

Polyurethanes with Long Fluorinated Side Chains

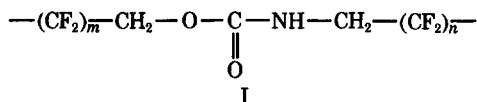
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Synopsis

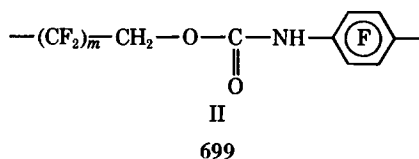
Copolymer triols were prepared from propylene oxide and glycidyl (α, α, ω -trihydrododecafluoroheptyl) ether or pentadecafluoroheptylepoxyethane. Cationic polymerization was used and block copolymers were obtained in the molecular weight range of 1,000 to 3,000. These copolymer triols were reacted with an 80/20 mixture of 2,4-/2,6-tolylene diisocyanate, giving polyurethanes with the same polymer backbone as the conventional polyurethanes based on polyoxypropylene triols and tolylene diisocyanate. It was found that these polyurethanes, containing between 0% and 45% fluorine, showed increasing adhesion to anodized aluminum with increasing urea bond content of the polymer. However, the fluorine content did not show the expected effect on adhesion. Isothermal gravimetric analysis showed that the heat stability of the fluorourethanes was lower than for conventional urethanes on a weight basis, only because the segments split off in heat degradation were heavier for the fluorourethane. This phenomenon might possibly also apply to urethanes with a fluorinated backbone. On a mole basis fluorourethanes might be as stable as nonfluorourethanes. It was also found that the thermostability, as measured by weight loss, increased with an increasing degree of crosslink density in the polymers.

INTRODUCTION

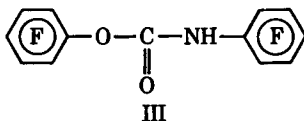
Urethanes with perfluorinated backbones have been recently synthesized.^{1,8,16} These investigations have shown that to obtain heat and hydrolytic stability, a CH_2 group had to be inserted between the isocyanate and the difluoromethylene groups.^{1,17} Furthermore, perfluoroalkyl diols are unstable and require also a CH_2 group between the CF_2 and the OH group. The only stable aliphatic fluorinated urethane structure was I shown below.



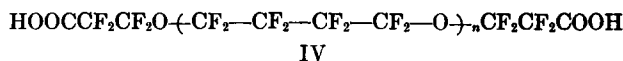
Another approach was to use aromatic perfluorinated diisocyanates, II.



Fluorourethanes prepared from aromatic perfluorodiols, III, were very slow to form but nevertheless were stable.



Fluorourethanes of types I, II, and III, however, are hard or brittle because of the short chains between urethane bonds. Fluorourethanes prepared from poly(perfluoroalkyl oxides) should, theoretically at least, be more flexible but have not been described in detail yet, although considerable work has been done on the preparation of dicarboxylic acids, IV, or amides of poly(perfluorobutylene oxide),² and on the preparation of perfluoropropylene oxide polymers.³



In this study, an attempt was made to prepare a urethane coating which would be at the same time highly flexible even at low temperatures and highly resistant to such diversified solvents as jet fuel, tetrahydrofuran, *m*-cresol, and alcohols. The approach taken was to conserve the conventional urethane backbone by using glycidyl ethers of fluoroalcohols to prepare the polyols. Fluorine-free diisocyanates were used and the reactivity of the urethane-forming ingredients was thus unchanged. It was quickly established that highly fluorinated linear urethanes (from diols and diisocyanates) were still soluble in various solvents. Crosslinking was thus needed and accomplished by the use of triols. The effect of the fluoroalkyl side chains on adhesion of the urethanes to metal, on heat stability, and on solvent resistance was then evaluated. One urethane based on a fluoroalkyl epoxyethane triol was also examined.

