TGA experiments, and $ZnC_2H_2N_2S_2$ at about 250°. The intractability of these coordination polymers in combination with their moderate thermal stability suggests a limited potential as useful polymeric materials.

Acknowledgment.—This work was supported in part by the Office of Naval Research. Analyses were performed by our Analytical Department. We are indebted to Miss R. A. Kossatz for the infrared spectroscopy, Mr. Harry Rein for the gas chromatography, Dr. J. G. Smith for the mass spectrometry, and Dr. J. R. Soulen for the TGA results. Experimental assistance was given by Mr. G. Mincarelli.

CONTRIBUTION FROM MONSANTO RESEARCH CORPORATION,
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Polymeric 1,3,2,4-Diazadiphosphetidine 2,4-Dioxide Compounds

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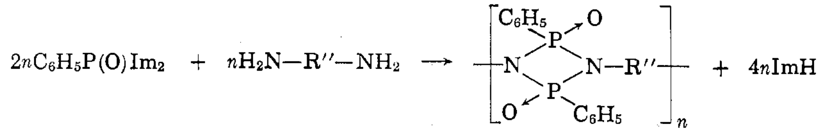
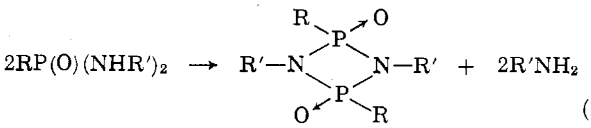
Received February 7, 1964

Controlled thermal decomposition of N,N′,N″-triphenylphosphoric triamide yielded a thermally stable, cross-linked polymer of the composition C_6H_4PON. Linear semi-inorganic homopolymers, containing four-membered $(PN)_2$ rings in the chain, were prepared by transamidative reaction of aromatic diamines with diimidazol-1-ylphenylphosphine oxide.



The feasibility of copolymer synthesis was demonstrated, using a mixture of amines. The indicated structure is supported by spectroscopic data and by physical properties of the polymers.

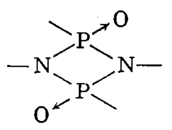
The work of Otto[1] and Michaelis and co-workers[2,3] established that phosphorus amides derived from primary aromatic amines decompose at rather low temperatures (~200°). Furthermore, it was demonstrated[3] that the decomposition can be represented as a specific condensation reaction.



(1)

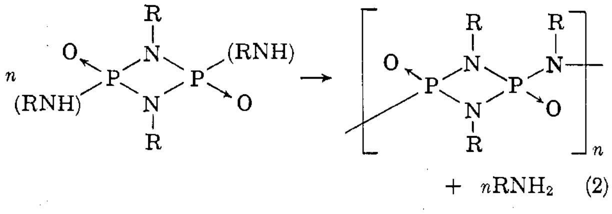
Their experimental description indicated that the 1,3,2,4-diazadiphosphetidine 2,4-dioxide (DAPO)[4] derivatives are thermally very stable compounds.

We substantiated these findings by determining quantitatively the thermal stability of tetraphenyl-DAPO.[5] It therefore appeared advisable to utilize the DAPO structural unit



in the chain of phosphorus-containing polymers, linking it through either the nitrogen or the phosphorus atoms. The tetrafunctionality of the cyclic unit seemed to provide the means for the synthesis of linear or cross-linked structures. To obtain linear polymers, two positions on the ring have to be blocked by unreactive groups.

Condensation and transamidation reactions were initially chosen for the synthesis of DAPO-type polymers. It appeared possible that 1,3-diaryl-2,4-bis(arylamino)-1,3,2,4-diazadiphosphetidine 2,4-dioxides would undergo condensation at elevated temperatures.



(2)

The transamidative approach was potentially more versatile. In view of the ready displacement of the imidazolyl group in diimidazol-1-ylphenylphosphine oxide (DIPPO),[6] this compound was chosen as the phosphorus-containing starting material. The following reaction was expected to yield linear DAPO-type polymers.

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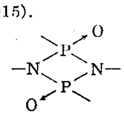
[1] P. Otto, *Ber*, **28**, 616 (1895).

[2] A. Michaelis and E. Silberstein, *ibid.*, **29**, 716 (1896).

[3] A. Michaelis, *Ann.*, **407**, 290 (1915).

[4] The abbreviated name of the  unit, DAPO, stems from the words di aza phosphetidine oxide, which indicate its chemical composition.

[5] L. Parts and M. L. Nielsen, to be published.

[6] R. Z. Greenley, M. L. Nielsen, and L. Parts, *J. Org. Chem.*, **29**, 1009 (1964).

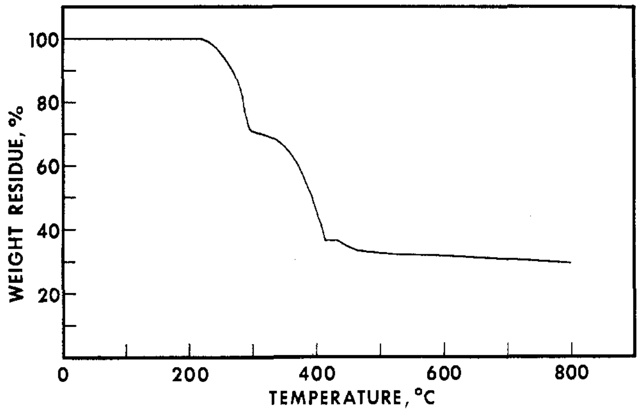
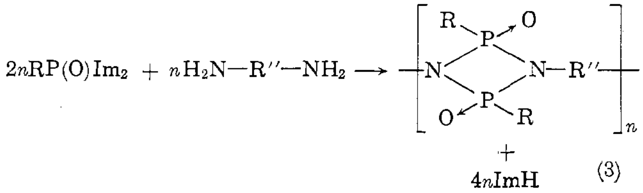
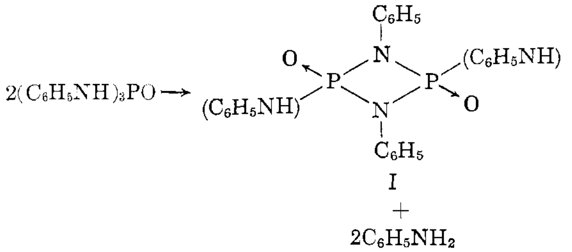


Fig. 1.—Thermogravimetric graph for the thermal decomposition of $(C_6H_5NH)_3PO$: sample weight 200 mg., heating rate 3°/min., helium atmosphere.


