this effect does not occur in III, it is apparent that the lack of a coordinate link of the tartrate to the metal ion results in the rotatory dispersion being similar to that of the free tartrate ion. Figures 1 and 2 indicate no observable interaction between the tartrate and the chromophoric center of III.

Optical rotatory dispersion has therefore indicated the noncoordination of a colorless (visible region) optically active coordinating agent in a system containing a colored complex. Further, there is a noticeable decrease in the rotational strength of the optical rotatory dispersion when the bidentate ligand becomes monodentate (Fig. 1), indicating that optical rotatory dispersion may also be a technique which can be utilized to differentiate between monodentate and polydentate character of optically active ligands. Similar studies on other systems are now in progress with a view toward testing this observation.

Acknowledgment.—The authors wish to express their sincere appreciation to the National Science Foundation for a fellowship grant (NSF-G34816) which contributed significantly to the progress of this investigation.

CONTRIBUTION FROM PENNSALT CHEMICALS CORPORATION,
TECHNOLOGICAL CENTER, KING OF PRUSSIA, PENNSYLVANIA

Polymeric Zinc Derivatives of Simple Bis-Chelating Agents

BY SELWYN H. ROSE, B. P. BLOCK, AND J. E. DAVIS

Received March 16, 1964

Infrared end-group analysis indicates a degree of polymerization of at least 20 for a zinc derivative of dithiooxamide prepared by the interfacial polymerization reaction of zinc acetate with dithiooxamide. The degrees of polymerization of zinc derivatives of 2,5-dihydroxy-*p*-benzoquinone prepared by two-stage reactions from diethylzinc and 2,5-dihydroxy-*p*-benzoquinone are estimated to be 4 and 27 by chemical end-group analysis. The conditions of the second step, the heating of the intermediate $C_2H_5ZnO_2C_6H_2O_2H$, determine the degree of polymerization.

Although considerable effort has been devoted to the synthesis of coordination polymers involving bis-chelating agents,[1] their characterization as polymers has not developed apace. This is undoubtedly due to the insolubility and intractability of most of the products. Typically these materials have been formulated as polymers from steric considerations and assigned a degree of polymerization on the basis of elemental analysis. Recently there have been attempts to estimate the degree of polymerization of some coordination polymers based on simple bis-chelating agents by other techniques.[2-6] We wish to record here the results of our efforts in this direction. We selected for study the one-to-one zinc derivatives of 2,5-dihydroxy-*p*-benzoquinone ($H_2C_6H_2O_4$) and dithiooxamide ($H_2C_2H_2N_2S_2$). $ZnC_6H_2O_4$ is a novel composition. Although $ZnC_2H_2N_2S_2$ has since been reported,[7] no attempt was made to measure its degree of polymerization.

Experimental

(A) **Apparatus.**—The reactions involving $(C_2H_5)_2Zn$ were carried out by standard manipulative techniques in a high vacuum apparatus. Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer.

(B) **Reactants.**—With the following exceptions all chemicals and solvents were reagent grade and were not further purified.

(1) A sample of $H_2C_2H_2N_2S_2$ supplied by Mallinckrodt Chemical Works was used without further purification. *Anal.* Calcd. for $C_2H_4N_2S_2$: C, 20.0; H, 3.3; N, 23.3. Found: C, 20.0; H, 3.4; N, 23.1.

(2) Technical grade $H_2C_6H_2O_4$ was purified by vacuum sublimation. *Anal.* Calcd. for $C_6H_4O_4$: C, 51.5; H, 2.8. Found: C, 51.7; H, 3.0.

(3) Commercial $(C_2H_5)_2Zn$ was purified by fractional distillation in the vacuum apparatus. Its vapor-phase infrared spectrum (bands observed at 2933–2882 (vs), 2809 (sh), 2740 (sh), 1468 (m), 1418 (m), 1379 (m), 1185 (m), 985 (s), and 949 (m) cm.$^{-1}$) correlated well with the reported liquid-phase spectrum.[8] Attempts to determine the exact purity by vapor-phase chromatography were unsuccessful because we were unable to elute the $(C_2H_5)_2Zn$ from the columns tried. A combination of vapor-phase chromatography and mass spectroscopy, however, revealed that the major impurity, diethyl ether, was present in larger amounts than all the other impurities combined. Comparison of the vapor-phase infrared spectrum of the sample with that of a low-pressure standard sample of diethyl ether indicated that the diethyl ether impurity (as represented by a very small peak in the 9.7 μ region) was approximately 0.2 mole % of the $(C_2H_5)_2Zn$ sample. The purity of the $(C_2H_5)_2Zn$ was therefore in excess of 99.5 mole %.

