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Sulfonated naphthalenic polyimides containing ether and ketone linkages as polymer electrolyte membranes

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ABSTRACT

Two series of sulfonated naphthalenic polyimides containing ether and ketone linkages (SPI-KK-X and SPI-K-X) were prepared by a one-pot polymerization reaction of sulfonated diamine monomers, 1,4-bis[3-sodium sulfonate-4-(4-aminophenoxy)benzoyl]benzene or 4,4-bis[3-sodium sulfonate-4-aminophenoxy]benzophenone, with 4,4-diaminodiphenyl ether and 1,4,5,8-naphthalenetetracarboxylic dianhydride. The membranes cast from the resulting polymers had good thermal and oxidative stability, dimensional stability and mechanical properties. At 80 °C, the proton conductivities of several samples, including SPI-KK-1, SPI-K-1 and SPI-K-2 were higher than 0.10 S/cm, which were comparable to that of Nafion. Methanol permeabilities of the obtained polymer electrolyte membranes (PEMs) were in the range of $1.43\text{--}2.03 \times 10^{-7} \text{ cm}^2/\text{s}$, which were several times lower than that of Nafion 117. It is interesting to note that the SPI-KK-X series, having a more rigid phenyl-ketone-phenyl-ketone-phenyl moiety, had a lower dimensional swelling ratio and lower methanol permeability in comparison with the corresponding SPI-K-X series at the same level of ion exchange capacity (IEC).

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1. Introduction

Fuel cells have drawn extensive attention in the 21st century as effective, clean and green energy technologies, since the world is facing an ever increasing problem of energy shortages and pollution. Polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) have been recognized as promising energy devices in automotive, stationary and portable electronic applications [1]. The characteristics of polymer electrolyte membranes (PEMs), which are the proton conducting core components of PEMFCs and DMFCs, have a great influence on the performance of fuel cells. Perfluorosulfonic acid type membranes, such as Nafion (DuPont) series, which possess excellent oxidative and dimensional stabilities and high proton conductivity, are the commercial state-of-the-art PEMs currently utilized in PEMFC and DMFC systems [2]. However, some deficiencies are well-recognized, such as its high cost, high fuel crossover, low operation temperature ($\leq 80^\circ\text{C}$) and environmental recycling uncertainty [3–5]. In this respect, much research effort is being directed to develop new PEMs with lower cost and good overall performance as alternatives to replace per-

fluorosulfonic acid type membranes [6–11]. Acid functionalized poly(arylenes), such as sulfonated polyarylether-type polymers (SPAEs), sulfonated polyimides (SPIs), polybenzimidazoles (PBIs) doped with phosphoric acid and sulfonated PBIs, have been widely studied as promising candidates for the next-generation PEMs, and some of them have been demonstrated to have attractive fuel cell performance [1,11].

Aromatic polyimides (PIs) have received widespread interest as PEMs, because of their excellent heat resistance, chemical stability, mechanical strength and excellent film-forming ability [12]. Unlike polyarylether-type polymers, such as polyetherketones and polyethersulfones, which can be acid-functionalized either by post-polymerization functionalization or by direct copolymerization of sulfonated monomers [4], the possible hydrolysis of PIs under acidic conditions limits the post-polymerization sulfonation approach; almost all of the reported SPIs were synthesized through the direct copolymerization of the sulfonated monomers. Thus, the preparation of the sulfonated monomers, for example, sulfonated diamines or dianhydrides, is especially important. Some sulfonated diamine monomers have been successfully prepared by sulfonation of commercially available diamines. A variety of SPIs based on these available monomers provides a good opportunity to better understand the structure–property relationships of these PEMs.

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Some interesting and useful results for SPIs were obtained by several research groups in recent years [13–21]. Mercier and co-workers reported the synthesis of a series of SPIs from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) and the results indicated that NTDA-based six-membered ring polyimides were more stable than five-membered ring PIs under fuel-cell conditions [15]. Okamoto and co-workers reported several series of SPIs based on sulfonated diamines and NTDA, some of which exhibited good fuel cell properties [22–26]. For example, sulfonated diamine monomers with flexible linkages, 4,4'-diaminodiphenylether-2,2'-disulfonic acid (ODADS) or 9,9-bis(4-aminophenyl)fluorene-2,7-disulfonic acid (BAPFDS) led to ODADS or BAPFDS-based polyimides that exhibited much better water stability than those derived from a widely used sulfonated diamine, 2,2'-benzidinedisulfonic acid [23,24]. Watanabe and Miyatake developed a SPI containing fluorenyl groups having a high proton conductivity of 1.67 S/cm at 120 °C under 100% relative humidity (RH), which is much higher than that of Nafion [25]. They also reported some SPIs containing aliphatic segments and a stability greater than 5000 h was even achieved under fuel cell operating conditions [26]. McGrath reported the synthesis of a novel sulfonated diamine, 3,3'-disulfonic acid-bis[4-(3-aminophenoxy)phenyl]sulfone (SA-DADPS), containing flexible sulfone and ether linkages, in an attempt to improve hydrolytic stability and membrane ductility [16]. Clearly, in order to improve understanding of the structure–properties relationships and further develop high-performance SPI-based PEMs, there is a continuing requirement to prepare additional SPIs having various new structures.

Most recently, several sulfonated polyaryletherketones containing rigid and regular phenyl–ketone–phenyl–ketone–phenyl linkages in the polymer backbones (SPEEKs) have been found to exhibit many attractive properties as PEMs for DMFCs [10]. In the present study, phenyl–ketone–phenyl–ketone–phenyl and ether linkages have been successfully incorporated into NTDA-based SPIs through copolymerization of a novel sulfonated diamine monomer, 1,4-bis[3-sodium sulfonate-4-(4-aminophenoxy)benzoyl]benzene (BSAPBB). The properties related to PEM materials for fuel cell applications, including thermal stability, mechanical properties, water uptake, dimensional swelling, methanol permeability and proton conductivity were thoroughly evaluated. Aimed at elucidating the structure–property relationships, another series of sulfonated polynaphthalimides with a comparable structure containing phenyl–ketone–phenyl and ether linkages have been synthesized, derived from 4,4-bis[3-sodium sulfonate-4-aminophenoxy]benzophenone (BSAPBP), and a detailed property comparison has been made.

