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ORIGINAL PAPER

Synthesis and hydrolytic stability of soluble sulfonated polybenzoxazoles derived from bis(3-sulfonate-4-carboxyphenyl) sulfone

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Abstract As a kind of high performance polymer, polybenzoxazoles are of interest as the matrix of proton exchange membrane (PEM). Soluble sulfonated polybenzoxazoles (sPBO) were synthesized by incorporation of the hexafluoroisopropylidene moieties into the polymer backbone, which show high molecular weight and excellent thermal stability. The hydrolytic stability of sPBO was investigated in detail in order to determine whether it is suitable for PEM applications or not. Contrary to expectation, sPBO membranes underwent hydrolysis under mild conditions. The hydrolysis of sPBO was confirmed by NMR, IR spectroscopy, and gel permeation chromatography. This work showed that sPBO membranes could not be used as PEM due to the poor hydrolytic stability.

Keywords Hydrolytic stability · Polybenzoxazoles · Proton exchange membrane · Sulfonated

Introduction

Proton exchange membrane (PEM) is one of the key components of proton exchange membrane fuel cells (PEMFC). Nafion is the state-of-the-art membrane for PEMFC due to its excellent properties. However, Nafion shows some drawbacks, such as limited operation temperature, high methanol permeability, and expensive cost, which hinder its widespread applications [1]. Recently, great effort has been made to

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develop nonfluorinated proton exchange membranes [2–6], including sulfonated poly(arylene ether sulfone)s [7–9], sulfonated poly(arylene ether ketone)s [10, 11], sulfonated poly(arylene thioether)s [12], sulfonated polymides [13–15], sulfonated poly(phthalazinone ether)s [16–19], sulfonated poly(arylene ether phosphine oxide)s [20, 21], sulfonated polybenzimidazoles [22–26] and so on.

Polybenzoxazoles (PBO), a kind of high performance polymers [27–29], are generally regarded as a promising candidate for the matrix of PEM [30]. However, PBO has not been used as PEM materials probably due to the poor solubility [31]. Besides, the hydrolytic stability of PBO should also be evaluated when used as PEM because it works under the moist environment [32]. In fact, there are only a few literatures on the hydrolytic stability of PBO [32–34]. The relevant studies at first focused on the hydrolytic stability of the model compound containing a benzoxazole moiety. So et al. [33] have found that the model compound with a benzoxazole ring was stable in 0.2 N H_2SO_4, 0.2 N NaOH, or 1% PPA. Moreover, they also observed that PBO showed no degradation after soaking in 0.2 N H_2SO_4, 0.2 N NaOH, or 1% PPA for 15 days [33]. On the contrary, Jackson et al. [35] investigated the hydrolytic stability of 2-methylbenzoxazole (2-MeBO) and discovered that the benzoxazole ring showed a ring cleavage under mild conditions. Similarly, Werstiuk and Ju found that 2-MeBO underwent hydrolysis to 2-acetamidophenol after exposed in neutral D_2O at elevated temperatures [36]. McGrath et al. observed that PBO showed a chain scission in 80 or 90% aqueous MSA solution, which are not experienced in normal applications [34]. These results relevant to the hydrolytic stability of the benzoxazole ring and PBO are limited and sometimes contradictory, thus the hydrolytic stability of PBO is still an open question.

Up to now, there are few reports on sulfonated polybenzoxazoles (sPBO). Sakaguchi et al. [30] prepared sPBO for the first time by polycondensation of 5-sulfoisophalic acid or 2-sulfoterephthalic acid, but the resulting polymers could not be cast into membrane in organic solvents due to their poor solubility, unsuitable for fuel cell applications. McGrath et al. [37] reported a kind of sPBO membranes in a conference proceeding, but the hydrolytic stability of sPBO was not mentioned. Therefore, it is significant to prepare soluble sPBO and investigate its hydrolytic stability so as to determine whether it is suitable for PEM applications or not.

In this paper, soluble sPBO were prepared by polycondensation of bis(3-sulfonate-4-carboxyphenyl) sulfone and bis(4-carboxyphenyl) sulfone with 2,2′-bis(3-amino-4-hydroxyphenyl)hexafluoropropane in polyphosphoric acid. The structure and properties of the resulting sPBO as PEM were investigated with particular emphasis on the hydrolytic stability.