(C) **Reactions.** (1) **Preparation of $ZnC_2H_2N_2S_2$.**—A solution of 25 mmoles of $Zn(C_2H_3O_2)_2\cdot 2H_2O$ in 50 ml. of water was added to a suspension of 25 mmoles of $H_2C_2H_2N_2S_2$ in 300 ml. of benzene in a Waring blendor. The mixture was agitated for 15 min. and then filtered. The precipitate, a pale yellow solid, weighed 3.2 g.

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[1] Much of this work has been reviewed recently. See, for example, J. C. Bailar, Jr., "Inorganic Polymers," Special Publication No. 15, The Chemical Society, London, 1961, p. 51; B. P. Block, Chapter 8 in "Inorganic Polymers," F. G. A. Stone and W. A. G. Graham, Ed., Academic Press, New York, N. Y., 1962; I. Haiduc, *Russ. Chem. Rev.*, **30**, 498 (1961); or C. N. Kenney, Chapter 9 in "Developments in Inorganic Polymer Chemistry," M. F. Lappert and G. J. Leigh, Ed., Elsevier Publishing Company, New York, N. Y., 1962.

[2] F. W. Knobloch, Ph.D. Dissertation, Rensselaer Polytechnic Institute, 1959.

[3] D. N. Chakravarty and W. C. Drinkard, Jr., *J. Indian Chem. Soc.*, **37**, 517 (1960).

[4] R. N. Hurd, G. DeLaMater, G. C. McElheny, and L. V. Peiffer, *J. Am. Chem. Soc.*, **82**, 4454 (1960).

[5] S. Kanda, *Nippon Kagaku Zasshi*, **81**, 1347 (1960), from *Chem. Abstr.*, **55**, 2294*e* (1961).

[6] S. Kanda, *Nippon Kagaku Zasshi*, **83**, 282, 560 (1962), from *Chem. Abstr.*, **58**, 13,404*gf* (1963).

[7] V. N. Odnoralova and G. I. Kudryavtsev, *Vysokomolekul. Soedin.*, **4**, 1314 (1962).

[8] H. D. Kaesz and F. G. A. Stone, *Spectrochim. Acta*, **14**, 360 (1959).

after extensive washing with 95% ethanol and overnight drying in a vacuum desiccator. The product failed to melt before decomposition and was insoluble in water and a wide range of common polar and nonpolar organic solvents. *Anal.* Calcd. for $C_2H_2N_2S_2Zn$: C, 13.1; H, 1.1; N, 15.3; S, 34.9; Zn, 35.6. Found: C, 13.2; H, 1.2; N, 15.0; S, 34.9; Zn, 34.8. Infrared absorption bands of a Nujol mull: 3236 (s); 1524–1504 (vs), 1332 (s), 1300 (s), 1033 (m), 936 (m), 841 (vs), 828 (sh), and 792 (s) cm.$^{-1}$.

(2) **Preparation of $ZnC_6H_2O_4\cdot 2H_2O$.**—To a mixture of 10 mmoles of $H_2C_6H_2O_4$ and 200 ml. of acetone in a Waring blendor was added 10 mmoles of $Zn(C_2H_3O_2)_2\cdot 2H_2O$. The mixture was stirred for 1 hr. and then filtered to yield a pinkish purple solid. The solid was washed with acetone and water and then dried in a vacuum desiccator for several hours. This product also failed to melt before decomposition and was insoluble in water and common polar and nonpolar organic solvents. *Anal.* Calcd. for $C_6H_6O_6Zn$: C, 30.1; H, 2.5; Zn, 27.3. Found[9]: C, 29.5; H, 2.9; Zn, 26.3. Infrared absorption bands of a Nujol mull: 3333 (m); 1538 (vs), 1266 (s), 816 (m), and 767 (m) cm.$^{-1}$.

