on a PTC Instruments Model 306L ASTM Type A Durometer.

Synthesis of Monomers and Oligomers

[3,3'-biisoxazole]-5,5'-diylbis(methylene) bis(phenylcarbamate) (2). A 50 mL round bottom flask equipped with a stir bar and drying tube was charged with 20 mL anhydrous MeCN and BIDO (**1**) (500 mg, 2.55 mmol). The resulting yellow slurry was stirred as phenyl isocyanate (0.835 mL, 7.65 mmol) was added dropwise. The solution became homogenous as the isocyanate was consumed and upon partial addition, a white precipitate formed. After the addition was completed the reaction stirred at room temperature for 2 hours. The precipitates were filtered, dried, and collected. The filtrate was concentrated *en vacuo* and the resultant white powder was purified by dissolution of the material in ethyl acetate and precipitation by hexanes. The collected precipitate from the reaction and the purified filtrate solids were combined thus affording the carbamate (**2**) in good yield. (706 mg, 1.62 mmol, Yield: 64%). X-Ray quality clear colorless plates were grown from a solution of the complex in acetone diffused into water. ^1H NMR (500 MHz, DMSO-d_6, δ): 5.40 (s, 4H), 7.02 (t, 2H), 7.14 (s, 2H), 7.29 (t, 4H), 7.46 (d, 4H), 9.96 (s, 2H). ^{13}C NMR (500 MHz, DMSO-d_6, δ): 56.58, 103.12, 118.78, 123.28, 129.31, 139.11, 153.03, 154.18, 169.85. Infrared (cm^{-1}, neat): 3315 (m), 3125 (m), 3053 (w), 2950 (w), 1706 (s), 1603 (m), 1538 (s), 1441 (m), 1317 (m), 1231 (s), 1083 (m), 1066 (m), 911 (m), 846 (m), 746 (s), 691 (s).

6:5 BIDO:1,4-Phenylene diisocyanate (BIDO:Phen, 3). To a round bottom flask equipped with a stir bar and drying tube was added **1** (500 mg, 2.55 mmol) in 20 mL anhydrous MeCN, generating a slurry. Next, 1,4-Phenylene diisocyanate (306 mg, 1.91 mmol) was dissolved in 20 mL anhydrous MeCN and added dropwise to the reaction. As the isocyanate was added the solution became cloudy and precipitate started to form. After complete addition the reaction was allowed to stir overnight retaining the cloudy white composition. The precipitate was collected via filtration, washed with acetone, then dried yielding a 6:5 ratio BIDO:Phen oligomer (**3**) as a chalky, white chips (680 mg, 0.344 mmol, 80% yield). ^1H NMR (500 MHz, DMSO-d_6): δ 4.66 (s, 4H), 5.37 (s, 20H), 5.80 (s, 2H), 6.88 (s, 2H), 7.13 (s, 10H), 7.39 (s, 20H), 9.86 (s, 10H). Infrared (cm^{-1}, neat): 3317 (w), 3119 (w), 1710 (vs), 1566 (m), 1526 (m), 1411 (m), 1314 (m), 1221 (s), 1066 (m), 912 (w), 815 (w). Heat of Formation: –2.41 kJ/g. Decomposition (peak): 316 °C.

3:2 BIDO:Hexamethylene diisocyanate (HDI) oligomer (BIDO:HDI, 4). To a round bottom flask equipped with a stir bar and drying tube was added **1** (2.0 g, 10.2 mmol) in 60 mL anhydrous MeCN. Next, HDI (1.14 g, 1.09 mL, 6.8 mmol) was added to the reaction vessel dropwise. Upon addition the solution became cloudy and the reaction stirred overnight forming a white precipitate. The precipitate was collected by filtration and washed with MeCN and acetone affording the 3:2 oligomer as white chips (3.05 g, 3.29 mmol, quantitative yield). ^1H NMR (500 MHz, DMSO-d_6, δ): 4.66 (s, 4H), 5.23 (s, 8H), 5.81 (s, 2H), 6.87 (s, 2H), 7.01 (d, 4H), 7.45 (t, 4H). Infrared (cm^{-1}, neat): 3318 (m), 3125 (w), 2936 (w), 2867 (w), 1696 (vs), 1538 (s), 1334 (m), 1262 (s), 1145 (m), 1052 (m), 1001 (m), 908 (m), 842 (w). Heat of Formation: –2.57 kJ/g. Melting Point: 154 °C. Decomposition (peak): 316 °C.

