Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Zollinger, J. L. , Throckmorton, J. R. , Ting, S. T. , Mitsch, R. A. and Elrick, D. E.(1969) 'Preparation and Curing of Poly (Perfluoroalkylene Oxides)†', Journal of Macromolecular Science, Part A, 3: 7, 1443 — 1464
To link to this Article: DOI: 10.1080/10601326908051836
URL: http://dx.doi.org/10.1080/10601326908051836

J. MACROMOL. SCI.–CHEM., A3(7), pp. 1443-1464, November, 1969

Preparation and Curing of Poly (Perfluoroalkylene Oxides)†

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SUMMARY

A series of functionally terminated poly(perfluoroalkylene oxides), a new class of curable, liquid, fluorinated polymers, has been prepared by the photopolymerization of perfluorooxydipropionyl fluoride, $O(CF_2CF_2COF)_2$, and related perfluoroacyl fluoride monomers. Polymerization proceeds by ultraviolet-induced scission of CF_2COF groups and coupling of the $CF_2\cdot$ radicals thus formed. Polymer molecular weight and functionality increase with photolysis time. The acid fluoride-terminated polymers ($\bar{M}_n$ 1000-5000, functionality 2-5) are liquids possessing low T_g (about -60°C) and excellent thermal stability. Other functional end groups (e.g., COOH, COOR, CH_2OH, etc.) have been prepared using standard reactions.

Carboxy-terminated polymer was converted to elastomers with bis(acyl aziridines), diepoxides, and bisoxetanes, with the cure rate decreasing in that order.

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†Contracts AF04(611)-11200 and AF04(611)-67-C-0030, Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California; Robert Corley, project engineer. Contribution No. 526 from the Central Research Laboratories, Minnesota Mining and Manufacturing Company, St. Paul, Minnesota.

Ester-terminated polymer afforded thermally and hydrolytically stable amide cross-linked rubbers on heating with diamines.

A new series of catalysts (trialkyl antimony dihydroxides) was found which effects quantitative room-temperature conversion of perfluoroalkanonitriles to triazines. Employing these catalysts, very thermally stable, transparent elastomers were prepared from the dinitriles, $NC(CF_2CF_2OCF_2CF_2)_nCN$, n = 1, 2, 4.

Liquid hydroxy-terminated perfluoro(tetramethylene oxide) prepolymers were cured with diisocyanates to yield elastomers possessing the best combination of properties of the rubbers that have been examined in this study. These urethane cross-linked elastomers have good physical properties, excellent hydrolytic and oxidative stability, and the necessary thermal stability for rocket propellant binders. These elastomers are also expected to have utility in other extreme environmental applications.

BACKGROUND

Earlier work [1] had shown that a fluorinated alkylene oxide backbone in a polymer was an excellent candidate to achieve the special physical and chemical requirements for a high-density binder prepolymer. The polymer referred to is poly(perfluorotetramethylene oxide) and was prepared by the ultraviolet irradiation of bis(2-iodotetrafluoroethyl)ether in the presence of mercury [1]:

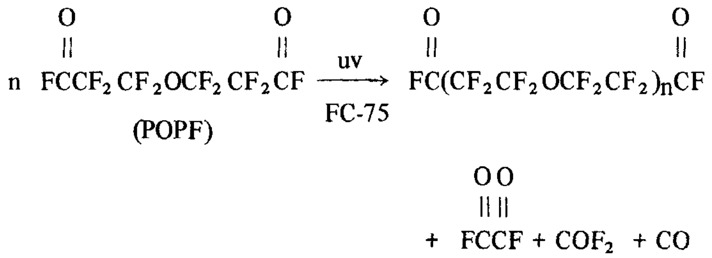
$$O(CF_2CF_2I)_2 \xrightarrow{\text{uv, Hg}^{\circ}} \left(CF_2CF_2CF_2CF_2O \right)_n \qquad (1)$$

Depending on molecular weight, the polymers range from oils to tacky rubbers with a T_g of about -65°C and excellent thermal stability as measured by DTA and TGA (10% weight loss between 515 and 530°C). However, polymers prepared in this manner were generally found to possess end-group functionality of about 1. Therefore, other synthetic routes to binder propolymer were sought.

POLYMER SYNTHESIS

A method which appeared worthy of consideration evolved from reports in the literature [2] which disclosed the formation of fluorocarbon dimers from photolysis of monofunctional perhaloacyl fluorides and the formation of a solid polymer from the photolysis of perfluoroglutaryl fluoride.

The ultraviolet irradiation of perfluorooxydipropionyl fluoride [3] (POPF) in FC-75† solution gives acid fluoride-terminated poly(perfluorotetramethylene oxide) in quantitative yield:



$$n\ \underset{\text{(POPF)}}{\mathrm{F\overset{\overset{O}{\|}}{C}CF_2CF_2OCF_2CF_2\overset{\overset{O}{\|}}{C}F}} \xrightarrow[\text{FC-75}]{\text{uv}} \mathrm{F\overset{\overset{O}{\|}}{C}(CF_2CF_2OCF_2CF_2)_n\overset{\overset{O}{\|}}{C}F} + \mathrm{F\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}F} + \mathrm{COF_2} + \mathrm{CO} \qquad (2)$$

The polymerization proceeds by the ultraviolet-induced cleavage of the $-\mathrm{CF_2}\!\not/\!\mathrm{COF}$ bond in the monomers (or growing polymer chain) with subsequent coupling of the $-\mathrm{CF_2}\cdot$ radicals thus formed. The volatile products, which include oxalyl fluoride, carbonyl fluoride, and carbon monoxide (all arising from the $\cdot$COF radical), are removed by a nitrogen purge or by distillation from the heated reaction mixture.

