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Development of Novel Fluoro / Fluoro-Nitro Energetic Binders for High Energy Applications

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Abstract— **Various high energetic materials (HEMs) like RDX and HMX are crystalline solids that are sensitive to shock. Suitable fluoro-nitro polymeric binders will be a potential replacement to the conventional stable but un-energetic hydroxyl-terminated polybutadiene (HTPB) for processing them in a shock insensitive and machinable form without decreasing the overall energy. Synthesis of fluoro-and nitro-substituted epoxy monomers followed by synthesis of the corresponding fluoro/fluoro-nitro polymeric binders via cationic ring-opening polymerization are discussed in this paper.**

Keywords-component; Energetic Materials; Binders; Fluorinated Polymers; Nitro Polymers

I. INTRODUCTION

The development of next-generation weapon systems envisions new explosives and propellant formulations with smart controls, better performance and enhanced stability during storage and transportation. Particularly, extensive programs for development of Insensitive Munitions (IM) that meets expectations of performances in addition to reducing vulnerability to un-expected hazardous stimuli are gaining increase global importance. One of the most efficient approach and current state-of-art to reduce the sensitivity of explosives is the use and development of cast-cured polymer bonded explosives (PBX). PBX is a tough elastomeric polymer matrix created and cured in-situ containing suspended explosive ingredients. The tough elastomeric polymer material acts as the binding matrix that provides improved mechanical properties to the propellant as well as the absorbing matrix for dissipating the energy from hazardous stimuli. The most common binding material used in PBX formulations is hydroxyl-terminated polybutadiene (HTPB), a polymer that is cross-linked with isocyanates in the presence of plasticizers such as dioctyl-adipate (DOA). Other common binding polymers include carboxy-terminated polybutadiene (CTPB) and hydroxyl-terminated polyethers (HTPE) [1]. Although these binder systems have excellent physical properties in reducing the vulnerability of explosive charges but their inert backbone reduces the overall energy output and performance of the propellant composition. Research into this problem has led to the emergence and development of new high performance explosives and advanced rocket propellants by designing new energetic polymers and / or plasticizers that contribute to the total energy of the composition. Recent literature in this field reports the inclusion of azido, nitro, fluoro, difluoroamine and other energetic functional groups into the polymer backbone and plasticizer for improving the overall internal energy and performance of the system [2].

The most common routes reported in literature for designing and developing energetic polymeric binders are by incorporating energetic functional groups such as azido, nitro including C-nitro, O-nitro and N-nitro and difuoramine groups [3, 4] into the polymeric backbone of conventional binders such as HTPB, HTPE etc. The critical requirements of these newly developed energetic polymeric binders are to improve the internal energy as well as the overall oxygen balance of the propellant formulations. [5, 6].

Fluorinated polymers usually show high chemical stability, have lower coefficients of friction, high densities, and good compatibility other energetic materials across a broad range of operating temperatures. [7, 8]. Moreover, fluoropolymer-metal compositions have shown to result in specific high reaction energies. [9]. For example, recent literature report magnesium, Teflon, and Viton system (MTV) yielding a significantly large specific reaction energy of 9.4 KJ/g, in comparison to TNT and RDX with only 3.72 KJ/g and 6.57 KJ/g respectively. [10]. Therefore, design, synthesis and applications of new fluorinated energetic binders is a novel, advanced and highly attractive research field in the high energy materials community.

Herein, we report the synthesis of a fluoro-substituted epoxy monomer and nitro-substituted epoxy monomer followed by synthesis of the corresponding fluorinated and fluoro-nitro polymeric binders via cationic ring-opening polymerization.

II. EXPERIMENTAL

A. Materials

2,2,2-trifluoroethanol and $BF_3.OEt_2$ were purchased from Avra Synthesis Pvt. Ltd. Anhydrous dichloromethane (DCM), NaOH, HNO_3, epichlorohydrin, sodium sulphate, sodium bicarbonate were purchased from Finar Ltd. 1,4-butane-di-ol (BDO) [>99.0%(GC)], were obtained from TCI Chemicals (India) Pvt. Ltd. Specially dried solvent grade was purchased and used for polymerization reaction. All other commercial chemicals were used without further purification.

