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Studies on Phosphorus-Containing Polymers. VI. Synthesis of Derivatives of Linear Phosphonitrile Chloride and Their Stability

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Studies on Phosphorus-Containing Polymers. VI. Synthesis of Derivatives of Linear Phosponitrile Chloride and Their Stability

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ABSTRACT

The synthesis of LPNC and its derivatives and the hydrolysis and heat resistance properties of these materials are discussed. Lack of stability to water and depolymerization are adverse properties of many inorganic polymers. In the case of LPNC, it was found that these properties were probably due to the terminal ionic structure, and when the ionic part is removed from LPNC, the properties could be somewhat improved.

INTRODUCTION

Applications of phosphonitrilic chloride (PNC) investigated until now chiefly have relied primarily on its heat and flame resistances. The material, however, has a disadvantage in that it tends to be

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hydrolyzed. In order to overcome this disadvantage, various syntheses of PNC derivatives have been studied [1-3]. If organic groups are substituted for all of the chlorines, the hydrolysis resistance increases, but then the heat resistance decreases. In the present study we have considered the possibility of synthesizing derivatives having both heat resistance and hydrolytic stability, in view of the fact that chlorines in the main chain are less reactive than the terminal chlorine toward nucleophilic reagents. In this study, linear phosphonitrilic chloride (LPNC) was treated with selected nucleophilic reagents, such as aniline and phenol, to synthesize derivatives in which the chain end did not show ionic behavior, and their heat resistance and hydrolytic stability were investigated in comparison with those of untreated LPNC.

EXPERIMENTAL

Reagents

Linear PNC was prepared as described elsewhere [4]. Phosphorus pentachloride (30 g) was treated with 6.2 g of ammonium chloride ($\text{PCl}_5/\text{NH}_4\text{Cl} = 5/4$) in a mixed solvent of nitrobenzene and sym-tetra-chloroethane (1:1) at 130°C for 4 hr. After the reaction was over, the reaction mixture was poured into petroleum ether. The precipitate was dissolved in chloroform and reprecipitated with petroleum ether. After washing the precipitate with benzene, a white powder was obtained. See Ref. 4 for analytical data on the product.

Aniline was a commercial preparation to which was added powdered zinc. After refluxing in the mixture for a few hours, the aniline was distilled off under reduced pressure in dry nitrogen atmosphere.

A commercial preparation of phenol was distilled in a dry nitrogen atmosphere under reduced pressure before use.

Metallic sodium was a commercial preparation used as received.

Conversion of LPNC

LPNC was placed in a four-necked flask fitted with a stirrer, a reflux condenser, and a N_2 introducing tube. The flask was heated in an oil bath at 255°C under dry nitrogen stream. After a fixed time (between 30 min and 12 hr), the reaction mixture was removed. The volatile component (phosphorus pentachloride) was completely removed in vacuo. The mixture was then allowed to stand in petroleum ether for one day, and the precipitate dried in vacuo.

Reaction of the Converted LPNC with Aniline

One mole of the converted LPNC is treated with a slight excess of 2 moles of aniline to obtain a partially substituted derivative. Thus,

in 50 ml of chloroform, 2.0 g (2.2×10^{-3} mole) of the converted LPNC is allowed to react with a slight excess of 0.38 g (4.4×10^{-3} mole) of aniline at 20°C for 3 hr under dry nitrogen gas flow. The by-product, anilinium chloride, is removed by filtration. The solvent is evaporated off from filtrate and residue is dried in vacuo.

In order to obtain a fully substituted derivative, one part (by molar proportion) (5 g = 0.043 unit mole) of LPNC is allowed to react with 5 parts (20 g = 0.23 mole) in benzene at 20°C. After 3 hr the reaction solution is washed with diluted solution of hydrochloric acid to remove the unreacted aniline and anilinium chloride by-product. The benzene solution is further washed several times with water, then benzene is evaporated off, and the residue is dried in vacuo.

