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SN-8275-F

PREPARATION OF LINEAR HYDROXY SUBSTITUTED POLYPHOSPHAZENES

By K. L. Paciorek, T. I. Ito, and R. H. Kratzer

October 1978

Final Report

Prepared Under Contract No. NAS2-8469

ULTRASYSTEMS, INC.
Irvine, California



NATIONAL AERONAUTICS & SPACE ADMINISTRATION
Ames Research Center

George Fohlen, Technical Manager

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George Fohlen, Technical Manager

FOREWORD

This Final Report describes the work performed by the Chemicals and Materials Research Department, Ultrasystems, Inc. under Contract NAS2-8469, "Preparation of Linear Hydroxy Substituted Polyphosphazenes". The investigations were carried out during the period from 23 July 1974 to 15 June 1977 by K. L. Paciorek, T. I. Ito, and R. H. Kratzer, project manager. This contract was administered by NASA Ames Research Center with Dr. George Fohlen as technical manager.

TABLE OF CONTENTS

	<u>Page No.</u>
1. SUMMARY	1
2. INTRODUCTION	3
3. RESULTS AND DISCUSSION	5
3.1 Model Studies	5
3.2 Polymer Studies	7
4. EXPERIMENTAL DETAILS AND PROCEDURES	20
4.1 General	20
4.2 Model Studies	20
4.3 Polymer Studies	26
5. REFERENCES	33

LIST OF TABLES

<u>Table No.</u>		<u>Page No.</u>
I	Summary of $(\text{PNCI}_2)_3$ Polymerizations at 250°C	10
II	Effect of Reagent Nature and Reaction Duration upon Completeness of Ethoxy Substitution of Poly(dichloro- phosphazenes)	12
III	Summary of Alkoxy Substitution Reactions of Poly(dichlorophosphazenes)	13

LIST OF FIGURES

<u>Figure No.</u>		<u>Page No.</u>
1	TGA of $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_3OCH_2CH_2OC-(O)NHC_6H_5$ (in nitrogen)	8
2	TGA of $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_3OCH_2CH_2OC-(O)NHC_6H_5$ (in air)	9
3	TGA of Poly(dimethoxyphosphazene) (in air)	15
4	TGA of Poly(diethoxyphosphazene) (in air)	16
5	TGA of $[(CH_3O)_x(OCH_2CH_2OH)_yPN]_z$ (in air)	17
6	Relative Viscosities of PAPI/Poly(methoxy, hydroxyethoxy-phosphazene) Solutions	19
7	DTA of $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_3OH$	22
8	DTA of $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_3OCH_2CH_2OC-(O)NHC_6H_5$	25

1. SUMMARY

The objective of this program was to investigate possible routes towards synthesis of partially hydroxy-substituted phosphazene prepolymers amenable to processing into cellular, flexible polyurethane foams. The selection of the phosphazene backbone was based on its flame retardant characteristics and the fact that phosphazenes produce very minor quantities, if any, of toxic compounds upon thermal oxidative decomposition.

Model studies conducted on a short chain phosphazene, $(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_3OH$, have shown that urethane formation does not proceed without side reactions when the hydroxyl group is situated directly on the phosphorus atom. Having the hydroxyl group attached to the phosphorus via an ethoxy linkage alleviates this difficulty as shown by the ready synthesis of $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_3OCH_2CH_2OC(O)NHC_6H_5$.

It has been established under this program that to attain reasonable yields of sufficiently high molecular weight poly(dichlorophosphazene) via the thermolysis of hexachlorocyclotriphosphazene, at $250^\circ C$ in the absence of solvent, requires trace quantities of air (oxygen). In view of the difficulties in producing large quantities of poly(dichlorophosphazene) via this process the majority of the substitution reactions was carried out utilizing a polymer sample prepared by Horizons Research Inc. via a solution process. This material appeared to be stable in bulk at $-78^\circ C$ and in 10% benzene solution at room temperature; however in bulk at room temperature some crosslinking took place after 14-29 days of storage.

No substitution of the chloro-moiety by ethanol was found to occur in the absence of a base. The extent of reaction using sodium ethoxide-ethanol and pyridine-ethanol reagents was strongly time dependent, with 50%

reaction being reached relatively fast. The char yield of poly(dimethoxyphosphazene) was significantly better than that of the diethoxy analogue as determined by thermal gravimetric analysis. Transesterification was unsuccessful in introducing hydroxyethoxy groups into poly(dimethoxyphosphazene). To obtain poly(hydroxyethoxy, methoxy-phosphazene) poly(dichlorophosphazene) was treated with a predetermined quantity of the mono-sodium salt of ethylene glycol followed by addition of sodium methoxide-methanol reagent. The polymer thus formed contained hydroxyl-groups and formed urethanes. The actual degree of hydroxyl substitution as compared to the theoretical value was not determined due to funds limitation.

2. INTRODUCTION

Flameproofing of a polyurethane can theoretically be accomplished in three ways: (a) by using a flame retarding isocyanate, (b) by using a flame retarding comonomer, e.g., diol, or (c) employing only flame retardant comonomers. If the flame retarding component employed is sufficiently effective it can be assumed that flameproofing of one of the two major polyurethane constituents will suffice. In view of the fact that the isocyanates normally employed are either low molecular weight oligomers or monomeric species it furthermore can be argued that flameproofing of e.g., a hydroxy-substituted prepolymer offers the most promising approach.

Permanent flame resistance (as opposed to incorporating physically admixed additives) can be achieved by chemically bonding elements of the fifth and seventh main group of the periodic table in or to the polymer backbone. These elements are nitrogen, phosphorus, arsenic, antimony, bismuth, and the halogens fluorine, chlorine, bromine, and iodine. All of these elements have been shown to be effective flame retardants, although antimony is normally used as an additive (ref. 1,2) and bismuth and iodine are not used in practical applications because of their high cost. If a further requirement is that the flame retardant does not contribute to the formation of toxic or otherwise hazardous thermal decomposition products arsenic and all halogens must also be eliminated from consideration (ref. 3-7). This leaves nitrogen and phosphorus as the two flame retarding elements, which have been shown to be effective without forming dangerous decomposition products. Of particular interest considering the program objectives is the synergism of phosphorus-nitrogen combinations in respect to flame retardation (ref. 8-11) and that these combinations, when in the form of phosphazenes, do not form toxic or otherwise hazardous products upon oxidative thermal decomposition (ref. 12,13).

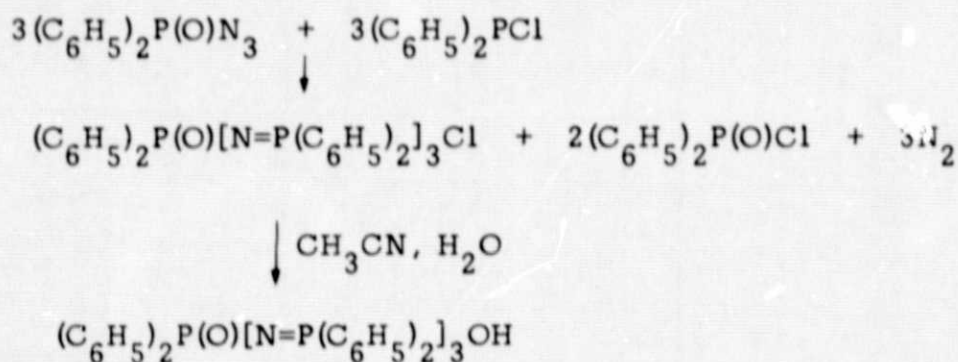
To prepare a hydroxy substituted phosphazene polymer amenable to urethane formation a number of factors had to be determined (a) the environment of the hydroxyl group, (b) the ease of hexachlorocyclotriphosphazene polymerization, (c) the nature of the non-reactive substituents and, (d) the mode of introduction of the hydroxyl entity. The specific approaches taken, the rationale of the selections made, and the results of this study are discussed in Section 3.

3. RESULTS AND DISCUSSION

The objective of this program was to develop a synthesis procedure leading to hydroxy substituted polyphosphazenes from which flexible foams could be produced using common urethane technology. Based on the criteria delineated in Section 2 the phosphazene backbone appeared to offer the required characteristics insofar as flame retardancy and toxic product evolution upon thermal degradation were concerned. The unresolved questions were (a) the bonding environment of the hydroxyl group to provide proper reactivity i.e. whether situated directly on phosphorus or as a part of a side chain (b) hexachlorocyclotriphosphazene polymerization aspects and (c) the substitution reactions of poly(dichlorophosphazene). For ease of presentation the discussion was thus divided into Model and Polymer Studies.

