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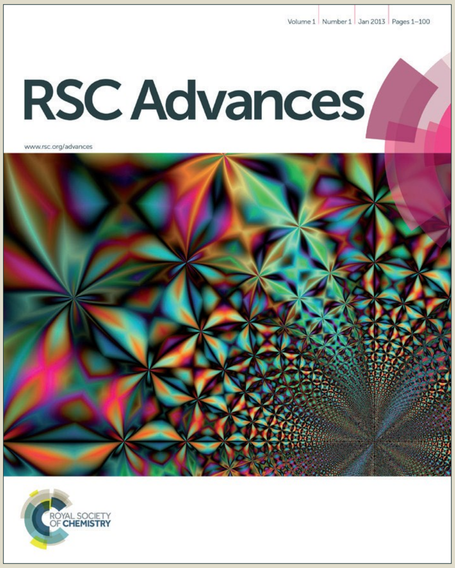

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Blend memebranes of quaternized poly (vinylbenzyl chloride-co-styrene) and quaternized polysulfone for anion-exchange membrane fuel cells

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Abstract

In this study, poly(vinylbenzyl chloride-co-styrene) (P(VBC-co-St)) copolymer is synthesized through emulsion copolymerization of vinylbenzyl chloride and styrene. The copolymerization process is optimized via orthogonal experiments of seven factors and three levels. The optimized P(VBC-co-St) and chloromethylated polysulfone (CMPSF) are blended in dimethylacetamide to prepare blend anion-exchange membranes (AEM) by solution casting, followed by quaternization and alkalization. The copolymerization and quaternization reactions are confirmed by using Fourier transform infrared attenuated total reflection and ^{1}H nuclear magnetic resonance spectrum. X-ray diffraction and scanning electron microscopy are employed to characterize the morphology of AEMs. The properties of AEMs including water uptake, mechanical property and ionic conductivity are investigated. The blend AEM consisted of 60% P(VBC-co-St) and 40% CMPSF is transparent, tough and flexible, showing a water uptake of 34.09±0.68 % and a ionic conductivity of 1.84×10^{-2} S cm^{-1} at 60 ^{o}C, a tensile strength of around 15.68±1.62 MPa and a moderate elongation rate at break of about 32.67±1.28 %. Moreover, at least 90 % of the original ionic conductivity can be kept after it is treated in 1M NaOH solution for 120h at 50 ^{o}C.

Keywords: Poly(vinylbenzyl chloride-co-styrene); Emulsion copolymerization; Blend; Anion exchange membrane; Ionic conductivity

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1. Introduction

As one of promising candidates for the next clean energy source systems, the polymer electrolyte membrane fuel cells have received considerable attention in the past several decades. After substantial endeavors have been made in proton-exchange membrane fuel cells (PEMFC), the commercial applications of PEMFC are still impeded by some tough problems, such as high cost and insufficient durability [1]. Consequently, research interests of polymer electrolyte membrane fuel cells are gradually drawing back to anion-exchange membrane fuel cells (AEMFC), which uses the anion exchange membrane (AEM) to transport hydroxide ions. AEMFC has several outstanding advantages over PEMFC, such as faster electro-kinetics, increased material stability, broader choice of fuels [2].

Anion-exchange membrane (AEM) is an important component in AEMFCs, which functions as ionic conductor, electronic insulator and fuel barrier. In order to develop high performance AEMs for AEMFC applications, various polymer backbones for AEMs containing quaternary ammonium groups have been investigated, including polysulfone[3], poly(arylene ether)s[4-6], polystyrene[7], polyphenylene[8], poly(2,6-dimethyl-1,4-phenylene oxide)[9]. The AEM of quaternized polysulfone (QPSF) has shown enough ionic conductivity at high ion-exchange capacity (IEC), but relatively low mechanical strength because it is difficult to balance the high ionic conductivity and sufficient mechanical properties [10]. The vinylbenzyl chloride (VBC), a vinyl monomer contain chloromethyl groups, is usually employed as co-monomer in order to control the IEC of resultant AEM [11-13]. When it and styrene (St) are used to synthesize poly(vinylbenzyl chloride-co-styrene) (P(VBC-co-St)) copolymers via free radical polymerization, their brittle mechanical properties can be anticipated, which makes them unfavorable for AEM solely. But it has been found that the alkali stability of the polystyrene backbones containing pendent trimethylammonium cationic groups is higher than that of the aromatic backbone analogues [14]. In order to utilize this advantage and enhance the ionic conductivity of quaternized P(VBC-co-St) (QP(VBC-co-St)), AEMs consisted of QPSF and quaternized P(VBC-co-St) (QP(VBC-co-St)) are proposed and such a research has not been reported at present.

In this work, the synthesis process of emulsion polymerization for P(VBC-co-St) is optimized. The P(VBC-co-St) from optimized synthesis process and chloromethylated polysulfone (CMPSF) are blended in dimethylacetamide (DMAc) for the resulting blend AEMs. The AEMs are charactered in terms of structural analysis, mechanical analysis, morphological analysis, water uptake and ionic conductivity measurements.

2. Experimental

2.1 Synthesis of P(VBC-co-St)

Styrene (99%) and 4-vinylbenzyl chloride (97%) were purchased from Sinopharm Chemical Reagent Co., Ltd and Sigma-Aldrich, respectively. P(VBC-co-St) copolymer was synthesized using St and VBC as monomers via free radical emulsion polymerization. Various influence factors and levels, including monomer ratio of St and VBC, the dosage of emulsifying agent, initiator, sodium hydroxide and water, the reaction time and temperature were list in table 1. A typical copolymerization reaction was as follows: 0.16 g sodium dodecyl benzene sulphonate (SDBS), 0.12 g potassium persulfate (KPS), 0.05 g sodium hydroxide (NaOH) were firstly dissolved in 100 mL deionized water, then 2.5 g St and 1.5 g VBC were added and reacted for 4 h at 70 ^{o}C with vigorous stir. Successionally, the reaction mixture was precipitated in 1 M sodium chloride (NaCl) aqueous solution. The precipitated copolymer was dissolved in chloroform and re-precipitated in methanol. At last, the precipitate was dried at 60 ^{o}C under vacuum to yield P(VBC-co-St) copolymer.