Experimental

Materials

Bis(4-carboxyphenyl) sulfone (BCPS), *p*-tolyl sulfone (TSF), and 2,2′-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6FAP) were purchased from Sigma-Aldrich and used as received. Phosphorous pentoxide, polyphosphoric acid (PPA), and other reagents or solvents were purchased from Shanghai Chemical Reagents Co. and used without further purification. Bis(3-sulfonate-4-carboxyphenyl) sulfone (BSCS) was synthesized according to our previous report [23].

Synthesis of sPBO

A typical polymerization procedure is shown as follows. 18.95 g of 80% PPA and 7.2 g of P_2O_5 were charged to a three-necked round bottom flask, equipped with a nitrogen inlet/outlet and a mechanical stirrer. The mixture was stirred at 170 °C for 5 h to incorporate P_2O_5. A mixture of 6FAP (6.5526 mmol), BCPS (3.2763 mmol), and BSCS (3.2763 mmol) was added to the flask and stirred at 100 °C for 16 h. The mixture was stirred at 195 °C for 6 h and held at 200 °C for 4 days. The extremely viscous solution was cooled and poured into deionized water. The fibrous product was washed with deionized water until the pH value of flush water reached 7, followed by drying in vacuo at 120 °C for 10 h.

Yield: 96%. ^{1}H NMR (DMSO-d_6, ppm): 8.60–8.40 (3H), 8.36–8.24 (2H), 8.20 (1H), 8.10–7.80 (5H), 7.50–7.30 (2H). FT-IR (KBr, cm^{-1}): 1,625, 1,050 (benzoxazole), 1,085, 1,023, 640 (–SO_3Na).

Membrane preparation

Sulfonated polybenzoxazoles polymer in the sodium form were dissolved in NMP (6 wt%), then the polymer solution was cast onto a glass plate and dried at 80 °C for 24 h. The membrane was peeled off from the glass plate by immersing in deionized water and dried under vacuum at 120 °C for 24 h.

Measurements

IR spectra were performed on a PE Paragon 1000 IR spectrometer. NMR spectra were recorded using a Mercury Plus 400 MHz NMR instrument. Gel permeation chromatography (GPC) was carried out on a PE 200 apparatus. Polystyrene standards were employed for calibration. Differential scanning calorimeter (DSC) measurements were conducted on a PE Pyris-1 instrument. The samples in the sodium form were preheated under nitrogen at 150 °C for 30 min to remove moisture before measurement. The DSC curves were recorded from 90 to 350 °C at a heating rate of 10 °C min^{-1}. The thermogravimetric analysis (TGA) was measured on a PE TGA-7 thermogravimetric analyzer in a nitrogen atmosphere at a rate of 20 °C min^{-1}. The TGA curves were in the range from 150 to 800 °C.

The hydrolytic stability of sPBO was examined under designated conditions. The membrane weight and solution volume for all the tests is 80 mg and 25 mL, respectively. The treated membranes were washed with deionized water until the flush water achieves a neutral pH, then dried under vacuum at 120 °C for 24 h.

The transmission electron microscope (TEM) measurements were performed on a JEOL-JEM2100F apparatus. The preparation procedure of the sample is similar to the previous report [20]. The silver form samples in the copper grid were used.

Results and discussion

Synthesis and characterization of sPBO

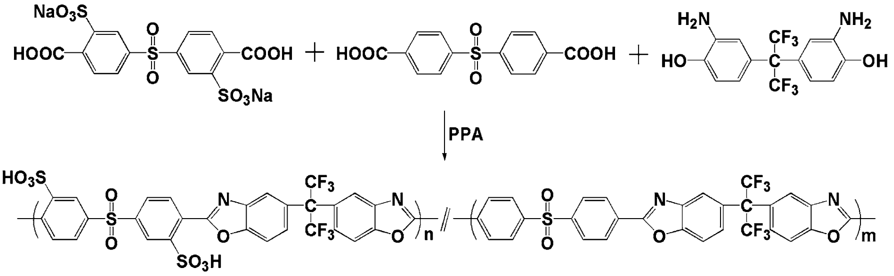
A series of sPBO with various degrees of sulfonation were synthesized by direct polycondensation of BSCS and BCPS with 6FAP in polyphosphoric acid (Scheme 1). The products were expressed as sPBO-*x*, the “*x*” of which is the molar fraction of BSCS in the entire dicarboxylic monomers. The polymerization was carried out at a concentration of 14 wt%. The results of polymerization are summarized in Table 1. The number average molecular weight (Mn) of sPBO is higher than 2.3×10^4 g mol^{-1}, and the polydispersity index (PDI) is in the range of $2.5 \sim 3.0$. All the resulting polymers could form transparent, tough, and flexible membranes, suggesting that the polymers were successfully synthesized.