Reaction of the Converted LPNC with Phenol

The converted LPNC is treated with sodium phenolate in dry benzene under dry nitrogen atmosphere as follows. To a slight excess of the equivalent of sodium is added an excess amount of phenol. The reaction is continued in boiling benzene until the sodium pieces are completely dissolved. Subsequently the supernatant layer of benzene is removed. The sodium phenolate is washed with fresh benzene to remove unreacted phenol as completely as possible. Then a solution of 2.0 g (2.20×10^{-3} mole) of the converted LPNC in 50 ml of benzene is added to the sodium phenolate. Reaction is carried out at 20°C for 4 hr in dry N₂ atmosphere. The by-product sodium chloride is removed from the reaction mixture by filtration. Benzene is removed by evaporation, and the product is dried at 80°C in vacuo. Synthesis of the fully substituted derivative carried out by treating one part of LPNC with 3 parts of sodium phenolate. The reaction conditions are the same as in the partial substitution. After the termination of the reaction, the reaction mixture is washed to remove the by-product sodium chloride and unreacted phenolate. After removing benzene by evaporation, the product is dried in vacuo.

Hydrolysis of the Derivatives

The starting materials (terminal anion-unconverted and -converted LPNC) and their various derivatives obtained according to the methods described above are compared for the weight change caused by slow hydrolysis due to moisture in the air. A fixed amount (100 mg) of a sample is placed in a sampling bottle. The bottle is allowed to stand in a closed chamber which is maintained at $23 \pm 2^\circ\text{C}$ and 80% RH. After a given time, the bottle is taken out and after vacuum drying at 80-100°C, weighed. Then the rate of weight loss is calculated. Also, the hydrolyzed samples are analyzed by infrared absorption spectroscopy to investigate the structural change.

Thermal Analysis of the Derivatives

For investigation of thermal properties of the various derivatives, thermogravimetric and differential thermal analyses are carried out by an automatic-recording differential thermobalance: Thus, 250 mg of the samples are heated at a rising temperature of $5^{\circ}\text{C}/\text{min}$ in air atmosphere.

RESULTS AND DISCUSSION

NMR Spectrum of LPNC

The structure of LPNC synthesized according to the method described [4] was investigated by infrared absorption and NMR spectroscopy. The infrared absorption spectrum has absorptions at around 1250 and 760 cm^{-1} , which are appropriate for the stretching vibration of LPNC [5]. The NMR absorption spectrum shown in Fig. 1 has three peaks. The groups of absorption in the vicinities of -1.5 , 10 , and 300 ppm can be associated with the terminal phosphorus atom, the phosphorus atom in the main chain, and the counteranion PCl_6^- respectively [6]. From the area ratios of these peaks, the average degree

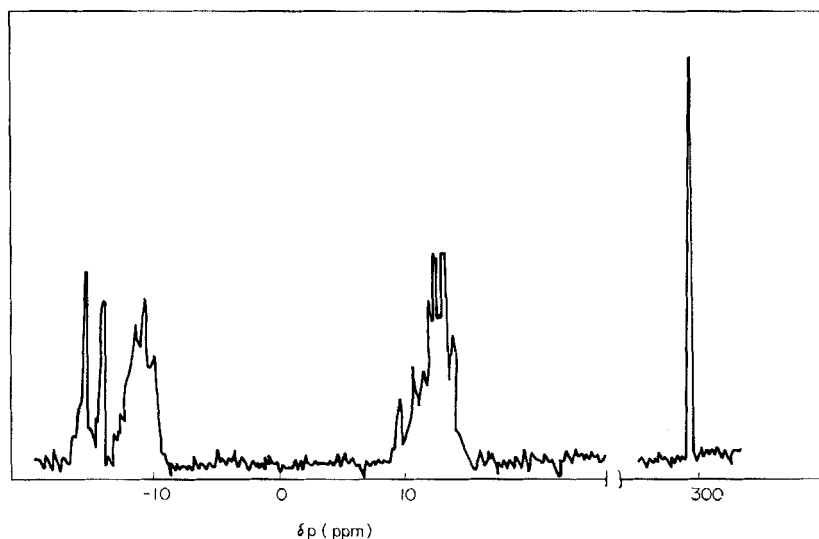
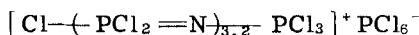


FIG. 1. ^{31}P -NMR spectrum of linear phosphonitrilic chloride obtained with phosphorus pentachloride and ammonium chloride.

