

Synthesis and Spectral Characterization of Hexahydroxy *Tris*-Cyclophosphazene Hexaacrylate

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Acrylic acid was mixed with hexahydroxycyclo phosphazene $[\text{NP}(\text{OH})_2]_3$ in equimolar ratio in DMF followed by conc. H_2SO_4 and refluxed for 6 h. The product, obtained, was analyzed, quantitatively, as well as, mass, IR and UV spectrometrically and formulated as $[\text{P}_3\text{N}_3(\text{OH})_2-\text{C}(\text{OOC}-\text{CH}=\text{CH})_2]_3$ as ionic polymer (trimer), having $(\text{CH}=\text{CH}-\text{COO})-\text{P}_3\text{N}_3(\text{OH})_2$ units.

Key Words: Synthesis, Hexahydroxy *Tris*-cyclophosphazene hexaacrylate.

INTRODUCTION

Being Lewis' base, the complexes of $(\text{NPCl}_2)_2$ and $(\text{NPH}_2)_3$, trimers have been reported¹⁻¹⁰. But neither complexations nor substitutional reactions of $[\text{NP}(\text{OH})_2]_3$ have been carried out till now. Therefore, $[\text{NP}(\text{OH})_2]_3$ was treated with acrylic acid in presence of conc. H_2SO_4 and investigations of product formed are being presented herewith.

EXPERIMENTAL

Hexahydroxy cyclophosphazene, $[\text{NP}(\text{OH})_2]_3$ was synthesized¹¹ by the reaction of NaOH on $(\text{NPCl}_2)_3$, using AnalaR grade chemicals. The product $[\text{NP}(\text{OH})_2]_3$ was mixed with acrylic acid in equimolar ratio in DMF followed by the addition of conc. H_2SO_4 and refluxed for 6 h until the completion of reaction. The mass formed was filtered, washed with DMF, benzene, alcohol and ether successively, dried and stored in a vacuum desiccator.

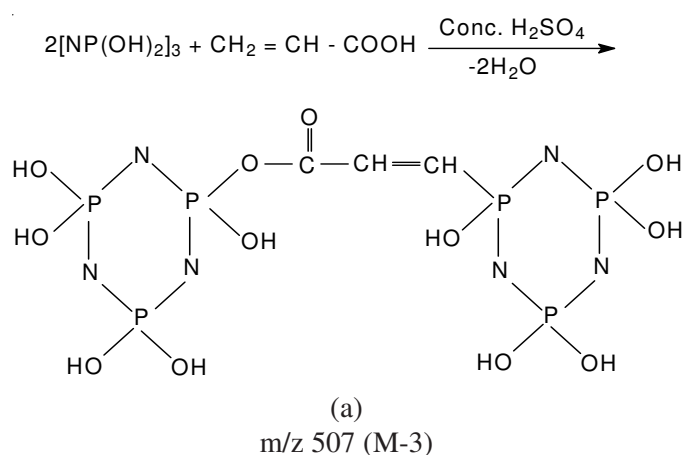
The quantitative estimations for the constituent elements of hexahydroxy *tris*-cyclophosphazene hexaacrylate (HTPHA) were performed as described¹². Jeol SX-102 (FAB), Shimadzu 8201 PC (4000-400 cm^{-1}) and Perkin-Elmer Lambda-15 (200-800 nm) spectrometers were used to record mass, IR and UV Spectra at CDRI, Lucknow.

