Supporting Information for

Temperature-Responsive Proton-Conductive Liquid Crystals
Formed by the Self-Assembly of Zwitterionic Ionic Liquids

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Figure S1. (a) SAXS patterns of [C_{12}IPS][C_{6}H_{5}SO_{3}H] aqueous mixture system with increasing IL content collected at 25 ºC; (b) Corresponding POM images collected at 25 ºC.
Figure S2. (a) SAXS patterns of [C$_{12}$IPS][CF$_3$SO$_3$H] aqueous mixture system with increasing IL content collected at 25 °C; (b) Corresponding POM images collected at 25 °C.
Figure S3. (a) SAXS patterns of [C$_{14}$IPS][CH$_3$SO$_3$H] and [C$_{16}$IPS][CH$_3$SO$_3$H] aqueous mixture systems with increasing IL content collected at 25 °C; (b) Corresponding POM images collected at 25 °C.
Table S1. Structural parameters for the liquid crystalline phases of \([C_nIPS][R-SO_3H]\) aqueous mixture systems.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\phi_L)</th>
<th>(a_0) (nm)</th>
<th>(r_H) (nm)</th>
<th>(r_p) (nm)</th>
<th>(d_W) (nm)</th>
<th>(a_s) (nm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{16}IPS/CH_3SO_3H) (H₁)</td>
<td>70</td>
<td>0.3492</td>
<td>4.7978</td>
<td>1.4885</td>
<td>1.8209</td>
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<td></td>
<td>80</td>
<td>0.3420</td>
<td>4.5587</td>
<td>1.3997</td>
<td>1.7594</td>
<td>0.6572</td>
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<tr>
<td>(C_{14}IPS/CH_3SO_3H) (Pm3n,H₁)</td>
<td>70</td>
<td>0.3237</td>
<td>9.2797</td>
<td>1.9767</td>
<td>1.7227</td>
<td>0.6162</td>
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<tr>
<td></td>
<td>80</td>
<td>0.3148</td>
<td>4.1935</td>
<td>1.2354</td>
<td>1.7227</td>
<td>0.6573</td>
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<tr>
<td>(C_{12}IPS/CH_3SO_3H) (Pm3n,H₁)</td>
<td>60</td>
<td>0.2588</td>
<td>8.0574</td>
<td>1.5930</td>
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<td>0.6629</td>
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<td>7.8690</td>
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<td>0.6624</td>
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<td>80</td>
<td>0.2608</td>
<td>3.2146</td>
<td>0.8619</td>
<td>1.4908</td>
<td>0.8168</td>
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<td>(C_{12}IPS/C_{16}H_6SO_3H) (H₁)</td>
<td>50</td>
<td>0.2144</td>
<td>4.9490</td>
<td>1.2033</td>
<td></td>
<td>2.5425</td>
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<td>1.1863</td>
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<td>0.3530</td>
<td>3.9239</td>
<td>1.2240</td>
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<td>1.4758</td>
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<tr>
<td>(C_{12}IPS/CF_3SO_3H) (H₁)</td>
<td>30</td>
<td>0.1288</td>
<td>6.9977</td>
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<td>3.7627</td>
<td>1.1774</td>
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<td>1.4079</td>
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</table>

\(\phi_L\) is the volume fraction of the hydrophobic long alkyl chain part; \(a_0\) is the lattice parameters of the liquid crystalline phases; \(r_H\) is the radius of cylinder unit in the hexagonal structure; \(r_p\) is the radius of the micelle unit in the Pm3n cubic structure; \(d_W\) is the thickness of the water channel of the liquid crystalline phases; \(a_s\) is the effective cross-sectional area.
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) and Pm3n micellar cubic (cubic lattice parameter) liquid crystalline phases were obtained according to Eq. (1) and (2), respectively.[1]

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

(1)

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

(2)

where $q(h,k)$ and $q(h,k,l)$ are the scattering vectors corresponding to the scattering peaks observed in the SAXS spectra for the hexagonal and Pm3n micellar cubic 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 $[\text{C}_n\text{IPS}][\text{R-SO}_3\text{H}]$ aqueous mixture system $\varphi_L$ is calculated by Eq. (3)[2]:

$$\varphi_L = \frac{\frac{W_C}{\rho_C} \times \frac{V_{C,L}}{V_C}}{\left( \frac{W_C}{\rho_C} + \frac{W_H}{\rho_H} + \frac{W_W}{\rho_W} \right)} = \frac{\frac{W_C}{M_C} \times V_{C,L}}{\left( \frac{W_C}{\rho_C} + \frac{W_H}{\rho_H} + \frac{W_W}{\rho_W} \right)}$$

(3)

where $W_C$, $W_H$ and $W_W$ are the weight fraction of $\text{C}_n\text{IPS}$, $\text{R-SO}_3\text{H}$ and water, respectively, and $\rho_C$, $\rho_H$ and $\rho_W$ are the densities of $\text{C}_n\text{IPS}$, $\text{R-SO}_3\text{H}$ and water, respectively. The density of $\text{C}_n\text{IPS}$ is obtained using a pycnometer as reported previously,[3] and the reference solvent is ethyl acetate ($\rho = 0.8944 \text{ g cm}^{-3}$). The densities of $\text{C}_{12}\text{IPS}$, $\text{C}_{14}\text{IPS}$, $\text{C}_{16}\text{IPS}$, $\text{CH}_3\text{SO}_3\text{H}$, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$, $\text{CF}_3\text{SO}_3\text{H}$ and water are 1.0227, 1.1098, 1.1595, 1.48, 1.32, 1.69 and 0.997 g cm$^{-3}$, respectively. $V_C$, $V_{C,L}$ and $M_C$ are molecular volume of $\text{C}_n\text{IPS}$, molar volume of alkyl chain and the molecular weight of $\text{C}_n\text{IPS}$. $V_{C,L}$ is calculated by Eq. (4)[4]:
\[ V_{C,L} = N_A \times 10^{-21} [0.027(m - 1) + 0.055] \]  \hspace{1cm} (4)

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 \( (r_H) \), the thickness of the water channel \( (d_W) \) and the effective cross-sectional area \( (a_s) \) could be obtained using Eq. (5), (6) and (7), respectively. \([5]\)

\[
\begin{align*}
r_H &= a_0 \frac{\sqrt{3\varphi_L}}{2\pi} \hspace{1cm} (5) \\
d_W &= a_0 - 2r_H \hspace{1cm} (6) \\
a_s &= \frac{2V_{C,L}}{r_HN_A} \hspace{1cm} (7)
\end{align*}
\]

For calculation of Pm3n micellar cubic liquid crystalline structural parameters, it is generally assume that the two kinds of micelles to be spherical with the same radius. \([6]\)

The radius of the micelle unit \( (r_p) \) and the effective cross-sectional area \( (a_s) \) could be obtained using Eq. (8) and (9), respectively. \([6]\)

\[
\begin{align*}
r_p &= a_0 \frac{\sqrt{3\varphi_L}}{2} \sqrt{\frac{4\pi}{3}} \hspace{1cm} (8) \\
a_s &= \frac{3V_{C,L}}{r_pN_A} \hspace{1cm} (9)
\end{align*}
\]

References