The ^{1}H NMR spectrum of sPBO-50 is shown in Fig. 1a. As seen from Fig. 1a, all the hydrogen atoms of sPBO-50 are assigned. No peak at around 10 ppm was observed, which is ascribed to the proton of the amide group of the intermediate products [38], indicating a complete cyclization of benzoxazole rings. The degree of sulfonation (DS), defined as the average number of the sulfonic acid group per repetitive unit, could be derived from the intensity of ^{1}H NMR signals of sPBO. In Fig. 1a, Peak H-3 is attributed to the hydrogen atom of the repetitive unit containing sulfonate groups, whereas Peak H-4 and H-4′ are assigned to the hydrogen atoms of the hexafluoroisopropylidene moiety. The DS of sPBO can be calculated by the following equation

$$\mathrm{DS} = 2i_3/(i_4 + i_{4'})$$

where i_3, i_4, and $i_{4'}$ are the intensity of Peak H-3, H-4, and H-4′, respectively. The value of DS obtained by ^{1}H NMR and by calculation is listed in Table 1. It can be seen that the measured value accords well with the theoretical one.

The IR spectra of PBO and sPBO with various DS are shown in Fig. 1b. All the polymers exhibit the characteristic absorption bands at 1,625 cm^{-1} (benzoxazole, C=N stretching) and 1,050 cm^{-1} (benzoxazole, C–O stretching) [39]. Moreover, all the sPBO indicate the absorptions at 1,085, 1,023, and 640 cm^{-1}, which were absent in the IR spectrum of PBO. The absorptions at 1,085 and 1,023 cm^{-1} are assigned to asymmetric and symmetric stretching vibration of the sulfonate group of sPBO,



Scheme 1 Synthesis of PBO and sPBO

Table 1 Synthesis and properties of the products

Polymer	BSCS/BCPS/6FAP Molar ratio	DS		GPC			Yield (%)	T_{d5}^{a} (°C)
		The calculated	The measured	Mn × 10^{-4}	Mw × 10^{-4}	PDI		
PBO	0/100/100	0	0	–[b]	–[b]	–[b]	98	557
sPBO-30	30/70/100	0.6	0.57	2.60	6.50	2.5	96	527
sPBO-40	40/60/100	0.8	0.75	3.72	9.09	2.4	96	523
sPBO-50	50/50/100	1.0	0.95	2.30	6.21	2.7	95	508
sPBO-60	60/40/100	1.2	1.16	4.24	13.0	3.0	97	502

[a] The 5% weight loss temperature

[b] Poor solubility in DMF

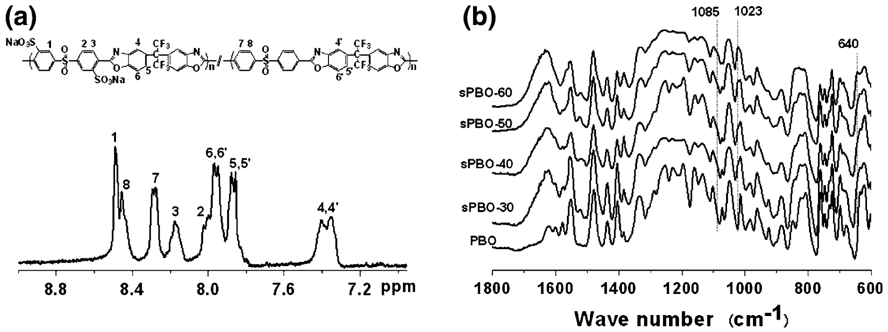


Fig. 1 **a** ^{1}H NMR spectrum of sPBO-50 and **b** IR spectra of PBO and sPBO

respectively, and the band at 640 cm^{-1} is attributed to the stretching vibration of the S–O of sulfonate groups [20, 21]. In addition, the peak intensity of the sulfonate group increases with increasing DS of sPBO. These demonstrated that sulfonate groups are successfully incorporated into the polymer backbone by polycondensation.

