

Synthesis and characterization of novel sulfonated polybenzimidazoles from 1,3-disulfonic acid sodium-4,6-bis(4-carboxyphenoxy)benzene

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Abstract: A novel sulfonated diacid, 1,3-disulfonic acid sodium-4,6-bis(4-carboxyphenoxy)benzene (DSBCPOB-Na) was successfully synthesized via sulfonation of 1,3-bis(4-carboxyphenoxy)benzene (mBCPOB). A series of sulfonated polybenzimidazoles (sPBIs) with different sulfonation degree were prepared by condensation polymerization of DSBCPOB-Na, 4,4'-dicarboxy-diphenyl ether (DCDPE) and 3,3'-diaminobenzidine (DAB) in phosphorus pentoxide/methanesulfonic acid (PPMA), and the copolymerization reactions were carried out via random manner. The structures of DSBCPOB-Na and sPBI were confirmed by FT-IR, ¹H NMR and ¹³C NMR. The obtained sPBIs showed good solubility, high thermal stability and excellent mechanical property. The 10% of weight loss of sPBI-11, 12, 13 and 14 were higher than 450 °C, and the membranes had tensile strength and elongation at break in the range of 89–96 MPa and 12–42%, respectively, showing adequate thermal and mechanical stability for fuel cell application.

Aromatic polybenzimidazoles (PBIs), known for their excellent thermal and thermoxidative stability, high mechanical strength, outstanding chemical resistance, have found important industrial applications. Moreover, PBIs can be well doped with a number of acids (typically phosphoric acid (PA)) due to the strong interactions between the basic imidazole rings of PBIs and acids. It has been reported the PA-doped PBIs displayed high proton conductivities even under anhydrous conditions which makes them very suitable for use in high temperature (150-200 °C) PEMFCs.

In this study, a novel sulfonated dicarboxylic acid, 1,3-disulfonic acid sodium-4,6-bis(4-carboxyphenoxy)benzene (DSBCPOB-Na), was synthesized and a series of sPBIs with different degrees of sulfonation (DS) were prepared via random copolymerization of DSBCPOB-Na, 4,4'-dicarboxydiphenyl ether (DCDPE) and 3,3'-diaminobenzidine (DAB) in the medium of phosphorus pentoxide/methanesulfonic acid (PPMA). The thermal stability, mechanical properties, radical oxidative stability, PA-doping and proton conductivity of these sPBI membranes were also investigated.

As shown in Scheme 1, DSDCPOB-Na was synthesized via three-step reactions. In the first step, 4-fluorobenzonitrile reacted with 1,3-dihydroxybenzene to form the intermediate product *m*BCNPOB at a high yield of 93%. Next, *m*BCNPOB was hydrolyzed in glycol to give the dicarboxylic acid product *m*BCPOB at a yield of 83%. Finally, *m*BCPOB was sulfonated to produce the sulfonated dicarboxylic acid monomer, DSBCPOB-Na, using 95% sulfuric acid as the sulfonating reagent. Scheme 2 shows the copolycondensation procedure of preparing sulfonated copolybenzimidazoles in PPMA at 140 °C. The DS was controlled by controlling the molar ratio between DSBCPOB-Na and DCDPE and the synthesized copolymers were denoted as sPBI-xy (the suffix 'xy' refers to the molar ratio of DSBCPOB-Na to DCDPE).

Figure 1 shows the FT-IR spectra of *m*BCNPOB, *m*BCPOB and DSBCPOB-Na. The absorption

band at 2230 cm^{-1} is assigned to $\text{-C}\equiv\text{N}$ stretching vibration of *m*BCNPOB (Fig. 1 (a)). In Fig. 1 (b) a new absorption band at 1694 cm^{-1} which is attributed to the carboxyl carbonyl groups appeared. This indicates that the $\text{-C}\equiv\text{N}$ groups have been completely hydrolyzed to carboxyl groups. In Fig. 1(c), the absorption bands at 1072 and 1034 cm^{-1} are assigned to the symmetric and asymmetric stretching of the sulfonic acid groups indicating that the sulfonation reaction has been successfully performed. The ^1H NMR spectrum of DSBCPOB-Na is shown in Figure 2. The peak assignments are just consistent with the chemical structure indicating that DSBCPOB-Na has been successfully synthesized.

