Facile Construction of Alkaline Anion Exchange Membrane with 3D

Interconnected Ionic Nano-channels

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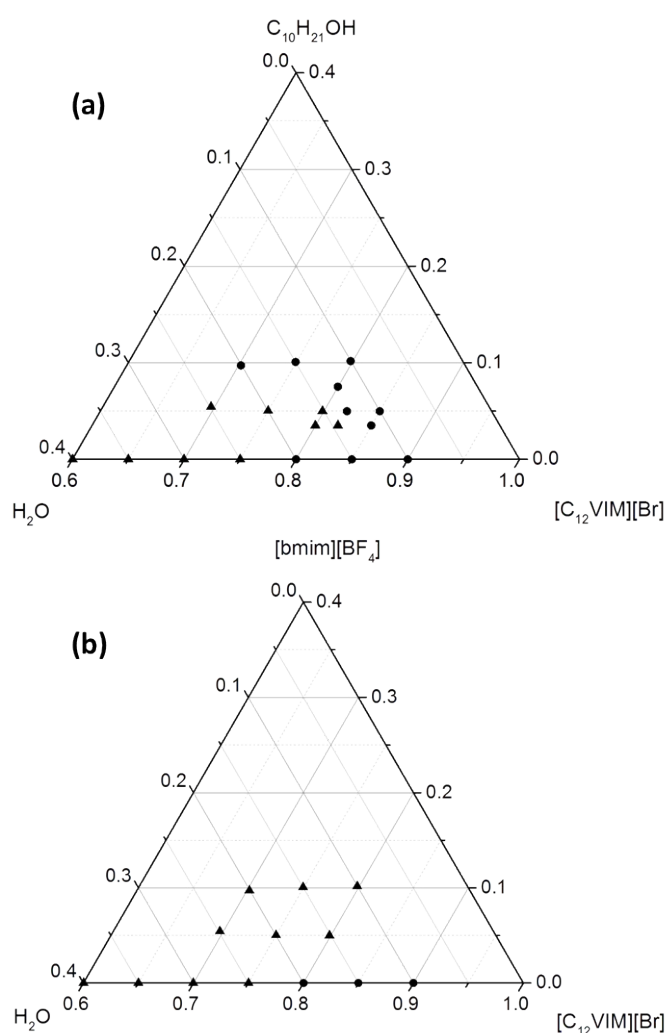
Figure S1. Ternary phase diagrams for $C_{12}VIMBr/C_{10}H_{21}OH/H_2O$ and $C_{12}VIMBr/$ bmimBF$_4$/H$_2$O systems at 25 ºC. H$_1$, hexagonal liquid crystalline phase (▲); L$_{\alpha}$, lamellar liquid crystalline phase (●).
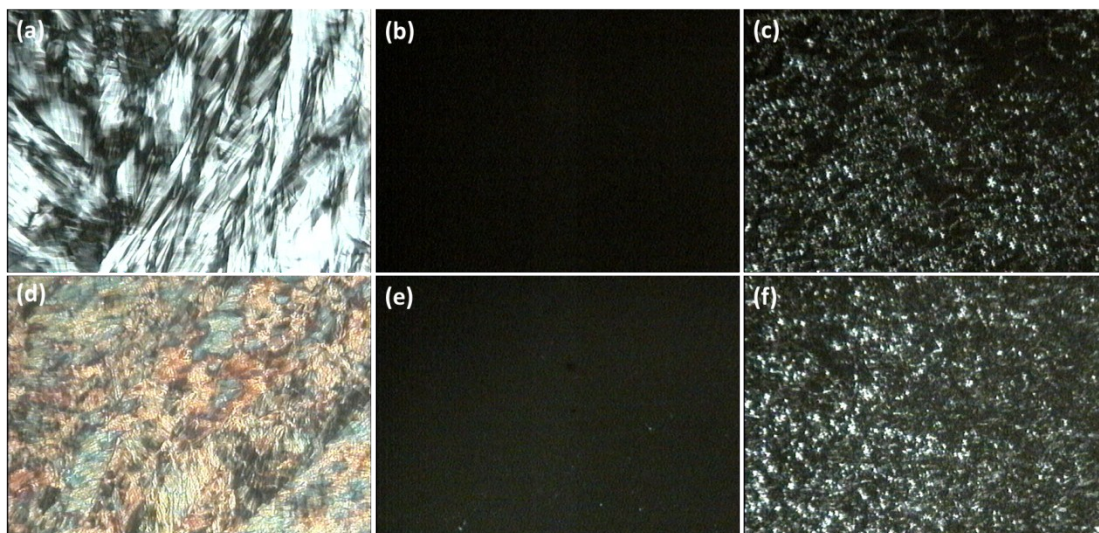
Figure S2. POM images for the typical liquid crystal phases before and after polymerization. Shown are H_1 before (a) and after (d), V_1 before (b) and after (e), and L_α before (c) and after (f) polymerization.

