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Features of Condensation of 4,4'-Dihydroxybiphenyl with Phenylphosphonous Tetraethyldiamide

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Abstract — 4,4'-Dihydroxybiphenyl was condensed with phenylphosphonous tetraethyldiamide. The molecular mass, chemical composition, and structural features of the product, oligo(4,4'-biphenylene phenylphosphonite), were elucidated using the method of matrix-activated laser desorption/ionization, with a time-of-flight (TOF) mass analyzer. The oligophenylphosphites containing labile P–N bond, which are unstable under conditions of recording mass spectra, were stabilized by conversion into oligophenylphosphonates. 1*H*-Tetrazole catalyzes the reaction of phenylphosphonous tetraethyldiamide with 4,4'-dihydroxybiphenyl. Cross-linking in the solid state of the oligo(4,4'-biphenylene phenylphosphonite) containing terminal phosphonamidite group leads to gradual increase in the molecular weight and is accompanied by redox processes.
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Arylene oligophosphonites are of interest as effective modifiers of coordination catalysts [1, 2]. However, conditions of synthesis and structure of arylene oligophosphonites as ligands have been studied inadequately [3, 4]. The catalytic properties of arylene oligophosphonite ligands can arise from unusual microprocesses in the bulk of the oligomer.

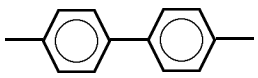
In this study we examined the condensation of 4,4'-dihydroxybiphenyl with phenylphosphonous tetraethyldiamide and the features of the chemical behavior of oligophenylphosphonite in the solid state. In the course of condensation, we used 1*H*-tetrazole exerting a catalytic effect on the alcoholysis of amides of trivalent phosphorus acids [5–7]. When discussing the results, we used the data obtained by the method of matrix-assisted laser desorption/ionization (MALDI) technique which is used, in particular, for mass-spectrometric analysis of phosphorus-containing polymers [4, 8, 9].

RESULTS AND DISCUSSION

Condensation of the bifunctional phosphorylating agent, phenylphosphonous teraethyldiamide, with 4,4'-dihydroxybiphenyl for the preparation of oligophenylphosphonites **I** and **II** was performed at the reactant molar ratio of 1:1 under argon with removing the released diethylamine. Compound **II** was prepared by the reaction in the presence of 1*H*-tetrazole:

$$n\mathrm{PhP(NEt_2)_2} + n\mathrm{HOArOH} \longrightarrow \underset{\mathbf{I,\ II}}{[\text{–OArOP(Ph)–}]_x},$$

Ar =



$x = n_1$ (**I**) $< n_2$ (**II**).

The reaction progress was monitored by ^{31}P NMR spectroscopy. The reaction was conducted until the signal at δ_P 98 ppm of the starting phenylphosphonous tetraethyldiamide disappeared; however, in contrast to the case described in [4], it was not exhaustive and was completed with the appearance of signals at δ_P 131 and 158 ppm corresponding to the compounds containing the fragments [–OArO–P(Ph)·NEt_2] and [–OArO–P(Ph)O–]. The integral intensity ratio of the signals at δ_P 131 and 158 ppm was 1 : 0.5 and 1 : 14 for compounds **I** and **II**, respectively. Oligophenylphosphonite **I** is a white viscous paste, and product **II** is a transparent colorless glassy substance with softening point 90–95°C.

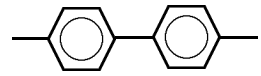
The oligophenylphosphonite samples for mass-spectral (MALDI) study were prepared by dissolution in THF, using 2,4,6-trihydroxyacetophenone as matrix. The oligophenylphosphonites containing labile

P–N bond [6] show instability in the MALDI experiments, manifested as irreproducibility of the mass spectra. To stabilize the oligophenylphosphonite samples, they were oxidized to the corresponding oligophenylphosphonates by the following procedure we developed. The oligomer was dissolved in THF containing peroxide and was oxidized in a thin layer on a metallic (Al–Ni, 1 : 1 by weight) support to form compounds **III** and **IV**, respectively:

$$[\text{–OArOP(Ph)–}]_x \xrightarrow{[O]} [\text{–OArOP(O)(Ph)–}]_x,$$

III, IV

Ar =



$x = n_1$ (**III**) $< n_2$ (**IV**).

The main processes (phosphorylation of 4,4'-dihydroxybiphenyl with phenylphosphonous tetraethyldiamide) and oxidation of the reaction products **I** and **II** can be described by the following equations:

$$n\text{HOArOH} + (n+1)\text{PPh(NEt}_2)_2 \xrightarrow{-2n\text{HNEt}_2} \text{Et}_2\text{NP(Ph)[–OArOP(Ph)–]}_n\text{NEt}_2,$$

Ia

$$n\text{HOArOH} + n\text{PPh(NEt}_2)_2 \xrightarrow{-(2n-1)\text{HNEt}_2} \text{H[–OArOP(Ph)–]}_n\text{NEt}_2,$$

Ib, IIb

$$(n+1)\text{HOArOH} + n\text{PPh(NEt}_2)_2 \xrightarrow{-(2n-1)\text{HNEt}_2} -2n\text{H[–OArOP(Ph)–]}_n\text{OArOH},$$

IIc

$$\text{Et}_2\text{NP(Ph)[–OArOP(Ph)–]}_n\text{NEt}_2 \xrightarrow{+(n+1)[O]} \text{Et}_2\text{NPO(Ph)[–OArOP(O)(Ph)–]}_n\text{NEt}_2,$$

IIIa

$$\text{H[–OArOP(Ph)–]}_n\text{NEt}_2 \xrightarrow{+n[O]} \text{H[–OArOP(O)(Ph)–]}_n\text{NEt}_2,$$

IIIb, IVb

$$\text{H[–OArOP(Ph)–]}_n\text{OArOH} \xrightarrow{+n[O]} \text{H[–OArOP(O)(Ph)–]}_n\text{OArOH}.$$

