

[54] **2-FLUORO-2,2-DINITROETHYL  
SUBSTITUTED POLYETHERS**

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[52] U.S. Cl. .... **260/615 BF**; 149/19.3; 149/19.4; 149/88; 149/92; 260/2 A; 260/348 R

[51] Int. Cl. .... **C07c 43/12**

[58] Field of Search. 260/2 EP, 2 A, 348 R, 615 BF

[56] **References Cited**

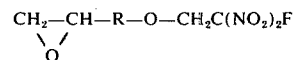
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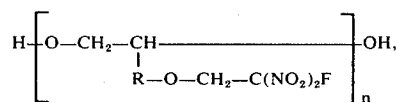
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[57] **ABSTRACT**

This invention is concerned with novel, energetic monomeric epoxy aliphatic ethers terminated with a dinitrofluoro moiety and with the polymers prepared therefrom. The monomers are of the general formula



and the polymers are of the general formula



wherein R is a lower alkylene of 1 to 4 carbon atoms, and wherein n is a positive number of from 4 to 25.

**2 Claims, No Drawings**

## 2-FLUORO-2,2-DINITROETHYL SUBSTITUTED POLYETHERS

### BACKGROUND OF THE INVENTION

This invention relates to new and useful monomeric and polymeric compositions of matter. More particularly, the present invention pertains to energetic, thermally stable, organic monomers and the polymers derived therefrom and wherein said products are useful as energetic binders for formulating both explosive and propellant compositions. Specifically, the subject invention is concerned with novel, energetic, explosive, monomeric lower alkyl nitrohalo-epoxides and the polymers made from said monomeric epoxides.

Chemical explosives and propellants of the aliphatic, aromatic and heterocyclic types are widely used by the scientific, military and commercial arts for many purposes. Often, the successful use of these chemical compositions necessitates their manufacture by casting, molding, extruding and like processes into items of predetermined shape and design. These manufacturing processes frequently require a mixing of the energetic explosive or propellant compound with a processing agent for fabricating the desired article. For example, the manufacture of many ordnance projectiles, cartridges for small arms, blasting and demolition explosives, the casting of a shaped propellant grain into a combustion chamber, and other like items demand a mixing of the explosive or propellant with a processing agent or binder for facilitating casting or filling, molding or extruding to successfully fabricate the desired commercial or military item. Presently, binders like asphalt, synthetic polybutadiene elastomers, reactive terminated elastomeric derivatives, polysiloxane type polymers, wax-like hydrocarbons, cellulose esters and other similar agents are used for processing purposes.

However, serious disadvantages are frequently encountered with present day binders for compounding explosive compositions and propellant grains. For example, one disadvantage often encountered with high melting point explosives is that they cannot be safely melt cast because some decomposition occurs before they reach their melting points. To overcome this disadvantage the high melting point explosives are conventionally mixed with a castable plastic essentially non-energetic binder, for example, a synthetic polyester for casting the desired item. The use of these inert, non-energetic synthetic binders has the definite disadvantage of lowering the total energy content of the formulated composition with a resultant decrease in energy performance for the given explosive system. Another disadvantage is that most of the prior art materials generally contain little oxygen and therefore consume a portion of the explosive or propellant oxidizer to facilitate their own combustion which results in a decreased performance for the explosive or propellant composition of matter. Thus, with this kind of binder it is often necessary to furnish a source of oxygen to overcome this inherent deficiency for the binder in the explosive or propellant charges. Other disadvantages frequently evidenced by the prior art binders are their poor storage characteristics, especially under different atmospheric conditions, such as over a temperature range of about  $-65^{\circ}\text{F.}$  to about  $300^{\circ}\text{F.}$ , a low density with non-energetic properties, their undesirable sensitivity to impact and other like unwanted disadvantages.

Accordingly, it is an object of the present invention to make available to the art energetic binders with improved thermal and impact stability and density, to preserve the energy of explosive systems.

Another object of the present invention is to provide novel energetic binders suitable for processing by casting and like techniques, high melting point explosives without lowering the energy content of the given explosive.

Still another object of the present invention is to provide energetic, thermally stable, impact stable, high energy monomers of the lower alkyl nitrohalo epoxide type suitable for manufacturing desired explosive and propellant systems without substantially decreasing the energy of the explosive or propellant.

Still another object of the present invention is to provide energetic, thermally stable, impact stable, high energy polymeric binders suitable for manufacturing desired explosive and propellant systems without substantially decreasing the energy of the explosive or propellant.