2. Experimental

2.1. Chemicals and materials

1,4-Bis(4-fluorobenzoyl)benzene was obtained from Jilin University, China. 4,4-Diaminodiphenyl ether (ODA) was purchased from Tokyo Chemical Industry. 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA) was supplied by Sigma–Aldrich, and dried at 160 °C in vacuo for 20 h prior to use. Benzoic acid (Tianjin Chemical Reagent, China), *m*-cresol (Shanghai Chemical Reagent, China), 4-aminophenol (Shanghai Chemical Reagent, China) and triethylamine (TEA, Tianjin Chemical Reagent, China) and fuming sulfuric acid (SO₃ 30%, Beijing Chemical Reagent, China) were used without purification. Potassium carbonate (Beijing Chemical Reagent, China) was ground into fine powder and kept at 120 °C prior to use. All other chemicals were obtained from commercial sources, and used without further purification.

2.2. Synthesis of sulfonated diamine monomers

2.2.1. Synthesis of 1,4-bis[3-sodium sulfonate-4-(4-aminophenoxy)benzoyl]benzene

2.2.1.1. Synthesis of 1,4-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene (BSFBB). The sulfonated precursor containing activated difluoro groups, BSFBB, was synthesized according to a reported procedure as follows [7]. A three-necked flask (250 mL) equipped with a mechanical stirrer and nitrogen inlet was charged with 1,4-bis(4-fluorobenzoyl)benzene (96.6 g) and fuming sulfuric acid (30%, 250 mL). The solution was kept at 110 °C for 6 h under stirring, and then the solution was cooled and poured into ice water. The sulfonated compound was precipitated by addition of NaCl, filtered, and then neutralized with sodium hydroxide until pH ~ 7. The crude product was recrystallized from a mixed solution of ethanol and water with the proportion of 1:1. Yield, 74%.

FTIR (KBr, cm⁻¹): 1093, 1047 (–SO₃Na); 1677 (C=O).

¹H NMR (DMSO-d₆, ppm): 7.39 (t, *J* = 8.4 Hz, 1H); 7.88–7.84 (m, 1H); 7.89 (s, 2H); 8.15 (dd, *J* = 6.8 Hz, 2.0 Hz, 1H).

2.2.1.2. Synthesis of 1,4-bis[3-sodium sulfonate-4-(4-aminophenoxy)benzoyl]benzene (BSAPBB). A typical synthesis procedure was as follows: BSFBB (10 mmol), 4-aminophenol (10.05 mmol) and anhydrous potassium carbonate (10.05 mmol), were added into a three-necked flask equipped with a Dean-Stark trap, condenser, mechanical stirrer and nitrogen inlet and outlet. Dimethylformamide (DMAc, 25 mL) and toluene (20 mL) were used as solvent and azeotropic reagent, respectively. The solution-mixture was refluxed at 125 °C for 3 h to dehydrate the system. After removal of toluene, the reaction temperature was increased to 145 °C and maintained at this temperature for another 4 h. After the reaction was complete, the solution was cooled below 80 °C and then poured into ethanol. The crude product was filtered and dried. The pure product was obtained by recrystallization from a mixture of ethanol and water in the proportion of 4:6. Yield, 67%.

FTIR (KBr, cm⁻¹): 1089, 1047 (–SO₃Na); 1677 (C=O); 3458 (–NH₂).

¹H NMR (DMSO-d₆, ppm): 5.06 (s, 4H); 6.61 (d, *J* = 7.5 Hz, 2H); 6.72 (d, *J* = 8.4 Hz, 4H); 6.80 (d, *J* = 7.5 Hz, 4H); 7.69 (d, *J* = 7.2 Hz, 2H); 7.72 (s, 4H); 8.25 (s, 2H).

2.2.2. Synthesis of 4,4-bis[3-sodium sulfonate-4-aminophenoxy]benzophenone (BSAPBP)

The synthesis of BSAPBP was accomplished using a procedure similar to BSAPBB. 4,4-Bis(3-sodium sulfonate)benzophenone was prepared from 4,4'-difluorobenzophenone using a similar synthesis and purification method as outlined in Section 2.2.1.1, to replace BSFBB. Yield, 58%.

FTIR (KBr, cm⁻¹): 1086, 1043 (–SO₃Na); 1674 (C=O); 3458 (–NH₂).

¹H NMR (DMSO-d₆, ppm): 5.03 (s, 4H); 6.61 (d, *J* = 7.5 Hz, 2H); 6.66 (d, *J* = 8.4 Hz, 4H); 6.77 (d, *J* = 8.8 Hz, 4H); 7.55 (d, *J* = 8.4 Hz, 2H); 8.15 (s, 2H).

2.3. Synthesis of the SPIs from BSAPBB and BSAPBP

2.3.1. Synthesis of the SPIs from BSAPBB (SPI-KK-X)

The preparation procedure of a sulfonated polynaphthalimide copolymer based on NTDA/BSAPBB/ODA monomers, SPI-KK-2, is described as follows: BSAPBB (2.2654 mmol), ODA (0.7346 mmol), 0.8 mL of TEA, and 15 mL of *m*-cresol were placed in a 50 mL three-necked round bottomed flask equipped with a magnetic stirring bar and N₂ inlet. The mixture was stirred under a nitrogen atmosphere. After a clear solution was obtained, NTDA (3.0 mmol) and benzoic acid (6.0 mmol) were added into the mixture and then the mixture was stirred at 175 °C for 15 h and then at 195 °C for 3 h under a

Table 1
Selected properties of sulfonated polynaphthalimides.

Polymer	η_{inh} (dL/g)	IEC (mequiv./g)	T_d (°C)		Water uptake (%)		Swelling ratio (%)	
			5%	10%	20 °C	100 °C	20 °C	100 °C
SPI-K-1	1.14	1.90	354	459	64	81	11	17
SPI-K-2	1.05	1.81	362	473	51	72	9	13
SPI-K-3	1.01	1.72	373	496	46	69	8	12
SPI-K-4	0.99	1.61	461	499	42	67	6	11
SPI-KK-1	1.20	1.91	358	463	62	76	9	15
SPI-KK-2	1.12	1.83	374	488	47	71	6	10
SPI-KK-3	1.09	1.70	386	501	42	68	5	7
SPI-KK-4	0.82	1.62	455	512	39	67	4	6

stream of N_2 . After the reaction, the mixture was poured into a large excess of acetone. The yellow precipitate was filtered, washed with acetone as much as possible, and dried at 80 °C under reduced pressure for 12 h to obtain the polyimide ionomer, SPI-KK-2 in the triethylammonium salt form.

