

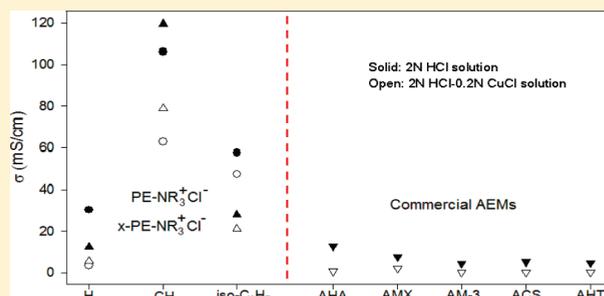
New Polyethylene Based Anion Exchange Membranes (PE–AEMs) with High Ionic Conductivity

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Supporting Information

ABSTRACT: This paper discusses a new class of high performance polyethylene-based anion exchange membranes (PE–AEMs) that contain a wide concentration range of pendant (flexible) ammonium chloride (NR_3^+Cl^-) groups and with or without a cross-linked PE matrix structure. The chemistry involves a metallocene-mediated polymerization of ethylene, silane-protected α,ω -aminoolefin [$\text{C}_x\text{N}(\text{SiMe}_3)_2$], with or without styrenic diene (cross-linker), to form ethylene/ $\text{C}_x\text{N}(\text{SiMe}_3)_2$ copolymers and ethylene/ $\text{C}_x\text{N}(\text{SiMe}_3)_2$ /diene terpolymers, respectively. The resulting co- and ter-polymers were completely soluble in common organic solvents and were solution-casted into uniform films (thickness, 50–70 μm ; without backing material) and then thermal cross-linked in ethylene/ $\text{C}_x\text{N}(\text{SiMe}_3)_2$ /diene case, further interconverting the silane-protected amino groups into the desired $-\text{NR}_3^+\text{Cl}^-$ groups (R: H, CH_3 , and C_3H_7) under solid state conditions. The resulting PE– NR_3^+Cl^- and cross-linked x-PE– $\text{N}(\text{CH}_3)_3^+\text{Cl}^-$ membranes were systematically studied to understand how the PE structure ($-\text{NR}_3^+\text{Cl}^-$ concentration, R group, cross-linking density, etc.) affects ionic conductivity, water uptake, film stability, and ion selectivity. For comparison, several commercially available AEMs were also examined. Evidently, an x-PE– $\text{N}(\text{CH}_3)_3^+\text{Cl}^-$ membrane, with 28.1 mol % $-\text{N}(\text{CH}_3)_3^+\text{Cl}^-$ groups and 0.2 mol % cross-linkers, shows moderate water swelling and outperforms all commercial membranes with exceptionally high ionic conductivities of 119.6 mS/cm in 2 N HCl solution and 78.8 mS/cm in 2 N HCl–0.2N CuCl solution at room temperature.



INTRODUCTION

Ion exchange membranes (IEMs) have been applied in many fields,^{1–5} such as the purification of pharmaceuticals, production of salt from seawater, wastewater treatment, and electrochemical devices (i.e., fuel cells, batteries, electrodialysis, electrolysis, electrodeionization, etc.). In electrochemical assembly, the ion exchange membrane provides two major functions—a selective ion transport (ion conductor) and electric insulation (separator) between two electrodes. Usually, a desirable membrane shall possess a stable (hydrophobic) matrix and some continuous ionic (hydrophilic) channels across the film with a high ion-exchange capacity (IEC) and good ion mobility, while maintaining its structural integrity and stability under particular conditions. Many experimental results^{6–8} have shown that the ion conductivity is directly related to a combination of the ion-exchange capacity, ion mobility, hydration level, and morphology. Indeed, it has been a scientific challenge to develop an inexpensive polymer that can perform a balanced set of properties with high ion concentration, good ionic conductivity, acceptable water swelling, and long-term chemical and structural stability under severe electrochemical conditions.

Several polymers, such as fluoropolymers,^{9–11} polysulfones,^{12–16} and cross-linked polystyrene,^{17–19} are commonly used as the

polymer backbones for preparing numerous cationic exchange membranes (CEMs) and anionic exchange membranes (AEMs). They show various advantages but also some shortfalls. Fluoropolymers are generally expensive and also cause major concerns in chemical stability^{20,21} under strong base conditions. The preparation of polysulfones by the polycondensation process requires high chemical purity and a precise functional group stoichiometry in the monomers to achieve a desirable high molecular weight. The cross-linked polystyrene is usually prepared on reinforced backing fabrics to increase its mechanical strength. Because of the insolubility of ion exchange membranes, most of the ion incorporation procedures in the preparation of AEMs involve free radical grafting reaction^{22–24} under heterogeneous condition, which usually produces ill-defined molecular structures. Many functionalization routes also involve carcinogenic chemicals, such as chloromethylstyrene²⁵ and chloromethyl methyl ether.²⁶ Coates et al.^{27,28} recently reported a new synthetic approach to prepare cross-linked AEMs via ring-opening metathesis copolymerization of cyclo-olefins and their quarter-ammonium derivatives. One of the comonomers contains

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two olefin units that engage in double enchainment to form a cross-linked structure. Some resulting cross-linked AEMs exhibit high anion conductivity and good mechanical properties.

Polyolefins, such as high density polyethylene (HDPE) and isotactic polypropylene (PP), are known to be very stable in severe electrochemical environments. As a matter of fact, the microporous PE and PP are the most common separators in rechargeable Li⁺ ion batteries.^{29–31} They exhibit a unique combination of chemical stability, hydrophobicity, high crystallinity, negligible swelling, and good mechanical properties under demanding environments, and are inexpensive. The combination also positions the polyolefins to be a very interesting polymer matrix for IEMs. The introduction of some continuous ion conductive channels through the polyolefin film may form IEMs with a stable hydrophobic membrane matrix and well-defined hydrophilic ionic channels that may offer a high IEC value, controllable water swelling, and high ionic conductivity. In the past there have been several papers^{32–36} discussing the polyolefin based ion-exchange membranes with some success. Because of synthesis difficulties—catalyst poison^{37,38} by a functional group in the direct Ziegler–Natta mediated α -olefin polymerization process, the most common functionalization routes have been based on the postpolymerization process, involving an irradiation-mediated free radical graft polymerization of a monomer-bearing ionic group or styrene followed by a functionalization reaction (sulfonation, alkaline hydrolysis, etc.) of benzyl groups. Unfortunately, the free radical process usually results in very complicated molecular structures.³⁹ The polymer structure and morphology have rarely been characterized. Recently, Coates et al.⁴⁰ extended the ring-opening metathesis copolymerization with the subsequent hydrogenation reaction to prepare solution-processable PE-based alkaline AEMs (without cross-linking). A desirable AEM with 1.5 mmol HO[−]/g IEC value, insoluble in both pure water and aqueous methanol at 50 °C, exhibits mechanical strength of 6 MPa at break and high hydroxide and carbonate conductivities (65 and 30 mS/cm at 50 °C, respectively).

Our research in developing new AEMs has stemmed from a nuclear hydrogen production program using a Cu–Cl thermochemical cycle.^{41,42} This process involves an electrolysis reaction ($2\text{CuCl} + 2\text{HCl} \rightarrow 2\text{CuCl}_2 + \text{H}_2$) in an aqueous solution at 25–80 °C. For producing H₂ in the cathode of the CuCl–HCl electrolyzer, an efficient Cl[−] conductive AEM is essential for selective Cl[−] ion diffusion from cathode to anode, without any diffusion of the Cu⁺ and Cu²⁺ species through the membrane. In this paper, we will discuss a new AEM preparation process, which involves a metallocene-mediated ethylene polymerization process to prepare soluble functional PE copolymers that can be solution-casted and further derived into PE-based Cl[−] ion conductive AEMs. The resulting PE–AEMs contain a wide range of ammonium chloride ($-\text{NR}_3^+\text{Cl}^-$) groups in the flexible methylene side chains and various degrees of cross-linking density (after thermal treatment). The effective chemical method to prepare functional polyethylene copolymers with well-controlled molecular structures allows us to carry out a systematic study to understand the structure–property relationship, including Cl[−] ion conductivity, water uptake, and ion selectivity under various conditions. The main objective is to identify the most suitable PE–AEM that can perform significantly higher Cl[−] ion conductivity and ion selectivity than commercial ones, while maintaining good chemical, thermal, and mechanical stability.