Still a further object of the instant invention is to provide energetic monomers and polymers that supply their own combustion oxygen.

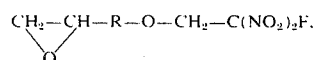
Yet still a further object of the instant invention is to provide novel monomeric epoxy aliphatic esters terminated with a dinitrofluoro moiety and the polymers produced therefrom.

Still a further object of the subject invention is to produce unique monomeric glycidyl ethers substituted with a dinitrofluoro group and the novel polymers synthesized therefrom.

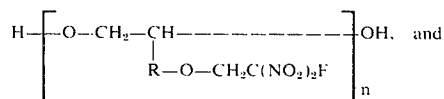
Other objects and advantages of the invention will become apparent from the following detailed description and the accompanying claims.

### SUMMARY OF THE INVENTION

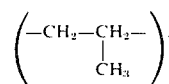
Briefly, the present invention is concerned with (1) novel energetic, monomeric compounds which can be represented by the following general formula:



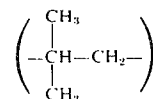
and with (2) novel energetic, polymeric compounds derived from said monomers and which polymers can be represented by the following general formula:



wherein R in (1) and (2) is a straight or branched chain lower alkylene of 1 to 4 carbon atoms such as methylene ( $-\text{CH}_2-$ ), ethylene ( $-\text{CH}_2-\text{CH}_2-$ ), isopropylene



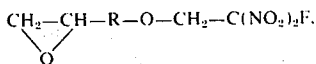
isobutylene



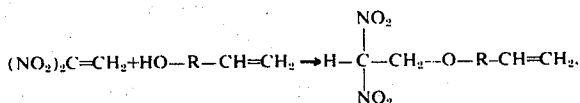
and the like, and wherein  $n$  is a positive integer of from 4 to 25.

### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

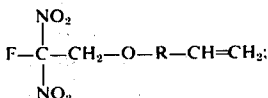
The novel monomeric compounds of the present invention of the general formula



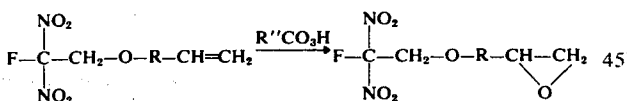
described supra, can be prepared by the following procedure: first, the addition of an unsaturated, lower aliphatic alcohol to an unsaturated, lower aliphatic dinitro substituted olefin to produce the corresponding unsaturated ether, as represented by the reaction equation,



wherein R is an alkylene of 1 to 4 carbon atoms; next, fluorinating said ether to form the unsaturated dinitro-fluoroether,

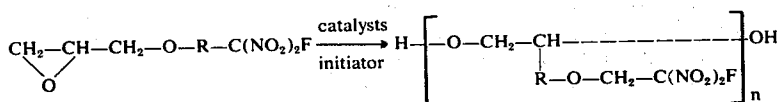
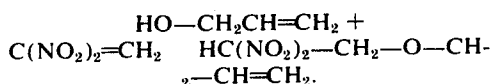


and finally, direct oxidation of the olefin to the epoxide with peracids, as depicted by the chemical reaction:



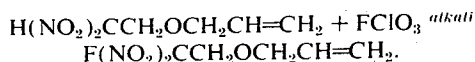
wherein R'' is an alkyl, trifluoroalkyl, or an aryl group such as phenyl, benzyl or the like.

The synthesis of a novel compound prepared according to the mode and manner of the present invention can be represented by the preparation of glycidyl 2,2-dinitro-2-fluoroethoxide. The first step of the synthesis consists in the preparation of allyl 2,2-dinitroethyl ether according to the procedure as set forth in *The Journal of Organic Chemistry*, Vol. 23, p. 813, 1958. This reaction consists in the addition of allyl alcohol to 1,1-dinitroethylene according to the following equation:

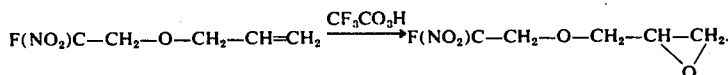


The 1,1-dinitroethylene is a reactive intermediate generated in situ from 2-bromo-2,2-dinitroethyl acetate, 1,2-dichloro-1,1-dinitroethane or 1,1,1-trinitroethane. For the synthesis described herein, the 1,1-dinitroethylene was generated from 1,2-chloro-1,1-dinitroethane according to the procedure as set forth in *The Journal of Organic Chemistry*, Vol. 31, p. 369, 1966.

