POLIMERY

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Telechelic oligomers made from ethylene oxide and phosphoric acid. Structure and transformation into organoaluminum polymers

The paper is dedicated to Professor Bożena Kolarz.

Summary — The reaction of phosphoric acid with ethylene oxide (EOX) in organic solvents or water has been studied at -5 °C to +30 °C by means of NMR and MALDI—TOF spectroscopy. Linear telechelic oligomers comprising 4—25 ethylene oxide monomeric units and 3 terminal hydroxyl groups were found to be the main products of this reaction. Side products include cyclic esters, condensation products containing 2—3 phosphorus atoms in the chain and oligodiols. The esters are stable at temperatures up to 170 °C; and in water exhibit strong resistance to hydrolysis up to approx. 80 °C. Aqueous medium at 100 °C in presence of aluminum oxohydroxide in the form of boehmite leads to hydrolysis of one ester bond, in situ yielding a diester, which reacts with the boehmite to form hybrid phosphate-alumoxane structures; with molar ratio of P:Al in such polymers of approx. 1.1. A transparent colloidal dispersion with a broad molecular weight spread of the polymer component and low limiting viscosity number (about 0.002 cm³/g) is formed. Lowest molecular weight fractions form true solutions in water and DMSO.
**Key words:** phosphoric acid, ethylene oxide, oligomeric phosphates, boehmite, hybrid phosphate-alumoxane polymers, chemical structure, MALDI TOF.

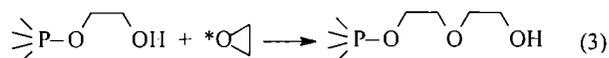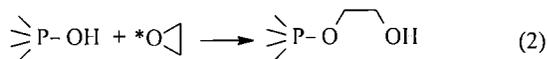The reaction of phosphoric acid with oxiranes leads to the formation of telechelic esters containing oxyalkylene units terminated with hydroxyl groups. The mechanism of oxiranes addition to the acids of phosphorus in anhydrous non polar media and the kinetics of ethylene oxide (EOX) addition to various OH groups present in these systems were studied in the early nineties by Biela, Kubisa and Penczek [1—3] by means of NMR spectroscopy. It was found that in the absence of
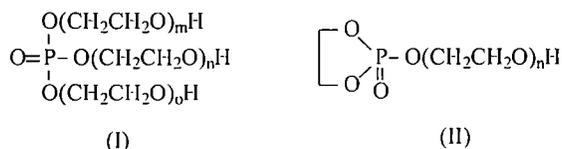
external acidic catalysts the reaction is self catalyzed by the P-OH group and can be described in terms of "activated monomer" polymerization. Monomer activation does not require ionization of the acid and proceeds predominantly with EOX activated by hydrogen bond formation:

$$\left[\mathord{>}O + H_3PO_4 \rightleftharpoons \left[\mathord{>}O\text{-}\text{-}H\text{-}O\text{-}P\mathord{<} = \left[\mathord{>}O^* \right. \right. \right. \tag{1}$$
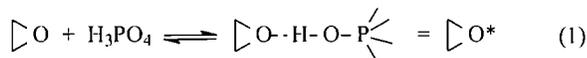
Further elementary steps involve addition of the activated monomer to the P-OH and C-OH bonds:

$$\mathord{>}P\text{-}OH + {}^*O\mathord{<} \longrightarrow \mathord{>}P\text{-}O\frown OH \tag{2}$$

$$\mathord{>}P\text{-}O\frown OH + {}^*O\mathord{<} \longrightarrow \mathord{>}P\text{-}O\frown O\frown OH \tag{3}$$
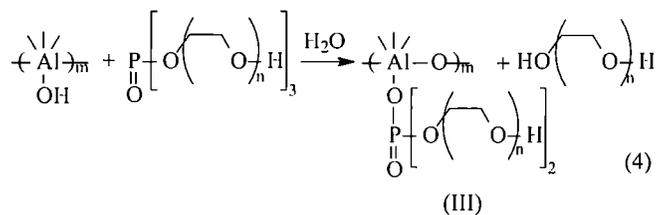
The reactivities of the subsequent P-OH groups in H_3PO_4 increase with an increase in the degree of substitution, which favors the formation of fully substituted esters (I).

$$\begin{array}{c} O(CH_2CH_2O)_mH \\ | \\ O{=}P\text{-}O(CH_2CH_2O)_nH \\ | \\ O(CH_2CH_2O)_oH \end{array} \qquad \left[\begin{array}{c} O \\ \diagdown \\ \diagup \\ O \end{array}\mathord{>}P\text{-}O(CH_2CH_2O)_nH \right.$$

(I)   (II)

The formation of a small amount of cyclic phosphate of the general formula (II) was also observed and attributed to the internal esterification or transesterification reactions; however, the structure of the final products obtained after complete conversion of the P-OH bonds was not studied in detail [2]. According to patent reports, the telechelic oligomers made from oxiranes and phosphoric acid are promising flame retardants that can be incorporated into various types of condensation polymers [4—8].

Studies carried out in our laboratory showed that they can serve also as an inexpensive source of organophosphorus ligands in the synthesis of hybrid inorganic-organic polymers. For example, polymeric aluminum diphosphonate (III) can be obtained by reacting oli-

$$\begin{array}{c} \diagdown | \diagup \\ {+}Al{\rightarrow}_m \\ | \\ OH \end{array} + P{-}\left[O\!\left(\frown O\right)_{\!n}\!H\right]_3 \xrightarrow{H_2O} {+}Al{-}O{\rightarrow}_m + HO\!\left(\frown O\right)_{\!n}\!H$$

$$\begin{array}{c} O \\ | \\ P{-}\left[O\!\left(\frown O\right)_{\!n}\!H\right]_2 \\ \| \\ O \end{array} \tag{4}$$

(III)

gomeric esters in an aqueous medium with boehmite, which is the most stable and naturally abundant aluminum oxohydroxide.

Particles consisting of small "boehmite like cores" and side organic ligands have received recently consi-

derable interest with respect to their potential applications as nanometer-sized, chemically reactive fillers, supports for metallocene catalysts and precursors of commercially important fine ceramics [9—11]. Metal organophosphates also play an important role in the preparation of new families of microporous and mesoporous materials [12, 13].

Therefore, it seems to be reasonable to obtain more detailed information about the structure of phosphorus-containing oligomers formed in the reaction of phosphoric acid with oxirane and their reactivity towards various mineral sources.

