

Synthesis and Characterization of Quaternized Poly(4-vinylpyridine-co-styrene) Membranes

Aibin Huang, Chaobo Xiao, Lin Zhuang

Department of Chemistry, Wuhan University, Wuhan 430072, People's Republic of China

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ABSTRACT: Copolymers of 4-vinylpyridine and styrene [P(4VP-St)s] with varied molar ratios were synthesized by means of radical mass polymerization with 2,2'-azobisisobutyronitrile as an initiator. The insoluble (linear) pyridinium-type polymers in the octyl-pyridinium bromide form, which possess various macromolecular chain compositions, were prepared by the reaction of each P(4VP-St) with 1-bromooctane. A series of membranes were prepared for use in electrochemistry. These membranes, prepared with quaternized poly(styrene-co-4-vinylpyridine), were characterized by IR spectroscopy, X-ray diffraction, differential scanning calorimetry, thermo-

gravimetry, tensile strength measurements, scanning electron microscopy, and an electrochemistry workstation. Our emphasis was to select a membrane with appropriate properties for use in the electrochemistry field. A promising membrane was selected to use in the field of electrochemistry by these characterizations. This study could be the preparation for a study on the electrochemical properties of pyridinium-type polymers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2146–2153, 2005

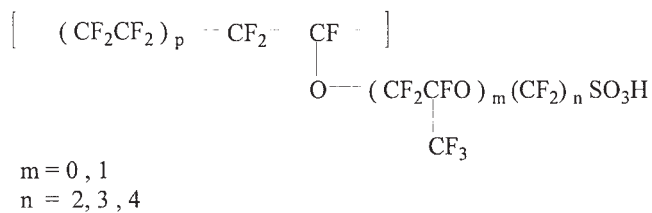
Key words: polyelectrolytes; quaternized copolymers; membrane

INTRODUCTION

Polymer electrolytes¹ have occupied an important position in solid-state ionics because of their unique properties, such as film-forming capabilities, good processibility, flexibility, light weight, elasticity (plasticity), transparency, a relatively high ionic conductivity, and a wide potential window. Some of these characteristics cannot be attained by hard inorganic solid electrolytes, including inorganic glasses, and thus, polymer electrolytes have been exploited to bridge a gap between fluid electrolyte solutions and hard inorganic solid electrolytes.²

Fuel cells³ are electrochemical converts, transforming chemical energy directly into electricity. In fuel cells, energy conversion depends on a polymer electrolyte membrane. The utilization of such polymer electrolyte membranes is diverse; they are used not only as separation membranes but also as functionally charged membranous materials.

A common separator membrane material in fuel cells is a hydrated perfluorosulfonic polymer, such as Nafion. Nafion has the following structure:



This main chain C—F structure defines the Nafion membrane's many advantages, including a high intensity and a high heat resistance: the sulfonic salt provides good ionic electric conductivity, and so on.^{4–8} However, a high production cost limits its use. It is a kind of proton-exchange polymer electrolyte. In fuel cells, it needs an electrode made of precious metal.⁹

To find a cheaper material that can replace Nafion and that does not require a noble metal electrode in fuel cells, a solid polymer electrolyte (SPE) membrane was synthesized. Poly(4-vinylpyridine) (4PVP), was used. PVP resin is a special functional resin. The nitrogen atom in the pyridine ring has a structure of a triamino group. It shows alkalinescence. The pyridine ring in PVP is a typical aromatic heterocycle that is

Correspondence to: C. B. Xiao (xiao@whu.edu.cn).

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short an electron. It can resist attack by an oxidant.¹⁰ PVP resin can be modified by an alkyl halide and turned into poly(vinyl-*N*-alkyl) pyridinium salts. It can adsorb bacteria from water.¹¹ In a poly(4-vinyl-*N*-alkyl) pyridinium salt, the halogen anion can be exchanged, so it can be made into an anion-exchange resin. When the number of carbons in the alkyl halide is more than eight, the poly(4-vinyl-*N*-alkyl) pyridinium salt is insoluble in water.¹² It is obvious that the poly(4-vinyl-*N*-alkyl) pyridine, quaternized by a longer chain alkyl halide, is hydrophobic, but as the side chain becomes longer and longer, the heat stability of such polymers deteriorate, so we chose 1-bromooctane as the alkylation reagent.

