

Synthesis, Characterization, and Energetic Properties of Nitrate Ester Acrylate Polymer

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Cite This: *ACS Omega* 2023, 8, 38879–38884



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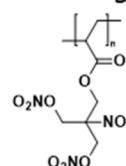
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Supporting Information

ABSTRACT: An energetic nitrate ester acrylate monomer (**4**) was synthesized in a total yield of 68% and polymerized to form the energetic nitrate ester acrylate polymer (NEAP). Compound **4** is a liquid at room temperature with a melting point of -8.6 °C and NEAP is a solid with a glass-transition temperature of -8.8 °C. Intermediates leading to **4** and NEAP were characterized by high-resolution mass spectrometry, elemental analysis, Fourier transform infrared spectroscopy, and proton and carbon nuclear magnetic resonance spectroscopies (^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR). Both **4** and NEAP have electrostatic discharge, friction, and impact sensitivities comparable to those of trinitrotoluene, making NEAP a potential candidate for advanced energetic formulations.

High Yielding Synthesis & Energetic Polymer



N-NEAP
 $n = 3 - 10$ units
 $M_w = 1,040 - 3,020$ g/mol



1. INTRODUCTION

Advancements in energetic systems such as propellants, explosives, and pyrotechnics rely on the optimization of the energetic formulations. The main components of an energetic formulation are the explosive material and a polymer that binds the explosive particles together to keep the formulation moldable and safe to handle. The combination of these polymers and plasticizers are typically referred to as binders, and these materials are typically fuel-rich and nonenergetic. While these binders are necessary to hold explosives together and reduce their sensitivities, they reduce the overall energetic performance compared with pure explosive materials. For example, explosive C-4 contains 91% of the explosive 1,3,5-trinitro-1,3,5-triazinane (RDX) and 9% binder. While C-4 has low mechanical sensitivities and can easily be molded for a variety of applications, it is less powerful than RDX on its own.¹ One of the major goals of energetic material research is to develop formulations with increased performance compared with conventional energetics, such as C-4. Obtaining these higher-performing energetic formulations is usually achieved through either using a more powerful explosive or by increasing the ratio of explosive to polymer. However, these methods typically result in materials that are more sensitive and less malleable, inhibiting their widespread application. To combat this, incorporating explosophores into the polymer backbone became a strategy to synthesize energetic binder materials that could be used to develop formulations with increased performance.² The energetic binder polyglycidyl nitrate [poly(GLN)]³ was developed in 1952 and since its first report, researchers have used it as an energetic binder in several explosive formulations,⁴ resulting in high-energy

systems that maintain their reduced vulnerability to mechanical insults, including impact, friction, and electrical discharge.⁵ While poly(GLN) increases an energetic formulation's properties, there are limitations in its use due to its relatively low decomposition temperature that results in decured poly-(GLN).^{6,7} Additionally, poly(GLN) has low density, oxygen balance, and heat of formation, giving it poor explosive performance properties compared with conventional explosives, like RDX.

To mitigate the thermal decomposition, acrylate-based polymers have been investigated for their enhanced mechanical properties and better stability, due to the strong C–C bonds that form upon polymerization.⁸ Furthermore, acrylates undergo a UV radical-catalyzed polymerization using a photo initiator that does not require harsh conditions that may be incompatible with energetic materials.⁹ Herein, we report the synthesis and characterization of the nitrate ester acrylate monomer 2-nitro-3-((nitrooxy)-2-((nitrooxy)methyl)propyl acrylate and its polymer nitrate ester acrylate polymer (NEAP), which has better sensitivity and predicted performance than poly(GLN).

