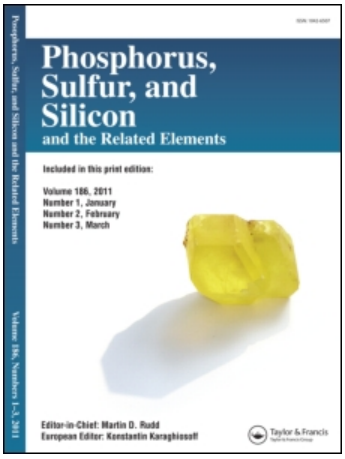

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Gita Seth[a]; Anjana Agarwal[a]; Mahesh K. Samota[a]; Yajula Garg[a]
[a] Department of Chemistry, University of Rajasthan, Jaipur, India

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Studies on Rare Earth Polyphosphate Glasses of the Composition $[Na_xM_{(1-x)/2a}Gd_{(1-x)/2a}PO_3]_n$

Gita Seth
Anjana Agarwal
Mahesh K. Samota
Yajula Garg
Department of Chemistry, University of Rajasthan, Jaipur, India

A fusion technique was used for the preparation of derivatives of the composition $[Na_xM_{(1-x)/2a}Gd_{(1-x)/2a}PO_3]_n$ (where M = bivalent metal like Cu(II), Ca(II), Zn(II), Ni(II), and Mg (II); x = 1/2, 3/4, & 2/3; and a = valency of metal). Composition of these polyphosphate glasses was confirmed by their analyses for metals and phosphorus. The polymeric nature of all polyphosphate glasses was confirmed by the determination of a number average molecular weight (M_n). The characteristic frequencies in the IR spectra are supportive of the presence of polyphosphate indicative of the polymeric nature of these derivatives. From X-ray diffraction, the amorphous nature of complex polyphosphates has been determined.

Keywords Polyphosphate glasses; rare earth

INTRODUCTION

The polyphosphate glasses have numerous applications in industries such as paints, inks, and detergents. The complex polyphosphate glasses have been known to possess various properties such as conductors, optical materials, flame-proofing agents, and fire retardants.[1,2] Rare earth phosphate compounds have gained commercial importance because of their suitable optical properties for laser applications.[3] A single crystal diffraction technique was employed for the structure determination of ultraphosphate,[4] in which as powder solution technology was used for the structure determination of metaphosphates.[5] Polyphosphate derivatives of lanthanides have been studied by many

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Address correspondence to Gita Seth, University of Rajasthan, Department of Chemistry, Jaipur 302004, India. E-mail: gita27@sify.com

workers.[6] A persual of literature revealed that complex polyphosphates containing rare earth cations and bivalent metal ions have not been studied in detail. In this article, studies on polyphosphate of bivalent metals such as Cu(II), Cd(II), and Zn(II) and Mg(II) with Gd(III) of the composition $[Na_xM_{(1-x)/2a}Gd_{(1-x)/2a}PO_3]_n$ are reported.

EXPERIMENTAL

The fusion method[7] was used for the preparation of various complex polyphosphates. Sodium dihydrogen orthophosphate, diammonium hydrogen orthophosphate, bivalent metal oxide ($M^{II}O$), and gadolinium oxide ($M_2^{III}O_3$) were taken in an appropriate molar ratio in platinum crucible and mixed well with a platinum stirrer and heated up to $900^\circ \pm 10^\circ C$ for 2 h. The products were obtained in the form of a transparent melt, which was chilled between two stainless steel plates. Compositions were confirmed by the estimation of alkali, bivalent metals, gadolinium, and phosphorus. Sodium was estimated flamephotometrically; phosphorus was estimated spectrophotometrically; bivalent metals were estimated by standard gravimetric and volumetric techniques; gadolinium was estimated complexometrically with a standard 0.05 M EDTA solution using Xylenol orange as an indicator.[8]

R_f values were measured with the help of TLC in a dioxane solvent system (30 mL dioxane + 75 mL water + 5 g trichloro acetic acid and ammonia solution). Dioxane is preferred over other solvent systems due to its miscibility in water, low dielectric constant, and moderately low viscosity. In this solvent, an excellent resolution is obtained in comparatively less running time.

The number of average molecular weights was determined by an end group titration technique,[9] with the help of a Systronic pH meter that had a glass and a calomel electrode. Aqueous solutions of the complex polyphosphate were prepared by dissolving about 0.1–0.15 g of a sample in 100 mL of double distilled water. The solution thus obtained was then titrated after adjusting the pH to 3.0 with 0.01N HCl against a 0.1N NaOH solution. The volume of alkali consumed between the two inflections in the titration curve around pH 4.5 and 9.0 units was used to calculate the number average molecular weight (M_n) as per formula in Eq. (1):

$$M_n = \frac{20{,}000 \times \text{weight of polymeric sample}}{\text{volume of 0.1N NaOH used}} \quad (1)$$

There are two end groups per chain, which are titrated by 0.1 N NaOH. The number average molecular weight (M_n) corresponds to the

weight of the polymeric sample equivalent to 1 g mole of the polymer. Hence it corresponds to $2 \times 1000/0.1$, that is 20,000.

