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Studies on Complex Polyphosphates of N-Heterocyclic Bases

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SUMMARY

A few novel complex polyphosphate derivatives of the general composition $(BHPO_3)_n$ (where B is pyridine, substituted methylpyridines, quinoline, morpholine, benzimidazole, and imidazole) have been synthesized by precipitation techniques. Viscosity average molecular weight values indicate their polymeric character which is similar to that of Graham's salt and other linear chain polymers. The viscosity average molecular weights of the precipitated polyphosphates have been found to be dependent on the basicities of the heterocyclic amines. The relation between the M_w and R_g values determined by paper chromatography also confirm their polymeric nature. Conductivity measurements at different dilutions indicate their polyelectrolytic behavior analogous to the Fuoss model.

INTRODUCTION

A number of studies on the synthesis of ammonium phosphates and polyphosphates have been reported (IONARS et al 1966 LAPINA 1968). These derivatives have been found to be useful as fertilizers, fire resistant materials and pigment additives. Recently the synthesis and characterization of a few organic poly (aminium phosphate)s have been communicated from these laboratories (VYAS et al 1979). The N-heterocyclic bases are important constituents in paints, pigments, pesticides, insecticides, fire resistant materials, and plant nutrients. They are sufficiently basic to influence the reactions of polyphosphates, used industrially, as well as the environment of the latter. A perusal of literature reveals that the reactions of cations of N-heterocyclic bases with polyphosphate anions have not been studied so far. In the present communication, the polyphosphate derivatives of

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N-heterocyclic bases have been synthesized by precipitation techniques (THILO 1962). The polymeric nature of these derivatives has been confirmed by the determination of their viscosity average molecular weights and by paper chromatographic studies. Conductivity measurements reveal their polyelectrolytic behavior.

EXPERIMENTAL

All the reagents used were of analytical grade. The poly(aminium phosphate)s of N-heterocyclic bases were prepared by the precipitation technique. An aqueous solution of the hydrochloride of the N-heterocyclic base was added to an aqueous solution of poly(lithiumphosphate) (1:1 molar ratio). The pH of the solution was adjusted below 4 units by addition of 0.02M hydrochloric acid. This is based on the assumption that lithium ions in contrast to H^+ ions, should be weakly associated with $(PO3)^-$ chain anions below pH 4. A turbid solution was obtained by the addition of 2-propanol, which settled down as a viscous mass after cooling in an ice bath. The viscous mass so obtained was repeatedly smeared with 2-propanol to extract as much water as possible. Finally, it was dried in vacuo at room temperature. The poly(aminium phosphate)s were obtained as amorphous, hygroscopic powders. On the basis of the analytical data for phosphorous and nitrogen their composition corresponds to the general formula $(BHPO_3)_n$. The viscosity average molecular weights were determined with the Ostwald viscometer at $30 \pm 0.1^{\circ}C$ in 0.035M NaCl as swamping electrolyte. Conductivity measurements were carried out with a Toshniwal conductivity bridge and Philips conductivity cell (cell factor 1.49). Paper chromatographic studies were conducted on a Whatman No.1 paper, using an Ebel (EBEL 1953) acidic solvent with ascending technique.

RESULTS AND DISCUSSION

The viscosity average molecular weights (M_w) of poly(aminium phosphate)s have been calculated according to

$$\eta = k\, M_w$$

where η is the intrinsic viscosity and k a constant (STRAUSS et al 1953). The M_w values are listed in Table 1.

TABLE 1

Viscosity average molecular weights (M_w) of poly(aminium phosphate)s of N-heterocyclic bases.

Name of the compound	M_w^*	M_w'
Poly (pyridinium phosphate)	1875	2840
Poly (2-methylpyridinium phosphate)	2272	3068
Poly (3-methylpyridinium phosphate)	2735	3295
Poly (4-methylpyridinium phosphate)	4687	4829
Poly (2,3-benzpyridinium phosphate)	4744	5681
Poly (1,4-tetrahydroxazinium phosphate)	5639	6250
Poly (imidazolinium phosphate)	6420	7500
Poly (benzimidazolinium phosphate)	6505	7571

*M_w by the STRAUSS METHOD
M_w' by the NAGY METHOD

As the M_w values determined by the viscosity method are susceptible to extrapolation errors in the low concentration region of the polymer, improved M_w' viscosity average molecular weights have been determined by extrapolation of the G vs. F plot (NAGY et al 1978) as shown in Fig.1.

where $G = AF + B$ and $F = \frac{X}{\alpha - X}$

$G = \frac{Y}{\alpha - X}$ and $\alpha = X_M + xm.$

The indices m and M denote the lowest and highest values of the independent variable, for example of the concentration, and Y denotes the specific viscosity. The improved values of viscosity average molecular weights (M_w') are recorded in Table 1.