The main goal of this work was to identify organophosphorus compounds which are formed in the reactions of EOX with phosphoric acid in bulk, aprotic solvents and in water by means of NMR and MALDI TOF techniques.

We also report the synthesis of aluminum phosphates by controlled hydrolysis of triesters in the presence of boehmite.

EXPERIMENTAL

Materials

Phosphoric acid (85 % aq., POCh, Poland), phosphoric acid (99.9 % anhydrous, Fluka), EOX (>99.8 %, Fluka), and boehmite (Catapal $D^{\circledR}$ alumina supplied by CONDEA-Vista) were used without purification. The solvents and other reactants were purified according to general procedures. The reactions, purification of starting materials and solvents as well as all other operations were performed in the atmosphere of dried and deoxidized nitrogen.

Synthesis of phosphoric acid organic esters

Synthesis of phosphoric acid esters with EOX

EOX was introduced at -78 °C to a weighed, nitrogen containing, glass pressure ampoule. Next, it was introduced into a cooled glass pressure ampoule containing anhydrous phosphoric acid (and the solvent when performing the reaction in its presence) by means of a stainless steel capillary.

Reactions with an aqueous solution of phosphoric acid were carried out in a 100 mL three-neck flask, equipped with a magnetic stirrer and dry ice condenser, to which a weighed amount of phosphoric acid was introduced first and EOX by means of a capillary, next. Since the reaction proceeds vigorously and is strongly exothermic, it was cooled with an acetone dry ice bath. EOX was introduced to the system in a continuous manner.

Synthesis of the aluminum organophosphate [compound (III)]

Reactions of the obtained oligoesters with boehmite were carried out in water for 48 hours at boiling point of

water under ambient pressure. The aluminum organo-phosphate obtained was purified by extraction of organic residue with acetonitrile.

Hydrolysis of EOX oligomeric triesters

Distilled water was added to a flask equipped with a magnetic stirrer and reflux condenser containing known amounts of the products obtained. Next, the mixture was heated at ca. 80 °C or in boiling water. Samples were taken in course of the heating for titration in order to determine the amount of the liberated P-OH groups.

Methods of characterization

Carbon, hydrogen, oxygen and phosphorus content were determined by the combustion method on a Carbo Elbo model 1108 apparatus.

Aluminum content was determined complexometrically.

^{13}C, ^{27}Al and ^{31}P NMR spectra of solid samples were recorded on a Bruker DSX 300 spectrometer.

Spectrometric molecular mass determination was performed by means of a MALDI TOF 4 mass spectrometer (Kratos Analytical). ^{1}H and ^{31}P NMR spectra were recorded on a Varian Mercury 400 spectrometer (CDCl$_3$ or DMSO, 25 °C). The ESI MS spectrum was recorded on a LC-MSD 110, Agilen Technologies mass spectrometer with electrospray ionization. The optimization of the Electrospray MS detection conditions was obtained for standards transported to the ionization source by light aspiration (25 µl · min^{-1}) obtained by the nebulizing gas stream 11 µl · min^{-1}. The chromatographic program LC Chemstation 3D (Hewlett Packard) was used for MS data, allowing observation of the mass spectra.

Acidic groups of the products obtained were determined by titrating the products in aqueous solutions with a 0.1 M NaOH solution. The end point of titration was determined by measuring changes of pH of the indicator electrode during titration.

GPC measurements were carried out on a Lab Alliance chromatograph equipped with a refractometric detector and PLaquagel-OH Mixed 8 µm chromatographic column using PEOX as a molecular weight standard. The measurement was performed in demineralized water at a 0.5 cm^3/min flow.

RESULTS AND DISCUSSION

Reactions in anhydrous conditions

Reactions of anhydrous phosphoric acid and EOX were carried out in bulk, as well as in acetonitrile and dioxane solutions using a 5 to 20-fold excess of the oxirane. ^{31}P{H} NMR spectra of the products (e.g. Fig. 1) indicate that phosphoric acid is completely converted
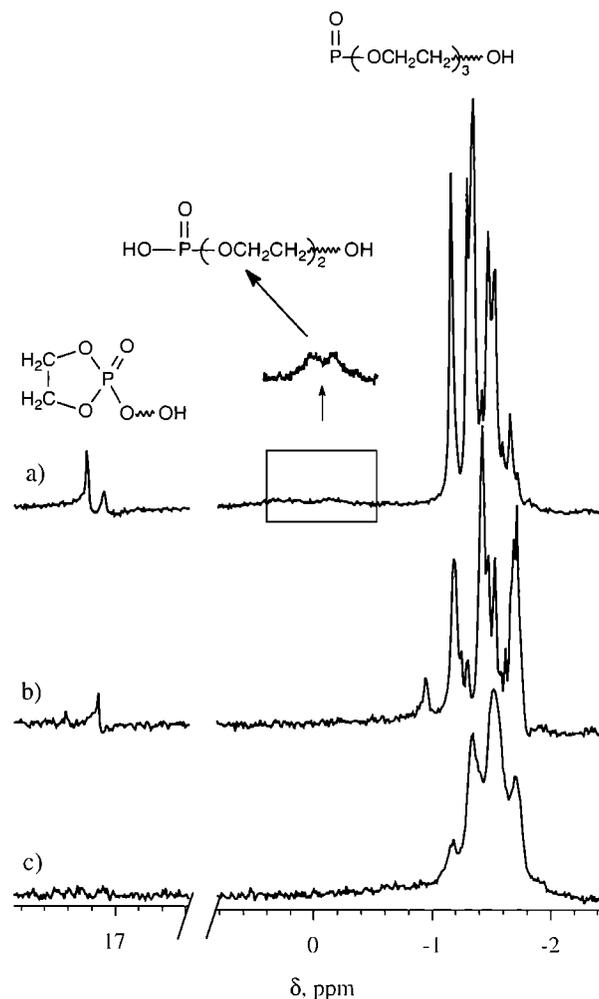

Fig. 1. ^{31}P NMR spectra of the EOX and EOX/H$_3$PO$_4$ reaction products: a) reaction carried out in acetonitrile; b) reaction carried out in bulk; c) reaction with 85 % H$_3$PO$_4$ aqueous solution

into esters under these conditions. The main signals in the range from -1.5 to -2.2 ppm accounting for 80—97 mol. % of total phosphorus, are due to the mixture of linear triesters, whereas the small signals at δ ≈ 17 ppm (1—3 % of P) are attributed to cyclic phosphates (II). Additional signals at -0.5— -1.0 ppm were reported in some spectra. They are probably the signals of diesters, since only one neutralization point (corresponding to pH change from 5 to 10) is observed during titration of the reaction mixture with 0.1 M NaOH solution. The total consumption of acidic P-OH group determined from the integration of signals in ^{31}P NMR spectra of the products reached 83—100 % (Table 1). Unreacted phosphoric acid at 2—4 ppm and of monoesters at δ -0.5—+3 ppm are observed (their chemical shifts depend on the esters to acid proportion) at an early stage of the reaction.