(3)

Results and Discussion

Controlled Thermal Decomposition of $(C_6H_5NH)_3PO$.—Michaelis and Silberstein[2] and Buck and Lankelma[7] have demonstrated that thermal decomposition of N,N′,N″-triphenylphosphoric triamide yields 1,3-diphenyl-2,4-bis(phenylamino)-DAPO (eq. 4), a solid which melts at 358–359°.[2,7] Michaelis and Silberstein did not state the conditions required to effect the condensation; Buck and Lankelma conducted the reaction at 225° (30 mm.).


(4)

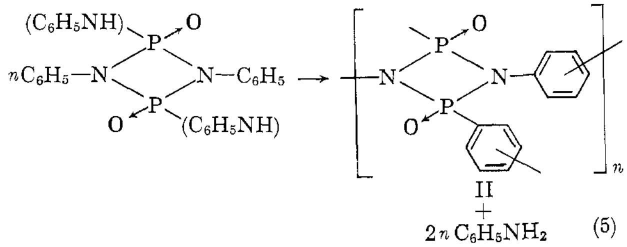
To establish the feasibility of reaction 2, we followed the condensation thermogravimetrically (Fig. 1). N,N′,N″-Triphenylphosphoric triamide was heated at a rate of 3°/min. in a helium atmosphere. The condensation began at 220°. The first sudden change of slope of the curve occurred at 300°, corresponding to 29% weight loss. Upon further heating, the sample continued to lose weight to 420°. Between 420 and 440° the weight remained constant, indicating loss of 62% of the original sample weight. Slow decomposition occurred between 440 and 800°.

Subsequently, preparative experiments were conducted in the thermogravimetric equipment and the condensation reactions were stopped at 300, 400, 420, 500, and 800°, respectively. The products were analyzed and additionally characterized by their infrared spectra and X-ray diffraction patterns.

The first break in the thermogravimetric analysis (TGA) curve, at 300°, corresponds to the formation of I (eq. 4). The observed weight loss (29%) is in agreement with the calculated value (28.8%). The product is crystalline; its infrared spectrum is identical with that of an authentic sample prepared by the method of Buck and Lankelma.[7]

The weight loss at the second break of the TGA curve (63%) is much higher than the calculated value (43.2%) for the desired reaction (eq. 2). The liquid formed in the condensation consists of pure aniline. The empirical composition of the pale yellow solid product corresponds to C_6H_4PNO. The polymer is insoluble in conventional solvents at room temperature; however it can be hydrolyzed almost completely in concentrated hydrochloric acid at 100°. Although the characterization of the hydrolysis products would establish the position of attachment of phosphorus on the benzene ring, we have not pursued the work in this direction.

It is concluded that at temperatures ranging from 300 to 420° the reaction shown in eq. 5 occurs. The somewhat higher experimental weight loss (63%) than calculated (57.6%) for eq. 5 is attributed to volatilization of I at elevated temperatures prior to condensation. The infrared spectral features in the P–N stretching region (8–12 μ) suggest that formula II represents a somewhat idealized picture of the chemical structure of this polymer. The broad spectral bands indicate that the thermal condensation is accompanied by $(PN)_2$ ring opening, the extent of which is not known. Consequently this polymeric product does contain also some linear PN fragments and/or larger than four-membered rings.



It is interesting to note that the polymer is fusible at elevated temperatures under high pressure ($T >$ 200°, $P \sim$ 10,000 p.s.i.). This is believed to be due to structural reorganization of the P–N bonds, which is indicated by sharpening of spectral bands attributable to P–N motions.

Heating of II to 800° causes relatively little weight loss and darkening of the sample. The composition of the black solid indicates that extensive hydrogen abstraction occurs in the 450–800° range.

We may thus recapitulate our findings. When N,N′,N″-triphenylphosphoric triamide is subjected to conditions conducive for thermal condensation, a linear polymer of the structure depicted in eq. 2 is not obtained. However, more extensive condensation

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[7] A. C. Buck and H. P. Lankelma, *J. Am. Chem. Soc.*, **70**, 2398 (1948).

polymerization occurs at higher temperatures (300–450°). As indicated by eq. 5, the polymerization involves hydrogen abstraction from the phenyl groups and yields a cross-linked resin which is fusible under pressure. The latter undergoes loss of hydrogen upon heating from 450 to 800° and degrades extensively above 800°.

Preparation of DAPO-Type Polymers by the Reaction of DIPPO with Diamines.—The initial experimental approach in attempting to synthesize linear DAPO-type polymers according to eq. 3 consisted of melt reaction of equivalent quantities of DIPPO and diamines. 4,4′-Oxydianiline yielded a polymer, and 96% of the calculated amount of imidazole was recovered. The polymer could be dissolved in quinoline; a 1% solution had a specific viscosity of 0.09 at room temperature.

