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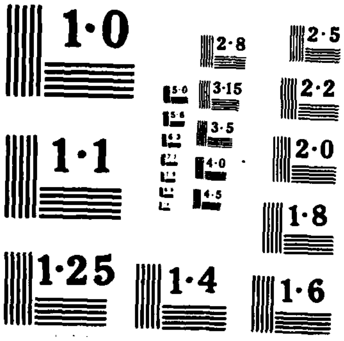
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PREPARATION OF ENERGETIC COMPOUNDS

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PREVIOUSLY EMPLOYED PREPARATIVE METHODS WERE SUCCESSFULLY SCALED UP TO PRODUCE SPECIFIC COMPOUNDS OF INTEREST TO THE U.S. NAVY. SPECIFICALLY, THE COMPOUNDS SYNTHESIZED WERE 4,5-BIS(FLUORODINITROMETHYL)-1,3-DIOXALANE; 1,3,3,5,7,7-HEXANITROOCTAHYDRO-1,5-DIAZOCINE; AND 2,2,3,3,4,4-HEXAFLUORO-1,5-PENTANEDIOL POLYFORMAL. IN ADDITION, A SMALL QUANTITY OF THE 2,4,4,5,5,6,6-HEPTAFLUORO-2-TRIFLUOROMETHYL-3-OXA-1,7-HEPTANEDIOL POLYFORMAL WAS SYNTHESIZED. THE NECESSARY DATA WERE OBTAINED ON THE SYNTHESIZED COMPOUNDS TO OBTAIN AN INTERIM SHIPPING CLASSIFICATION FROM THE NAVY. THE COMPOUNDS WERE SUBSEQUENTLY SHIPPED TO THE NAVAL WEAPONS CENTER AND THE NAVAL SURFACE WEAPONS CENTER FOR EVALUATION AS INGREDIENTS IN HIGH ENERGY EXPLOSIVE COMPOSITIONS.

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PREFACE

The research reported herein was supported by the Office of Naval Research, Mechanics Division, with Dr. R. S. Miller as the scientific officer. This report covers the period 1 May 1984 through 30 June 1986. The program was directed by Dr. M. B. Frankel. Contributing to this program were Dr. J. F. Weber and Mr. M. A. Cunningham. Dr. L. R. Grant served as the program manager. Dr. H. G. Adolph of the Naval Surface Weapons Center provided valuable technical guidance and his help is gratefully acknowledged.

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INTRODUCTION

There is a continual quest to upgrade the performance of state-of-the-art propellants and explosives. The three principal ingredients of these systems are the oxidizer, plasticizer, and polymeric binder. Consequently, a major effort has been carried out in the past years to synthesize and characterize high-energy, high-density compounds that could be utilized for these applications. Recent research work by Dr. H. G. Adolph at the Naval Surface Weapons Center (NSWC) has revealed three attractive new propellant and/or explosive ingredients. These compounds are 1,3,3,5,7,7-hexanitrooctahydro-1,5-diazocine, a high-energy solid oxidizer candidate; 4,5-bis(fluorodinitromethyl)-1,3-dioxalane (DHFEFO), a high-density liquid plasticizer candidate; and certain fluorinated polyformals, which are high density prepolymer candidates. The objective of this program was to synthesize and characterize sufficient quantities of these materials so that they could be more fully evaluated by the technical staffs at NSWC and the Naval Weapons Center (NWC).

DISCUSSION

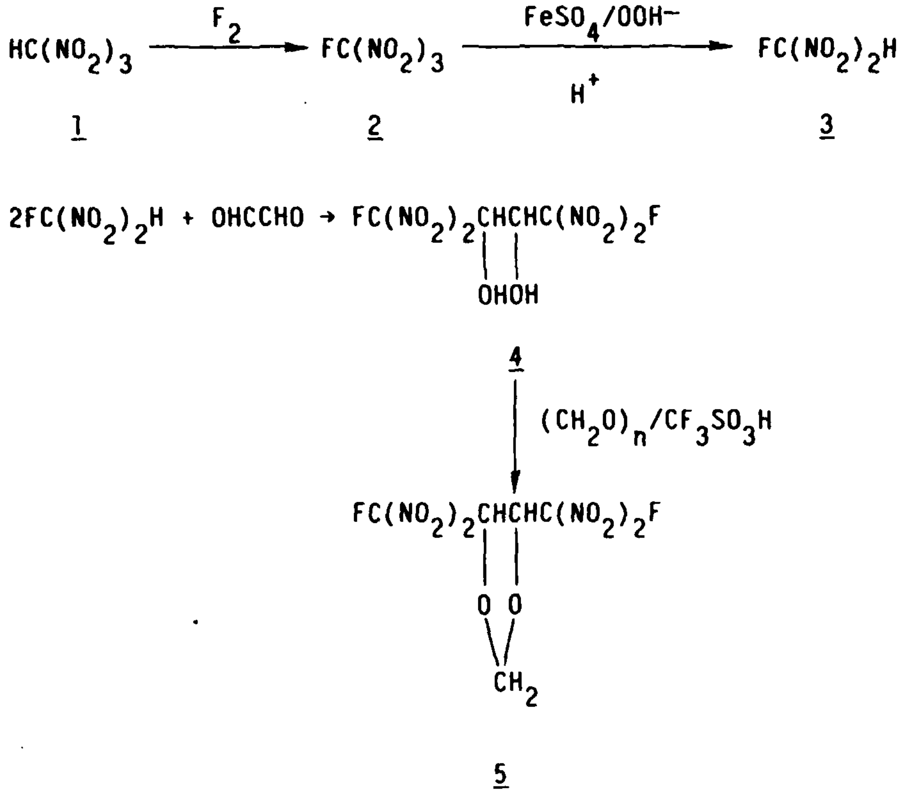
4,5-BIS(FLUORODINITROMETHYL)-1,3-DIOXALANE

In the continuing search for new plasticizer candidates with improved energy and physical properties, attention was centered on 4,5-bis(fluorodinitromethyl)-1,3-dioxalane (DHFEFO), a new compound discovered by Dr. H. G. Adolph at NSWC (Ref. 1). DHFEFO was reported to have a higher density than the plasticizer bis(2,2,2-fluorodinitroethyl) formal (FEFO). The higher density of DHFEFO is an important factor since the detonation pressure of an explosive ingredient is proportional to the square of its density. In addition, the freezing point of DHFEFO was reported to be significantly lower than that of FEFO, which is a very desirable property for a plasticizer. These attractive features of DHFEFO warranted its evaluation in advanced explosive compositions being developed by the Navy.

A two-phase, DHFEFO production program was anticipated. During the first phase, a quantity less than 1 pound of DHFEFO would be prepared and characterized at Rocketdyne. A DOT shipping classification would be obtained from the Navy and the material then shipped to the NWC for evaluation as an explosive ingredient. If this evaluation proved to be favorable, then an additional 15 pounds of the material would be prepared for further testing. On the other hand, if the evaluation was unfavorable, additional efforts on DHFEFO would not be warranted, and the work would be terminated.