EXPERIMENTAL

Preparation of Glycidyl Ethers

Glycidyl (α,α,ω -Trihydrododecafluoroheptyl) Ether—Sodium Hydroxide Method

A 5-liter three-necked flask was filled with 1992 g (6 moles) of α,α,ω -trihydrododecafluoroheptanol [$\text{H}(\text{CF}_2\text{CF}_2)_5\text{CH}_2\text{OH}$], 1860 g epichlorohydrin (20 moles), and 50 ml water (2.5% by weight based on fluoroalcohol). After heating the mixture to 80°C, sodium hydroxide pellets were added in 20 portions of 12 g each (240 g, 6 moles) over a period of 3 hr. The sodium hydroxide addition was timed so as to keep the temperature at 92°–97°C, since the reaction was exothermic. After 3 hr, the mixture was heated for another 4 hr at 95°C.

After cooling, the sodium chloride formed was filtered. The liquid was washed with 500 ml water in a separatory funnel. The water layer was added to the filtered sodium chloride and analyzed (290 g NaCl or 82%

TABLE I
Fluoroalkyl Glycidyl Ethers: $R_f\text{CH}_2\text{—O—CH}_2\text{—CH—CH}_2$

R_f	bp, °C	F calcd, %	Yield, %
$\text{HC}_6\text{F}_{12}\text{—}$	102 at 10 mm	58.7	70
$\text{C}_7\text{F}_{15}\text{—}$	80 at 2.0 mm	62.5	72

conversion). The organic layer was dried on 5A molecular sieves and distilled at 10 mm Hg. *Anal.* Calcd for glycidyl (α,α,ω -trihydrododecafluoroheptyl) ether: oxirane oxygen, 4.13%; found 4.03%. VPC assay, 84.5%; yield, 70%. (See Table I.)

Glycidyl (α,α -Dihydropentadecafluorooctyl) Ether—Sodium Hydride Method

In a typical experiment, 29.5 g sodium hydride dispersion in mineral oil (53% concentration; metal hydrides, 0.65 mole) was treated with four portions each of 300 ml diethyl ether to remove mineral oil. Then, to the slurry of NaH and 1 liter diethyl ether, 1,1-dihydropentadecafluorooctanol (Columbia Organics, redistilled, bp 158°–159°C; 0.50 mole) dissolved in 600 ml diethyl ether was added with stirring (air stirrer) during a 1.25-hr period at room temperature. Epichlorohydrin (0.60 mole; Fisher Scientific) was added and the reaction mixture stirred overnight. After removal of 1.25 liters diethyl ether, an additional quantity of 300 g epichlorohydrin was added. Upon removal of the last traces of ether, the reaction mixture was refluxed for 4 hr (with stirring). (Good stirring is recommended during these operations to avoid local overheating. Fear et al.¹⁷ reported violent degradation of solid $\text{CF}_3\text{CH}_2\text{ONa}$ when heated to 180°C.)

Water (750 ml) was added to the cooled reaction mixture. The organic layer was separated and the aqueous layer extracted with three 350-ml portions each of diethyl ether. The combined organic layers were dried (MgSO_4). Distillation provided a center fraction, bp 80°C/2.0 mm, 100°C/11 mm; n_D^{25} 1.3288 (VPC, main component, 98.0%); wt 163.9 g (71.8% yield). *Anal.* Calcd for $\text{C}_{11}\text{H}_7\text{O}_2\text{F}_{15}$: C, 28.96; H, 1.55; F, 62.48. Found: C, 29.04; H, 1.62; F, 62.25. $\text{C}_7\text{F}_{15}\text{CH}_2\text{OCH}_2\text{—CH—CH}_2$ had strong

oxirane absorption at 11.0, 11.68, and 11.91 μ . (See Table I.) This glycidyl ether was used in the early phases of the study and was subsequently replaced by the glycidyl (α,α,ω -trihydrododecafluoroheptyl) ether, without noticeable change in polymer properties.¹⁹

