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CHEMISTRY

Synthesis and Properties of New Poly(benzimidazole) Based on AB-type Monomer

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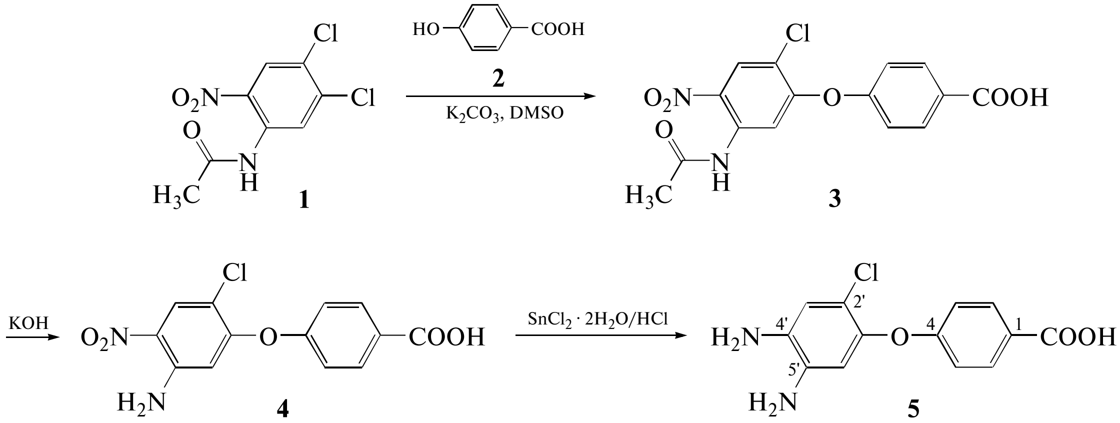
Proton-conducting membranes based on complexes of poly(benzimidazole)s with phosphoric acid are one of the most promising solid polymer electrolytes for high-temperature fuel cells (FC) [1].

Previously, we prepared poly[2-(4'-oxyphenylene)-5-benzimidazole] (POPBI) based on AB-type monomer [2]. These polymers attract interest due to the fact that they have more ordered structure and show good thermomechanical properties [3]. In continuation of these studies, in this work, we describe the synthesis of a new monomer, 4-(2'-chloro-4',5'-diaminophenoxy)benzoic acid (Scheme 1, compound **5**), which was further used for the preparation of previously unknown poly(benzimidazole) under homopolycondensation conditions.

According to preliminary computer simulations performed by A.A. Askadskii (Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences) with the use of Kaskad software, polymer based on acid **5** should show certain improved characteristics as compared with POPBI: the better film-forming ability. Other physicochemical characteristics should not degrade. The latter agrees well with literature data [4]. Furthermore, the presence of halogen atoms in poly(benzimidazole)s favors better binding of the polymer with the doping agent [5]. These advantages should be favorable for the preparation of an efficient polymer proton-conducting membrane for fuel cells.

The synthesis of the new monomer of AB type was conducted according to the procedure proposed for 4-(3',4'-diaminophenoxy)benzoic acid [2]:



Scheme 1.

However, the conditions of S_NAr reaction previously optimized for the synthesis of 4-(4'-nitro-5'-acetamidophenoxy)benzoic acid were found to be inapplicable in this case because of formation of a considerable amount of a byproduct.

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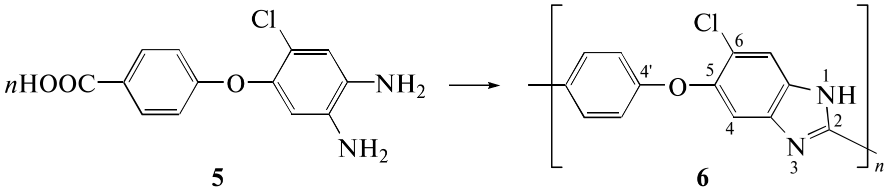
With the aim to obtain acid **3** (Scheme 1), we studied the features of this reaction and revealed that the S_NAr reaction should be conducted at 110°C for 4 h at the 1 : 2 substrate-to-nucleophile ratio with gradual addition of a solution of *N*-acetyl-2-nitro-4,5-dichloroaniline (**1**) to the reaction mixture. The target product was obtained in 87% yield.