Signals characteristic for POCH$_2$ groups form complicated multiplets in the δ from 3.6 to 4.1 ppm range in the proton resonance spectra (Fig. 2). One sharp peak for

T a b l e 1. Conversion of P-OH group and oxirane consumption in the reaction of phosphoric acid (PhA) with ethylene oxide (EOX) in various solvents[a]

Solvent	EOX/PhA mole ratio	P-OH conversion mol %	Mole ratio	
			EOX/P	EOX/P-OCH2
Bulk	15	92	9.1	3.3
	20[b]	100	8.7	2.9
Acetonitrile[c]	5	83	5.0	2.0
	20	96	5.8	2.0
Dioxane[c]	15	100	5.4	1.8
Water	1[d]	9	0.9	3.5
	3[d]	19	1.8	3.2
	8[d]	90	7.3	2.8
	20[d]	97	12.3	4.2
	20[d]	100	12.9	4.3
	20[e]	100	10.2	3.4
Water-dioxane[f]	20	100	8.8	2.9

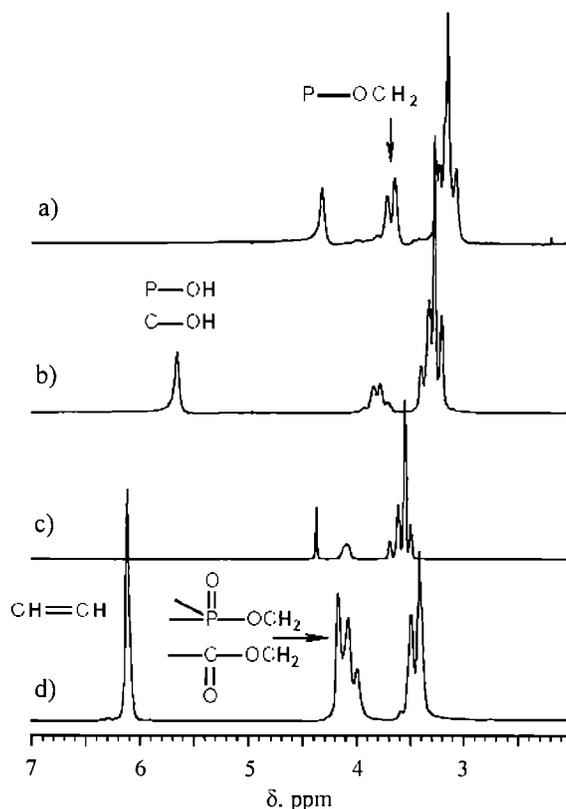[a] Determined by ^{31}P[H] and ^{1}H NMR.
[b] Reaction carried out for 14 days at -5 °C.
[c] 10 mL per 1 g of PhA.
[d] 85 wt. % of PHA (PhA:water mole ratio = 1:1).
[e] 70 wt. % of PHA (PhA:water mole ratio = 1:1).
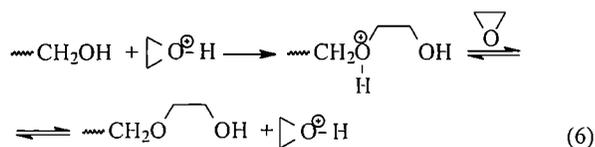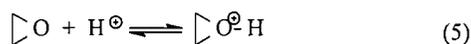[f] PhA:water:dioxane mole ratio = 1:1:5.

Fig. 2. ^1H NMR spectra of the EOX/H₃PO₄ reaction products: a) reaction carried out in acetonitrile; b) reaction with 85 % H₃PO₄ aqueous solution; c) reaction carried out in bulk; d) product of the reaction carried out in acetonitrile after esterification with maleic anhydride (temp. 60 °C, two-fold excess of anhydride)

both groups is observed due to the fast proton exchange in systems, in which alcoholic and acidic OH groups are present. The position of this signal depends on the proportion between the acidic and alcoholic groups and on concentration (at the 90—96 % conversion of the P-OH groups and about 10 % concentration of the product in CDCl₃ δ_{OH} occurs usually between 3.4 and 4.3 ppm). Degree of conversion in these systems can be determined on the basis of the relative intensity of the OH and P-OCH₂ groups signals. It is very close to the value determined on the basis of signal intensity in the phosphorus spectrum (±1 %) and on the basis of titration (±3 %). A comparison of the intensity of the P—OCH₂ and other methylene groups signals allows estimation of the mole ratio of EOX monomeric units (m.u.) to the phosphate m.u. in the products obtained (Table 1). The validity of these methods was confirmed by another procedure based on the esterification of terminal alcoholic OH groups with maleic anhydride. The degree of EOX oligomerization after esterification can be calculated from the integration ratio of the signals at δ ~4 ppm and δ ~3.5 ppm (Fig. 2d) characteristic for terminal (-POCH₂ and -C(O)OCH₂) and internal (-CH₂OCH₂) methylene groups, respectively. Both methods gave the same results (±5 %) within inaccuracy in determination of the signals intensities. The relative intensity of the CH=CH group signal at 6.1 ppm and terminal methylene group signal allow to determine the number of alcoholic OH groups per one P-OCH₂ bond. Integration ratio of the signals at δ 6.1 ppm and ~4 ppm under anhydrous conditions is between 0.49 and 0.51, which means that the molar ratio of POCH₂/OH groups is close to unity, as expected.
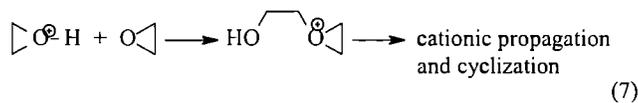
Molar ratio of EOX m.u. to phosphate m.u. for reactions carried out in dioxane is about 1.8, and is slightly higher than the value predicted on the basis of kinetic data for the reaction carried out at 25 °C (1.5) [6]. Average length of the EOX m.u. sequences in the oligomers formed increases with an increase in the polarity of the reaction medium. In reactions carried out in acetonitrile it is ~2.0, and in those carried out in bulk 3.3 (this value decreases to *ca.* 2.9 if the reactions are carried out below 0 °C). In the absence of a solvent the reactions proceed at first in a two-phase system and the system becomes homogeneous only after a certain time. Under these conditions at least part of the products are formed in a strongly polar medium of highly concentrated phosphoric acid and its esters.

