

Synthesis and Properties of Sulfonated Poly[2,2'-(*p*-oxydiphenylene)-5,5'-bibenzimidazole]

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ABSTRACT: A novel sulfonated polybenzimidazole, sulfonated poly[2,2'-(*p*-oxydiphenylene)-5,5'-bibenzimidazole] (SOPBI), were successfully prepared by post-sulfonation reaction of poly[2,2'-(*p*-oxydiphenylene)-5,5'-bibenzimidazole] (OPBI) using concentrated and fuming sulfuric acid as the sulfonating reagent at 80 °C, and the degree of sulfonation (DS) were regulated by controlling the reaction conditions. No significant polymer degradation was observed in the post-sulfonation processes. The resulting SOPBIs showed good solubility in dimethyl sulfoxide (DMSO), high mechanical strength, superior radical oxidative stability and reasonably high proton conductivities.

INTRODUCTION

Polybenzimidazoles (PBIs) have attracted much attention in the past decade because of their potential important application in polymer electrolyte membrane fuel cells (PEMFCs).[1-16] Sulfonated polybenzimidazoles (SPBIs) have been reported to have higher proton conductivities than the corresponding non-sulfonated PBI membranes when doped with phosphoric acid.[10-18] The synthesis of SPBIs can be achieved by three approaches: grafting [10,11], direct polymerization [12-14] and post-sulfonation [15-18]. Direct polymerization method can give SPBIs with exactly desired structure and precisely controlled degree of sulfonation, but almost all the sulfonated monomers are not commercially available and needed to be synthesized. Post-sulfonation method is quite simple, however, it is reported that cross-linked and/or fragile membranes with low degree of sulfonation were often obtained because of the too high reaction temperature which is essential for sulfonation due to the rather low reactivity of poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (a commercial PBI) and poly(2,5-benzimidazole) (ABPBI). If the reactivity of PBIs is enhanced, sulfonation reaction might be carried out under relatively mild conditions. In this presentation, we report on the synthesis of a new sulfonated polybenzimidazole, sulfonated poly[2,2'-(*p*-oxyphenylene)-5,5'-bibenzimidazole] (SOPBI), via both direct polymerization method and pos-sulfonation method and their mechanical properties, radical oxidative stability, and proton conductivities are also described.

EXPERIMENTAL

3,3'-Diaminobenzidine (DABz) were purchased from Acros Organics and used without further purification. 4,4'-dicarboxydiphenyl ether (DCDPE) was kindly supplied from Peakchem (Shanghai) and vacuum dried at 80 °C prior to use. Methanesulfonic acid (MSA), phosphorus pentoxide, polyphosphoric acid (PPA), fuming sulfuric acid, 96% concentrated sulfuric acid, dimethylsulfoxide (DMSO), 1-methyl-2-pyrrolidinone (NMP) and N,N-dimethylacetamide (DMAc) were purchased from SCRC. Organic solvents were distilled under reduced pressure and dried over 4A molecular sieves before use. Other materials were used as received. Poly[2,2'-(*p*-oxydiphenylene)-5,5'-bibenzimidazole] (OPBI) was synthesized by condensation polymerization of DCDPE and DABz in PPMA at 140 °C for 160 minutes.[19]

4,4'-Dicarboxydiphenyl ether-2,2'-disulfonic acid disodium salt (DCDPEDS) was synthesized by sulfonation of DCDPE at 80 °C for 12 h using fuming sulfuric acid (30% SO₃) as the sulfonating reagent. Yield: 62%. ¹H NMR (DMSO-d₆), δ 13.02 (2H, -COOH), 8.371 (s, 2H), 7.885 (d, 2H), 6.809 (d, 2H).

SOPBIs were prepared by three methods: 1) post-sulfonation using concentrated sulfuric acid or fuming sulfuric acid as the sulfonating reagent at 80 °C for a given time (5-20 h); 2) direct polymerization of DCDPEDS and DABz in PPA at 190 °C for 20 h; 3) direct polymerization of DCDPEDS and DABz in PPMA at 140 °C for 20 h. Membranes were prepared by casting SOPBI solutions in DMSO at 80 °C for 5 h. The as-cast membranes were proton exchanged with 1.0 M sulfuric acid solution at 80 °C for 10 h.