5:4 BIDO:1,3-Bis(isocyanatomethyl)cyclohexane oligomer (BIDO:Cy, 5). To a round bottom flask equipped with a drying tube was added **1** (1 g, 5.1 mmol) in 20 mL of anhydrous THF. Next, 1,3-bis(isocyanatomethyl)cyclohexane (0.791 g, 0.719 mL, 4.08 mmol) was added dropwise, neat into the reaction mixture. The solution became cloudy white as the isocyanate was added then homogenous with a light-yellow tint. The reaction stirred overnight. The solvent was removed *en vacuo* affording an off-white semi-crystalline powder (1.81 g, 1.03 mmol, quantitative yield). ^1H NMR (500 MHz, DMSO-d_6, δ): 4.66 (s, 4H), 5.22 (s, 16H), 5.79 (s, 2H), 6.85 (s, 2H), 7.00 (s, 8H), 7.43 (dt, 8H). Infrared (cm^{-1}, neat): 3316 (w), 3124 (w), 2915 (w), 2851 (w), 1696 (vs), 1536 (m), 1238 (s), 1143 (m), 1026 (m), 1001 (m), 906 (m), 767 (w). Heat of Formation: –1.76 kJ/g. Decomposition (peak): 332 °C.

4:3 BIDO:Isophorone diisocyanate oligomer (BIDO:Iso, 6). To a round bottom flask equipped with a stir bar and drying tube was added **1** (2 g, 10.2 mmol) in 40 mL anhydrous THF generating a slurry. Next, Isophorone diisocyanate (1.69 g, 1.61 mL, 7.65 mmol) was added dropwise, neat to the reaction. The slurried particulates became dissolved as the isocyanate was added and remained homogenous as the reaction stirred overnight. The solvent was removed by rotary-evaporation and the resultant oil was triturated with acetone and pumped to dryness removing any residual THF thus affording the 4:3 BIDO:Iso oligomer as an off white powder (3.71 g, 2.55 mmol, quantitative yield). ^{1}H NMR (500 MHz, DMSO-d$_6$ δ): 4.66 (s, 4H), 5.24 (d, 12H), 5.79 (s, 2H), 6.88 (s, 2H), 7.01 (s, 6H), 7.37 (dd, 4H), 7.49 (t, 2H). Infrared (cm^{-1}, neat): 3323 (w), 3142 (w), 2951 (w), 1703 (vs), 1519 (s), 12335 (s), 1125 (m), 1033 (s), 902 (s), 810 (m), 771 (m). Heat of Formation: –1.71 kJ/g. Decomposition (peak): 338 °C.

Polymer Synthesis

4:3 BIDO:Iso Polymer (7). To a round bottom flask equipped with a stir bar, reflux condenser, and drying tube was added **6** (1 g, 23 mg OH) in 30 mL anhydrous THF. Next, Capa 8025E (100 mg, 8.2 mg OH) was added neat, followed by toluene-2,4-diisocyanate terminated poly(propylene glycol) (867 mg, 31.2 mg NCO) and the reaction was allowed to stir at 65 °C overnight. The turbid, yellow mixture was evaporated under vacuum affording a yellow oil. The oil was triturated with acetone and pumped to dryness resulting in a stiff, translucent solid. The material was placed under vacuum overnight to remove any residual solvent. Glass Transition (T_g): −18.4 °C. Decomposition (peak): 320 °C. Thermogravimetric Analysis (TGA) (onset): 253 °C. Density (He pycnometry): 1.17 g/cm^3. Shore A Hardness: 81.

Results and Discussion

The urethane (carbamate) linkage is of interest, as mentioned previously, for its ease of synthesis and oxygen content as well as stable and robust bonding characteristics. Polymerization of isocyanates occurs with the reaction of an alcohol or amine to form a carbamate or urea linkage, respectively. Generally speaking, the reaction rates of the protic materials are as follows: primary alkyl amines > secondary alkyl amines >> aromatic amines > primary alcohols > water > secondary alcohol >> carboxylic acids. Additionally, aryl isocyanates tend to react faster than alkyl isocyanates due to charge delocalization by the ring.[36]

Synthesis and Characterization of BIDO Oligomers

Initial attempts to synthesize heterocyclic based pre-polymers included reactions with Lawrence Livermore Material (LLM) precursors (Figure 3, Left). The electron deficiency of the amines precluded the formation of small molecule intermediates like **2** (Figure 4, A) even in the presence of base (1,4-diazabicyclo[2.2. 2]octane, triethylamine), heat, and common catalysts. The LLM precursor materials were too unreactive – due to the basicity of the amines – and were replaced by the BIDO heterocycle. BIDO exhibits a methylene group separating the alcohol functionality from the isoxazole ring allowing for the protic group to retain its acidity thus promoting reaction with more basic isocyanate monomers. In similar veins of research, ongoing studies are being conducted to ascertain if alkyl linkers can be appended to the LLM precursors of interest to mitigate the electron deficiency problems described above.