Participation of oxonium ions should be taken into consideration in a polar medium. In our opinion, their addition to the terminal hydroxyl groups leads to the formation of higher oligomers.

As was shown earlier, contribution of the reaction pathway involving protonated EOX species is negligibly small in reactions carried out in dioxane [5], however it plays a significant role in the presence of external catalysts (*e.g.* HBF₄). The formation of oxonium ions in reac-

$$\triangleright O + H^{\oplus} \rightleftharpoons \triangleright \overset{\oplus}{O} H \qquad (5)$$

$$\text{---}CH_2OH + \triangleright \overset{\oplus}{O} H \longrightarrow \text{---}CH_2\overset{\oplus}{\underset{H}{O}} \overset{}{\diagup} OH \overset{\triangledown}{\underset{O}{\rightleftharpoons}}$$

$$\rightleftharpoons \text{---}CH_2O \overset{}{\diagup} OH + \triangleright \overset{\oplus}{O} H \qquad (6)$$
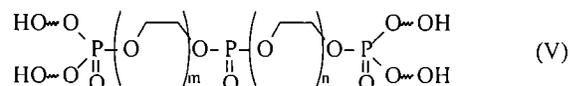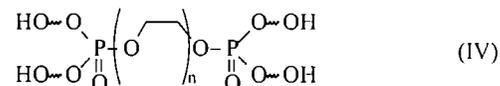
tions carried out in bulk is indicated also by the formation of small amounts of dioxane and higher cyclic EOX oligomers (that were detected by MS electron spray spectroscopy of the reaction mixture).

$$\triangleright \overset{\oplus}{O} H + O\triangleleft \longrightarrow HO \overset{}{\diagup} \overset{\oplus}{O}\triangleleft \longrightarrow \text{cationic propagation and cyclization}$$

$$(7)$$

MALDI TOF spectra (Fig. 3) of the reaction mixture show that oligoesters comprising one phosphorus atom (I) are the main products formed in the systems studied. Two main series of signals correspond usually to adducts with the proton and Na^+ cation. Molecular weight of signals corresponds to oligomers comprising from 4 to 18 EOX m.u. in the case of products of reactions carried out in solution and from 4 to 25 EOX m.u. of those carried out in bulk. Mean EOX m.u. content in the products determined on the basis of the relative intensity of signals in the MALDI TOF spectrum in this molecular weight range is on average higher than that determined

$$HO\text{---}O \overset{}{\underset{HO\text{---}O'}{\diagdown}} \overset{}{\underset{O}{\overset{\|}{P}}} \overset{}{\diagup} O \overset{}{\diagup} \Big)_n O - P \overset{O\text{---}OH}{\underset{O\text{---}OH}{\diagup}} \qquad (IV)$$

$$HO\text{---}O \overset{}{\underset{HO\text{---}O'}{\diagdown}} \overset{}{\underset{O}{\overset{\|}{P}}} - O \overset{}{\diagup} \Big)_m O - P - \overset{}{\diagup} O \overset{}{\diagup} \Big)_n O - P \overset{O\text{---}OH}{\underset{O\text{---}OH}{\diagup}} \qquad (V)$$

by the NMR method (in the case of the series with a proton by 1—3 units, and in that of Na^+ by 3—5 units). Oligomers of lower molecular weights probably undergo faster degradation under the measurement conditions. Their content decreases with an increase in the power of the radiation applied.
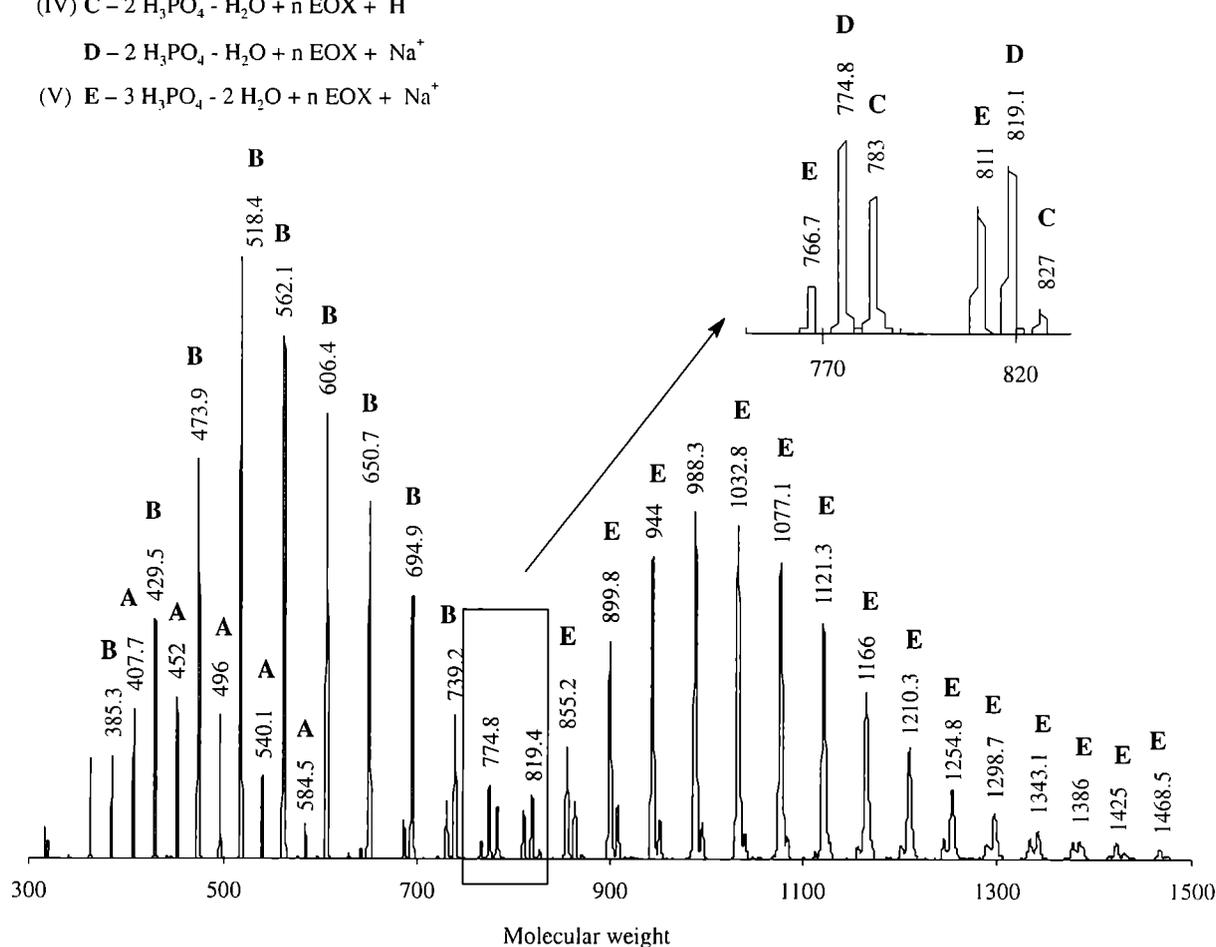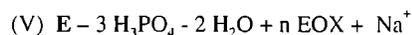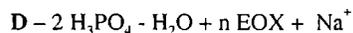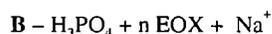
(I) $A - H_3PO_4 + n\,EOX + H^+$

