

Poly(phosphoramidites)—Polycondensation Products of Phosphorous Triamides with Aliphatic Diols and Dibasic Phenols

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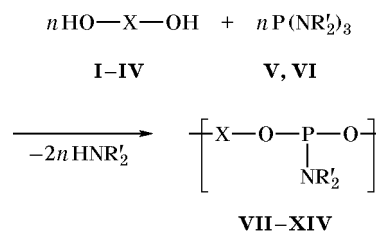
Abstract—Phosphorous triamides react with aliphatic diols and dibasic phenols: 1,6-hexanediol, 2,2'-(4-hydroxyphenyl)propane, 1,4-hydroquinone, and 4,4'-dihydroxybiphenyl in the temperature range 80–110°C in diethylene glycol dimethyl ether or without a solvent to afford phosphorus-containing regular high-molecular products having an $O_2P(NR_2)$ moiety in the monomeric unit. The resulting poly(phosphoramidites) are capable of swelling in organic solvents, and they can be used as macroligands in the catalytic hydrogenation of styrene over rhodium(I) complexes.

Phosphorus-containing polymers are used in various fields of science and technology, specifically in chemical technology, biotechnology, and many other fields, e.g., as ligands for heterogeneous and homogeneous metal-complex catalysis [1, 2]. There are three approaches to synthesis of such compounds: (1) modification of finished polymeric materials [3–6], (2) polymerization of phosphorus-containing monomers [7], and (3) polycondensation of di- and polyfunctional compounds [8]. The first of these ways, modification of finished polymeric materials, has essential limitations, for not all functional groups therein are accessible; moreover, it is difficult to attain regular arrangement of phosphorus-containing fragment along the polymeric chain. Polymerization of phosphorus-containing monomers implies preliminary synthesis of appropriate monomers and specific catalysts, which undoubtedly narrows the scope of application of that approach. Unlike the above two methods, the polycondensation technique seems to be the most appropriate. It allows the use of accessible di- and polyfunctional compounds, e.g., diols. It is also promising to involve in the polycondensation process phosphorylating agent based on phosphorous and phosphonous acid amides in which the P–N bond readily undergoes alcoholysis [9–12].

The goal of the present study was to examine the conditions of synthesis and properties (including the catalytic activity of the corresponding macroligand complexes in the hydrogenation processes) of poly-

condensation products derived from phosphorous triamides and dibasic phenols or aliphatic diols. As diols we chose 1,6-hexanediol (**I**), 2,2'-(4-hydroxyphenyl)propane (**II**), hydroquinone (**III**), and 4,4'-dihydroxybiphenyl (**IV**). These compounds are characterized by different spatial arrangements of the hydroxy groups, which should give rise to polymeric products with a definite distance between the phosphorus-containing fragments. The phosphorylating agents were hexamethyl- and hexaethylphosphorous triamides **V** and **VI**. The reactions were carried out with equimolar amounts of reactants without a solvent (method *a*) or in diethylene glycol dimethyl ether (method *b*) with removal of the liberated amine by distillation (Scheme 1). The resulting poly(phosphoramidites) were isolated in 76–99% yield. They are resinous or

Scheme 1.



I, VII, XIa, XIb, X = $(\text{CH}_2)_6$; **II, VIIIa, VIIIb, XII**, X = $p\text{-C}_6\text{H}_4\text{CMe}_2\text{C}_6\text{H}_4\text{-}p$; **III, IXa, IXb, XIII**, X = $p\text{-C}_6\text{H}_4$; **IV, Xa, Xb, XIV**, X = $p\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{-}p$; **V, VII–X**, R' = Me; **VI, XI–XIV**, R' = Et.

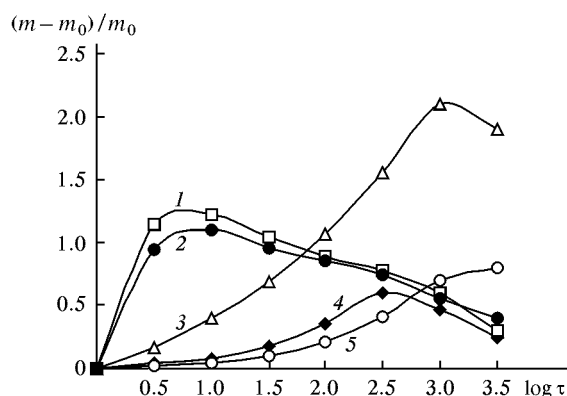


Fig. 1. Swelling of polymer **VIIIa** in different solvents at 25°C; m_0 is the initial polymer weight, m is the weight of swelled polymer, and τ is time, s; (1) diethylene glycol dimethyl ether, (2) dimethylformamide, (3) chloroform, (4) dioxane, (5) hexane.

