

Second Annual Summary Report

"DEVELOPMENT OF THERMALLY STABLE PHOSPHONITRILE
ELASTOMERS FOR ADVANCED AEROSPACE STRUCTURES"

Contract No. NAS8-25184

DCN 1-1-50-13631

April 24, 1971 to April 23, 1972

Authors

Kennard A. Reynard
Selwyn H. Rose

June 1972

to

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812

FACILITY FORM 602

(NASA CR OR TMX OR AD NUMBER)

W73-13593
(ACCESSION NUMBER)

50
(PAGES)

Q3
(CODE)

18
(CATEGORY)

(THRU)

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ABSTRACT

Attempts to prepare low molecular weight, curable poly(fluoroalkoxyphosphazenes) have been successful. Derivatization of $[\text{Cl}_2\text{PN}]_n$ polymer with alkoxides derived from $\text{CF}_3\text{CH}_2\text{OH}$, $\text{C}_3\text{F}_7\text{CH}_2\text{OH}$, and $\text{CH}_3\underset{\text{OH}}{\text{C}}\text{HCH}_2\text{CH}_2\text{OH}$ or $\text{C}_2\text{H}_5\text{NHCH}_2\text{CH}_2\text{OH}$ gave functionally reactive terpolymers. These terpolymers could be crosslinked with polyisocyanates at room temperature.

Attempts to control molecular weight have not been as successful. The effects of $(\text{Cl}_2\text{PN})_3$ monomer purity, use of $(\text{Cl}_2\text{PN})_{3,4}$ mixture, and early termination of the bulk polymerization of $(\text{Cl}_2\text{PN})_3$ were studied briefly. Both low and high molecular weight polymers were obtained. Reaction of NH_4Cl with PCl_5 with subsequent heating to give chain extension gave either gels or oils with molecular weights of several thousand.

The stabilization of poly(fluoroalkoxyphosphazene) was investigated. The results generally were inconclusive, but acids were found to be deleterious while bases had little discernible effect. Improvements in stability by modification of end groups was inconclusive.

High molecular weight $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$ copolymer was compounded, cured, and supplied to NASA. A copolymer rich in $\text{C}_3\text{F}_7\text{CH}_2\text{O}$ - and a $[(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$ homopolymer which were plastics also were supplied.

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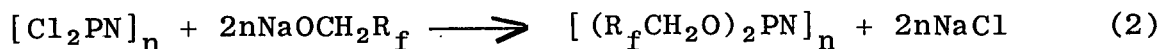
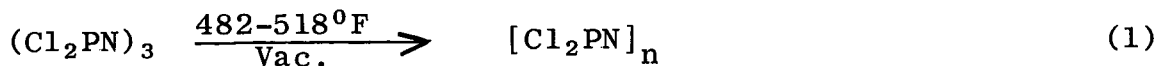
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"DEVELOPMENT OF THERMALLY STABLE PHOSPHONITRILE
ELASTOMERS FOR ADVANCED AEROSPACE STRUCTURES"

1.0 INTRODUCTION AND SUMMARY

A research program to develop high strength, chemically resistant polymers which retain properties over a wide temperature range was begun several years ago at Horizons Incorporated. This research has resulted in the preparation of a series of poly(fluoroalkoxyphosphazene) elastomers and plastics which have a unique combination of properties. These materials have very good low temperature properties, excellent solvent resistance and are flame retardant. These materials appear to have a thermal capability of 300°F in long term use and the potential of being developed for use at considerably higher temperatures. The elastomers have been cured to give high strength samples (1800-2500 psi, 100-200% elongation).

The synthetic route to poly(phosphazenes) involves the preparation and subsequent reaction of soluble poly(dichlorophosphazene) as shown in equations (1) and (2).



If a mixture of alkoxides is used, substitution occurs in a nonregular fashion and a copolymer is obtained.

While $[(CF_3CH_2O)_2PN]_n$ is a crystalline plastic which is soluble in various oxygenated solvents [Ref. 1], the $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ copolymer is an elastomer which is soluble only in certain fluorinated solvents [Ref. 2]. The copolymer has a glass transition temperature (DTA) of $-77^{\circ}C$ ($-107^{\circ}F$) [Ref. 3] and has an initial decomposition point of $300^{\circ}C$ ($572^{\circ}F$) in air on a thermobalance at a heating rate of $2.8^{\circ}C$ per minute [Ref. 4]. Intrinsic viscosities of the polymer as high as 2.4 dl/g at $30^{\circ}C$ have been observed in $F[CF(CF_3)CF_2O]_2CHFCF_3$.

The copolymer appears unaffected after prolonged immersion in boiling water, concentrated alkali or mineral acids, and common organic solvents, but is soluble in the Freon solvents TA, TF and E-2. When placed in a direct flame, the material softens and vaporizes but will not burn. This material was evaluated at the U. S. Army Natick Laboratories and was found to have "the best combination of fuel resistance and low temperature properties to date of any fluorine-containing elastomer developed under the long term Army rubber research effort" [Ref. 5].

Two other highly interesting elastomers, $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$ and $[(HCF_2CF_2CH_2O)_2PN-(HCF_2C_5F_{10}CH_2O)_2PN]_n$, have shown good solvent resistance to benzene and hydrocarbons but are soluble in many polar organic solvents [Ref. 6]. Both elastomers vaporize without ignition in a

direct flame. These copolymers have glass transition temperatures of -67°C and -64°C , respectively. The intrinsic viscosities of these copolymers generally are between 2 and 5 dl/g at 30°C in acetone. They have initial decomposition points similar to $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$.

An interesting family of plastics also has been developed [Ref. 6]. These plastics are based on homopolymers and copolymers which contain the heptafluorobutoxy-substituent. The homopolymer, $[(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$, is a fibrous plastic which does not darken or melt on heating in air to 572°F . Copolymers of the type $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$ which are rich in the $\text{C}_3\text{F}_7\text{CH}_2\text{O}$ - substituent have been prepared. These materials are translucent plastics but they have a wider degree of solubility than the $[(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$ homopolymer. These copolymers are soluble in Freon TA and are easily cast to form solvent resistant coatings.

The objectives of this second year's effort on Contract NAS8-25184 (April 24, 1971 to April 23, 1972) are to prepare poly(fluoroalkoxyphosphazenes) in a variety of molecular weight ranges and to crosslink these materials under mild conditions. The resultant materials are to be developed as sealants, potting compounds, coatings and elastomers for service in the presence of fuels at 500°F and for short time exposure up to 700°F .

Some successes were achieved during this year's effort. Two elastomeric terpolymers were prepared and were cured at room temperature. Also, several methods for preparation of low molecular weight poly(dichlorophosphazene) were investigated and three routes appeared to be successful. Attempts to improve thermal stability were less successful. An attempted modification of the end groups of the poly(dichlorophosphazene) before derivatization was inconclusive. Incorporation of several fillers into the derivatized material had little effect on thermal stability.

