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

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Introduction

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

- (COOCH2CH2)n
- (CH2CH2)n

The major role of telcho acids, mostly poly(glycerol-1,2- or -3- phosphate), is transporting Ca²⁺ and Mg²⁺ 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 these structures in order to explore this particular ability [2-5].

Synthesis of poly (alkylene phosphates).

Ring opening polymerization of five- and six-membered phosphorus containing monomers:

Transesterification of glycols with H-phosphonates, with further condensation of the poly (H-alkylene phosphonates) to the poly (alkylene phosphates); Polymer with Mn up to 40·10⁴ was prepared. Elaboration of BCPO or BPO₄ diazides and catalyzed, polycondensation of acids with some polyols. If H₂PO₄ was used (diprotic acids), then the resulting in polymers P-F function was oxidized, like in the poly (alkylene phosphates). Catalyzed polycondensation is a novel and unexplored method and will be presented with results being still under way [6].

Hydrolytic stability.

Although all the phosphoric acids and the corresponding poly (alkyl <9> alkylene phosphates) are hydrolytically stable (in trimethyl phosphite the rate of hydrolysis of the first methyl group is comparable to the rate of hydrolysis of methylene), hydrolytic stability increases dramatically passing to diesters of phosphoric acid [3b]. The rates of hydrolysis depend on:

- (CH₂O)n
- (CH₂)n

The 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 dicarboxylic acids are attached, e.g.,

- (CH₂CH₂O)n
- (NHCOOH)ⁿ

then the pH profile for the ratio of rates is even more pronounced [7,3]. 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 carrier and drug delivery with these polymers [9]. In our laboratory scaffolds are explored based on polyphosphates-CaCO₃ hybrids.

Specific interactions and liquid membranes.

Synthesis of analogues of T.A. allowed understanding the structure-binding ability relationship. It has particularly been shown that 1,2-glycerol units are specific for Ca²⁺ and 1,3-glycerol units for Mg²⁺. 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-ship macromolecules were even more powerful, because of the faster flow when transporting cations (due to smaller hydrodynamic radius). Monomers of phosphoric acid are either located on the cores 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 phosphates) taken as a template and complexation with preferred macromolecules, with basic units (e.g. -polycyclic) [11].

Non-specific interaction with inorganic salts. Polymer-Inorganic hybrids.

Linear-organic block copolymers of poly(alkylene phosphates) are powerful modifiers of the crystallization processes of inorganic solids. Various shapes of CaCO₃ crystals were observed during crystallization in presence of these block copolymers with poly(alkylene phosphates) units. Size and dispersion of these could also be controlled. Block copolymers are strongly anchored to nanocrystals, forming this way polymer-inorganic hybrid material [12].

References: