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CROSSLINKING OF PERFLUOROCARBON POLYMERS

ULTRASYSTEMS, INC.
2400 MICHELSON DRIVE
IRVINE, CALIFORNIA 92715

MAY 1978

TECHNICAL REPORT AFML-TR-78-65
Interim Report for Period 16 February 1977 through 16 February 1978

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AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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NOTICE

This technical report has been reviewed and is approved for publication.

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Nonmetallic Materials Division

AIR FORCE/56780/2 August 1978 — 100

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Crosslinking investigations of perfluorinated systems via fluorine abstraction and functional epoxide approach are reported. To promote fluorine abstraction metalloid compounds, triphenylphosphine, tetraphenyldiphosphine, and related materials as well as zirconium sponge were studied. Fluorine abstraction was observed, but no coupling appeared to take place.

A functional epoxide, 4-bromoheptafluoro-1,2-epoxybutane was

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synthesized and successfully copolymerized with hexafluoropropene oxide and hexafluoropropene oxide derived acid fluorides. Transformation of the bromine-containing acid fluorides to hydrogen terminated compounds was accompanied by substitution of bromine by hydrogen; this interference was absent in the copolymers of 4-chloroheptafluoro-1,2-epoxybutane. U.V. irradiation in the presence of mercury was found effective in coupling the bromo-substituted perfluoroalkylether nitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)CN$, and the bromine-containing triazines.

FOREWORD

This report was prepared by Ultrasystems, Inc., Irvine, California under Contract No. F33615-76-C-5054, "Crosslinking of Perfluorocarbon Polymers", and covers work performed during the period 16 February 1977 through 16 February 1978. The Contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 04, "New Organic and Inorganic Polymers". The investigations were carried out by R. H. Kratzer, J. Kaufman, T. I. Ito, J. H. Nakahara, and K. L. Paciorek, Project Manager. This contract was administered under the direction of the Air Force Materials Laboratory, Polymer Branch, Dr. R. C. Evers (AFML/MBP), Project Engineer.

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SUMMARY

Crosslinking investigations of perfluorinated systems via fluorine abstraction and functional epoxide approach are reported. To promote fluorine abstraction metalloid compounds, triphenylphosphine, tetraphenyldiphosphine, and related materials as well as zirconium sponge were studied. Fluorine abstraction was observed, but no coupling appeared to take place.

A functional epoxide, 4-bromoheptafluoro-1,2-epoxybutane was synthesized and successfully copolymerized with hexafluoropropene oxide and hexafluoropropene oxide derived acid fluorides. Transformation of the bromine-containing acid fluorides to hydrogen terminated compounds was accompanied by substitution of bromine by hydrogen; this interference was absent in the copolymers of 4-chloroheptafluoro-1,2-epoxybutane. U.V. irradiation in the presence of mercury was found effective in coupling the bromo-substituted perfluoroalkylether nitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)CN$, and the bromine-containing triazines.

I. INTRODUCTION

Synthetic as well as natural gums must be crosslinked to establish three-dimensional networks in order to exhibit good viscoelastic properties and to provide practical elastomers. In the case of the fluorinated polymers, as exemplified by $-(CF_2)_n-$, $-[CF_2CF_2CF_2CF(CF_3)]_n-$, $[CF(CF_3)CF_2O]_n-$ and $-[(CF_2)_xO]_n-$ compositions to preserve the inherent chemical inertness and high thermal and oxidative stability the ideal crosslink should leave the basic structure of the polymer unchanged.

Fluorine abstraction followed by the establishment of a C-C linkage appeared to offer the simplest approach to obtain this objective.[1] Work by others[2,3] indicated that compounds such as e.g. triphenylphosphine are effective agents for this process.[2,3] Unfortunately, studies performed under the first phase of this program employing various metalloid compounds were unsuccessful in promoting this type of a reaction.[1] Under the current phase of this project only a minimal effort was therefore expended on this direct approach. The major emphasis was centered on synthesis and incorporation of functional monomers into perfluoroalkylether systems to provide chemically inert as well as thermally and oxidatively stable crosslinks.

II. DISCUSSION

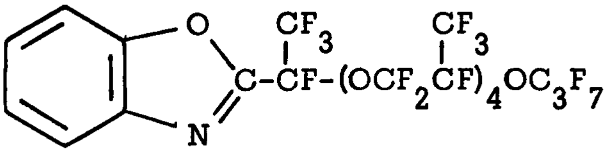
In view of the to date unsuccessful attempt to establish crosslinks via fluorine abstraction the investigations performed under the current phase of the program were centered on functional monomer synthesis, co-polymerization feasibility, and crosslink formation. Only a very limited effort was devoted to further exploration of the direct crosslinking approach, mainly to conclude the previously initiated work.

For ease of presentation the technical discussion was divided into three sections:

1. Crosslinking investigations of nonfunctional fluorocarbons
2. Monomer and model compound syntheses and investigations
3. Polymer studies

1. Crosslinking Investigations of Nonfunctional Systems

At 300°C tetraphenyldiphosphine failed to abstract fluorine from "free" perfluoroalkylethers as represented by E-fluids; however reaction was observed when a perfluoroalkylether chain was attached to a benzoxazole ring. Thus at 300°C 25% of benzoxazole, I,



I

was found to undergo degradation. Under these conditions, if any crosslinking took place, a char-like material was produced. In view of these results it appeared that using more moderate conditions, namely lower temperature, should hopefully lead to the desired cross-linking. Interaction of equimolar quantities of tetraphenyldiphosphine and benzoxazole at 250°C in vacuo for 139 hr gave a two phase liquid system together with some black deposit. The bottom layer was subsequently found to consist mainly of the benzoxazole I whereas $(C_6H_5)_2PFO$ was the major component of the upper layer. The composition of the total reaction mixture is given in Table I. Based on these data it can be deduced that under the conditions employed tetraphenyldiphosphine provides an effective fluorine abstracting agent since 1.73 mmol of $(C_6H_5)_2PFO$ were formed, which corresponds to a 51% yield. The fact that the molar ratio of benzoxazole employed to phosphinyl fluoride formed is one is a coincidence . However, in view of the high recovery of the starting material it has to be concluded that the fluorine abstraction occurs at several sites of one molecule and does not produce radicals which can couple, but rather leads to progressive degradation of a given chain. This action must be promoted by the benzoxazole ring, since it was not observed with "free" polyperfluoroalkylethers i.e. E-fluids.

If one compares the differences in the free energy of formation between various metal or metalloid-fluorine bonds, M-F, and the free energy of formation of the carbon-fluorine bond, C-F, it is apparent, based on the compilation given in Table 2, that phosphorus does not present the most favorable system. Furthermore since in all the studies utilizing tetraphenyldiphosphine the dissociation into free radicals

$$(C_6H_5)_2PP(C_6H_5)_2 \longrightarrow 2\ (C_6H_5)_2P\cdot$$

had to occur prior to fluorine abstraction the actual free energy change

TABLE 1

PRODUCTS OBTAINED ON INTERACTION OF $RCF(CF_3)[OCF_2CF(CF_3)]_4OC_3F_7$ AND $(C_6H_5)_4P_2$

Compound[a]	mg	%
$R-CF(CF_3)[OCF_2CF(CF_3)]_4OC_3F_7$	1536.05	83.77
$R-CF(CF_3)H$	13.79	0.75
$C_3F_7O[CF(CF_3)CF_2O]_3CF(CF_3)H$	10.792	0.59
$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)H$	6.092	0.33
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2H$	0.128	0.01
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)H$	6.564	0.36
$C_3F_7OCF(CF_3)H$	2.083	0.11
CF_3CF_2H	0.068	T
C_6H_6	0.408	0.06[b]
$C_6H_5CH_3$	0.033	0.01[b]
$(C_6H_5)_2PFO$	380.59	60.24[b]
$C_6H_5PF_2O$	1.58	0.25[b]
CO_2	5.196	0.28
PF_3	5.538	0.30
SiF_4	53.536	2.92

a) R = benzoxazole ring. b) These percentages are given with respect to tetraphenyldiphosphine; all the other values are based on the benzoxazole originally employed.

TABLE 2

COMPARISON OF FREE ENERGY DIFFERENCES BETWEEN M-F AND C-F BONDS AT 500°K[4]

Element M	Compound	ΔF_f^o(M-F) Kcal	ΔF_f^o(M-F) - ΔF_f^o(C-F) Kcal
Al	AlF_3	-108.7	-57.9
Zr	ZrF_4	-104.0	-53.2
Si	SiF_4	-92.3	-41.5
Ti	TiF_4	-89.5	-38.7
B	BF_3	-87.7	-36.9
P	PF_5	-69.8	-19.0
C	CF_4	-50.8	

for the formation of each PF-bond must be lower than -19.0 kcal/mol as given in Table 2. By comparison, the free energy change for a process such as

$$\text{Zr} + \text{C-F} \longrightarrow \text{Zr-F} + \text{C}$$

may be estimated to be quite large (-53.2 kcal/mol). Accordingly, high surface area zirconium sponge (3.150 mmol) was heated with perfluoro-(methylcyclohexane) (2.853 mmol) in vacuo at 300°C for 24 hr. Since this reaction resulted in recovery of 99.94% of unchanged starting material the direct crosslinking approach via fluorine abstraction was abandoned.

2. Monomer and Model Compound Syntheses and Studies

As an alternative to direct crosslinking, discussed above, the introduction into a perfluoroalkylether polymer of bromine-containing side chains was considered. One of the advantages of such a system would be the establishment on curing of the thermally, oxidatively and chemically stable $-CF_2-CF_2-$ linkage. The incorporation of such an entity into a perfluoroalkylether system by copolymerization of e.g. hexafluoropropene oxide and 4-bromoheptafluoro-1,2-epoxybutane seemed to offer the best approach. The precursor olefin was successfully synthesized during the first phase of the program[1] via a 3-step reaction sequence from 1,1,1-trichloro-5-bromoperfluoropentane. Due to the relative difficulty in obtaining large quantities of the starting material, 1,1,1-trichloro-5-bromoperfluoropentane, work was carried out on model systems to optimize the epoxide synthesis conditions and the subsequent telomerization and tranformation processes. The initial model studies were performed using perfluoroheptene-1. Under the current phase the closely related 1,1,1,5-tetrachloroperfluoropentane was kindly made available by Dr. W. H. Gumprecht of Du Pont. Utilizing this compound the study and optimization of the various reactions became possible.