2.2 Synthesis of CMPSF

CMPSF was synthesized according to literatures [10]. Briefly, the procedure was as follows: 11g polysulfone (Udel P3500, Solvay) was dissolved in 300 mL dichloromethane and then treated with 16 mL chloromethyl ether (CME) in the presence of 3 mL anhydrous tin chloride at 30 ^{o}C for 30min to obtain the CMPSF. At last, the mixture was treated in 3 L ethanol for obtain CMPSF precipitate, followed by filtration, washing with water and evaporation.

2.3 Fabrication of AEMs

At first, P(VBC-co-St) and CMPSF were dissolved in dimethylacetamide (DMAc) to make two 15% (w/v) solutions, followed by stir, and filtration. The corresponding solutions were referred as solution A and solution B, respectively. Five groups containing two solutions with different proportions were confected for casting films. Before casting, N,N,N′,N′-tetramethylethylenediamine (TMEDA) was added into the casting solution as crosslinking agent (0.2 mL / 10 g casting solution) for forming partial crosslink in membranes. Then the film was dried under vacuum at 80°C for 24h. The resultant membrane was immersed into 30 wt% trimethylamine (TMA) solution for 24h to induct quaternary groups into the membrane, thereafter, the membrane was put into 1M KOH solution for another 24 h. At last, the resultant membrane was washed several times with distilled water and naturally dried to obtain AEMs (Scheme 1) under ambient environment to avoid great shrinkage with water losing. Depending on the content of CMPSF (10 g A+ 0 g B, 6 g A+ 4 g B, 5 g A+ 5 g B, 4 g A+ 6 g B, 0 g A+ 10 g B) in casting solution, the obtained AEMs were designated as QP(VBC-co-St), QP(VBC-co-St)/40%QPSF, QP(VBC-co-St)/50%QPSF, QP(VBC-co-St)/60%QPSF and QPSF.

2.4 Structure characterizations

In order to study the molecular structure of the P(VBC-co-St) copolymer, ^{1}H nuclear magnetic resonance (NMR) spectrum of it was recorded using a BRUKER Avance DMX600 NMR spectrometer. Dueturated chloroform was as the solvent and tetramethylsilane was as the internal standard. Fourier transform infrared attenuated total reflection (ATR-FTIR) spectra of AEMs were recorded using a VERTEX70 spectrometer. X-ray diffractometer (X'Pert PRO) was adopted to determine the crystal. Cu Kα (λ=1.54Å) was used as an X-ray source at d-generator voltage of 45 kV and current of 80 mA. Samples were scanned in 2θ ranges from 2° to 15°, in steps of 0.02° and counting time 2 s per step. The surface morphology of samples was examined through a scanning electron microscopy (SEM, JEOL JSM-6510). After the sample was dried, it was vacuum-deposited with a thin Au film for the SEM examination.

2.5 Ion-exchange capacity

IEC of AEMs was determined using back titration method. A weighted dry AEM sample was immersed in 100 mL of 1M NaCl solution for 48 at room temperature. Then the NaCl solution was titrated with 0.1 M HCl solution. Based on the titration results, IEC (mmol/g) of the membrane was calculated as follows:

$$\mathrm{IEC} = \frac{\mathrm{N}_{HCl}}{\mathrm{M}_{dry}} \qquad (1)$$

where N_{HCl} and $\mathrm{M}_{\mathrm{dry}}$ are the amount of HCl in mmol and the mass of the dried sample, respectively. The measurements were carried out with an accuracy of 0.001 mmol g^{-1}.

2.6 Water uptake

All membranes were vacuum dried at 100 ^{o}C before water uptake testing. Then the AEMs were soaked in deionized water for 24h at a certain temperature. Weights of dry and wet membranes were measured. The water uptake content was the average of the two measurements with an error within ±3.0% and calculated by uptake content (%) = $\frac{\omega_{wet} - \omega_{dry}}{\omega_{dry}} \times 100$ (2)

where ω_{dry} and ω_{wet} are the masses of dried and wet samples, respectively.

2.7 Mechanical properties

Tensile strength was measured by using INSTRWN5566 Mechanical Testing Machine. The membrane samples were cut into 0.5 cm × 5.0 cm and immersed in water for 48 h at room temperature before testing. The samples were examined at an elongation rate of 10 mm /min. Triplicate analyses were carried out and the average values for the determination of the tensile strength were taken. The tensile strength was calculated with the following equation:

$$\text{Tensile strength} = \frac{\text{Maximum load}}{\text{Cross sectional area}} (\text{N/mm}^2) \quad (3)$$

2.8 Hydroxide ion conductivity

Ionic conductivity (σ) of the membranes was measured by two-probe AC method from 1Hz to 500 KHz and 10 mV AC perturbation on an Autolab work station. A sample with size of 15 mm × 15 mm was placed in an open, temperature controlled cell where it was clamped between two platinum electrodes. Specimens were soaked in deionized water for at least 48 h prior to the test. The impedance measurement was performed with 100% relative humidity (RH) at desired temperature. The σ of the membrane in the direction perpendicular to the surface was calculated from the impedance data, using the formula:

$$\sigma = \frac{d}{R \cdot A} \quad (4)$$

where d and A are the thickness and face area of the sample, respectively, and R is derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the Z axis. The conductivities were highly reproducible, and multiple measurements found an average error of <5%, so this uncertainty is smaller than the plot symbols, hence error bars are omitted.

2.9 Alkaline solution stability

The alkaline solution stability of the membranes was evaluated by ionic conductivity after the membrane was immersed in 1M NaOH solution at 50 ^{o}C for 120 h.

3. Results and discussion

3.1 Copolymerization process and structural analysis

Table 1

Table 1 showed the effects of seven factors on the yield of P(VBC-co-St) copolymer via an orthogonal experiment of seven factors and three levels. From the range analysis to these influence factors, it could be found that the order of relative importance of the seven factors was as follow: monomer ratio of St and VBC > dosage of emulsifying agent > dosage of initiator and temperature > weight of NaOH > reaction time > volume of water. The optimized reaction condition was 2.5 g St, 1.5 g VBC, 0.16 g SDBS, 0.12 g KPS and 0.05 g NaOH in 100 mL deionized water at 70 ^{o}C for 4 h. The P(VBC-co-St) copolymer from the optimized reaction condition, whose yield exceeded 87 %, was used for the following measurements.

