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Synthesis of New Monomer 3,3'-Diamino-4,4'-bis{*p*-[(diethoxyphosphoryl)methyl]phenylamino}diphenyl Sulfone and Polybenzimidazoles on Its Basis

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Polyheteroarylenes (PHAs) are of great interest for application as thermo-, heat-, fire-, and chemically-resistant systems and some of them also as components of solid-polymer proton-conducting membranes of hydrogen (methanol)–air fuel cells (FCs) [1]. Thus, for example, film materials based on PHA containing ionogenic acid groups (SO_3H, COOH) were successfully tested in such FCs. The chemical structure of these polymeric electrolytes can be easily modified in desired direction, they show high moisture absorption and sufficient proton conduction at temperatures below 100°C in a wet state. The further development in this field is associated with a possibility to obtain polymers showing proton-conducting properties at temperatures above 120°C under anhydrous conditions. Polymers comprising phosphoryl groups can meet this requirement because they can provide proton transfer in the absence of water [1, 2].

Polybenzimidazoles (PBIs) are one of the most studied types of PHAs used in fuel-cell membranes as polymer–electrolyte complexes with orthophosphoric acid [2–7]. It has been found, however, that free orthophosphoric acid migrates from membrane into electrode space while the fuel cell is in use, this decreases proton conductance and cell efficacy. Therefore, it is rather reasonable to develop methods for the synthesis of PBIs that involve ionogenic acid phosphorus-containing groups chemically bound to the polymer chain. To provide high chemical and thermal stability of this polymer, it is optimal to include phosphorus atom into the main chain of polymer via P–C bonds [8]. Only few reports on the synthesis of phosphorylated polybenzimidazoles (PPBIs) are available in the literature: phosphonethylated ones prepared by polymer-analogous reactions [8], copolymers derived from 5-phosphonoisophthalic acid [9], high-molecular-weight film-forming PBI based on 10-dihydroxy-10-oxo-10H-dibenzo[*b*,*e*][1,4]oxaphosphinine-2,8-dicarboxylic acid [8,10].

The measurements of proton conductivity of pressed or film samples based on the above polymers showed values within 10^{-3} to 10^{-5} S/cm, whereas the conductivity of PBIs doped with phosphoric acid reached 0.15 S/cm [5–7]. Such a large difference in proton conductivity is likely due to the fact that doped systems contain up to 5–6 molecules of H_3PO_4 per monomer unit of polymer, which is equivalent to 15–18 P–OH groups, while the obtained PPBIs comprise only 1–2 groups, which is insufficient for efficient proton transport.

In this work, we have synthesized high-molecular-weight PPBIs containing 4–5 P–OH groups covalently attached to the polymer chain and assessed their physicochemical properties and possibility of application in a real fuel cell.

EXPERIMENTAL

4,4'-Dichlorodiphenyl sulfone (**1**), 4,4'-oxydibenzoic acid (**6**), diethyl 4-aminobenzylphosphonate (**3**), polyphosphoric acid (PPA), Eaton's reagent (ER), *N*-methylpyrrolidone (NMP), and formic acid were purchased from Sigma-Aldrich and used without additional purification.

3,3-Bis(*p*-carboxyphenyl)phthalide (**7**) received from Soyuzglavreaktiv was purified by recrystallization from methanol with activated carbon and dried in vacuum (0.133 Pa) at 90–100°C, 10-hydroxy-10-oxo-10H-10λ^5-phenoxaphosphine-2,8-dicarboxylic acid (**8**) was obtained by procedure [10].

