Preparation of Poly(alkylene H-phosphonate)s and Their Derivatives by Polycondensation of Diphenyl H-Phosphonate with Diols and Subsequent Transformations

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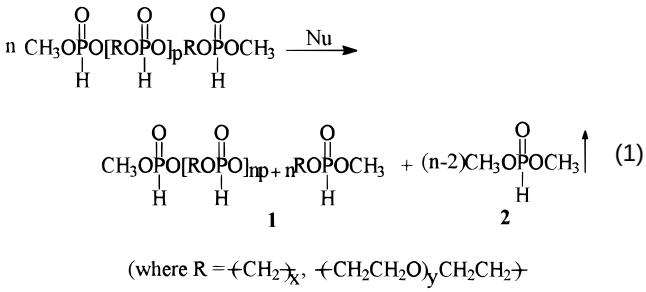
ABSTRACT: A new method of preparation of poly(alkylene H-phosphonate)s (**1**) by polycondensation of diphenyl H-phosphonate with diols such as 1,10-decanediol or tetra(oxyethylene) glycol is described. These polymers can be converted into poly(alkylene phosphate)s—mimicking backbones of nucleic acids and other biomacromolecules. The described method is the only one allowing simple preparation of this important class of polymers. This method eliminates the major side reaction taking place when dialkyl H-phosphonates are used and is related to the C-alkylation and formation of the unreactive ether end groups. Reaction of diphenyl H-phosphonate with alcohols is practically irreversible and can be performed without removing phenol, formed as a byproduct of condensation. It can be carried out in solvent or in bulk at temperature 80−200 °C. Removing phenol enhances, however, formation of polymers with higher $\bar{M}_n$. Polymers with $\bar{M}_n \sim 30 \times 10^3$ were obtained and characterized as such or in the form of their derivatives. Chlorination of **1** with gaseous Cl_2 leads to corresponding poly(alkylene chlorophosphate)s transformed readily into further derivatives, for instance, poly(alkyl alkylene phosphate)s, poly(alkylene phosphate) salts, or/and acids, using the poly(alkylene phosphorimidazolide) as the reactive intermediate.

Introduction

Poly(alkylene phosphate)s are based on backbones mimicking biomacromolecules. These macromolecules can readily be prepared from poly(alkylene H-phosphonate)s (**1**). Phosphonate groups of these polymers can readily be transformed into strong acidic groups (dialkyl phosphoric acid group) linked together by by variety of units, e.g., polymethylenes $(-(CH_2)_nOP(O)(OH)O-)$[1]or poly(oxyethylene)s $(-(CH_2CH_2O)_nP(O)(OH)O-)$[2]. We have recently described a new method of synthesis of **1**, based on polytransesterification of short oligomers, ended with methyl H-phosphonate units:



(where R = $-(CH_2)_x-$, $-(CH_2CH_2O)_yCH_2CH_2-$)

During polytransesterification the dimethyl H-phosphonate (**2**), volatile at the synthesis conditions, is removed from the chain ends and a higher polymer is formed. In this way **1** with $\bar{M}_n$ up to 20×10^3 were obtained. The starting short oligomers are prepared by reacting the corresponding diols with an excess of **2**.

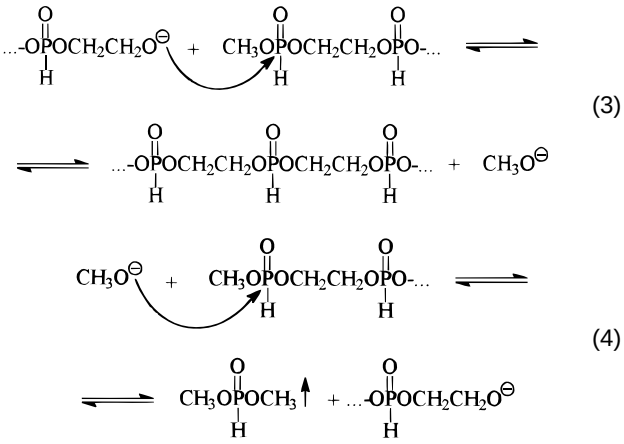
Poly(alkylene H-phosphonate)s (**1**) are particularly versatile functional-reactive polymers, since they contain reactive H-phosphonate units, in which the P-H bond can be converted into a number of derivatives, like P−OH, P−SH, and P−NR_2. Many of these reactions proceed in mild conditions with practically quantitative conversion. These classes of high-molecular-weight polymers have been prepared for the first time (except a limited number of similar polymers prepared previously by a ring-opening polymerization[3,4]). Some of these polymers degrade relatively easily by hydrolysis;[5] other are known to be stable (like DNA) in spite of their polyester backbone. All of these reasons make the poly(alkylene H-phosphonate)s particularly attractive in a number of areas of polymer chemistry.