Synthesis and Characterization of DHFEFO

Adolph's procedure for the synthesis of DHFEFO involves a four-step reaction sequence as shown below:



$$\underset{\underline{1}}{HC(NO_2)_3} \xrightarrow{F_2} \underset{\underline{2}}{FC(NO_2)_3} \xrightarrow[H^+]{FeSO_4/OOH^-} \underset{\underline{3}}{FC(NO_2)_2H}$$

$$2FC(NO_2)_2H + OHCCHO \rightarrow \underset{\underline{4}}{FC(NO_2)_2\underset{OH}{CH}\underset{OH}{CH}C(NO_2)_2F}$$

$$\underline{4} \xrightarrow{(CH_2O)_n/CF_3SO_3H} \underset{\underline{5}}{FC(NO_2)_2\underset{O}{CH}\underset{O}{CH}C(NO_2)_2F \quad (O\text{—}CH_2\text{—}O)}$$

The aqueous fluorination of nitroform (1) gave fluorotrinitromethane (2), Ref. 2. Reduction of 2 to fluorodinitromethane (3) was then carried out, using the ferrous salt catalyzed acid peroxide reaction (Ref. 3). The Michael addition of 3 to glyoxal produced 1,4-difluoro-1,1,4,4-tetranitrobutane-2,3-diol (4), Ref. 4. The first four steps proceeded smoothly according to the published procedures. The final step in this procedure involved the cyclization of 4 with trioxane in the presence of trifluoromethanesulfonic acid to yield 4,5-bis(fluorodinitromethyl)-1,3-dioxalane (5). DHFEFO had only been prepared on a gram scale at NSWC and its physical properties were not completely characterized. Furthermore, only a very limited effort had been previously expended on this preparative procedure. Therefore, a series of larger size runs (10 to 500 grams) were conducted to determine any scaling problems associated with the final step of the sequence, and to provide sufficient quantities of DHFEFO for its evaluation by NWC.

Table 1 summarizes the results obtained on the basis of 10 runs. The 10-gram-size runs were conducted primarily to determine the effects of reaction temperature, time, and alteration of the glycol to trioxane molar ratio on the yield of 5. The best yield of 39% was obtained from Run 7, which employed a reaction time of 20 hours and a maximum temperature of 60 C. In all of these runs, a contributing factor to the low yields was the recovery of significant amounts (63 to 82%) of unreacted glycol.

On the basis of the results obtained from these small-scale runs, the larger size runs (50 to 500 grams of the glycol) were generally conducted at a reaction temperature of 60 C and for a period of approximately 24 hours. The yields of 5 varied from 5.6 (Run 4) to 34.7% (Run 9), and decreased with increasing amounts of glycol utilized. There was an obvious scaling problem associated with this reaction, but no definitive reasons for this or solutions to the problem were determined.

The 130 grams of 5 that were produced from the above 10 runs was of high purity based on its liquid chromatographic and infrared analyses (Fig. 1). The data summarized in Table 2 also confirmed the compound's previously reported high density, low freezing point, and relative insensitivity to impact. Although the differential scanning calorimetery (DSC) results indicated DHFEFO to be thermally stable, the weight loss data at 74 C (Table 2) revealed it to be quite volatile.

Evaluation of DHFEFO

An interim shipping classification of "Class B Explosive" was obtained for DHFEFO and 107 grams were shipped to the NWC for evaluation. The DHFEFO was formulated with other materials to give a final composition consisting of 75 HMX/18.75 DHFEFO/6.25 BAMO-NMNC. This system cured well, no compatibility problems were noted, and it exhibited very good mechanical properties. However, during the accelerated aging studies, it was found that 36 w/o of the DHFEFO was lost after 40 days at 55.6 C (132 F). This high rate of plasticizer loss is unacceptable for an explosive ingredient and, therefore, it was recommended that no further work be done on the DHFEFO. The program was then modified to replace the intended

TABLE 1. PREPARATION OF 4,5-BIS(FLUORODINITROMETHYL)-1,3-DIOXALANE (DHFEFO)*

RUN NO.	GLYCOL, g (mol)	TRIOXANE, g (mol)	CF_3SO_3H, g (mol)	TEMPERATURE, C	TIME, (hours)	RECOVERED GLYCOL, g (%)	DHFEFO YIELD, g (%)
1	50 (0.163)	5 (0.056)	574 (3.82)	60	61	37.0 (74)	10.3 (19.9)
2	10 (0.033)	1 (0.011)	115 (0.764)	78	24	7.6 (76)	2.4 (22.9)
3	10 (0.033)	2 (0.022)	115 (0.764)	66	19	8.2 (82)	1.4 (13.3)
4	500 (1.63)	50 (0.56)	5736 (38.2)	53-60	24	455 (91)	29.3 (5.6)
5	10 (0.033)	1 (0.011)	115 (0.764)	64	24	-----	0.8 (7.6)
6	50 (0.163)	5 (0.056)	574 (3.82)	62.5	24	35.7 (71.4)	14.3 (27.6)
7	10 (0.033)	1 (0.011)	115 (.764)	50-60	20	6.3 (63)	4.1 (39)
8	100 (0.327)	10 (.11)	1147 (7.64)	60	24	86.5 (86.5)	12.4 (11.9)
9	50 (0.163)	5 (0.056)	574 (3.82)	60	22	32.9 (65.8)	18.0 (34.7)
10	368 (1.2)	37 (0.41)	4426 (28.1)	60	24	347.6 (91.1)	37.1 (9.7)

* Molar ratios employed in all experiments:

Glycol/Trioxane	2.9 (except for Run 3 which utilized a ratio of 1.5)
CF_3SO_3H/Glycol	23
CF_3SO_3H/Trioxane	68 to 70 (except for Run 3 which employed a ratio of 35)

