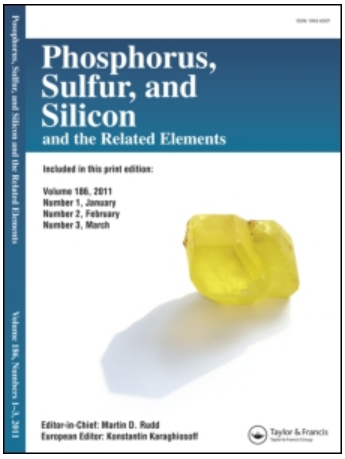

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POLYMERIZATION OF CYCLIC MONOMERS CONTAINING PHOSPHORUS

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The mechanism of polymerization is discussed, in which cyclic esters of phosphoric acid, and related compounds are converted into linear macromolecules, modelling nucleic and teichoic acid backbones. Structures like deoxyribose polyphosphate and glycerol polyphosphate were prepared from the corresponding cyclic compounds.

These polymerizations involve heterolytic breaking of the P—O bond in the corresponding cyclic monomer and proceed by ionic mechanisms. Both 5- and 6-membered monomers have been polymerized. The thermodynamic parameters of the ring-chain interconversion were determined; the 5-membered ring polymerization is driven by the exothermicity of the ring-opening, whereas polymerization of several 6-membered rings is endothermic and allowed because of the positive change of entropy.

Anionic polymerization, and particularly the coordinate-anionic polymerization provides, in contrast to the cationic processes, high-molecular weight polymers with more uniform structure. Anionic polymerization proceeds mostly (in the applied conditions) on the macroion-pairs. The elementary reactions consist of the nucleophilic attack of the paired macroanions on the phosphorus atom in the cyclic monomer molecule. Rate constants of the elementary reactions for the model monomers are discussed.

INTRODUCTION

Polymer chemistry contributes in various ways to the present progress in biology, biochemistry and medicine, providing new methods for preparing and studying macromolecules as well as providing new, highly specified materials. One of these ways, we are particularly interested in, is the synthesis of new polymers, structurally related to the natural biopolymers with poly(alkylenephosphate) main chains. We assume, that for a number of applications it is not necessary to duplicate exactly the actual structure of natural biopolymers in order to provide the desired functions.

SYNTHESIS OF POLYPHOSPHATES: THE CONTRIBUTION OF POLYMER CHEMISTRY

Biopolymers with polyphosphate backbones belong to the most intensively studied areas in chemistry, biochemistry and biology. These are related to polynucleotides, comprising DNA and several types of RNA, as well as to teichoic acids: polyphosphates of glycerol or ribitol and several other sugar-containing polyphosphates of medium molecular weights (up to $1.0 \cdot 10^4$). Teichoic acids (TA) are important constituents of the cell walls, particularly of some bacteria.[1] Phospholipids, the lower molecular weight esters, are also membrane constituents.[2,3] The common chemical

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feature of these products is the presence of the phosphoalkylene unit, either in the repeating units (DNA, RNA, TA) or as one of the chemical groups (phospholipids).

Some research groups are using the already existing organic and polymer chemistry in attempts to formulate the supermolecular structures and entities of biological importance. We think, that this is a perfectly legitimate approach, but, on the other hand, the activity at the borderline between polymer chemistry and biochemistry and biology requires that another gap is filled, namely between the structurally crude macromolecules, prepared till now by polymer chemists, and much more structurally sophisticated biopolymers.

Thus, we have undertaken a program directed toward synthesis of polymeric alkylenephosphates, related to nucleic acids (NA) and teichoic acids (TA). In this paper we summarize our recent and older work mostly on the synthesis and on some applications of these polymers.

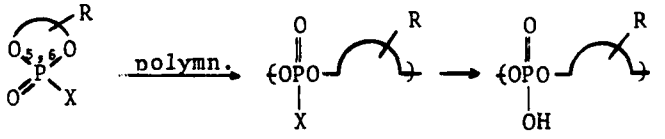
Several authors elaborated methods of modelling DNA by using vinyl or ring-opening polymerization. These works started from polymerizing vinyl monomers derived from NA bases, like vinyl adenine, uracil, or thymine.

