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Partially sulfonated poly(arylene ether sulfone)-*b*-polybutadiene for proton exchange membrane

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Abstract

A novel block copolymer based on poly(arylene ether sulfone)-*b*-polybutadiene (SPAES-*b*-PB) was synthesized and its flexible segment was sulfonated by electrophilic addition reaction with acetyl sulfate. This could be a new approach to prepare suitable alternative proton exchange membranes to Nafion®. Only a single glass transition temperature (T_g) of copolymer measured by differential scanning calorimeter (DSC) indicated good compatibility between PAES block and PB block. A tough and transparent membrane based on SPAES-*b*-PB exhibited higher proton conductivity (0.0302 S/cm at 25 °C and 100% relative humidity) even with relatively low ion exchange capacity (IEC) of 0.624 mmol/g compared to other sulfonated block copolymer membranes such as sulfonated polystyrene-*b*-poly(ethylene-ran-butylene)-*b*-polystyrene (SSEBS), sulfonated poly(styrene-isobutylene-styrene) (S-SIBS), sulfonated hydrogenated poly-butadiene-styrene copolymer (HPBS-SH) as a result of selected sulfonation of the flexible segments facilitating sulfonated groups to aggregate to form ion-rich channels.

Keywords: Block copolymer; Proton exchange membrane; Sulfonation

1. Introduction

A great deal of efforts have been made for the development of proton exchange membrane fuel cells (PEMFC) in recent years because of their promising applications in new clean power source [1–3]. Although Nafion® membrane has been mainly used in PEMFC because of its excellent chemical stability and high conductivity, its high cost and other drawbacks limit its wide applications. Intensive research work in this field has focused on the study of new suitable proton conducting polymer membranes as alternatives to Nafion®. But few of these membranes have been practically used for proton conduction in PEMFC [4,5]. So study of the structure of Nafion® will be helpful to prepare novel proton exchange membrane.

It is well known that perfluorosulfonate ionomer has high proton conductivity due to existence of ion channels [6–8], even with lower ion exchange capacity. That is reasonable since Nafion® has high phase-separated hydrophilic and hydrophobic domains. The hydrophilic sulfonated groups close to each other to produce cylindrical channels for water and ion transportation. Nafion® is also found to exhibit high proton conductivity at low water content via segmental motions [9] (presumably main chain or side chain) because of their flexibilities. Recently there have been considerable advances on sulfonated block copolymers consisting of hard and flexible segments due to their excellent mechanical properties and good abilities to develop the structure of phase separation [10–13].

In this work, we report synthesis of a new block copolymer that consists of poly(arylene ether sulfone) and polybutadiene segments through polycondensation, and post-sulfonation of selected flexible block fragment. A series of membranes in different sulfonation degree made from it were characterized and compared with other block copolymer membranes. These membranes exhibit excellent

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mechanical property and higher conductivity even with lower IEC. It is very promising to be used as a candidate for polyelectrolyte in PEMFC and the relationship between structure and property of such copolymer is studied.

2. Experimental

2.1. Materials

4,4′-dichlorodipenyl sulphone was obtained from Acros. Carboxyl-terminated polybutadiene (CTPB) was purchased from Chinese Lanzhou Latex Research Center (Mn = 4250). 4,4′-isopropylidenediphenol obtained from Shanghai Reagents Company was recrystallized from absolute ethanol before use. Other common chemicals were all analytical grade and used without further purification.

2.2. Polymer preparation

2.2.1. Synthesis of chloro-terminated poly(arylene ether sulfone) (PAES-Cl)

The synthesis of chloro-terminated poly(arylene ether sulfone) was performed according to a procedure described by McGrath et al. [14] by base catalyzed solution polycondensation. 4,4′-dichlorodiphenyl sulphone (0.021 mol), 4,4′-isopropylidenediphenol (0.020 mol), potassium carbonate (0.023 mol) were added to a 150 mL three-necked flask equipped with nitrogen inlet and Dean Stark trap. Toluene (20 mL) and *N*-methyl-2-pyrrolidone (NMP) (30 mL) were added to afford a concentration of 20 wt% solids. The mixture was heated at 160 °C for 4 h and at 190 °C for 16 h. The subsequent viscous solution was filtered before precipitation of the polymer in 200 mL ethanol. The precipitate was filtered, washed twice with hot deionized water (80 °C) and vacuum dried at 100 °C for 24 h. Yield: 81%.