The intrinsic viscosity [η] of the optimized P(VBC-co-St) copolymer was determined through using an Ubbelohde viscometer with the capillary diameter of 0.54 mm (See ESI). The [η] of P(VBC-co-St) in N,N-dimethylformamide at 35 ^{o}C ± 0.1 ^{o}C was 88.93 mL/g. Because the K and α values of P(VBC-co-St) for the Mark-Houwink equation were absent, the K (0.0318 mL/g) and α (=0.603) values of polystyrene under same conditions were adopted [15]. It was estimated that the viscosity average molecular weight (*Mv*) of P(VBC-co-St) was about 519744 g/mol.

Fig. 1

In order to elucidate the structure of P(VBC-co-St) copolymer, the ^{1}H-NMR spectrum of it was shown in Fig. 1. The peaks appeared at 6.2-7.2 ppm were generated by the protons of aromatic rings, and the peaks between 0.9 ppm and 2.1 ppm were associated with the $–CH_2$ and –CH protons on the aliphatic chains. The characteristic peak of protons in -CH_2Cl groups had shifted to around 4.5 ppm because of deshielding effect from chlorine. The results suggested that the copolymerization of St and VBC had been successfully carried out. Furthermore, molar content of VBC in P(VBC-co-St) copolymer could be calculated at 18.0% according to the areas of peak around 4.5ppm and peaks between 0.9 and 2.1 ppm. The value was less than the original molar content of VBC in total monomers (29.0 %), which might be attributed to the difference of their reactivity ratios.

Fig. 2

The quaternization reactions of AEMs were characterized by ATR-FTIR spectra of them (Fig. 2). It was obvious that the intensity of peaks between 2851 and 3060 cm^{-1}, which was mainly produced by C-H stretching vibrations of the –CH_2 and –CH on the aliphatic chains of QP(VBC-co-St), were gradually weakened with the increase of QPSF content. The broad peak at 3390 cm^{-1} was associated with vibrations of the hydroxyl groups. The peaks at 1486 cm^{-1} and 1635 cm^{-1} were assigned to the stretching vibration of quaternary ammonium groups, confirming the successful quaternization [16].

Fig. 3 Fig. 4

When the QP(VBC-co-St) membrane was fully humidified at room temperature, it demonstrate acceptable flexibility (Fig.3a). But it would become brittle after it became dry, which might be explained by its structure. As shown in Fig. 4, there existed a main diffuse peak at 20^{o} of 2θ, which indicated the amorphous structure in the QP(VBC-co-St) membrane. Moreover, there were two XRD diffraction peaks at 31.5^{o} and 46.2^{o} of 2θ, which meant the existence of partial crystallization in the QP(VBC-co-St) membrane. As a consequence, the brittleness of the QP(VBC-co-St) membrane could be forecast owing to the physical crosslink induced by the crystals and the chemical crosslink formed by TMEDA.

After combining with QPSF, transparent blend membranes with tough and flexible properties were prepared (Fig.3b). Even up to magnifications of 10,000×, the SEM image of the QP(VBC-co-St)/40%QPSF membrane did not show any evidence of phase separation (Fig.3c), revealing rather good miscibility between QP(VBC-co-St) and QPSF.

3.2 IEC, Water uptake and mechanical property

Table 2

The IEC, water uptakes and mechanical property of AEMs were listed in table 2. The IECs of blend membranes displayed a linear dependence relation with the contents of QP(VBC-co-St) and QPSF. The QPSF membrane exhibited the highest water uptake of 186.21±3.24% at 95 ^{o}C due to the highest IEC and the enhancement of polymer segment motions at 95 ^{o}C. After QPSF was incorporated into QP(VBC-co-St), the water uptake decreased with the increased content of QP(VBC-co-St) in blend membranes. The water uptake of QP(VBC-co-St)/40%QPSF membrane was only 87.61 ± 1.08 % 95 ^{o}C, which reduced by 52.9 % as compared with the value of QPSF membrane.

Generally, the stiff polymer should show high tensile strength and low elongation rate, but the QPSF showed low tensile strength and low elongation rate after absorbing water. The wet QPSF showed a tensile strength of around 5.60±0.34 MPa and an elongation rate at break of 62.67±2.95 % because of the plasticization of water molecules and its high IEC. The wet QP(VBC-co-St) membrane displayed a tensile strength of 14.74±0.56 MPa and an elongation rate at break of 14.78±0.45 %, which was consistent with its structure containing crystals and crosslink. For the blend membranes, the QP(VBC-co-St)/40%QPSF demonstrate the highest tensile strength of 15.68±1.62 MPa and a moderate elongation rate at break of 32.67±1.28 % probably because the physical crosslink in QP(VBC-co-St) was replaced by stronger chemical crosslink in the QP(VBC-co-St)/40%QPSF membrane. Hence, in the QP(VBC-co-St)/40%QPSF was more appropriate for applications in AEMFC in terms of mechanical properties.

After alkaline solution stability test, the tensile strength of QP(VBC-co-St) membrane was maintained about 90% of its original tensile strength, while the tensile strength of QPSF membrane was only maintained about 39% of its original tensile strength. The results were induced by different IEC and degradation mechanism. Firstly, the QPSF membrane with rather high IEC was prone to functional group degradation due to the attacks of OH^-. Secondly, the aryl-ether cleavage of polysulfone backbones was likely to occur under high pH environments [17]. On the contrary, the QP(VBC-co-St) membrane with rather low IEC only suffered from slightly functional group degradation, which endowed QP(VBC-co-St) membrane with better alkaline solution stability [2].

3.3 Ionic conductivity and alkaline solution stability

Fig.5

The ionic conductivities of all AEMs at different temperature were plotted in Fig.5. All of them increased with the ascending of temperature. The positive correlation between the ionic conductivity and temperature could be attributed to the increase of free volume in favour of ion transport and the mobility of anions with rising temperature. The apparent activation energies (E_a) of ionic conductivity varied from 9.95 kJ/mol to 16.82 kJ/mol, which indicated that OH^- ions were transported in these AEMs via Grotthuss-type mechanism. The ionic conductivities of QPSF and QP(VBC-co-St)/60%QPSF at 95 °C achieved 3.82×10^{-2} S cm^{-1} and 4.27×10^{-2} S cm^{-1}, respectively. But the relatively poor mechanical properties and high water uptakes restricted the applications of them in AEMFC. While QP(VBC-co-St)/40%QPSF and QP(VBC-co-St)/50%QPSF displayed more balanced performances. The ionic conductivities of them were 1.84×10^{-2} S cm^{-1} and 2.14×10^{-2} S cm^{-1} at 60 °C, which could meet the basic requirements of applications in AEMFC.

