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AFRPL-TR-67-177

(Unclassified)

HIGH DENSITY, HIGH TEMPERATURE BINDERS FOR SOLID PROPELLANTS

R. A. Mitsch
J. R. Throckmorton
J. L. Zollinger
G.C. Britz

Minnesota Mining and Manufacturing Company

Final Report AFRPL-TR-67-177

1 October 1965 to 31 March 1967

Contract No. AF 04(611)-11200

May 1967

Air Force Rocket Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
Edwards Air Force Base, California 93523

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FOREWORD

(U) The work described in this report was performed under Contract No. AF 04(611)-11200, sponsored and administered by Air Force Rocket Propulsion Laboratory, Research and Technology Division, with Mr. James L. Trout and Mr. Robert E. Corley as Project Engineers.

(U) The photolytic polymerizations described in this report were performed by Dr. James R. Throckmorton, with non-technical assistance by Mr. Merritt L. Stigen. Potential curing reactions were studied by Dr. J. LaMar Zollinger, assisted by Mr. Wayne H. Swanson. Polymerization scale-up studies were carried out by Dr. Galen C. Britz with non-technical assistance by Mr. Gordon T. Frank.

(U) This report covers work conducted from 1 October 1965 to 31 March 1967.

(U) This report is classified CONFIDENTIAL because of performance data involved.

(U) This report has been reviewed and is approved.

W. H. EBELKE, Colonel, U.S.A.F.
Chief, Propellant Division

CONFIDENTIAL ABSTRACT

(U) The ultraviolet photopolymerization of perfluorooxydipropionyl fluoride, $O(CF_2CF_2CFO)_2$, to yield functionally-terminated poly(perfluorotetramethylene oxide) polymers is discussed, with attention given to factors influencing molecular weight, extent of branching, and functionality.

(U) Rate studies were carried out with model perfluorocarboxylic acids and various aziridines, epoxides, olefins, oxetanes, acyl pyrrolidines, and azetidines.

(U) Carboxyl-terminated poly(perfluorotetramethylene oxide) polymer was cured with epoxides, oxazolines and oxetanes.

(C) The high yield, room temperature catalytic trimerization of perfluoroalkanonitriles has been investigated in detail. A large number of organometallics were screened for catalytic activity. To date, the most effective catalyst is tributyl antimony oxide. Tributyl antimony oxide, in low concentration, effects quantitative trimerization of perfluoroalkanonitriles to perfluoroalkyltriazines in one day at room temperature. The thermal stability and redistribution of the resulting perfluoroalkyltriazines has also been studied.

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I. INTRODUCTION

(C) Under a contract[1,2] supported by the Air Force Materials Laboratory, Wright-Patterson Air Force Base, the 3M Company has developed a series of perfluoroalkylene oxide polymers containing the $-OCF_2CF_2CF_2CF_2-$ unit. These show excellent low- and high- temperature properties; the glass transition temperature for $\{OCF_2CF_2CF_2CF_2\}_n$ is below -65°C. (-85°F.), in differential thermal analysis in air (or in nitrogen) no change is noted below 380°C. (716°F.), and 10% weight loss in air is observed thermogravimetrically at 515°C. (959°F.).

(C) The density of the perfluoroalkylene oxide polymers permits one to achieve the minimum target density impulse of 510 seconds (with a calculated specific impulse of over 240 seconds) at a binder level of 27%.

(C) The perfluoroalkylene oxide polymers obtained in the earlier contract work had carboxyl-termination of at most about 1.0. The present report describes the preparation of such polymers with carboxyl-, ester-, and amide- termination of 2.0 and, with branched products still higher values by the solution photopolymerization of perfluorooxydipropionyl fluoride.

(U) Work on the curing of carboxyl-terminated poly(perfluoroalkylene oxides) has also been started. This report describes studies of potential curing reactions on model compounds with some effort devoted to polymers.

(U) A novel perfluoroalkanonitrile trimerization reaction involving the use of organometallic agents has been discovered. The various parameters of the reaction, including catalytic redistribution and properties of the resulting triazines, are discussed.

II. DISCUSSION

A. (U) MONOMER PURIFICATION

1. (U) Background.- Although the original work in the area of prepolymer preparation from oxygen-containing diacyl flourides was carried out on monomer of 80-85% purity, it waa immediately apparent that the monomer purity was an important variable in a syatematic study of photopolymerization. For this reason, a considerable amount of effort was devoted to perfluoroöxydipropionyl fluoride purification.

2. (U) Purification of $O(CF_2CF_2CFO)_2$ by distillation, b.p. 66-69°C./740mm., afforded a material of 73% purity (by vapor phase chromatography). This monomer resisted any significant increase in purity by repeated distillation. The F^{19} n.m.r. analysis showed $\underline{CF}$: $C\text{-}\underline{CF_2}$: $\underline{CF_2}O$ weight ratios of 1:3:2.4 rather than the required 1:2:2 weight ratios for pure monomer. In addition, preliminary infrared data suggested that the major portion of the impurity consisted of acyl fluoride containing species.

(U) The inability to purify perfluoroöxydipropionyl fluoride by distillation led to an investigation of purification by chemical methods. The procedure used here has been outlined and used successfully by others. In the present work, two fractions of perfluoroöxydipropionyl fluoride, b.p. 60-66°/740 mm. (about 60% by VPC) and b.p. 66-69°/740 mm. (about 73% by VPC), obtained by distillation were used. These fractions were hydrolyzed with water, the water solution treated with a dilute potassium hydroxide solution followed by solid calcium hydroxide, and filtered to give a solution of the acid salt. Distillation of the acid from a 36N sulfuric acid solution of the dried salt gave purified perfluoroöxydipropionic acid, b.p. 94-96°/0.3 mm. Purity was estimated to be better than 95%.

(U) The purified acid was converted to perfluorooxydipropionyl chloride (b.p. 76-77°C/150mm.) of 98% purity in yields of 80-85% by treatment with thionyl chloride using a pyridine catalyst.

(U) The final step in the chemical purification scheme was effected by the successful conversion of the diacyl chloride to perfluorooxydipropionyl fluoride in 92-93% yields by treatment with "anhydrous" potassium fluoride. The crude diacyl fluoride, as removed from the reaction mixture, was 94.1% pure as determined by vapor phase chromatography. The sample contains one major impurity (5.2%) and two minor impurities (totaling 0.7%). The F^{19} n.m.r. spectrum and mass spectrum of a pure sample of the major impurity are consistent for a diacyl fluoride isomeric with the desired monomer with the following structure, $OFCCF_2CF_2OCF(CF_3)CFO$

Thus, the isomeric diacyl fluoride monomer mixture, prepared by the chemical purification scheme, and capable of photopolymerization is 99.3% pure. Based on these results, it is apparent that a satisfactory monomer purification technique which should be applicable to large scale separations has been established. It is possible that the isomeric monomer mixture as obtained will prove to be advantageous in the polymerization by providing a limited, yet controlled, amount of branching, as well as a slightly decreased CF_2:O ratio in the polymer backbone. These modifications would be expected to improve the glass transition temperature.

B. (U) POLYMER PREPARATION

1. (U) Polymers from Perfluorooxydipropionyl Fluoride. - Recently Harris[3] has described the photolysis of monofunctional perfluoroacyl fluorides and has reported yields of up to 81% of the coupled products.

$$Cl(CF_2)_8\overset{O}{\overset{\|}{C}}F \xrightarrow{h\nu} \underset{(81\%)}{Cl(CF_2)_{16}Cl} + CO + COF_2$$

In addition, Harris[3] photolyzed perfluoroglutaryl fluoride and obtained what appeared to be the expected polymer although little characterization was attempted. As is apparent, this technique when applied to a perfluoro ether diacyl fluoride, either as a monomer or as a co-monomer with different perfluoro ether diacyl fluorides or other

perfluoro diacyl fluorides, may be expected to permit a study of the maximum variation in the CF_2:O ratio as well as lead directly to a prepolymer with a functionality of at least two. The perfluoro ether diacyl fluoride which is presently being investigated as a monomer for photopolymerization is perfluoroöxydipropionyl fluoride, $O(CF_2CF_2\overset{O}{\overset{\|}{C}}F)_2$.

(U) In the early phases of this program, in order to study the photopolymerization of perfluoro ether diacyl fluorides, perfluoroöxydipropionyl fluoride was purified by distillation, b.p. 66.5-67.0°/740 mm. Fluorine nuclear magnetic resonance spectra indicated the monomer to be about 80-85% pure. The contaminants, however, were indicated to be non-functional and were not considered to be harmful for the polymerization study. Subsequent studies on the purification of this monomer, as described in the preceding section, have indicated that the contaminants are, in fact, monofunctional acyl fluorides as well as isomeric difunctional acyl fluorides. Thus, the chemical purification scheme has been adopted as the method of choice although most of the studies described herein were carried out on monomer purified by distillation.

(U) The photopolymerization of dilute solutions (10-17%) of perfluoroöxydipropionyl fluoride in FC-75[4] solvent has been carried out over a temperature range of 0-105°C. The ultraviolet source was of the immersion type using a quartz insert and a Hanovia 450-watt lamp. The off-gases collected during the photolysis were identified as oxalyl fluoride primarily, with lesser amounts of carbon monoxide and carbonyl fluoride.

$$FC\overset{O}{\overset{\|}{C}}F_2CF_2OCF_2CF_2\overset{O}{\overset{\|}{C}}F \xrightarrow{h\nu} FC\overset{O}{\overset{\|}{C}}F_2CF_2\left[O(CF_2)_4\right]_n OCF_2CF_2\overset{O}{\overset{\|}{C}}F + FC\overset{O}{\overset{\|}{C}}F +$$

$$CO + COF_2$$

(U) The resultant poly(perfluorotetramethylene oxides) obtained after removal of the solvent under vacuum, are colorless, viscous liquids, generally soluble in all proportions in FC-75. Identification by infrared and F^{19} nuclear magnetic resonance spectra demonstrates the acyl fluoride termination. The resultant polymer possesses a certain amount of branching, the degree of which is to some extent dependent on the temperature of the photopolymerization.

(U) Hydrolysis, methanolysis, or ammonolysis of the acyl fluoride-terminated polymer affords the corresponding acid-, ester-, or amide-terminated poly(perfluorotetramethylene oxide).

$$O(CF_2CF_2\overset{O}{\overset{\|}{C}}F)_2 \xrightarrow{h\nu} \xrightarrow{ROH} ROC\overset{O}{\overset{\|}{C}}F_2CF_2\left[O(CF_2)_4\right]_nOCF_2CF_2\overset{O}{\overset{\|}{C}}OR$$

$R = H-, CH_3-$

$$O(CF_2CF_2\overset{O}{\overset{\|}{C}}F)_2 \xrightarrow{h\nu} \xrightarrow{NH_3} H_2N\overset{O}{\overset{\|}{C}}CF_2CF_2\left[O(CF_2)_4\right]_nOCF_2CF_2\overset{O}{\overset{\|}{C}}NH_2$$

(C) The low glass transition temperature (-80°F. to -58°F.) and relatively high thermal stability (10% weight loss by 476°F. in air) exhibited by samples of carboxyl-terminated poly(perfluorotetramethylene oxide) polymer prepared by the above process suggested that this area was worthy of continued investigation. Thus, during the past year, the photopolymerization of perfluoro-oxydipropionyl fluoride has been studied over a range of reaction conditions utilizing a number of different reactor modifications.

Table I contains typical results of photopolymerization of perfluorooxydipropionyl fluoride; photolysis time and temperature being varied. The results of photopolymerization with photolysis time as the only variable are also shown in a graphical form in Figure 1. All runs were carried out on an initial monomer charge of 25-30 g. In the initial experiments (runs 1 and 2) the acid fluoride groups were converted to the methyl esters, and the resultant mixture separated

Table I.

Photopolymerization Results
Perfluorooxydipropionyl Fluoride

Run No.	Radiation Time, Hours	Temp., °C.	$\bar{M}_n$	Additional Comments
1	3	105	950	Methyl esters separated by distillation
2	5	105	1510	Methyl esters separated by distillation
3	10	105	3700	Acid-terminated, functionality = 2.7
4	12	105	4900	Acid-terminated, functionality = 2.8
5	14	105	6800	Acid-terminated, functionality = 2.7
6	14	25	2700	Acid-terminated, no nitrogen purge, f = 2.5
7	20	25	3000	Acid-terminated, no nitrogen purge, f= 2.5
8	8	8	1800	Acid-terminated, nitrogen purge
9	11	8	4500	Acid-terminated, nitrogen purge
10	10	8	--	Amide-terminated

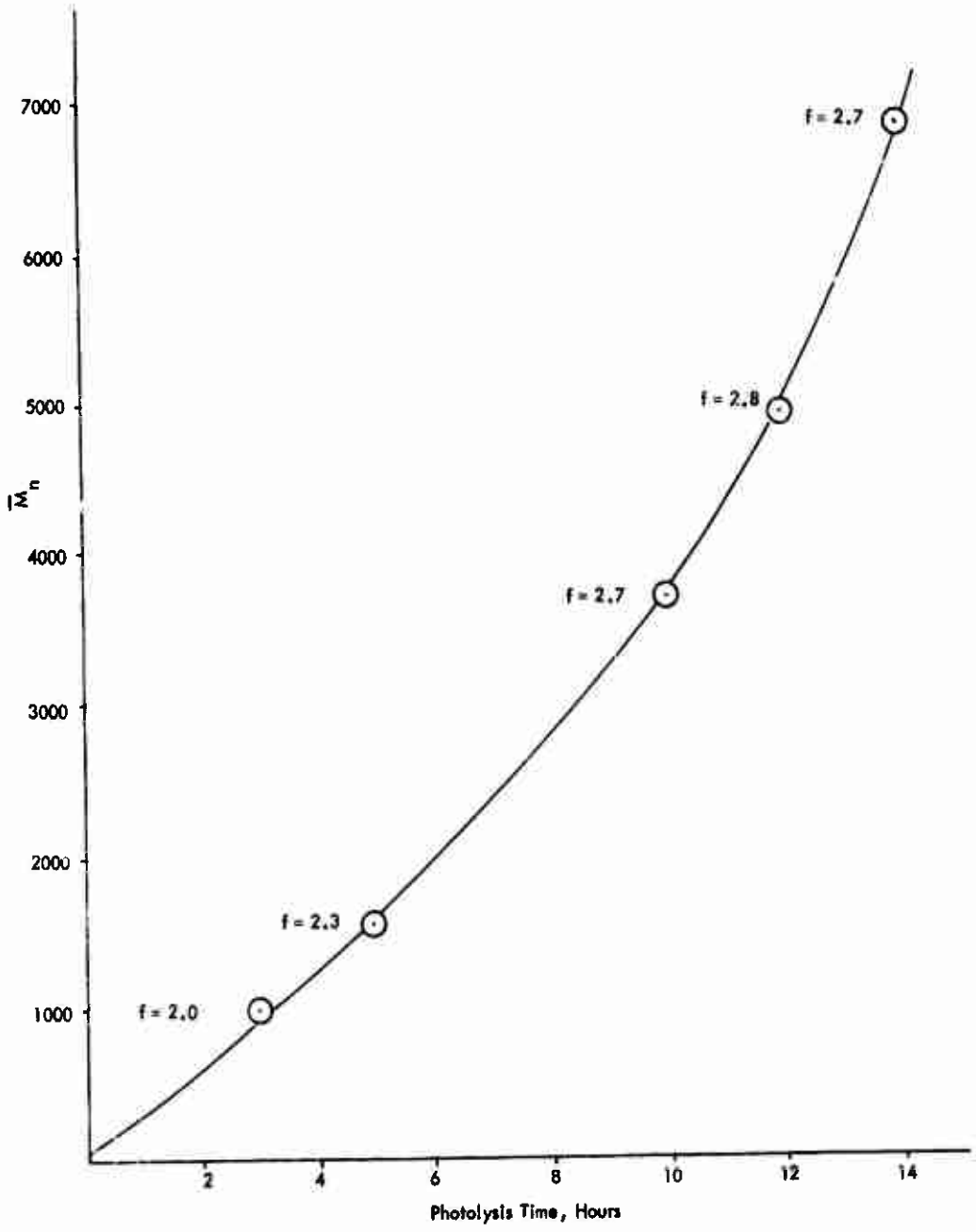


Figure 1. $\bar{M}_n$ vs. Photolysis Time (20-30 grams of monomer in 135 cc. of FC-75 at 100-105°C.)

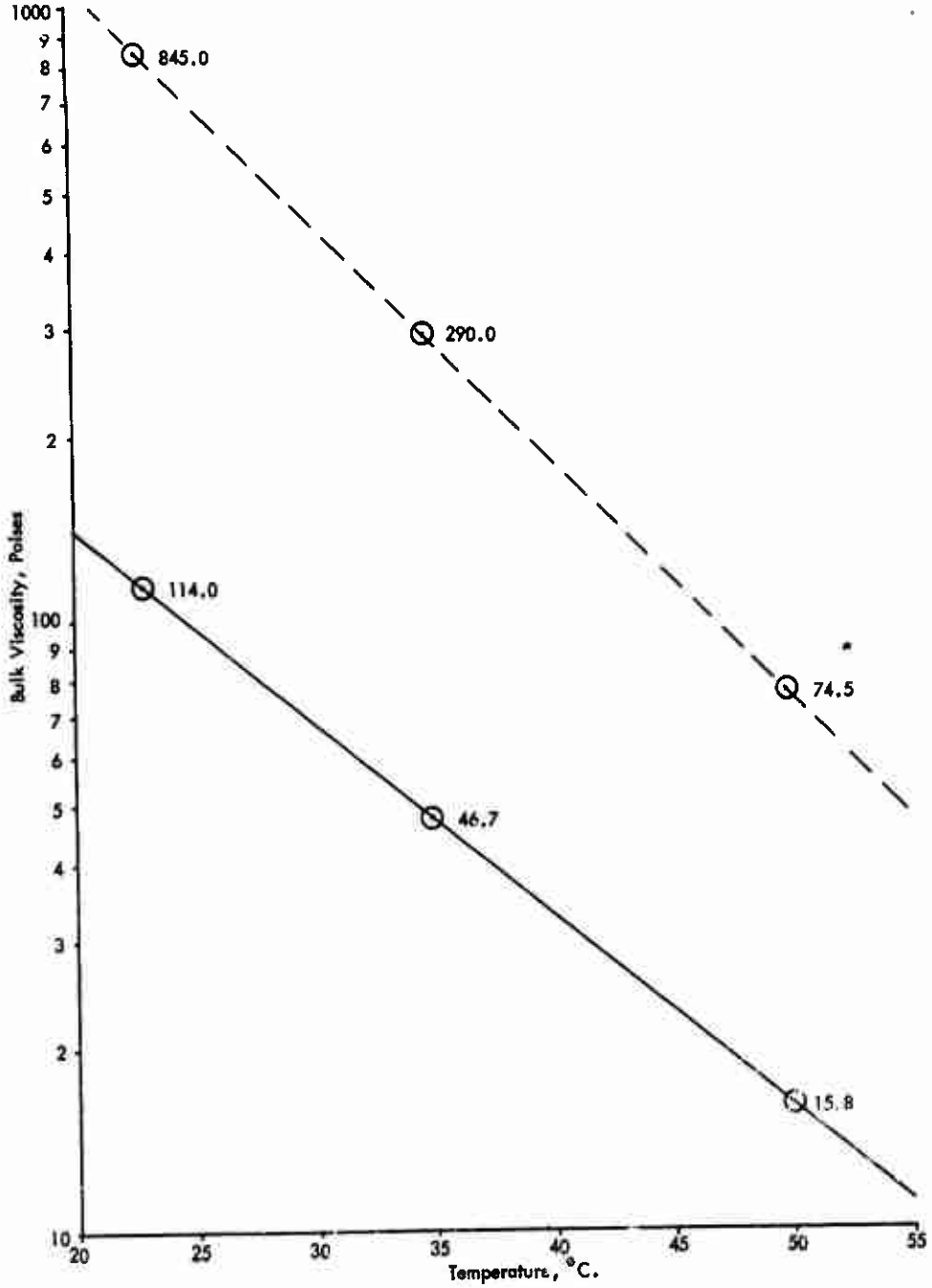


Figure 2. Bulk Viscosity of Perfluoropolyethers vs. Temperature
(——: $\bar{M}_n$ = 3100, f=1.9; – – –: $\bar{M}_n$ = 6800, f=2.7)

by distillation. In runs 3 and 4, hydrolysis was used to convert the polymeric acyl fluoride to the acid directly.