IVc

The mass spectrum of **III** is typical of a polymeric material (Fig. 1). The maximum mass is registered at *m/z* 2733.7. The mass spectrum contains peaks corresponding to several series of ions owing to the formation of oligomers differing in the terminal groups. It is noteworthy that these series differ in the peak intensity, but all have the same mass, 308 Da, of the monomeric unit, which corresponds to [–OArOP(O)(Ph)–]. The spectrum contains two major groups of peaks, belonging to completely and partially protonated products of complete phosphorylation of 4,4'-dihydroxybiphenylphenyl: $\{\text{Et}_2\text{NP(O)(Ph)}\cdot[\text{–ArOP(O)(Ph)–}]_n\text{NEt}_2 + \text{H}\}^+$ (**IIIa**) and $\{\text{H[OAr}\cdot\text{OP(O)(Ph)]}_n\text{NEt}_2 + \text{H}\}^+$ (**IIIb**) (Fig. 1, Table 1).

Compound **II** was obtained by the reaction in the presence of a five-membered heteroaromatic compound, 1*H*-tetrazole, added in a catalytic amount. The reaction progress was monitored by ^{31}P NMR spectroscopy. Comparison of the ^{31}P NMR spectra of compounds **I** and **II** showed that the contribution of the terminal groups [–ORO–P(Ph)NEt$_2$] to the composition of the oligomer obtained with 1*H*-tetrazole decreased considerably. This is seen from the relative intensity of the signal at 158 ppm. The intensity ratio of the signals at 131 and 158 ppm for this compound is 1 : 14. Stepwise (308 Da) accumulation of the mass of the oligomer prepared with 1*H*-tetrazole begins at *m/z* 495.1, which corresponds to the mass of the protonated molecule of the compound H[OArOP(O)·(Ph)]OArOH, and ends at the *m/z* value corresponding to the oligomer H[–OArOP(O)(Ph)–]$_{14}$OArOH (**IVc**). The compounds with the phosphonamide terminal group [–OArOP(O)(Ph)–]$_n$NEt$_2$ are represented by a group of signals that are smaller in number and less intense (Fig. 2, Table 2). The maximum mass corresponds to *m/z* 4499.1 Da. Thus, condensation of 4,4'-dihydroxybiphenyl with phenylphosphonous tetraethyldiamide in the presence of 1*H*-tetrazole is characterized by higher degree of phosphorylation and leads to the product of the higher molecular weight as compared to the noncatalytic process. Note that the products of reaction of 4,4'-dihydroxybiphenyl with phenylphosphonous tetraethyldiamide in the presence of 1*H*-tetrazole contain no residual azole.

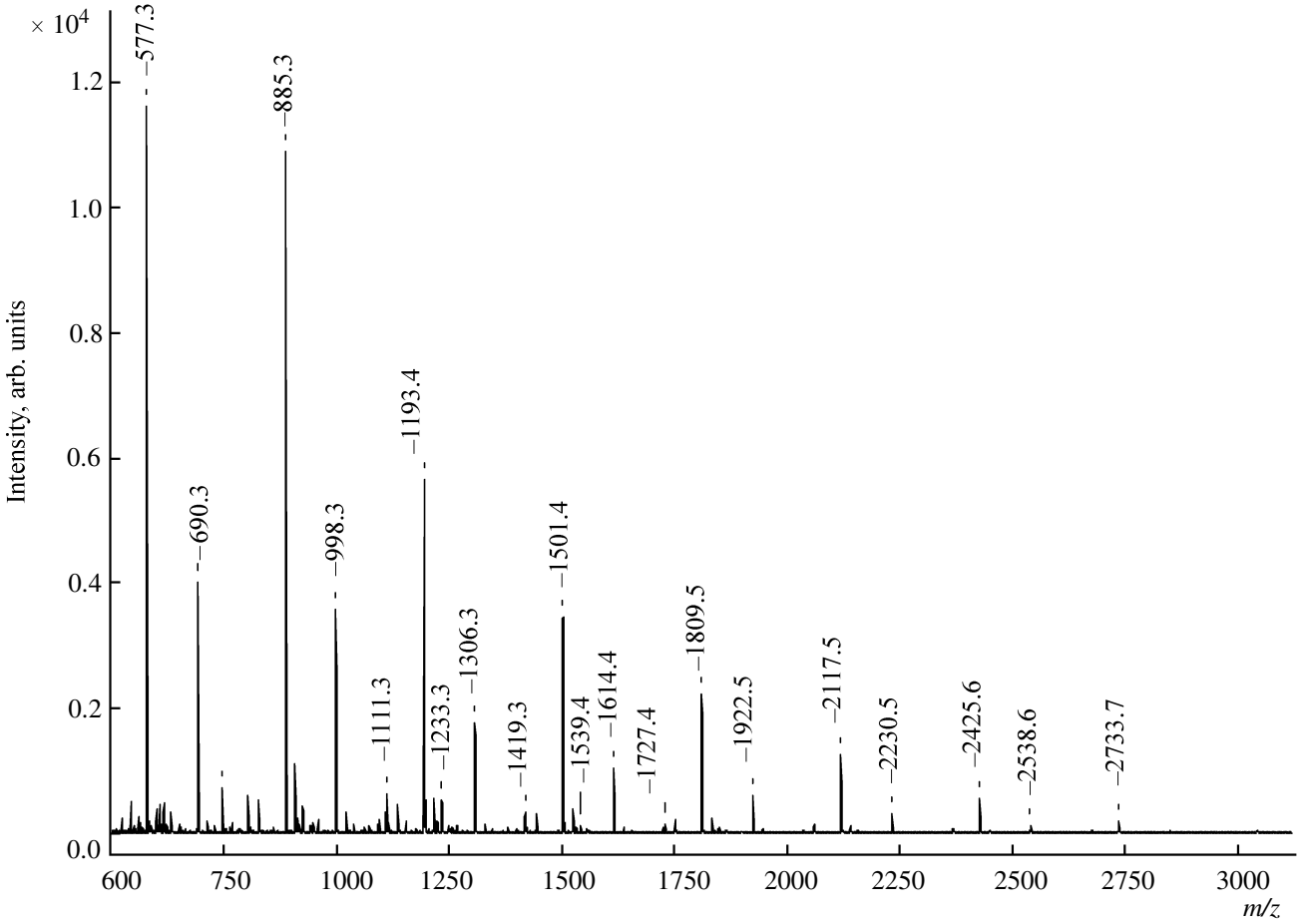


Fig. 1. Mass spectrum of oxidized form **III** of oligo(4,4'-biphenylene phenylphosphonite) **I** obtained in the linear mode.