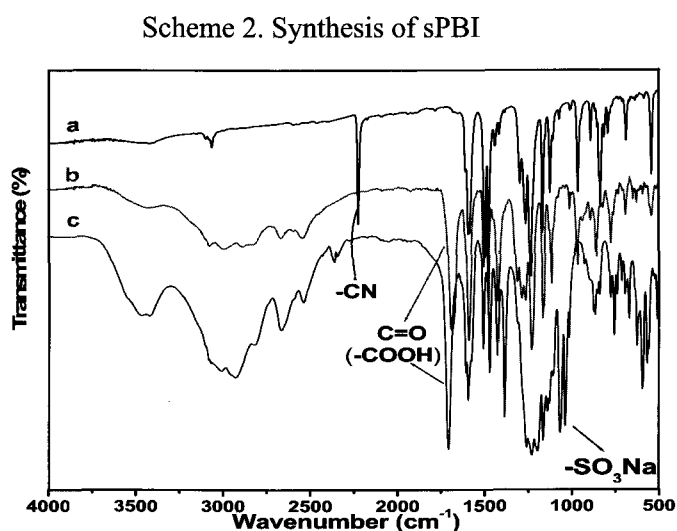
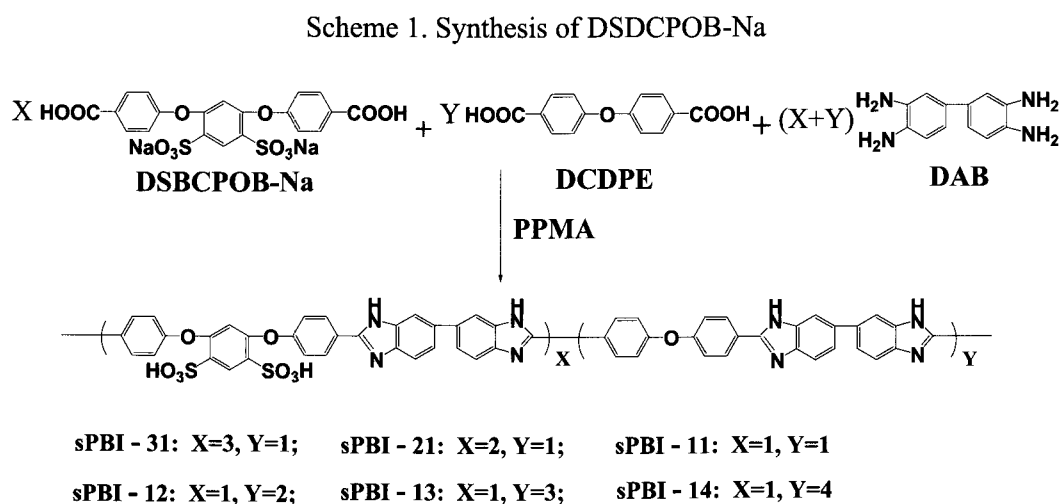
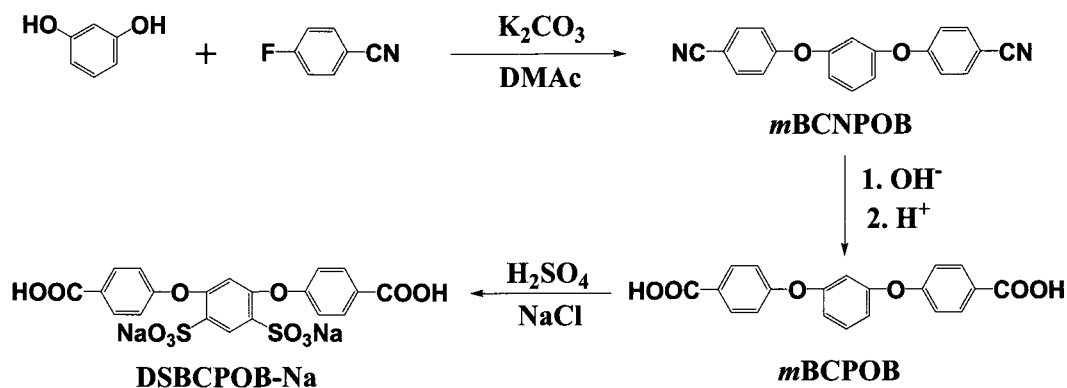


