

*Supporting Information for:*

**Preparation of Poly(ionic liquid) Nanoparticles through  
RAFT/MADIX Polymerization-Induced Self-Assembly**

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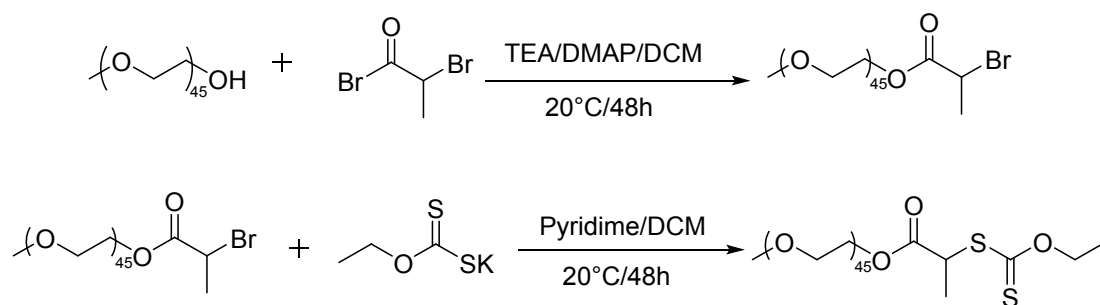
## **Experimental Section**

**Materials:** Poly (ethylene glycol) monomethyl ether (mPEG<sub>45</sub>-OH, Mn = 2000 g/mol), 2-bromopropionyl bromide (98%), potassium ethylxanthate (85%), 1-bromododecane (98.5%), vinylimidazole (98%) and 4-dimethylaminopyridine (DMAP, 99%) were all purchased from Energy Chemical and used without further purification. 2,2'-Azobis(2-methylpropionamide) dihydrochloride (V-50, 97%, Energy Chemical) was recrystallized from methanol/water mixed solvent and stored under refrigeration at 4 °C prior to use. All the aqueous solutions were prepared from deionized (DI) water. Other chemicals were of analytic grade and used without further purification.

### **Characterization:**

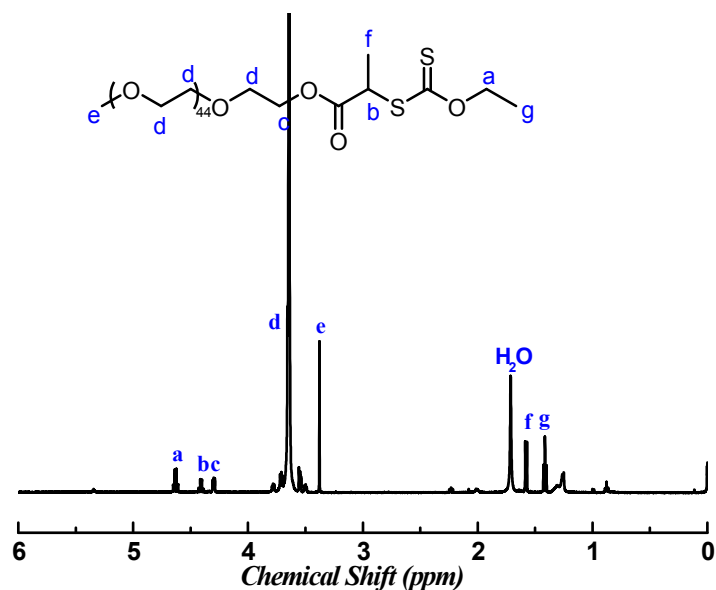
<sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> using Bruker Avance III 500 MHz NMR Spectrometer. Zetazizer ZS90 (Malvern, UK) dynamic light scattering (DLS) was used to determine the hydrodynamic diameter (D<sub>h</sub>) and polydispersity (PDI) of nanoparticles. Transmission electron microscopy (TEM) was conducted on Titan-G<sup>2</sup> 80-200 chemi STEM FEI transmission electron microscope operated at 80 kV. The TEM samples of PIL nanoparticles were diluted to concentrations of 0.2 ~ 1% and stained by uranyl acetate dehydrate before TEM observation.