After immersing the polymer in 1 M H_2SO_4 for 24 h at room temperature (see Section 2.4), SPI-KK-2 in the acid form was obtained.

FTIR (KBr, cm^{-1}): 1083, 1191 ($-SO_3H$); 1350 (C–N); 1672, 1713 (C=O).

1H NMR (DMSO- d_6 , ppm): 7.09 (d, $J=8.0$ Hz); 7.21 (d, $J=8.5$ Hz); 7.31 (d, $J=8.0$ Hz); 7.49 (d, $J=8.0$ Hz); 7.56 (d, $J=7.0$ Hz); 7.87 (d, $J=7.0$ Hz); 7.91 (s, $J=8.0$ Hz); 8.32 (s); 8.75 (s).

All the other SPI-KK-X polymers with different ion exchange capacity (IEC) values were similarly synthesized by adjusting the monomer feed ratios. SPI-KK-0 homopolymer was obtained by polymerization of NTDA and BSAPBP. The calculated IEC values of SPI-KK-1, SPI-KK-2, SPI-KK-3 and SPI-KK-4 were 1.97, 1.86, 1.75, and 1.67 mequiv./g, respectively.

2.3.2. Synthesis of the SPIs from BSAPBP (SPI-K-X)

The sulfonated polynaphthalimides based on NTDA/BSAPBP/ODA, named as SPI-K-X, were prepared using the same procedure as the above SPI-KK-X series. SPI-K-0 is the homopolymer derived from NTDA and BSAPBP. The calculated IEC values of SPI-K-1, SPI-K-2, SPI-K-3 and SPI-K-4 copolymers obtained by adjusting the monomer feed ratios of NTDA/BSAPBP/ODA were 1.97, 1.86, 1.75, and 1.67 mequiv./g, respectively.

2.4. Membrane preparation

Sulfonated PI (0.5 g) was dissolved in 10 mL of dimethylacetamide overnight. The solution was then filtered with a fine glass frit filter funnel and then the filtrate was directly cast onto a flat and clean glass plate. After drying at 60 °C for 12 h and vacuum drying at 120 °C for 24 h, clear film in the salt form was obtained. The salt-form polynaphthalimide membrane was immersed in a 1 M H_2SO_4 at room temperature for 24 h to convert it to the acid form by proton exchange. The acidified film was soaked in, and washed thoroughly with deionized water. The thickness of the cast films was in the range of 30–60 μm .

2.5. Characterization

2.5.1. Analysis and measurements

The viscosities of the obtained copolymers were measured by using a thermostatically controlled Ubbelohde viscometer with polymer concentrations of 0.5 g/dL in DMSO at 25 °C. FTIR spectra were obtained on a Nicolet Impact 410 Fourier-transform infrared spectrometer. 1H NMR experiments were carried out at room temperature on a Bruker 510 spectrometer (500 MHz for 1H) using DMSO- d_6 as solvent.

2.5.2. Thermal properties of membranes

Differential scanning calorimeter (DSC) measurements were performed using a Mettler Toledo DSC821e instrument from 80 to 200 °C at heating rates of 20 K min^{-1} under nitrogen atmosphere at a constant flow of 200 mL min^{-1} , rapidly cooling to room temperature, then reheating to 400 °C. Thermogravimetric analysis (TGA) was used to evaluate thermal stability of membranes with a Netzsch Sta 449c thermal analyzer system. Before analysis, the films were dried and kept in the TGA furnace at 100 °C in a nitrogen atmosphere for 10 min, and then reheated to 800 °C at 20 K min^{-1} , and the temperatures at 5% and 10% weight loss were recorded for each sample.

2.5.3. Water uptake and swelling ratio measurements

The film samples (10 mm \times 30 mm) were dried at 120 °C for 24 h before measurements. After recording the lengths and weights of dry membranes, the samples were immersed into deionized water for 24 h at the desired temperatures. Before measuring the lengths and weights of membranes, the water was wiped from the membrane surface with a paper towel. The water uptake was calculated from the change of film weight as follows:

$$\text{Water uptake (\%)} = \left(\frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \right) \times 100\%$$

where W_{dry} and W_{wet} are the weights of dried and wet samples, respectively.

The dimensional swelling ratio was calculated from the change of film length using the following equation:

$$\text{Swelling ratio (\%)} = \left(\frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} \right) \times 100\%$$

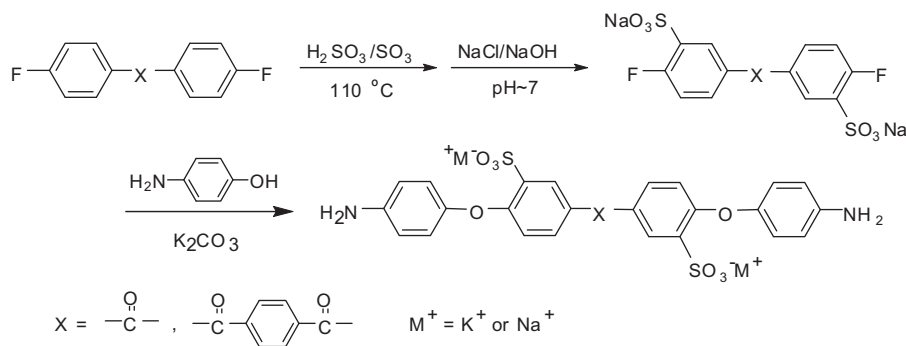
where l_{dry} and l_{wet} are the lengths of the dry membrane and the wet membrane, respectively.

2.5.4. Oxidative stability

Oxidative stability of the films were measured by soaking them in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C. The oxidative stability was evaluated by the dissolution time (t) of the polymer membranes.