Terpolymers of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ were prepared which contained a small amount of a third constituent which was introduced in an effort to facilitate low temperature crosslinking. The reaction moieties investigated were the amine, $C_2H_5NHC_2H_4O-$ and the secondary alcohol, $CH_3CH(OH)C_2H_4O-$. Both terpolymers, $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-(C_2H_5NHC_2H_4O)_2PN]_n$ and $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_2PN]_n$, were readily cured at room temperature with the use of diisocyanates in the presence of a catalyst. Both TDI and PAPI were used, and the catalyst was dibutyltin diacetate. A third terpolymer which contained the $C_2H_5SC_2H_4O-$ moiety was prepared but crosslinked upon standing.

A variety of different approaches were tried in an attempt to prepare low molecular weight poly(dichlorophosphazene) which after derivatization would be suitable for

sealant and potting compound applications. Several of these approaches appeared to be successful. Bulk polymerization of mixtures of purified hexachlorophosphazene and purified octachlorophosphazene produced oils, greases, and flowable gums. Bulk polymerization of unpurified hexachlorophosphazene gave oils and elastomers. The reaction of PCl_5 with NH_4Cl followed by chain extension produced oil fractions.

The modification of high molecular weight poly(dichlorophosphazene) by reaction with sulfur dioxide before derivatization was attempted. After derivatization a copolymer which had different solution properties was obtained. However, the resultant copolymer did not appear to age differently than the same copolymer prepared from poly(dichlorophosphazene) which was not pretreated with SO_2 .

Several additives were mixed with $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$ gum stock in an effort to improve thermal stability. These additives were taken from acidic, amphoteric and basic classes, but little change in thermal stability was observed.

A variety of samples were supplied to NASA for evaluation as flame-retardant materials. Several different specimens of $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$ were submitted. These specimens included the raw gum, a cured unfilled sample and a cured filled sample. Also, the $[(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}-(\text{C}_7\text{F}_{15}\text{CH}_2\text{O})_2\text{PN}]_n$ elastomer and the $[(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$ homopolymer

were furnished. A $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ composition which was rich in the heptafluorobutoxy- substituent was provided for evaluation as a potential conformal coating for circuit boards.

2.0 EXPERIMENTAL

2.1 Preparation of Terpolymers of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$

2.1.1 Preparation of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_2PN]_n$

An alkoxide mixture was prepared by the reaction of CF_3CH_2OH (18.0 g, 0.18 mole), $C_3F_7CH_2OH$ (36.0 g, 0.18 mole) and $CH_3CH(OH)C_2H_4OH$ (10.8 g, 0.12 mole) with sodium (10.1 g, 0.44 mole) in 400 ml of dry tetrahydrofuran. The alkoxide mixture was stirred overnight at room temperature and refluxed for 3 hours but additional glycol (5.4 g, 0.06 mole) was added to complete the reaction of the sodium (three hour reflux). The $[Cl_2PN]_n$ polymer (23.2 g, 0.20 mole) in dry benzene was added to the alkoxide solution at reflux in about 1.5 hours. After the addition was complete, the reaction mixture was stirred for 0.5 hour and allowed to cool to room temperature. The liquid layer was decanted, and the solid portion was washed with water. The solid product was dissolved in 600 ml of Freon TA and washed with water until the aqueous layer was free of chloride ion. Upon precipitation into benzene, an opaque white rubbery solid (26 g) was obtained. The terpolymer had an intrinsic viscosity of 0.83 dl/g in Freon TA at 28°C. Anal. Calcd. for the title terpolymer which contains 11.4 mole percent of $CH_3CH(OH)C_2H_4O-$: C, 22.7; H, 1.7; N, 4.3; Cl, 0.0. Found: C, 22.7; H, 1.7; N, 4.6; Cl, 0.2. The proton nuclear magnetic resonance data (NMR) are given in Table I. By integration, the amount of $CH_3CH(OH)C_2H_4O-$ was calculated to be about 20 mole percent.

TABLE I.

H¹ Nuclear Magnetic Resonance Data for High Molecular Weight
Poly(fluoroalkoxyphosphazene) Terpolymers
cps, Downfield from TMS

Compound	CF ₃ CH ₂ O- CF ₃ CF ₂ CF ₂ CH ₂ O- -CH ₂ O-	Termonomer				Solvent
[(CF ₃ CH ₂ O) ₂ PN-(C ₃ F ₇ CH ₂ O) ₂ PN- {CH ₃ CH(OH)C ₂ H ₄ O} ₂ PN] _n 1782-29		CH ₃ -CH-CH ₂ -CH ₂ O- OH				Freon TF
		CH ₃ -,	-CH-,	-CH ₂ - (-CH-CH ₂ -)	-CH ₂ -	
	267	80	267	120	267	
	unequ. triplet	doublet	unequ. triplet	broad singlet	unequ. triplet	
[(CF ₃ CH ₂ O) ₂ PN-(C ₃ F ₇ CH ₂ O) ₂ PN- (C ₂ H ₅ NHC ₂ H ₄ O) ₂ PN] _n 1782-31		CH ₃ -CH ₂ -NH-CH ₂ -CH ₂ -O-				Freon TF D ₆ acetone
		CH ₃ -	-CH ₂ - (-CH ₂ -NH)	-CH ₂ - (NH-CH ₂ -)	(-CH ₂ -O-)	
	284	75	185	185	185	
	unequ. triplet	triplet	broad singlet	broad singlet	broad singlet	

2.1.2 Cure of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_2PN]_n$

Curing studies with diisocyanates (TDI and DDI) were carried out. A 10% polymer solution in Freon TA was prepared, crosslinking agents were added and the mixture was observed at room temperature. The curing data are summarized in Table II.

TABLE II

Room Temperature Cures of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_2PN]_n$

Cure Mixture Terpolymer Solution (5 g)			Time of Observation (hrs.)	Remarks (b)
TDI (g)	DDI (g)	Catalyst (a) (micro liters)		
	0.15		240	no cure, evaporate and heat to 80-90°C for several hours, cured
	0.15	15	5	very slight cure
	0.1	10	5	very slight cure
	0.2	20	5	yellowish color very slight cure
0.05		5	5 24	no cure moderate cure
0.08		8	5 12	no cure tight cure

(a) dibutyltin diacetate

(b) cured samples in bulk form were hazy to opaque.

All cured samples were stable on standing in the presence of solvent.