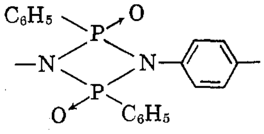
When a melt reaction was attempted with benzidine, only 88.8% of the imidazole was recovered. The product of the incomplete condensation reaction solidified at the reaction temperature (285°) and the condensation became prohibitively slow. It appeared advisable to conduct the polymerizations in solution.

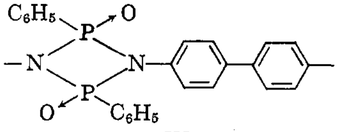
Quinoline (b.p. 237°) was used as the solvent for solution polymerizations. Reactions have been conducted at temperatures ranging from 25 to 300° and the solvent has not interfered. At temperatures much higher than the boiling point of quinoline, the remaining solvent functions as a plasticizer. The advantage of using a solvent for the synthesis of DAPO-type polymers has also been indicated by the analytical results of the products and viscosities of polymer solutions.

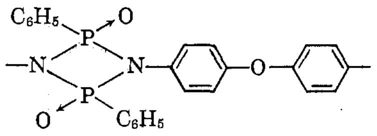
The reaction of 4,4′-oxydianiline with DIPPO was repeated in quinoline solution. The specific viscosity of a 1% solution of the resultant polymer was 0.22. A homogeneous solution of benzidine and DIPPO in quinoline was obtained by rapid heating prior to formation of the insoluble polymer. When conducted in solution, the latter polymerization proceeded to completion.

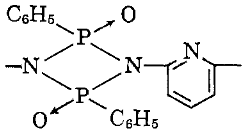
Several DAPO-type polymers were synthesized by the solution technique. Besides 4,4′-oxydianiline and benzidine, *p*-phenylenediamine and 2,6-diaminopyridine were used for the synthesis of homopolymers. Also, a copolymer was prepared by allowing DIPPO to react with an equimolar mixture of 4,4′-oxydianiline and benzidine. Whereas during homopolymerization of benzidine with DIPPO the quinoline-insoluble polymer precipitated from solution, the reaction mixture remained homogeneous in the copolymerization experiment. The product was structurally more rigid and higher melting than the homopolymer prepared from 4,4′-oxydianiline. The copolymerization experiment is perhaps best indicative of the scope of chemical variations that can be incorporated in DAPO-type polymers.

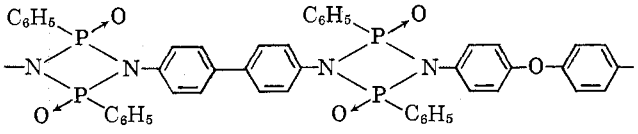
Polymers containing the repeating units III–VII were synthesized. The structural formula VI indicates the copolymeric nature of the material. It does not imply regular alternation of 1,1′-biphenylene and 1,1′-(4,4′-oxydiphenylene) units in the polymer chain.


III


IV


V


VII


VI

Several unsuccessful attempts were made to devise a synthesis for DAPO-type polymers for which hydrolytically stable phosphorus compounds could be utilized. 4,4′-Oxydianiline was the diamine used in these experiments. It was found that the condensation reaction with phenylphosphonic diamide did not proceed to completion; dipyrrol-1-ylphenylphosphine oxide was not sufficiently reactive. The low reactivity of the latter compound is attributed to the relatively nonpolar nature of the P–N bonds and the low stability of anions formed in nucleophilic displacement reactions.

Undesired side reactions occurred with phenylphosphonic acid and diphenyl phenylphosphonate. The latter two attempts to synthesize the DAPO-type polymer by alternative methods indicated that potential side reactions must be seriously considered when condensations are conducted at elevated temperatures. Multicomponent systems that are stable at moderate temperatures, and in which reactions can be effected in this temperature range catalytically, cannot be assumed to remain unreactive in the absence of catalysts in the 150–300° temperature range.

Some properties of the polymers which were synthesized are summarized in Table I. The physical characteristics vary greatly, depending upon the structure. The polymer prepared from 4,4′-oxydianiline is appreciably soluble in quinoline. It can be molded into transparent, physically tough objects; flexible fibers can be drawn from the melt. Based on X-ray diffraction analysis, the polymer as obtained from the reaction is amorphous. However, crystallization has been observed upon cooling a quinoline solution of the polymer. The copolymer prepared from DIPPO, 4,4′-oxydianiline, and benzidine resembles the above described homopolymer in its properties.

The homopolymer prepared from DIPPO and 2,6-diaminopyridine was found to be a brittle, amorphous, moldable resin. The polymers obtained from DIPPO