Polytransesterification involving methyl H-phosphonate end groups has two weak points. The first is typical for this kind of a process: it requires application of the high-purity starting materials. They have to be handled carefully, since, for instance, **2** easily hydrolyzes and a monoester is formed:

$$CH_3OP(O)(H)OCH_3 + H_2O \rightarrow HOP(O)(H)OCH_3 + CH_3OH \quad (2)$$

The formation of monoester breaks the material chain growth and a high-molecular-weight polymer cannot be obtained.

Transesterification proceeds with alcoholate anions as the "growing species": coupling of two macromolecules is followed by re-formation of the growing polyalcoholate anion and re-formation of **2**, as shown below.



(3)

(4)

However, the alcoholate anions react with dialkyl H-phosphonates ambidently, attacking either phospho-

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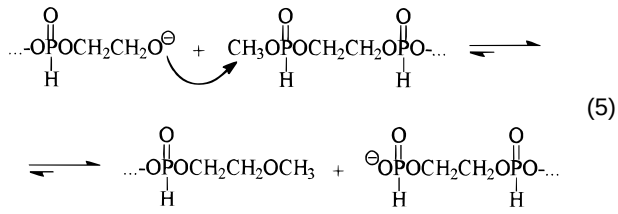
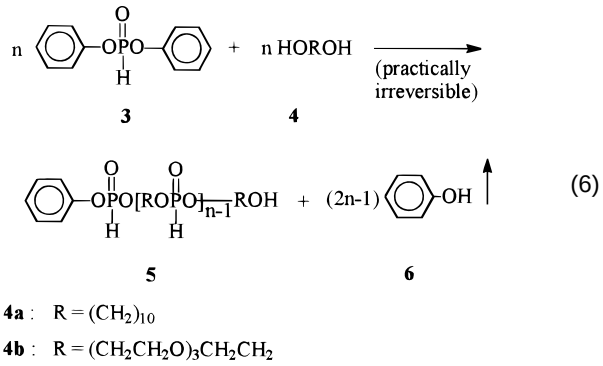
rus (as shown above) or carbon atoms.[6] The latter reaction results in dealkylation and formation of the unreactive chain ends.



(5)

This secondary reaction (dealkylation from the end group) could be eliminated, when the diphenyl H-phosphonate ($C_6H_5OP(O)(H)OC_6H_5$) (**3**) is used. Besides, it has been known that diphenyl H-phosphonate reacts with aliphatic alcohols almost irreversibly.[6] Indeed, elimination of dealkylation allowed preparation of **1** by the simple polycondensation reaction, described in this paper. When medium-molecular-weight polymers are required ($\bar{M}_n \leq 10^4$), then elimination of C_6H_5-OH during the polycondensation is not necessary.



(6)

4a: $R = (CH_2)_{10}$

4b: $R = (CH_2CH_2O)_3CH_2CH_2$

Letters (**a**) and (**b**) in symbols of compounds, in the text below, indicate derivatives of 1,10-decanediol ($R = -(CH_2)_{10}-$) and tetraethylene glycol ($R = -(CH_2CH_2O)_3CH_2CH_2)-$), respectively.

Another possible approach, namely increase of the steric hindrance at the carbon atom to be attacked (e.g., application of the neopentyl H-phosphonates), gave less promising results.

Experimental Part

Solvents. CH_2Cl_2 was purified conventionally and dried finally with a sodium mirror. 1,2-Dichlorobenzene was refluxed for 2 h over P_2O_5 and then distilled and refluxed again for 2 h over CaH_2. Finally 1,2-dichlorobenzene was distilled just before use (bp 182 °C/760 mmHg). C_6H_6 was purified conventionally and dried with and kept over sodium/potassium alloy. $CDCl_3$ was dried with calcium hydride.