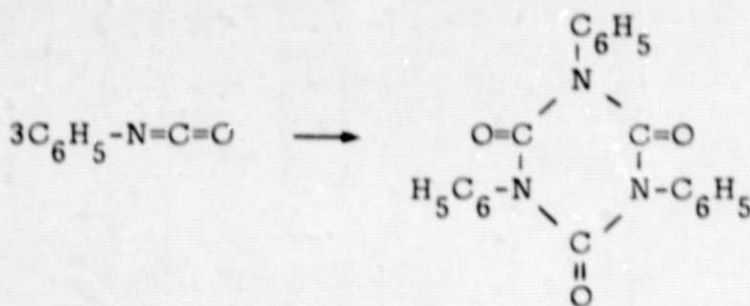
3.1 MODEL STUDIES

The synthesis of a linear hydroxy-terminated phosphazene via the reaction sequence given below was described previously (ref. 13):



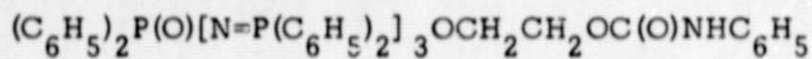
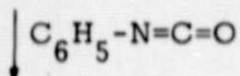
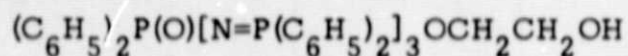
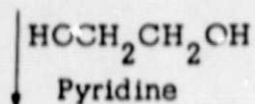
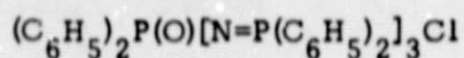
Following this procedure the hydroxy-terminated material was obtained in an overall 27% yield. This material failed to react with phenylisocyanate in benzene at 70°C; however in the absence of solvent on prolonged heating at 95-103°C reaction did occur. Unfortunately, it was not the formation of the

desired urethane, $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_3OC(O)NHC_6H_5$. The evolution of carbon dioxide together with the observation of $N=C=N$ linkages in the involatile residue showed that one of the occurring processes was carbodiimide formation, which can be catalyzed by phosphinioxides (ref. 14). The major reaction, however, was the cyclization of phenylisocyanate into triphenyl isocyanurate,



This self condensation is known to be catalyzed by phosphorus compounds e.g., triphenylphosphine (ref. 15). None of the desired urethane was isolated from the reaction mixture. Thus it must be concluded that a hydroxyl group bonded directly to phosphorus is unreactive towards isocyanate. Consequently this type of a linkage does not appear suitable for potential polyurethane foam production.

To obtain a model system wherein the hydroxyl group is separated from the phosphorus atom the chloro-terminated intermediate, $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_3Cl$, was treated with ethylene glycol in the presence of pyridine. The reaction proceeded without difficulty and the hydroxyethoxy compound afforded readily the corresponding urethane, e.g.,



This material was thermally and oxidatively stable up to $\sim 185^\circ\text{C}$, as shown by the thermogravimetric (TGA) curves given in Figures 1 and 2; it also failed to hydrolyze on prolonged exposure to hot water, thus proving the suitability of this arrangement for urethane foam application.

3.2 POLYMER STUDIES

Polymerization of hexachlorocyclotriphosphazene into linear poly(dichlorophosphazenes) has been described by Allcock (ref. 16). Following exactly his procedure, i.e. conducting the process with rigid exclusion of air or moisture gave only a very low yield of the polymer. Addition of a trace amount of air (oxygen) apparently promoted the reaction. To evaluate the influence of air presence, starting material purity and reaction period a number of tests were carried out and these are summarized in Table I. The need to use pure trimer is shown by Run No. 3, where the employment of an impure sample resulted in a crosslinked product.

A reasonable polymer yield, $\sim 25\%$ in some instances, was obtained by conducting the reaction over extended periods of time (compare Runs 5 and 6).

PART NO. 990088

236 TGA

SCALE 50
WEIGHT 0.5
FLOW RATE 67 ml/min
GAS N₂

TAXIS

SCALE 50
WEIGHT 0.5
FLOW RATE 67 ml/min
GAS N₂

DTA/DSC

SCALE 50
WEIGHT 0.5
FLOW RATE 67 ml/min
GAS N₂

TGA

SCALE 0.5
WEIGHT 0.5
FLOW RATE 67 ml/min
GAS N₂

TMA

SCALE 0.5
WEIGHT 0.5
FLOW RATE 67 ml/min
GAS N₂

DUPONT Instruments

MEASURED VARIABLE

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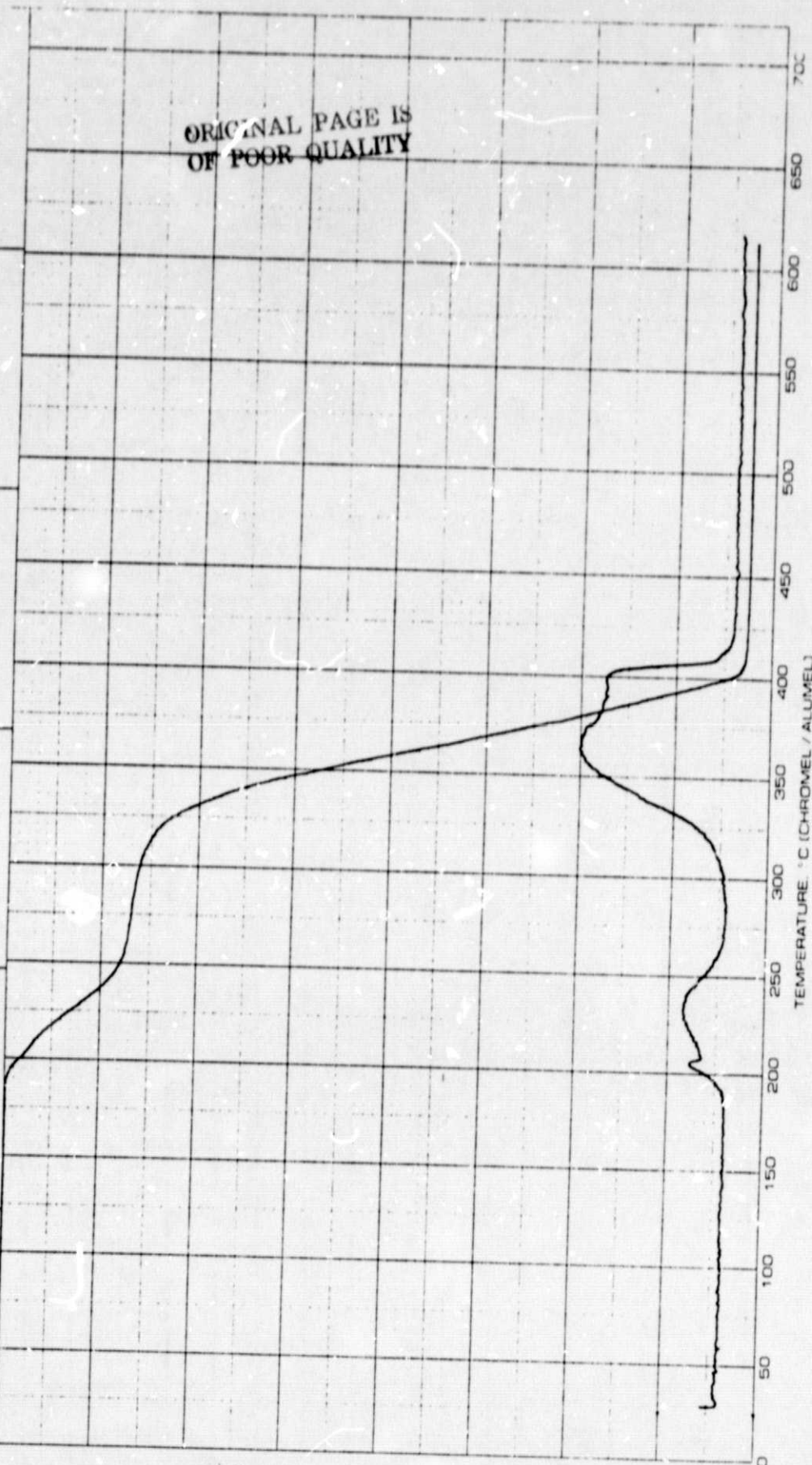


Figure 1: TGA of $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_3OCH_2CH_2OC(O)NHC_6H_5$ (in nitrogen)