RESULTS AND DISCUSSION

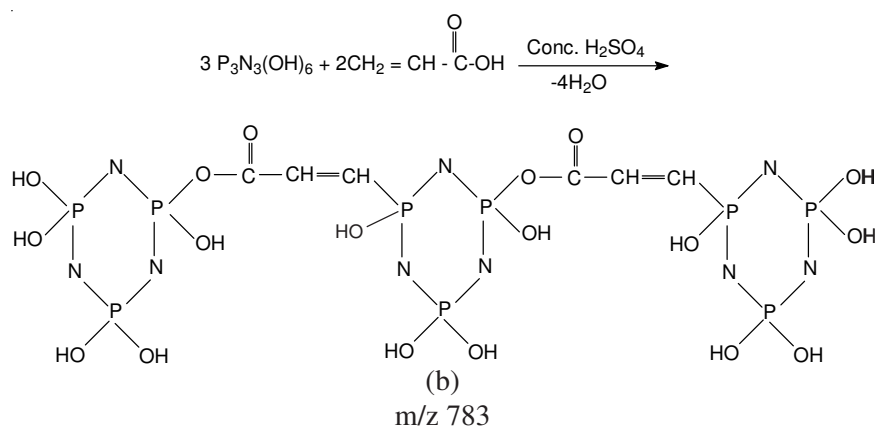
Hexahydroxy *tris*-cyclophosphazene hexaacrylate (HTPHA) is white semi-crystalline solid, soluble in water, P and N were tested as PO_4^{3-} and NH_4^+ , respectively and found positive, chemical data based on its mass

spectrum and gravimetric analysis are as % found (calcd.) C 23.25 (23.30), H 1.94 (1.95), N 13.56 (13.59), P 30.03 (30.09) and m.w. 929.0 (927.0) g mol⁻¹ assigning HTPHA as [P₃N₃(OH)₂-(OOC-CH=CH)₂]₃ for which mass line at m/z 929 (M + 2) has occurred in its mass spectrum.

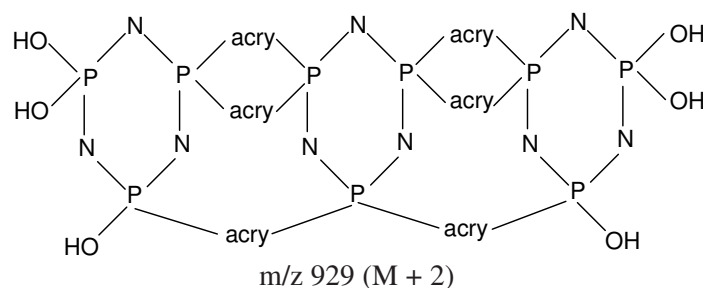
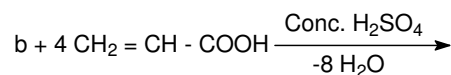
The prominent mass lines at m/z 352 and 387 for (P₃N₃O)₂-O-C-C=C (M - 2) and (P₃N₃O₂)₂-O-C-CH = CH (M-1), respectively explain that one molecule of acrylic acid has reacted to two OH groups of two P₃N₃ ring in bigging, bridging two P₃N₃ rings as:



The mass line at m/z 586 for [P₃N₃(OH)₂]₂-(O=C-CH=CH)₂-P₃N₂O (M+1) fragment suggest that two molecules of acrylic acid have reacted to three molecules of [NP(OH)₂]₃ molecules in presence of conc. H₂SO₄, with the elimination of 4 water molecules as confirmed by mass line at m/z 783 for N₉P₉-(OH)₁₄-(OOC-CH=CH)₂ fragment, according to following reaction.