More recently Overberger,[4] and Takemoto[5] used other chains, mostly polyamines or polypeptides, to impart hydrophilicity to the corresponding polymers. There are several comprehensive reviews published by Overberger,[6-8] Takemoto[9,10] and Ise[11] on the synthesis, properties, and applications of these polymers. The biological activity of these products, at least according to Pitha, is not promising.[12] This is, in Pitha's judgement,[12] mostly due to their electroneutral properties differing in this basic feature from the natural products: the surface of the cells does not contain groups that could bind strongly enough electroneutral vinyl polymers. The biomolecules that would have to interact are all located inside of the cells and thus isolated from the circulating polymer by membranes that these polymers cannot penetrate.[12]

However, some polymers belonging to this group, like poly-1-vinylcytosine, are effective inducers of interferon in some human cells.[12,13]

Thus, missing in this development there were polyphosphates and poly(alkylenephosphates), modelling the backbone itself and eventually leading to the simpler models of polynucleotides. These contain bases or sugars alone, or all of the components of biopolymers attached to the poly(alkylene-phosphate) polyanion, avoiding the above discussed drawbacks of the electroneutral polymers. Mechanism of both anionic and cationic polymerization of the cyclic phosphates and related monomers leading to these structures has already been discussed by one of us.[14] Some preliminary data on the more advanced models of biopolymeric polyphosphates were also reviewed by us at the meeting on "Phosphorus Chemistry Towards Biology"[15] and at more recent IUPAC Symposium.[16]

Application of the ring-opening polymerization requires some preliminary comments. The final chain is a polyanion, the required ring-opening polymerization is the ionic process, therefore, the corresponding monomer **1** in the form of a cyclic alkylenephosphate cannot be directly polymerized:



(1)

The substituents around the P atom in **1** (the exocyclic groups) should be chosen in such a way that they would not hamper the ionic polymerization and would easily be convertible into the acidic groups in the macromolecule, without altering the polymerization degree. Hopefully, cyclic compounds containing the tetracoordinated penta- or tervalent and tricoordinated tervalent phosphorus atoms offer ample possibilities to fulfil these requirements. Both 5- and 6-membered monomers were studied, remembering that although DNA has 6-atom repeating units, some of the teichoic acids are based on 5-atom units.

THERMODYNAMICS OF POLYMERIZATION

Some synthetic limitations come from the polymerization thermodynamics. Below, in Figure 1, we compiled the ΔH_p and ΔS_p from our works.[17-20] It is remarkable, that the enthalpy of polymerizaion of the six-membered cyclic phosphates, phosphites, and phosphoramidites is close to 0. The sign of ΔH_p may depend on the conditions of polymerization (whether in bulk or in the appropriate solvent).

The significance of the compensation plot for the six-membered cyclic phosphates (we put in Figure 1 data on cyclic six-membered phosphite as well as one five-membered cyclic phosphate) was already discussed by us.[14] Suffice it to say, that the

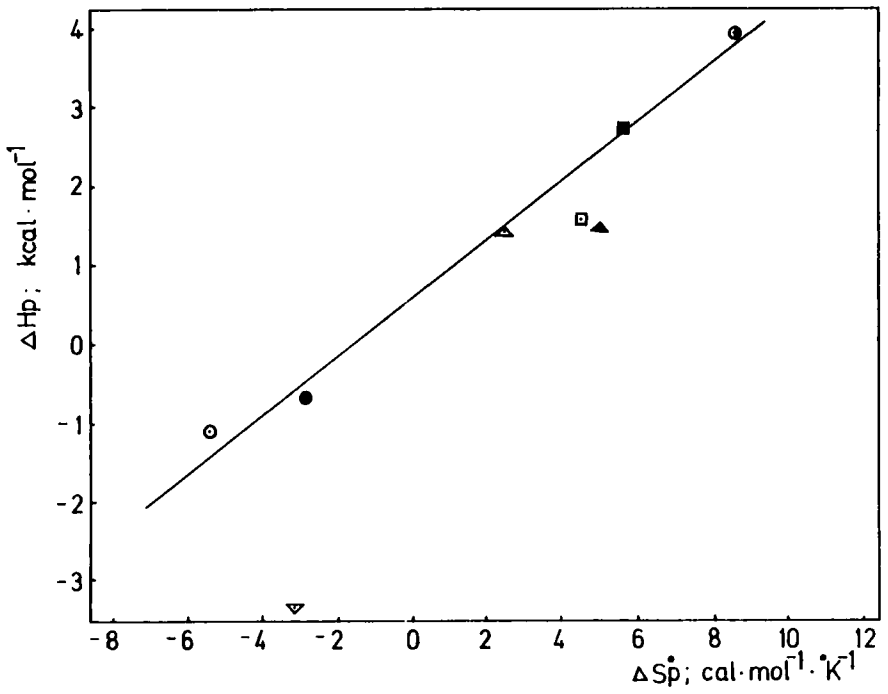
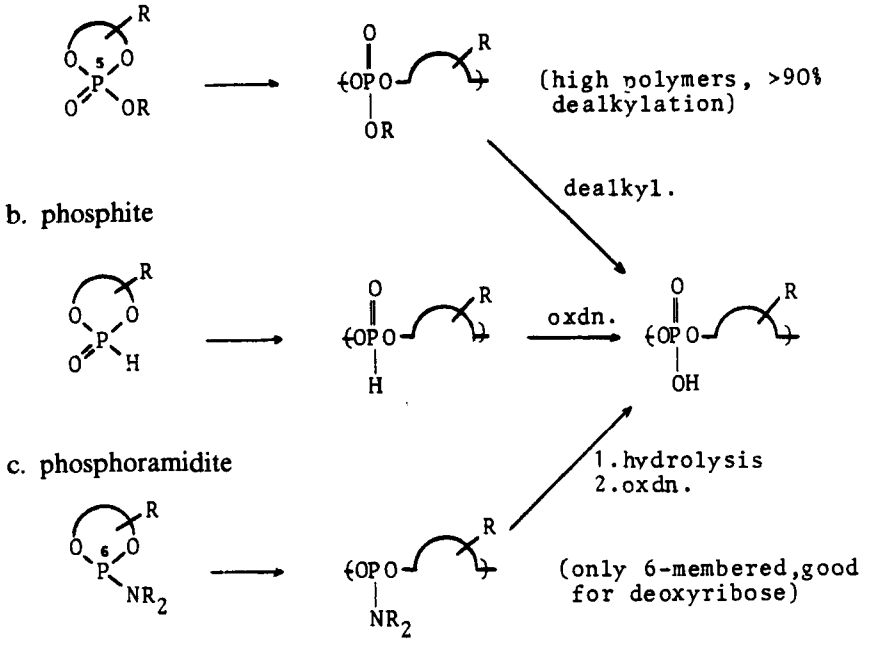