PART NO. 99008B

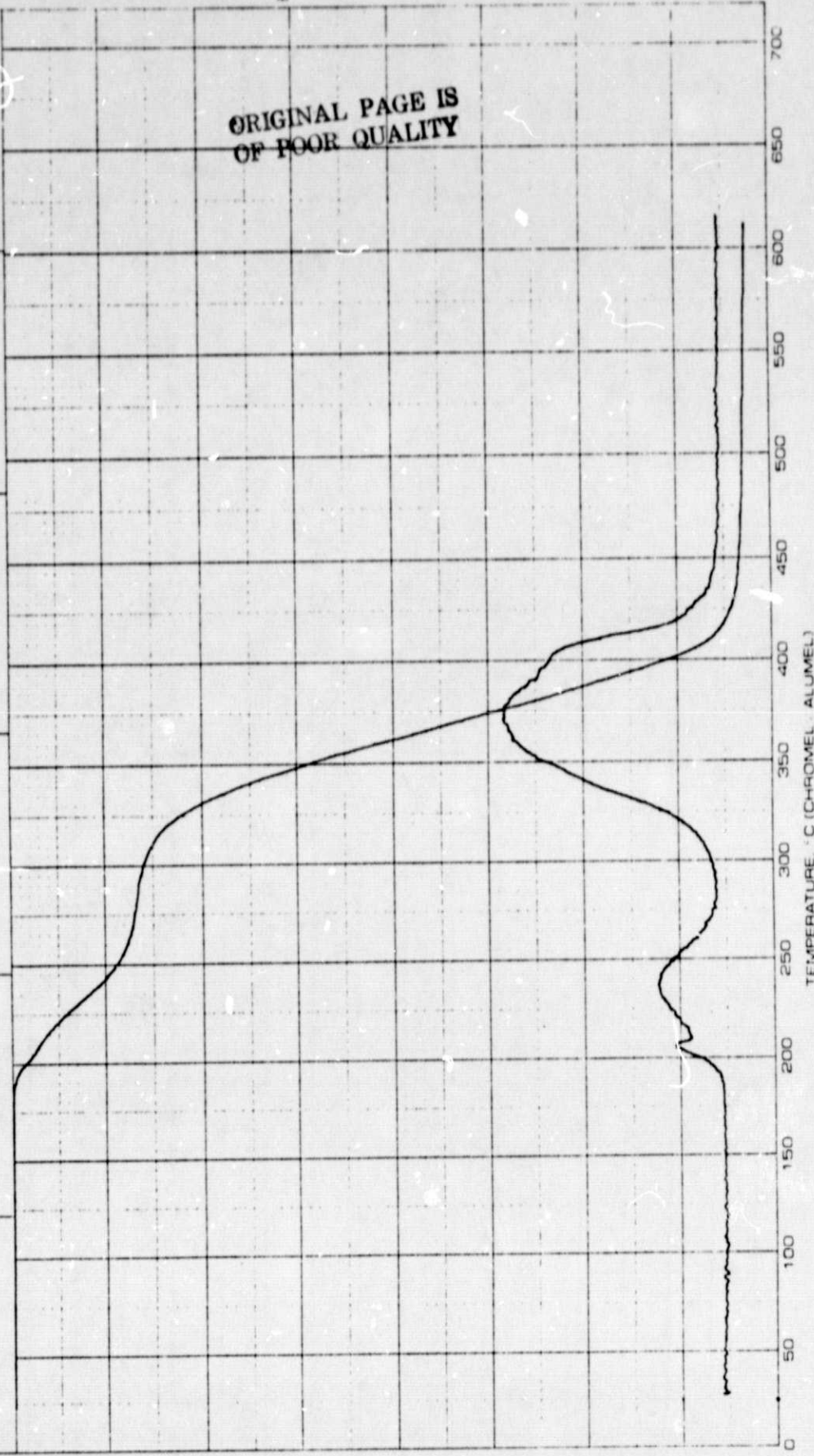
TGA 235 TGA 235 TGA 235 TGA 235

SCALE: 50
 FLOW RATE: 50 ml/min
 IR: 400-1500 cm⁻¹
 AT: 150
 FLOW RATE: 67 ml/min

DTA/DSC
 SCALE: 0.1 mV
 WEIGHT: 100 mg
 REFERENCE:

TGA
 SCALE: 1.0 mg
 WEIGHT: 0.72 mg
 TGA (100%): 1
 TGA (100%): 0.2

TMA
 SCALE: 100 μm
 MOJE
 SAMPLE SIZE
 LOAD: 4
 (10X) (macro) m



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OF POOR QUALITY

Figure 2: TGA of $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_3OCH_2CH_2OC(O)NHC_6H_5$ (in air)

TABLE I
SUMMARY OF $(\text{PNCI}_2)_3$ POLYMERIZATIONS AT 250°C

Run No.	$(\text{PNCI}_2)_3$ ^a Amount g	Reaction Time hr	$(\text{PNCI}_2)_x$ Amount g	Conversion %	Air Pressure mm
1	28.53	48	0.49	3.49	0
2	14.98	48	3.73	25.00	0.13
3	14.68 ^b	48	2.23 ^c	n.d. ^d	0.13
4	14.65	984	2.97	20.27	0
5	24.78	72	3.93	15.86	0.19
6	21.28	120	5.94	23.97	0.19
7	21.28	120	3.19	14.9%	0.12
8	19.02	648	3.04	15.98	0.12

a) The $(\text{PNCI}_2)_3$ used was freshly crystallized from heptane. b) In this case $(\text{PNCI}_2)_3$ was employed as received from ROC/RIC Corp. c) This was cross-linked material only. d) Not determined.

This was especially true in the case when "no air" (less than 10^{-3} mm) was present (see Run No. 4). However, regardless of conditions, the highest yield realized was 25% which, considering the tediousness of the polymerization and isolation method, did not seem to offer a practical process for the production of large quantities of poly(dichlorophosphazenes). Accordingly, for the majority of the substitution studies a poly(dichlorophosphazene) sample, prepared by Horizons Research, Inc. via their solution process, was utilized.

To determine the effect of (a) reaction times, (b) polymer and alcohol concentrations, and (c) the nature and concentration of base employed upon the extent of substitution the series of tests summarized in Table II was performed. Based on these data it is apparent that 50% of substitution takes place relatively readily which would tend to indicate that with the geminal chlorine arrangement present in dichlorophosphazenes substitution of the first chlorine occurs faster than that of the second. Considering the completion of the reaction there does not seem to be much difference between sodium ethoxide and pyridine. To reach completion extended reaction periods were necessary. In the case of the sodium ethoxide-ethanol reagent system only sodium ethoxide, not the free ethanol, was consumed in the substitution reaction. This is proven clearly by Test No. 5 where no consumption of free ethanol occurred. Based on this finding it can be deduced that in partial substitutions, di-hydroxy alcohols, having an excess of alcohol over the monosodium salt will assure absence of crosslinking and/or exocyclic substitution on phosphorus.

Following essentially the procedures of Allcock (ref. 16) poly(diethoxyphosphazenes) and poly(dimethoxyphosphazenes) were prepared in yields ranging from 36 to 59%. These experiments are summarized in Table III. The ultimate application of the polymers is for flame retardant, high

TABLE II
EFFECT OF REAGENT NATURE AND REACTION DURATION
UPON COMPLETENESS OF ETHOXY SUBSTITUTION
OF POLY(DICHLOROPHOSPHAZENES) ^a

Test No.	Polymer mg	Reagent		$\frac{C_6H_6}{ml}$	Reac. Period Days	$\frac{C_2H_5OH}{\text{Consm.}} \%$
		Type	Mole % ^b			
1 ^d	915.7	$C_2H_5OH-C_5H_5N$	100	10	5	58
2 ^d	856.1	$C_2H_5OH-C_5H_5N$	90	11	1	45
3	832.2	C_2H_5ONa	90	20	2	60
4	690.4	C_2H_5ONa	97	25	4	84
5 ^e	2010	$C_2H_5ONa-C_2H_5OH$	90	50	33	0

a) All the reactions were performed at room temperature. b) This is given with respect to the polymer chlorine content. c) This is based on the ethanol content in the aliquot as determined either by mass spectral or gas chromatographic analysis. In Runs 1, 2 and 5 a measured aliquot was withdrawn, distilled in vacuo at room temperature and the collected volatiles were analyzed by an appropriate technique. In Runs 3 and 4 a small quantity of water was added prior to distillation to liberate ethanol from sodium ethoxide. d) The quantities of ethanol and pyridine were equimolar. e) The quantities of sodium ethoxide and ethanol were equimolar and added up to 90% of the polymer chlorine content.