The crude polymers obtained in this photopolymerization range in molecular weight from about 500 to 15,000 with functionalities from about 2 to 8. Longer irradiation time yields polymers of higher molecular weight and functionality. The more linear polymer, e.g., functionality of 2.5, $\bar{M}_n$ of 1250, may be separated from polymer having higher functionality (and molecular weight), by hydrolysis of the crude acid fluoride polymer to carboxy-terminated perfluorotetramethylene oxide (CTPFO) polymer, followed by extraction with Freon-113.* Data from the extraction of crude CTPFO polymer from a typical polymerization are presented in Table 1. Additional experimental data are plotted in Fig. 1.

The effect of photolysis time is also illustrated in Fig. 1, where the $\bar{M}_n$ of crude polymer is seen to rise from 875 at 2.5 hr to 1600 at 6 hr. The apparent decrease in $\bar{M}_n$ of crude and residual polymer after about 9 hr is due to formation of some high-molecular-weight, cross-linked gel which was not included in the sample used for $\bar{M}_n$ determination. The $\bar{M}_n$ of

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†An inert fluorocarbon liquid manufactured by the 3M Company.

*A fluorinated fluid manufactured by the du Pont Company.

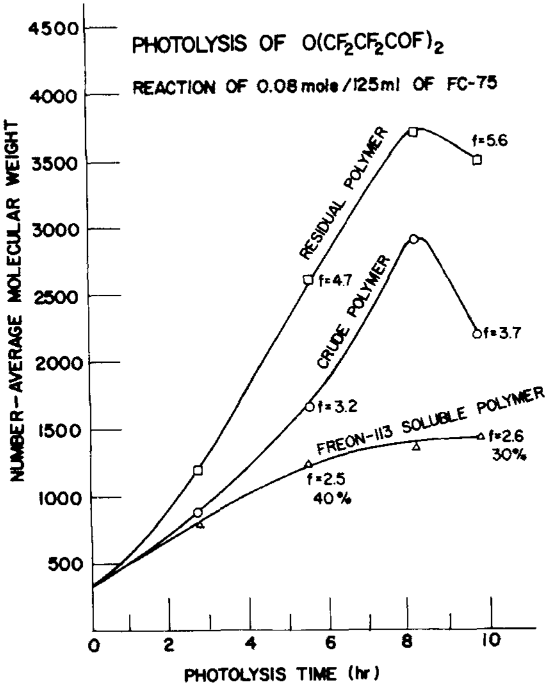


Fig. 1. $\overline{M}_n$ (and Functionality) of $FCO(CF_2CF_2OCF_2CF_2)_nCOF$ vs. photolysis time at 50°C.

Table 1. Extraction of $HOOC(CF_2CF_2OCF_2CF_2)_nCOOH$[a]

% Extracted[b]	Fraction	$\overline{M}_n$[c]	Functionality
–	Crude	1650	3.2
40	Extract	1250	2.5
–	Residue	2600	4.7

[a] From 5-hr photolysis of POPF (0.65 M in FC-75) at 50°C followed by hydrolysis.

[b] 15 ml of Freon-113 per gram of crude polymer.

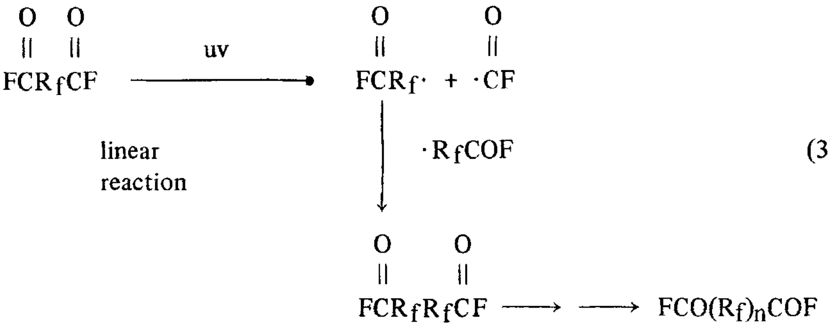
[c] Vapor-phase osmometry in Freon-113 solution.

Freon-113-soluble polymer is observed to plateau after about 6 hr. Further irradiation serves to form Freon-113-insoluble polymer of higher functionality at the expense of the more soluble, linear polymer. Thus, there is an optimum photolysis time of about 5.5 hr for best yields of the more linear CTPFO polymer under the conditions of this series of experiments.