FIGURE 1 Isoequilibrium dependence for 2-oxo-1,3,2 λ^5-dioxaphosphorinanes (6-membered) substituted in a 2-position; substituents: (○): methoxy (cationic), (●): methoxy (anionic), (△): ethoxy, (■): n-propoxy, (◑): trimethylsilyloxy, (□): hydrogen; and for comparison, (▲): 2-*N*,*N*-diethylamino-1,3,2-dioxaphosphorinane, (▽): 2-metoxy-2-oxo-1,3,2-dioxaphospholane (5-membered).[21]

larger the exocyclic substituent the lower exothermicity of polymerization, which is actually driven for larger substituents by the positive change in entropy.

Three major synthetic routes were elaborated in our group, all based on the above-described principle, these are:

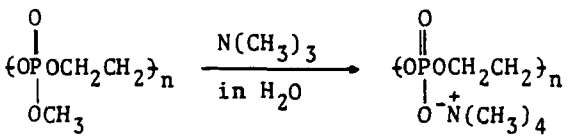


SCHEME 1

The triester route can only be applied for the 5-membered rings. This is because an extensive chain transfer in the much less strained 6-membered ones does not allow us to prepare higher polymers.[17,18] More recently however Nakamura *et al.*[22] observed that monomer with the *t*-C_4H_9O-exocyclic group leads to polymers with $\overline{M}_n$ up to $2.5 \cdot 10^4$.

In our hands, application of the organometallic initiators in the polymerization of 1,3,2-dioxaphospholanes allowed the preparation of the linear polymers with $\overline{M}_n$ in the range 10^4–10^5.

The passage from the poly(alkylalkylenephosphate) to poly(alkylenephosphate) requires dealkylation. This was elaborated for poly(2-methoxy-2-oxo-1,3,2-dioxaphospholane) (poly(methylethylenephosphate)) (**2**) and over 90% of dealkylation was obtained with less than 30% of decrease in the polymer $\overline{DP}_n$:[23]

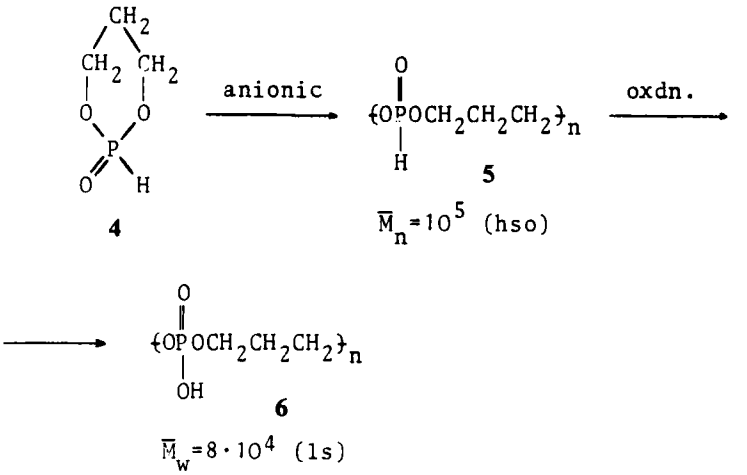


(2)