Table S1 Structure Parameters for the LC Phase of $C_{12}VIMBr$/p-xylene/H_2O system

Phase	[C_{12}VIM][Br] (wt%)	H_2O (wt%)	P-xylene (wt%)	ϕL	a_0 (nm)	d_H (nm)	$2l$ (nm)	d_L (nm)	d_W (nm)
H_1	75.12	19.78	5.109	0.4885	4.130	1.516			1.099
V_1	75.20	14.70	10.10	0.5429	5.882		1.305		1.144
L_α	75.03	9.916	15.05	0.5944	3.421			2.034	1.387

φ_L is the volume fraction of hydrophobic alkyl chains in surfactant molecule; a_0 is the lattice parameters of LC phase; d_H is the radius of cylinder unit in H_1 phase; d_L is the thickness of hydrophobic domain in L_α phase; d_W is the thickness of water channel in LC phase.
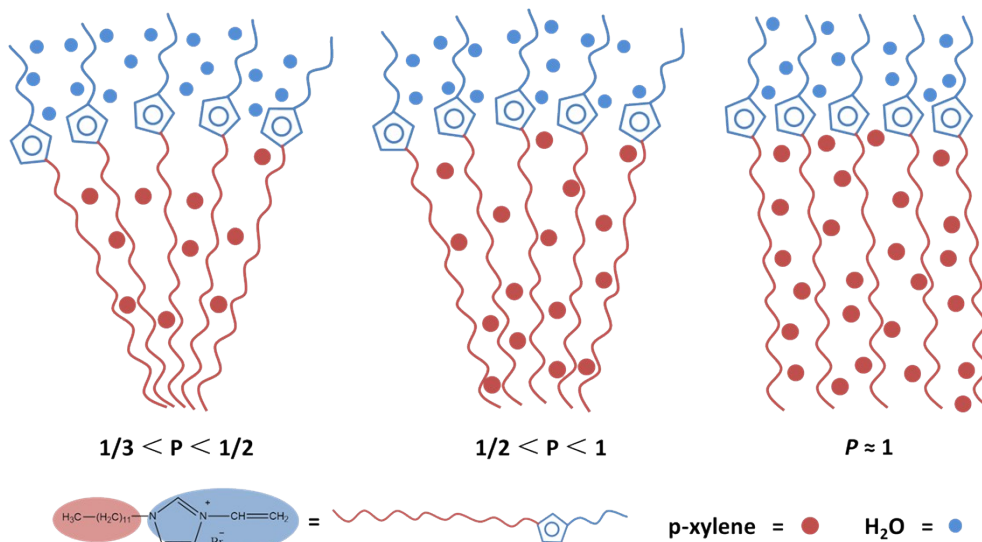
Scheme S1. Schematic illustration of phase transition mechanism in C_{12}VIMBr/p-xylene/H_2O system. Critical packing parameter (P) is defined as $P = v/a_0l$, where v is the effective hydrophobic chain volume, a_0 is the effective headgroup area of the surfactant molecules, and l is the surfactant alkyl chain length.