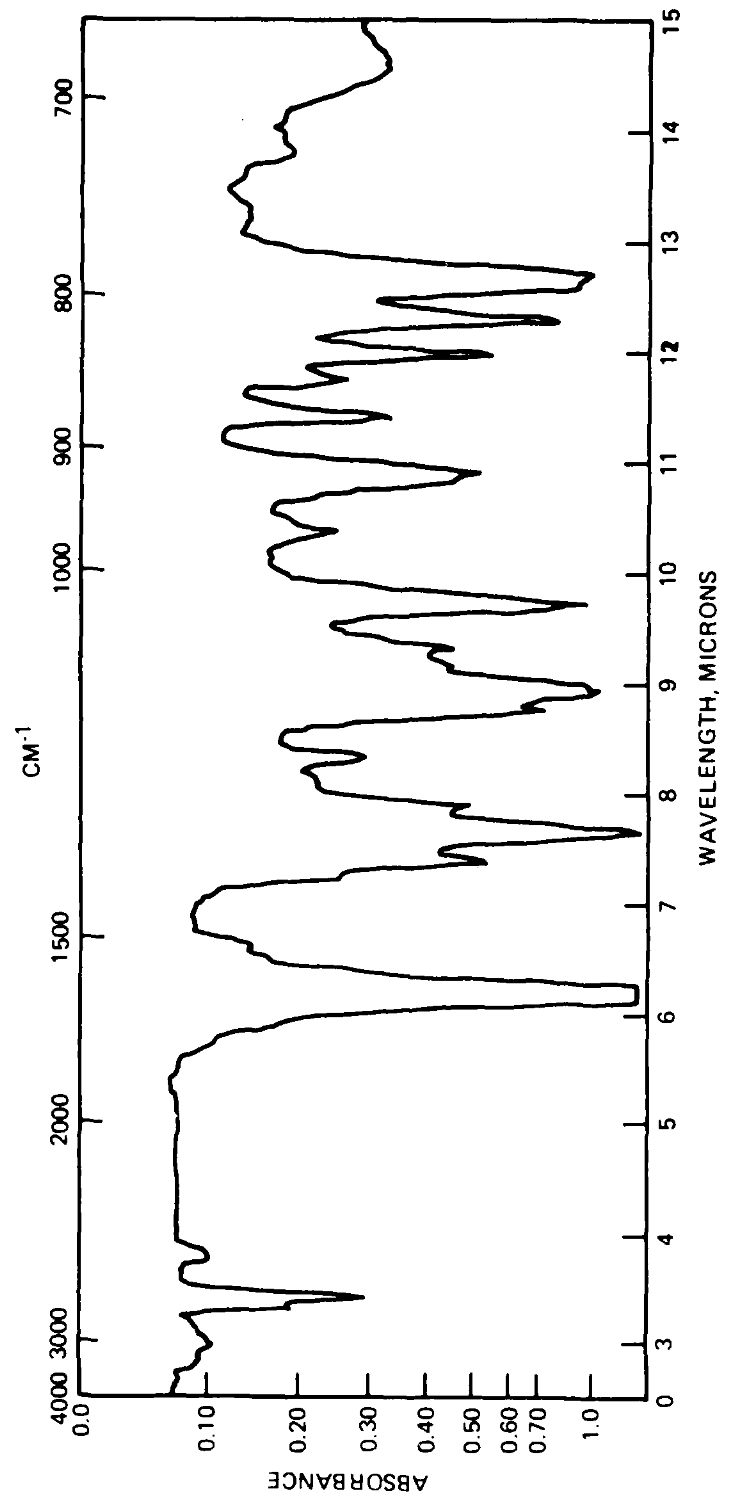
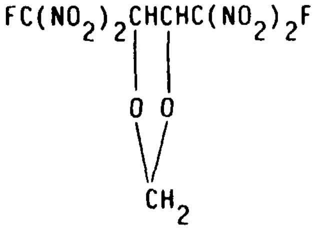


Figure 1. Infrared Spectrum of DHFEFO

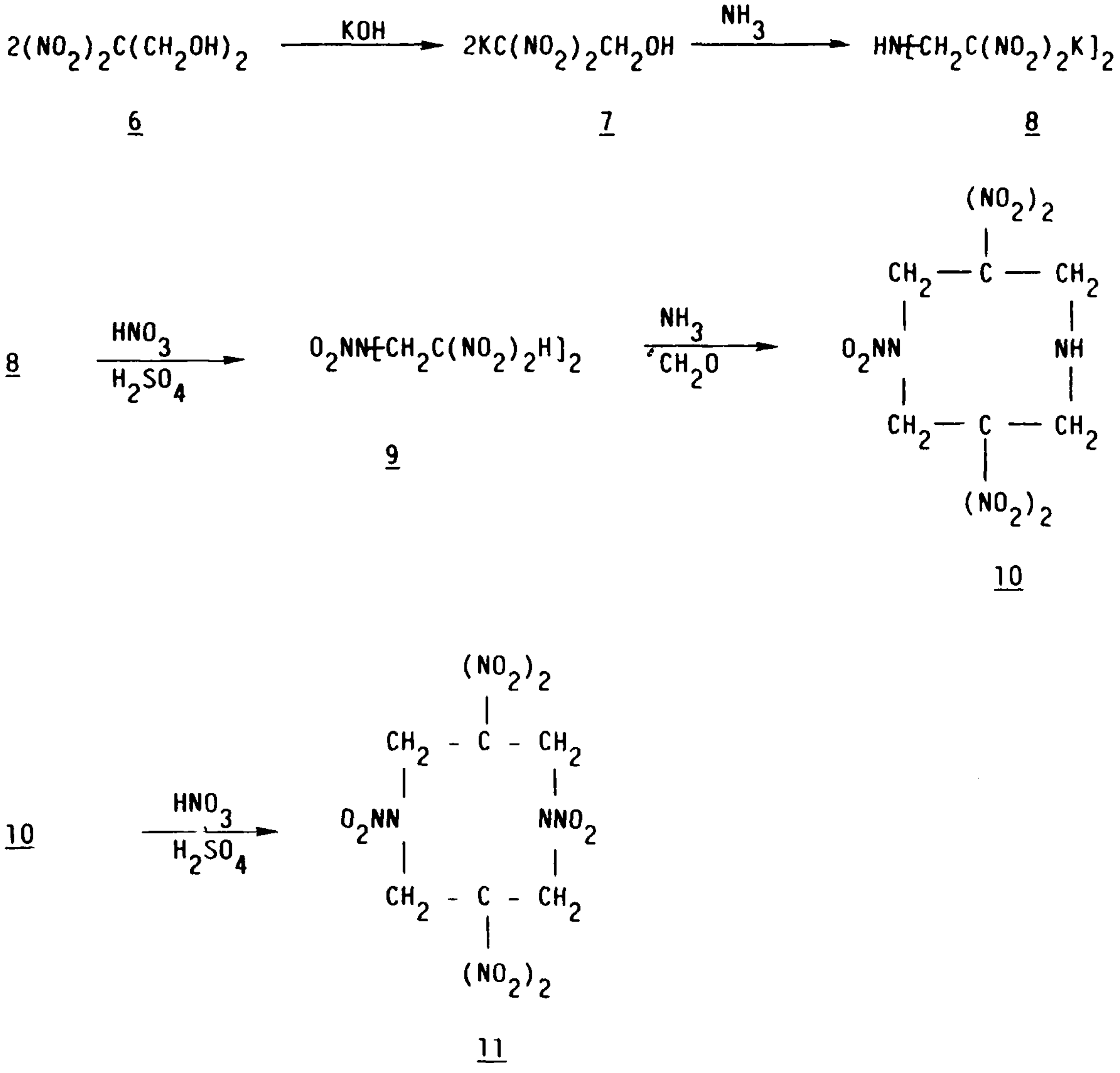
TABLE 2. DATA SHEET FOR DHFEFO

NAME	4,5-BIS(FLUORODINITROMETHYL)-1,3-DIOXALANE
STRUCTURE	
FORMULA	$C_5H_4F_2N_4O_{10}$
MOLECULAR WEIGHT	318
DENSITY	1.675 g/cc at 25 C
FREEZING POINT	-50 C
IMPACT SENSITIVITY	89 in.-lb
THERMAL STABILITY	184 C (onset of exotherm, based on DSC measurements)
WEIGHT LOSS (74 C), %	
24 HOURS	15.0
51 HOURS	40.3
72 HOURS	55.3
SHIPPING CLASSIFICATION	Class B Explosive (25 w/o solution in CH_2Cl_2)

scaleup work on DHFEFO with the synthesis of 1,3,3,5,7,7-hexanitrooctahydro-1,5-diazocine and the specific fluorinated polyformals described below.