    $B - H_3PO_4 + n\,EOX + Na^+$

(IV) $C - 2\,H_3PO_4 - H_2O + n\,EOX + H^+$

    $D - 2\,H_3PO_4 - H_2O + n\,EOX + Na^+$

(V) $E - 3\,H_3PO_4 - 2\,H_2O + n\,EOX + Na^+$
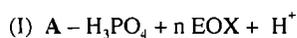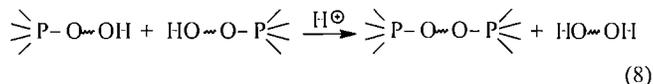

Fig. 3. MALDI TOF spectrum of the reaction product of anhydrous H_3PO_4 and EOX carried out in dioxane (explanation in text)

Signals of condensation products comprising 2 (IV), and in some cases also 3 phosphorus atoms (V) are present in spectra of all the products studied:

— These products probably result maily from the intermolecular transesterification [eq. (8)] with the elimination of diols, since direct esterification of phosphoric acid with alcohols requires a much higher temperature [14—16].

$$\underset{/}{\overset{\backslash}{>}}P\!-\!O\!\sim\!OH \ + \ HO\!\sim\!O\!-\!P\underset{\backslash}{\overset{/}{<}} \ \xrightarrow{H^{\oplus}} \ \underset{/}{\overset{\backslash}{>}}P\!-\!O\!\sim\!O\!-\!P\underset{\backslash}{\overset{/}{<}} \ + \ HO\!\sim\!OH$$

(8)

— The addition reactions of EOX to diphenylphosphoric acid in bulk and in acetonitrile were carried out using a 10-fold excess of the oxirane, in a similar way as the reactions with phosphoric acid, in order to confirm the possibility of transesterification in the systems studied.

$$(C_6H_5O)_2POH \xrightarrow{\overset{\bigtriangledown}{O}} (C_6H_5O)_{2-a}P\left[O\left(\overbrace{}O\right)_n H\right]_{1+a} + \ a\ C_6H_5OH$$
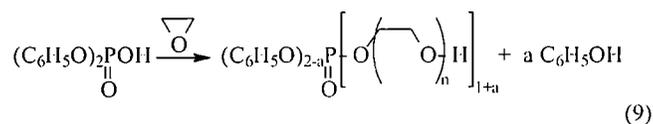
a = 0.6—0.9

(9)

On the basis of analysis of ^1H NMR spectra it was found that about 29 % of the oxyphenyl groups undergo transesterification at complete conversion of the P-OH bonds in the reaction carried out in acetonitrile, and in that in bulk about 19 %. The average number of EOX m.u. falling in these reactions per one $P\text{-}OCH_2$ bond is slightly lower than that in the reactions with phosphoric acid, and is equal to 1.7 for reactions carried out in acetonitrile and 2.4 for those in bulk. This results from the smaller concentration of P-OH groups which catalyze the oxirane oligomerization.