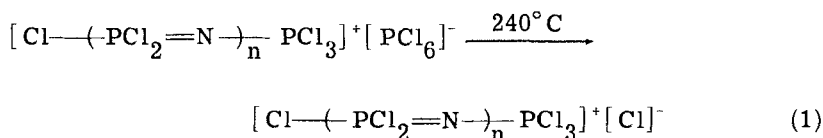
of polymerization (n) is determined to be 3.2. The structure of LPNC is, therefore, described as follows:



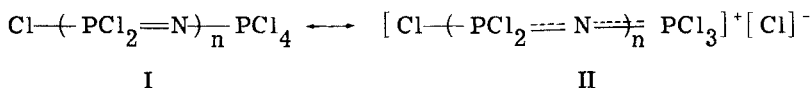
This structure is also supported by the results of phosphorus analysis (P content = 20.7%).

Counteranion Conversion of LPNC

If LPNC is heated to above 240°C, its counteranion changes to chlorine ion:



This structural change of LPNC was investigated by ^{31}P -NMR spectroscopy. The spectra are given in Fig. 2. The absorption at 300 ppm is still seen after 30 min heating. After 2 hr heating, this peak disappears, and only the absorptions at 2.8-5.5 ppm and 18 ppm, which are due to the phosphorus atoms of the chain end and the main chain, respectively, remain. If PCl_6^- still remains, the NMR spectrum is similar to that of unconverted LPNC; while the completely converted LPNC gives a NMR spectrum in which the absorptions corresponding to the terminal and main-chain phosphorus atoms shift to considerably higher magnetic field. Two reasons may account for this fact: one is that the heating process produces thermal polymerization of LPNC and the dislocalization of positive electric charge on the terminal and main chain's phosphorus atoms become lower; the other is that the converted LPNC probably resonates between structures I and II.



It is conceivable that owing to such an un-ionized structure (I), the converted LPNC is higher in electron density on the phosphorus atom than the unconverted LPNC. It seems likely that the increase of the electron density on each phosphorus atom causes chemical shifts to higher magnetic fields according to the increasing shading effect.

Furthermore, comparison between the NMR spectra for 2 and 12 hr reaction shown in Fig. 2 reveals that the peak area due to the

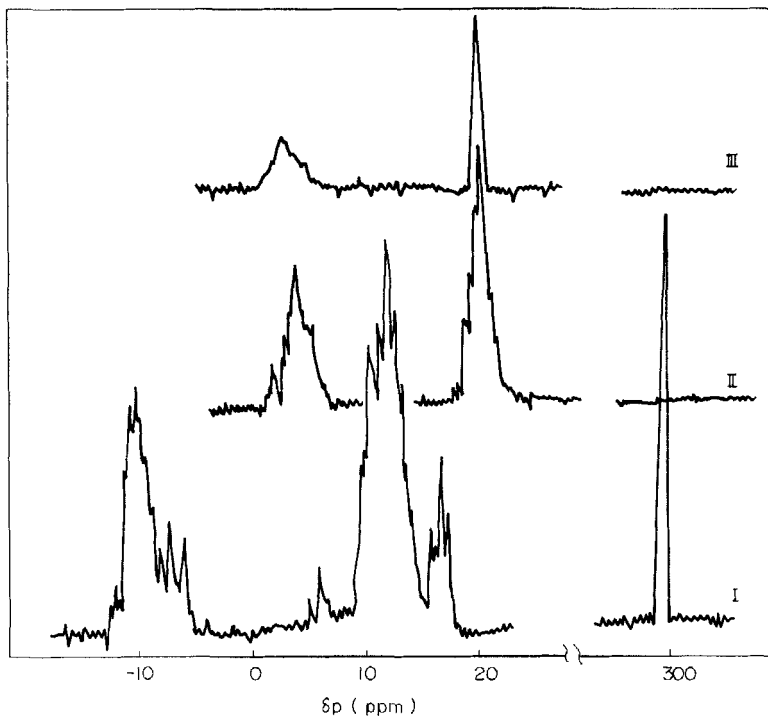


FIG. 2. ^{31}P -NMR spectra of linear phosphonitrilic chloride at various times: (I) after 0.5 hr; (II) after 2 hr; (III) after 12 hr.

phosphorus atoms of the main chain relatively increases. This fact suggests that the degree of polymerization of LPNC increases on heating. The temperature of the conversion is preferably $240\text{--}300^\circ\text{C}$ because a heat-polymerized polymer is known to depolymerize gradually at about 300°C and over. If heated for a long time, it is converted into an insoluble polymer, and so the period of heating is preferably about 2-8 hr.