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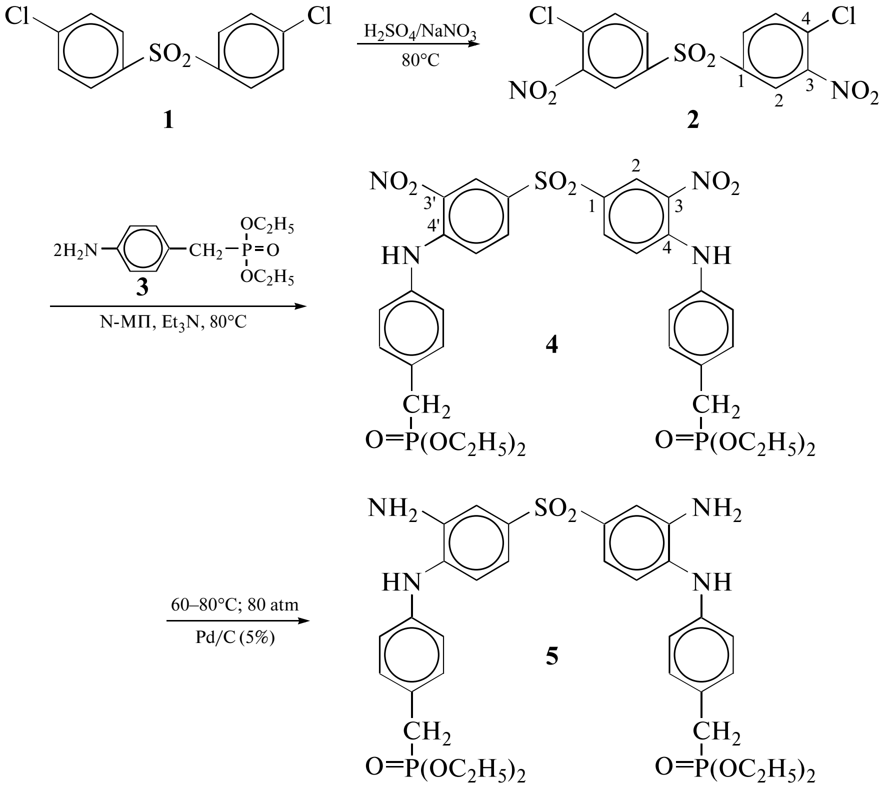
Synthesis of Initial Compounds

4,4'-Dichloro-3,3'-dinitrodiphenyl sulfone (2) (Scheme 1) was obtained by in-house procedure. 4,4'-Dichlorodiphenyl sulfone (**1**) (57.4 g, 0.2 mol) was dissolved under stirring in 250 mL of concentrated H_2SO_4 at 80°C in a 500-mL two-necked flask equipped with a helical-blade stirrer. After dissolution (1–1.5 h), 37.4 g (0.44 mol) of $NaNO_3$ was added in small portions with stirring over 20–30 min. The resultant white suspension was stirred for 5 h (monitoring by TLC for product formation, toluene as eluent). The suspension was cooled to ambient temperature, poured on ice and distilled water was added to total volume of 1000 mL. The precipitate was filtered off, washed with water to pH 7, and recrystallized from 1000 mL of acetic acid to give 71.69 g (95%) of compound **2**. After drying (100°C, $P_{\text{res}} = 10^{-2}$ Torr) mp 200–201.5°C.

^{1}H NMR ($CDCl_3$, δ, ppm): 8.43 (d, 2H, $^4J_{\text{HH}}$ = 2.0 Hz), 8.07 (dd, 2H, $^3J_{\text{HH}}$ = 8.4 Hz, $^4J_{\text{HH}}$ = 2.0 Hz), 7.78 (d, 2H, dd, 2H, $^3J_{\text{HH}}$ = 8.4 Hz).



Scheme 1

4,4'-Bis{*p*-[(diethoxyphosphoryl)methyl]phenylamino}-3,3'-dinitrodiphenyl sulfone (4) (Scheme 1) was obtained by reaction of diethyl 4-aminobenzylphosphonate (**3**) with sulfone **2**. Compound **3** (16 g, 0.044 mol) was added in argon flow at ambient temperature to 26 mL of *N*-methylpyrrolidone containing 5.6 g (0.02 mol) of sulfone **2**. After homogeneous solution formed, the temperature was raised to 80°C and the reaction was continued until disappearance of compound **2** in the reaction mixture (monitoring by TLC, toluene–acetone, 5 : 1, as eluent). After completion of the synthesis (~6 h), the reaction mixture was cooled to ambient temperature and diluted with 150 mL of ethanol. The resulting bright yellow fine precipitate was filtered off, dried in air, and recrystallized from ethanol to give 12.02 g (80%) of compound **4**, mp 154–156°C.

