

Simple and Green Synthesis of a Novel Fluoro-Nitrato Energetic Plasticizer

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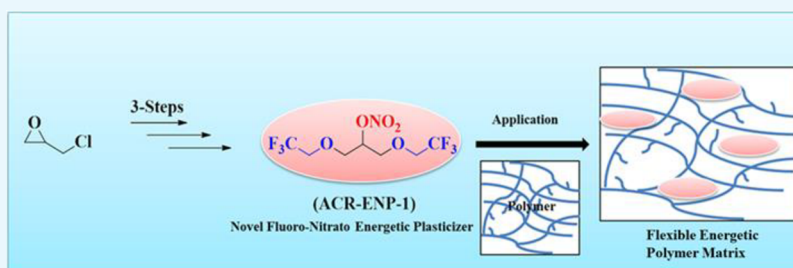
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ABSTRACT: Herein, we report a facile, simple, cost-effective, and green synthesis of a new fluoro-nitrato energetic plasticizer, 2-nitrato-1,3-di(trifluoroethoxy)propane (ACR-ENP-1). Compatible mixtures of ACR-ENP-1 with known binders demonstrated far impressive energetic and mechanical properties of the composite compared to similar composites of same binders with known energetic plasticizers.

1. INTRODUCTION

The general role of plasticizers is to increase the flexibility or processability of plastics/polymers used in a wide range of applications from automobile industry to healthcare and consumer products. Plasticizers help in improving the mechanical properties of the composite matrix, especially the binder.¹ The conventional plasticizers usually have inert and stable carbon–hydrogen-based backbone and are used in all kinds of applications. However, for energy-based applications, mixing the ingredients of the composite polymer matrix with nonenergetic plasticizers dilutes the overall energy content of the energetic system. Over the last few decades, research into development of novel energetic plasticizers has been gaining a lot of interest, for example, bis(2,2-dinitro propyl)acetal, dinitro-diaza-alkanes (DNDA-57), 1,2,4-butanetrioltrinitrate (BTTN), and *N,N*-butyl-*N'*(2-nitroxy-ethyl) nitramine as energetic plasticizers for poly(3-nitratomethyl-3-methyloxetane) (poly-NIMMO)⁹ and novel geminal dinitro esters as energetic plasticizers for glycidyl azide (GAP) binder¹¹ have shown interesting results. The main focus of energetic plasticizers is to enhance the mechanical properties and safety characteristics of the energetic formulation without diluting the overall energy content of the system. This is mainly achieved by softening the polymer matrix with lowering of the glass transition temperature (T_g) and making it more flexible to ease processing. The higher energy characteristics of the energetic plasticizer along with its ability to improve the mechanical strength of the composite enable tailoring higher performance with less loading of the energy content, thereby making future energetic composite polymer materials safer and greener.¹

The first energetic plasticizer developed for commercial application and still widely used is nitroglycerine (NG) or glyceroltrinitrate. NG was first discovered in 1846. It has a high oxygen balance of +3.5 that improves the energy content of the overall composite mixture. However, it has a relatively high melting point of 14 °C and glass transition temperature of around –68 °C. NG has excellent plasticizing property; however, it is highly shock-sensitive and has poor thermal stability (decomposes around 50 °C). Moreover, NG is reported to cause major physiological effects such as dilation of arteries and severe headaches.² Several alternate nitrate esters including BTTN, trimethylol ethane trinitrate, triethyleneglycoldinitrate, and ethyleneglycoldinitrate (nitroglycol) with carbon content and greater stability have been later developed as a practical replacement to NG for overcoming the limitations of NG.²

In contrast to relatively unstable nitro-compounds, fluorinated organic compounds generally demonstrate high thermal, chemical, and electrochemical stability. Also, the density of a system is usually found to increase by introducing fluorine groups into the structure.³ Therefore, designing new plasticizer structures having both nitro and fluoro moieties are considered to be a suitable method toward developing novel energetic and

