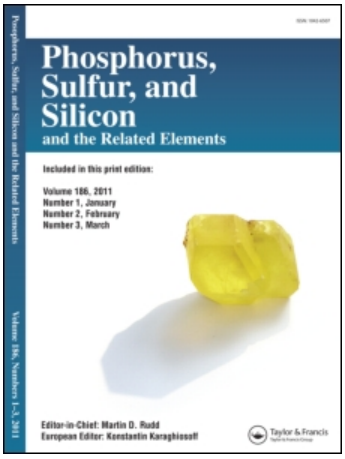


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

STUDIES ON ALKALINE-EARTH METAL POLYMETAPHOSPHATES PREPARED BY PRECIPITATION AND DEHYDRATION

A. Packter[a]; W. O. S. Doherty[a]
[a] Chemistry Department, North-East London Polytechnic, London, England

To cite this Article Packter, A. and Doherty, W. O. S.(1983) 'STUDIES ON ALKALINE-EARTH METAL POLYMETAPHOSPHATES PREPARED BY PRECIPITATION AND DEHYDRATION', Phosphorus, Sulfur, and Silicon and the Related Elements, 17: 2, 125 — 133
To link to this Article: DOI: 10.1080/03086648308077533
URL: http://dx.doi.org/10.1080/03086648308077533

Phosphorus and Sulfur, 1983, Vol. 17, pp. 125–133
0308-664X/83/1702-0125/$18.50/0

STUDIES ON ALKALINE–EARTH METAL POLYMETAPHOSPHATES PREPARED BY PRECIPITATION AND DEHYDRATION

A. PACKTER and W. O. S. DOHERTY

Chemistry Department, North-East London Polytechnic, London E.15, England

(*Received June 20, 1983, in final form July 26, 1983*)

Barium, strontium, calcium and magnesium polymetaphosphate hydrate powders were prepared by precipitation from aqueous solution and their dehydrations to amorphous anhydrous powders were studied in detail by a variety of physico-chemical methods. Anhydrous barium and strontium polymetaphosphates were formed through two dehydration processes whereas calcium and magnesium polymetaphosphates were formed through dehydration, hydrolysis (with depolymerisation) and repolymerisation processes, over the temperature range 20–450°C.

Batch samples of amorphous anhydrous alkaline–earth metal polymetaphosphate powders were then prepared by controlled dehydration and their properties studied. All these powders consisted of "peapod"-shaped aggregates of three to fourteen "spherules" of highly microcrystalline material of average diameter d_{av} = 0.17 μm. Their general composition was $[MP_2O_6]_n$; chain-lengths (n) varied from 8 to 22 (and molecular-weights varied from about 800–2200). Their glass transition temperatures (T_g) were similar to the values reported for amorphous polymetaphosphates prepared by high-temperature methods and increased with reciprocal cation radius from 453–530°C. The annealing of the amorphous powders above T_g was also studied by the above techniques: crystallisation started onto heterogeneous nuclei at initial temperatures $T_i = T_g$ + 20–30°C and reached maximum rates at temperatures $T_{x\,max} = T_g$ + 50–70°C.

INTRODUCTION

The alkaline–earth metal polymetaphosphates form a group of inorganic polymers of some applied interest: their glass transition temperatures are in the range 400–600°C and so they would exhibit satisfactory rheological properties at appreciably higher temperatures than most organic polymers.[1–3] These materials have generally been prepared by the dehydration of the corresponding alkaline–earth metal dihydrogen orthophosphate powders[4,5] and by the dehydration of the metal ammonium dihydrogen orthophosphate melts.[2,6] Recently, there has been some interest in the preparation of amorphous polymetaphosphate powders and films by precipitation of the polymetaphosphate hydrates from metal chloride—sodium polymetaphosphate solutions and dehydration of the hydrate precursors.[7–12] The reports on these studies were generally of a qualitative inorganic preparative character.

This paper then describes a more detailed investigation of the properties of amorphous barium, strontium, calcium and magnesium polymetaphosphate powders prepared by dehydration of the hydrate precipitates. The dehydration and related hydrolysis, depolymerisation and repolymerisation processes were monitored by a variety of physico-chemical methods. Batch samples of the amorphous materials, free of low molecular-weight hydrolysis products, were prepared and their chemical and physical properties were studied. Some preliminary studies were also carried out

on the crystallisation of the amorphous powders by annealing at temperatures above the glass transition temperatures.