Preparation of Pentadecafluoroheptylepoxyethane

The procedure described by Witterholt⁴ was employed. Diazomethane in diethyl ether was prepared in the usual manner⁵ from 0.45 mole N-methyl-N-nitroso-*p*-toluenesulfonamide (Diazald, Aldrich) in 825 ml diethyl ether, 200 ml diethylene glycol monoethyl ether (Polysolv-DE), and 0.45 mole of potassium hydroxide in 45 ml water. Perfluorooctanal (0.174 mole, Peninsular Chem. Research, redistilled from P₂O₅, bp 120°–122°C) was then added with stirring to the ether solution of diazomethane at 0°C over a 20-min period and then stirred at room temperature for 65 hr. Glacial acetic acid (50 ml) was added over a 5-min period, the reaction mixture was stirred for 15 min and then successively washed with water (500 ml), saturated sodium bicarbonate solution (500 ml), and two 500-ml portions each of water. The dried (Drierite) ether solution was distilled to give a center fraction, bp 158°–160.5°C, n_D^{25} 1.3053, wt 27.5 g (38.3% yield). *Anal.* Calcd for C₇F₁₅H₃O: C, 26.23; H, 0.73; F, 69.16. Found: C, 26.62; H, 0.89; F, 68.95. The product had strong infrared absorption at 10.97 μ , which is characteristic of epoxy groups. (Reported for C₇F₁₅CH-CH₂: bp 81°C/44 mm; n_D^{20} 1.3076.)⁴



Preparation of Triols

Polyol Preparation by Block Copolymerization

A mixture of 250 g (0.25 mole) Poly-G 1030PG (Olin Mathieson Chemical Corporation) (OH number 168, mol wt = 1000, triol) previously stripped on a flash evaporator at 80°C and 1 mm Hg, and 250 g (0.65 mole) of glycidyl (α,α,ω -trihydroperfluoroheptyl) ether was made in a three-neck flask (stirrer, nitrogen flush). Then 4 ml BF₃ etherate was added slowly while the temperature rose to 50°C, at which point ice cooling was applied. When the exotherm was finished, heating was applied for 5 hr (at 50°C). Then 200 ml methylene chloride and 4.5 ml triethylamine were added and the neutralized mixture washed with 100 ml water. The organic layer was separated, dried on molecular sieves, filtered, and concentrated on a rotary evaporator at 80°C and 1 mm Hg. *Anal.* OH number polyol, 88.7; % free glycidyl ether by VPC, 0%; % fluorine, 27.7 (theory 29.8%); mol wt calculated from OH number, 1900. (See Table II, Triol 4.)

Polyol Preparation by Random Copolymerization

The same polyol as above could be prepared at 5° or 20°C by random copolymerization by substituting the Poly-G 1030 by a mixture of glycerol and a calculated amount of propylene oxide to give a triol of the desired molecular weight, e.g., 23 g glycerol and 227 g propylene oxide.

The completion of the reaction was monitored after 24 hr by adding the same amount of BF₃·Et₂O as at the start of the reaction. Absence of an exotherm indicated complete reaction, which was then further confirmed

TABLE II
Preparation of Triols by Block Copolymerization

Number	Original triol ^a	Weight ratio, triol/glyc. ether ^b	Final MW _{OH}	OH number, mg KOH/g	F, %
1	Poly-G 430PG	1/1	1060	158	29.3
2	Poly-G 430PG	1/2	1320	127	39.4
3	Poly-G 430PG	1/8	3090	54.4	52.2
4	Poly-G 1030PG	1/1	1900	88.4	29.3
5	Poly-G 1030PG	1/2	2690	62.7	40.7
6	Poly-G 1030PG	1/1 (c)	1723	94.0	29.1

^a 430PG = Polyoxypropylene triol MW 430; 1030PG = polyoxypropylene triol MW 1000.

^b $\text{HC}_6\text{F}_{12}\text{CH}_2\text{---O---CH}_2\text{---CH---CH}_2$

^c $\text{C}_7\text{F}_{15}\text{CH---CH}_2$



by OH number determination and gel permeation chromatography on the purified polyol.