Table 3

Table 3 showed the ionic conductivity values reported in the literature for different AEMs. Although the ionic conductivity was sample-dependent and tended to vary from laboratory to laboratory, the comparison still demonstrated qualitatively that that the ionic conductivity of the QP(VBC-co-St)/40%QPSF membrane had a same magnitude as those of the reported values.

Fig.6

Fig. 6 presented the alkaline solution stability of QP(VBC-co-St)/40%QPSF. After it was treated in 1M NaOH solution for 120 h at 50 ^{o}C, its ionic conductivity could be maintained at least 90%, suggesting good alkaline solution stability. The result was in agreement with the mechanical properties measurement of AEMs after alkaline solution stability test.

4. Conclusions

In summary, the optimized reaction condition for emulsion copolymerization of St and VBC was 2.5 g St, 1.5 g VBC, 0.16 g SDBS, 0.12 g KPS and 0.05 g NaOH in 100 mL deionized water at 70 ^{o}C for 4h. The P(VBC-co-St) copolymer was confirmed through ^{1}H-NMR spectrum and the quaternization reactions of AEMs were approved by ATR-FTIR. The blend membranes of QP(VBC-co-St)/40%QPSF and QP(VBC-co-St)/50%QPSF showed better comprehensive performance. The QP(VBC-co-St)/40%QPSF displayed a water uptake of and 34.09±0.68 % and a ionic conductivities of 1.84×10^{-2} S cm^{-1} at 60 ^{o}C, a tensile strength of 15.68±1.62 MPa and a moderate elongation rate at break of 32.67±1.28 %. Furthermore, it also had good alkaline solution stability. These results suggested that it had a promising potential as AEM for AEMFC.

Acknowledgments

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Table Caption

1. Orthogonal experimental design of copolymerization with seven factors and three levels
2. IEC, Water uptake and mechanical properties of the AEMs
3. Ionic conductivity values reported in the literature for different AEMs

Scheme Caption

1. Synthesis and crosslinked structure schemes of QP(VBC-co-St)/QPSF blend membranes

Figure Captions

1. ^{1}H-NMR spectrum of P(VBC-co-St) copolymer
2. ATR-FTIR spectra of all AEMs
3. (a) Digital photo of QP(VBC-co-St) membrane, (b) Digital photo and (c) SEM image of QP(VBC-co-St)/40%QPSF membrane
4. X-ray diffraction patterns of QP(VBC-co-St) membrane
5. Ionic conductivity of all AEMs at different temperature
6. Ionic conductivity of QP(VBC-co-St)/40%QPSF membrane after the alkaline solution stability test

No.	Factors							Yield of copolymer (%)
	St:VBC (g:g)	KPS (g)	Temperature (^{o}C)	SDBS (g)	Time (h)	NaOH (g)	H_2O (mL)	
1[a]	2.5/1.5	0.08	50	0.08	3	0.03	50	7.32±0.34
2[b]	2.5/1.5	0.10	60	0.12	4	0.05	70	10.46±0.52
3[a]	2.5/1.5	0.12	70	0.16	5	0.07	100	87.91±1.56
4[b]	2/2	0.08	50	0.12	4	0.07	100	8.57±0.43
5[a]	2/2	0.10	60	0.16	5	0.03	50	12.78±0.58
6[a]	2/2	0.12	70	0.08	3	0.05	70	76.69±1.11
7[b]	1.5/2.5	0.08	60	0.08	5	0.05	100	9.44±0.47
8[b]	1.5/2.5	0.10	70	0.12	3	0.07	50	11.35±0.56
9[b]	1.5/2.5	0.12	50	0.16	4	0.03	70	10.79±0.54
10[a]	2.5/1.5	0.08	70	0.16	4	0.05	50	83.73±1.25
11[a]	2.5/1.5	0.10	50	0.08	5	0.07	70	14.33±0.56
12[a]	2.5/1.5	0.12	60	0.12	3	0.03	100	12.41±0.36
13[a]	2/2	0.08	60	0.16	3	0.07	70	7.58±0.13
14[a]	2/2	0.10	70	0.08	4	0.03	100	70.89±1.42
15[b]	2/2	0.12	50	0.12	5	0.05	50	13.52±0.67
16[a]	1.5/2.5	0.08	70	0.12	5	0.03	70	14.56±0.31
17[b]	1.5/2.5	0.10	50	0.16	3	0.05	100	10.15±0.51
18[a]	1.5/2.5	0.12	60	0.08	4	0.07	50	9.81±0.31
K_1	216.16	131.20	131.20	188.48	125.50	128.75	138.51	
K_2	190.03	129.96	129.96	70.87	194.25	203.99	134.41	
K_3	66.1	211.13	211.13	211.13	152.54	139.55	199.37	
k_1	72.05	43.73	43.73	62.83	41.83	42.92	46.17	
k_2	63.34	43.32	43.32	23.62	64.75	68.0	44.80	
k_3	22.03	70.38	70.38	70.38	50.85	46.52	66.46	
R	50.02	27.06	27.06	46.76	22.92	25.08	21.66	
Optimized[c]	2.5/1.5	0.12	70	0.16	4	0.05	100	87.23±1.09

[a] The values were averaged from two experiments.

[b] One point data, the estimated errors of these measurements were less than 5%.

[c] The values were averaged from eleven experiments.