Infra red spectra were obtained on an FTIR spectrophotometer (IR Magna 550, nicolet) in the region of 4000–400 cm^{-1}. To get the IR spectra, a powdered form of polyphosphate glass was mixed with KBr in a 1:1000 ratio, ground together into fine powder, dried to remove moisture, and pressed at r.t. under high pressure into a small transparent KBr pallet. All the spectra were calibrated with the help of a polystyrene film.

The X-ray diffraction (XRD) spectra of complex polyphosphates were recorded on a Philips make powder diffractrometer PW 1840 at $\lambda Fek_{\alpha}1.937355$Å (the conditions of measurements were as follows: speed $0.10^{\circ}2\theta$/s, range 2×10^{3}, and 2θ was 3.6° to 90°. The value of the glass transition temperature of these complex polyphosphates was also determined by measuring the heat flow versus the temperature with the help of Differential scanning calorimeter 3210B.

RESULTS AND DISCUSSION

The various polyphosphate derivatives synthesized for this article were analyzed for their constituents, i.e., phosphorus, alkali/bivalent metals and gadolinium (see Table I). The R_f and Rg values for various complex polyphosphates were calculated with the help of TLC and are reported in Table II. R_f values of these polyphosphates closely resemble those of poly(lithium phosphate) and Graham's salt, indicating that these are polymeric in nature. Chromatograms of these derivatives also show two spots of very weak intensity along with those of polyphosphates. The R_f values of these spots correspond to ortho- and trimetaphosphates. These spots are probably due to an initial hydrolysis of a polyphosphate chain

TABLE I Elemental Analysis of Complex Polyphosphate Glasses

Formula of Compound	Percent of P Obs. (Cal.)	Percent Na Obs. (Cal.)	Percent of M obs. (Cal.)	Percent of Gd Obs. (Cal.)
$[NaPO_3]_n$	3.15 (3.29)	4.21 (4.43)	—	—
$[Na_{24}Mg_3Gd_2(PO_3)_{36}]_n$	29.47 (29.48)	14.45 (14.59)	3.03 (3.14)	8.16 (8.29)
$[Na_{24}Ca_3Gd_2(PO_3)_{36}]_n$	29.10 (29.12)	14.29 (14.41)	1.87 (1.92)	8.10 (8.19)
$[Na_{24}Ni_3Gd_2(PO_3)_{36}]_n$	28.63 (28.70)	14.11 (14.20)	4.42 (4.51)	8.27 (8.34)
$[Na_{24}Cu_3Gd_2(PO_3)_{36}]_n$	28.46 (28.59)	14.01 (14.15)	4.80 (4.88)	8.01 (8.04)
$[Na_{24}Zn_3Gd_2(PO_3)_{36}]_n$	28.49 (28.55)	14.01 (14.13)	4.99 (5.01)	8.01 (8.03)
$[Na_{36}Ca_3Gd_2(PO_3)_{48}]_n$	29.35 (29.42)	16.27 (16.38)	3.26 (3.37)	6.14 (6.22)
$[Na_{36}Ni_3Gd_2(PO_3)_{48}]_n$	29.02 (29.10)	16.11 (16.20)	3.37 (3.43)	6.12 (6.15)
$[Na_{36}Cu_3Gd_2(PO_3)_{48}]_n$	28.93 (29.01)	16.03 (16.16)	3.66 (3.71)	6.07 (6.13)

TABLE II TLC Data and R_g Values of Various Complex Polyphosphate Derivative in Dioxane Solvent

Complex Polyphosphate	M_n	$-\text{Log } n_c$	R_f	R_g
NaH_2PO_4	—	—	0.920	—
$[NaPO_3]_n$	4725	$\bar{2}.2286$	0.039	0.042
$[Na_{24}Mg_3Gd_2(PO_3)_{36}]_n$	2913	$\bar{2}.5570$	0.060	0.065
$[Na_{24}Ca_3Gd_2(PO_3)_{36}]_n$	3348	$\bar{2}.5019$	0.052	0.056
$[Na_{24}Ni_3Gd_2(PO_3)_{36}]_n$	3362	$\bar{2}.5064$	0.054	0.059
$[Na_{24}Cu_3Gd_2(PO_3)_{36}]_n$	3627	$\bar{2}.4751$	0.050	0.054
$[Na_{24}Zn_3Gd_2(PO_3)_{36}]_n$	2350	$\bar{2}.6642$	0.067	0.073
$[Na_{36}Ca_3Gd_2(PO_3)_{48}]_n$	2600	$\bar{2}.6072$	0.061	0.066
$[Na_{36}Ni_3Gd_2(PO_3)_{48}]_n$	3540	$\bar{2}.4783$	0.049	0.053
$[Na_{36}Cu_3Gd_2(PO_3)_{48}]_n$	4383	$\bar{2}.3865$	0.033	0.036

in aqueous solutions, which has been considered to be less than 2–2.5%. This is in agreement with observations reported in the literature.[10] The plot of R_f versus the negative log of chain length is a straight line, which indicates the long chain polymeric character of polyphosphate derivatives. The chain length was obtained by using Eq. (2):