Polyols prepared and their properties are given in Table II.

Preparation of Prepolymers

The triols were reacted with TDI (80/20 mixture of 2,4- and 2,6-tolylene diisocyanate) at 90°C under nitrogen for 2 hr. The NCO/OH ratio was 2/1. These prepolymers were used in bulk or in a solvent to cast films and cured with moisture from the air.

When needed, moisture-cured systems were catalyzed with 1,4-diazo-bicyclo-[2,2,2]-octane.

Testing Procedures

TGA. Heat stability of unsupported films was measured by determination of the weight loss for 2 hr at 250°C in air in a du Pont thermogravimetric analyzer, Model 950.

Glass Transition Temperature. Determined with a du Pont thermo-mechanical analyzer, Model 940. Heating rate 20°C/min.

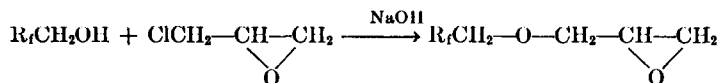
Gel Permeation Chromatography. Waters Associates, Model 100, tetrahydrofuran solvent.

RESULTS AND DISCUSSION

Preparation of Epoxides

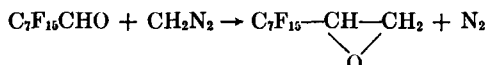
Glycidyl ethers were prepared from α, α, ω -trihydrododecafluoroheptanol, a tetrafluoroethylene telomer,¹⁵ and α, α -dihydropentadecafluorooctanol (Table I). Only the first glycidyl ether was fully evaluated since no difference in urethane properties between the two was found.

Originally, the glycidyl ethers were prepared according to the method of DeAcetis and Naps,⁶ in which the sodium alcoholate, prepared from sodium hydride and the fluoroalcohol, was reacted with an excess epichlorohydrin. Yields were around 50%–70%. The method was, however, lengthy and somewhat hazardous. As a result, the procedure for the preparation of glycidyl ethers with aqueous NaOH⁷ was modified to give better yields and used with the telomer alcohols.



Yields and purity were the same as when prepared by the sodium hydride method.

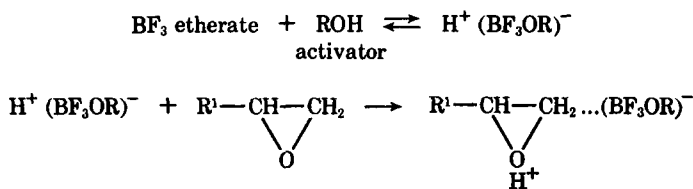
The pentadecafluoroheptylepoxyethane was prepared from perfluoro-octanal and diazomethane.⁴



Preparation of Triols

Homopolymer triols were prepared from the perfluoroalkyl glycidyl ethers by cationic polymerization with BF₃ etherate as catalyst and a calculated amount of glycerol as activator or chain initiator.

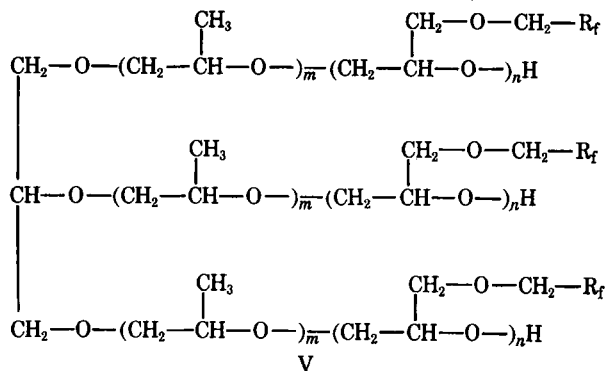
The initial step in the cationic polymerization of alkylene oxides⁹ is generally assumed to be the formation of a hydroxonium ion:



As the substituent R¹ becomes more electronegative, as in the series CH₃ < CH₂O < CF₂, it can be expected that the formation of the polymerization-initiating hydroxonium ion is accordingly less favored. It was found that the ease of polymerization decreased effectively in the series propylene oxide > glycidyl ethers > perfluoroalkyl epoxyethane. In fact, the latter compound would not polymerize with BF₃ etherate, and antimony pentachloride had to be used as catalyst.