BRANCHING REACTION

The formation of polymers having functionalities greater than 2 indicates that a branching reaction is taking place during the photopolymerization in addition to the expected linear reaction. Model compound studies have demonstrated that the branching reaction involves the attack of a $-CF_2\cdot$ radical on the oxygen atom of an acid fluoride group, leading to a new radical, which on coupling with another radical yields a branch on the polymer backbone.

Equations (3) and (4) illustrate, respectively, the mechanism of the linear and branching reactions for a diacyl fluoride.



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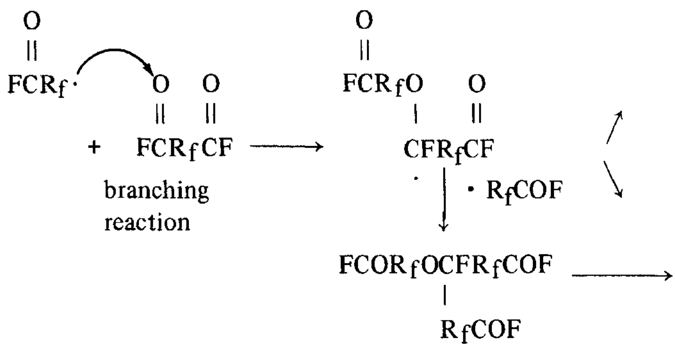


(4)

Reaction temperature (in the 0-100°C range) does not appear to influence the extent of branching taking place in the photolysis.

Other Monomers and Copolymerization

Photopolymerizations have also been conducted with other monomers. Perfluorooxydiacetyl fluoride (POAF) and the dimer of POPF (POPF-D) have been successfully converted to polymers.

$$\underset{\text{POAF}}{O(CF_2COF)_2} \xrightarrow{uv} FCO(CF_2OCF_2)_nCOF \qquad (5)$$

$$\underset{\text{POPF-D}}{FCO(CF_2CF_2OCF_2CF_2)_2COF} \xrightarrow{uv} FCO(CF_2CF_2OCF_2CF_2)_nCOF \qquad (6)$$

As expected, POPF-D, which has an initial molecular weight of 526 and a functionality of 2, yields polymer of higher molecular weight and lower functionality for a given photolysis time when compared with POPF.

Copolymerization of various molar ratios of POAF and perfluoroglutaryl fluoride (PGF), $FCO(CF_2)_3COF$, affords polymers having different CF_2/O ratios in the backbone. Higher CF_2/O ratios (corresponding to a higher proportion of PGF) yield polymers of higher glass transition temperatures, T_g, as shown in Table 2.

Table 2. Photopolymerization of Perfluorooxydiacetyl Fluoride (POAF) and Perfluoroglutaryl Fluoride (PGF)[a]

Monomer charge	Reaction conc., moles/140 ml	Mole ratio, POAF/PGF	Product		
			$\overline{M}_n$	f	T_g, °C
POAF	0.073	1/0	750	2.6	-48
POAF and PGF	0.073	5/1	1100	3.4	-45
POAF and PGF	0.074	2/1	1000	2.5	-30
POAF and PGF	0.071	1/1	1000	2.7	-13

[a] Photolysis time of 5 hr at a temperature of 5-35°C.

Scale-up

The scale-up of the photopolymerization reaction utilizes a stirred, cylindrical quartz reactor. The FC-75 solution of POPF (80% by weight) is irradiated by means of ultraviolet lamps (450-500 W, medium-pressure mercury) with elliptical reflectors which concentrate the radiation in the solution adjacent to the reactor wall. Several 0.75-lb batches of monomer have been converted to polymer ($\overline{M}_n$ 1700-3300, functionality 2.4-3.3) in this reactor. Polymer is isolated by stripping off the solvent (and very low-molecular-weight polymer) under reduced pressure.

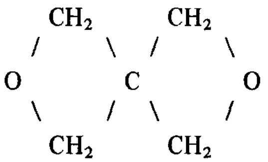
CURING STUDIES

The types of functional groups available in the prepolymer include the acid fluoride obtained in the polymerization process, ester, amide, carboxylic acid, 1,1-dihydroalcohol, and other acid-derived functions. These various end groups are obtained by conventional organic reaction procedures. The results of polymer curing studies and some model compound work are described for some of these functional groups. Emphasis was given those reactions which do not have volatile by-products. Difunctional curing agents were considered adequate for cross-linking because of the greater-than-2 functionality of the prepolymer.

Carboxylic Acid Reactions

Early screening reactions (Table 3) revealed that acyl aziridines and epoxy compounds, which are useful for curing carboxy-terminated hydrocarbon polymers, react too rapidly with carboxy-terminated perfluorotetramethylene oxide (CTPFO) prepolymers, because of the strongly acidic nature of the perfluoroacid end groups, to provide the desired pot life for use as propellant binders. Gelation of liquid CTPFO prepolymers at 25°C takes place within minutes with acyl aziridines and in less than 1 hr with diepoxides.