Storage of oligo(4,4'-biphenylene phenylphosphonite), which contains phosphonamidite terminal group, leads to appreciable changes in the physicochemical properties of the oligomer. After 3-month keeping of an ether solution of oligo(4,4'-biphenylene phenylphosphonite) **II** in an inert atmosphere at 20°C, the signal of the [–OArO–P(Ph)NEt_2] fragment in its ^{31}P NMR spectrum at δ_P 131 ppm decreased in intensity, whereas the signal of [–OArO–P(Ph)O–] at 158 ppm increased. The integral intensity ratio became 1 : 26 (signals *1* and *2*, Fig. 3). Also, low-field signals (*3–7*, Fig. 3) of several organophosphorus compounds appeared in the ^{31}P NMR spectra. The growth of the signal at 158 ppm of phenylphosphonous acid diester is associated with the condensation processes continuing in the compact oligomer. Chain elongation in oligomer **II** and its conversion to the phosphinate form **VI** for mass-spectral studies can be represented by the following set of equations:

$$\underset{\textbf{IIb}}{H\text{–}[OArOP(Ph)]_n\text{–}NEt_2} + \underset{\textbf{IIc}}{H[\text{–}OArOP(Ph)\text{–}]_nOArOH} \xrightarrow{-HNEt_2} \underset{\textbf{Vc}}{H\text{–}[OArOP(Ph)\text{–}]_{2n}OArOH},$$

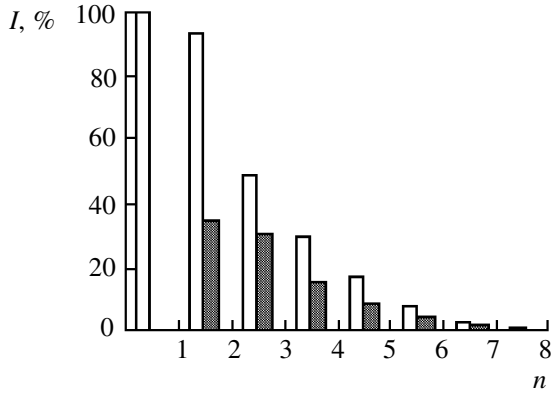
$$\underset{\textbf{Va}}{H\text{–}[OArOP(Ph)\text{–}]_{2n}OArOH} \xrightarrow{+2n[O]} \underset{\textbf{VIa}}{H[\text{–}OArOP(O)(Ph)\text{–}]_{2n}OArOH}.$$

The largest detected mass of compound **VIa** (Fig. 4) is approximately 1000 Da higher than the largest mass of oligomer **IVc** (Fig. 2).

It is interesting that in the mass spectrum of sample **VI** the intensities of the peak at *m/z* 745.3 and the related peaks (increment 308 Da), assigned to oxidized forms of phosphonium salts **VIb**, sharply increase.

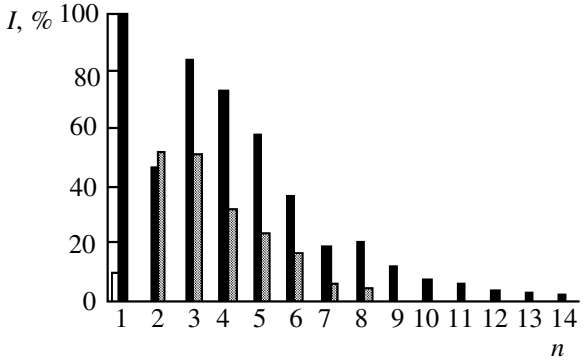
In ^{31}P NMR spectra unoxidized sample **V** in THF,

Table 1. Ions corresponding to oxidized forms **III** of oligo(4,4'-biphenylene phenylphosphonite) (**I**) with n = 1–8. Bars: (white) diamide and (grey) monoamide



Comp. no.	Ion	*m/z*	*I*, %
IIIa	$Et_2NP(O)Ph–[OArOP(O)Ph]–NEt_2$ + H^+	577.3	100.0
IIIb	$H–[OArOP(O)Ph]_2–NEt_2$ + H^+	690.3	34.4
IIIa	$Et_2NP(O)Ph–[OArOP(O)Ph]_2–NEt_2$ + H^+	885.3	93.8
IIIb	$H–[OArOP(O)Ph]_3–NEt_2$ + H^+	998.3	30.7
IIIa	$Et_2NP(O)Ph–[OArOP(O)Ph]_3–NEt_2$ + H^+	1193.4	48.7
IIIb	$H–[OArOP(O)Ph]_4–NEt_2$ + H^+	1306.3	15.2
IIIa	$Et_2NP(O)Ph–[OArOP(O)Ph]_4–NEt_2$ + H^+	1501.4	29.5
IIIb	$H–[OArOP(O)Ph]_5–NEt_2$ + H^+	1614.4	8.6
IIIa	$Et_2NP(O)Ph–[OArOP(O)Ph]_5–NEt_2$ + H^+	1809.5	16.9
IIIb	$H–[OArOP(O)Ph]_6–NEt_2$ + H^+	1922.5	4.4
IIIa	$Et_2NP(O)Ph–[OArOP(O)Ph]_6–NEt_2$ + H^+	2117.5	7.6
IIIb	$H–[OArOP(O)Ph]_7–NEt_2$ + H^+	2230.5	2.5
IIIa	$Et_2NP(O)Ph–[OArOP(O)Ph]_7–NEt_2$ + H^+	2425.6	3.0
IIIb	$Et_2NP(O)Ph–[OArOP(O)Ph]_8–NEt_2$ + H^+	2733.7	1.5

