

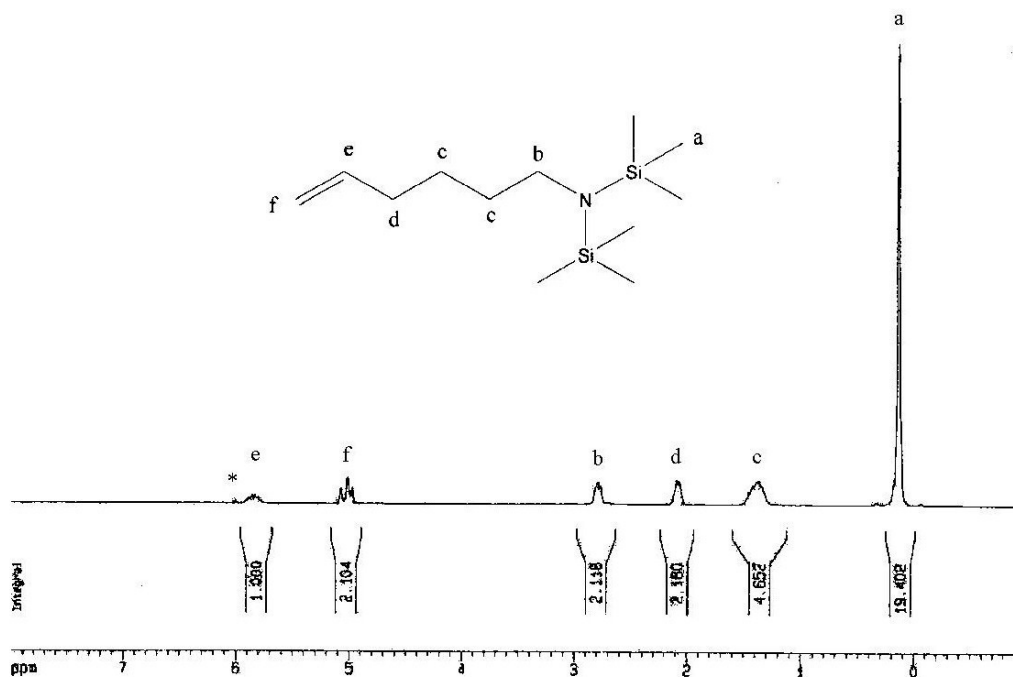
## Supporting Information

### Controlled Functionalization of Poly(4-methyl-1-pentene) Films for High Energy Storage Applications

*Min Zhang, Lin Zhang,\* Meng Zhu, Yiguang Wang,\* Nanwen Li, Zhijie Zhang, Quan Chen, Linan An, Yuanhua Lin\* and Cewen Nan*

#### 1. Synthesis of 6-bis(trimethylsilyl)amino-1-hexene

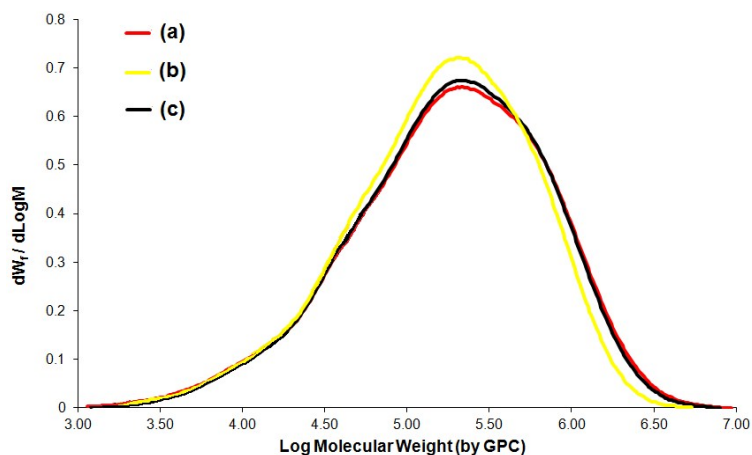
6-Bis(trimethylsilyl)amino-1-hexene was prepared in two reaction steps. In a 500 mL flask equipped with a magnetic stirring bar, 50 g (0.299 mol) of lithium bis(trimethylsilyl)amide dissolved in 200 mL of THF was slowly added into a mixture of 25 mL (0.329 mol) of chloromethyl methyl ether and 50 mL 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 CaH<sub>2</sub> to obtain 6-bis(trimethylsilyl)amino-1-hexene in 73% yield. <sup>1</sup>H NMR (300 MHz, 25 °C, CDCl<sub>3</sub>): 5.81 (m, 1 H, -CH=CH<sub>2</sub>), 5.07 (m, 2 H, -CH=CH<sub>2</sub>), 2.77 (t, 2 H, -CH<sub>2</sub>-N-), 2.14 (m, 2 H, -CH<sub>2</sub>-CH=CH<sub>2</sub>-), 1.38 (m, 4 H, -CH<sub>2</sub>-CH<sub>2</sub>-), 0.21 (s, 18 H, -NSi<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub>).