Bisoxetanes, higher-ring homologs of the diepoxides, were found to cure CTPFO prepolymers at a slower, more satisfactory rate (3-hr pot life at 60°C), because of the slower ring-opening reaction (Table 3). The bisoxetane curing agent, 2,6-dioxa-4-spiroheptane,

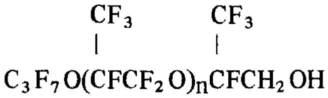


was found to be readily soluble in the CTPFO prepolymer and gave cured rubbers having improved hydrolytic stability compared with polymer cured with diepoxides. (Diepoxide-cured polymers hydrolyze slowly in air under ambient conditions.) This improved stability is attributed to the steric hindrance afforded (by the neopentyl-type structure) to the carboxylate ester groups formed in the cross-link, $-CF_2CO_2CH_2C(CH_2OH)_2CH_2O_2CCF_2-$. However, the steric hindrance is insufficient since oxetane-cured polymers slowly (10 days) revert to liquid on standing in water at room temperature.

Attempts to cure CTPFO polymer with chromium trifluoroacetate gave weak rubbers.

Ester Reactions

Methyl ester-terminated perfluorotetramethylene oxide prepolymers have been cured by amide formation with a fluorinated diamine, $H_2NCH_2(CF_2)_8CH_2NH_2$, to yield thermally stable (220°C) and hydrolytically stable (water, 70°C) rubbers. The reaction required several days at 100°C. Methyl alcohol was eliminated in this curing reaction and caused bubble formation. However, when a long-chain (molecular weight, ~900), nonvolatile, fluorinated alcohol,



$$C_3F_7O(\underset{CF_3}{CF}CF_2O)_n\underset{CF_3}{CF}CH_2OH$$

was employed as the alcohol portion of the ester-terminated polymer, curing with the fluorinated diamine at 100°C liberated the high-molecular-weight alcohol, which acted as a plasticizer for the bubble-free rubber.

Perfluoronitrile Reactions

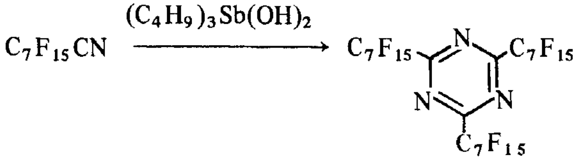
A series of catalysts was discovered during this work which converts perfluoroaliphatic nitriles to the very stable perfluoroalkyl triazines in high yields at room temperature and ordinary pressures. One of the most effective catalysts is tributyl antimony dihydroxide:

Table 3. Relative Reaction Rates of Various Ring Compounds (0.5 N) with Perfluoropropionic Acid (0.5 N) in Chloroform at 25°C

Ring compound	T 1/2, hr[a]
N-acyl aziridines[b]	<0.1
N-p-toluenesulfonyl aziridine	0.5
Glycidyl phenyl ether	3
Butadiene diepoxide	10
Epichlorohydrin	13
3,3-Bis(chloromethyl) oxetane	>100 (60°C)

[a] Time at which one-half of small ring structure had reacted, as measured by proton NMR analysis.

[b] N,N′,N″-tris(1,2-butylene) trimesamide or N-phenyl-N′-ethylene urea.



(7)

Previous methods [4] for the synthesis of perfluoroalkyl triazines from perfluoroaliphatic nitriles have required high temperatures and pressures, usually in the presence of high concentrations of volatile catalysts (HCl, NH_3).

The rate of reaction in this new triazine synthesis is increased by increased catalyst concentration and higher temperatures, although with 1-2% catalyst, reaction for 1 day at 25°C affords a greater than 90% conversion to the triazine.

A solid triazine polymer is obtained when this catalyst is employed with a fluorinated dinitrile. The homopolymer from perfluorosebaconitrile, $NC(CF_2)_8CN$, is a rather hard, opaque solid [Eq. (8)]. Cross-linking and hardness are decreased via chain extension by incorporation of a mononitrile, e.g., $C_5F_{11}CN$ [Eq. (9)]. The resulting copolymer is elastomeric.

A series of fluoroaliphatic ether dinitriles, $NC(CF_2CF_2OCF_2CF_2)_nCN$, $n = 1, 2, 4$, was prepared† and converted to triazine cross-linked homopolymers, by means of the above antimony catalyst (or ammonia). In

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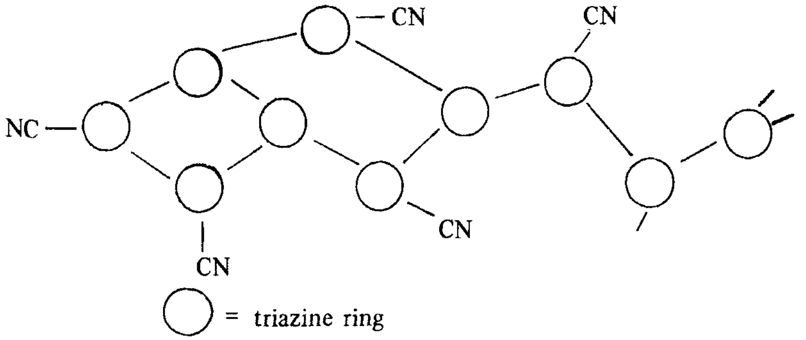
†From the corresponding acid fluorides [see Eq. (2)] by conversion to amide and dehydration. Nitrile properties are given in Table 4.