The acetamide bond cleavage was achieved in the course of base hydrolysis. The nitro group in compound **4** (Scheme 1) was reduced with tin(II) chloride in 36% hydrochloric acid. As a result, the monomer of 99.93% purity was obtained in 67.14% total yield. The structure and composition of intermediate compounds and target product **5** were confirmed by elemental analysis data, ^{1}H NMR spectroscopy, and mass spectrometry.

Synthesized monomer **5** was used in the reaction of homopolycondensation (Scheme 2) for preparing a new poly(benzimidazole), poly[2-(6-chloro)-(4'-oxyphenylene)-5-benzimidazole] (6-Cl-POPBI, compound **6**).



5 **6**

Scheme 2.

The synthesis of PBI from AB-type monomers is usually carried out in a polyphosphoric acid medium (180–200°C) [6] or Eaton's reagent [7]. The application of this reagent is more preferable because of the high reaction rate at relatively low temperatures (100–140°C), as well as good solubility of initial compounds, which allows one to conduct the synthesis under homogeneous conditions. Therefore, Eaton's reagent was used to obtain an unknown poly(benzimidazole). The homopolymerization reaction was carried out at 140°C. Reaction course was monitored by visually observing the growth of the reaction mixture viscosity.

Five hours after reaction beginning, a portion of the reaction mixture was poured into water for polymer precipitation. The isolated polymer after washing and drying proved to be poorly soluble in N-MP, DMF, and DMA even on heating. The resulting 6-Cl-POPBI is dissolved only on heating in amide solvents in the presence of 1–4% lithium chloride toward polymer weight. The rest of the reaction mixture was heated at 140°C for another 1 h. A sharp increase in reaction mixture viscosity was observed 6 h after reaction beginning. Polymer **6** was completely precipitated from water at this point. This fraction seems to be a cross-linked polymer insoluble in amide solvents even on addition of lithium chloride. Most likely, crosslinking proceeds via reaction of the terminal carboxy group with the secondary nitrogen atom of the imidazole fragment. Cross-linked polymer is likely to result also from Friedel–Crafts reaction because it is known that Eaton's reagent is used for producing acylium cation in the synthesis of benzophenones [8].

With the aim to obtain high-molecular-weight organo-soluble 6-Cl-POPBI, we studied the effect of reaction time on viscosity characteristics of the polymer (table).

It is seen from our data that homopolycondensation in Eaton's reagent for 5–6 h leads to low-soluble polymers poorly processable into film. Poly(benzimidazole prepared over 3–4 h was well soluble in N-MP, DMF, DMA and insoluble in toluene, chloroform, hexane and had η_{red} = 0.68–0.89 dL/g. Poly(benzimidazole) prepared over 4.5 h had a higher reduced viscosity of 0.98 dL/g. The polymer was well soluble in amide solvents on slight heating. This fraction was further used to cast films and to study the structure and physicochemical characteristics of polymer **6**.

The IR spectrum of the obtained polymer (Fig. 1) shows characteristic absorption bands of the benzimidazole system in the range 1630–1580 cm^{-1} corresponding to the stretching vibrations of C=N (1622 cm^{-1}), C=C (1608 cm^{-1}), and C=C nodal atoms (1595 cm^{-1}) [9, 10]. Absorption bands at 1487, 1448, and 1423 cm^{-1} are also related to the stretching vibrations of the benzimidazole moiety [11]. Bands at 3405 and 3065 cm^{-1} correspond to stretching vibrations of free N–H group and aromatic C–H bonds [6, 9, 10, 12]. The absorp-

Reaction time and reduced viscosity (η_{red}) of 6-Cl-POPBI solution in N-MP (reaction temperature 140°C)

Time, h	3.0	3.5	4.0	4.5	5.0	5.5	6.0
η_{red}, dL/g	0.68	0.76	0.89	0.98	1.13 [a]	1.17 [b]	See [c]

[a] Polymer is dissolved on heating with LiCl.
[b] For the polymer fraction dissolved on heating with LiCl.
[c] Polymer is insoluble.