The next step in the synthesis is the fluorination of allyl 2,2-dinitroethyl ether with perchloryl fluoride to form the corresponding allyl 2,2-dinitro-2-fluoroethyl ether which fluorination can be represented by the reaction



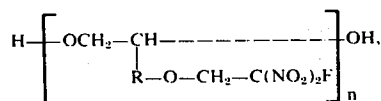
The final step of the synthesis consists in the epoxidation of the allyl 2,2-dinitro-2-fluoroethyl ether with peroxytrifluoroacetic acid to form the desired glycidyl 2,2-dinitro-2-fluoroethoxide. The epoxidation reaction can be represented by the equation



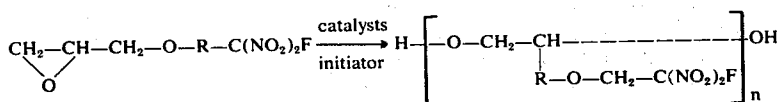
Additional compositions of matter can easily be prepared by the above described synthesis by employing a suitable alcohol such as 3-butene-1-ol or 2-methyl-3-butene-1-ol.

Generally, the above described dinitroethylation, fluorination and epoxidation reactions are carried out under normal atmospheric conditions. The initial temperature of the dinitroethylation reaction was usually about 15°C. to 25°C. followed by agitation or stirring at room temperature for 10 to 15 hours. The beginning temperature of the fluorination process was its refluxing temperature followed by a reaction temperature of about 20°C. to 25°C. for about 3 to 4 hours. The epoxidation reaction was carried out at its refluxing temperature for about 1 to 3 hours. The above reactions were usually performed in the presence of an inert solvent, such as methylene chloride, carbon tetrachloride, chlorobenzene, chloroform or any other inert solvent that does not adversely affect the reactions.

The novel polymeric compounds of the present invention of the general formula



as described supra, can be conveniently prepared by converting the subject monomers, as synthesized according to the mode and manner of the invention, to hydroxy-terminated liquid prepolymers of varying molecular weight by a catalytic reaction using a Lewis acid catalyst, and, initiator containing OH groups in the presence of an organic solvent. The polymeric reaction can be represented by the following equation:



wherein R was as defined supra.

Briefly, the polymerization process consists in weighing a quantity of monomer and introducing it into a reaction flask containing solvent, then adding a catalyst and allowing the polymerization reaction to proceed to produce the desired polymer. The course of the reaction can be followed by the disappearance of the epoxy group and the polymerization reaction can be terminated by the addition of water or any suitable quenching material. The polymer is isolated from the reaction medium by first water extracting the solvent to remove the catalysts and then drying the extracted solvent and extracting the polymer with alcohol. Finally, the alcohol is evaporated to give the polymer.

Exemplary of the Lewis acid catalysts suitable for polymerizing the monomers are catalysts such as aluminum chloride, zinc chloride, ferric chloride, boron trifluoride, boron trifluoride hydrate, stannic chloride and like metal halides.

Representative of initiator compounds containing an OH group suitable for the polymerization reaction are compounds such as water, glycerine, glycols like ethylene glycol, polypropylene glycol, polyethylene glycol, mixed polyethylene polypropylene glycols, glycerol and the like.

Solvents, suitable for the polymerization reaction, generally include methylene chloride, carbon tetrachloride, ethylene chloride, methylene dichloride, methyl bromide, propyl chloride and like hydrocarbon solvents.

The above discussion is merely illustrative of the mode and manner of carrying out the present invention, and it is to be understood that the discussion is not intended to be limited to the instant disclosure, as other techniques may be successfully employed.

The following examples are representative of embodiments of the present invention and these examples are not to be construed as limiting as other obvious embodiments will be readily apparent to those versed in the art.

#### EXAMPLE I

Preparation of allyl 2,2-dinitroethyl ether: 50 grams (0.264 mole) of 1,2 dichloro-1,1-dinitroethane were added dropwise over a 15 minute period to a well stirred mixture of 200 ml of methylene chloride, 85.5 grams (1.48 moles) of allyl alcohol and 219 grams (1.32 moles) of potassium iodide. The slightly exothermic reaction was controlled at 20°-25°C. with an ice bath. The resulting red solution was stirred at room temperature for 12 hours. About 200 ml of water was added to dissolve the inorganic salts and the layers were separated. The water layer was extracted with methylene chloride and the combined organic portion was then washed several times with a 10 percent sodium thiosulfate to remove iodine. After a final water wash, the methylene chloride solution was dried over magnesium sulfate. Removal of excess methylene chloride yielded a red oil and a white solid. These materials were separated by crystallization of the solid from carbon tetrachloride. The white solid was found to be 1,2 diiodopropanol and the red oil was crude allyl 2,2-dinitroethyl ether. The crude allyl 2,2-dinitroethyl ether was purified by first forming the potassium salt through reaction with potassium hydroxide, recrystallization