### **1. Synthesis of PEG-Xanthate macro-CTA:**



mPEG<sub>45</sub>-OH (8.0 g, 4 mmol), triethylamine (0.4 g, 4 mmol), DMAP (4.8 mg, 0.04 mmol) and 80 mL of anhydrous DCM were charged into a dry flask. A solution of 2-bromopropionyl bromide (0.6 mL, 5 mmol) in 30 mL of anhydrous DCM was added slowly at 0 °C, after which the reaction was allowed to proceed at room temperature for 24 h. The reaction mixture was washed thoroughly with 300 mL of deionized water (three times) and dried with Na<sub>2</sub>SO<sub>4</sub>. After the solvent was removed, the product was collected by precipitation in cold diethyl ether, followed by vacuum drying at room temperature, to afford white powder mPEG<sub>45</sub>-Br (6.95 g) with a yield of 81%.

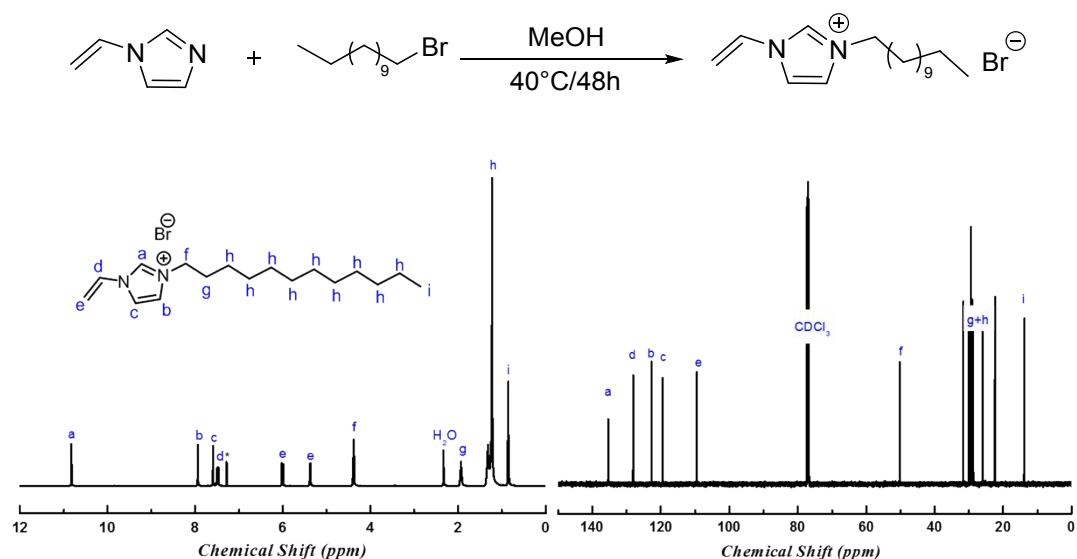
mPEG<sub>45</sub>-Br (3.2 g, 1.5 mmol), potassium ethylxanthate (0.721 g, 4.5 mmol), pyridine (6 mL) and anhydrous DCM (30 mL) were mixed and were allowed to react at room temperature for 48 h. After the solvent was removed, the purified product PEG-xanthate (2.73 g, 84%) was obtained via precipitation in cold diethyl ether, followed by vacuum drying.



**Figure S1.**  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  of PEG-xanthate.

**Synthesis of 3-n-Dodecyl-1-vinylimidazolium bromide ( $\text{C}_{12}\text{VIm-Br}$ ):**

1-Vinylimidazole (3.86 g, 41 mmol), 1-bromododecane (10 g, 40 mmol) and 3 mL of methanol were added into a 25 mL reactor and were stirred at  $40^\circ\text{C}$ . After 48 h, the product was precipitated in cold diethyl ether, and dried at room temperature until constant weight, yielding white solid of 72% conversion.

