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ScienceDirect
Mendeleev Commun., 2012, **22**, 162–163
Mendeleev Communications

Poly(*N*-phenylenebenzimidazoles) as an alternative to classical polybenzimidazoles

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DOI: 10.1016/j.mencom.2012.05.018

A new thermally stable polybenzimidazole film has been synthesized by nucleophilic aromatic substitution, transformed into a complex with phosphoric acid and tested as a proton-conductive membrane.

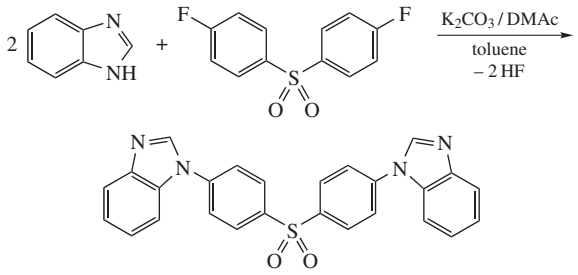
Polybenzimidazoles (PBIs) are important heterocyclic polymers, which can be used as thermally stable heat- and fire-resistant materials[1] and polymer electrolyte membranes (PEMs) for fuel cells (FCs).[2] A PBI-based PEM is a complex proton-conductive material, where the polymer is doped with a large amount of phosphoric acid. As a result, the proton conductivity rises greatly, there is no need to humidify the membrane during FC functioning, and a FC itself can work at temperatures above 120 °C, unlike Nafion-type membranes. The most effective and thoroughly investigated PBI types are Celazole (BASF), ABPBI[2] and PBI-O-PHT.[3–7]

However, there are several disadvantages to the widely used industrial and laboratory methods for PBI synthesis: firstly, expensive toxic tetraamines that are unstable to oxidation during storage; secondly, highly corrosive solvents like polyphosphoric acid and Eaton's reagent at high temperatures (140–220 °C); thirdly, high quantities of acid and salt drains during polymer precipitation and purification. Marvel's method of PBI synthesis[8] and reductive polyheterocyclization[9] also have specific technological limitations.

We propose a new promising and more environment-friendly PBI synthesis based on nucleophilic aromatic substitution involving NH groups of bis(benzimidazole) monomers, and commercially available 4,4′-dichlorodiphenylsulfone and 4,4′-difluorodiphenylsulfone as the opposite-type electrophilic monomers. Note that Hlil *et al.*[10] attempted to synthesize PBI *via* similar nucleophilic substitution in a sulfolane solution at 200–210 °C. Even though cheap and simple bis(benzimidazole) monomers were successfully synthesized from *o*-phenylene diamine and isophthalic or terephthalic acid in PPA, the resulting homopolymer was of a rather low molecular weight (η_{inh} = 0.22 dL g^{-1}) compared to ordinary PBI types and, therefore, inappropriate for FC membrane preparation. Possibly, polymer chain formation in that case was sterically hindered by the structure of bis(benzimidazole) monomers applied. Bis(benzimidazole) monomer type described further appears to be more reactive in nucleophilic substitution.

The model reaction illustrates the synthetic approach involving benzimidazole NH groups in nucleophilic substitution for activated halogen (Scheme 1, for experimental details, see Online Supplementary Materials). The ^{1}H NMR spectrum of the identified product helped us to analyze more complex spectra of the monomer and polymers further obtained.

The bifunctional benzimidazole monomer† was synthesized on the basis of 3,3′,4,4′-tetraaminodiphenyl oxide, which is used as a monomer in traditional PBI synthesis in Eaton's reagent media.[4–6] Two benzimidazole heterocycles are readily formed by the inclusion of formic acid fragments, but appropriate monomer



