

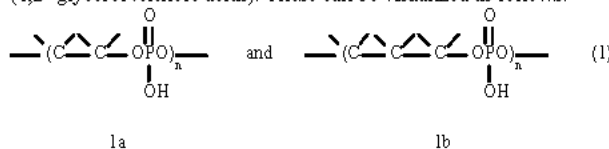
Polymers with Phosphodiester Bonds: from Models of Biopolymers to Liquid Membranes and Polymer-Inorganic Hybrids

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Introduction

The backbones of nucleic and teichoic acids are built on the poly(alkylene phosphate) chains i. e. macromolecules with phosphodiester repeating units with six atoms (nucleic acids) or five (1,2-glycerol teichoic acids). These can be visualized as follows:



The major role of teichoic acids, mostly poly(glycerol-1,2 <or 1-3> phosphate), is transporting Ca^{2+} and Mg^{2+} cations through the cell walls. This is related to the strong binding of these cations by the phosphodiester units [1]. Thus, we elaborated several methods of synthesis of the chains of these structures in order to explore this particular ability [2-5].

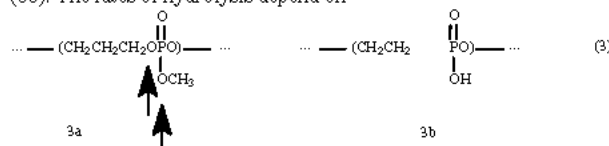
Synthesis of poly(alkylene phosphates).

Ring-opening polymerization of five- and six-membered phosphorous containing monomers;

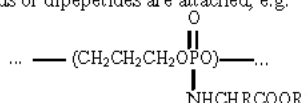
Transesterification of glycols with H-phosphonates, with further oxidation of the poly(H-alkylene phosphonates) to the poly(alkylene phosphates); Polymers with M_n up to $40 \cdot 10^3$ were prepared. Direct polyaddition of H_3PO_4 or H_3PO_3 to diepoxides and catalyzed direct polycondensation of acids with some polyols. If H_3PO_3 was used (diprotic acids), then the resulting in polymers P-H function was oxidized, like in the poly-H-phosphonates. Catalyzed polycondensation is a novel and unexpected method and will be presented with results being still under way [6].

Hydrolytic stability.

Although triesters of phosphoric acids and the corresponding poly(alkyl <aryl> alkylene phosphates) are hydrolytically labile (in trimethyl phosphate the rate of hydrolysis of the first methyl groups is comparable to the rate of hydrolysis of methylbenzoate), hydrolytic stability increases dramatically passing to diesters of phosphoric acid (3b). The rates of hydrolysis depend on



pH and the pH profile for hydrolysis of the structures shown above will be presented. Moreover, the ratio of the rates of hydrolysis of the main and side groups (red and blue arrows in 3a) also depends on pH. When amino acids or dipeptides are attached, e.g.



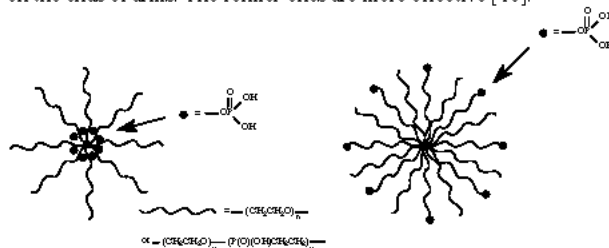
then the pH profile for the ratio of rates is even more pronounced [7,8]. From all of these data it follows, that the hydrolytic stability can be tailored according to the polymer structure.

Biomedical applications.

On the basis of the developed chemistry, and taking into account the controlled degradability of the poly(alkylene phosphates), several groups are working on gene carriers and drug delivery with these polymers [9]. In our laboratories scaffolds are explored based on polyphosphates- CaCO_3 hybrids.

Specific interactions and liquid membranes.

Synthesis of analogues of TA allowed understanding the structure-binding ability relationship. It has particularly been shown that 1,2-glycerol units are specific for Ca^{2+} and 1,3-glycerol units for Mg^{2+} . Further developments lead to the synthesis of polymers, serving as specifically interacting either ionically with simple cations or with other macromolecules by H-bonding. In the liquid membranes star-shaped macromolecules were even more powerful, because of the faster flow when transporting cations (due to smaller hydrodynamic radius). Monoesters of phosphoric acid are either located on the core or on the ends of arms. The former ones are more effective [10].



Another example of specific interaction is a complex formed during polymerization of basic monomers on the poly(alkylene phosphate) taken as a template and complexation with preformed macromolecules, with basic units (e.g.: polyaniline) [11].

Nonspecific interaction with inorganic salts. Polymer-inorganic hybrids.

Ionic-nonionic block copolymers of poly(alkylene phosphates) are powerful modifiers of the crystallization processes of inorganic salts. Various shapes of CaCO_3 crystals were observed during crystallization in presence of these block copolymers with poly(alkylene phosphate) units. Size and dispersity of sizes could also be controlled. Block copolymers are strongly anchored to nanocrystals, forming this way polymer-inorganic hybrid material [12].

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