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stable plasticizer for future energetic applications. For example, bis (2-fluoro-2,2-dinitroethyl)formal (FEFO) is a fluoro-nitro energetic plasticizer having a melting point of 14 °C and is reported to have the highest density (1.60 g/cc) for any energetic plasticizer currently in use.³ However, it is a highly toxic compound, causing severe skin irritation, which makes it difficult to use in a large scale setup. Also, the synthesis of FEFO involves complex and stringent chemical reaction conditions.³

In terms of developing new advanced energetic polymer composite for various applications, there is a long felt need to develop a new energetic plasticizer having a lower melting point and glass transition temperature than known systems, having good compatibility with known energetic binders, having a higher safety, handling and stability performance, reasonable oxygen balance, and higher decomposition temperature. There is also a need for a greener method of synthesis of an energetic plasticizer, which does not require the use of any solvent and the purification method involves simple, safe, and cost-effective procedures and that could be easily scaled for industrial applications.^{1,2} Herein, we report a facile and green synthesis of a new fluoro-nitrate energetic plasticizer, ACR-ENP-1, along with the preliminary investigations of its scope and applicability as an energetic plasticizer in energetic applications.

2. RESULTS AND DISCUSSION

The designed structure of ACR-ENP-1 was an attractive candidate for a potential energetic plasticizer because it was analogous to the structure of NG (Figure 1), with an oxygen

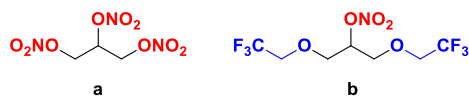


Figure 1. Structure of (a) nitroglycerine and (b) ACR-ENP-1.

balance of -71.7 and a theoretical heat of formation of -1810 kJ/mol. Moreover, for practical application, its synthetic process outlines an environment-friendly process to overcome the challenges and limitations of the previous systems.

The synthesis of ACR-ENP-1 follows a three-step simple synthetic procedure. The first step is an environment-friendly, simple nucleophilic substitution of epichlorohydrin by

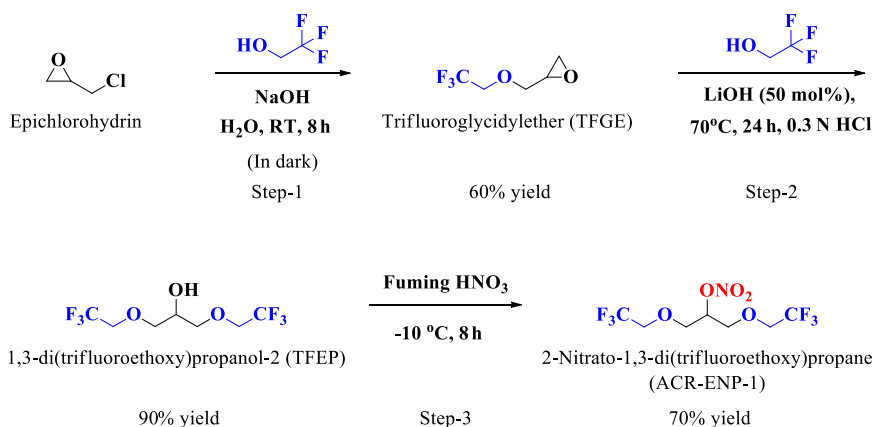
trifluoroethanol (TFE) in basic water to give $\sim 60\%$ trifluoroglycidylether⁴ (TFGE) as isolated yields.

It is important to note that TFGE was found to be light-sensitive. Hence, the synthesis was performed in the dark in the presence of free-radical scavenger 2,6 di-tertiarybutyl-4-methyl phenol. When the reaction was performed in the presence of light or in the absence of the scavenger, multiple side products were detected, thereby lowering the yield of the isolated product, TFGE. The purification of TFGE was accomplished via distillation without using any column purification techniques. The 1154 cm^{-1} stretching frequency of the C–F bonds in the FT-IR (Supporting Information) indicated the nucleophilic substitution of the C–Cl bond by TFE with the disappearance of 756 cm^{-1} (stretching frequency of C–Cl). The second step is the ring opening of TFGE with TFE in the presence of lithium hydroxide, producing a fluoro-alcohol intermediate, 1,3-di(trifluoroethoxy)propanol-2 or TFEP (Step-2) in $\sim 90\%$ yield. The opening of the three-membered oxirane ring to give an alcohol was indicated by the broad FT-IR absorption of the –OH bond around 3440 cm^{-1} . Lithium hydroxide was preferred over sodium hydroxide or potassium hydroxide due to higher yields. In this step, excess of TFE was used that served both as a reagent and as solvent for the synthesis. After the reaction, the excess of TFE was recovered via rotary evaporation. The final step of the synthesis is a nitration of TFEP with $\sim 98\%$ concentrated nitric acid at $-10\text{ }^\circ\text{C}$ to give the desired compound 2-nitrate-1,3-di-(trifluoroethoxy)propane or ACR-ENP-1 in $\sim 70\%$ yield as shown in Step 3 (Scheme 1).