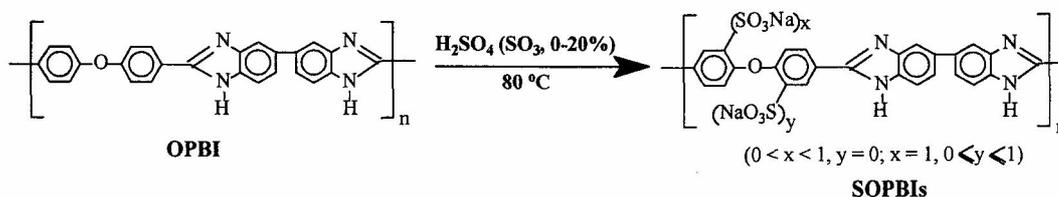
Proton conductivity (σ) was measured using a four-point-probe electrochemical impedance spectroscopy technique over the frequency range from 100 Hz to 100 KHz (Hioki 3552) [20]. Tensile measurements were performed with an Instron 4456 instrument in ambient atmosphere at a crosshead speed of 1 mm/min.

RESULTS AND DISCUSSION

Three methods were employed to synthesize a series of SOPBIs with different sulfonic acid group content: 1) post-sulfonation using concentrated sulfuric acid or fuming sulfuric acid as the sulfonating reagent at 80 °C (Scheme 1); 2) condensation polymerization of DCDPEDS, DCDPE and DABz in PPA at 190 °C for 20 h; 3) condensation polymerization of DCDPEDS, DCDPE and DABz in PPMA at 140 °C for 20 h. The SOPBIs prepared by the post-sulfonation method are well soluble in some organic solvents such as DMSO and NMP, whereas the direct polymerization methods always yielded insoluble gels. This suggests that cross-linking occurred during the direct polymerization process. To confirm this issue, we dissolved the SOPBI (prepared by post-sulfonation method in sulfuric acid at 80 °C for 5 h) in PPMA and then heated the solution mixture to 140 °C. Gelation was observed after about 4 h and the resulting polymer became completely insoluble in DMSO and pure methanesulfonic acid in which the SOPBI was well soluble before this treatment. Similar phenomenon was observed by treating the polymer in PPA at 170 °C. These results clearly demonstrated that cross-linking did occur in the direct polymerization processes.

Figure 1 shows the FT-IR spectra of OPBI, the sulfonated homo-polybenzimidazole synthesized by method 3 and the sulfonated polymer prepared by post-sulfonation in concentrated sulfuric acid at 80 °C for 5 h. The characteristic absorption bands around 3000-3500 cm⁻¹ (-NH), 1630 cm⁻¹ (-C=N), 1440 cm⁻¹ (in-plane deformation of imidazole rings) in the three spectra suggest the formation of imidazole rings, while the absorption bands around 1240 cm⁻¹, 1090 cm⁻¹ and 1030 cm⁻¹ in Figure 1 (b) are assigned to the stretch vibration of sulfonic acid groups.

Scheme 1 Post-sulfonation of OPBI



For the post-sulfonation method, the degree of sulfonation (DS) of the polymers can be regulated by controlling the sulfonation reaction conditions. For example, the DS (determined by ¹H NMR) increased from 60% to 100% when the reaction time extended from 5 h to 20 h using

concentrated sulfuric acid as the sulfonating reagent at 80 °C. Higher DS was achieved when fuming sulfuric acid was used instead of concentrated sulfuric acid. SOPBIs with the DS of 92% and 154% were prepared by using 10% and 20% sulfur trioxide containing fuming sulfuric acid as the sulfonating reagent at 80 °C for 5 h, respectively. Moreover, it should be noted that the post-sulfonation treatment did not cause significant degradation of the polymer judging from the high tensile strength of SOPBIs (Table 1). This indicates that OPBI has unusually high tolerance to oxidation even in fuming sulfuric acid containing 20% sulfur trioxide at 80 °C, which is superior to many other hydrocarbon polymers such as polystyrene and its derivatives, poly(ether sulfone)s and poly(ether ketone)s.

Table 1 Tensile strength properties, radical oxidative stability, water uptake (WU), and proton conductivity of OPBI and SOPBIs.