Model mixtures of triesters comprising different amounts of condensation products were obtained in the reaction of $POCl_3$ with ethylene, diethylene and triethylene glycols. On the basis of analysis of NMR spectra it was found that distinct differences in the chemical shifts of signals characteristic for triesters comprising one phosphorus atom (I) and for the condensation products occur only in the case of ethylene glycol derivatives in which phosphorus atoms in the condensation products are bonded via a single EOX m.u. (Fig. 4). The signal of protons in the $P\text{-}OCH_2CH_2O\text{-}P$ moiety is especially characteristic, being shifted by about 0.2 ppm towards the lower field with respect to the signal of protons of other $P\text{-}OCH_2$ groups due to the induction effect of the two ester groups. This last signal is clearly visible in the spectra of products of all the reactions carried out
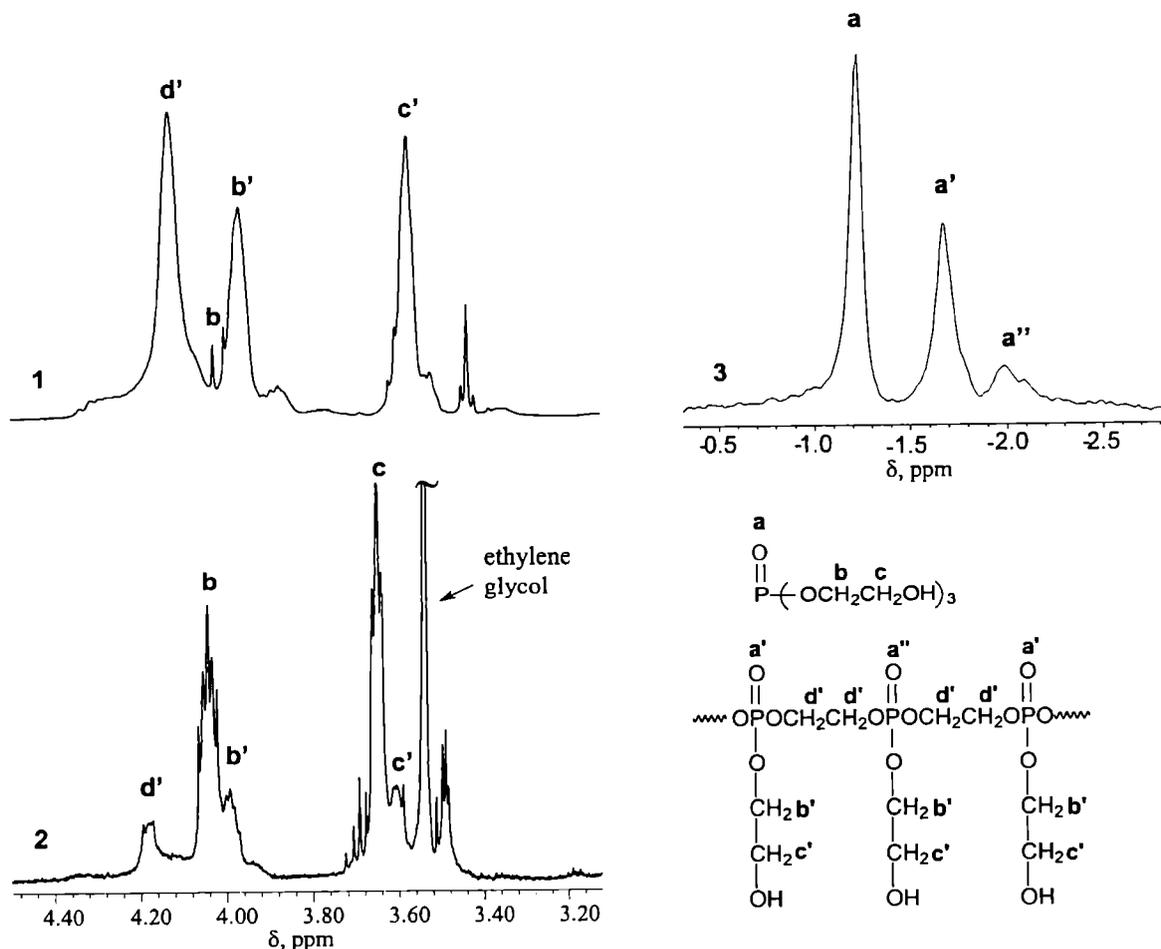

Fig. 4. ^1H NMR (1, 2) and ^{31}P NMR (3) spectra of the condensation products of $POCl_3$ and ethylene glycol

in solvents (Fig. 2a). On the basis of the intensities of these signals it can be estimated that 25—30 % of the EOX m.u. in the ester groups in products of reactions carried out in dioxane or acetonitrile form bridges linking the phosphorus atoms. However, such a clear differentiation of the condensation products signals is not observed in the products of reactions performed without a solvent (Fig. 2c). Phosphorus atoms in the condensation products of such systems are probably linked mainly *via* bridges comprising two or more EOX m.u. due to the higher degree of oligomerization.

Reactions with phosphoric acid aqueous solutions

An 85 wt. % aqueous solution of phosphoric acid is approximately an equimolar mixture of the acid and water. At room temperature this mixture reacts vigorously with EOX. The reaction can be carried out in a controlled manner by dosing the reactants at 0—5 °C and, next, increasing the temperature to ambient. P-OH groups conversion degree reaches 90—100 % at a twenty-fold oxirane excess. Triesters of a linear structure are the main phosphoroorganic products (80—97 %). Signals characteristic for the condensation products in which the phosphorus atoms are linked by a single EOX m.u., are present in the NMR spectra of the products, similarly as in reactions carried out in dioxane or acetonitrile [they constitute 20—25 % of all the triesters (Fig. 2c)].

A series of signals corresponding to the products comprising 2 phosphorus atoms (IV) and from 8 to 17 EOX m.u. (13 at an average) is present in the MALDI TOF spectra. Signals of products comprising one phosphorus atom (I) are attributable to oligomers in which the number of EOX m.u. varies from 4 to 17.

Diols are also formed besides esters. Mass spectra obtained by the "electron spray" technique (Fig. 5) show that the number of EOX m.u. in the diols formed varies from 2 to 14. Weak signals characteristic for cyclic esters (II) and a series of signals attributable to esters (I) of 3 to 15 EOX m.u. are also visible in these spectra. The average content of these m.u. is 8.8, which gives *ca.* 2.9 m.u. per one ester bond.

Molar ratio of the terminal CH_2OH groups to the $P-OCH_2$ groups (determined on the basis of the relative intensity of signals at δ ~4 ppm and 6.1 ppm in the ^1H NMR spectra of the products obtained after esterification with maleic anhydride) ranges between 1.6—1.7, *i.e.* close to the theoretical value (5/3) at complete conversion of the OH bonds in the acid and water. This means that part of the oxirane molecules act as a "drying agent" in these systems affording ethylene glycol, which competes with phosphoric acid as a starter for the oxirane polymerization according to the "activated monomer" polymerization. Molar ratio of all the EOX m.u. to the $P-OCH_2$ groups in these products is *ca.* 13, which means that at an average of 2.6 molecules of the oxirane undergo addition to each of the OH bonds in the acid and water. It is higher than that in the products of the reaction carried out in dioxane and acetonitrile, caused by higher polarity of the reaction medium and greater participation of oxonium ions in the propagation step [eq. (6)]. Dilution of the system with water or dioxane causes a decrease in the degree of oligomerization (Table 1). For example, about 10 moles of EOX are consumed (average degree of oligomerization is ~1.5 per one OH bond) at complete conversion of OH groups in two moles of water and 1 mole of acid. However, higher oligodiols and small amounts of esters are also formed besides ethylene glycol, even at a 40—50-fold excess of water with respect to the acid. It should be noticed that phosphoric acid esters are formed already in the initial reaction steps, when water is still present in the system. At the conversion of 0.9 moles of EOX per one mole of the acid and one mole of water (Table 1) about 27 % of EOX m.u. form ester bonds (mainly monoesters), and about 15 % of the m.u. is present in the form of ethylene glycol. Conversion of one P-OH bond at this stage is accompanied by the reaction of 3.4 molecules of the oxirane, and about 4.3 molecules at complete conversion of the acidic groups. Therefore, the "drying" of the system proceeds parallel to the EOX addition to P-OH and C-OH bonds. Thus, one can expect that the acid molecules are only partly dissociated and oxirane activation resulting from the formation of hydrogen bonds with phosphoric acid is still possible.