(3) **Preparation of $ZnC_6H_2O_4$. (a) Dehydration of $ZnC_6H_2O_4\cdot 2H_2O$.**—A sample of $ZnC_6H_2O_4\cdot 2H_2O$ was dried in an Abderhalden over P_2O_5 for 5 hr. at 139° to yield a brown solid. The solid was stored and analyzed under anhydrous conditions. *Anal.* Calcd. for $C_6H_2O_4Zn$: C, 35.4; Zn, 32.2. Found: C, 35.2; Zn, 31.7. On exposure to the atmosphere, the anhydrous brown solid gradually turns into the pinkish purple dihydrate.

(b) **The Reaction of $(C_2H_5)_2Zn$ with $H_2C_6H_2O_4$.**—To a reaction tube on the vacuum apparatus containing a rigorously anhydrous mixture of 7.64 mmoles of $H_2C_6H_2O_4$ and 20 ml. of diethyl ether frozen to −196° was added 7.81 mmoles of $(C_2H_5)_2Zn$. The $(C_2H_5)_2Zn$ was measured as a liquid (d_{20} 1.205[10]) in a graduated tube and then distilled into the reaction vessel. The mixture was allowed to warm to 0° and then was stirred by means of an electromagnetic spiral type stirrer until no additional ethane evolution was evident. The ethane was separated from the reaction mixture by fractional distillation and measured as a gas at room temperature in a calibrated volume connected to a mercury manometer. Calcd. for reaction of one acid H per $H_2C_6H_2O_4$: 7.64 mmoles. Found: 7.60 mmoles.

The mixture was then allowed to react at room temperature for a total of 25 hr. The evolved ethane was removed periodically, and the reaction ultimately produced a total of 13.48 mmoles of ethane (vapor pressure at −111.6° 178 mm.; calculated 180 mm.[11]). The reaction mixture was then filtered through a fritted disk by rotation of the filtration apparatus to which the reaction tube was attached; a brown solid and a colorless solution resulted. The colorless nature of the solution indicated that essentially all of the $H_2C_6H_2O_4$ had reacted since even a very dilute solution would be a pale yellow. The amount of unreacted $(C_2H_5)_2Zn$ in the filtrate was determined to be 0.19 mmole by hydrolysis and subsequent measurement of the resulting ethane. The brown solid was analyzed, under water- and oxygen-free conditions, for carbon and for ethyl end groups (by measurement of ethane evolution on hydrolysis with dilute sulfuric acid). *Anal.* Calcd. for $C_2H_5(ZnC_6H_2O_4)_4H$: C, 37.0; 1.2 mmoles of C_2H_6/g. Found: C, 37.2; 1.3 mmoles of C_2H_6/g.

In a similar preparation the brown solid was heated at 145° for 2.5 hr. The polymerization proceeded further as shown by the production of more ethane (identified by its mass spectrum). An ethyl-end-group analysis of 0.18 mmole/g. indicates that the degree of polymerization is approximately 27. *Anal.* Calcd. for $C_2H_5(ZnC_6H_2O_4)_{\sim 27}H$: C, 35.7; Zn, 32.0. Found: C, 35.6; Zn, 30.8.

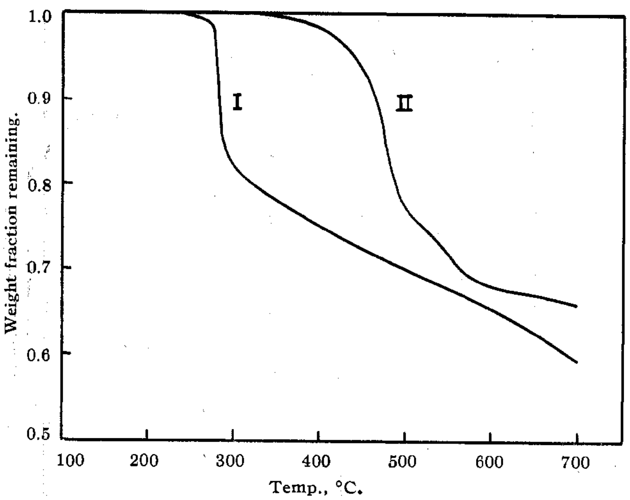


Fig. 1.—TGA of $ZnC_2H_2N_2S_2$, curve I, and $ZnC_6H_2O_4$, curve II, in nitrogen; heating rate 5°/min.