Table 1

membranes	IEC (meq g^{-1})	Water uptake (%) at		Tensile strength (MPa)		Maximum elongation (%)	
		60 ^{o}C	95 ^{o}C	Original value	Residual value [a]	Original value	Residual value [a]
QP(VBC-co-St)	1.06	17.23±0.42	41.56±0.68	14.74±0.56	13.24±0.32	14.78±0.45	13.16±0.34
QP(VBC-co-St)/40%QPSF	1.14	34.09±0.68	87.61±1.08	15.68±1.62	14.14±0.53	32.67±1.28	28.37±0.42
QP(VBC-co-St)/50%QPSF	1.16	36.39±0.77	95.61±2.07	12.45±1.06	10.95±0.68	27.61±0.94	21.85±0.84
QP(VBC-co-St)/60%QPSF	1.20	39.74±0.92	103.01±1.47	9.14±0.64	6.87±0.46	23.30±1.17	18.29±1.08
QPSF	1.28	42.71±1.16	186.21±3.24	5.60±0.34	2.18±0.12	62.67±2.95	32.18±1.86

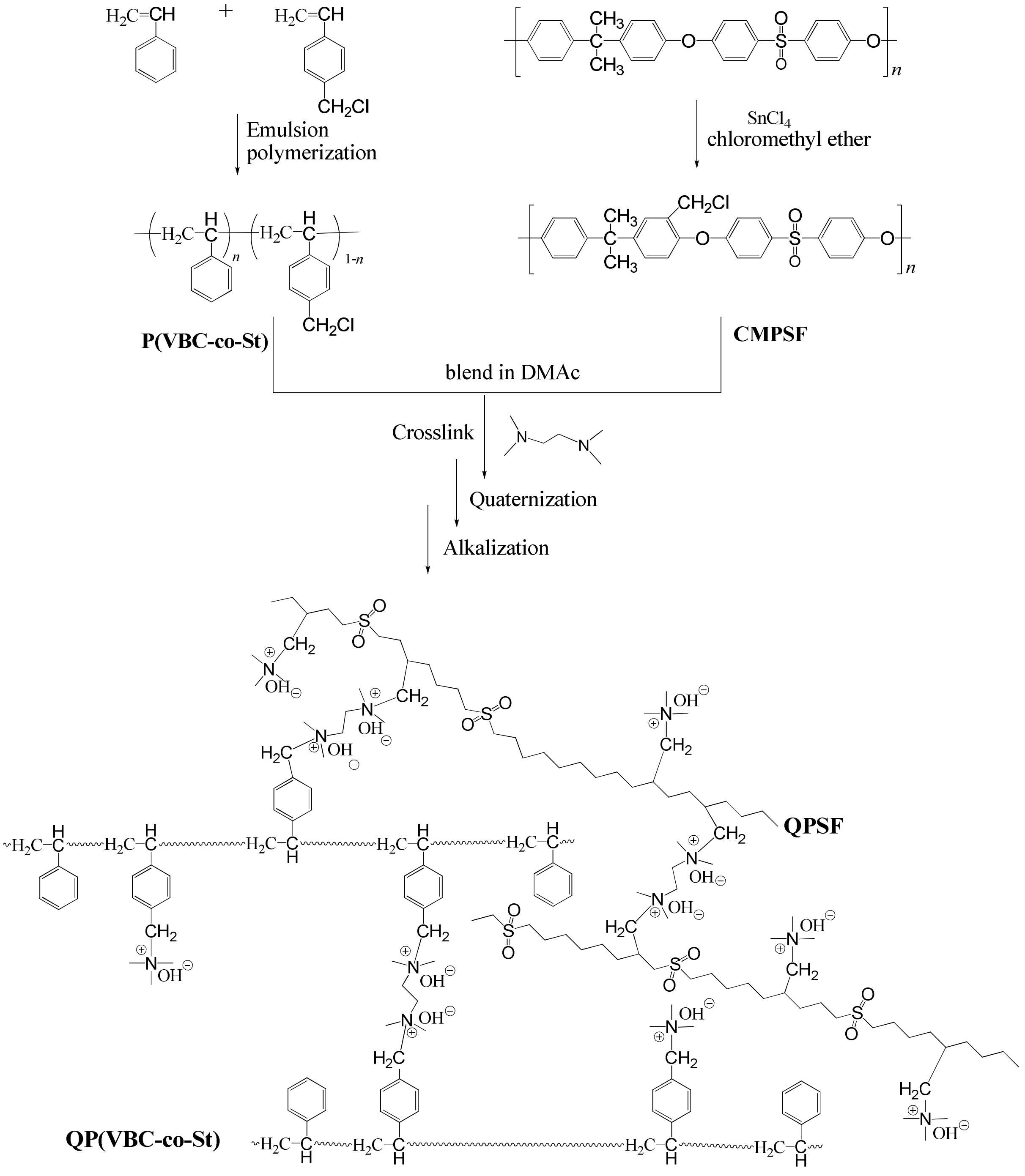
[a] The mechanical properties of the membranes after treatment with 1M NaOH.

Table 2

Membrane material	Functional groups	IEC (meq g^{-1})	Conductivity (×10^{-2} S cm^{-1})	Reference
QP(VBC-co-St)/40%QPSF	Quaternary Ammonium	1.14	1.84 (60 °C)	This study
Quaternary phosphonium polysulfone	TPQPOH[a]	1.17	4.50 (20 °C)	18
QPMBV[b]	Quaternary Ammonium	1.25	0.82 (80 °C)	19
Imidazolium-based PVBC-g-PAES[c]	Imidazolium	1.65	3.11 (60 °C)	20
Dimethylimidazolium-based (VBC-co-St)	Dimethylimidazolium	1.33	2.08 (60 °C)	21
QPEN[d]	Quaternary Ammonium	2.91	5.60 (60 °C)	22
Imidazolium-based PAES[e]	Imidazolium	2.50	1.46 (20 °C)	23
Quaternary Ammonium ETFE-g-VBC[f]	Quaternary Ammonium	1.49	7.90 (50 °C)	24
Quaternary ammonium PAES	Quaternary Ammonium	2.07	7.10 (80 °C)	25
PPO-b-PVBTMA[g]	Quaternary Ammonium	2.50	1.60 (60 °C)	26
Quaternary Ammonium PPO[h]	Quaternary Ammonium	2.13	7.50 (60 °C)	27
QPSF	Quaternary Ammonium	1.18	3.40 (60 °C)	28

[a]TPQPOH = methylene quaternaryphosphonium-hydroxide. [b]QPMBV = poly(methyl methacrylate-co-butyl acrylate-co-vinylbenzyl chloride). [c]PVBC-g-PAES = poly(4-vinylbenzylchloride)-graft-poly(arylene ether sulfone). [d]QPEN = quaternized benzylmethyl-containing poly(arylene ether nitrile). [e]PAES = poly(arylene ether sulfone). [f]ETFE = poly(ethylene-co-tetrafluoroethylene). [g]PPO-b-PVBTMA = poly(2,6-dimethyl-1,4-phenylene oxide)-b-poly(vinylbenzyltrimethylammonium). [h]PPO = poly(2,6-dimethyl-1,4-phenylene oxide).