Materials. Commercial diphenyl H-phosphonate (Aldrich) was found to contain about 15% phenol, according to the ^1H NMR spectrum. Phenol was removed under vacuum until no signals of phenol were observed in the ^1H NMR spectrum. Then a small grain of sodium was added prior to the final fractional distillation. The fraction at bp 132 °C/0.5 mmHg was collected. The purity was close to 99.0%, according to ^1H and ^{31}P NMR spectra. Diphenyl H-phosphonate was freshly distilled just before polycondensation. Otherwise high-molecular-weight polymer (over 10^4) could not be prepared. 1,10-Decanediol (**4a**) (EGA/CHEMIE) was purified by vacuum distillation in the presence of a small grain of sodium (bp 115 °C/0.5 mmHg). Tetraethylene glycol (**4b**) (Aldrich-Chemie) was purified like 1,10-decanediol. The fraction at bp 130 °C/0.2 mmHg was collected (purity over 99.9%, according to GLC).

Polycondensation. (1) Without Solvent. Polycondensation was performed in a vacuum distillation apparatus equipped with a Teflon-covered magnetic stirring bar and a large Rotaflo stopcock, separating the distillation flask from the condenser, which was attached to the vacuum through a trap immersed in liquid N_2. Equimolar amounts of diphenyl H-phosphonate and diol (1,10-decamethylene or tetraethylene) were placed and stirred together in this apparatus (with or without ~0.5% wt sodium used as catalyst) for 1 h at 100 °C/25 mmHg. Phenol formed during the reaction was continuously distilled off. During the next hour the temperature was gradually increased to 150 °C and the pressure was decreased to 0.01 mmHg. The viscosity of the reaction mixture increased rapidly in the last 15 min, and stirring was not possible when the mixture reached 200 °C. The final product was a transparent, colorless solid.

(2) In Solvent (without Removing Phenol). In Benzene. 1,10-Decanediol (0.59 g, 0.0034 mol) and diphenyl H-phosphonate (0.80 g, 0.0034 mol) in 9 mL of dry benzene were placed in an one-neck round bottom flask and refluxed under dry Ar, avoiding any contact with the atmosphere. The $^{31}P\{^1H\}$ NMR spectra were recorded after various time intervals until no further changes in the spectra were observed. The total reaction time was over 100 h.

In 1,2-Dichlorobenzene. Diphenyl H-phosphonate (1.66 g, 0.0071 mol), 1,10-decanediol (1.24 g, 0.0071 mol), and 3.8 mL of 1,2-dichlorobenzene were placed in a glass ampule with a Rotaflo stopcock and heated at 140 °C in an Ar atmosphere until no more changes in spectra were observed (about 20 h). The $^{31}P\{^1H\}$ NMR spectra were recorded after 0.5, 1.5, 6.5, and 19.5 h.

Poly(alkylene chlorophosphate)s were prepared by chlorination of **5a** and **5b** alike by the known procedure of chlorination of the low-molecular-weight dialkyl H-phosphonates.[8] Dry Cl_2 was passed through gels of **5a** or **5b** swollen in CH_2Cl_2 (30 mmol of repeating units of polymer in 15 mL of CH_2Cl_2). Gels were dissolved during chlorination. Addition of Cl_2 was stopped at the first appearance of a persistent yellow color. At this stage the original absorption in $^{31}P\{^1H\}$ NMR spectra (corresponding to the $-OP(O)(H)O-$ units) disappeared and instead a singlet due to the $-OP(O)(Cl)O-$ units appeared. The excess of Cl_2 was removed under vacuum until a colorless solution resulted. This solution was further used for preparation of different derivatives without polymer isolation. Imidazole derivatives **8a** and **8b** were prepared by a direct reaction of crude poly(alkylene chlorophosphate)s **7a** and **7b** with an excess of imidazole, avoiding contact with the atmosphere, according to the procedure described by us previously.[9]

Poly(1,10-decamethylene phosphoric acid) (**9a**) was prepared by acidic hydrolysis of **8a**: 5 g of crude **8a** (not isolated from the reaction mixture after preparation) in 20 mL of CH_2Cl_2 was poured into 100 mL of 1 M HCl with vigorous stirring. The white precipitate was separated by filtration, washed twice with 50 mL of 1 M HCl and several times with water until neutral pH was reached, and finally dried at 50 °C under reduced pressure.