EXPERIMENTAL SECTION

Materials and Instrumentation. All O₂ and moisture sensitive manipulations were carried out inside an argon filled Vacuum Atmospheres drybox. Methylaluminoxane (MAO) (Ethyl) was purified by vacuum-pumping to remove trimethylaluminum (TMA) at 70–80 °C for 6 h. *rac*-CH₂(3-*tert*-Butyl-Ind)₂ZrCl₂ catalyst⁴³ and 4-(3-butenyl)-styrene⁴⁴ were prepared using the published procedures. Polymerization-grade ethylene (Matheson) was used as received. Toluene (Wiley Organics) was distilled over CaH₂ under argon. Allyl bromide (99%), lithium bis(trimethylsilyl)amide (97%), iodomethane (99%), and 2-iodopropane (Sigma-Aldrich) were used as received.

All high-temperature ¹H NMR spectra were recorded on a Bruker AM-300 instrument in 1,1,2,2-tetrachloroethane-*d*₂ at 110 °C. The melting temperatures of the polymers were measured by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 instrument controller with a heating rate of 20 °C/min. All mechanical properties (tensile strength, tensile modulus, elongation at break, etc.) were measured according to the ASTM D-1708 method. The dog-bone specimens (38 mm × 15 mm overall size and 5 mm × 22 mm in the gauge area) were die cut and performed using an Instron 5866 universal tester, with a load cell of 100 N and a constant cross head speed of 1 mm/min. At least five samples were tested in order to minimize possible errors.

Synthesis of 6-Bis(trimethylsilyl)amino-1-hexene. This monomer was prepared in two reaction steps. In a 500 mL flask equipped with a magnetic stirring bar, 50 g (0.299 mol) of lithium bis(trimethylsilyl)amide dissolved in 200 mL of THF was slowly added into a mixture of 25 mL (0.329 mol) of chloromethyl methyl ether and 50 mL of THF at 0 °C under a nitrogen atmosphere. Once the addition was complete, the solution was allowed to warm to room temperature for 2 h before evaporating the excess chloromethyl methyl ether and THF solvent. *N,N*-Bis(trimethylsilyl)methoxymethylamine (80% yield) was isolated by distillation. In the second step, 6-bis(trimethylsilyl)amino-1-hexene was prepared by treating *N,N*-bis(trimethylsilyl)methoxymethylamine with 4-pentenemagnesium bromide. In a 500 mL flask equipped with a magnetic stirring bar and a condenser, 5.2 g magnesium powder (0.22 mol) was suspended in 200 mL of dry ether, and 25 mL (0.21 mol) of 5-bromo-1-pentene diluted with 50 mL of dry ether was then introduced dropwise through the condenser. The solution was refluxed overnight before adding 41 g (0.20 mol) of *N,N*-bis(trimethylsilyl)methoxymethylamine over a period of 2 h under room temperature. The reaction was allowed to proceed at room temperature for another 2 h before adding 100 mL of aqueous NaOH solution (30%). The organic layer was separated and dried, and the crude product was then distilled over CaH₂ to obtain 6-bis(trimethylsilyl)amino-1-hexene in 73% yield. ¹H NMR (300 MHz, 25 °C, CDCl₃): 5.81 (m, 1 H, $-\text{CH}=\text{CH}_2$), 5.07 (m, 2 H, $-\text{CH}=\text{CH}_2$), 2.77 (t, 2 H, $-\text{CH}_2-\text{N}-$), 2.14 (m, 2 H, $-\text{CH}_2-\text{CH}=\text{CH}_2-$), 1.38 (m, 4 H, $-\text{CH}_2-\text{CH}_2-$), 0.21 (s, 18 H, $-\text{NSi}_2(\text{CH}_3)_6$).

Co- and Ter-Polymerization of Ethylene, 6-bis(trimethylsilyl)amine-1-hexene, and Divinylbenzene. A typical copolymerization reaction was carried out in a 250 mL glass flask with a magnetic stirrer, which was charged with 50 mL of toluene, 6-bis(trimethylsilyl)amine-1-hexene, dry MAO (Al/Zr = 1000), and ethylene (14 psi). Zirconium catalyst (1 μ mol) in 3 mL of toluene solution was then injected into the reactor to initiate the copolymerization. After 60 min of polymerization at constant temperature and ethylene pressure, the reaction solution was quenched by acetone and filtered, washed extensively with acetone to remove residual monomer and then dried under vacuum at room temperature for 12 h.

Terpolymerization of ethylene/6-bis(trimethylsilyl)amine-1-hexene/divinylbenzene was carried out under a similar condition. In a 250 mL glass flask with a magnetic stirrer, ethylene, 2-hex-5-enyl-1,1,1,3,3,3-hexamethyldisilazane, divinylbenzene, and dry MAO (Al/Zr = 1000) were charged

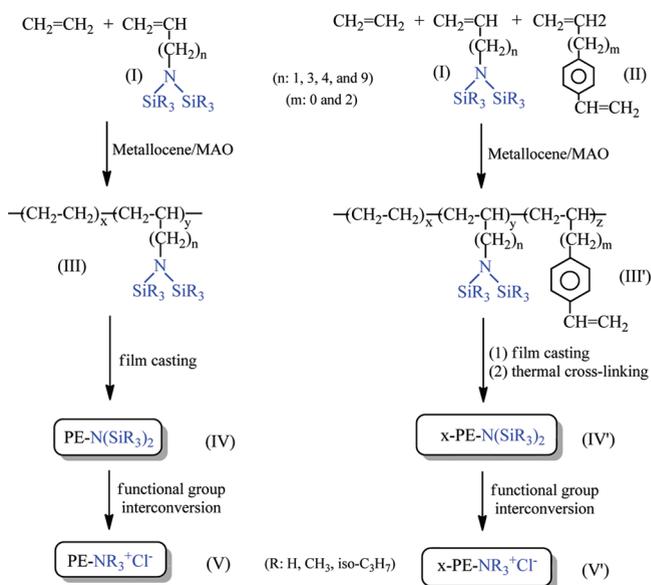
before injecting zirconium catalyst (1 μmol) in 3 mL toluene solution to initiate the terpolymerization reaction. After 30 min of polymerization at 50 $^{\circ}\text{C}$ and constant ethylene pressure (20 psi), the reaction was quenched by acetone and filtered, washed extensively with acetone to remove residual monomer and then dried under vacuum at room temperature for 12 h.