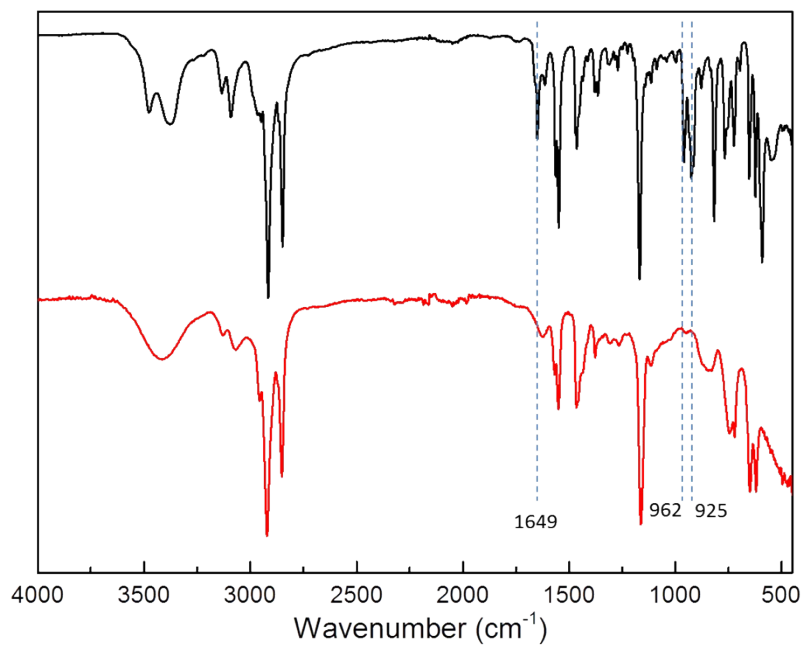
Figure S3. Comparative FT-IR spectra of IL monomer C_{12}VIMBr (black) and poly(C_{12}VIMBr) membrane (red). Successful polymerization was confirmed by the disappearance of characteristic absorption peaks of vinyl, including C=C stretching modes at 1649 cm^{-1}, =CH$_2$ rocking modes at 962 cm^{-1} and =CH bending modes at 925 cm^{-1}.
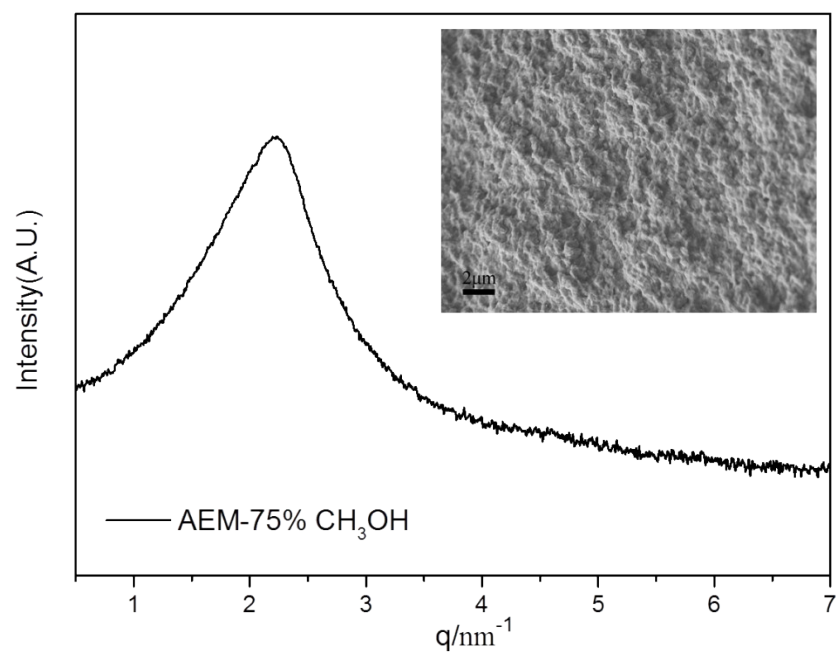
Figure S4. SAXS pattern of AEM-75wt% obtained by photopolymerization of 75 wt% $C_{12}VIMBr$ methanol solution. Insert shows the cross-section SEM image of this control membrane.
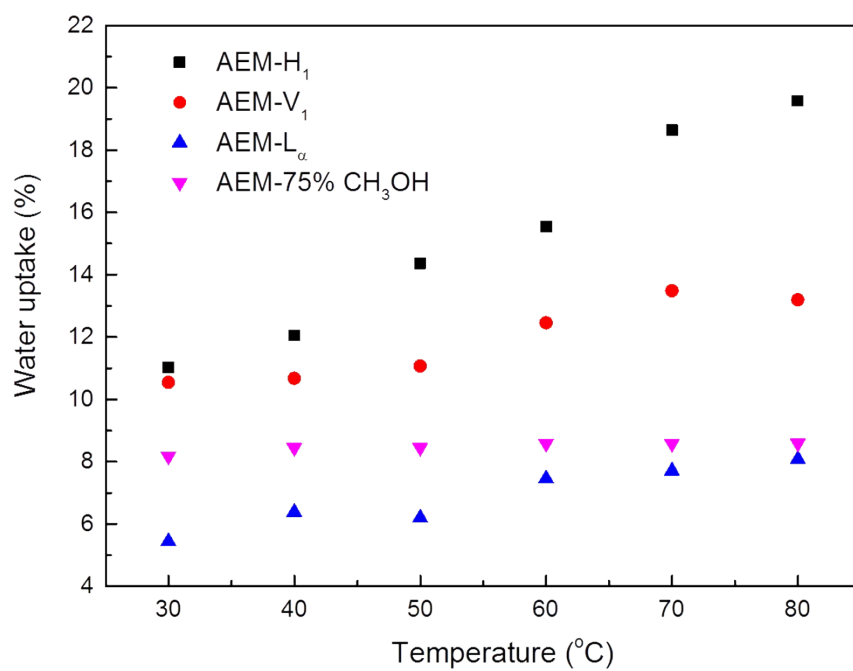
Figure S5. Water uptake of the obtained membranes at a varied temperature. AEM-H_1 (black squares), AEM-V_1 (red circles), AEM-L_α (blue triangles) and AEM-75% CH_3OH (pink triangles).