The olefin 4-chloroperfluorobutene-1 was obtained in an overall 71% yield from the tetrachloro-precursor. Difficulties were experienced in the preparation of the epoxide due to the material's volatility and the facile reaction of the initially formed oxide with methanol to yield a methyl ester, most likely of the form $ClCF_2CF_2CF(OCH_3)CO_2CH_3$, in analogy with the hexafluoropropene oxide studies of Sianesi et al.[5] This reaction did not appear to interfere with the oxide formation in case of perfluoroheptene-1.[1] Zapevalov[6] reported a yield of 65% for the chloro-epoxide; it is believed that using larger starting material quantities yields higher than 35% would have been attained. Employing the optimized procedure for the preparation of the bromo-analogue yields of 35% were realized and in most instances olefin-free product was obtained which eliminated the bromination step necessary for olefin removal.

A number of routes are known to afford coupling via a bromo- or an iodo-moiety. For a polymer system a peroxide based cure appeared to offer several advantages especially as this type of vulcanization has been used for the fluoroelastomers in the past.[7] Unfortunately, treatment of the model compound, perfluoro-n-heptyl bromide, with benzoyl peroxide resulted in predominant substitution of bromine by hydrogen; no coupling was observed. Coupling proceeded readily with zinc in the presence of acetic anhydride; however, the product isolation using this system appeared to be unsuitable for cross-linking small polymer samples. Ultraviolet irradiation in the presence of mercury was found to yield the desired coupled product, C_7F_{15}-C_7F_{15}, without any side reactions or isolation problems.

The telomers obtained from cesium fluoride catalyzed epoxide additions are acid fluoride terminated. These can be readily transformed into methyl esters; however, it has been reported[8] that esters when subjected to UV irradiation undergo dimerization accompanied by carbon dioxide, ethane and perfluoroacetyl fluoride evolution. This process would be expected to interfere with the coupling reaction.

Whether carboxyl groups behave in a similar fashion was unknown. There was a possibility that here production of hydrogen-terminated materials accompanied by carbon dioxide evolution might take place i.e.:

$$R_fCOOH \xrightarrow{h\nu} R_fH + CO_2$$

To determine the feasibility of this transformation perfluoro-n-octanoic acid was subjected to ultraviolet radiation. The major volatiles formed were carbon dioxide and silicon tetrafluoride together with traces of water, $C_7F_{15}H$, and $C_7F_{14}H_2$. The solid residue was composed of unreacted perfluorooctanoic acid and unidentified coupled olefinic compounds. Thus, it can be concluded that the major reaction is liberation of hydrogen atoms and carbon dioxide i.e.

$$n\text{-}C_7F_{15}COOH \xrightarrow{h\nu} n\text{-}C_7F_{15}^{\bullet} + H^{\bullet} + CO_2$$

followed by some coupling of the primary fluorocarbon free radicals. This reaction is accompanied by fluorine abstraction by the hydrogen atoms forming hydrogen fluoride which in the presence of glass is transformed into the isolated silicon tetrafluoride. It is noteworthy that the SiF_4 to CO_2 mole ratio found was 1 : 4, which indicates clearly that for every carbon dioxide molecule liberated a hydrogen fluoride molecule was formed. Based on this result it became apparent that prior to ultraviolet irradiation of the bromine-containing telomers the end-group carboxyl functionality must be replaced by an ultraviolet resistant moiety.

The transformation of carboxyl to hydrogen-end groups via pyrolysis either of the ammonium salts or of the alkali metal salts (the latter in the presence of ethylene glycol) offered an attractive avenue.[9] To ascertain the applicability of this method to high molecular weight materials the tests listed in Table 3 were carried out. In Runs No. 1 and 2 telomers derived from hexafluoropropene oxide were employed whereas in Runs No. 3 and 4 co-polymers of hexafluoropropene oxide and 4-chloroheptafluoro-1,2-epoxybutane were used. The ammonium salt route appeared to present a number of advantages as compared to the sodium salt approach, the major one being the absence of involatile salt residues and possibly alkali metal hydroxide after reaction completion. Unfortunately, using ammonium salts formation of olefinic linkages and the presence of residual carbonyl groups was observed. Thus, the alkali metal salt procedure had to be adopted.

TABLE 3

TRANSFORMATIONS OF R_fOR_fCOOH TELOMERS INTO R_fOR_fH PRODUCTS

Run No.	Material Origin	Amount		NaOH	ethylene glycol	NH_4OH conc	Product yield	Remarks
		g	mmol	mmol	mmol	ml	%	
1	R-1[a]	1.69	0.60	0.58	32	n.a	80[b]	no carbonyl, no olefin
2	R-2[a]	1.93	0.55	n.a	n.a	1	58[b]	no carbonyl, no olefin
3	R-10[a]	0.85	0.65	n.a	n.a	1	39[b]	carbonyl and olefin present
4	R-11[a]	0.60	0.46	0.50	21	n.a	33[b]	no carbonyl, no olefin present

a) In these tests the involatile "polymers" described in Table 6 were employed.

b) This is the yield of the involatile polymeric material; in view of the small size samples used the low yield recorded is due to mechanical loss.

The applicability of this hydrogen termination reaction to bromine-containing materials had to be tested next. No suitable model compounds are available; consequently these had to be synthesized. The best approach appeared to be the co-telomerization of an acid fluoride with the bromo-epoxide. To optimize the process a number of tests given in Tables 4 and 5 were conducted with 4-chloroheptafluoro-1,2-epoxybutane. It would appear from this compilation that changing the catalyst to acid fluoride ratio and the cesium alkoxide formation conditions has no effect on the yield of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_2CF_2Cl)COF$, which stayed constant at ~ 40%. On the other hand utilizing the shorter chain acid fluoride a 1:1 proportion of cesium fluoride to acid fluoride resulted in significantly lower quantities of the desired telomer than the 1:2 ratio (compare tests No. 16 and17). The yield of the mono-adduct (see Table 5) obtained utilizing the bromo-epoxide was higher than that observed under parallel conditions with the chloro-analogue; also the relative quantities of the di- and tri-adducts were increased. The major portion of the mono-adduct was collected in the condensible volatiles of which it constituted 84%.

The transformation of $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_2CF_2Cl)COF$ telomer to the hydrogen terminated product $C_3F_7O[CF(CF_3)CF_2O]$-$CF(CF_2CF_2Cl)H$ using the ethylene glycol-sodium hydroxide reagent system was accomplished quantitatively. Unfortunately, the telomer mixture of $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)COF$ and $C_3F_7OCF(CF_3)$-$CF_2OCF(CF_2CF_2Br)CF_2OCF(CF_2CF_2Br)COF$ under these conditions afforded mainly products wherein both the carbonyl and the bromine entities were substituted by hydrogen.

In view of the failure to prepare the hydrogen-terminated, bromine-containing materials another terminal group had to be considered. As

TABLE 4

SUMMARY OF TELOMERIZATION REACTIONS[a]

	Reagents						Recovered		Conditions[c]					
	A			B			A	B	(I)		(II)			
Run No.	Type[b]	g	mmol	Type	g	mmol	wt %	wt %	Temp °C	Time hr	Temp °C	Time hr	CsF mole % of A	ml tg/mg CsF
13	HHHCOF	1.00	2.01	C_4F_7ClO	0.47	2.02	29	-	-23 0	2 2	-20	16	52	0.002
14[d]	HHHCOF	1.20	2.42	C_4F_7ClO	0.57	2.46	34	-	-23 0	2 2	-20	17	90	0.002
15	HHHCOF	1.00	2.01	C_4F_7ClO	0.47	2.02	49	-	-19	2	-20	19	90	0.0015
16	HHCOF	0.69	2.09	C_4F_7ClO	0.49	2.10	32	-	24 0 -20	2 1 1	-20	16	50	0.002
17[d]	HHCOF	7.09	2.13	C_4F_7ClO	0.49	2.12	47	-	0 24 -20	1 2 1	-20	16	84	0.0015
18	HHCOF	0.38	1.14	C_4F_7BrO	0.32	1.14	13	-	24 0 -20	1 2 1	-20	16	52	0.0015

a) All the telomerizations were conducted in a 25 ml evacuated round bottomed flask; into Cs-tg first A was condensed then B. b) H corresponds to hexafluoropropene oxide moiety. c) Conditions (I) apply to Cs-tg plus A; conditions (II) apply after B was introduced. d) Stirring was very ineffective in this test.

TABLE 5

PRODUCT DISTRIBUTION IN TELOMERIZATION REACTIONS

	Products[a]					
Run No.	R		RX		RXX	
	weight[b] %	recovery[c] %	weight[b] %	yield[c] %	weight[b] %	yield[c] %
13[d]	20	29	54	53	17	13
14[d]	23	34	42	41	21	16
15[d]	33	47	40	39	14	10
16[e]	19	32	56	55	8	5
17[e]	29	47	18	17	16	11
18[e,f]	7	13	61	60	19	13

a) R pertains to the acid fluoride employed; X denotes 4-chloroperfluorobutene-1 oxide segment in Runs 13-17 and 4-bromoperfluorobutene-1 oxide segment in Run No. 18. b) This is the weight percent of a given product in the reaction mixture as determined from gas chromatography assuming each constituent to give the same response. c) Based on the acid fluoride employed. d) In this test $C_3F_7OCF(CF_3)CF_2OCF(CF_3)COF$ was employed. e) In this test $C_3F_7OCF(CF_3)COF$ was employed. f) In this test 3% yield of RXXX was obtained.

discussed previously methyl ester and carboxyl terminal groups cannot be utilized in processes employing ultraviolet irradiation. Nitriles are relatively readily prepared from acid fluorides; thus a nitrile termination could be considered. No literature data could be found on the behavior of perfluorinated nitriles under ultraviolet radiation in the presence of mercury. Apparently, nitriles are unaffected by ultraviolet radiation since the perfluoroalkylether nitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$, was recovered quantitatively after such a treatment. The nitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)CN$, was thus synthesized and subjected to ultraviolet radiation in the presence of mercury. The coupled product, $C_3F_7OCF(CF_3)CF_2OCF(CN)(CF_2)_4CF(CN)OCF_2CF(CF_3)OC_3F_7$ was obtained in a quantitative yield thereby establishing the feasibility of this overall process.