Functional Group Interconversion. The incorporated bis(trimethylsilyl)amine ($-\text{N}(\text{SiMe}_3)_2$) groups in the co- and ter-polymers were further converted to the desired $-\text{NR}_2$ and $-\text{NR}_3^+\text{Cl}^-$ groups (R: H, CH_3 , and C_3H_7). One example is to interconvert ethylene/ $\text{C}_x\text{N}(\text{SiMe}_3)_2$ copolymer into various PE- NR_2 copolymers. About 1 g of ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2$ copolymer was suspended in 50 mL of THF at 50 $^{\circ}\text{C}$ before adding dropwise 2 N methanolic hydrogen chloride solution. The mixture was stirred for 4 h at 50 $^{\circ}\text{C}$, and then poured into 1 N methanolic NaOH solution. The resulting polymer was collected by filtration and washed with 1 M aqueous ammonia and water under a nitrogen atmosphere. After drying at 50 $^{\circ}\text{C}$ under vacuum for overnight, the resulting PE- NH_2 copolymer was obtained with quantitative yield. The pendant NH_2 groups in PE were further alkylated to PE- $\text{N}(\text{CH}_3)_2$ and PE- $\text{N}(\text{iso-C}_3\text{H}_7)_2$ copolymers using various alkyl iodides. In a typical example, 1 g of PE- NH_2 copolymer was suspended in 50 mL of dry isopropyl alcohol in the presence of 2.76 g of potassium carbonate (0.02 mol) under N_2 . The solution was refluxed for 1 h and then 1.51 g of 2-iodopropane (0.01 mol) was added and the whole solution was stirred under reflux for 5 days. The resulting polymer was collected by filtration and washed with THF, 1 M aqueous ammonia and water subsequently under nitrogen atmosphere. After vacuum-drying at room temperature for overnight, the resulting PE- $\text{N}(\text{iso-C}_3\text{H}_7)_2$ copolymer was obtained with quantitative yield. Similar experimental procedures were carried out in ethylene/ $\text{C}_x\text{N}(\text{SiMe}_3)_2$ /diene terpolymer. However, the terpolymer was usually solution-casted into film, then thermally cross-linked to form the corresponding cross-linked terpolymer film, before carrying out amino group interconversion under solid state conditions. As will be discussed, the amino group reactions are also very effective in film form.

Membrane Preparation and Evaluation. Membranes were prepared by casting a viscous xylene solution of ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2$ copolymer or ethylene/ $\text{C}_x\text{N}(\text{SiMe}_3)_2$ /diene terpolymer onto a Teflon substrate using an Elcometer 4340 Automatic Film Applicator at an elevated temperature, assuring no precipitation of the polymer due to crystallization of the PE segments. To avoid air bubbles, films were casted several times by gradually increasing the film thicknesses. The resulting solution-casted films (size 4 in. \times 6 in.) were heated at 110 $^{\circ}\text{C}$ for 2 h to remove the remaining solvent. Some films were further compressed at 150 $^{\circ}\text{C}$ under a pressure of 24000 psi to remove any defects and obtain a uniform thickness. In the ethylene/ $\text{C}_x\text{N}(\text{SiMe}_3)_2$ /diene terpolymer case, the membranes were further treated at 220 $^{\circ}\text{C}$ for 2 h under vacuum to complete the cross-linking reaction. The $-\text{N}(\text{SiMe}_3)_2$ groups in the resulting membranes were then converted to the desired $-\text{NR}_2$ groups (R: H, CH_3 , and C_3H_7), following the previously discussed procedures. All films were soaked in 0.5 M HCl solution for 24 h to transfer all amine groups to ammonium salt ($-\text{NR}_3^+\text{Cl}^-$).

All membranes were characterized with the degree of water swelling (DS), water content (λ), ion exchange capacity (IEC), and ionic conductivity, all measured at ambient temperature. The DS value (g $\text{H}_2\text{O}/100$ g dry film) was determined by $(W_w - W_d)/W_d$, where W_w and W_d are the weight of a wet (equilibrated with water) and dry membrane, respectively. The water content (λ) is calculated based on a molar ratio of water to ammonium chloride. The IEC value is based on Cl^- concentration that was measured by chloride precipitation using an AgNO_3 solution and AgCl precipitation, with K_2CrO_4 as an end-point indicator. The membrane conductivity was measured in a clip-type conductivity cell (Figure S1 in the Supporting Information). Two titanium disk electrodes are applied to both sides of the membrane. Both compartments of the cell were filled with various solutions of a desired concentration. The conductivity measurements were performed by a two-electrode electrochemical impedance spectroscopy using the

Scheme 1. Two Parallel Synthetic Routes To Prepare PE- NR_3^+Cl^- and x-PE- NR_3^+Cl^- Membranes



Gamry Electrochemical Measurements system. The experimental details are discussed in the Supporting Information.

RESULTS AND DISCUSSION

Synthesis and Characterization of PE- NR_3^+Cl^- and x-PE- NR_3^+Cl^- Membranes. Scheme 1 illustrates two parallel synthesis routes to prepare PE- NR_3^+Cl^- membranes (V) and their cross-linked counterpart x-PE- NR_3^+Cl^- membranes (V'). The chemistry involves a metalocene-mediated polymerization of ethylene, bis(trimethylsilyl)amine-protected α,ω -amino-olefins [$\text{C}_x\text{N}(\text{SiMe}_3)_2$] (I), with or without diene cross-linkers (II), to obtain the intermediate ethylene/ $\text{C}_x\text{N}(\text{SiMe}_3)_2$ copolymer (III) and ethylene/ $\text{C}_x\text{N}(\text{SiMe}_3)_2$ /diene terpolymer (III'), respectively. The resulting PE copolymer (III) and terpolymer (III') intermediates contain various concentrations of pendant silane-protected amino groups, and few percentages of styrene moieties (cross-linkers)^{45,46} in the terpolymers. They are completely soluble in common organic solvents, and the silane-protected amino groups can be further modified into the desired $-\text{NR}_3^+\text{Cl}^-$ groups in solution or in solid state conditions with simple chemicals. However, due to the low solubility of PE polymers containing a high concentration of $-\text{NR}_3^+\text{Cl}^-$ groups (R: H, CH_3 , iso- C_3H_7) both PE copolymer (III) and terpolymer (III') intermediates were usually solution-casted into films with a thickness of 50–70 μm , followed by thermal cross-linking reaction in the PE terpolymer (III') cases. A subsequent functional group transformation reaction occurs in a solid state to obtain the desired PE- NR_3^+Cl^- (V) and x-PE- NR_3^+Cl^- membranes (V').

In the first step of metalocene-mediated polymerization reactions to prepare ethylene/ $\text{C}_x\text{N}(\text{SiMe}_3)_2$ copolymers (III) and ethylene/ $\text{C}_x\text{N}(\text{SiMe}_3)_2$ /diene terpolymers (III'), the suitable metalocene catalysts shall be free from interacting with $-\text{N}(\text{SiMe}_3)_2$ group and exhibit good reactivity toward α -olefin moieties in all three monomers, as well as performing selective mono- or chain-termination of diene monomers (II). In addition, it is essential to identify the most effective $\text{C}_x\text{N}(\text{SiMe}_3)_2$ and

Table 1. Summary of Metallocene-Mediated Co- and Terpolymerization Reactions between Ethylene, α,ω -Aminoolefins, and Dienes

run	catalyst ^a	polymerization condition			yield (g)	M_v^d (kg/mol)	polymer composition		
		ethylene (psi)	$[C_xN(SiMe_3)_2]^b$ (M)	diene ^c (M)			ethylene (mol %)	$[C_xN(SiMe_3)_2]^b$ (mol %)	diene ^c (mol %)
A-1	A	14	1.5 ($n = 3$)	0	3.0	153	100	0	0
A-2	A	14	0.5 ($n = 6$)	0	1.5	89	85.8	14.2	0
A-3	A	14	1.0 ($n = 6$)	0	1.0	73	77.9	22.1	0
A-4	A	14	1.5 ($n = 6$)	0	0.6	58	72.8	27.2	0
A-5	A	14	2.0 ($n = 6$)	0	0.4	46	69.0	31.0	0
B-1	B	14	1.5 ($n = 3$)	0	3.0	271	100	0	0
B-2	B	14	0.5 ($n = 6$)	0	1.8	148	85.9	14.1	0
B-3	B	14	1.0 ($n = 6$)	0	1.2	119	77.6	22.4	0
B-4	B	14	1.5 ($n = 6$)	0	0.7	97	74.6	25.4	0
B-5	B	14	2.0 ($n = 6$)	0	0.4	74	69.5	30.5	0
B-6	B	14	1.5 ($n = 11$)	0	0.2	46	91.4	8.6	0
C-1	A	14	0.5 ($n = 6$)	0.4 (DVB)	0.6	78	87.3	12.2	0.5 (DVB)
C-2	A	14	1.5 ($n = 6$)	0.4 (DVB)	0.5	49	73.0	26.6	0.4 (DVB)
C-3	A	14	2.0 ($n = 6$)	0.4 (DVB)	0.3	43	71.1	28.5	0.4 (DVB)
C-4	A	14	1.5 ($n = 6$)	0.4 (BSt)	0.8		cross-linked polymer		
C-5	A	14	1.5 ($n = 6$)	0.1 (BSt)	0.6	50	73.7	26.1	0.2 (BSt)
C-6	A	14	2.0 ($n = 6$)	0.1 (BSt)	0.4	43	70.8	29.0	0.2 (BSt)
D-1	B	14	0.5 ($n = 6$)	0.4 (DVB)	1.6	133	85.5	13.9	0.6 (DVB)
D-2	B	14	1.5 ($n = 6$)	0.4 (DVB)	0.6	101	69.7	29.8	0.5 (DVB)
D-3	B	14	2.0 ($n = 6$)	0.4 (DVB)	0.5	74	66.2	33.4	0.4 (DVB)
D-4	B	14	2.0 ($n = 6$)	0.4 (BSt)	0.4		cross-linked polymer		
D-5	B	14	2.0 ($n = 6$)	0.1 (BSt)	0.5	78	68.3	31.5	0.2 (BSt)
D-6	B	14	1.5 ($n = 6$)	0.1 (BSt)	0.6	97	71.7	28.1	0.2 (BSt)