2.1.3 Preparation of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-(C_2H_5NHC_2H_4O)_2PN]_n$

An alkoxide mixture was prepared in 400 ml of dry tetrahydrofuran from sodium (10.1 g, 0.44 mole), CF_3CH_2OH (18.0 g, 0.18 mole), $C_3F_7CH_2OH$ (36.0 g, 0.18 mole) and 2-ethylaminoethanol (10.7 g, 0.12 mole). The mixture was stirred overnight and refluxed for 3 hours. Considerable sodium remained and additional 2-ethylaminoethanol (5.3 g, 0.06 mole) was added, and reflux was continued for 3 more hours whereupon the sodium was consumed. Over a period of 1.5 hours, $[Cl_2PN]_n$ polymer (23.2 g, 0.20 mole) in 330 ml of dry benzene was added to the light yellow alkoxide mixture at reflux and reflux was continued for 1/2 hour. The next day the liquid ($pH > 10$) was decanted and evaporated to give an oil fraction. The solid was water washed, and dissolved in 600 ml of Freon TA, and washed with water until the aqueous layer was free of chloride ion. The polymer was isolated by precipitation into 1-1/2 volumes of benzene. The procedure was repeated a second time. A slightly yellowish elastomer (28 g) was obtained which had an intrinsic viscosity of 0.55 dl/g at $28^\circ C$ in Freon TA. Anal. Calcd. for the title terpolymer which contains 10 mole percent of $C_2H_5NHC_2H_4O$: C, 22.5; H, 1.7; N, 5.1; Cl, 0.0. Found: C, 22.2; H, 1.7; N, 5.6; Cl, 0.3. Proton NMR showed that the -NH- proton which is usually quite broad and difficult to locate was not observed. Upon integration the amount of $C_2H_5NHC_2H_4O$ - was calculated to be about 10 mole percent.

2.1.4 Cure of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-(C_2H_5NHC_2H_4O)_2PN]_n$

A solution of the terpolymer (10%) in Freon TF/acetone (1v/1v) was treated with TDI or DDI at room temperature. The samples were retained in solution in closed containers and observed periodically. The data are summarized in Table III.

TABLE III

Room Temperature Cures of
 $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-(C_2H_5NHC_2H_4O)_2PN]_n$

Cure Mixture Terpolymer Solution (5 g)			Time of Observation (hrs.)	Remarks (b)
TDI (g)	DDI (g)	Catalyst (a) (micro liters)		
	0.15	none	1	slight cure
	0.15	none	240	slight cure
	0.15	1.5	2	moderate cure
	0.1	10	2	moderate cure
	0.2	20	2	moderate cure
0.05		5	2	tightly cured and clear in bulk form
0.08		8	2	tight cure
0.1		10	2	tight cure

(a) dibutyltin diacetate

(b) cured samples in bulk form were hazy to opaque except where indicated.

Samples which were cured with DDI appeared to partially redissolve on standing and with some samples loss of viscosity also took place. This phenomenon is unexplained and was not observed with the TDI cured samples.

2.1.5 Attempted Preparation of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-(C_2H_5SC_2H_4O)_2PN]_n$

An alkoxide mixture was prepared by the reaction of CF_3CH_2OH (19.8 g, 0.198 mole) and $C_3F_7CH_2OH$ (39.6 g, 0.198 mole) with sodium (9.30 g, 0.404 mole) in 400 ml of dry tetrahydrofuran. The alkoxide mixture was stirred overnight, and sodium was still present when ethylthioethanol (4.6 g, 0.044 mole) was added to the mixture which was heated to $60^\circ C$. A light yellow color developed and the sodium was consumed in 3 hours. The $[Cl_2PN]_n$ polymer (21.3 g, 0.18 mole) was dissolved in 400 ml of dry benzene and added to the mixture at reflux in about 1.5 hours. After the addition was complete, the reaction mixture was heated at reflux for 16 hours before the liquid layer was decanted. The solid portion was washed once with tetrahydrofuran and three times with water. The sticky solid was dissolved in 300 ml of Freon TA and washed with water until the aqueous layer was free of chloride ion. The polymer solution was added to 3 liters of benzene but precipitation did not take place. The solution was evaporated to dryness, and the residue was extracted with acetone to give an acetone soluble fraction and an acetone

insoluble fraction. Neither fraction contained appreciable amounts of sulfur as determined by elemental analysis.

The preparation of the title terpolymer by an interchange reaction also was attempted. Ethylthioethanol (1.17 g, 0.011 mole) was added to sodium (0.23 g, 0.01 mole) in 30 ml of dry tetrahydrofuran. The mixture was stirred overnight at 40°C and the solution turned dark brown (pH >12). The solution was added to a $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ copolymer (3.43 g, 0.01 mole) in 70 ml of Freon E-2. The mixture was stirred for 3 hours at 50°C and was added to 400 ml of a 1:1 benzene/acetone mixture without formation of a precipitate. The solution was evaporated to give a rubbery film which was water washed and dissolved in 75 ml of Freon TA. The solution was water washed until the aqueous layer was free of chloride ion. After precipitation into 750 ml of benzene, 2.6 g of a snappy solid was obtained. This product on standing at room temperature for 2-3 days became insoluble in Freon TA.

2.2 Synthesis of Low Molecular Weight $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ Copolymers and Terpolymers

2.2.1 Polymerization of Purified $(Cl_2PN)_3$ in the Presence of Purified $(Cl_2PN)_4$

Hexachlorophosphazene (m.p. 112-114°C) and octachlorophosphazene (m.p. 122.8-123.8°C) were polymerized under vacuum, purified and derivatized to form $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ in normal fashion. Characterization data for

the copolymers are summarized in Table IV. Polymerization temperature differences were due to fluctuations in the bath in which the samples were polymerized. Increased amounts of octachlorophosphazene appear to lead to longer polymerization times, lower percent conversions and lower molecular weight poly(dichlorophosphazene).

The copolymer with intrinsic viscosity of 0.40 dl/g was aged at 150°C for 24 hours and 48 hours in air. Values of 0.32 dl/g and 0.28 dl/g, respectively, were obtained.

In addition to the materials that were obtained by precipitation, other fractions were isolated by evaporation of reaction solvents, and solvents used for purification. These fractions are described in Table V.