^{1}H NMR (DMSO-d_6, δ, ppm): 1.19 (t, 12H, $^3J_{\text{HH}}$ = 7.0 Hz), 3.28 (d, 4H, $^2J_{\text{HP}}$ = 21.6 Hz), 3.97 (dq, 8H, $^3J_{\text{HH}}$ = 7.2 Hz, $^3J_{\text{HP}}$ = 7.4 Hz), 7.08 (d, 2H, $^3J_{\text{HH}}$ = 9.2 Hz), 7.28–7.38 (m, 8H), 7.90 (dd, 2H, $^3J_{\text{HH}}$ = 9.2 Hz, $^4J_{\text{HH}}$ = 2.4 Hz), 8.56 (d, 2H, $^4J_{\text{HH}}$ = 2.4 Hz).

^{31}P{^{1}H} NMR (DMSO-d_6, δ, ppm): +27.8 (s).

3,3'-Diamino-4,4'-bis{*p*-[(diethoxyphosphoryl)methyl]phenylamino}diphenyl sulfone (5) (Scheme 1) was obtained by reduction of 7.91 g (0.01 mol) of sulfone **4** with hydrogen in an autoclave (60–80°C, P_{H_2} = 80 atm) over 5% Pd/C in 210 mL of ethanol during 8 h. The hot solution of **4** after reduction was filtered through silica gel layer and cooled. Tetramine **5** crystallized as fine beige crystals. After drying in vacuum (100°C, $P_{\mathrm{res}} = 10^{-2}$ Torr), 6.21 g (85%) of the product was obtained with mp 118–120°C.

For $C_{34}H_{44}N_4O_8P_2S$ anal. calcd. (%): C, 55.51; H, 6.22; N, 7.58; P, 8.40; S, 4.52.

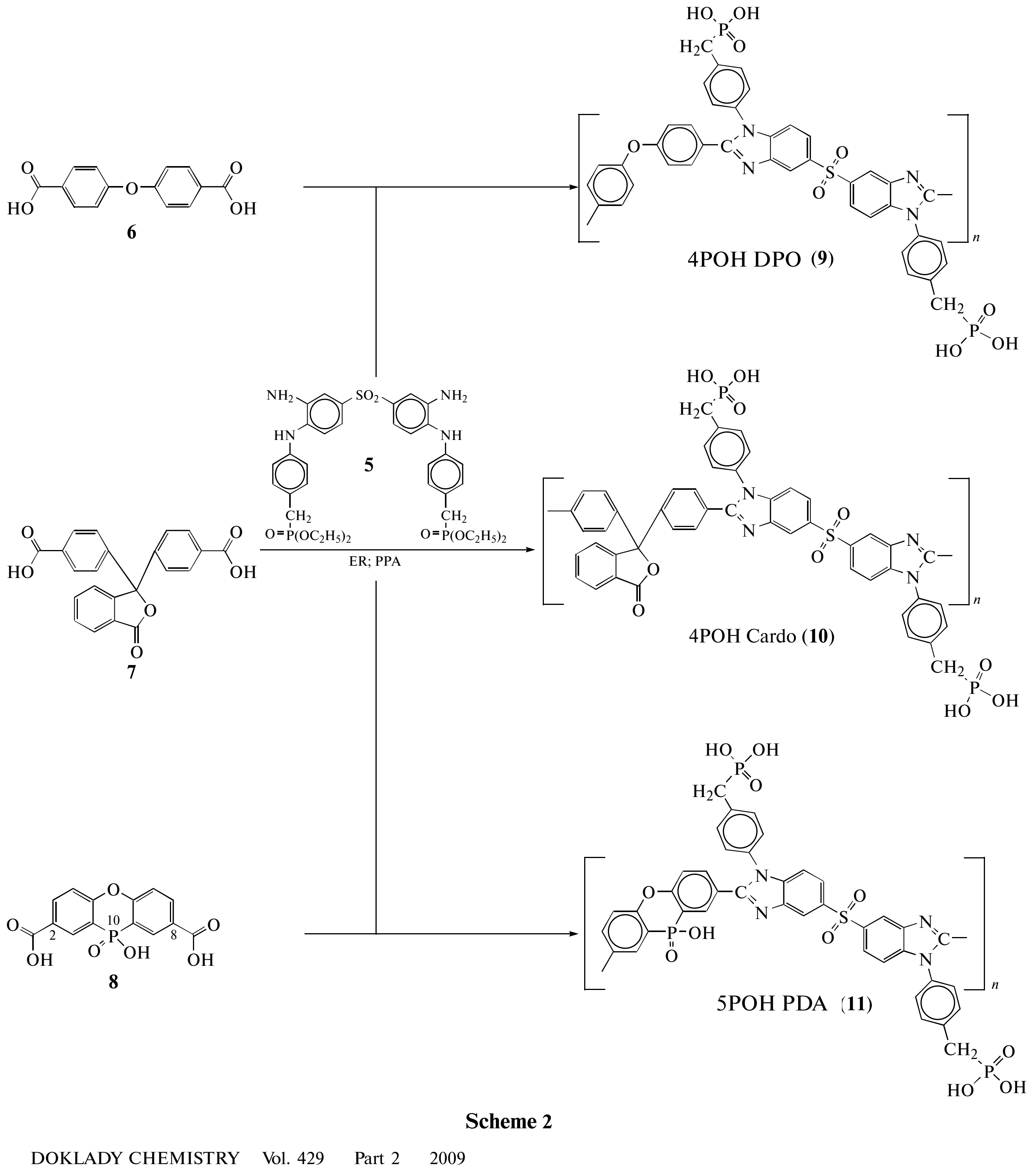
Found (%): C, 55.88; H, 6.07; N, 7.67; P, 8.48; S, 4.39.