The propagation reaction was assumed to occur as follows:

The same type block copolymers could also be obtained by oxyalkylating commercially available polyoxypropylene triols, prepared by anionic polymerization, with the fluoroalkyl glycidyl ethers, again with BF_3 etherate as catalyst. The structure of these copolymers are shown below (V).



In the above structure, $m = 1.98$ for Poly-G 430PG and $m = 5.4$ for Poly-G 1030PG; n varies between 0.37 and 2.94; $m + n =$ number of alkylene oxide units per triol chain.

Properties of Fluorourethanes

Adhesion to Anodized Aluminum

Sharpe and Schonborn¹² have, on the basis of theoretical calculations, predicted that fluorinated polymers should be universal adhesives because of their tendency to wet other surfaces very well (although the fluoropolymer surface itself has low wettability by other products). To measure adhesion, the fluorourethane prepolymers described were applied in a 1 × 6 in. strip

TABLE III
Adhesion and Urethane Composition^a

Number	Urethane no. (Table II)	TDI, %	Urea, %	Peel strength, lb/in.
1	3	11.7	2.4	1.6
2	5	16.2	3.3	2.1
3	4	21.6	4.4	2.5
4	2	28.5	5.8	8.0
5	1	31.2	6.4	7.0
6	Poly-G 1030-TDI-H ₂ O	26.0	1.5	1.2
7	Poly-G 1030-TDI-H ₂ O	34.3	6.8	9.0
8	Poly-G 1030-TDI-Ox.An. ^b	28.6	0	2.0
9	Poly-G 1030-TDI-Ox.An. ^b	28.6	0	0.8
10	Poly-G 1030-TDI-Quadrol	30.0	0	9.0
11	6	23.2	4.7	2.7

^a NCO/OH = 2/1 in all samples, except #6 with an NCO/OH = 1.2/1.

^b Ox.An.: Oxypropylated aniline.

to chromic anodized aluminum (2024 T3), cured by air moisture for two weeks, and the 180° peel strength was then measured (lb/in.). All prepolymers were made with TDI. Several nonfluorinated urethanes were included as shown in Table III. It was found that the peel strength correlated well with the percentage of urea groups counted as —NH—CO—NH—. Other correlations attempted failed to be valid for all data collected. When the logarithm of the peel strength was plotted as a function