TABLE III
SUMMARY OF ALKOXY SUBSTITUTION REACTIONS
OF POLY(DICHLOROPHOSPHAZINES)^a

Run No.	Polymer		Reagent A		ROH ^d ml	Reagent B Type	mmol ^c	P(OH) ₂ ^d ml	C ₆ H ₆ ml	Product		Initial Condition		Final Condition	
	g	mmol ^b	Type	mmol ^c						g	%	Temp. °C	Period hr, d	Temp. °C	Period hr, d
6	3.57	6.2 x 10	NaOEt	8.2 x 10	30	-	-	-	70	2.1	49	RT ^f	6 d	-	-
7	3.73	6.4 x 10	NaOEt	4.8 x 10	150	-	-	-	150	2.5	59	RT	7 d	-	-
8	1.49	2.6 x 10	NaOMe	3.2 x 10	9	-	-	-	30	0.5	36	Refl ^g	7 hr	-	-
9 ^h	29.69	5.2 x 10 ²	NaOMe	2.4 x 10 ³	150	-	-	-	300	13.3	37	Refl	4 hr	RT	3 d
10 ^h	5.02	1.0 x 10 ²	NaOEt	1.3 x 10 ²	65	-	-	-	100	3.1	44	RT	3 d	-	-
11	2.99	5.2 x 10	NaOMe	4.7 x 10	13	NaO(CH ₂) ₂ OH	20.9	5	60	1.8	63	Refl	5 hr	RT	3 d
12	1.43	2.5 x 10	NaOMe	2.4 x 10	6	NaO(CH ₂) ₂ OH	0.9	0.5	30	0.5	37	RT	21 hr	Refl	7 hr ⁱ
13	14.86	2.6 x 10 ²	NaOMe	2.4 x 10 ²	75	NaO(CH ₂) ₂ OH	30	8	250	13.6	93	Refl	7 hr	RT	16 hr
14	15.00	2.6 x 10 ²	NaOMe	2.5 x 10 ²	75	NaO(CH ₂) ₂ OH	7.4	3	250	9.2	65	Refl	7 hr	RT	16 hr
15	14.73	2.5 x 10 ²	NaOMe	2.4 x 10 ²	60	NaO(CH ₂) ₂ OH	22	5	250	9.8	71	Refl	3 hr	RT	16 hr

a) Typical experimental procedures for a representative reaction system is given in Section 4. b) These are mmoles of the theoretically available chlorine. c) The mmoles are based on the sodium metal used. d) This is the alcohol from which the sodium alkoxide originated. e) Hours are denoted as hr, days as d. f) Ambient temperature. g) Refluxing. h) The polymer used in this experiment was partially crosslinked due to storage in bulk at room temperature; however it was soluble in benzene-alcohol solvent. i) In this instance following the addition of ethylene glycol-alkoxide mixture and stirring at ambient temperature for 21 hr volatiles were removed in vacuo then C₆H₆. MeOH, and NaOMe were added and the mixture refluxed.

char foams thus the presence of side chains with the least potential of forming volatiles was of advantage. Consequently, the major synthetic effort was concentrated on the methoxy substituted materials inasmuch as these, in agreement with the theoretical postulations, showed at 500°C a char yield of 68% as compared to 48% exhibited by the poly(diethoxyphosphazenes) (compare Figures 3 and 4).

To obtain hydroxyethoxy substituted materials, a grouping found amenable to urethane formation by the model studies, transesterification of poly(dimethoxyphosphazenes) with free ethylene glycol and sodium hydroxyethoxide was attempted. In neither case did the exchange occur as proven by the absence of liberated methanol. However, interaction of poly(dichlorophosphazene) with a selected proportion of ethylene glycol-sodium hydroxyethoxide reagent mixture (aiming at a specified abundance of hydroxyethoxy substituents) followed by reaction with an excess of sodium methoxide-methanol gave high yields, up to 93%, of materials which exhibited in the infrared spectra hydroxyl absorption and which did form urethanes. The introduction of the limited number of hydroxyethoxy groups did not result in deterioration of the material's thermal stability as shown by the TGA (see Figure 5) which indicates even a higher char yield at 500°C than the homopolymer (76 versus 68%).

In order to prove that the hydroxyl group concentration and distribution of such a hydroxy substituted poly(methoxy, hydroxyethoxy-phosphazene) is adequate for polyurethane formation, in particular foam production, a twenty five percent solution of this material was treated with a solution of PAPI (obtained from NASA Ames Research Center, composition unknown). In view of the small sample available and the effect of air and moisture on the urethane formation 0.25 ml aliquots of the polymer solution were placed in

PART NO. 970088

TGA 280 DATE 12 MAR 74
OFFER/ICR
SAMPLE
NP(OcM₂)₂
8275-4-24-81-1
ATTA RIR
FLOW RATE .75 ml/min

T-AXIS

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

DTA/DSC

SCALE °C/in
INTEGRATION
WEIGHT, mg
REFERENCE

TGA

SCALE mg/in 1.0
SUPPRESSION mg 0 (30)
WEIGHT mg 9.93
TIME LEFT min 1
dV (mg-min)/in 0.2

TMA

SCALE mil/in
MODE
SAMPLE SIZE
LOAD g
dV (10X)(mil/min)/in



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Figure 3: TGA of Poly(dimethoxyphosphazene) (in air)

PART NO. YEARS

TGA

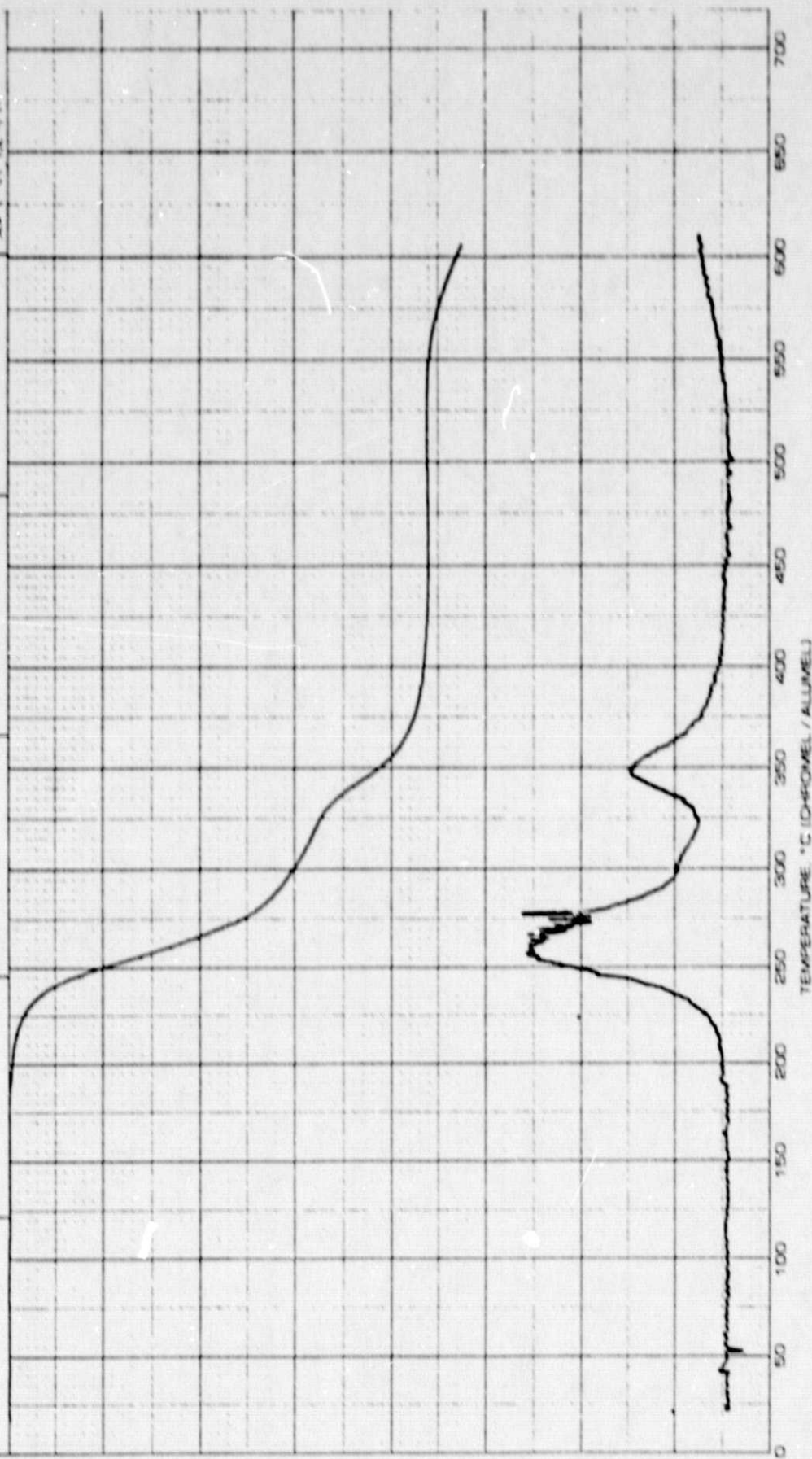
DATE: 8/10/76
 OPERATOR: ACJ
 SAMPLE: [P(000)]₄ 8.325-9-75
 10.652
 ATM: AIR
 FLOW RATE: 50 ml/min

T. AXIS
 SCALE: C/m 50
 PROG. RATE: C/min 5
 HEAT: COOL 150
 SHIFT: 0

DTA/DSC
 SCALE: C/m
 WEIGHT: mg
 REFERENCE

TGA
 SCALE: mg/g 1
 SUBPRESSION: mg 0
 WEIGHT: mg 10.17
 TMA LOAD: mg 1
 DT (mg/min): min. 0.2

TMA
 SCALE: micron
 MODE
 SAMPLE SIZE
 LOAD: g
 DT (micron/min):



DUPONT Instruments

MEASURED VARIABLE

Figure 4: TGA of Poly(dieoxyphosphazene) (in air)

