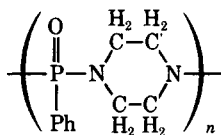


## Inorganic Polymers. IV. Reactions of Poly(P-phenylphosphonic Imide). The Replacement Polymerization of Poly(P-phenylphosphonic Imide) with Piperazine

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### Synopsis

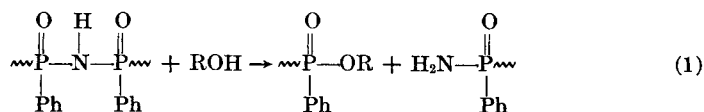
Poly(P-phenylphosphonic imide) reacts with a variety of compounds containing reactive hydrogen atoms, due to the instability of the —P—N—P— linkage to such reagents. Utilization of this property of the polymer may provide convenient routes to prepare various types of P-phenylphosphonic diamides,  $\text{Ph(O)P(NH}_2\text{)(NR}'_2\text{)}$ , phosphonamidates,  $\text{PhP(O)(NH}_2\text{)(OR)}$ , etc. ( $\text{R} = \text{H, alkyl, aryl, etc.}$ ). The reaction of the polyimide with piperazine results in a polymer containing



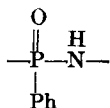
structural units. The polymer thus obtained is however only partially soluble in the usual organic solvents, and this insolubility is probably due to crosslinking catalyzed by piperazine. The product polymer was found to be thermoplastic.

### INTRODUCTION

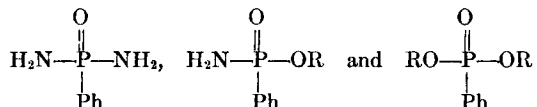
Poly(P-phenylphosphonic imide) reacts with various compounds, in particular with those containing reactive hydrogen atoms, such as acids, alcohols, amines, etc.<sup>1,2</sup> This reactivity indicates that the unmodified polymer itself may be of only limited practical use, but that it may provide a starting material of considerable interest whose behavior may be characteristic for polymers of this type. Thus, the reaction of the polymer with an alcohol would be expected to lead initially by means of chain scission to an ester and an amide grouping:



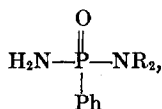
Assuming the polymer to possess an unbranched linear or cyclic structure consisting of



units, and that complete degradation to monomeric units occurs, one might expect a priori the following three compounds as the reaction products:

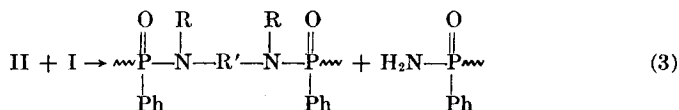
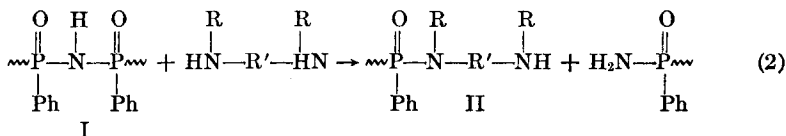


In reactions with amines, e.g.,  $\text{NHR}_2$ , unsymmetric P-phenylphosphonic diamides,

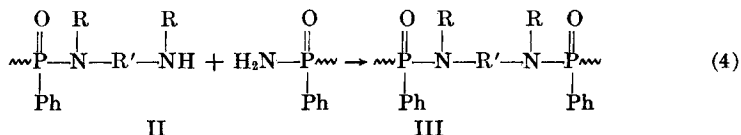


might be obtained.

The reactions of the polymer with bifunctional reagents such as diamines, dialcohols, etc., are of particular interest. With a diamine, for example, the following reactions are expected to occur, it being assumed that the imide linkage is more susceptible to nucleophilic attack than the amide linkage:



Under conditions where the amide groups formed can condense with the evolution of ammonia with the amines II, polymer I can be converted to polymer III:



A polymer of type III, with a N.A.D.P. of 5-20, has been reported by Nielsen and co-workers<sup>3</sup> who prepared it by the reaction of dichlorophenylphosphine oxide with diamines.

In this paper, the results of preliminary experiments on the reactions of poly(P-phenylphosphonic imide) with reagents containing reactive hydrogen atoms are described. Detailed investigations will be published later.

## EXPERIMENTAL

### Preparation of Poly(P-phenylphosphonic Imide)

P-Phenylphosphonic diamide, prepared by the reaction of dichlorophenylphosphine oxide with ammonia,<sup>2</sup> was polymerized at 240°C for 30 min under vacuum. The number-average molecular weight of the polymer thus obtained and used in our studies was in the range of 2500–2700.

### Reaction of the Polymer with Isopropyl Alcohol

The polymer, 2–3 g, was dissolved in isopropyl alcohol and the solution was refluxed for ten days.

### Reaction of the Polymer with Diethylamine

Anhydrous diethylamine was distilled from barium oxide before use. Benzene was dried over sodium before use. Reactions were carried out both in benzene with a 1:1 molar ratio of diethylamine to polymer unit and in an excess of diethylamine, by refluxing the solutions for 7–10 days.

### Reaction with Piperazine

Anhydrous piperazine was purified by sublimation before use. The reaction was carried out in benzene solution or, in the absence of a solvent, either in sealed tubes or under an atmosphere of nitrogen.