Poly(1,10-decamethylene phosphate) sodium salt (**10a**) was prepared by basic hydrolysis of **8a**: 5 g of crude **8a** (16 mmol of repeating units) in 20 mL of CH_2Cl_2 was poured into 100 mL of 0.2 M Na_2CO_3 solution. Then the water layer was ultrafiltrated in the Amicon Ultrafiltration Stirred Cell (200 mL) using a membrane with the molecular weight cutoff equal to 1000. The resulting mixed HIm^+/Na^+ polymer salt was converted into Na^+ salt using cation exchange resin Dowex 50W in the Na^+ form.

Poly(tetra[oxyethylene] phosphoric acid) (**9b**) was prepared from the mixed HIm^+/Na^+ salt of poly(tetra[oxyethylene] phosphoric acid) (prepared according to the above procedure) by passing its solution in water through the column with cation exchange resin Dowex 50W (in the H^+ form). The final product was obtained by evaporating off water and then dried at 50 °C under reduced pressure.

Poly(methyl tetra[oxyethylene] phosphate) (**11b**) was prepared by dropping of a mixture of 0.75 mL (0.019 mol) of methanol and 1.5 mL (0.019 mol) of pyridine in 10 mL of CH_2Cl_2 into a solution of 5 g (0.018 mol) of **7b** in 15 mL of CH_2Cl_2 at 25 °C. After 24 h volatile components were distilled off

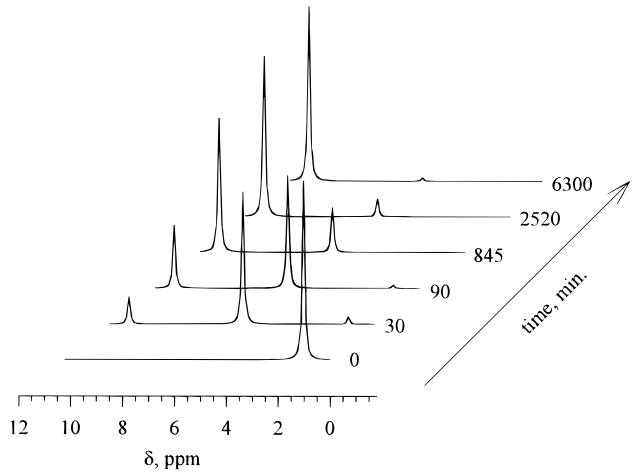


Figure 1. Development of the $^{31}P\{^1H\}$ NMR spectra during polycondensation of diphenyl H-phosphonate (**3**) with 1,10-decanediol (**4a**). Conditions: $[\mathbf{3}]_0 = [\mathbf{4a}]_0 = 0.36$ mol/L, in boiling C_6H_6, without catalyst added. Chemical shifts of signals at $\delta = 1.18$, $\delta = 5.16$, and $\delta = 8.79$ ppm correspond to the P atoms in **3**, polymer end groups (PhOP(O)(H)O−...), and polymer repeating units (−OP(O)(H)O$(CH_2)_{10}$−...), respectively.

under vacuum at room temperature. Pyridinium hydrochloride was removed by ultrafiltration of an aqueous solution of **11b** (carried out until no precipitate was detected after addition of $AgNO_3$). Pure product was obtained by freeze drying the resulting solution.

Measurements. ^1H (200 MHz), ^{13}C (50 MHz), and ^{31}P (81 MHz) NMR spectra were recorded with a Bruker AC200 spectrometer using $CDCl_3$ (and D_2O in the case of salts) as solvent. All spectra were recorded at room temperature, and standard acquisition parameters were applied. Whenever the quantitative data are given, they are of ±15% accuracy due to the conditions of spectra acquisition.

Molecular Weight Measurements. The number-average molecular weights ($\bar{M}_n$) were measured on a Knauer membrane osmometer in highly purified dry CH_2Cl_2 and by size exclusion chromatography (SEC) on the basis of PEG standards calibration. SEC analyses were performed using an LKB 2150 HPLC pump and TSK G3000 HXL column. A Wyatt Optilab 903 interferometric refractometer was applied as a detector. $CHCl_3$ was used as eluent. The weight-average molecular weights ($\bar{M}_w$) were determined with a MALLS Dawn F laser photometer (Wyatt Technology Corp.) in H_2O solvent.

Gas Liquid Chromatography (GLC). GLC measurements were performed using a Hewlett Packard 5890 apparatus and HP17 10 m column.

Results and Discussion

The high purity of starting compounds, namely of diphenyl H-phosphonate (**3**) and of the used glycols, is of the utmost importance. If one fails to prepare the pure compounds (cf. Experimental Part and below), to analyze them correctly, and then to proceed with polycondensation in an anhydrous and (preferably) oxygen free atmosphere (to prevent oxidation of the P−H function), then the synthesis will not lead to a high-molecular-weight polymer.