3. Polymer Studies

To obtain a perfluoroalkylether system leading to elastomers it was felt that relatively high molecular weight materials needed to be produced. Accordingly, low reaction temperatures and low catalyst concentrations were initially selected for telomerization of the epoxides.[10] The tests performed are summarized in Table 6. Preliminary work to optimize the polymerization conditions as well as subsequent studies to verify catalyst activity and the absence of contamination were carried out using hexafluoropropene oxide.

The first copolymerization reaction resulted in incorporation of only ca 50% of all perfluoroheptene oxide available; yet the consumption of hexafluoropropene oxide, was better than that observed on homopolymerization. This would indicate that a) perfluoroheptene oxide is less reactive than hexafluoropropene oxide; b) perfluoroheptene oxide

TABLE 6

SUMMARY OF TELOMERIZATION REACTIONS [a]

Run No.	Reagents					Recovered		Low MW Telom.	Polymer		Conditions[e]		CsF	
	C_3F_6O		Oxide-2			C_3F_6O	Oxide-2		Yield	MW[d]	Temp	Time	mole %[c]	ml to mg CsF
	g	mmol	Type	g	mmol	Wt %[b]	Wt %[b]	Wt %[c]	Wt %[c]		°C	hr		
1	5.08	30.58	-	-	-	5.4	-	3.1	91	3600	-[f]	-[f]	0.33	0.002
2	2.34	14.09	-	-	-	40.5	-	2.6	57	2600	-23	8	0.33	0.002
3	5.09	30.69	-	-	-	18.2	-	0.4	81	3500	-23	16[g]	0.33	0.002
4	4.09	24.63	$C_7F_{14}O$	2.31	6.32	1.2	55.6	?	79	2800	-23	16[g]	0.33	0.002
5C[h]	0.16	1.00	C_4F_7ClO	0.23	1.00	-	1.0	80[i]	none	n.a.	0	16	6.5	0.002
6	5.07	30.53	-	-	-	1.1	-	1.5	97	n.d.	-23	8	0.33	0.002
7	0.71	4.28	C_4F_7ClO	0.50	2.14	-	-	1.3	99[j]	1700	0	17	2.0	0.002
8	0.71	4.28	C_4F_7ClO	0.49	2.11	-	-	1.3	99[j]	2200	-23	20	2.0	0.002
9	0.34	2.05	C_4F_7ClO	0.24	1.03	15.8	15.1	11.2[i]	73[j]	1200	24	4.5	4.2	0.002
10	1.00	6.03	C_4F_7ClO	0.69	2.98	-	-	3.3	97[j]	1300	0	15	6.5	0.002
11	0.50	3.04	C_4F_7ClO	0.69	2.98	-	-	5.2	95[j]	1300	0	15	6.5	0.002
12[k]	0.25	1.51	C_4F_7ClO	0.35	1.52	-	-	32.2[i]	67[j]	800	40	2	6.6	0.005
19A	0.50	3.03	C_4F_7BrO	0.43	1.55	100	100	-	-	-	-23	16	0.3	0.002
19B[h]	0.50	3.03	C_4F_7BrO	0.43	1.55	52	26	41	-	-	-23	16	1.4	0.002
19C[h]	0.24	1.47	C_4F_7BrO	0.32	1.15	100	100	-	-	-	-23	16	2.5	0.002
20	2.54	15.28	-	-	-	-	-	~ 1	98	n.d	-23	16	0.43	0.002
21	0.35	2.14	C_4F_7BrO	0.30	1.08	-	27	?	87	1900	-23	16	2.0	0.002
22A	0.90	5.45	C_4F_7BrO	0.75	2.72	29	59	57	-	-	-23	48	2.5	0.002
22B[h]	0.53	3.20	C_4F_7BrO	0.44	1.60	45	55	49	-	-	-13	24	2.1	0.002
22C[h]	0.23	1.39	C_4F_7BrO	0.25	0.88	100	100	-	-	-	-23	24	2.8	0.002
23	2.54	15.35	-	-	-	40	-	60	-	-	-26	16	0.43	0.002
24	2.46	14.84	-	-	-	10	-	?	~90	n.d	-23	16	0.45	0.002
25	2.53	15.27	-	-	-	1.6	-	-	98	n.d	-23	16	0.43	0.002
27	0.79	4.77	C_4F_7BrO	0.66	2.37	?	?	~11	89	~1600	-23	51	1.8	0.002

a) All the telomerization reactions at -23 and 0°C were conducted in a 25 ml evacuated round bottomed flask into which the reagents were condensed. b) Percent of oxide originally employed. c) Percent of total oxide or oxides used. d) The molecular weight was determined on the methyl esters using Krytox MLO-71-6 (MW 5500) as a standard. e) In the experiments conducted at 0°C and below the reaction mixture was stirred at the given temperature for the denoted period of time then the volatiles were pumped away initially at the reaction temperature then at room temperature. f) In this experiment the reaction mixture was stirred at -23°C for 14 hr, at 0°C for 2 hr, at room temperature for 1 hr. g) In these tests whenever the total reaction time exceeded 8 hrs the mixture was kept overnight (16 hr) at -78°C. h) The starting materials used in this test were recovered from the proceeding test (after removal of acid fluoride by passing through an Ascarite column). In the case of the test series 5 the Runs 5A and 5B are not listed. i) The composition is given in Table 7). j) The composition is given in Table 8. k) The pressure used here was originally 400 mm; as reaction proceeded it decreased to 11 mm.

performs a solvent function for the polymerization process. The ratio of $C_7F_{14}O$ to C_3F_6O units in the resultant polymer was calculated to be 1 : 7.8 based on the recovered perfluoroheptene oxide. This value is in good agreement with the ratio of 1 : 7.5 obtained by NMR analysis at the Air Force Materials Laboratory. The NMR data also confirmed that indeed a true copolymer was formed. Utilizing a 1 : 8.87 ratio of 4-chloroheptafluoro-1,2-epoxybutane to hexafluoropropene oxide and the same conditions as those given for Run No. 4 (see Table 6) resulted mainly in starting material recovery with some production of low molecular weight telomers. After removal of the acid fluoride terminated compounds an attempt was made again to co-telomerize the two oxides (Test No. 5C); again only low molecular weight products were obtained (for composition see Table 7). Apparently, co-telomerization is the major process with homo-telomerizations taking place to a very limited extent only. Conducting the C_3F_6O - C_4F_7ClO telomerization at 0^oC and -23^oC under otherwise identical conditions showed, based on the product's average molecular weight and component distribution (see Tables 6 and 8, Runs No. 7 and 8), that lower temperatures favor longer chain species whereas higher catalyst concentrations result in decreased chain length (compare Runs No. 7 and 10). The epoxide relative ratio, however seem to have no effect on the product's average molecular weight and distribution (Runs No. 10 and 11, Tables 6 and 8). The pronounced influence of temperature is best shown by Run No. 12 wherein room temperature volatile telomers were afforded in 32% yield (for volatile product distribution see Table 7) and also the involatile materials were of low molecular weight (see Tables 6 and 8). In none of these experiments was predominantly a single compound found.

The conditions employed in the copolymerization runs with the

TABLE 7

LISTING OF THE LOW MW TELOMERS OBTAINED IN SELECTED TESTS[a]

Compound[b]	Run 5C Wt %[c]	Run 9 Wt %[c]	Run 12 Wt %[c]
H	-	-	0.1
C	-	-	0.1
HH	-	-	0.8
HHH	-	-	2.8
HC	14	-	2.8
CH	7.1	-	0.8
HHHH	-	1.1	1.7
HHC	4.3	-	2.9
CHH	7.2	-	2.6
HHHHH	-	2.0	0.4
CC	-	-	0.2
CHC	24.7	-	5.7
HHHC	-	4.1	?
CHHH	-	-	2.6
HCC	-	-	4.2
HCHC	13.1	1.5	?
HHCC	-	-	0.8
CCC	-	-	0.6
CHCC	-	-	0.1

a) The test conditions are summarized in Table 6; in Tests 5C and 9 only the major species are listed. b) H corresponds to hexafluoropropene oxide moiety, whereas C corresponds to the 4-chloroperfluorobutene-1 oxide. Thus, HC is $C_3F_7OCF(CF_2CF_2Cl)CO_2Me$ whereas CH is CF_2ClCF_2-$CF_2CF_2OCF(CF_3)CO_2Me$. c) Weight percent of oxides used.

TABLE 8

C_3F_6O and C_4F_7ClO TELOMERIZATIONS COMPOSITION OF 25°C INVOLATILE MATERIALS[a]

Compound[b]	r.t. min.	R-7 Area %(18)	R-8 Area %(18)	R-9 Area %(18)	R-10 Area %(18)	R-11 Area %(18)	R-12 Area %(18)
HHH	4.2	-	-	-	1.0	-	-
HC	5.6	-	-	-	0.2	-	-
CH	6.1	-	-	-	0.1	-	-
HHHH	6.7	-	-	-	2.1	-	0.4
HHC	8.3	-	-	-	1.0	1.6	-
CHH	8.7	-	-	-	1.3	1.2	1.3
HHHHH	9.4	-	-	-	4.5	2.6	2.0
HHHC CHC	11.2	-	-	17.2	15.2	19.0	35.0
HHHHHH	12.1	15.9	-	14.3	7.6	4.3	-
HCC	13.7	8.2	15.1	63.8	37.7	45.0	64.0
HHCHH HCHC HHHHHHH	14.4	2.2	?	?	9.0	4.3	-
HHCC HHCHC CHHC	16.0	42.2	38.5	90.6	75.7	77.2	91.9
HHHCC CHHHC	18.0	100	100	100	100	100	100
HHHHCC HHHCHC CHHHHC	20.0	184	131	93.7	112	118	95.6
HHHCHHC HHHHCHC CHHHHHC	21.6	255	188	110	119	119	115
n.d.	23.3	339	283	63.2	114	117	57.0
n.d.	26.4	344	820	37.8	180	192	60.5
n.d.	28.5	274	358	22.9	50.7	56.1	16.9
n.d.	30.3	170	440	16.3	22.5	40.6	13.9
n.d.	33.3	98.6	360	3.9	24.5	29.1	5.4
n.d.	36.7	63.8	351	1.8	13.4	20.9	3.6
n.d.	39.8	-	377	1.6	11.8	14.4	3.1
n.d.	44.5	-	257	-	7.5	8.0	-
n.d.	50.0	-	200	-	-	-	-
n.d.	59.0	-	190	-	-	-	-

a) The telomerization conditions are summarized in Table 6; the GC was performed using 10' x 1/8" 4% OV-101 on chromosorb G column, programmed at 7°C/min from 50-220°C. b) H corresponds to hexafluoropropene oxide moiety, whereas C corresponds to the 4-chloroperfluorobutene-1 oxide. Thus HC is $C_3F_7OCF(CF_2CF_2Cl)CO_2Me$ whereas CH is $CF_2ClCF_2CF_2CF_2OCF(CF_3)CO_2Me$.