The low molecular weight diols formed in the reaction of EOX with concentrated phosphoric acid can be distilled off under vacuum at 150—170 °C. Molar ratio of the $P-OCH_2$ groups to the terminal OH groups after this
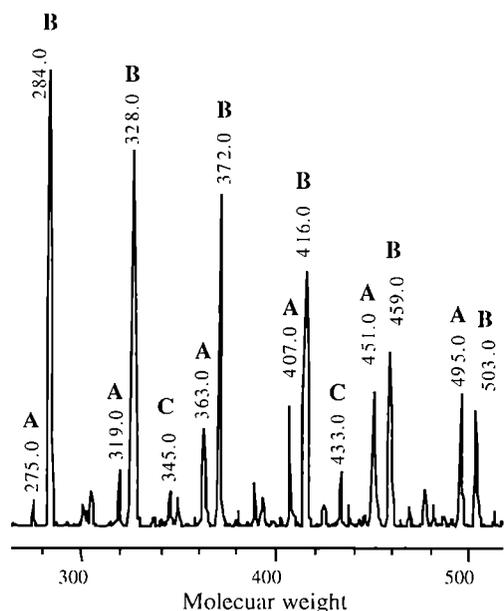

Fig. 5. ESI MS spectrum of the EOX and 85 % H_3PO_4 aq. reaction product: A: H_3PO_4 + p EOX (I) (p = m + n + o); B: H_2O + n EOX; C: ethylene phosphate + n EOX (II)

operation is about 1.2 and the average number of EOX m.u. falling per one ester bond is about 3. Slow decomposition of the ester groups occurs with the formation of P-OH bonds at a higher temperature of the process, starting from 180 °C.

Hydrolysis of oligomeric esters of phosphoric acid

Mono- and diesters of phosphoric acid have a higher value of the first ionization constant than the parent acid [7]. Therefore, one can expect that these products can react with a variety of inorganic oxides or hydroxides. Oligomeric mono- and diesters are formed in the reaction of phosphoric acid with oxiranes. However, due to kinetic reasons, their concentration in the reaction mixture is small after complete conversion of the acid [2]. Content of these compounds can be increased by hydrolysis of the triesters. The rate of hydrolysis of phosphoric acid esters is known to depend on pH and the mechanism of these reactions in acidic and basic media is well known [17, 18]. In the case of reaction products of phosphoric acid and oxiranes, the pH value of their aqueous solutions ranges usually between 5—5.5, which results from the small amount of diesters present in the final products.

A mixture of triesters and 20—25 % of diesters can be obtained by controlled hydrolysis of reaction products of phosphoric acid with EOX 80 °C (Table 2). pH value of the reaction mixture is then 2.7—2.8. It is known that phosphoric acid diesters in a weakly acidic medium occur mainly in the form of $(RO)_2PO^-$ anions, which are resistant toward a nucleophilic attack of water molecules [17, 18]. A gradual decrease in pH with the triester hydrolysis progress leads to a decrease in the anion concentration and hydrolysis of the diester neutral form, which is catalyzed by the protonation of oxygen atoms.

T a b l e 2. Hydrolysis of triesters[a]

Initial composition mol %		pH	Temp. °C	Time h	Final composition mol %		pH
triesters	diesters				triesters	diesters	
98	2	5.2	80	8	96	4	3.6
96	4	3.6	80	4	94	6	3.3
94	6	3.3	80	10	76	23	2.8
76	23	2.8	80	14	56	26	2.5
95	5	3.4	100	4.5	38	18	1.9
95	5	3.4	100	6.5	3	49	1.9

[a] Reaction mixture obtained in the reaction of 85 wt. % phosphoric acid with ethylene oxide.

Hydrolysis of triesters at 100 °C is accomplished already after several hours of reaction. pH of the reaction mixture drops below 2 and the diesters undergo partial decomposition to monoesters and phosphoric acid.

Hydrolysis in the presence of boehmite

Hydrolysis of triesters proceeds practically in the pH 2.7—3.5 range in the presence of boehmite, since part of the P-OH bonds formed react with Al-OH groups.

Composition of the hybrid linkages formed depends on the reaction time and P/Al ratio in the starting mixture. Hydrolysis carried out for 48 hours at 100 °C at a P/Al ratio = 3 leads to a product soluble in water and DMSO. ^1H NMR spectrum of this product (Fig. 6) re-
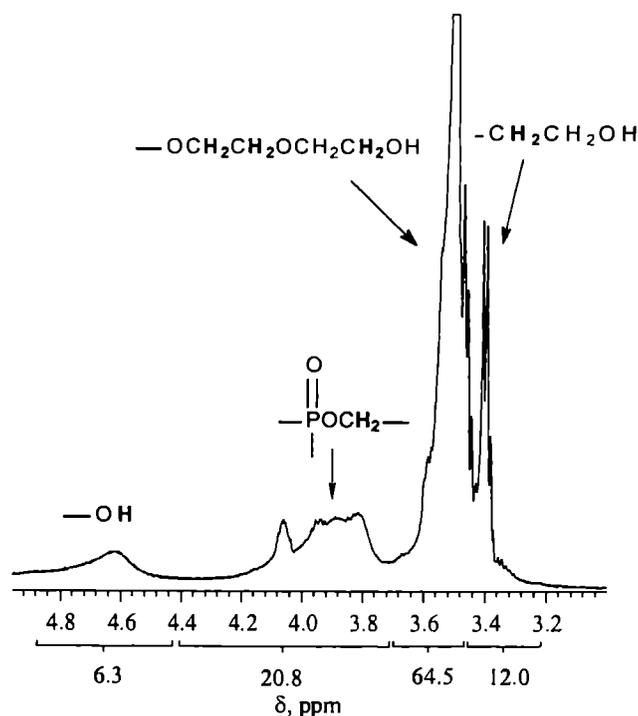