Table 2. Ions corresponding to oxidized forms **IV** of oligo(4,4'-biphenylene phenylphosphonite) (**II**) with n = 1–14. Bars: (white) diamide and (grey) monoamide



Comp. no.	Ion	*m/z*	*I*, %
IVc	$H–[OArOP(O)Ph]–OArOH$ + H^+	495.1	100.0
IVa	$Et_2NP(O)Ph–[OArOP(O)Ph]–NEt_2$ + H^+	577.2	9.1
IVb	$H–[OArOP(O)Ph]_2–NEt_2$ + H^+	690.2	52.3
IVc	$H–[OArOP(O)Ph]_2–OArOH$ + H^+	803.2	46.8
IVb	$H–[OArOP(O)Ph]_3–NEt_2$ + H^+	998.3	50.6
IVc	$H–[OArOP(O)Ph]_3–OArOH$ + H^+	1111.3	84.1
IVb	$H–[OArOP(O)Ph]_4–NEt_2$ + H^+	1306.3	31.5
IVc	$H–[OArOP(O)Ph]_4–OArOH$ + H^+	1419.4	73.7
IVb	$H–[OArOP(O)Ph]_5–NEt_2$ + H^+	1614.4	22.8
IVc	$H–[OArOP(O)Ph]_5–OArOH$ + H^+	1727.4	58.0
IVb	$H–[OArOP(O)Ph]_6–NEt_2$ + H^+	1922.4	15.5
IVc	$H–[OArOP(O)Ph]_6–OArOH$ + H^+	2035.4	37.1
IVb	$H–[OArOP(O)Ph]_7–NEt_2$ + H^+	2230.4	5.2
IVc	$H–[OArOP(O)Ph]_7–OArOH$ + H^+	2343.3	18.5
IVb	$H–[OArOP(O)Ph]_8–NEt_2$ + H^+	2538.4	4.3
IVc	$H–[OArOP(O)Ph]_8–OArOH$ + H^+	2651.3	19.6
IVc	$H–[OArOP(O)Ph]_9–OArOH$ + H^+	2960.2	11.7
IVc	$H–[OArOP(O)Ph]_{10}–OArOH$ + H^+	3268.5	7.2
IVc	$H–[OArOP(O)Ph]_{11}–OArOH$ + H^+	3577.0	5.0
IVc	$H–[OArOP(O)Ph]_{12}–OArOH$ + H^+	3884.4	3.4
IVc	$H–[OArOP(O)Ph]_{13}–OArOH$ + H^+	4192.6	2.6
IVc	$H–[OArOP(O)Ph]_{14}–OArOH$ + H^+	4499.1	2.0

the corresponding [10] signal of the phosphonium salt appears as two peaks of approximately equal intensity at 44 and 41 ppm (*3*, *4* in Fig. 3). This fact indirectly indicates that exchange reactions leading to elongation of the oligomer chain in the course of cross-linking of oligo(4,4'-biphenylene phenylphosphonite) containing phosphonamidite terminal group are accompanied in the solid phase by gradual redox processes of the type

$$2H–[–OArOP(Ph)–]_n–NEt_2 \longrightarrow \underset{Et_2N}{\overset{Et_2N}{\diagdown\!\overset{+}{P}\!\diagup}}Ph\,{}^{-}OArO–[OArOP(Ph)]_{n-1}–$$