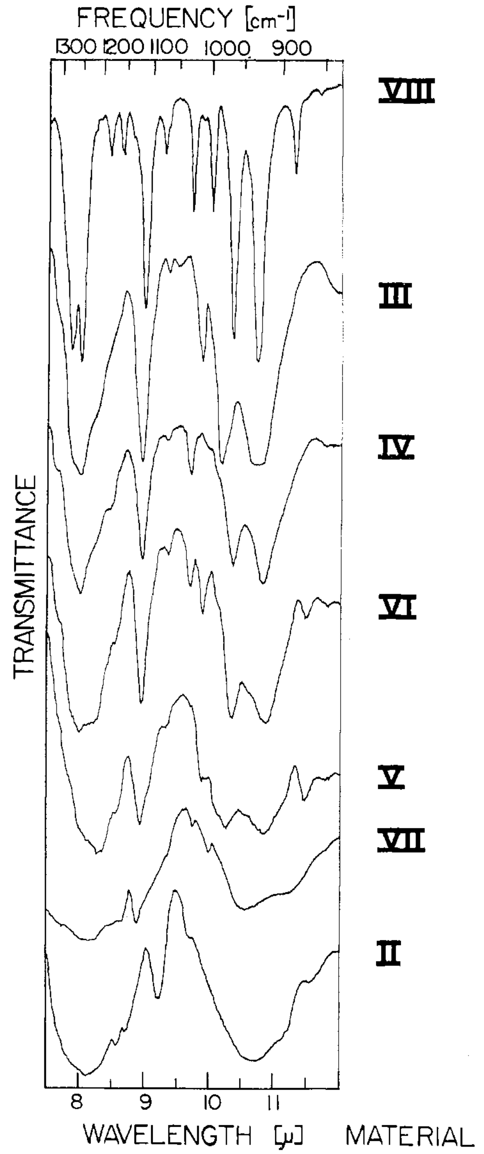


Fig. 2.—Infrared spectra of 1,3,2,4-tetraphenyldiazadiphosphetidine 2,4-dioxide and of DAPO-type polymers in the P–N stretching region.

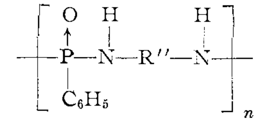
with *p*-phenylenediamine and benzidine are structurally perhaps most interesting. These materials are insoluble in quinoline, they do not melt below 360°, the infrared absorption bands are sharp, and powder X-ray diffraction patterns indicate some degree of three-dimensional ordering. Apparently in these polymers we achieved the highest degree of intermolecular and intramolecular order, largely due to the rigidity of the polymer chains.

Table I
Some Properties of DAPO-Type Polymers

Polymer[a] no.	Melting range, °C.	Density, g./cc.	Onset temp. of decompn., °C.[b]	10% wt. loss, at °C.[b]	Residue wt. at 800°, % of orig. wt.[b]
III	>360	1.31	170	380	44
IV	>360	1.25	280	445	62
V	250–280	1.27	390	448	56
VI	278–295	1.26	350	425	59
VII	290–300	1.37	350	415	67

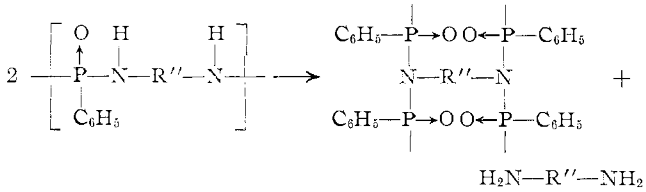
[a] Compressed pellets of the polymers had the following physical characteristics: III and IV, light yellow, opaque, brittle; V, brownish yellow, transparent, tough; VI, caramel-brown, transparent, tough; VII, reddish brown, transparent, brittle. [b] Based on thermogravimetric measurements in helium atmosphere. Sample weights 200 mg., heating rate 3°/min.

It is of interest to note a recent publication by Gutmann, Hagen, and Utvary.[8] Materials which according to the authors have the structure



$$\left[-\overset{O\uparrow}{\underset{C_6H_5}{P}}-\overset{H}{N}-R''-\overset{H}{N}-\right]_n$$

were heated under high vacuum. It is stated[8] that the following reactions occurred



and cross-linked, glassy products were obtained. The reported infrared spectra do indicate disordered structures. The incomplete analytical data do not allow one to calculate the extent of condensation, nor do these reflect the compositions of the products. The condensations reported by Gutmann and coworkers did not yield polymers which would possess the composition of completely condensed products. The latter materials would have identical elemental compositions with the structurally ordered DAPO-type polymers prepared from the same diamines, which we are reporting.

The extent of structural information pertaining to four-membered $(PN)_2$ ring compounds is presently quite limited. Molecular weight measurements on aromatically-substituted DAPO derivatives[3,9] indicate dimeric structure. Factors affecting the dimerization of N-aryliminotrichlorophosphoranes, $ArN{=}PCl_3$, have been discussed by Zhmurova and Kirsanov.[10] Trippett[11] extended the qualitative reasoning to four-membered $(PN)_2$ ring compounds in general. Infrared absorption at 847 cm.$^{-1}$ has been attributed to P–N stretching vibration of N-methyliminotrichlorophosphorane dimer.[12]

We have observed that DAPO-type polymers possess strong infrared absorption bands in the 1200–1300 and 885–985 cm.$^{-1}$ regions. These wave lengths correspond closely to those of the monomeric model compound, tetraphenyl-DAPO. Absorption maxima for the latter compound were observed at 1280, 1256, 970, and 935 cm.$^{-1}$. A graphical comparison of the infrared spectra of the polymers and of the monomeric model compound tetraphenyl-DAPO (VIII) is pre-

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(8) V. Gutmann, D. E. Hagen, and K. Utvary, *Monatsh. Chem.*, **93**, 627 (1962).

(9) A. Michaelis, *Ann.*, **326**, 129 (1903).

(10) I. N. Zhmurova and A. V. Kirsanov, *J. Gen. Chem. USSR*, **30**, 3044 (1960).

(11) S. Trippett, *J. Chem. Soc.*, 4731 (1962).

(12) A. C. Chapman, W. S. Holmes, N. L. Paddock, and H. T. Searle, *ibid.*, 1825 (1961).