(C) Differential thermal analysis and thermogravimetric analysis have been obtained on the crude, uncured acid-terminated polymer from the ten hour photopolymerization ($\bar{M}_n$ = 3700, functionality = 2.7). The T_g of this sample was -59° to -46°C. (-74° to -51°F.). The sample showed 10% weight loss by 260°C. (500°F.) in air which undoubtedly represents the temperature at which the fluorocarbon acid (uncured) undergoes decarboxylation.

(U) The bulk viscosities of typical acid-terminated perfluorotetramethylene oxide polymers, $\bar{M}_n$ = 3100, functionality = 1.9, and $\bar{M}_n$ = 6800, functionality = 2.7 have also been measured and are shown in Figure 2. Note the relatively large viscosity-temperature coefficient indicated by the slope of the lines.

(U) As is evident from the results shown in Table I, the crude polymer has a functionality greater than two and apparently has a certain amount of branching. Area measurements of the F^{19} n.m.r. spectra peaks afford added confirmatory evidence for the presence of branching.

(U) Although branching is indicated in the crude polymers obtained via photopolymerization, separation of the more nearly linear polymer from the more highly branched material can be accomplished by a simple solvent extraction with Freon-113. The results of this extraction technique with the crude acid terminated polymer from run 3 ($\bar{M}_n$ = 3700, functionality = 2.7) and run 4 ($\bar{M}_n$ = 4900, functionality = 2.8) are shown in Table I below. The columns in Table II show percent extracted, as well as the $\bar{M}_n$ and functionality of each fraction.

Table II. Extractions of Polymers

	Run 3	Run 4
1st Extraction*	52% extracted $\bar{M}_n$ = 2500 Functionality = 1.9	46% extracted $\bar{M}_n$ = 3100 Functionality = 1.9
2nd Extraction	12% extracted	9% extracted $\bar{M}_n$ = 4100 Functionality = 3.1
Residue	36% $\bar{M}_n$ >10,000 Functionality >8	45%

*10-15 cc. of Freon-113 per gram of polymer at 23° C.

(U) The aforementioned branching in the photopolymerization of perfluorodiacyl fluorides has been thought to arise by reaction (3) in the following scheme although recent spectroscopy results have not afforded confirmatory evidence for this speculation. The desired coupling for polymerization is shown by reaction (2).

$$R_f\overset{O}{\overset{\|}{C}}F \xrightarrow{h\nu} R_f\text{-}\overset{O^*}{\overset{\|}{C}}\text{-}F \longrightarrow R_f\cdot + \cdot\overset{O}{\overset{\|}{C}}F \longrightarrow F\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}F \qquad (1)$$

$$R_f\cdot + R_f\cdot \longrightarrow R_f\text{-}R_f \qquad (2)$$

$$R_f\cdot + F\overset{O}{\overset{\|}{C}}\text{-}R_f \longrightarrow R_f\text{-}O\text{-}CFR_f \xrightarrow{R_f\cdot} R_f\text{-}O\text{-}\underset{R_f}{\overset{\cdot}{C}}FR_f \qquad (3)$$

If the above has any factual basis as a reprcsentation of the reactions involved in the photopolymerization, changing the temperature, the concentration, or both in the reaction may be expected to decrease the extent of branching. The activation energy of the radical coupling reaction (reaction 2) would be expected to be near zero whereas reaction (3) should have a definite activation energy. Thus, we would expect that the amount of branching could be decreased considerably by carrying out the photopolymerization at a much lower temperature.

(U) By means of experiments at 8 and 25°C., it was found that lowering the reaction temperature does indeed reduce the amount of branching. Although the functionalities of the crude polymer obtained at room temperature still suggest branching, the functionality of the crude polymer is less (2.5 vs. 2.7). However, more meaningful are the results of extraction experiments. The ability of Freon-113 to separate the more nearly linear polymer from the highly branched material has been discussed above. Thus, extraction with Freon-113 removed 46% of carboxyl-terminated polymer of $\bar{M}_n$ = 3100 and a functionality of 1.9 from a crude polymer of $\bar{M}_n$ = 4900 and a functionality of 2.8. In all samples extracted to date, only 46-55% of the crude polymer obtained from photopolymerization at 105° was soluble in Freon-113. On the other hand, polymerization at 25° resulted in a polymer of which 61-82% was soluble. See Table III for typical examples. Thus, 75% of the crude acid-terminated polymer from run 7 ($\bar{M}_n$ = 3000, f = 2.5) was soluble in the first extraction with Freon-113. The extracted polymer was found to have a $\bar{M}_n$ of 2400 and a functionality of 1.8.

Table III. Polymer Extraction Results

Run*	3	4	5	6	7
Temp.	105	105	105	25	25
$\bar{M}_n$	3700	4900	6800	2700	3000
f	2.7	2.8	2.7	2.5	2.5
% Extracted**	52	46	55	75	75
$\bar{M}_n$	2500	3100	3000	2000	2400
f	1.9	1.9	2.2	1.8	1.8

* Run numbers refer to Table I

** 15 cc. Freon-113 per gram of polymer.

(U) Lowering the reaction temperature to decrease the amount of branching was not without difficulties, however. At the lower reaction temperatures, problems were experienced with removal of the volatile by-products, such as oxalyl fluoride. As a consequence, radical recombination and solvent-cage effects presumably resulted in an inefficient system and yielded molecular weights of less than 3000 even after extended photolysis periods. Thus, after 14 hours of photolysis at 25°, a $\bar{M}_n$ of 2700 was achieved, whereas at 105° the same photolysis time afforded a polymer of $\bar{M}_n$ = 6800.

(U) This difficulty has been circumvented to a certain degree by purging the reaction with dry, oxygen-free nitrogen during polymerization. The results of the nitrogen purge can be shown by a comparison of runs 6 and 9 (Table I). In run 6, 14 hours of photolysis at 25° (without nitrogen purge) gave a polymer of $\bar{M}_n$ = 2700, whereas in run 9, 11 hours of photolysis (with nitrogen purge) at a lower temperature

resulted in the formation of a polymer with a $\bar{M}_n$ of 4500. The reactor modification to permit the use of the nitrogen purge also allowed slightly larger polymerization runs to be made.

(U) Attempts to demonstrate reproducibility in polymer preparation using the nitrogen purge system have indicated the need for close control of reaction variables, especially the nitrogen-purge flow rate, monomer charge, and photolysis time. Although carboxyl-terminated polymers with molecular weights in the 3000 to 4500 range were readily prepared, molecular weights of 5000 to 10,000 have been more difficult to achieve. High molecular weight semi-solid, elastomeric gels occurred in two cases, in which a high nitrogen purge flow rate and a monomer charge 10% less than normal were utilized. These results strongly indicate the need for a means of monitoring the molecular weight of the polymer during polymerization. To this end, inherent viscosity, infrared, and measuring the amount of, and nature of the reaction volatiles are under study. For larger polymerization runs, it will be very desirable to have the capability of following the $\bar{M}_n$ during polymerization.

(U) One final reactor modification, which eliminates the need for a nitrogen purge during photopolymerization has been incorporated into the system during the present reporting period. The photopolymerization was carried out essentially as described above at 8-10°C. with a reactor modified to contain an inlet and outlet port for pump circulation of the reaction mixture. The experimental data from each run carried out and the properties of the 100 g. blend of polymer which was transmitted to our subcontractor, Allegany Ballistics Laboratory, are summarized in Table IV. In all cases, hydrolysis of the resulting acyl fluoride-terminated polymer was used to prepare samples with carboxyl-termination.

(U) The yields of polymer shown in Table IV, considering the monomer purity problems discussed above, appear to be nearly quantitative. However, expected trends between exposure times, molecular weights, and functionality of polymer are absent. Curiously, attempted extraction of linear polymer from the crude carboxyl-terminated polymer with Freon-113 gave polymer

having in some cases a higher molecular weight and functionality than the crude. This was suspected to be due to incomplete hydrolysis of the original acyl fluoride-terminated polymer by the relatively small volume of water used. Slow hydrolysis of the unconverted acyl fluoride groups by atmospheric moisture in subsequent operations could then be expected to give hydrogen fluoride which would give a disproportionate decrease in the acid equivalent weight and an increase in the functionality. Recently, however, a small portion of the polymer blend in a small amount of FC-75 was washed thoroughly with 200 ml. of water overnight. The polymer was worked up as described above and then extracted with Freon-113. Only a small trace of material failed to dissolve. The Freon-113 soluble material had a $\bar{M}_n$ of 2200 and a functionality of 3.2 (triple check) which is essentially the same as reported in Table IV.

(U) Fluorine n.m.r. analysis of the untreated polymer blend showed a $-\underline{CF_2}O- \cdot -\underline{CF_2}\overset{O}{\overset{\|}{C}}-$ weight ratio of about 3 to 1 and several peaks which have been attributed to cyclic structures. A linear polymer of $\bar{M}_n$ = 2200 would require a weight ratio of about 10:1. Thus, the n.m.r. analysis as well as the functionality indicate the polymer had some degree of cross-linking. The apparent lack of methine fluorine absorption indicates that the dominant cross-linking reaction may not be attack of a carbonyl oxygen atom by a perfluorocarbon radical as previously suspected.

(U) In order to determine the cause of the faint cloudiness associated with some of the polymer samples, a sample was analyzed for water and trace metal content. Metal analysis showed only 4 ppm magnesium, 80 ppm silicon, 2 ppm aluminum, 7 ppm calcium, 8 ppm sodium, and 7 ppm potassium. Thus, formation of metal fluorides by attack of hydrogen fluoride on the glassware followed by dissolution of the metal fluorides in the polymer does not appear to be significant. The sample also contained 0.4% water which may account for the faint cloudiness observed in this and other polymers obtained by this process. In most cases, the cloudiness could be removed by repeated treatment with sodium sulfate in warm FC-75 solution.

Table IV. Photopolymerization Results

	Run Number							
	3	4	7	9	5	8	10	6
Monomer Charge	34.5 g.	32 g.	30 g.	50 g.	50 g.	50 g.	50 g.	50 g.
Exposure time (hr.)	4	5-5/6	6	8	8-1/4	8-1/4	8-1/2	9
Weight $R_f(COF)_2$	17	19.5	21	27.5	28.4	30.5	27.7	-
Weight $R_f(CO_2H)_2$	8.5	14.5	17	24.3	14.0	18.6	25.3	23
Properties								
$\bar{M}_n$	1000	1250	2000	1800	1230	1540	2200	980
f	1.8	2.0	3.3	3.0	1.9	2.4	3.3	1.6
$<n>$	0.014	0.019	0.012	0.019	0.018	0.018	0.026	0.024
Lineor								
$R_f(CO_2H)_2$	8.5g.	11.4g.	11 g.	16.4g.	12.7g.	15 g.	15 g.	15 g.
extracted	100%	91%	73%	72%	90%	90%	63%	70%
Properties								
$\bar{M}_n$	1000	1800	1800	1500	1500	1560	3000	1500
f	1.8	2.7	2.8	2.7	2.3	2.4	4.6	2.3
$<n>$	0.014	0.018	0.019	0.013	0.016	0.017	0.016	0.017
Residue	-	0.5	4.2	5.9	0.5	1.0	5.0	6.1
Blend of lineor	$\bar{M}_n$ = 2,200; f = 3.4; $<n>$ = 0.014; T_g -80° to -58°F; 10% weight loss by 476°F. in oir.							
Blend of residue	$\bar{M}_n$ = 3,300; $<n>$ = 0.02; f = 4.7							

2. (U) Polymer Scale-Up

(U) Scale-up of the photopolymerization of perfluoro-oxydipropionyl fluoride has been initiated.

(U) Data for the preliminary photopolymerization experiments run during this reporting period are tabulated in Table V. The main purpose of these experiments was to check out the apparatus and gather engineering scale-up data. While only a limited amount of scale-up information was gained, the techniques for handling the monomer and the polymer workup procedures were established.

(U) The monomer (perfluoro-oxydipropionyl fluoride) is easily hydrolyzed and has a pungent odor. Therefore, pipetting it into the reactor, as was done in the first two runs, is undersirable. A standard monomer charging procedure, in which the monomer is distilled directly into the reactor, has been devised. The distillate receiver consists of an accurately calibrated buret so the monomer can be accurately metered into the reactor.

(U) The 100-ml. reactors have a nitrogen purging tube and an outlet arm which can be connected to a condenser. The nitrogen purge serves two purposes - to agitate the solution and to help expel the by-product oxalyl fluoride. In the first two runs the nitrogen purge rate was too fast because some FC-75 escaped through the condensers. The last two runs were made with a much slower purge rate and with new, more efficient condensers. Even with these changes, some of the FC-75 was carried over into the cold trap. All of the reactions were carried out with a 550-watt ultraviolet lamp.

The polymer workup procedure on the first three runs was:

1. Heat reaction solution to drive off trapped oxalyl fluoride or unreacted monomer.
2. Add water and hydrolyze by refluxing.
3. Separate the water and FC-75 phases.

Table V

Run No.	Monomer (gm)	Concentration (Wt.%)	Acid Terminated Polymer H_2O Phase	FC-75 Phase	Total	% Yield	Time (hr.)	Temp. (°C.)	N_2 Flow Rate (liters/hr.)
1T	15.9	10.1	----	0.6	0.6	6.1	7.0	97	0.4
2T A	5.3	5.0	1.9	0.2	2.1	63.7	8.0	20	0.2
B	10.5	10.0	3.9	0.3	4.2	64.3	8.0	20	
C	47.7	48.7	12.2	0.2	12.4	41.8	8.0	20	
D	10.5	10.0	2.5	0.2	2.7	41.4	8.0	20	
3T	10.6	10.0	5.8	0.5	6.3	95.5	11.0	20	0.05
4T A	15.9	10.1	----	----	8.5	86.1	12.0	37	0.05
B	15.9	10.1	----	----	9.7	98.3	12.0	37	0.05

(Unclassified)

4. Strip the solvent from each phase on a roto-vac.
5. Dissolve in ether, then strip off the ether.

The water phase always contained more material than the FC-75 phase, but the FC-75 phase was more viscous. The weight of the water phase reported in Table V includes a white solid material. An analysis of this material from Run 3T showed that its equivalent weight is 680. Further analyses to completely characterize the material will be made. The workup procedure for Run 4T was changed. Instead of separating the two phases after hydrolysis, the solution was filtered and then the entire solution was stripped.

Referring to Table V, Run 1T was made to test the apparatus and see if polymer could be made in it. Run 2T was for the same purpose, but we also hoped to see a concentration effect. Unfortunately, our controls and procedures were poor and no useful information about concentration was gained. Results from the first two runs indicated low $\bar{M}_n$ polymer. Run 3T was photolyzed for 16 hours in an attempt to increase the $\bar{M}_n$ by longer U.V. exposure. The polymer in the water phase had an $\bar{M}_n$ of about 1000 and a functionality of about 2.8. This weight was lower than desired and possibly was caused by the inefficient use of the U.V. light in the reactor setup. In the present setup the four 100-ml. reactors surround the U.V. lamp and are equidistant from it. An immersed light source is more efficient, but before changing to this design concept Run 4T was made with the reactors one-half inch closer to the lamp. The original center-to-center distance between the lamp and reactor was 2-5/8" as compared to 2-3/16" in Run 4T. Two reactors were used in Run 4T to check reproducibility. The reproducibility was satisfactory, $\bar{M}_n$ = 772 and f = 2.1 for 4TA and $\bar{M}_n$ = 660 and f = 2.3 for 4TB. However, the molecular weight was still low.

(U) Recognizing the need for the development of a technique to follow large scale photopolymerization reactions, vapor phase chromatography, infrared, and refractive index have been examined.

(U) The collection of gas samples periodically during the polymerization was not effective. The amount of oxalyl fluoride in each sample was so small that it could not be measured accurately by vapor phase chromatography.

(U) On the other hand, infrared and refractive index look promising. Liquid samples were withdrawn with a syringe in Run 4T. The solution (1 cc.) was added to 2 cc. of methyl alcohol. After esterifying the polymer, the solvent was pulled off with a vacuum. Both infrared and refractive index measurements were made on the samples. The rate of end-group disappearance was measured by plotting the ratio of the ester peak at 5.6 microns to the C-F penk at 8.3 microns versus time (Figure 3). The refractive index of the esterified polymer is plotted as a function of time in Figure 4. Additional data is necessary before conclusions concerning the use of these can be made.

(U) The advantages of the 100-ml. reactor apparatus may be offset by its disadvantages. The advantages of the apparatus are the small monomer charge and the ability to run four levels of a variable simultaneously. The primary disadvantage is the inability to use the U. V. lamp effectively because it is located outside of the solution rather than being immersed in it. This is evident by the low $\bar{M}_n$ polymers that have been made to date. Another problem has been the small amount of polymer available for workup due to the small sample size.

(U) New reactor designs are being contemplated and may be used if higher $\bar{M}_n$ polymer cannot be obtained with the present apparatus. In addition, it remains to establish reproducibility in photopolymerizations, correlate a physical property measurement to the desired polymer properties, establish the effect of variables on photolysis and to produce quality polymer on a large scale.

3. (U) Nitrile-Termination.

