Preparation of an Anion-Exchange Membrane by the Amination of Chlorinated Polypropylene and Polyethyleneimine at a Low Temperature and Its Ion-Exchange Property

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ABSTRACT: An anion-exchange membrane was prepared by the amination of chlorinated polypropylene and polyethyleneimine at a low temperature and was investigated with respect to not only its physical properties but also its electrochemical properties. The degrees of amination were 50.16, 53.76, 57.11, and 65.29% at 30, 40, 50, and 55°C, respectively. The base polymer membrane had no water uptake, whereas that of the aminated polymer membrane was 0.254, 0.296, 0.298, and 0.319 g of H_2O/g of dry membrane, respectively, with increasing amination. The prepared membranes pos- sessed an ion-exchange capacity in the range of 1.257–2.000 mequiv/g of dry membrane and a fixed ion concentration in the range of 4.492–6.261 mequiv/g of H_2O. The ionic conduc- tivity of the aminated polymer membrane was highest when the water uptake was highest. Those of the prepared mem- brane were in the range of 0.89×10^{-2} to 1.36×10^{-2} S/cm. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 830–835, 2009

Key words: crosslinking; ion exchangers; membranes; synthesis

INTRODUCTION

The development of synthetic ion-exchange mem- branes, reported by Juda in 1949[1] and by Juda and McRae in 1950,[2] stimulated both commercial and academic interest in such membranes and the related process.[3] Nowadays, synthetic ion-exchange membranes have been improved by various meth- ods and have many practical uses.[4,5]

Amination method is considered one of the most important ways of functionalize polymers, in which the polymers are usually dissolved in organic solvents to enhance the effectiveness of the amination reaction. Generally, aminated polymers become more hydro- philic, biocompatible, adhesive, and selective, and they are widely used as ion exhangers,[6,7] biomateri- als,[8] coatings,[9] and membranes in electrochemical devices.[10–12]

Recently, Wang et al.[13] prepared anion-exchange materials via amination between chlorinated poly- propylene (CPP) and polyethyleneimine (PEI) under hydrothermal conditions. However, these were pre- pared in porous powders and also were insoluble in any common solvents. Therefore, they were not suited to preparing anion-exchange membranes through direct casting.

It is known that not only amination and dehydro- chlorination but also crosslinking occur.[13,14] Like- wise, the amination of a chlorinated polymer is a well-known substitution-type or SN_2-type reac- tion,[14,15] which is favored substitution in polar sol- vents, at lower reaction temperatures, and in lower nucleophile concentration reactions.[16,17]

In this work, to prepare anion-exchange mem- branes effectively, the amination reaction was initi- ated with a highly polar aprotic solvent at controlled temperatures (<60°C). New anion-exchange mem- branes were prepared directly from aminated poly- mer solutions, and then membrane properties, such as the structure, water uptake, ion-exchange capacity (IEC), fixed ion concentration (FIC), and ion conduc- tivity, were examined.

EXPERIMENTAL

Amination procedure

Chemicals

CPP (2 g; weight-average molecular weight = 150,000; Sigma–Aldrich Co., St. Louis, MO) was dis- solved in 25 mL of toluene (high-performance liquid

chromatography grade; Sigma–Aldrich) in a flask. Also, 3 g of PEI (weight-average molecular weight = 423; Sigma–Aldrich) was dissolved in 50 mL of acetone (high-performance liquid chromatography grade; Sigma–Aldrich) in another flask. After the two polymers were wholly dissolved, water in the polymers was removed with anhydride magnesium sulfate ($MgSO_4$; Sigma–Aldrich). Thereafter, the dissolved polymers were poured into a round-bottom flask that contained a polytetrafluoroethylene-coated magnetic stirring bar.

A Claisen adapter was connected to the round-bottom flask. To the straight part of this adapter, a second adapter with a gas inlet for argon was connected. Also, a Graham condenser was connected to the curved arm of the Claisen adapter. Argon was purged into the system during the entire experiment. Temperatures (30, 40, 50, and 55°C) were controlled with a water bath for 48 h. The pH values of these aminated solutions were measured with a pH meter (FE20-FiveEasyTM, Mettler–Toledo, Ltd., Giessen, Germany).

Membrane preparation

After the amination reaction, membranes were obtained by the casting of an aminated solution onto a clean glass plate, and they were dried at room temperature for 24 h. Aminated membranes were peeled off the glass plate and were washed repeatedly with deionized water until the pH was neutral. Then, they were dried in an oven at 60°C for 24 h, and they were dried overnight at 105°C.