4-bromoheptafluoro-1,2-epoxybutane were parallel to those utilized in Run No. 8 conducted with the chloro-analogue. It should be noted that with the exception of Test No. 19C no reaction took place in the test series 19. The lack of reaction was not due to the cesium fluoride or tetraglyme contamination as proven by the results of Run No. 20 using hexafluoropropene oxide itself. It could be that the absence of polymerization was caused by 4% of residual 4-bromoheptafluorobutene-1 present in the sample of the bromo-epoxide. Using olefin-free epoxide in Run No. 21 gave the desired co-polymer. This material was readily transformed into the nitrile and in the form of the nitrile it was subjected to GC-MS (see Table 9) and elemental analysis. The results of the elemental analysis are in good agreement with the GC-MS component determinations.

The recovery of the bromo-epoxide in Run No.21 shows that the reaction period employed was possibly too short. This stipulation is further supported by the initially slow pressure drop observed. The occurrence of copolymerization is proven by the nature of the lower molecular weight oligomers listed in Table 9. It should be noted that the mass spectral data is reliable insofar as the terminal group is concerned due to the nitrile identifying action. However, whether the bromo-epoxide fragment initiates the chain or is incorporated within the chain is not that readily ascertained in the higher molecular weight chains (more than 4 segments). Most of the GC peaks contain a mixture of positional isomers as indicated by mass spectral breakdown patterns.

In the test series 22 the same batch of the epoxide was employed as that used in Run No. 21. As can be seen from the data listed in Table 6 repurification of the epoxides and process repetitions failed

TABLE 9

C_3F_6O AND C_4F_7BrO TELOMERIZATIONS COMPOSITION OF TEST NO. 21 NITRILE TERMINATED MATERIAL[a]

Compound[b]	r.t. min.	Area %(21.8)
HHHHH	9.7	2.9
BHB HBB	11.7	5.4
HHHHB	11.9	10.0
HHHHHB	13.1	27.3
BHHB HHBB	14.5	31.8
HHHHHHB	15.5	42.3
BHHHB HHHBB	16.7	55.1
HHHHHHHB	17.7	26.4
BHHHHB HHHHBB	18.8	67.7
HHHHHHHHB	19.6	13.2
BHHHHHB HHHHHBB	20.6	93.2
BHHHHHHB HHHHHHBB	21.8	100.0
BHHHHHHHB HHHHHHHBB	22.9	84.8
BHHHHHHHHB HHHHHHHHBB	24.0	64.5
BHHHHHHHHHB HHHHHHHHHBB	25.2	48.8
n.d.	26.7	33.1
n.d	28.4	7.9
n.d	29.6	6.5

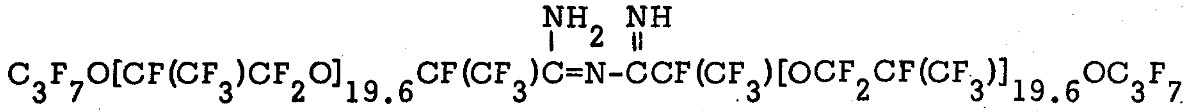
a) The telomerization conditions are summarized in Table 6 Test No. 21 the GC was performed using 10' x 1/8" 4% OV-101 on chromosorb G column, programmed at 7°C/min from 50-220°C.

b) H corresponds to hexafluoropropene oxide moiety, whereas B corresponds to the 4-bromoperfluorobutene-1 oxide. Thus HB is $C_3F_7OCF(CF_2CF_2Br)CN$ whereas BH is $CF_2Br\ CF_2CF_2CF_2$-$OCF(CF_3)CN$.

to afford polymerization. Inasmuch as the homopolymerization of hexafluoropropene oxide performed in the subsequent test Run No. 23 also failed, contamination of catalyst and/or tetraglyme was suspected. Run No. 24 was conducted with freshly dried cesium fluoride and tetraglyme. The same ingredients were employed in Test No. 25, the results of which were comparable to Run No. 20 indicating that hexafluoropropene oxide, cesium fluoride, tetraglyme and the overall equipment were free of contamination. The copolymerization of hexafluoropropene oxide and 4-bromoheptafluoro-1,2-epoxybutane using the same conditions as those employed in Test No. 21 with the exception of a longer reaction time afforded a comparable degree of polymerization as indicated by volatiles recovered and the molecular weight of the "polymeric" material.

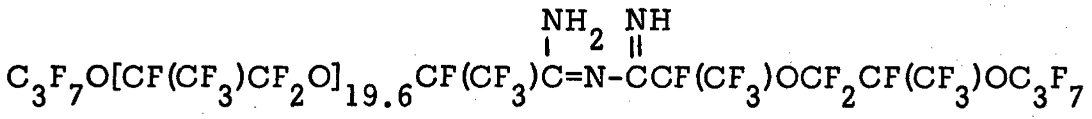
As described in a previous section of this dicussion bromo-substituted perfluoroalkylether nitriles are amenable to coupling when subjected to ultraviolet radiation in the presence of mercury. However, in the case of a relatively high molecular weight material the isolation would require acid washing to remove the mercury salts, this in turn would be expected to result in the hydrolysis of the nitrile groups. To alleviate this occurrence the transformation of the nitrile to a triazine seemed advisable. To determine the applicability of this process to polymeric materials this synthesis was performed on the perfluoroalkylether obtained in Run No. 1 (see Table 6). The nitrile preparation proceeded readily, however treatment with ammonia yielded an imidoylamidine-amidine mixture. This was not surprising in view of the data generated under other programs.[11] Interaction of this mixture with a volatile perfluoroalkylether nitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$ showed that the original mixture contained 54% of amidine the remainder being the imidoylamidine I.

Since both imidoylamidines



$$C_3F_7O[CF(CF_3)CF_2O]_{19.6}CF(CF_3)\overset{\overset{NH_2}{|}}{C}=N-\overset{\overset{NH}{\|}}{C}CF(CF_3)[OCF_2CF(CF_3)]_{19.6}OC_3F_7$$

I



$$C_3F_7O[CF(CF_3)CF_2O]_{19.6}CF(CF_3)\overset{\overset{NH_2}{|}}{C}=N-\overset{\overset{NH}{\|}}{C}CF(CF_3)OCF_2CF(CF_3)OC_3F_7$$

II

were formed in the mole ratio of 1 : 2.36, the average molecular weight of the resultant triazine mixture (obtained after $C_3F_7OCF(CF_3)COF$ treatment) was calculated to be 5268 in good agreement with the found molecular weight of 5300. The overall triazine yield with respect to the methyl ester starting material was 53%.

Using the above reaction sequence the bromo-substituted triazine (MW, 2100) was prepared in an overall 39% yield. This material was a liquid which after ultraviolet irradiation in the presence of mercury was transformed into a waxy solid showing the feasibility of crosslinking bromine-containing perfluorocarbons.

III. EXPERIMENTAL DETAILS AND PROCEDURES

1. General

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B), under nitrogen by-pass, or in vacuo. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means.

Infrared spectra were recorded using a Perkin-Elmer Corporation Infrared Spectrophotometer Model 21, depending on the physical state of sample, e.g. as gas, neat liquid, or in form of double mulls (Kel-F oil No. 10 and Nujol) for solids. Thermal analyses were conducted using a DuPont 951/990 Thermal Analyzer system. The mass spectrometric analyses were obtained employing a DuPont 21-491B double focusing mass spectrometer attached to a Varian Aerograph Model 204, equipped with a flame ionization detector, and a DuPont 21-094 data acquisition and processing system. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

2. Crosslinking Investigations of Non-Functional Systems

These investigations were performed in evacuated sealed ampoules of ca 25 ml volume over the specified period of time and at the denoted temperatures. At the conclusion of an experiment the ampoules were cooled in liquid nitrogen, and were opened to the vacuum system. The liquid nitrogen noncondensibles, if produced, were measured with the aid of a Sprengel pump and determined by mass spectrometry. The liquid nitrogen condensibles, which were volatile at room temperature, were fractionated from a warming trap through traps kept at -23, -78°C into a liquid nitrogen cooled trap. Each fraction was measured, weighed and analyzed by infrared spectroscopy and gas chromatography/mass spectrometry. The residue itself was weighed and subjected to GC-MS, infrared spectral analyses, and differential thermal analysis.