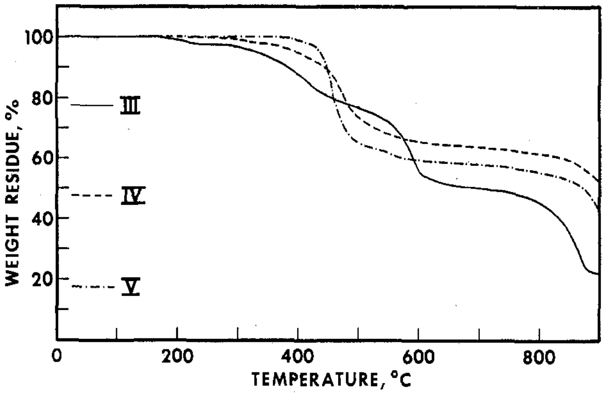


Fig. 3.—Thermogravimetric graph for DAPO-type polymers III, IV, and V: sample weight 200 mg., heating rate 3°/min., helium atmosphere.

sented in Fig. 2. The close similarity of the spectral features (*i.e.*, frequencies, relative intensities) in the above-mentioned spectral regions, especially for the first five structures, is noteworthy. In view of the lack of more complete spectroscopic data, absence of structural data for the DAPO molecular unit, and the fact that only spectra of solid samples were recorded, no attempt will be made to assign vibrational frequencies associated with ring stretching motions to normal vibrations; only some qualitative statements will be made.

The doublet structure in the 1200–1300 cm.$^{-1}$ region is attributed to P–O stretching and asymmetric $(PN)_2$ ring stretching. The two strong absorption bands in the 885–985 cm.$^{-1}$ region are believed to be due to ring breathing vibration and the second asymmetric $(PN)_2$ ring stretching vibration. The frequencies assigned to asymmetric P–N stretching and to ring breathing vibrations in the phosphonitrile chloride trimer are[13] 1218 and 875 cm.$^{-1}$.

Zhmurova and Kirsanov[10] and Chapman with coworkers[12] have referred to the analogy in bonding between phosphonitriles and the dimers of phosphorane imines. As indicated above, this analogy appears to be reflected also in the vibrational spectra of 1,3,2,4-diazadiphosphetidine 2,4-dioxide derivatives.

The similarity of spectral features in the $(PN)_2$ ring stretching region for the model compound and for polymers indicates that the DAPO structural units are present in polymers. Additional evidence for the DAPO structure is the solubility of polymers with more flexible chains in quinoline and three-dimensional ordering of polymers with rigid chain units in the solid state.

Thermal Stability of DAPO-Type Polymers.—The information pertaining to thermal stability is summarized in Table I and is presented graphically in Fig. 3 and 4. A very noticeable feature in Fig. 3 is the low thermal stability of the polymer prepared from *p*-phenylenediamine. Initial weight loss was observed at 170°. The instability is attributed to the possibility for the formation of quinone imine structure which would represent the first step in thermal decomposition.

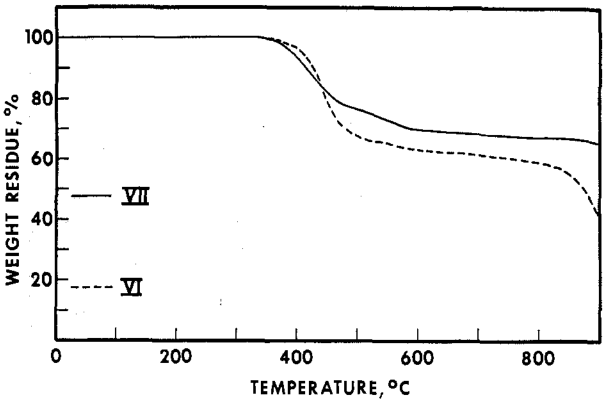
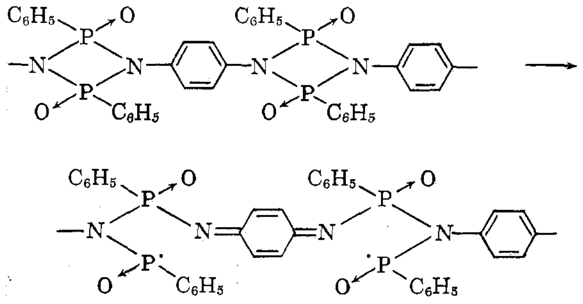


Fig. 4.—Thermogravimetric graph for DAPO-type polymers VI and VII: sample weight 200 mg., heating rate 3°/min., helium atmosphere.



The possibility for the formation of a quinoid structure does not exist in the polymer which contains the diphenyl ether linkage in the chain, and the product remains stable to 390°.

Experimental

Quinoline, used as the solvent for most of the polymerization reactions, was refluxed over zinc and calcium hydride, distilled in nitrogen atmosphere, and stored over calcium hydride. The amines were purified by vacuum distillation or sublimation. Apparatus was assembled and the reactions were conducted in a dry nitrogen atmosphere. The solid polymers could be handled in air. All melting temperatures have been corrected. Elemental analyses were performed by Galbraith Laboratories, Inc. Thermogravimetric measurements were made with an Aminco thermobalance in a helium atmosphere, heating at the rate of 3°/min.

Polymer from Thermal Decomposition of N,N',N''-Triphenylphosphoric Triamide.—Samples of $(C_6H_5NH)_3PO$, 0.200 g. each, were heated to 300, 500, and 800°, respectively, at constant heating rate in TGA apparatus. The thermogravimetric graph obtained in the last experiment is presented as Fig. 1. Samples of solid residues were recovered and submitted for infrared and elemental analysis (Table II).

TABLE II

Max. temp., °C.	Elemental compn. of product, %				Appearance
	C	H	N	P	
300	62.56[a]	4.97	12.29	13.61	Colorless, crystalline solid
500	52.76[b]	3.15	9.64	21.04	Yellow, rigid foam
800	52.10	0.83	8.96	22.73	Black, rigid foam

[a] Calcd. for $(C_6H_5NH)_2[P(O)NC_6H_5]_2$: C, 62.61; H, 4.82; N, 12.17; P, 13.46. [b] Calcd. for $[C_6H_4P(O)N]_n$: C, 52.57; H, 2.94; N, 10.22; P, 22.60.