Table S2. Water uptake, swelling degree, and conductivities of recently reported AEMs. In each cited paper, we choose the AEMs with similar IEC values for comparison with our results.

IEC (mmol/g)	w.u. (%)	s.d. (%)	conductivity ($\times 10^{-2}$ S/cm)	ref
1.18	13.19	6.38	2.22 (80℃)	AEM-V$_1$
1.22	81.9	35.4	2.31 (60℃)	1
1.35	68	N	4.65 (80℃)	2
1.38	39.6	N	1.59(Cl$^-$,90℃)	3
1.41	87.07	24.23	1.77 (60℃)	4
1.43	96.5	25.5	6.77 (80℃)	5
1.52	63	32.4	2.59 (60℃)	6
1.94	61	14	3.0 (30℃)	7
1.95	50.9	32.3	5.62 (70℃)	8
2	92	34	6.6 (23℃)	9

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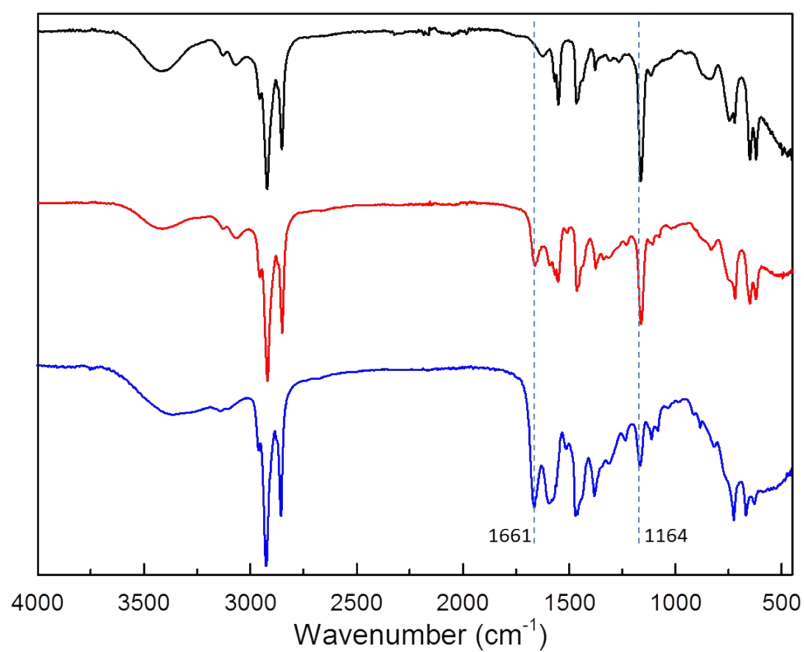(9) A. M. Park, R. J. Wycisk, X. Ren, F. E. Turley and P. N. Pintauro, *J. Mater. Chem. A*, 2016, **4**, 132.

Figure S6. FT-IR spectra of AEM-V$_1$ before (black) and after the accelerated alkaline stability test by exposure to 4 M aqueous KOH at 80 °C for 96 h (red) and 120 h (blue).
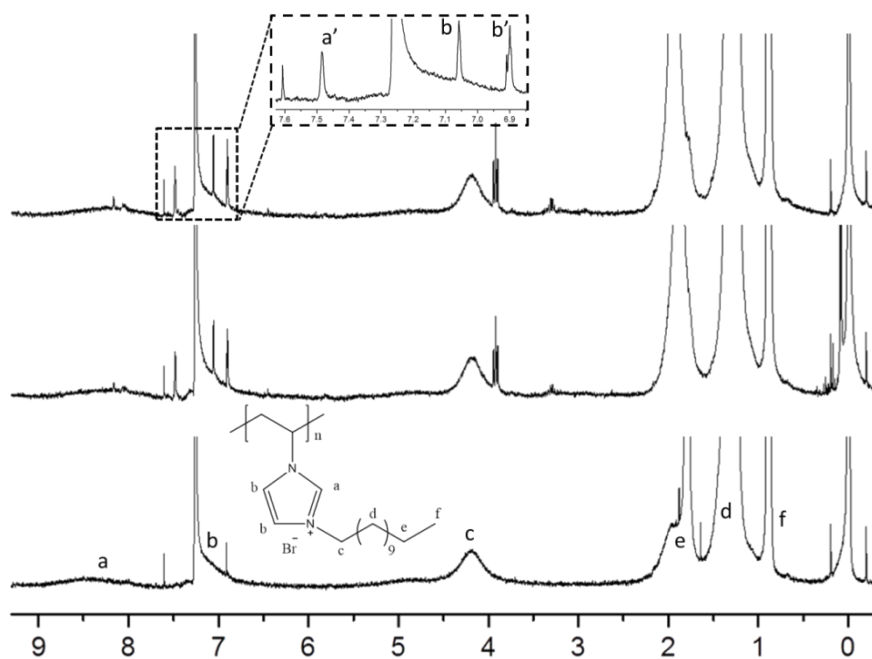
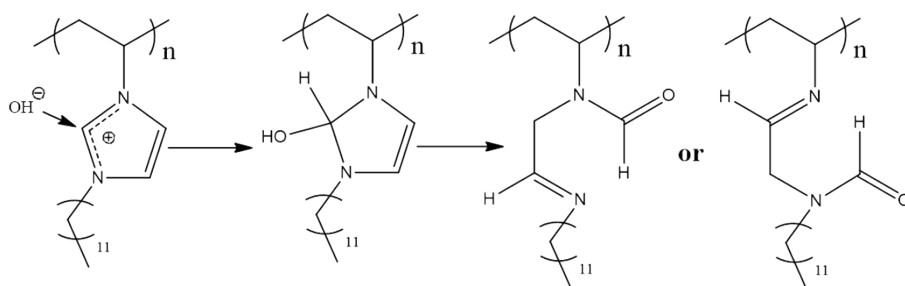**Figure S7.** ^{1}H NMR spectra (CDCl$_3$) of AEM-V$_1$ before (bottom) and after the accelerated alkaline stability test by exposure to 4 M aqueous KOH at 80 °C for 96 h (middle) and 120 h (upper).