Membrane properties

Fourier transform infrared (FTIR) spectrometry

An FTIR spectrometer (Spectrum GX, PerkinElmer Co., Waltham, MA) was used to record the spectrum. The base polymer was dissolved in a solvent, and then the water in the polymer was eliminated with a drying agent. The aminated solution sample and base polymer solution sample were mixed with KBr, respectively. The mixture was dried and then was pressed to form pellets to record the FTIR spectrum. An average of 20 scans with a resolution of 1 cm^{-1} was recorded.

Structure of the membranes

The cross-sectional morphologies of the membranes were observed with a scanning electron microscope (6300F, JEOL, Tokyo, Japan). The membrane samples, frozen in liquid nitrogen, were broken and coated with gold before scanning electron microscopy analysis.

Thermogravimetry (TG)

Thermal analysis was performed with a Pyris 1 thermogravimetric analyzer (PerkinElmer). All tests were conducted in an N_2 purge (40 mL/min) with sample weights of 3–7 mg over a temperature range of 30–700°C at heating rate of 5°C/min.

Elemental analysis

The base polymer membrane and the aminated polymer membrane sample prepared for elemental analysis were dried in a vacuum oven at 60°C for 1 day.

All analyses were carried out by the Institute of Chemistry of the Chinese Academy of Sciences (Beijing, China).

Degree of amination

The degree of amination was calculated with the following formula:[18]

$$\text{Degree of amination (\%)} = \frac{C_1 - C_2}{C_1} \times 100 \quad (1)$$

where C_1 and C_2 are the Cl concentrations (mmol/g) of the base polymer membrane and the aminated polymer membrane, respectively. The Cl concentration was determined by a titration method.[7,13]

IEC

The nitrogen analysis, which indicated the possible extent of amination, was performed with the Mohr method. The aminated membrane (0.5 g) was treated in a $1M$ HCl solution at room temperature for 5 h for conversion into the chloride salt. After filtration and washing, the membrane in the chloride form was immersed in a $0.5M$ NaOH solution for 1 h. After 10 mL of the chloride-ion solution released from the membrane was taken, it was neutralized with a $0.1M$ HNO_3 solution and then was determined by a titration of a $0.1M$ $AgNO_3$ solution with K_2CrO_4 as an indicator. IECs were calculated from the released chloride ions and the mass of the dried membrane:[4,11]

IEC (mequiv/g of dry membrane)

$$= \frac{\text{mequiv of ion-exchange capacity}}{\text{g of dry membrane}}$$

$$= \frac{(a - b) \times f \times \frac{1}{V}}{\text{g of dry membrane}} \times 10,000 \quad (2)$$

where a and b are the volumes (mL) of $0.1M$ $AgNO_3$ for the titration and base test, respectively; f is the factor of $0.1M$ $AgNO_3$; and V is the volume of the sample.
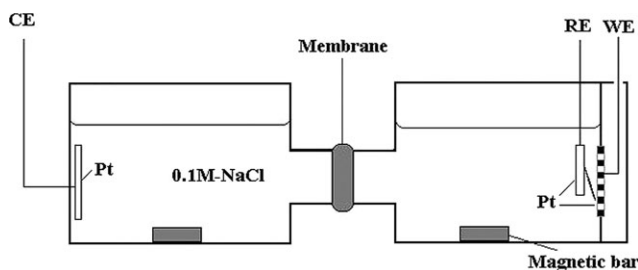
Figure 1 Schematic diagram for the measurement of the ion conductivity of the membranes. RE, reference electrode; CE, counter electrode; WE, working electrode.