2.5.5. Proton conductivity

Proton conductivity experiments were carried out by using AC impedance spectroscopy (Solartron-1260/1287 impedance analyzer) with frequency range and oscillating voltage of 10–10⁷ Hz, 50–500 mV, respectively. Membranes (50 mm \times 10 mm) were placed in a four-point test cell comprising two outer gold wires that provided feed current to the sample and two inner gold wires that were used to measure the voltage drops. The films were fully hydrated in deionized water for 48 h before measurement, and the temperature was regulated by a wrap-around resistance heater with a temperature controller. The impedance measurement experiments were performed in water vapor at 100% RH at



Scheme 1. Synthesis of sulfonated diamine monomers, BSAPBP and BSAPBB.

the desired temperatures. The conductivity (σ) of the membranes, measured longitudinally, was calculated by the following equation:

$$\sigma = \frac{D}{LBR}$$

where D is the distance between the two electrodes, and R is the measured resistance. L and B are the thickness and width of the film samples, respectively.

2.5.6. Methanol permeability

The methanol diffusion coefficient was measured by using a cell made up of two-half-cells separated by the membrane being measured, which was fixed between two rubber rings. Aqueous methanol (10M) was placed on one side (A) of the diffusion cell, and deionized water was placed on the other side (B). The liquids in both compartments were stirred magnetically to ensure solution uniformity. The methanol concentrations in B cell were periodically surveyed by using SHIMADSU GC-8A chromatograph. The methanol permeability coefficient was calculated using the following formula.

$$C_B(t) = A \times DK \times C_A(t - t_0) / V_B L$$

where DK is the methanol diffusion coefficient (cm^2/s), $C_B(t)$ is concentration of methanol in B cell (mol/L), C_A is concentration of methanol in A cell (mol/L), A is membrane area (cm^2), L is thickness of membrane (cm) and V_B is the volume of the diffusion cell.

3. Results and discussion

3.1. Synthesis and characterization of sulfonated diamine monomers

While some available diamines could be theoretically sulfonated, only a few diamine monomers containing $-\text{SO}_3\text{H}$ groups have been successfully obtained for the preparation of SPIs due to the complexity of the sulfonation reaction [16,21–26]. Thus, it is important to explore further approaches to incorporate $-\text{SO}_3\text{H}$ groups into diamines. A synthetic approach for preparing diamine monomers, based on the reaction of activated difluoro/dichloro compounds and 4-aminophenol, has been developed for the preparation of polyetherimides [27]. Recently, this synthetic strategy was also applied to the preparation of disulfonated diamine monomers, such as 3,3'-disulfonic acid-bis[4-(3-aminophenoxy)phenyl]sulfone [16] and 4,4'-bis(4-aminophenoxy)benzophenone-3,3'-disulfonic acid [28].

In this study, a new sulfonated monomer, 1,4-bis[3-sodium sulfonate-4-(4-aminophenoxy)benzoyl]benzene (BSAPBB) was prepared first by sulfonation of 1,4-bis(4-fluorobenzoyl)benzene [7], followed by nucleophilic aromatic substitution ($\text{S}_{\text{N}}\text{Ar}$) reaction between 1,4-bis(3-sodium sulfonate-

4-fluorobenzoyl)benzene and 4-aminophenol, as shown in Scheme 1. Sulfonated diamine monomer, 4,4-bis[3-sodium sulfonate-4-aminophenoxy]benzophenone (BSAPBP), was similarly synthesized. It should be noted that the starting dihalo-compound, target product, reaction conditions and purification procedure for the preparation of BSAPBP were quite different from the reported work by Riande and co-workers [28], in which a dichloro compound was the starting material and the prepared sulfonated diamine was in the acid form.

The chemical structures of both BSAPBB and BSAPBP monomers were confirmed by FTIR and ^1H NMR spectroscopies. Representative FTIR and ^1H NMR spectra for BSAPBB monomer are shown in Figs. 1 and 2.

3.2. Synthesis and characterization of polymers

A one-pot, high-temperature polycondensation method was employed in the presence of TEA and benzoic acid (catalyst) to synthesize six-membered ring polyimides [21–26]. By varying the molar ratio of the sulfonated to non-sulfonated diamine monomers, sulfonated polynaphthalimide copolymers, SPI-KK-X based on NTDA/BSAPBB/ODA and corresponding SPI-K-X based on NTDA/BSAPBP/ODA were synthesized, as shown in Scheme 2. Tough and ductile membranes were prepared by DMSO solutions of SPIs in the salt form onto glass plates, followed by a drying procedure. The triethylammonium salt form membranes were converted into their corresponding acid forms by immersing the membranes in 1M H_2SO_4 for 24 h at room temperature. The IEC values (1.61–1.91 mequiv./g) of the membranes by titration were close to the calculated ones, as shown in Table 1.

Fig. 3 is the FTIR spectra of SPI-KK-X copolymers in their salt forms. The spectra display the naphthalimide adsorption bands