Scheme S2. A possible schematic illustrating the ring-opening degradation of imidazolium cations.
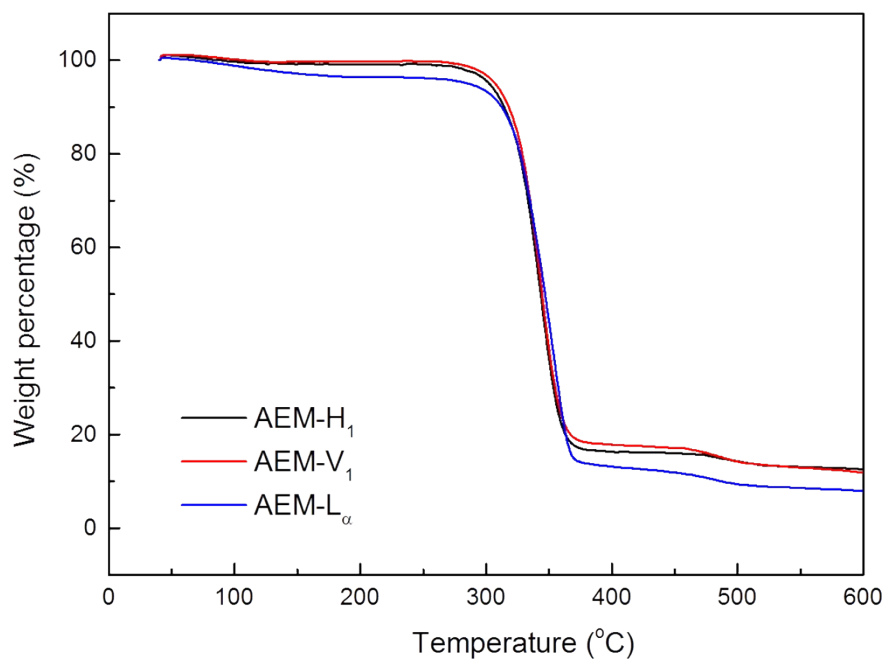
Figure. S8 TGA curves of the produced membranes under a nitrogen flow at a heating rate of 10 °C min⁻¹.

Experimental

Materials.

1-Vinylimidazole (99%), 1-bromododecane (98%), p-xylene (98%), n-decyl alcohol (98%) and the photoinitiator 2-hydroxy-2-methylpropiophenone (97%) were purchased from J&K Scientific Ltd. $C_{12}VIMBr$ and $bmimBF_4$ were synthesized according to the literature method. All the materials were used as received without any purification. Deionized water was used throughout all the experiments.

Phase Diagram.

The samples were prepared by weighing the selected amount of components in sealed glass vials (in weight percent, wt%). The composition interval was selected as 5 wt% for a rough mapping, while smaller interval of 2 wt% was selected for the region in the vicinity of the phase boundaries. The mixtures were homogenized and equilibrated repeatedly through vortex mixing and centrifugation. The types of liquid crystals were identified by polarized optical microscope (POM) and small-angle X-ray scattering (SAXS).

Preparation of Nanostructured Membranes.