RESULTS
THE DEHYDRATION OF ALKALINE-EARTH METAL POLYMETAPHOSPHATE HYDRATE POWDERS

Barium and Strontium Polymetaphosphate Hydrates

T.G.A. The dehydration of the hydrate powders was first studied in some detail by different physico-chemical techniques, to monitor the various chemical changes occurring and to determine the most suitable methods for the preparation of anhydrous polymer materials free of low molecular-weight hydrolysis and/or depolymerisation products. The T.G.A. thermograms[7] indicated a mass loss at 30 to 185°C—corresponding to the loss of the first 1.5 to 2 molecules of cation hydrate water—to form $[BaP_2O_6 \cdot H_2O]_n$ and $[SrP_2O_6 \cdot 1.5H_2O]_n$. There was then a second mass loss at 200 to 400°C, corresponding to the loss of the remaining 1 to 1.5 molecules of polyanion hydrate water to form anhydrous $[BaP_2O_6]_n$ and $[SrP_2O_6]_n$.

D.T.A. The D.T.A. thermograms for the dehydration at 10°C min^{-1} showed a predominant endothermic reaction at 50–60°C to 170°C; there was then a second less endothermic reaction at 200°C to 350–400°C.[7]

I.r. spectrophotometry. The infra-red spectra before and after heating confirmed the thermal analysis.[7] The initial hydrates showed strong water bands at $\nu = 3340$ and 1635 cm^{-1} and medium P=O bands at $\nu = 1260$ cm^{-1}: rapid continuous heating to 200°C and then 400°C reduced the intensities of and then completely eliminated the water bands but left the P=O bands unchanged.

X-ray diffraction and paper chromatography. Analysis of samples heated to 200°C and then 400°C indicated no change in the diffuse X-ray diffraction patterns and no formation of new low molecular-weight phosphates. This confirmed that the mass losses were related to dehydration only.

End-group analysis. There was some overall depolymerisation; this reduced the average chain-lengths of the two types of hydrates from initial values of 14–15 and 30–31 to final values of 12 and 22, respectively.

Calcium Polymetaphosphate Hydrates

D.T.A. The D.T.A. thermograms, for dehydration at 10°C min^{-1}[7] showed an endothermic reaction from 60 to 180°C; this would correspond to the loss of the loosely-bound and the first two cation water molecules to form $[CaP_2O_6 \cdot 2H_2O]_n$. There were then several additional peaks, corresponding to further dehydration of the above product and other chemical changes, from 200 to 400°C.

I.r. spectrophotometry. The infra-red spectra were similar to those of the barium salt but there was some modification of the P=O band at higher temperatures.[7]

X-ray diffraction and paper chromatography. Analysis of samples heated to 200°C confirmed loss of water with no change in structure. However, analysis of samples heated to 350°C indicated the formation of a mixture of crystalline products (from the amorphous 200°C hydrate): paper chromatography indicated the formation of a mixture of low molecular-weight products $Ca(H_2PO_4)_2$ and $CaH_2P_2O_7$. Analysis of samples kept at 300–400°C for prolonged periods indicated in turn depletion of these crystalline products and reformation of amorphous high molecular-weight polymetaphosphate $[CaP_2O_6]_n$.[7]

End-group analysis. Overall there was appreciable depolymerisation; the average chain-lengths decreased from initial values of 12 and 22 to final values of 8 and 14, respectively.

Recrystallisation. More prolonged holding (8–16 hr) at 350°C leads to recrystallisation of the amorphous polymetaphosphate. Rapid heating to 400°C and then holding at this temperature even for 2–3 hr also leads to recrystallisation.

Magnesium Polymetaphosphate Hydrates

D.T.A. The D.T.A. thermograms, for dehydration at 10°C min^{-1}, showed an endothermic reaction now from 90 to 200°C; this would correspond to the loss of the loosely-bound and the first two cation water molecules to form $[MgP_2O_6 \cdot 1.5H_2O]_n$. There were then additional peaks, corresponding to further dehydration of the above products and several other chemical changes, from 200 to 500°C.