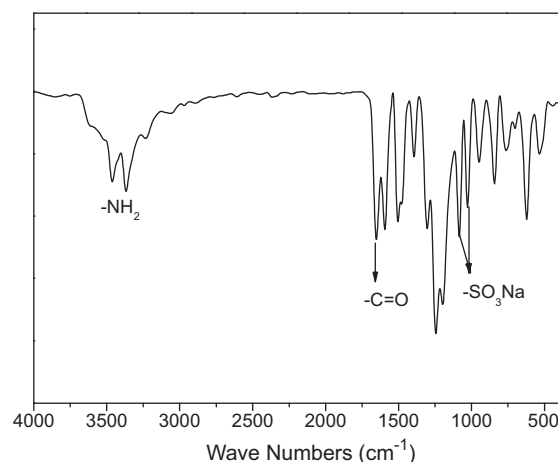
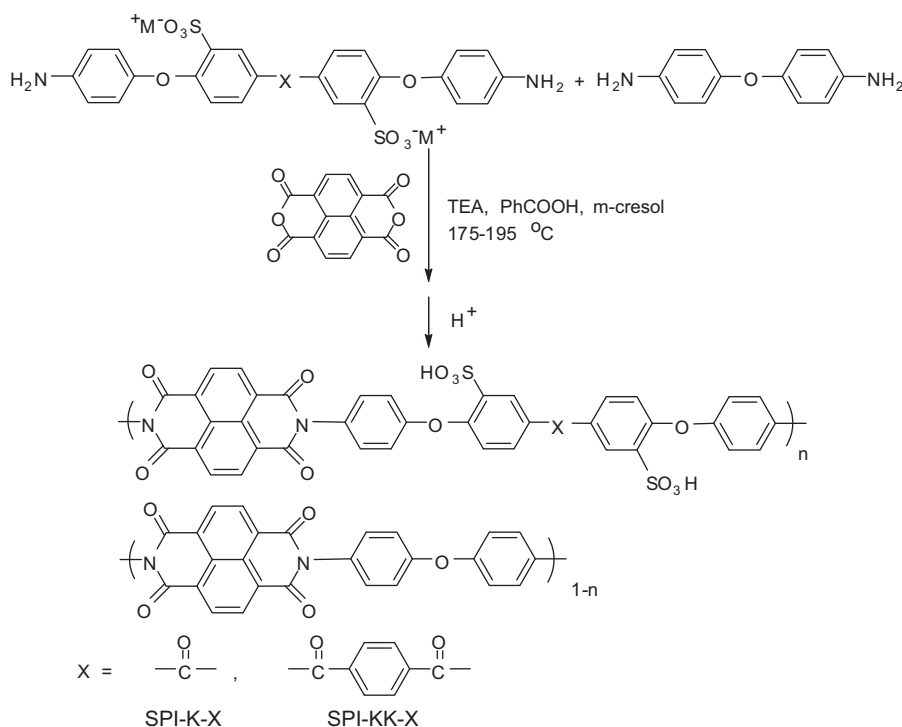


Fig. 1. FTIR spectrum of BSAPBB monomer.



at 1716, 1678, and 1349 cm^{-1} corresponding to the symmetric, asymmetric vibration of C=O groups and vibration of C–N groups of the six-membered imide rings, respectively. The band around 1083 cm^{-1} is assigned to the stretching vibration of sulfonic acid groups, whose intensities increased with the value of IEC.

^1H NMR spectra of sulfonated polynaphthalimide polymers in DMSO- d_6 are shown in Fig. 4(A) and (B). The spectral signals were assigned to the protons of the polymeric structure. Copolymer compositions, as expected from the feed monomer ratios, were confirmed from the integration ratios of the signals. No residual amide and carboxylic protons were observed, indicating that the imidization reaction was complete. As shown in Fig. 4(A), compared with SPI-KK-0 homopolymer, additional signals (e' and f') corresponding to the protons of ODA for all SPI-KK-1, 2, 3 and 4 copolymers appeared. With the increase of the IEC values, the proportion of signals e and e' increased. Similar behavior is evident in the spectra of the SPI-K-X series of polymers, as shown in Fig. 4(B).

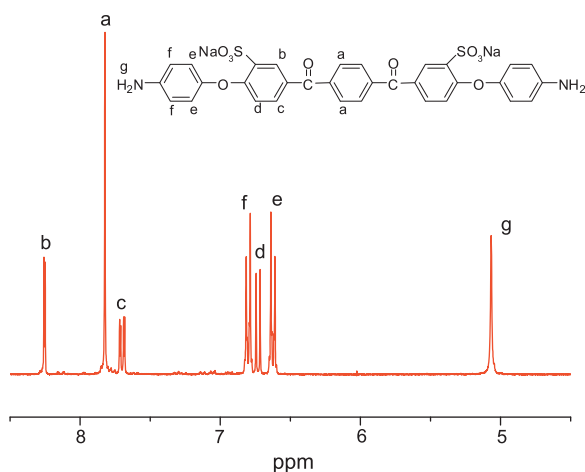


Fig. 2. ^1H NMR spectrum of BSPABB monomer.

3.3. Thermal properties

Thermal properties of the SPI membranes were studied by DSC and TGA measurements. No obvious glass transitions were observed, which might be due to the strong interactions of ionic groups, imide groups and rigid backbones. Fig. 5 shows the typical TGA curves of the sulfonated polynaphthalimides with various IEC values. Two-stage weight loss curves were obtained as expected. The initial weight loss around 300 °C was due to the decomposition of sulfonic acid groups, and the secondary weight loss started from 500 °C indicated the decomposition of the polyimide backbone. Furthermore, as IEC increased, the weight losses at the same temperature increased. The TGA results listed in Table 1 clearly indicate that this class of sulfonated polyimides has good thermal stability.

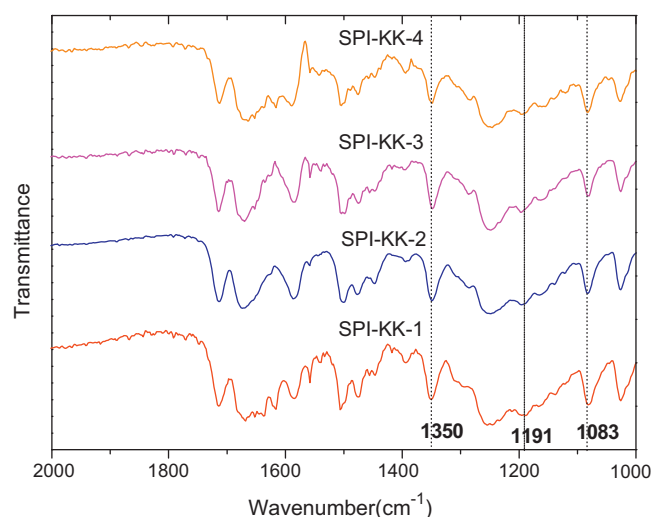


Fig. 3. FTIR spectra of SPI-KK-X copolymers in their salt forms.