IIb **Vb**

$$+ \{H–[–OArOP(Ph)–]_n–H\}.$$

Vc

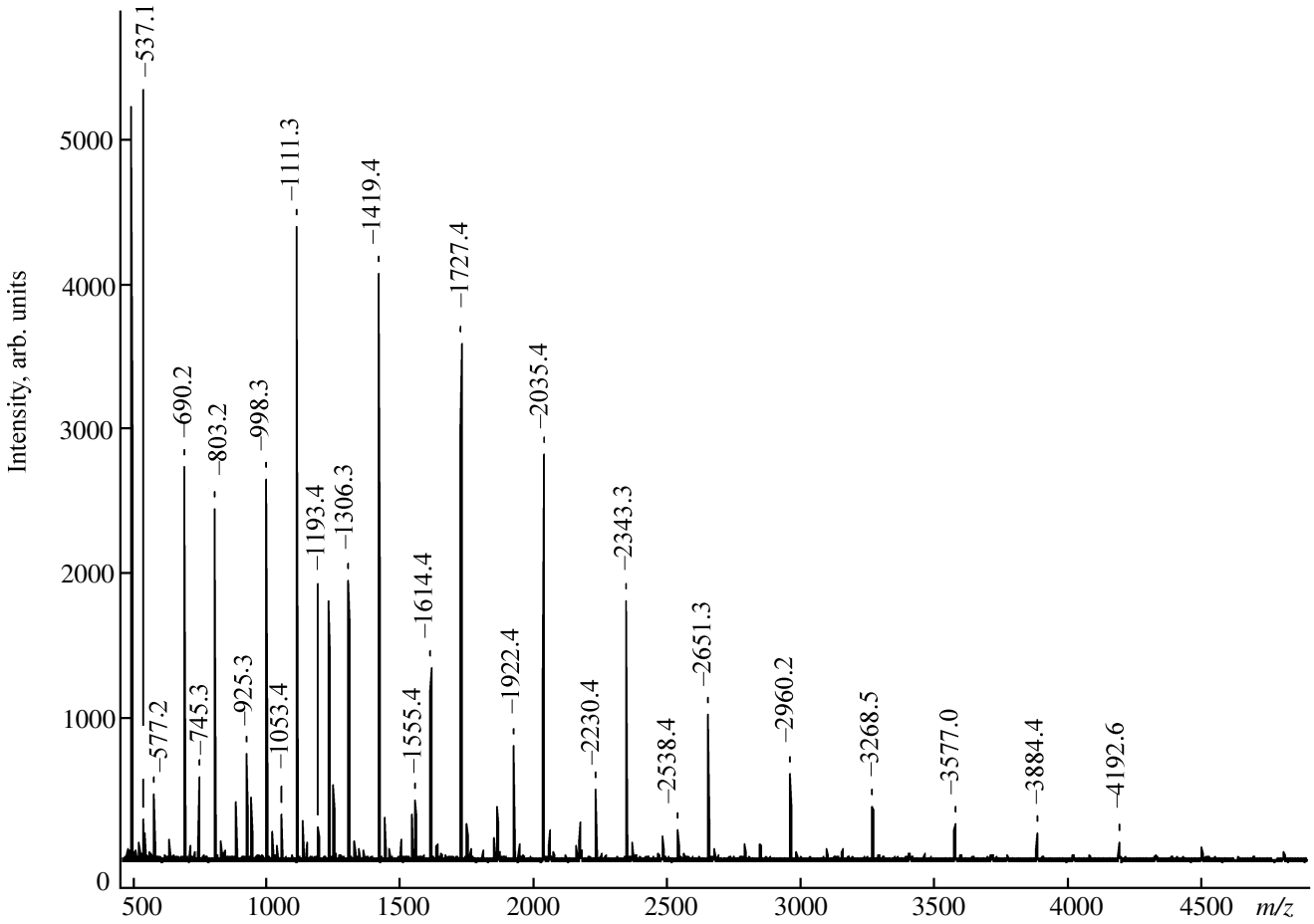


Fig. 2. Mass spectrum of oxidized form **IV** of oligo(4,4'-biphenylene phenylphosphonite) **II** obtained in the linear mode.

Compounds **Vc**, the products of the redox process involving compounds of type **IIb**, were not detected by mass spectrometry, probably because of their conversion into more complicated structures, cyclic esters of phenylphosphonous acid **Vd** and cyclic esters of hypophosphorous acid in phosphinite form **Ve**:

$$\{H\text{–}[\text{–OArOP(Ph)–}]_n\text{–}H\} + 2H\text{–}[\text{–OArOP(Ph)–}]_n\text{–}NEt_2$$

Vc **IIb**

$$\xrightarrow{-2PhH} PPh\begin{matrix}[OArOP(Ph)]_{n-1}\\ OArO\end{matrix}$$

Vd

$$+ HP\begin{matrix}[OArOP(Ph)]_{n-1}OArO\\ OArO\text{–}[\text{–P(Ph)OArO}]_{n-1}\end{matrix} PH \times Et_2N\text{–}NEt_2$$

Ve

Formation of compounds of type **Ve** type in the bulk of the oligomer is suggested by appearance in the ^{31}P NMR spectrum of compound **V** of the typical signals of a P–H bond (*5–7*, Fig. 3) [10].

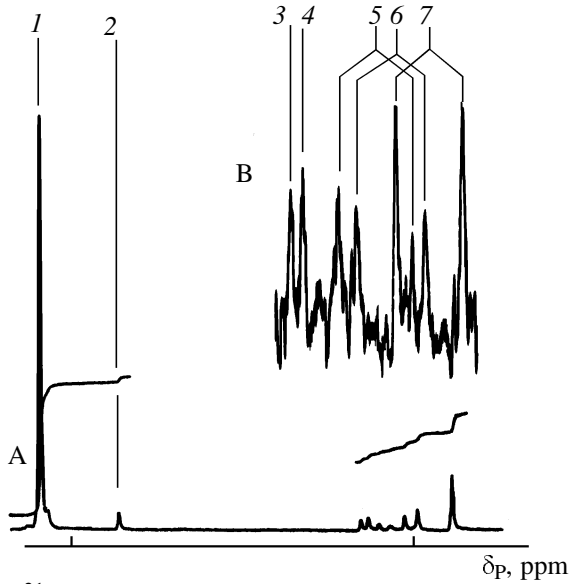


Fig. 3. ^{31}P NMR spectra of oligophosphonite **V** in THF. Main signals in spectrum A, ppm: (*1*) 158.1, [–OArO–P(Ph)O–]; (*2*) 131.2, [–OArO–P(Ph)NEt_2]. Spectrum B is the right part of spectrum A recorded without proton decoupling. Main signals in spectrum B, ppm ($^1J_{PH}$, Hz): (*3, 4*) 44.2, 41.1 (**Vb**); (*5–7*) 28.4 (584.9), 23.8 (584.9), 11.1 (507.3) (**Ve**).