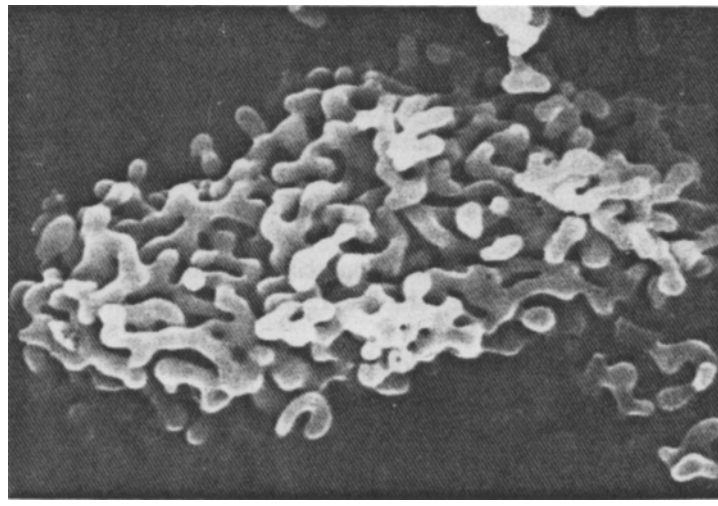
I.r. spectrophotometry. The infra-red spectra were similar to those of the other hydrates.

X-ray diffraction and paper chromatography. Analysis of samples heated to 200°C confirmed loss of water with no change in structure. However, analysis of samples heated to 250°C indicated that the 200°C hydrate was converted to crystalline $Mg(H_2PO_4)_2$. Analysis of samples heated to 250–450°C showed that this latter orthophosphate was in turn converted to crystalline $MgH_2P_2O_7$. Then analysis of samples after further heat treatment (24 hr holding) at 500°C indicated depletion of the low molecular-weight crystalline material and reformation of amorphous high molecular-weight polymetaphosphate $[MgP_2O_6]_n$.

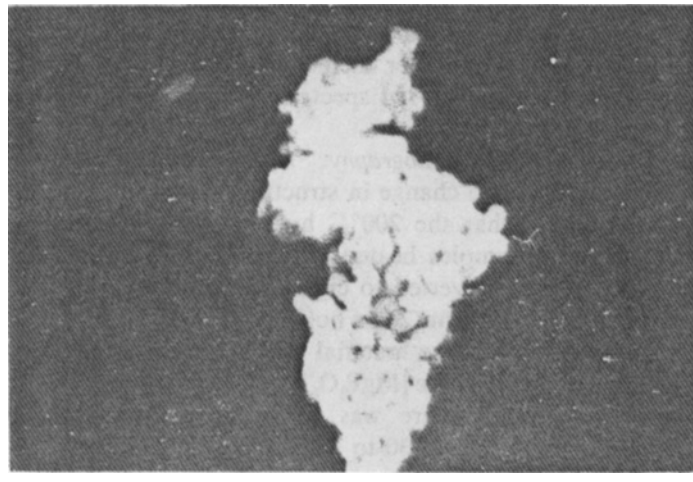
End-group analysis. Overall there was some depolymerisation; the average chain-lengths decreased from 14 and 30 to 10 and 17, respectively.

Crystallite Morphologies

Typical scanning electron micrographs of the dehydration products of barium polymetaphosphate hydrate are presented in Micrographs 1 and 2. Dehydration, by rapid heating to 200°C, leads to the formation of slightly larger spherules of average diameter $d_{av} = 0.12$ μm with increase in average volume to $V_{av} = 0.002$ μm^3: these spherules were in turn aggregated to form "pea-pod" and "boomerang"-shaped particles, each consisting of two to four spherules. Complete dehydration, by rapid heating to 400°C, leads to formation of rather larger spherules of $d_{av} = 0.005$ μm and a four–five fold increase in volume to $V_{av} = 0.005$ μm^3: these spherules were in turn aggregated to "pea-pods" of three to fourteen units.



MICROGRAPH 1 Barium polymetaphosphate hydrate powder after partial dehydration at 200°C: magnification ×20,000.



MICROGRAPH 2 Barium polymetaphosphate hydrate powder after complete dehydration at 400°C (the amorphous anhydrous powder): magnification ×20,000.