An in-phase photopolymerization method was used for the preparation of membranes with LC nanostructures. The photopolymerizable sample was prepared according to the phase diagram. 2-hydroxy-2-methylpropiophenone (0.5 wt% to the monomer) was added as photoinitiator. The polymerizable LC sample was sandwiched between two quartz substrates and equilibrated for 1h before photopolymerization. UV irradiation was carried out using a 365 nm UV-LED lamp (LUYOR-3109) at room temperature for 30 min. The thickness of the samples was approximately 100 μm. For comparison, membranes without LC nanostructures were prepared following the same procedure except methanol was used instead of water.

Characterization.

A polarized optical microscope (Olympus BX51p) equipped with cooled CCD (Evolution MP5.1RTV, Q-imaging, Canada) was used to observe textures of the LC phase. Small-angle X-ray scattering (SAXS) measurements were carried out on the SAXSess mc^2 X-ray scattering system (Anton Paar). SAXS measurement was

performed with Cu Kα radiation operating at 2 kW (50 kV and 40 mA). The distance between the sample and detector was about 264.5 mm and the wavelength of X-rays was 1.542 Å. The exposure time was 600 s for all samples. The morphologies of the polymeric films were investigated by scanning electronic microscopy (SEM, JEOL JSM-7600F) after extraction of the solvent and gold sputter coating. Thermo gravimetric analysis (TGA) was performed with a Rheometric Scientific TGA 1500 (Piscataway, NJ) under a nitrogen flow from 30 to 600 °C at a heating rate of 10 °C/min.

Ionic Conductivity Measurements. The resistance value of the produced membranes was measured using electrochemical impedance spectroscopy in the frequency of 1-10^6 Hz using a CHI760D workstation. The temperature was varied from 20 to 80 °C by steps of 10 K. During the conductivity measurement, the membranes were immersed in N_2-saturated deionized water. The ionic conductivity was calculated as

$$\sigma = \frac{l}{RWd}$$

Where l is the interelectrode separation (= 1 cm for the test cell used), R is the resistance of the membrane, W and d are width (here 1 cm) and thickness of the membrane, respectively. To prepare the membranes in OH⁻ form, the membranes were immersed in a N_2-saturated 1 mol/L KOH solution for 24 h. The above process was repeated three times to ensure a complete displacement. The membranes in OH⁻ form were then rinsed thoroughly with deionized water until the pH of the residual water was neutral.

Ion Exchange Capacity (IEC) Determinations. The membrane ion exchange capacities were measured using a back-titration method. A produced membrane in OH⁻ form was soaked in standard HCl solution (0.1 mol/L, 40 mL) for 24 h. Then the resulting solution was titrated with a KOH standard solution to pH 7. The membrane ion exchange capacities can be obtained as follows

$$IEC = \frac{n_{i(H^+)} - n_{f(H^+)}}{m_{dry}}$$

Where $n_{i(H^+)}$ and $n_{f(H^+)}$ are the initial and final amounts of proton in the HCl

solution determined by titration, m_{dry} is the weight of membranes in dry conditions. The test was conducted at least three times to reach an average value.

Water Uptake and Swelling Degree. The water uptake and the swelling degree of the membranes can be evaluated by weight analysis and linear expansion ratio, respectively. The water uptake of the membrane *w.u.* (%) and the membrane swelling degree *s.d.* (%) can be calculated from

$$w.u. = \frac{w_w - w_d}{w_d} \times 100\%$$

$$s.d. = \frac{x_w - x_d}{x_d} \times 100\%$$

Where w_w and x_w are the weight and lengths of the hydrated membranes, respectively, while w_d and x_d are the weight and lengths of the dry membranes, respectively.

Accelerated Alkaline Stability Tests. The membranes were immersed in 4 M aqueous KOH solution at 80 °C for different time periods. Then the membranes were washed several times with deionized water and dried under vacuum. Chemical structural changes occurring in the membrane during the test were detected by ^{1}H NMR spectroscopy and FT-IR spectroscopy.