The ACR-ENP-1 acronym is a short form of “ACRHEM-ENERGETIC PLASTICIZER-1,” where ACRHEM refers to the center where this research was carried out. Sharp FT-IR absorption around 1639 cm^{-1} confirms the presence of –ONO_2 groups in the final product, ACR-ENP-1 (Supporting Information). Each of the products in Steps 1, 2, and 3 was thoroughly characterized by FT-IR, ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectroscopic studies. Furthermore, high resolution mass analysis through HRMS of the final compound, ACR-ENP-1 at $m/z = 302$ and more than 99% purity as shown in HPLC studies successfully confirms the synthesis and high purity isolation of the desired product.

One of the most important properties of a plasticizer is its glass transition temperature. The lower the glass transition temperature of a plasticizer, the higher will be its potential ability to impart more flexibility, processing ability, and

Scheme 1. Synthesis of ACR-ENP-1



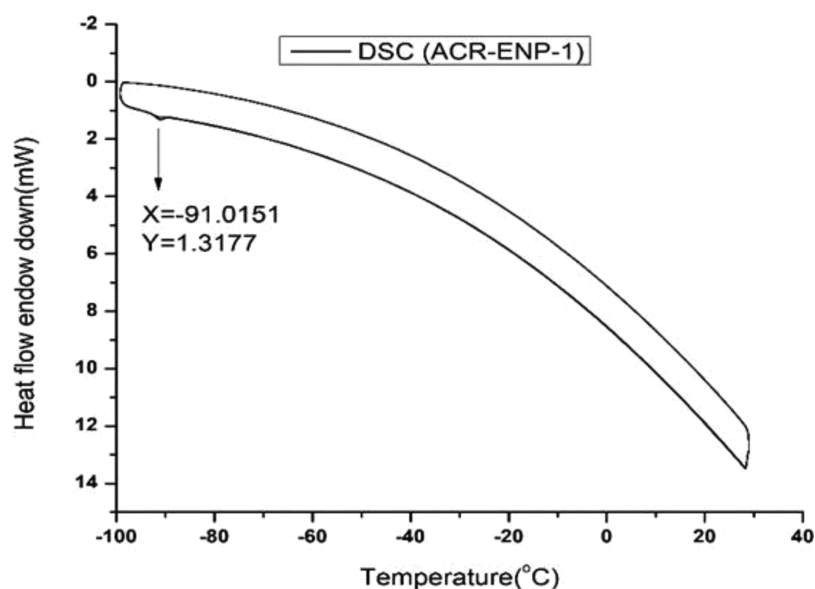


Figure 2. DSC profile of ACR-ENP-1.