Polymer	DS ^a (%)	Tensile Property		Fenton Reagent Test ^b		WU ^c (%)	! ^d "#\$%&'
		Stress (MPa)	Strain (%)	T (°C)	τ (h)		
OPBI	0	129	14.9	25	>650	29	NM
				80	43		
SOPBI	60	98	15.2	25	>650	65	0.0069
	92	90	11.6	25	96	121	0.034
	154	81	12.3	25	<2	320	0.185

^aDetermined by ¹H NMR. ^b30% H₂O₂ containing 30 ppm FeSO₄. ^cMeasured at room temperature.

^dMeasured at 60 °C in water. NM: not measured.

Fenton's reagent test was carried out with these polymer membranes to examine the radical oxidative stability of OPBI and SOPBIs. The membranes (thickness: 10-20 μ m) were soaked in 30% H₂O₂ containing 30 ppm FeSO₄ and the stability was characterized by the elapsed time (τ) that the membranes started to become brittle (broke into pieces). As shown in Table 1, OPBI and SOPBI with a DS of 60% showed the stability of more than 650 h at 25 °C indicating unusually high radical oxidative stability of the polymers.

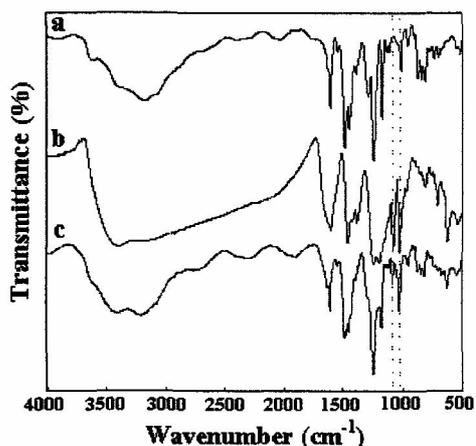


Figure 1 FT-IR spectra of OPBI (a), the sulfonated homo-polybenzimidazole prepared by direct polymerization method in PPMA (b), and SOPBI prepared by post-sulfonation in concentrated sulfuric acid at 80 °C for 5 h (c).

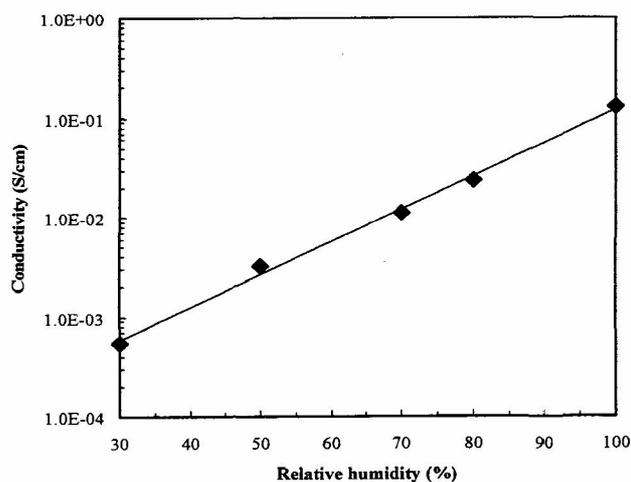


Figure 2 Variation of proton conductivity of SOPBI (DS = 154%) as a function of relative humidity (RH) at 60 °C.

The proton conductivity strongly depended on the DS and it increased from 0.0069 S/cm for the membrane of DS = 60% to 0.185 S/cm for the one of DS = 154%. The variation of proton conductivity of SOPBI (DS = 154%) as a function of relative humidity (RH) at 60 °C is shown in Figure 2. The conductivity increased with an increase in RH. This is a common phenomenon which has been observed with many other sulfonated polymer membranes and it is expected that the conductivity at low RH could be greatly enhanced by phosphoric acid-doping treatment.

CONCLUSIONS

Post-sulfonation method is very useful and facile for preparing SOPBIs with controlled degrees of sulfonation. No significant polymer degradation was observed in the post-sulfonation process even when fuming sulfuric acid containing 20% sulfur trioxide was used as the sulfonating reagent at 80 °C. The resulting SOPBIs showed good solubility, excellent mechanical properties, superior radical oxidative stability and reasonably high proton conductivities.

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