Solubility of PBO and sPBO

The solubility of products was evaluated at a concentration of 0.1 g mL^{-1}. The testing results are compiled in Table 2. Generally, most of PBO show poor solubility due to the rigid rod structure. In Table 2, this PBO however dissolves in NMP on heating though it forms a gel after cooling. Similar to the literature, this is due to the incorporation of the flexible hexafluoroisopropylidene moieties into the backbone of PBO [40]. sPBO-30 is soluble in NMP and sulfolane at elevated temperatures. sPBO-40 dissolves in most of the aprotonic solvents on heating. sPBO-50 is soluble in NMP, DMF, and DMAc even at 25 °C. The solubility of sPBO-60 is best among all the sPBO. These indicate that the solubility of sPBO increases with increasing DS. These sPBO are soluble in common solvents and can

Table 2 Solubility of PBO and sPBO

Polymer	Solvents					
	NMP	DMAc	DMF	DMSO	Sulfolane	Methanol
PBO	+[a]	±	±	±[a]	±[a]	−
sPBO-30	+	±	±	±[a]	+	±
sPBO-40	+	+	+	±[a]	+	±
sPBO-50	++	++	++	+[a]	+	±
sPBO-60	++	++	++	++	+	+

++, Soluble at room temperature; +, soluble on heating; ±, partially soluble on heating; −, insoluble even on heating

[a] Gel formation after cooling

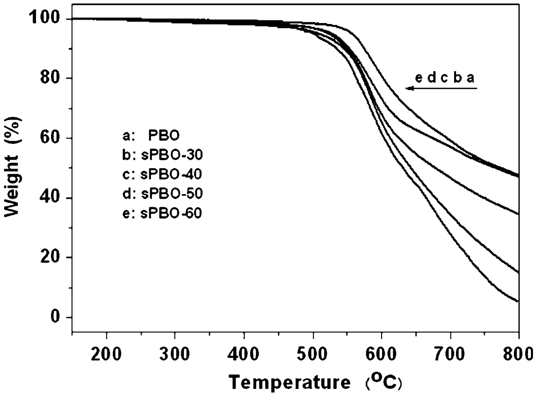


Fig. 2 TGA traces of PBO and sPBO

be cast into tough films. To our knowledge, only McGrath et al. have reported soluble sPBO with high molecular weight in a reference proceeding prior to us [37]. It is necessary that sPBO exhibits good solubility when used as PEM materials.

Thermal behavior

The TGA curves of PBO and the sodium form sPBO are displayed in Fig. 2 and the 5% weight loss temperature (T_{d5}) of them is listed in Table 1. It can be seen from Fig. 2 that PBO has a one-step degradation pattern at about 550 °C, which is ascribed to the decomposition of the main chain. In contrast, sPBO-60 displays a two-step degradation profile. The first stage of degradation is assigned to desulfonation, and the second one is ascribed to the degradation of polymer backbones like the literatures [20, 21]. However, the TGA curves of sPBO-30, -40, and -50 look like a one-step degradation pattern probably because their degradation temperature of the sulfonate group is close to that of polymer backbone. In Table 1, the T_{d5} of PBO is 557 °C, while the T_{d5} of sPBO is lower than 530 °C. Moreover, the T_{d5} of sPBO decreases with the increase of DS. These are due to the fact that the first degradation step of sulfonated polymers is attributed to the elimination of

–SO_3Na. In addition, there is no exothermal peak, endothermal peak, and glass transition in the DSC curves of PBO and sPBO at temperatures ranging from 90 to 350 °C.

Hydrolytic stability of sPBO

The hydrolytic stability of sPBO was studied by observing the change of the membrane samples after treatment. At first, the hydrolytic stability of sPBO as a function of DS was investigated at 80 °C for 24 h in 1 M HCl. On the other hand, as a typical example, the hydrolysis behavior of sPBO-60 was investigated under designated conditions. The reagents for hydrolytic stability test include deionized water, 1 M HCl, 1% PPA, 1% MSA, and 1 M NaOH. The treated membranes were characterized by NMR, IR spectroscopy, and GPC.