3. Monomer and Model Compound Syntheses and Investigations

a. Preparation of 5-Chlorooctafluoromethylpentanoate

Following essentially the procedure of Kim, et al.[12], to a stirred mixture of $Cl(CF_2CF_2)_2CCl_3$, (100.05 g, 282.75 mmol), Hg_2SO_4 (1.09 g, 2.19 mmol) and $HgSO_4$ (5.08 g, 17.12 mmol) was added 30% oleum (75 ml) over a period of 30 min. Subsequently, the mixture was refluxed under a nitrogen by-pass for 88 hr at 98-100°C. The cooled solution was then added dropwise over a period of 1.5 hr to methanol (76 ml) stirred in an ice-bath. This was followed by stirring at room temperature overnight. The methanolic solution was added into 275 ml of ice and water. A clear organic layer composed of the desired ester (71.35 g, 85.7% yield) separated at the bottom.

b. Preparation of 5-Chlorooctafluoro-sodium-pentanoate

Sodium hydroxide (5.17 g, 129.25 mmol) was dissolved in water (25 ml). To the warm solution was added dropwise $Cl(CF_2)_4CO_2CH_3$ (25.00 g, 84.88 mmol) over a period of 14 min. The resulting mixture was stirred at ambient temperature for 4 days. The alcohol was subsequently removed under reduced pressure and the solution acidified with concentrated sulfuric acid (5 ml). The solution was then subjected to continuous ether extraction over a period of 4 days. Removal of ether by distillation followed by evaporation in vacuo yielded a slightly orange liquid (27.69 g). Direct titration of this liquid with 0.9233 N sodium hydroxide to pH 7.05 gave after water removal and drying an 84.6% yield of the sodium salt (yield based on the quantity of ester employed).

c. Preparation of 4-Chloroperfluorobutene-1

Pyrolysis of $Cl(CF_2)_4COONa$ at 277-300°C was carried out in a 100 ml round bottom flask attached to a vacuum system via three liquid nitrogen cooled traps. The olefin was purified by vacuum fractionation from a warming trap through -78, -96, -112 into -196°C cooled traps. The desired product was collected in the -78, -96, and -112°C traps; $VP_{0^\circ C}$=182 mm. As shown by gas chromatographic analysis the material consisted of 99% 4-chloroperfluorobutene-1 admixed with ca 0.4% of $CF_2ClCF{=}CF_2$, 0.5% of $ClCF_2CF{=}CFCF_3$ and 0.1% of $CF_3CF_2CF{=}CF_2$. The pyrolysis runs are summarized in Table 10, whereas the olefin's mass spectrum is given in Table 11.

d. Epoxidation of 4-Chloroperfluorobutene-1

All the reactions summarized in Table 12 were carried out employing 60% H_2O_2 and identical relative quantities of H_2O_2, methanol, and potassium hydroxide; the differences in yields were caused by different reaction conditions and workup procedures. The difficulty in working with this compound is due to its high vapor pressure $VP_{0^\circ C}$=182 mm, which results in material loss. Thus it was found that the sample cannot be washed at 0°C with water, since most of the material is just lost (Run No. 1). Using E-7 fluid during the washing procedure to solubilize the epoxide followed by vacuum distillation of the bottom layer gave also very low yields (Run No. 2). Runs No. 3 and 4 were very similar with the exception that in Run No. 3 a -78°C reflux condenser was employed, whereas in Run No. 4 the apparatus was closed to the atmosphere.

TABLE 10

SUMMARY OF $Cl(CF_2)_4COONa$ PYROLYSIS EXPERIMENTS

Run No.	$Cl(CF_2)_4COONa$ g	Temperature °C	Time hr	Yield %
1	10.27	277-289	2.50	98
2	10.68	282-296	2.50	97
3	13.54	284-300	2.00	98
4	13.63	282-295	1.25	98

TABLE 11

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF 4-CHLOROPERFLUOROBUTENE-1

m/e		m/e		m/e	
31	58.4	85	46.2	147	62.7
35	8.2	87	16.3	149	21.1
47	6.1	93	59.6	162	12.0
50	14.7	94	5.8	181	54.3
55	10.1	100	14.2	182	7.3
62	12.0	109	9.1	197	14.7
66	9.0	112	20.4	199	8.4
69	66.5	116	11.5	216	27.5
74	14.8	131	100.	218	13.2
81	14.9	132	15.5		

a) Peaks having intensities less than 5% of the base peak are not reported.

TABLE 12

SUMMARY OF EPOXIDATION REACTIONS PERFORMED ON 4-CHLOROPERFLUOROBUTENE-1

Test No.	Olefin g	Temp °C	Time KOH addn min	React. Period hr	Epoxide Yield %	Comments
1	2.03	-23	6	3.75	27	product loss on washing, high ester content
2	2.03	-23	9	4.0	11	olefin content, 60%
3	2.18	-15 to -20	14	3.75	26	olefin content, 40%
4	3.03	-15 to -20	8	5.00	27	olefin content, 16%
5	5.47	-15 to -20	2	5	mainly olefin	poor stirring
5A[a]	a	-10 to -20	1	5	mainly ester	vigorous stirring
6	5.01	-15 to -25	20	8	22	product loss prior to transfer; trace olefin present
7	5.66	-20 to -25	120	10	22	product loss prior to transfer; low yield due to olefin
7A[b]	3.63	-21 to -19	120	7	35	olefin content, 0.4%
8	5.21	-21 to -18	90	7.5	34	olefin content, 0.4%

a) The materials obtained from reaction 5 was utilized here. b) The material obtained from reaction 7 was utilized here.

A typical procedure is given below. The olefin, 3.03 g, was condensed into a round bottom flask at -196°C in vacuo; subsequently the flask was warmed to -20°C and brought to atmospheric pressure with nitrogen. To the olefin at -20°C was added methanol (1.5 ml) followed by a solution of 60% H_2O_2 (3.7 ml) in methanol (1.5 ml). To the stirred mixture was then added over a period of 8 min methanolic potassium hydroxide (2.71 g in methanol, 3 ml). This was followed by stirring at -15 to -20°C for 5 hr. Subsequently, the material was distilled from the flask kept at -20°C into vacuum traps kept at -196°C via a column packed with calcium chloride and Drierite. The reason for this elaborate procedure was the facile reaction of the initially formed oxide with methanol to yield a methyl ester. The material collected in the vacuum system was fractionated from a warming trap via traps held at -47, -63, -78 into -196°C trap. The product obtained in the -196°C trap consisted of the epoxide admixed with the olefin. The yields given in Table 12 are based on this fraction and are corrected for the olefin content based on infrared spectral analysis.

e. Olefin Removal from 4-Chloroheptafluoro-1,2-epoxybutane via Bromination

In vacuo at 0°C to an epoxide-olefin mixture (3.212 g, 13.954 mmol) was added bromine (0.2 ml) and the resulting solution, after standing for 3.5 hr at 0°C (with occasional shaking), was treated with sodium thiosulfate solution (3 g in 5 ml H_2O). Subsequently, the volatiles were distilled at 0°C via an Ascarite-filled column into a liquid nitrogen cooled trap. Fractionation from a warming trap through -63, -78, -112 and -196°C cooled traps gave the desired oxide 12.246 mmol (87.8 yield) in the -78 and -112°C traps; $VP_{0^\circ C}$ =199 mm; MW, 233 (calcd. for C_4F_7ClO, 232.48). The infrared spectrum showed absence of the olefin; this was confirmed by the mass spectrum (see Table 13).

f. Epoxidation of 4-Bromoheptafluorobutene-1

The procedure used was basically that employed for the synthesis of 4-chloroheptafluoro-1,2-epoxybutane. Thus to the olefin, 2.87 g, (which was condensed into the reaction flask at -196°C in vacuo, warmed to -20°C, and brought to atmospheric pressure with nitrogen) was added at -20°C 60% hydrogen peroxide (2.5 ml) followed by methanol (2.2 ml). Subsequently to the stirred mixture was introduced over a period of 45 min a methanolic potassium hydroxide solution (2.22 g in methanol 5.4 ml). The reaction mixture was then stirred at -21 to -19°C for 6 hr; this was followed by vacuum distillation at -23°C into traps kept at -196°C via a column packed with calcium chloride and Drierite. The product thus obtained was fractionated repeatedly from a warming trap through traps held at -47, -63, -78 into a -196°C trap to remove the methanol which was largely retained into the -47°C trap. Finally the material was distilled onto freshly dried calcium chloride and was further purified by passing through an Ascarite-packed column. The material thus obtained, (1067 mg, 35.6%); VP_{0^oC} =99 mm; MW 273, (calcd for C_4F_7BrO, 276.9) was olefin-free; its mass spectral breakdown pattern given in Table 14 and the infrared spectrum are in agreement with the assigned structure.

g. Coupling of Perfluoro-n-heptyl Bromide

i) Using Zinc-Acetic Anhydride. A mixture of perfluoro-n-heptyl bromide (10.01 g, 22.30 mmol), 40 mesh zinc (4.55 g, 69.6 mmol), acetic anhydride (12.61 g, 133.3 mmol), and 1,1,2-trichlorotrifluoroethane (Freon-113), (30 ml) were heated under a nitrogen atmosphere at reflux temperature (~ 68°C bath) with stirring for 24 hr. A white precipitate formed during this period. To the cooled reaction mixture

TABLE 13

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF 4-CHLOROHEPTAFLUORO-1,2-EPOXYBUTANE

m/e		m/e		m/e	
31	71.8	81	21.8	119	23.5
35	8.9	85	94.9	128	4.8
47	38.2	87	50.0	131	57.1
49	4.3	93	17.5	132	5.9
50	39.0	97	29.2	135	28.1
62	11.1	100	33.4	137	15.8
66	17.7	109	6.6	147	16.2
68	8.1	112	11.0	149	8.2
69	91.0	116	100.	166	4.8
70	6.3	117	9.6	169	19.3
74	6.8	118	52.1	185	4.9
78	8.5				

a) Peaks having intensities less than 3% of the base peak are not reported.

