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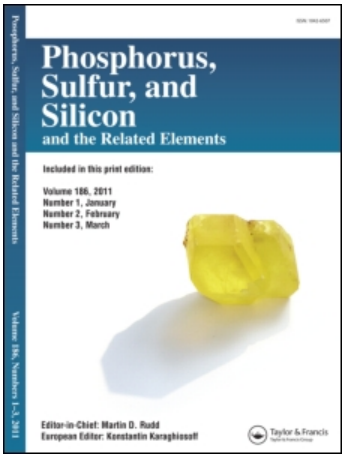

Phosphorus, Sulfur, and Silicon and the Related Elements

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Poly(Alkylene Phosphate)S Related to Nucleic and Teichoic Acids

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POLY(ALKYLENE PHOSPHATE)S RELATED TO NUCLEIC AND TEICHOIC ACIDS

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Abstract Preparation, some properties and applications of the bioanalogous poly(alkylene phosphate)s, obtained according to the methods elaborated in these authors laboratory, are reviewed. Ring-opening polymerization, polyaddition, and two-step polycondensation methods are effective in the synthesis of polymers with various moieties of nucleic and teichoic acids (NA and TA respectively). The major aim of the work is to find relatively simple methods, allowing high molecular weight polymers to be prepared. Thus, preparation of poly(glycerol phosphate), poly(trimethylene phosphate) bearing NA bases, and other related polymers with $\bar{M}_n > 10^4$ are described.

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INTRODUCTION

Backbones of both nucleic and teichoic acids (NA and TA, respectively) are composed of diesters of phosphoric acids: poly(alkylene phosphate)s.

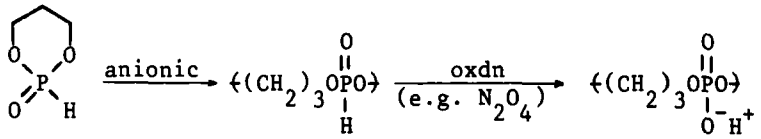
Synthetic polymers of this structure, mimicking NA and/or TA, may find applications, either as models of the parent polymers or as bioanalogous polymers with functions related to these, exhibited by the parent biopolymers. Some of these polymers can be prepared in relatively large quantities by simple polymerization processes. Several poly(alkylene phosphate)s prepared in our group[1,2] have been shown to have unusual cation-binding properties. These polymers are highly selective and can be used as liquid membranes[3], in analogy with some TA functions.

It has to be mentioned, that extensive work has been devoted to the synthesis of models of NA, differing from polymers discussed in this paper. These models contain sugar and/or bases linked to chains with repeating units differing from alkylene phosphate segments. The earlier work was reviewed comprehensively by Jones[4], whereas the more re-

cent work has been discussed by Overberger[5] and by Takemoto[6].

SYNTHESIS OF SIMPLE POLY(ALKYLENE PHOSPHATE)S CHAINS

It seems, that the first high molecular weight, simple poly(alkylene phosphate) was prepared in our laboratory[1]. For this purpose ring-opening polymerization of a cyclic phosphite, with further oxidation of the resulting poly(alkylene phosphite) was used:



(1)

1 2

Poly(trimethylene phosphate) (2) with $\bar{M}_w = 8 \cdot 10^4$, obtained from 1 with $\bar{M}_n = 10^5$, has, according to ^1H-, ^{13}C-, and ^{31}P-NMR, perfectly regular structure. This polymer is soluble in H_2O and highly hydrophilic films can be cast from H_2O or H_2O/CH_3OH solution.

Since this first polymer was prepared, several simple-chain poly(alkylene phosphate)s were synthesized by other methods, involving both polymerization and polycondensation approaches.

Polycondensation, in order to be successful, requires special methods. We elaborated three ways, that can also be applied to the more complicated system, and are involving dialkyl phosphites, tetraalkyldiamide of phosphorous acid or bis(diethylamino)methoxyphosphine as phosphorylating agents.

All of these three methods of phosphorylation have already been known for the low mol.wt compounds. However, in order to obtain relatively high molecular weight polymers ($\bar{M}_n > 10^4$) the new multistep syntheses with dimethyl phosphite had to be applied in order to avoid side reactions.

POLY(ALKYLENE PHOSPHATE)S WITH SUGARS OR ITS ANALOGUES IN THE CHAIN

The next synthetic step, after having established general methods of preparing high molecular weight simple chains, involved preparation of polymers with further elements, existing in NA and TA. Polyphosphates of glycerol or ribitol belong to simplest TA. The former has been prepared by polymerization of the properly substituted cyclic monomer, the corresponding 5-membered cyclic phosphite[7].