(U) In view of the discovery of an excellent nitrile-trimerization catalyst, reported in a later section, work has been initiated to prepare nitrile-terminated

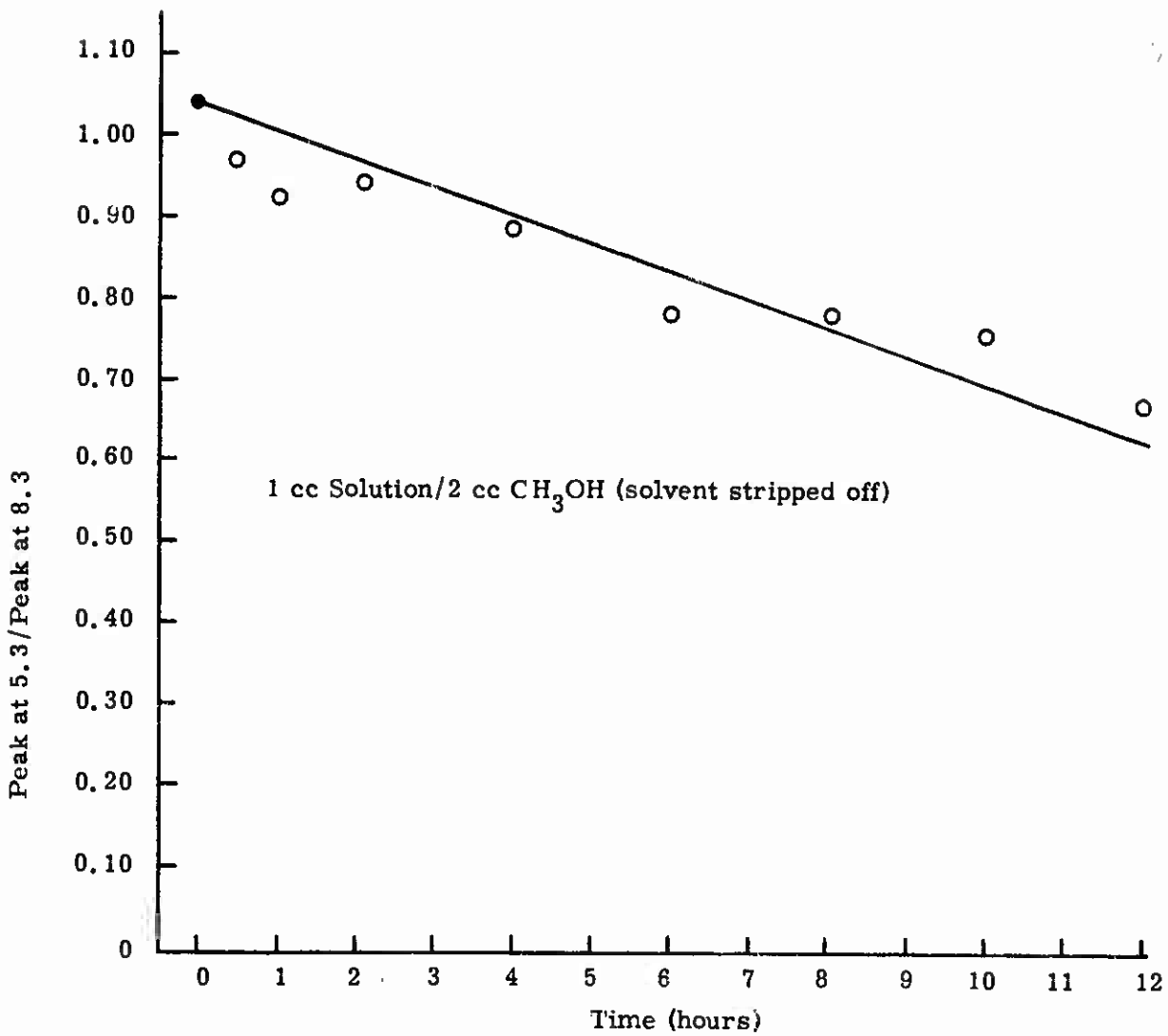


Figure 3. Rate of End-Group Disappearance (I.R. Data: Ratio of $\overset{O}{\overset{\|}{C}}-OCH_3$ Peak to C-F Peak)

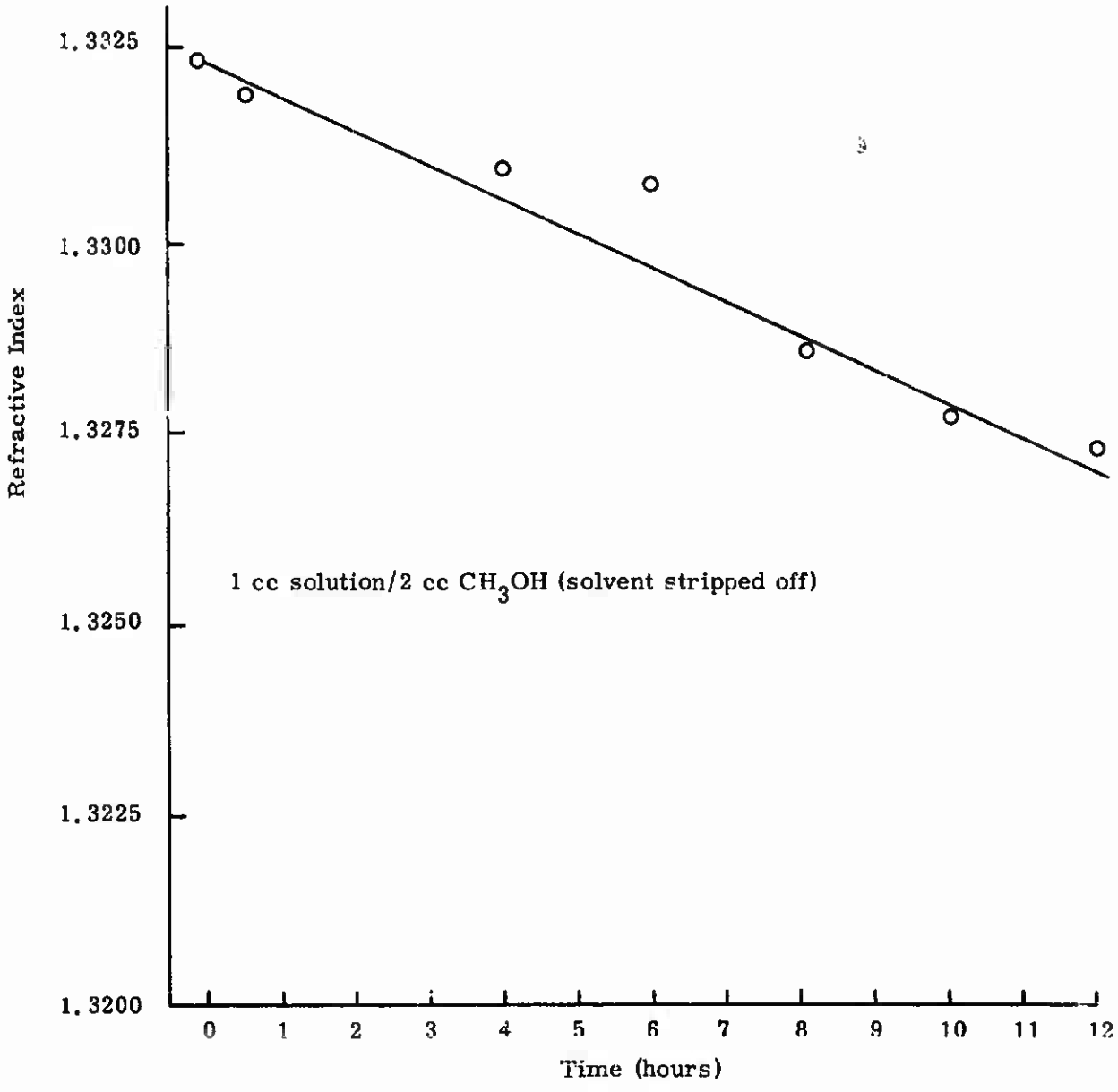


Figure 4. Refractive Index as a Function of Photolysis Time

polyperfluoroethers. Photopolymerization of perfluorooxydipropionyl fluoride followed by bubbling ammonia gas through the crude polymer mixture has afforded the corresponding amide-terminated polymer. Both the polymer and ammonium fluoride precipitate from the reaction mixture. Removal of the salt is readily accomplished by washing with water. Two attempts at dehydration by means of P_2O_5 have led, at best, to a low conversion to nitrile-terminated polymer.

$$H_2N\text{-}\overset{O}{\overset{\|}{C}}CF_2CF\left[O(CF_2)_4\right]_nOCF_2CF_2\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow[-H_2O]{P_2O_5} N{\equiv}CCF_2CF_2\left[O(CF_2)_4\right]_n$$

$$-OCF_2CF_2CN$$

(U) Perhaps of more interest would be the sequence of photopolymerization to afford acyl fluoride-terminated polymer followed by the addition of N_2F_4 and continued photolysis.

$$-O\text{-}CF_2CF_2\overset{O}{\overset{\|}{C}}F \xrightarrow[h\nu]{N_2F_4} -OCF_2CF_2NF_2 \xrightarrow{\phi_3P} -O\text{-}CF_2CN + \phi_3PF_2$$

Defluorination could then be accomplished by means of a reducing agent such as triphenyl phosphine or dicumene chromium.[5] Experiments to this end are in progress.

4. (U) Future Work. - Larger amounts of polymer will be prepard so that the subcontractor, Hercules Powder Company, may study the material at the Allegany Ballistics Laboratory facilities.

(U) The most economical and efficient way to improve on the method of preparation of prepolymer appears to be through a factorial design experiment. A modified design has been suggested in which the complete factorial experiment is restricted in certain well-defined ways. This design will cover the four variables; concentration, nitrogen purge rate, exposure time, and temperature, each at five levels.

(U) Computer analysis of the data from the factorial experiment will be possible using a preselected computer program set up in conjunction with the design. The computer analysis will yield the effect of a change of each variable on the polymer properties, the possible ways this effect may be modified by variation of another variable, and measure the effects of any complex interactions between variables.

(U) The four variables presented above and their importance in affecting polymer properties have been discussed in previous reports. The assignment of a range of values for exposure time, temperature, and nitrogen purge rates would appear to be possible utilizing the data from these previous photopolymerization studies. A few initial probes at various concentrations should serve to fix the concentration levels.

(U) A second approach which has not yet been completely ruled out is a graphical approach. Essentially the graphical method would approach the experiment in a biased manner based on previous experimental data and experience. Data from each individual run would be plotted on a graph so that a step-by-step progression could be seen. Undesirable levels of concentration, temperature, etc., if chosen, could then be eliminated at the outset and new levels incorporated.

(U) The polymer properties which we initially plan to follow are as follows: number-average molecular weight, viscosity, functionality, thermal stability by thermogravimetric analysis, and glass transition temperature by differential thermal analysis. Ultimately, computer analysis or graphical analysis of the data relating polymer properties to a change in level of the factors will allow a choice of reaction conditions to produce a polymer with specified properties.

(U) Increasing attention will be directed toward the preparation of nitrile-terminated polymer, either by introduction of nitrile groups during the polymerization, or by conversion of polymers with other termination.

C. (U) CURING STUDIES

1. (C) Discussion. - A satisfactory curing agent for the present work should meet several requirements. It should:

a. Give elastomers having the desired physical properties, including a glass transition temperature of -75°F.
b. Give thermally stable cures. (The cross-link site is considered the weakest point in fluorocarbon polymer vulcanizates.[8])
c. Cure at a reasonable rate and temperature. (The rate of cure of the liquid polymers should be slow enough at the usual processing temperature (120-140°F.) to allow formulation with about 80% solids and still give a castable system.) Should cure below 350°F. and at or near room temperature, if possible.
d. Permit good cures in the presence of ammonium perchlorate and aluminum (as well as in the unfilled polymer).
e. Give elastomers whose physical properties do not change appreciably with age under the conditions of ultimate use. (Should have good thermal and hydrolytic stability.)
f. Yield bubble-free cured binder. (The curing reaction should preferably not eliminate a volatile product.)
g. Be commercially available or conveniently synthesized.

(U) The types of functional groups available in the prepolymer include the acid fluoride obtained in the initial process and many of its derivatives. A partial list of these derivatives with possible curing agents are outlined in Table VI. Since the initial acid fluoride terminated polymer is sensitive to moisture, conversion to the acid is usually carried out. Thus, initial curing studies with the polymer involved reactions with acid end groups.

Table VI
Types of Possible Curing Agents

Functional Groups in Polymer		Possible Curing Agents
Acid fluoride	$R_fC(=O)F$	Polyols, polyamines
Acid	$R_fC(=O)OH$	Epoxides, acyl aziridines, metal salts, polyols, olefins
Esters	$R_fC(=O)OR$	Polyamines, polyols, 3,3'-dihydroxybenzidine (benzoxazole formation)
Amides	$R_fC(=O)NHR$	Acylaziridines (?)
Nitriles	R_fCN	3M Catalyst System (Gives triazines)
Alcohols	R_fCH_2OH	Diisocyanates

(U) The approach used in selecting satisfactory curing agents was to screen likely systems using model compounds. Promising candidates were tested out with the prepolymer itself. Perfluorobutyric acid (PFBA), b.p. 120°C., and perfluoropropionic acid (PFPA) were selected as models to represent the carboxyl-terminated fluorocarbon polymers. Reaction rates between PFBA and PFPA and possible curing agents were studied by titration techniques and proton n.m.r. spectroscopy. Infrared and gas chromatographic data were also used for following the extent and course of reactions.

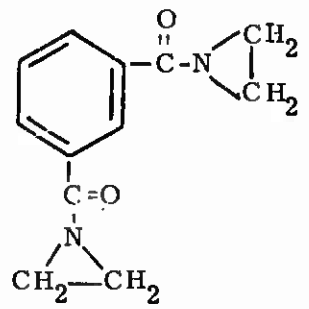
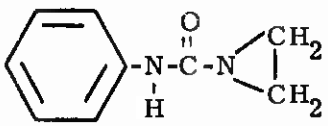
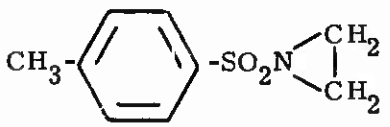
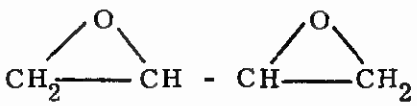
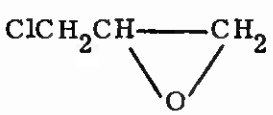
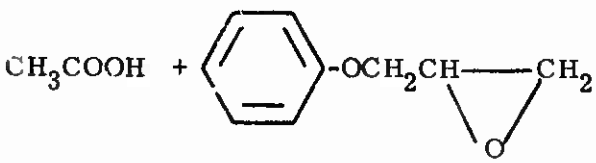
2. (U) Model Compounds. - Model compounds with several types of functionality have been studied. Potentiometric titration, H^1 n.m.r. and gas-liquid chromatographic analysss were used to follow the rates of reaction.

(U) Perfluorocarboxylic Acids with Aziridines. - Four acyl aziridines N,N'-bis(ethylene)-isosebacamide (HX-740), N,N',N''-tris(1,2-butylene)trimesamide (HX-868), N,N'-bis (ethylene)isophthalimide (HX-742) and N-phenyl-N'-ethyleneurea were reacted with PFBA and/or PFPA at room temperature. In all cases, an exothermic reaction ensued and 60-80% of the fluorocarbon acid was consumed within a few minutes with no further loss of acid on standing. H-n.m.r. obtained within a few minutes after mixing revealed complete opening of the aziridine ring. N-(p-toluene-sulfonyl) aziridine reacted with PFPA at a slower rate, but still very rapidly compared with epoxy compounds, so that the reaction could be followed by H-n.m.r. analysis. These data are presented in a tabular form in Table VII.

(U) Perfluorocarboxylic Acids with Epoxides. - The reaction of epoxy compounds with perfluorobutyric and propionic acid was found to be quite rapid, as measure by titrating unreacted acid, when compared with published data for hydrocarbon aliphatic acids and epoxies. Precise rate results confirmed the results for acid consumption but indicated a faster rate for epoxy reaction. Both unreacted acid and oxirane groups were determined by potentiometric titration techniques. Figure 5 shows the reaction of 0.50 N glycidyl phenyl ether with two concentration levels of acid and demonstrates that a small amount of catalytic polymerization of epoxide was taking place. The opening of the oxirane ring was also followed by H-n.m.r. analysis. When the n.m.r. probe was cooled from the usual 43°C. operating temperature to 25°C., excellent agreement was obtained for these different analytical procedures for determining epoxy content

Table VII

Reaction Rates of PFPA with Aziridines and Epoxides

Ring Compound	Temp.	$T_{1/2}$
	25°	1 min.
	25°	1 min.
	25°	24 min.
	25°	2.8 hrs.
	25°	9 hrs.
	25°	13 hrs.
	125°	350 hrs.

(Figure 6). The rates of oxirane ring opening for three epoxies as determined by H-n.m.r. are presented in Figure 7.

(U) The solvents which were used in these rate studies were carefully dried and redistilled. Chloroform (a phosgene former when pure) was kept in the dark under nitrogen. Stock solutions of epoxy compounds in this purified chloroform did not show evidence for ring opening while duplicate samples were undergoing rate studies with perfluoropropionic acid (PFPA). PFPA was used for most of the rate work instead of PFBA because of its greater solubility in common solvents.

(U) Nitrobenzene gave enhanced reactivity when employed as a solvent, when compared with carbon tetrachloride. PFBA and glycidyl phenyl ether (GPE) reacted exothermally at concentrations of 1.0 N or 0.50 N in nitrobenzene. H-n.m.r. spectra obtained immediately revealed complete reaction of the oxirane ring. Benzene and chloroform as solvents showed little difference in their effect on reaction rates of PFPA and GPE.

(U) The reaction product from epichlorohydrin and PFPA was isolated and found to be mainly 3-chloro-2-hydroxy-1-propyl perfluoropropionate.

(U) The reaction rates of three typical epoxides with PFPA and the corresponding rate data for the reaction of acetic acid with glycidyl phenyl ether are listed in Table VII.

(U) Perfluorocarboxylic acids with Olefins. - The cross-linking reaction desired in the case of olefins is the addition of a fluorocarbon acid to the double bond to form esters of secondary alcohols as reported[6] for trifluoroacetic acid and olefins.

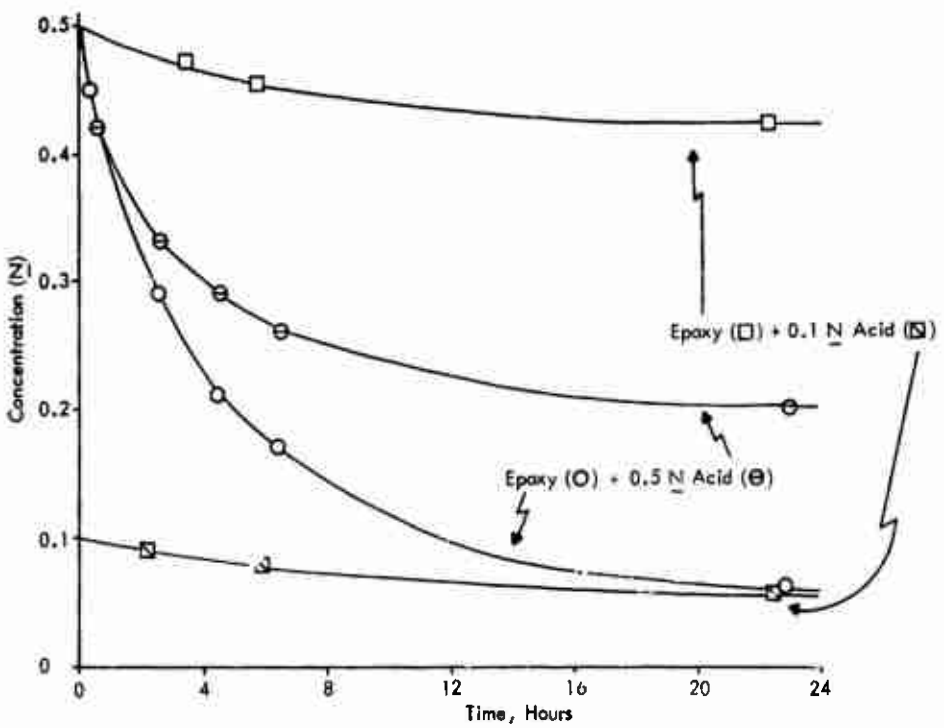


Figure 5. Rate of Reaction of Perfluoropropionic Acid (0.50 and 0.10 N) with Glycidyl Phenyl Ether (0.50 N) in Chloroform Solution at 25°C.

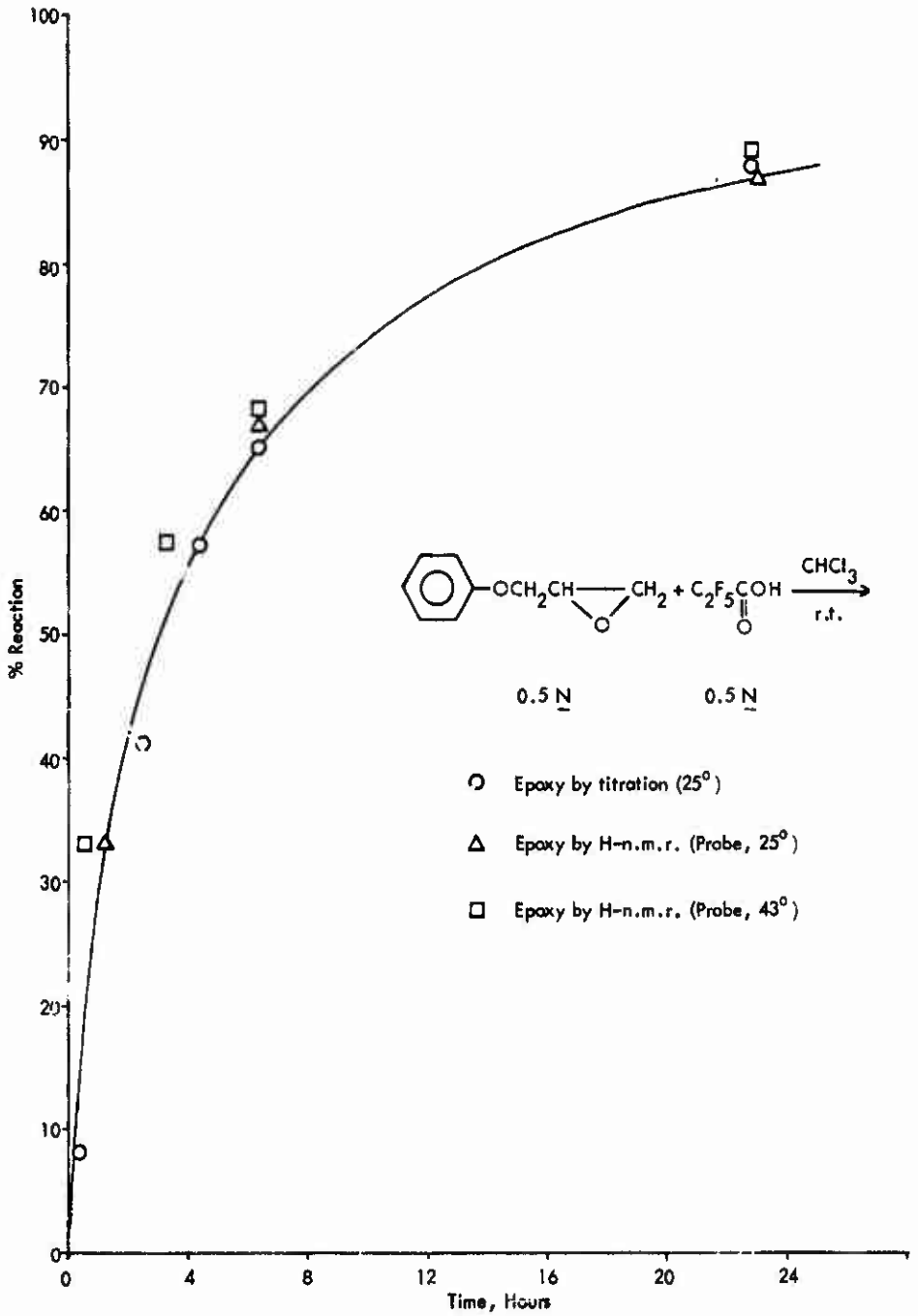


Figure 6. Comparison of Epoxy Ring-Opening Reaction Rates by Titration and H-n.m.r. at 25°C.