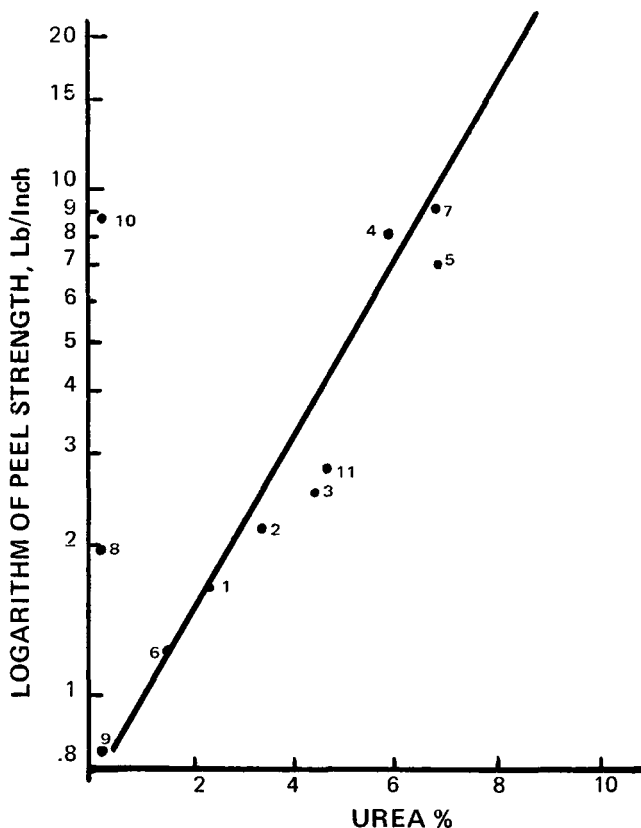


Fig. 1. Logarithm of the peel strength as a function of the urea content. TDI urethanes: (1-5) F-polyols; (6,7) 1030PG (NCO variable); (8,9) 1030PG, oxypropamine; (10) 1030PG, Quadrol; (11) F-epoxy polyol.

of urea content, a straight line was obtained (Fig. 1). The following conclusions could be reached:

1. In the range of 0% to 45% fluorine in the polymer, no dependency could be detected between adhesion and fluorine content.

2. When a triol was reacted with TDI in a 2/1 NCO/OH ratio, 1.5 urea linkages per triol were formed. When the ratio was 1/1, no urea linkages were formed. In Table III, #6, urethane was made at a 1.2/1 NCO/OH ratio. Its adhesion, expected to be around 6-8 lb/in., was only 1.2 lb. It was

concluded that urethane bonds did not contribute to the adhesion at all, only the urea bonds did.

3. Cure by Quadrol (oxypropylated ethylenediamine) produced films with no urea groups also. The adhesion was, however, very high. This might be attributed to the high basicity of the tertiary nitrogen groups introduced by the Quadrol. On the other hand, cure by oxypropylated aniline, containing aromatic tertiary nitrogen, did not produce good adhesion. Apparently, the basicity of these nitrogens was not high enough.

The perfluoroheptylepoxyethane-derived urethane fitted the curve also.

From unpublished data, it was found that prepolymers made with aliphatic diisocyanates, such as hexamethylene diisocyanate (HDI) or methylenebis-(4,4'-cyclohexylisocyanate) (H₁₂MDI) did not fit relationship and gave very poor adhesion. Urea groups formed by cure with methylenebis-(*o*-chloroaniline) were almost, but not quite, as effective as these formed by moisture cure.¹⁸

It was also noticed that very slow cure would increase the adhesion to some degree, possibly because prolonged mobility of the polymer molecules produced a higher number of bonds with the metal. To avoid fluctuations due to differences in cure rate, all systems in Table III had been catalyzed to produce a full cure within one day from application. The catalyst was 1,4-diazobicyclo[2,2,2]octane. The adhesion to Alclad aluminum was poor in all cases, which confirms the applicability of Pearson's principle of hard and soft acids¹³ to the case of adhesion. In fact, anodized aluminum, having an aluminum oxide surface, would produce bonds between a hard acid (Al³⁺) and a hard base (NH⁻). In Alclad aluminum, the much softer acid (Al⁰) should produce fewer or weaker bonds with the hard base.

Heat Stability

To gain some idea of the resistance of these fluorourethanes to heat, they were isothermally decomposed in air at 250°C for 2 hr by TGA. Two conventional urethanes were included also in this series. Care was taken to use, as much as possible, films of comparable thickness (10–15 mil).

By plotting the weight loss, in % of the original weight, as a function of the square root of time, the more stable systems showed a linear relationship between 5% and 30% decomposition (Fig. 2). For those systems decomposed beyond 30%, a linear relationship between weight loss and the logarithm of time was found (Fig. 3). The former type of relationship is generally interpreted as a decomposition process controlled by Fickian diffusion.¹⁴

By determining the time needed to reach 25% weight loss, it could be concluded that the decomposition rate was inversely related to the number of crosslinks per unit weight for three fluorourethanes (Fig. 4).