^{1}H NMR (DMSO-d_6, δ, ppm): 1.18 (t, 12H, $^3J_{\mathrm{HH}} = 7.0$ Hz), 3.13 (d, 4H, $^2J_{\mathrm{HP}} = 21.2$ Hz), 3.94 (dq, 8H, $^3J_{\mathrm{HH}} = 7.2$ Hz, $^3J_{\mathrm{HP}} = 7.4$ Hz), 5.28 (br s, 4H), 6.95–7.16 (m, 14H), 7.39 (s, 2H).

^{31}P{^{1}H} NMR (DMSO-d_6, δ, ppm): +28.43 (s, P).

Synthesis of PPBI in Polyphosphoric Acid (PPA) and Eaton's Reagent (ER) Medium

Polymer 4POH DPO (**9**) was obtained in PPA and ER from monomers **5** and **6** (Scheme 2).



Scheme 2

Properties of phosphorus-containing polybenzimidazoles prepared in polyphosphoric acid (PPA) and Eaton's reagent (ER) medium

Polymer	Medium	η_{red}, dL/g (0.5%, 25°C in H_2SO_4)	τ, h	Solubility				T_{deg}, °C (TGA, air)
				H_2SO_4	CF_3COOH	HCOOH (100%)	NH_4OH (28%)	
4POH DPO (**9**)	PPA	0.53	40	+	+	++	+++	500
	ER	0.80	30	+	+	++	+++	475
4POH Cardo (**10**)	ER	3.24	30	+	+	++	+++	450
5POH PDA (**11**)	PPA	0.42	40	+	+	++	+++	475
	ER	1.33	35	+	+	±	+++	475

Note: The sign "+" indicates polymer solubility below 1%, "++" indicates that polymer is soluble, "+++" indicates that polymer is readily soluble, "±" indicates that polymer is soluble in part.

Synthesis in PPA medium. A two-necked flask equipped with a mechanical stirrer was charged with 0.731 g (0.001 mol) of monomer **5** and 0.258 g (0.001 mol) of monomer **6**. Polyphosphoric acid (4.37 g) was added to the monomers and the mixture was heated to 75°C. After 2-h keeping, the temperature was raised to 120°C, 2.1 g of P_2O_5 was added, and the mixture was kept for 4 h. The temperature was elevated to 180°C and the reaction was continued for 32 h. The reaction mixture was cooled to 120°C and the resultant polymer was precipitated with water. The precipitate was collected by filtration, washed with water, and dried in vacuum (0.133 Pa) at 100°C for 5 h to give 0.94 g (95%) of polymer **9**.