Table 3


Emulsion polymerization
$SnCl_4$
chloromethyl ether
P(VBC-co-St)
CMPSF
blend in DMAc
Crosslink
Quaternization
Alkalization
QPSF
QP(VBC-co-St)

Scheme 1

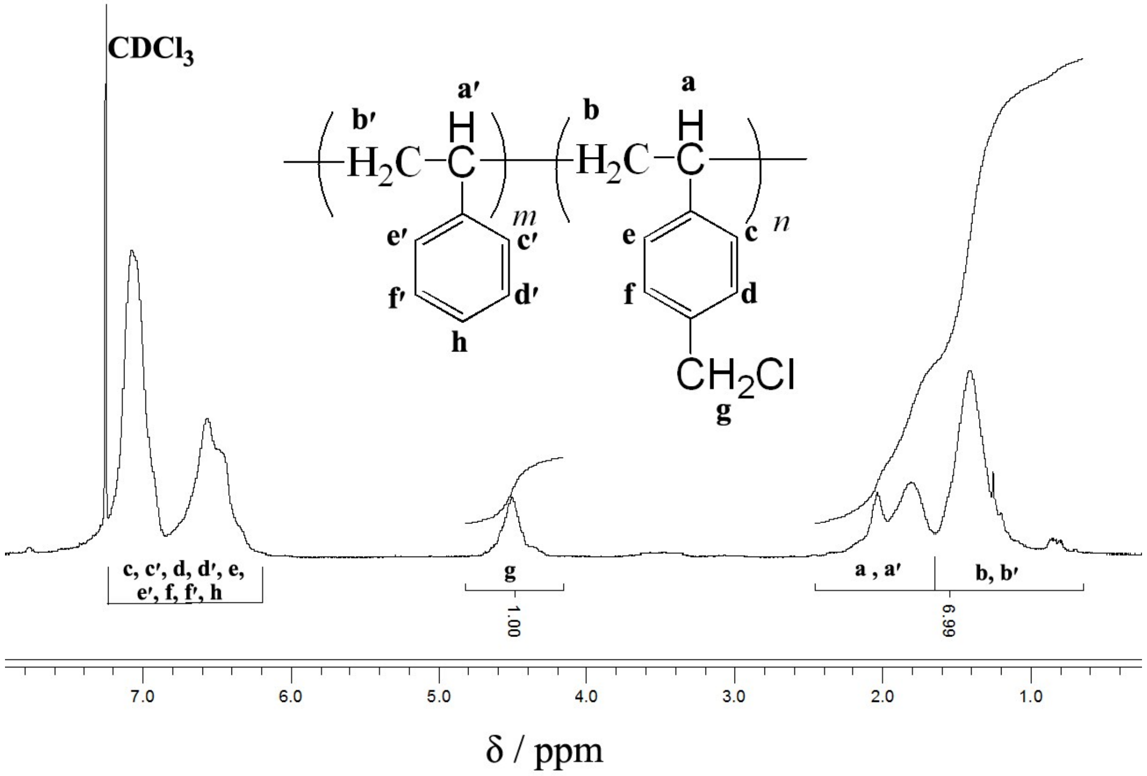

CDCl$_3$
a′
b′
a
b
m
n
e′
c′
f′
d′
h
e
c
f
d
CH$_2$Cl
g
c, c′, d, d′, e, e′, f, f′, h
g
1.00
a , a′
b, b′
6.99
7.0
6.0
5.0
4.0
3.0
2.0
1.0
δ / ppm

Fig.1

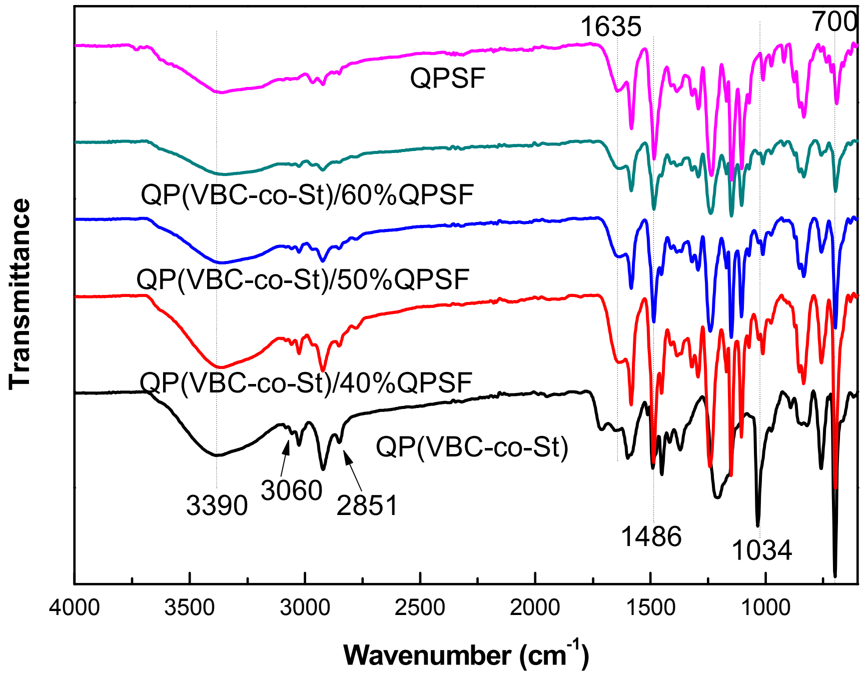

Transmittance
Wavenumber (cm^{-1})
4000
3500
3000
2500
2000
1500
1000
QPSF
QP(VBC-co-St)/60%QPSF
QP(VBC-co-St)/50%QPSF
QP(VBC-co-St)/40%QPSF
QP(VBC-co-St)
1635
700
3390
3060
2851
1486
1034