2.2.2 Bulk Polymerization of Unpurified (Cl₂PN)₃

Commercial hexachlorophosphazene (El Monte Chemical Corp.) is a mixture comprised mostly of cyclic materials (70-80% hexachlorophosphazene, 15-20% octachlorophosphazene) with some linear materials possibly present. Bulk polymerization of this mixture gave [Cl₂PN]_n polymer which was quite fluid at 100°C which indicated a low molecular weight. Normal derivatization to form [(CF₃CH₂O)₂PN-(C₃F₇CH₂O)₂PN]_n gave low molecular weight copolymers. Some of these materials were gummy rubbers with extensive cold flow and some were pourable oils. A summary of synthesis and characterization data for these derivatized low molecular weight materials is found in Tables VI and VII. Upon evaporation of reaction solvents

TABLE IV

Characterization of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ Elastomers
 Obtained from Polymerization of $(Cl_2PN)_{3,4}$ Mixtures

$(Cl_2PN)_4$ Present (wt. %)	Poly. Time (hrs.)	Poly. Temp. (°C)	$[\eta]$ at 28°C of $[Cl_2PN]_n$ in Benzene (dl/g)	$[\eta]$ at 28°C in Freon E-2 (dl/g)	F ¹⁹ NMR (mole %)		Remarks
					CF_3CH_2O-	$C_3F_7CH_2O-$	
10	13	270	-	0.40	49.5	50.5	stringy elastomer no cold flow at room temperature
50	8	265	0.34	0.30	50.5	49.5	snappy elastomer no cold flow at room temperature
50	5	270	-	0.20	50.0	50.0	stringy material no cold flow
70	16	265	0.38	0.19	52.5	47.5	elastomeric cold flow at room temperature

TABLE V

[(CF₃CH₂O)₂PN-(C₃F₇CH₂O)₂PN]_n Products Obtained
from Polymerization of (Cl₂PN)_{3,4} Mixtures

(Cl ₂ PN) ₄ Present (wt. %)	Main Fraction (g) (from precipitation) See Table IV	Fraction (g) from Evaporation of Reaction Solvents (Benzene-THF)	Fraction (g) from Evaporation of First Precipitation (Freon TA-Benzene)	Fraction (g) from Evaporation of Second Precipitation (Freon TA-Benzene)
10 (a)	60.4	11.4 yellow liquid	6.2 white viscous oil	3.0 very viscous white oil
50	9.5	37.8 yellow liquid	1.3 gray viscous liquid	0.8 gray semisolid
50	12.7 (a)	40.0 yellow liquid	1.8 white viscous oil	1.1 white semisolid
	1.2	8.4 white liquid	1.1 white viscous oil	2.0 white semisolid
70	1.1	2.7 yellow viscous liquid	3.9 [η] = 0.22 soft rubber with cold flow	2.6 gray soft rubber

(a) hydrolysis of sample with dilute acid

TABLE VI

Characterization of Low Molecular Weight $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$
Elastomers Obtained from Polymerization of Unpurified $(Cl_2PN)_3$

Sample Number	Polymerization		Conversion (%)	$[\eta]$ at 28°C [$(CF_2CH_2O)_2PN-$ $(C_3F_7CH_2O)_2PN$] _n in Freon E-2 (dl/g)	CF ₃ CH ₂ O-,	C ₃ F ₇ CH ₂ O-	Cl Content (%)	Cold Flow
	Time (hrs.)	Temp. (°C)						
1699-30	96	250	80	0.46	58	42	0.2	several days
1755-18	94	250	80	0.62 (a)	50	50	0.2	none
1755-46	16	270	80	0.39 (acid hydrolysis)	51.5	48.5	0.2	weeks
				0.22 (water hydrolysis)	51.2	48.8	0.1	weeks

(a) the $[Cl_2PN]_n$ had $[\eta]$ of 0.25 in benzene at 28°C

(benzene-tetrahydrofuran) and precipitation solvent mixtures (benzene-Freon TA), lower molecular weight fractions were isolated and they are summarized in Table VII.

2.2.3 Early Termination of Bulk Polymerization of Purified $(Cl_2PN)_3$

Hexachlorophosphazene was polymerized under vacuum and the polymerization was terminated when the melt became slightly viscous. The purified $[Cl_2PN]_n$ polymer was derivatized to the $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ copolymer in routine manner. A snappy elastomer (3.3 g) with very slow cold flow was obtained. The intrinsic viscosity of the copolymer was determined to be 0.44 dl/g in Freon E-2 and the composition of the copolymer was determined by $F^{19}NMR$ to be 1.3(CF_3CH_2O-):1($C_3F_7CH_2O-$). Upon evaporation of the reaction solvents (benzene-tetrahydrofuran) 0.3 g of yellow viscous liquid was obtained. The two solvent mixtures from purification (Freon TA-benzene) were evaporated and 0.6 g of yellow gummy solid and 0.4 g of white soft solid were obtained.

2.2.4 Reaction of NH_4Cl with PCl_5

Phosphorus pentachloride was sublimed before use. Ammonium chloride was prepared by reaction of ammonia with hydrogen chloride in chlorobenzene. Chlorobenzene was distilled from anhydrous $MgSO_4$ under an atmosphere of N_2 after a large forerun was discarded.

TABLE VII

Fractions of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ Copolymers
Obtained from Polymerization of Unpurified $(Cl_2PN)_3$

Sample Number	Main Fraction (g) (from precipitation)	Fraction (g) from Evaporation of Reaction Solvents (Benzene-THF)	Fraction (g) from Evaporation of First Precipitation (Freon TA-Benzene)	Fraction (g) from Evaporation of Second Precipitation (Freon TA-Benzene)
1699-30	14.3 elastomer cold flow	33.6 yellow, waxy solid	22.0 gummy elastomer cold flow	-
1755-18 (a)	47.5 elastomer without cold flow	24.3 yellow oil	8.6 white, opaque oil [η]=0.02 dl/g (Freon E-2) mw=2115 (Freon TF)	7.0 white, viscous solid
1755-46	34.3 elastomer with slow cold flow	27.0 colorless oil	6.9 white, viscous oil	2.8 very viscous, white oil
1755-46 (a)	4.7 elastomer with slow cold flow	4.9 colorless oil	2.0 very viscous white oil	3.9 white semisolid slow cold flow

(a) hydrolysis with water

Liquid ammonia (24 g, 1.41 moles) was dried over sodium and slowly vaporized into 1.2 liters of chlorobenzene. Simultaneously, hydrogen chloride (>1.41 moles) was passed through concentrated sulfuric acid into the chlorobenzene solution. The heat of reaction raised the temperature of the slurry to 67°C and the addition time was 3 hours.

Chlorobenzene (200 ml) was distilled to insure anhydrous conditions and to remove excess HCl. Phosphorus pentachloride (346 g, 1.66 moles) was added under nitrogen at room temperature and the reaction mixture was heated to reflux ($\approx 135^\circ\text{C}$). Hydrogen chloride began to evolve at 70°C and was collected in a solution of NaOH. After 2 hours at reflux the reaction mixture was a clear yellow-green solution. The NaOH solution titer indicated that 98% of the theoretical amount of HCl was evolved. Chlorobenzene was distilled under vacuum until a yellow-white solid remained. Three 250 ml portions of n-pentane (distilled from CaH_2) were used to extract 95.6 g of $(\text{Cl}_2\text{PN})_3$ from the solid. A yellow-green oil remained which was heated at 160°C under 10 mm in a sublimator for 15 minutes. However, a sublimate (which would consist of unreacted NH_4Cl and PCl_5) was not observed. The oil (113 g) had a refractive index of 1.6112 at 23°C and crystallized upon standing. The infrared spectrum showed a broad intense peak centering at 1300 cm^{-1} and another strong band at 770 cm^{-1} . The product was assumed to be

$\text{Cl}[\text{Cl}_2\text{PN}]_n\text{PCl}_3^{\oplus}\text{PCl}_6^{\ominus}$, in which n was about 8. Anal. Calcd. for $\text{N}_8\text{P}_{10}\text{Cl}_{26}$: N, 8.3; P, 23.0; Cl, 68.6, molecular weight 1345. Found: N, 8.5; P, 23.5; Cl, 67.7, molecular weight (VPO) 1249 (benzene) and 816 (chloroform). The difference in molecular weight values may be due to the insolubility of lower molecular weight fractions in benzene, which led to selective fractionation.