Theory for calculation of structural parameters of liquid crystalline phase

The lattice parameters a_0 of the hexagonal (distance between the centers of adjacent cylinders), Im3m bicontinuous cubic (cubic lattice parameter) and lamellar (lamellar periodicity) liquid crystalline phases were obtained according to Eq. (1), (2)and (3), respectively.[10]

$$q_{(h,k)} = \frac{4\pi}{\sqrt{3}a_0} \cdot (h^2 + k^2 + hk)^{1/2} \tag{1}$$

$$q_{(h,k,l)} = \frac{2\pi}{a_0} \cdot (h^2 + k^2 + l^2)^{1/2} \tag{2}$$

$$q_{(l)} = \frac{2\pi}{a_0} \cdot l \tag{3}$$

where q(h,k), q(h,k,l) and q(l) are the scattering vectors corresponding to the

scattering peaks observed in the SAXS spectra for the hexagonal，Im3m bicontinuous cubic and lamellar phase, respectively, h, k, l are Miller indexes, and a_0 is the lattice parameter. From the results of SAXS, several structural parameters characterizing the structure of the liquid crystalline phase could be calculated as follows.

The volume fraction of the hydrophobic long alkyl chain part in $[C_{12}VIM][Br]$/p-xylene/H_2O mixture system φ_L is calculated by Eq. (4)[11]:

$$\varphi_L = \frac{\dfrac{W_S}{\rho_S} \times \dfrac{V_{S,L}}{V_S}}{(\dfrac{W_S}{\rho_S} + \dfrac{W_O}{\rho_O} + \dfrac{W_W}{\rho_W})} = \frac{\dfrac{W_S}{M_S} \times V_{S,L}}{(\dfrac{W_S}{\rho_S} + \dfrac{W_O}{\rho_O} + \dfrac{W_W}{\rho_W})} \tag{4}$$

where W_S, W_O and W_w are the weight fraction of $[C_{12}VIM][Br]$, p-xylene and water, respectively, and ρ_S, ρ_O and ρ_W are the densities of $[C_{12}VIM][Br]$, p-xylene and water, respectively. The density of $[C_{12}VIM][Br]$ is obtained using a pycnometer as reported previously, and the reference solvent is ethyl acetate ($\rho = 0.8944\ g \cdot cm^{-3}$). The densities of $[C_{12}VIM][Br]$, p-xylene and water are 1.015, 0.861 and $0.997 g \cdot cm^{-3}$, respectively. V_S, $V_{S,L}$ and M_S are molecular volume of $[C_{12}VIM][Br]$, molar volume of alkyl chain and the molecular weight of $[C_{12}VIM][Br]$. $V_{S,L}$ is calculated by Eq. (5)[12]:

$$V_{D,L} = N_A \times 10^{-21}[0.027(m-1) + 0.055] \tag{5}$$

where N_A is Avogadro's number and m is the number of methylene in alkyl chain.

For hexagonal liquid crystalline, the radius of cylinder unit (r_H) could be obtained using Eq. (6)[13]:

$$r_H = a_0\sqrt{\frac{\sqrt{3}}{2\pi}\varphi_L} \tag{6}$$

For Im3m bicontinuous cubic liquid crystalline, the hydrophobic part length (2l) could be obtained using Eq. (7)[14]

$$\varphi_L = 4.69\left(\frac{l}{a_0}\right) - \frac{16\pi}{3}(\frac{l}{a_0})^3$$

(7)

For lamellar liquid crystalline, the thickness of hydrophobic domain (d_L) could be obtained as:[15]

$$d_L = a_0 \cdot \varphi_L$$

(8)

Furthermore, the thickness of water channel (d_W) of hexagonal, Im3m bicontinuous cubic and lamellar liquid crystalline phases is given by Eq. (9), (10) and (11), respectively.

$$d_W = a_0 - 2r_H$$

(9)

$$d_W = 0.305a_0 - l$$

(10)

$$d_W = a_0 - d_L$$

(11)

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