Polymer from Thermal Decomposition of N,N',N''-Triphenylphosphoric Triamide (II), Preparative Experiment.—The experi-

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[13] A. C. Chapman and N. L. Paddock, *J. Chem. Soc.*, 635 (1962).

ment was conducted in the TGA apparatus. The rate of heating was 3°/min. Sample weight was not recorded automatically.

Triphenylphosphoric triamide (15.573 g., 0.0481 mole), contained in a wide test tube, was heated to 425° in helium atmosphere. Vacuum was applied slowly. Evaporation of volatile matter in the beginning of the evacuation cooled the sample to 400°. Heating was continued for 1 hr. at 400–425°.

Pale yellow liquid, 7.2 g., evolved during the condensation, was recovered from the trap (n^{25}D 1.5854, reported[14] for aniline 1.5840) and was identified as aniline (0.077 mole) by its infrared spectrum. The spectrum also indicated the absence of benzene in the liquid. Incomplete recovery (80%) is attributed to mechanical losses during transfer of the liquid from the trap. However, the sample used for identification was representative of the total liquid condensate.

A small amount of $(C_6H_5NH)_2[P(O)NC_6H_5]_2$, identified spectroscopically, was evolved from the sample during evacuation and deposited in cold sections of the apparatus.

The light yellow solid product (5.835 g.) constituted an 88.5% yield of $[C_6H_4P(O)N]_n$.

Anal. Calcd. for C_6H_4NOP: C, 52.57; H, 2.94; N, 10.22; P, 22.60. Found: C, 52.30; H, 3.68; N, 10.27; P, 22.20.

Preparation of Diimidazol-1-ylphenylphosphine Oxide (DIPPO).—The following procedure represents a simplification of the synthesis which we have previously reported.[6] The imidazol-1-ylpotassium is not isolated; the product can conveniently be purified on a larger scale by distillation.

To pieces of potassium (46.9 g., 1.20 g.-atoms), suspended in 400 ml. of dimethoxyethane (DME), was added a solution of imidazole (81.7 g., 1.20 moles) in 300 ml. of the same solvent. The reaction mixture was heated to the melting point of potassium. Imidazole was added at a rate to maintain the metal in the molten state. Stirring was continued for a brief time after addition of imidazole had been completed.

Phenylphosphonic dichloride (117.0 g., 0.60 mole), dissolved in 300 ml. of DME, was added over a period of 70 min. The reaction temperature rose from 29 to 51°. Subsequently the reaction mixture was heated to 70–80° for 1 hr. and was centrifuged upon cooling to room temperature. The solid was extracted with 800 ml. of DME. DIPPO was recovered by vacuum removal of the solvent.

The crude solid was recrystallized from toluene and was further purified by vacuum distillation at 150–240°, using a large air-cooled condenser. At the completion of the distillation, the colorless product was melted and allowed to flow into a receiver. The yield was 100.6 g. (64.8%).

Anal. Calcd. for $C_{12}H_{11}N_4OP$: C, 55.81; H, 4.29; N, 21.70; P, 12.00. Found: C, 56.04; H, 4.48; N, 21.44; P, 11.94.

Poly[1,1′-(4,4′-oxydiphenylene)-2,4-diphenyl-1,3,2,4-diazadiphosphetidine 2,4-Dioxide] (V) from DIPPO and 4,4′-Oxydianiline. Melt Reaction.—DIPPO (12.91 g., 0.050 mole) and 4,4′-oxydianiline (5.01 g., 0.025 mole) were weighed in a drybox and transferred into a reaction flask equipped with a Z-shaped air-cooled condenser. The assembly was removed from the drybox, connected to a nitrogen bypass line, and immersed in an oil bath at 176°. A reaction started immediately. Initially the mixture became gel-like, but upon further heating became a viscous reddish brown liquid. After 70 min. of heating, during which the temperature had been raised to 226°, the system was evacuated to remove imidazole. The evacuation was continued for 65 min. The contents of the flask were converted to a rigid foamy solid. The foam was crushed in a drybox and was heated at 250° for 4 hr. The condenser contained 96% of the calculated amount of imidazole.

A 4-g. sample of the product was heated to 300° for 1 hr. under vacuum. A small amount (0.03 g.) of 4,4′-oxydianiline was evolved. The polymer softened and sintered during the heating.

Anal. Calcd. for $C_{24}H_{18}N_2O_3P_2$: C, 64.87; H, 4.08; N, 6.30; P, 13.94. Found after heating to 240°: C, 63.66; H, 4.09; N, 6.51; P, 13.43. Found after heating to 300°: C, 62.70; H, 4.03; N, 6.22; P, 13.51. The specific viscosity of a 1% solution in quinoline at 25° was 0.09.

The product obtained at 230° was a noncrystalline solid (by X-ray diffraction), soluble in dimethyl sulfoxide and in quinoline. Upon heating to 300° the polymer became very tough and could not be dissolved in dimethyl sulfoxide. However, it was still soluble in quinoline.

Polymer from DIPPO and 4,4′-Oxydianiline (V). Solution Polymerization.—DIPPO (12.91 g., 0.05 mole), 4,4′-oxydianiline (5.01 g., 0.025 mole), and quinoline (20.03 g.), contained in a flask equipped with an air-cooled condenser, formed a homogeneous solution when the flask was immersed in a heating bath at 170°. In 1 hr. the temperature was raised to 250°.

The flask was evacuated slowly. A small amount of reaction mixture splashed into the condenser, leading to a nonquantitative yield of the polymer. The evacuated system was heated for 3.5 hr. at temperatures ranging to 288°. The evacuation and heating were interrupted once in order to crush the polymer foam which solidified in the neck of the flask. The yield of the light yellow, tough polymer was 9.82 g. (88.4%). By X-ray diffraction the polymer was noncrystalline.