Figure 3a shows the ^1H NMR spectra of sPBO with various DS after treatment at 80 °C for 24 h in 1 M HCl. The ^1H NMR spectra of all the sPBO show a group of peaks centred at 11.4, 10.2, 9.7, and 4.7 ~ 4.1 ppm, respectively, which are absent in those of the pristine sPBO. These peaks are assigned to the carboxylic acid (11.4 ppm), amide (10.2 ppm), hydroxyl (9.7 ppm), and amino groups (4.7 ~ 4.1 ppm), respectively, suggesting that the benzoxazole moieties underwent hydrolysis. Moreover, the intensity of these peaks exhibits an increasing tendency with the increase of DS. This illustrates that the hydrolysis of sPBO is more and more obvious with increasing DS under the same conditions.

Figure 3b shows the IR spectra of the pristine and hydrolyzed sPBO. Different from the IR spectra of the pristine sPBO, those of the hydrolyzed sPBO show the absorption bands at 3,422 (N–H strentching), 1,730 (carboxyl C=O strentching), 1,512 cm^{-1} (N–H bending), and a “satellite” band at 1,652 (amide C=O strentching). This is similar to the Werstiuk’s report, which stated that the benzoxazole moiety was hydrolyzed to an intermediate 2-hydroxy-benzoxazoline, then encountered further hydrolysis to 2-aminophenol and carboxylic acid [32, 36]. As can be found from Fig. 3b, the intensity of the absorption bands of carboxyl and

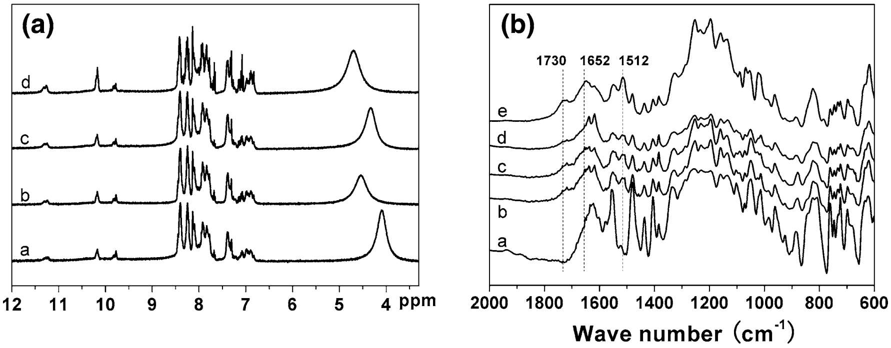


Fig. 3 **a** ^1H NMR spectra of the sPBO samples immersed at 80 °C for 24 h in 1 M HCl: *a* sPBO-30, *b* sPBO-40, *c* sPBO-50, *d* sPBO-60; **b** IR spectra of the pristine sPBO-30 (*a*) and hydrolyzed sPBO samples: *b* sPBO-30, *c* sPBO-40, *d* sPBO-50, *e* sPBO-60

amide groups enhances with increasing DS, fitting well with the above results of the ^{1}H NMR. The reason may arise from the microstructure of sPBO with various DS and would be explained in the following part.

The ^{1}H NMR spectra of the sPBO-60 samples hydrolyzed in various reagents are displayed in Fig. 4a. In Fig. 4a, curve "*a*", "*b*", "*c*" and "*d*" are the ^{1}H NMR spectra of the pristine sPBO-60 and sPBO-60 samples hydrolyzed at 80 °C for 24 h in 1 M HCl, 1% MSA, and 1% PPA, respectively. In Fig. 4a, the profile of curve "*c*" is similar to that of curve "*b*", as illustrates that sPBO-60 show similar hydrolysis in 1% MSA like in 1 M HCl. It could also be observed that sPBO-60 exhibited less hydrolysis in 1% PPA than in 1 M HCl or 1% MSA. Curve "*e*" is the ^{1}H NMR spectrum of the sPBO-60 sample hydrolyzed in 1 M NaOH, which displays a very weak peak at 10.2 ppm (–CONH–) and no peaks at 11.4 (–COOH), 9.7 (–OH), and 4.7 ~ 4.1 ppm ($-NH_2$), unlike that of the sPBO-60 samples hydrolyzed in acid solutions. The reason may be that sPBO-60 was hydrolyzed to an intermediate product in 1 M NaOH like the Werstiuk' report [36], i.e., the benzoxazole rings of sPBO were hydrolyzed to the phenol salt containing amido groups. Besides, curve "*f*" and "*g*" in Fig. 4a are the ^{1}H NMR spectra of sPBO-60 after soaking in deionized water at 80 °C for 24 h and 10 days, respectively. Compared with curve "*a*", curve "*f*" hardly shows any difference, suggesting that sPBO-60 almost undergoes no hydrolysis at 80 °C for 24 h in deionized water. However, curve "*g*" exhibits the amide peak (10.2 ppm) and hydroxyl peak (9.7 ppm) but no peaks at 11.4 ppm (–COOH) and 4.7 ppm ($-NH_2$), indicating that the hydrolysis of benzoxazole rings appears but stay at the intermediate step in deionized water at 80 °C for 10 days. This can be further confirmed by its excellent mechanical strength. Proton exchange membranes are usually needed to be acidified at room temperature for 48 h in 1 M HCl in order to be converted into the acid form membrane. sPBO-60 membrane was treated under the exact conditions so as to evaluate its structural change. Its ^{1}H NMR spectrum (curve "*h*") is shown in