TABLE 14

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF 4-BROMOHEPTAFLUORO-1,2-EPOXYBUTANE

m/e		m/e		m/e	
31	47.3	93	30.5	147	4.0
47	29.6	97	33.2	160	62.2
50	39.7	100	42.4	162	59.4
62	9.6	110	15.4	169	35.9
66	3.4	112	22.2	179	20.7
69	61.4	119	29.2	181	19.9
70	3.7	129	57.3	191	9.1
74	6.8	131	100.	193	9.6
79	9.0	132	10.7	210	16.5
81	35.0	141	3.8	212	14.2
91	4.0	143	3.6		

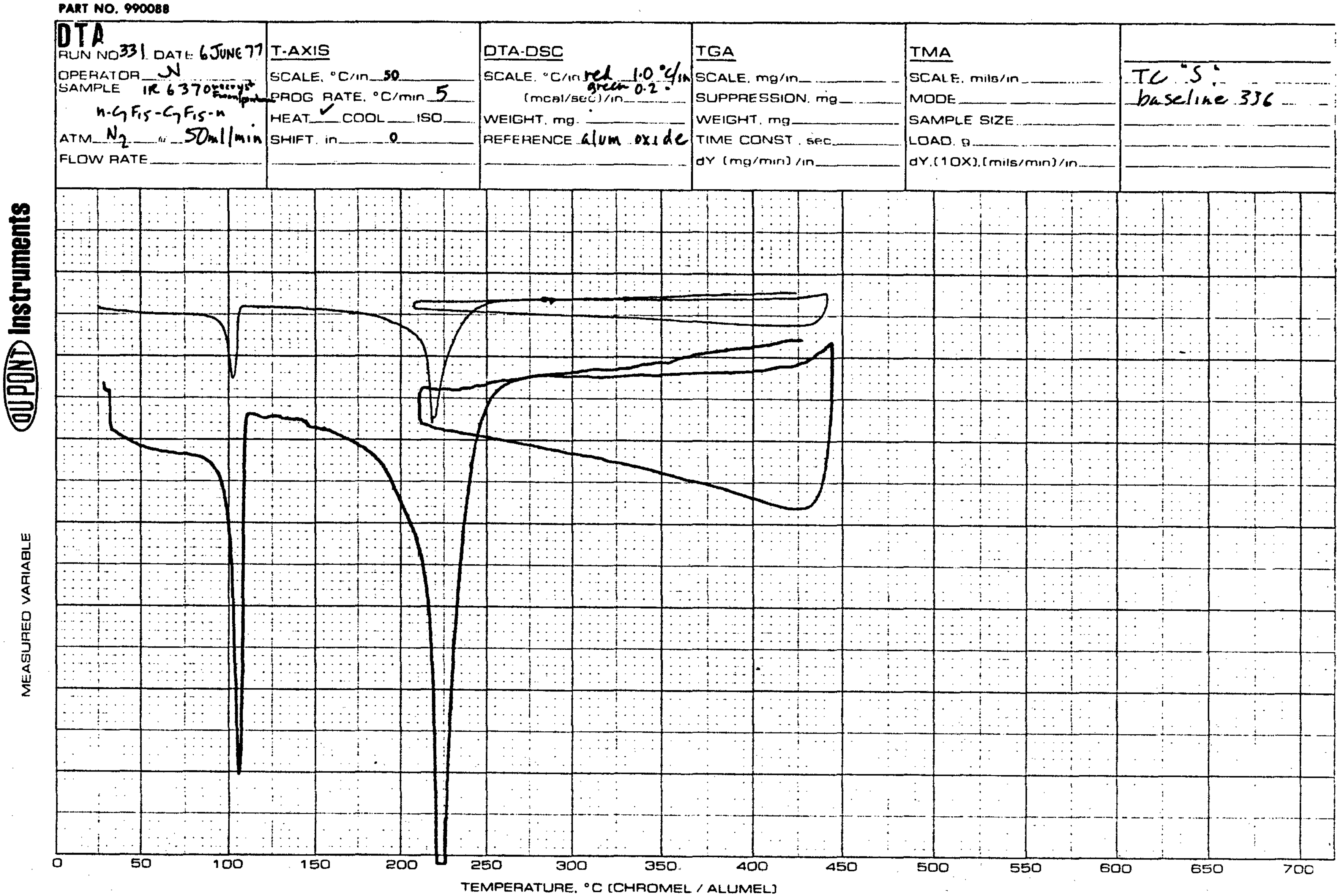
a) Peaks having intensities less than 3% of the base peak are not reported.

additional 1,1,2-trichlorotrifluoroethane (30 ml) was added; this was followed by filtration and washing of the solution with water and 10% sodium bicarbonate. The GC-MS of the solution showed in addition to the solvent and the coupled product n-$C_{14}F_{30}$ only a trace of the starting material. Purification of the perfluorotetradecane by distillation was unsuccessful since the product is a solid and sublimes readily even at 100°C at atmospheric pressure. Thus it was purified by sublimation followed by crystallization from a 1,1,2-trichlorotrifluoroethane-pentane mixture giving 2.62 g (32% yield) of pure product, mp $\sim$ 102°C, bp $\sim$ 118°C as shown by the DTA curve in Figure 1. The reported low yield is due to the workup procedure, not the production of by-products or incomplete reaction.

ii) Using U.V. Irradiation in the Presence of Mercury. In a Vycor tube of approximately 20 ml volume were sealed in vacuo perfluoro-n-heptyl bromide (2.08 g, 4.63 mmol) and mercury (19.81 g, 98.78 mmol). The resulting mixture was then shaken horizontally over a period of 23 hr while being irradiated by a 450 watt Hanovia lamp from a distance of 20 cm. At the end of the reaction period no liquid was visible; when the tube was opened to the vacuum system only a trace (10 mg) of condensibles was obtained; no noncondensibles were noticed. The organic residue was dissolved in Freon-113 and filtered from the mercury salts. On removal of solvent 1.29 g (75% yield) of a white solid was obtained. Its infrared spectrum, GC-MS and DTA trace were identical with that exhibited by the zinc-coupled product described above. The less than quantitative yield is due to the workup procedure, not incomplete or side reactions.

h. Interactions of Benzoyl Peroxide and Perfluoro-n-heptyl Bromide

i) Under Nitrogen By-Pass at 100°C. Heating of perfluoro-n-heptyl bromide (10.00 g, 22.27 mmol) with benzoyl peroxide (1.82 g,



PART NO. 990088

DTA

RUN NO 331 DATE 6 JUNE 77
OPERATOR JN
SAMPLE IR 6370 recryst [illegible]
n-C7F15-C7F15-n
ATM N2 " 50ml/min
FLOW RATE

T-AXIS

SCALE, °C/in 50
PROG RATE, °C/min 5
HEAT ✓ COOL ISO
SHIFT, in 0

DTA-DSC

SCALE, °C/in red 1.0 °C/in green 0.2 "
(mcal/sec)/in
WEIGHT, mg
REFERENCE alum oxide

TGA

SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST, sec
dY (mg/min)/in

TMA

SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY,(10X),(mils/min)/in

TC "S"
baseline 336

Figure 1: DTA of n-Perfluorotetradecane

7.51 mmol), using the latter as a suspension in the stirred bromide solution, resulted in an explosion when the heating bath reached ~ 100°C.

ii) <u>In Vacuo up to 316°C.</u> Heating of perfluoro-n-heptyl bromide (1.98 g, 4.42 mmol) with benzoyl peroxide (0.18 g, 0.75 mmol) in a sealed tube for 24 hr at 100°C followed by 24 hr at 230°C and finally 48 hr at 316°C gave a dark discolored residue admixed with a clear liquid. The room temperature volatiles consisted of the materials listed in Table 15 in addition to 37.3 mg (0.848 mmol) of carbon dioxide and 84.73 mg of silicon tetrafluoride. The carbon dioxide produced corresponds to 56.5% of theory based on peroxide originally employed.

TABLE 15

PRODUCTS FORMED ON THE INTERACTION OF PERFLUORO-n-HEPTYL BROMIDE AND BENZOYL PEROXIDE UP TO 316°C

Compound	Weight %[a]	Compound	Weight %
$C_6F_{13}H$	0.1	Bromobenzene	5.2
$C_7F_{15}H$	22.3	$C_6H_5C_7F_{15}$	0.9
$C_7F_{15}Br$	50.6	$C_6H_4Br_2$	0.1
$C_7F_{14}HBr$	5.3	$BrC_6H_4C_7F_{15}$	0.1
Benzene	2.4	$C_7F_{15}\text{-}C_7F_{15}$	0.1
$C_7F_{13}H_2Br$	1.6		

a) Based on the quantity of perfluoro-n-heptyl bromide used.

iii) <u>In Vacuo at 100°C.</u> Heating of perfluoro-n-heptyl bromide (1.92 g, 4.27 mmol) with benzoyl peroxide (0.19 g, 0.80 mmol) in a sealed ampoule at 100°C for 72 hr afforded on cooling a white solid in a clear liquid. The room temperature volatiles consisted of the products listed in Table 16; the starting material was the major species present. The unaccounted fluorocarbon portion was most likely in the form of brominated and C_7F_{15} substituted carboxylic acid and/or ester moieties as indicated by infrared spectral analysis of the involatile residue. The evolved carbon dioxide corresponded to 67% of theory based on peroxide originally used.

TABLE 16

VOLATILE PRODUCTS FORMED ON THE INTERACTION OF PERFLUORO-n-HEPTYL BROMIDE AND BENZOYL PEROXIDE AT 100°C FOR 72 HR

Compound	Weight %[a]	Compound	Weight %
$C_7F_{15}H$	0.4	Benzene	4.7
$C_6F_{13}Br$	0.3	$C_7F_{13}H_2Br$	0.6
$C_7F_{15}Br$	75.8	Bromobenzene	7.3
$C_7F_{14}HBr$	2.9	$C_6H_5C_7F_{15}$	0.2

a) Based on the quantity of perfluoro-n-heptyl bromide used.

i. U.V. Irradiation of Perfluoro-n-octanoic Acid

Perfluoro-n-octanoic acid 1.01 g (2.35 mmol) was sealed in vacuo in a 20 ml Vycor tube and was irradiated by a 450 watt Hanovia lamp from a distance of 20 cm. During the 16 hr irradiation period the tube was shaken horizontally. At the end of the experiment a white crystalline solid was deposited on the walls of the tube. The condensibles consisted of 1.412 mmol of carbon dioxide and 0.338 mmol of silicon tetrafluoride together with traces of $C_7F_{15}H$ and $C_7F_{14}H_2$, and water. The solid residue was composed of unreacted perfluorooctanoic acid and unidentified coupled olefinic compounds.

j. Telomerization Reactions of Acid Fluoride and Halo-epoxide

The telomerization reactions are summarized in Tables 4 and 5. In a typical procedure to prepare the cesium fluoride complex onto the denoted quantity of cesium fluoride and tetraglyme was condensed the perfluoroalkylether acid fluoride; this was then followed by stirring at the specified temperature for specified periods of time. Subsequently the epoxide was condensed (at -196°C) onto the cesium complex-tetraglyme solution and the telomerization reaction was carried out at -20°C for a given period of time. At the conclusion of the reaction the unreacted reagents and the volatile products were removed in vacuo, originally at -20°C, then at 0°C, and finally at room temperature. The volatiles were fractionated using high vacuum line techniques and the individual fractions were analyzed as the methyl esters by GC-MS. The room temperature involatile residues were analyzed in an analogous fashion. The mass spectral breakdown patterns of the three major compounds thus prepared $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_2CF_2Cl)CO_2Me$, $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Cl)CO_2Me$, and $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)CO_2Me$ are given in Tables 17 and 18.

k. Preparation of $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_2CF_2Cl)H$

The volatile condensibles from the telomerization experiments No. 13 and 14 (see Table 4) which consisted of a 1:1 mixture of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)COF$ and $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_2CF_2Cl)COF$ were washed with water followed by addition of 2.5 ml of 0.92 N sodium hydroxide. Water was then removed at ~ 60°C using

TABLE 17

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7O[CF(CF_3)CF_2O]_xCF(CF_2CF_2Cl)CO_2Me^a$

m/e	x=1	x=2	m/e	x=1	x=2
15	71.3	20.8	131	16.2	13.7
31	16.1	7.2	135	16.7	10.8
33	5.4		137	7.4	
47	12.2	6.6	147	13.0	17.3
50	8.5	6.1	150	11.6	16.8
59	100.	100.	169	66.5	58.1
60	11.0	7.2	170	7.0	
69	85.1	57.4	181	7.0	5.1
81	39.2	22.6	197	13.3	13.1
85	14.2	13.5	199	6.3	5.9
87	8.1	5.7	225	17.8	18.6
97	9.6	7.5	227	10.0	10.8
100	20.8	16.3	335	15.8	9.3
109	16.0	8.2	391	11.0	16.5
116	6.4		393		6.4
119	31.7	19.1	541	13.0	
129	5.3		707		9.2

a) Peaks having intensities less than 5% of the base peak are not reported.