Anal. Calcd. for $C_{24}H_{18}N_2O_3P_2$: C, 64.87; H, 4.08; N, 6.30; P, 13.94. Found: C, 64.70; H, 4.34; N, 6.34; P, 14.09. The specific viscosity of a 1% solution in quinoline at 25° was 0.22.

Polymer from Phenylphosphonic Diamide and 4,4′-Oxydianiline.—Phenylphosphonic diamide was prepared by reaction of phenylphosphonic dichloride with liquid ammonia.[15] The excess of ammonia was allowed to evaporate, and ammonium chloride was removed with concentrated ammonium hydroxide. The crude product (86.8%) was purified by recrystallization from dimethyl sulfoxide, yielding 61.8% of pure phenylphosphonic diamide. Although the melting point has been reported (191°), we found it to be unreliable as an indication of purity since the compound begins to decompose thermally 50° below the melting point.

Anal. Calcd. for $C_6H_9N_2OP$: C, 46.15; H, 5.81; N, 17.94; P, 19.84. Found: C, 46.01; H, 5.80; N, 17.74; P, 20.04.

Phenylphosphonic diamide (7.81 g., 0.05 mole) and 4,4′-oxydianiline (5.01 g., 0.025 mole) were suspended in 20.20 g. of quinoline. The reaction flask was equipped with a bubbler which indicated ammonia evolution. The reactants were immersed in a bath preheated to 216°. Ammonia evolution began before complete dissolution occurred. The solution became more viscous and solid flakes were observed in the foam above the reaction mixture. Upon further heating, the solution became reddish brown and the solid flakes disappeared.

In 2.5 hr. the temperature of the reaction mixture was raised to 284° and evolution of ammonia ceased. The flask and its contents were allowed to cool to 145° and removal of quinoline by evacuation was begun. The reaction mixture set up to a rigid red foam which was crushed mechanically.

Upon further heating under vacuum the reaction mixture melted, foamed, solidified, and had to be crushed twice before removal of volatile materials was complete. The final condensation temperature was 284°. No 4,4′-oxydianiline evolved in the course of the heating. The remaining product, weighing 10.38 g., was composed of red, hard, noncrystalline solid. It was more brittle than the polymer obtained upon condensation of DIPPO with 4,4′-oxydianiline. A small amount of product was lost due to splashing of the solution into the condenser during the removal of quinoline.

Anal. Calcd. for $C_{24}H_{18}N_2O_3P_2$: C, 64.87; H, 4.08; N, 6.30; P, 13.94. Calcd. for $C_{48}H_{39}N_5O_6P_4$: C, 63.65; H, 4.34; N, 7.73; P, 13.68. Found: C, 62.70; H, 4.59; N, 7.56; P, 13.11.

The analytical results for the product are in fair agreement with values calculated for seven-eighths removal of ammonia.

Attempted Reaction of Dipyrrol-1-ylphenylphosphine Oxide with 4,4′-Oxydianiline.—Dipyrrol-1-ylphenylphosphine oxide[6] (12.81 g., 0.05 mole) and 4,4′-oxydianiline (5.01 g., 0.025 mole)

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(14) J. C. Smith, N. J. Foecking, and W. P. Barber, *Ind. Eng. Chem.*, **41**, 2289 (1949).

(15) W. C. Smith and L. A. Audrieth, *J. Org. Chem.*, **22**, 265 (1957).

were suspended and partly dissolved in 16.5 g. of quinoline. The flask was equipped with a microdistillation column and take-off head. The reaction was conducted under nitrogen. After 6.5 hr. of heating with the temperature ranging to 266°, only 0.70 g. of pyrrole had distilled from the reaction mixture, which had become dark brown. Since dipyrrol-1-ylphenylphosphine oxide begins to decompose below this temperature,[6] the experiment was discontinued.

Reaction of Phenylphosphonic Acid with 4,4′-Oxydianiline.—Phenylphosphonic acid (7.90 g., 0.05 mole) and 4,4′-oxydianiline (5.01 g., 0.025 mole) were allowed to react under nitrogen. The reaction time was 1.5 hr. and the reaction temperature ranged from 173 to 270°. Evolution of vapors was observed immediately after reactants began to melt. When the temperature reached 197°, and the reactants had melted only partly, the liquid mixture became violet. At 250° the reaction mixture consisted of a blue, somewhat viscous liquid. Vacuum was applied at 265–270°. The liquid condensate, weighing 1.2 g., consisted of approximately equal volumes of water and an organic phase. The major component of the latter phase was identified spectroscopically as aniline; it did not contain a detectable amount of *p*-aminophenol.

Upon cooling to room temperature the nonvolatile reaction product was a blue solid. A degradative reaction occurred and the desired product was not obtained.

Attempted Reaction of Diphenyl Phenylphosphonate with 4,4′-Oxydianiline.—Diphenyl phenylphosphonate (15.51 g., 0.05 mole) was allowed to react with 4,4′-oxydianiline (5.01 g., 0.025 mole). At 192° condensation of a colorless, crystalline solid, presumably phenol, was observed. Condensation continued as the temperature was raised. Above 225° the reaction mixture darkened, acquiring blue coloration, and evolution of phenol ceased. The experiment was discontinued.

Reaction of DIPPO with Benzidine. Attempted Melt Polymerization.—The following amounts of reactants were transferred into a flask equipped with an air-cooled condenser: 12.91 g. (0.05 mole) of DIPPO and 4.61 g. (0.025 mole) of benzidine. The flask was then immersed in an oil bath maintained at 175°. Melting began immediately; however, formation of threads of polymer was observed in solution before the mixture melted completely. At no time during the experiment was the reaction mixture completely homogeneous. The reaction temperature was raised to 285° within 3 hr. Upon vacuum removal of imidazole (6.05 g., 88.8%), the product (11.40 g.) consisted of a dark brown, foamy solid.