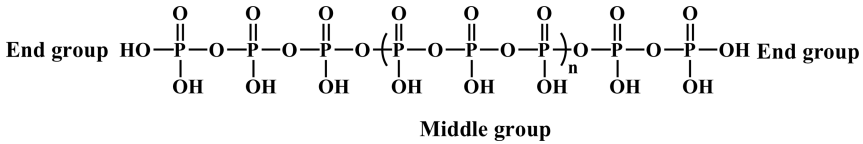
$$\text{chain length } (n_c) = \frac{\text{number average molecular weight}}{\text{weight of single phosphate unit}} \tag{2}$$

The number average molecular weights of complex polyphosphate glasses are reported in Table III. The M_n values lies in the range of 2000–4000, indicating a chain length (n_c) equal to 20 to 40 units, which is in agreement with the reported values in the literature.[11] The existence of two inflections in the titration curve is indicative of the presence

TABLE III Number Average Molecular Weight (M_n) Determined by End Group Titration. W = Weight of the polymer sample used in titration. V = Volume of 0.1 N NaOH consumed between 4.5 to 9.0 pH

Complex Polyphosphate	W (g)	V (mL)	M_n
$[NaPO_3]_n$	0.1701	0.72	4725
$[Na_{24}Mg_3Gd_2(PO_3)_{36}]_n$	0.1616	1.11	2913
$[Na_{24}Ca_3Gd_2(PO_3)_{36}]_n$	0.1389	0.83	3348
$[Na_{24}Ni_3Gd_2(PO_3)_{36}]_n$	0.1647	0.98	3362
$[Na_{24}Cu_3Gd_2(PO_3)_{36}]_n$	0.1632	0.90	3627
$[Na_{24}Zn_3Gd_2(PO_3)_{36}]_n$	0.1116	0.95	2350
$[Na_{36}Ca_3Gd_2(PO_3)_{48}]_n$	0.1144	0.88	2600
$[Na_{36}Ni_3Gd_2(PO_3)_{48}]_n$	0.2000	1.13	3540
$[Na_{36}Cu_3Gd_2(PO_3)_{48}]_n$	0.2016	0.92	4383

of strong and weak acidic groups in the polyphosphate derivatives. As the nature of the titration curves obtained are similar to those of Grahm's salt, it can be concluded that the polyphosphate derivatives consist of end and middle groups in the chain-like polymeric anion (see Scheme 1).



SCHEME 1

The IR spectra of these polymeric derivatives show broad bands, which may be ascribed to their amorphous polymeric character. The absorption frequencies observed are in close agreement with the values reported for Grahm's salt. The IR spectra of all long chain polyphosphate derivatives contains a very strong broad band with an absorption maxima at 1270 cm^{-1}, which is ascribed to the P═O stretching vibration. The absence of a triplet band at $\simeq$1330 cm^{-1} and a sharp band at 770–745 cm^{-1} attributed to trimetaphosphate and cyclic phosphate indicates the absence of the trimetaphosphate anion and cyclic phosphate. The absorption bands in the region of 1100–1800 cm^{-1} and 1115–1170 cm^{-1} related to PO_2 or P—O ionic character, attributed to long chain polyphosphates, are observed in these derivatives. A weak broad band characteristic of amorphous phosphates is also observed at 1030–990 cm^{-1}. The absorption at 890–870 and 720 cm^{-1} are ascribed to vibrations in the P—O—P chain.[12]

From IR spectral studies and other studies previously mentioned, it can be suggested that these complexes are long chain polymers containing a polyphosphate $(PO_3)_n^{-n}$ chain. From XRD, the amorphous nature of complex polyphosphates has been determined and it was found that the glass transition temperature of these complex polyphosphate derivatives lie in the range of $\approx$300°C.

CONCLUSION

The R_f and R_g values of Grahm's salt and complex polyphosphate synthesized are very close to each other. This confirms the chain-like polymeric character of these derivatives. The M_n values lie between 2000–4000, indicating a chain length (n_c) equal to 20–40 units. From XRD, the amorphous nature of complex polyphosphates has been determined.

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