Portions (5-6 g) of the solidified oil were placed in a small sublimator and heated under nitrogen at 250°C for different periods of time. A white solid normally sublimed onto the cold finger and the oils became darker. Upon heating for 10 and 16 hour periods, gelation occurred and insoluble material was formed. Reportedly [Ref. 4], soluble products of higher molecular weight should be obtained when the sample is heated at 250°C for 48 hours.

Soluble chain extended oils were derivatized to $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$ copolymers. Characterization of the chain extended products and their $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$ derivatives is summarized in Table VIII. Except for sample 1755-32, which was a thick grease, the other samples were oils.

The data are informative from the experiments which employed identical low molecular weight polymer but different types of hydrolysis during purification. Acid treatment

TABLE VIII

Characterization of Chain Extended Products

Sample Number	Chain Extension Time (hrs.)	Temp. (°C)	%Cl	Molecular Weight (a) in Acetone	Composition by ^{F19} NMR	
					CF ₃ CH ₂ O-	C ₃ F ₇ CH ₂ O-
1717-12	0		67.7	816 (c)	-	-
1717-44			<0.1	1300	1.17	1.0
1717-21	4	250	<0.1	1931	1.27	1.0
1717-30	6	250	<0.1	2460	1.21	1.0
1717-32	8	250	<0.1	2420	1.23	1.0
1755-14	4	250	-	1390 (c)	-	-
1755-15A			0.4	1290	1.15	1.0
1755-15B (b)			0.5	1770	1.20	1.0
1755-28	16	200	-	1310 (c)	-	-
			<0.1	1750	1.19	1.0
1755-32	6	250	-	2600 (c)	-	-
			<0.1	3300	1.25	1.0

(a) by vapor pressure osmometry

(b) hydrolyzed in the absence of acid

(c) underivatized and determined in CHCl₃

(1755-15A) gave more degradation than treatment carried out in the absence of acid (1755-15B).

2.2.5 Preparation and Attempted Cure of Low Molecular Weight $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_2PN]_n$

Low molecular weight poly(dichlorophosphazene) was prepared from unpurified $(Cl_2PN)_3$ as described in Section 2.2.2 and was derivatized and purified in the same manner as described in Section 2.1.1 except acid hydrolysis was employed. Summary of polymerization data and characterization of the derivatized products are given in Table IX. The low molecular weight fractions, 1820-03T and 1820-13T, were chosen for curing studies. Analytical and molecular weight data obtained for these two oils are given in Table X. The calculated mole percent of $CH_3CH(OH)C_2H_4O-$ in 1820-03T and 1820-13T, on the basis of elemental analyses, was about 33 and 38%, respectively. Integration of the NMR data indicated mole percents of about 62 and 66, respectively. The infra-red spectra of these terpolymers were very similar and showed a shoulder in the OH stretching frequency region 3400-3500 cm^{-1} .

An attempt was made to cure 1820-03T with TDI in the absence of solvent and the data are summarized in Table XI. The cures were not successful and an isocyanate with higher isocyanate functionality was investigated. The use of polymethylene polyphenyl isocyanate (PAPI) necessitated

TABLE IX

Low Molecular Weight $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_2PN]_n$

Sample Number	Polymerization			Purified Polymer Fraction			Other Fractions (g)		
	Time (hrs.)	Temp. (°C)	Conversion (%)	$[\eta]$ (a) (dl/g)	Cl (%)	Remarks	Fraction 1 (b)	Fraction 2 (c)	Fraction 3 (d)
1820-03	4	270	37	0.34	0.0	1.7 g gray weak rubber	17.5 viscous oil (1820-03T)	0.9 yellow viscous oil	0.2 very viscous yellow oil
1820-13	7	270	12	0.12	0.2	2.8 g white sticky taffy	4.2 yellow sticky taffy with very slow cold flow (1820-13T)	-	-

(a) in Freon E-2 at 28°C

(b) from evaporation of reaction solvents (benzene-THF)

(c) from evaporation of first precipitation solvents (Freon TA-benzene)

(d) from evaporation of second precipitation solvents (Freon TA-benzene)

TABLE X

Characterization of Low Molecular Weight
 $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_2PN]_n$

Sample Number	Analysis (%) (a)				Approximate (b) Mole % of $CH_3CH(OH)C_2H_4O$	Molecular Weight (c) (Mw)
	C	H	N	Cl		
1820-03T	26.3 (26.3)	2.8 (2.8)	5.3 (4.6)	0.0 (0.0)	33	980
1820-13T	27.3 (27.3)	3.1 (3.1)	5.6 (4.7)	0.2 (0.0)	38	2860

(a) calculated values in parentheses on the basis of a 1:1 ratio of $CF_3CH_2O:C_3F_7CH_2O$

(b) calculated from elemental analysis

(c) by VPO in acetone

TABLE XI

Attempted Curing of Low Molecular Weight
 $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_2PN]_n$
 (1820-03T)

Terpolymer Oil (g)	TDI (g)	PAPI (g)	Catalyst (a) microliters	Tetra- hydrofuran (ml)	Remarks
1.66	0.07		7		No cure at room temperature, heat to 80°C (20 hrs) and the oil became quite viscous but remained soluble
1.66	0.09		9		
1.66	0.11		11		
0.5		0.14	20	2	No cure at room temperature
0.5		0.27	20	2	" "
0.5		0.40	20	2	" "
0.8		0.13	13	2	No cure at room temperature or when heated to 50°C (6 hrs)

(a) dibutyltin diacetate

the use of tetrahydrofuran in order to render the system miscible. Neither isocyanate gave a successful cure and sufficient time was not available to allow curing studies of 1820-13T.

2.3 Attempted Stabilization of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$

2.3.1 Effect of Purification Procedures

During a normal preparation of a copolymer of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$, excess alkoxides were used to insure complete substitution of the P-Cl bonds in the $[Cl_2PN]_n$ polymer. After reaction, dilute acid usually was added to neutralize the excess alkoxides before polymer purification.