2.2.2. Synthesis of amino-terminated poly(arylene ether sulfone) (PAES-NH_2)

PAES-NH_2 was synthesized by a reaction of PAES-Cl and a specific weight of 4-amoniphenol using similar method depicted above. The only difference was the reaction solution was kept at 150 °C for 20 h. Yield: 75%.

2.2.3. Synthesis of acidylated CTPB (PBCOCl)

A solution of CTPB (0.00534 mol) and $SOCl_2$ (0.0427 mol) in 100 mL toluene was added to a 250 mL three-necked flask fitted with nitrogen inlet and condenser. The mixture was kept at 75 °C for 2 h, and then the reaction temperature was raised to 90 °C and kept for 20 h. The obtained solution was distilled to remove excessive $SOCl_2$ and stored for later use. Yield: 95%.

2.2.4. Synthesis of block copolymer PAES-b-PB

A solution of PAES-NH_2 (3.0 g) and PBCOCl (5.1 g) in NMP/toluene (5/2 v/v) mixture solvent was added to a 150 mL flask equipped with condenser. The reaction mixture was heated at 50 °C for 24 h, and then poured into 200 mL ethanol to get precipitate. The product was washed with deionized water and dried under vacuum at 100 °C for 24 h. Yield: 96%. ^{1}H NMR (in DMSO-d_6) δ (ppm): 6.92–7.90 (aromatic), 5.4 (2H, CH=CH), 2.0 (4H, $2CH_2$), 1.68 (6H, $2CH_3$). FT-IR (KBr): 3030 (ν_s, aromatic, C-H), 1687 (ν_s, C=O), 1640 (ν_s, C=C), 966 (δ, =CH). $M_n = 4.581 \times 10^5$, polydispersity = 1.241.

2.2.5. Synthesis of sulfonated PAES-b-PB (SPAES-b-PB)

Sulfonating reagent acetyl sulfate was prepared following the procedure described in literature [11]. Acetic anhydride was cooled to 0 °C, and then reacted with corresponding volume of 98% concentrated sulfuric acid at 0 °C for 6 h. Fresh acetyl sulfate was prepared and stored in refrigerator just prior to adding to the following reaction mixture.

PAES (2 g) was dissolved in 50 mL tetrahydrofuran (THF). After it was completely dissolved, calculated amount of acetyl sulfate prepared above was added. The clear solution was kept at 75 °C under nitrogen atmosphere for 12 h, and then most of solvent was evaporated off by rotating evaporation. The obtained viscous deep brown solution was poured into 4-fold ethanol, and 1.5 M NaOH solution was added drop-wise until pH reached 7. The sulfonated polymer was isolated, washed twice with absolute ethanol to remove residual acid, dried under vacuum at 80 °C for 24 h. The crude product was washed with hot deionized water (80 °C) and dried under vacuum again. Yield: 90%.

2.3. Membrane preparation

A solution of sulfonated copolymer in NMP (8 wt%) was prepared and filtered. The filtered solution was cast onto glass plates and dried by infrared lamp until most of solvent was evaporated. The residual solvent was completely removed under vacuum at 120 °C for 48 h. The membranes were detached from the glass plates after they were immersed into hot deionized water (50 °C) for 5 min, and then immersed into 1.5 M H_2SO_4 solution overnight. Finally the membranes were thoroughly washed with deionized water and dried under vacuum at 100 °C for 24 h.

2.4. Characterization

Fourier-Transform IR (FTIR) spectra were scanned using a Perkin–Elmer Paragon1000 FTIR spectrometer. ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Mercury Plus 400 MHz spectrometer in DMSO-d_6. Gel permeation chromatography (GPC) was performed with dimethyl formamide (DMF) as the eluent using a Perkin–Elmer Series 200 apparatus. The molecular weight was calculated with respect to linear polystyrene (PS) standards.