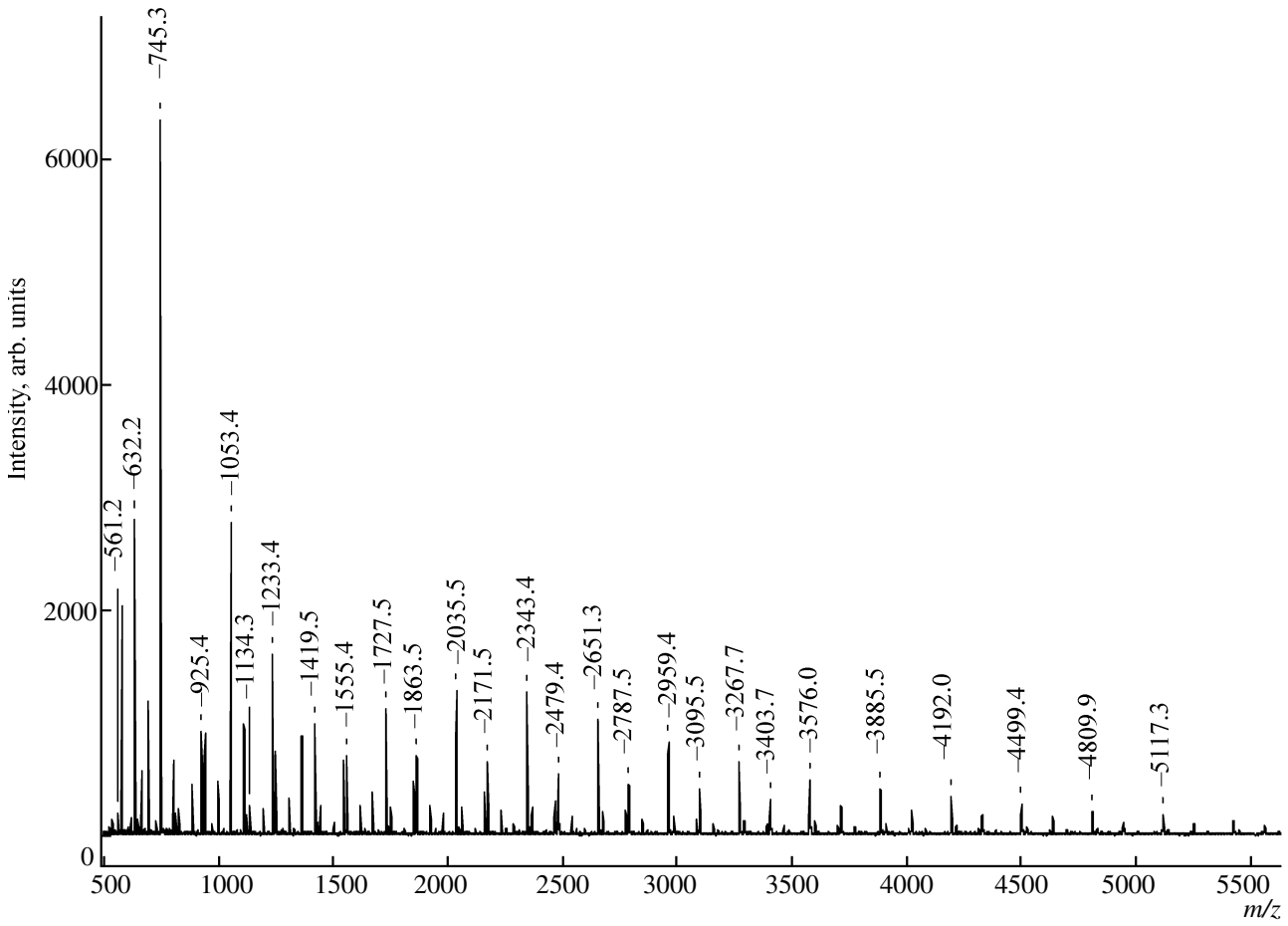
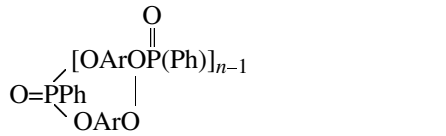
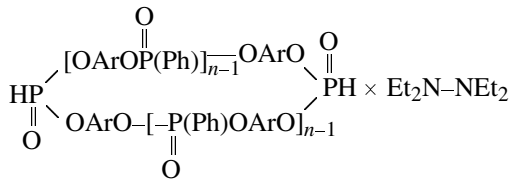


Fig. 4. Mass spectrum of oxidized form **VI** of oligo(4,4'-biphenylene phenylphosphonite) **V** obtained in the linear mode.

In the mass spectra, the peaks corresponding to cyclic compounds **Vd** and **Ve** were recorded as ions of the corresponding oxidized species **VId**, **VIe**:



VId



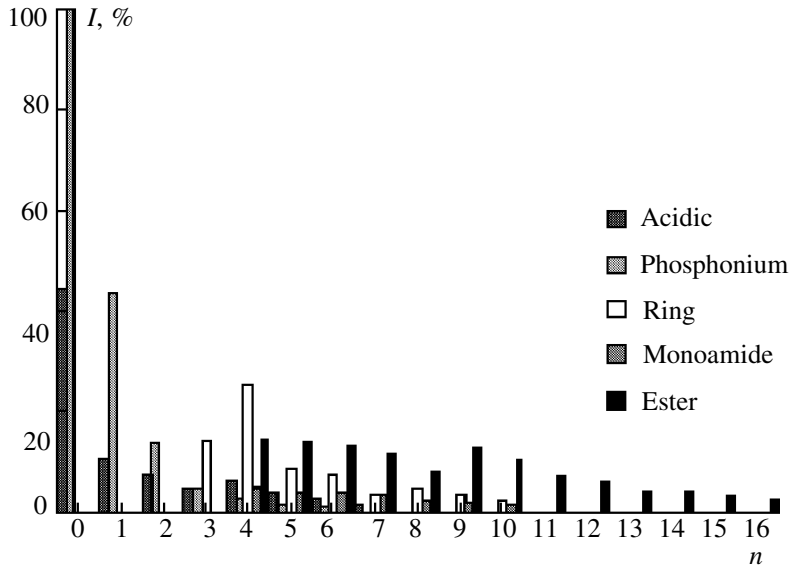
VIe

An interesting feature of cyclic compounds **VIe** is that they are recorded in the mass spectrum as MNa^+ ions. This is true for all the compounds with the number of monomeric units $(n - 1) > 0$. In the case of the parent compound **VIe** with a two-unit ring $[(n - 1) = 0]$, a peak of a higher mass, 632.2, was detected; it can be assigned to the MNa^+H^+ dication (Table 3). Thus, we established that 1*H*-tetrazole catalyzes condensation of 4,4'-dihydroxybiphenyl with phenylphosphonous tetraethyldiamide. The MALDI method used for measuring the molecular mass and structural features of oligophenylphosphonites containing labile P–N bond can be better applied to stable oxidized forms of the oligomers. Cross-linking in the solid state of oligo(4,4'-biphenylene phenylphosphonite) with phosphonamidite terminal group leads to growth of its molecular weight and is accompanied by redox processes, which is due to steric hindrance in the oligomer body and to hindered diffusion of diethylamine.