Table 4. Fluoroether Dinitriles and Homopolymers

$NC(CF_2CF_2OCF_2CF_2)_nCN$					
n	Molecular weight	Boiling point, °C	d_4^{20}, g/cc	$n_D^{23.5\,°C}$	T_g of triazine homopolymers,[a] °C
1	268	62	1.42	1.2762	+14 to +23
2	484	132	1.61	1.2867	-36 to -29
4	916	125/10 mm	1.73	1.2935	-49 to -43

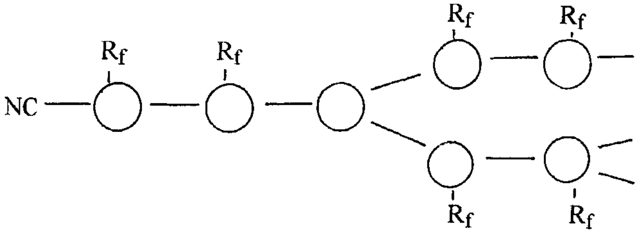
[a] T_g was determined from DTA (differential thermal analysis) of the polymers [obtained by $(C_4H_9)_3Sb(OH)_2$ catalysis: 1-2% catalyst, sealed tubes, 90-100°C].

$$NC(CF_2)_8CN \xrightarrow{\text{catalyst}} \text{hard, opaque solid}$$



(8)

$$NC(CF_2)_8CN + C_5F_{11}CN \xrightarrow{\text{catalyst}} \text{transparent elastomer}$$



(9)

remarkable contrast to the hard, opaque polymer obtained from $NC(CF_2)_8CN$, the polymers from these ether-containing dinitriles are transparent elastomers. The glass transition temperature (T_g) of these rubbers decreases as n increases. Some properties of the dinitriles and the T_g of the homopolymers are shown in Table 4.

The triazine elastomers are very thermally stable (Table 5) and have good hydrolytic stability. One of the deficiencies noted for the organo antimony-catalyzed system is moisture sensitivity during cure. Nitrile-catalyst complexes appear to be converted to amide if moist air is present. The triazine polymers prepared using ammonia in a sealed tube had better thermal stability than the triazine polymers containing the antimony catalysts.

Table 5. Heat-Aging and TGA Data in Air for Triazine Polymers

Monomers and prepolymers	Curing agent or catalyst	Temp.,[a] °C	Weight loss			TGA[c] temp. at 10% wt loss
			%	Days	Rate[b] %/hr	
$NCCF_2CF_2OCF_2CF_2CN$	$Bu_3Sb(OH)_2$	260	9	361	0.0046	453
$NCCF_2CF_2OCF_2CF_2CN$	NH_3	260	3	25	0.0004	500
$NCCF_2CF_2OCF_2CF_2CN$	NH_3	315	6	25	0.011	–
$NC(CF_2CF_2OCF_2CF_2)_2CN$	$Bu_3Sb(OH)_2$	260	11	25	0.013	–
$NC(CF_2CF_2OCF_2CF_2)_4CN$	$Bu_3Sb(OH)_2$	260	18	25	0.01	400
$NC(CF_2CF_2OCF_2CF_2)_4CN$	NH_3	260	3	25	0.0054	450
$NC(CF_2)_8CN + C_5F_{11}CN$	$Bu_3Sb(OH)_2$	260	7	25	0.006	348

[a] Temperature at which polymer was heated in air (open glass tube). All samples were still rubbery after test.

[b] Rate determined between 3rd and 6th day.

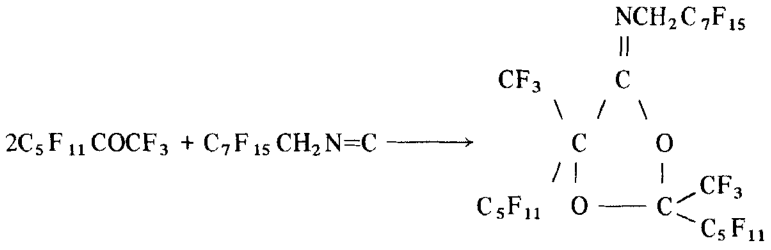
[c] 5°C/min temperature rise, in air.

Perfluoroketone Reactions

A potential cure system for fluoroether polymers was envisioned through the utilization of a new reaction between two molecules of a perfluoroalkyl ketone and one of alkyl isocyanide to yield a stable (thermal and hydrolytic) iminodioxolane compound [5]. We have found that the reaction works best on a trifluoromethyl perfluoroalkyl ketone, and that the presence of a perfluoroalkyl group in the isonitrile gives a miscible system and also a slower reaction rate (complete in about 1 day at 25-40°C instead of about 1 hr observed with the alkyl isocyanides). Perfluoroheptanone-2 and 1,1-dihydroperfluorooctyl isocyanide gave complete conversion overnight at 40°C to the iminodioxolane shown in Eq. (10). The perfluoroisopropyl ketone group, which is relatively easy to prepare [6]

$$(-COF + CF_3CF{=}CF_2 \xrightarrow{F^-} -COCF(CF_3)_2\ ),$$

does not react with isonitriles under the conditions tried (60°C) using a model compound, $(CF_3)_2CFCOCF_2CF_2OCF_2CF_2COCF(CF_3)_2$.