Ion exchange capacity (IEC) was determined by titration. Membrane samples were soaked in 50 mL of 1 M NaCl solution for 24 h, and then titrated with 0.01 M NaOH solution.

Water uptake of membrane was determined in acid form. Membranes were first thoroughly dried under vacuum at 100 °C for 24 h to a constant weight, which was recorded as W_{dry}. The dried membranes were then immersed in deionized water at 70 °C for 4 h. The wet membranes were taken out, wiped with tissue paper and weighed quickly (W_{wet}). Water uptake was calculated using the following equation:

$$\text{Water uptake} = \frac{W_{\mathrm{wet}} - W_{\mathrm{dry}}}{W_{\mathrm{dry}}} 100\% \tag{1}$$

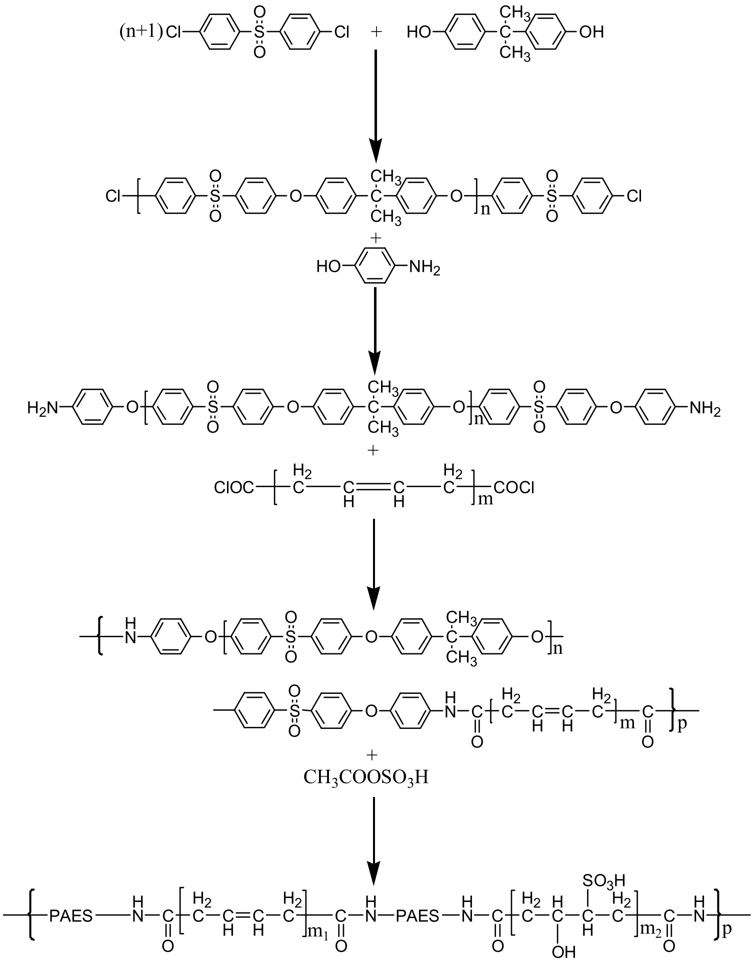
Tensile dumbbell membrane specimens were tested by Instron 4465 electron tensile tester (Instron Corp., USA) at a crosshead speed of 10 mm/min. The gauge length and width of dumbbell tensile specimens were 25 mm and 6 mm respectively. The thickness of membrane samples ranged from 36 to 54 μm.

The glass-transition temperatures were determined on Perkin–Elmer DSC-7 under a protective nitrogen atmosphere. Samples were heated from −70 to 180 °C at heating rate of 10 °C/min.

Proton conductivity of membranes was measured with a two-electrode cell. AC impedance of samples was carried out in the frequency range 100 Hz–1 MHz with amplitude of 10 mV using Solartron SI 1260 Impedance/Gain-phase analyzer. The membranes were immersed in deionized water (25 °C) at least 1 h before being measured. The resistance value associated with the membrane conductivity was determined from the frequency that produced the minimum imaginary response.