As a type of cationic polymer containing both hydrophilic cationic groups (i.e., pyridinium groups) and a hydrophobic (nonpolar) segment in the macromolecular chains, pyridinium-type polymers may be homopolymeric, containing almost one charge per monomer unit, such as a polyelectrolyte or a copolymer of one monomer containing a charge and another containing no charge. The latter possesses a lower charge density than conventional polyelectrolytes and so have been called *ionomers*. Eisenberg studied ion aggregation¹³ in ionomers and models of ionomers. Soluble (linear) pyridinium-type polymers, whose backbone chains contain 4-vinylpyridine (4VP) units and styrene (St) units, exhibit typical polyelectrolyte solution behavior in that the viscosity of the polymer/polar solvent system increases with dilution. This fact implies that ion-containing polymers, whether their charge density is high or low, possess the common characteristic of being able to interact strongly with opposite charges.

In our group experiments, the quaternized 4VP homopolymer by 1-bromooctane was still hydrophilic although it was insoluble in water, and the membrane made from it was not strong enough (this experiment was done and proven by our group). A hydrophobic monomer (St) had to be introduced for copolymerization to improve the strength of the membrane and to drop its degree of swelling in water. For this study, a series of membranes, with different unit ratios, were synthesized, and some physical properties were characterized. Considering these properties, we selected a solid polymer electrolyte with an appropriate unit

TABLE I
Data for the Different Monomer Ratios

	4VP (mol)	St (mol)	AIBN (g)
A	0.028	0.113	0.0116
B	0.047	0.094	0.0116
C	0.071	0.071	0.0117
D	0.094	0.047	0.0116
E	0.105	0.035	0.0116

AIBN monomer = 0.05% (molar ratio).

TABLE II
Volume of the 1-Bromooctane in the Copolymers with Different Ratios

	Copolymer (3 g)				
	A	B	C	C	E
1-bromooctane (mL)	4.5	7.0	8.5	10.0	12.0

ratio to use in the electrochemistry field. In this article, we mainly discuss the relationship between the properties and structure of such membranes by physical property characterization. A promising membrane for use in the electrochemistry field was selected.

EXPERIMENTAL

Materials

The 4VP monomer (Aldrich) was dried over calcium hydride overnight and fractionally distilled under reduced pressure (12 mmHg) at 59–61 °C, with the first and last 10% of the monomer discarded. St (Chemistry Reagent Factory, Beijing) was washed three times with a 5% aqueous solution of sodium hydroxide to remove the inhibitor, washed five times with pure water to a neutral pH, and dried over anhydrous sodium sulfate overnight. It was then distilled under reduced pressure (21–22 mmHg) at 47–48°C, with the first and last 10% of the monomer discarded. As the initiator of polymerization, 2,2'-azobisisobutyronitrile (AIBN, The Fourth Reagent Factory, Shanghai) was refined by recrystallization twice, with CH₃OH (A.R. Chemistry Reagent Factory, Shanghai) as the solvent. 1-Bromooctane (Chemistry Reagent Factory, Shanghai) and other reagents were used without further purification.

Preparation of the polymer samples

Synthesis of the copolymers containing pyridine rings

The copolymerization reaction of 4-VP and St was carried out in a two-necked, round-bottom flask equipped with a nitrogen inlet, a reflux condenser, a bubbling device, and an electromagnetic stirrer. A series of the poly(4-vinylpyridine-styrene) copolymers of varying composition were synthesized by mass polymerization with AIBN as an initiator.¹⁴ The reaction proceeded under a continuous nitrogen atmosphere at 60°C; the reaction process needed at least 20 h. The copolymer was dissolved several times in methanol and reprecipitated in dry ether for to remove excess monomer. The product was put in a vacuum drying oven at 50°C for 24 h. The ratios of different reagents are shown in Table I.