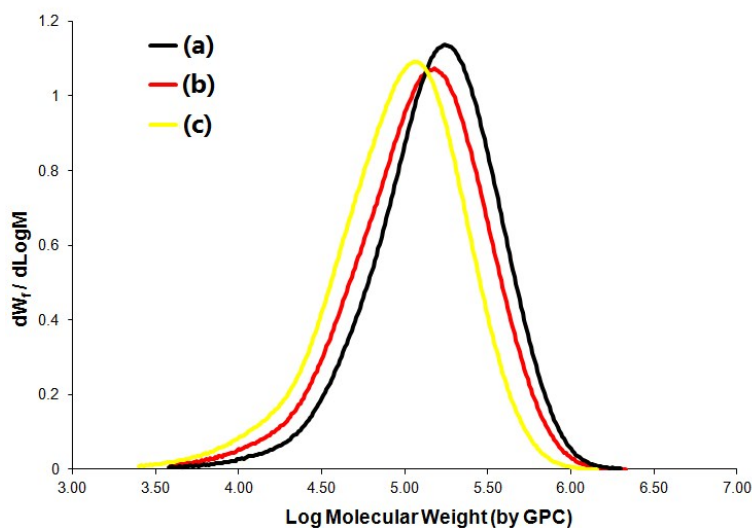
**Figure S1.**  $^1\text{H}$  NMR spectrum of 6-bis(trimethylsilyl)amino-1-hexene in 1,1,2,2-tetrachloroethane- $d_2$  at 25 °C.

## 2. GPC measurement

The polymer molecular weights were also analyzed on a PL-220 series high temperature gel permeation chromatography (GPC) unit equipped with four PLgel Mixed-A (20 $\mu\text{m}$ ) columns (Polymer Laboratory Inc.). The oven temperature was at 150 °C and the temperatures of autosampler's hot and the warm zones were at 135 °C and 130 °C respectively. The solvent 1, 2, 4-trichlorobenzene (TCB) containing ~200 ppm tris(2,4-di-tert-butylphenyl) phosphite (Irgafos 168) was nitrogen purged. The flow rate was 1.0 mL/min and the injection volume was 200  $\mu\text{l}$ . A 2 mg/mL sample concentration was prepared by dissolving the sample in  $\text{N}_2$  purged and preheated TCB (containing 200 ppm Irgafos 168) for 2.5 h at 160 °C with gentle agitation.



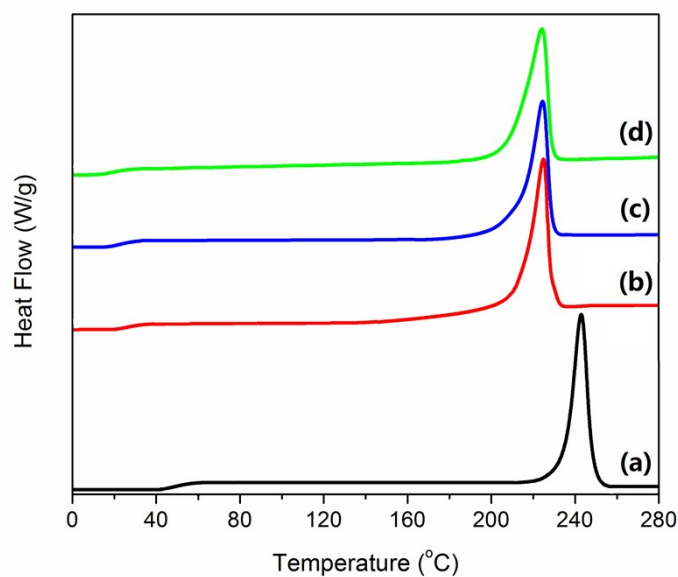
**Figure S2.** GPC molecular weight distribution overlay of three PMP copolymers with incorporation of (a) 1.9%, (b) 3.1% and (c) 4.5% by Ziegler-Natta catalyst.