PHYSICO-CHEMICAL PROPERTIES OF AMORPHOUS ALKALINE-EARTH METAL POLYMETAPHOSPHATE POWDERS

Preparation and Chemical Composition

Batch samples of the anhydrous amorphous barium, strontium, calcium and magnesium polymetaphosphate powders were then prepared from the corresponding hydrate powder by controlled heat treatment in a muffle furnace (to produce

TABLE I

Properties of amorphous alkaline–earth metal polymetaphosphates

	This work: prepared from				Eisenberg (n = 4–20)	Jeffes (n = 4–5)
	$[NaPO_3]_n$		$[NaPO_3(II)]_n$			
	n	T_g/°C	n	T_g/°C	T_g/°C	T_g/°C
$[NaPO_3]_n$	11	272	21	300	280	287
$[BaP_2O_6]_n$	12	456	22	455	470	—
$[SrP_2O_6]_n$	12	480	22	480	485	—
$[CaP_2O_6]_n$	8	455	14	460	—	522
$[MgP_2O_6]_n$	10	530	17	535	—	—
$[ZnP_2O_6]_n$		—			520	510
$[CdP_2O_6]_n$		—			450	—

materials free of low molecular-weight hydrolysis and/or depolymerisation products). Their chemical compositions and average molecular-weights were rechecked (by chemical analysis, paper chromatography and end-group analysis) and are collated in Table I.

These products in fact all contained over ninety-nine percent polymetaphosphate with general composition $[MP_2O_6]_n$. The chain-lengths of the materials prepared from sodium polymetaphosphate $[NaPO_3(I)]_n$ varied from 8 to 12 while those of the materials prepared from sodium polymetaphosphate $[NaPO_3(II)]_n$ varied from 14 to 22; so molecular-weights varied from about 800 to 2200.

Crystallite Morphologies

Crystallite spherule form and sizes were similar to those of the materials prepared in the dehydration studies on smaller hydrate samples.

Glass Transition Temperatures

The mechanical properties of amorphous glassy polymer products deteriorate markedly above the "glass transition temperatures." Samples of the micro-crystalline anhydrous polymetaphosphate spherules were re-examined by differential thermal analysis from ambient temperature to above 550°C. The ΔT vs. T thermograms, for analysis at 10°C min^{-1} heating rate, showed distinct inflexions in a glass transition range.[7] The glass transition temperatures (T_g) were then determined at these inflexions;[2,7,20] the results are included in Table I, together with the values for the sodium polymetaphosphate starting materials for comparison. The glass transition temperatures of the alkaline–earth metal polymetaphosphate powders were from 160–230°C higher than the sodium polymetaphosphate values. Generally they were similar to the values reported by Eisenberg[1] and Jeffes[2] for materials, of similar molecular-weight, prepared by other methods: the low values for the calcium polymetaphosphate spherules may be related to some frozen-in dislocations from the dehydration process.[21,22] Eisenberg[1] has proposed the following relation for metal polymetaphosphate glasses;

$$T_g = f\left[q/(r_M + r_O)\right],$$

where q is the cation charge, r_M, r_O are the ionic radii of the M^{2+} cation and the O^{2-} anion in the metaphosphate molecule. The glass transition temperatures of the materials prepared by dehydration of hydrate precipitates also showed this relation; the T_g values generally increased in the order of cation charge and reciprocal radius,

$$Mg^{2+} > Sr^{2+} > \underset{Ca^{2+}}{Ba^{2+}} \gg Na^{+}.$$

Devitrification

Metal polymetaphosphate glasses are in turn generally rapidly devitrified when annealed at temperatures above the glass transition temperatures.[2,7] Some preliminary studies were then made on the annealing of the amorphous microcrystalline powder spherules, using different physico-chemical methods. Optical microscopy indicated increased birefringence but scanning electron microscopy showed no formation of any crystallites within the amorphous spherules. However differential thermal analysis showed up devitrification clearly;[7] generally a marked exothermic recrystallisation process started at initial temperatures T_i = 470–510°C (about 20–30°C above the glass transition temperatures T_g) whilst for magnesium polymetaphosphate powders, this process started at T_i = 570°C (about 50°C above T_g). Analysis of the Avrami plots indicated that these crystallisations occurred through heterogeneous nucleation processes. The rates of crystallisation were rather low near T_i but increased rapidly with increasing temperature and reached maximum values at temperatures $T_{x\max}$ about 50–70°C above T_g for the barium, strontium and calcium salts and at $T_{x\max}$ about 90°C above T_g for the magnesium salt. The rates of crystallisation then decreased as the spherules were depleted of amorphous material; for the first three salts, the annealing process was complete at 520–570°C (about 70–100°C above T_g and for the magnesium salt at 680°C (about 160°C above T_g).