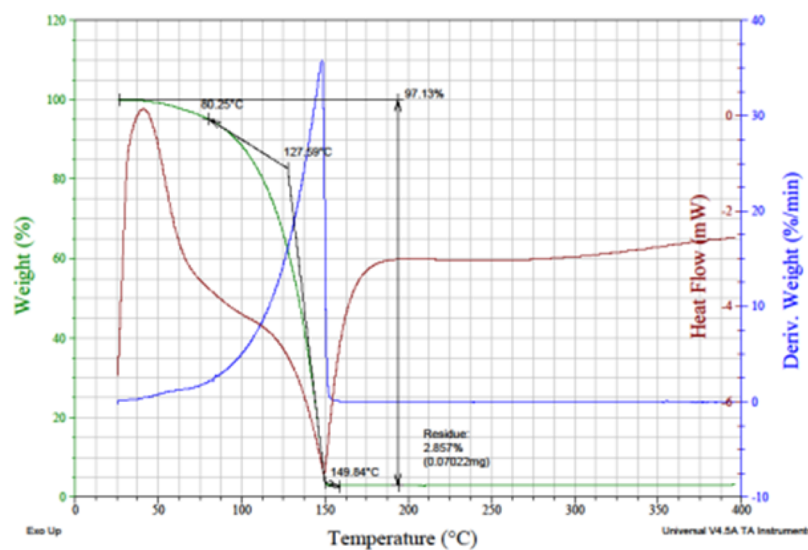


Figure 3. TGA profile of ACR-ENP-1.

mechanical strength to the composite for practical applications. The glass transition temperature of ACR-ENP-1 was found to be ~ -91 °C (Figure 2), which was much lower compared to already known fluoro-nitro plasticizers such as 2,2,2-fluorodinitroethyl 2-nitroalkyl acetals,⁵ 2,2-dinitropropyl 2-fluoro-2,2-dinitroethyl formal,⁶ bis (2-fluoro-2,2-dinitroethoxy)(1-fluoro-1,1-dinitro-2-propoxy)methane,⁷ and 3,3-bis(difluoroamino)-1,5-dinitratopentane.⁸

Also, the theoretical density of ACR-ENP-1 was found to be 1.78 g/cc compared to 1.6 g/cc for FEFO.³ FEFO has been reported to have the highest density among all the energetic plasticizers known so far.³ Density is important for energetic plasticizers as it is a characteristic measure of the energetic content of a molecule. Furthermore, in terms of thermal stability, T_{dmax} of ACR-ENP-1 was found to be ~ 128 °C (Figure 3), which was much higher than most commonly used energetic plasticizer NG and other nitro-based energetic plasticizers.²

The friction sensitivity of ACR-ENP-1 was found to be 160 N, which was also much higher and indicated much greater stability than that of NG.^{3,8} Furthermore, the energetic nature of ACR-ENP-1 is clearly evident from the exothermic nature of the heat flow (brown curve), as shown in the TGA profile in Figure 3. For an energetic plasticizer to be useful for practical applications, previous report suggests that physical miscibility and material compatibility with the binder used in the manufacture of the composite material is the most important criteria to determine its usefulness for various potential applications.^{2,9,10} In our work, similar physical miscibility tests were performed and analyzed by simply mixing the two components (plasticizer and binder) and observing the nature of the mixed state (miscible or immiscible). Miscible components will completely mix with each other as a single phase and immiscible components will either precipitate, become turbid, or remain immiscible as it is. If miscible, the components were further tested for compatible studies on the basis of their combined glass transition temperatures. If after

mixing both the components, the mixture gives a single glass transition temperature of the mixed phase, the components are considered to be compatible.^{2,9} Immiscible components were not further tested for compatibility studies.

According to the current state-of-art, hydroxy-terminated-polybutadiene (HTPB) is the most common binder (non-energetic) used for high energy materials applications.¹ Among energetic binders, GAP¹⁰ and poly(3-nitratomethyl-3-methyl-oxetane) also known as Poly-NIMMO² are two of the most preferred and known energetic binders.^{2,10} On the other hand, Viton is a vital fluoro-polymer elastomer used in various energetic materials applications. In our work, we have checked and analyzed the miscibility and compatibility of ACR-ENP-1 with poly-NIMMO, GAP, Viton, poly-GLN, Poly-TFGE, and HTPB in a 1:1 ratio by weight, as shown in Table 1. ACR-