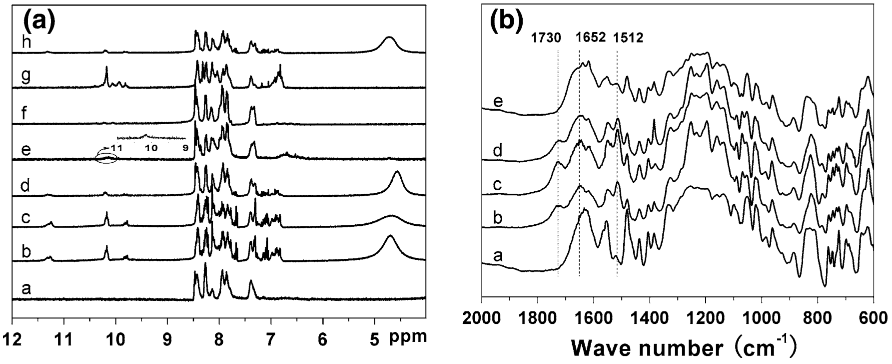


Fig. 4 **a** ^{1}H NMR spectra of the pristine sPBO-60 (*a*) and sPBO-60 samples hydrolyzed in various reagents: *b* in 1 M HCl, *c* in 1% MSA, *d* in 1% PPA, *e* in 1 M NaOH, *f* in deionized water at 80 °C for 24 h, *g* in deionized water at 80 °C for 10 days, *h* in 1 M HCl at room temperature for 48 h; **b** IR spectra of the pristine sPBO-60 (*a*) and hydrolyzed sPBO-60 samples: *b* in 1 M HCl, *c* in 1% MSA, *d* in 1% PPA, *e* in 1 M NaOH

Fig. 4a, which shows the cognizable peaks at 11.4, 10.2, 9.7, and 4.7 ppm. This indicates that sPBO-60 membrane was hydrolyzed to some extent at room temperature for 48 h in 1 M HCl.

The corresponding IR spectra of the pristine and hydrolyzed sPBO are display in Fig. 4b. Different from the pristine sPBO-60, the sPBO samples hydrolyzed in acid show the distinct absorption bands at 1,730 (carboxyl C=O strentching), 1,512 cm^{-1} (N–H bending), and a "satellite" peak 1,652 (amide C=O strentching). In contrast, the IR spectrum of the sPBO-60 sample hydrolyzed in 1 M NaOH displays a group of distinct absorption bands at 3,422 (N–H strentching), 1,652 (amide C=O strentching), and 1,512 cm^{-1} (N–H bending) but no absorption band at 1,730 cm^{-1} (carboxyl C=O strentching), consistent with the result of the ^{1}H NMR.

As seen from the above analysis, sPBO was hydrolyzed to the product containing polar groups such as hydroxyl and amide by acid or alkali solution, the molecular weight of which is inconvenient to be determined by GPC due to the strong interaction between the above polar groups and the fixed phase. Therefore, as an exclusive example, the molecular weight of the hydrolyzed sPBO-60 (treated at 80 °C for 24 h in 1 M HCl) is measured by GPC. The GPC chromatographs of the pristine sPBO-60 and hydrolyzed sPBO-60 are shown in Fig. 5. The latter exhibits longer elution time than the former, that is to say, the hydrolyzed product shows lower molecular weight than the pristine sPBO-60, further confirming that sPBO-60 sample was hydrolyzed in 1 M HCl.