Water uptake and FIC

The membranes were dried at $100 \pm 5°C$ for 1 day to obtain the unchanged weight. The dried membranes were weighed (W_1) and then were soaked in water for 1 day. Then, the membrane samples were removed from the water and weighed immediately after the free surface water was blotted (W_2). The water uptake of the membrane (W_M) was calculated with the following formula:[4,11,19,20]

$$W_M \left(g \text{ of } H_2O/g \text{ of dry membrane} \right) = \frac{(W_2 - W_1)}{W_2} \quad (3)$$

The FIC (A_f), which is known as a factor related to the selectivity, can be calculated with the following formula:[4,11,18]

$$A_f \left(\text{mequiv/g of } H_2O \right) = \frac{\text{IEC}}{W_M} \quad (4)$$

Ion conductivity

The ion conductivity of the aminated membrane was measured with an impedance analyzer (μAutoLab III AFR2, Eco Chemie B.C., Ulrecht, Netherlands). The impedance spectra were recorded at the frequency of 1 kHz with an alternating-current single amplitude of 10 mV and at room temperature. As shown in Figure 1, the aminated membrane for the impedance measurement was fastened between the two compartments with a Teflon ring clamper. Before the experiments, the membrane was conditioned for 1 day in a $0.1M$ NaCl electrolyte solution. The contents of the two compartments were kept stirred with magnetic stirring bars during the experiments. The ion conductivity was obtained with the following formula:[4,11,20]

$$K = \frac{1}{\rho} = \frac{L}{(R_1 - R_2) \cdot S} \quad (5)$$

where K is the ion conductivity (S/cm); ρ is the specific resistance (cm/S); L is the thickness of the membrane (cm); S is the area of the membrane

(cm²); and R_1 and R_2 are the cell alternating-current impedances (Ω) with and without the membrane, respectively.

RESULTS AND DISCUSSION

FTIR analysis

The chemical structures of the polymer and aminated polymer were analyzed with an FTIR spectrometer. In the FTIR spectrum of the base polymer membrane (Fig. 2), the absorption band at 723–682 cm^{-1} arises from stretching vibrations of C—Cl bonds. The absorption band at 2950–2840 cm^{-1} is assigned to the C—H stretching vibrations. The peaks at 1455 and 1378 cm^{-1} are attributed to the bending of C—H and stretching of C—C bonds. The band at 973 cm^{-1} is ascribed to the CH$_2$ vibration. After amination, the intensities of the band at 723–682 cm^{-1} evidently drop. Also, new absorption bands appear at 3419 and 1654 cm^{-1} because of amination. In contrast to the standard spectra, the broad band at 3419 cm^{-1} is due to the symmetrical and asymmetrical stretching vibrations of NH and NH$_2$, whereas the peak at 1654 cm^{-1} is due to the vibration of C—N—H or C=N.

Structure of the membrane

Figure 3(a,b) presents the cross-sectional morphologies of the base polymer membrane and aminated polymer membrane, which were observed with scanning electron microscopy. When the chlorinated polymer was aminated with a monoamine (PEI), rugged textures with pores were observed. This was
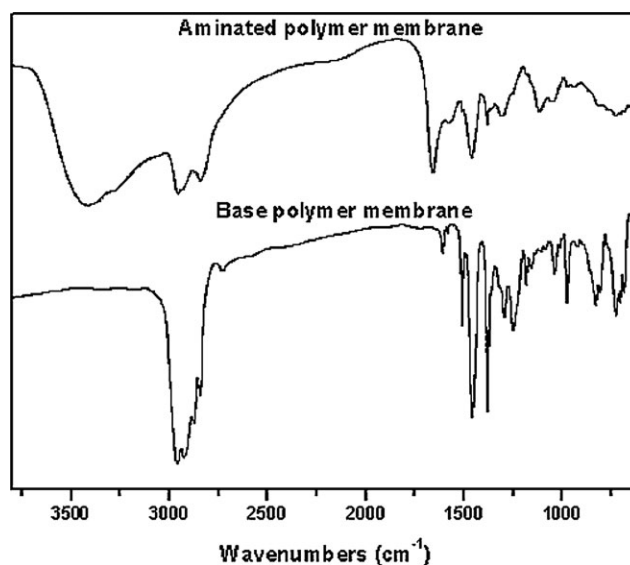