The infrared absorption spectrum shows only absorptions at about 1300 and 760 cm^{-1} , which are due to the P-N stretching. From these results, we confirmed that the terminal anion was converted without changing the polymer structure.

The conversion is accompanied by changes in the properties. Namely, the starting material LPNC is a white, waxlike solid insoluble in benzene, while the product is a yellow viscous liquid which is soluble in benzene.

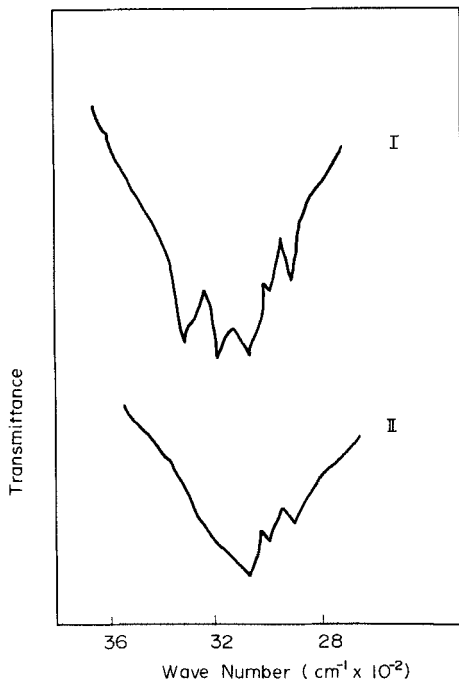


FIG. 3. Infrared spectra of the reaction products of the converted LPNC with aniline only in the range of high wavenumber: (I) LPNC-A (f. s.); (II) LPNC-A (p. s.).

Reaction of the LPNC with Aniline

The reaction of the LPNC converted with aniline was investigated. Depending on the mixing ratios between the two materials, various partially substituted products [abbreviated LPNC-A (p. s.)] are obtainable. Also fully substituted products [abbreviated LPNC-A (f. s.)] can be prepared.

The infrared absorption spectra of these products with different degrees of substitution in the range of high wavenumber are shown in Fig. 3.

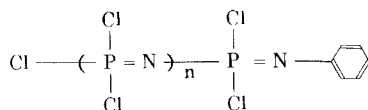
For the fully substituted product, the absorption spectra appear at about 3300 cm^{-1} due to the ν_{NH} stretching of the secondary amine and in addition at $3200\text{--}2900\text{ cm}^{-1}$ due to the ν_{CH} stretching. The partially substituted product has an absorption at about 3100 cm^{-1} (ν_{CH}), but there is no absorption due to the ν_{NH} of secondary amine as is seen in fully substituted products.

TABLE 1. Elementary Analysis of Reaction Products

Sample ^a	Analysis (found)		Number of substitution introduced groups per molecule
	P (%)	Cl (%)	
LPNC-A(p. s.)	19.3	50.5	1.1
LPNC-A(f. s.)	11.8	4.36	18.8
LPNC-Ph(p. s.)	20.4	30.2	7.7
LPNC-Ph(f. s.)	8.60	2.42	19.5

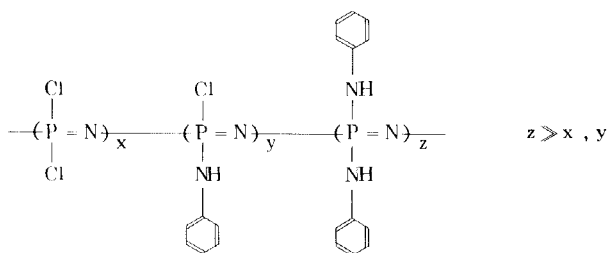
^aIn the synthesis of the partially and fully substituted products, converted LPNC having the average values of degree of polymerization (\bar{n}) of 5.7 (p. s.) and 8.4 (f. s.), respectively, were used.