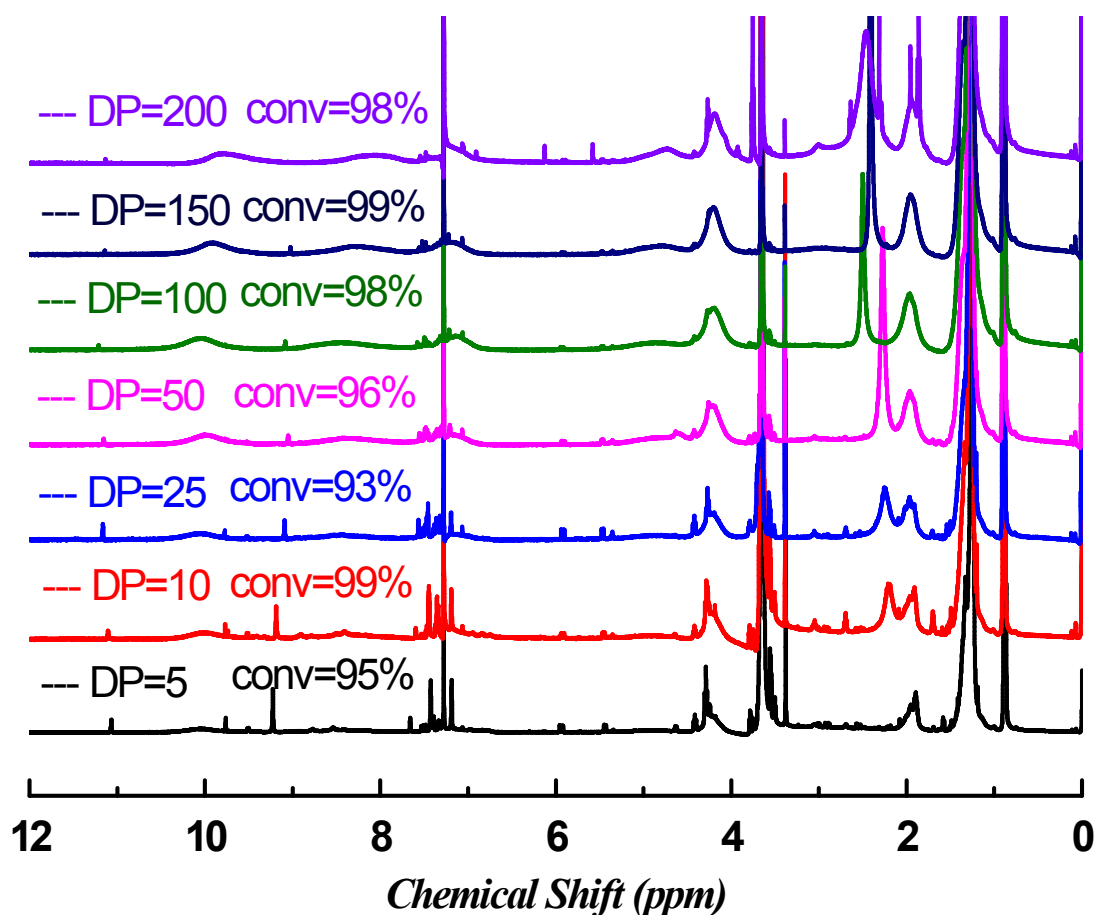


**Figure S2.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$  of  $\text{C}_{12}\text{VIm-Br}$ .

## **Synthesis of PEG-b-PIL Nanoparticles via RAFT Aqueous Dispersion**

### **Polymerization:**

PEG-b-PIL nanoparticles were synthesized by using different molar ratios of C<sub>12</sub>VIm-Br/PEG-xanthate macro-CTA at different solids contents. In a typical experiment (Run 5 in Table 1: [C<sub>12</sub>VIm-Br]/[PEG-xanthate]/[V-50] = 100/1/0.5, solids contents = 5 wt%), C<sub>12</sub>VIm-Br (0.343 g, 1 mmol), PEG-xanthate (22 mg, 0.01 mmol), V-50 (1.4 mg, 0.005 mmol), and water (6.9 g) were charged into a 25 mL round bottom flask to form a homogenous solution. The reaction mixture was purged with argon for 1h, sealed, and immersed into a 65 °C pre-heated oil bath. The reaction was conducted for 24 h under magnetic stirring and quenched by immersing into an ice-water bath. The final conversion of C<sub>12</sub>VIm-Br was around 98%, as indicated by <sup>1</sup>H NMR analysis.