1,3,3,5,7,7-HEXANITROOCTAHYDRO-1,5-DIAZOCINE

Interest in 1,3,3,5,7,7-hexanitrooctahydro-1,5-diazocine (11) as a dense, high-energy oxidizer is based on its structural similarity to HMX, wherein the symmetry of HMX is maintained by replacement of two nitramino groups with dinitromethylene moieties. The preparative procedure for 11 was based on a four-step reaction sequence (Ref. 5):



The first step, treatment of 2,2-dinitro-1,3-propanediol (6) with potassium hydroxide, gave quantitative yields of potassium 2,2-dinitroethanol (7). This salt, as well as the other compounds prepared in this sequence of reactions, were considered to be impact-sensitive materials and were always handled solvent wet. Consequently, only approximate yields were obtained, which were based on drying a small aliquot of the wet products. The synthesis of 7 was scaled up twice to the 8.68 mole size, which gave about 1500 g of product (m.p. 123-124 d) per run.

The preparation of 8, by the Mannich condensation of 7 with ammonia was based on the original procedure of Klager (Ref. 6). This procedure was found to give substantial amounts of the tris(potassio-2,2-dinitroethyl) amine (8a) as well as the desired 8:

$$\underline{7} \xrightarrow{NH_3} \underset{\underline{8}}{HN[CH_2C(NO_2)_2K]_2} \overset{NH_3}{\rightleftarrows} \underset{\underline{8a}}{N[CH_2C(NO_2)_2K]_3}$$

The formation of 8a was eliminated by the incremental addition of ammonia during the reaction. The synthesis of 8 was scaled up twice to the 4.14 mole size, which yielded about 600 g per run of salt, m.p. 145-146 d.

Nitration of 8 to 9 was carried out on a 1 to 2 mole scale and product yields in the range of 60 to 70% were obtained. Five nitration runs were conducted which gave several pounds of 9, m.p. 100-102 d (Ref. 5, m.p. 98.5-99.5 d). The Mannich condensation of 9 with ammonia and formaldehyde yielded 1,3,3,7,7-pentanitro-octahydro-1,5-diazocine (10). The product yields from this reaction were low (34%) and a total of five 1-mole runs had to be carried out to provide sufficient amounts of this material for conversion to the requisite amount of 11 for shipment. Each of the 1-mole runs gave about 113 g of 10, m.p. 122-140 d (Ref. 5, m.p. 160 d). The final step, nitration of 10, produced the desired 1,3,3,5,7,7-hexnitrooctahydro-1,5-diazocine (11). A total of 600 g of 11 was prepared in 6 runs, m.p. 250-252 d (Ref. 5, m.p. 250 d), in yields ranging from 73 to 91%. Elemental analyses confirmed the identity and purity of the product.

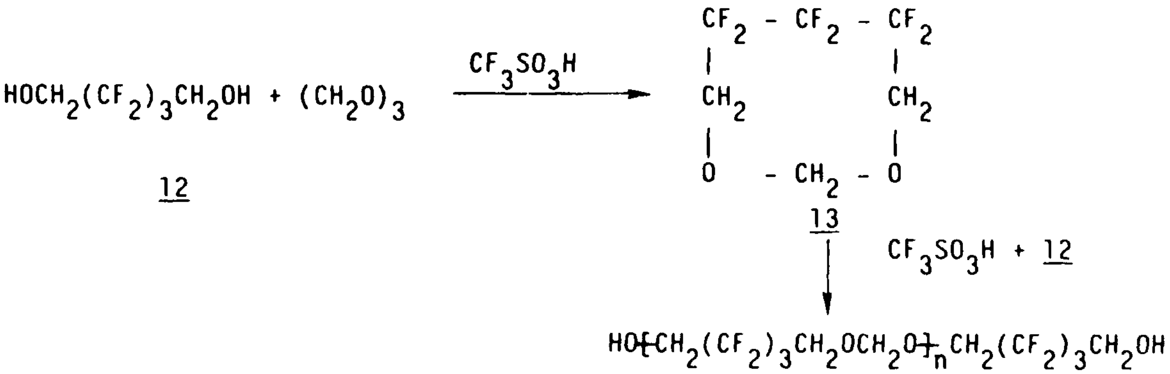
The impact sensitivity of 11 was found to be 30 in.-lb (HMX = 40). On this basis, an interim DOT shipping classification as a "Class A Explosive" was obtained from the Navy and the material was shipped to NSWC for evaluation.

FLUOROPOLYFORMALS

Hydroxy-terminated fluoropolyformals are of interest as binders for high-energy, castable, explosive compositions, primarily because of the high density that the fluoropolymer contributes to the system. Two fluorinated polyformals, based on 2,2,3,3,4,4-hexafluoro-1,5-pentanediol (12) and 2,4,4,5,5,6,6-heptafluoro-2-trifluoromethyl-3-oxa-1,7-heptanediol (15), were synthesized during this program employing preparative methods (Ref. 7) developed by Dr. H. G. Adolph of the NSWC. The following sections present the results of these investigations.

2,2,3,3,4,4-Hexafluoro-1,5-Pentanediol Polyformal

The initial efforts made to prepare the polyformal of 12 were based on the condensation of 12 with trioxane in the presence of trifluoromethanesulfonic acid. The products of these reactions were low molecular weight polymers. The polyformal of 12, with a more desirable number average molecular weight (Mn) of 2500 to 5000, had been prepared by Adolph via the intermediate cyclic monomer (13) as shown below:



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This procedure was followed in the subsequent preparative runs.

The cyclic monomer, (13), was prepared by the trifluoromethanesulfonic acid (triflic acid) catalyzed condensation of the diol with paraformaldehyde in methylene chloride at ambient temperature. Thirteen pounds (5.9 kg) of the diol (12), supplied by 3M, were converted to the cyclic formal in four large-scale runs of approximately 3 pounds (1.4 kg) each. The product was isolated, after neutralization of the acid, by a careful fractional distillation of the solvent, unreacted formaldehyde (as trioxane), and product in the order given. As described below, the quality of the cyclic monomer is crucial in the subsequent polymerization reactions. The yields of 13 averaged about 80% for the four runs. The remaining quantity of 12 (~500 g) was reserved for use as part of the catalyst system for the polymerization reactions.

Polymerization of the cyclic monomer is initiated with a catalytic amount of diol 12 and triflic acid. The relative amounts of 12 and 13 determine the molecular weight of the resultant polymer. As a rough approximation, dividing the total weight of 12 and 13 by the number of moles of 12 gives a good estimate of the resultant polymer's Mn:

$$\text{Mn} \approx \frac{\text{mass of diol + mass of formal}}{\text{moles of diol}}$$

The Mn values shown in Table 3 were determined experimentally by means of high-pressure gel permeation chromatography (GPC). This method measures the relative size distribution of the polymers. The absolute Mn values are assigned by comparison with a set of standards of known molecular weights. Ideally, known oligomers of the polymer being studied are used as standards. This method was used by NSWC, because their chromatographic system resolved the oligomers from dimer to at least the pentamer. The instrument used at Rocketdyne did not resolve these oligomers and was standardized with known polypropylene glycol samples. Consequently, the resultant experimental values obtained at Rocketdyne were lower than the NSWC values, and the size of this error was larger for the higher molecular weight polymers.