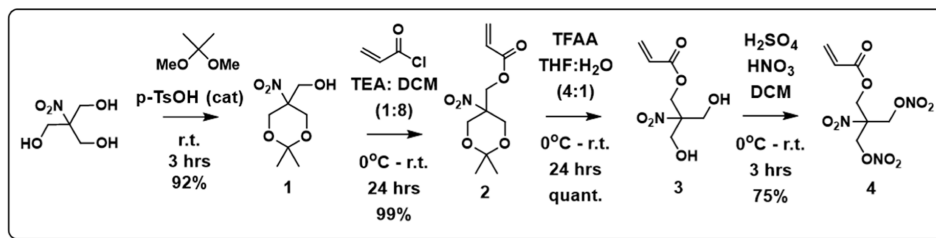
Received: April 20, 2023

Accepted: September 27, 2023

Published: October 13, 2023



Scheme 1. Synthesis of Monomer 4



2. RESULTS AND DISCUSSION

2.1. Synthesis of Energetic Acrylate: Monomer 4. The synthesis of 2-nitro-3-(nitrooxy)-2-((nitrooxy)methyl)propyl acrylate (**4**) began with the acid-catalyzed acetal protection of commercially available tris(hydroxymethyl)nitromethane to form compound **1** (Scheme 1). Originally, we pursued other routes using selective nitration¹⁰ and mono acrylation^{11,12} of tris(hydroxymethyl)nitromethane to minimize the number of synthetic steps, but these reactions resulted in mixtures that were difficult to purify. Morin and Sello reported acetal-protected compound **1** by using 2,2-dimethoxypropane as an acetone surrogate, preventing the generation of water in the process, thus preparing **1** in quantitative yield after 15 h.¹³ In a similar method, we were able to isolate compound **1** in 92% yield after only reacting for 3 h. Methyl signals in the proton nuclear magnetic resonance (¹H NMR) spectrum at 1.40 and 1.23 ppm and carbon (¹³C{¹H}) NMR signals at 20.0 and 26.9 ppm confirmed the established protecting group of compound **1**. Subsequent acryloylation of the remaining alcohol group on compound **1** was conducted under basic conditions using an 8:1 mixture of dichloromethane (DCM) and triethylamine (TEA) and dropwise addition of acryloyl chloride at 0 °C. The reaction was allowed to warm to room temperature and compound **2** was isolated after 24 h in near quantitative yield (Scheme 1). The identity of compound **2** was confirmed through chemical characterization via ¹H and ¹³C{¹H} NMR spectroscopies. New signals at 6.33, 6.15, and 6.01 ppm with splitting patterns matching acrylate substitution were observed in the ¹H spectrum. The ¹³C{¹H} NMR also had new signals at 164.4, 133.1, and 127.1 ppm corresponding to the acrylate group (see Experimental Methods and the Supporting Information). After acrylation, acetal deprotection of **2** produced compound **3** in quantitative yield, using a modified literature procedure,¹⁴ consisting of trifluoroacetic acid in a solution of 4:1 tetrahydrofuran (THF) and water (Scheme 1). By keeping the reaction at or below room temperature, the acid-labile acrylate group remained intact. Compound **3** was characterized through the loss of the dimethyl acetal group in the ¹H and ¹³C{¹H} NMR spectra. Compound **3** was subjected to mixed acid nitration using fuming (90%) nitric acid and sulfuric acid (85%) in DCM chilled to 0 °C. After neutralization and extraction of the organic layer, monomer **4** was obtained in 75% yield. Additionally, all compounds (**1**–**4**) were isolated as pure materials after either rotary evaporation (compounds **1** and **3**) or aqueous workup and extraction (compounds **2** and **4**) with little to no purification necessary.