X-ray diffraction studies confirmed the formation of monoclinic or orthorhombic crystalline alkaline–earth metal polymetaphosphate material.

EXPERIMENTAL

Materials and Solutions

Sodium polymetaphosphates $[NaPO_3(I)]_n$ (n = 12) and $[NaPO_3(II)]_n$ (n = 20) were supplied by Albright and Wilson Ltd., West Midlands, England.

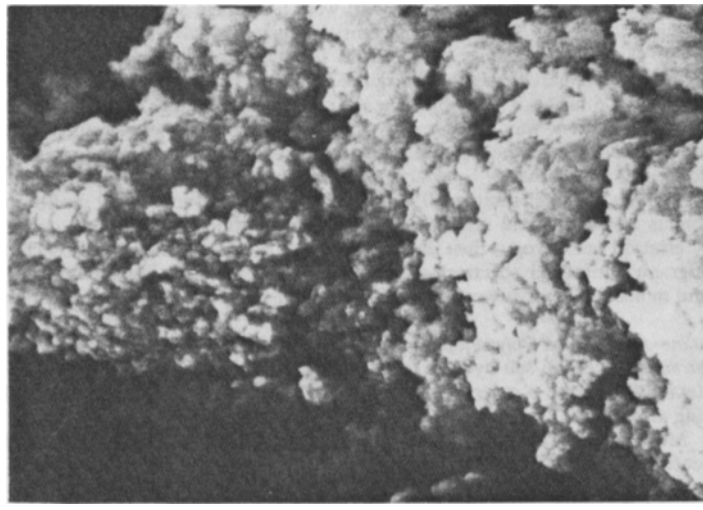
Barium, strontium, calcium and magnesium chlorides were "Analar" materials supplied by British Drug House Ltd.

Stock solutions were prepared in cold CO_2-free distilled water and stored at 10°C.

Alkaline–Earth Metal Polymetaphosphate Hydrate Powders

Preparation. Barium, strontium and calcium salts were prepared free of low molecular-weight cyclic and linear metaphosphates and disodium alkaline–earth metal salts by the following method.[13] Sodium polymetaphosphate solution (1 dm^3 of 0.1M) was added rapidly to equivalent metal chloride solution (1 dm^3 of 0.1M) at PO_3/M ratio = 2 : 1 the precipitation temperature was 20°C. The solutions were gently stirred for 30 min. The final precipitates were then filtered off by centrifugation and washed with cold distilled water. To remove low molecular-weight phosphates, the samples were then washed three more times with cold distilled water, then with ethanol and ether. Residual solvents were removed by drying at ambient temperature, over calcium chloride granules under vacuum, to constant weight. The magnesium salt was precipitated similarly from equivalent 0.1M solutions in twenty percent aqueous acetone and washed and dried as above.

Crystallite morphologies. A typical scanning electron micrograph of barium polymetaphosphate hydrate powder is presented in Micrograph 3. All the precipitated hydrate powders consisted of spherical



MICROGRAPH 3 Barium polymetaphosphate hydrate powder precipitated from 0.1M solution at ambient temperature: magnification ×10,000.

amorphous particles ("spherules") of very low particle size; average diameters varied from d_{av} = 0.05–0.1 μm. The X-ray diffraction patterns were all highly diffuse and confirmed the micro-crystalline character of these hydrates.