TABLE 3. PREPARATION OF 2,2,3,3,4,4-HEXAFLUORO-1,5-PENTANEDIOL POLYFORMAL

RUN NO.	REACTANTS			MOLECULAR WEIGHT VALUES		COMMENT
	CYCLIC FORMAL (13), g (mol)	DIOL (12), g (mol)	CF_3SO_3H, ml	Mn (ROCKETDYNE)*	Mn (NSWC)**	
1	20.6 (0.09)	1.63 (0.008)	0.175	2124	2424	---
2	198.2 (0.88)	12.0 (0.06)	2.6	(1954)***	4189	---
3	109.4 (0.49)	8.5 (0.04)	0.940	2351	3600	EMPLOYED TRIOXANE-CONTAMINATED 13
4	110.6 (0.49)	12.4 (0.06)	0.940	--	--	MAINLY MONOMER ISOLATED
5	52.5 (0.23)	5.0 (0.02)	0.450	--	4100	USED TRIOXANE-CONTAMINATED 13
6	57.0 (0.25)	6.8 (0.03)	0.450	--	--	USED TRIOXANE-CONTAMINATED 13
7	50.0 (0.22)	4.0 (0.02)	0.500	2288	3300	USED TRIOXANE-CONTAMINATED 13
8	50.0 (0.22)	6.0 (0.03)	1.00	2712	3250	USED TRIOXANE-CONTAMINATED 13
9	50.5 (0.22)	4.5 (0.02)	0.480	1754	2350	SPECIALLY PURIFIED 13 USED
10	251.0 (1.12)	18.7 (0.09)	2.40	1958	--	PRODUCT COMBINED WITH THAT FROM RUN 12
11	51.8 (0.23)	2.0 (0.009)	0.500	2672	--	PRODUCT COMBINED WITH THAT FROM RUN 13
12	1010.5 (4.51)	76.8 (0.36)	10.0	2164	2571	
13	1301.8 (5.81)	52.1 (0.25)	13.0	2994	5453	PREPARED FROM TRIOXANE-FREE 13
14	1317.3 (5.88)	85.2 (0.40)	13.0	2343	2746	

*DETERMINED BY GPC USING POLYPROPYLENE GLYCOL AS STANDARDS (150 TO 4,000)

**DETERMINED BY GPC USING POLYFORMAL OLIGOMERS AS STANDARDS

***SAMPLING ERROR RESULTED IN A VERY LOW VALUE

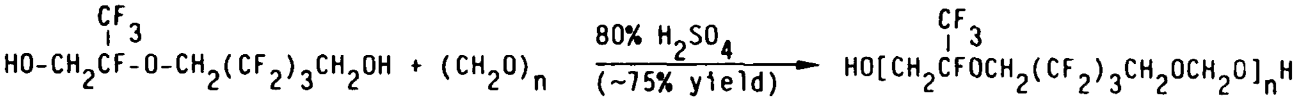
In all, 14 polymerizations were carried out on a scale from ~22 g to ~1400 g of starting material (Table 3). The first two runs (Runs 1 and 2) were conducted with small samples of the cyclic formal which were prepared separately and carefully purified. These served as pilot runs to assess the polymerization reaction prior to the larger scale preparations.

After synthesis of the first three large batches of 13, trial polymerizations were carried out to prepare a polymer with a nominal Mn of 2500 (Runs 3-9). The molecular weights of the products from the first six reactions (3 through 8) were erratic and, aside from unreacted 13, were considerably higher than the desired Mn. Examination of the NMR spectra of the cyclic formal used for these polymerizations indicated that it contained a significant (~ 10 mol%) amount of formaldehyde (determined as trioxane). The presence of this impurity was shown to be the cause for formation of the lower Mn materials. For example, the cyclic intermediate used for Run 9 was trioxane-free and, as a result, a product with the expected Mn value was obtained. (Compare Mn values for Runs 9 and 5.)

Following these runs, a final large-scale preparation of 13 was carried out. This product and all of the 13 on hand was carefully fractionally distilled to produce ~ 3.9 kg of trioxane-free (by NMR) product. The next 5 runs (10 through 14) used this very pure material. The objective of these particular runs was to produce approximately 2 pounds each of the polyformal with a Mn of approximately 2500 and 5000, and any residual 13 was to be converted to a material exhibiting a Mn of ~ 3500. Runs 10 and 12 were conducted under conditions expected to yield a product with a Mn of ~ 2500, whereas 11 and 13 were performed to produce a 5000 Mn polymer. The last run was scheduled to synthesize the 3500 Mn material. The total quantities of the polyformals synthesized were: 2.15 pounds (Mn = 2571), 1.93 pounds (Mn = 5453) and 2.17 pounds (Mn = 2746). The Mn values given are those obtained by NSWC. Only in the latter case was the Mn value of the polymer less than desired. The average polymer yield from Runs 10 through 14 was 71%, with 20% of the starting cyclic formal recovered during workup.

2,4,4,5,5,6,6-Heptafluoro-2-Trifluoromethyl-3-Oxa-1,7-Heptanediol Polyformal

A small sample (~ 50 g) of diol 15, received from 3M, was converted to its polyformal (16) by the acid catalyzed condensation with formaldehyde (generated from paraformaldehyde):



$$\mathrm{HO{-}CH_2\overset{CF_3}{\overset{|}{C}}F{-}O{-}CH_2(CF_2)_3CH_2OH + (CH_2O)_n \xrightarrow[(\sim 75\%\ yield)]{80\%\ H_2SO_4} HO[CH_2\overset{CF_3}{\overset{|}{C}}FOCH_2(CF_2)_3CH_2OCH_2O]_nH}$$

15 16

The resultant polymer was not very soluble in methylene chloride and NSWC determined that it was incompatible with the energetic plasticizer FEFO. For this reason, no further work on this polymer was pursued.

EXPERIMENTAL

Many of the compounds reported herein are sensitive explosives and should be handled with appropriate care. Melting points are uncorrected and the microanalyses were performed by Galbraith Laboratories. NMR spectra were run as deuteriochloroform solutions in a Varian EM-390 spectrophotometer. Chemical shifts are reported in parts per million (ppm) down field from internal tetramethylsilane.

SYNTHESIS OF 4,5-BIS(FLUORODINITROMETHYL)-1,3-DIOXALANE

The typical experimental conditions employed for synthesis of the intermediate diol (4) and its dioxalane derivative are described in the following paragraphs.

1,4-Difluoro-1,1,4,4-Tetranitrobutane-2,3-Diol (4)

A solution of 874.5 g (7.05 mol) of fluorodinitromethane in 2500 g of methylene chloride was cooled in an ice bath and diluted with 1680 ml of water. To the stirred mixture was added 648.5 g (3.36 mol) of 30% aqueous glyoxal during 85 minutes, while maintaining the reaction temperature at 2-5 C by external cooling. During addition of the glyoxal, an aqueous sodium bicarbonate solution was added as required to buffer the reaction mixture at a pH of 6.5-7.5. The reaction mixture was subsequently acidified with dilute hydrochloric acid, saturated with sodium chloride and extracted with 4 x 850 ml portions of ether. The combined extracts were dried over anhydrous sodium sulfate and concentrated to 857.8 g (83.4%) of crude product (m.p. 104-169 C). Two recrystallizations from ethylene dichloride at a ratio of 7 ml/g gave 640.3 g (62.3%) of the purified product with an m.p. of 178-180 C.