from methanol, and then acidifying to pH of 1 with hydrochloric acid. The resulting pure allyl 2,2-dinitroethyl ether, was obtained in 55 percent overall yield as a colorless oil,  $n_D^{27.5}$  1.4527,  $d^{25}$  1.3. The calculated elemental analysis for  $C_5H_8N_2O_5$  was C, 34.09; H, 4.55; N, 15.19. The found analysis was C, 34.20; H, 4.29; N, 16.11. Infrared spectrum for the compound, in Nujol, exhibited maximum peaks at 6.35, 7.5, and 9.0 microns.

#### EXAMPLE II

Preparation of allyl 2,2-dinitro-2-fluoroethyl ether: The pure allyl 2,2-dinitroethyl ether, prepared according to the procedure set forth in Example I, was added (4.11 grams; 0.0234 moles) slowly to a well stirred solution of sodium hydroxide (0.935 grams; 0.0234 mole) water (15 mls) and methanol (35 mls). The slightly exothermic reaction yielded an immediate orange color; the final pH was approximately 8. Perchloryl fluoride was then metered into the system to which was added a dry ice reflux condenser to prevent excess perchloryl fluoride from sweeping out of the reaction flask. When the perchloryl fluoride began to reflux vigorously, it was shut off and under slight nitrogen flow reflux was maintained for about 4 hours. The reaction temperature was maintained between 20°-25°C. with a water bath. The reaction mixture had changed from deep orange to pale orange in color. Water (50 mls) was added and a yellow oil dropped out of solution. The mixture was then extracted with 3-60 ml portions of methylene chloride. The methylene chloride extracts were washed with 3-30 ml portions of 3 percent sodium hydroxide and finally with water. After dryings with magnesium sulfate, excess methylene chloride was removed under vacuum and the residual liquid was distilled through a small Vigreux column. The distillation yielded 2.4 grams (53 percent yield) of allyl, 2,2-dinitro-2-fluoroethyl ether b.p. 42°C./1.1 mm,  $n_D^{25}$  1.4240,  $d^{25}$  1.28. The calculated elemental analysis for  $C_5H_7N_2O_5$  was C, 30.93; H, 3.64; N, 14.43. The found analysis was C, 30.86; H, 3.45; N, 14.43. The infrared spectrum for the compound, in Nujol, exhibited maximum peaks at 6.2, 7.6 and 9.0 microns.

#### EXAMPLE III

Preparation of glycidyl 2,2-dinitro-2-fluoroethoxide: A solution of peroxytrifluoroacetic acid was prepared from 0.78 ml (0.028 mole) of 90 percent hydrogen peroxide, 4.73 ml (0.0335 mole) of trifluoroacetic anhydride and 10 ml of methylene chloride. This reagent was added over a 25 minute period to a well stirred boiling mixture of 3.18 g. (0.0164 mole) of allyl 2,2-dinitro-2-fluoroethyl ether, 25 ml methylene chloride, and 12.4 g. (0.088 mole) of disodium hydrogen phosphate (pre-dried in vacuum oven overnight at 50°C.). After the mild exothermic reaction had subsided, the solution was heated under reflux for 2 additional hours. The resulting mixture was stirred with 60 ml of water until all the inorganic salts had dissolved. The organic layer was separated and the aqueous layer was extracted with 3-25 ml portions of methylene chloride. The combined methylene chloride portion was washed with 50 ml of 10 percent sodium bicarbonate

and dried over magnesium sulfate. The solvent was removed at reduced pressure and the residual liquid was fractionated through a small Vigreux column to yield 1.99 g. (58 percent yield) of glycidyl 2,2-dinitro-2-fluoroethoxide b.p. 66°C./0.15 mm,  $n_D^{25}$  1.4350,  $d_4^{25}$  1.45. The calculated elemental analysis for  $C_5H_7N_2O_6F$  was C, 28.6; H, 3.36; N, 13.33. The found analysis was C, 28.78; H, 3.29; N, 13.46. The infrared spectrum for the compound, in Nujol, exhibited maximum peaks at 6.25, 7.65, 9.4 and 11.10 microns.