EXPERIMENTAL

The ^{31}P NMR spectra were recorded on a Bruker WP-80 instrument with operating frequency of 32.4 MHz, external reference 85% H_3PO_4. The MALDI mass spectra were taken on an Autoflex II instrument (Bruker Daltonics, Germany) with a nitrogen laser (λ = 337 nm) in the mode of recording pos-

Table 3. Ions corresponding to oxidized forms **VI** of oligo(4,4'-biphenylene phenylphosphonite) (**V**) with n = 1–16



Comp. no.	Ion	*m/z*	*I*, %
VIe	{–OArOP(OH)–OArOP(OH)–}×(Et_2NNEt_2) + Na^+ + H^+	632.2	44.2
VIa	{–OArOP(O)(Ph)–[OArOP^+(NEt_2)$_2$(Ph)]–} + H^+	745.3	100.0
VId	{–[OArOP(O)(Ph)]$_3$–} + H^+	925.4	14.5
VIe	{–OArOP(OH)–[OArOP(O)(Ph)]–OArOP(OH)–}×(Et_2NNEt_2) + Na^+	939.5	10.7
VIa	{–OArOP(O)(Ph)–[OArOP(O)(Ph)]–[OArOP^+(NEt_2)$_2$(Ph)]–} + H^+	1053.4	43.7
VIa	H[OArOP(O)(Ph)]$_3$OArOH + H^+	1111.2	15.5
VId	{–[OArOP(O)(Ph)]$_4$–} + H^+	1233.4	25.4
VIe	{–[OArOP(O)(Ph)]–OArOP(OH)–[OArOP(O)(Ph)]–OArOP(OH)–}×(Et_2NNEt_2) + Na^+	1247.5	10.5
IVb	H–[OArOP(O)(Ph)]$_4$–NEt_2 + H^+	1306.3	5.2
VIa	{–OArOP(O)(Ph)–[OArOP(O)(Ph)]$_2$–[OArOP^+(NEt_2)$_2$(Ph)]–} + H^+	1361.4	13.8
VIa	H–[OArOP(O)(Ph)]$_4$–OArOH + H^+	1419.5	14.9
VId	{–[OArOP(O)(Ph)]$_5$–} + H^+	1541.3	8.9
VIe	{–[OArOP(O)(Ph)]$_2$–OArOP(OH)–[OArOP(O)(Ph)]–OArOP(OH)–}×(Et_2NNEt_2) + Na^+	1555.4	9.3
IVb	H–[OArOP(O)(Ph)]$_5$–NEt_2 + H^+	1614.4	4.1
VIa	{–OArOP(O)(Ph)–[OArOP(O)(Ph)]$_3$–[OArOP^+(NEt_2)$_2$(Ph)]–} + H^+	1669.5	5.1
VIa	H–[OArOP(O)(Ph)]$_5$–OArOH + H^+	1727.5	14.5
VId	{–[OArOP(O)((Ph)]$_6$–} + H^+	1849.4	7.6
VIe	{–[OArOP(O)(Ph)]$_2$–OArOP(OH)–[OArOP(O)(Ph)]$_2$–OArOP(OH)–}×(Et_2NNEt_2) + Na^+	1863.5	7.6
IVb	H–[OArOP(O)(Ph)]$_6$–NEt_2 + H^+	1922.5	4.1
VIa	{–OArOP(O)(Ph)–[OArOP(O)(Ph)]$_4$–[OArOP^+(NEt_2)$_2$(Ph)]–} + H^+	1977.5	3.0
VIa	H–[OArOP(O)(Ph)]$_6$–OArOH + H^+	2035.4	13.4
VId	{–[OArOP(O)(Ph)]$_7$–} + H^+	2157.4	3.7
VIe	{–[OArOP(O)(Ph)]$_3$–OArOP(OH)–[OArOP(O)(Ph)]$_2$–OArOP(OH)–}×(Et_2NNEt_2) + Na^+	2171.5	6.0
IVb	H–[OArOP(O)(Ph)]$_7$–NEt_2 + H^+	2230.5	3.5
VIa	{–OArOP(O)(Ph)–[OArOP(O)(Ph)]$_5$–[OArOP^+(NEt_2)$_2$(Ph)]–} + H^+	2285.6	1.6
VIa	H–[OArOP(O)(Ph)]$_7$–OArOH + H^+	2343.5	11.8
VId	{–[OArOP(O)((Ph))–]$_8$–} + H^+	2465.5	4.8
VIe	{–[OArOP(O)(Ph)]$_3$–OArOP(OH)–[OArOP(O)(Ph)]$_3$–OArOP(OH)–}×(Et_2NNEt_2) + Na^+	2479.4	4.8
IVb	H–[OArOP(O)(Ph)]$_8$–NEt_2 + H^+	2538.6	2.6
VIa	{–OArOP(O)(Ph)–[OArOP(O)(Ph)]$_6$–[OArOP^+(NEt_2)$_2$(Ph)]–} + H^+	2593.7	1.0

Table 3. (Contd.)