As seen from the studies above, sPBO encounters obvious hydrolysis under mild conditions, leading to the result that they are unsuitable for PEM applications.

Microstructure of sPBO membranes

The microstructure of sPBO membranes were investigated by TEM. The previous studies have demonstrated that the silver form sample can improve the contrast of micrographs [20]. Therefore, sPBO samples used for TEM were transformed into the Ag^+ form. As the typical representatives, the TEM micrographs of sPBO-30 and -60 are shown in Fig. 6. As seen from Fig. 6, the dark area represents hydrophilic ionic domains, while the bright area stands for hydrophobic aromatic segments.

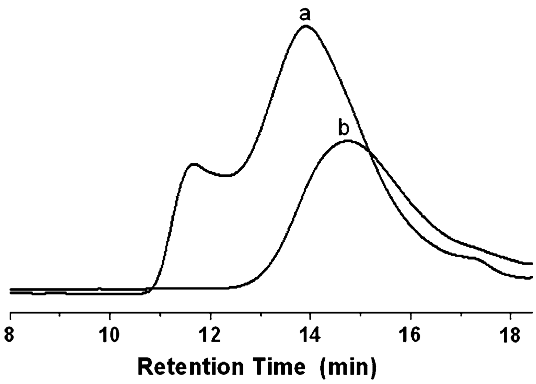


Fig. 5 GPC curves of the pristine (**a**) and hydrolyzed (**b**) sPBO-60

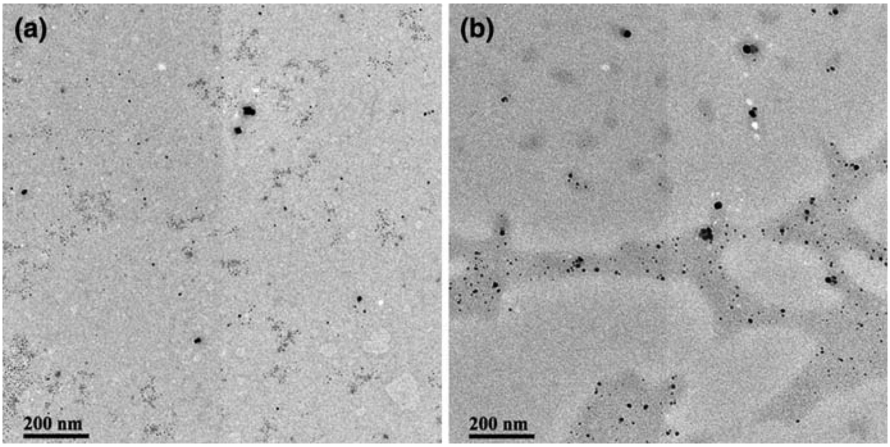


Fig. 6 TEM micrographs of: **a** sPBO-30, **b** sPBO-60

sPBO exhibits a nanophase separation morphology as indicated by the dark and light regions, which is similar to other ionomers [20]. sPBO-30 shows the isolated ionic clusters. However, for sPBO-60, the ionic clusters aggregate and thus form the continuous ionic channels. Generally, the hydrophobic segments of ionomer membranes provide the mechanical strength while the hydrated hydrophilic domains are responsible for proton conduction [3]. The formation of continuous ionic channel is favorable to absorb water, thus promotes the hydrolysis of sPBO. Therefore, sPBO membranes show more and more obvious hydrolysis with increasing DS, consistent with the above testing results.

Conclusion

Soluble sulfonated polybenzoxazoles were prepared by incorporation of the hexafluoroisopropylidene moieties into the polymer backbone. The properties of the resulting sPBO as PEM were investigated with particular emphasis on the hydrolytic stability. sPBO show high molecular weight and excellent thermal stability. Contrary to expectation, sPBO membranes show hydrolysis even in 1 M HCl at room temperature for 48 h. The hydrolysis of sPBO was confirmed by NMR, IR spectroscopy, and GPC. The hydrophilic domains of sPBO become continuous with the increase of DS and are favorable to absorb water, leading to the result that the hydrolysis of sPBO enhances with increasing DS. The studies demonstrated that sPBO membranes could not be used as proton exchange membranes due to their poor hydrolytic stability.

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