Table 1. Summary of Miscibility and Compatibility Analyses Data of ACR-ENP-1 with a Range of Known Binders Used in High Energy Material Applications

binder (wt %)	T_g 100% binder (°C)	miscibility, 50 wt % binder + 50 wt % ACR-ENP-1	T_g 50 wt % binder + 50 wt % ACR-ENP-1 (°C)	compatible
poly-NIMMO	-33.11	yes, clear phase	-50.04	yes
GAP	-47.01	yes, clear phase	-57.03	yes
Viton	-19.37	yes, clear phase	-48.96	yes
poly-GLN	-30.49	yes, clear phase	-48.52	yes
poly-TFGE	-56.03	yes, clear phase	-67.50	yes
HTPB	-70	no, immiscible, two separate phase	NA ^a	NA ^a

^aNA: not applicable

ENP-1 and HTPB were found to be completely insoluble with each other irrespective of the weight ratios taken and separated out as two distinct phases. However, on mixing 50 wt % of ACR-ENP-1 with 50 wt % of poly-NIMMO or GAP or Viton or poly-GLN or poly-TFGE produces a clear phase, thereby showing complete physical miscibility of the mixed components. The DSC analysis of the same mixtures was found to show only one glass transition temperature of the mixed state, thereby verifying the compatibility of the systems. Also, it was noteworthy to find that the glass transition temperature of the compatible mixture was much lower than the corresponding pristine binder. The lower glass transition temperature of the binder–plasticizer mixture clearly indicated the improvement in flexibility and mechanical properties of the binders with addition of the new plasticizer, ACR-ENP-1. These properties of ACR-ENP-1 as a new energetic plasticizer underscored its application potential toward the development of various new energetic composite systems having higher energy but with greater flexibility and mechanical stability. Furthermore, from an environmental point of view, the toxicity of this compound was found to be low, as it showed some anti-cancer activity toward cancerous cells, while not much of an effect was detected on healthier cells. This investigation is still under progress, and a detailed study will be reported in near future.

3. CONCLUSIONS

In summary, we have developed a simple, green, and cost-effective process for the synthesis of a new fluoro-nitrato energetic plasticizer, ACR-ENP-1, in high yields and high

purity. The entire synthetic process mostly includes solventless or water-based reactions in contrast to highly sophisticated and stringent conditions for synthesis of other known energetic fluoro-nitro systems. The high potential of ACR-ENP-1 as an energetic plasticizer can be justified on the basis of its structure, which was designed similar to NG but with an objective to have higher stability. The preliminary properties of ACR-ENP-1 far exceeded its targeted expectations when compared to conventional and extensively used NG and other conventional energetic plasticizers, as ACR-ENP-1 demonstrated far better and excellent mechanical and compatibility properties when mixed with known energetic binder systems. Currently, we are investigating the effect of ACR-ENP-1 in multicomponent energetic systems and will report the findings in the near future.

4. EXPERIMENTAL SECTION

4.1. Materials. Epichlorohydrin, sodium hydroxide, hydrochloric acid, TFE, lithium hydroxide monohydrate, sulfuric acid, sodium nitrate, dichloromethane, sodium chloride, acetone, sodium sulfate anhydrous, and all other chemicals were purchased from Avra Synthesis Pvt. Ltd. The deuterated solvents for NMR were purchased from Sigma Aldrich. All the solvents were used as received without further purification.

4.2. Synthesis of TFGE. In an amber-colored round bottom flask, 9% aqueous solution of NaOH was prepared by using 16.8 g of NaOH pellet (0.42 mol), and to that solution, 2,2,2-TFE (30 mL, 0.42 mol) was added at room temperature and kept for overnight stirring. After the required amount of stirring, 64 mg of 2,6-di-*tert*-butyl-4-methylphenol (equivalent to 0.02 wt % of epichlorohydrin) was added to the reaction mixture as a free-radical scavenger. Then, epichlorohydrin (22 mL, 0.28 mol) was slowly added to the reaction mixture solution over 1 h via addition funnel at room temperature. After the addition was complete, the mixture was allowed to stir at room temperature for 7 h. After completion of the reaction, the crude product was found to be immiscible with water and separated as an immiscible layer in the reaction mixture. The immiscible layer was separated and washed three times with distilled water in an amber-colored separating funnel and dried over anhydrous Na₂SO₄. The crude filtrate obtained after removal of Na₂SO₄ was first distilled under normal conditions, followed by vacuum distillation, and the pure product was isolated in 60% yield (26.12 g). The pure fraction was collected under the following conditions: pot temperature = 120 °C, pressure = 23 mm in Hg.