#### EXAMPLE IV

Polymerization of glycidyl 2,2-dinitro-2-fluoroethoxide: To a reaction flask, consisting of a two-necked 100-milliliter round-bottom flask wherein one neck was fitted with a 4-millimeter vacuum stopcock and the other neck stoppered for use in the introduction and removal of reagents and samples, was added 1.50 grams (7.13 mmoles) of glycidyl 2,2-dinitro-2-fluoroethoxide and 20 milliliters of methylene chloride. The contents of the flask were next frozen in a liquid nitrogen bath, and the flask was opened to the vacuum line. After pumping the flask down to 20 microns, 60.1 cc of boron trifluoride at a pressure of 100 millimeters was condensed into the reaction flask. The reaction flask was then removed from the vacuum line and gently warmed to room temperature, and, as soon as the monomer solution thawed, stirring was done with a magnetic stirring bar. The reaction was allowed to proceed for 1-2 hours, or, until the 11.1 micron epoxide band in the infrared spectrum had disappeared. The samples were removed for infrared examination by first opening the reaction flask's stopcock under a nitrogen flow, and after the contents of the flask were blanketed with nitrogen, the side-arm stopper was removed and a sample was withdrawn with a hypodermic syringe. After completion of the reaction, approximately 10 milliliters of water was added to the reaction flask and stirring continued for several minutes. The contents of the flask were then transferred to a 125-milliliter separatory funnel. After two additional water washes of the methylene chloride solution, the sample was dried over anhydrous sodium sulfate, and the sodium sulfate was washed with methylene chloride several times. The washes were combined with the decanted solution. Finally, the methylene chloride was evaporated under vacuum. The polymer residue produced was dissolved in methanol and filtered through a conventional Millipore filter to remove small quantities of insoluble solids. Following vacuum removal of the methanol, the liquid polymer was dried in a vacuum oven at 40°C. for several days. The yield of polymer was quantitative.

#### EXAMPLE V

Other polymers of this invention were prepared according to the procedure of Example IV and they are set forth in Table I immediately below:

Table I

POLYMERIZATION OF GLYCIDYL 2,2-DINITRO-2-FLUOROETHOXIDE				
Monomer/ Catalyst (Molar) (2)	H <sub>2</sub> O/BF <sub>3</sub> (Molar)	Temper- ature	Functionality (3)	$\bar{M}_n$ (4)
8:1	0.34	RT	0.8	1068
17:1	0.7	RT	0.71	1257
33:1	1.35	RT	0.74	1378
68:1	2.8	RT	1.1	1473

Table I-Continued

POLYMERIZATION OF GLYCIDYL 2,2-DINITRO-2-FLUOROETHOXIDE				
Monomer/ Catalyst (Molar) (2)	H <sub>2</sub> O/BF <sub>3</sub> (Molar)	Temper- ature	Functionality (3)	$\bar{M}_n$ (4)
22:1	1.0	RT	0.58	1157
11:1	0.5	-78°	0.66	1643
22:1	10.0	RT	*	850
5.5:1	0.67	RT	0.85	1311
22:1	0.076	RT	0.57	866
22:1	0.11 <sup>(1)</sup>	RT	1.5	2660
22:1	10.0	RT	1.9	784
22:1	5.0	RT	1.6	1060
22:1	0.29 <sup>(1)</sup>	RT	1.2	2460

\* Strong OH in infrared.

<sup>(1)</sup>Solvent was carbon tetrachloride, all other runs carried out in methylene chloride solvent.

(2) Catalyst was Lewis acid BF<sub>3</sub>.

(3) Functionality indicates the average number of OH groups per polymer chain.

(4)  $\bar{M}_n$  indicates the average molecular weight of the polymer.

The parameters that were used to characterize the prepolymers are functionality and molecular weight. Functionality is indicative of the number of hydroxyl groups per polymer molecule and was determined by the diborane method. This method involves the reaction of diborane with prototonic material and subsequent measurement of the evolved hydrogen:  $B_2H_6 + 6 ROH \rightarrow 2B(OR)_3 + 6H_2$ . The apparatus consists of a reaction vessel fitted with a serum cap and a manometer. The vessel contains excess diborane-tetrahydrofuran solution into which the weighed, carefully dried sample is injected with a syringe. The resulting hydrogen evolution is then measured. The method was modified somewhat in that the diborane-tetrahydrofuran solution was metered onto a carefully weighed unknown sample contained in a vessel evacuated on a vacuum system. The hydrogen evolved is then removed with a Toepler pump and carefully measured. The analysis is quite rapid requiring approximately 30 minutes per sample. The method is especially suitable for epoxy compounds, and sterically hindered hydroxyl compounds. Nitro, nitrate, and other energetic groups do not interfere with the analysis. The other parameter, that is, molecular weight, was measured with the Mechrolab Vapor Phase Osmometer.

