Electronic Supplementary Information

Title: Ionic liquid-derived charged polymers to show highly thermoresponsive LCST-type transition with water at desired temperatures

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Materials

Tributylhexylphosphonium bromide ([P\textsubscript{4446}]Br; Hokko Chemical Industry Co.) and potassium 3-sulfopropylmethacrylate (K[C3S]; Tokyo Chemical Industry Co.) were used as received. α,α’-azobis(isobutyronitrile) (AIBN; Wako Chemical Industry Co.) was recrystallised with ethanol prior to use. A series of poly(sodium \(p\)-styrenesulfonate) (PSS) with well-defined molecular weight distribution were purchased from Polymer Standard Service.

Synthesis of tributylhexylphosphonium 3-sulfopropylmethacrylate ([P\textsubscript{4446}][C3S])

[P\textsubscript{4446}]Br was dissolved in pure water, and an excess amount of K[C3S] was added to the solution. This solution was stirred over 24h at room temperature. The resulting product was extracted with dichloromethane and washed with water for several times. The dichloromethane layer was then evaporated and dried in vacuo for at least 24h at room temperature. The [P\textsubscript{4446}][C3S] was obtained as a colourless liquid with glass transition temperature of -72.4 °C (See Fig. S4, black line).

\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}, \(\delta\)ppm relative to TMS): 0.90(t, 3H, CH\textsubscript{3}), 0.97(t, 9H, CH\textsubscript{3}), 1.31-1.32(m, 4H, CH\textsubscript{2}), 1.51-1.56(m, 16H, CH\textsubscript{2}), 1.92(t, 3H, CH\textsubscript{3}), 2.19-2.38(m, 11H, CH\textsubscript{2}), 2.89-2.93(m, 2H, CH\textsubscript{2}), 4.26(t, 2H, CH\textsubscript{2}), 5.52(dd, 1H, CH), 6.08(dd, 1H, CH).

Gel permeation chromatography (GPC)

Weight-average molecular weight (\(M_w\)) of poly([P\textsubscript{4446}][C3S]) was determined by GPC using
water/acetonitrile mixture (water : acetonitrile = 6 : 4) containing 50 mM LiCl as an eluent. The GPC curve was recorded by Shimadzu instruments equipped with Shimadzu SPD-20A UV-vis detector ($\lambda$ = 215 nm), LC-20AD solvent delivery unit, and a poly(vinyl alcohol) gel column (Shodex Asahipak GF-7M HQ, 0.4 ml min$^{-1}$). The column was heated at 40 °C using a column oven (Shimadzu CTO-20AC). A calibration curve was prepared using PSS as a standard. The GPC curves of both monomeric and polymerised [P$_{4446}$][C3S] was shown in Fig. S6. In the GPC curve of poly([P$_{4446}$][C3S]), there was no distinct peak derived from monomeric [P$_{4446}$][C3S]. The $M_w$ value of the prepared poly([P$_{4446}$][C3S]) was 3.6 × 10$^5$. 
Fig. S1 Phase transition temperature ($T_c$) of [P$_{4446}$][C3S] after mixing with different amounts of water.
Fig. S2 $^1$NMR chart of [P$_{4446}$][C3S] in CDCl$_3$. 
Fig. S3 $^1$NMR chart of poly([P$_{4446}$][C3S]) in CDCl$_3$. 
Fig. S4 DSC charts of [P$_{4446}$][C3S] (black line) and poly([P$_{4446}$][C3S]) (red line).
Fig. S5 TG/DTA charts of $[\text{P}_{446}]\text{[C3S]}$ (black line) and poly($[\text{P}_{446}]\text{[C3S]}$) (red line).
**Fig. S6** GPC curves of [P$_{4446}$][C3S] (black line) and poly([P$_{4446}$][C3S]) using water/acetonitrile with 50 mM LiCl as an eluent.
Fig. S7 Transmittance change of poly([P₄₄₄₄][SS]) (blue line) and poly([P₄₄₄₆][C₃S]) (red line) after mixing with pure water. Concentration of the polymers was respectively 10 wt%.
Fig. S8 Reversible liquid-to-gel transition of polymer phases precipitated from aqueous media with different $C_{\text{salt}}$ (mM). $C_{\text{salt}}$ was 0 (1), 100 (2), 200 (3), and 300 (4), respectively. The transition temperature ($T'_{c}$) value of the polymer phases was described in Table S1.
**Fig. S9** DSC charts of four polymer phases precipitated from aqueous media with different $C_{\text{salt}}$. $C_{\text{salt}}$ was 0 (black line), 100 (red line), 200 (blue line), and 300 (green line), respectively.
Table S1 Properties of polymer-rich phases precipitated from aqueous media having different salt concentration (C$_{salt}$)

<table>
<thead>
<tr>
<th>Entry</th>
<th>C$_{salt}$</th>
<th>$T_c^{a}$</th>
<th>W$_{aq}$/wt%$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>37.0</td>
<td>59 ± 3</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>32.0</td>
<td>51 ± 2</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>25.4</td>
<td>60 ± 1</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>18.5</td>
<td>58 ± 2</td>
</tr>
</tbody>
</table>

$^a$ $T_c$' value was determined as endothermic peaks during heating detected by DSC method.  
$^b$ W$_{aq}$ value was determined by weight loss of water as measured by TG/DTA method.