Hydrolysis of the brown solid with distilled water and subsequent vacuum drying yielded $ZnC_6H_2O_4\cdot 2H_2O$. *Anal.* Calcd. for $C_6H_6O_6Zn$: C, 30.1; H, 2.5; Zn, 27.3. Found: C, 29.4; H, 3.3; Zn, 27.0.

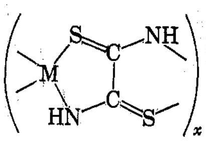
An attempt, in a separate experiment, to drive the polymerization even further by prolonged heating at 275° resulted in decomposition of the brown solid.

One $(C_2H_5)_2Zn$–$H_2C_6H_2O_4$ reaction was terminated when the ratio of C_2H_6 evolved to $H_2C_6H_2O_4$ used was 1.51:1. The reaction mixture was removed from the vacuum system, filtered, and washed with diethyl ether. *Anal.* Calcd. for $C_{12}H_8O_{10}Zn_2$: C, 32.5; H, 1.8; Zn, 29.5. Found: C, 32.5; H, 3.0; Zn, 28.4.

(D) **Thermogravimetric Analysis.**—Both $ZnC_2H_2N_2S_2$ and $ZnC_6H_2O_4$ were subjected to our usual thermogravimetric analysis procedure on a modified Chevenard thermobalance[12] in a nitrogen atmosphere at a heating rate of 5°/min. The resulting weight–temperature relationships are shown in Fig. 1.

Discussion

Bivalent metal derivatives of $H_2C_2H_2N_2S_2$ have been considered to be polymeric since Jensen suggested that the $C_2H_2N_2S_2^{2-}$ ion could not act as a quadridentate ligand but must instead be a bridging group.[13] Currently the bonding is believed to be as shown in I.[14]



I

Since the composition of our zinc derivative, prepared by an interfacial reaction between $Zn(C_2H_3O_2)_2\cdot 2H_2O$ in water and $H_2C_2H_2N_2S_2$ in benzene, corresponds quite well to $ZnC_2H_2N_2S_2$, the degree of polymerization is high enough to be undeterminable by elemental analysis. It is interesting to note that attempts to prepare the compound by the same procedure used by Hurd, *et al.*, to prepare analogous nickel compounds[4] yielded poorly defined products. Conventional techniques for the direct determination of molecular weight could not be used because $ZnC_2H_2N_2S_2$ is insoluble and infusible.

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[9] The purity of the material leaves something to be desired because of the difficulty of removing adsorbed water without removing coordinated water. R. S. Bottei and P. L. Gerace, *J. Inorg. Nucl. Chem.*, **23**, 245 (1961), have experienced similar difficulties with metal–naphthazarin hydrates.

[10] G. Jander and L. Fischer, *Z. Elektrochem.*, **62**, 965 (1958).

[11] R. R. Dreisbach, Advances in Chemistry Series, No. 22, American Chemical Society, Washington, D. C., 1959, p. 12.

[12] J. R. Soulen and I. Mockrin, *Anal. Chem.*, **33**, 1909 (1961).

[13] K. A. Jensen, *Z. anorg. allgem. Chem.*, **252**, 227 (1944).

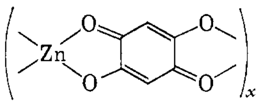
[14] J. R. Barceló, *Spectrochim. Acta*, **10**, 245 (1958).

Consequently we resorted to end-group analysis in an attempt to determine the degree of polymerization.