B. Characterization

NMR data were recorded in Bruker-500 MHz instrument using TMS as a standard reference and deuterated chloroform as solvent. FTIR spectra were collected using Bruker Tensor II FTIR spectrometer (neat) within the spectral range from 4000 - 400 cm^{-1}. DSC analysis was performed using a Perkin Elmer

DSC8000 instrument. The samples were mounted on a closed aluminum pan and heated at the heating rates of 10ºC min^{-1} under nitrogen atmosphere having a flow rate at 40 mL/min. The TG-DTA experiments were carried out on a TA instrument Q600 SDT under nitrogen atmosphere having a flow rate of 100 mL/min. Molecular weights of the polymers were measured with Thermo GPC Ultimate 3000 using Tetrahydrofuran (THF) as eluent and calibrated with polystyrene standards.

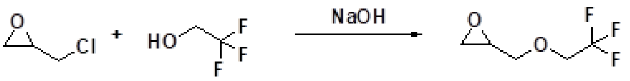
C. Synthesis

- *Synthesis of 2,2,2-trifluoroethoxy-glycidylether (TFGE)*: In an amber colored round bottom flask, 9% aqueous NaOH solution was prepared with NaOH pellet (0.42 mol), and to that solution 2,2,2-trifluoroethanol (0.42 mol) was added at room temperature and kept for overnight stirring. Then epichlorohydrin (0.28 mol) was slowly added to it over 1 hour via addition funnel at room temperature. After the addition was complete, the mixture was allowed to stir at room temperature for 7 hours. After completion of reaction, the immiscible layer of crude product in water was separated, washed 3 times with distilled water in an amber colored separating funnel and dried over anhydrous Na_2SO_4. The crude filtrate obtained after removal of Na_2SO_4 was first distilled in normal condition followed by vacuum distillation and the pure product was isolated in 60% yield. The pure fraction was collected under the following conditions: pot temperature = 120ºC, pressure = 23 in Hg) was collected.
  FTIR (cm^{-1}): 2990, 1312, 1150, 915, 820, 689
  ^{1}H NMR (500MHz, $CDCl_3$, δ): 2.62 (m, 1H), 2.81 (m, 1H), 3.16 (m, 1H), 3.48 (m, 1H), 3.89 (m, 3H)
- *Synthesis of Glycidylnitrate (GLN): Epichlorohydrin* (0.294 mol) was slowly added over 1.2 h, via a solid addition funnel, to a rapidly stirred solution of 70% aqueous nitric acid (0.311 mol) at -15° C under nitrogen atmosphere. The epichlorohydrin addition rate was controlled so as to maintain a reaction temperature of less than 10° C. After the addition was complete, the mixture was allowed to stir for 2.5 h at 10° C under nitrogen atmosphere. The reaction mixture was then cooled to -10° C and 50% aqueous NaOH (0.404 mol) was added dropwise over 0.75 h at a rate so as not to exceed a reaction temperature of 10° C. The resultant solution was allowed to stir for 30 min, while the reaction temperature was allowed to rise to about 25° C. Additional distilled water (31 mL) was then added and the reaction solution extracted with dichloromethane. The combined dichloromethane extract was dried over anhydrous Na_2SO_4, filtered and was stored in a freezer for 12 h. The solvent was then evaporated under vacuo to give a yellow oil (88% yield). This material was purified by fractional distillation (pot temp.=45° C., head temp. =27°-28° C., P=0.370 mm) to afford glycidyl nitrate (GLN) as a colorless liquid in 30% yield.
  FTIR (cm^{-1}): 3071, 3009-2905, 1642, 1427, 1360, 1285, 866, 758.
  ^{1}H NMR (500MHz, $CDCl_3$, δ): 4.78 (dd, J=2.6, 12.6 Hz, 1H), 4.33 (md, 1H), 3.27 (m, 1H), 2.90 (m, 1H), 2.71 (m, 1H).
- *Synthesis of Poly-TFGE:* A three-neck flask was flame dried under vacuum to remove air and moisture. 1,4-butane-di-ol (0.0025 mol) was added to the flask via syringe under N_2 atmosphere and rapidly stirred. To the stirred solution, boron trifluoride etherate (0.0025 mol) was added under N_2. The $BF_3.OEt_2$ addition was maintained so as not to exceed a reaction temperature of 20° C. After the addition was complete, the solution was allowed to stir for 1 h and the ether was removed under high vacuum. Anhydrous CH_2Cl_2 was added to the resulting viscous residue forming a solution followed by cooling to 10° C. Under N_2 atmosphere, a solution of monomer TFGE (0.05 mol) in anhydrous CH_2Cl_2 was then added dropwise to the solution at a rate so as to maintain a reaction temperature of 10°C. After the addition was complete (40 min total addition time), the reaction was continued for additional 24 h at room temperature. The mixture was then quenched with brine (5 mL) and was washed with saturated aqueous $NaHCO_3$ (3x5 mL). The organic fraction was then dried over anhydrous Na_2SO_4, filtered, and the CH_2Cl_2 was evaporated in vacuo to get polymer, poly-TFGE in ~45% yield.
  FTIR (cm^{-1}): 2931, 2980, 1443, 1274, 1147, 966, 826, 667.
  ^{1}H NMR (500MHz, $CDCl_3$, δ): 3.98 (m), 3.67 (m).
- *Synthesis of Poly(TFGE-r-GLN):* A three-neck flask was flame dried under vacuum to remove air and moisture. 1,4-butane-di-ol (0.0025 mol) was added to the flask via syringe under N_2 atmosphere and rapidly stirred. To the stirred solution, boron trifluoride etherate (0.0025 mol) was added under N_2. The $BF_3.OEt_2$ addition was maintained so as not to exceed a reaction temperature of 20° C. After the addition was complete, the solution was allowed to stir for 1 h and the ether was removed under high vacuum. Anhydrous CH_2Cl_2 was added to the resulting viscous residue forming a solution followed by cooling to 10° C. Under N_2 atmosphere, a solution of monomer TFGE (0.025 mol) and monomer GLN (0.025 mol) in anhydrous CH_2Cl_2 were then added dropwise to the solution at a rate so as to maintain a reaction temperature of 10°C. After the addition was complete (40 min total addition time), the reaction was continued for additional 24 h at room temperature. The mixture was then quenched with brine (5 mL) and was washed with saturated aqueous $NaHCO_3$ (3x5 mL). The organic fraction was then dried over anhydrous Na_2SO_4, filtered, and the CH_2Cl_2 was evaporated in vacuo to get the copolymer, poly (TFGE-r-GLN) in ~40% yield.

