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# Chemical Modification of Cardo Poly(benzimidazole) Using "Click" Reaction for Membranes of High-Temperature Hydrogen Fuel Cells

Iv. I. Ponomarev, I. I. Ponomarev, E. I. Goryunov, Yu. A. Volkova, D. Yu. Razorenov, Z. A. Starikova, I. V. Blagodatskikh, M. I. Buzin, and Academician A. R. Khokhlov Received July 20, 2012

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Poly(benzimidazole)s (PBIs) are one of the most promising and studied classes of polymers used as membranes in high-temperature hydrogen fuel cells (HTFC) as polymer–electrolyte complexes with orthophosphoric acid [1, 2].

Phosphonethylated poly(benzimidazole)s (PEP-BIs) were obtained for the first time in the Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, by the polymer analogous reaction of high-molecular-weight PBI–O–PT polymer [3] via the reaction with *O*,*O*-diethyl vinylphosphonate [4] (Scheme 1) and successfully studied in the construction of the membrane-electrode block (MEB) of the hydrogen HTFC.



#### Scheme 1.

The current–voltage characteristics of the MEB based on PEPBI–O–PT membrane are comparable with the best commercial products of BASF, Celtec<sup>®</sup>-P1000, and Celtec<sup>®</sup>-V [4–7]; however, such MEBs need further improvement.

Earlier [5], we also obtained rather high-molecular-weight N-aryl-substituted PBIs with five –P–OH groups per repeat unit of the polymer. However, films prepared from these PBIs were found to have insufficiently high strength and could not be used for assembling MEBs [5].

In this work, we have studied an approach that consists in a two-step polymer analogous reaction of filmforming high-molecular-weight PBI-O-PT with propargyl bromide followed by transformation into a phosphorylated analogue by 1,3-dipolar addition of diethyl (4-azidobenzyl)phosphonate (Scheme 2, compound 3). For this purpose, we also studied in this

Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia

work for the first time such reactions by using model 2phenylbenzimidazole (2-PBI, 1) as an example. We also carried out the polymer analogous transformations of high-molecular-weight PBI–O–PT into phosphorylated triazolopolybenzimidazole (PTPBI) (Scheme 3), which was used to prepare proton-conducting membranes tested in a model of MEB of HTFC.

## **EXPERIMENTAL**

Dimethyl sulfoxide, *N*-methylpyrrolidone (N-MP), 2-phenylbenzimidazole (2-PBI), diethyl (4-aminobenzyl)phosphonate, propargyl bromide (PB), sodium hydroxide, potassium carbonate, triethylamine, copper(I) iodide, sodium azide, and 85% phosphoric acid were purchased from Sigma–Aldrich and used as received.



Scheme 2.

## Methods of Study of Individual Compounds and Polymers

The <sup>1</sup>H and <sup>31</sup>P NMR spectra of obtained compounds were recorded on a Bruker Avance-400 spectrometer (operating at 400.13 and 161.98 MHz, respectively) in a DMSO- $d_6$  or HCOOD solution. Chemical shifts ( $\delta$ ) were calculated using residual proton signals of a deuterated solvent as an internal reference (<sup>1</sup>H) and 85% H<sub>3</sub>PO<sub>4</sub> as an external reference (<sup>31</sup>P).

The IR absorption spectra were recorded on a Nicolet Magma-IR 750 IR Fourier-transform spectrophotometer in the range of  $4000-400 \text{ cm}^{-1}$  as thin films or KBr pellets. Thermogravimetric studies (TGA) were performed on a MOM Derivatograph-C instrument (Hungary) in air at a heating rate of 5 K/min using ~15 mg samples.

The reaction course and the purity of the initial reagents and isolated products were monitored by TLC on Silufol UV-254 plates with visualization under UV light or in iodine vapors.

The reduced viscosity of PBI was measured in a capillary Ubbelohde viscometer at  $25^{\circ}$ C at the concentration of polymer solutions of 0.5 g/dL.

Molecular-weight characteristics were analyzed by GPC on an Agilent 1100 chromatograph equipped with a diode array detector and column with hydroxycontaining methyl acrylate sorbent by procedure [3] using a solution of LiCl in DMF (50 mmol/L) as an eluent. The calibration curve was plotted with the use of polystyrene standards.

#### Synthesis of Individual Compounds

Poly(benzimidazole) PBI-O-PT was obtained by procedures developed by us [3]. Polymer with  $\eta_{red} = 2.1 \text{ dL/g} (0.5\% \text{ solution in N-MP at } 25^{\circ}\text{C})$  was used in the reaction with propargyl bromide.