^{1}H NMR (HCOOD, δ, ppm): 4.90 (d, $^2J_{HP}$ = 22.0 Hz), 8.65–9.22 (m, aromatic protons).

^{31}P{^{1}H} NMR (HCOOD, δ, ppm): +25.91 (s).

Synthesis in ER medium. A two-necked flask equipped with a mechanical stirrer was charged with 0.7308 g (0.001 mol) of monomer **5**, 0.2582 g (0.001 mol) of monomer **6**, and 3 mL of ER. The monomers were dissolved in argon flow for 1 h at 100°C with stirring. The resultant homogeneous solution was strengthened with 2 g of P_2O_5 and stirred additionally for 1 h. The temperature was elevated to 145°C over 2 h and then 2 mL of ER was added. The reaction was carried out for 24 h, the temperature was decreased to 100°C and the polymer was precipitated with water. The precipitate was collected by filtration and Soxhlet extracted with isopropanol. The polymer was dried in vacuum (0.133 Pa) at 100°C for 5 h. Yield 0.95 g (96.1%).

^{1}H NMR (HCOOD, δ, ppm): 4.90 (d, $^2J_{HP}$ = 22.0 Hz), 8.65–9.22 (m, aromatic protons).

^{31}P{^{1}H} NMR (HCOOD, δ, ppm): +25.91 (s).

Polymers 4POH Cardo (**10**) and 5POH PDA (**11**) were obtained in PPA and ER similarly to polymer **9** from monomers **7** and **5** as well as **8** and **5** in more than 95% yields (Scheme 2). The table shows the properties of polymers **9**–**11**.

Study of Individual Compounds and Polymers

^{1}H and ^{31}P NMR spectra of the studied compounds were recorded on a Bruker Avance 400 spectrometer operating at 400.13 and 161.98 MHz, respectively, in DMSO-d_6 or HCOOD solutions. Chemical shifts in δ scale were calculated using residual proton signals of the deuterated solvent as an internal reference (^{1}H) and 85% H_3PO_4 as an external reference (^{31}P).

Dynamic TGA was carried out with a MOM Q-1000 derivatograph (Hungary) in air at a heating rate of 5 K/min, sample weight of 40–60 mg.

Melting points were measured on a Boetius heating bench and not corrected.

Reaction course and purity of isolated products were monitored by TLC using Silufol UV-254 plates, visualization under UV light or by exposing to iodine vapors.

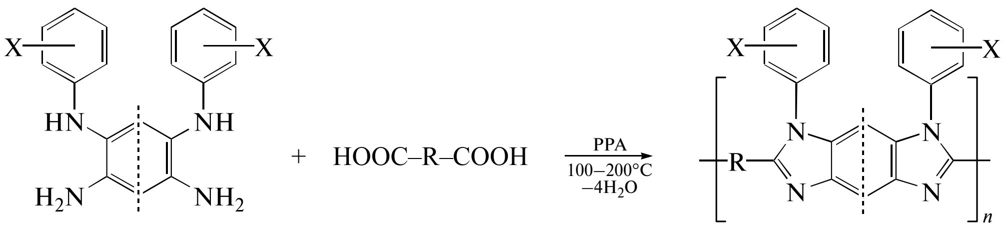
Reduced viscosity was measured at 25°C with a capillary Ubbelohde viscometer at polymer concentration of 0.5 g/dL.

RESULTS AND DISCUSSION

Tetramine **5** was obtained for the first time according to Scheme 1.

At the first stage, the nitration of 4,4'-dichlorodiphenyl sulfone (**1**) with sodium nitrate in 98% H_2SO_4 at 80°C afforded 4,4'-dichloro-3,3'-dinitrodiphenyl sulfone (**2**) in high yield. The latter was further used for the synthesis of 4,4'-bis{*p*-[(diethoxyphosphoryl)methyl]phenylamino}-3,3'-dinitrodiphenyl sulfone (**4**) by reaction with 2 equivalents of diethyl 4-aminobenzylphosphonate (**3**) in *N*-methylpyrrolidone in the presence of triethylamine. Dinitro compound **4** was reduced with hydrogen over Pd/C (5%) in EtOH solution in an autoclave at 60–80°C. After crystallization of reduction product **5** from ethanol, its composition and chemical structure were confirmed by elemental analysis and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

It is known that, in general, the polycondensation of 1,3-diamino-4,6-dianilines with dicarboxylic acids in PPA medium leads to N-phenyl-substituted PBIs [2] (Scheme 3).