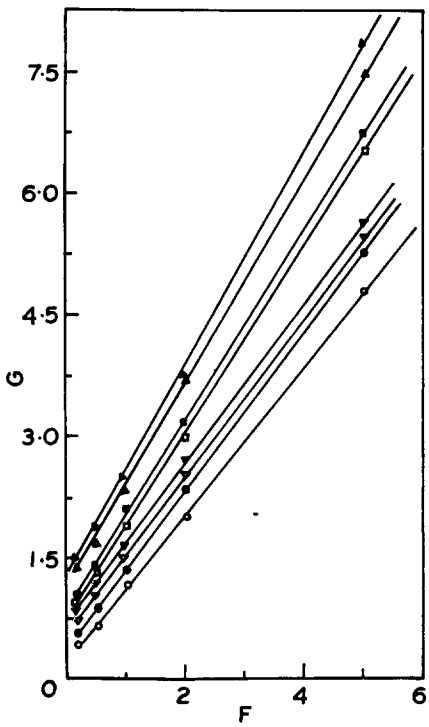


Fig.1 : Plot of G versus F for various poly-(aminium phosphate)s of N-heterocyclic bases.
o - Poly(pyridinium phosphate) a;
● - Poly(2-methylpyridinium phosphate) b;
▽ - Poly (3-methylpyridinium phosphate) c;
▼ - Poly (4-methylpyridinium phosphate) d;
□ - Poly (2,3-benzpyridinium phosphate) e;
■ - Poly (1,4-tetrahydroxazinium phosphate) f;
△ - Poly (imidazolinium phosphate) g;
▲ - Poly (benzimidazolinium phosphate) h;

The linear relationship between intrinsic viscosities and M_w values confirms the reliability of viscometric data (Fig.2).

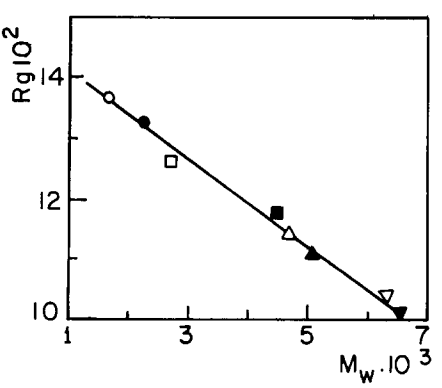


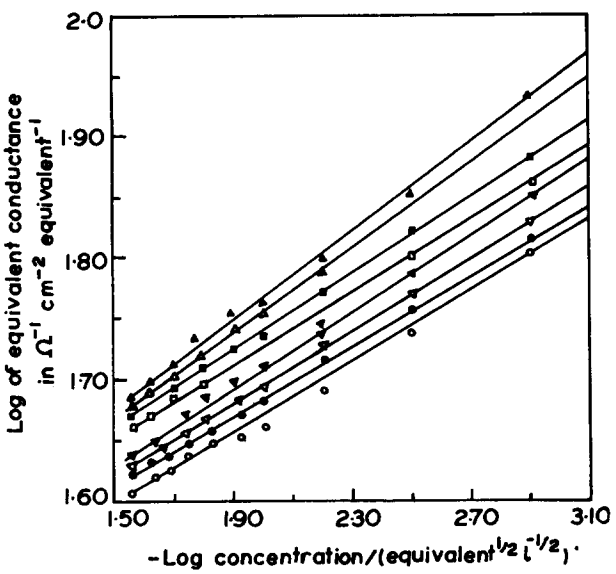
Fig.2: Plot of intrinsic viscosities versus M_w values of various poly-(aminium phosphate)s of N-heterocyclic bases*

● -a ; o -b
▲ -c , △ -d
■ -e , □ -f
▼ -g , ▽ -h

(* For further information see Legend to Fig.1).

The M_w values of the precipitated polyphosphates probably depend on the basic nature of the amine as well as on the molar volumes. More basic amines are able to precipitate higher molecular weight polyphosphate chains. The plot of the log of the equivalent conductivity versus the -log concentration is similar to that of Graham's salt and typical of polyelectrolytes (FUOSS 1951).

Fig.3: Plot of equivalent conductivities versus -log concentrations.



▲ -a; Δ -b
■ -c; □ -d
▼ -e; ∇ -f
● -g; o -h

(For further information see legend to Fig. 1)

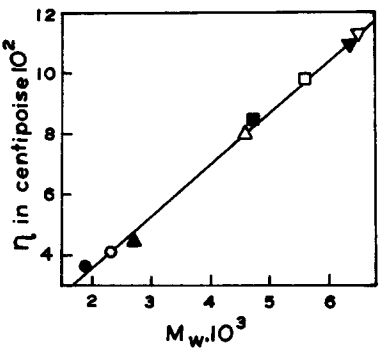


Fig.4: Plot of R_g values versus M_w values for various poly(aminium phosphate)s

○	-a	●	-b
□	-c	■	-d
△	-e	▲	-f
▽	-g	▼	-h

The polymeric nature of these polyphosphates was further established by paper chromatographic studies. The R_f and R_g values were found to be in the range (0.08 to 0.1069 and 0.101 to 0.1360 respectively. These vary according to the degree of polymerization. A plot of R_g values versus M_w values yields a straight line (Fig.4). A similar relationship was observed in the case of poly(alkali metaphosphates).

In conclusion it can be stated that these poly(aminium phosphate)s of N-heterocyclic bases consist of $(BHPO_3)_n$ units.

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