Synthesis of 2-phenyl-1-prop-2'-ynyl-1*H*-benzimidazole (2) and its X-ray diffraction study. A mixture of 1.94 g (0.01 mol) of 2-PBI (1), 1.40 g (0.011 mol) of potassium carbonate, and 1.30 g (0.011 mol) of PB was stirred in 10 mL of N-MP at 50°C in a dry argon flow for 10 h with intermittent sonication. The reaction was monitored by TLC using toluene as an eluent. The reaction solution was poured into water, neutralized with acetic acid to pH 6, and 1 was extracted with diethyl ether ( $3 \times 30$  mL). The extract was dried with calcium chloride, filtered, and concentrated to 20 mL. The filtrate was placed in a refrigerator, the precipi-



Fig. 1. Crystal structure of 2-phenyl-1-prop-2'-ynyl-1*H*-benzimidazole acetate (2).

tated colorless crystals were filtered off and dried in a vacuum at  $60^{\circ}$ C to give 2.1 g (90%) of crystalline compound **2**, mp 71–73°C (lit.: 72°C).

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>,  $\delta$ , ppm, *J*, Hz): 3.52 (t, 1H, HC=C, <sup>4</sup>J<sub>HH</sub> 2.5), 5.16 (d, 2H, CH<sub>2</sub>, <sup>4</sup>J<sub>HH</sub> 2.5), 7.28–7.38 (m, 2H, H<sup>5,6</sup>), 7.57–7.66 (m, 3H, *m*-+*p*-C<sub>6</sub>H<sub>5</sub>), 7.68–7.75 (m, 2H, H<sup>4,7</sup>), 7.84–7.90 (m, 2H, *o*-C<sub>6</sub>H<sub>5</sub>).

Pale yellow needle-like crystals of acetate of compound **2** were obtained from diethyl ether,  $C_{16}H_{12}N_2 \cdot CH_3COOH$  (FW = 293.3), monoclinic, at 100 K a = 10.9958(8) Å, b = 7.6562(5) Å, c = 18.2065(13),  $\beta = 101.944(1)^\circ$ , V = 1499.6(2) Å<sup>3</sup>, space group  $P2_1/n$ , Z = 4,  $d_{calcd} = 1.295$  g/cm<sup>3</sup>. The experimental set of 18 887 reflections was obtained on a Bruker APEX II CCD area detector diffractometer at 100 K ( $\lambda MoK_{\alpha}$  radiation,  $2\theta_{max} = 60.0^\circ$ ) from a single crystal of 0.35 × 0.20 × 0.16 mm in size. All calculations were performed with the SHELXTL PLUS 5 software package.

Atomic coordinates, bond lengths, bond angles, and thermal parameters are deposited with the Cambridge Crystallographic Data Center (CCDC no. 770666) and are available free upon request through http://www.ccdc.cam.uk/conts/retrieving.html (or from CCDC, 12 Union Road, Cambridge CB2 1EZ; fax: +44 1223 335 033; or deposit@ccdc.cam.ac.uk).

DOKLADY CHEMISTRY Vol. 447 Part 1 2012

The structure contains molecules of **2** and acetic acid (Fig. 1) bound by the strong hydrogen bond N2…H–O1S (distances N2–O1S are 2.699(2) Å, N2…H 1.81(2) Å, H–O1S 0.90(2) Å, H–O1S 0.90(2) Å, angle N2…H–O1S 172(1)°) and the weak hydrogen bond C16–H16…O2S (distances C16…O2S 3.212(2), H16…O2S 2.44(2) Å, and C16–H16 0.95(2) Å, angle C16–H16…O2S 138(1)°).

Synthesis of *O*,*O*-diethyl (4-azidobenzyl)phosphonate (3). Diazonium diethyl (4-aminobenzyl)phosphonate was obtained by a standard procedure. Then, the equivalent amount of 30% aqueous solution of sodium azide was added to an aqueous solution of the diazonium salt cooled to 0°C in such a manner that temperature did not rise above 5°C. The supernatant above the precipitated oil was decanted, and the oil was washed twice with water. The oil was dried in a vacuum over  $P_2O_5$ . The yield of azide **3** is quantitative.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm, *J*, Hz): 1.17 (t, 6H, CH<sub>3</sub>, <sup>3</sup>*J*<sub>H-H</sub> 7.1), 3.23 (d, 2H, CH<sub>2</sub>P, <sup>2</sup>*J*<sub>H-P</sub> 21.5), 3.95 (dq, 4H, CH<sub>3</sub>CH<sub>2</sub>, <sup>3</sup>*J*<sub>H-H</sub> ~ <sup>3</sup>*J*<sub>H-P</sub> 7.3), 7.04–7.12 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 7.28–7.36 (m, 2H).