Scheme 3

We assumed that the polycondensation reaction of the above monomers **5**–**8** will proceed similarly both in PPA and ER [11], which in recent time is widely used for the synthesis of PHA and PBI (see, in particular, [11–13]). Polymer concentrations in the syntheses varied within 10–20%. The syntheses involved strengthening of both PPA and ER by adding phosphoric anhydride during polycondensation (taking into account water evolved). The use of this technique makes it possible to increase considerably the molecular weight of resulting PPBI. The syntheses in PPA and ER were carried out at 180–200°C and 140–145°C, respectively.

We used the following dicarboxylic acids as comonomers for sulfone **5**: 4,4'-oxydibenzoic acid (**6**), because its polymers show high film-forming properties [2], 3,3-bis(*p*-carboxyphenyl)phthalide (**7**), whose use provides cardo polymers and enhances their solubility [2, 13], and 10-hydroxy-10-oxo-10H-10λ^5-phenoxaphosphine-2,8-dicarboxylic acid (**8**) as a carrier of one P–OH group [8, 10].

^1H and ^{31}P NMR spectra confirm the chemical structure of polymers **9**–**11**, which contain after precipitation only free phosphonate groups showing phosphorus chemical shifts at 25.9 ppm [8]. Thus, the polycyclocondensation and isolation of polymers **9**–**11** is accompanied by the total hydrolysis of diethyl phosphonate group of monomer and complete retention of benzylphosphonate side groups.

The structure of the polymers was also confirmed by the data of IR spectroscopy. IR spectra show wide bands of associated hydroxy groups in the region of 2500–3800 cm^{-1} and strong bands of stretching vibrations of phosphonate groups within 1150–1280 cm^{-1}.

The table shows that η_{red} values for 0.5% solutions of the polymers in H_2SO_4 at 25°C are of 0.42–3.24 dL/g, which indicates rather high molecular weights of obtained PPBIs, which, however, exhibit limited solubility in formic and trifluoroacetic acids and in concentrated ammonia solutions upon heating to 60–80°C. A solution of polymer 5POH PDA (**11**) in aqueous ammonia shows distinct thixotropic properties and gives elastic physical gel upon cooling, whose slow drying at ambient temperature results in good films.

The table also shows that all obtained polymers, according to the data of dynamic TGA in air (heating rate of 5 K/min), have high thermal stability comparable with that of the best known polymers of PBI family [1–3]. Their onset degradation temperatures are above 500°C.

The preliminary testing of proton conductivity of a film of 5POH PDA (**11**) obtained from a gel in 28% aqueous ammonia solution followed by treatment with 2% H_2SO_4 showed conductivity about 1–2 mS/cm at 160°C, whereas PPBI obtained in the work [10] based on PDA under these conditions showed 100 times lower proton conductivity. For the practical application of membranes in high-temperature fuel cell, the proton conductivity should be at least of 5 mS/cm at 150–200°C, better value is 50 mS/cm and above. Therefore, the use of films of obtained PPBIs in a pure form seems to be doubtful. The attempts to dope them with phosphoric acid lead to rather mechanically weak membranes providing no opportunity to make efficient membrane-electrode assembly (MEA). The obtained PPBIs were successfully used as thickening agents for phosphoric acid for application as storage for proton-conducting electrolyte in a three-layer membrane based on traditional PBIs. The resource testing of these MEAs (with working surface area of 5 cm^2) in a hydrogen–air fuel cell with the use of

Celtec P1000® industrial electrodes (BASF) in a galvanostatic mode (current density of 0.4 A/cm^2, 160°C) showed stable potential difference of ΔU = 0.560–0.580 V during 2200 h of continuous operation.

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