2 **3**

Further conversion of the polysalt **3** into polyacid is quantitative with applying the cation exchange resin.[23]

Particularly successful has been the cyclic phosphite route. Polymerization of the six-member 1,3-propylene phosphite (**4**), initiated anionically or with aluminum alkyls, gives high linear polymers **5**. Further oxidation yielded the first high molecular weight poly(alkylenephosphate) (**6**) with the sequence of atoms in the main chain identical to biopolymers, namely three carbons, two oxygens, and one phosphorus atom:



(3)

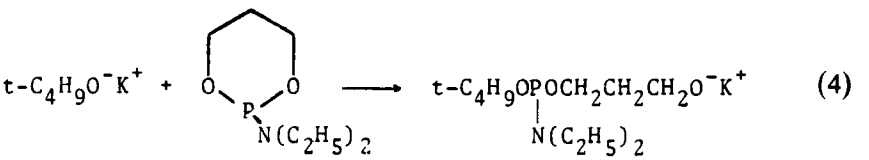
The high molecular weight poly(1,3-propylenephosphate) (**6**) is a solid rubbery product, soluble and stable in water solution. Sometimes it crystallizes during precipitation from solution and its water solubility decreases, apparently due to the formation of the strong intermolecular hydrogen bonds.

SOME ELEMENTS OF THE POLYMERIZATION MECHANISM

Cyclic phosphates and cyclic phosphites polymerize with anionic or "crypto-anionic" initiators (by crypto-anionic we mean the non-ionic initiators like trialkoxy-aluminum, providing either anionic or coordinate anionic polymerization). Cationic polymerization is less favorable; monomers either cannot be polymerized at all or polymerize with some side reactions, decreasing the degree of polymerization of the resulting polymers.

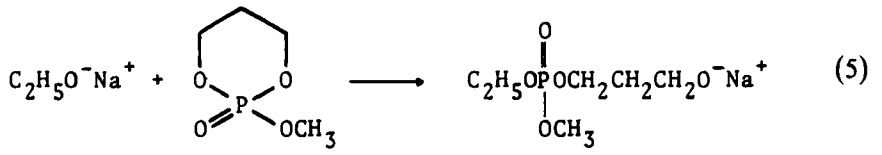
Anionic initiators were shown to react with monomers by a direct nucleophilic attack on the phosphorus atom. This has been established by NMR, allowing us to observe the direct addition of the fragment of initiator to the first monomer molecule.[20]

e.g.:



(4)

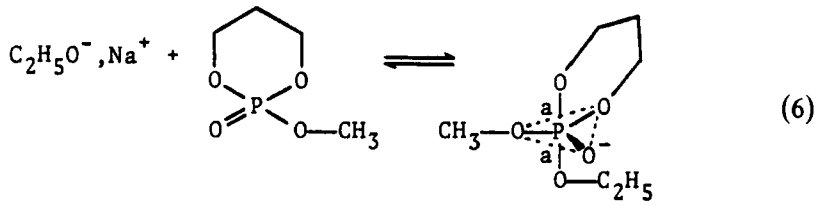
The presence of the t-C_4H_9O-group, attached directly to the P atom (and not, for instance, to the carbon atom of the CH_2 group), follows from the observed multiplicities (due to splitting by a nearby P atom) in ^1H- and ^{13}C-NMR. Similarly, initiation with $C_2H_5O^-Na^+$ of the cyclic phosphate also generates growing alcoholate anion:[17]



(5)

Chain propagation in these conditions is mostly governed by the behavior of the alcoholate anions in the given media. Large size cations have to be used to ensure the breakdown of the nonreactive aggregates.

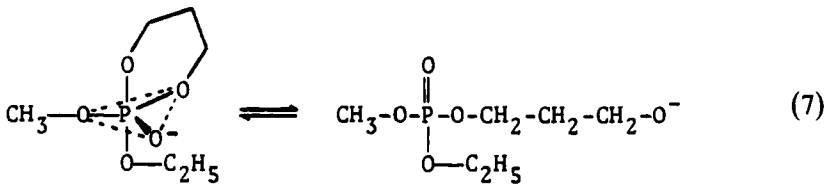
The nucleophilic attack on phosphorus atom leads to the trigonal bipyramid:



(6)