(10)

Reactions of Hydroxy-Terminated Polymer

Preparation. The acid fluoride and methyl ester-terminated polymers have been reduced to hydroxy-terminated perfluorotetramethylene oxide (HTPFO) prepolymer by treatment with $LiAlH_4$ or $NaBH_4$ in ether solvents.

$$ROOC(CF_2CF_2OCF_2CF_2)_nCOOR + LiAlH_4 \longrightarrow$$

$$HOCH_2(CF_2CF_2OCF_2CF_2)_nCH_2OH \qquad (11)$$

Curing. Curing HTPFO prepolymers with diisocyanates yields urethane cross-linked elastomers possessing good physical properties compared with epoxy- and oxetane-cured polymers. The hydrolytic stability of the urethane cross-linked polymers is excellent. The thermal stability is only moderate, but is believed to be adequate for use as a propellant binder.

A typical HTPFO prepolymer employed in the curing studies with diisocyanates has the properties listed in Table 6.

Table 6. Typical Properties of $HOCH_2(CF_2CF_2OCF_2CF_2)_nCH_2OH$

Molecular weight, $\bar{M}_n$	1700
Equivalent weight	680
Functionality	2.5
Viscosity at 65°C (poise)	4-5
Density, g/ml	1.82
T_g, °C	<-55

Fluorinated and unfluorinated aliphatic and aromatic diisocyanates have been screened as curing agents (Table 7). Oxydi(ethylisocyanate) (ODEI) and oxybis(1,1-dihydroperfluoropropylisocyanate) OBDI) are new diisocyanates.

All of the diisocyanates in Table 7 are initially insoluble in HTPFO prepolymer at 80°C but dissolve (by partial reaction) in less than 45 min on stirring, except for TDI which requires 1-2 hr at 100°C.

Cure Rates. The various classes of isocyanates react at different rates, as noted by gel times and infrared analysis of equivalent quantities of polymer and curing agents. The fluorinated aromatic isocyanate, TPDI, effects the most rapid cure (2 hr to gel at 80°C), while TDI is the slowest (20 hr to gel at 100°C). The decreasing order of reactivity for all of the diisocyanates is TPDI > OBDI > ODEI > HDI > TDI.

A plot of viscosity vs. time for TPDI- and TDI-cured HTPFO polymer systems at 65°C is instructive (Fig. 2). The rate of viscosity change for the uncatalyzed HTPFO-TDI system (even with preheating at 90-100°C for 50 min to obtain miscibility) is similar to that for a conventional carboxy-terminated polybutadiene (CTPB) prepolymer-epoxide-catalyst system which is plotted for comparison. It thus appears that highly filled slurries containing HTPFO-TDI as a binder will remain sufficiently fluid at about

Table 7. Isocyanate Curing Agents

Abbreviation	Name	Structure	Boiling point, °C/mm
TDI	Tolylene diisocyanate	$CH_3-C_6H_3(NCO)_2-2,4$	120/10
HDI	Hexamethylene diisocyanate	$OCN(CH_2)_6NCO$	130/14
ODEI	Oxydi(ethylisocyanate)	$O(CH_2CH_2NCO)_2$	93/3
TPDI	Tetrafluoro-m-phenylene diisocyanate[a]	$C_6F_4(NCO)_2-1,3$	61/1
OBDI	Oxybis(1,1-dihydroperfluoropropylisocyanate)	$O(CF_2CF_2CH_2NCO)_2$	62/0.4

[a] Peninsular Chem Research.

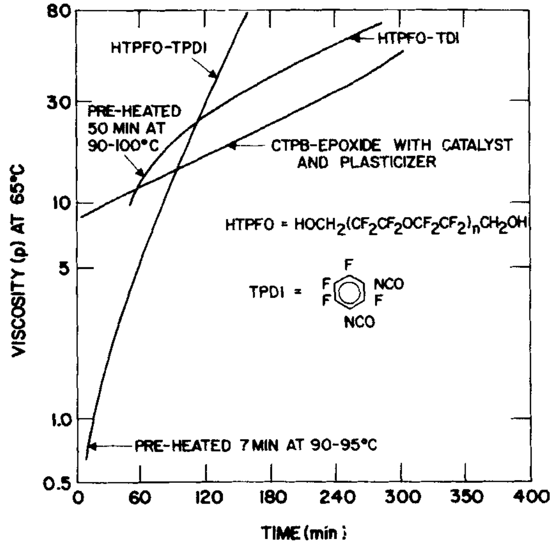


Fig. 2. Viscosity change of curing liquid rubbers vs. time at 65°C.

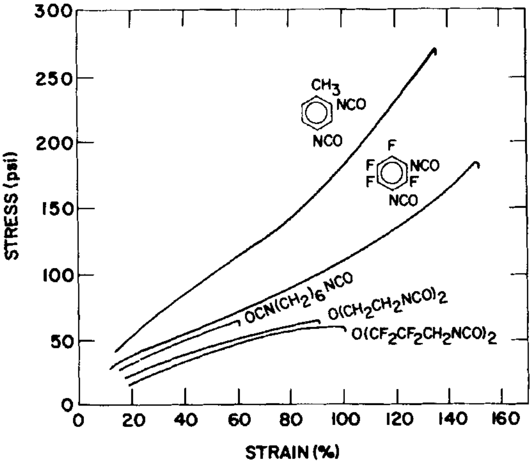


Fig. 3. Stress vs. strain for isocyanate-cured $HOCH_2(CF_2CF_2OCF_2CF_2)_nCH_2OH$ (cured 4 days at 80°C, run at 25°C).