**In Benzene Solution.** The polymer, 2 g, and a 3–4 times molar excess of piperazine were dissolved in 250 ml of dry benzene and the mixture was refluxed for eight days. The benzene was then distilled off and unreacted piperazine was sublimed out at 100°C under vacuum.

**In Sealed Tubes.** The reaction was carried out in sealed Pyrex glass tubes (1 cm inner diameter and 7–8 cm long) sealed under vacuum with various molar ratios of the polymer to piperazine. The tubes were then heated at 200°C for 100 hr.

**Under Nitrogen Atmosphere.** The polymer, 5–10 g, was placed together with varying amounts of piperazine in the reaction vessel which was fitted with a stirrer. Nitrogen gas was passed into the vessel. The reactions were carried out initially for 2 hr at 140°–150°C to dissolve the polymer in the molten piperazine. When a transparent, viscous, homogeneous liquid had been obtained, the temperature was slowly raised to 240°C and kept at this temperature with stirring for varying lengths of time. After the reaction the products were ground to a powder and washed thoroughly with absolute ethanol to extract unreacted piperazine and the alcohol-

soluble fraction of the product. The ammonia eliminated was passed into dilute hydrochloric acid and was determined by titration.

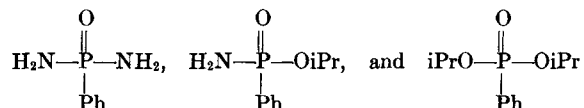
### Molecular Weight Measurements

The number-average molecular weights of the soluble products were determined using a Mechrolab vapor pressure osmometer, Model 301 A, at 65°C with 1,2-dichloroethane or absolute ethanol as solvent.

## RESULTS AND DISCUSSION

### Reactions of Poly(P-phenylphosphonic Imide) with Monofunctional Reagents

**Reaction with Isopropyl Alcohol.** If the reaction, shown by eq. (1), is complete, the following three reaction products may be expected to be formed:



In the present work a crystalline compound of mp 205°C and molecular weight 200 (shown to be pure by thin-layer chromatography) was obtained in about 30% yield. Its infrared spectrum was in keeping with that of an isopropyl P-phenylphosphonamidate, but an elemental analysis has not yet been obtained. The remaining 70% of the product consisted of a viscous, colorless material whose average molecular weight was 570. It is likely that this viscous material is a mixture of oligomers with a N.A.D.P. of 4-5 and it is likely that further degradation to the above-mentioned crystalline compound and/or other monomeric species may be attained with longer reaction times.

Further work is in progress to determine whether the unsymmetric compound is the only product when the reaction goes to completion.

**Reaction with Diethylamine.** The product obtained from the reaction of the polymer with diethylamine was very different from that with isopropyl alcohol. No crystalline compound was observed; instead, a soft resin-like material soluble in most organic solvents was obtained. The molecular weights of these products were found to be in the range of 1000-1100, apparently independent of the concentration of diethylamine used in this work. The reaction seemed to be very slow compared to those involving isopropyl alcohol, ammonia,<sup>2</sup> and water.<sup>2</sup> It may nevertheless be possible to obtain various unsymmetric phosphonic diamides by this route.

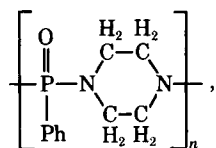
### Reaction of Polymer with Bifunctional Reagents

The product obtained by the reaction of the polymer with a large excess of piperazine in benzene solution had a number-average molecular weight

of 400–500. More than 50% of the piperazine required for the complete reaction, i.e., the replacement of every —P—N—P— unit by a —P—N—R'—N—P— unit, was found to be consumed.

The products from the sealed-tube reactions were all only partially soluble in most organic solvents, and hence their molecular weights could not be measured. The products were very hard amber-colored resins with softening points of about 250°C. Ammonia as well as small amounts of phosphine were detected when the sealed tubes were opened. The latter suggests that some decomposition of the polymer takes place on heating with piperazine at temperatures above 200°C. Although undoubtedly some crosslinking of the polymer occurred, thus decreasing its solubility considerably, it was nevertheless still thermoplastic.

The amounts of ammonia eliminated from the reaction under an atmosphere of nitrogen were determined by titration. In most cases, 75%–85% of the theoretical amount of ammonia (cf. above) was eliminated. It seems therefore likely that the recondensation reaction, eq. (4), is of considerable importance leading to structural units of the type



but there is also some evidence that the amine acts also as a catalyst in the crosslinking reaction. The products thus obtained were washed with absolute ethanol to remove excess piperazine and to extract the ethanol-soluble polymer fraction whose number-average molecular weight was in the range of 400–500.

The ethanol-insoluble white resinous powder which remained had a softening point of about 220°C but did not melt below 300°C, while a polymer sample prepared from dichlorophenylphosphine oxide and piperazine had softening and melting points of about 200°C and 220°C, respectively. The latter polymer was completely soluble in the usual organic solvents and had a number-average molecular weight of 1300–1400. The infrared spectra of these piperazine polymers were all very similar, regardless of their method of preparation.

The reaction of poly(P-phenylphosphonic imide) with hexamethylene diamine gave a polymer similar to that obtained with piperazine. With *p*-phenylenediamine, a violet-black product indicating considerable decomposition was obtained.

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