7

In structure 7 the negative charge is distributed among the oxygen atoms and, in principle, the P—O bond could be broken at any ligand, but the apical bonds are preferred because of their enhanced weakness. The six-membered ring is shown in 7 to occupy the axial-equatorial position, because this is the preferred structure the ring compounds have according to the X-ray studies.[24] Therefore, in 7 the apical (marked a in 7) bond is broken, and the new alcoholate anion is produced; this is already a growing center of propagation:



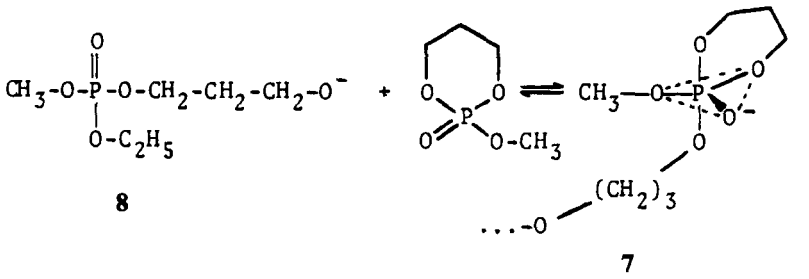
(7)

7 8

Thus formed growing anionic center participates in the chain growth by attacking the phosphorus atom in the next monomer molecule and reproducing a structure similar to 7.

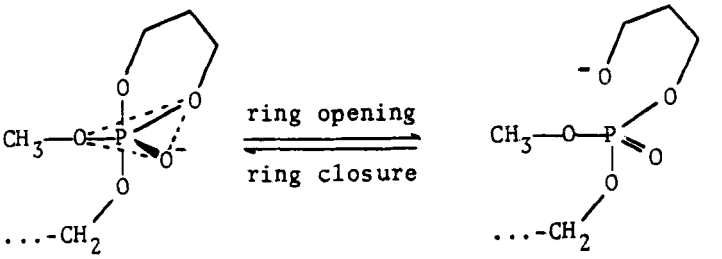
Thus, in short, the growing active species have the structure of the alcoholate anion and the chain propagation consists of an attack by these species on the electrophilic phosphorus atom in the monomer molecule. This attack is directed

along the apical position and leads to the formation of the transition state (or a high energy intermediate product), having the structure of a trigonal bipyramid.



8 **7** (8)

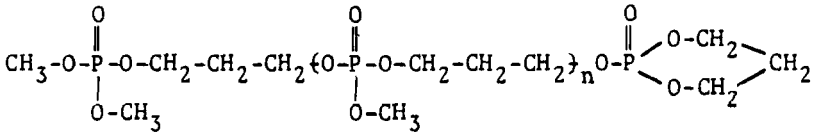
Chain growth is reversible and ring opening ⇌ ring closure equilibrium should use the same reaction pathway. Both involve an attack along the apical position, as shown according to eq. (8) and (9):



(9)

ANIONIC CHAIN TRANSFER

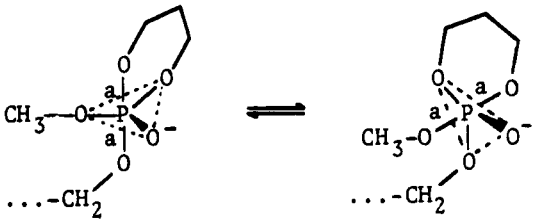
Polymers prepared by anionic polymerization of 2-alkoxy-2-oxo-1,3,2-dioxaphosphorinanes have rather low molecular weights and every macromolecule has one cyclic end-group, as shown in **9**:



9

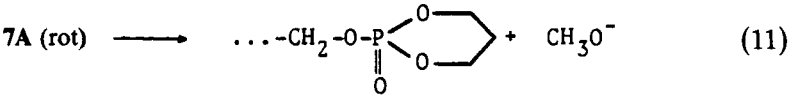
This could easily be explained if we assume that in the transition (intermediate) state **7A** the ring remains intact and that the other axial P—O bond breaks, giving a CH_3O^- anion and a neutral macromolecule with a ring at its end. This would, however, require the exocyclic group to leave from a much more stable equatorial position. A similar problem has been faced in the hydrolysis of the cyclic phosphates and it was proposed that structures similar to **7A** can change the position of substituents by a pseudorotation. Application of this theory to the explanation of the

anionic chain transfer calls for the exchange of the equatorial position exocyclic group with the apical one. This is possible if structure **7A** is allowed to pseudorotate along the P—O^- bond taken as a pivot. This pseudorotation is formally equivalent to changing the positions of the methoxy and polymeric chain substituents:

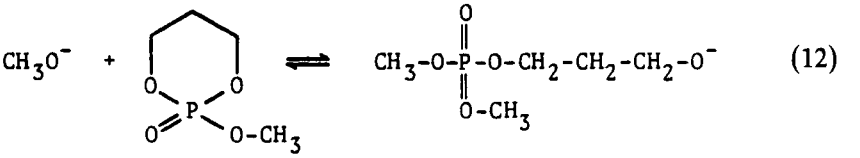


7A **7A (rot)** (10)

The exocyclic methoxy group, located (**7A** (rot)) at the apical position, leaves the growing chain as a methoxy anion, which reinitiates a new chain:



(11)



(12)

Thus, in this way the chain transfer (eq. (11)) provides a cyclic end-group and coupled to reinitiation (eq. (12)) produces a second end-group, a shown in polymer structure **9**.