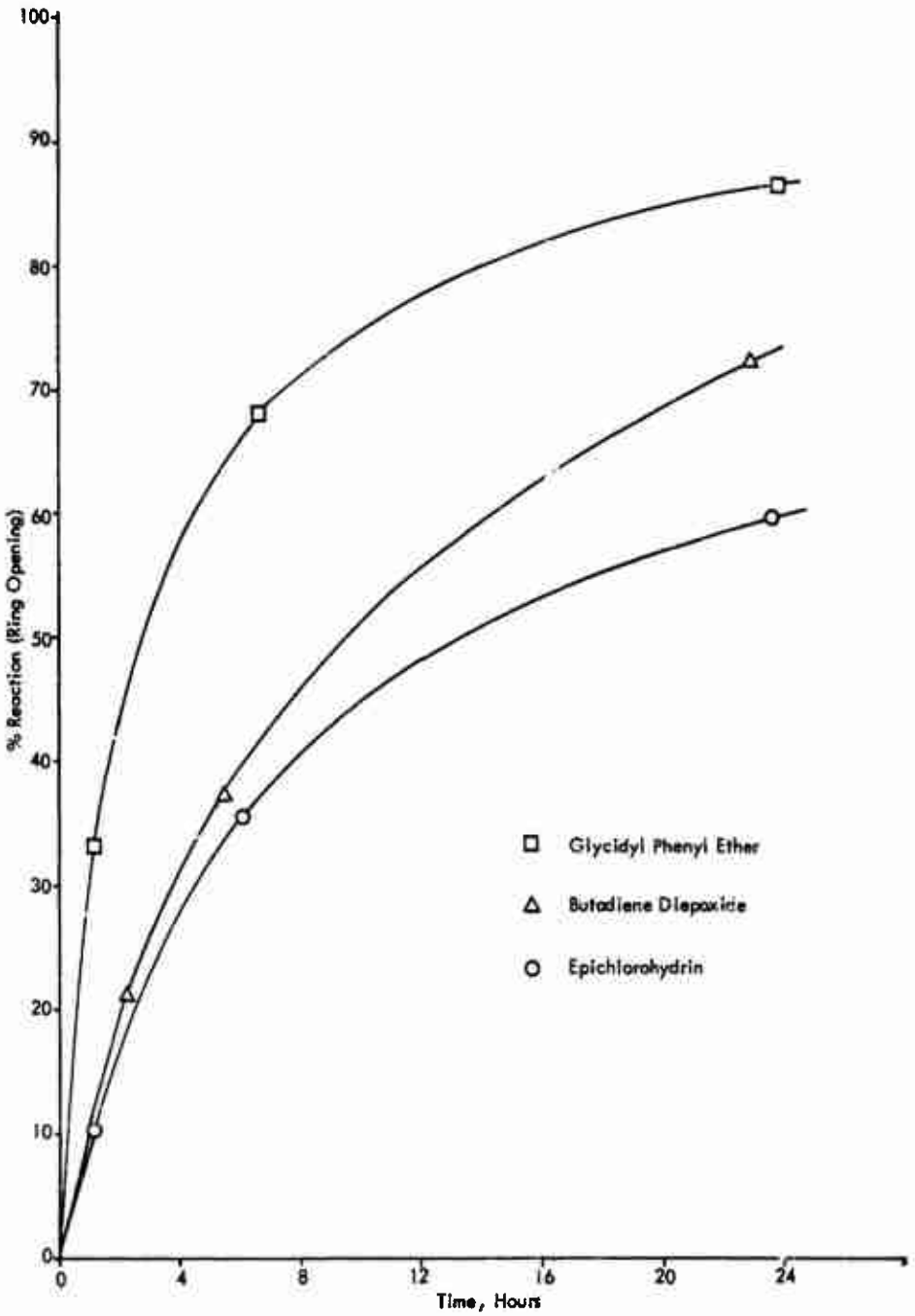


Figure 7. Rate of Reaction of Perfluoropropionic Acid (0.5 N) with Epoxy Compounds (0.5 N) in Chloroform at 25°C. (by H-n. m. r.)

(U) Vinycyclohexane gave no evidence for reaction with PFBA in acetonitrile after two days at room temperature as shown by titration or infrared analysis. In addition, no reaction was noted for an equimolar solution of PFPA and allyl benzene after 22.5 hours at 60.5°C. Addition of 1.5 mole % of benzenesulfonic acid and continued heating at 80°C. for 63 hours also failed to effect the desired reaction (see Experimental Section for successful reaction at 70°C. without solvent).

(U) Attempted reaction of PFPA and triallyl cyanurate caused cleavage to cyanuric acid.

(U) A twofold (equivalent) excess of PFPA was sealed in an n.m.r. tube with allyl ether. The tube was heated 36 hours at 60.5°C. with no evidence for reaction by H-n.m.r. Further heating at 78°C. for 64 hours gave only a slight indication of an addition reaction. The presence of the oxygen atom apparently deactivates this olefin.

(U) Oxetanes. - In a proton n.m.r. study, 3,3-bis(chloromethyl) oxetane (PENTON monomer) was reacted with a slight excess of PFBA in $CFCl_3$ (Me_4Si reference) at room temperature. After two hours, the n.m.r. spectra showed only peaks due to starting materials but on heating 18 hours at 80°C., complete reaction was indicated with evidence for the ring opening reaction giving a hydroxy ester.

(U) In a second experiment, a sealed n.m.r. tube containing the above oxetane and PFPA as 0.50 N solutions in benzene was heated at 60.5°C. No reaction was noted after 36.5 hours and only slight reaction (~ 5%) after 102 hours by H-n.m.r. analysis. (A bisoxetane has been used to cure polymer. See later sections).

(U) With Azetidines. - A solution of N-(p-toluene sulfonyl)-azetidine and PFPA, each 0.50 N in chloroform, was heated at 60.5°C. Only a minor amount of ring opening was noted after 36.5 hours, but 80-90% reaction had

taken place in 102 hours. At least two products were noted by H-n.m.r., apparently including the expected Tos-$NHCH_2CH_2CH_2OCOR_f$ and possibly Tos-$NHCH_2CH_2CH_2OH$. The reaction rates of azetidines, oxetanes and olefins are shown in Table VIII.

(U) Acyl Pyrrolidines. - N-Butyryl pyrrolidine failed to react with PFBA in $CFCl_3$, as noted by proton n.m.r., when heated 38 hours at 80°C.

(U) Amides of Perfluorocarboxylic Acids. - It was hoped to obtain a ring opening reaction with an amide of a perfluorocarboxylic acid and an acyl aziridine:

$$R_fCONH_2 + RCONCH_2CH_2 \xrightarrow{?} R_fCONHCH_2CH_2NHCOR$$

The resulting product would have only amide functions, which are more stable than ester groups obtained in many other curing reactions.

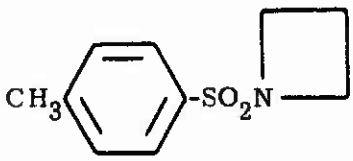
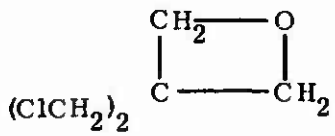
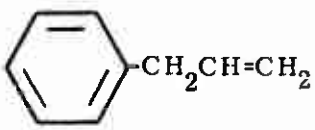
(U) Equivalent quantities of N,N'-bis(ethylene)isophthalamide and perfluorobutyramide were dissolved in 0.5 cc. of deuterated acetone (the only convenient mutual solvent) and the solution sealed in an n.m.r. tube. Heating at 60.5° · 36.5 hours gave no evidence for a ring opening reaction by H-n.m.r., only some deuterium-proton exchange. Heating an addition 64 hours at 78°C. gave indication of 33-50% reaction. Product identification by H-n.m.r. was not possible due to dilution of proton concentration from the exchange reaction with the solvent.

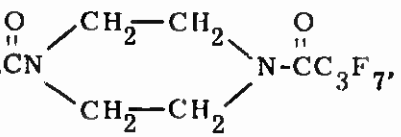
(U) Heating perfluorobutyramide and the above bis(aziridine) at 75° without solvent gave a glassy polymeric solid insoluble in DMSO, DMF, and trifluoroacetic acid.

(U) Some N-methyl perfluorobutyramide was prepared for further reactions with acyl aziridines.

Table VIII

Reaction Rates of R_fCOOH with Azetidines, Oxetanes and Olefins (0.5 N in $CHCl_3$)

Compound	Temperature, °C.	$T_{1/2}$ Hours
	60°C.	75
	60°C.	>102
	80°	>>63
$(CH_2=CH-CH_2)_2O$	80°	>>64 (neat)

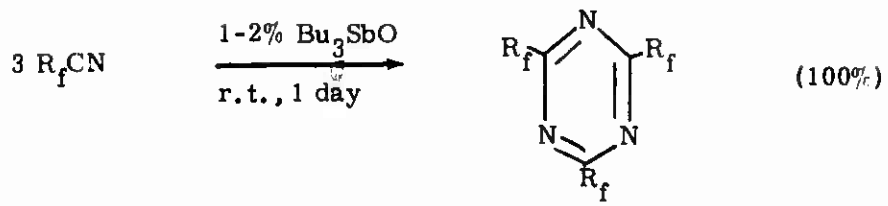
(U) A bis(amide), not containing -NH bonds,  , m.p. 109°C., was prepared and tested. It had moderate stability in boiling H_2O, but showed poor thermal stability at 500°F.

(U) Also, $C_6H_5NHCO_2CH_2(CF_2)_3CH_2CO_2NHC_6H_5$, m.p. 135°C., a model compound representing a 1,1-dihydro alcohol-terminated polymer cured with an isocyanate, exhibited excellent stability in H_2O at 100°C., but had only fair thermal stability at 500°F.

(U) Perfluoroalkanonitrile Trimerization. - As a class, the perfluoroalkyltriazines are among the most thermally stable organic compounds and as such, suitable synthetic routes, as well as properties of the resulting triazines, have been under extensive investigation over the past few years.

(U) Previous methods of synthesis from perfluoroalkanonitriles include heating the nitriles alone at high temperatures and pressures, treating the nitrile with large concentrations (20-50%) of anhydrous hydrogen chloride under pressure at temperatures from 20-150°C. in an autoclave and heating the nitrile with ammonia under pressure. It is obvious from an examination of the above techniques that none are suitable for curing a nitrile-terminated polymer in the presence of ammonium perchlorate and aluminum. Work under the present contract[3] has resulted in a major advancement in the nitrile-triazine state-of-the-art.

(U) A series of catalysts has been discovered which converts perfluoroalkanonitriles to 2,4,6-tris(perfluoroalkyl)-1,3,5-triazines at room temperature and ordinary pressures. With the most effective catalyst, tributylantimony oxide, quantitative conversions are obtained in less than a day at room temperature and atmospheric pressure.



(U) This new, high conversion reaction to produce triazines under ambient conditions is a significant improvement over existing methods and appears to offer great potential for crosslinking nitrile-terminated fluorocarbon polymers (see Experimental Section), and producing high boiling perfluoroalkyl triazines as high performance fluids. Polymers and fluids containing perfluoroalkyl-triazine groups are among the most thermally-stable organic materials.[7,8]

(U) The catalyst was initially prepared by the method of Dyke and Jones[9], who reacted tributyl antimony and mercuric oxide in ethyl alcohol. Free mercury is liberated and the tributylantimony oxide recovered by concentration of the alcohol solution. It was found, however, that the catalyst prepared by this method was complexed with ethanol which is very difficult to remove, even on heating under reduced pressure. Thus, the catalyst employed in many of the preparations and rate studies in this report had the approximate composition $(C_4H_9)_3SbO \cdot (C_2H_5OH)_{1.5}$ as determined by elemental, infrared, and H-n.m.r. analysis.

(U) A more active form of tributylantimony oxide catalyst is a liquid product prepared in acetone according to the following equation:

$$(C_4H_9)_3Sb + HgO \xrightarrow{\text{Acetone}} (C_4H_9)_3SbO\text{"A"} + Hg$$

The amber liquid formed here is designated "A" to distinguish it from the solid oxide obtained in a different synthesis described below and the ethanol complexed material above. Bu_3SbO"A" was freed from acetone by heating under reduced

pressure, but elemental analysis has revcaled a carbon content a fcw percent below theory, and emission spectroscopy has shown the presence of somc complexed mercury.

(U) A purer product was prepared by a longer route, in which $(C_4H_9)_3Sb$ was converted to the dibromide and an alcoholic solution of the latter converted to the $(C_4H_9)_3Sb(OH)_2$ by passing it through the hydroxide form of an anionic exchange resin. The dihydroxide obtained on evaporation of the alcohol was a colorless liquid which readily lost one mole of water on heating (100^{o}) in a vacuum to yield the solid $(C_4H_9)_3SbO$. Elemental analyses of the dihydroxide and oxide were in good agreement with theory for these compounds.

(U) The extent of trimerization for the higher nitriles was conveniently followed by periodic infrared examination of the reaction mixture noting the disappearance of the 4.4 micron band due to nitrile and the growth of the 6.4 micron absorption of the triazine product. The trimerization rate for $C_5F_{11}CN$ was determined using vapor phasc chromatography (VPC).

(U) Figure 8 compares the relative effectiveness of two Bu_3SbO catalysts on the rate of trimerization of $C_5F_{11}CN$. The least reactive was complexed with ethanol and also contained traces of water because of frequent usc. The other catalyst was prepared using acctone as a solvent (as noted above) and also contained traces of moisture but was still much more effective. In fact, a mild exotherm was noted at the start of the reaction when run on about 5 g. of nitrile.

(U) The effect of temperature is illustrated by the plots in Figure 9. The reaction run at $60^{o}C$. was much more rapid in the early minutes, being 82% complete in 0.5 hours, compared with 40% conversion for the room tempc ature reaction. Both reactions were virtually quantitative after one day.

(U) The effect of catalyst concentration is shown in Figure 10 for the system

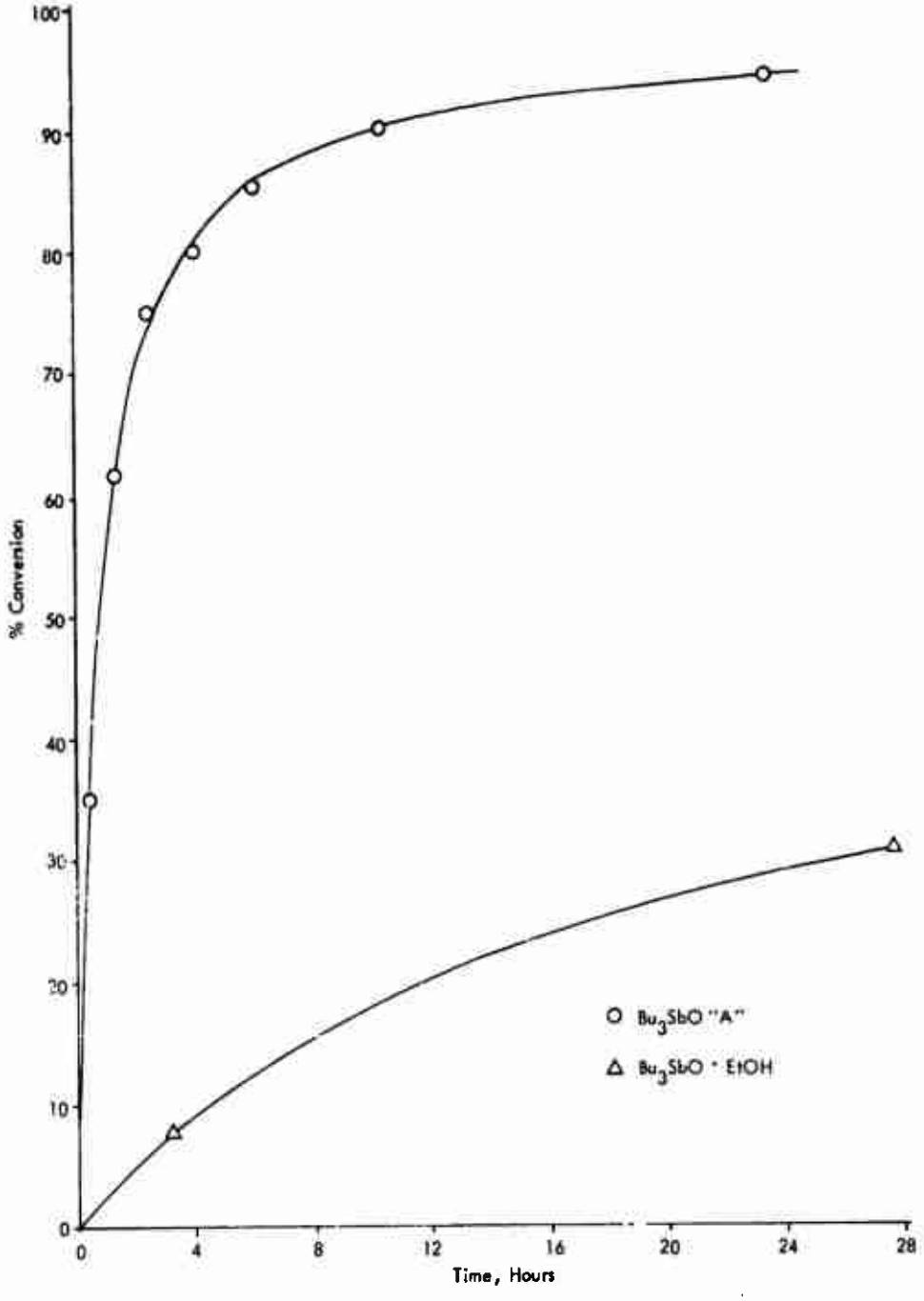


Figure 8. The Effect of Catalyst on Trimerization Rate of $C_5F_{11}CN$ at 25°C. (by VPC)

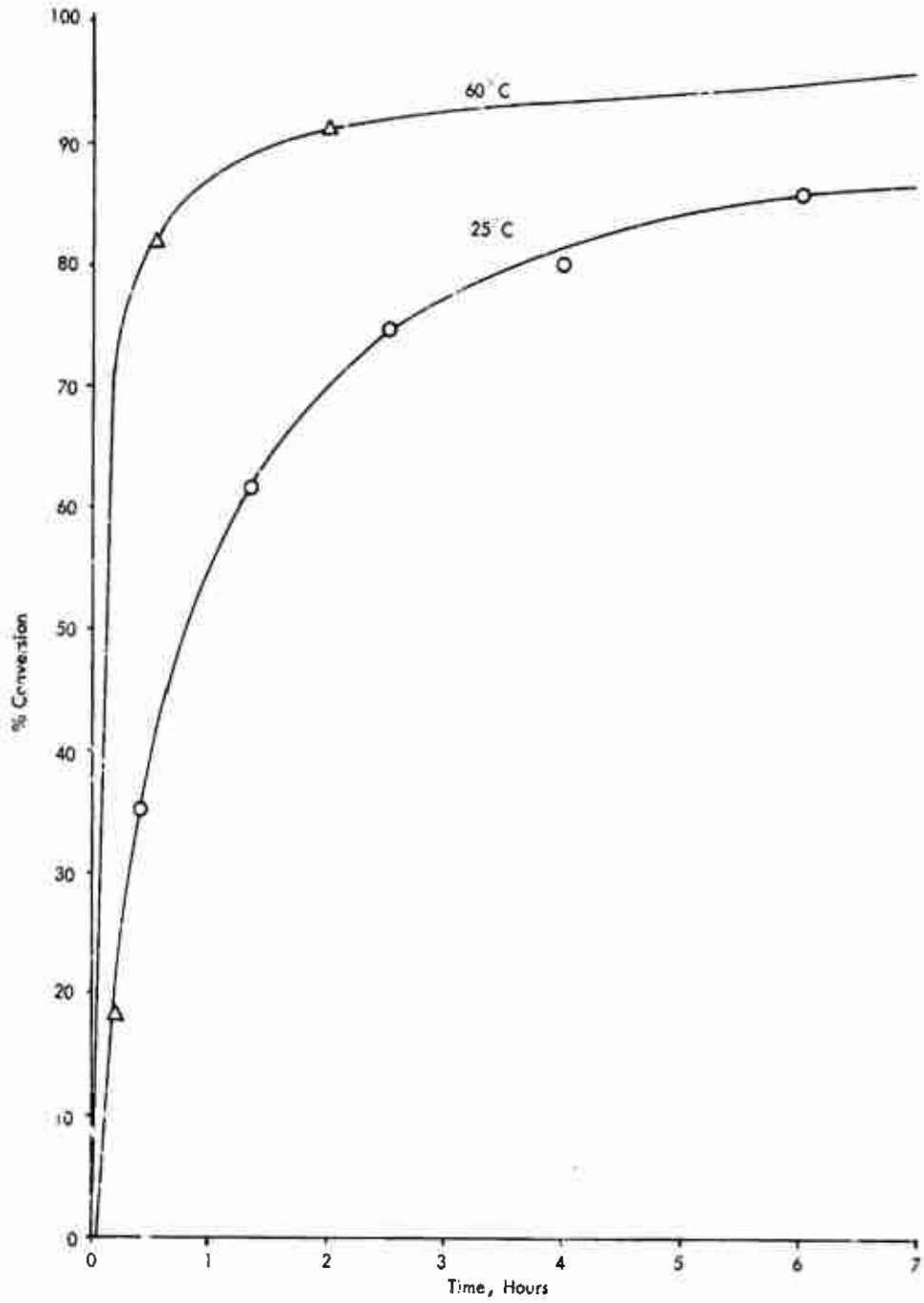


Figure 9. The Effect of Temperature on Trimerization Rate of $C_5F_{11}CN$ (by VPC) (2.4% Bu_3SbO)

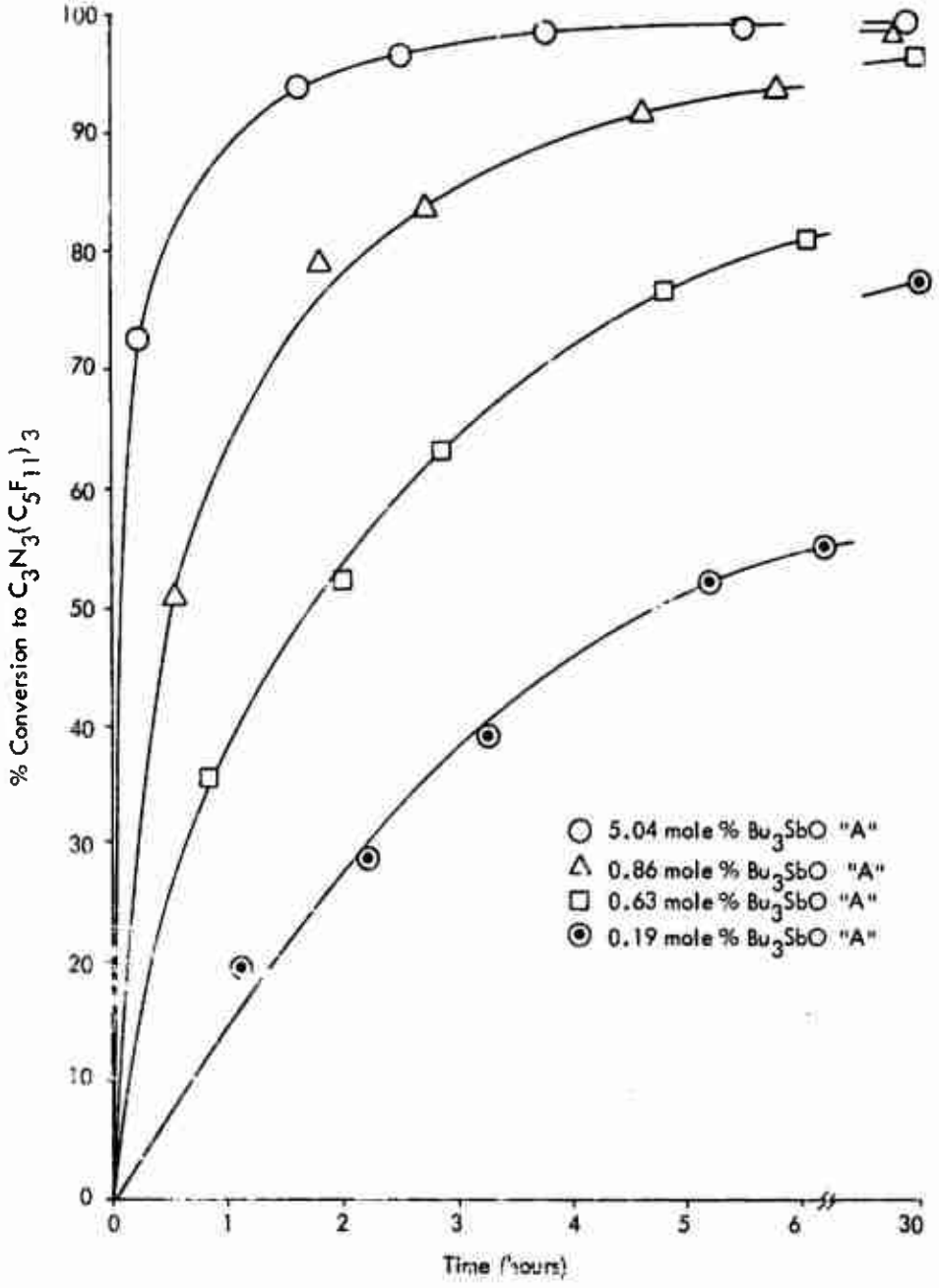


Figure 10. The Effect of Catalyst Concentration on the Trimerization Rate of $C_5F_{11}CN$ at 25°C. (by VPC)

$C_5F_{11}CN$ and $Bu_3SbO"A"$. A marked rate increase was observed with increased catalyst concentration. A mild exotherm was noted at 5 mole % catalyst, with a 90% conversion to trimer being obtained after one hour, and 99.5% after 5.5 hours at room temperature. The 0.63 and 0.86 molc % catalyst concentrations achieved over a 95% conversion to the triazine after 30 Hours.

(U) Experiments were run to determine the reason for the greater catalytic activity of $(C_4H_9)_3SbO"A"$, prepared from tributylantimony and mercuric oxide in acetone solution compared with the purer tributylantimony dihydroxide. It was surmised that the reason for the difference might be due to: 1) the formers greater solubility as a liquid in R_fCN, 2) presence of mercury, or 3) residual acetone.

(U) To test these possibilities small amounts of mercury, mercuric oxide, acetone, and $ClCF_2CFCl_2$ were mixed with pure tributylantimony oxide and $C_5F_{11}CN$ added to yield mixtures containing 1.7 mole % antimony catalyst (based on nitrile). All were slower than the control, except that after 24 hours the mixture containing mercuric oxide and the control both showed quantitative conversion to triazine. The mercuric oxide mixture will receive some further study.

(U) In order to gain some information concerning the mechanism of the nitrile trimerization reaction, the reaction of $C_5F_{11}CN$ in the presence of high Bu_3SbO concentrations was examined spectroscopically.

(U) When an equimolar quantity of $Bu_3SbO"A"$ and $C_5F_{11}CN$ were mixed, a mild exotherm was noted and within a minute or two, the initially insoluble mixture became homogeneous. An infrared examination of the non-volatile liquid indicated an adduct formation. The nitrile band at 4.4 microns was no longer present and there was no evidence for the triazine structure (6.4 microns), but a new strong band at about 6.0 microns ($-\overset{|}{C}=N$) and a moderate absorption at 5.8 microns ($-\overset{|}{C}=O$) were present. At a catalyst - $C_5F_{11}CN$ ratio of 1:2, a similar reaction occured. The infrared showed no nitrile, a small amount of triazine (6.4 microns) and the

following peaks: 5.8 (w), 6.0 (m) and 6.2 (m) microns. The product from a 1:3 catalyst-nitrile mixture was similar to the 1:2 product, except slightly more triazine was present. Figure 11 shows the trimerization rates of $C_5F_{11}CN$ using these adducts as catalysts on the day following their preparation. It is apparent that they are good catalysts. These experiments give strong evidence that the trimerization of R_fCN with these catalysts proceeds through successive insertion of the nitrile group of R_fCN into R_fCN-Bu_3SbO adducts. Two possible adduct structures which could account for the infrared absorptions observed are shown below.

$$Bu_3Sb{=}N\{C(R_f){=}N\}_n C(R_f){=}O \qquad Bu_3Sb{-}O(N{=}CR_f)_n$$

Final elimination of the triazine product results in regeneration of the catalyst or the initial active adduct. This is similar to a mechanism proposed by Bloodworth and Davies[10] for the trimerization of RNCO by Bu_3SnOR catalysts.

(U) Following the discovery of tributylantimony oxide as a trimerization catalyst, a number of available organometallics were screened for activity with $C_7F_{15}CN$, $C_5F_{11}CN$ and CF_3CN during the past year. The results are shown in Table IX with a more detailed examination of the more active catalysts compared in Table X. Several of the compounds were synthesized specially for this work as noted.

(U) These screening tests were usually run in a screw-top vial with $C_5F_{11}CN$ and about 5% of the potential catalyst. The mixture was shaken and let stand at room temperature with periodic sampling for analysis by infrared and vapor phases chromatography over at least a one-week period.

(U) In initial studies, tributylantimony itself appeared to be an active trimerization catalyst, but it was surmised that it was because of air oxidation to the active oxide. This was borne out by running the experiment under nitrogen and sampling the mixture through a rubber septum. There was no trimerization in a month under these new conditions.

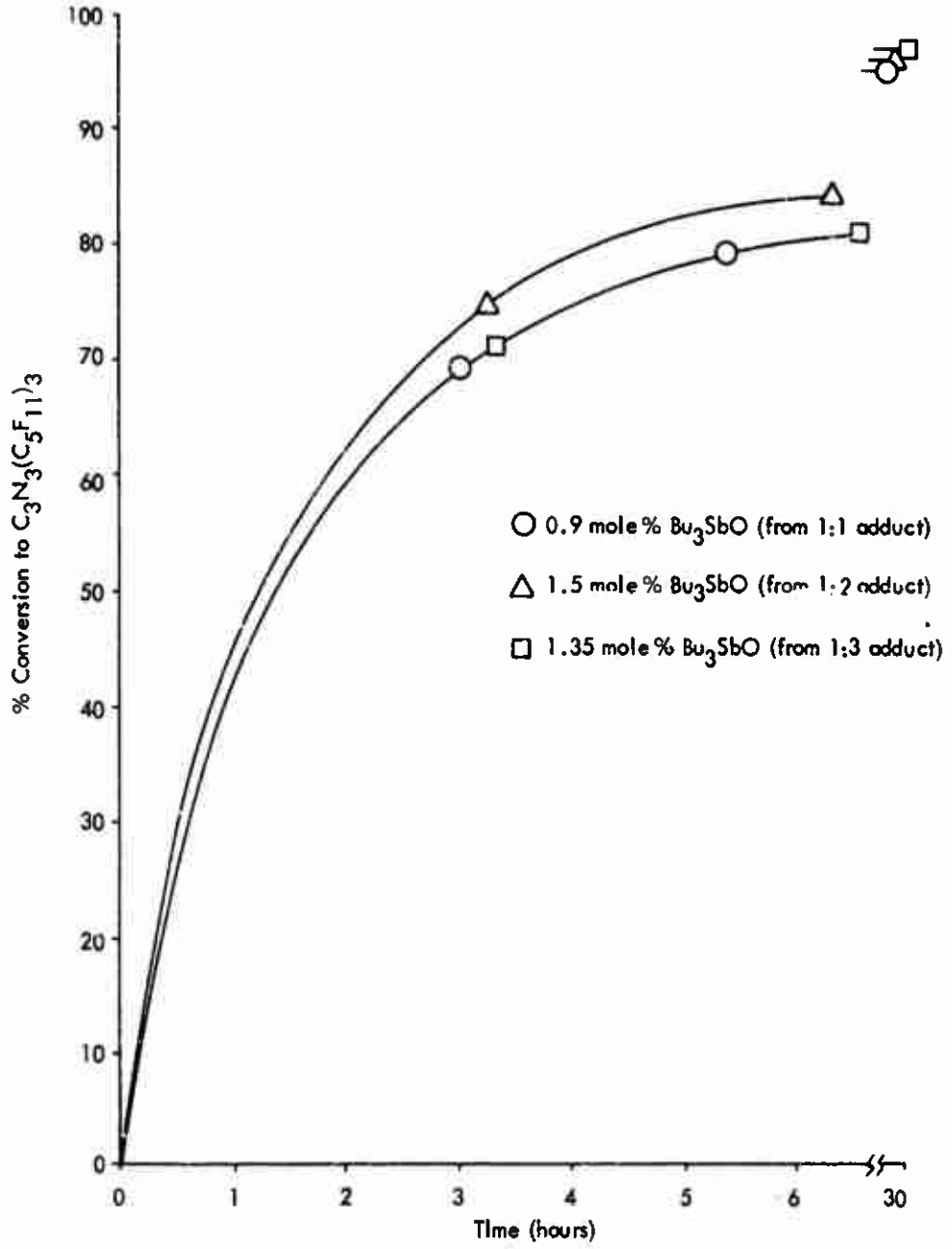


Figure 11. Trimerization Rate of $C_5F_{11}CN$ with $(C_4H_9)SbO$"A"-$C_5F_{11}CN$ Adducts as Catalysts at 25°C. (by VPC)

(U) A comparison of $Bu_3Sb(OH)_2$ and pure Bu_3SbO as catalysts for $C_5F_{11}CN$ trimerization is presented in Figure 12 and rate curves for $Me_3Sb(OH)_2$ and Me_3SbO are shown in Figure 13. Except for $Bu_3Sb(OH)_2$, these compounds were initially insoluble in $C_5F_{11}CN$ and the rate curves reflect this. $Bu_3Sb(OH)_2$, a liquid was mostly soluble and thus began its catalysis immediately, whereas Bu_3SbO a solid, formed a solid ball which only slowly dispersed to begin its activity. Both gave greater than 90% conversion after two days. Since both $Me_3Sb(OH)_2$ and Me_3SbO were initially insoluble in $C_5F_{11}CN$, it seems reasonable that the true relative activity of dihydroxides and oxides is shown in Figure 13. Even though the dihydroxide was present in almost twice the molar concentration, its rate of nitrile trimerization was significantly slower than that of the oxide.

(U) An examination of the results shown in Table X illustrates the superiority of the first catalyst, Bu_3SbO"A" over the pure Bu_3SbO and the others in the list.

(U) The fluorinated alkylantimony oxide, $(C_3F_7CH_2CH_2)_3SbO$, was studied since it was believed that it would be soluble in the fluorocarbon nitriles whereas other catalysts are insoluble or only slightly soluble. It was found to be completely miscible throughout the trimerization reaction. However, reaction rates with this catalyst at room temperature were low compared with rates using the other alkylantimony compounds (Figure 14). This effect is apparently due to the electron withdrawing character of the perfluoroalkyl groups (triphenylantimony oxide, another organoantimony oxide with negative groups, is not a catalyst at room temperature). A higher reaction temperature (100°C.) accelerated the trimerization and brought it to completion after 100 hours (Figure 15), while at room temperature, the reaction appeared to have stabilized at about 20% conversion after 100 hours.

Table IX

Compounds Screened as Potential R_fCN Trimerization Catalysts at 25°C. (1 week or as noted)

Name	Active (+) Inactive (-)	Comments
Antimony		
Tributyl antimony	-	Run under N_2 one month.
Tributyl antimony dihydroxide	+	One day. High conversion.
Tributyl antimony oxide	+	One day. High conversion.
Trimethyl antimony dihydroxide	+	One day. High conversion.
Trimethyl antimony oxide	+	One day. High conversion.
Trimethyl antimony dimethoxide	+	Trace in 4 days, 20 percent in 3 weeks.
Triphenyl antimony oxide	-	One month. No nitrile or triazine.
Antimony triethoxide	-	
Triphenyl antimony dichloride	-	
Antimony pentoxide	-	
Triphenyl antimony	-	
Triphenyl antimony diacetate	-	Trace of solid.
Antimony tartrate	-	
Antimony pentasulfide	-	
Antimony pentachloride	-	6.0μ peak (IR)
Tributyl antimony	+	80% 2 days (in air).
Triphenoxy antimony	-	
Antimony metal	-	

Table IX Continued

Arsenic		
Trimethyl arsenic dihydroxide	+	Some triazine, mostly solid adduct.
Trimethyl arsenic oxide	+	Partial conversion to triazine.
Triphenyl arsenic oxide hydrate	-	Crystalline adduct at 25° or 60°.
Triphenyl arsine	-	Trace of solid
Arsenic trioxide	-	
Phosphorus		
Tributyl phosphorus oxide	-	
Triphenyl phosphorus sulfide	-	
Trimethyl phosphate	-	
Triphenyl phosphorus oxide	-	
Tributyl phosphite	-	
Tributyl phosphate	-	
Tributyl phosphorus	-	
Tin		
Bis(tributyl tin)oxide	+	Erratic. Active at 25°, slight at 60°.
Dibutyl tin oxide	-	Small amount of an adduct.
Tributyl tin acetate	-	
Triphenyl tin hydroxide	-	
Tributyl tin methoxide	-	Evidence for an adduct.
Tributyl tin chloride	-	
Dibutyl tin chloride	-	
Tributyl tin sulfide	-	
Tetrabutyl tin	-	

Table IX Continued

Tin Con't.		
Tin metal	-	
Dibutyl tin acetate	-	
Miscellaneous		
Ferrocene	-	
Tributyl borate	-	
Zirconium acetyl acetonate	-	
Aluminum powder	-	
Ammonium perchlorate	-	
Triphenyl lead chloride	-	
Titanium acetyl acetonate	-	
Aluminum isopropoxide	-	Trace of solid.
Diphenyl mercury	-	
Triphenyl bismuth	-	
Ferric acetyl acetonate	-	
Sodium methoxide	(+)	Trace at 6.4μ.
Potassium acetate	-	

Table X

Decreasing Order of Catalyst Efficiency in the Room Temperature Trimerization of $C_5F_{11}CN$ in the Absence of a Solvent.