Figure 1. FT-IR spectra for: (a) *m*BCNPOB; (b) *m*BCPOB; (c) DSBCPOB-Na

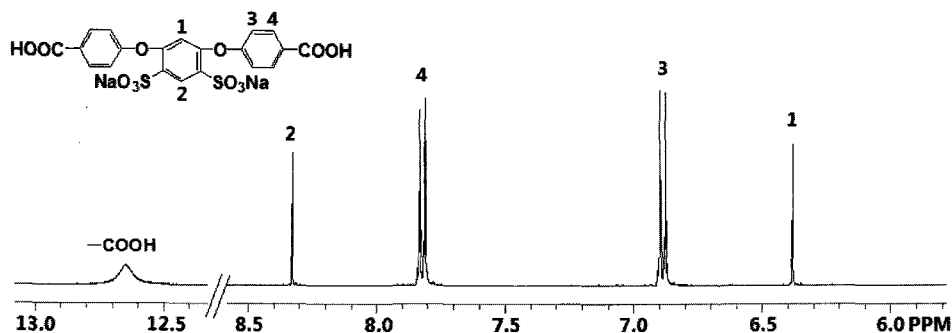


Figure 2. ^1H NMR spectrum of DSBCPOB-Na

The FT-IR spectra of the synthesized sPBIs are shown in Figure 3. 1634 cm^{-1} (C=N stretching) and 1480 cm^{-1} (in-plane deformation of imidazole rings) are clearly observed, while the characteristic absorption band of carboxyl carbonyl groups of the dicarboxylic acid monomers at 1694 cm^{-1} completely disappeared. This indicates that the complete formation of imidazole rings.

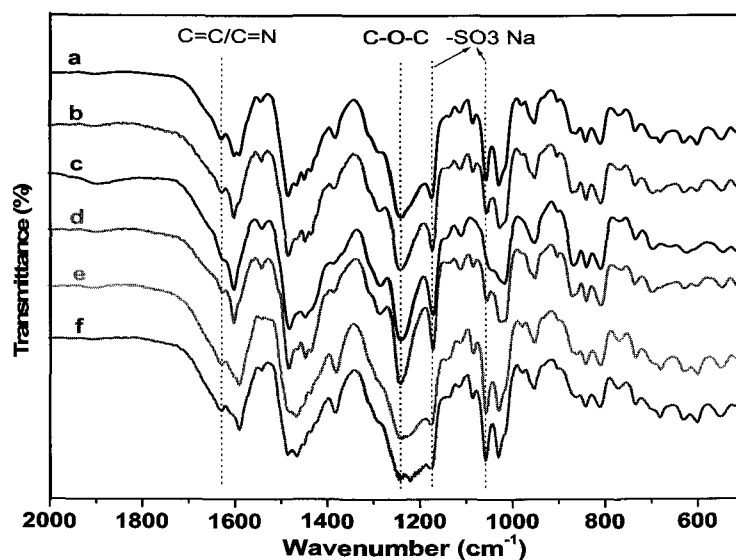


Figure 3. FT-IR spectra of sPBIs (A) (a: sPBI-11; b: sPBI-12; c: sPBI-13; d: sPBI-14; e: sPBI-21; f: sPBI-31)

The sPBIs in their proton form with different DS were subjected to thermogravimetric analysis (TGA) in air to evaluate their thermal stability. As shown in Figure 4, in which the degradation of the membranes displayed two steps. From $290\text{ }^\circ\text{C}$ to $450\text{ }^\circ\text{C}$, the first weight loss region are found, which is ascribed to the desulfonation. The temperature of 5% weight loss of all copolymers is higher than $400\text{ }^\circ\text{C}$, indicating adequate thermal stability for fuel cell application.