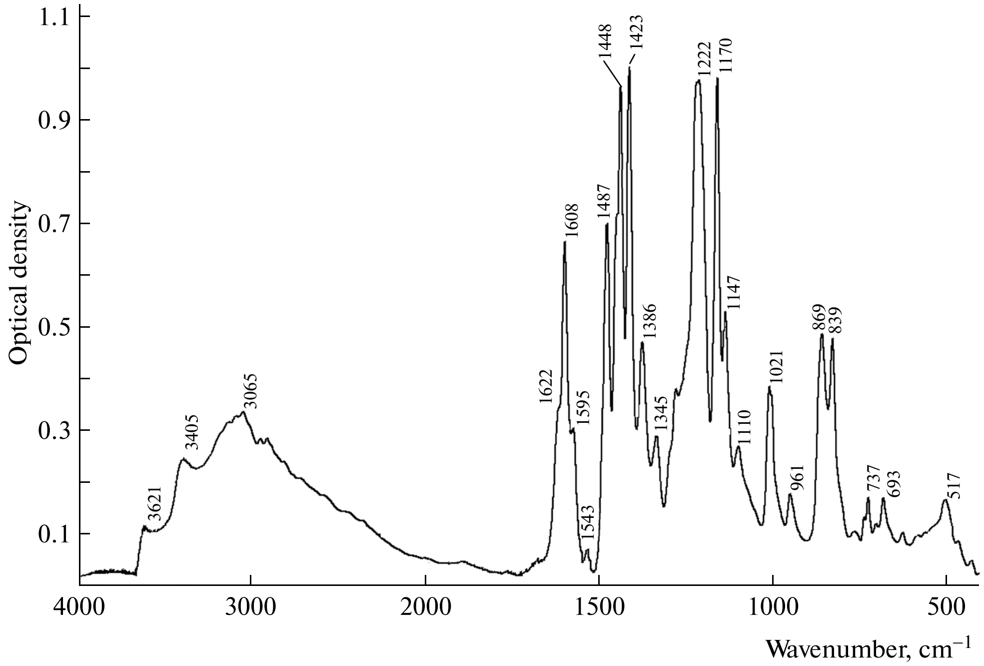


Fig. 1. IR spectrum of polymer **6** (in KBr pellet).

tion band of stretching vibrations of Ar—O—Ar ether bonds was detected in the IR spectrum at 1222 cm^{-1} [9]. Peaks at 1021 and 839 cm^{-1} belong to *para*-substituted benzene ring [11]. Absorption bands of C—Cl stretching vibrations were found in the range 800–600 cm^{-1} [13].

The lack of absorption bands in the IR spectrum of the polymer at 3389, 3308, and 1694 cm^{-1} typical of the stretching vibrations of amino and carboxy groups [13] of initial monomer indicate the high conversion of the terminal groups under used reaction conditions.

Thus, the analysis of IR spectral data allows us to draw a conclusion that homopolymerization resulted in a polymer with the structure corresponding to poly[2-(6-chloro)-(4'-oxyphenylene)-5-benzimidazole] (**6**).

Thermal-oxidative stability of the polymer was assessed by the data of DTGA in air (Fig. 2). Thermal degradation began at 390°C, while 10 and 50% weight loss temperatures were 454 and 509°C, respectively. We obtained similar results previously for the thermal-oxidative stability of poly[2-(4'-oxyphenylene)-5-benzimidazole] [2]. The weight loss of the polymer (2.3%) in the temperature range up to 100°C is explained by the loss of water absorbed by poly(benzimidazole) owing to high water capacity (up to 15%) of polymers of this type [14].

Thermomechanical characteristics of polymer **6** were studied for film specimens at a heating rate of 5 K/min in air with a constant load of 10 kg/cm^2. Polymer softening occurred under these conditions at 310°C.

Testing the mechanical strength characteristics of polymer **6** showed that cast films have a tensile strength of 82–84 MPa, an elongation at rupture of 6–8%, and a bulk modulus of 2060–2100 MPa (Fig. 3).