^a Catalyst A: *rac*-Et(Ind)₂ZrCl₂/MAO. Catalyst B: *rac*-CH₂(3-*t*-Butyl-Ind)₂ZrCl₂/MAO. ^b 3-Bis(trimethylsilyl)aminopropylene ($n = 3$); 6-bis(trimethylsilyl)aminohexene ($n = 6$); 11-bis(trimethylsilyl)aminoundecene ($n = 11$). ^c 1,4-Divinylbenzene (DVB); 4-(3-butenyl)styrene (BSt). ^d Estimated by intrinsic viscosity of polymer/decalin dilute solution at 135 °C with the standard of polyether ($K = 6.2 \times 10^{-2}$ mL/g, and $\alpha = 0.7$).

diene comonomers for obtaining PE copolymers (III) and terpolymer (III') with high molecular weights and controllable amounts of amino groups and pendant styrenic moieties (cross-linkers). Table 1 summarizes four comparative reaction sets using *rac*-Et(Ind)₂ZrCl₂/MAO and *rac*-CH₂(3-*t*-Butyl-Ind)₂ZrCl₂/MAO catalysts that have been shown to have a good combination of free of catalyst poison, high reactivity toward α -olefin moieties, and selective monoinsertion of 1,4-divinylbenzene (DVB) or 3-butenylstyrene (BSt). Sets A and B compare ethylene/ α,ω -aminoolefin copolymerization using three functional comonomers, including 3-bis(trimethylsilyl)aminopropylene [$C_3N(SiMe_3)_2$], 6-bis(trimethylsilyl)aminohexene [$C_6N(SiMe_3)_2$], and 11-bis(trimethylsilyl)aminoundecene [$C_{11}N(SiMe_3)_2$], and two catalyst systems, respectively. The [$C_3N(SiMe_3)_2$] comonomer, having only 1 methylene spacer, did not engage in the copolymerization reaction; the short spacer may not be sufficient to prevent the amino group from interfering with the metallocene-mediated α -olefin insertion. On the other hand, the [$C_{11}N(SiMe_3)_2$] comonomer is too big to effectively compete with the small ethylene during the copolymerization. The maximum [$C_{11}N(SiMe_3)_2$] content in the copolymer was 8.6 mol % (run B-6). It is interesting to note that there was a paper⁴⁷ reporting a similar ethylene/ $C_{11}N(SiMe_3)_2$ copolymerization by *rac*-Me₂Si(Benz[e]Ind)₂ZrCl₂/MAO catalyst, which produced

only insoluble copolymer with a maximum 3.7 mol % [$C_{11}N(SiMe_3)_2$] content.

Evidently, the most suitable amino-comonomer is [$C_6N(SiMe_3)_2$] having four methylene spacers. Although the catalyst activity systematically decreases with the increase of the [$C_6N(SiMe_3)_2$] comonomer feed, the comonomer content in the copolymer increases correspondingly. We have prepared soluble ethylene/ $C_6N(SiMe_3)_2$ copolymers (III) with up to 30 mol % [$C_6N(SiMe_3)_2$] contents in both catalyst systems. In detail, by comparing every comparative run (A-2 vs B-2, A-3 vs B-3, A-4 vs B-4, A-5 vs B-5) between two catalyst systems, the *rac*-CH₂(3-*t*-Butyl-Ind)₂ZrCl₂/MAO catalyst shows better performance with higher yields, higher $C_6N(SiMe_3)_2$ incorporation, and higher copolymer molecular weight.

Sets C and D show the results of ethylene/ $C_6N(SiMe_3)_2$ /diene terpolymerization reactions using the same two catalyst systems. In addition to select the $C_6N(SiMe_3)_2$ functional comonomer, the focus was shifted to the monoinsertion of diene comonomers (i.e., DVB and BSt), which shall result in soluble ethylene/ $C_6N(SiMe_3)_2$ /diene terpolymers (III') containing pendant styrenic moieties (cross-linkers). It is interesting to note that both *rac*-Et(Ind)₂ZrCl₂ and *rac*-CH₂(3-*t*-Butyl-Ind)₂ZrCl₂ catalysts prepare ethylene/ $C_6N(SiMe_3)_2$ /DVB terpolymers with good solubility, but only forming soluble

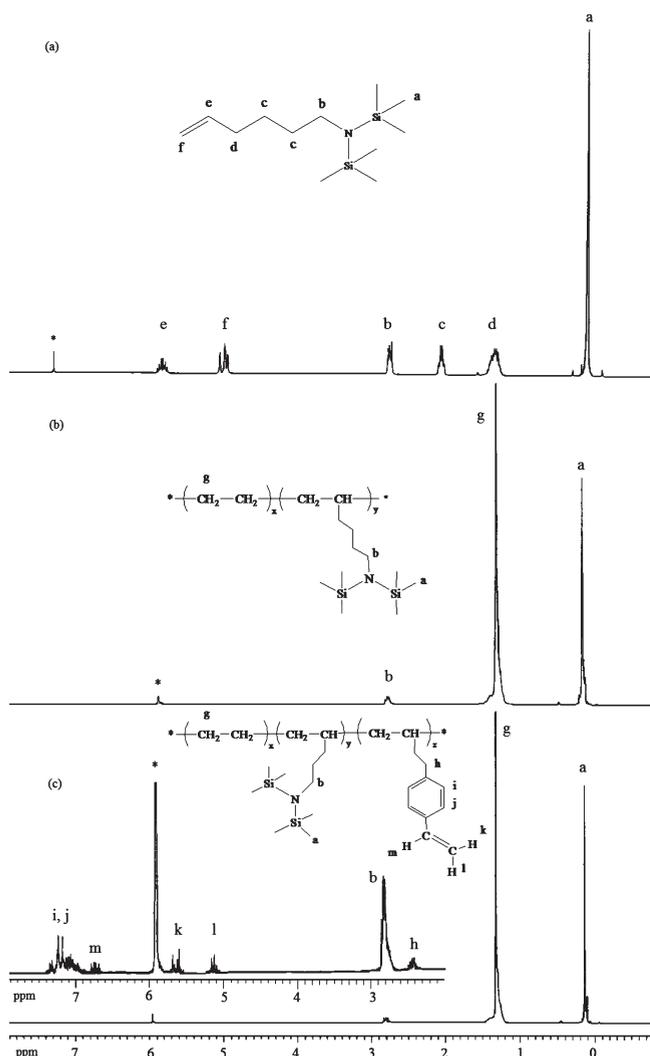


Figure 1. ^1H NMR spectra of (a) $\text{C}_6\text{N}(\text{SiMe}_3)_2$ comonomer, (b) ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2$ copolymer containing 14.2 mol % $\text{C}_6\text{N}(\text{SiMe}_3)_2$ units (run A-2), and (c) ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2$ /DVB terpolymer having 12.2 mol % $\text{C}_6\text{N}(\text{SiMe}_3)_2$ and 0.5 mol % DVB contents (run C-1). (Inset: the chemical shift assignments for $\text{C}_6\text{N}(\text{SiMe}_3)_2$ comonomer.)

ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2$ /BSt terpolymers with a relatively low BSt concentration (runs C-5, C-6, D-5, and D-6). With the increased BSt concentrations, both catalysts produce insoluble ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2$ /BSt terpolymers (runs C-4 and D-4). The double-enchainment activity may be slightly higher in the BSt case than in the DVB case, which may be associated with the kinetic availability of the pendant styrene moieties after mono-enchainment. The flexible pendant styrene moieties in the BSt case may be more inviting to engage in a second enchainment reaction, especially in these soluble (completely amorphous) PE terpolymers with a high concentration of comonomer units. Note that our previous results⁴⁶ showed no detectable cross-linking reaction in propylene/BSt copolymerization reactions, which form PP copolymers with high crystallinity that may prevent the second enchainment. However, the BSt asymmetric diene, containing both α -olefin and styrenic olefin, shows a higher incorporation than the DVB symmetric diene, due to higher catalyst reactivity toward the α -olefin moiety. Furthermore, the

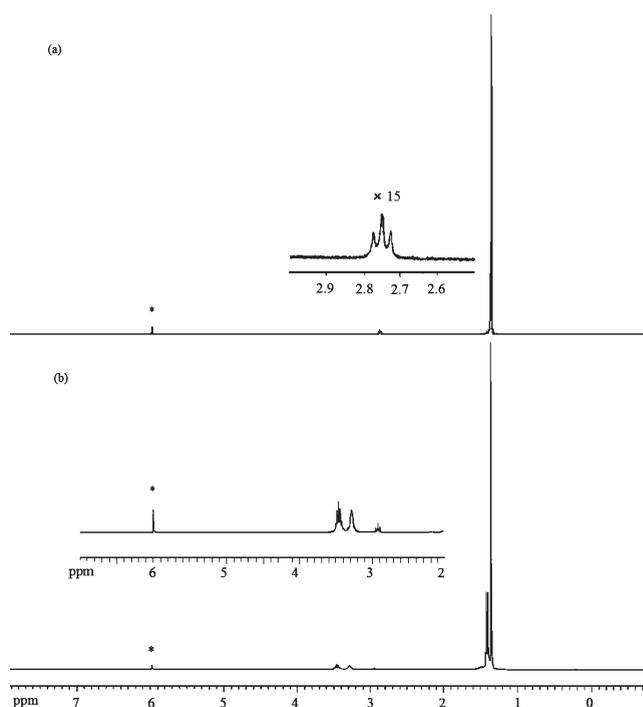


Figure 2. ^1H NMR spectra of (a) PE- NH_2 copolymer containing 3.2 mol % of $-\text{NH}_2$ groups and (b) PE- $\text{N}(\text{iso-C}_3\text{H}_7)_2$ copolymer containing 14.2 mol % of $-\text{N}(\text{iso-C}_3\text{H}_7)_2$ groups.

flexible pendant styrene moieties in the polymer chain are essential to enhance an interchain cyclo-addition reaction⁴⁸ that offers high cross-linking efficiency. With all experimental results and considerations, all cross-linked x-PE- NR_3^+Cl^- membranes (discussed later) are based on ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2$ /BSt terpolymers with low BSt contents, prepared by the *rac*- $\text{CH}_2(3\text{-tert-Butyl-Ind})_2\text{ZrCl}_2/\text{MAO}$ catalyst system.

Figure 1 compares three ^1H NMR spectra between $\text{C}_6\text{N}(\text{SiMe}_3)_2$ functional comonomer, an ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2$ copolymer (run A-2), and an ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2$ /DVB terpolymer (run C-1). Figure 1a exhibits the expected chemical shifts and intensities for a pure $\text{C}_6\text{N}(\text{SiMe}_3)_2$ comonomer (with the inserted chemical structure and chemical shift assignments). Figure 1b shows a major peak at 1.35 ppm, corresponding to ethylene units, and two chemical shifts at $\delta = 2.77$ ppm (t, 2 H, $-\text{CH}_2-\text{N}$) and $\delta = 0.21$ (s, 18 H, $-\text{NSi}_2(\text{CH}_3)_6$) indicating 14.2 mol % $\text{C}_6\text{N}(\text{SiMe}_3)_2$ content in the ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2$ copolymer (run A-2). Figure 1c displaces the expected chemical shifts at $\delta = 2.77$, 1.35, and 0.21 ppm in the ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2$ /DVB (87.3/12.2/0.5 mol ratio) terpolymer (run C-1). In addition, the expanded spectrum (inserted) also show several minor chemical shifts at 5.2 and 5.7 ppm (doublet, $\text{CH}=\text{CH}_2$) and 6.7 ppm (doublet of doublet, $\text{CH}=\text{CH}_2$); aromatic proton peaks occur between 7.1 and 7.4 ppm (C_6H_4), corresponding to the incorporated DVB units (0.5 mol %). The peak intensity ratios indicate that the mole ratio of the vinyl group to the phenyl group is near unity, implying mono-enchainment of DVB units during the metallocene-mediated polymerization.

The silane-protected amino groups in the ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2$ copolymer were further interconverted to various amino groups. For the solution ^1H NMR study, polymer modifications were carried out in solution, and all resulting polymers maintained good solubility in common organic solvents. Figure 2

shows ^1H NMR spectra of two PE copolymers containing 3.2 mol % of $-\text{NH}_2$ groups and 14.2 mol % of $-\text{N}(\text{iso-C}_3\text{H}_7)_2$ groups, respectively. Because of strong polar group interactions, the PE- NH_2 copolymer with the higher $-\text{NH}_2$ content (>4 mol %) becomes insoluble in common organic solvents. In Figure 2a, the combination of a complete disappearance of a sharp peak at $\delta = 0.21$ ppm ($-\text{NSi}_2(\text{CH}_3)_6$) and the coexistence of the chemical shift at $\delta = 2.77$ ppm (t, 2 H, $-\text{CH}_2-\text{NH}_2$)—a similar peak in the starting ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2$ copolymer—indicates a successful deprotection reaction of bis(trimethylsilyl)amino groups by HCl to form NH_2 groups. Figure 2b shows a ^1H NMR spectrum of the PE- $\text{N}(\text{iso-C}_3\text{H}_7)_2$ copolymer prepared from the ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2$ copolymer containing 14.2 mol % of $\text{C}_6\text{N}(\text{SiMe}_3)_2$ comonomer units (run A-2). The functional group modification involves two steps: the same silane deprotection reaction to form the NH_2 group and the subsequent alkylation of the $-\text{NH}_2$ group to the $-\text{N}(\text{iso-C}_3\text{H}_7)_2$ group. Although both the starting ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2$ and final PE- $\text{N}(\text{iso-C}_3\text{H}_7)_2$ copolymers are soluble in common organic solvents, the PE- NH_2 intermediate having 14.2 mol % NH_2 was insoluble. In other words, most of the reaction processes were under a heterogeneous reaction condition. In Figure 2b, the absence of a chemical shift at $\delta = 0.21$ ppm [$-\text{NSi}_2(\text{CH}_3)_6$] implies effective silane deprotection in forming $-\text{NH}_2$ groups, despite the insoluble PE- NH_2 copolymer. There are several new chemical shifts, including $\delta = 1.41$ ppm ($-\text{CH}_2-\text{N}[\text{CH}(\text{CH}_3)_2]_2$), 2.9 ppm ($-\text{CH}_2-\text{NH}[\text{CH}(\text{CH}_3)_2]$), 3.3 ppm ($-\text{CH}_2-\text{N}[\text{CH}(\text{CH}_3)_2]_2$), and 3.5 ppm ($-\text{CH}_2-\text{N}[\text{CH}(\text{CH}_3)_2]_2$). Evidently, the second step of the alkylation reaction of $-\text{NH}_2$ groups was not completed. There are approximately 10% monoalkylation moieties ($-\text{NH}[\text{CH}(\text{CH}_3)_2]$) coexisting in the PE- $\text{N}(\text{iso-C}_3\text{H}_7)_2$ copolymer. Overall, the amino functional group interconversion reactions under heterogeneous condition are quite effective, which is significant in the preparation of cross-linked x-PE- NR_3^+Cl^- membranes.