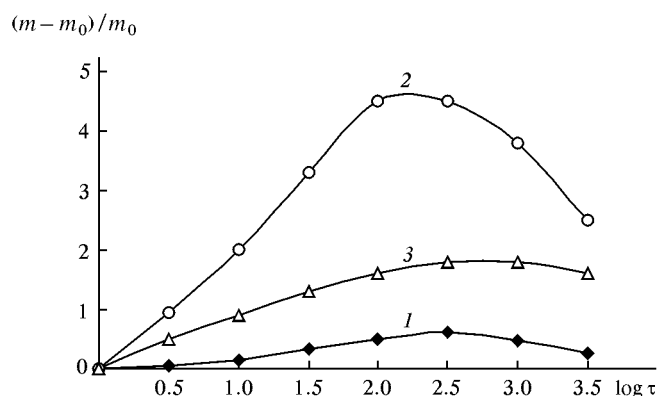
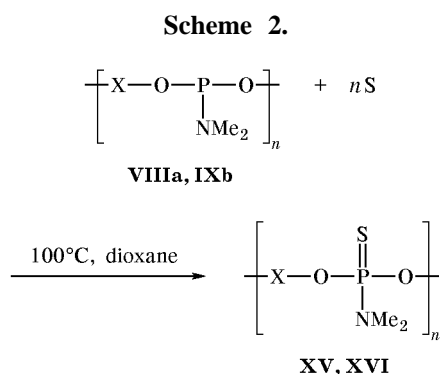


Fig. 2. Swelling of polymers (1) **VIIIa**, (2) **VIIIb**, and (3) **IXb** in dioxane.

glassy substances melting in a relatively wide temperature range (16°C). The molecular weight of the products ranges from 5000 to 15000.

Poly(phosphoramidites) **VIIIa**, **VIIIb**, and **IXb** readily swell in organic solvents (such as chloroform, diethylene glycol dimethyl ether, and dioxane; see Figs. 1, 2), so that we succeeded in recording their ^{31}P (δ_{p} 139–146 ppm) and ^1H NMR spectra (see Experimental) and bringing them into some reactions typical of trivalent phosphorus compounds.

After swelling in dioxane, polymers **VIIIa** and **IXb** reacted with elemental sulfur at 100°C to give the corresponding poly(phosphoramidothioates) (Scheme 2).



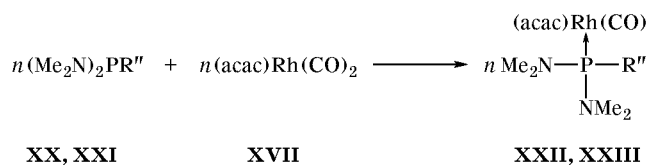
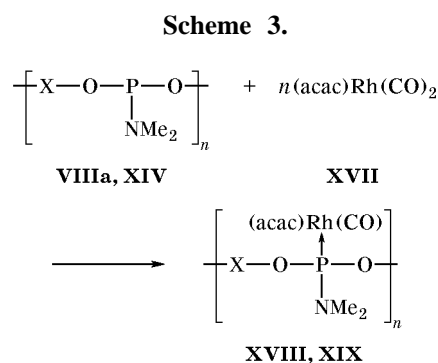
VIIIa, **XV**, X = $p\text{-C}_6\text{H}_4\text{CMe}_2\text{C}_6\text{H}_4\text{-}p$; **IXb**, **XVI**, X = $p\text{-C}_6\text{H}_4$.

The ^{31}P NMR spectra of compounds **XV** and **XVI** contain signals at δ_{p} 69 and 53 ppm, which belong to the amidothiophosphate fragments. Their ^1H NMR spectra are also consistent with the assumed structures (see Experimental). Compound **XV** is a yellowish vitreous substance melting in the temperature range

from 230 to 240°C; product **XVI** is a yellowish resilient substance melting within the range 170–175°C. Both products are resistant to atmospheric moisture.

It should be noted that the stability of the initial poly(phosphoramidites) on storage in air is almost the same as that of their sulfur derivatives. Even after storage for 3 months on exposure to air, their ^{31}P NMR spectra displayed no P(V) signals. This property of the products may be very useful from the viewpoint of their practical application.