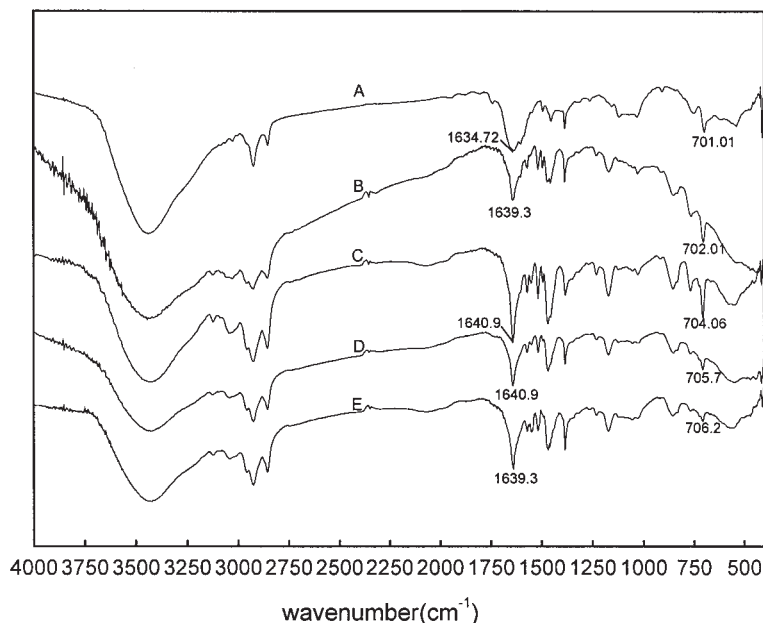


Figure 1 IR spectra of the membranes in the range 4000 to 400 cm^{-1} .

Synthesis of insoluble pyridinium-type polymers

The copolymers (3.0 g) were quaternized by the addition of excess 1-bromooctane to a 5% solution of the polymer in nitromethane (60 mL)¹⁵ and refluxing under nitrogen for 72 h. The crude product was obtained by evaporation of the reagents under vacuum. The copolymer was dissolved in ethanol and precipitated from the solution in excess dry ether. The volumes of the 1-bromooctane added to the copolymers with different ratios are shown in Table II.

Preparation of the membranes

The solution of dissolved copolymer (1.0 g) in 10 mL of nitromethane was cast on a Teflon gasket, and the nitromethane was allowed to evaporate at room temperature. The membrane, was dislodged carefully and then subjected to further drying *in vacuo* for 2 days. Dried membranes of thicknesses ranging from 50 to 60 μm were obtained.

Mensuration of the resistance of the membranes

The square membranes (2 cm^2) made by the quaternized copolymers were immersed into a 0.1 mol/L NaOH solution (25°C) for half an hour. The membranes changed from colorless to red. This process was reversible when the red membrane was immersed into 0.1 mol/L HCl. Clearly, groups were exchanged between OH^- and the haloid ion. The

resistances of the membranes exchanged by OH^- were measured by an electrochemistry workstation.

Characterization of the membranes

IR spectra of the membranes were measured with a Nicolet 170SX Fourier transform infrared (FTIR) spectrometer (Madison, WI) with KBr pellets, wide-angle X-ray diffraction (WAXD) patterns of the membranes $55 \pm 5 \mu\text{m}$ in thickness were recorded with a Shimadzu XRD-6000 (Japan) diffractometer with a $\text{Cu K}\alpha$ target at 40 kV and 30 mA with a scan rate of $4^\circ/\text{min}$. The diffraction angle ranged from 5 to 45° . The tensile strength and breaking elongation of the membranes were measured on an electron tensile tester (XINSANSI-cmt6202, Shenzhen, China) with a tensile rate of 5 mm/min at a gauge length of 50 mm and a width of 10 mm. The temperature and relative humidity were 25°C and 60%, respectively. Differential scanning calorimetry (DSC) tests of the sample membranes were performed in a nitrogen atmosphere with a Sysstsys 16TG/DAT/DSC thermal analyzer instrument (France), and the temperature was raised from 20 to 500°C at a heating rate of $10^\circ\text{C}/\text{min}$. The morphology of the membrane surface was examined with a Hitachi-570 scanning electron microscope (Japan). The membranes were frozen under liquid nitrogen, fractured, and coated with gold under 13.3-Pa vacuum conditions before the scanning electron microscopy (SEM) experiments. The resistances of the exchanged membranes were measured by an elec-