Chemical compositions. Chemical and thermogravimetric analysis, paper chromatography and end-group analysis confirmed that these hydrates were products of general composition $[MP_2O_6 \cdot hH_2O]_n$, free of low molecular-weight phosphates ($n < 5$) and the $[Na_2MP_4O_{12}]_n$ products: h represents the total number of molecules of hydrate water per MP_2O_6 group, while n represents the average chain-length. In turn,[13]

$$h = (h_{ads} + h_1 + h_2),$$

where h_{ads} is the loosely-bound adsorbed water,
h_1 is the cation bound water,
h_2 is the polyanion bound water.
The different h and n values were as follows:

	h_{ads}	h_1	h_2	h	n
$[BaP_2O_6(I) \cdot hH_2O]_n$	—	1.5	1.0	2.5	14
$[BaP_2O_6(II) \cdot hH_2O]_n$	0.5	1.5	1.0	3.0	30
$[SrP_2O_6(I) \cdot hH_2O]_n$	—	1.5	1.5	3.0	15
$[SrP_2O_6(II) \cdot hH_2O]_n$	1.0	1.5	1.5	4.0	31
$[CaP_2O_6(I) \cdot hH_2O]_n$	—	2.0	2.0	4.0	18
$[CaP_2O_6(II) \cdot hH_2O]_n$	0.5	2.0	2.0	4.5	34
$[MgP_2O_6(I) \cdot hH_2O]_n$	—	2.0	1.5	3.5	14
$[MgP_2O_6(II) \cdot hH_2O]_n$	1.0	2.0	1.5	4.5	30

Dehydration of Hydrate Powders

Thermogravimetric analysis. Samples (0.3 g) were heated in silica crucibles in a "Stanton" Thermobalance at 600°C hr^{-1} from ambient temperature to 500°C. The total weight loss (ΔW_T) and residual weight (W_T) were recorded as a function of temperature (T); the final residual weight (W_{fin}) was also noted. Then the hydrate number (h_T) at any temperature was determined as

$$\frac{\Delta W_T}{W_{fin}} = \frac{18h_T}{(M + 2P + 6O)}$$

where
M = r.a.m. of Ba, Sr, Ca and Mg,
P = r.a.m. of P,
O = r.a.m. of O.

Differential thermal analysis. Samples (10–30 mg) were heated (in sample holders) through different heating schedules in a "Stanton Redcroft" Differential Thermal Analyser Model 673/4 from ambient temperature to 500°C; most runs were carried out at 10°C min^{-1}. The reference sample was calcined alumina ground to the same particle size as the sample powder. The samples and reference holders were quartz ampoules 3 cm × 6 mm × 4 mm bore. The differential temperature vs. temperature thermograms were recorded. The instrument was calibrated by measurements of the temperatures and enthalpies of fusion of measured weights of pure benzoic acid, tin and potassium sulphate. Some preliminary studies on the kinetics of dehydration were made by analysis of the thermograms by Borchardt's method.[14]

Muffle furnace heating. Larger samples (0.3–1 g) were then heated in a small muffle furnace through different continuous and isothermal schedules. The crystal morphologies of these dehydrated samples were studied by electron microscopy; their chemical compositions were monitored by chemical analysis, paper chromatography, infra-red spectrophotometry and X-ray powder diffraction and their average chain-lengths and molecular-weights were determined by end-group potentiometric analysis.

Anhydrous Alkaline-Earth Metal Polymetaphosphate Powders (Batch Sample Preparation)

Barium and strontium. Metal salt hydrate powders (1 g) were heated at 10°C min^{-1} to 450°C.

Calcium. Metal salt hydrate powders (1 g) were heated at 10°C min^{-1} to 350°C and then held for 5 hr further heating at 350°C.

Magnesium. Metal salt hydrate powders (1 g) were heated at 10°C min^{-1} to 450°C and then held for 24 hr further heating at 450°C.

Glass Transition and Crystallisation of Amorphous Powders. Amorphous powder samples (10–30 mg) were reanalysed in the Differential Thermal Analyser at 10°C min^{-1} from ambient temperature to 700°C. The differential temperature vs. temperature thermograms were recorded.[13,20]

Chemical Compositions and Properties—before and after Dehydration

Chemical analysis. Dried powder samples (0.1 g) were dissolved in dilute hydrochloric acid and hydrolysed to the orthophosphates. Mg(Ca, Sr, Ba)O contents were determined by titration of the metal cation solutions against standard sodium E.D.T.Aate solution.[15a]

P_2O_5 contents were determined by precipitation as magnesium ammonium orthophosphate hydrate—after removal of the cation.[13,15b]

H_2O (hydrate water) contents were determined from loss on ignition at 500°C.[15c]

Paper chromatography. Orthophosphates, pyrophosphates, linear and cyclic tri- and tetraphosphates were determined by the standard Karl-Kroupa method, as described in a recent paper.[13,16]