Thus, polymer **6** has high physicochemical characteristics similar to those of poly[2-(4'-oxyphenylene)-5-benzimidazole], which is used in the manufacture of a solid polymer electrolyte [15]. Polymer **6** will be used for the production of proton-conducting membrane

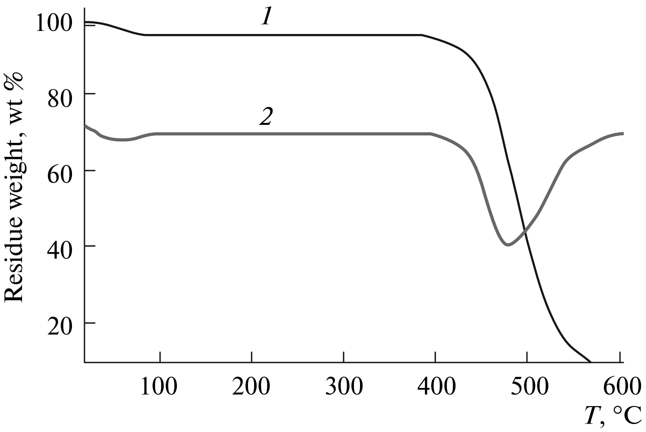


Fig. 2. (*1*) TGA and (*2*) DTGA curves for polymer **6** (air, 10 K/min).

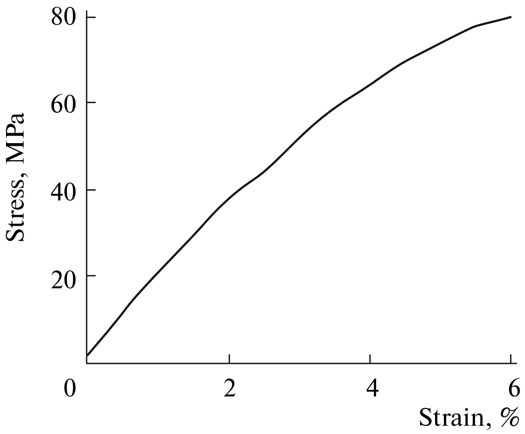


Fig. 3. Stress–strain curve for polymer **6**.

for fuel cells and its performance characteristics will be studied in future.

EXPERIMENTAL

Methods of Studying Individual Compounds and Polymers

NMR spectra were recorded on a Bruker DRX500 SF spectrometer operating at 500 MHz in a DMSO-d_6 + CCl_4 solvent with TMS as an internal reference. Mass spectra were recorded on a FINNIGAN MAT. INCOS 50 instrument at an ionizing voltage of 70 eV. Elemental composition was determined on a CHN-1 elemental analyzer. IR absorption spectra were recorded on a Thermo-Nicolet Nexus IR Fourier-transform spectrometer in the range 4000–400 cm^{-1} in KBr pellets.

Thermogravimetric analysis (TGA) was performed on a MOM Derivatograph C (Hungary) at a sample weight of ≈15 mg and a heating rate of 10 K/min in air. Thermomechanical analysis of film specimens of polymers was carried out on a TA Instruments Q400 apparatus at a heating rate of 5 K/min in air, a punch diameter of 2.5 mm, and a constant load of 10 kg/cm^2.

Analysis of film specimens of polymers was conducted on a Lloyd Instrument LR5K Plus apparatus at the strain rate 50 mm/min in air.

Synthesis of Monomer **5**

4-(2'-Chloro-4'-nitro-5'-acetamidophenoxy)benzoic acid (3). A mixture of 8.3 g (0.06 mol) of K_2CO_3 and 2.8 g (0.02 mol) of 4-hydroxybenzoic acid (**2**) in 200 mL of DMSO was heated for 15 min at 75°C and then 2.5 g (0.01 mol) of N-acetyl-2-nitro-4,5-dichloroaniline (**1**) in 100 mL of DMSO was added during 2 h. The reaction mixture was stirred for 4 h at 110°C. After cooling, the mixture was poured into water and filtered. Then, the filtrate was treated with hydrochloric acid until pH 6, the resultant precipitate was separated by filtration, dried, and crystallized from a mixture of alcohol and DMF.

Yield 3.1 g (88%), mp 273–276°C.

^{1}H NMR (DMSO-d_6, δ, ppm, *J*, Hz): 2.05 (s, 3H, CH_3), 7.25 (d, 2H, $H^{3',5'}$, *J* 8.72), 7.42 (s, 1H, H^6), 8.04 (d, 2H, $H^{2',6'}$, *J* 8.7), 8.29 (s, 1H, H^3), 10.31 (s, 1H, NH), 13.05 (s, 1H, COOH).