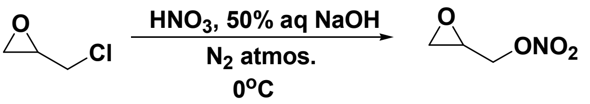
^{1}H NMR (500MHz, $CDCl_3$, δ): 4.5 (s), 4.0 (m), 3.3-3.8 (m).

III. RESULTS AND DISCUSSION

As described in the experimental section, the synthesis of monomer TFGE and monomer GLN were accomplished by substitution of the chloro-functional group in epichlorohydrin as shown in Scheme 1 and Scheme 2 below.



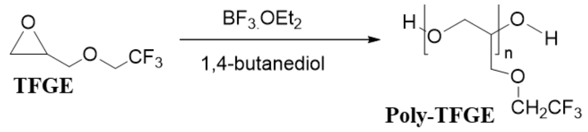
Scheme 1. Synthesis of TFGE from Epichlorohydrin



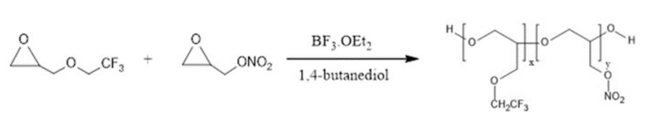
Scheme 2. Synthesis of GLN from Epichlorohydrin

The structure of the monomers, TFGE and GLN were confirmed through detailed spectroscopic analyses by FTIR, ^{1}H NMR and ^{13}C NMR. However, it must be cautioned that for synthesis of TFGE, the reaction and the purification were conducted in amber coloured glass apparatus. TFGE was found sensitive to light and underwent decomposition when the reaction and/or purification was conducted in transparent glass apparatus. Investigations are currently under progress to understand the cause and mechanism of decomposition under visible light.