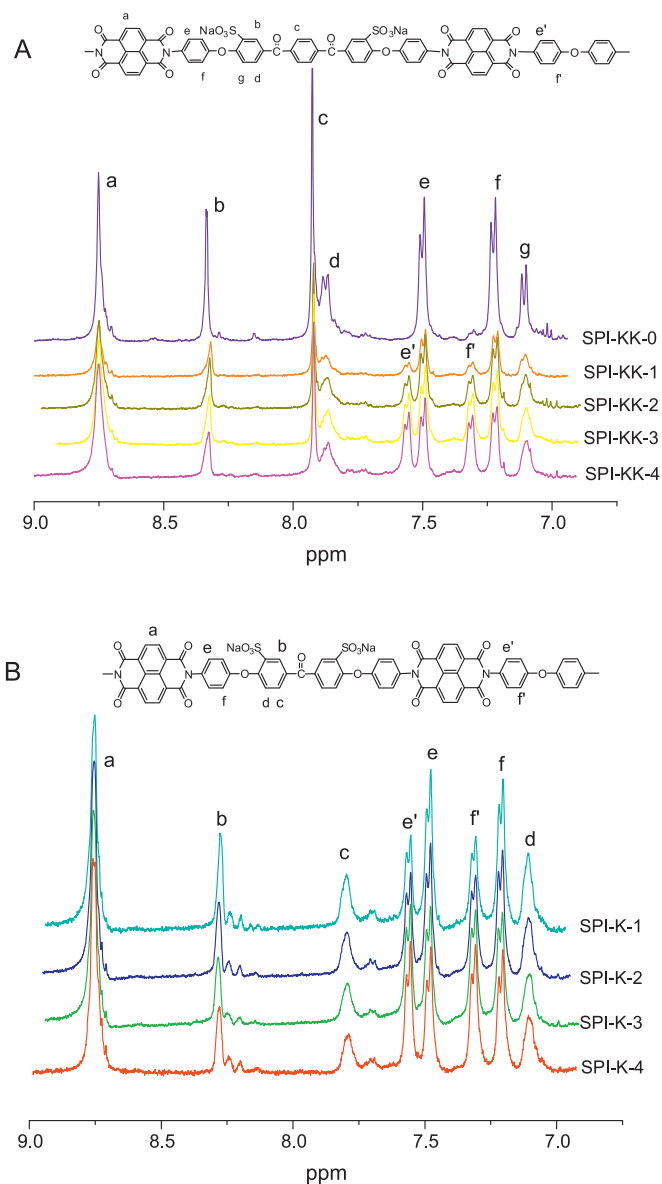


Fig. 4. ^1H NMR spectra of the polymers in DMSO-d_6 . (A) SPI-KK-X; (B) SPI-K-X.

3.4. Water uptake and dimensional swelling ratio

Water absorption is related to proton conductivity and dimensional stability of the membranes. To maintain high proton conductivity, the membranes must have an ability to retain a sufficient amount of water, which is often associated with the

Table 3
Mechanical properties of the membranes.

Polymer	Tensile strength (MPa)		Young's modulus (GPa)		Elongation at break (%)	
	Dry	Wet	Dry	Wet	Dry	Wet
SPI-K-1	82.9	30.3	1.30	0.44	23	44
SPI-K-2	71.5	28.5	1.20	0.43	18	33
SPI-K-3	68.5	28.4	1.17	0.42	17	23
SPI-K-4	63.3	24.1	1.03	0.41	15	18
SPI-KK-1	85.2	31.2	1.31	0.50	24	30
SPI-KK-2	78.8	29.8	1.25	0.49	23	25
SPI-KK-3	73.4	29.3	1.19	0.48	22	25
SPI-KK-4	70.3	24.8	1.05	0.47	17	22

The samples in wet state were obtained by immersing them in water for 72 h, and the samples in dry state were obtained by putting them in a vacuum oven at 100°C for 12 h.

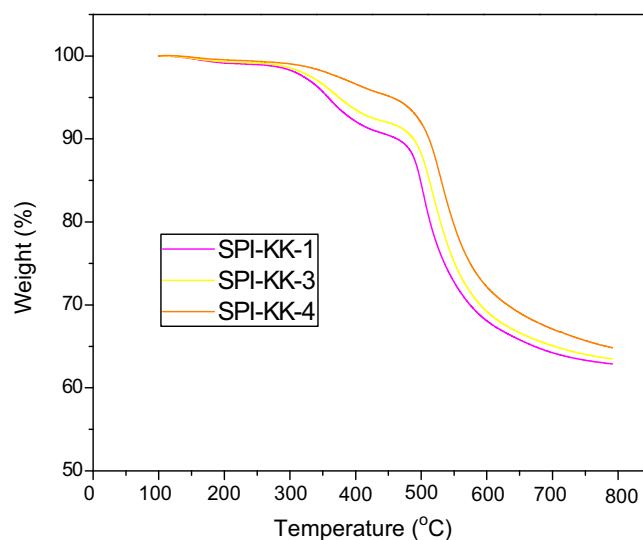


Fig. 5. TGA curves of typical polynaphthalimide copolymers.

Table 2
Proton conductivity (σ), oxidative stability and methanol permeability of the PEMs.

Polymer	Methanol permeability ($\text{cm}^2 \text{s}^{-1}$)	σ (S/cm)		Oxidative stability t (h)
		20°C	80°C	
SPI-K-1	2.03×10^{-7}	0.039	0.110	4
SPI-K-2	1.90×10^{-7}	0.036	0.101	>6
SPI-K-3	1.81×10^{-7}	0.029	0.074	>6
SPI-K-4	1.60×10^{-7}	0.020	0.062	>6
SPI-KK-1	1.84×10^{-7}	0.037	0.107	4.5
SPI-KK-2	1.70×10^{-7}	0.020	0.068	>6
SPI-KK-3	1.60×10^{-7}	0.018	0.059	>6
SPI-KK-4	1.43×10^{-7}	0.014	0.043	>6

t : time at which the membranes dissolved in Fenton's reagent.

high content of acidic groups. On the other hand, excessive water uptake would destroy the dimensional integrity and mechanical properties, especially at elevated temperature in a humidified environment. An important goal in preparing PEMs is achieving both high proton conductivity and low dimensional swelling. As shown in Table 1, all the PEMs exhibited very good water absorption and dimensional swelling throughout the temperature range tested. At 20°C , the water uptake and dimensional swelling were in the range of 64–39% and 11–4%, respectively. At 100°C , the values of both water uptake (81–67%) and swelling ratio (17–6%) increased, though not excessively. Fig. 6 shows that the values of water uptake and the dimensional swelling increased with the test temperature. For each series, the values increased with the IEC values, as expected. Interestingly, at comparable IEC values,