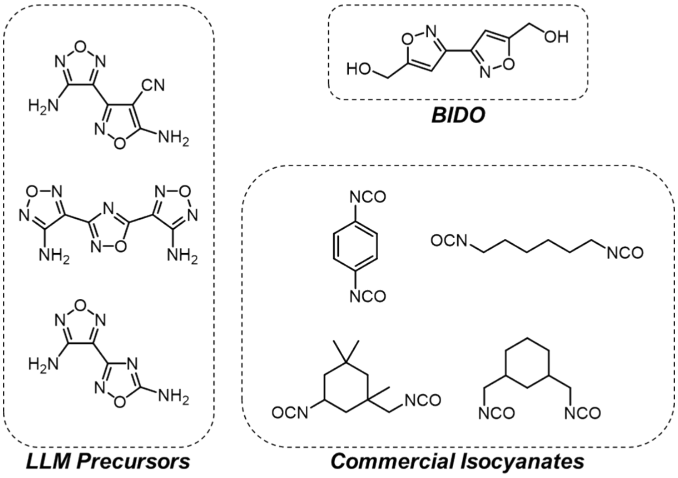


Figure 3. Prospective LLM precursors (left), BIDO (top right), and commercial isocyanates (bottom right).

Ensuing reactions with BIDO and phenyl isocyanate resulted in formation of compound **2**. This small molecule rendered the following analyses (SCXRD, NMR, IR) possible which are not accessible to most polymeric materials. The crystal data obtained provided a view into the packing of the molecule in the solid state (Figure 4, B and C) demonstrating that BIDO was a viable material for polyurethane chemistry and indicated that the stacking properties of the flat BIDO portion of the molecule would prove difficult in our attempts to synthesize room temperature liquid prepolymers. Indeed, BIDO spans 8.7 Å between CH_2 terminations providing excellent opportunity for ring stacking leading to increased crystallinity and therefore strength of BIDO based polymers. The two isoxazole rings were in an ‘up-down’ orientation (as opposed to ‘up-up’) to minimizing steric repulsion of the aryl C – H moieties (Figure 4, A), and the torsion between the two isoxazole rings was 0.3° making the BIDO portion extremely planar. The amide portion of compound **2** has a wide range of torsion (81 – 99°) in reference to the BIDO plane which is acting as a the ‘flexible’ portion of these materials (Figure 4, B) and gives some dampening effect to the dominant ring stacking. This behavior could be expected in all the oligomers developed herein which would give additional evidence behind their solid nature despite vastly differing isocyanate counterparts.

While these oligomers likely form strong hard resins if crosslinked with a triol and oligomeric poly-isocyanate, our intent was to make room temperature liquid oligomers. To that end, reactions with four different difunctionalized isocyanates: phenyl diisocyanate (Phen), hexamethylene diisocyanate (HDI), 1,3-bis(isocyanatomethyl) cyclohexane (Cy), and isophorone diisocyanate (Iso) were chosen specifically in an attempt to overcome the ring stacking propensity of BIDO and produce a room temperature liquid prepolymer. Our methodology was not conventional as the isocyanate portion of polymers is generally considered the ‘hard’ segment of a material. In our studies we utilized them as ‘soft’ segments to mitigate the rigid and stacking nature of BIDO. Materials ranging from 900–1800 molecular weight were obtained from the ensuing reactions (3�6) and each presented as a solid, thus confirming that the large flat BIDO core is not amenable to forming liquid prepolymers, even at very small masses. However, our lowest molecular weight material (**4**) did exhibit a melting point of 154 °C, the only one of our materials to melt before decomposing, indicating the change the isocyanate did in fact produce differences in the physical properties of the materials.