Homopolymer Poly TFGE and random copolymer Poly(TFGE-r-GLN) were synthesized via cationic polymerization using BDO as an initiator and $BF_3.OEt_2$ as a catalyst in CH_2Cl_2 (Scheme 3 and Scheme 4). A general reaction mechanism for carbocationic polymerization of TFGE to form poly-TFGE is demonstrated in Fig.1.



Scheme 3. Synthesis of Poly-TFGE via cationic polymerization



Scheme 4. Synthesis of Poly (TFGE-*r*-GLN) via cationic polymerization

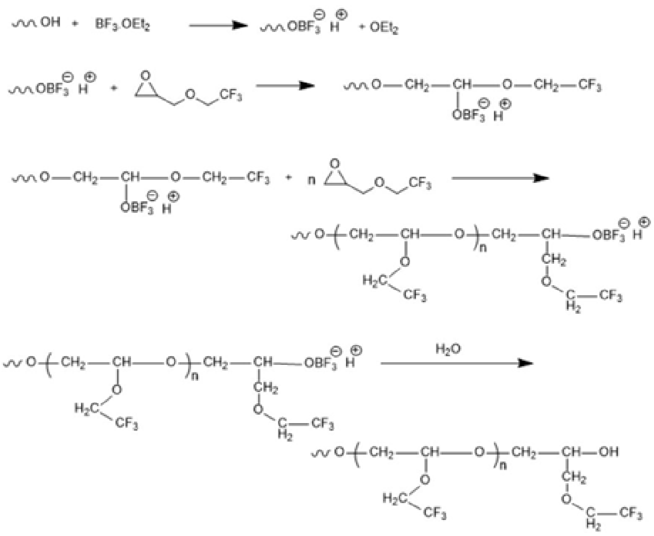


Fig. 1. Synthetic mechanism for formation of poly-TFGE via cationic polymerization

The polymerization reactions were confirmed via ^{1}H NMR comparisons between the corresponding monomers and polymers. The average molecular weight of poly-TFGE and Poly(TFGE-*r*-GLN) analysed via size exclusion chromatography were found to be 1628 g/mol and 750 g/mol with a poly-dispersity (PDI) index of 1.56 and 1.47 respectively. The thermal stability of Poly-TFGE and Poly (TFGE-*r*-GLN) were measured with TGA method and the decomposition temperature (T_{max}) for Poly-TFGE and Poly(TFGE-*r*-GLN) were found to be 312 ^oC and 193 ^oC respectively. The glass transition temperatures of Poly-TFGE and Poly (TFGE-*r*-GLN) were measured with DSC method and T_g for Poly-TFGE and Poly(TFGE-*r*-GLN) were found to be -55 ^oC and -45 ^oC respectively. Friction sensitivity of Poly-TFGE and Poly(TFGE-r-GLN) were found to be 252N and 168N respectively.

IV. CONCLUSIONS

In conclusion, in this paper, we report the synthesis of fluoro-substituted epoxy monomer and nitro-substituted epoxy monomer followed by synthesis of the fluorinated homopolymer: Poly-TFGE and fluoro-nitro random copolymer: Poly(TFGE-*r*-GLN) via cationic ring-opening polymerization. Preliminary characterization of the homopolymers and copolymers via TGA, DSC, GPC analyses and friction sensitivity methods underscores the potential of these systems to be used as energetic binders for high energetic applications. Further investigation of these materials are under progress and will be reported in near future.

V. ACKNOWLEDGMENT

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