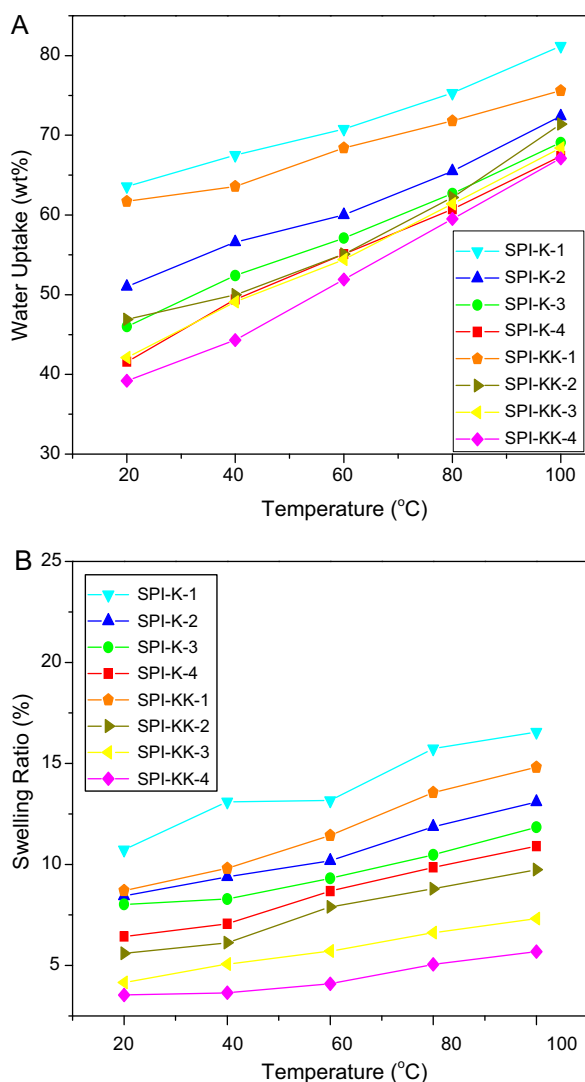


Fig. 6. Water uptake (A) and swelling ratio (B) of SPI-KK-X and SPI-K-X copolymers at different temperatures.

SPI-KK-X membranes always had lower water uptake and dimensional swelling than SPI-K-X membranes. A comparative plot is given in Fig. 7. This could be explained by the more rigid backbones of $\text{-Ph-ketone-Ph-ketone-Ph-}$ linkages, which might affect the molecular chain packing and the aggregation of ionic clusters.

3.5. Hydrolytic-oxidative stability and mechanical properties

As shown in Table 2, the samples even with high IEC values did not dissolve in Fenton's reagent within 4 h at the temperature of 80 °C, which suggested good oxidative stability. In addition, no obvious differences oxidative stability for two series copolymers was observed.

As shown in Table 3, all the membranes exhibited good mechanical properties. In the dry state, the PEM membranes possessed high tensile strength in the range of 63.3–85.2 MPa and Young's moduli of 1.03–1.31 GPa, with elongations at break of 15–24%. These tensile results are comparable with or better than some reported SPIs, and also this tensile behavior is similar to the unsulfonated polyimides [27]. After hydrating the membranes in water for more than 72 h, all the membranes showed good mechanical properties, though with lower values of tensile stress of 24.1–31.2 MPa,

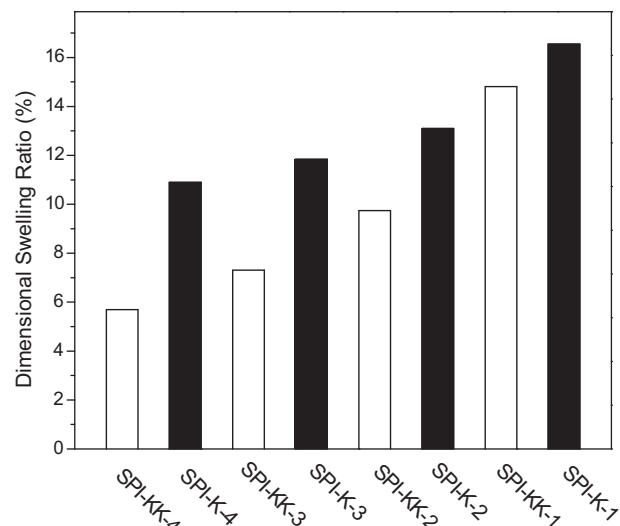


Fig. 7. A comparison of dimensional swelling ratios between SPI-KK-X and SPI-K-X at 100 °C.

Young's moduli of 0.41–0.50 GPa and elongations at break of 18–44%.

The hydrolytic stability is very important for SPI materials targeted for fuel cell applications [29,30]. Hydrolytic stability of the SPI membranes in hot water was examined by immersing the sample sheets into water at 80 °C. All of the membranes maintained sufficient mechanical properties after 24 h, and SPI-K-3,4 and SPI-KK-3,4 membranes with low IEC values could maintain their mechanical properties even after 120 h. The mechanical properties of the four selected membranes before and after treatment in hot water are listed in Table 4.

3.6. Proton conductivity and methanol permeability

A combination of high proton conductivity and low fuel permeability of PEMs is relevant to enhancing the performance of PEMFCs and DMFCs. The proton conductivities of the membranes estimated from AC impedance spectroscopy are presented in Fig. 8 and Table 2. The membranes possessed conductivities in the range of 0.014–0.039 S/cm at room temperature. The conductivities of all the samples showed dependence on temperature and IEC values.