Anal. Calcd. for $C_{24}H_{18}N_2O_2P_2$: C, 67.29; H, 4.24; N, 6.54; P, 14.46. Found: C, 65.90, 65.69; H, 4.90, 4.73; N, 9.49, 9.26; P, 11.82, 11.69.

Polymer from DIPPO and Benzidine (IV). Solution Polymerization.—The starting reaction mixture consisted of 12.91 g. (0.05 mole) of DIPPO, 4.61 g. (0.025 mole) of benzidine, and 20.49 g. of quinoline. There was no indication of extensive dissolution in quinoline, nor of a reaction at room temperature.

The flask containing the reactants was immersed in a bath maintained at 140°. A homogeneous solution formed initially, from which a colorless suspended solid later separated. Within 1.5 hr. the temperature was raised to 275°. During the subsequent vacuum removal of quinoline and imidazole the temperature was maintained at 275–285°. The weight of the pale yellow, hard solid product was 10.65 g. (99.4%).

Anal. Calcd. for $C_{24}H_{18}N_2O_2P_2$: C, 67.29; H, 4.24; N, 6.54; P, 14.46. Found: C, 67.22; H, 4.36; N, 6.47; P, 14.25.

By X-ray diffraction analysis the polymer was largely noncrystalline. Weak, broad, and diffuse maxima were observed in the diffraction pattern, indicating some three-dimensional ordering.

Copolymerization of 4,4′-Oxydianiline and Benzidine with DIPPO in Quinoline Solution.—4,4′-Oxydianiline (2.50 g., 0.0125 mole), benzidine (2.30 g., 0.0125 mole), DIPPO (12.91 g., 0.050 mole), and quinoline (20.04 g.) were transferred into a flask equipped with a condenser and a trap. When the flask was immersed in an oil bath at 175°, a homogeneous pale yellow solution was formed. In 1.5 hr. the temperature was raised to 274°; the product remained in solution. The system was evacuated slowly and in 1.5 hr. the temperature was increased to 287°. The flask was removed from the bath to crush the foamy polymer which had expanded into the neck. Subsequently, heating was continued for 2 hr. at 280–28 °, the product remaining solid. The caramel-brown product (VI) weighed 11.44 g. (calcd. 10.91 g.).

Anal. Calcd. for $C_{48}H_{36}N_4O_5P_4$: C, 66.06; H, 4.16; N, 6.42; P, 14.20. Found: C, 65.07; H, 4.64; N, 7.66; P, 13.07.

A portion (4.87 g.) of the incompletely condensed polymer was suspended in quinoline (24.36 g.). Upon heating to 200°, the solution became homogeneous. Within 1.5 hr. the reaction mixture was heated to 270°. Vacuum was applied and heating was continued for 4 hr. at temperatures ranging to 293°. The tough, light caramel-colored product weighed 4.68 g.

Anal. Found: C, 65.91; H, 4.35; N, 6.36; P, 13.96.

Polymer from DIPPO and *p*-Phenylenediamine (III).—*p*-Phenylenediamine (2.70 g., 0.025 mole), DIPPO (12.91 g., 0.05 mole), and quinoline (20.0 g.) were transferred into a flask equipped with a condenser and a trap. The flask was immersed in an oil bath maintained at 205°. The reactants dissolved completely, but within a short period an insoluble colorless solid had formed, and in 6 min. the contents of the flask formed a rigid immobile gel. After the initial 20 min. of heating the reaction mixture became a mobile suspension, containing a light tan granular solid. After 2 hr. the system was evacuated for the removal of quinoline and imidazole. Over a period of 3.75 hr. the temperature of the oil bath was raised to 293°. The weight of the granular, very light tan product was 8.56 g. (97.2%).

Anal. Calcd. for $C_{18}H_{14}N_2O_2P_2$: C, 61.37; H, 4.01; N, 7.95; P, 17.59. Found: C, 58.42; H, 4.64; N, 8.16; P, 15.19.

In view of the low decomposition temperature of the polymer, the discrepancy in analytical values is attributed to slow thermal decomposition, especially during the later stages of heating.

The X-ray diffraction pattern indicated three-dimensional ordering in the polymeric product and preferential crystal growth in one direction. The three strongest lines correspond to interplanar spacings of 6.21, 8.6, and 5.07 Å.

Polymer from DIPPO and 2,6-Diaminopyridine (VII).—DIPPO (12.91 g. 0.05 mole), 2,6-diaminopyridine (2.73 g., 0.025 mole), and quinoline (20.1 g.) were transferred into the polymerization vessel in a drybox. The reaction was conducted in a nitrogen atmosphere. The flask was immersed in an oil bath maintained at 140°. Within 30 min. the temperature was raised to 230°. Formation of a light tan suspended solid was observed. During the following 1.5 hr. the reaction temperature was raised to 267°. The solid disappeared and the reaction mixture was converted to a viscous red solution. The solvent and imidazole were removed by evacuation at temperatures ranging to 305°. The yield was quantitative.

Anal. Calcd. for $C_{17}H_{11}N_3O_2P_2$: C, 57.80; H, 3.71; N, 11.90; P, 17.54. Found: C, 57.68; H, 3.86; N, 11.79; P, 17.36.

Acknowledgments.—Financial support of this work by AF Materials Laboratory, Research and Technology Division, Air Force Systems Command, under Contract No. AF 33(616)-7853, is gratefully acknowledged. For instrumental analytical services we are indebted to D. Q. Douglas, R. R. Ferguson, C. Fritsch, and M. J. Ross.