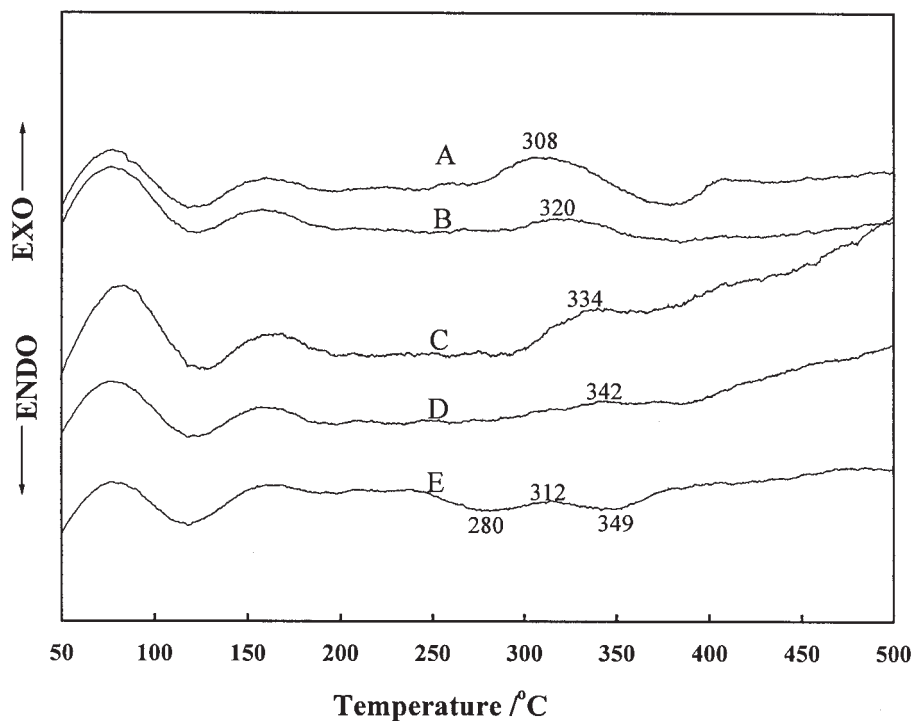


Figure 2 DSC curves of the membranes.

trochemistry workstation made by Chenhua Instrument Co. (Shanghai).

RESULTS AND DISCUSSION

FTIR

The FTIR spectra of the compounds are shown in Figure 1. As shown in Figure 1, every compound had a band at about 1640 cm^{-1} (A = 1634.72 , B = 1639.3 , C = 1640.9 , D = 1640.9 , and E = 1639.3 cm^{-1}), which is the characterization peak of the pyridinium-type polymers.¹⁶ With increasing pyridinium salt units in the compounds, the band at 700 cm^{-1} , which was assigned to the out-of-plane bending of the benzyl ring moved to a low frequency¹⁷ (A = 701.01 , B = 702.1 , C = 704.6 , D = 705.7 , and E = 706.2 cm^{-1}). This could be explained by the fact that the 4VP unit caused a change in the electron distribution of the benzyl ring.

These compounds did not appear as a peak at 1414 cm^{-1} , which showed that the compounds were quaternized completely.¹⁸

Thermal stability

The DSC results of the compounds are shown in Figure 2. The compounds degraded in the region $280\text{--}380^\circ\text{C}$, according to Figure 2. At about 120°C , of endothermic peak in each compound in the DSC results was assigned to loss of water adsorbed because the

pyridinium salt was prone to adsorb water. Exothermic peaks for compounds A, B, C, D, and E were centered at 308 , 320 , 334 , 342 , and 312°C , respectively. These exothermic peaks were assigned to the degradation of these polymers.

Thermogravimetry (TG) is a good method for monitoring polymer stability. TG results of the compounds are shown in Figure 3. As shown in Figure 3, the weight loss appearing in the $110\text{--}130^\circ\text{C}$ region for the TG of these compounds was water loss (because the pyridinium salt was prone to adsorb water). Compounds A and B showed obvious two-step weight losses. For compound A, the weight loss temperatures were at 308 and 377°C ; for compound B, they were at 320 and 382°C . Compounds C, D, and E showed one-step weight losses at 334 , 342 , and 280°C , respectively.

As shown by the DSC and TG peaks of the compounds, the thermal stability order was $E < A < B < C < D$. From the TG results of compounds A and B (they lost weight by stages), we deduced that microdomains of polystyrene and quaternized PVP existed in their mass.