Poly(phosphoramidites) **VIIIa** and **XIV** were brought into complex formation with rhodium(I) using

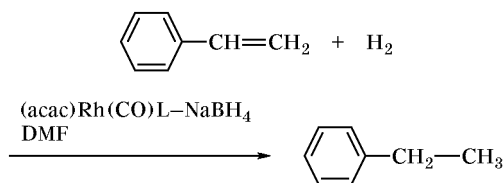


VIIIa, **XVIII**, X = $p\text{-C}_6\text{H}_4\text{CMe}_2\text{C}_6\text{H}_4\text{-}p$; **XIV**, **XIX**, X = $p\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{-}p$; **XX**, **XXII**, R'' = $i\text{-Pr}$; **XXI**, **XXIII**, R'' = OPh.

(acetylacetonato)(dicarbonyl)rhodium(I) (**XVII**). The reaction was carried out in diethylene glycol dimethyl ether at 20°C (reaction time 1 h; Scheme 3). According to the IR spectra, only one carbonyl group in complex **XVII** is replaced (see table). Signals of the initial poly(phosphoramidite) disappeared from the ^{31}P NMR spectrum, while a new doublet signal appeared with a characteristic direct P–Rh coupling constant (see table). Comparison of the spectral parameters of complexes **XVIII** and **XIX** with those of model complexes **XXII** and **XXIII**, which were obtained by reaction of simple phosphorous amides with (acetylacetonato)(dicarbonyl)rhodium(I) (**XVII**) (Scheme 3, see table), showed that the polymeric complexes contain an $\text{O}_2\text{P}(\text{NR}_2)$ fragment in the monomeric unit.

The catalytic activity of poly(phosphoramidite) complexes **XVIII** and **XIX** was tested in the hydrogenation of styrene according to Scheme 4. The reaction was carried out at 50°C under a hydrogen pressure equal to atmospheric. The rate of styrene hydrogenation over complexes **XVIII** and **XIX** was twice as high, as compared with analogous known catalysts [1]. A fairly high stability of polymeric rhodium complexes **XVIII** and **XIX** should also be noted: they retain their catalytic activity after hydrogenation of 1600 mol of the substrate per 1 mol of the metal.

Scheme 4.



EXPERIMENTAL

The ^1H NMR spectra were recorded on Bruker AC-200 and Bruker AM-400a instruments in CDCl_3 using tetramethylsilane as reference. The ^{31}P NMR spectra were obtained on a Bruker WP-80 (32.4 MHz) instrument in dioxane or diethylene glycol dimethyl ether relative to 85% H_3PO_4 . The molecular weights were determined by gel-permeation chromatography using a Waters device equipped with 10^3 -Å and 10^5 -Å Styragel columns, a Waters-410 diffusimeter–refractometer as detector, and a Waters-590 pump; the data were processed using a DataModul-730 integrator; the calibration was performed against Waters PS standards. The IR spectra were measured on a Specord 75IR spectrometer.

Spectral parameters of rhodium complexes with polymeric and monomeric phosphoramidites

Complex no.	^{31}P NMR spectrum ^a		IR spectrum, ν , cm^{-1}
	δ_{P} , ppm	$^1J_{\text{P-Rh}}$, Hz	
XVIII	134	262	1985
XIX	134	261	1985
XXII	124	220	1960
XXIII	135	265	1985

^a In diethylene glycol dimethyl ether.

Poly(phosphoramidites) were synthesized either in diethylene glycol dimethyl ether (method *a*) or without a solvent (method *b*).

Poly(phosphoramidite) VII. Phosphorous triamide **V**, 0.825 g (5.1 mmol), was added to 0.597 g (5.1 mmol) of diol **I** in 2 ml of diethylene glycol dimethyl ether, and the mixture was stirred for 4 h at 80–90°C. The solvent was distilled off under reduced pressure (80°C, 1 mm), and the residue was dried in a vacuum. Yield 0.96 g (95%), mp 260–275°C. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.38 s (4H, CH_2), 2.6 d (6H, NMe_2 , $^3J_{\text{H,P}} = 8.47$ Hz), 1.6 s (4H, CH_2), 3.6 m (4H, CH_2 , $^3J_{\text{H,H}} = 1.6$ Hz). ^{31}P NMR spectrum (dioxane), δ_{P} , ppm: 145, 139 (5:1). *M* 5500.

Poly(phosphoramidite) VIIIa was synthesized as described above for compound **VII** from 2.673 g (11.7 mmol) of phenol **II** in 3 ml of diethylene glycol dimethyl ether and 1.909 g (11.7 mmol) of phosphorous triamide **V**; reaction time 5 h (80°C). Yield 3.53 g (99%), mp 290–300°C. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.62 s [6H, $\text{C}(\text{CH}_3)_2$], 2.77 d [6H, $\text{N}(\text{CH}_3)_2$, $^3J_{\text{H,P}} = 9.35$ Hz], 6.92 d (4H, H_{arom} , $^3J_{\text{H,H}} = 8.29$ Hz), 7.11 d (4H, H_{arom} , $^3J_{\text{H,H}} = 8.25$ Hz). ^{31}P NMR spectrum (diethylene glycol dimethyl ether): δ_{P} 139 ppm. *M* 15000.