Table 8. Physical Properties of Urethane Cross-linked Rubbers[a]

Isocyanate	Hardness shore A2	T_g[b], °C	Density,[c] g/cc	Tensile strength,[d] psi	Elongation,[d] %
TDI	50	-5	1.81	270	135
TPDI	45	-18	1.88	184	150
HDI	30	-52	1.74	65	60
ODEI	24	-40	1.80	65	90
OBDI	15	-24	1.85	60	100

[a] Equivalent quantities of isocyanate and $HOCH_2(CF_2CF_2OCF_2CF_2)_nCH_2OH$ ($\bar{M}_n$ 1500, E.W. 600), cured for 4 days at 80°C.

[b] T_g determined from DTA (average of broad temperature range).

[c] Mercury intrusion method.

[d] Determined at 25°C on small dumbbells at a strain rate of 240%/min, duplicates. There was no permanent set when measured 10 min after the specimens had broken.

65°C to allow time for mixing and casting. However, the HTPFO-TPDI system may not be satisfactory because of the rapid viscosity increase at 65°C.

Physical Properties of Elastomers

Tensile-elongation data are plotted in Fig. 3 and listed in Table 8 for HTPFO polymer cured with equivalent amounts of five diisocyanates. Table 8 also includes glass transition temperature (T_g), hardness, and density for each of these five elastomers.

The aromatic diisocyanate-cured elastomers exhibit the highest tensile strength and elongation for this group of isocyanates. However, one cannot safely conclude that the aromatic isocyanates are inherently better unless the comparison is made over a reasonably wide temperature range. At 25°C, the aliphatic diisocyanate-cured rubbers are farther above their T_g than the aromatics (Table 8) and thus may exhibit poorer mechanical properties. Furthermore, maximum properties are not necessarily obtained at the same isocyanate-to-hydroxyl ratios for aromatic and aliphatic isocyanates. High tensile strengths are not expected for the cured perfluorotetramethylene oxide polymers because of the low molar cohesion of the fluorinated polymer chains. Elongation is also limited by the relatively short polymer chain lengths between functional groups (and thus between polymer cross-links). The use of higher-molecular-weight polymer of the same functionality should improve elongation and tensile strength, and lower the T_g. Using more than the stoichiometric amount of diisocyanate curing agent increases the modulus of the cured rubber, as shown in Fig. 4 for TPDI.

Hydrolytic Stability

Urethane cross-linked elastomers prepared from the reaction of HTPFO prepolymer with a fluorinated isocyanate, TPDI, and a nonfluorinated isocyanate, TDI, have good hydrolytic stabilities. Less than 1% weight gain and no observable physical property changes were noted over a 94-day period for samples immersed in water at room temperature. No noticeable effect was observed on rubber properties after 12 days of immersion in water at 70°C.

Thermal Stability

Heat-aging studies on isocyanate-cured HTPFO polymer at 177°C in air

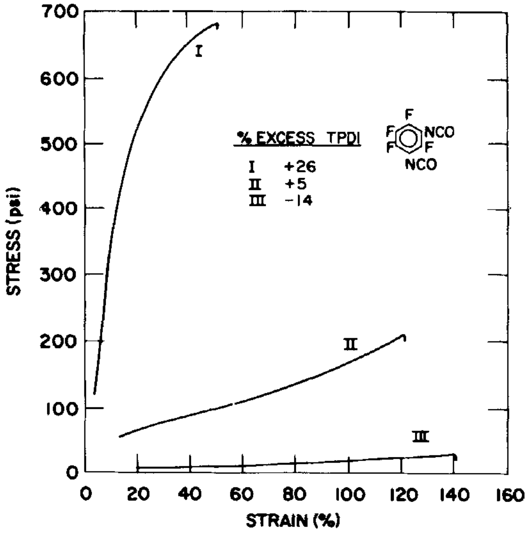


Fig. 4. Stress vs. strain (at 25°C) for $HOCH_2(CF_2CF_2OCF_2CF_2)_nCH_2OH$ cured with various amounts of tetrafluorophenylene-diisocyanate (cured 1 day at 80°C and 1 day at 125°C).

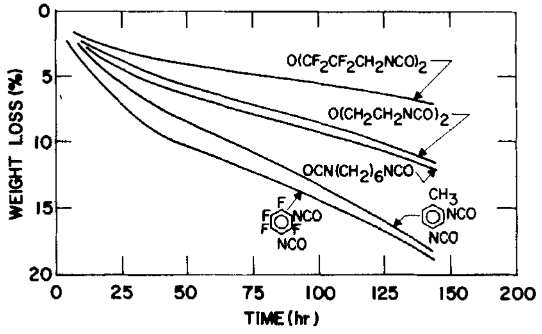


Fig. 5. Weight loss vs. time for $HOCH_2(CF_2CF_2OCF_2CF_2)_nCH_2OH$ cured with various diisocyanates. Run in air at 177°C.