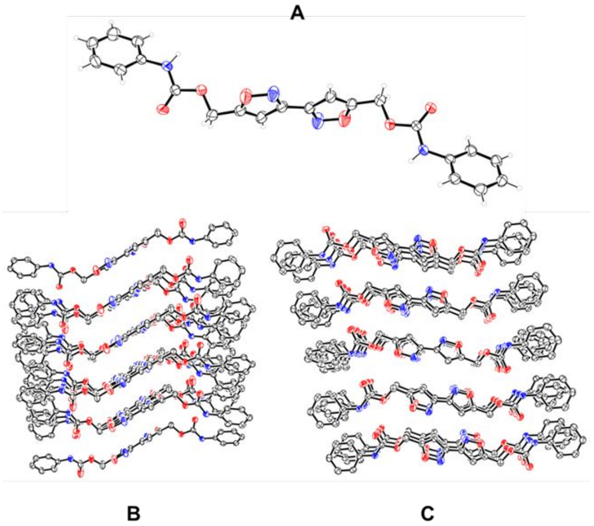


Figure 4. Crystal structure of **2** (thermal ellipsoids 30%) displaying the asymmetric unit cell (A) and packing of the molecule (B/C).

Oligomers (**3�6**) were characterized via ^{1}H NMR, IR, combustion calorimetry, and differential scanning calorimetry (DSC). The proton spectra (Figure 5) confirmed the synthesis of the small chain oligomers in the 1000–2000 molecular weight range. Interestingly, if the reactions were performed at elevated temperatures, the input and output ratios of the materials would not always align. An example: BIDO and isophorone were mixed in a 4:3 ratio at 50 °C in anhydrous MeCN. The reaction analysis (^{1}H NMR) demonstrated the oligomer was composed of a 10:9 ratio of isoxazole to isocyanate moieties opposed to the 4:3 ratio obtained at room temperature in the same solvent. Furthermore, if the input ratio was increased to 10:9, a 25:24 product ratio was the result.

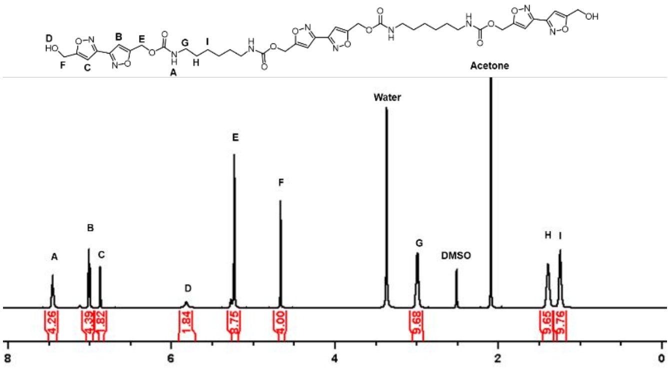


Figure 5. NMR Spectrum of **4** confirming oligomerization. Spectrum Parameters: DMSO-d$_6$, 23 °C, 500 MHz, δ in ppm.

At a composition ratio of 25:24 the material formed a plastic, recalcitrant to solvation (Figure S11, *Supplementary Information*). Ratios of the BIDO to isocyanate in the oligomer shifting when at elevated temperatures is not yet understood and is being further researched. Short chain (3:2, 4:3, 5:4) oligomers were utilized for polymer synthesis as they were soluble enough for further reaction.

The DSC scans of **3�6** gave an indication of the thermal stability of the materials. Decomposition temperatures (T$_d$) ranged between 316–338 °C for the oligomers, indicating high thermal stability (Figure 6). Materials that exhibit high thermal stability are of interest for the obvious safety benefits, but also for high temperature applications such as deep oil rock fracturing[37] or reliable stage separation for space exploration.[38] Furthermore, the oligomeric derivatives all exhibited decomposition temperature similar to BIDO indicating the addition of the fuel-rich diisocyanate links did not completely stabilize BIDO to the point it offers no energetic benefit.

Heat of formation values were determined by combustion calorimetry and were the quantitative metric of choice to compare energetic prowess with that of more common energetics. The data gleaned from the experiments can be found in Table 1 below. The BIDO monomer has a ΔH_f value of –2.01 kJ/g but is improved when oligomerized into **5** and **6** at –1.76 and –1.71 kJ/g, respectively. These in comparison with inert materials like CAB and Estane® (–4.93 kJ/g and −3.97 kJ/g respectively) show promise, but when compared to truly energetic polymers like GAP, polyBAMO, polyAMMO, whose heat of formations near or surpass zero, show that the BIDO based polymers would fall in-between the inert and energetic polymeric boundaries as intended.