The novel compounds of the invention prepared by the above described processes are thermally stable and very energetic. The compound glycidyl 2,2-dinitro-2-fluoroethoxide has an explosive power of 117 as compared to trinitrotoluene with an explosive power of 100. The energetic epoxy compounds of the invention can be used in pure form for their explosive effects or they can be utilized in admixtures with other explosives like nitroglycerin, pentaerythritol tetranitrate, ammonium nitrate, picric acid, trinitrotoluene and the like.

The novel polymers of the invention are ideally suited for casting explosives into items of predetermined and diverse geometric shapes. The polymer can be loaded with a high percentage of oxidizer and fuel and then cast, and finally cured into a tough resilient explosive composition or composite propellant. For example, a castable explosive composition was formulated by intimately blending 80 weight percent of cyclotrimethylenetrinitroamine (HMX), and 20 weight percent of the polymer of glycidyl 2,2-dinitro-2-fluoroethoxide. This castable composition had an explosive force 62 percent greater than TNT. Another castable composition was formulated consisting of 80

weight percent HMX, 10 weight percent of a polymer of 2,2-dinitro-2-fluoroethanoxide and 10 weight percent of a plasticizer bis (2,2-dinitro-2-fluoroethyl) formal. This explosive composition had an explosive force 67 percent greater than TNT.

In Table II, immediately below, is further set forth the unobvious and unexpected results obtained by formulating explosive compositions employing binders made according to the mode and manner of the instant invention. The explosive power obtained for a composition consisting essentially of HMX and a non-energetic binder polybutadiene, and the explosive power obtained for a composition consisting essentially of HMX and an energetic binder poly(glycidyl 2,2-dinitro-2-fluoroethanoxide) are compared against the explosive power of the standard reference explosive TNT.

weight percent, will give acceptable working properties.

The energetic compounds and compositions of matter formed by mixing the compounds with other explosives can be used for many other endeavors such as, oil well shooting, ordnance, demolition, incendiary compositions, rockets, projectiles and the like.

Obviously, many modifications and variations of the instant invention are possible in the light of the above teaching. It is, therefore, to be understood that within the scope of the disclosure and appended claims, the invention may be practiced otherwise than as specifically described.

We claim:

1. A polymer of the formula

Table II

Explosive	PERFORMANCE FOR EXPLOSIVE COMPOSITIONS				Explosive Power <sup>(4)</sup>
	Weight Percent	Binder	Weight Percent	Plasticizer	
HMX	100				1.859
HMX	80	Poly-butadiene <sup>(1)</sup>	20		1.017
HMX	80	PGDNFE <sup>(2)</sup>	20		1.616
HMX	80	PGDNFE	10	FEFO <sup>(3)</sup>	1.667
TNT	100				1.000

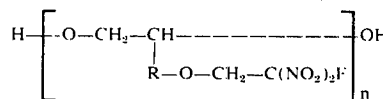
<sup>(1)</sup>Commercially available carboxy-terminated polybutadiene.

<sup>(2)</sup>Poly(glycidyl 2,2-dinitro-2-fluoroethanoxide).

<sup>(3)</sup>Bis-(2,2-dinitro-2-fluoroethyl) formal.

<sup>(4)</sup>Explosive power is measured by detonation pressure.

The novel hydroxy-terminated prepolymers prepared herein can be cured with conventional curing agents. Generally, about up to 5 weight percent of isocyanate type curing agent is employed for formulating the energetic compositions. Such diisocyanates as hexamethylene diisocyanate, bis-isocyanatophenyl methane, toluene diisocyanate, 3-nitroazabicyclo-1.5-pentane diisocyanate and the like will give a satisfactory cure. Energetic nitro plasticizers such as bis(2,2-dinitro-2-fluoroethyl) formal and the like, usually in a concentration of 0 to 40



in which R is alkylene of 1 to 4 carbon atoms and n is an integer of from about 4 to 25.

2. The polymer of claim 1 in which R is methylene.

\* \* \* \* \*

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