Synthesis of O,O-diethyl 4-{4'-[(2"-phenyl-1"*H*benzimidazol-1"-yl)methyl]-1'*H*-1',2',3'-triazol-1'yl}benzylphosphonate (4). Compound 2 (2.32 g, 0.01 mol) and 2.69 g (0.01 mol) of azide 3 was heated at reflux in 20 mL of ethanol for 2 h in the presence of 0.2 g (0.001 mol) of CuI and 0.5 mL of triethylamine. The reaction course was monitored by TLC using toluene-methanol as an eluent. After reactants 2 and 3 disappeared, the reaction solution was filtered through a thin layer of silica gel, concentrated to 5-6 mL, and allowed to crystallize in a refrigerator to give pale yellow crystals, mp 114–116°C.

For C<sub>27</sub>H<sub>28</sub>N<sub>5</sub>O<sub>3</sub>P anal. calcd. (%): C, 64.66; H, 5.63; N, 13.96; P, 6.18, FW = 501.52.

Found (%): C, 64.51; H, 5.68; N, 13.76; P, 6.13.

<sup>1</sup>H NMR (DMSO-d<sub>6</sub> + CF<sub>3</sub>COOD,  $\delta$ , ppm, J, Hz): 1.15 (t, 6H, CH<sub>3</sub>,  ${}^{3}J_{\text{HH}}$  6.8), 3.30 (d, 2H, CH<sub>2</sub>P,  ${}^{2}J_{\text{HP}}$ 21.6), 3.95 (dq, 4H, CH<sub>2</sub>O,  ${}^{3}J_{HH} \sim {}^{3}J_{HP}$  7.1), 5.84 (s, 2H, CH<sub>2</sub>N), 7.46 (d, 2H, C<sub>6</sub>H<sub>4</sub><sup>2,6</sup>, <sup>3</sup>J<sub>HH</sub> 7.7), 7.58– 7.67 (m, 2H,  $H^{5",6"}$ ), 7.71–7.84 (m, 5H, *m*-+*p*-C<sub>6</sub>H<sub>5</sub>+ C<sub>6</sub>H<sub>4</sub><sup>3,5</sup>), 7.85–7.93 (m, 1H, H<sup>4</sup>"), 8.05–8.16 (m, 3H,  $o-C_6H_5 + H^{7"}$ ), 8.94 (s, 1H, H<sup>5'</sup>).

<sup>31</sup>P{<sup>1</sup>H} NMR (DMSO-d<sub>6</sub>, δ, ppm): 26.00 s.

Alkylation of PBI-O-PT with propargyl bromide. Alkylation (Scheme 3) was carried out using the samples of PBI–O–PT with  $\eta_{red}$  = 1.4–3.0 dL/g (0.5% solution in N-MP at  $25^{\circ}$ C), which corresponds according to GPC data to  $M_w = 60000-90000$  [3]. The polymer (0.532 g, 1 mmol) was dissolved in 6 mL of N-MP, 0.3 g (~2.2 mmol) of K<sub>2</sub>CO<sub>3</sub> was added, and the mixture was stirred for 30 min on a water ultrasound bath at 40–50°C. Then, a solution of 0.5 g (~4.4 mmol) of propargyl bromide (freshly distilled

fraction of polymer.

over methylhydroquinone) in 5 mL was added dropwise, and stirring was continued (24, 48, 72, and 96 h) with intermittent sonication for 20-30 min at 40-50°C and sampling for <sup>1</sup>H NMR analysis of the substitution extent. The polymer was precipitated with water, acidified with acetic acid to pH 5, filtered, and the polymer powder was refluxed twice in distilled water for 1-2 h each to remove the solvent. The powder was dried at 100°C in a vacuum. Depending on conditions and reactant ratio, the alkylation degree may be 25-100%. Propargyl-containing PBI-O-PT-Pg is readily soluble in amide solvents and DMSO.

1,3-Dipolar addition of 4-azidobenzylphosphonate (3) to PBI-O-PT-Pg to form PTPBI. PBI-O-PT-Pg (0.608 g, 1 mmol) was dissolved in 6 mL of DMSO, a solution of 0.55 g (~2.2 mmol of azide 3 in 5 mL of DMSO and a solution of 0.04 g of CuI, 0.5 mL of Et<sub>3</sub>N in 3 mL of DMSO were added. The reaction mixture was stirred for 8 h at 60-80°C, filtered through a fritted glass filter, and precipitated with 1% aqueous ammonia solution. The precipitate was separated by filtration, dried at 100°C in a vacuum, and studied by NMR and IR spectroscopy and by elemental analysis. In all cases, irrespective of the alkylation extent of PBI-O-PT, the polymer analogous "click" reaction proceeded quantitatively. Completely alkylated PBI-O-PT undergoes 100% addition of azide to give PTPBI containing 5.2% of phosphorus at a calculated value of 5.18%. The polymer is soluble in amide solvents, DMSO, and HCOOH.