Since a trifunctional prepolymer will give a linear chain when two out of the three NCO groups react, the third NCO group should be counted as one half of a crosslink per mole prepolymer. The degree of crosslinking was thus calculated by dividing one half by the molecular weight of the pre-

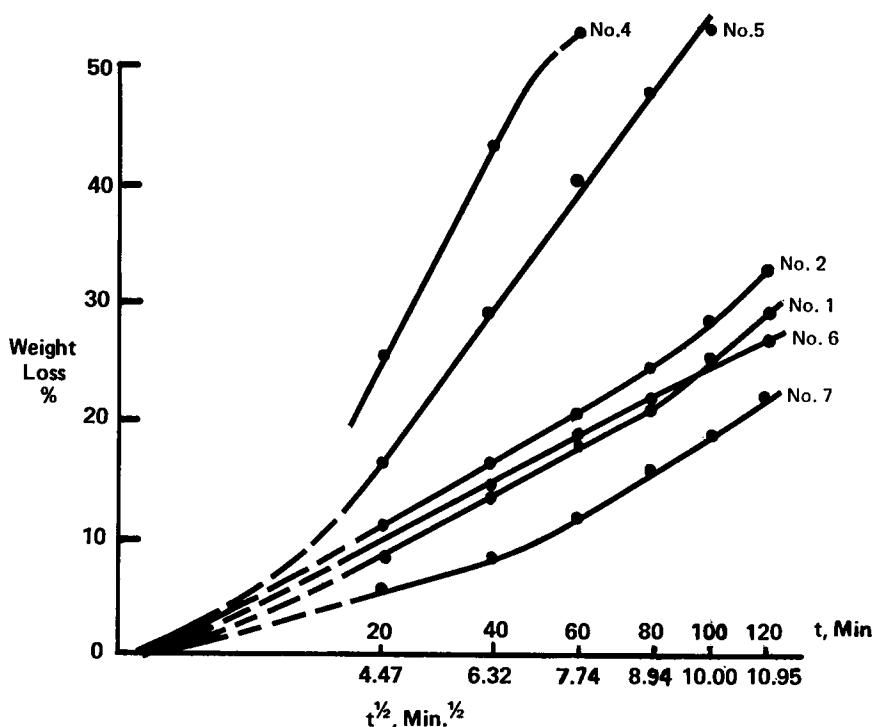


Fig. 2. Weight loss in per cent at 250°C as a function of the square root of time of polyurethanes in Table IV.

polymer (Table IV). The fourth fluorourethane did not fit the curve perfectly, most likely because the film was made without catalyst and took several days to cure. It seems reasonable to assume that the effective number of crosslinks is lower than the number calculated from stoichiometry. As a result, the decomposition rate was faster than expected. The conventional urethane gave a much lower decomposition rate than expected for its crosslink density. This was anticipated since the breaking of one ether bond in the fluorourethane will split off a fluoroalkyl glycidyl

TABLE IV
Heat Stability

Prepolymer no. (Table II)	Prepolymer MW	Crosslink/g $\times 10^4$	Time to 25% wt loss	T_g , °C
1	1580	3.17	100	+17
2	1840	2.72	83	+59
4	2420	2.08	20	-23
5	3210	1.56	34	-22
Poly-G 3030PG-TDI (6)	3520	1.42	100	-56
Poly-G 1030PG-TDI (7)	1520	3.29	147	+21
C ₇ F ₁₅ epoxyethane	2255	2.25	53	-51