4,5-Bis(Fluorodinitromethyl)-1,3-Dioxalane (5)

To 574 g (3.82 mol) of triflic acid was added 5 g (0.056 mol) of trioxane. The mixture was stirred at ambient temperature until the trioxane had dissolved. 1,4,-Difluoro-1,1,4,4-tetranitrobutane-2,3-diol, 50 g (0.163 mol), was then added and the reaction mixture heated at 60 C for 22 hours, cooled to 5-10 C, and filtered to recover 32.9 g (65.8%) of unreacted diol. The filtrate was quenched in ice and extracted with methylene chloride. The methylene chloride solution was washed with water, 4% sodium bicarbonate, water, dried, and passed through a chromatographic column of basic alumina and silica gel. Concentration of the solution gave 18.0 g (34.7%) of product.

PREPARATION OF 1,3,3,5,7,7-HEXANITROOCTAHYDRO-1,5-DIAZOCINE

The experimental conditions utilized for the synthesis of the target compound and its intermediates were as follows.

Potassium 2,2-Dinitroethanol (7)

A solution of 1440 g (8.68 mol) of 2,2-dinitro-1,3-propanediol in 3360 g of isopropyl ether was cooled in an ice bath and a solution of 571.9 g (8.68 mol) of potassium hydroxide in 2.7 ℓ of methanol added during 1.5 hours, while keeping the reaction temperature at 5-10 C. The reaction mixture was stirred for an additional 30 minutes and the yellow solid was then collected in a quantitative yield, washed with 2 x 1 ℓ of methanol and stored solvent wet. A dried sample of the product melted at 123-124 d.

Bis(Potassio-2,2-Dinitroethyl) Amine (8)

To a mixture of 702 g (4.14 mol) of potassium 2,2-dinitroethanol and 900 ml of water was added 500 ml of 28-30% ammonium hydroxide. The mixture was stirred for 1 hour at ambient temperature, then heated to 55 C for 2 hours. An additional quantity of 160 ml of ammonium hydroxide was added and the reaction mixture then maintained at 55 C for 1 hour. A final portion of 80 ml of ammonium hydroxide was added after this time. After another hour at 55-60 C, the reaction mixture was cooled in an ice bath. The product was then collected, washed with 3 x 250 ml of methanol and 3 x 250 ml of methylene chloride. The dried material exhibited a m.p. of 145-146 d. The solvent wet salt was stored in a refrigerator until used for the next reaction.

Bis(2,2-Dinitroethyl) Nitramine (9)

A mixture of 681 g (2.07 mol) of bis(potassio-2,2-dinitroethyl) amine and 3.5 ℓ of methylene chloride was cooled to 0 C. A solution of 736 ml (17.54 mol) of 98% nitric acid and 132 ml of 96% sulfuric acid was added during 45 minutes at -5 to 0 C. An additional 1260 ml of 96% sulfuric acid was then added over a 1-hour period, while maintaining the reaction temperature at -5 to 0 C. The mixture was then stirred for 2.5 hours at 0-3 C and the product collected and washed sequentially with cold 80%, 60%, 30%, 10%, and 1% sulfuric acid and ice water to give 352.9 g of a water-wet white solid. The product had a m.p. of 100-102 d.

1,3,3,7,7-Pentanitrooctahydro-1,5-Diazocine (10)

A mixture of 1872 ml of 40% aqueous methanol and 89 ml of glacial acetic acid was cooled in an ice bath and 292 g (0.98 mol) of bis(2,2-dinitroethyl) nitramine added at 0-10 C. Concentrated ammonium hydroxide, 194 ml (1.46 mol), was added over an interval of 45 minutes at 5-10 C, followed by the addition of 243 ml (3.0 mol) of 37% formaldehyde. The pH was then adjusted to 4.8-5.0 and the reaction mixture stirred for 2 hours at ambient temperature. The yellow solid was collected, washed with 3 x 350 ml of water, dissolved in 1100 ml of acetone, and filtered to remove a solid impurity. Concentration of the acetone solution gave 113.3 g (34.1%) of product, melting at 122-140 d.

1,3,3,5,7,7-Hexanitrooctahydro-1,5-Diazocine (11)

To 464 ml of 98% sulfuric acid was added 113 g (0.33 mol) of 1,3,3,7,7-pentanitrooctahydro-1,5-diazocine at 0-5 C. A mixed acid solution of 170 ml of 98% nitric acid and 232 ml of 98% sulfuric acid was added during 30 minutes at 5-10 C. The reaction mixture was stirred for 45 minutes at 5-10 C and quenched on ice. The white solid formed was collected, washed with water, and dried to give 116.8 g (91.3%) of product, m.p. 252 d. Elemental analyses: calculated for $C_6H_8N_8O_{12}$: C, 18.75; H, 2.08. Found: C, 18.60; H, 2.43.

SYNTHESIS OF FLUOROPOLYFORMALS

The preparative reaction conditions used for the intermediate cyclic formal (13) and the fluoropolyformals of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol and 2,4,4,5,5,6,6-heptafluoro-2-trifluoromethyl-3-oxa-1,7-heptanediol were as follows.

5,5,6,6,7,7-Hexafluoro-1,3-Dioxocane (13)

The following is representative of the conditions employed for the preparation of the cyclic formal (13). To a 12 ℓ flask charged with 1401.3 g (6.61 mol) of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol and 260 g (8.67 mol) of paraformaldehyde in 6 ℓ of methylene chloride was added 585 ml of trifluoromethanesulfonic acid (992 g; 6.61 mol) in about 25 minutes. The temperature dropped to 15 C initially, then rose to 24 C at the completion of the addition. This mixture was stirred at ambient temperature for 2 hours and then the reaction was stopped by addition of 3 ℓ of ice water. The layers were separated, and the aqueous layer was extracted with 2 ℓ of methylene chloride. The organic layers were combined, washed twice with 2 ℓ of a saturated NaCℓ solution, dried (Na_2SO_4), and filtered into a distillation pot. The solvent was removed by distillation through a short Vigreux column at ambient pressure. A forerun fraction, containing trioxane and some product, was collected at 70-165 C. The undistilled material was then cooled and transferred to a smaller pot and the product distilled at 65-70 C (20 mm Hg) into an ice-cooled receiver to give 1241 g (86% yield) of the purified 13. The forerun from this distillation, which was about 65% 13, was saved for later redistillation. NMR ($CDCℓ_3$) of the distilled product: singlet at 4.70 ppm, multiplet at 4.07 ppm (trioxane resonates at 5.07 ppm as a singlet).

2,2,3,3,4,4-Hexafluoro-1,5-Pentanediol Polyformal (14)

The following procedure used for Run 13 is representative of the preparation of the various polyformals.