Fourier transform infrared (FT-IR) spectroscopy comparisons of compounds **1** and **4** are shown in Figure 1 to highlight the overall transformations from this route. Where compound **1** (blue, top spectrum) has a strong O–H hydroxyl stretch at 3328 cm⁻¹ (red vertical marker) and an N–O nitro stretch at

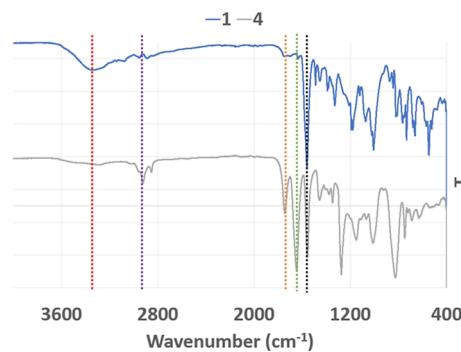


Figure 1. FT-IR data comparing compounds **1** and **4**. Highlighted wavenumbers correspond to hydroxyl (red, 3328 cm⁻¹), alkene (purple, 2921 cm⁻¹), carbonyl (orange, 1743 cm⁻¹), alkene (green, 1641 cm⁻¹), and nitro (black, 1556 cm⁻¹) stretches for each **1** and **4**.

1556 cm⁻¹ (black vertical marker). However, compound **4** lacks the hydroxyl stretch yet gained the C=C alkene stretch (purple, 2921 cm⁻¹), C=O carbonyl stretch (orange, 1743 cm⁻¹), other C=C alkene stretch (green, 1641 cm⁻¹), and maintained the N–O nitro stretch (black, 1556 cm⁻¹). Despite the acid lability of the ester acrylate group, this data along with high-resolution mass spectrometry (HRMS) (see Experimental Methods) confirm that the nitration took place without compromising the ester acrylate group.

X-ray quality crystals of compound **2** were obtained through slow evaporation of a solution containing **2** in THF and confirmed the successful acrylation of **1**. Compound **2** was determined to have an orthorhombic crystal system with a *P*2₁2₁2₁ space group, as illustrated in Figure 2. Intermolecular

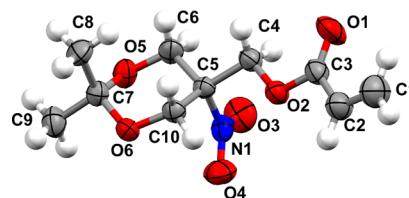


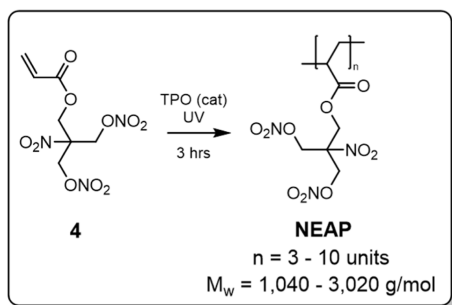
Figure 2. Molecular conformation of **2**, non-hydrogen atoms are shown as 50% probability displacement ellipsoids. Ellipsoids of **2** are shown at 50% probability.

interactions with the neighboring residue likely dictate the crystal packing with short contact distances of 2.4–2.6 Å measured between the acrylate carbonyl oxygen (O1) and the hydrogen atoms from carbons C6 and C10. Intramolecular interactions between hydrogen atoms from C4 and acrylate carbonyl oxygen (O1) also had similar short contact distances of 2.4–2.6 Å. The bond distance between C1 and C2 at 1.304(4) Å is consistent with typical C=C bond distances of

related acrylates^{15,16} and is in agreement with IR and NMR data.

2.2. Synthesis of NEAP. Compound **4** underwent radical polymerization using the photo cationic initiator diphenyl-(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) irradiated at 350 nm to form NEAP (Scheme 2), producing a flexible,

Scheme 2. Synthesis of NEAP under Photochemical Conditions^a



^aMolecular weight (M_w) and number of repeating units (n) determined only for the low-molecular-weight material via GPC (1 mg/mL in ethyl acetate), due to the insolubility of the majority of the NEAP polymer.