WAXD of the membranes

The WAXD results for the membranes are shown in Figure 4. As shown in Figure 4, the intensity of the diffraction peaks of the compounds descended gradually with increasing pyridinium salt unit ratio in the compounds, which implied that the degree of crystal-

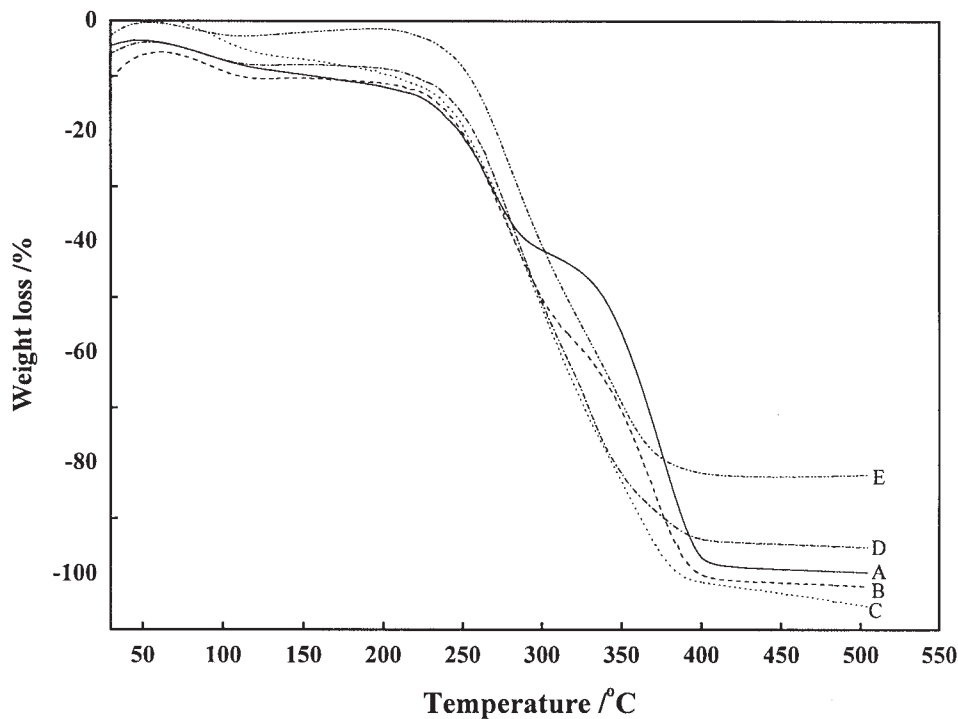


Figure 3 TG curves of the membranes.

lization gradually decreased. This showed that the structures of the compounds tended to be more amorphous as the pyridinium salt unit ratio increased. Another phenomenon was that the angle of diffraction became wider with increasing pyridinium salt unit

ratio in the compounds. For E, the diffraction peak was so weak that the 2θ peak could hardly be found, which indicated that the amorphous areas became bigger. Unlike inorganic salts, this kind of SPE is prone to have a more amorphous structure with in-