A 2 ℓ, three-necked round bottom flask with a mechanical stirrer, nitrogen inlet, and small addition funnel was charged with 1301.8 g (5.81 mol) of the cyclic formal (13) and 52.1 g (0.246 mol) of the diol (12). This mixture was then heated to 60 C in an oil bath for 1 hour. To the homogeneous solution was added 13.0 ml of trifluoromethanesulfonic acid (22.0 g, 0.147 mol) over a 70-minute period. The mixture was stirred under nitrogen for 20 hours at 60 C, then cooled to room temperature and diluted with 3 ℓ of $CH_2C\ell_2$. The resulting solution was poured into one consisting of 800 ml of 30% H_2O_2, 1.6 ℓ of 10% KOH, and 2.4 ℓ of saturated NaCℓ and stirred for 1 hour. The layers were separated and the aqueous layer was extracted with 1 ℓ of $CH_2C\ell_2$ The combined organic layers were washed with 5 ℓ of saturated NaCℓ. An emulsion formed which was slow to separate. The very wet organic layer was dried with $MgSO_4$, filtered, and concentrated. Final stripping was carried out on a rotary evaporator at 105 C under a hard vacuum. The vacuum traps collected 265 g (20%) of unreacted cyclic monomer. The cloudy product was turbid with fine suspended solids, so it was redissolved in 3 ℓ of $CH_2C\ell_2$, filtered through 250 g of silica gel, and reconcentrated to give 840 g (62%) of a clear, viscous polymer. GPC analysis of this material (see Fig. 2), using polypropylene glycol standards, gave: Mn = 2994, Mw = 4109, Q = 1.37. The NSWC values obtained on the same polymer were: Mn = 5453, Mw = 10960, Q = 2.01.

Neither emulsion formation nor the aforementioned solids' problems were encountered during the isolation of the other two (lower molecular weight) polymers prepared. Consequently, these materials were not purified further by the silica gel treatment. The Rocketdyne GPC analytical curves for the other two fluoropolyformals are shown in Figs. 3 and 4 for which the Mn values obtained by NSWC were 2571 (Fig. 3) and 2746 (Fig. 4), respectively.

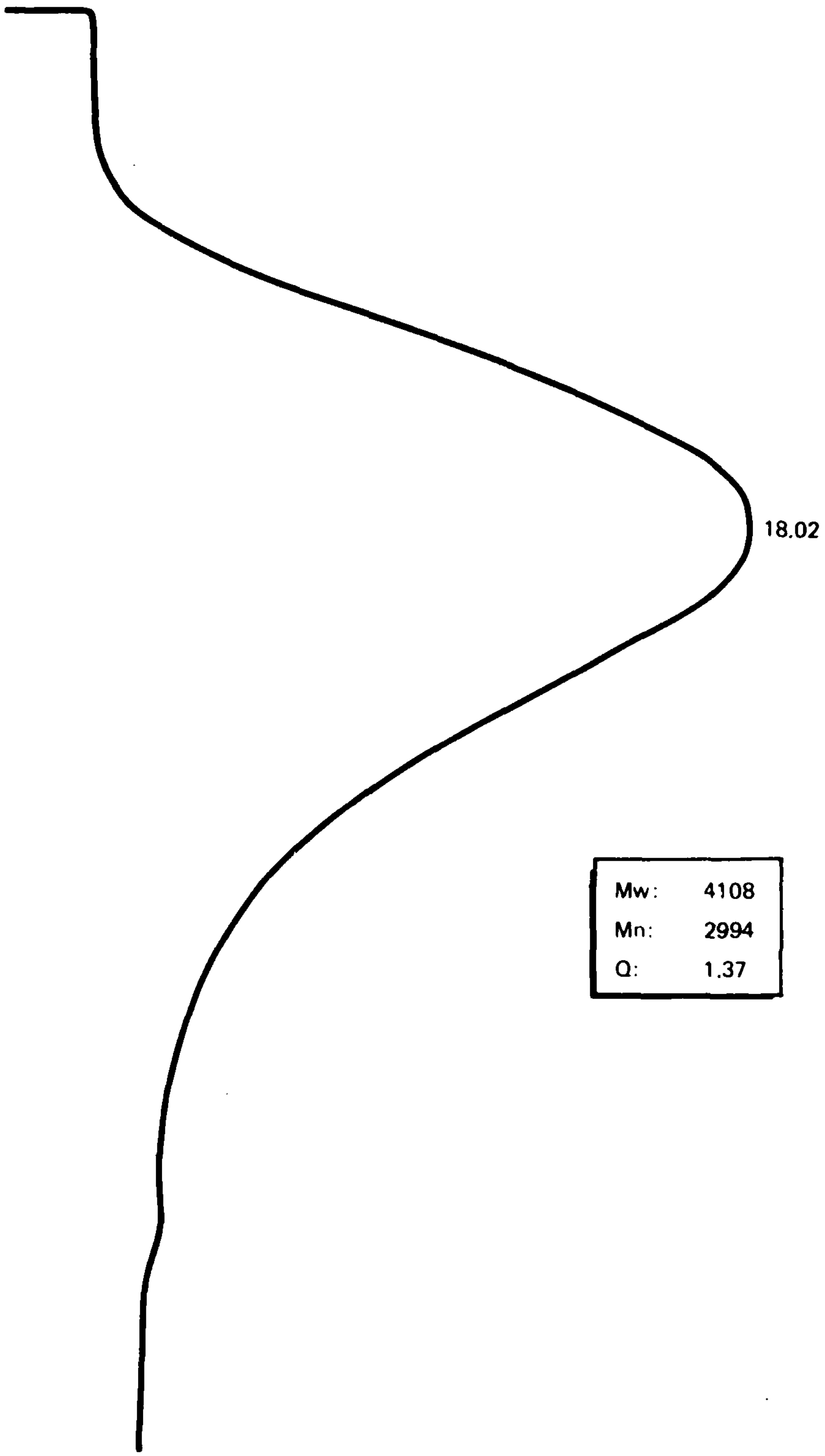


Figure 2. Rocketdyne's GPC Analysis of Fluoropolyformal, 14 (Table 3, Run 13)