Although the ionic conditions (ion-pair, size of counterion, free ionic state) can influence the extent of transfer but in order to get high polymers from the six-membered monomers we turned to compounds with exocyclic groups different from the endocyclic ones.

Although other routes are also being studied in our laboratory, in one of the successful preparations of the high molecular weight polymers having the structure of 1,3-propylene phosphates, 2-hydro-2-oxo-1,3,2-dioxaphosphorinane was used as a monomer (eq. (3)). Apparently, formation of the high-molecular weight polymers is connected with the absence of the exocyclic ester group, which is responsible in 2-alkoxy-2-oxo-1,3,2-dioxaphosphorinanes for an extensive chain transfer, as described in previous paragraphs.

In ^{1}H-NMR of **4** absorption of H—P is observed as a doublet, centered at 6.90 δ (J_{PH} = 675 Hz) and in **5** at 6.95 δ (J_{PH} = 725 Hz).

Oxidation of **5** by N_2O_4 in CH_2Cl_2 at 0° according to Denney[25] (eq. (3)), led to the corresponding poly(1,3-propylene phosphate): a highly elastic, transparent solid material.

TABLE I

Polymerization of 2-*N*,*N*-diethylamino-1,3,2-dioxaphosphorinane (M) initiated by t-C_4H_9OK (I) in THF solvent at 25°C[20]

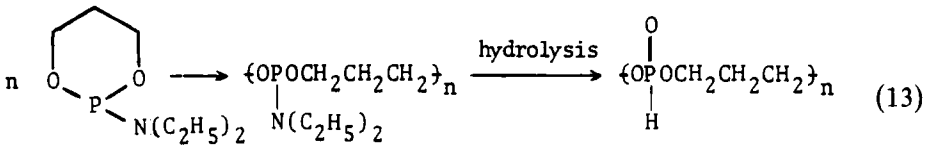
$[M]_o$ (mol · L^{-1})	$[M]_e^*$ (mol · L^{-1})	$[I]_o \cdot 10^2$ (mol · L^{-1})	$\frac{[M]_o - [M]_e}{[M]_o}$ (conversion)	$\overline{M}_n$ calcd	$\overline{M}_n^{**}$ detd
3.7	0.88	4.3	0.76	11.500	12.000
3.25	0.72	6.9	0.78	6.500	6.500
3.2	1.2	4.2	0.62	8.000	9.800
2.74	1.07	5.2	0.61	5.700	6.200

*Determined by ^{31}P-NMR.
**By vpo.

Transformation of **5** into **6** leads to the complete disappearance of the H atoms bound to P atoms, and observed in ^{1}H-NMR as a characteristic doublet with the large coupling constant given above.

We have shown recently,[20] that 2-*N*,*N*-diethylamino-1,3,2-dioxaphosphorinane (**10**) also polymerizes without an appreciable transfer or termination. This clearly follows from the data given in Table I.

Indeed, the calculated polymerization degree, given by the ratio of monomer consumed to the initiator used: $\overline{DP}_n(\text{calcd}) = ([M]_o - [M]_e)/[I]_o$, agrees well with the measured value, $\overline{DP}_n$(detd). Poly(*N*,*N*-diethyl-1,3-propylenephosphoramidite) (**11**) can easily be converted to the corresponding polyphosphite **5** by mild hydrolysis; thus:



(13)

10 **11** **5**

Application of the "phosphoramidite route" has been particularly rewarding in the polymerization of deoxyribose derivatives. The corresponding cyclic phosphite bearing deoxyribose moiety did not polymerize at all whereas its phosphoramidite analogue polymerized easily to the fairly high molecular weight polymer.[26]