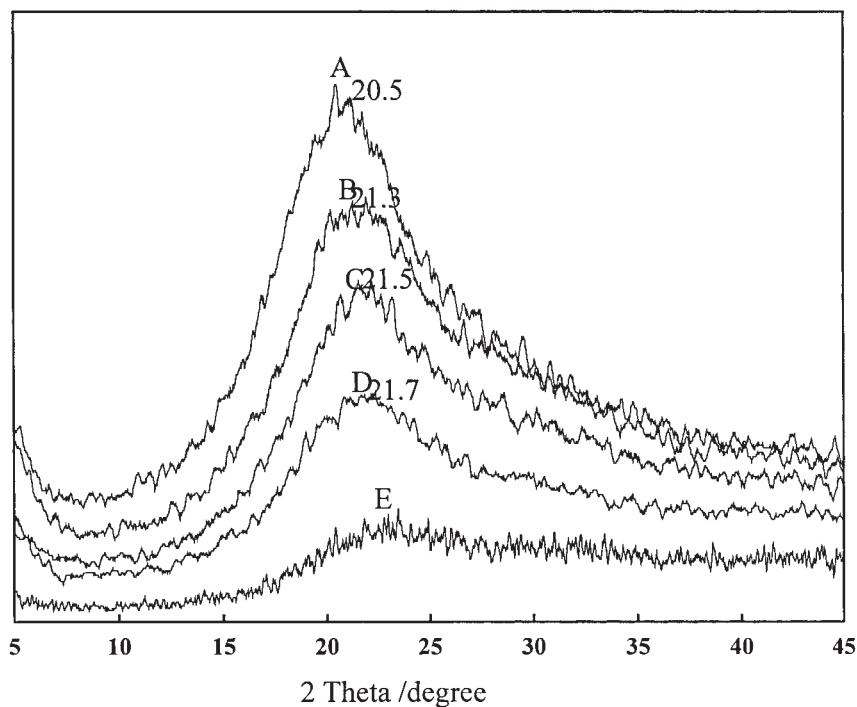
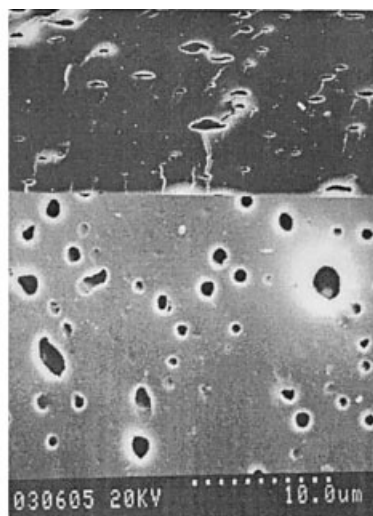
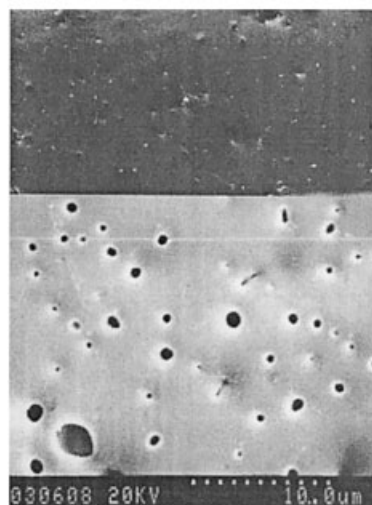


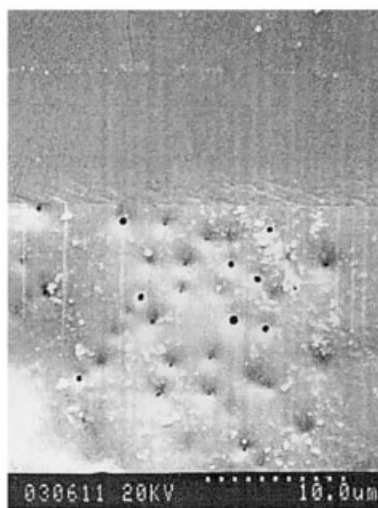
Figure 4 WAXD patterns of the membranes.



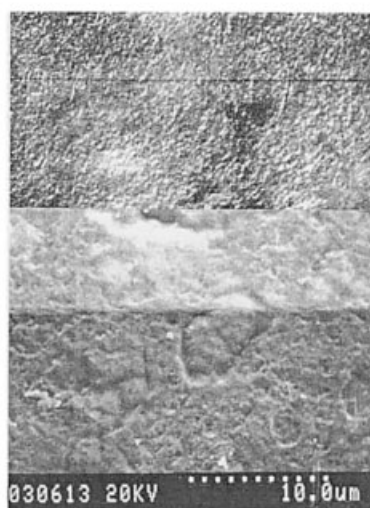
A



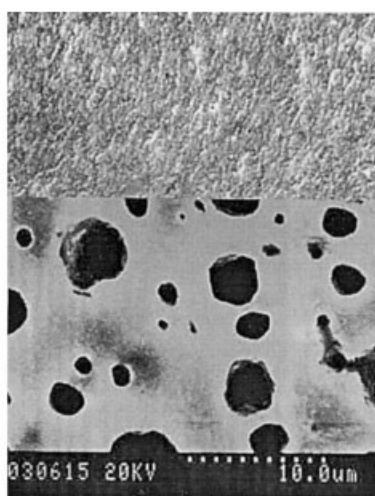
B



C



D



E

Figure 5 SEM results for the membranes.

creasing exchangeable groups. The WAXD results showed that the ratio of the two units in the copolymers had an effect on the crystallization of the compounds. A possible explanation is that the chains of copolymer became coiled, which caused a more amorphous structure with increasing exchangeable groups.¹⁹