The infrared spectrum of $ZnC_2H_2N_2S_2$ contains a band at 6.30 μ which has been assigned to a deformation mode of $-NH_2$,[15] but there is no indication of the presence of $C_2H_3O_2^-$ in the spectrum. In the spectrum of a reference mixture of $ZnC_2H_2N_2S_2$ containing 4.6 mole % $H_2C_2H_2N_2S_2$ (9.2 mole % $-NH_2$ groups), the band at 6.30 μ was over three times as large. Correction for the background contribution from the $-NH_2$ end groups in $ZnC_2H_2N_2S_2$ leads to the conclusion that the concentration of polymer end groups is about one-half the concentration of $-NH_2$ groups added *via* the $H_2C_2H_2N_2S_2$, *i.e.*, about 4.6 mole %. A band at 6.40 μ, which has been assigned to the $C_2H_3O_2^-$ group, was observed in a reference mixture of $ZnC_2H_2N_2S_2$ containing 3.8 mole % $Zn(C_2H_3O_2)_2 \cdot 2H_2O$, but not in the $ZnC_2H_2N_2S_2$. The concentration of $C_2H_3O_2^-$ end groups in the $ZnC_2H_2N_2S_2$ in thus less than half the concentration of $C_2H_3O_2^-$ groups from the added $Zn(C_2H_3O_2)_2 \cdot 2H_2O$, for a peak one-third as large as that observed in the reference mixture would be clearly visible.

If we assume that $ZnC_2H_2N_2S_2$ is a linear polymer as shown in I with one H end group and one $C_2H_3O_2^-$ end group, *i.e.*, $C_2H_3O_2(ZnC_2H_2N_2S_2)_xH$, the degree of polymerization exceeds 20 units. On the other hand, it exceeds 40 if the end groups are H and $HC_2H_2N_2S_2$, *i.e.*, $HC_2H_2N_2S_2(ZnC_2H_2N_2S_2)_xH$.

There seems to be little doubt that the coordination number of the metal in the $MC_2H_2N_2S_2$ polymers is four. Although it has been suggested that zinc may have a coordination number of six in systems closely related to $ZnC_6H_2O_4 \cdot 2H_2O$,[16] we believe that zinc has a coordination number of four in its $H_2C_6H_2O_4$ derivatives and will develop this thesis later. Consequently we consider that the $ZnC_6H_2O_4$ polymers have structure II with appropriate end groups. Others have suggested an analogous structure for various $MC_6H_2O_4$ derivatives.[17] Like $ZnC_2H_2N_2S_2$, $ZnC_6H_2O_4$ is intractable, but its infrared spectrum is not as amenable to end-group study so we had to use a different technique to estimate its molecular weight. Kanda has been quite active in trying to determine the degree of polymerization of other $MC_6H_2O_4$ polymers, in particular $CuC_6H_2O_4$. He has employed light scattering by the solid,[5] X-ray and electron diffraction,[6] and magnetic susceptibility[18] and concludes that $CuC_6H_2O_4$ polymer chains contain at least nine copper atoms. Our approach differs from his in that we have studied the extent of the reaction between $(C_2H_5)_2Zn$ and $H_2C_6H_2O_4$ *via* ethane evolution and measured the number of ethyl end groups chemically.

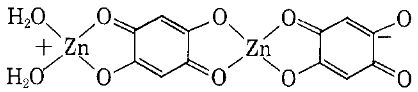


II

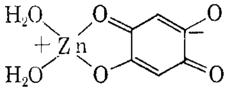
Under suitable conditions $(C_2H_5)_2Zn$ reacts with $H_2C_6H_2O_4$ in stepwise fashion. Thus at 0° only one mole of ethane was collected per mole of the $(C_2H_5)_2Zn-H_2C_6H_2O_4$ mixture. This indicates that at 0° the reaction is $(C_2H_5)_2Zn + H_2C_6H_2O_4 \rightarrow C_2H_5ZnC_6H_2O_4H + C_2H_6$. At higher temperatures more ethane is evolved, presumably from the conversion of $C_2H_5ZnC_6H_2O_4H$ to $C_2H_5(ZnC_6H_2O_4)_xH$. At room temperature reaction appears to cease when x is about 4, whereas at 145° x reaches 27. Decomposition occurs at 275°. In the reactions at room temperature, and at 145°, the quantity of ethane produced by hydrolysis of the polymers and the carbon content of the polymers correspond to the degrees of polymerization given.

The amount of ethane collected during the room-temperature polymerization corresponds to the formation of $C_2H_5(ZnC_6H_2O_4)_{4.2}H$, in good agreement with the end-group and chemical analyses. The complete consumption of the $H_2C_6H_2O_4$ and the consumption of only sufficient $(C_2H_5)_2Zn$ for exact 1:1 stoichiometry also support a polymer of this type and strongly suggest one H end group for each C_2H_5 end group.