TGA 2.85 (DATE) 2 APR 76 T-AXIS

OPERATOR RCJ
 SAMPLE B275-4-74-91-28
 WEIGHED 12.15
 ATM P.P.
 FLOW RATE 50 ml/min

SCALE °C/m 50
 PROG RATE C/min 5
 HEAT COOL ISO
 SHIFT m 0

DTA/DSC
 SCALE °C/m
 WEIGHT mg
 REFERENCE

TGA
 SCALE mg/m
 SUPPRESSION mg
 WEIGHT mg 12.15
 TIME CONST sec 1
 dY (10K) (ml/min)/m

TMA
 SCALE ml/m
 MODE
 SAMPLE SIZE
 LOAD g

20. P. 54. BL. 8. 1. 2.

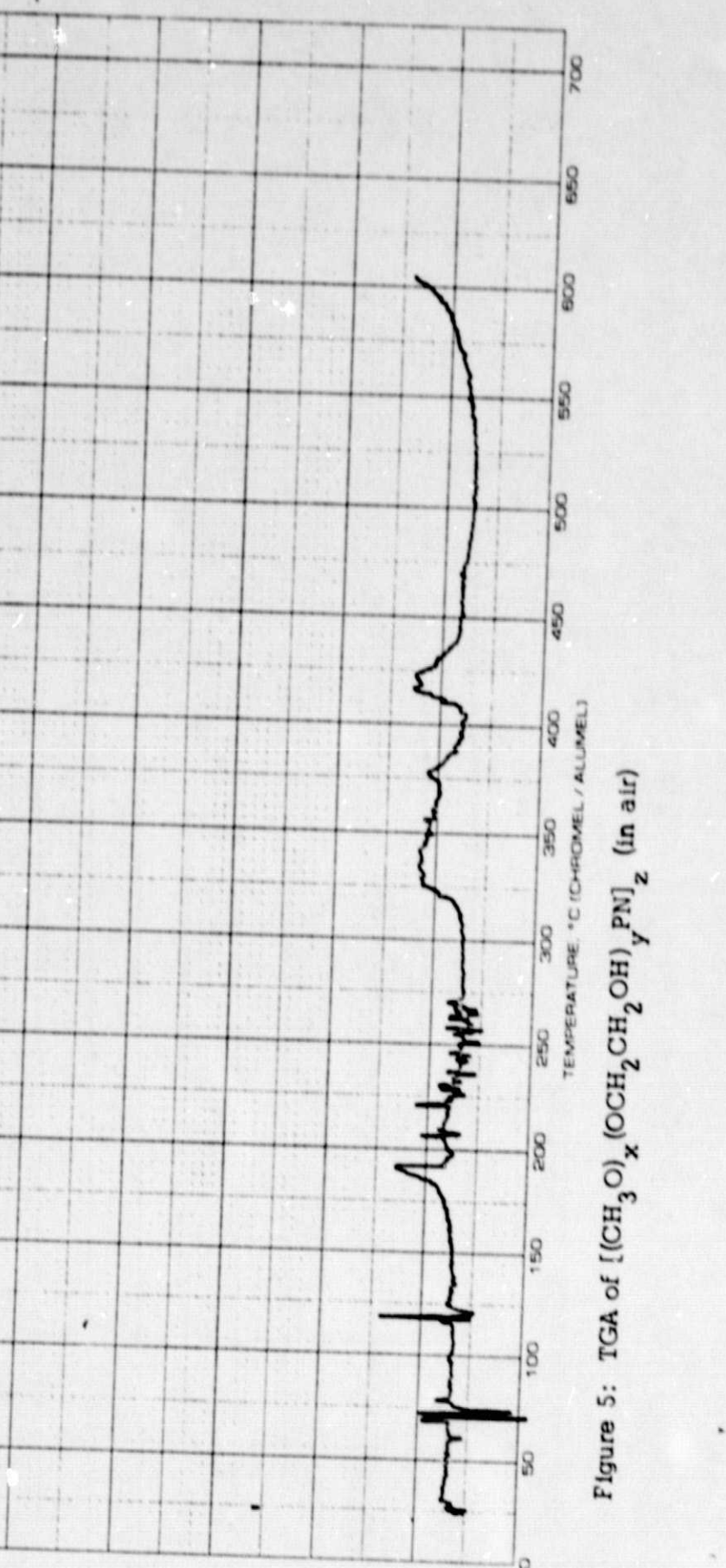


Figure 5: TGA of $[(CH_3O)_x(OCH_2CH_2OH)_yPN]_z$ (in air)

ampoules of equal size, followed by addition of various amounts of the above mentioned polyisocyanate solution, sealing and heating to 60°C for 2 hrs. As can be seen from Figure 6, the four volume ratios of polymer and crosslinking agent solutions employed produced mixtures of distinctly different flow characteristics, with the mixture of one part polymer solution and 0.2 parts PAPI solution causing gelation. The fact that gelation did occur proves that the hydroxyl group distribution along the polyphosphazene chain is sufficiently random for infinite network formation. The failure of the samples to rise, e.g. to produce a foam, must be attributed to the small sample sizes employed, for which the rate of heat dissipation is larger than the rate of heat production due to urethane formation.

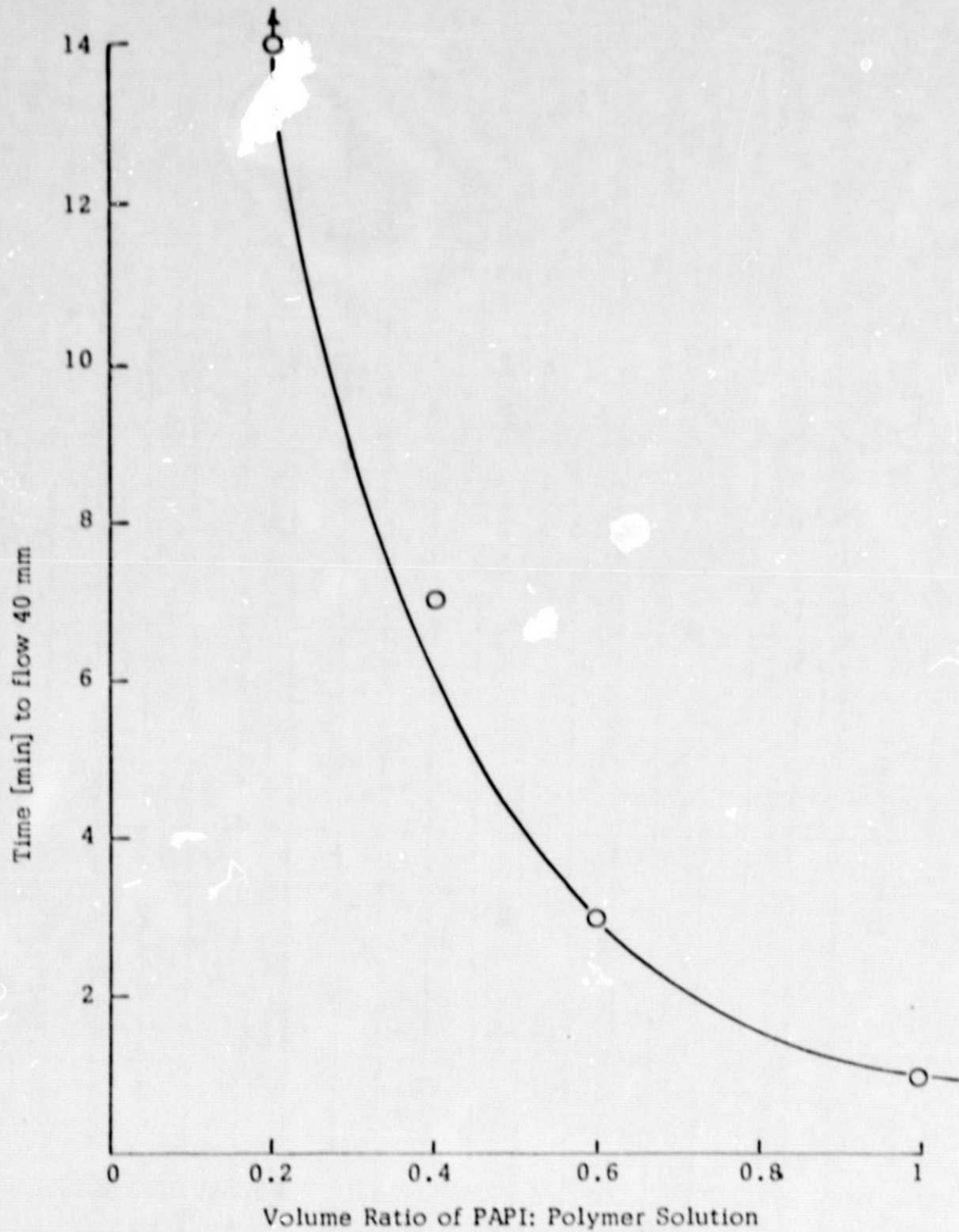


Figure 6: Relative Viscosities of PAPI/Poly(methoxy, hydroxyethoxy-phosphazene) Solutions.