TABLE 18

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)CO_2Me$[a]

m/e		m/e		m/e	
15	87.3	82	13.0	170	14.5
31	25.1	93	8.2	179	17.6
33	8.9	97	14.2	181	29.7
43	10.1	100	63.6	241	21.1
44	8.1	106	6.8	243	18.9
47	16.8	109	34.4	269	32.7
50	16.4	112	6.5	271	33.4
59	65.4	119	77.7	275	5.0
60	17.5	120	5.8	309	5.0
61	7.9	129	22.3	335	68.8
62	5.2	131	35.8	337	8.7
69	82.2	143	5.8	435	18.7
70	7.7	147	26.1	437	20.1
78	12.4	150	49.7	513	6.8
79	7.1	160	10.2	541	37.5
80	5.8	162	10.5	542	9.3
81	<u>100</u>.	169	93.7		

a) Peaks having intensities less than 5% of the base peak are not reported.

a stream of nitrogen. After addition of ethylene glycol (1.13 g) the resulting mixture was heated at 175-190°C for 3 hr under nitrogen by-pass with the outlet leading to a liquid nitrogen cooled trap. After cooling to room temperature the condensible volatiles were collected in vacuo in a trap cooled to -196°C. This condensate consisted of two layers, the bottom layer (350 mg, 60% yield) was found by GC-MS to be composed of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)H$ and $C_3F_7[OCF(CF_3)CF_2]_2OCF$-$(CF_2CF_2Cl)H$ (see the respective breakdown patterns in Tables 19 and 20) in a 1:3 ratio. The relative loss of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)H$ is attributed to its higher volatility and therefore greater rate of evaporation during the final separation of the two phases, which was conducted under atmospheric conditions.

TABLE 19

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7OCF(CF_3)CF_2OCF(CF_3)H^a$

m/e		m/e		m/e		m/e	
31	24.5	81	10.2	147	57.6	217	19.9
47	16.6	82	14.2	148	6.2	235	10.6
50	12.6	97	43.1	150	15.2	245	13.5
51	60.3	100	60.4	167	55.5	267	39.4
69	92.9	101	100.	168	5.4	333	6.9
70	8.1	102	11.9	169	86.7	335	18.3
78	9.0	119	56.6	170	13.8	383	7.4
79	16.3	131	10.0	195	12.1	433	6.8

a) Peaks having intensities less than 5% of the base peak are not reported.

TABLE 20

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_2CF_2Cl)H$[a]

m/e		m/e		m/e	
31	20.5	102	12.3	217	45.9
47	14.1	113	36.4	233	9.7
50	12.8	116	8.5	235	58.0
51	36.0	117	19.7	236	5.6
63	5.0	119	52.9	263	8.7
66	7.0	128	6.6	285	12.0
67	20.9	129	9.1	313	13.4
69	79.7	131	23.9	317	49.1
70	8.7	132	9.5	333	51.6
75	5.6	135	6.4	334	6.9
78	7.9	145	10.9	335	70.7
79	5.2	147	63.5	336	13.8
81	9.4	148	6.5	479	5.6
82	41.7	150	59.8	501	61.9
85	66.9	151	14.4	502	12.2
86	5.0	167	96.3	549	8.9
87	53.6	168	18.6	580	6.6
93	5.7	169	100.	649	12.3
97	23.0	170	20.7	665	29.9
98	9.8	185	11.6	666	6.8
101	59.9	187	5.9	667	10.9

a) Peaks having intensities less than 5% of the base peak are not reported.

l. Attempted Preparation of $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)H$

The procedure adopted was that described for the chloro-analogue. The material used (348 g) was the involatile fraction of Test No. 18 (Table 4) which consisted of equal portions of telomers, $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)COF$ and $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)CF_2OCF(CF_2CF_2Br)COF$ together with ~ 15% by weight $C_3F_7OCF(CF_3)COF$ and a trace of the trimer adduct. The volatiles collected in the liquid nitrogen cooled traps during the heating period and the subsequent evacuation contained as the two major products $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2H)H$ and $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2H)CF_2OCF(CF_2CF_2H)H$ admixed with smaller quantities (~ 20% of the above main components) of $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)H$ and $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2H)CF_2OCF(CF_2CF_2Br)H$. The mass spectral breakdown patterns of $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2H)H$ and $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)H$ are given in Table 21.

m. Preparation of $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)CN$

To the acid fluoride, $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)COF$ (137.7 mg, 0.226 mmol; Test No.18, Table 4, condensible volatiles), was added in vacuo methanol (1.344 mmol) and after 1 hr at room temperature the excess of methanol was removed; the amount consumed was 0.281 mmol. Subsequently, onto the methyl ester was condensed ammonia and on warming the pressure drop was monitored. This was repeated 4 times until no pressure drop was observed anymore. Thus the amide formation was assumed to be completed. The amide was then heated with P_2O_5 (200 mg) under 450 mm of nitrogen (in a closed system) at 180-190°C for 2.5 hr. After cooling to room temperature the product was distilled in vacuo and purified by vacuum fractionation from a

TABLE 21

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2X)H$[a]

m/e	X=H	X=Br	m/e	X=H	X=Br	m/e	X=H	X=Br
31	16.1	14.9	113	15.9	22.6	213	11.3	60.4
45	22.1		119	55.9	48.2	214		5.2
47	10.6	9.5	129		59.2	217	31.1	16.3
50	11.9	11.4	131	12.1	62.6	227	9.9	
51	91.4	30.3	132		5.6	229		6.0
61	5.4		133	94.2		231		5.0
63	5.8		134	12.8		235		14.4
64	14.4		147	26.1	18.1	277	7.6	
69	100.	100.	150	15.4	14.6	285	5.6	
70	7.3	7.4	151		17.7	295		9.3
78	7.4		161		8.0	299	19.2	
79		7.7	163		8.8	313	15.2	5.7
80		6.0	169	87.8	86.3	317		24.3
81	6.6	12.5	170	14.9	14.1	335	69.3	74.0
82	28.9	31.6	185	6.2		336	11.4	12.1
83	8.9		199	59.7		365	7.9	
97	25.7	14.2	200	6.2		383	11.1	7.8
100	43.2	41.1	211		66.4	465	10.8	
101	14.2	9.9	212		5.7	483		15.7
111	6.3	7.8						

a) Peaks having intensities less than 5% of the base peak are not reported.

warming trap through traps held at 0,-23, -47 and -196°C. The material present in the -23 and -47°C cooled traps (55 mg) was found to consist of 95% pure nitrile $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)CN$, $VP_{23.5^\circ C}$=1.8 mm. The mass spectrum given in Table 22 is consistent with the assigned structure based on m/e, 508 (M-Br) and m/e, 179, 181 (CF_2CF_2Br).

n. Preparation of $C_3F_7OCF(CF_3)CF_2OCF(CN)(CF_2)_4CF(CN)-OCF_2CF(CF_3)OC_3F_7$

The nitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)CN$, (45 mg) was sealed in vacuo with mercury (2.37 g) in a 20 ml Vycor tube. The resulting mixture was then shaken horizontally and irradiated with a 450 watt Hanovia lamp over a period of 14 hr; only a trace (~ 2 mg) of condensible volatiles were collected. The room temperature involatile residue was taken up in Freon-113 and subjected to GC-MS analysis. Based on this analysis the main component (90%) dissolved in the Freon-113 was the desired coupled product. The mass spectrum given in Table 23 is consistent with the assigned structure. Although no parent peak m/e, 1016 was recorded, the M-F peak m/e, 997, is present in high abundance (23.3%), as well as other peaks such as m/e, 990 (M-CN); m/e, 831 ($M-OC_3F_7$); m/e 665 ($M-OCF_2CF(CF_3)OC_3F_7$) etc.

4. Polymer Studies

a. Telomerization Reactions

The telomerizations and co-telomerizations performed are summarized in Table 6. All telomerizations were conducted in 25 ml carefully dried evacuated round bottom flasks. In a typical reaction the epoxide or epoxides (purified by a final passage through an Ascarite column) were condensed at -196°C onto the appropriate tetraglyme-cesium fluoride mixture; subsequently the flask was isolated from the remainder

TABLE 22

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)CN$[a]

m/e		m/e		m/e	
28	11.5	112	8.2	209	9.0
31	50.6	119	80.0	213	5.9
47	18.7	120	7.4	229	15.2
50	22.1	126	10.4	231	12.9
54	13.5	129	73.1	235	7.8
57	7.0	131	79.9	236	55.0
66	7.3	136	9.1	237	6.4
69	100.	138	18.3	238	54.2
70	13.8	147	55.6	239	6.6
76	18.2	148	6.2	242	7.0
78	11.9	150	44.1	245	7.3
79	11.0	157	7.9	254	5.9
81	19.8	160	14.0	276	12.2
88	11.1	162	12.5	285	7.1
93	8.3	167	5.0	292	6.1
97	47.7	169	95.9	323	6.6
100	82.5	170	18.7	325	6.6
101	7.6	176	14.7	335	97.6
107	63.1	179	36.1	336	18.8
108	6.0	181	31.0	342	7.6
110	6.0	207	8.2	508	46.5
				509	9.7

a) Peaks having intensities less than 5% of the base peak are not reported.