Evaluation of PE- NR_3^+Cl^- and x-PE- NR_3^+Cl^- Membranes. On the basis of the polymerization results (Table 1), the *rac*- $\text{CH}_2(3\text{-tert-Butyl-Ind})_2\text{ZrCl}_2/\text{MAO}$ catalyst system was applied to prepare membrane precursor polymers, ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2$ copolymers (III) and ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2/\text{BSt}$ terpolymers (III'), with a combination of high molecular weight, high $\text{C}_6\text{N}(\text{SiMe}_3)_2$ comonomer content, and only 0.2 mol % BSt units in the terpolymer, in order to ensure good solubility. Both precursor polymers were solution-casted into films (thickness: 50–70 μm). During the film drying step under elevated temperatures, the ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2/\text{BSt}$ terpolymers also engaged in a cross-linking reaction by cyclo-addition⁴⁸ between two pendant styrene units, resulting in cross-linked x-PE- $\text{N}(\text{SiMe}_3)_2$ films. The combination of a high molecular weight terpolymer and effective cross-linking reaction is crucial to obtain a complete 3-D network structure. The pendant $-\text{N}(\text{SiMe}_3)_2$ groups were then deprotected to form $-\text{NH}_2$ groups by treating them in an aqueous HCl solution. Under acidic conditions, they converted into PE- NH_3^+Cl^- and x-PE- NH_3^+Cl^- membranes with high purities. A further solid-state treatment of $-\text{NH}_2$ groups with alkyl iodine reagents was also carried out to obtain PE- NR_3^+Cl^- (V) and x-PE- NR_3^+Cl^- (V') membranes (R: CH_3 and $\text{iso-C}_3\text{H}_7$), with different alkylation efficiencies (discussed later). Table 2 summarizes physical properties of several PE- NR_3^+Cl^- and x-PE- NR_3^+Cl^- membranes containing high concentrations of pendant $-(\text{CH}_2)_4-\text{NR}_3^+\text{Cl}^-$ groups. For comparison, several commercially available Cl^- ion

conductive membranes were also evaluated side-by-side. They include four Neosepta type AEMs produced by Tokuyama Soda and a Selemion high temperature AEM produced by Asahi Glass. They are based on cross-linked styrene/divinylbenzene copolymers with various concentrations of quaternary ammonium chloride groups and cross-linking densities, with or without Supporting Information. However, their detailed structural compositions are not available.

As shown in Table 2, all Neosepta type commercial membranes have relatively low IEC values (between 1 and 2 mmol/g) and low water swelling with a DS value below 30%. The lowest one is the ACM membrane with only 1 mmol/g of Cl^- ion concentration and 7.5% DS value, which also reflects in low ionic conductivity. On the other hand, our PE- NR_3^+Cl^- and x-PE- NR_3^+Cl^- membranes show significantly higher IEC and DS values. The ion exchange capacity (IEC) of PE- NR_3^+Cl^- and x-PE- NR_3^+Cl^- membranes was not only measured by titration but also estimated from the $-\text{N}(\text{SiMe}_3)_2$ content of the polymers, measured by ^1H NMR. As summarized in Table 2, all membranes show an IEC value well above 2.5 mmol/g. In addition to high $-\text{NR}_3^+\text{Cl}^-$ content, the small ethylene mass also contributes to the high IEC value. Note that both IEC values in PE- NR_3^+Cl^- membrane (set B) are very close, only slightly lower in their titration values. However, there is a significant difference in the cross-linked x-PE- NR_3^+Cl^- membranes (set D)—the titration value is only about two-third of the estimated value. The results indicate that the interconversion of $-\text{N}(\text{SiMe}_3)_2$ groups in the non-cross-linked PE matrix was quite efficient. However, the same reaction in the cross-linked PE matrix was much more difficult. The limited swelling in the cross-linked matrix may have slowed down the diffusion of chemical reagents and reduced the overall interconversion efficiency.

Figure 3 compares degree of water swelling (DS) and water content (λ) vs IEC for PE- NH_3^+Cl^- membranes at room temperature. Generally, the water swelling follows with the IEC value. When comparing membranes B-2, B-3, B-4-a, and B-5, with a systematic increase of NH_3^+Cl^- content in PE copolymers, the DS value increases from 29 to 240%, as well as λ value from 5.2 to 27.8. The degree of hydration per ammonium chloride (λ) increases with the ammonium chloride concentration, indicating a morphological change to become more continuous domains (channels) in PE- NH_3^+Cl^- to ease water swelling. The PE- NH_3^+Cl^- membrane with 30.5 mol % $-\text{NH}_3^+\text{Cl}^-$ groups (sample B-5) absorbs too much water (DS value: 240%) and almost loses its structure integrity. High water uptake also dilutes the ion concentration and results in low ionic conductivity (discussed later). On the other hand, by introducing a very small amount (~ 0.2 mol %) of BSt cross-linker units in the similar PE copolymer (set D-6) the water swelling dramatically reduces. As shown in Figure 4 they are scaled back to 30% for x-PE- NH_3^+Cl^- (sample D-6-a), 57% for x-PE- $\text{N}(\text{CH}_3)_3^+\text{Cl}^-$ (sample D-6-b), and 45% for x-PE- $\text{N}(\text{iso-C}_3\text{H}_7)_3^+\text{Cl}^-$ (sample D-6-c). It is also interesting to note that the $-\text{N}(\text{CH}_3)_3^+\text{Cl}^-$ group shows a higher hydration number than both the $-\text{NH}_3^+\text{Cl}^-$ and $-\text{N}(\text{iso-C}_3\text{H}_7)_3^+\text{Cl}^-$ groups in both cross-linked (set D-6) and non cross-linked (set B-4) membranes.

In addition, these cross-linked membranes exhibit very good (tough) mechanical strength. Table 3 shows tensile properties of two x-PE- NH_3^+Cl^- membranes (x-D-5 and x-D-6), derived from D-5 and D-6 ethylene/ $\text{C}_6\text{N}(\text{SiMe}_3)_2/\text{BSt}$ terpolymers (Table 1), respectively. As discussed before, during the membrane preparation, both D-5 and D-6 membranes experienced

Table 2. Summary of Physical Properties of PE-NR₃⁺Cl⁻, x-PE-NR₃⁺Cl⁻, and Several Commercial Anion-Conductive Membranes

samples	polymer composition			ionic conductivity (mS/cm)					
	ethylene/C ₆ ²⁻ NR ₂ /BST (mole ratio)	R group	IEC ^a (mmol/g)	IEC ^b (mmol/g)	DS ^c (%)	λ ^d value	2 N HCl	2 N HCl- 0.2N CuCl	
B-2	85.9/14.1/0	H	3.3	3.1	29	5.2	2.5	0.1	
B-3	77.6/22.4/0	H	4.3	3.6	82	12.6	14.6	0.3	
B-4-a	74.6/25.4/0	H	4.6	4.0	126	17.5	30.1	3.6	
B-4-b	74.6/25.4/0	CH ₃	4.1	3.9	135	19.2	106.1	62.9	
B-4-c	74.6/25.4/0	iso-C ₃ H ₇	3.3	3.1	97	17.4	57.6	47.3	
B-5	69.5/30.5/0	H	5.1	4.8	240	27.8	18.2	0.8	
D-6-a	71.7/28.1/0.2	H	4.9	3.1	30	5.4	12.4	5.6	
D-6-b	71.7/28.1/0.2	CH ₃	4.3	2.9	57	10.9	119.6	78.8	
D-6-c	71.7/28.1/0.2	iso-C ₃ H ₇	3.4	2.6	45	9.6	27.7	21.1	
AHA ^e	no backing material (205 μm)		-	2.0	22	6.1	12.61	0.66	
AMX ^e	with backing fabric (140 μm)		-	1.5	28	10.4	7.65	2.06	
AM-3 ^e	highly cross-linked (150 μm)		-	1.7	20	6.5	4.45	0.25	
ACS ^e	monoanion permselective (110 μm)		-	1.7	25	8.2	5.30	0.22	
ACM ^e	cross-linked (100um)		-	1.0	7.5	4.2	4.59	0.005	
AHT ^f	high temperature membrane (350 μm)		-	1.8	10	3.1	4.82	0.11	