4. EXPERIMENTAL DETAILS AND PROCEDURES

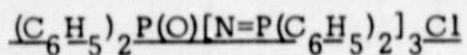
4.1 GENERAL

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

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

4.2 MODEL STUDIES

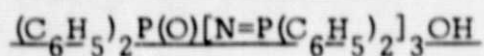
Synthesis of Chloride Terminated Linear Phosphazene,



Following a previously developed procedure (ref. 13) 33.91 g (139.43 mmol) of diphenylphosphinyl azide and 30.82 g (139.68 mmol) of diphenylchlorophosphine were refluxed in diethyl ether with stirring for seven days. (The diphenylphosphinyl azide required for this reaction was prepared by treating diphenylphosphinyl chloride with an excess of trimethylsilyl

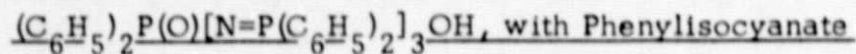
azide in the absence of solvent (ref. 17)). After cooling to room temperature the solids formed were collected on a sintered glass disc, dried, boiled with 250 ml benzene, and filtered hot. The benzene insoluble products were then extracted with 225 ml of boiling acetonitrile, and filtered hot giving 11.84 g (30.6% yield) of the desired compound identified by its infrared spectrum and melting point of 335-340°C (mp 338-345°C, ref. 13).

Preparation of Hydroxy-terminated Linear Phosphazene,



The chloro-terminated linear phosphazene, $\text{(C}_6\text{H}_5\text{)}_2\text{P(O)[N=P(C}_6\text{H}_5\text{)}_2\text{]}_3\text{Cl}$ (6.10 g, 7.20 mmol) was hydrolyzed by refluxing with aqueous acetonitrile (ref. 13). The solid, insoluble product obtained after washing with water and drying amounted to 4.8 g (87.7%), mp 171.7-172.9°C (mp 171-171.5°C, ref. 13). Its DTA scan is given in Figure 7, its infrared spectrum was identical with that of an authentic sample (ref. 13).

Interaction of Hydroxy-terminated Linear Phosphazene,



a) In refluxing benzene. Into a 100 ml round bottom flask were placed 2.007 g (2.460 mmol) of $\text{(C}_6\text{H}_5\text{)}_2\text{P(O)[N=P(C}_6\text{H}_5\text{)}_2\text{]}_3\text{OH}$ and dissolved in 50 ml of benzene by heating the suspension to 71°C. After a clear solution was obtained it was cooled to ~ 9°C and 298 mg (2.502 mmol) of phenylisocyanate, dissolved in 15 ml of benzene was added during a 20 min period. The still clear solution was then heated for 2 hr under reflux, cooled, and the volatiles were removed at room temperature under vacuum. A white residue remained, the infrared spectrum of which showed it to be unreacted phosphazene proving that no reaction took place.

b) In the absence of solvent at 91-92°C. Into a ~ 25 ml ampoule

DATE: 28/06/74
DSC
DSC
d.p. (NO₃)₃OH
ATTA Nu
FLOW RATE 50 ml/min

T-AXIS
SCALE: C/min 50
PROG RATE: C/min 5
HEAT: 1.00L ISC
SHIFT: 0

DTA/DSC
SCALE: C/min
WEIGHT mg
REFERENCE alum oxide
red 1.0 g/in
green 0.2 g/in

TGA
SCALE: mg/min
SUPPORT: SSION mg
WEIGHT mg
TIME CONST: sec
(BY (mg/min) / m)

TMA
SCALE: mly/in
MODE
SAMPLE SIZE
LOAD g
(BY (10X) (mly/min) / in)

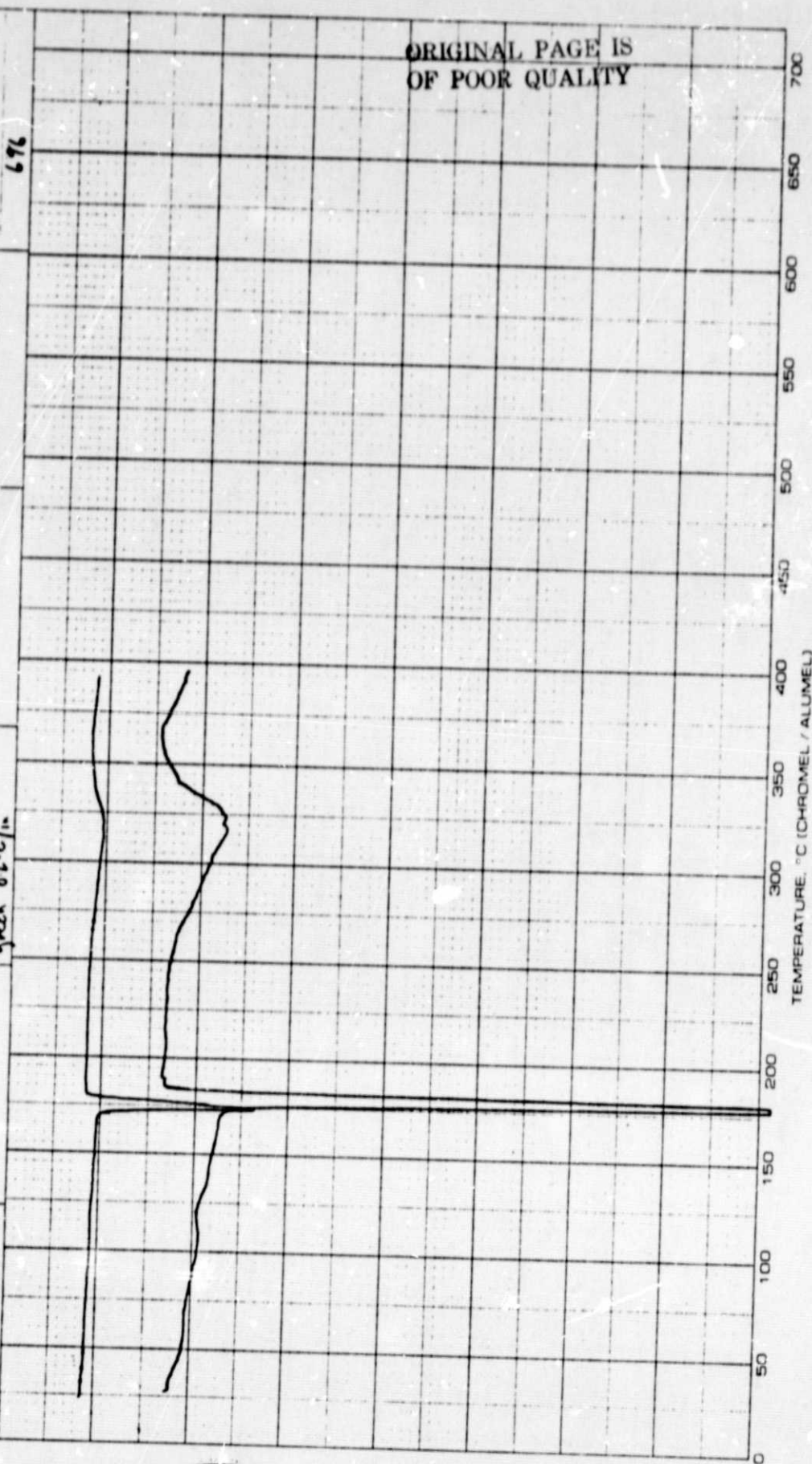


Figure 7: DTA of (C₆H₅)₂P(O)[N=P(C₆H₅)₂]₃OH

were placed 2.010 g (2.464 mmol) of $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_3OH$; after evacuation on the high vacuum line 3.891 g (32.660 mmol) of pure phenylisocyanate were distilled onto the phosphazene. The sealed ampoule was then heated at $91-92^\circ C$ for 15 hr, cooled in liquid nitrogen, and opened to the high vacuum line. No noncondensable gases were observed. The volatile materials present were then distilled out of the ampoule, first at room temperature, finally at $\sim 75^\circ C$. The volatiles thus distilled off the reaction residue were separated by fractional condensation using -78 and $-196^\circ C$ traps. The condensate in the liquid nitrogen cooled trap, 2.047 mmol, was identified by infrared spectroscopy and molecular weight determination as carbon dioxide. The condensate in the trap cooled to $-78^\circ C$ was a water clear liquid and was identified by infrared spectroscopy to be pure phenylisocyanate. This fraction amounted to 0.834 mg (21%). The involatile residue exhibited in its infrared spectrum a number of carbonyl bands as well as absorption at 4.70μ indicative of the presence of the carbodiimide, $N=C=N$, grouping. From the residue triphenyl isocyanate (1.27 g, 33% yield), mp $282-282.5^\circ C$, was isolated by treatment with benzene. No linear hydroxy-terminated phosphazene, $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_3OH$, was recovered.

c) In the presence of Dabco. A mixture of $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_3OH$ (1.13 g, 1.39 mmol), phenylisocyanate (0.15 ml, 0.16 g, 1.39 mmol) and Dabco (triethylenediamine, 0.11 g, 0.98 mmol) was heated at $60^\circ C$ for 22 hr. During the heating process benzene (1.3 ml) was added in two portions. After cooling the solid (0.96 g, 85% recovery) was filtered off, washed with benzene and dried. Based on the comparison of the melting point and infrared spectrum with that of the authentic $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_3OH$ sample it was established that no reaction had taken place.