In addition, it is also evident that the crosslinking reactions between two molecules of LPNC and one molecule of aniline did not take place, because the converted LPNC which is the starting material has a molecular weight of 870 while this partially substituted LPNC has a molecular weight of 878, the difference between before and after the reaction being negligible. Elementary analyses of the reaction products are shown in Table 1. From these results, the partially substituted LPNC may have the structure III.



III

On the other hand, fully substituted products generally have the structure IV.



IV

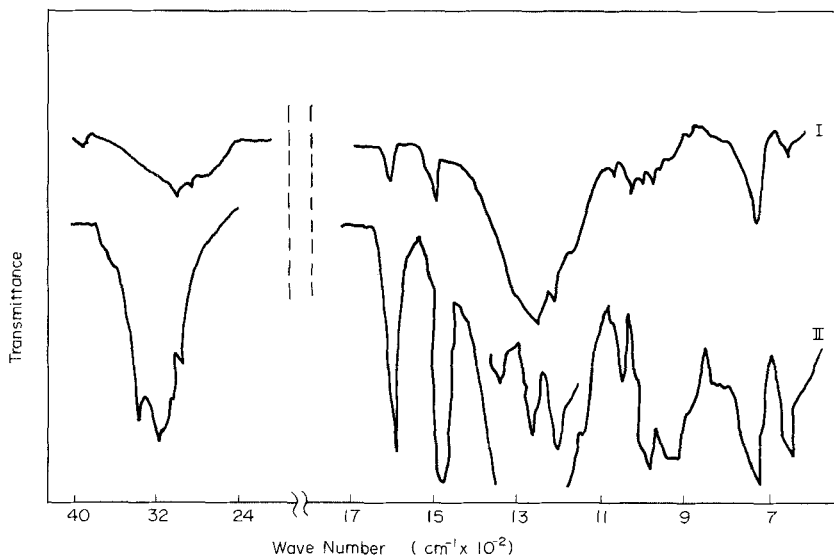
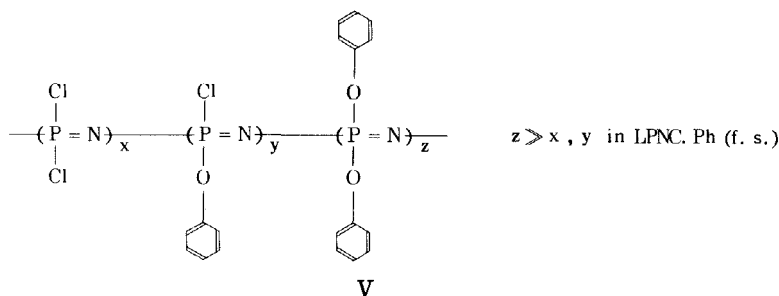


FIG. 4. Infrared spectra of the reaction products of the converted LPNC with phenol: (I) LPNC-Ph (p. s.); (II) LPNC - Ph (f. s.).

In this case, the end structure and the manner of substitution are still unclear. It is supposed that the terminal ionic group disappears on the introduction of the reagent. Furthermore, the infrared absorption spectrum indicates that these anilide groups do not exist in the form of chloride salt.

Reaction of the Converted LPNC with Phenol

The reaction of the converted LPNC and sodium phenolate proceeds as rapidly as the reaction of the converted LPNC and aniline. The partially and fully substituted products [LPNC-Ph(p. s.) and LPNC-Ph(f. s.), respectively] are both yellow viscous liquids. The infrared absorption spectra of both products, which are shown in Fig. 4, are the same. It is observed that for the fully substituted product, the spectrum has relatively stronger absorption maxima due to phenyl ring and P-O-Ar(C₆H₅) than that due to PN stretching vibration. Consequently it is conceivable that phenoxy radicals are introduced in the same type of combination into the main chain and the chain end. Also elementary analyses of reaction products are shown in Table 1. From these results, the probable structure of both products is V.



In this case also, details of the end structure or the position of the remaining chlorine atoms are still unclear, but it is conceivable that the ionic structure of the end is caused to disappear by the substitution.

Hydrolytic Stability of the Derivatives

Weight losses accompanied by hydrolysis of unsubstituted and substituted LPNC are given in Fig. 5.