Comp. no.	Ion	*m/z*	*I*, %
VIa	$H–[OArOP(O)(Ph)]_8–OArOH + H^+$	2651.6	8.2
VId	$\{–[OArOP(O)(Ph)]_9–\} + H^+$	2773.5	3.4
VIe	$\{–[OArOP(O)(Ph)]_4–OArOP(OH)–[OArOP(O)(Ph)]_3–OArOP(OH)–\} \times (Et_2NNEt_2) + Na^+$	2787.5	7.0
IVb	$H–[OArOP(O)(Ph)]_9–NEt_2 + H^+$	2846.6	2.2
VIa	$H–[OArOP(O)(Ph)]_9–OArOH + H^+$	2959.4	13.1
VId	$\{–[OArOP(O)(Ph)]_{10}–\} + H^+$	3081.6	2.6
VIe	$\{–[OArOP(O)(Ph)]_4–OArOP(OH)–[OArOP(O)(Ph)]_4–OArOP(OH)–\} \times (Et_2NNEt_2) + Na^+$	3095.5	6.5
IVb	$H–[OArOP(O)(Ph)]_{10}–NEt_2 + H^+$	3154.7	1.5
VIa	$H–[OArOP(O)(Ph)]_{10}–OArOH + H^+$	3267.7	10.4
VIe	$\{–[OArOP(O)(Ph)]_5–OArOP(OH)–[OArOP(O)(Ph)]_4–OArOP(OH)–\} \times (Et_2NNEt_2) + Na^+$	3403.7	5.1
VIa	$H–[OArOP(O)(Ph)]_{11}–OArOH + H^+$	3576.0	7.8
VIe	$\{–[OArOP(O)(Ph)]_5–OArOP(OH)–[OArOP(O)(Ph)]_5–OArOP(OH)–\} \times (Et_2NNEt_2) + Na^+$	3711.6	4.1
VIa	$H–[OArOP(O)(Ph)]_{12}–OArOH + H^+$	3885.5	6.3
VIe	$\{–[OArOP(O)(Ph)]_6–OArOP(OH)–[OArOP(O)(Ph)]_5–OArOP(OH)–\} \times (Et_2NNEt_2) + Na^+$	4019.5	3.6
VIa	$H–[OArOP(O)(Ph)]_{13}–OArOH + H^+$	4192.0	4.4
VIe	$\{–[OArOP(O)(Ph)]_6–OArOP(OH)–[OArOP(O)(Ph)]_6–OArOP(OH)–\} \times (Et_2NNEt_2) + Na^+$	4327.5	3.0
VIa	$H–[OArOP(O)(Ph)]_{14}–OArOH + H^+$	4499.4	4.3
Ve	$\{–[OArOP(O)(Ph)]_7–OArOP(OH)–[OArOP(O)(Ph)]_6–OArOP(OH)–\} \times (Et_2NNEt_2) + Na^+$	4635.6	2.7
Va	$H–[OArOP(O)(Ph)]_{15}–OArOH + H^+$	4809.9	3.3
Ve	$\{–[OArOP(O)(Ph)]_7–OArOP(OH)–[OArOP(O)(Ph)]_7–OArOP(OH)–\} \times (Et_2NNEt_2) + Na^+$	4943.6	1.8
Va	$H–[OArOP(O)(Ph)]_{16}–OArOH + H^+$	5117.3	2.9

itive ions. The spectra were obtained with a time-of-flight mass analyzer operating in the linear mode. The matrix was chosen on the basis of comparison of MALDI spectra obtained with 2,5-dihydroxybenzoic acid, 9-nitroanthracene, or 2,4,6-trihydroxyacetophenone. The following characteristics were taken for the comparison: reproducibility of the spectra, resolution, and signal-to-noise ratio. The best results were achieved with 2,4,6-trihydroxyacetophenone, and it was taken as a matrix for measurements. The samples were prepared by the "dried drop" technique, with THF as a solvent for the matrix and polymer; the matrix to polymer molar ratio was about 500 : 1.

Oligo(4,4'-biphenylene phenylphosphonite) (I). To 2.02 g of phenylphosphonous teraethyldiamide, we added 1.49 g of 4,4'-dihydroxybiphenyl. The mixture was stirred under argon atmosphere and gradually heated to 110°C over a period of 30 min. In so doing, 4,4'-dihydroxybiphenyl completely dissolved. The reaction flask was then connected to a vacuum pump, and the mixture was heated for 60 min under reduced pressure (15 mm Hg) at 110°C. The yield of phenylphosphonous acid diesters under these conditions was 35% based on the released diethylamne. The product is a white viscous substance soluble in dioxane, THF, and DMSO. ^{31}P NMR spectrum, (THF, δ_P, ppm; in parentheses, integral intensity): 131.2 (1), 159.4 (0.5). Molecular mass (MALDI): up to 2700 Da.

Oligo(4,4'-biphenylene phenylphenylphosphonite) (II). To 2.02 g of phenylphosphonous teraethyldiamide, we added 1.49 g of 4,4'-dihydroxybiphenyl and 0.05 g (0.7 mmol) of 1*H*-tetrazole. The mixture was stirred under argon and gradually heated over a period of 30 min to 110°C. In so doing, 4,4'-dihydroxybiphenyl dissolved completely. The reaction flask was connected to a vacuum pump, and the mixture was heated for 60 min at 110°C at reduced pressure (15 mm Hg). The yield of phenylphosphonous acid diesters under these conditions was 94% based on the released diethylamine. The product is a colorless transparent glassy substance soluble in dioxane, THF and DMSO; softening point 125–130°C. ^{31}P NMR spectrum (THF, δ_P, ppm; in parentheses, integral intensity): 131.1 (1), 159.0 (14). Molecular mass (MALDI): up to 4500 Da.

Oxidation of oligo(4,4'-biphenylene phenylphenylphosphonites) I and II and their transformation to **III** and **IV** for mass-spectrometric study were performed in air. The thin films were formed on a metallic surface (Al–Ni, 1 : 1 by weight) from solutions in THF containing peroxide.

Cross-linking of oligo(4,4'-biphenylene phenylphenylphosphonite) (sample **V**) was performed by keeping solid oligomer **II** under argon at 20°C for 3 months. Oligo(4,4'biphenylene phenylphosphonite) **V** for mass-spectrometric studies was oxidized into compound **VI** in air similarly to compounds **I** and **II**.

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