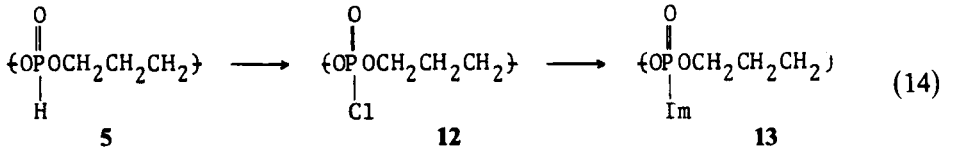
As indicated above (eq. (4)), anionic polymerization of 2-*N*,*N*-diethylamino-1,3,2-dioxaphosphorinane involves nucleophilic attack of an anion on the phosphorus atom in the monomer molecule. As it has recently been shown, anionic polymerization conducted in THF solvent proceeds predominantly on the macroion-pairs when K^+ is the counterion. The dissociation constants of these macroion-pairs are very low ($K_D \simeq 10^{-10}$ mol · L at 25°) and, thus, the concentration of ions is negligible for the applied concentrations of the growing species.

One of us with Kałużyński[27] determined the rate constants of propagation on the macroion-pairs (with K^+ counterion): thus $k_p^{\pm}(25°) = 1.5 \cdot 10^{-3}$ L · mol^{-1} · s^{-1}. This value is several orders of magnitude lower than the rate constant of propagation

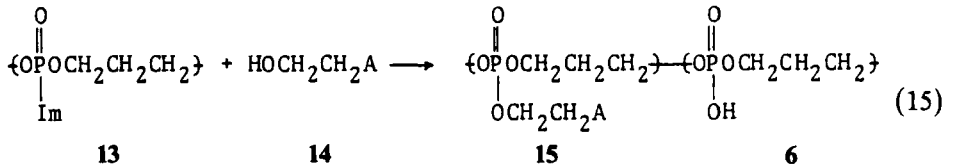
(for the same macroion-pair $\sim CH_2CH_2O^-,K^+$) determined in our laboratory for ε-caprolactone (12.0 $L \cdot mol^{-1} \cdot s^{-1}$) and for ethylene oxide, determined by Kazanski *et al.*[28] This indicates that the electronic factors are more important than the ring strain. The presence of the electron pair on P in phosphoramidite dramatically reduces the rate constant of nucleophilic attack by a macroanion pair.

POLYPHOSPHATES BEARING *N*-SUBSTITUTED ADENINE IN THE SIDE CHAIN

We elaborated recently[29] several synthetic methods of preparing poly(alkylenephosphates) with different side groups. One of these methods, leading to polymers containing nucleic bases moieties in the side chains, is described below, taking adenine as an example;[30]



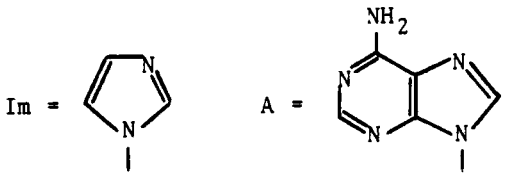
5 **12** **13** (14)



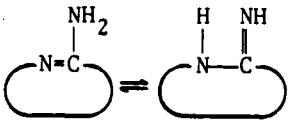
13 **14** **15** **6** (15)

$\leqslant 85\%$ $\geqslant 15\%$

(the complete elimination of units **6** is discussed below) where:



The contribution of units **15** does not exceed 85%. This is because the presence of adenine in two tautomeric forms:



provides the wrong addition of N^6-2′-hydroxyethyladenine to polymer **13** and gives eventually, after the usual work-up of the resulting polymer, the acidic units **6**. When

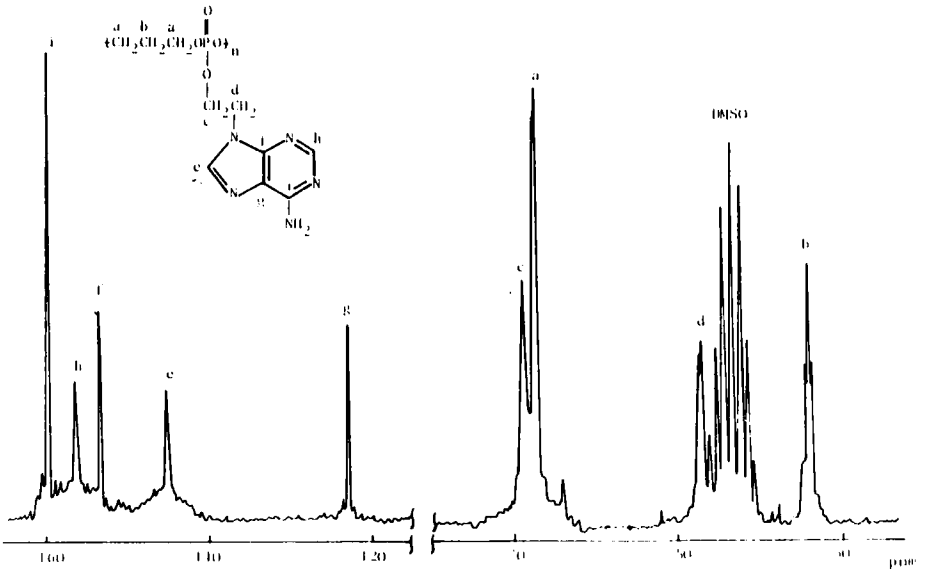
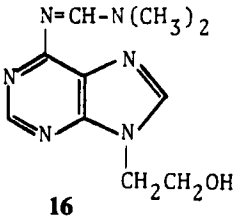