Companion reactions were conducted in which purification procedures were varied. Identical $[Cl_2PN]_n$ was derivatized with an identical alkoxide mixture to form $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ copolymer. Acid hydrolysis and hydrolysis in the absence of acid were investigated. The yields of copolymers were 69% (acid treated) and 77% (water treated). Anal. Calcd. for $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ (1:1): C, 21.0; H, 1.2; N, 4.1; F, 55.4; Cl, 0.0. Found (acid hydrolysis): C, 20.6; H, 1.3; N, 4.0; F, 54.2; Cl, 0.03. Found (water hydrolysis): C, 20.7; H, 1.6; N, 4.1; F, 54.2; Cl, 0.7. From the F^{19} NMR data, both copolymers gave $(CF_3CH_2O^-):(C_3F_7CH_2O^-)$ mole ratios of 1:1. The intrinsic viscosities of the two copolymers in Freon E-2 at 28°C were quite

different: $[\eta] = 0.75$ dl/g (acid hydrolysis) and $[\eta] = 1.35$ dl/g (water hydrolysis). This large discrepancy in intrinsic viscosity values for the two copolymers was quite unexpected. Upon repetition of the experiment, intrinsic viscosity trends were verified. The acid hydrolyzed sample had an intrinsic viscosity of 0.4 dl/g and the water hydrolyzed sample gave 1.8 dl/g.

2.3.2 Effect of Modification of End Groups

The $[\text{Cl}_2\text{PN}]_n$ polymer in benzene was treated with gaseous SO_2 , was purged with nitrogen and was derivatized normally to $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$ copolymer. The presence of the phosphoryl group in this copolymer was not conclusively demonstrated, but the copolymer differed in its solubility in Freon E-2 from the control $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$ copolymer which was prepared from identical untreated $[\text{Cl}_2\text{PN}]_n$. The SO_2 treated copolymer gave a milky jelly-like solution which completely dissolved upon addition of acetone. This behavior suggested a high degree of molecular aggregation which would occur if polar groups, such as $\text{P}=\text{O}$, were present. Anal. Calcd. for $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$ (1:1): C, 21.0; H, 1.2; N, 4.1; Cl, 0.0. Found: C, 19.9; H, 1.3; N, 4.1; Cl, 0.1.

A portion of the same $[\text{Cl}_2\text{PN}]_n$ polymer was not treated with SO_2 and was derivatized to $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$. The intrinsic viscosity of the copolymer was 2.3 dl/g in Freon E-2 at 28°C . Aging studies of the SO_2

treated copolymer were carried out at 150°C but thermal stability was not improved.

2.3.3 Effect of Additives

The effect of various acids and acid acceptors on $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ was studied at 149-151°C. Two acid additives, HCl and p-toluenesulfonic acid, and one acid acceptor additive, ethylene oxide, were studied.

A sample of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ copolymer (0.5 g) was weighed into each of two vials and Freon TA (25 ml) was added to each vial. An aqueous solution of 10% HCl (0.17 g) was added to one vial. Gaseous ethylene oxide (15-20 g) was bubbled into the other copolymer solution. Volatiles were removed from both samples by a stream of air. Similarly, p-toluenesulfonic acid monohydrate (0.02 g) was added to the $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ copolymer. Amphoteric materials such as Al_2O_3 were also investigated. Summary of data is presented in Table XII.

The data appear to indicate that treatment of the copolymer with HCl had a negligible effect. The presence of HCl in the copolymer was not determined in the isolated sample prior to aging. No change in stability would be expected if HCl was not present during the test.

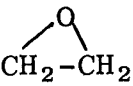
The p-toluenesulfonic acid had a pronounced deleterious effect. Most of the p-toluenesulfonic acid (b.p. 146-147°C, 0.1 mm) would be expected to be retained during the

aging study. The presence of water in this acid may co-catalyze depolymerization.

The ethylene oxide treated sample was somewhat less stable than the untreated sample. The amount of ethylene oxide retained in the copolymer is unknown, but the copolymer appeared slightly less stable. The addition of $\text{Al}(\text{OH})_3$ seemed to be slightly detrimental while the addition of Al_2O_3 seemed to slightly improve the thermal stability of the copolymer.

TABLE XII

Aging Studies of $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$ in Air at 150°C .

<u>Additive</u>	<u>Time (hrs.)</u>	<u>Final $[\eta]$ (a) in Freon-E-2 at 28°C</u>	<u>Weight Loss (%)</u>
None	24.5	0.85	0
None	48	0.70	0
None	96	0.14	0.13
HCl	25	0.84	0
	25	0.54	0
$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$	25	0.07	0
$\text{Al}(\text{OH})_3$	24	0.43	0.18
Al_2O_3 (Type V) ^(b)	24	0.99	0
Al_2O_3 (Type V) ^(b)	48	0.32	0
Al_2O_3 (Type V) ^(b)	96	0.24	0.56

(a) the initial viscosity of copolymer was 1.4 dl/g

(b) aluminum oxide (cationotropic), activity Grade V, from M. Woelm, Eschwege, Germany

2.4 Preparation and Characterization of High Molecular Weight Poly(fluoroalkoxyphosphazenes) for Evaluation by NASA

2.4.1 Preparation and Compounding of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$

Distilled hexachlorophosphazene (850 g) was polymerized at 249-251°C for 37 hours. Purified $[Cl_2PN]_n$ (170 g, 1.46 moles) was dissolved in 3.4 liters of dry benzene and was added to a mixture of alkoxides prepared from CF_3CH_2OH (175 g, 1.75 moles) and $C_3F_7CH_2OH$ (350 g, 1.75 moles) and sodium (74 g, 3.22 moles) in 3.1 liters of dry tetrahydrofuran. The copolymer was isolated by filtration and was rinsed with tetrahydrofuran several times. It was dissolved in 6 liters of Freon TA and washed exhaustively with water until the aqueous layer was free of chloride ion. The copolymer was isolated by precipitation into 7 liters of benzene. A white elastomer (424 g) was obtained which had an intrinsic viscosity of 0.62 dl/g in Freon E-2 and a Cl analysis of 0.05%. NMR results are given in Table XIII.

TABLE XIII

Nuclear Magnetic Resonance Data for $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ Upfield from $CFCl_3$, cps

<u>Compound</u>	<u>CF_3CH_2O- CF_3</u>	<u>CF_3</u>	<u>$CF_3CF_2CF_2CH_2O-$ CF_2 (CF_3-CF_2-)</u>	<u>CF_2 $(-CF_2-CH_2-O-)$</u>	<u>Solvent</u>
$[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ (1717-15)	4304 triplet	4625 triplet	7223 singlet	6880 broad singlet	Freon TA

Mixing of the copolymer with fillers, peroxides, and additives was accomplished in a high shear helicone type mixer with spiral blades. Molding of samples was carried out with conventional compression molding equipment, and samples were cooled under pressure. Samples 1768-02 and 1768-08 were supplied to NASA, and their formulations are given in Table XIV.