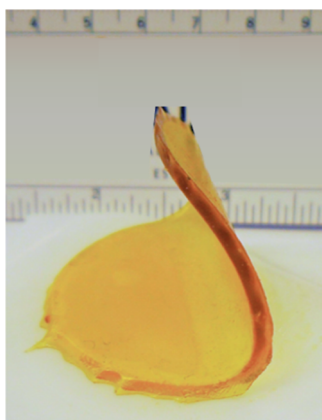


Figure 3. Photograph of the NEAP film directly after releasing clamped edges.

plastic-like material (Figure 3). Attempts to accurately determine the molecular weight via gel permeation chromatography (GPC) were unsuccessful with only partial dissolution of NEAP in the GPC mobile phase. Photographs of NEAP in solutions of dimethyl sulfoxide, *N,N*-dimethylformamide, acetone, ethyl acetate, and THF show that the polymer swells, absorbing the solvents without complete dissolution (see Supporting Information, S10). While the majority of the polymer is insoluble, GPC measurements show that the dissolved material has low molecular weights between 1040 and 3020 g mol⁻¹, implying that only the lower-molecular-weight oligomers and polymers are soluble and that higher-molecular-weight polymers are unaccounted for.

The average molecular weight of the dissolved NEAP at 2030 g mol⁻¹ is about 82% of the mass of poly(GLN) (2484 g mol⁻¹) (Table 1).¹⁷ The higher-molecular-weight chains of the dissolved NEAP were relatively low, at 3020 g mol⁻¹, corresponding to about 10 units. In addition to the insolubility

Table 1. Calculated and Measured Energetic Properties of 4 and NEAP

	4	NEAP	TNT	poly(GLN)
ρ (g cm ⁻³)	1.64 ^a	1.57	1.65 ^a	1.46 ^a
ΔH_f^a (kcal mol ⁻¹)	-36.3	-58.0 ^e	-15.1	-68.1
D_p^a (GPa)	25.08	18.75 ^e	20.13	16.74
D_v^a (km s ⁻¹)	7.45	7.07 ^e	7.21	6.82
OB _{CO₂} % ^a	-46.0	-47.7 ^e	-74.0	-85.3 ^e
M_n (g mol ⁻¹) ^f		2030		2484
T_d (°C) ^g	150	144	240	214
T_g (°C)	-67.6	14.9		-35
T_m (°C)			80	
IS ^b (cm)	140 ± 2.0	162.0 ± 2.0	150	124.4
FS ^c (N)	>360	>360	>360	>360
ESD ^d (J)	0.250	0.250	0.06	0.0625

^aCalculated values. ^bLANL type 12, 50% drop height, 2.5 kg weight. Neyer d-optimal method. ^c50% load Bruceton up/down method. ^dABL spark, 3.4% threshold initiation level (TIL). ^eMolecular weight calculated for three repeating units. ^fAverage molecular weight determined by GPC. ^gOnset of decomposition exotherm. Poly(GLN) data refs 17, 23–25. TNT data refs 26, 27.

of the majority of NEAP, the low molecular weight could also be due to radical quenching by the nitro groups on the monomer during UV curing. Similar processes have been reported where radical polymerization in the presence of nitro groups on acryl-based monomer structures act as radical scavengers and inhibit polymer growth.¹⁸

2.3. Mechanical Testing. The rubber-like properties of NEAP implied that it could be a useful component in pliable energetic formulations. To quantify the mechanical properties of NEAP, rheometry measurements were performed to measure the stress and strain for the material in shear (See Supporting Information, supplemental figures S20–S22). Here, stress is defined as the deforming force per unit area of the material, and strain is the amount of distortion experienced by the material. Stress and strain allow for an accurate description and prediction of elastic, plastic, and fluid behavior of polymeric materials.²⁰ Figure 4 illustrates the measured stress relaxation curve of NEAP measured at room temperature.

This curve is a time-dependent decrease in storage modulus under constant strain²⁰ and is plotted as the storage modulus [G' (Pa)] or elasticity of the material as a function of time (s).