Compound	State	Approx. Rates 2% Catalyst, 22°C.			Solubility (r.t.)	
		T 1/2 Hrs.	% Conversion 4 hrs.	1 day	R_fCN	$Cl(CF_2CFCl)_2Cl$
$(C_4H_9)_3SbO$"A"	Liquid[a]	0.3	97	100	sl. sol.	-
$(C_4H_9)_3Sb(OH)_2$	Liquid[b]	0.8	65	86	soluble	soluble
$(C_4H_9)_3SbO$	Solid[c]	2.5	70	99	insoluble	sl. sol.
$(CH_3)_3SbO$	Solid	12	20	70	insoluble	-
$(CH_3)_3Sb(OH)_2$	Solid	18[d]	15[d]	57[d]	insoluble	insoluble
$(C_4H_9)_3SbO \cdot C_2H_5OH$	Liquid	-	10	30	sl. sol.	-
$(C_3F_7CH_2CH_2)_3SbO$	Solid	-	5	13	soluble	soluble
$\left[(C_4H_9)_3Sn\right]_2O$	Liquid	-	2	15	sl. sol.	soluble
$(CH_3)_3AsO$	Solid	-	-	30[e]	sl. sol.	-
$(CH_3)_3As(OH)_2$	Solid	-	-	tr.[e]	sl. sol.	-
$(CH_3)_3Sb(OCH_3)_2$	Liquid	-	-	tr.[e]	sl. sol.	-
$(C_4H_9)_3SnOCH_3$	Liquid	-	-	tr.[e]	sl. sol.	soluble
CH_3ONa	Solid	-	-	tr.[e]	insoluble	-
$N(CH_2CH_2)_3N$	Solid	-	-	tr.[e]	insoluble	-

[a] From Bu_3SbO + HgO in acetone. Contains combined mercury.

[b] From Bu_3SbBr_2 + Resin $^+OH^-$ in alcohol.

[c] M. P. 152-153°C., from dehydration of $Bu_3Sb(OH)_2$

[d] 3.8 mole % catalyst

[e] After more than 4 weeks.

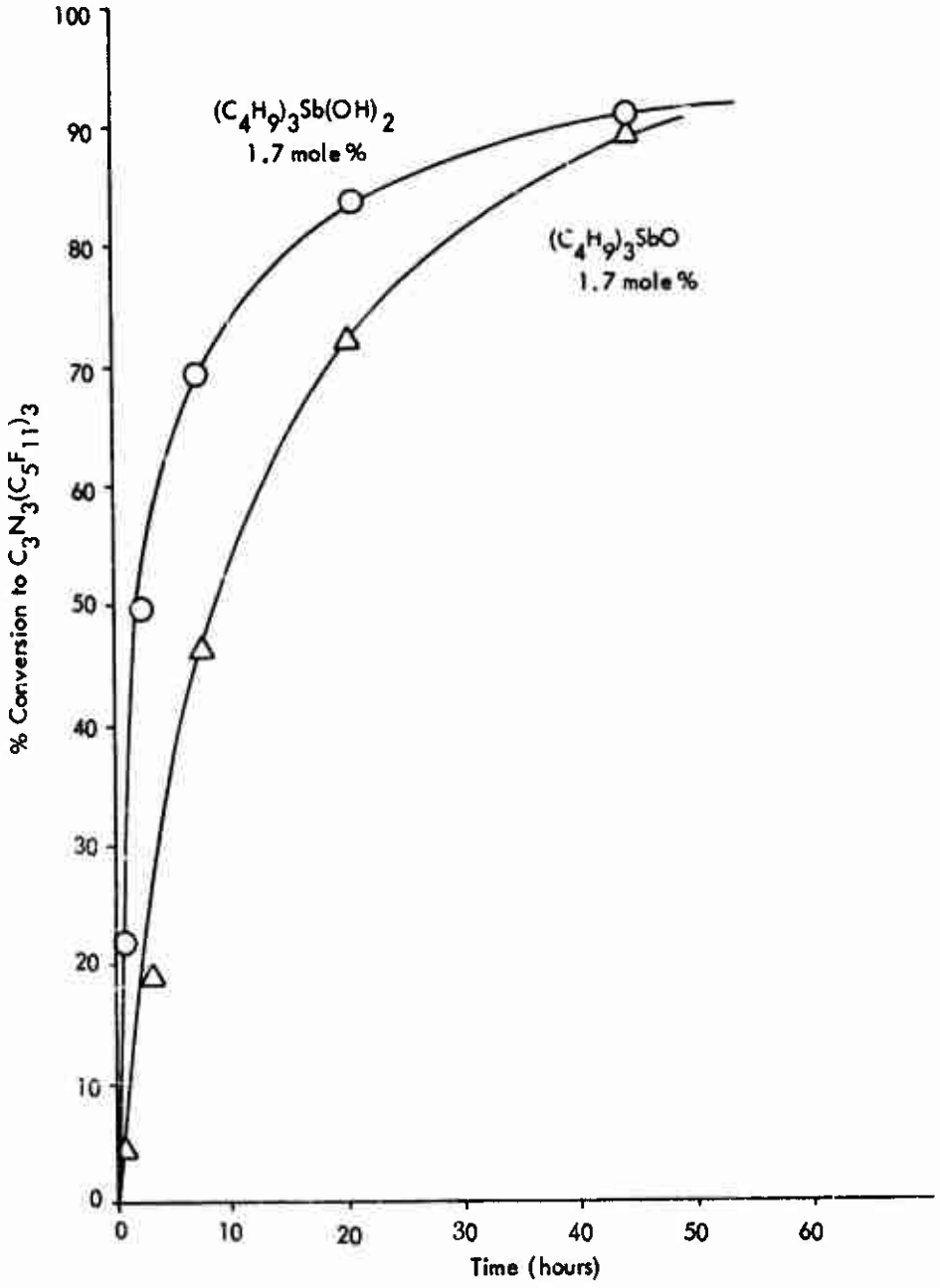


Figure 12. Trimerization Rate of $C_5F_{11}CN$ with $(C_4H_9)_3SbO$ and $(C_4H_9)_3Sb(OH)_2$ Catalysts at 25°C. (by VPC)

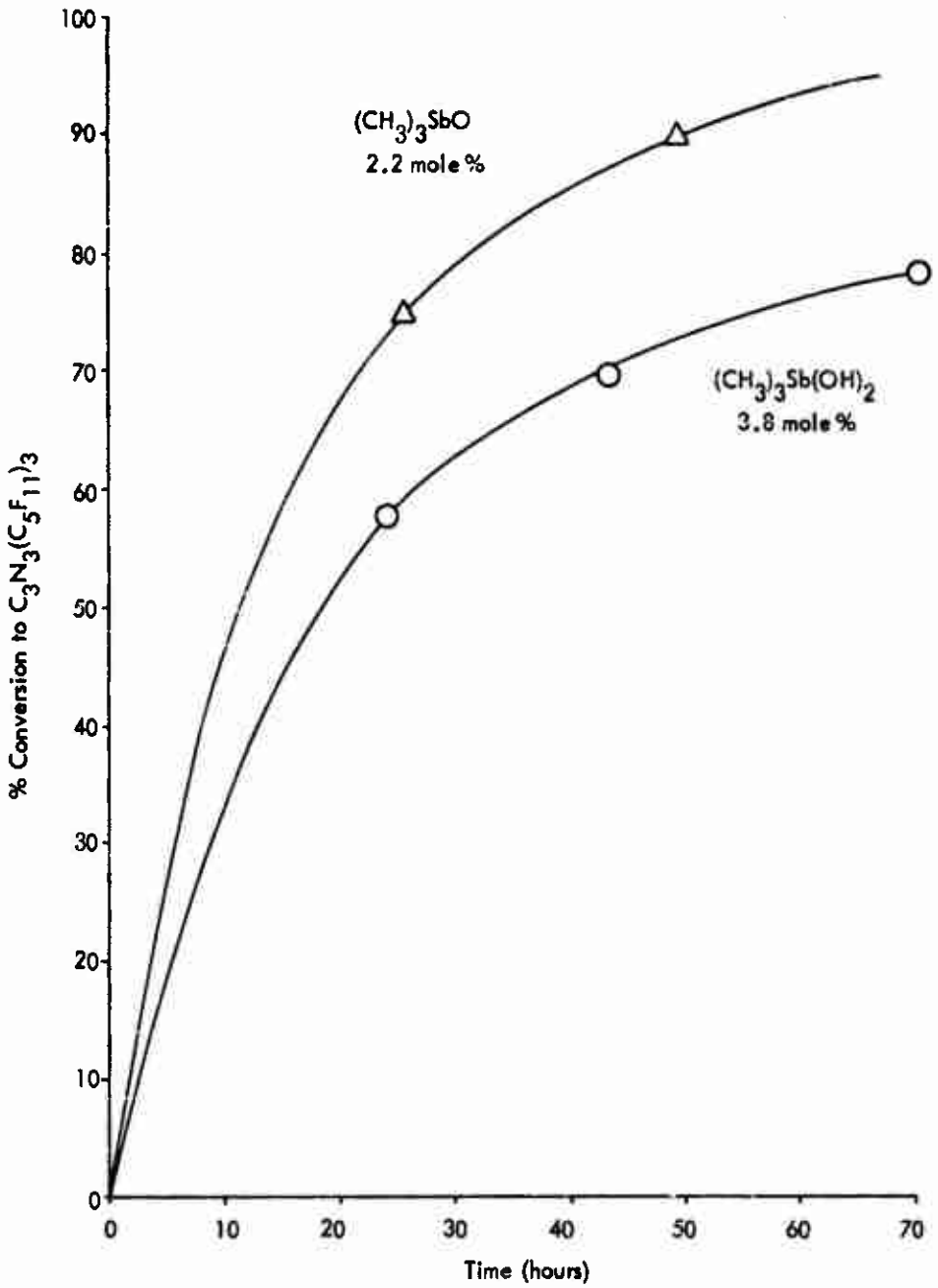


Figure 13. Trimerization Rate of $C_5F_{11}CN$ with $(CH_3)_3SbO$ and and $(CH_3)_3Sb(OH)_2$ Catalysts at 25°C. (by VPC)

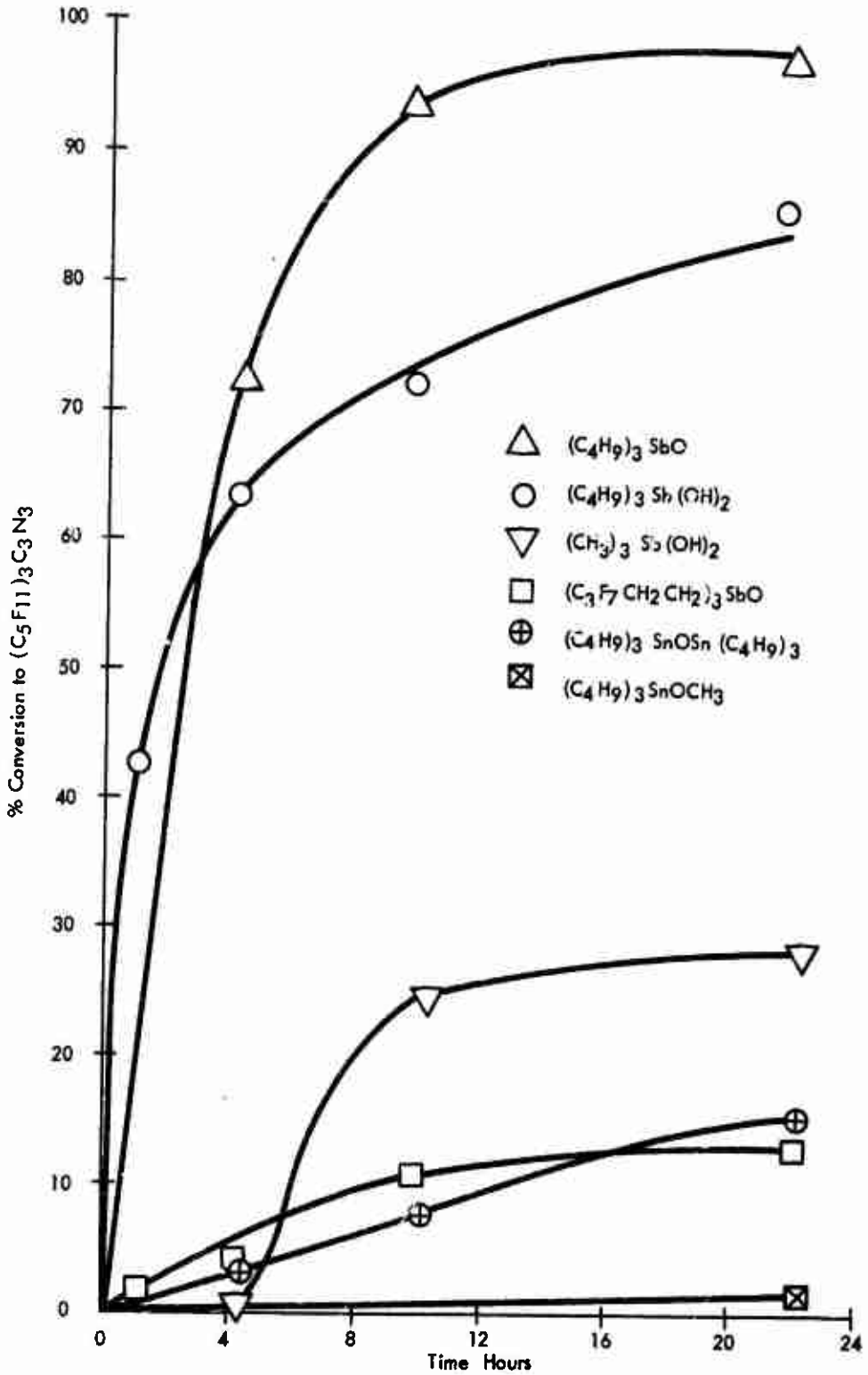


Figure 14. The Trimerization of $C_5F_{11}CN$ with Various Catalysts (1.9 mole %) at 22°C.

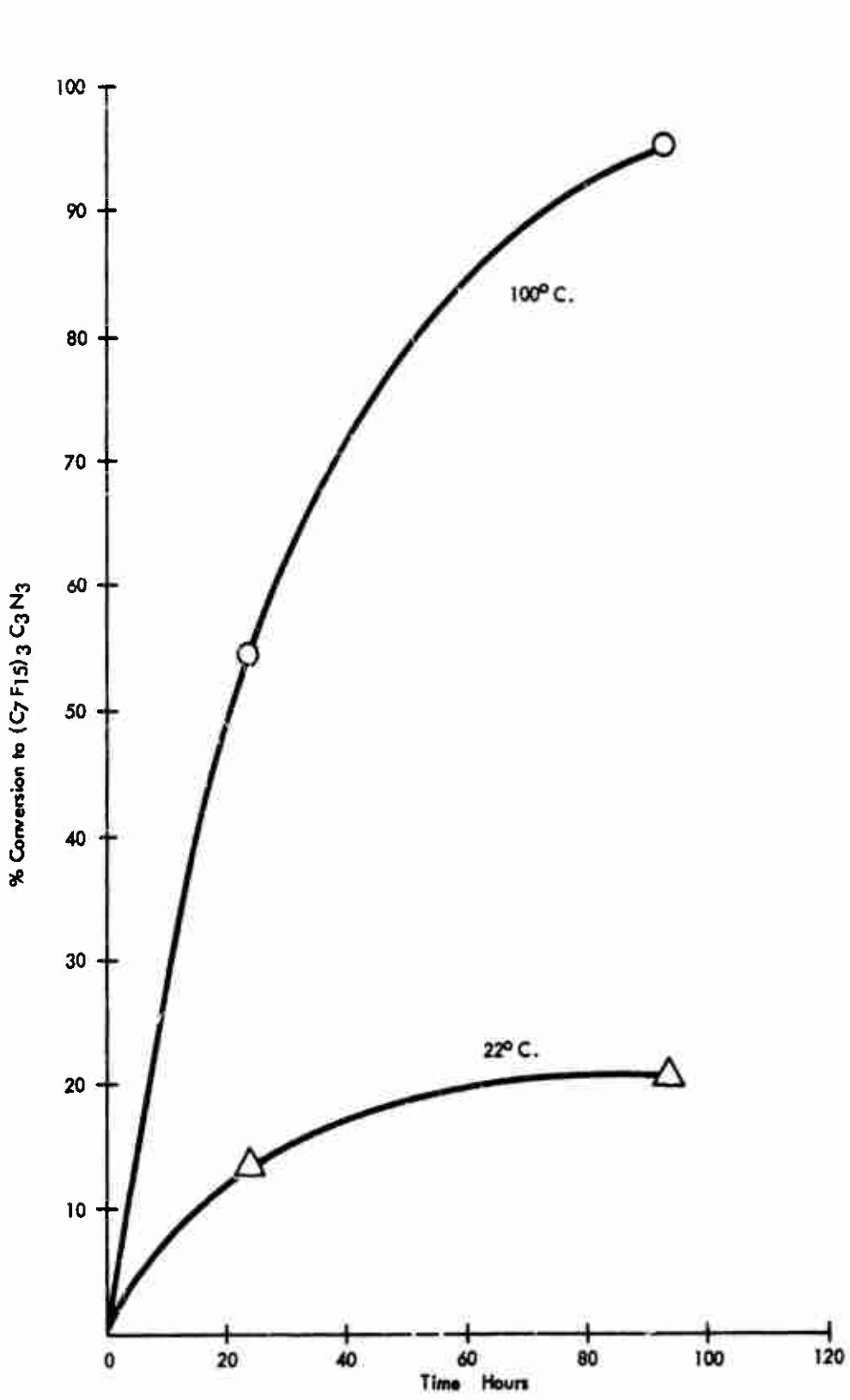


Figure 15. The Effect of Temperature on Trimerization Rate of $C_7F_{15}CN$ with $(C_3F_7CH_2CH_2)_3SbO$ (5.8 mole%)

(U) The use of a solvent, $Cl(CF_2CFCl)_2Cl$, decreased reaction rates (Figure 16). When these solution trimerizations were heated, a rate increase was observed for $(C_4H_9)_3Sb(OH)_2$ and $(CH_3)_3Sb(OH)_2$ and a decrease for $(C_4H_9)_3SbO$ and $(C_3F_7CH_2CH_2)_3SbO$. However, these observations were preliminary and should be rechecked.

(C) Thermal Stability of Perfluoroalkytriazines. - Pure perfluoroalkyltriazines are known to be very thermally stable. Should trialkylantimony oxide catalysts prove useful in curing nitrile-terminated perfluoroalkylene oxide prepolymers, it is hoped that the resulting elastomer will be thermally stable, and that the residual catalyst which will be unavoidably present in the system will not cause decomposition or reversion of the triazine crosslinks to nitrile. Thus, the thermal stability of some triazine systems has been examined.

(C) Heating tris(perfluoropentyl)triazine containing 3.2 mole % residual tributylantimony oxide catalyst in a sealed glass tube overnight at 205-260°C. (500°F) caused the evolution of some gases including HF (as evidenced by the presence of SiF_4), CO_2, some volatile hydrocarbon and fluorocarbon fragments, and the deposition of antimony metal. The dark residual liquid was substantially unchanged triazine (by infrared examination); there was no reversion to nitrile. It is expected that triazines containing residual Me_3SbO catalyst will produce fewer gaseous products.

(C) When the triazine containing the 3.2 mole % catalyst was extracted with acetone to remove residual catalyst, and freed from traces of solvent under reduced pressure, it was stable and remained essentially colorless after heating for 100 hours at about 270°C. in glass.