In the $^{31}P\{^1H\}$ NMR spectrum of the purified **3** there is sometimes a small peak at $\delta = 128.6$ ppm, which we assigned to triphenyl phosphite, which is formed by disproportionation of diphenyl H-phosphonate.[10] This impurity was effectively removed to the level below 1% by vacuum distillation. Starting from a not purified **3** polycondensation results in polymers of $\bar{M}_n$ below 10^3. Purification of **3** is described in detail in the Experimental Part. Application of purified **3** gives polymers with $\bar{M}_n$ well above 10^4.

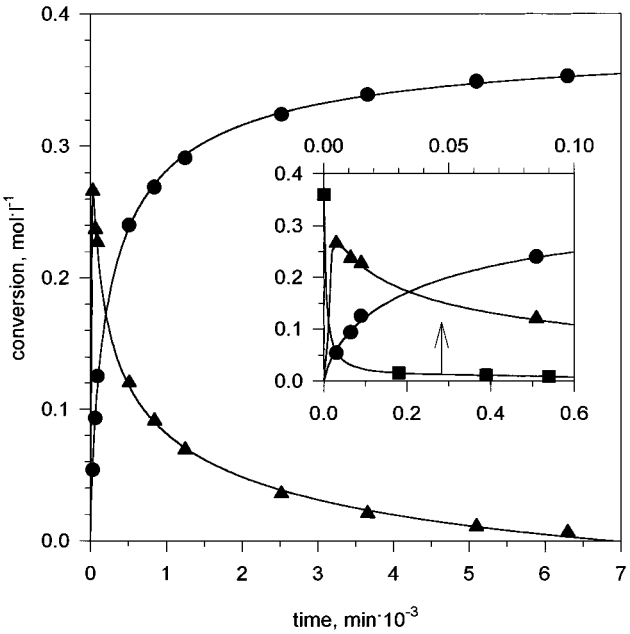


Figure 2. Kinetics of polycondensation of **3** with **4a**: (■) decreasing **3** concentration; (▲) changing polymer end groups concentration; (●) increasing **5a** concentration. Conditions are as in Figure 1.

Polycondensation. (1) In Solution. Two different modes of polycondensation were developed. The solution polycondensation was carried out without removing phenol (**6**) from the reaction mixture. We conducted polycondensation in benzene solution at 80 °C and in 1,2-dichlorobenzene at 140 °C (both systems were well protected from the atmosphere). At these conditions we could obtain $\overline{DP}_n$ up to 50 (i.e., $\bar{M}_n = 11\,600$ for 1,10-decamethylene glycol) (according to the end groups measured at $^{31}P\{^1H\}$ NMR spectra with standard conditions of spectra acquisition; thus it is within ±15% of the measured value[7]). Polycondensation takes more than 100 h although polymer is obtained directly in solution.

When polycondensation was performed according to this method (eq 6), we could easily follow conversion of **3** into the polymer end groups and then to the monomer units in the $^{31}P\{^1H\}$ NMR (chemical shifts in the ^{31}P NMR spectrum for the corresponding phosphorus atoms are given in Figure 1).

The corresponding typical kinetic curves of polycondensation **3** with **4a** in benzene at 80 °C and in 1,2-dichlorobenzene at 140 °C are given in Figures 2 and 3, respectively.

(2) In Bulk. Polymerization in bulk, with continuous removal of phenol (**6**), gives the highest $\bar{M}_n$ (up to 35×10^3 when tetraethylene glycol was used); however, the product at the end of the reaction is solid even at 200 °C and it takes some time to dissolve it for further treatment. The whole process (cf. Experimental Part) takes no more than 2.5−3 h and does not require (in contrast to transesterification[7]) any catalyst. Polycondensation in bulk is conducted at 100 °C with a continuous increase of temperature to 150 °C over 2−2.5 h and then kept at this temperature for approximately 1 h.

All of the polycondensations in bulk were conducted under vacuum in a flask fitted with a Rotaflo stopcock with a side arm condenser, attached to the vacuum line.

Poly(H-phosphonate)s of 1,10-decamethylene glycol (**5a**) and tetraethylene glycol (**5b**) were prepared by this method.