Another metric to consider is oxygen balance (OB) (Equation 3). Generally, as OB approaches zero for an explosive material the impact and other physical and shock related sensitivities

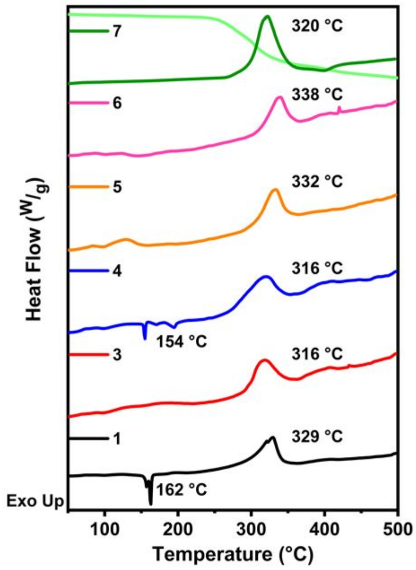


Figure 6. Differential Scanning Calorimetry traces of BIDO, oligomeric materials **3�6** and polymer **7**. TGA measurement of **7** included (light green) displaying that the mass loss aligns with the thermal decomposition of **7**.

increase.[26] However, low OB does maximize gaseous products as more carbon is oxidized to CO/CO_2 gas. In our low performance oligomer examples, **3–6** the sensitivity is not measured as the BIDO core is not considered an explosive, therefore maximizing OB is only a benefit in our oligomers. Inert binders like HTPB (OB% =−325%) and Estane® (OB% =−196%) have very negative oxygen balance, meaning, that under detonation conditions significant quantities of carbonaceous soot form which does not benefit the pressure volume work.[39, 40] Materials like GAP and PGN display less negative numbers (OB% = −121% and OB% = −60% for GAP and PGN respectively) adding to their performance, and in some cases sensitivity. The oligomers developed herein exhibit OB% numbers ranging between −142% and −173% which fall between that of the inert and energetic prepolymers described, following suit with other metrics presented in Table 1.

$$OB\% = \frac{1600}{MW}\left(z - 2x - \frac{y}{2}\right) \qquad Eq.\ 3$$

Where: MW = Molecular Weight, x = # of carbon atoms, y = # of hydrogen atoms, z = # of oxygen atoms

Material	ΔH_f (kJ/g)	T_d (°C)	T_g (°C)	OB (%)
BIDO	−2.01	329	—	−130.5
3	−2.41	316	—	−142.1
4	−2.57	316	—	−152.2
5	−1.76	332	—	−163.8
6	−1.71	338	—	−173.1
7	—	320	−18.4	—
HTPB	0.20	375	−70	−325.4
CAB	−4.93	—	80	−159.8
Estane	−3.97	390	−32	−196.2
GAP	1.44	231	−45	−121.1
PGN	−2.39	195–215	−35	−60.5
polyNIMMO	−2.67	200	−25	−114.2
polyBAMO	2.79	231	−37	−123.7
polyAMMO	0.18	—	—	—

Table 1. Thermal data depicting heat of formation (ΔH_f), decomposition temperature (T_d), glass transition temperature (T_g), and calculated oxygen balance (OB%) for oligomers **3–6**, polymer **7**, and commercial prepolymers.

Synthesis and Characterization of a BIDO Polymer

Due to the solid nature of **3–6**, either an additive or a solvent was necessary to dissolve the 'OH portion' of the formulation to a produce cross-linked urethane polymer. Initial attempts to perform solvent-free crosslinking were unsuccessful. An example solvent-free attempt is as follows; the most soluble oligomer **6** (56 wt%) was added to 1,4-butane diol (11 wt%) and polycaprolactone triol Capa 8025E (5 wt%). Even constant stirring with heating for days would not dissolve **6** in this mixture. After numerous failed attempts at solvating **6** into similar mixtures with other low viscosity polyols a shift was made to utilize **6** as an 'additive' to the mixture instead of it being the main component. Even as an additive (< 5% by mass) the compound **6** would not dissolve in 1,4-butane diol and Capa 8025E even at elevated temperatures. This solvation issue was deemed to be a function of polarity and resulted in further search of a suitable reaction medium.