6.5 0 3.5 4.0 4.5 5.0 5.5 6.0  $\log M$ Fig. 2. Molecular weight distribution function relative to PS (lower axis) and hydrodynamic radius distribution (upper axis) for (1) PBI-O-PT, (2) PBI-O-PT-Pg (modification extent of 80%), and (3) the corresponding PTPBI-O-PT. W is the weight



# **RESULTS AND DISCUSSION**

In this work, we have studied in detail the model reactions of 2-PBI (1) with propargyl bromide followed by the reaction of intermediate alkyne 2 with phosphorylated azide 3 to give 4 (Scheme 2).

The chemical structure of products **2** and **4** was confirmed by the data of <sup>1</sup>H and <sup>31</sup>P NMR, Fourier-transform IR spectroscopy, and X-ray crystallography.

The IR spectrum of compound **2** lacks a broad band of stretching vibrations of benzimidazole NH group at 3200–3400 cm<sup>-1</sup> and shows a new band of stretching vibrations of the  $\equiv$ CH terminal acetylene fragment at 3290 cm<sup>-1</sup>. The IR spectrum of the product of the "click" reaction (**4**) displays a strong band of stretching vibrations of phosphonate P=O group at 1272 cm<sup>-1</sup>.

According to X-ray diffraction data (Fig. 1), molecule **2** is nonplanar, the phenyl ring is turned by  $45.8^{\circ}$  relative to benzimidazole plane, and the propynyl substituent is disposed orthogonally (dihedral angle is  $84.9^{\circ}$ ). The bond lengths and angles have common values. Molecules in crystal form chains extended along the *a* axis.

The data obtained in the study of model reactions were further used to examine polymer analogous reactions of PBI–O–PT. The general scheme of PTPBI– O–PT synthesis (Scheme 3) is shown above.



The alkylation of PBI–O–PT with propargyl bromide was monitored by NMR and IR spectroscopy and GPC. Figure 2 shows the molecular-weight distribution curves for initial PBI, its propargyl-containing products, and final PTPBI–O–PT, as well as the calculated hydrodynamic radius distribution (using the Stokes equation and the determined Mark-Houwink constants for PS in eluent:  $K = 4.07 \times 10^{-4} dL g$ , a = 0.53). GPC data indicate an increase in the hydrodynamic size of chains caused by the first stage of modification and the extension of size distribution. This fact can be explained by both the increase in chain rigidity on account of hindered rotation around virtual bonds and the improvement of thermodynamic qual-

DOKLADY CHEMISTRY Vol. 447 Part 1 2012

ity of the solvent. As a result, the apparent values of  $M_w$  (relative to PS) alter from 60 000 to 166 000 and 184 000, while  $M_w/M_n$  ratio is changed from 2.05 to 5.3 and 5.9, respectively.

The obtained polymers, according to the data of TGA in air, have a high thermal stability comparable with that of the known polymers of the PBI family [1-6]. Their intense decomposition temperatures are above 580°C, the onset of oxidative destruction occurs at ~350°C for diethoxyphosphoryl form of PTPBI-O-PT and ~400°C for PBI-O-PT-Pg. To transform the diethoxyphosphoryl groups of the polymers into acidic groups, PTPBI films were refluxed for 5 h in 18% hydrochloric acid to give phosphonic acids as probed by <sup>31</sup>P NMR:  $\delta \sim 19.5$  ppm (HCOOD). Such a PTPBI-O-PT is readily soluble in formic acid but forms rather friable films. An increase in the molecular weight  $M_{\rm w}$  of initial PBI-O-PT (to about 90000, GPC) did not produce the PTPBI-O-PT polymer capable of forming proton-conducting membranes with favorable strength characteristics. The prepared PTPBI-O-PT polymers were tested as "thickeners" of phosphoric acid for the reservoir of the nine-layered MEB [4–6]. This MEB has worked with commercial electrodes Celtec®P-1000 [7] in galvanostatic mode (current density of 0.4 A/cm<sup>2</sup>) for 200 h at 160°C and 350 h at 180°C showing a stable potential difference U = 0.580 and 0.602 V, respectively, at a constant open-circuit voltage of ~0.94 V.

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