Scheme 1

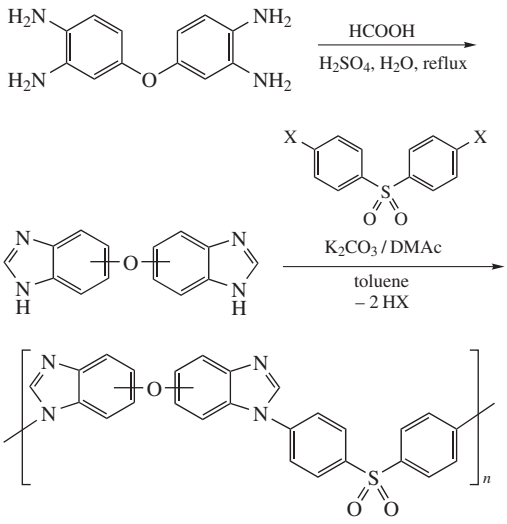
preparation appeared to be tricky: it was not expected that the substance was likely to form a hydrate.

The use of the monomer in a hydrate form in polymer synthesis causes a disbalance in monomer ratio, and hence a low molecular weight of the resulting polymer. DSC data of the reaction product contain significant endothermic peaks at 119 °C for hydrate form, and peaks at 227 and 241 °C for free product in isomeric forms. Recrystallization followed by azeotropic drying in toluene was found a reliable monomer preparation procedure. ^{1}H NMR spectra, along with the DSC data of the monomer, show the presence of two isomeric forms.

The polymer synthesis‡ was carried out in a dimethylacetamide (DMAc) solution using anhydrous K_2CO_3 as a basic agent. Other solvents (*N*-methylpyrrolidone, *N*,*N*-dimethylformamide and

† For synthesis and characteristics of 5(6),5′(6′)-bis(benzimidazole)oxide monomer, see Online Supplementary Materials.

‡ 5(6),5′(6′)-Bis(benzimidazole)oxide (1.5015 g, 6 mmol) and K_2CO_3 (0.91 g, 6.6 mmol or 1.82 g, 13.2 mmol) were mixed with DMAc (5 ml) and toluene (1 ml) in a flask equipped with a stirrer. The mixture was heated under dry argon flow at 90 °C for 1 h; then, 4,4′-dichlorodiphenylsulfone (1.5255 g, 6 mmol) or 4,4′-difluorodiphenylsulfone (1.7230 g, 6 mmol) was added. Polymer synthesis continued at 170 °C (X = Cl) or 140 °C (X = F) for 24–48 h. With increasing the mixture viscosity, extra DMAc quantities (up to 10 ml total) were added. In some experiments, an ultrasonic impact was applied by the periodic interruption of heating and immersing the reaction flask in an ultrasonic bath (3–5 times for 10 min each). The reaction mixture was diluted with DMAc (15 ml) and poured into 0.1 M HCl (200 ml). Precipitated polymer flakes were filtered off, washed with hot water, extracted in a Soxhlet extractor with methanol and dried. ^{1}H NMR (DMSO-d_6) δ: 8.66–8.49 (m, 2H), 8.29–8.09 (m, 4H), 8.02–7.83 (m, 4H), 7.78–7.58 (m, 2H), 7.44–7.25 (m, 2H), 7.13–6.90 (d, 2H). ^{13}C NMR (DMSO-d_6) δ: 154.46–153.98, 144.27, 144.10, 143.67, 140.11, 139.67, 139.43, 133.06, 129.75, 128.66, 124.38, 120.99, 116.33–115.31, 112.27, 108.96–108.62, 101.90–101.38. TMA: Tg = 300 °C. TGA: 5% weight loss at 450 °C.



Scheme 2

sulfolane) and basic agents (NaH, LiH and Bu^{t}OK) were found less effective. Table 1 summarizes the characteristics of the resulting polymers. It is obvious that the reaction of nucleophilic substitution for F (in 4,4′-difluorodiphenylsulfone) goes easier than that for Cl (in 4,4′-dichlorodiphenylsulfone). Thus, the procedure using 4,4′-difluorodiphenylsulfone as a monomer results in the formation of higher molecular weight polymers with higher viscosities. On the one hand, an excess of K_2CO_3 increases the reaction rate in general, but, on the other hand, it increases the inhomogeneity and reaction mixture viscosity and thus causes the formation of a hardly soluble K_2CO_3 polymer agglomerate. In some cases, this process leads to polymer gelation. Ultrasonic treatment prevented agglomeration and keeped K_2CO_3 solid particles evenly dispersed in polymer solution. We suppose that it can also refresh the surface of K_2CO_3 excluding KF or KCl layers and providing better catalytic activity towards the monomers.