3. Results and discussion

Acidylation reaction was used to synthesize acidylated CTPB (PBCOCl). CTPB is a special polybutadiene bearing two carboxyls at the end of main chain, and their existence remarkably improves the flexibility of backbone of copolymers. In this article, PBCOCl was used to react with PAES-NH_2 to synthesize hard-*block*-flexible



Scheme 1. Synthesis of sulfonated poly(arylene ether sulfone)-*b*-polybutadiene.

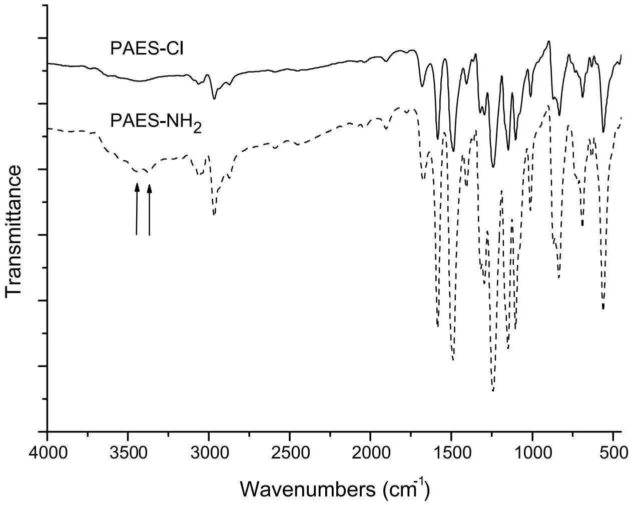


Fig. 1. FT-IR spectra of PAES-Cl and PAES-NH$_2$.

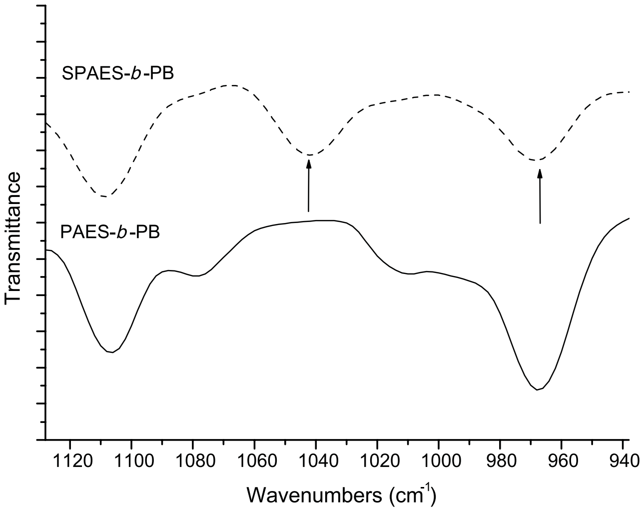


Fig. 2. FT-IR spectra of sulfonated SPAES-*b*-PB and PAES-*b*-PB.

copolymer. Measurement of block copolymer's molecular weight was performed by GPC. Its high molecular weight (M_n) of 4.581×10^5 attributes to higher reactivity of acyl chloride groups than carboxyl groups.

Chloro- and amino-terminated PAES were synthesized by direct high-temperature polycondensation as illustrated in Scheme 1. Excess of 4,4′-dichlorodiphenyl sulphone was used to ensure formation of chloro-terminated structure. Feed ratio of reactants is very crucial in controlling the molecular weight and degree of functionality of hard segment of the resulting block copolymer. No significant difference between ^{1}H NMR spectra of PAES-Cl and PAES-NH$_2$ was observed due to very low content of end groups comparing to the whole copolymer backbone. But the alteration of structure could be clearly confirmed by IR spectra of PAES-Cl and PAES-NH$_2$ shown in Fig. 1. Peaks at 3459 and 3373 cm^{-1} assigned to the stretching vibration of NH$_2$ appeared after the reaction indicates successful reaction of condensation.

Sulfonation of block copolymer was carried out via double bond addition reaction as shown in Scheme 1. The flexible segment of copolymer was selectively sulfonated by acetyl sulfate. Aromatic rings in hard segment are free of being sulfonated under such sulfonating condition. Degree of sulfonation (DS) of copolymers can be controlled by controlling the ratio of sulfonating agent to the double bonds of flexible segment. Successful introduction of sulfonated groups was confirmed by IR spectroscopy shown in Fig. 2. A clear difference between the spectra of the neat copolymer and sulfonated copolymer was observed. The new arising peak at 1040 cm^{-1} is assigned to the symmetric stretching vibration of sulfuric acid groups. As expected, the absorption peak at 966 cm^{-1} assigned to C=C double bond shows a decrease in intensity. It means that the concentration of C=C double bond in the flexible segment decreased after sulfonation, which also proved that sulfonation of flexible segment occurred.