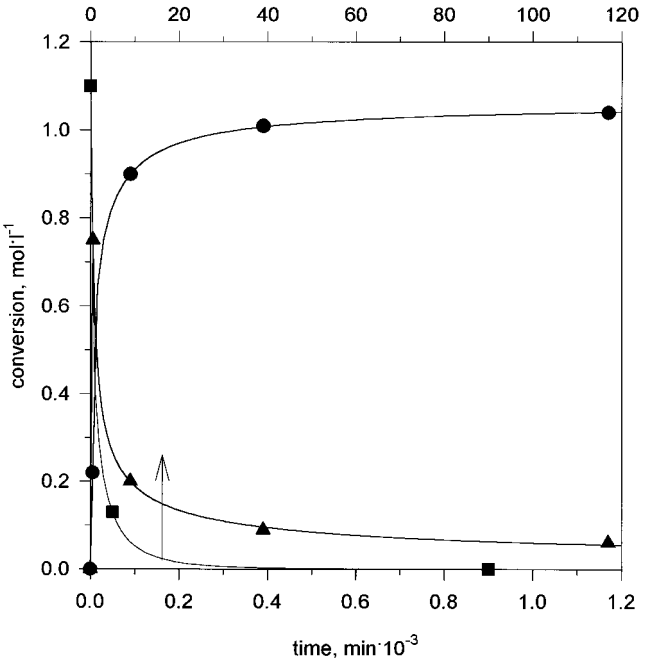
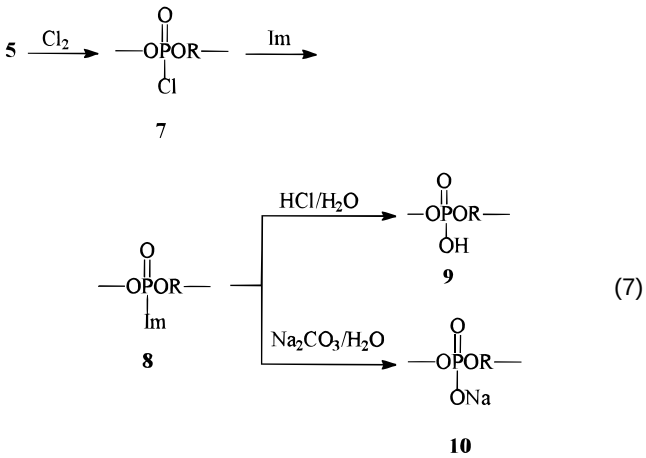


Figure 3. Kinetics of polycondensation of **3** with **4a**: (■) decreasing **3** concentration, (▲) changing polymer end group concentration; (●) increasing of **5a** concentration. Conditions: $[\mathbf{3}]_0 = [\mathbf{4a}]_0 = 1.1$ mol/L in 1,2-dichlorobenzene at 140 °C, without catalyst added.

Chemical shifts in ^{1}H, ^{13}C, and ^{31}P NMR spectra of the obtained polymers **5a** and **5b** are given in Table 1.

There was only one signal in the ^{31}P{^{1}H} NMR spectrum corresponding to the polymer repeating units,[1,2,4] indicating that $\overline{DP}_n$ is above 10^2.

Derivatives. Polymers **5a** and **5b** were transformed to polyacids **9a** and **9b** via P−Cl (**7a**, **7b**) and P−Im (**8a**, **8b**) derivatives (eq 7).



(7)

Thus obtained polymers were chlorinated in CH_2Cl_2 solution with gaseous Cl_2 without isolation from the reaction mixture. In the ^{31}P{^{1}H} NMR spectra of these polymers only one signal at $\delta = 5.09$ ppm (**7a**) or $\delta = 5.26$ ppm (**7b**) was observed.

The chlorinated polymers (**7**) were transformed to their P−imidazole (**8**) derivatives in a reaction with an excess of imidazole. The imidazole derivatives (**8**) were then hydrolyzed and converted into free acids (**9**) by precipitation into 1 M HCl or they were converted to their sodium salts (**10**) by treating **8** with Na_2CO_3 solution. This is the best way of preparing **9** and **10**. Some other methods were less successful. For instance,