Morphological characteristics of the membranes

The SEM photographs are shown in Figure 5. The upper section of each photograph indicates the cross-section of the membrane, and the bottom section indicates the surface of the membrane. As shown in Figure 5, D had the smoothest surface in the five pictures; C was also smooth, whereas A, B, and E were coarse and had some cavities in their surfaces. The cause of the holes was not clear. This phenomenon corresponded to the WAXD results of the membranes. According to the Bragg equation, $d = \lambda/2 \sin \theta$, θ got higher from A to D, and d got smaller in this order. This meant that the structure of the membranes got more compact. The holes became smaller from A to D (no holes), this may have accounted for the structure of the membranes getting more compact. The phenomenon that A, B, and E had coarse surfaces could be explained in that A, B, and E showed an obvious two-phase separation, which C and D did not show. However, what caused A, B, and E to have an obvious two-phase separation? The copolymers contained St and pyridinium-salt units: these two units are different in hydrophilicity, which causes phase separation.²⁰ Because the St and pyridinium salt units in D were close to the identical copolymerization point ($r_{4VP} = 0.62$, $r_{St} = 0.50$),²¹ the distribution of the two units was symmetrical. When the distribution of the two units was not symmetrical, as for the A, B, and E copolymers, they had obvious phase separation. This result was consistent with the results of DSC and TG for the membranes. This result (phase separation) was not consistent with other literature,¹⁸ the reason being that the ratio of ionic groups was different in that work.¹⁸ This implies that the copolymers D and C had good electrochemical properties.

TABLE III
Mechanical Performance of the Membranes

	Tensile strength (MPa)	Elongation at break (%)
A	13.74	1.41
B	10.82	1.82
C	10.22	4.31
D	7.59	4.80
E	6.53	6.86

TABLE IV
 Q_w of the Membranes Made by Quaternized Copolymers

	Dry weight (g)	Wet weight (g)	Q_w (%)
A	0.0249	0.0274	10.04
B	0.0328	0.0401	22.26
C	0.0174	0.0227	30.46
D	0.0361	0.0496	37.40
E	0.0176	0.0312	77.27

Mechanical properties of the membranes

The mechanical properties of a membrane are very important for its application. The mechanical performances of the membranes are shown in Table III. With increasing pyridinium salt units the tensile strengths of the membranes gradually fell, whereas the elongations at break increased gradually. It may be that the electrostatic effect made the strength of the membrane decrease and made the elongation at break increase with increasing of pyridinium salt content in the compounds, too. The phenomenon was in accord with the model of MacKnight and Earnest.¹⁹

Water swelling properties

The degree of swelling (Q_w) of a membrane can indicate its probable stability in a working situation. Membranes of the five compounds were immersed in pure water for 24 h:

$$Q_w = (\text{Wet weight} - \text{Dry weight}) / \text{Dry weight} \times 100\%$$

The degrees of swelling of the membranes made by quaternized copolymers are shown in Table IV.

As shown in Table IV, with increasing pyridinium salt content, the degree of swelling of the membranes gradually increased. Because the pyridinium salt unit is hydrophilic, such a result was reasonable.

Resistance of the exchanged membrane

The resistances of the membranes exchanged by OH^- were measured by the electrochemistry workstation, and the results are listed in Table V. As shown in Table V, an obvious result was found: the resistances of the membranes decreased step by step according to the

TABLE V
Resistance of the Membranes Exchanged by OH^- (25°C)

	A	B	C	D	E
Resistance ($\Omega \text{ cm}^2$)	36.0	19.0	9.0	5.6	—

order $A > B > C > D$. Because the exchangeable group content increased from A to D gradually, the ionic conductance of the membranes increased in the same order. However, because membrane E had bad mechanical performance and a high degree of swelling in water, it could not be measured by the electrochemistry workstation. The resistances of the membranes decreased with decreasing degree of crystallization. The closest analog to this phenomenon is the phenomenon of the SPE of the poly(ethylene oxide) salt type. As is generally known, with a SPE of the poly(ethylene oxide) salt type, increasing chain flexibility by decreasing its degree of crystallization can be helpful in improving its ionic conductivity.²² The resistance of membrane D could be explained by electrochemistry.

CONCLUSIONS

For this study, a series of quaternized copolymers were synthesized and characterized by the measurement of their properties. We found that compound D had the best heat-resistance performance and electrical resistance performance, whereas compound A had the best mechanical performance of the five compounds. All things considered, compound D was most appropriate for use in fuel cells. The integrity of the membrane needs to be improved: how to improve this and the electrochemical performance of the membrane made by this compound, will be reported in our next article.

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