**Figure S3.** GPC molecular weight distribution overlay of three PMP copolymers with incorporation of (a) 0%, (b) 2.2% and (c) 4.1% by metallocene catalyst.

### 3. DSC measurement

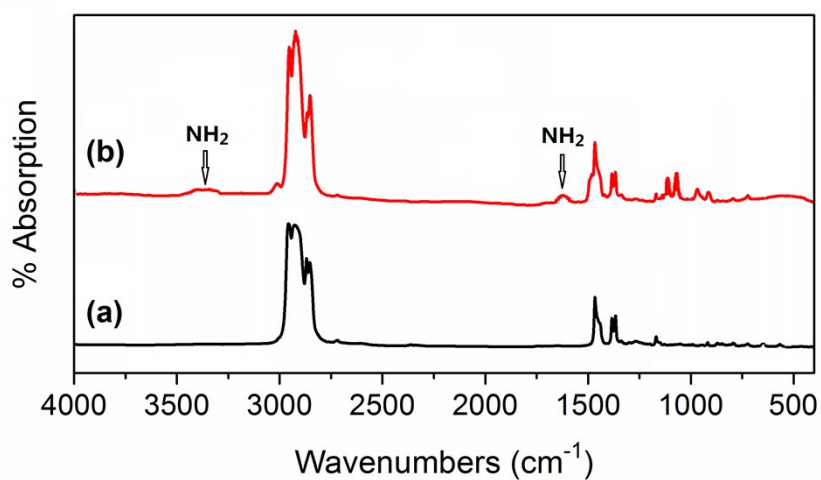
The melting temperatures and glass transition temperatures of the polymers were measured by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 instrument controller with a heating rate of 20 °C/min.



**Figure S4.** DSC thermographs obtained for (a) PMP, (b) PMP-N(SiMe<sub>3</sub>)<sub>2</sub>-1.9, (c) PMP-N(SiMe<sub>3</sub>)<sub>2</sub>-3.1 and (d) PMP-N(SiMe<sub>3</sub>)<sub>2</sub>-4.5 by Ziegler-Natta catalyst.

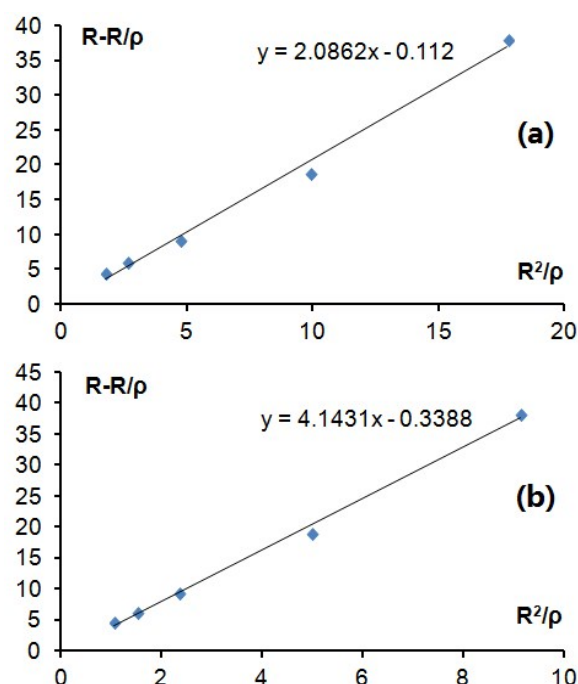
#### 4. FT-IR measurement

Fourier transform infrared spectroscopy (FTIR) was recorded on a PE-1710 spectrometer from 4000 to 400 cm<sup>-1</sup> with a 4 cm<sup>-1</sup> resolution in 64 scans using polymer thin films.