Figure 2 FTIR spectra of the base polymer and aminated polymer membranes.
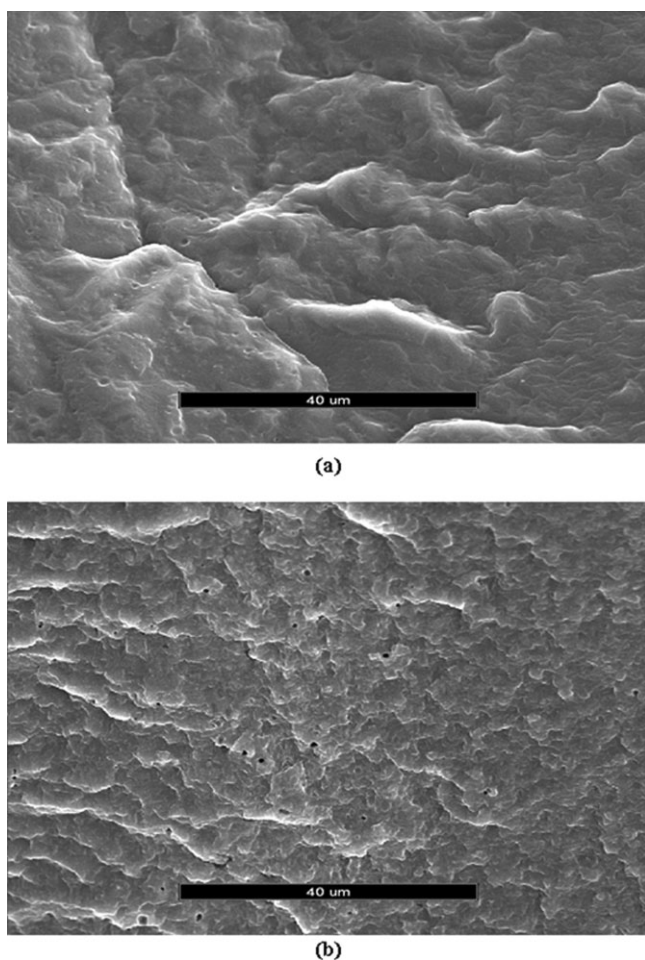
Figure 3 Cross sections of the (a) base polymer and (b) aminated polymer membranes.

thought to have happened because the polymer had a crosslinked structure after amination. Likewise, when the solubility of the aminated membrane was tested in various solvents such as tetrahydrofuran, dimethyl sulfoxide, dimethylformamide, chloroform, and toluene, the aminated membrane did not dissolve but merely swelled in these solvents. The result was due to the crosslinked aminated structure versus the base polymer.

TG

Figure 4 shows the TG curves of the base polymer membrane and the aminated polymer membrane prepared with CPP and with CPP and PEI. The aminated polymer membrane experienced more mass loss than the base polymer membrane. Moreover, the decomposition temperature of the base polymer membrane was about 350°C, but that of the aminated polymer membrane was about 300°C. At a low temperature (<300°C), the mass loss was likely due to decomposition of the functional groups. At a

high temperature (>300°C), it was likely due to deamination of the aminated polymer membrane at about 300°C. These results imply that the decomposition of the aminated polymer membrane was accelerated at a high temperature because its backbone was attacked by the decomposed amine groups during the deamination reaction.[19]

As the temperature reached beyond around 450°C, the masses of both membranes tended to be stable. However, the aminated membrane produced more residues (carbon). This was thought to have happened because PEI chains randomly attached to CPP chains, leading to partially crosslinked interpenetrating structures. This was evidenced by the fact that the aminated membrane was insoluble in a common solvent.

Elemental analysis and titration

The elemental analysis and titration results for the base polymer membrane and aminated polymer membranes at various temperatures for 48 h are summarized in Table I. The titration for the nitrogen analysis was determined with the Mohr method.[7,13] The chlorine content of the base membrane was 9.18 mmol/g, and those of the aminated membranes were 4.58, 4.25, 3.94, and 3.19 mmol/g at 30, 40, 50, and 55°C, respectively. Likewise, the aminated polymer membranes had nitrogen contents ranging from 7.33 to 9.73 mmol/g. In addition to the amination reaction (substitution reaction), which gave rise to the anion exchange of the polymer membrane, the elimination reaction between Cl and its adjacent H caused additional Cl loss, which could be seen by a comparison of the changes in the Cl content before and after amination and in the N content of the
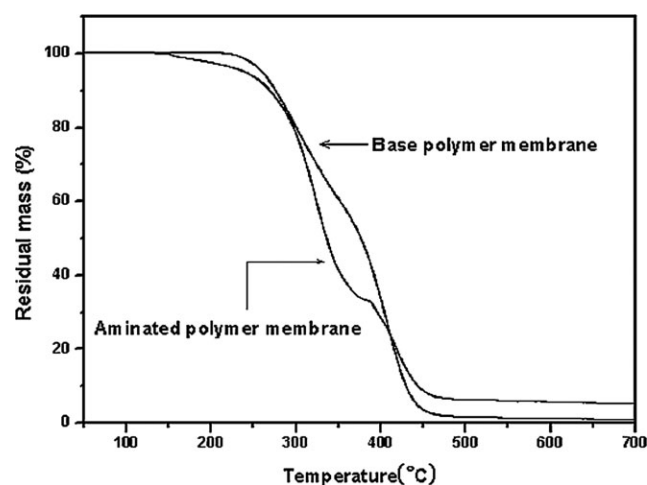

Figure 4 TG curves of the base polymer and aminated polymer membranes.

