

# **Self-assembly of Diblock Copolymers Containing Thermo- and Photo-responsive LCST Phase Behavior Polymer with Tunable Assembly Temperature in Ionic Liquids Mixture**

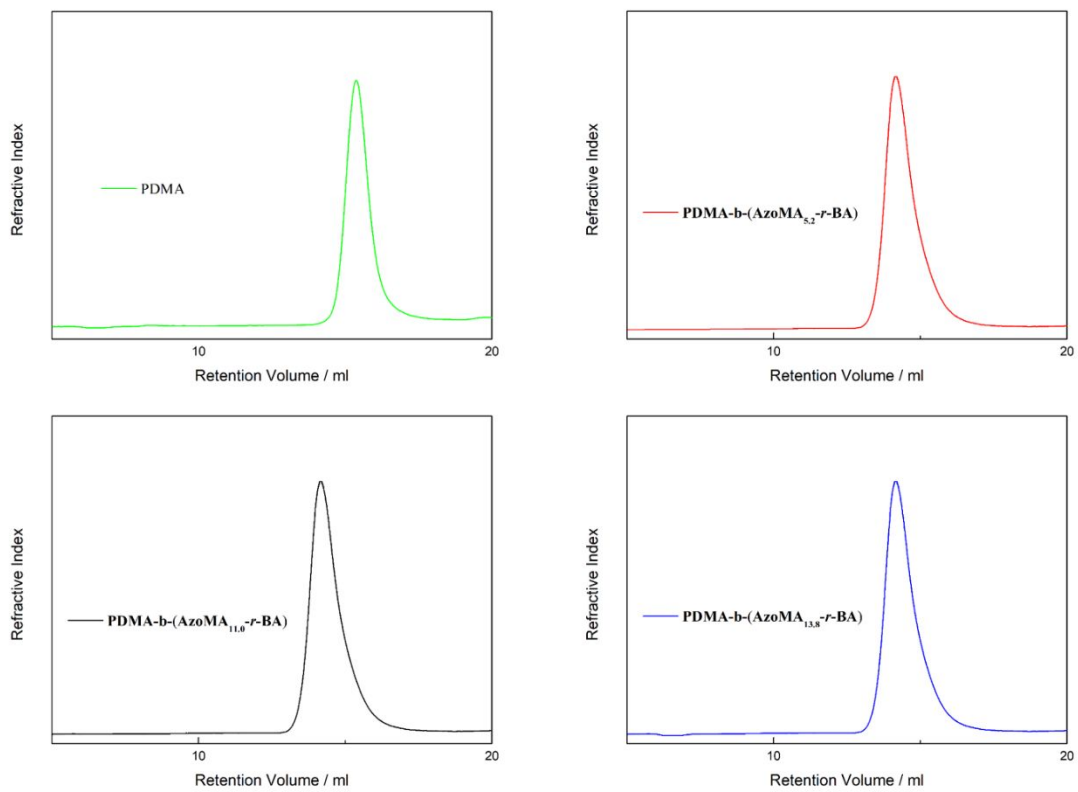