Fig.2

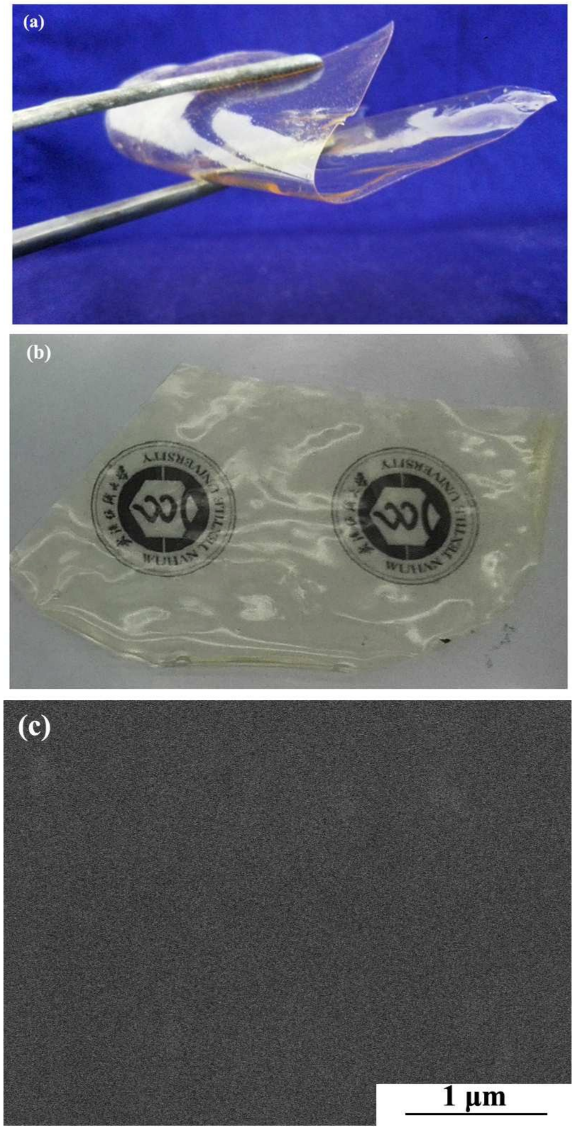


Fig.3

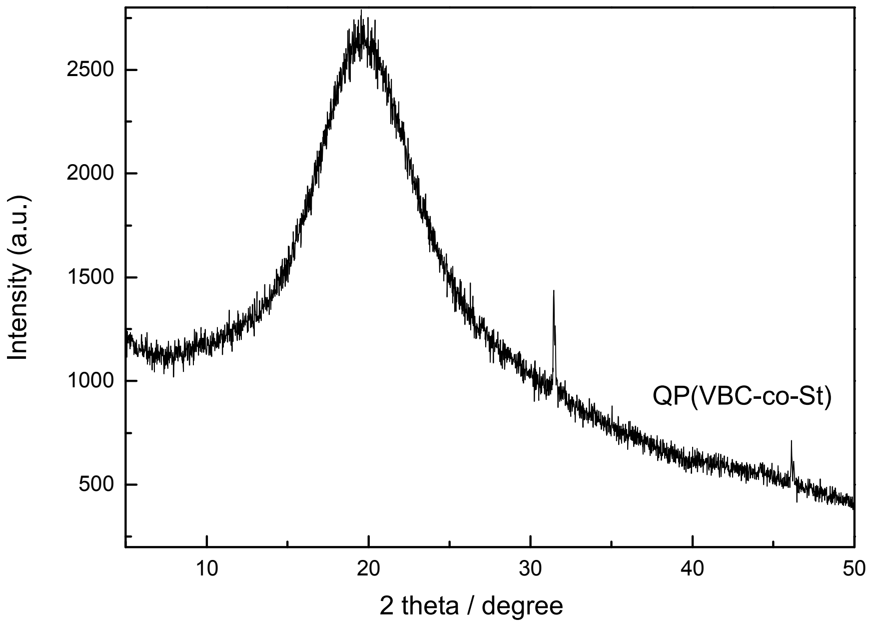

Intensity (a.u.)
2500
2000
1500
1000
500
10
20
30
40
50
2 theta / degree
QP(VBC-co-St)

Fig.4

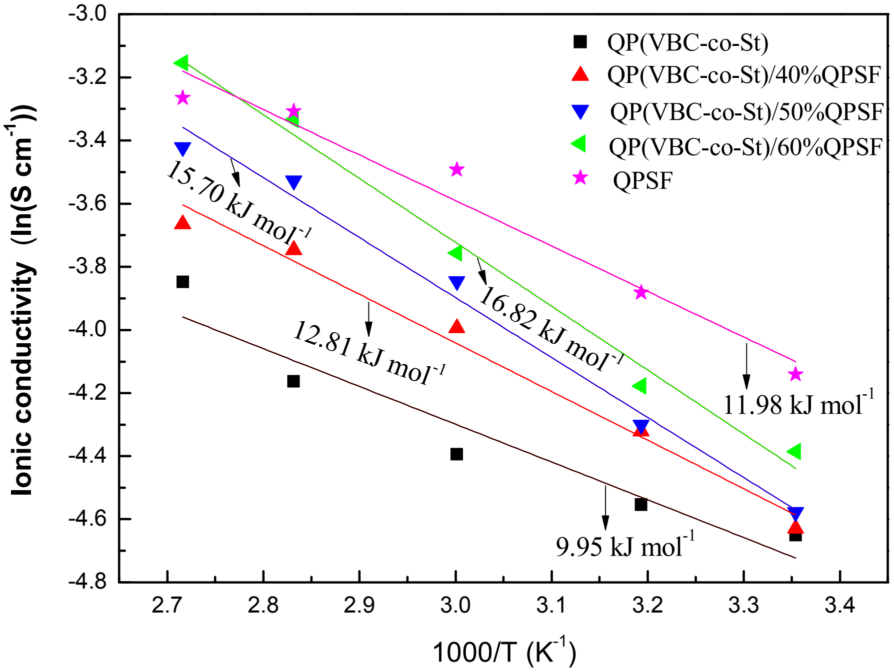

-3.0
-3.2
-3.4
-3.6
-3.8
-4.0
-4.2
-4.4
-4.6
-4.8
2.7
2.8
2.9
3.0
3.1
3.2
3.3
3.4
Ionic conductivity (ln(S cm^{-1}))
1000/T (K^{-1})
■ QP(VBC-co-St)
▲ QP(VBC-co-St)/40%QPSF
▼ QP(VBC-co-St)/50%QPSF
◀ QP(VBC-co-St)/60%QPSF
★ QPSF
15.70 kJ mol^{-1}
16.82 kJ mol^{-1}
12.81 kJ mol^{-1}
11.98 kJ mol^{-1}
9.95 kJ mol^{-1}