Poly(phosphoramidite) VIIIb was synthesized as described above for compound **VII** from 3.356 g (14.7 mmol) of phenol **II** in 3 ml of diethylene glycol dimethyl ether and 2.39 g (14.7 mmol) of phosphorous triamide **V**; reaction time 4 h (70–80°C). Yield 4.09 g (92%), mp 252–260°C. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.62 s [(6H, $\text{C}(\text{CH}_3)_2$), 2.75 d [6H, $\text{N}(\text{CH}_3)_2$, $^3J_{\text{H,P}} = 9.39$ Hz], 6.92 d (4H, H_{arom} , $^3J_{\text{H,H}} = 8.53$ Hz), 7.12 d (4H, H_{arom} , $^3J_{\text{H,H}} = 8.11$ Hz). ^{31}P NMR spectrum (diethylene glycol dimethyl ether): δ_{P} 139 ppm. *M* 9500.

Poly(phosphoramidite) IXa. Phosphorous triamide **V**, 1.076 g (6.59 mmol), was added to 0.725 g

(6.59 mmol) of phenol **III**, and the mixture was stirred for 3 h at 70–80°C. It was then evacuated for 2 h at 80°C (1 mm). Yield 1.19 g (98%), mp 290–297°C. ¹H NMR spectrum (CDCl₃), δ, ppm: 2.75 d [6H, N(CH₃)₂], ³J_{H,P} = 9.39 Hz), 6.87 s (4H, H_{arom}, ³J_{H,H} = 8.09 Hz). ³¹P NMR spectrum (diethylene glycol dimethyl ether): δ_p 140 ppm.

Poly(phosphoramidite) IXb was synthesized as described above for compound **VII** from 0.321 g (2.92 mmol) of phenol **III** in 1.5 ml of diethylene glycol dimethyl ether and 0.476 g (2.92 mmol) of phosphorous triamide **V**; reaction time 9 h, 100–110°C. Yield 0.86 g (76%), mp 284–290°C. ¹H NMR spectrum (CDCl₃), δ, ppm: 2.75 d [6H, N(CH₃)₂], 6.87 s (2H, H_{arom}), 7.08 s (2H, H_{arom}). ³¹P NMR spectrum (diethylene glycol dimethyl ether): δ_p 139 ppm.

Poly(phosphoramidite) Xa was synthesized as described above for compound **VII** from 0.602 g (3.2 mmol) of phenol **IV** in 1.5 ml of diethylene glycol dimethyl ether and 0.527 g (3.2 mmol) of phosphorous triamide **V**; reaction time 8 h, 100°C. Yield 1.21 g (79%), mp 185–190°C. ³¹P NMR spectrum (dioxane): δ_p 140 ppm.

Poly(phosphoramidite) Xb was synthesized as described above for compound **Xa** from 0.872 g (4.6 mmol) of phenol **IV** and 0.764 g (4.6 mmol) of phosphorous triamide **V** at 100°C (14 h). Yield 1.16 g (95%), mp 264–280°C. ³¹P NMR spectrum (dioxane), δ, ppm: 140, 139 (4:1).

Poly(phosphoramidite) XIa was synthesized as described above for compound **VII** from 0.235 g (1.98 mmol) of diol **I** in 2 ml of diethylene glycol dimethyl ether and 0.492 g (1.98 mmol) of phosphorous triamide **VI** at 100–110°C (25 h). Yield 0.39 g (89%), mp 248–258°C. ¹H NMR spectrum (CDCl₃), δ, ppm: 1.13 m [6H, N(CH₂CH₃)₂], 1.38 s (4H, CH₂), 1.6 s (4H, CH₂), 2.6 d [4H, N(CH₂CH₃)₂, ³J_{H,P} = 8.47 Hz], 3.6 m (4H, CH₂, ³J_{H,H} = 1.6 Hz). ³¹P NMR spectrum (dioxane), δ_p, ppm: 146, 139 (10:1).

Poly(phosphoramidite) XIb was synthesized as described above for compound **IXa** from 0.374 g (3.17 mmol) of diol **I** and 0.815 g (3.17 mmol) of phosphorous triamide **VI** at 80–90°C (3 h). Yield 0.72 g (98%), mp 274–280°C. ³¹P NMR spectrum (dioxane), δ_p, ppm: 146, 139 (4:1).