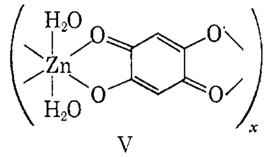
When the second stage of the $(C_2H_5)_2Zn-H_2C_6H_2O_4$ reaction at room temperature was stopped after the evolution of 1.51 moles of ethane per mole of $H_2C_6H_2O_4$, the product presumably was $C_2H_5(ZnC_6H_2O_4)_2H$. After exposure to the atmosphere the product gave an analysis corresponding approximately to $ZnC_6H_2O_4 \cdot H_2O$, which might reasonably be expected to have structure III (or its tautomer). It is difficult to formulate an octahedral configuration for the zinc. The infrared spectrum, including the far-infrared, of $ZnC_6H_2O_4 \cdot H_2O$ was identical with that of $ZnC_6H_2O_4 \cdot 2H_2O$. This similarity suggests the possibility that the dihydrate has the structure IV (or its tautomer), similar to III, and not the polymeric structure V. In this connection it seems possible that other dihydrates of this general class which have been assumed to be polymeric[16,19] might instead be monomeric.



III



IV



V

Treatment of the $x = 27$ product with water yielded $ZnC_6H_2O_4 \cdot 2H_2O$. Its infrared spectrum was identical with that of the $ZnC_6H_2O_4 \cdot 2H_2O$ prepared from $Zn(C_2H_3O_2)_2 \cdot 2H_2O$. It thus is likely that the same polymer is formed by both reaction routes.

$ZnC_6H_2O_4$ starts to lose weight at about 350° in our

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(15) T. A. Scott and E. L. Wagner, *J. Chem. Phys.*, **30**, 465 (1959).

(16) R. S. Bottei and P. L. Gerace, *J. Inorg. Nucl. Chem.*, **23**, 245 (1961).

(17) S. Kanda and Y. Saito, *Bull. Chem. Soc. Japan*, **30**, 192 (1957).

(18) S. Kanda, *Kogyo Kagaku Zasshi*, **66**, 641 (1963).

(19) R. H. Bailes and M. Calvin, *J. Am. Chem. Soc.*, **69**, 1886 (1947).

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.

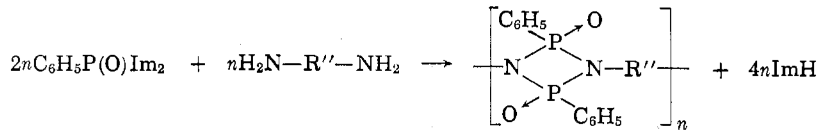
CONTRIBUTION FROM MONSANTO RESEARCH CORPORATION,
DAYTON LABORATORY, DAYTON 7, OHIO

Polymeric 1,3,2,4-Diazadiphosphetidine 2,4-Dioxide Compounds

BY L. PARTS, MORRIS L. NIELSEN, AND JOHN T. MILLER, JR.

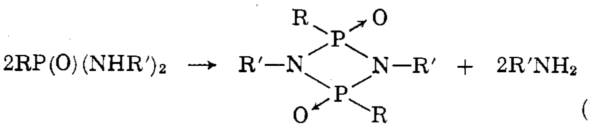
Received February 7, 1964

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.

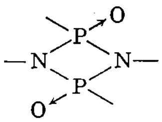
The work of Otto[1] and Michaelis and co-workers[2,3] established that phosphorus amides derived from primary aromatic amines decompose at rather low temperatures (~200°). Furthermore, it was demonstrated[3] that the decomposition can be represented as a specific condensation reaction.



(1)

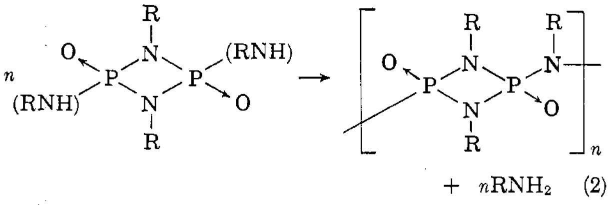
Their experimental description indicated that the 1,3,2,4-diazadiphosphetidine 2,4-dioxide (DAPO)[4] derivatives are thermally very stable compounds.

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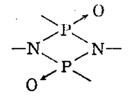
[1] P. Otto, *Ber.*, **28**, 616 (1895).

[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).