TABLE XIV
 Compounding and Cure Data for
 $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ Copolymers
Formulation (expressed in parts/hundred)

Sample No.	1768-08		1768-02	
Batch No.	1715-15	1632-14B	1715-15	1468-25B
	50	50	50	50
Zn ₂ B ₆ O ₁₁	-			60
Dicumyl peroxide	3			3
Mix time (minutes)	30			75
Mix temperature (°C)	16-20			8-21
Mixer RPM	100			100
Cure time (minutes)	60			60
Temperature (°F)	284			356
Comments	-			Elastic, not very strong

2.4.2 Preparation of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ Rich in $C_3F_7CH_2O$ - Functionality

An alkoxide mixture was prepared from CF_3CH_2OH (5.8 g, 0.06 mole), $C_3F_7CH_2OH$ (46.4 g, 0.23 mole) and sodium (6.1 g, 0.27 mole) in 400 ml of dry tetrahydrofuran. The solution was heated to reflux and $[Cl_2PN]_n$ polymer (14.0 g, 0.12 mole) in 200 ml of dry benzene was added. After the addition was complete, the reaction mixture was refluxed overnight. The yellowish-brown liquid was decanted and the solids were dissolved in 750 ml of Freon TA and thoroughly washed with water. On precipitation into 1500 ml of benzene, a white, fibrous copolymer (27.5 g) was obtained. The intrinsic viscosity was 0.57 dl/g in Freon TA at 28°C and the % Cl was 0.0.

2.4.3 Preparation of $[(C_3F_7CH_2O)_2PN]_n$

Heptafluorobutanol (86.4 g, 0.43 mole) was slowly added to sodium (9.1 g, 0.40 mole) in 400 ml of dry tetrahydrofuran. After the addition, the mixture was stirred overnight at room temperature and refluxed for 2 hours whereupon the mixture was homogeneous. The $[Cl_2PN]_n$ polymer (20.9 g, 0.18 mole) was dissolved in 450 ml of dry benzene and added to the alkoxide solution at reflux. The heterogeneous mixture was refluxed for 16 hours after the completion of addition. The mixture was cooled, filtered and the solid

was washed with tetrahydrofuran and with water. The resultant white powder was dissolved in 800 ml Freon TA/Freon E-2 (1v/1v) and washed with water until free of chloride ion. The homopolymer (41.7 g) was obtained by addition of the solution to 1600 ml benzene/acetone (1v/1v). The polymer did not melt or discolor at 300°C. (572°F). The polymer was insoluble in Freon E-2 and common organic solvents, partially soluble in Freon TA, and completely soluble in Freon E-1. The intrinsic viscosity was 3.3 dl/g in Freon E-1 at 28°C and Cl analysis was 0.1%. A thick film (1" x 3") was submitted to NASA for evaluation.

3.0 DISCUSSION

In view of the ambitious objectives of this program, a rapid demonstration of feasibility in several areas was attempted. The problem areas which were addressed were: (1) develop room temperature cures, (2) prepare materials with lower molecular weights than had been previously prepared, (3) increase thermal stability of the poly(fluoroalkoxyphosphazenes). Some success in the first and second areas was attained but thermal stability was not improved in the limited studies which were conducted.

In order to demonstrate the feasibility of a room temperature cure most rapidly, the preparation of elastomeric terpolymers was undertaken. This approach obviated the development of new technology except in the introduction of appropriate termonomer groups. The preparation of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ polymers which contained small amounts of termonomer groups was easily accomplished when the termonomer groups were $CH_3CH(OH)C_2H_4O-$ and $C_2H_5NHC_2H_4O-$. Soluble terpolymers which contained $C_2H_5SC_2H_4O-$ could not be prepared. Terpolymers were prepared by the addition of a solution of $[Cl_2PN]_n$ to a mixture of the alkoxides of CF_3CH_2OH , $C_3F_7CH_2OH$ and the termonomer. This synthesis probably did not give totally random distribution of the termonomer group along the backbone due to differences in reactivity ratios. However, the procedure was the most expedient and did, in fact, prove to be satisfactory. If totally random distribution of

the terpolymer group is desired, ligand exchange reactions could be conducted with a $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ copolymer [Ref. 7] or the alkoxide of the termonomer could be prereacted with $[Cl_2PN]_n$.

The amount of termonomer groups present in the terpolymers is not known accurately. Elemental analyses of terpolymers show small changes in carbon, hydrogen and nitrogen values with changes in amounts of termonomer groups. Adding to the uncertainty in the calculation of the amount of crosslinking sites available is the lack of sensitivity of carbon and hydrogen values. Also, the NMR figures for these terpolymers are derived by a difference method. Possibly, the peak areas used for integration have more than the assigned number of components in them and erroneously high values for the component attributed to the crosslinking site would be calculated. However, the $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-(C_2H_5NHC_2H_4O)_2PN]_n$ terpolymer gave good agreement in the elemental analyses and NMR for 10 mole percent of $C_2H_5NHC_2H_4O-$.

Terpolymers which contained $CH_3CH(OH)C_2H_4O-$ or $C_2H_5NHC_2H_4O-$ were easily cured, whereas the neat terpolymer which contained $C_2H_5SC_2H_4O-$ crosslinked on standing. Cures were accomplished at room temperature with diisocyanates in the presence of dibutyltin diacetate.

Several different isocyanates, TDI, DDI, and PAPI, were investigated. While TDI successfully cured both terpolymers, some cures of the $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-(C_2H_5NHC_2H_4O)_2PN]_n$ terpolymer accomplished with DDI seemed to undergo reversion. The terpolymer crosslinked and precipitated, but upon standing some material appeared to go back into solution without an increase in the viscosity of the solution. The cause of this behavior was not investigated. This problem was not observed when TDI was used to cure this terpolymer.

Because the materials had very high molecular weights, the use of solution cures was required even though this was known to be undesirable. However, since the feasibility of this type of cure for the poly(fluoroalkoxyphosphazenes) was successfully demonstrated, an effort was made to extend this chemistry to lower molecular weight materials. Thick oils would not require the use of solution cures, provided compatibility problems with the curing agents were not encountered.

The mechanism of the ring opening which forms poly(dichlorophosphazene) has not been elucidated [Ref. 8], and the manipulations to control molecular weight were of necessity somewhat empirical. Past bulk polymerizations of hexachlorophosphazene typically have led to a mixture which contained very high molecular weight material and

very low molecular weight material with little intermediate species observed. In these polymerizations hexachlorophosphazene was polymerized until a very high melt viscosity was attained.