**Figure S5.** FT-IR spectra obtained for (a) PMP and (b) PMP-NH<sub>2</sub>-4.5 by Ziegler-Natta catalyst.

## 5. Reactivity ratios measurement



**Figure S6.** Fineman-Ross plots for the copolymerisation of 4-methyl-1-pentene/6-bis(trimethylsilyl)amino-1-hexene using (a) *rac*-Me<sub>2</sub>Si[2-Me-4-Ph(Ind)]<sub>2</sub>ZrCl<sub>2</sub>/dMAO as catalyst and (b) a Ziegler-Natta catalyst ( $R = M_1/M_2$ ,  $\rho = [M_1]/[M_2]$ ).

**Table S1** Summary of 4-methyl-1-pentene/6-bis(trimethylsilyl)amino-1-hexene copolymerization reaction at low conversion by *rac*-Me<sub>2</sub>Si[2-Me-4-Ph(Ind)]<sub>2</sub>ZrCl<sub>2</sub> catalyst

Entry <sup>a</sup>	T (°C)	M <sub>2</sub> (ml)	Polymer (g)	[M <sub>2</sub> ] <sup>b</sup> (%)	R <sup>c</sup>	ρ <sup>c</sup>	R <sup>2</sup> /ρ	R-R/ρ
1	25	1	3.4	1.19	38.40	83.07	17.75	37.94
2	25	2	2.6	2.61	19.20	37.27	9.89	18.68
3	25	4	1.9	4.88	9.60	19.49	4.73	9.11
4	25	6	1.1	6.03	6.40	15.58	2.63	5.99
5	25	8	0.6	7.12	4.80	13.04	1.77	4.43

<sup>a</sup> 15 μmol of *rac*-Me<sub>2</sub>Si[2-Me-4-Ph(Ind)]<sub>2</sub>ZrCl<sub>2</sub> catalyst, 1.0 g of dMAO, M<sub>1</sub>= 20 mL of 4-methyl-1-pentene, 15 min;

<sup>b</sup> [M] indicates the comonomer content (mol %) in the copolymers by <sup>1</sup>H NMR under 110 °C in 1,1,2,2-tetrachloroethane-d<sub>2</sub>

<sup>c</sup> R=M<sub>1</sub>/M<sub>2</sub>, ρ= [M<sub>1</sub>]/[M<sub>2</sub>].

**Table S2** Summary of 4-methyl-1-pentene/6-bis(trimethylsilyl)amino-1-hexene copolymerization reaction at low conversion by Ziegler-Natta catalyst

Entry <sup>a</sup>	T (°C)	M <sub>2</sub> (ml)	Polymer (g)	[M <sub>2</sub> ] <sup>b</sup> (%)	R <sup>c</sup>	ρ <sup>c</sup>	R <sup>2</sup> /ρ	R-R/ρ
1	25	1	3.9	0.62	38.40	161.33	9.14	38.16
2	25	2	2.2	1.33	19.20	74.19	4.97	18.94
3	25	4	1.4	2.49	9.60	39.16	2.35	9.35
4	25	6	1.0	3.58	6.40	26.93	1.52	6.16
5	25	8	0.4	4.38	4.80	21.83	1.06	4.58

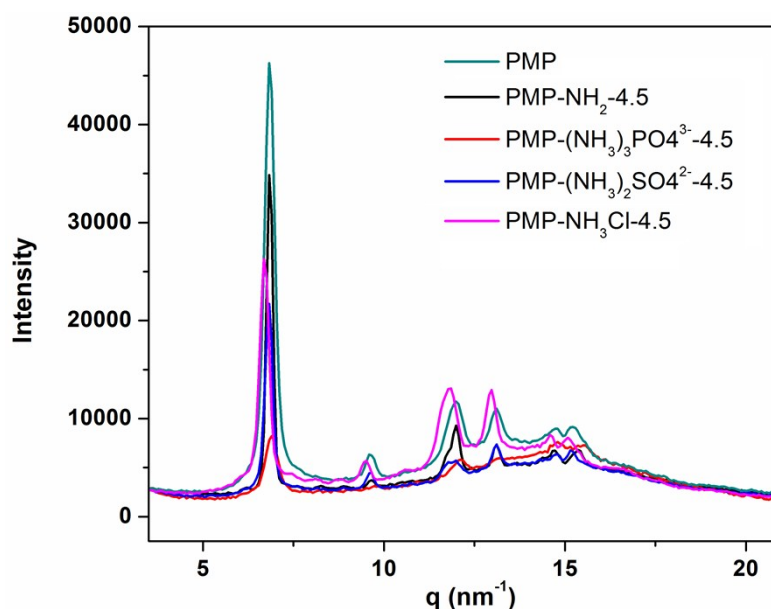
<sup>a</sup> 15 umol Ziegler-Natta catalyst, 5.0ml of 10 wt. % AlEt<sub>3</sub>, M<sub>1</sub>=20 mL of 4-methyl-1-pentene, 15 min;