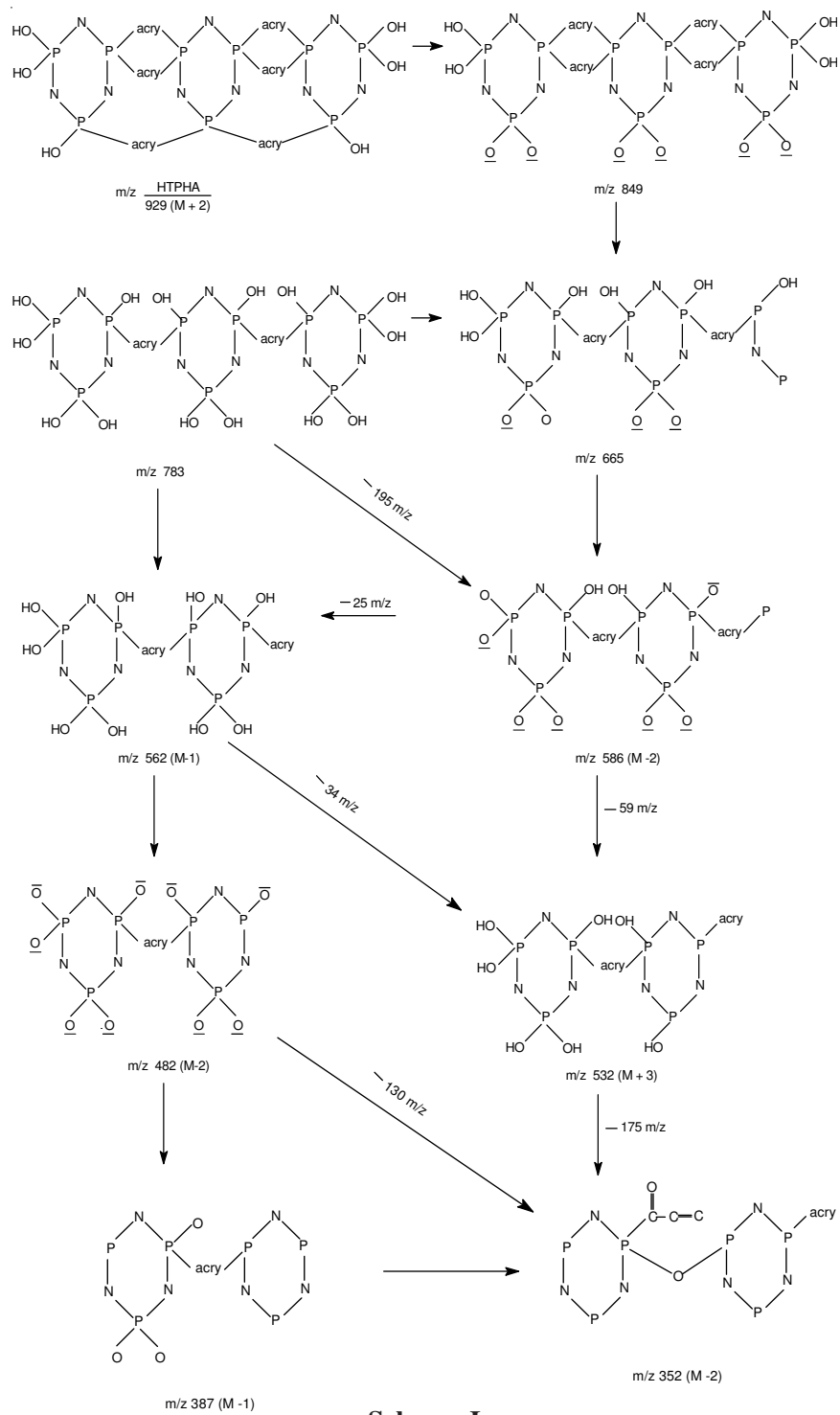
Four molecules of acrylic acid have again reacted with 'b' forming HTPHA, bridging three acrylate ($\text{CH}=\text{CH}-\text{COO}^-$) groups between three P_3N_3 rings. The reaction may be as follows:



The other prominent mass line in its mass spectrum (FAB) may be processed for various fragments as given in **Scheme-I**.

The formation of HTPHA is supported by comparative IR spectra (Fig. 1) in which the vibration, observed at 620 cm^{-1} for symmetric O-H group in $[\text{NPOH}]_2_3$ trimer, has triplicated shifted to 662 cm^{-1} and reduced in intensity, depicting that three O-H groups out of six of $[\text{NPOH}]_2_3$ have reacted to acrylic acid in presence of conc. H_2SO_4 . Similarly, broad band at 1113 cm^{-1} for P-O band in trimer has condensed and divided in HTPHA into three vibrations at 936 , 1009 and 1099 cm^{-1} for P-O band, linked to other group. No frequency has appeared in IR spectrum of $[\text{NP}(\text{OH})_2]_3$ at 1410 cm^{-1} , while the IR spectrum consist a broad and weak band at 1412 cm^{-1} for C=O (ketonic) group linked to $\text{CH}=\text{CH}$ group of acrylic acid and P-O group of HTPHA ring. The vibrations at 2102 and 2251 cm^{-1} for P-N bands in $[\text{NP}(\text{OH})_2]_3$ have diminished and a new broad (weak) band at 2259 cm^{-1} has occurred suggesting the strain on P-N ring during the HTPHA formation, while a sharp frequency (triplet) at 3495 cm^{-1} , found in trimer has lowered, become more intense and broad inferring the bonding of P-OH to acrylic acid, because this vibration is not for free O-H band ($3650\text{-}3590 \text{ cm}^{-1}$)¹³.