(C) The thermal stability of $(C_5F_{11})_3C_3N_3$ containing residual trimethylantimony oxide catalyst was improved over the triazine containing the corresponding tributylantimony oxide. The triazine catalyst mixture was refluxed in an open tube at about 260°C. (500°F.) for 129 hours with only 3.6% weight loss, believed

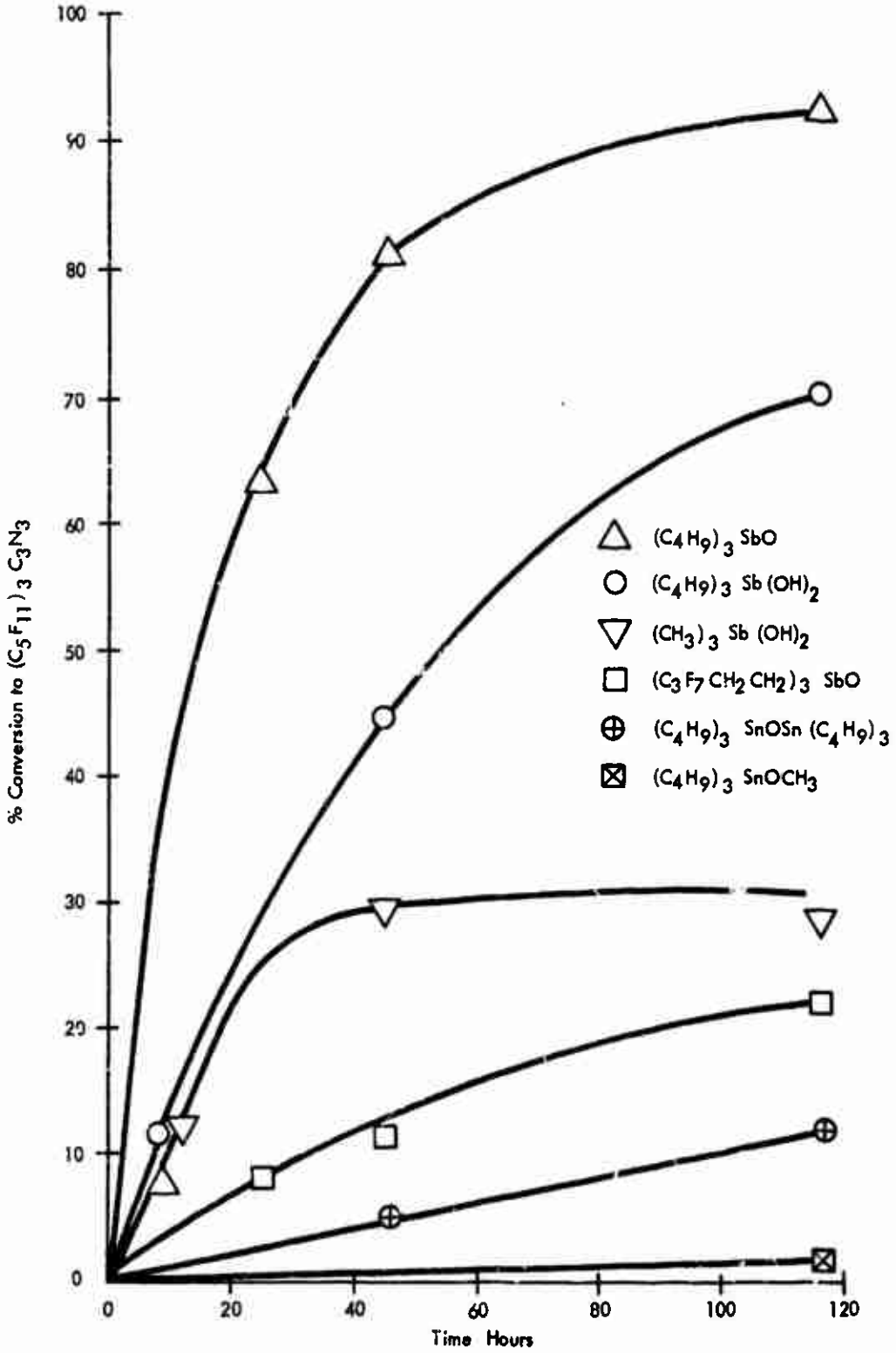


Figure 16. The Trimerization of $C_5F_{11}CN$ in $Cl(CF_2CFCl)_2Cl$ (1:1 by vol.) with Various Catalysts (2.0 mole %) at 22°C.

mostly due to volatilization. The residual liquid had darkened, but was essentially all triazine, as determined by infrarcd and vapor phase chromatography.

(U) Perfluoroalkyl Redistribution in Triazines. - Redistribution of the perfluoroalkyl groups in triazine crosslinked polyperfluoroalkylene oxides is undesirable. Thus, experiments were carried out to determine the extent of possible catalytic redistribution.

(U) An equimolar solution of $C_5F_{11}CN$ and $C_7F_{15}CN$ was treated with $(C_4H_9)_3Sb(OH)_2$ (4 mole %) at room temperature. In 24 hours, a quantitative conversion to the four possible triazine products had taken place in essentially the theoretical distribution of 12.5, 37.5, 37.5, 12.5 (1:3:3:1): $(C_5F_{11})_3C_3N_3$ (11.5%; $(C_5F_{11})_2C_7F_{15}C_3N_3$ (38%); $C_5F_{11}(C_7F_{15})_2C_3N_3$ (39%); $(C_7F_{15})_3C_3N_3$ (11.5%) The % values were obtained from peak areas from gas chromatography runs.

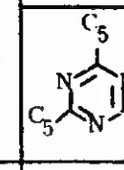
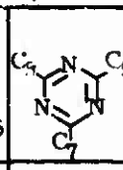
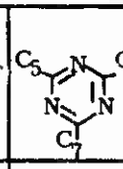
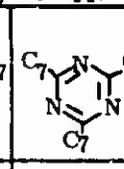
(U) Having established that the two triazines containing mixed alkyl groups could be monitored, equimolar mixtures of $(C_5F_{11})_3C_3N_3$ and $(C_7F_{15})_3C_3N_3$ were treated under various conditions to note any redistribution of alkyl groups. The results of these experiments are summarized in Table XI. It was found that some redistribution was noted in all cases where tributylantimony oxide was known to be present. In the absence of catalyst, no rearrangement was observed. The theoretical equilibrium distribution was never reached, but probably could be under appropriate conditions. The maximum noted was 25% mixed triazine in 10 days at 100°C.

(U) Apparently, there is an equilibrium between a triazine-catalyst complex (I) and a nitrile-catalyst adduct (II) which lies mostly to the left:

$$(R_f)_3C_3N_3 + \text{catalyst} \rightleftharpoons \underset{\text{(I)}}{(R_f)_3C_3N_3 \cdot \text{catalyst}} \rightleftharpoons \underset{\text{(II)}}{R_fCN \cdot \text{catalyst}}$$

Table XI

The Catalytic Redistribution of Perfluoroalkyl Groups in Equimolar Mixtures of $(C_5F_{11})_3C_3N_3$ and $(C_7F_{15})_3C_3N_3$ (by VPC)

Catalyst (Bu_3SbO), Mole %	Time	Temp. °C.	Product Composition, Mole % (C_5=C_5F_{11}, C_7=C_7F_{15})				
							$C_5F_{11}CN$ $C_7F_{15}CN$
0	28 days	100	50	0	0	50	0
tr.[a]	7 days	100	50	0	0	50	0
2.8	1 day	100	47.5	2.5	2.5	47.5	0
2.8	4 days	100	42	8	8	43	0
2.8	10 days	100	38	12	13	37	0
2.8	29 days	100	35	12	12	41	0
9.7	1 hour	210	46.7	2.5	2.5	46.7	1.5
9.7	4 hours plus	210	45	4.5	4.5	45	1
	23 days	22	45.5	4	4	45.5	1
9.7	10 days	22	44	6	6	44	0
9.7	23 days	22	40	10	10	40	0
Theoretical (b)			12.5	37.5	37.5	12.5	

a. Residual soluble catalyst. (Major portion insoluble on walls of original trimerization vessels.)

b. Theoretical distribution at equilibrium.

(U) It appears that the only way to prevent a redistribution of alkyl groups in triazines is to deactivate the catalyst after triazine formation. An attempt at catalyst-deactivation by thermal means has been carried out.

(U) A mixture of the C_5F_{11}- and C_7F_{15}- triazines and $(C_4H_9)_3SbO$ catalyst was heated at 210°C. A relatively rapid redistribution to 5% mixed triazines occurred in the first hour, increasing only 4% (to 9%) over the next three hours. This treatment apparently destroyed the catalyst since no significant redistribution took place in the mixture during a subsequent 23 days at room temperature. A control run at 22°C., produced 20% mixed triazines in 23 days.

(U) Other redistribution experiments include the following: to $(C_5F_{11})_3C_3N_3$ containing residual catalyst from the trimerization was added $C_7F_{15}CN$. The nitrile trimerized and after four weeks at 50°C., 5% mixed triazines were present. To $(C_7F_{15})_3C_3N_3$ containing residual catalyst from the trimerization was added an equivalent amount of redistilled $(C_5F_{11})_3C_3N_3$. After four weeks at 50°C., a 20% conversion to mixed triazines had taken place.

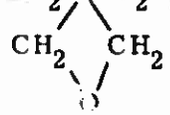
3. (U) Polymer Curing Studies. - Small samples of carboxy-terminated perfluoroalkyleneoxide polymer ($\bar{M}_n$=2400, functionality = 2.3) have been cured by two diepoxides to yield transparent rubbery solids within two hours at room temperature. These cure rates are consistent with the moderate reaction rates observed with perfluorocarboxylic acids and epoxy compounds described earlier in this report.

(U) One liquid polymer sample (1.65 meq.) was mixed with 0.43 meq. of STE 6 Epotuf (a trifunctional glycidyl derivative of trimethylol propane) and 1.1 meq. of butadiene deipoxide. Two other polymer samples (2 and 3) were mixed with equivalent amounts of STE 6 Epotuf and butadiene diepoxide, respectively. After mixing, the samples were poured into small polytetrafluoroethylene molds. Samples containing the trifunctional epoxy, STE 6 Epotuf,

began gelling so rapidly that they were difficult to cast, even though the operations were carried out in less than a minute. These samples contained bubbles. After one hour at room temperature, all samples had gelled, but only sample 2 was tack-free. After one day at room temperature, samples 1 and 3 were still slightly tacky. Heating at 70°C. for 2 hours caused little change but further heating for 1 hour at 110°C. gave tack-free specimens. After two more hours at 110°C., the cured samples were removed from the dumbell-shaped molds. Sample 2 broke easily on removal and was crumbly. Samples 1 and 3 were intact but lacked strength. They were rubbery but could not be bent greater than about 30° without cleaving. Small samples of 1 and 2 (cured as above) were heated further at 110°C. for 16 hours with no apparent change. They remained weak and crumbly.

(U) After one month in a polyethylene capped vial, the rubber sample 1, which had received a final cure of 3 hours at 110°C., had softened somewhat and become slightly tacky. Rubber sample 3 under these conditions was unchanged. Samples of 1 which had been cured further (overnight at 110°C.) had reverted to liquid polymer on standing in air for a month, while rubber sample 2 with the same exposure was still a solid but was very slightly tacky. It appears from these results that curing reactions yielding ester groups of the type, $-CF_2COOR-$; e.g., acid-epoxy, acid-alcohol, acid-acyl aziridine, do not give hydrolytically stable cures.

(U) The rapid gelling of perfluorocarboxylic acid polymers with conventional epoxy reagents, as well as the hydrolytic instability as reported above will prevent their use in binder preparation. On the other hand, rate studies reported above indicate that oxetanes, ring homologues of oxiranes, react much more slowly with perfluoroacids than the smaller ring. This slower rate was also shown to apply in the reaction of the carboxy-terminated polymer and a bis oxetane. A tacky rubber was obtained in two days at room temperature in one experiment, and a firm elastomer after 1.3 hours heating at 105°C. in another case.

(U) A fluorine-containing oxetane, $(CF_3)_2C(C_6H_4OCH_2\text{-}C\text{-}C_2H_5)_2$, 

m.p. 133-134°C., was prepared in the hope that it would have some solubility in the carboxyl terminated fluorocarbon polymer.

(U) The above bis(oxetane) was used to cure a sample of carboxyl-terminated perfluorotetramethylene oxide polymer. The bis(oxetane) was essentially insoluble at room temperature. Nevertheless, the viscosity of the mixture increased during a one day period at room temperature, but gelled after 2.5 hours at 65°C. Further curing was carried out at 110°C. to yield a very firm transparent solid containing air bubbles. The air was apparently entrapped in the fluffy bis(oxetane) and remained in the cured specimen after the curing reaction.

(U) A solid oxazoline, 1,3,5-tris(ethyl-2-oxazolinyl) benzene, cured the carboxyl-terminated polymer within a few minutes at room temperature in regions where the two immiscible materials were in intimate contact. This is nearly as rapid as the acyl aziridine (HX-868) precursor of this compound cured a similar polymer sample.

(C) The thermal stability of the polymer cured with dicyclopentadienylether diepoxide was determined by TGA. Results (in air): -10% weight loss at 260°C.

(C) The polymer cured with the bis oxetane gave about the same results. TGA: -10% weight loss at 250°C. These values are about the same as those for the uncured carboxy-terminated polyalkylene oxide polymer (-10% weight loss at 260°C.).

(U) The room-temperature trimerization of perfluoroalkanonitriles to perfluoroalkyltriazines using the new catalyst, tributyl antimony oxide, has been disclosed earlier in this report. When this catalyst (1%) was mixed with perfluorosebaconitrile, b.p. 148°C., a white, waxy solid formed overnight at room temperature. The solid hardened on standing.

(U) Addition of catalyst to an equimolar mixture of the dinitrile and a mononitrile, $C_5F_{11}CN$, resulted in a rubbery transparent gel during a similar reaction period at room temperature. The presence of mononitrile apparently increased the chain extension while decreasing crosslinking in the trimerization. The success in crosslinking a perfluorodinitrile demonstrates the feasibility of crosslinking nitrile-terminated perfluoroalkyleneoxide polymers.

(C) The thermal stability of the $C_5F_{11}CN$ chain extended triazine system as determined by DTA is shown below in Table XII.

Table XII
Decomposition of Triazine Cross-Linked
Polymers Based on $NC(CF_2)_8CN$

Composition (Mole %)			Decomposition Temperature	
$NC(CF_2)_8CN$	$C_5F_{11}CN$	$(C_4H_9)_3SbO$	10% wt. loss	50% wt. loss
98.3	0	1.7	298°C.	502°C.
54	44.6	..4	348°C.	509°C.

(U) A carboxy-terminated perfluoroalkyleneoxide polymer was cured at room temperature in the presence of a mixture of aluminum powder and ammonium perchlorate using a diepoxide.

(C) The perfluoronitrile, $C_5F_{11}CN$, was converted to the corresponding triazine in the presence of aluminum and ammonium perchlorate using the room-temperature catalyst, tributyl antimony oxide.

(U) The reaction rate for the above two experiments did not appear to be changed by the presence of the added metal and oxidizer (see Experimental section for further details).

D. (C) PROPELLANT EVALUATION.

(U) Propellant evaluation at Allegany Ballistics Laboratory was initiated during the course of this contract on a 100-ml. sample of carboxyl-terminated poly(perfluorotetramethylene oxide). The prepolymer was characterized by the following properties: $\bar{M}_n$ = 2200, acid equivalent weight 641, functionality 3.4, $[\eta]_{inh}$ = 0.014 and having HF, COF_2, CO and OFCCFO as possible contaminants.

(C) Carboxyl-terminated poly(perfluorotetramethylene oxide) gave satisfactory results (no significant pressure increase) with ammonium perchlorate (AP) and aluminum in one-day modified Taliani tests at 93°C. No pressure increase was noted in three-day tests at 93°C. with dry or wet AP (2% water) although there was some "carbonization" at the top of both samples.

(U) As expected, the polymer reacted exothermally with several epoxides. Either viscosity increase or gelling occurred, but the reaction appeared to stop abruptly before a significant amount of ester was formed, judged from infrared spectroscopy studies. In a typical example, the polymer was reacted with (1) an equivalent amount of DER-332 and (2) about 50% of an equivalent amount of DER-332. A hard gel resulted in both cases but infrared spectra indicated that essentially no ester was formed (5.75μ) and that both acid group (5.6μ) and epoxide group (12.1μ) remained. Of possible significance is the fact that samples prepared with less than an equivalent amount of epoxide appeared to generate more ester (5.75μ) than the gels formed from 1:1 equivalent COOH: epoxide.

(U) A similar result was noted when an attempt was made to follow the rate of reaction of DER-736 with the polymer; infrared spectrum was unchanged from 10 minutes to four hours after mixing. The gel obtained from the polymer-DER-736 reaction was softer than that obtained from the polymer -DER-332 reaction. Gel was not improved by adding 0.1% chromium octoate as catalyst or by heating six days at 55°C.

(U) UNOX-221 appeared to react instantaneously with the carboxyl-terminated polymer. Previous studies had indicated that UNOX-221 andERLA-0510 reacted faster with a carboxyl-terminated polybutadiene than other epoxides. A viscosity increase was noted when the polymer and limonene dioxide were heated. Because of the initial fast reaction, solution of the polymer and epoxides could not be deaerated and no attempt was made to prepare samples for mechanical property tests at this time.

(U) The polymer-DER-736 gel can be hydrolyzed in water to a liquid. There is evidence to indicate this can be reversed; a presumably hydrolyzed polymer-DER-736 solution was re-geiled by a three-day exposure to 55°C.

(C) The glass-transition temperature of carboxyl-terminated poly(perfluoro-tetramethylene oxide) at a cooling rate of 1°C./minute was measure in the ABL strain gage T_g apparatus and found to be -54.2°C. $\pm$ 0.3°C. (-66°F.).

III. EXPERIMENTAL

A. (U) PHOTOPOLYMERIZATION

(U) The reactor consists of an outer Pyrex jacket (volume 215 cc.) which is jointed so as to permit introduction of a water-cooled quartz immersion well. The reactor also contains an outlet for a condenser and a dry-ice trap, in series, and sample inlet.

(U) In a typical experiment, the reactor is flamed-out under vacuum, cooled to -196°C., and 25-30 g. of perfluoro-8-oxydipropionyl fluoride introduced by vacuum distillation. The FC-75 solvent (190 cc.) is then added by a simple pouring technique, under slight vacuum, in the absence of air. The reactor and its contents are then heated to and maintained at 100-105°C. The reaction mixture is stirred with a magnetic stirring bar while being photolyzed with a 450-watt Hanovia ultraviolet source. Upon completion of the desired photolysis time, the reactor is cooled to room temperature and the contents are poured into a flask suitable for removal of the solvent. The solvent is removed on a rotating evaporator, followed by heating the residual, non-volatile polymer for about 4 hours at 100°C. at a pressure of about 0.01 mm. to 0.1 mm. Conversion to the acid or ester is accomplished by addition of water or alcohol, respectively, to a solution of the acid fluoride-terminated polymer in FC-75, ,followed by removal of solvent, excess nucleophile and hydrogen fluoride under vacuum.

B. (U) CATALYSTS AND CURING AGENTS

1. (U) Preparation of $(CH_3)_3Sb(OH)_2$ - Trimethylantimony was prepared from freshly distilled antimony trichloride and methylmagnesium bromide in ether as described by Long, Doak and Freedman[11]. To 6 g. (0.036 mole) of $(CH_3)_3Sb$ in CCl_4 was added under N_2 a solution of Br_2 in CCl_4 until the bromine color persisted. The crude precipitated solid $(CH_3)_3SbBr_2$ weighed 14.2 g. Eleven grams were recrystallized from about 75 ml. of acetone to yield 6.8 g. thick needles. An additional 2 g. were recovered from the filtrate. A solution of the 7.8 g. of the dibromide in 400 ml water was passed through a column of BIORAD AG1-X4 ion exchange resin in the hydroxide form. The resulting aqueous effluent gave

5.8 gm. of an oil which solidified on touching with a spatula. Dissolving in 300 cc. hot acetone and cooling yielded 4.7 g. of feathery crystals. Infrared analysis was consistent for $(CH_3)_3Sb(OH)_2$. Elemental and proton n.m.r. analysis indicated the presence of water. Calculated for $C_3H_{11}O_2Sb \cdot 3/4\ H_2O$: C, 16.8; H, 5.9. Found: C, 16.9; H, 5.8.

2. (U) Preparation of $(CH_3)_3SbO$- Heating $(CH_3)_3Sb(OH)_2$ overnight at 140°C. and about 0.1 Torr caused sublimation and dehydration to yield $(CH_3)_3SbO$ (by infrared analysis).