TABLE I
Elemental Analysis and Titration Results

Sample				Element				
	C (%)	H (%)	O (%)	Cl (%)	Cl (mmol/g)	N (%)	N (mmol/g)	$N_{titration}$ (mmol/g)
CPP	57.64	8.36	1.44	32.53	9.18	<0.30	—	—
CPP–PEI (30°C)	50.54	7.86	15.11	16.22	4.58	10.27	7.33	7.38
CPP–PEI (40°C)	50.91	8.22	14.59	15.05	4.25	11.23	8.02	7.69
CPP–PEI (50°C)	51.24	8.89	13.62	13.96	3.94	12.30	8.78	8.16
CPP–PEI (55°C)	52.47	8.66	13.94	11.30	3.19	13.64	9.73	9.33

aminated membranes. Because of this elimination reaction, the polymer chains were crosslinked during the amination, as evidenced by the fact that the aminated membrane was insoluble in various solvents such as tetrahydrofuran, dimethyl sulfoxide, dimethylformamide, chloroform, and toluene. Moreover, the reaction temperature had a signification influence on the degree of substitution and elimination. The elimination was slow below 50°C, whereas both amination and elimination reactions were more favored at 55°C. By comparing the nitrogen contents obtained with elemental analysis and titration, we can see that the majority of functional groups, such as NH and NH_2, were accessible. It can be concluded that the chlorinated aliphatic polymer was successfully functionalized, and the aminated polymer membranes exhibited an anion-exchange capacity.

Likewise, the pH value of the base polymer solution was 12.79, but those of the aminated solution showed a slight decline to 11.74, 11.35, 11.12, and 10.82 at the reaction temperatures. This was thought to have happened because the chlorine and its adjacent hydrogen were substituted and eliminated from the CPP polymer during the amination reaction.
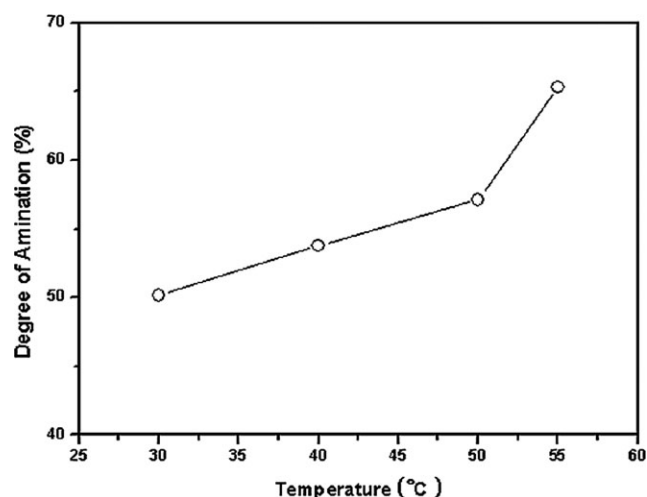
Degree of amination

Figure 5 shows the degree of amination of the aminated polymer membranes at various temperatures for 48 h. After amination, those of the polymer membranes were 50.16, 53.76, 57.11, and 65.29% at 30, 40, 50, and 55°C, respectively. The degree of amination below 50°C was lower than those at 55°C. As shown in Table I, this was thought to have happened because the conversion rate was slow when the Cl functional group of CPP was substituted with an N functional group such as NH or NH_2 below 50°C. On the other hand, the elimination reaction was slow below 50°C, whereas both the amination and elimination reactions were more favored at 55°C.