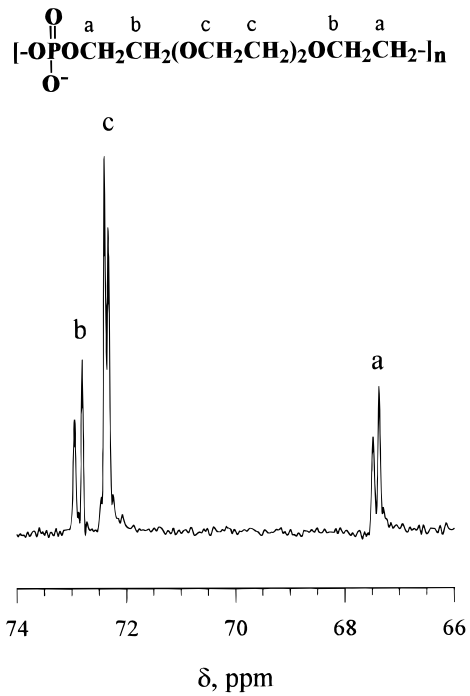


Figure 4. ^{13}C{^{1}H} NMR spectrum of poly(sodium tetra[oxyethylene] phosphate) (**10b**), 5% solution of polymer in D_2O. Chemical shifts of signals are given in Table 2.

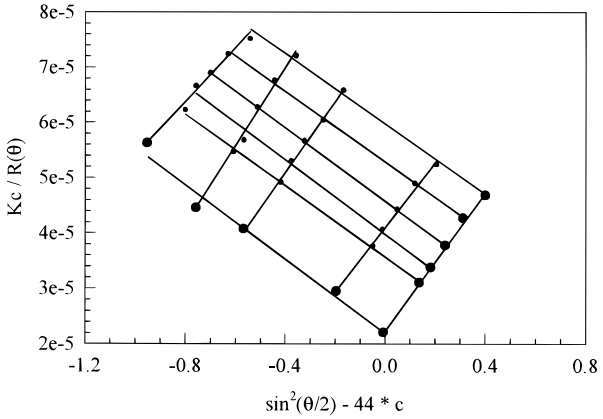


Figure 5. Zimm plot of the poly(tetra[oxyethylene]phosphoric acid) (**9b**). *c* is the concentration (in g/L), Θ the scattering angle, *K* an optical constant, and *R*(Θ) the excess scattered intensity ratio of the solution of concentration *c* and at angle Θ. H_2O at 25 °C was used as the solvent for measurement.

direct hydrolysis of the P−Cl derivatives provides pyrophosphoric intermolecular units, difficult to hydrolyze. These units were never detected when P−imidazole derivatives were applied. Salts **10** were also obtained by dissolving **9** in the corresponding base (e.g., NaOH).

^{1}H and ^{13}C{^{1}H} NMR spectra of poly(sodium salts) (**10**) contain only signals corresponding to polymer repeating units (see Table 2).

The ^{13}C{^{1}H} NMR spectrum of poly(sodium [tetraoxyethylene] phosphate) (**10b**) is given in Figure 4. In the ^{31}P{^{1}H} NMR spectrum, besides a signal of the polymer repeating units ($\delta = 1.18$ ppm), there is a small signal at $\delta = -0.32$ ppm assigned to the trialkyl phosphoric groups. These are most probably the branching points, which can originate from the triphenyl phosphite present (an impurity) in the substrate diphenyl H-phosphonate or formed by the disproportionation reaction.[10]

Molecular Weight Determination. Values of $\bar{M}_n$ of one of the samples of **5b** and of poly(methyl tetra-

Table 1. Chemical Shifts in ^1H, ^{13}C, and ^{31}P NMR Spectra of Poly(H-phosphonate)s 5a and 5b