TABLE 23

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF

$C_3F_7OCF(CF_3)CF_2OCF(CN)(CF_2)_4CF(CN)OCF_2CF(CF_3)OC_3F_7$[a]

m/e		m/e		m/e	
28	11.2	138	35.8	336	26.2
31	15.5	147	55.7	342	7.6
47	12.4	150	36.9	408	7.9
50	10.7	169	100.	442	6.6
54	9.8	170	23.8	470	6.7
69	68.6	176	11.2	499	5.7
70	7.0	213	6.5	529	6.4
76	14.0	219	14.3	636	5.7
78	6.4	245	13.9	665	43.0
81	6.1	247	10.8	666	11.0
97	45.5	276	16.6	753	8.1
100	54.4	285	10.0	831	9.2
107	18.0	292	6.6	947	6.8
119	68.9	304	10.5	990	33.1
126	7.9	333	7.7	992	9.8
131	29.1	335	81.4	997	23.3
				999	6.2

a) Peaks having intensities less than 5% of the base peak are not reported.

of the vacuum system, warmed to the specified temperature at which temperature the contents were then stirred for the denoted period of time. At the end of the reaction the volatiles were distilled off into a liquid nitrogen cooled trap, initially at the reaction temperature, then at room temperature. In this way the production of low molecular weight telomers was largely prevented. A somewhat different technique was utilized when the telomerization process was conducted at room temperature or above. In these instances the epoxide or epoxides were not condensed onto the catalyst but the stirred tetraglyme-cesium fluoride mixture was exposed initially to ~ 400 mm pressure of the epoxide or epoxide mixture. The progress of the reaction was monitored by pressure drop.

In all instances the products formed were subjected to analysis, specifically GC-MS (see Tables 7 and 8) and molecular weight determinations, in the form of their methyl esters. A number of hexafluoropropene oxide homo-telomerizations were carried out to ascertain the catalyst's effectiveness and the absence of impurities in the oxide itself.

b. Hydrogen Termination of Telomerization Products

In a typical reaction, the room temperature involatile telomerization mixture containing R_fOR_fCOF, CsF and tetraglyme was washed four times by decantation with 5-10 ml of water. Subsequently the designated quantity of either sodium hydroxide solution (0.9N) or concentrated ammonia was added. In the case of the sodium salt the sample was washed with water to remove the excess of sodium hydroxide and then dried at 50-55°C under a stream of nitrogen over a period of ~ 5-12 hr. In the case of the ammonium salt the washing step was omitted. The pyrolysis was conducted under nitrogen by-pass at 175-190°C over a period of 3-4 hr. All the volatiles were collected during the heating process in a liquid nitrogen cooled trap. In the case of the sodium salts the specified quantity of ethylene glycol was added prior to heating. At the conclusion of the reaction the involatile residue was subjected to vacuum at room temperature and the volatiles thus collected were distilled from a 0°C trap into a -196°C cooled trap using standard high vacuum techniques. The involatile residues were taken up in Freon-113, washed with water (to remove sodium salts and the glycol) and the solution dried over sodium sulfate. After solvent removal the material was subjected to infrared spectral and GC-MS analysis.

c. Preparation of $[C_3F_7(OCF(CF_3)CF_2)_xOCF(CF_3)][C_3F_7OCF(CF_3)CF_2OCF(CF_3)][C_3F_7OCF(CF_3)]C_3N_3$

To 1.04 g (0.28 mmol) of the oligomer, $C_3F_7O(CF(CF_3)CF_2O)_{19.6}CF(CF_3)CO_2Me$, MW 3600 (see Table 6, Test No. 1) in ether (2 ml), cooled to 0°C, was added liquid ammonia (~ 2 ml) via a Dry Ice condenser. Refluxing was continued for 1 hr; subsequently the Dry Ice condenser was removed and the mixture was warmed to room temperature. Ether and the last traces of ammonia were removed in vacuo. The resultant amide was heated with phosphorus pentoxide (1.45 g) at 190-200°C for 2 hr. In an inert atmosphere enclosure the mixture was then extracted with 3 x 4 ml of Freon-113; on removal of solvent 0.94 g (90% yield) of product was obtained which exhibited in its infrared spectrum a weak band at 4.42 μ and no absorption in the 5-6 μ region. This material, in Freon-113, was added with stirring to liquid ammonia (7-8 ml) kept in a bath at -20°C. Refluxing, using a -78°C condenser, was continued for 1 hr; subsequently ammonia and the solvent were removed in vacuo at room temperature leaving 870 mg (93% yield) of an amidine-imidoylamidine mixture.

To transform all the amidine groups into imidoylamidine linkages to this mixture was added on a vacuum line $C_3F_7OCF(CF_3)$-$CF_2OCF(CF_3)CN$ (520.1 mg). After stirring overnight at room temperature the excess of nitrile was removed; the amount reacted was 61.3 mg (0.13 mmol). Based on this it can be calculated that the original mixture contained 54% of amidine. Treatment of the imidoylamidines with $C_3F_7OCF(CF_3)COF$ (350 mg, 1.05 mmol), followed by solution in Freon-113 and washing with 10% sodium bicarbonate and water, gave on solvent removal the triazine (860 mg, 63% yield); MW 5300. Molecular weight of 5268 was calculated based on the original amidine-imidoylamidine mixture.

d. Nitrile Terminated 4-Bromoheptafluoro-1,2-epoxybutane Hexafluoropropene Oxide Copolymer

The copolymer (500 mg) prepared in Test No. 21, Table 6 was treated with methanol (1 ml); subsequently the material was taken up in Freon-113, washed with water, and dried over magnesium sulfate. On removal of the solvent 460 mg of ester was obtained which exhibited an infrared spectrum consistent with the expected structure. The respective amide and the nitrile were prepared following exactly the procedure employed in the synthesis of nitrile terminated hexafluoropropene oxide telomer (see part c. above). To attain complete transformation of the amide to the nitrile the last reaction had to be performed twice. The yield of product based on acid fluoride originally employed was low, 32% (160 mg), due to mechanical losses associated with the small sample. The component distribution of this material is given in Table 9. The average molecular weight and elemental composition were calculated based on the area factors of each of the components. Anal Calcd.: C, 20.43%; F, 60.84%; Br, 10.32%; N, 1.04%; MW, 1488. Found:

C, 20.72%; F, 62.40%; Br, 10.71%; N, 1.37%; MW, 1900.

e. Preparation of 4-Bromoheptafluoro-1,2-epoxybutane Hexafluoropropene Oxide Copolymer Substituted Triazine

From the copolymer (1.11 g), prepared in Test No. 27 Table 6, the respective nitrile was obtained in 62% yield following the procedure given in part d. The amidine, imidoylamidine and finally the triazine (0.65 g, 39% overall yield) were prepared following exactly the procedure delineated in part c. The average molecular weight and elemental composition were calculated based on the copolymer nitrile analysis, and contributions from $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$ and $C_3F_7OCF(CF_3)COF$ reagents. Calcd. for $C_{41}F_{77}Br_2N_3O_{10}$: C, 21.25%; F, 63.13%; Br, 6.90%; N, 1.81%; O, 6.91%; MW, 2317.17. Found: C, 21.28%; F, 63.87%; Br, 8.26%; N, 2.36%; MW, 2100.

The higher than calculated bromine-content is most likely caused by the formation of some imidoylamidine in the preparation of the amidine from bromo-substituted nitrile.

f. U.V. Irradiation of Bromo-substituted Triazine

The triazine (228 mg) prepared in part e. was subjected to ultraviolet radiation in the presence of mercury (2.9 g) for 21 hr using essentially the procedure given in the preceding section, part n. After dissolving mercury and mercury salts in dilute nitric acid, the semi-solid material was taken up in Freon-113 and washed with water. Removal of solvent followed by drying in vacuo at 90°C afforded a semi-solid product (176 mg). The solubility of this material in Freon-113 indicates that chain extension, not crosslinking took place which is to be expected inasmuch as on average there were only two bromine atoms present per triazine molecule.

IV. CONCLUSIONS AND RECOMMENDATIONS

A. Direct Crosslinking Using Metalloid Compounds or Metals

A number of metalloid compounds namely, triphenylphosphine, tetraphenyldiphosphine, potassium diphenylphosphide, and tetrakis-(pentafluorophenyl)diphosphine were studied at temperatures up to 300°C as potential curing agents for perfluorocarbon and perfluoroalkylether systems. In some cases above 200°C fluorine abstraction was observed; however in no instance was a well defined coupled product isolated. Fluorine abstraction was invariably accompanied by material degradation as evidenced by charring and volatiles formation. In the limited investigations, metals such as zirconium sponge were found to be totally ineffective as fluorine abstractors.

Based on the above results it has to be concluded that direct crosslinking of fluorocarbon systems does not look promising and at present additional exploration of this concept would not seem warranted.

B. Crosslinking via Functional Groups

Bromine was selected as the candidate functional group since on crosslinking the thermally and oxidatively stable $-CF_2CF_2-$ linkage is established. To introduce bromine into the perfluoroalkylether chain the synthesis of 4-bromoheptafluoro-1,2-epoxybutane was devised and accomplished. Its copolymerization with hexafluoropropene oxide and hexafluoropropene oxide derived acid fluorides was successfully carried out incorporating pendant bromo-groups into the perfluoroalkylether chain. To obtain material amenable to crosslinking the terminal carbonyl function had to be transformed into a group unaffected by the crosslinking process visualized, in this case ultraviolet radiation.

Hydrogen termination interfered with the bromine substituent. The carbonyl group was thus transformed into a nitrile and the latter was found to be unaffected by ultraviolet radiation which permitted the coupling to occur quantitatively. Carrying the transformation further bromo-substituted triazine was synthesized and crosslinked.

To summarize a) feasibility of functional oxide synthesis b) its copolymerization with hexafluoropropene oxide and c) crosslinking of the resultant perfluoroalkylether polymer have been demonstrated. Further research is necessary to optimize the polymerization process to obtain high molecular weight materials reproducibly and to explore curing processes other than ultraviolet radiation.

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