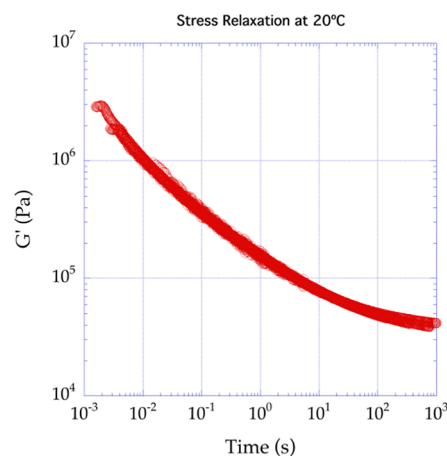


Figure 4. Stress relaxation curve for NEAP at 20 °C.

NEAP can recover by a factor of 10 Pa within the first second of the measurement, indicating that NEAP has viscoelastic properties as shown in Figure 4. This property is desirable for polymers used in energetic formulations, since high polymer flexibility generally results in formulations that are more malleable.

2.4. Energetic Properties. The physicochemical parameters of materials 4, NEAP, TNT, and poly(GLN) are listed in Table 1. The density and heat of formation of compound 4 were calculated using the method developed by Byrd and Rice and entered into the CHEETAH thermochemical code to determine the detonation pressures and velocities.^{19–21} These calculations determined that compound 4 has the highest density at 1.64 g cm⁻³, followed by TNT (1.65 g cm⁻³) and poly(GLN) (1.46 g cm⁻³). Using the same Byrd and Rice method, the calculated density for the three repeating units of NEAP was determined to be 1.68 g cm⁻³. While this information gives a narrow window of theoretical density for three repeating units, due to the molecular weight distribution of the polymer ($n = 3–10$) this could also influence a density distribution which warranted further analysis. Qualitative density of NEAP was completed by observation of the polymer in solutions of deionized water (0.99 g cm⁻³), dichloromethane (1.33 g cm⁻³), and chloroform (1.47 g cm⁻³) (see Supporting Information, S11). NEAP sank to the bottom of the vials in each of these solutions, including the solutions from GPC solubility testing, indicating that it is more dense than the solutions tested. Further quantitative analysis of NEAP density was conducted using gas pycnometry of an averaged three sample volume measurements (1.3027 cc) exhibiting an average density of 1.572 g cc⁻¹ (See Supporting Information, S12). Using the gas pycnometry density of NEAP, the detonation pressure and velocity data were calculated for the polymer using the CHEETAH thermochemical code. From the values obtained for density and heat of formation, compound 4 was calculated to have a higher detonation pressure (Dp) at 25.08 GPa and velocity (Dv) at 7.45 km s⁻¹ than NEAP (Dp 18.75 GPa and Dv 7.07 km s⁻¹), TNT (Dp 20.13 GPa and Dv 7.21 km s⁻¹), and poly(GLN) (Dp 16.74 GPa and Dv 6.82 km s⁻¹). The performance of 4 is calculated to be better than that of NEAP likely due to the higher energy of the alkene C=C bonds in 4 compared to C–C bonds in NEAP. Despite the better performance of 4 over NEAP, NEAP is a rubbery solid that has detonation properties superior to those of poly(GLN), with a detonation pressure and velocity less than those of TNT. Thermal decomposition (T_d) comparisons show that TNT ($T_d = 240$ °C) and poly(GLN) ($T_d = 214$ °C) have higher thermal stabilities than those of 4 ($T_d = 150$ °C) and NEAP ($T_d = 144$ °C). Homolytic cleavage of the C–N bond produces carbon-based radicals. The thermal stability of nitrocarbons typically follows the order of 1° > 2° > 3° because the tertiary radicals are more highly stabilized than secondary and primary radicals. The tertiary nitro groups of 4 and NEAP are likely the culprit of their low thermal stability. Glass-transition temperatures (T_g) for 4, NEAP, and poly(GLN) show that poly(GLN) ($T_g = -35.0$ °C) has a lower transition temperature than NEAP ($T_g = 14.9$ °C) but is a higher transition than 4 ($T_g = -67.6$ °C). This high transition temperature for NEAP is desirable for applications where high mechanical strength and rigidity are required.²² Within the T_g measurement for compound 4, the exotherm between 60 and 110 °C likely corresponds to the thermal polymerization of the monomer. Melt temperature