^a IEC value (ion exchange capacity; mmolCl/g of dry polymer film) is estimated from ¹H NMR spectrum. ^b IEC value is measured by titration. ^c Degree of swelling: g H₂O/100 g dry polymer film. ^d Water content λ (molar ratio of water to ammonium chloride). ^e Membrane manufacturers: Tokuyama Soda. ^f Membrane manufacturers: Asahi Glass.

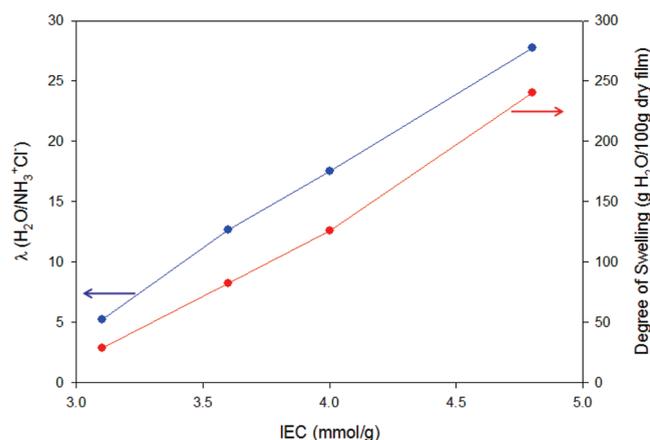


Figure 3. Water content (λ) and degree of water swelling (DS) vs IEC value for PE-NH₃⁺Cl⁻ membranes (samples B-2, B-3, B-a, and B-5 in Table 2) at room temperature.

temperature of up to 150 °C for a short period of time, which may have resulted in a partially cross-linked structure. On the other hand, x-D-5 and x-D-6 membranes were further treated at 220 °C for 2 h to complete the cross-linking reaction. The tensile strength at yield of the x-D-6 membrane reaches about 20 MPa with an elongation at break of 181%, which is more than sufficient to function as an ion conductive membrane in most electrochemical assemblies.

Conductivity of the membrane was measured in 2 N HCl aqueous solution and 2 N HCl–0.2 N CuCl aqueous solution to model the catholyte and anolyte solutions in the CuCl–HCl electrolyzer used for hydrogen production.^{43,44} All membranes were equilibrated in the same solutions for 20 h before we began measurements. The conductivity is impacted by the combination of the IEC value, water swelling, and ion mobility. All Neosepta

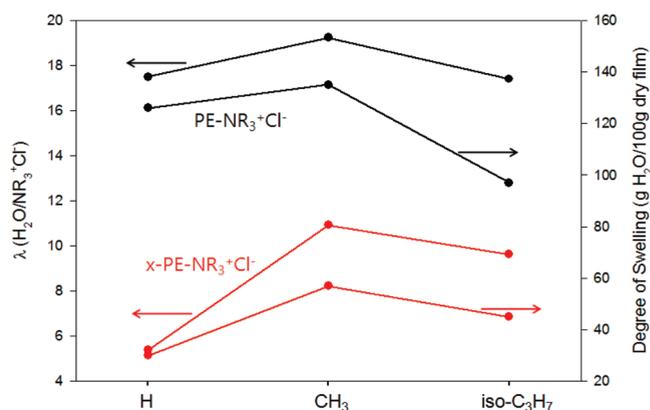
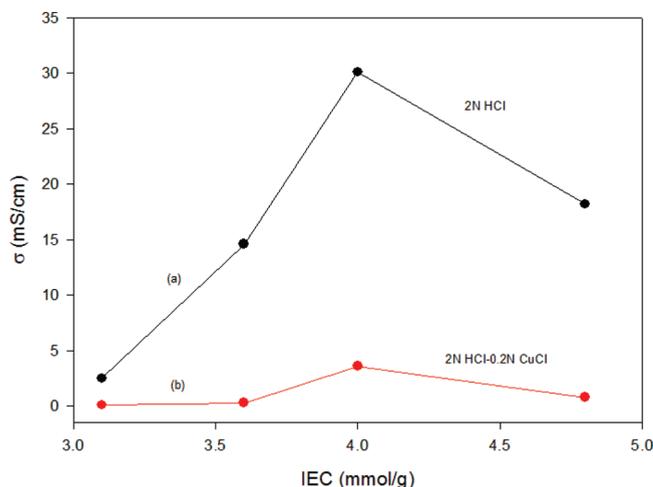


Figure 4. Comparison of water content (λ) and degree of water swelling (DS) between PE-NR₃⁺Cl⁻ and x-PE-NR₃⁺Cl⁻ (R: H, CH₃, iso-C₃H₇) membranes at room temperature.

type commercial membranes (Table 2) show moderate ionic conductivity (4–13 mS/cm) in 2 N HCl solution and significantly lower conductivity (0.11–2.06 mS/cm) in 2 N HCl–0.2 N CuCl solution. The AHA membrane shows the highest conductivity (12.61 mS/cm) in 2 N HCl solution among the tested commercial AEMs. The AMX membrane has a similar composition with AHA but with additional reinforcement to provide higher mechanical strength and reduced thickness. It demonstrated a small reduction of the ionic conductivity (7.65 mS/cm) in 2 N HCl solution but exhibited the highest conductivity (2.06 mS/cm) in 2 M HCl + 0.2 M CuCl solution among the tested membranes. The AM-3 membrane is highly cross-linked. In spite of moderate conductivity, a positive effect of high cross-linking on the membrane performance is to decrease the Cu permeability. The ACS membrane is designed as a monoanion permselective AEM, which allows for the selective

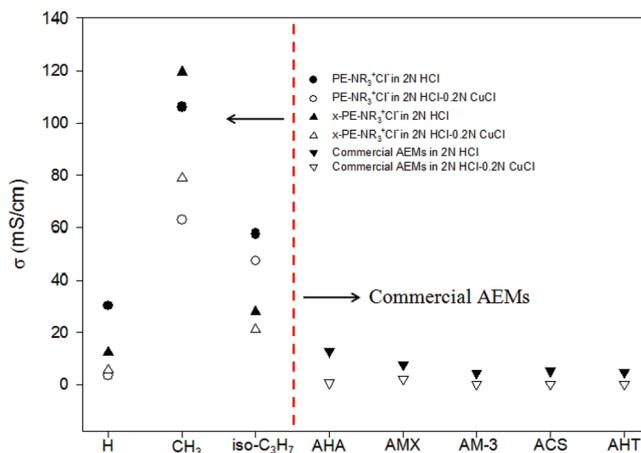
Table 3. Tensile Properties of Two PE-NH₃⁺Cl⁻ Membranes before and after Thermal Treatment

membranes	tensile modulus (MPa)	tensile strength at yield (MPa)	elongation (%)
D-5	233 ± 52	10 ± 2	210 ± 42
x-D-5	311 ± 50	19 ± 2	141 ± 30
D-6	273 ± 50	12 ± 2	255 ± 44
x-D-6	358 ± 53	20 ± 2	158 ± 30

**Figure 5.** Comparison of Cl⁻ ion conductivity vs IEC of PE-NH₃⁺Cl⁻ membranes (samples B-2, B-3, B-4-a, and B-5 in Table 2) with various concentrations of -NH₃⁺Cl⁻ groups in (a) 2 N HCl and (b) 2 N HCl-0.2 N CuCl solutions at room temperature.

transport of chloride in preference to multivalent anions. The AHT, a Selemion membrane designed for high temperature applications, was also tested. It shows relatively low Cl⁻ ion conductivity, especially in 2 N HCl-0.2 N CuCl solution. Note that the Cl⁻ ion conductivity in 2 N HCl-0.2 N CuCl solution is always lower than that in 2 N HCl solution, which may be due to the association between Cu⁺ species and some amino groups in the polymer, therefore reducing the quaternary ammonium chloride (Cl⁻ carrier) concentration. In fact, during the measurement in 2 N HCl-0.2 N CuCl solution the starting clear solution in the cathode gradually changes to a blue hue in all cases, indicating some type of Cu²⁺ species diffusion throughout the commercial membranes.