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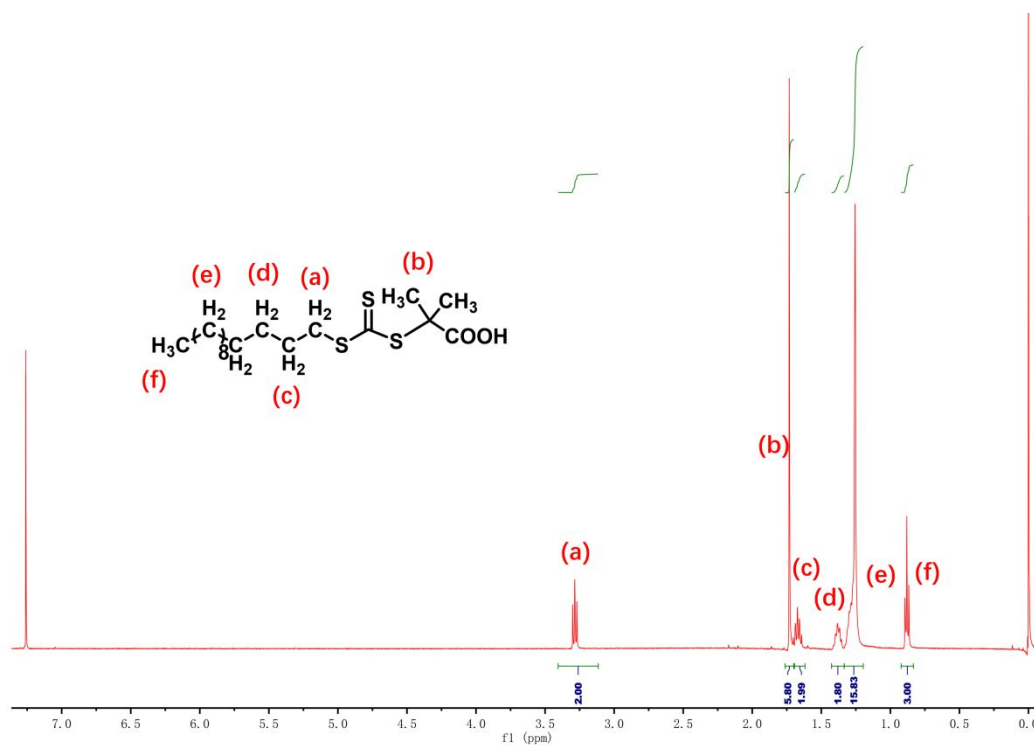
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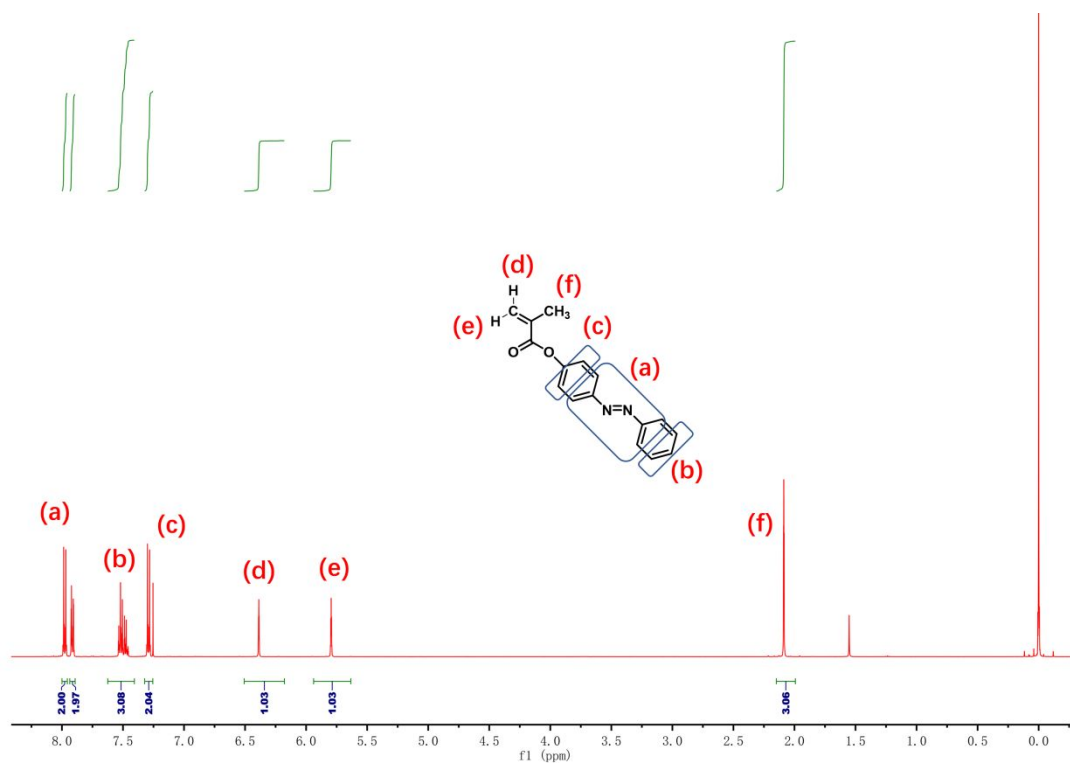
**Figure S 1.** The SEC traces of diblock copolymer