MS (m/z (I_{rel}, %)): 350 (7) $[M]^+$, 308 (22), 304 (16), 227 (3), 183 (15), 76 (5), 65 (12), 43 (100).

For $C_{15}H_{11}ClN_2O_6$ anal. calcd. (%): C, 51.36; H, 3.14; N, 7.99.

Found (%): C, 51.34; H, 3.05; N, 8.05.

4-(2'-Chloro-4'-nitro-5'-aminophenoxy)benzoic acid (4). Fourteen grams (0.04 mol) of 4-(2'-chloro-4'-nitro-5'-acetamidophenoxy)benzoic acid (**3**) was stirred in 200 mL of 20% aqueous solution of KOH at 60°C. The resultant precipitate was collected by filtration and treated with acetic acid. Yield 11.97 g (97%), mp 226–228°C.

^{1}H NMR (δ, ppm, *J*, Hz): 6.57 (s, 1H, $H^{6'}$), 7.20 (d, 2H, $H^{3,5}$, *J* 9.5), 7.46 (s, 2H, NH_2), 8.04 (d, 2H, $H^{2,6}$, *J* 10.0), 8.12 (s, 1H, $H^{3'}$), 13.00 (s, 1H, COOH).

MS (m/z (I_{rel}, %)): 308 (7) $[M]^+$, 292 (4), 256 (11), 188 (26), 136 (100), 90 (7).

For $C_{13}H_9ClN_2O_5$ anal. calcd. (%): C, 51.57; H, 2.92; N, 9.08.

Found (%): C, 51.54; H, 2.95; N, 9.06.

4-(2'-Chloro-4',5'-diaminophenoxy)benzoic acid (5). A mixture of 9.26 g (0.03 mol) of 4-(2'-chloro-4'-nitro-5'-aminophenoxy)benzoic acid (**4**) and 22.6 g (0.10 mol) of $SnCl_2 \cdot 2H_2O$ was stirred in 100 mL of 36% HCl at 90°C for 1 h. After cooling, the reaction mixture was treated with 25% aqueous ammonia solution until pH 7–8. The precipitate was separated by filtration, dried at 60°C, added to 400 mL of anhydrous isopropyl alcohol, heated at reflux on stirring for 0.5 h and filtered. The precipitate deposited from the filtrate was separated by filtration. Yield 7.52 g (90%), mp 231–232°C.

^{1}H NMR (δ, ppm, *J*, Hz): 6.38 (s, 1H, $H^{6'}$), 6.64 (s, 1H, $H^{3'}$), 6.86 (d, 2H, $H^{3,5}$, *J* 9.5), 7.88 (d, 2H, $H^{2,6}$, *J* 10.0). There are no proton signals of NH_2 and COOH groups owing to fast deuterium exchange.

MS (m/z (I_{rel}, %)): 279 (73) $[M]^+$, 242 (17), 226 (27), 198 (15), 166 (100), 110 (68), 92 (9), 74 (28).

For $C_{13}H_{11}ClN_2O_3$ anal. calcd. (%): C, 56.01; H, 3.95; N, 10.05.

Found (%): C, 55.58; H, 3.95; N, 10.07.

Synthesis of Polymer 6

Poly[2-(6-chloro)-(4'-oxyphenylene)-5-benzimidazole] (6). One gram of 4-(2'-chloro-4',5'-diaminophenoxy)benzoic acid (**5**) and 20 mL of Eaton's reagent were placed into a three-necked flask equipped with a mechanical stirrer, a thermometer, and a capillary tube for gas inlet. The flask was purged with argon for 30 min and placed on a silicone-oil bath preliminary heated to 100°C. The temperature was increased to 140°C over 1 h. After 4.5 h, the mixture was poured in a thin stream into water. The precipitated polymer was washed with distilled water until neutral pH, kept in aqueous ammonia solution for 1 h and washed with water again. The resultant polymer **6** was dried in air and then in a vacuum of 0.1 bar at 100°C to constant weight. Yield 92%.

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