The two peaks at 200 nm (49800 cm^{-1}) for charge transfer transition and 333.6 nm (29976 cm^{-1}) due to $p\pi-p\pi$ transition caused by P-N ring are observed in electronic spectrum of HTPHA. The value of oscillator strength 'f' 3.93×10^{-5} esu for spin allowed laporate forbidden transition also indicate the spin orbital coupling between $[\text{NP}(\text{OH})_2]_3$ and acrylic acid. The value of dipole moment¹⁴ found, $\mu = 2.06 \times 10^{-4}$ Dye infers the ionic character of HTPHA (Fig. 2).



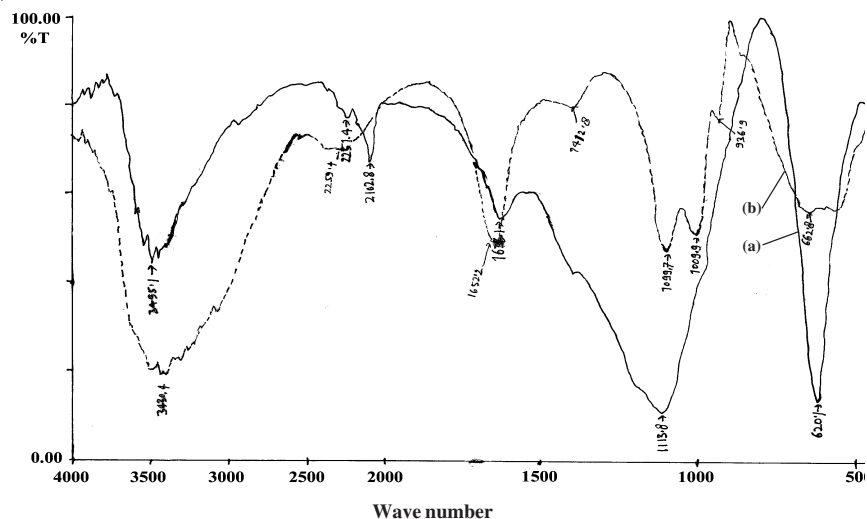


Fig. 1. IR Spectra (a) $[NPCOH]_3$ (b) HTPHA

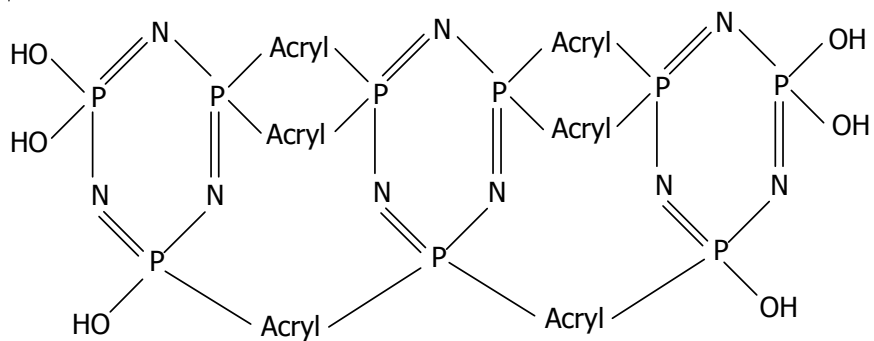


Fig. 2. Structure of HTPHA, $[P_3N_3(OH)_2-COO-C-CH=CH_2]_3$
 Note: $C^+H=CH-COO^-$ is shown as acryl

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