(T_m) comparisons for the solid TNT ($T_m = 80$ °C) are included for full data reporting purposes. Mechanical sensitivities including impact (IS), friction (FS), and electrostatic discharge (ESD) were measured for compound 4 and NEAP and compared to literature values for poly(GLN)^{17,23–25} and TNT.^{26,27} Both compounds 4 and NEAP were sensitive to impact at 140 ± 2.0 and 162.0 ± 2.0 cm, respectively. These materials have comparable sensitivity to impact to TNT (150 cm) but are less sensitive than poly(GLN) (124.4 cm). All four materials, 4, NEAP, TNT, and poly(GLN) were not sensitive to friction measurements with no response at >360 N. Lastly, electrostatic discharge measurements indicated that compound 4 and NEAP are both at 0.25 J, which is less sensitive than poly(GLN) at 0.0625 J and TNT at 0.06 J.

3. CONCLUSION

Compound 4 is a liquid at room temperature and was synthesized in an overall yield of 68% in four steps. Polymerization of 4 resulted in the novel energetic polymer, NEAP, that has viscoelastic, rubber-like properties. The predicted detonation properties of NEAP are better than poly(GLN) and comparable to TNT making it a good energetic binder candidate material.

4. EXPERIMENTAL METHODS

NMR data were collected on a Bruker AVANCE III 400 MHz NMR spectrometer at room temperature. Spectra were referenced to residual DMSO (proton 2.50 ppm, carbon 39.52 ppm) with chemical shifts reported in δ values (ppm) and J values in Hertz (Hz). The following abbreviations are used to describe peaks: d (doublet), brs (broad singlet), and m (multiplet). The GPC instrument used for this analysis is the Malvern OMNISEC (Westborough, MA, USA) equipped with quad detection: refractive index (RI), UV/vis photodiode array (PDA), multiangle light scattering, and a viscometer. A sample injection volume of 100 μ L of the polymer in ethyl acetate was used with a mobile phase flow rate of 1 mL/min. For all analyses, two serially coupled PL Gel Mixed C columns (Agilent Technologies, Palo Alto, CA, USA) were implemented. DSC measurements were conducted on a DSC Q-2000 from TA Instruments with temperature sweeps ranging from -80 to 400 °C. Melting temperatures were acquired using the DSC Q-2000 from TA Instruments by heating the materials to 100 °C followed by cooling to -80 °C and warming at 10 °C min⁻¹ ramp to 100 °C. Gas pycnometry was collected on a Quantachrome instrument with helium purge and averaged over three measurements.

Caution! The compounds presented are highly energetic with sensitivity to various stimuli. While we encountered no issues while working with this material, proper protective measures (Kevlar gloves, face shield, and grounded equipment) should still be used at all times.

4.1. (2,2-Dimethyl-5-nitro-1,3-dioxan-5-yl)methanol (1). Trishydroxy nitromethane (75.089 g, 0.497 mol) is added to a solution of 2,2-dimethoxypropane (100 mL) and stirred at room temperature. Catalytic *p*-toluenesulfonic acid monohydrate (0.760 g, 0.004 mol) is slowly added over many portions to the solution. Upon complete addition of catalyst, the solution became clear, and the mixture is left to stir overnight. After completion, the reaction is rotary evaporated using minimal heat to obtain 1 as a white powder in 92% yield