**Figure S 2.** <sup>1</sup>H NMR of 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic Acid (CTA),

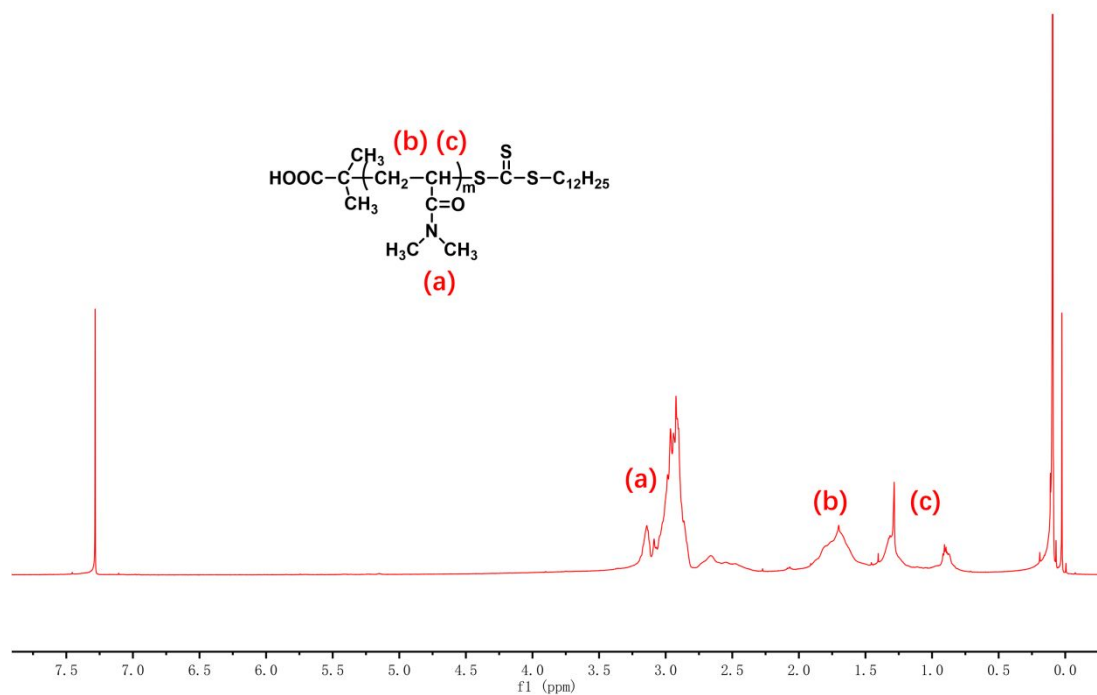
(a)~(f): used to mark the attribution of each hydrogen

<sup>1</sup>H NMR (500MHz CDCL<sub>3</sub>) δ=3.28 (t, J=7.5 Hz, 2H, CH<sub>2</sub>CS<sub>3</sub>), 1.73(s, 6H, C(CH<sub>3</sub>)<sub>2</sub>COOH), 1.70-1.64(m, 2H, CH<sub>2</sub>CH<sub>2</sub>CS<sub>3</sub>), 1.41-1.34(m, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CS<sub>3</sub>), 1.32-1.28(m, 16H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>), 0.88(t, 3H, J=7 Hz, CH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>)