Fig.5

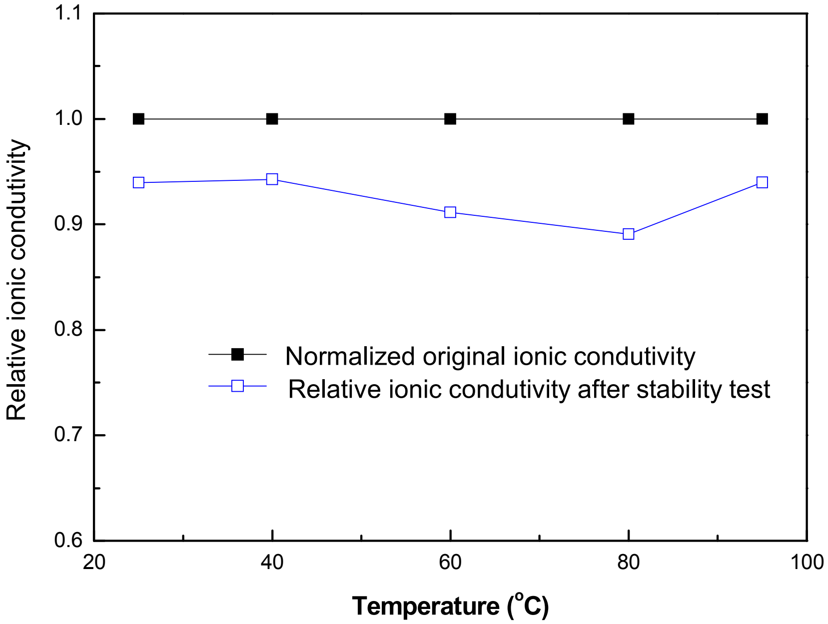
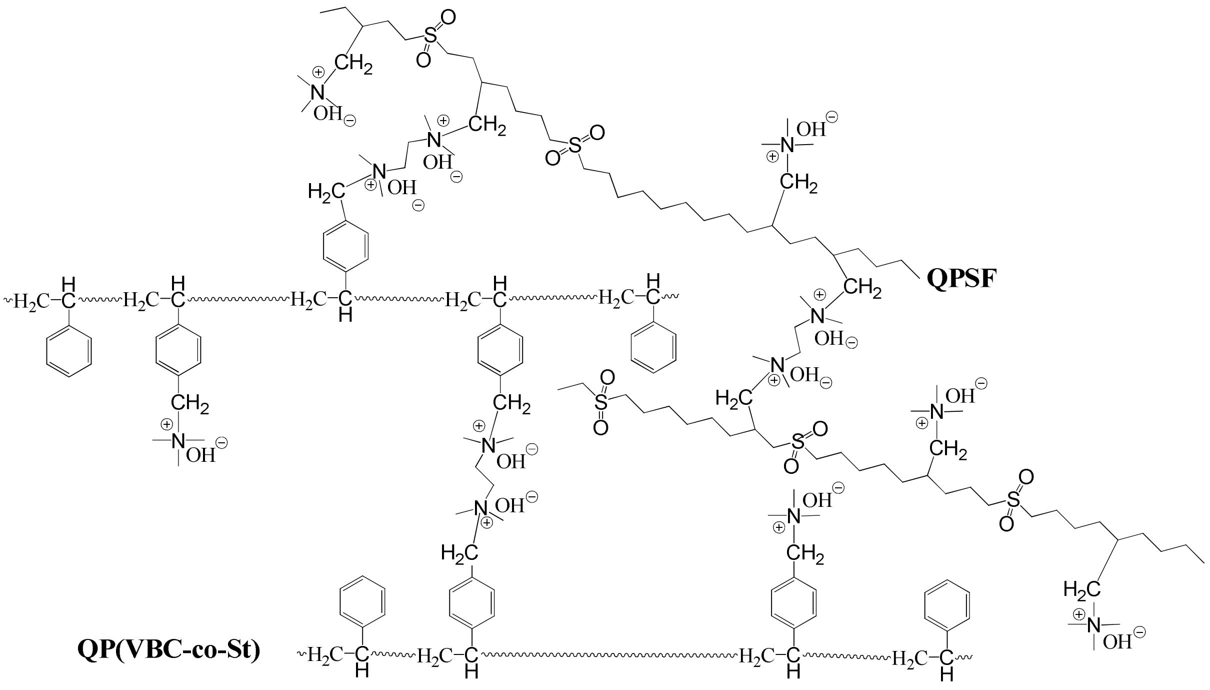
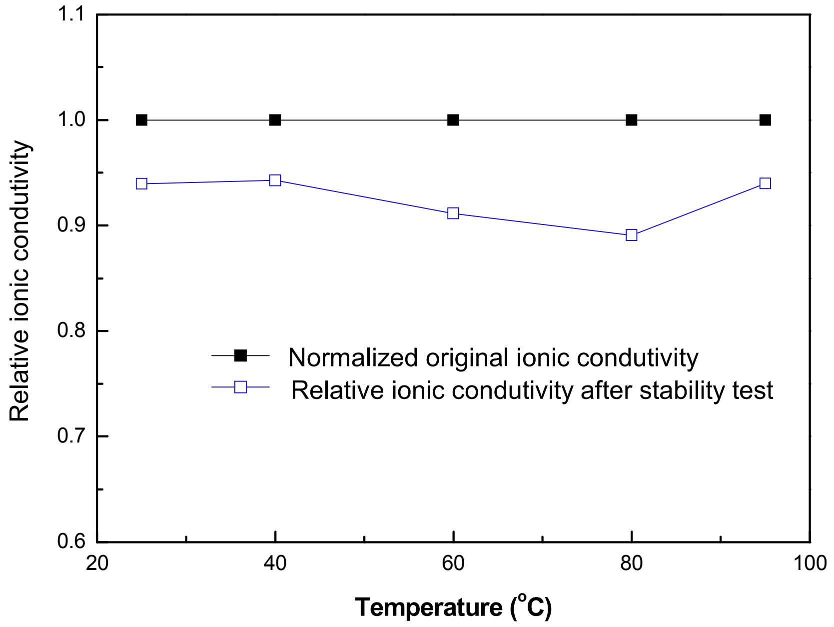

1.1
1.0
0.9
0.8
0.7
0.6
Relative ionic condutivity
20
40
60
80
100
Temperature (°C)
■ Normalized original ionic condutivity
□ Relative ionic condutivity after stability test

Fig.6





The blend AEM consisted of 60% P(VBC-co-St) and 40% CMPSF showed improved alkaline solution stability.