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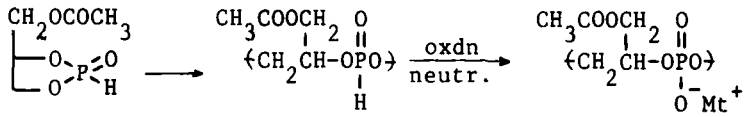
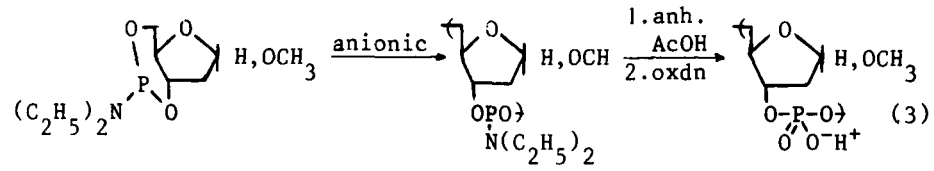


(2)

According to the ^{31}P-NMR spectra these polymers ($\overline{M}_n = 1.5 \cdot 10^4$) do not have unique structures; besides the required head-to-tail enchainment the other two (irregular) linkages are also present.

The deoxyribose containing polymer was also prepared by both polycondensation and polymerization methods. The highest $\overline{DP}_n = 46$ was obtained in the anionic polymerization of cyclic amide of phosphorus acid [8]:

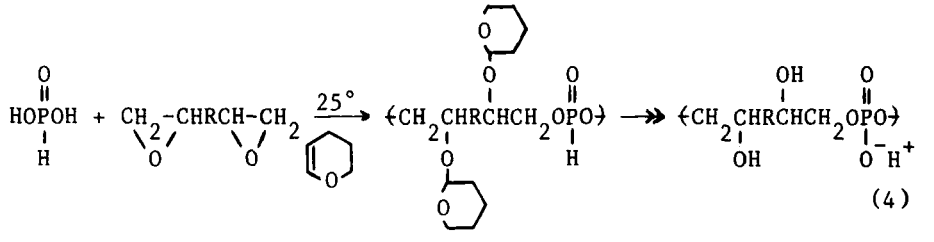


(3)

Closely related to these TA models are polyphosphates bearing cyclic furanoside like rings. Thus, poly(1,4-anhydroerythritol phosphate) has recently been prepared [9].

Polyaddition of H_3PO_3 or H_3PO_4 and their derivatives to diepoxides. A new route to polyphosphates.

Below, a scheme of reaction of H_3PO_3 with diepoxide is shown. In this way high molecular weight product is formed, containing hydroxyl groups in the repeating unit, like in some TA. As diepoxides either diepoxybutane or diglycidyleters of ethylene glycols have been used [10]:



(4)

Dihydropyran has been used to block *in statu nascendi* the hydroxyl groups, to prevent branching due to the subsequent addition of epoxy group.

An interesting novel family of water soluble polymers was prepared by direct addition of phosphoric acid to diepoxides. At certain conditions insoluble but highly swelling in water polymers are obtained.

Linear polymer with less branching were prepared recently by polyaddition of diepoxides to disilyl esters of methylphosphoric acid [11].

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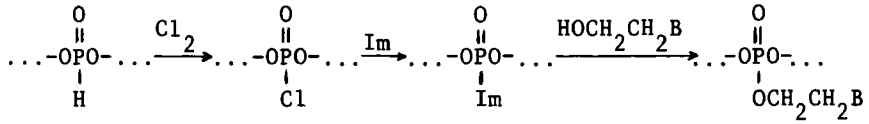
POLY(ALKYLENE PHOSPHATE)S WITH BASES IN THE CHAINS

As indicated in the introduction, several polymers, containing NA elements, nucleosides or bases only, attached to various chains, have been prepared in various laboratories. These polymers are mostly hydrophobic and studies of their interactions in water solutions thus not possible. Only recently synthesis of elements of NA, attached to hydrophilic chains, has been undertaken by Overberger[5] and Takemoto[6].

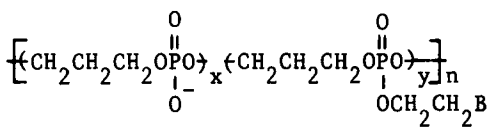
NA analogous polymers have also been prepared in our laboratory by attaching NA bases directly to the P-atom through a spacer. The general method of preparation is based on the following polymer-analogous reactions (only the phosphoryl unit is shown):



(5)

where B = Ade,Ura

Polymers with unique or mixed structures were prepared; e.g.:



; where x>0

When only a fraction of acidic groups in phosphodiester units are substituted, polymers are water soluble[12]. The $\bar{M}_n$ of these polymers are up to $1.2 \cdot 10^4$ (when B is N-substituted imidazole)[13].

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