3. (U) Preparation of $(C_4H_9)_3Sb(OH)_2$- Tributyl antimony (3.1 g.) was converted to $(C_4H_9)_3SbBr_2$ by treatment with bromine in CCl_4 solution under nitrogen. The orange solution was concentrated to yield 4.6 g. of an oil. This was dissolved in 100 ml. of 95 percent ethyl alcohol and passed through the BIORAD AG1-X4 ion exchange column (as above for $(CH_3)_3SbBr_2$). Concentration at the aspirator and finally at the vacuum pump gave mostly an oil with some solid on the upper walls. (The solid is mostly $(C_4H_9)_3SbO$). The colorless oil was analyzed. Calculated for $(C_4H_9)_3Sb(OH)_2$: C, 44.1; H, 8.9. Found: C, 44.1; H, 8.9. Exposure of this material to the air for three days caused no change in the elemental analysis or infrared analysis.

4. (U) Preparation of $(C_4H_9)_3SbO$- Heating the liquid $(C_4H_9)_3Sb(OH)_2$ (0.909 g., 2.78 mmole) at about 100°C. bath temperature and at full pump vacuum (about 0.1 Torr) caused the facile loss of water (0.050 g., 2.80 mmole) to yield a solid, weight 0.859 g., 2.80 mmole (calculated as the oxide). Calculated for $(C_4H_9)_3SbO$: C, 47.1; H, 8.9. Found: C, 46.8; H, 9.5. The infrared analysis is consistent for the oxide.

5. (U) Preparation of $(C_4H_9)_3SbO$"A"- In a dry 200 ml. r.b. flask was placed 100 ml. reagent acetone (Merck, treated with Drierite), 22 g. (0.1 mole) powdered HgO and 19 ml (22.7 g., 0.077 mole) tributylantimony (Metal and Thermite Company, oxidizes rapidly in air). A Teflon covered, football shaped

magnetic stirrer was added, the flask purged with N_2, stoppered and stirred magnetically at r.t. for two days. The mixture was allowed to settle, the acetone layer decanted and concentrated at the aspirator. The oil-solid mixture was stirred with about 50 ml. of dry acetone, allowed to settle and the acetone layer removed and concentrated under vacuum. Final traces of acetone were removed at about 0.1 mm Hg pressure for 1 day. The liquid product was mainly $(C_4H_9)_3SbO$, complexed with about 5% mercury. It was stored over a small amount of Drierite.

6. (U) Preparation of $(CH_3)_3As(OH)_2$ and $(CH_3)_3AsO$- Trimethyl arsenic dibromide, a hygroscopic solid, was prepared from arsenic trichloride by the method of Wittig and Torsell[12]. The crude dibromide was dissolved in 95 percent ethanol and passed through the anion exchange column described above. Evaporation of the effluent gave $(CH_3)_3As(OH)_2$ as a dark yellow oil. This was partially decolorized by treatment with active charcoal in acetone. Sublimation of $(CH_3)_3As(OH)_2$ yielded an oily solid, believed to be mostly $(CH_3)_3AsO$. Proton n.m.r. showed a strong peak at 8.31τ due to CH_3 groups plus two small impurity peaks.

7. (U) Preparation of $(CH_3)_3Sb(OCH_3)_2$- Sodium methoxide, from 1.4 g. of sodium, in 20 ml. of methyl alcohol was added dropwise to a suspension of $(CH_3)_3SbBr_2$ in 100 ml. of methyl alcohol. The resulting homogeneous solution was allowed to stand several days then concentrated at the aspirator. The solid-liquid mixture was treated with CCl_4, centrifuged to precipitate sodium bromide and the CCl_4 solution was concentrated. A solid-liquid mixture was again produced. An infrared of the liquid gave support for $(CH_3)_3Sb(OCH_3)_2$, although a moderate peak was present in the OH region. This material was a weak catalyst for R_fCN trimerization.

8. (U) Preparation of $(C_4H_9)_3SnOCH_3$- This compound was prepared by the method of Alleston and Davies[13] from tributyltin chloride and sodium methoxide. The compound is a mobile liquid boiling at 98°C./0.1 Torr. (Lit.[13] b.p. 97-99°/0.06 Torr.)

9. (U) Preparation of $C_3F_7CH_2CH_2I$. - n-$C_3F_7CH_2CH_2I$, b.p. 118-120°C., was prepared by the peroxide-catalyzed addition of C_3F_7I to ethylene.

10. (U) Preparation of $(C_3F_7CH_2CH_2)_3Sb$. - In a 1 liter, 3 neck flask fitted with a stirrer, condenser, drying tube and dropping funnel, was placed 5.9 g. (0.24 mole) of Mg turnings. The flask was flamed, purged with N_2 and 125 ml. dry ether containing a few ml. of $C_3F_7CH_2CH_2I$ added. The reaction started immediately. The balance of $C_3F_7CH_2CH_2I$ (total 71 g., 0.22 mole) in 125 ml. ether was added over a period of 2 hours with stirring and spontaneous reflux. The mixture was refluxed 3 hours, stirred overnight and decanted through glass wool away from 1.1 g. unreacted Mg.

(U) To this stirred solution under nitrogen was added dropwise 100 ml. ether containing 11.5 g. (0.05 mole) $SbCl_3$ (redistilled). The resulting mixture was treated with 125 ml. of water (exotherm). The organic phase was separated and the aqueous phase washed with ether. The combined organic layer was dried over Na_2SO_4 and concentrated to yield 42 g. of a cloudy liquid. Distillation through a short Vigreux column yielded 18.3 g. (0.026 mole, 35% conversion) of a colorless liquid, b.p. 93-96°C./0.5 mm, $n_d^{20} = 1.3698$. Calculated for $C_{15}H_{12}F_{21}Sb$: C, 25.2. Found: C, 25.1. F-n.m.r.: H-n.m.r. and I.R. spectra are consistent. The compound oxidizes rapidly in air.

11. (U) Preparation of $(C_3F_7CH_2CH_2)_3SbBr_2$. - A slight excess of bromine as a 20% solution in CCl_4 was added slowly to a stirred solution of 17 g. (0.024 mole) of $(C_3F_7CH_2CH_2)_3Sb$ in 60 ml. of CCl_4. The orange solution was concentrated at the water aspirator to yield 19.5 g. of an oil which crystallized. Recrystallization of 14 g. from about 7 ml. of n-butyl alcohol gave 9.7 g. white crystals, m.p. 39-39.5°C. A sample was sublimed and analyzed. Calculated for $C_{15}H_{12}Br_2F_{21}Sb$ (872.8): C, 20.6; Br, 18.3. Found: C, 20.7; Br, 18.4. H-n.m.r. and I.R. spectra are consistent.

12. (U) $(C_3F_7CH_2CH_2)_3Sb(OH)_2$ and $(C_3F_7CH_2CH_2)_3SbO$- A solution of 9.7 g. of $(C_3F_7CH_2CH_2)_3SbBr_2$ in 100 ml. of 95% ethyl alcohol was passed through a column of BIORAD AGI-X4 ion exchange resin in the hydroxide form. The effluent was concentrated under vacuum to yield 8.2 g. of an oil which appeared to be a mixture of the dihydroxide and oxide by infrared analysis. Heating at 100°C. under vacuum gave a white solid on cooling, m.p. 58°C. It is hygroscopic, liquifying overnight in air. Calculated for $C_{15}H_{12}F_{21}SbO$(729): C, 24.7. Found: C, 24.7. Infrared analysis is consistent for the oxide.

13. (U) Preparation of $(CF_3)_2C(C_6H_4OCH_2\text{-}C\text{-}C_2H_5)_2$ (with CH_2 CH_2 / O)

This compound was prepared by the addition of about 0.1 mole $C_6H_5SO_2OCH$ (CH_2 CH_2 / O) $C\text{-}C_2H_5$ in ethanol to 0.05 mole $(CF_3)_2C(C_6H_5OH)_2$ in ethanol containing 0.1 mole NaOH. The solution was refluxed one hour. A dark oil was obtained which was washed with water. Some crystals formed on standing. The mixture was treated with a small amount of methanol and the solid filtered. This was recrystallized successively from heptane and methanol to yield white crystals; m.p. 133-134°C. Anal. Calculated for $C_{27}H_{30}F_6O_4$: C, 60.9; H, 5.7; F, 21.4. Found: C, 60.8; H, 5.4; F, 21.3.

C. (U) MODEL COMPOUNDS

1. (U) Preparation of 1-methyl-2-phenylethyl perfluorobutyrate. - In a 15 cc. glass ampoule fitted with a polytetrafluoroethylene Fischer and Porter valve was placed 6.5 cc. (10.7 g., 0.05 mole) of perfluorobutyric acid and 5.7 cc. (5.1 g., 0.04 mole) of allylbenzene. The liquids were immiscible. The mixture was heated 16 hours at 70°C. to yield a reddish brown liquid. Analysis by vapor phase

chromatography (VPC) obtained at this point indicated about 50% completion. After a total of 36 hours at 70°C., the conversion to high boiling product was about 80%. A sample isolated by VPC was a colorless liquid, $n_D^{21.5} = 1.4017$. It was shown to have the following structure by H-n.m.r.:

$$C_6H_5-\underset{7.06\tau}{C\underline{H}_2}-\underset{\underset{8.67\tau}{C\underline{H}_3}}{\underset{|}{C\underline{H}}}\underset{5.66\tau}{OCOC_3F_7}$$

(U) Anal. Calculated for $C_{13}H_{11}F_7O_2$: C, 47.0; F, 40.1; H, 3.3
Found: C, 46.7; F, 40.2; H, 3.8.

2. (U) Preparation of 3-chloro-2-hydroxy-1-propyl perfluoropropionate and isomer. - An equimolar solution of epichlorohydrin (4.6 g.) and perfluoropropionic acid (8.2 g.) in 50 cc. of chloroform was refluxed overnight to give essentially complete conversion to the ester product. A pure sample was isolated by preparative VPC on a 1 meter x 1/2" FS-1265 column (10% on Fluoropak 80) at 100°C. and 250 cc. He/min. carrier gas flow. The $CHCl_3$ solvent eluted at 0.35 min. and the product at 8.2 min. under these conditions. The ester, $n_D^{23} = 1.3772$, was a mixture of isomers as determined by H-n.m.r. (τ values)

$$C_2F_5\overset{\underset{O}{\|}}{C}-OC\underset{5.48\ d}{\underline{H}_2}-\underset{\underset{7.15}{O\underline{H}}}{\underset{|}{C\underline{H}}}-C\underset{6.36\ d}{\underline{H}_2}Cl \qquad 88\%$$

$$C_2F_5\overset{\underset{O}{\|}}{C}OC\underset{4.66}{\underline{H}}-\underset{\underset{6.08\text{ or }6.22\ d}{C\underline{H}_2OH}}{\underset{|}{C}}\underset{6.08\text{ or }6.22\ d}{\underline{H}_2}Cl \qquad 12\%$$

3. (U) Preparation of 2,4,6-tris(perfluoropentyl)-1,3,5-triazine, $C_3N_3(C_5F_{11})_3$. - Perfluorohexanonitrile (19.0 g.) and $(C_4H_9)_3SbO\text{-}C_2H_5OH$ complex (0.37 g., 2 wt. %) were placed in a closed 15 cc. glass ampoule. The mixture was heated at 60°C. for 12.5 hours. Infrared analysis indicated about a 90% conversion to trimer. (Note: Heating is not necessary for complete overnight reaction if the more active catalyst prepared in acetone is used, as observed in the text. Longer reaction

time with the ethanol complexed catalyst at room temperature will also give high conversion.) The product was distilled through a short column packed with glass helices to yield a colorless liquid, b.p. 151-152°/38 mm., n_D^{23} 1.3160, d_4^{20} 1.800. The infrared spectrum shows a strong band at 6.39 microns due to the triazine ring. Anal. calculated for $C_{18}N_3F_{33}$: C, 24.4. Found: C, 24.5

(U) Three trace by-products obtained in this distillation are $C_5F_{11}CONH_2$, m.p. 116°C., $C_5F_{11}COOC_2H_5$, and $C_5F_{11}\overset{NH}{\overset{\|}{C}}-OC_2H_5$, n_D^{22} 1.3177; IR. NH, 2.98μ C= N, 5.94μ (Calculated for $C_8H_6F_{11}NO$: C, 28.2; H, 1.7. Found: C, 28.3; H, 1.7.) This trimerization was also successfully carried out in the presence of aluminum powder and ammonium perchlorate with no apparent rate change.

4. (U) Preparation of $C_3N_3(C_7F_{15})_3$. - About 2 cc. of $C_7F_{15}CN$, b.p. 108°, was shaken with 2 drops of $(C_4H_9)_3SbO \cdot (C_2H_5OH)_{1.5}$ in a closed vial. After 3 days at room temperature a nonvolatile pale yellow liquid of increased viscosity had formed. Infrared examination showed a strong band at 6.42 microns consistent with the triazine structure. Little if any nitrile absorption was evident.

5. (U) Preparation of $C_3N_3(CF_3)_3$. - CF_3CN was partially converted to the trimer by catalysis with $(C_4H_9)_3SbO.(C_2H_5OH)_{1.5}$ in (a) a stainless steel cylinder without solvent and in (b) a glass ampoule in chloroform solution. The reactions were conducted at room temperature. The triazine was isolated by VPC. The product was colorless liquid, $n_D^{22.5}$ 1.3208. The infrared spectrum gave strong bands at 6.33 and 11.57 microns, due to triazine. Mass spectral analysis produced a large peak due to the parent compound.

D. (U) POLYMER CURING

1. (U) Curing of carboxy-terminated perfluoroalkyleneoxide polymer with and without aluminum powder and ammonium perchlorate. - Small samples of liquid

polymer $\bar{M}_n$ 3000, functionality of about 2.2 (equivalent weight 1350), were cured with epoxy compounds at room temperature.

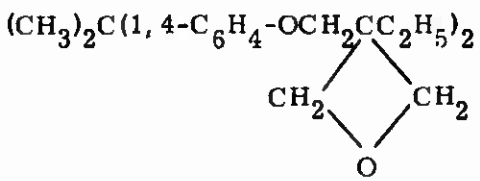
(a) Liquid polymer (1.2 g., 0.9 meq.) was mixed with 0.070 g. (0.7 meq.) dicyclopentenylether diepoxide (ERLA 0400) to give a clear homogeneous mixture at room temperature. The viscosity gradually increased to a tacky rubber in 0.5 hour, and a nontacky, bubble-free, transparent elastomer in 2 hours.

(b) The above cure was repeated in the presence of 0.2 g. of aluminum powder and 0.1 g. of ammonium perchlorate crystals. A nontacky, rubbery product formed in slightly over 2 hours at room temperature.

(c) Liquid polymer (0.9 g., 0.67 meq.) and 0.025 g. (0.58 meq.) of butadiene diepoxide were mixed to give a homogeneous system which gelled to a transparent bubble-free elastomer in 2 hours at room temperature.

2. (C) Curing of carboxy-terminated perfluoroalkyleneoxide polymer with an oxetane. -

(C) (a) The liquid polymer ($\bar{M}_n$ 2200, functionality about 2) 0.6 g. (0.55 meq.), was mixed with 0.09 g. (0.42 meq.) of bisoxetane of the following structure:



The crystalline oxetane appears insoluble. The mixture was heated at 105°C. in an air oven. After 20 minutes, the solid appeared to dissolve to yield a viscous oil. After 1.3 hours, the mixture had cured to a nontacky firm rubber, containing some air bubbles (possibly introduced when mixing the fluffy oxetane). Heating an additional 2 hours at 105°C. caused no change in appearance. The T_g of this rubber as determined by differential thermal analysis is -60°C.

(C) (b) The cure with the bisoxetane was repeated with the same proportions of reagents. After warming a few minutes at about 60°C., the viscous, fluid mixture, containing some undissolved oxetane, was allowed to stand at room temperature for two days. The viscosity gradually increased during this period to yield a tacky rubbery gel. Some crystals of oxetane still appeared to be present.

3. (U) Crosslinking perfluorosebaconitrile by catalytic triazine formation at room temperature. -

(U) (a) $NC(CF_2)_8CN$ (0.98 g., 1.9 mmole), b.p. 148°, and 0.012 g. (0.037 mmole) of $(C_4H_9)_3SbO$ were mixed in a glass vial and let stand at room temperature. After standing overnight, a white waxy solid had formed. Infrared examination revealed a strong 6.4 micron peak due to triazine formation and a moderate 4.4 micron peak due to starting nitrile. The solid hardened on further standing.

(U) (b) Modification with $C_5F_{11}CN$. - In a dry, screw-top glass vial was placed 1.0 g. (2.2 mmole) of $NC(CF_2)_8CN$, 0.53 g (1.8 mmole) of $C_5F_{11}CN$, and 0.018 g. (0.057 mmole) of $(C_4H_9)_3SbO$. The mixture was shaken and let stand at room temperature. Infrared examination of the liquid mixture after 4 hours revealed a strong triazine peak at 6.4 and a nitrile peak at 4.4 micron. On standing overnight, a very viscous transparent liquid had formed, which in two more days was a slightly tacky, transparent gel. Infrared indicated a high conversion to triazine, with some free nitrile groups present.

REFERENCES

1. Minnesota Mining and Manufacturing Company, Perfluoro Alkylene Oxide Polymers as High-Temperature Sealants, Contract No. AF 33(615)-1658, Annual Report, July 1964 to June 1965.

2. Minnesota Mining and Manufacturing Company, Perfluoro Alkylene Oxide Polymers as High-Temperature Sealants, Technical Report AFML-TR-65-216, Part II, July 1966.

3. J. F. Harris, J. Org. Chem., 30, 2182 (1965).

4. Minnesota Mining and Manufacturing Company.

5. R. A. Mitsch, J. Am. Chem. Soc., 87, 328 (1965) and other unpublished 3M work.

6. P. E. Peterson, C. Casey, E. Y. P. Tao, A. Agtarak and G. Thompson, J. Am. Chem. Soc., 87, 5163 (1965).

7. (a) W. L. Reilly and H. C. Brown, J. Org. Chem., 22, 698 (1957).
   (b) E. R. Bissell and R. E. Spengler, J. Org. Chem., 24, 1147 (1959)
   (c) Hooker Chemical Corp., Perfluoroalkylenetriazine Elastomeric Polymers, Contract No. AF 33(615)-1636, Quarterly Progress Report No. 6, 1 December to 28 February 1966.
   (d) Peninsular Chem. Research, Inc., Synthesis of New Fire Resistant Hydraulic Fluids, Contract No. NObs-92265, Bimonthly Status Report No. 3, 25 July 1965 to 25 September 1965.

8. Firestone Tire and Rubber Company, High Temperature Resistant Elastomeric Compounds, Contract No. AF 33(616)-6998, Technical Document Report No. WADC-TR-56-331, January, 1963.

9. W. J. C. Dyke and W. J. Jones, J. Chem. Soc., 1921 (1930).

10. A. J. Bloodworth and A. G. Davies, J. Chem. Soc., 6858 (1965).

11. G. G. Long, G. O. Doak and L. D. Freedman, J. Am. Chem. Soc., 86, 209 (1964).

12. G. Wittig and K. Torssel, Acta. Chim. Scand., 7, 1293 (1953).

13. D. L. Alleston and A. G. Davies, J. Chem. Soc., 2050 (1962).

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13. ABSTRACT

(U) Chemical purification of perfluorooxydipropionyl fluoride has resulted in good yields of high purity monomer for photopolymerization reactions.
(U) Extensive photopolymerization studies were conducted on perfluorooxydipropionyl fluoride to analyze the factors which influence molecular weight, extent of branching, and functionality.
(U) A variety of curing reactions have been carried out on model compounds and polymer samples using epoxides, oxazolines and oxetanes.
(U) A high yield, room temperature catalytic trimerization of perfluoroalkanonitriles was discovered under this contract. A variety of possible catalysts have been screened, and the most active of these, tributyl antimony oxide, was used to prepare perfluoroalkyl triazines for thermal and hydrolytic stability studies.
(C) Polymer samples have been evaluated in the presence of aluminum and ammonium perchlorate to determine their compatibility with propellant mixtures.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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