Water uptake and ionic conductivity

The ionic conductivities and water uptake of the aminated polymer membranes are shown in Figure 6. These values were measured at room temperature. The water uptake of the aminated polymer membrane increased with an increasing degree of amination. There was no water uptake in the base polymer membrane, whereas the water uptake of the aminated polymer membrane was 0.254, 0.296, 0.298, and 0.319 g of H_2O/g of dry membrane when the degrees
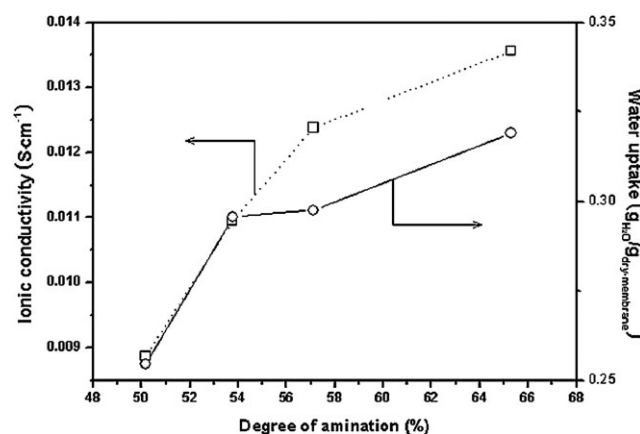

Figure 5 Degree of amination at different temperatures.

Figure 6 Variations of the ionic conductivity and water uptake with the degree of amination of the polymer.
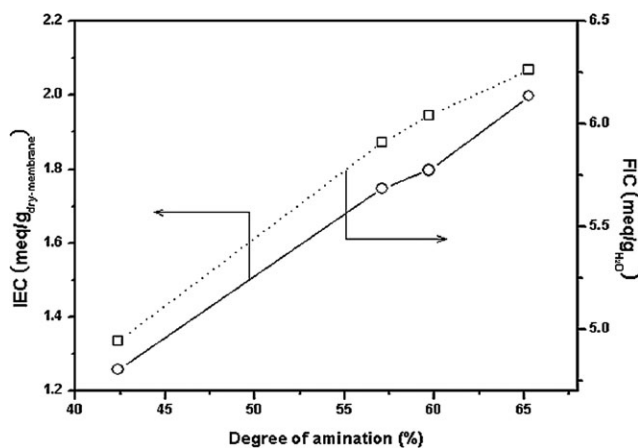
Figure 7 Variation of the IEC and the FIC with the degree of amination.

of amination were 50.16, 53.76, 57.11, and 65.29%, respectively. As Figure 5 shows, increasing the degree of amination led to an increase in the water uptake. In other words, the increasing water uptake implied that the chloride groups of the base polymer membrane were substituted by many amine groups.

The base polymer membrane showed an ionic conductivity of 5.75×10^{-7} S/cm at room temperature, whereas, as Figure 6 shows, the aminated polymer membranes showed ionic conductivities of 0.89×10^{-2}, 1.10×10^{-2}, 1.24×10^{-2}, and 1.36×10^{-2} S/cm when the degrees of amination were 50.16, 53.76, 57.11, and 65.29%, respectively. Ionic conductivities were high when the water uptake was high, as Figure 5 shows. This implies that amination affected the water uptake, and the water uptake affected the selective permeation of the membrane. Therefore, when the water uptake was highest, the ionic conductivity of the aminated polymer membrane also was highest, as is known.[4,19]

IEC and FIC

Figure 7 illustrates the relation between the IEC and FIC and the degree of amination. With an increase in the degree of amination, the IEC and FIC were increased. In general, increasing the FIC led to an increase in the IEC, as the results showed. From the data in Figure 7, it seems that to obtain a higher IEC, the membrane should have a high FIC and a high degree of amination. The prepared membranes possessed IECs in the range of 1.257–2.000 mequiv/g of dry membrane and FICs in the range of 4.942–6.261 mequiv/g of H_2O.

CONCLUSIONS

1. Anion-exchange membranes were prepared by the amination of CPP and PEI at low temperatures. The degrees of amination were 50.16, 53.76, 57.11, and 65.29% at 30, 40, 50, and 55°C, respectively.
2. The base polymer membrane had no water uptake, whereas the water uptake of the aminated polymer membrane was 0.254, 0.296, 0.298, and 0.319 g of H_2O/g of dry membrane with increasing amination.
3. The ionic conductivity of the aminated polymer membrane was highest when the water uptake was highest. The prepared membrane possessed ionic conductivity in the range of 0.89×10^{-2} to 1.36×10^{-2} S/cm.
4. The prepared membranes possessed IECs in the range of 1.257–2.000 mequiv/g of dry membrane and FICs in the range of 4.942–6.261 mequiv/g of H_2O.

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