Most of our PE-NR₃⁺Cl⁻ and x-PE-NR₃⁺Cl⁻ membranes, containing >25 mol % of NR₃⁺Cl⁻ content (Table 2), show significantly higher ionic conductivity in both 2 N HCl and 2 N HCl-0.2 N CuCl solutions. Figure 5 compares several PE-NH₃⁺Cl⁻ membranes (B-2, B-3, B-4-a, and B-5) with various IEC values. Generally, the higher -NH₃⁺Cl⁻ concentration will have the higher conductivity, with the conductivity increasing more than one order to 30.1 mS/cm in 2 N HCl solution and 3.6 mS/cm in 2 N HCl-0.2 N CuCl solution when the IEC value increases from 3.1 (B-2) to 4.0 mmol/g (B-4-a). The combination of DS, λ, and conductivity data implies a morphology change to form more continuous ion conductive domains embedded in the hydrophobic PE matrix. In fact, the further increase of the IEC value (sample B-5) results in lower

**Figure 6.** Comparison of Cl⁻ ion conductivity between PE-NR₃⁺Cl⁻ (samples B-4-a, B-4-b, and B-4-c), x-PE-NR₃⁺Cl⁻ (D-6-a, D-6-b, and D-6-c) membranes and several commercial membranes in 2 N HCl and 2 N HCl-0.2 N CuCl solutions at room temperature.

conductivity, due to the higher IEC leads to higher water swelling that dilutes the concentration of the Cl⁻ ion. In addition, high water swelling significantly weakens the mechanical properties of the B-5 membrane. Overall, it seems that the PE-NH₃⁺Cl⁻ with about 25 mol % (sample B-4-a) is a suitable composition for the anion membrane. In the subsequent study, we decided to further investigate this specific composition range with some structure alternations, including the NR₃⁺Cl⁻ group (with R: H, CH₃, and iso-C₃H₇) and cross-linking feature in the PE matrix.

Figure 6 compares the ionic conductivity for two sets of PE-NR₃⁺Cl⁻ (B-4-a, B-4-b, and B-4-c) and x-PE-NR₃⁺Cl⁻ (D-6-a, D-6-b, and D-6-c) membranes in 2 N HCl and 2 N HCl-0.2 N CuCl solutions, respectively. In each set, they have the same -NR₃⁺Cl⁻ concentration, but a changing R group from H, CH₃, to iso-C₃H₇. It is clear that the conductivity shows strong dependence on R groups, especially in 2 N HCl-0.2 N CuCl solution. Evidently, the bulkier R groups significantly reduce the ionic association between the Cl⁻ ion and stationary -NR₃⁺ group, therefore increasing Cl⁻ ion mobility and the ionic conductivity. In the B-4 set, the PE-N(CH₃)₃⁺Cl⁻ membrane (B-4-b) exhibits impressive conductivities of 106.1 mS/cm in 2 N HCl solution and 62.9 mS/cm in 2 N HCl-0.2 N CuCl solution; both are 1 order of magnitude higher than that shown in commercial membranes. However, when further increasing the size of the R group to the bulkier iso-C₃H₇ group, the IEC value decreases along with its conductivity, due to the dilution effect. A similar trend was also observed in x-PE-NR₃⁺Cl⁻ membranes (set D-6). As discussed, cross-linking dramatically reduces water swelling and increases ion concentration, which is helpful in ion conductivity. However, cross-linking may also reduce the ion mobility. The commercial cross-linked AM-3 membrane shows a slight reduction in conductivity from the corresponding non cross-linked AHA membrane. When comparing two parallel D-6 and B-4 sets with similar -NR₃⁺Cl⁻ (R: H, CH₃, and iso-C₃H₇) concentration, but with or without cross-linking, the conductivity difference is relatively small. In fact, the x-PE-N(CH₃)₃⁺Cl⁻ membrane (D-6-b) shows slightly higher conductivities of 119.6 mS/cm in 2 N HCl solution and 78.8 mS/cm in 2 N HCl-0.2 N CuCl solution. High mobility of the Cl⁻ ion in the flexible side chains may

minimize the negative ion mobility effect induced by cross-linking. Evidently, the x-PE-N(CH₃)₃⁺Cl⁻ membrane (D-6-b), containing 28.1 mol % of C₆N(CH₃)₃⁺Cl⁻ units, possesses the structure that results in the best combination of high Cl⁻ ion concentration and mobility.

All four PE-N(CH₃)₃⁺Cl⁻ (B-4-b), PE-N(iso-C₃H₇)₃⁺Cl⁻ (B-4-c), x-PE-N(CH₃)₃⁺Cl⁻ (D-6-b), x-PE-N(iso-C₃H₇)₃⁺Cl⁻ (D-6-c) membranes display close ionic conductivities in 2 N HCl and 2 N HCl–0.2 N CuCl solutions. In addition, the solution in the cathode side remains colorless during the measurement in 2 N HCl–0.2 N CuCl solution, indicating no Cu²⁺ species diffusion through the membrane. The bulky R groups may significantly reduce the association between Cu species and amino groups, therefore providing selective Cl⁻ ion diffusion throughout the membranes. This explanation is also in agreement with a phenomenon observed in PE-NH₃⁺Cl⁻ (B-4-a) and x-PE-NH₃⁺Cl⁻ (D-6-a) membranes, with the ionic conductivity in 2 N HCl–0.2 N CuCl solution gradually decreasing with the measurement time; this is because the Cu species slowly consumes the ammonium salt.

CONCLUSION

A new class of high performance polyethylene-based anion exchange membranes has been developed, which contains flexible ammonium chloride (–NR₃⁺Cl⁻) groups and a cross-linking PE network structure. The combination of direct metallocene-mediated copolymerization and effective functional group interconversions in film form allows us to prepare a wide range of well-defined x-PE–NR₃⁺Cl⁻ membranes with good mechanical strength and relatively low thickness (50–70 μm; without backing material). A systematic structure–property study on both PE–NR₃⁺Cl⁻ and x-PE–NR₃⁺Cl⁻ membranes was performed in order for us to understand the PE structure's effect (concentration of –NR₃⁺Cl⁻ groups, R in the quaternary ammonium group, cross-linking density, etc.) on the water uptake and ionic conductivity. The most desirable x-PE–NR₃⁺Cl⁻ membrane contains 28.1 mol % –N(CH₃)₃⁺Cl⁻ groups in the flexible side chains and possesses a fully cross-linked hydrophobic PE matrix (formed by 0.2 mol % BSt units). This membrane offers an excellent combination of desirable properties, including adequate water swelling, high thermal stability, and exceptionally high ionic conductivities of 119.6 mS/cm in 2 N HCl solution and 78.8 mS/cm in 2 N HCl–0.2 N CuCl solution (one order higher than all commercially available AEM membranes).

ASSOCIATED CONTENT

S Supporting Information. Membrane evaluation procedure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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