Table 1 shows physical properties of SPAES-*b*-PB membranes and comparison of conductivity between SPAES-*b*-PB and other sulfonated block copolymer membranes. Water uptake for membranes of different sulfonation degree increased with increasing IEC values. It displayed a linear relationship with IEC. The high tensile strength

Table 1
Physical properties of SPAES-*b*-PB membranes and comparison of conductivity between SPAES-*b*-PB and other sulfonated block copolymer membranes

Sample	Thickness (μm)	IEC (mmol/g)	DS[a]	Water uptake (%)	Tensile strength (MPa)	T_g (°C)	Proton conductivity (S/cm)
1	36	0.107	0.019	10	27.31	−37.7	0.0074
2	54	0.122	0.022	12	25.83	−32.7	0.0101
3	38	0.186	0.034	21	178.70	−28.1	0.0133
4	36	0.310	0.057	33	176.60	−9.2	0.0166
5	38	0.624	0.115	62	193.50	−4.5	0.0302
SSEBS	313	–	0.15	–	–	–	0.0013[b]
S-SIBS	–	0.7	–	–	–	–	0.0190[c]
HPBS-SH	–	–	>0.15	–	–	–	0.0081[d]

[a] Calculated from the content of PB block and IEC.
[b] Conductivity value for SSEBS was from Ref. [11]. It was measured at room temperature after immersion in water at least for 3 h.
[c] Conductivity value for S-SIBS was from Ref. [15]. It was measured at 21–22 °C and 100% relative humidity.
[d] Conductivity value for HPBS-SH was from Ref. [16]. It was measured at 50 °C after 1 h hydration.

values, which increased remarkably from 25.83 to 178.70 MPa while IEC varied from 0.122 to 0.186 mmol/g due to increasing intermolecular interaction of sulfonated groups, indicated excellent mechanical strength of membrane samples. In addition, only a single glass transition temperature was observed for the copolymer membranes in this study as listed in Table 1, indicating good compatibility between hard segment and flexible segment. It was also observed that T_g rises with increasing degree of sulfonation, which was probably due to hydrogen bond and ionic crossing intra and inter sulfonated copolymer chains.

As expected, proton conductivity of these membranes increases with increasing IEC. It ranged from 0.0074 to 0.0302 S/cm at 25 °C. Comparing with other sulfonated block copolymers, sample 5 exhibited higher proton conductivity even with lower IEC or degree of sulfonation. This is supposed to attribute to the nature of flexible segment of the copolymer. CTPB is a typical rubber whose glass transition temperature is very low. Introduction of PB segment into sulfonated copolymer remarkably improves the flexibility of copolymer backbone. Flexible PB segment of copolymer provides great mobility for sulfonated groups to move together to form the ion-rich pathways. On the contrary, for other sulfonated block copolymers of which sulfoanted groups were incorporated to the aromatic rings, the rigid aromatic rings would restrict the motion of the sulfonated groups and formation of ion-rich pathways, which is believed to contribute much to proton conductivity, especially at low water content. In order to improve conductivity, membranes based on such sulfonated block copolymers have to increase degree of sulfoantion but when the degree of sulfonation reaches a certain value, membranes prepared from these copolymers would severely swell and even be soluble in water.

4. Conclusion

A new method for preparing polyelectrolyte material for proton exchange membrane was developed. Novel sulfonated PAES-*b*-PB was synthesized via condensation reaction and selective post-sulfonation of flexible segment. Tough film in acid form exhibits high conductivity (0.0302 S/cm, 25 °C) even at relatively low IEC. This result implies that sulfuric acid groups on flexible segment of block copolymer are easier to gather together to form ion pathways. Further studies on detailed properties and relationship between morphology and conductivity of membranes are conducted.

Acknowledgements

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