(87.575 g, 0.458 mol). ^1H NMR (400 MHz, DMSO- d_6 , δ): 5.48 (t, $J = 6$ Hz, 1H, OH), 4.35 (d, $J = 13$ Hz, 2H; CH $_2$), 4.05 (d, $J = 13$ Hz, 2H; CH $_2$), 3.72 (d, $J = 5.7$ Hz; CH $_2$), 1.40 (s, 3H; CH $_3$), 1.25 (s, 3H; CH $_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, DMSO- d_6 , δ): 98.5 (C), 87.5 (C), 62.4 (CH $_2$), 61.2 (2x CH $_2$), 26.9 (CH $_3$), 20.1 (CH $_3$); IR (cm $^{-1}$): $\nu = 3415, 1538, 821$; HRMS (ESI) m/z : $[\text{M} + \text{CH}_3\text{COO}]^-$ calcd for C $_9$ H $_{16}$ NO $_7$, 250.0932; found, 250.0922. Elemental Analysis calcd for C $_7$ H $_{13}$ NO $_5$, C 43.98, H 6.85, N 7.33; found, C 43.66, H 6.72, N 7.01.

4.2. (2,2-Dimethyl-5-nitro-1,3-dioxan-5-yl)methyl Acrylate (2). Compound 1 (2.345 g, 0.012 mol) is dissolved in a mixture of dichloromethane (25 mL) and triethylamine (3 mL). The solution is stirred and cooled to 0 °C via an ice bath. Acryloyl chloride (1.20 mL, 0.015 mol) is added dropwise to the chilled reaction. After complete addition, the solution was allowed to warm to room temperature and reacted overnight, during which the triethylamine hydrochloride salt began precipitating out of solution. The byproduct salt is vacuum filtered out, and remaining mother liquor is collected. This solution is diluted with more dichloromethane (50 mL) and saturated sodium bicarbonate (50 mL) to perform an aqueous workup. The organic layer is extracted, washed again three times with DI water (50 mL each), dried using magnesium sulfate, gravity filtered, and rotary evaporated to give 2 as a yellow-tan solid in 99% yield (2.980 g, 0.012 mol). ^1H NMR (400 MHz, DMSO- d_6 , δ): 6.34 (d, $J = 17$ Hz, 1H, CH $_2$), 6.15 (dd, $J = 10$ Hz, 1H; CH), 6.01 (d, $J = 10$ Hz, 1H; CH $_2$), 4.54 (s, 2H, CH $_2$), 4.42 (d, $J = 13$ Hz, 2H; CH $_2$), 4.20 (d, $J = 13$ Hz, 2H; CH $_2$), 1.44 (s, 3H, CH $_3$), 1.27 (s, 3H, CH $_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, DMSO- d_6 , δ): 164.4 (C=O), 133.1 (C=C), 127.1 (C=C), 98.7 (C), 84.8 (C), 63.1 (CH $_2$), 61.0 (2x CH $_2$), 26.8 (CH $_3$), 20.0 (CH $_3$); IR (cm $^{-1}$): $\nu = 2996, 1717, 1631, 1548, 1183, 812$; HRMS (ESI) m/z : $[\text{M} + \text{CH}_3\text{COO}]^-$ calcd for C $_{12}$ H $_{18}$ NO $_8$, 304.1037; found, 304.0653. Elemental Analysis calcd for C $_{10}$ H $_{15}$ NO $_6$, C 48.98, H 6.17, N 5.71; found, C 47.63, H 5.96, N 5.33.

4.3. 3-Hydroxy-2-(hydroxymethyl)-2-nitropropyl Acrylate (3). Compound 2 (1.466 g, 0.006 mol) is dissolved in a mixture of THF: H $_2$ O (4:1, 10 mL total), and the vessel is chilled via an ice bath. Trifluoroacetic acid (5 mL) is added dropwise, and the reaction is allowed to warm to room temperature overnight. Following completion, the reaction mixture is dried at room temperature by rotary evaporation to afford 3 as a yellow oil in 99% yield (1.95 g, 0.01 mol). ^1H NMR (400 MHz, DMSO- d_6 , δ): 6.35 (d, $J = 16$ Hz, 1H, CH $_2$), 6.18 (dd, $J = 10$ Hz, 1H; CH), 5.99 (d, $J = 10$ Hz, 1H; CH $_2$), 4.83 (s, 2H, OH), 4.50 (s, 2H; CH $_2$), 3.81 (q, $J = 12$ Hz, 4H; CH $_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, DMSO- d_6 , δ): 164.7 (C=O), 132.4 (C=C), 127.8 (C=C), 93.4 (C), 67.1 (CH $_2$), 59.7 (CH $_2$), 25.2 (CH $_2$); IR (cm $^{-1}$): $\nu = 3415, 1715, 1546, 1162, 1036, 979$; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for C $_7$ H $_{11}$ NO $_6$, 204.0514; found, 204.9701.