Preparation of $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_3OCH_2CH_2OH$

In an inert atmosphere enclosure $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_3Cl$ (2.14 g, 2.565 mmol) was treated with ethylene glycol (6.72 g, 108.3 mmol) and pyridine (0.49 g, 6.195 mmol). Subsequently, the reaction mixture was heated under nitrogen by-pass at 70-75°C for 1.5 hr. On cooling a white deposit formed on the bottom. The liquid was then separated from the solid mass which was followed by heating of the liquid portion at 60-90°C for an additional 3 hr. On cooling again a white deposit was noted. Subsequently, the excess ethylene glycol (6.38 g, 102.8 mmol) was distilled in vacuo at 90°C (bath temperature). The original deposit was combined with the distillation residue, dissolved in ethanol, and precipitated with a tenfold quantity of water affording 1.05 g (48% yield) of the desired product, mp 78-81°C.

Preparation of the Urethane, $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_3OCH_2CH_2-OC(O)NHC_6H_5$

In an inert atmosphere $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_3OCH_2CH_2OH$ (334.6 mg, 0.389 mmol) was heated with phenyl isocyanate (0.048 ml) and benzene (0.3 ml) at 58-65°C for 5 hr. Subsequently the solid mass was treated with more benzene and filtered affording 189.5 mg (50% yield) of white crystals mp 183-189°C. Crystallization from benzene gave a material mp 189-189.5°C (for DTA see Figure 8). Anal. Calcd. for $C_{57}H_{50}N_4O_4P_4$: C, 69.94; H, 5.13; N, 5.72; P, 12.66; MW, 979. Found: C, 70.71; H, 5.25; N, 5.61; P, 12.61; MW, 976. Thermogravimetric analysis in nitrogen (Figure 1) and air (Figure 2) shows this compound to be thermally and oxidatively stable to ~185°C, then to lose weight to form a product stable to ~250-300°C. The almost identical stabilities in nitrogen and air are very surprising and may be speculated to be due to the presence of the phosphazene backbone.

DTA RUN NO. 79 DATE: 21 JUN 74 OPERATOR: JH SAMPLE: 12 415B recpt. ATTN: N FLOW RATE: 50 ml/min (100 ml/min) (100 ml/min)	T-AXIS SCALE: °C/min 50 PROG RATE: °C/min 5 HEAT: <input checked="" type="checkbox"/> COOL HEAT: <input type="checkbox"/> COOL OFFSET: in 0 (100 ml/min) (100 ml/min)	DTA/DSC SCALE: °C/in (mg/ml/min) (in) WEIGHT: mg REFERENCE: alum oxide prep 0.2 wt% prep 1.0	TGA SCALE: mg/in SUPPRESSION: mg WEIGHT: mg TIME CONST: 100 dY (mg/min) / in	TMA SCALE: mils/in MODE: SAMPLE SIZE: LOAD: g dY (10X) (mils/min) / in
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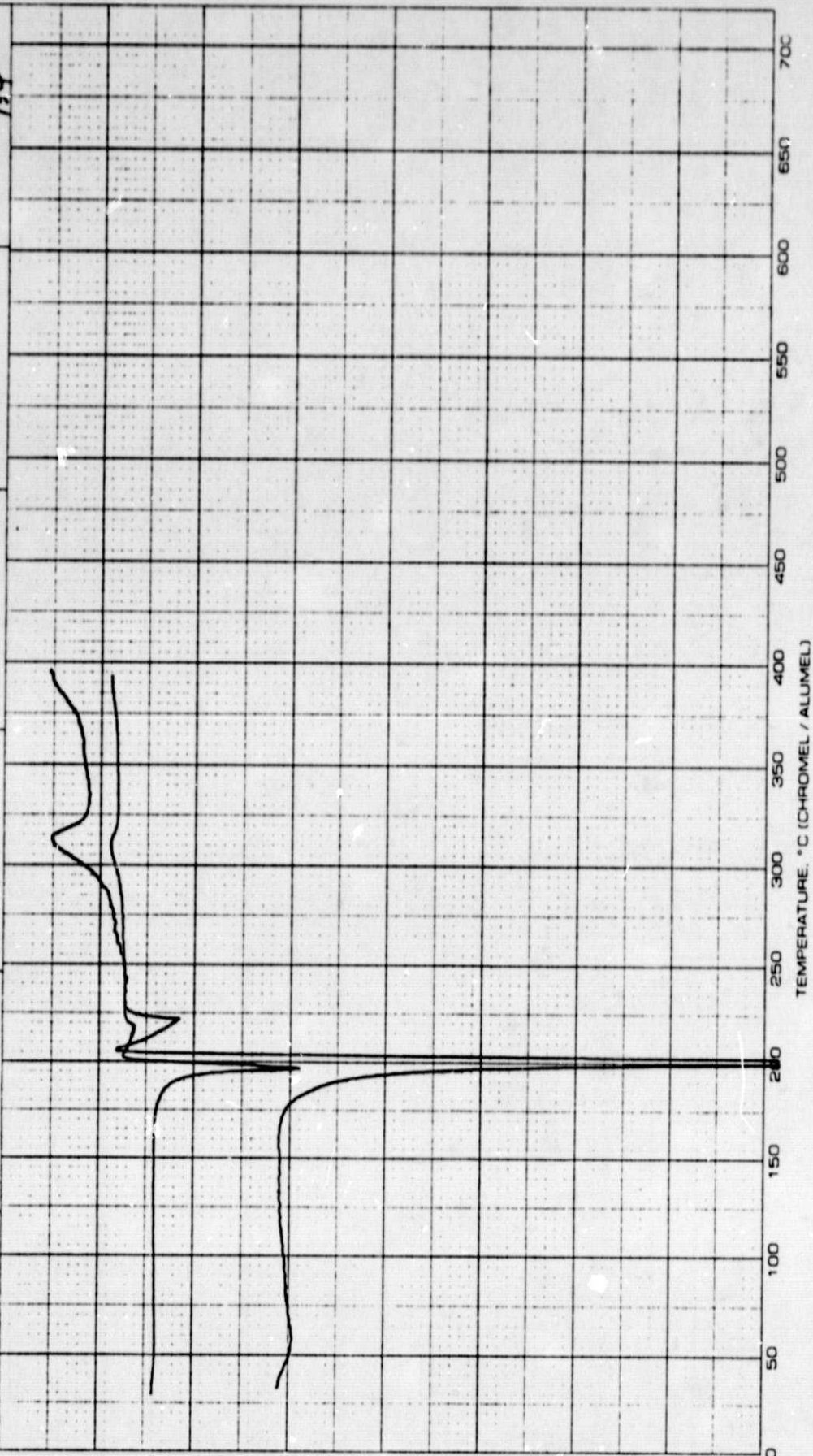


Figure 8: DTA of $(C_6H_5)_2P(O)[N=(C_6H_5)_2]_3OCH_2CH_2OC(O)NHC_6H_5$

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Evaluation of the Hydrolytic Stability of $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_3$
 $OCH_2CH_2OC(O)NHC_6H_5$

A mixture of the urethane (36 mg, 0.037 mmol) and distilled water (3 ml) was heated for 5 hr at 56°C. After cooling to ambient temperature the solid was filtered, washed with distilled water and dried (mp 189.5-190.5°C). Comparison of the melting point characteristics and the infrared spectrum with those of the starting material shows clearly that no hydrolysis took place.

4.3 POLYMER STUDIES

Purification of Hexachlorocyclotriphosphazene

The phosphonitrilic chloride trimer obtained from ROC/RIC Corporation (product P-07, 99.5% pure trimer) was dissolved below 75°C in dry n-heptane (100 g in 150 ml) inside an inert atmosphere chamber. To remove a slight yellow discoloration activated carbon was added, the solution filtered hot and then allowed to cool. The precipitated product was collected and dried in vacuo at room temperature, yield 62.5%.

Polymerization of Hexachlorocyclotriphosphazene

A number of polymerizations of $(Cl_2PN)_3$ were conducted at 250°C varying the reaction time, air pressure, starting material quantity, and starting material purity. All of these are summarized in Table I. In every instance the procedure employed was to place the trimer into an ampoule (30 mm diameter, 250 mm long) equipped with a seal-off constriction. This ampoule was evacuated to < 0.001 mm Hg, the contents molten, and this evacuation-melting operation was repeated twice. When the polymerization was conducted in vacuo the ampoule was sealed off at this stage. In those instances where air was used as "catalyst", pure dry breathing air was

introduced to produce the required pressure before the ampoule was sealed. After cooling to room temperature a given ampoule was opened inside an inert atmosphere enclosure and the contents stirred with dry benzene (ca 10 ml/g of $(Cl_2PN)_3$ employed). A clear solution indicated the absence of cross-linked material. It should be pointed out that in Run No. 3, wherein unpurified trimer was employed, 2.23 g of gel (crosslinked polymer) could be isolated at this stage. To isolate the non-crosslinked polymer, the benzene solution was poured slowly with stirring into a five-fold excess of dry heptane, which resulted in precipitation of the polymer. After filtration, washing with heptane, and drying at room temperature in vacuo the desired polymer was obtained.