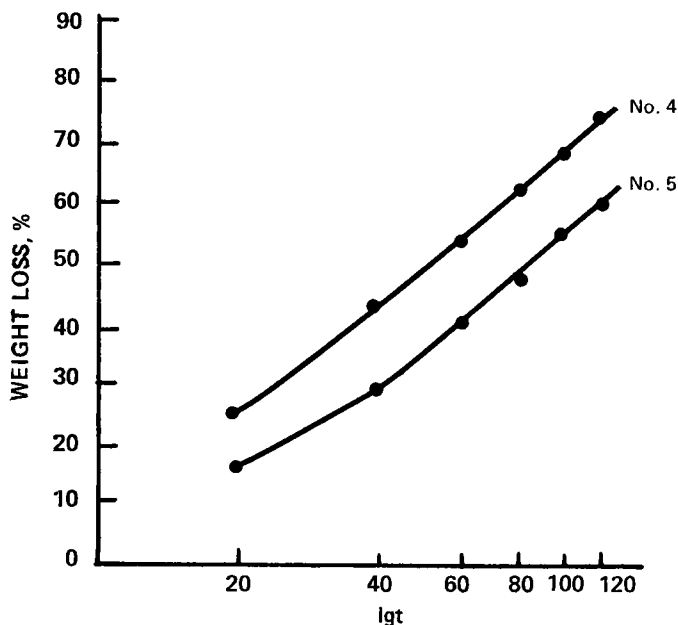


Fig. 3. Weight loss in per cent at 250°C as a function of the logarithm of time for polyurethanes in Table IV.

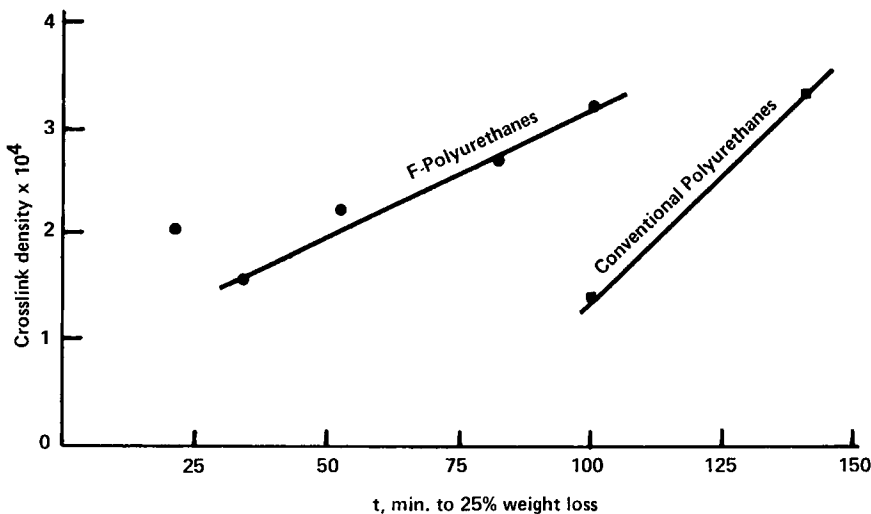


Fig. 4. Relationship between crosslink density and time to 25% weight loss (Table IV).

ether radical of molecular weight 380, compared to only 53 for the propylene oxide radical in the conventional urethane. The fluorourethanes seem to have lower heat stability, not so much because of lower bond strengths, but because of the heavier segments lost for every broken bond. The fluorourethane derived from the C_7F_{15} epoxyethane fitted the data of the other fluorourethanes, showing that the proximity of the CF_2 group to the backbone ether oxygen did not affect the heat stability.

Glass transition temperatures were measured by TMA and showed that, in general, the glass transition temperature decreased with the degree of crosslinking (Table IV). The tensile strengths and elongations varied between 350 psi and 350%, respectively for the lowest crosslinked urethanes to 5,000 psi and 50% for the highest crosslinked urethane. A urethane with medium crosslinking gave 1,500 psi tensile strength and 490% elongation.

Solvent resistance to aliphatic and aromatic hydrocarbons was improved for the fluoroalkyl glycidyl ether urethanes. Resistance to ethers, chlorinated solvents, or alcohols became a complex function of the degree of crosslinking and fluorination and depended also on whether the fluoroalkyl epoxy ethane was used or the fluoroalkyl glycidyl ethers.

This work was performed under Contract Numbers N0w-66-0323d, N00019-67-C-0339, and N00019-68-C-0166 for Naval Air Systems Command. We wish to thank Mr. J. Gurtowski of Naval Air Systems Command for his continued support in this work. We wish to thank also Messrs. J. E. Schingh and W. Glowa for their assistance in TGA and GPC analysis.

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Received August 7, 1969

Revised October 20, 1969