Unconverted and converted LPNC are rapidly hydrolyzed within 2 hr. During that period, their weight losses are 32% and 19%, respectively. This difference is conceivably due to the fact that the unconverted LPNC has a relatively greater number of chlorine atoms per molecule than the converted LPNC, since there are differences in the counter-anion and molecular weight. Over the 2-hr period, the weight change of both compounds is very slow.

That these unsubstituted LPNC show the same hydrolysis curve is probably due to the fact that both of these compounds have ionic structures.

Compared to the converted and unconverted LPNC, the partially substituted LPNC undergoes hydrolysis only very slowly. For example, the phenoxide-substituted product (chlorine content = 30.2%) remained unchanged after 24 hr standing. Compared with this product, the anilide-substituted product (chlorine content = 50.5%) showed a greater weight loss. Both substitution products are considerably more stable than unsubstituted LPNC. It is conceivable that the difference in the pattern of hydrolysis between unsubstituted LPNC and the partially substituted LPNC is due to the different terminal structures.

On the other hand, it is possible that the partially substituted products have no ionic structures at the chain end. The anilide partial-substitution product is merely subjected to disassociation of chlorine at the other end, which has a relatively low ionic behavior. This probably explains the relatively slow decrease of weight. The phenoxide-substituted product, of which the substitution rate for chlorine is great, is very stable because both chain ends would be substituted.

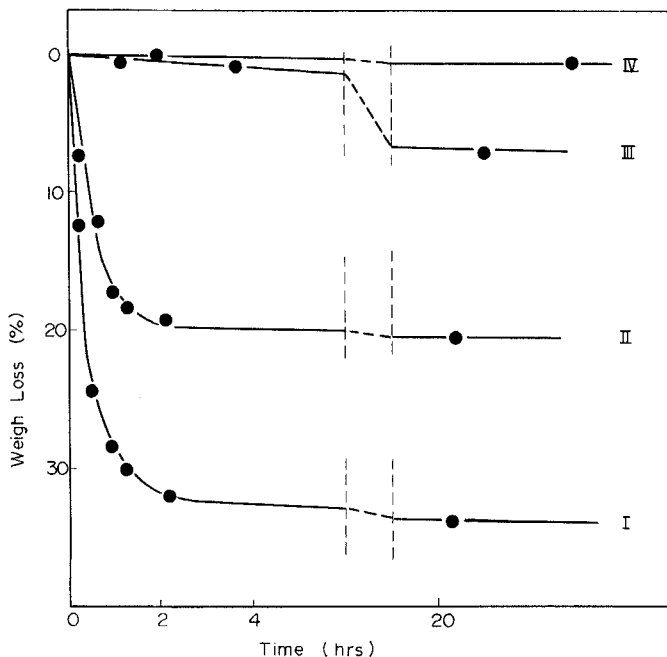


FIG. 5. Hydrolysis of LPNC and its various derivatives: (I) $[\text{Cl}-(\text{PCl}_2 = \text{N})_n \text{PCl}_3]^+ [\text{PCl}_6]^-$; (II) $[\text{Cl}-(\text{PCl}_2 = \text{N})_n \text{PCl}_3]^+ [\text{Cl}]^-$; (III) LPNC-A (p. s.); (IV) LPNC-Ph(p. s.).

Thermal Properties of the Derivatives

Thermogravimetric analysis was carried out of the unsubstituted LPNC and the various derivatives, and the results are given in Fig. 6. The unsubstituted LPNC undergoes change in two steps: polymerization begins at about 150°C , accompanied by a loss of weight, and thereafter the change proceeds in quite the same manner as in polyphosphonitrilic chloride (PPNC). Subsequently depolymerization begins at $300\text{--}350^\circ\text{C}$, accompanied by a decrease in weight. The weight loss is probably due to the fact that the main chain splits and the liberated low molecular PNC evaporates.

On the other hand, the derivatives obtained by substitution for most of the chlorines begin to decompose at considerably low temperatures. The anilide-substituted product begins to decrease in weight at about 100°C , accompanied by endothermic reaction, and thereafter changes unstably. Also the phenoxide-substituted product shows the same tendency as the anilide-substituted product.