Poly(phosphoramidite) XII was synthesized as described above for compound **VII** from 1.551 g (6.79 mmol) of phenol **II** in 2 ml of diethylene glycol dimethyl ether and 1.681 g (6.79 mmol) of phosphorous triamide **VI** at 80°C (25 h). Yield 1.95 g (87%), mp 310–315°C. ¹H NMR spectrum (CDCl₃),

δ, ppm: 1.04 t [6H, N(CH₂CH₃)₂, ³J_{H,P} = 6.83 Hz], 1.61 s [6H, C(CH₃)₂], 3.21 t [4H, N(CH₂CH₃)₂], 6.92 d (4H, H_{arom}, ³J_{H,H} = 8.97 Hz), 7.1 d (4H, H_{arom}, ³J_{H,H} = 8.54 Hz). ³¹P NMR spectrum (dioxane): δ_p 140 ppm.

Poly(phosphoramidite) XIII was synthesized as described above for compound **IXa** from 0.467 g (4.2 mmol) of phenol **III** and 1.04 g (4.2 mmol) of phosphorous triamide **VI** at 100°C (6 h). Yield 0.96 g (91%), mp 280–287°C. ³¹P NMR spectrum (dioxane), δ_p, ppm: 142, 129 (15:1).

Poly(phosphoramidite) XIV was synthesized as described above for compound **IXa** from 0.6257 g (3.36 mmol) of phenol **IV** and 0.831 g (3.36 mmol) of phosphorous triamide **VI** at 100°C (4 h). Yield 0.88 g (91%), mp 290–300°C. ³¹P NMR spectrum (dioxane): δ_p 140 ppm.

Poly(phosphoramidothioate) XV. Finely powdered sulfur, 0.091 g (2.8 mmol), was added to 0.854 g (2.8 mmol) of poly(phosphoramidite) **VIIIa** in 1.5 ml of dioxane, and the mixture was stirred for 3 h at 60–70°C. The solvent was distilled off under reduced pressure. Yield 0.92 g (97%), mp 230–240°C. ¹H NMR spectrum (CDCl₃), δ, ppm: 1.75 s [6H, C(CH₃)₂], 2.6 d [6H, N(CH₃)₂], 6.98 m (4H, H_{arom}), 7.15 m (4H, H_{arom}, ³J_{H,H} = 7.11 Hz). ³¹P NMR spectrum (dioxane): δ_p 67 ppm.

Poly(phosphoramidothioate) XVI was obtained as described above for compound **XV** from 0.059 g (0.35 mmol) of poly(phosphoramidite) **IXb** in 2.3 ml of dioxane and 0.0113 g (0.35 mmol) of sulfur. Yield 0.069 g (96%), mp 170–175°C. ³¹P NMR spectrum (dioxane): δ_p 69 ppm.

Rhodium(I) complexes XVIII, XIX, XXII, and XXIII. A solution of 2 mmol of compound **VIIIa**, **XIV**, **XX**, or **XXI** in diethylene glycol dimethyl ether was added to a solution of 2 mmol of (acac)(CO)₂Rh in 1 ml of diethylene glycol dimethyl ether, and the mixture was kept for 2 h at 20°C. The solvent was distilled off under reduced pressure, and the residue was dried in a vacuum at (70–80°C). The ³¹P NMR and IR spectral parameters of the products are given in table.

Hydrogenation of styrene over catalysts XVIII and XIX. The reaction was carried out following the procedure described in [1]. A solution of catalyst precursor was prepared in air by the action of the corresponding organophosphorus compound on 4.3 × 10⁻⁵ mol of (acac)(CO)₂Rh in 5 ml of DMF. The subcatalyst was activated with 10⁻³ g of NaBH₄ over a period of 5 min. The hydrogenation was carried out in a common glass reactor at 50°C under hydrogen pressure equal to atmospheric. The solution of catalyst

precursor was placed in the reactor and was purged with a 5-fold volume of hydrogen; styrene was added through a silicone membrane with a syringe (the substrate-to-rhodium ratio 100:1). The mixture was stirred by swinging; the reaction was assumed to start when the swinging was initiated (at a rate of ~ 700 – 800 min^{-1}). The progress of the reaction was monitored following the amount of hydrogen absorbed per unit time and also by GLC using an LKhM-8MD chromatograph equipped with a thermal-conductivity detector; carrier gas helium (flow rate 40 ml/min); 3-mm \times 1.5-m column packed with 15% of SE-30 on Chromaton HMDS.

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