End-group analysis. Average chain-lengths (and molecular-weights) were determined by the standard van Wazer potentiometric titration method, as described in the recent paper.[13,17]

Infra-red spectrophotometry. Sample powder (2–3 mg) was ground in an agate mortar to < 2 μm and dispersed in a Nujol mull. The infra-red spectrum was recorded on an I.R. Grating Spectrophotometer (Perkin-Elmer Model 337) from 4000–600 cm^{-1}: optical absorbances were measured at the principal regions for absorption by P=O groups and by OH groups.[13,18]

X-ray powder diffraction. Samples were prepared by pre-grinding in an agate mortar to < 10 μm. The fine powder was then "loaded" into one of the four cavities in the specimen holder of the X-ray Diffraction Camera. The X-ray powder diffraction analysis was performed at the Laboratories of Albright and Wilson Ltd, using a Nonius Guinier focussing Camera in conjunction with a Philips PW 1130 X-ray generator giving CuK_α radiation. The crystalline phases present were identified by matching the diffraction patterns of the unknown substances to standards from the J.C.P.D.S. diffraction file and from the Albright and Wilson library.[13,19]

Scanning electron microscopy. Finely-ground powder was rapidly heated at 100°C to remove loosely-bound water that could lead to chemical reaction in the electron beam. The dried powder, insufflated onto a sticky aluminium stub, was coated under high vacuum with gold: the coated sample was then examined in the Scanning Electron Microscope ("Jeol" Instrument Model T 200) at a tilt of ten degrees and at magnification from ×10,000 to ×40,000. 20 to 40 particles from each micrograph were studied and the average particle diameters (by weight) were determined.[13]

ACKNOWLEDGMENTS

We would like to thank Mr. R. A. Smith and colleagues of Albright and Wilson Ltd. Phosphates Division (Oldbury, W. Midlands, England) for their continuous interest in these studies and for valuable discussions on the topic.

REFERENCES

1. A. Eisenberg, *J. Pol. Sci.*, **A2, 4** 855 (1966); *Adv. Pol. Sci.*, **5**, 59 (1967).
2. J. H. E. Jeffes, *Phys. Chem. Proc. Metall. I.M.M. Conf.*, **1973**, 233 (1973).
3. N. Ray, *J. Non. Cryst. Solids*, **15**, 423 (1974).
4. A. Boulé, *C.R.*, **202**, 1434 (1936).
5. E. Thilo, *Z. Anorg. Chem.*, **290**, 223 (1957).
6. R. Mehrotra, *J. Pol. Sci.*, **A3**, 2535 (1965).
7. W. O. S. Doherty, C.N.A.A., Ph.D. Thesis (April 1983).
8. R. Klement, *Chem. Ber.*, **93**, 1956 (1960).
9. R. Mehrotra, *Ind. J. Chem.*, **4**, 356 (1966).
10. S. Ohashi, *Bull. C.S. Japan*, **33**, 1437 (1960).
11. R. Pfanstiel, *J. Amer. Chem. Soc.*, **78**, 5510 (1956).
12. E. Thilo, *J. Prakt. Chem.*, **7**, 46 (1958).
13. A. Packter and W. O. S. Doherty, *Cryst. Res. Tech.*, **18**, 535 (1983).
14. J. Borchardt, *J. Amer. Chem. Soc.*, **78**, 41 (1957).
15. A. I. Vogel, "Quantitative Inorganic Analysis," Longmans (1962), a) Ch. IV.4, 419; b) Ch. V.65, 576; c) Ch. V.4, 459.
16. E. Karl-Kroupa, *Anal. Chem.*, **28**, 1091 (1956).
17. J. R. Van Wazer, *J. Amer. Chem. Soc.*, **72**, 639 (1950).
18. D. E. C. Corbridge, *J.C.S.*, **1954**, 493 (1954).
19. P. H. Klug and L. E. Alexander, "X-Ray Diffraction Procedures," J. Wiley (1954), Chs. 6, 7.
20. A. Packter and M. S. Nerurkar, *Z. Polymere*, **229**, 7 (1969).
21. M. Natarajan, *Trans. Faraday Soc.*, **65**, 3088 (1969).
22. Y. Abé, *J. Amer. Ceram. Soc.*, **59**, 487 (1976).