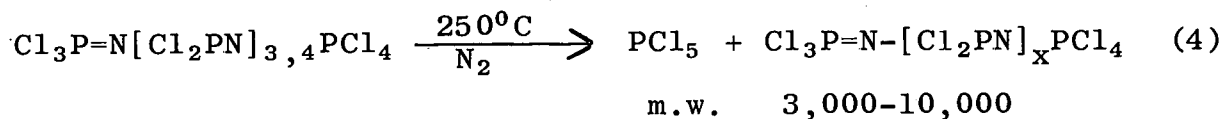
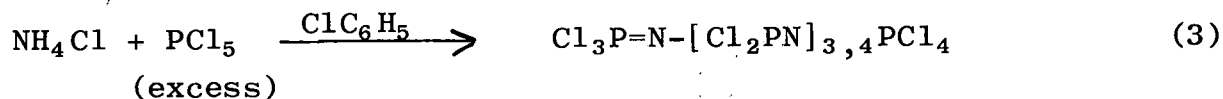
Several different procedures were employed in an effort to prepare lower molecular weight poly(dichlorophosphazene). These investigations led to the preparation of a wide variety of molecular weight ranges. However, time was not available to study reproducibility or production of a single molecular weight range by any particular method.

Hexachlorophosphazene and octachlorophosphazene mixtures were polymerized in bulk to high melt viscosities. After derivatization, the products were obtained as thin oils, as viscous oils, and in many cases as solids which underwent cold flow.

Undistilled hexachlorophosphazene was polymerized in bulk to high melt viscosities and upon derivatization gave low molecular weight fractions. However, the molecular weight of the products appeared to be higher than was obtained when octachlorophosphazene mixtures were used. Some thin oils were obtained but very viscous oils or waxy solids which underwent cold flow were more common. Also, elastomeric fractions which did not undergo cold flow were obtained.

Termination of the bulk polymerization of distilled hexachlorophosphazene before a high melt viscosity was reached did not successfully give low molecular weight materials. Instead, the percent conversion to poly(dichlorophosphazene) was reduced and upon derivatization the product was elastomeric. This result indicates that high molecular weight material was formed early in the polymerization.

A brief investigation of the reaction of PCl_5 with NH_4Cl was conducted. Other investigators had reported [Ref. 9] that upon heating the resultant products were converted to high molecular weight oils with the concomitant loss of PCl_5 as shown in equations (3) and (4).



The chain extension reaction as conducted at Horizons proved to be extremely sensitive. Low molecular weight oils were produced, but once gel formation began it was extremely rapid. However, if heating times were kept short, oils with molecular weights between 1300 and 2600 generally were prepared.

Replacement of the chlorine atoms in these linear, low molecular weight oily polymers with $\text{CF}_3\text{CH}_2\text{O}$ - and $\text{C}_3\text{F}_7\text{CH}_2\text{O}$ - should give approximately a three-fold increase in molecular weight, provided no other changes take place in the polymer molecule. However, molecular weight data (Table VIII) indicated that chain scission may have taken place. The cause of the observed lower molecular weight may have been due to imperfections in the starting oils (trace hydrolysis), or to attack of the backbone during the course of derivatization. Alternately, the apparently high molecular weight of $[\text{Cl}_2\text{PN}]_n$ polymer that was observed may have been due to non-ideal solvent-solute interactions. Such interactions would not be observed in the derivatized product, and a true molecular weight would be obtained for the poly(fluoroalkoxyphosphazene). These circumstances also would give the appearance of a reduction of molecular weight on derivatization.

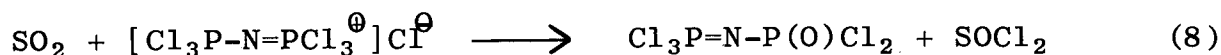
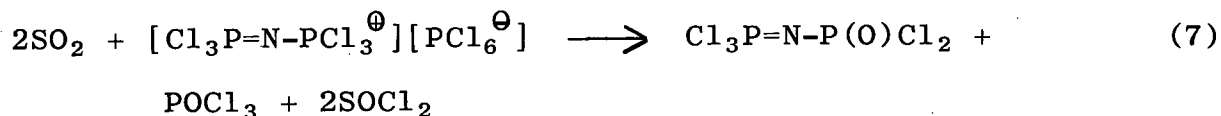
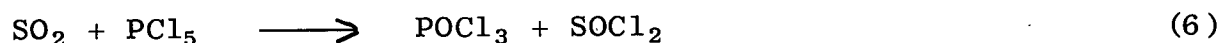
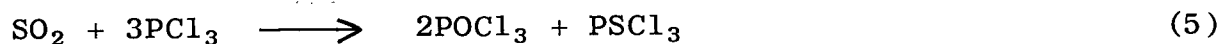
One method to control molecular weight was not investigated due to lack of time. Solution polymerization could be effective in the preparation of low molecular weight poly(dichlorophosphazenes). Previous work [Ref. 10] has shown that hexachlorophosphazene can be polymerized in solution to give a mixture of insoluble and soluble polymers whose molecular weights ranged from 1,500 to 130,000.

Attempts were made to extend the crosslinking chemistry, developed for the elastomeric terpolymers, to the oily terpolymers. One experiment was conducted with an oil fraction which contained the secondary alcohol. The oil was not

successfully crosslinked but this may be attributed to a molecular weight that was too low. The use of higher molecular weight oils for crosslinking should be more meaningful, as these materials will have termonomer functionality sufficient to lead to crosslinking.

In an attempt to influence the thermal stability of the poly(fluoroalkoxyphosphazenes), two different studies were begun. The first study was an attempt to modify the end groups of the derivatized polymer and thereby influence the mechanism of thermal decomposition. The second study was an attempt to stabilize the materials through the use of additives.

The nature of the end groups in poly(dichlorophosphazene) is unknown. However, a variety of phosphorus halides are known to undergo reaction with SO₂ as shown in equations (5) through (8). [Refs. 11, 12, 13, 14].



A solution of poly(dichlorophosphazene) was treated with gaseous SO₂ and subsequently was purged with nitrogen. The product was not isolated before derivatization to form [(CF₃CH₂O)₂PN-(C₃F₇CH₂O)₂PN]_n copolymer. While the presence of phosphazene groups in the SO₂ treated material could not be conclusively demonstrated, the material did have decidedly different solubility properties than untreated material. However, on aging the copolymer behaved no differently than untreated material.

Stabilization of many other polymer systems has been achieved through the incorporation of additives into the gum stock. Additives generally perform their function either by reaction with materials which cause decomposition or by formation of an adduct with the polymer which inhibits the mechanism of decomposition. A very brief investigation of the effect of acidic, amphoteric and basic additives on [(CF₃CH₂O)₂PN-(C₃F₇CH₂O)₂PN]_n copolymer was undertaken, but the results were inconclusive. Much more effort will be required for these studies to reach fruition.

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