¹H-NMR (500 MHz, CDCl₃, δ ppm): 2.62 (m, 1H), 2.81 (m, 1H), 3.16 (m, 1H), 3.48 (m, 1H), 3.89 (m, 3H).

¹³C-NMR (125 MHz, CDCl₃, δ ppm): 43.68, 50.41, 68.78, 72.79, 77.04, 125.04.

¹⁹F-NMR (400 MHz, CDCl₃, δ ppm): -74.672.

FT-IR (cm⁻¹): 3065.47, 3007.29, 2934.41, 456.25, 1411.91, 1276.50, 1153.17, 999.05, 963.23, 901.59, 850.42, 828.78, 763.14, 666.82, 609.55, 554.15, 535.57, 428.18, 413.60.

4.3. Synthesis of TFEP. In a two-neck round bottom glass flask, 206.4 mL of TFE (2.88 mol), followed by 2.3 g of anhydrous lithium hydroxide, LiOH (0.0961 mol), was added. Then, the reaction mixture was heated to 70 °C. After about 5–10 min at 70 °C, LiOH melted in the reaction mixture. Then, 30 g of TFGE (0.19 mol) prepared in Step 1 was slowly added to the reaction mixture in a dropwise addition method. The reaction mixture was then stirred and heated at 70 °C under a nitrogen atmosphere for 24 h. Then, after 24 h, the

reaction was stopped and cooled to room temperature and neutralized with 0.3 N HCl solution. The pure product, TFEP was isolated from the crude reaction mixture by solvent extraction with dichloromethane/water for three times. The organic solvents were separated by rotary evaporation, giving the pure compound TFEP in 90% yield (44.30 g).

$^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ ppm): 4.00(m, 1H), 3.90(q, 4H), 3.71(m, 4H), 2.5(s, 1H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ ppm): 68.41, 68.68, 68.96, 69.23, 69.34, 73.05, 120.48, 122.70, 124.92, 127.14.

$^{19}\text{F-NMR}$ (400 MHz, CDCl_3): -74.62.

FT-IR (cm^{-1}): 3440.29, 3020.58, 2936.77, 2892.01, 1459.11, 1443.79, 1413.11, 1276.12, 1216.25, 1145.69, 995.46, 967.57, 875.86, 827.868, 754.08, 667.27, 545.95, 498.87.

4.4. Synthesis of di(Trifluoroethyl-ether)2-nitrato-propanol or ACRHEM-Energetic Plasticizer-1 or ACR-ENP-1. In a two-necked round bottom flask, 1 g of TFEP (3.32 mmol) was slowly added dropwise under a nitrogen atmosphere to a stirring solution of 8 mL of concentrated nitric acid (~98% fuming nitric acid freshly obtained from distillation of sulfuric acid and sodium nitrate) at $-10\text{ }^\circ\text{C}$. Then, the reaction mixture was stirred at $10\text{ }^\circ\text{C}$ under a nitrogen atmosphere for 8 h. After the completion of the reaction, the reaction mixture was slowly and carefully poured into crushed ice. The crude reaction mixture in the crushed ice was solvent-extracted for three times with a dichloromethane/water mixture to give the desired product, di(trifluoroethyl-ether)2-nitrato-propanol or ACR-ENP-1 in 70% yield (757 mg).

$^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ ppm): 3.91(m, 8H), 5.33(m, 1H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ ppm): 68.48, 68.76, 69.03, 69.13, 69.31, 79.74, 120.23, 122.51, 124.73, 126.95.

$^{19}\text{F-NMR}$ (400 MHz, CDCl_3): -74.46.

FT-IR (cm^{-1}): 2945.85, 1769.86, 1639.16, 1444.52, 1272.64, 1149.26, 967.445, 903.09, 844.55, 753.35, 666.22, 554.59.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c00808>.

Characterization of compound by NMR, mass spectrometry, FT-IR, and HPLC (PDF)

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Notes

The authors declare no competing financial interest.

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