FIGURE 2 ^{13}C-NMR spectrum of polyphosphate with adenine residue (**15**). Recorded as ~ 30% solution in DMSO-d_6 at r.t. 90-MHz Bruker HX-72.[30]

adenine with blocked —NH_2 group (**16**) was applied instead of **14**



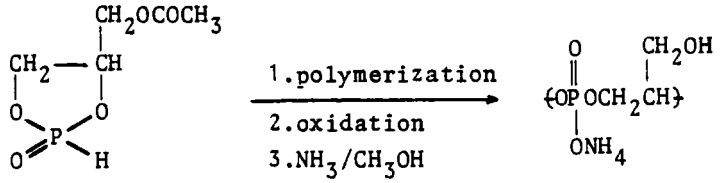
16

the complete conversion of **13** into **15** (the triester structure) was obtained. In the subsequent step the blocking group was removed quantitatively. The resulting polymer **15** is stable in water at room temperature for at least for 1 month, according to the ^{31}P-NMR spectra. ^{13}C-NMR spectrum of **15**, containing 100% of substituted units, is shown above in Figure 2.

APPLICATIONS OF THE RING-OPENING POLYMERIZATION TO THE SYNTHESIS OF BIOPOLYMERS

We have previously described preparation of a simple model of glycerol teichoic acid.[31] This polymer was obtained by the ring-opening polymerization of a cyclic substituted phosphite, namely, 4-acetoxymethyl-2-hydro-2-oxo-1,3,2-dioxaphos-

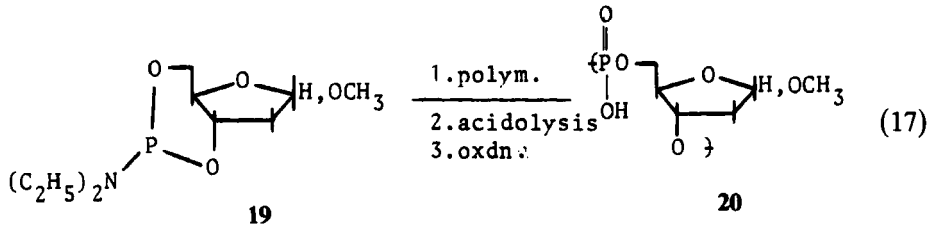
phorinane (**17**). The oxidation of the polymer thus obtained, followed by reaction with methanolic ammonia gave poly(glycerolo-1,2-phosphate ammonium salt) (**18**).



(16)

17 **18**

The phosphoramidite route was applied to the preparation of the poly(alkylenephosphate) bearing deoxyribose units.[26] This polymer was obtained by the ring-opening polymerization of the corresponding cyclic phosphoramidite (**19**). The simple model of DNA chain (**20**) was obtained after the two-step transformation as shown below (eq. (17)):



(17)

19 **20**

Thus, in the previous sections we described application of the ring-opening polymerization, namely the triester, phosphite, and phosphoramidite routes to obtain models of biopolymers with polyphosphate chains: simple poly(alkylenephosphates), teichoic acids, poly(alkylenephosphates) bearing bases and finally the poly(alkylenephosphate) with deoxyribose unit in the main chain.

THE ACTUAL AND POTENTIAL APPLICATION OF POLY(ALKYLENEPHOSPHATES)

The present and potential applications of polyphosphates, related to analogues of the natural products, can be divided into two groups, namely the biodegradable and non-biodegradable polyphosphates:

Biodegradable polyphosphates:

–biologically active polymers: polymers with biological activity originating from their inherent chemical and structural features
–drug carriers, allowing targeting, and then undergoing biodegradation
–components increasing pinocytosis, enhancement of the penetration of the carriers through the cell membranes

Non-biodegradable polyphosphates:

–components of synthetic membranes
–drug delivery systems
–models of enzyme functions and other biopolymeric systems
–chelating agents, including chelating of some metal ions, influencing in this way the antimicrobial activity

The application of the poly(alkylenephosphates) is being studied in several laboratories.

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