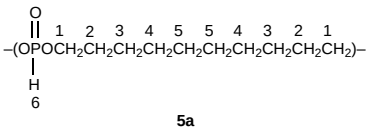
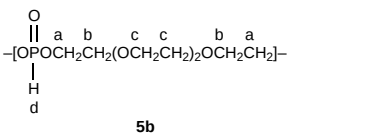
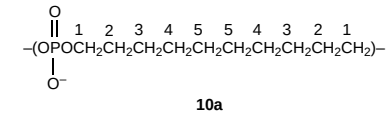
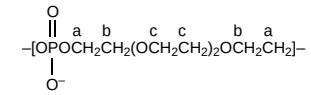
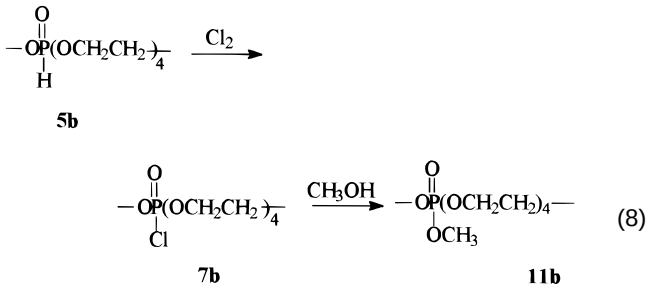
polymer structure	NMR spectra, δ in ppm		
	^1H	^{13}C	^{31}P
 **5a**	1.2−1.5 (m) (H_3, H_4, H_5), 1.6−1.8 (m) (H_2), 4.1−4.4 (m) (H_1), 6.76 (d, $\lvert^1J_{PH}\rvert$ = 691.8 Hz) (H_6)	25.36 (m) (C_3), 28.94 and 29.25 (two s) (C_4, C_5), 30.28 (d, $\lvert^3J_{PC}\rvert$ = 6.33 Hz) (C_2), 65.59 (d, $\lvert^2J_{PC}\rvert$ = 5.58 Hz) (C_1)	8.56
 **5b**	3.4−3.8 (m) (H_b, H_c), 4.0−4.4 (m) H_a,6.90 (d, $\lvert^1J_{PH}\rvert$ = 716.3 Hz) (H_d)	64.51 (d, $\lvert^2J_{PC}\rvert$ = 5.73 Hz) (C_a), 69.92 (d, $\lvert^3J_{PC}\rvert$ = 4.23 Hz) (C_b), 70.31 (m) (C_c)	9.84

Table 2. Chemical Shifts in the ^1H, ^{13}C, and ^{31}P NMR Spectra of Polyphosphates 10a and 10b

polymer structure	NMR spectra, δ in ppm		
	^1H	^{13}C	^{31}P
 **10a**	1.1−1.5 (m) (H_3, H_4, H_5), 1.5−1.7 (m) (H_2), 3.7−3.9 (m) (H_1)	28.31 (s) (C_3), 32.41 and 32.48 (two s) (C_4, C_5), 33.00 (d, $\lvert^3J_{PC}\rvert$ = 6.63 Hz) (C_2), 68.70 (d, $\lvert^2J_{PC}\rvert$ = 5.18 Hz) (C_1)	1.17
 **10b**	3.5−3.7 (m) (H_b, H_c), 3.9−4.0 (m) (H_a)	67.43 (d, $\lvert^2J_{PC}\rvert$ = 5.38 Hz) (C_a), 72.37 (s) (C_c), 72.88 (d, $\lvert^3J_{PC}\rvert$ = 7.32 Hz) (C_b)	1.18

[oxyethylene] phosphate) (**11**), prepared from the same **5b** by chlorination and subsequent methanolysis (eq 8), were determined by membrane (high speed) osmometry. The following results were obtained: $\bar{M}_n$ (**5b**) = 32 800 ($\overline{DP}_n$ = 137) and $\bar{M}_n$ (**11**) = 38 200 ($\overline{DP}_n$ = 141).

SEC of **5b** gave $\bar{M}_n$ (**5b**) = 40 000 (on the basis of PEG standards).



5b **7b** **11b** (8)

$\bar{M}_n$ and $\bar{M}_w$ of polyacid **10b** (obtained from another sample of **5b**) were determined using membrane osmometry and MALLS, respectively. The corresponding Zimm plot is given in Figure 5. The resulting values ($\bar{M}_n$ = 21 100, $\overline{DP}_n$ = 82 and $\bar{M}_w$ = 46 200, $\overline{DP}_w$ = 180) gave the molecular weight distribution $\bar{M}_w/\bar{M}_n$ = 2.19, close to the value expected for polycondensation polymers. $\bar{M}_w$ could be measured directly in water, because polyacids (poly(alkylene phosphates)) are strong acids, approximately equal in acidity to the first acidic group of H_3PO_4. Therefore, they should not be associated in solution.

Conclusions

Polycondensation of diphenyl H-phosphonate with diols gives high-molecular-weight poly(alkylene H-phosphonate)s ($\bar{M}_n$ up to 3×10^4) and allowed elimination of the side reactions, inevitable when dialkyl H-phosphonates are used. It was shown that these reactive polymers can readily be transformed into a series of derivatives including poly(alkyl alkylene phosphate)s and poly(alkylene phosphoric acid)s, without decreasing their polymerization degrees.

References and Notes

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