Table 9. TGA Data for Isocyanate-Cured HTPFO

Isocyanate	10% Weight loss temp.,[a] °C
OBDI	320
ODEI	295
HDI	290
TDI	285
TPDI	280

[a] 5°C/min temperature rise in air.

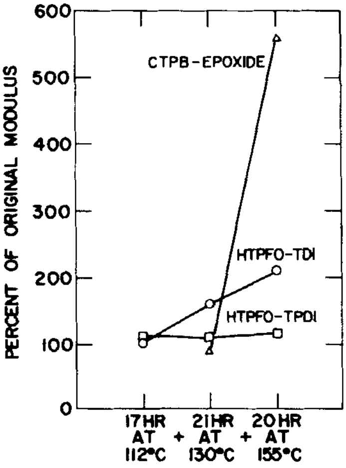


Fig. 6. Plot of modulus change vs. heating periods in air for cured rubbers.

revealed three different degrees of stability, depending on the type of isocyanate used. The decreasing order of stability is: fluorinated aliphatic (OBDI) > aliphatic (ODEI and HDI) > aromatic (TDI and TPDI). These data are plotted in Fig. 5. Thermogravimetric analyses (TGA) data (Table 9) for these five rubbers are consistent with the heat-aging data.

A comparison of the thermal oxidative stability of the urethane cross-linked, hydroxy-terminated, fluorinated ether polymers with an epoxy-cured, carboxy-terminated polybutadiene (CTPB) polymer reveals the high resistance of the fluorinated polymer to air oxidation compared with the CTPB polymer. The data are plotted in Fig. 6 and were obtained by successive determinations of the stress at 10% strain, after air-aging (static) of polymer rods for approximately 1-day periods at 112, 130, and 155°C. The fluorinated polymers (cured with TDI and TPDI) showed little change in modulus. In contrast, the epoxide-cured CTPB exhibited a large increase in modulus (became hard) due to air oxidation during the same period.

ACKNOWLEDGMENTS

The authors wish to thank D. M. Connor, M. L. Stigen, A. H. Stoskopf, and W. H. Swanson for help in conducting experiments; J. J. McBrady for interpretation of spectroscopic data; C. D. Green, J. J. Neumayer, and P. B. Olson for quantitative analytical determinations; R. L. Bohon and R. J. Wann for physical property measurements on cured polymers.

REFERENCES

[1] D. E. Rice, *J. Polymer Sci.*, B(6), 335-340 (1968).
[2] J. F. Harris, Jr., *J. Org. Chem.*, **30**, 2182 (1965).
[3] 3M Company, British Pat. 858,671 (1961).
[4] W. L. Reilly and H. C. Brown, *J. Org. Chem.*, **22**, 698 (1957); E. R. Bissell and R. E. Spenger, *ibid.*, **24**, 1147 (1959); C. G. Fritz and J. L. Warnell (duPont), U.S. Pat. 3,347,901 (1967).
[5] W. J. Middleton, D. C. England, and C. G. Krespan, *J. Org. Chem.*, **32**, 948 (1967).
[6] F. S. Fawcet and R. D. Smith (duPont), U.S. Pat. 3,185,734 (1965).

Accepted by editor May 27, 1969
Received for publication June 16, 1969

Discussion of Paper by J. L. Zollinger et al.

Preparation and Curing of Poly(Perfluoroalkylene Oxides)

A. H. Muenker: Did you look at the reactivity of trans-2,3-dimethyl-substituted sulfonyl aziridines with the carboxyl-terminated perfluoroalkylene oxide prepolymers? They may have significantly lower reactivity than mono- or unsubstituted sulfonyl aziridines.

J. L. Zollinger: We did not look at these particular aziridines. However, even if the cure rates were satisfactory, the elastomers would not be satisfactory because of hydrolytic instability of the fluorinated ester cross-links formed ($-CF_2COOCHCH_3-$) in the ring opening cure reaction.

R. F. Landel: I would have some reservations about interpreting the low tensile properties as resulting from low cohesion between the chains. In the work that Dr. Fedors and I have carried out on ultimate properties, the details of the chain architecture are immaterial–one obtains essentially the same results on a fluorinated rubber (Viton), hydrocarbon rubber, and even a protein rubber.

J. L. Zollinger: My statement was based on comments from a rheologist at 3M. A fluoroether polymer backbone has much lower chain molar cohesion than the polymers you mention.

R. F. Landel: The drastic change in the shape of the stress-strain curves with excess curing agent suggests an association. Is the excess material soluble; do the rubbers remain transparent?

J. L. Zollinger: They are transparent, no precipitation.

R. F. Landel: Then there must be secondary reactions; what happens to the excess isocyanates?

J. L. Zollinger: Infrared shows little isocyanate left even at 25% "excess" curing agent. There may be further reaction of NCO groups with urethane cross-links which gives a higher cross-link density and higher tensile strength.