Fig. 6. ^1H NMR spectrum (DMSO$_{d6}$) of the reaction product of phosphoric acid aliphatic oligoesters with boehmite

veals signals characteristic for hydroxyl groups (δ ~4.6 ppm), P-OCH$_2$ groups (3.8—4.15 ppm) and the remaining methylene groups in the EOX m.u. (3.4—3.6 ppm). Relative intensity of these signals shows that the average number of EOX m.u. per one P—OCH$_2$ bond is close to 3. Elemental analysis (C 32.6 %, H 6.5 %, P 6.5 %, Al 5.2 %) indicates that the phosphorus to aluminum molar ratio is ~1.1, and about 6.5 EOX m.u. fall per one phosphorus atom. Thus, it can be assumed that diester salts are the main reaction products; elongation of the reaction time leads to gradual hydrolysis of the P—OCH$_2$ bonds in the derivative formed. An analysis of the ^{27}Al NMR spectra indicates that the coordination number of aluminum in the hybrid polymers obtained is 6, i.e. it forms octahedral structures. Two signals were detected in the ^{27}Al MAS NMR spectra of the solid product, at δ -3.2 and -25.6 ppm. On the basis of studies of the model reaction of triethylaluminum with diphenylphosphate acid we attribute the signals at δ -25.6 ppm to the alumi-

num nuclei bridged by phosphate ligands Al-O-P = O → Al. The signal at δ -3.2 ppm is probably due to the residual boehmite core, which contains Al-O-Al bonds. XRD patterns for the products show that the product is amorphous, but residual peaks characteristic for boehmite at 2θ: 14°, 27°, 38° and 49° can be detected. Therefore, we assume that the polymer obtained is of a gradient structure and that structures of the boehmite (VI) dominate inside whereas that aluminum phosphate (VII) on the surface.

(VI)   (VII)
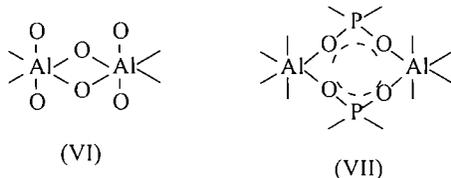
Position of signals in the ^{27}Al NMR spectra changes after dissolution in DMSO or in water. In the first case, two signals are present, at δ ≈-6 and -13 ppm, whereas in water a group of signals is observed in the δ range from -9 ppm to +1.5 ppm. This is probably connected with the solvating effects and partial dissociation of the Al-O-P bonds.

Preliminary chromatographic studies (Fig. 7) show that a broad molecular weight distribution takes place in aqueous solutions. However, the limiting viscosity number of these solutions are relatively low (~0.002 cm^3/g), which suggests that fractions of high molecular
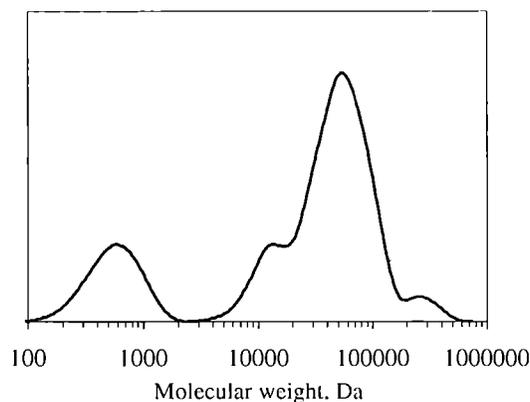

Fig. 7. GPC traces of polymeric organoaluminum phosphates

weight are not soluble in water but form transparent nanodispersions, only.

A more detailed description of these systems will be presented in a forthcoming paper.

CONCLUSIONS

Mixtures of telechelic oligomers comprising from 2 to 5 terminal hydroxyl groups and from 0 to 3 phosphorus atoms are formed in reactions of EOX and phosphoric acid. They resulted from the oxirane addition to phos-

phoric acid [eqs. (2) and (3)], followed by the condensation reaction [eq. (8)] that occurs at ambient temperature.

The average degree of EOX oligomerization ranges between 1.8—3.3, depending on the polarity of the solvent used and acid concentration. Monofunctional cyclic esters are also formed in these reactions at low yield (1—3 wt. %), as well as trace amounts of cyclic EOX oligomers. The amount of side products increases considerably in the case of using substituted oxiranes.

Practical utilization of such a complicated mixture of products for the synthesis of organic condensation polymers seems to be rather difficult. However, hydrolysis of phosphorus containing oligomers in the presence of boehmite or other metal hydroxides can potentially become an economically attractive method of modifying inorganic fillers to improve their miscibility with organic polymers.

REFERENCES

1. Biela T., Kubisa P.: *Makromol. Chem.* 1991, **192**, 73.
2. Biela T., Kubisa P.: *Makromol. Chem.* 1993, **194**, 285.
3. Biela T., Kubisa P., Penczek S.: *Makromol. Chem.* 1992, **193**, 1147.
4. *US Pat.* 2 372 244 (1945); *CA* 1946, 40:1029.
5. *US Pat.* 3 419 642 (1968); *CA* 1969, **70**:58 591e.
6. *US Pat.* 5 759 691 (1998), *EP Pat.* 794 236 (1997); *CA* 1997, **127**:249 458x.
7. *US Pat.* 5 728 746 (1998), *EP Pat.* 771 810 (1997); *CA* 1997, **127**:34 982c.
8. Polish patent appl. P.358 023 (2002).
9. Callender R. L., Harlan C. J., Shapiro N. M., Jones C. D., Callahan D. L., Wiesner M. R., MacQueen D. B., Cook R., Barron A. R.: *Chem. Mat.* 1997, *9*, 2418.
10. Vogelson C. T., Koidey Y., Alemany L. B., Barron A. R.: *Chem. Mat.* 2000, **12**, 795.
11. Obrey S. J., Barron A. R.: *Macromolecules* 2002, **35**, 1499.
12. Maeda K., Kiyozumi Y., Mizukami F.: *Angew. Chem. Int. Ed.* 1994, **33**, 2335.
13. Tanaka H., Chikazava M.: *Materials Res. Bull.* 2000, **35**, 75.
14. "Methoden der Organischen Chemie", Houben-Weyl [Ed. (Hrsg.) Müller Eu.], Thieme Verlag, Stuttgart 1963, vol. 12/1.
15. Pillai C. K. S., Prasad V. S., Sudha J. D., Bera S. C., Menon A. R. R.: *J. Appl. Polym. Sci.* 1990, **41**, 2487.
16. Van Wazer J.: "Phosphorus and its Compounds", Interscience Publishers, Inc., New York 1972.
17. Cox J. R. Jr, Ramsay O. B.: *Chem. Rev.* 1964, **64**, 317.
18. Bunton C. A.: *Ac. Chem. Res.* 1970, *3*, 257.