<sup>b</sup> [M] indicates the comonomer content (mol %) in the copolymers by <sup>1</sup>H NMR under 110 °C in 1,1,2,2-tetrachloroethane-d<sub>2</sub>

<sup>c</sup> R=M<sub>1</sub>/M<sub>2</sub>, ρ= [M<sub>1</sub>]/[M<sub>2</sub>].

## 6. XRD measurement

X-ray diffraction (XRD) analysis was carried out with a Bruker D8 advance (Germany). The wavelength of the X-rays was 1.542 Å (Cu Kα radiation, 40 kV and 100 mA), and the scanning rate was 4° min<sup>-1</sup>.



**Figure S7.** XRD curves of PMP-based ionomers.

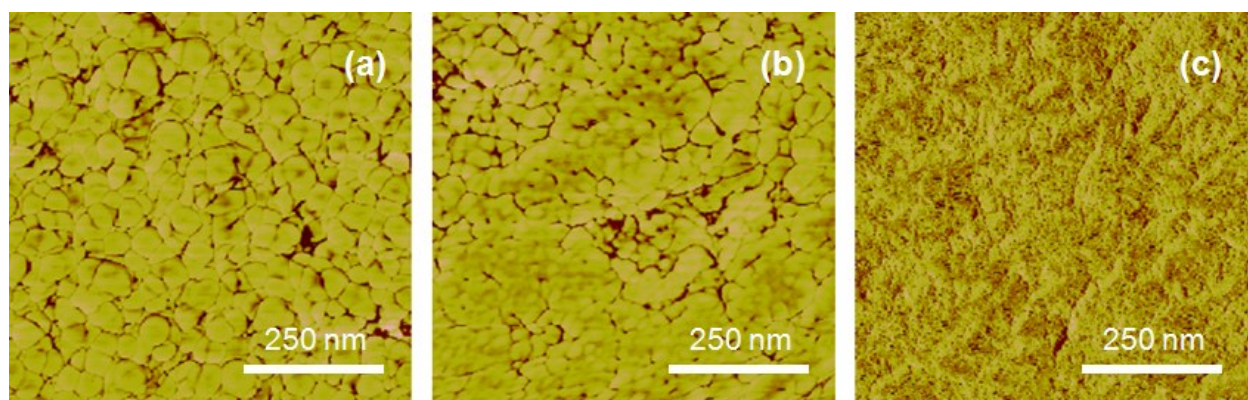
## 7. PMP-based ionomers solubility tests

**Table S3.** Solubility properties of the synthesised PMP ionomers.

	PMP	PMP-NH <sub>2</sub> -4.5	PMP-NH <sub>3</sub> <sup>+</sup> Cl <sup>-</sup> -4.5	PMP-(NH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> <sup>2-</sup> -4.5	PMP-(NH <sub>3</sub> ) <sub>3</sub> PO <sub>4</sub> <sup>3-</sup> -4.5
Tetrahydrofuran (60 °C)	–	–	–	–	–
Acetone (50 °C)	–	–	–	–	–
DMF (150 °C)	–	–	–	–	–
DMSO (150 °C)	–	–	–	–	–
NMP (150 °C)	–	–	–	–	–
Toluene (110 °C)	+/-	+/-	+/-	+/-	+/-
Xylene (130 °C)	+	+	+/-	+/-	+/-
1,2-dichlorobenzene (130 °C)	+	+	+/-	+/-	+/-
1,1,2,2-tetrachloroethane (110 °C)	+	+	+/-	+/-	+/-
Decalin (130 °C)	+	+	+/-	+/-	+/-
isopropyl alcohol (100 °C)	–	–	–	–	–
Methyl ethyl ketone (80 °C)	+/-	+/-	+/-	+/-	+/-
2,4,6-trichlorobenzene (150 °C)	+	+	+/-	+/-	+/-

+: soluble; -: insoluble; +/-: partially soluble.