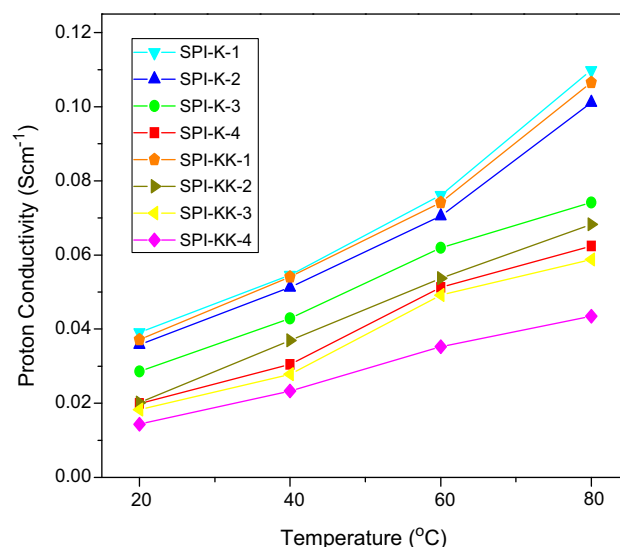
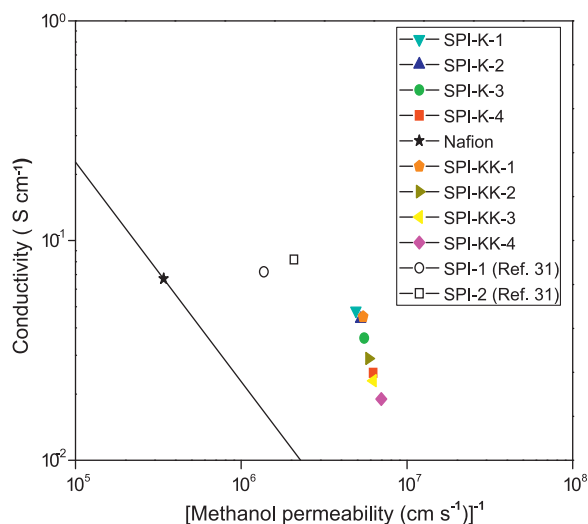


Fig. 8. Proton conductivities of the membrane at different temperature.

Table 4

Mechanical properties of the membranes before and after immersion in 80 °C water.

Polymer	Tensile strength (MPa)			Young's modulus (GPa)			Elongation at break (%)		
	RT ^a	6 h ^b	12 h ^c	RT	6 h	12 h	RT	6 h	12 h
SPI-KK-1	31.2	27.1	14.2	0.50	0.40	0.39	30	13	8
SPI-KK-2	29.8	20.2	16.9	0.49	0.37	0.35	25	9	5
SPI-K-1	30.3	25.3	16.2	0.44	0.39	0.38	44	21	9
SPI-K-2	28.5	17.2	11.7	0.43	0.31	0.29	33	11	9

^a After immersing the membranes in water at room temperature for more than 72 h.^b After immersing the membranes in water at room temperature for more than 3 weeks and then treated in water at 80 °C for 6 h.^c After immersing the membranes in water at room temperature for more than 3 weeks and then treated in water at 80 °C for 12 h.**Fig. 9.** Proton conductivity versus methanol permeability of the membranes.

At 80 °C, the proton conductivities of SPI-KK-1, SPI-K-1 and SPI-K-2 were higher than 0.10 S/cm, and comparable to Nafion.

Although the SPI-K-X series may have higher proton conductivity than the corresponding SPI-KK-X series at the same IEC value, SPI-KK-X membranes with more rigid backbones exhibited better methanol resistance. At the same IEC values, methanol permeability of SPI-KK-X ($1.43\text{--}1.84 \times 10^{-7} \text{ cm}^2/\text{s}$) were lower than those of SPI-K-X ($1.60\text{--}2.03 \times 10^{-7} \text{ cm}^2/\text{s}$) and are several times lower than the value of Nafion 117 ($2.94 \times 10^{-6} \text{ cm}^2/\text{s}$). In order to eval-

uate the combined effect of the proton conductivity and methanol crossover, a trade-off plot [4] containing both methanol permeability (at 30 °C) and proton conductivity (at 30 °C) is shown in Fig. 9. It is clear that the preferred membranes, which have higher proton conductivity and low methanol permeability, are situated at the right top corner of the plot. The membranes of SPI-KK-1, SPI-K-1 and SPI-K-2 were found to have good performance. To clearly elucidate this relationship, their selectivity, obtained by a calculation from the ratio of proton conductivity and methanol permeability, is given in Fig. 10. Obviously, SPI-KK-1, SPI-K-1 and SPI-K-2 had very good selectivity, and among them, SPI-KK-1 had the best selectivity, which may be a promising PEM material for DMFC applications.

4. Conclusions

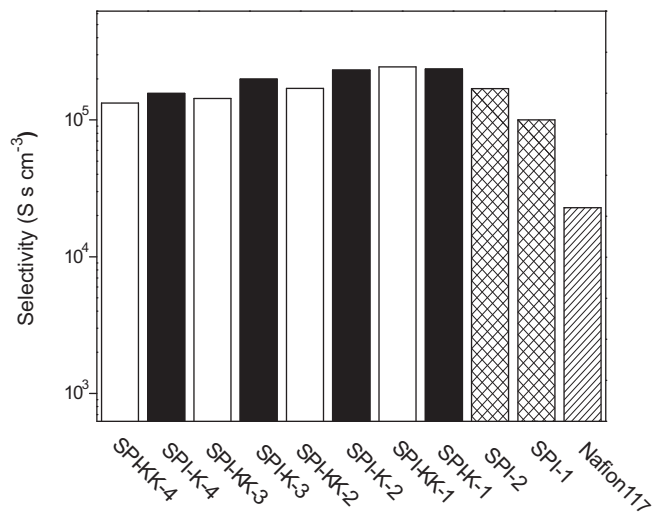
Two sulfonated monomers, 1,4-bis[3-sodium sulfonate-4-(4-aminophenoxy)benzoyl]benzene and 4,4-bis[3-sodium sulfonate-4-aminophenoxy]benzophenone were synthesized via nucleophilic aromatic substitution reactions of activated difluoro sulfonated compounds and 4-aminophenol. Two series of SPIs containing ether and ketone linkages were prepared through a copolymerization method. The properties, including thermal stability, mechanical properties, water uptake, swelling, methanol permeability and proton conductivity were evaluated. The proton conductivities of three obtained PEMs were higher than 0.10 S/cm at 80 °C, and they possessed other attractive properties, such as low methanol permeability, good oxidative and dimensional stability. It was found that the SPI-KK-X series, having more rigid phenyl-ketone-phenyl-ketone-phenyl moieties, had lower dimensional swelling ratio and methanol permeability in comparison with the SPI-K-X series at the same IEC values. Several obtained PEMs exhibited high selectivity for DMFC applications.

Acknowledgments

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**Fig. 10.** Selectivity of the membranes. SPI-1 and SPI-2 refer to NTDA-BAPBDS/BAPB and NTDA-3,3'-BSPB/BAPB from Ref. [31].

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