Volatile Content and Stability Determination of
Poly(dichlorophosphazene) Prepared by Horizons Research, Inc.

a) Volatiles Content. A 15.0 g sample of the polymer prepared in solution by Horizons Research, Inc. was subjected to vacuum, 0.001 mm Hg, over a period of 13 days. The products obtained, 1.53 g (10% of the original sample) consisted of hexachlorocyclotriphosphazene (80 mg, 0.5%); the major component, ~ 10% of the original sample, was 1,2,4-trichlorobenzene.

b) Stability. The bulk polymer was stable, when stored at room temperature (in an inert atmosphere), for 14 days as determined by its solubility in benzene. Between the 14th and 29th day crosslinking took place as shown by the material's insolubility in benzene. A 10% benzene solution of the polymer did not crosslink (no gel formed) on stirring at room temperature (in an inert atmosphere) over a period of 7 weeks. At $-78^{\circ}C$ the bulk polymer was stable for at least 6 months, judged by its solubility in benzene. The benzene insoluble "crosslinked" polymer was soluble in benzene-ethanol and benzene-methanol.

Poly(dichlorophosphazene) Ethoxy-Substitution Study

The experiments performed are summarized in Table II. In a typical test the given quantity of the polymer was dissolved in a stipulated volume of benzene and this solution was treated with the given quantity of the reagents. After stirring at room temperature for the denoted period of time a sample aliquot, usually 1 ml, was withdrawn, (treated with a small quantity of water if sodium alkoxide reagent was present) and then distilled in vacuo at room temperature. The distillate was subsequently analyzed by gas chromatography and/or quantitative mass spectrometry to determine the alcohol content. Knowing the original alcohol and/or sodium alkoxide concentration the consumption of the reagent was calculated.

Preparation of Poly(diethoxyphosphazenes)

In a typical preparation to an approximately 5% solution of poly(dichlorophosphazene) in benzene was added dropwise (to avoid a temperature rise) a solution of sodium ethoxide in ethanol (which was prepared by dissolving the required quantity of sodium metal in a 10 fold excess of dry ethanol). The reaction mixture was then stirred at room temperature for several days. At the conclusion of the reaction the solution was neutralized with concentrated hydrochloric acid and after addition of water (volume corresponding to that of the original polymer solution) the organic phase was separated and washed with additional water. To remove any insoluble material the solution was filtered through a sintered glass funnel. The filtrate was subsequently slowly added to a five fold volume of petroleum ether to precipitate the desired polymer. Usually the polymer was reprecipitated from benzene into petroleum ether and then dried in vacuo at ambient temperature.

Preparation of Poly(dimethoxyphosphazenes)

Basically two procedures were employed depending on the nature of

the poly(dichlorophosphazene) polymer; representative examples are given below.

a) Using benzene soluble (uncrosslinked) material. To a stirred solution of sodium methoxide prepared from sodium (0.74 g, 0.03 g-atom) and methanol (8.5 ml) was added a solution of poly(dichlorophosphazene) (1.49 g, 0.013 unit mol) over a period of 30 min. The mixture was then refluxed for 7 hr. Subsequently more methanol was added and benzene was distilled off azeotropically. This was followed by the addition of concentrated hydrochloric acid; an attempt at removal of NaCl by filtration was unsuccessful due to the viscous nature of the solution. The purification was effected by two precipitations of the methanolic polymer solution into diethyl ether (followed by washing with water) and one precipitation into benzene. After drying in vacuo 0.50 g (36% yield) of white rubbery material was obtained.

b) Using benzene partially insoluble "crosslinked" polymer. A solution of sodium methoxide prepared from sodium (14.23 g, 2.4 g-atom) and methanol (150 ml) was slowly added over a period of 1 hr to a mixture of the "crosslinked" poly(dichlorophosphazene) (29.69 g, 0.26 unit mol) in dry benzene (300 ml). An exotherm was observed. The mixture was refluxed for 4 hr and stirred at ambient temperature for 3 days. Subsequently, methanol (250 ml) was added and the benzene was distilled off azeotropically. The resultant mixture was acidified with concentrated hydrochloric acid followed by the removal of water and methanol under reduced pressure. The residue was dissolved in chloroform (250 ml) and washed with water (8 x 200 ml). Both chloroform and residual water were removed in vacuo. The polymeric material thus obtained was precipitated twice from methanol solution into diethyl ether, and the precipitate was then dried under vacuum at room

temperature. The product (13.3 g, 36.7%) was an opaque, elastic material which was soluble in benzene.

Preparation of Poly(methoxy, hydroxyethoxy-phosphazenes)

The procedure given below was found to afford the best poly(methoxy, hydroxyethoxy-phosphazenes)

To a mixture of crosslinked poly(dichlorophosphazene) (14.86 g, 0.13 unit mol) in benzene (250 ml) were added in succession 8.99 g of sodium hydroxyethoxide/ethylene glycol (sodium, 0.69 g, 0.03 g-atom; ethylene glycol, 8 ml) and sodium methoxide/methanol (sodium, 5.50 g, 0.24 g-atom; methanol, 75 ml). A slight exotherm was noted during the addition of the sodium methoxide solution. The mixture was refluxed for 7 hr, then stirred overnight at room temperature. The mixture was acidified (concentrated hydrochloric acid) and the solvents removed under reduced pressure. The residue was then taken up in chloroform. The chloroform solution was washed with water until the wash water gave a negative chloride test (silver nitrate). The solvents were removed in vacuo and the product dried in vacuo to give 13.58 g of an opaque elastomer which based on infrared spectral analysis did contain hydroxyl groups. It should be stressed at this juncture that the polymer once isolated from chloroform could not be redissolved in this solvent.

Attempted Transesterification of Poly(dimethoxyphosphazene)

a) Using 20 mole percent of ethylene glycol (with respect to PN units). Ethylene glycol (0.055 ml, 0.95 mmol) was added to poly(dimethoxyphosphazene) (0.51 g, 4.76 unit mmol) in chloroform (10ml). The mixture was heated below reflux temperature (65-70°C) for 6 hr under nitrogen. After cooling to room temperature all volatile material was distilled under vacuum. Mass spectral data indicated negligible extent of transesterification (based upon absence of m/e 31 peak enhancement).

b) Using 100 mole percent of ethylene glycol (with respect to PN units). To poly(dimethoxyphosphazene) (0.48 g, 4.48 unit mmol) in chloroform (10 ml) was added ethylene glycol (0.25 ml, 4.5 mmol). The mixture was refluxed for 6 hr under nitrogen, cooled, then distilled in vacuo. Mass spectral analysis indicated negligible extent of transesterification (based upon absence of m/e 31 peak enhancement).

c) Using Sodium Hydroxyethoxide. To a solution of poly(dimethoxyphosphazene) (1.01 g, 9.4 unit mmol) in dry tetrahydrofuran (25 ml) was added 0.38 g of sodium hydroxyethoxide/ethylene glycol (sodium 0.02 g, 0.0009 g-atom and ethylene glycol 0.36 g). The mixture was stirred and refluxed for 6 hr under nitrogen, cooled, a trace of water added, then distilled in vacuo. Mass spectral analysis indicated negligible extent of transesterification (based upon absence of m/e 31 peak enhancement).

Phenyl Urethane of Poly(methoxy, hydroxyethoxy-phosphazene)

A mixture of poly(methoxy, hydroxyethoxy-phosphazene) (1.93 g, containing in theory 12% of hydroxyethoxy substituents and 88% of methoxy groups), phenyl isocyanate (2.09 g, 17.5 mmol), and benzene (2 ml) was stirred and heated (56-74°C) for 5 hr under nitrogen by-pass. During heating the mixture slowly solubilized. The solution was washed with ether to give 1.58 g of an amorphous solid whose infrared spectrum exhibited a carbonyl absorbance at 5.80 μ indicating the presence of an urethane moiety.

Polyurethane of Poly(methoxy, hydroxyethoxy-phosphazene)

(Containing Theoretically 9% of Hydroxyethoxy Substituents, 91% of Methoxy Groups)

To four aliquots (0.25 ml) of 25% polymer solution (in chloroform) in 12 mm O.D. x 50 mm ampoules were added 50, 100, 150 and 250 μ l, respectively,

of PAPI 901 obtained from NASA Ames Research Center. After sealing, each of the resulting solutions was heated at 60°C for 2 hr. In view of the small sample sizes available the relative viscosities of the four solutions were determined at room temperature by tipping the four ampoules from the vertical into a horizontal position and measuring the time needed by the solution to flow 40 mm. The results are expressed graphically in Figure 6.

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