4.4. 2-Nitro-3-(nitrooxy)-2-((nitrooxy)methyl)propyl Acrylate (4). Compound 3 (0.160 g, 0.8 mmol) is diluted with a prechilled solution of dichloromethane (10 mL) and stirred at 0 °C via an ice bath. 90% nitric acid (1 mL) is slowly added to the reaction mixture. Concentrated sulfuric acid (1 mL) is added dropwise to the mixture and continued reacting at 0 °C. The ice bath is allowed to warm to room temperature while stirring the reaction for 3 h. Upon completion, the solution is poured over ice, neutralized to a pH of 7 using a sodium bicarbonate solution. This solution is diluted with

more dichloromethane (50 mL) and an aqueous work up is performed. The organic layer is extracted, washed again three times with DI water (50 mL each), dried using magnesium sulfate, gravity filtered, and rotary evaporated to give 4 as a yellow-orange oil in 75% yield (0.150 g, 0.508 mmol). ^1H NMR (400 MHz, DMSO- d_6 , δ): 6.39 (d, $J = 1.3$ Hz, 1H, CH $_2$), 6.17 (dd, $J = 10.4$ Hz, 1H; CH), 6.04 (d, $J = 10.4$ Hz, 1H; CH $_2$), 5.25 (dd, $J = 12.4$ Hz, 4H; CH $_2$), 4.76 (s, 2H; CH $_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, DMSO- d_6 , δ): 164.2 (C=O), 133.4 (C=C), 127.0 (C=C), 87.3 (C), 69.0 (2x CH $_2$), 61.6 (CH $_2$), 54.9 (CH $_2$); IR (cm $^{-1}$): $\nu = 1545, 1178, 1007, 547$; HRMS (ESI) m/z : $[\text{M} + \text{NO}_3]^-$ calcd for C $_7$ H $_9$ N $_3$ O $_4$, 357.0166; found, 357.0174. Elemental Analysis calcd for C $_7$ H $_9$ N $_3$ O $_{10}$, C 28.48, H 3.07, N 14.24; found, C 30.25, H 3.40, N 13.38.

4.5. NEAP. Compound 4 (2.023 g, 6.85 mmol) is added to a pan followed by diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) (0.020 g, 0.005 mmol). Both materials are mixed until homogeneous, and the pan is placed under UV irradiation (350 nm) and reacted for 3 h. Irradiation was halted to obtain a yellow, rubbery solid (1.9 g). IR (cm $^{-1}$): $\nu = 1747, 1645, 1558, 1273, \text{ and } 822$. GPC/SEC: 1040–3020 g mol $^{-1}$.

■ ASSOCIATED CONTENT

Supporting Information

The following files are available free of charge. Supporting Information (PDF) The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c02725>.

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, FT-IR data, DSC data, and TGA data for all compounds (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the LANL Science Campaign for the Harold Agnew Postdoctoral fellowship provided to V. A. Kuehl. We would like to thank Hongzhao Tian, Lisa

Klamborowski, Chris Freye, and Taylor Dehner of Los Alamos National Laboratory for providing thermal stability, sensitivity testing, high-resolution mass spectrometry, and molecular weight analyses. The authors also thank Ed Byrd for density and heat of formation calculations of the reported compounds along with Kyle Spielvogel for helpful crystallography discussion. Document released for publication under LA-UR-22-30525.

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