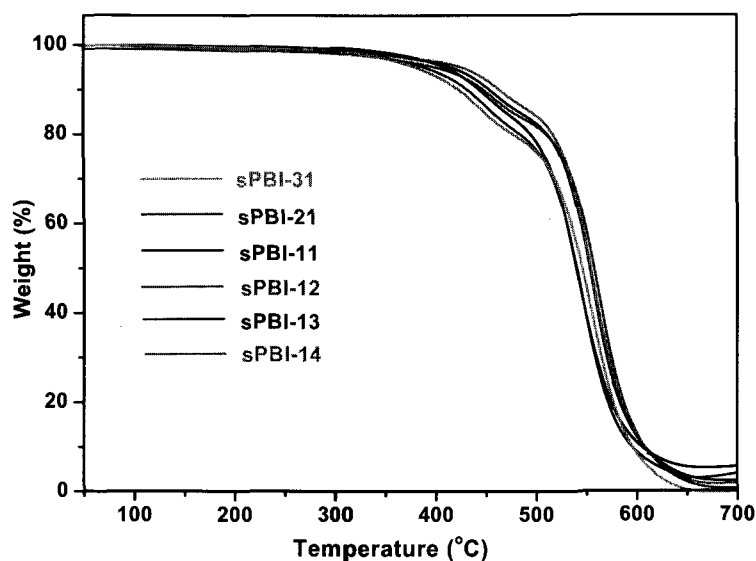


Figure 4. TGA curves of copolymers in air.

The dynamic mechanical properties of sPBIs membranes were investigated by DMA. Figure 5 shows the storage modulus and tangent delta of all sPBIs membranes. The glass transition temperature (T_g) based on the peak of tangent delta. It is found that the T_g and maximum storage modulus increase slightly with the increase of sulfonation degree of sPBIs. It illustrates the formation of ionic cross-linking between the sulfonic acid group and imidazole ring, resulting in higher T_g and maximum storage modulus. Furthermore, the formation of ionic cross-linking is confirmed by the value of tensile strength and elongation, as measured by Mechanical tensile measurements. However, higher DS also resulting in fragile of membrane when they are in dried state. For the sPBI- 31 and 21 membranes, the mechanical properties couldn't be measured because the membranes are too fragile.

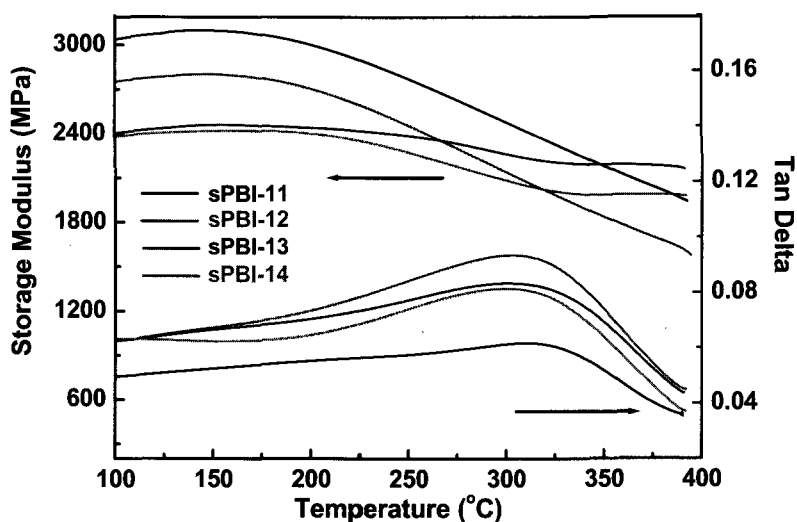


Figure 5. DMA curves of sPBI in nitrogen.

(Refs omitted)