On the contrary the anilide partial-substitution product begins to

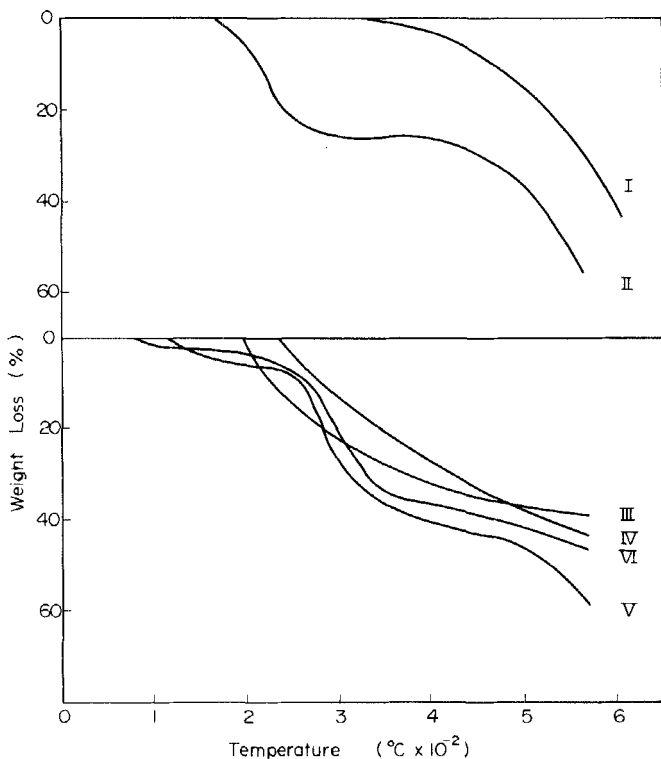


FIG. 6. Weight loss of polyphosphonitrilic chloride (PPNC), linear phosphonitrilic chloride oligomer (LPNC), and its various derivatives in air at a heating rate of $5^{\circ}\text{C}/\text{min}$: (I) PPNC; (II) LPNC; (III) LPNC-A (p. s.); (IV) LPNC-Ph (p. s.); (V) LPNC-A (f. s.); (VI) LPNC-Ph (f. s.).

lose its weight at about 200°C , accompanied by endothermic reaction, and thereafter changes slowly, the weight loss begin 35% at 600°C . Also the phenoxide partial-substitution product begins to decrease in weight at about 250°C and shows much the same pattern as the anilide-substituted product, the weight loss being about 40% at 600°C .

The unsubstituted LPNC is compared in thermal properties with the end-substituted products. If depolymerization, in which the main chain is split at random and the liberated PNC having a lower molecular weight evaporates, had occurred, the end-substituted derivatives would have begun to lose weight rapidly at about 400°C in the same manner as in the polymer, since they have the same main chain structure. It is therefore inferred that the thermal difference between them is due to the disappearance of the ionic structure at the end.

It was proposed that depolymerization of PPNC could proceed from

the chain end under ionic action by the backbiting mechanism [7-8]. The above-mentioned substitution products, the chain end of which has a nonionic structure, change slowly because such a mechanism of decomposition is hard to obtain.

REFERENCES

- [1] Imperial Chemical Industries Ltd., Brit. Pat. 89,325 (Apr. 4, 1962).
- [2] Albright & Wilson Ltd., Ger. Pat. 1,176,841 (Aug. 27, 1964).
- [3] M. Kajiwara, H. Saito, and T. Saito, Kobunshi Kagaku, **30**, 374 (1973).
- [4] F. Yamada, I. Horii, T. Yasui, and I. Shinohara, Nippon Kagaku Kaishi, **11**, 2191 (1974).
- [5] L. J. Bellamy, The Infrared Spectra of Complex Molecules, Methuen, London and Wiley, New York, 1958, p. 311.
- [6] E. Fluck, Z. Anorg. Allgem. Chem., **315**, 181 (1962).
- [7] F. G. R. Gimblett, Inorganic Polymer Chemistry, Butterworths, London, 1963, Chap. 7.
- [8] J. R. McCallum and A. R. S. Wernick, J. Macromol. Sci.-Chem., **A5**, 653 (1971).

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