The BIDO oligomer **6** (51 wt%) was finally polymerized using Capa 8025 E triol (5 wt%) and equimolar (OH:NCO) amounts of toluene-2,4-diisocyanate terminated poly(propylene glycol) (44 wt%) dissolved in THF. The reaction produced a turbid yellow solution that was dried by rotary evaporation. After trituration of the THF with acetone and placement under high vacuum overnight, a translucent rubber was recovered. Characterization of **7** by DSC (Figure S12, *Supplementary Information*) exhibited a T_g at −18.4 °C, a pronounced endotherm (123.4 °C broad, 5.58 J/g) we are attributing to residual crystalline BIDO regions melting, and a peak-exotherm around 320 °C. Thermogravimetric analysis (TGA) was conducted on **7** exhibiting an onset of mass loss at 253 °C (Figure 6, Light Green) coinciding with the onset of decomposition peak of **7** (Figure 6, Dark Green). Roughly 63% mass loss was recorded over the span of the decomposition.

Glass transition is a valuable metric to determine the temperature range over which a polymer will behave as an elastomer and when it will become brittle. In most applications explosives being stable at 0 °C and lower is often required to minimize shrinkage induced void and crack formation that increases the physical and thermal sensitivity of the explosive.[41, 42] The T_g value exhibited by **7** is approaching an acceptable temperature range for usability with a T_g almost as low as materials like PGN, polyNIMMO, Estane®, and polyBAMO.

It was also determined that the Shore A hardness of **7** was 81 which is double or more than that of several PGN based polymers (15-41)[15]. An HTPB material was tested[43] finding hardness levels between 50 and 60 indicating that our ring based polymer system does in fact add stiffness to the materials produced.

Conclusions

Presented herein are a family of oligomeric materials based on the BIDO heterocycle constituting our first approach of synthesizing heterocyclic based oligomers absent sensitive explosophores. The spectral and thermal properties of these materials were presented within the context of energetic polymers for HE formulations exhibiting decomposition temperatures between 315340 °C and ΔH_f values between −2.57 and −1.71 kJ/g. The BIDO:Iso oligomer (**6**) was utilized to generate polymer **7** which was tested for its thermal properties by glass transition temperature (−18 °C) and thermal decomposition (320 °C) and was compared with commonly utilized inert and energetic polymers. It was found that the energetic prowess of the BIDO materials in the current state was in between inert materials and known energetic polymers for common energetic indicators (ΔH_f values, thermal decomposition, and oxygen balance). A crystal structure collected on a surrogate small molecule with the BIDO core capped in monofunctional phenyl isocyanates (**2**) demonstrated strong BIDO core stacking. While the room temperature solid phase of the presented BIDO based oligomers **3–6** was not our desired target, we are performing further research into the mechanical property benefits of such heterocyclic-based core stacking polymers. Additional future work targeting room temperature liquid oligomers will research more flexible multi-ring structures and numerous single-ring heterocycle-based oligomers as well as more flexible monomer linkage chemistry such as esters, and vinyl/acrylate radical based systems that can still be crosslinked to a final polymer.

In a first effort, our materials show increased energetic utility compared to that of HTPB, Estane® and CAB materials by way of optimizing ΔH_f values, thermal decomposition, and oxygen balance. These metrics are encouraging as we seek to develop future materials that have better physical and mechanical properties to compete with commonly utilized energetic polymers. Utilization of a smaller ring system to decrease the propensity of ring stacking could provide a route to liquid prepolymers at room temperature, and the development of energetic isocyanates, or other reactive media for polymerization are also being considered to enhance the oxygen balance, chemical composition, and density which could help bridge the gap between inert polymers and energetic ones. Further research into liquid prepolymers based on heterocycles is of utmost interest to develop high loading percent energetic binder materials that could be used to achieve the safety and performance directives of the industry.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

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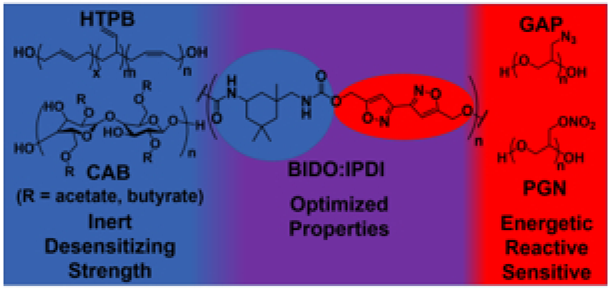
Heterocyclic energetic polymers can bridge the gap between inert and detonable energetic materials.



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