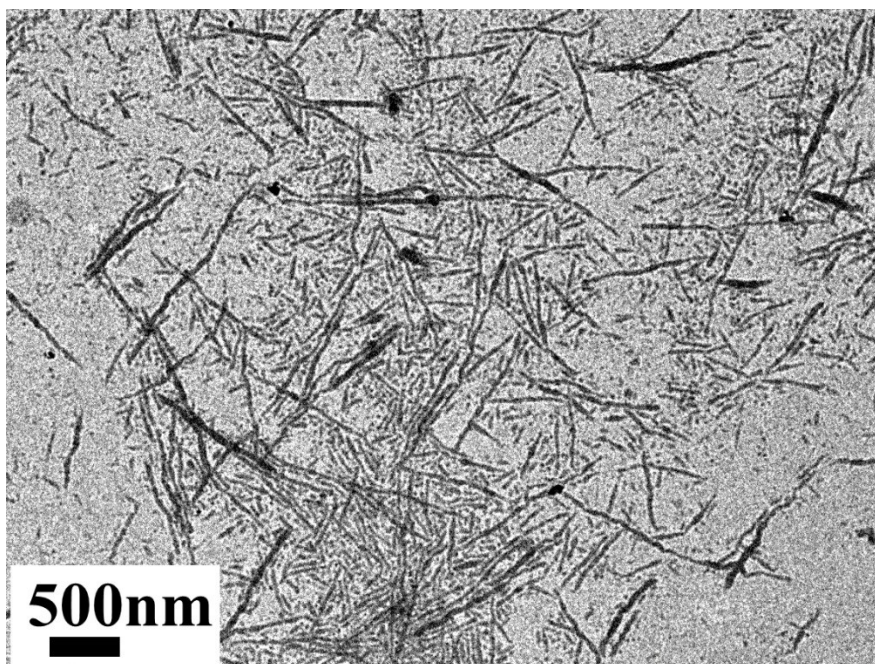


**Figure S3.**  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  of  $\text{PEG-b-P}(\text{C}_{12}\text{VIm-Br})_n$  of different DPs at solids content of 5 wt%. All the runs were carried out at 65 °C for 24h, with a constant  $[\text{PEG-xanthate}]/[\text{V-50}]$  ratio of 2:1.

The monomer conversions were calculated based on the following equation:

$$\text{Conv.} = \frac{A_1/2}{A_2/3} \times 100\%$$

Where  $A_1$  is the area integration of the peaks at chemical shifts of 5.4 and 6.1 ppm (2H of the residual vinyl group), and  $A_2$  is the area integration of the peak at chemical shifts between 0.7 and 0.9 ppm (3H of the methyl group in both  $\text{C}_{12}\text{VIm-Br}$  and  $\text{PEG-b-P}(\text{C}_{12}\text{VIm-Br})_n$ ).



**Figure S4.** TEM micrographs for PEG<sub>5k</sub>-b-P(C<sub>12</sub>VIm-Br)<sub>50</sub> prepared at solids content of 10 wt% (reaction was carried out at 65 °C for 24h, with a [PEG<sub>5k</sub>-xanthate]/[V-50] ratio of 2:1).