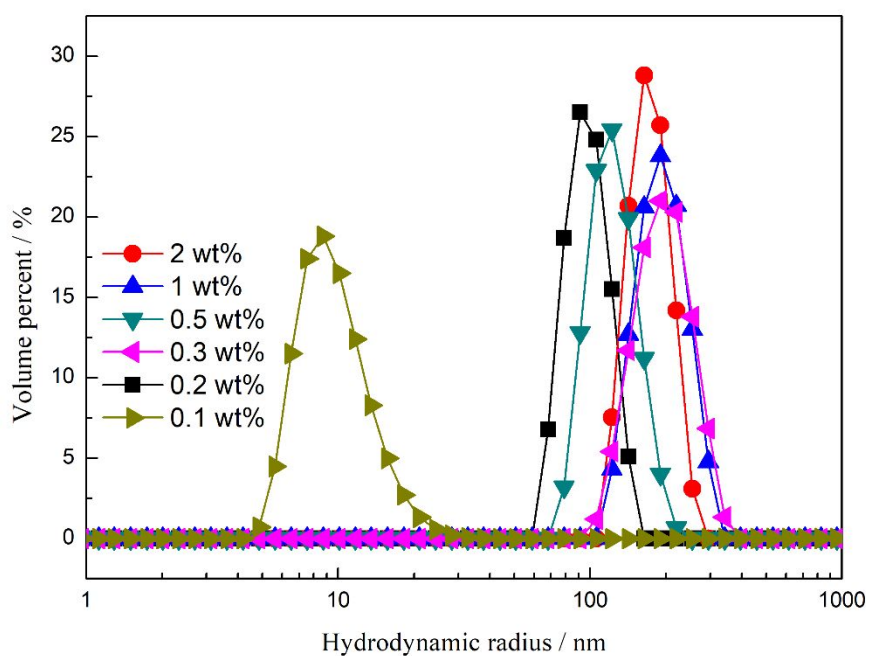


**Figure S 3.** <sup>1</sup>H NMR of 4-phenylazophenylmethacrylate (AzoMA), (a)~(f): used to mark the attribution of each hydrogen

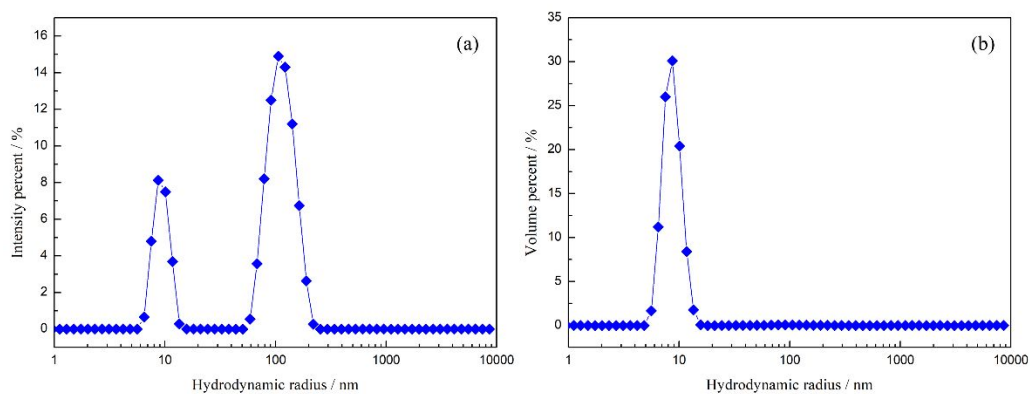
<sup>1</sup>H NMR (600MHz CDCl<sub>3</sub>) δ=7.99-7.96 (m, 4H, Ar-H ortho to N=N ), 7.54-7.45(m, 2H, Ar-H meta to N=N), 7.31-7.27 (m, 2H, Ar-H ortho to COO), 6.39- 6.38 (m, 1H, CH<sub>2</sub>) 5.80-5.79(m, 1H, CH<sub>2</sub>), 2.09 (t, J=2 Hz, 3H, CH<sub>3</sub>)