Polymer films were cast from a 10% polymer solution in *N*-methylpyrrolidone on glass plates heated at 60–80 °C. After solvent evaporation (8–12 h), the films were heated in a vacuum at 160 °C for 2 h, extracted with hot water and placed in 2% H_2SO_4 for 24 h at room temperature, and then heated in an oven with air circulation for 1 h at 350 °C for the three-dimensional cross-linking of polymer chains. The cross-linked films were doped with 77% H_3PO_4 at 60 °C for three days to obtain membrane materials. Before assembling, membranes were stored in 85% H_3PO_4 at room temperature. Material weight was controlled several times during the doping procedure, and at the end it reached 480%. We used a common procedure for PBI membrane preparation that includes thermal (at 350 °C) cross-linking of material treated with 2% H_2SO_4 and followed by doping with 77% H_3PO_4.

The membrane-electrode assembly (MEA) was constructed with a 5 cm^2 membrane using industrial Celtec P-1000 (BASF) electrodes, a 320 μm thick anode and a 260 μm thick cathode, with polyimide and polyether ketone gaskets.[3] A standard Arbin Instruments cell was used with a Khimelectronika GVCh-12 H_2 generator, air compressor and MOSFET-based electronic load. The FC test was carried out at 160 °C with air stream corresponding to the cathode stoichiometry λ = 2.5, at atmospheric pressure of both air and H_2. The performance characteristics of the FC (Figure 1) are close to those of the industrial BASF Celtec P 1000 MEA (*i.e.*, 0.600 V at 0.4 A cm^{-2}).[11] Our FC exhibited 0.570 V in the galvanostatic mode at j = 0.4 A cm^{-2} and 0.880 V in the open-circuit mode after 24 h of performance.

We consider that the above poly(*N*-phenylenebenzimidazoles) are a challenging alternative for classical PBI types used in FC and other applications. The reported synthetic procedure leads to high-molecular-weight film-forming polymers. The further development of this synthetic approach implies the synthesis of bis(benzimidazole) monomer analogues starting from other tetraamines and diamines (which are usually less toxic) and the study of active dihalogen compounds.

Table 1 Results of the polymer synthesis.

Entry	X	K_2CO_3 to monomer ratio	Time/h	T/°C	Ultrasonic impact	Viscosity η_{red}/dL g^{-1}
1	Cl	2.2 : 1	48	170	–	1.09
2	F	2.2 : 1	24	140	–	2.40
3	F	1.1 : 1	48	140	–	1.82
4	F	1.1 : 1	48	140	+	2.72

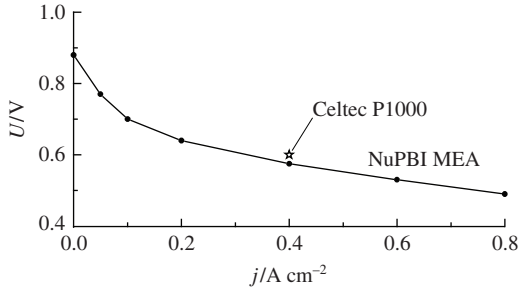


Figure 1 Fuel cell polarization curve.

This work was supported in part by the Russian Academy of Sciences, Programme no. 7 of the Division of Chemistry and Materials Science. We are grateful to Dr. P. V. Petrovskii for performing NMR studies and to Academician A. R. Khokhlov for supporting the fuel cell experiments.

Online Supplementary Materials

Supplementary data associated with this article (graphical NMR, DSC, TMA and TGA data, and additional experimental details) can be found in the online version at doi:10.1016/j.mencom.2012.05.018.

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Received: 25th October 2011; Com. 11/3822