## 8. PMP-based ionomers AFM measurement



**Figure S8.** The AFM images of comb-shaped (a) PMP-NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup>-4.5, (b) PMP-(NH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub><sup>2-</sup>-4.5 and (c) PMP-(NH<sub>3</sub>)<sub>3</sub>PO<sub>4</sub><sup>3-</sup>-4.5 membranes.

AFM micrographs were recorded with a bioatomic force microscopy (Bio-AFM). AFM tapping-mode height profiles were acquired with a JPK Instruments AG multimode

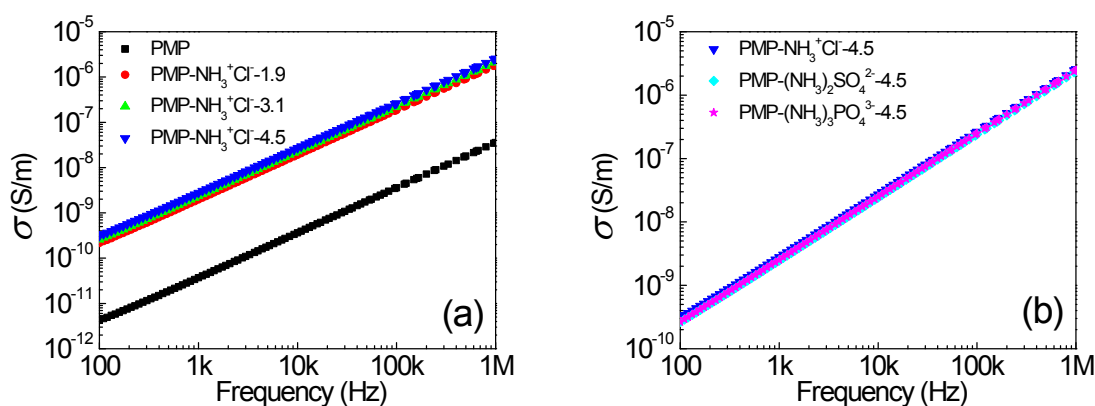
NanoWizard (Germany). The instrument was equipped with a NanoWizard scanner. For tapping-mode AFM, a commercial Si cantilever (TESP tip) of about 320 kHz resonant frequency from JPK was used.

## 9. PMP-based ionomers conductivity measurement

PMP-based ionomers conductivities were further calculated using dielectric related data. If the measured response is treated as the dielectric response only, the electric conductivity would contribute to the measured imaginary part of the permittivity as

$$\sigma = 2\pi f \varepsilon_0 \varepsilon_r \tan \delta$$

where  $\varepsilon_0$  is the vacuum permittivity ( $8.85 \times 10^{-12}$  F/m),  $\varepsilon_r$  is the relative dielectric constant,  $\tan \delta$  is the dielectric loss, and  $f$  is frequency. As shown in Figure S9 (a), the conductivities of PMP-NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup>-1.9, PMP-NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup>-3.1 and PMP-NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup>-4.5 are high than pure PMP which is due to the relatively high loss. The PMP-NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup>-4.5, PMP-(NH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub><sup>2-</sup>-4.5 and PMP-(NH<sub>3</sub>)<sub>3</sub>PO<sub>4</sub><sup>3-</sup>-4.5 membranes show very similar conductivities because the very closed value of dielectric constant and loss. There is a linear relationship of the conductivity versus frequency which indicates these polymers still show good dielectric properties.



**Figure S9.** The calculated conductivities of PMP-based ionomers (a) PMP, PMP-NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup>-1.9, PMP-NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup>-3.1 and PMP-NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup>-4.5, (b) PMP-NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup>-4.5, PMP-(NH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub><sup>2-</sup>-4.5 and PMP-(NH<sub>3</sub>)<sub>3</sub>PO<sub>4</sub><sup>3-</sup>-4.5 membranes.