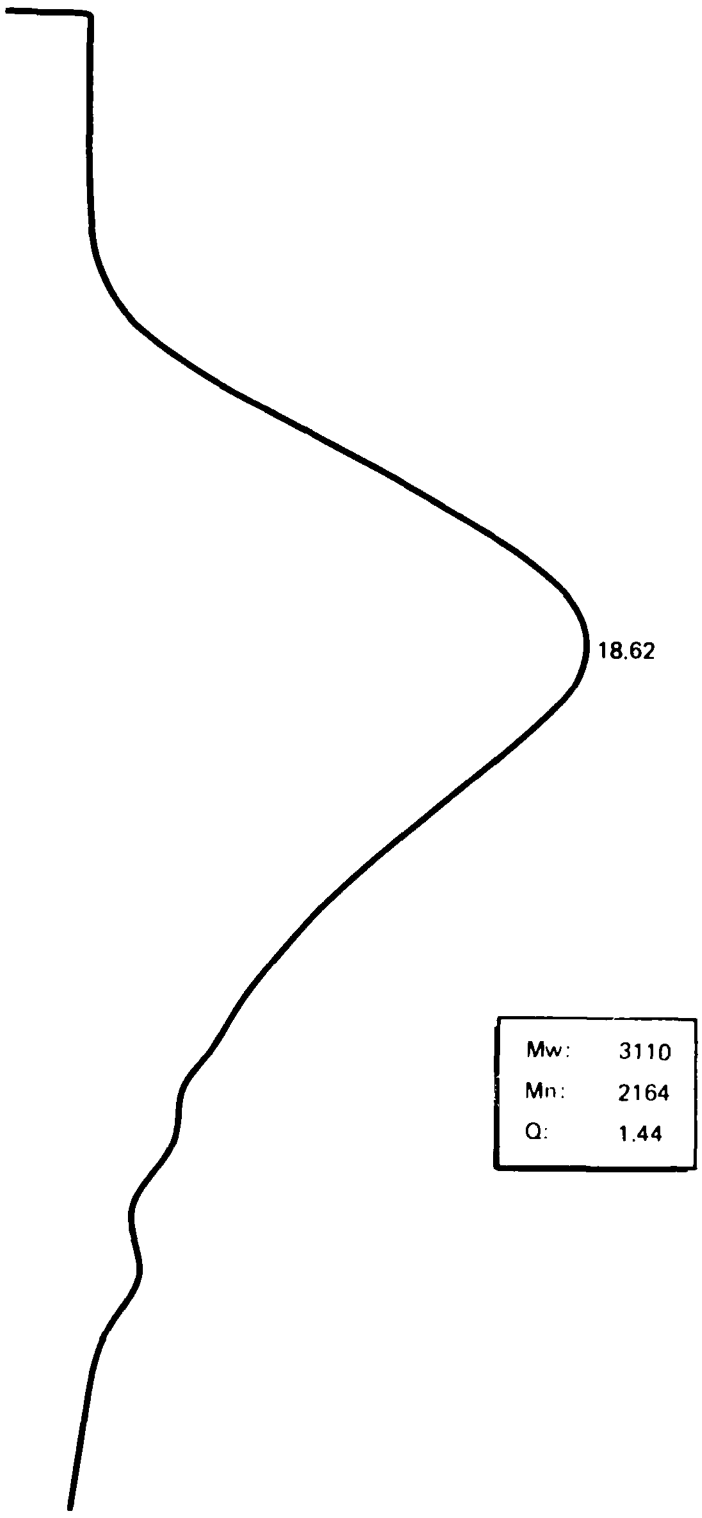


Figure 3. Rocketdyne's GPC Analysis of Fluoropolyformal 14 (Table 3, Run 12)

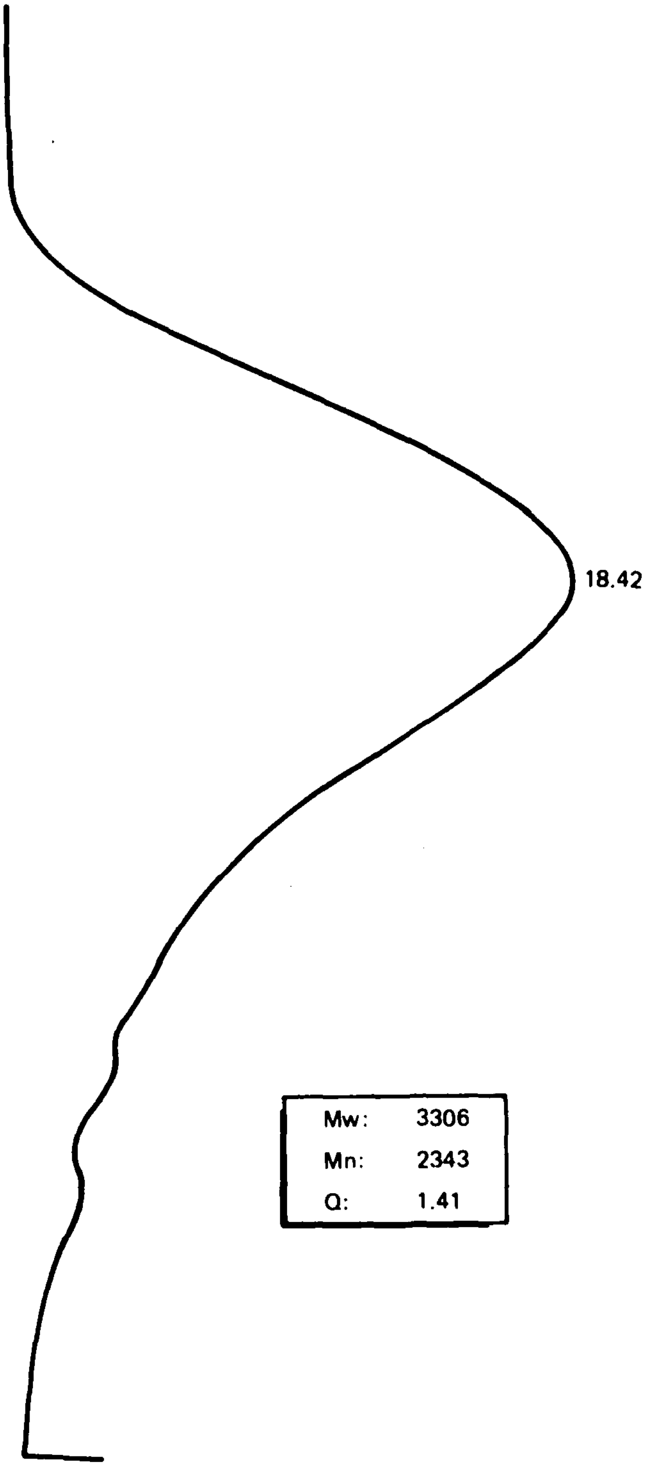


Figure 4. Rocketdyne's GPC Analysis of Fluoropolyformal 14 (Table 3, Run 14)

2,4,4,5,5,6,6-Heptafluoro-2-Trifluoromethyl-3-Oxa-1,7-Heptanediol Polyformal (16)

In a 500 ml, three-neck round bottom flask, 50.1 g (0.153 mol) of the diol (15) and 30 ml of 80% H_2SO_4 were stirred at room temperature until homogeneous, and 40 ml of $CH_2C\ell_2$ was then added. The milky mixture was cooled in an ice bath and a solution of 4.6 g (0.153 mol) of paraformaldehyde in 23 ml of 90% H_2SO_4 added dropwise. The mixture was stirred at room temperature for 24 hours, and the light brown mixture then poured over 300 g of ice and stirred with 300 ml of ether and 30 ml of 30% H_2O_2. After stirring for 1 hour, the layers were separated and the organic phase was washed with 250 ml of 5% KOH and 15 ml of 30% H_2O_2 followed by two brine washes. The solution was dried and concentrated under a GN_2 sparge. The resulting mixture was stripped of volatiles under a high vacuum while heating at 110 C overnight. The light brown, cloudy residue was dissolved in 250 ml of $CH_2C\ell_2$, filtered through 20 g of silica gel, and reconcentrated to give 37 g (74%) of polymer. GPC analyses of this material, using polypropylene glycol standards, gave: Mn = 1291, Mw = 2074, Q = 1.61.

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GLOSSARY

BAMO	3,3-Bis(azidomethyl)oxetane
DHFEFO	4,5-Bis(fluorodinitromethyl)-1,3-dioxalane
DSC	Differential Scanning Calorimetry
FEFO	Bis(2,2,2-fluorodinitroethyl) formal
GPC	Gel Permeation Chromatography
HMX	Cyclotetramethylene tetranitramine
Mn	Number Average Molecular Weight
Mw	Weight Average Molecular Weight
NMMO	3-Nitratomethyl-3-methyloxetane
NSWC	Naval Surface Weapons Center
NWC	Naval Weapons Center
Q	Dispersity (Mw/Mn)
Triflic Acid	Trifluoromethanesulfonic Acid

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APPENDIX A

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