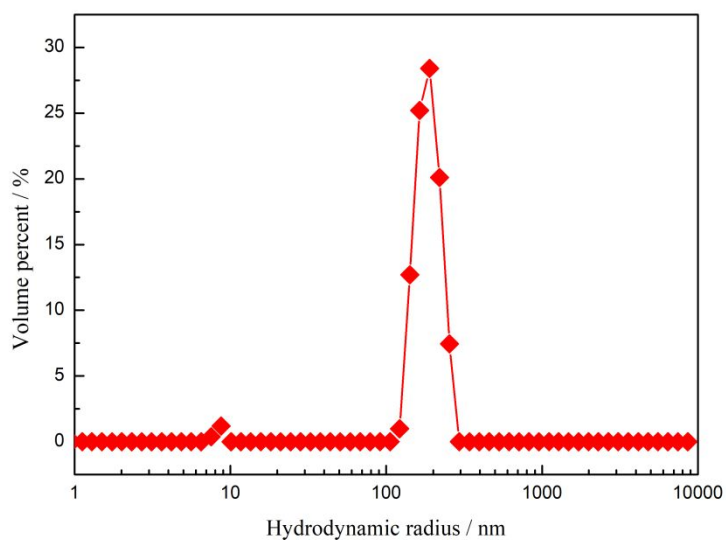
**Figure S 4.** <sup>1</sup>H NMR of PDMA-CTA, (a)~(c): used to mark the attribution of each hydrogen



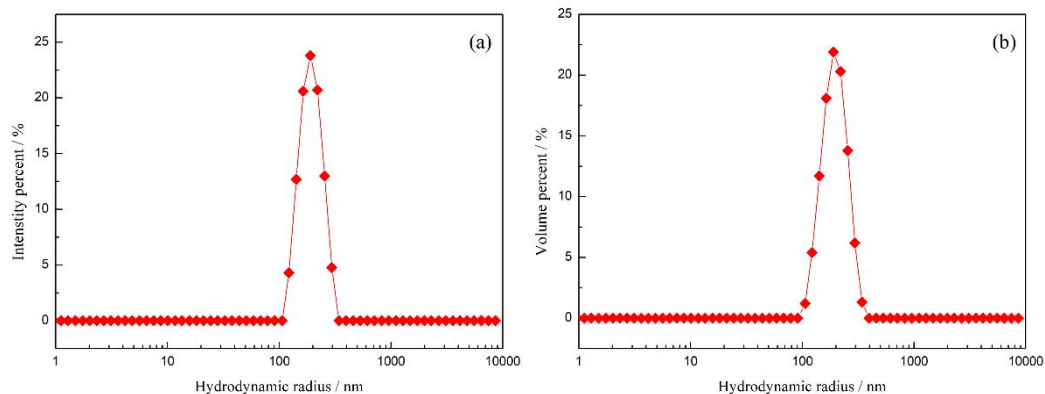
**Figure S 5.** The volume percent of diblock copolymer in  $[\text{C}_2\text{mim}][\text{NTf}_2]$  with different concentration based on DLS measurements



**Figure S 6.** The intensity percent (a) and volume percent (b) of PDMA-b-P(AzoMA<sub>13.8</sub>-*r*-BA) in ionic liquids mixture ([C<sub>2</sub>mim][NTf<sub>2</sub>]/[C<sub>4</sub>mim][NTf<sub>2</sub>]=1/2.5 by weight ) at 32 °C



**Figure S 7.** The volume percent of PDMA-b-P(AzoMA<sub>13.8</sub>-*r*-BA) in ionic liquids mixture ([C<sub>2</sub>mim][NTf<sub>2</sub>]/[C<sub>4</sub>mim][NTf<sub>2</sub>]=1/2.5 by weight ) at 36 °C



**Figure S 8.** The intensity percent (a) and volume percent (b) of PDMA-*b*-P(AzoMA<sub>13.8</sub>-*r*-BA) in ionic liquids mixture ([C<sub>2</sub>mim][NTf<sub>2</sub>]/[C<sub>4</sub>mim][NTf<sub>2</sub>]=1/2.5 by weight ) at 42 °C

It is noted that the intensity distribution shows bimodal distribution function at low temperature below the LCMT, while the particles corresponding to the larger  $R_h$  peak actually occupied little, which is fact that the lager  $R_h$  particle can absorb more lights and the DLS signal of intensity percent is heavily weighted by the large particles. The intensity percent is generally six power of the size of the micelle while the volume percent is just linear to that<sup>[1]</sup>.

Reference

[1] Shibayama, M., Karino, T., Okabe, S. Distribution analyses of multi-modal dynamic scattering data. *Polymer* **2006**, 47, 6446-6456.