Double-Stimuli-Responsive Spherical Polymer Brushes with a Poly(ionic liquid) Core and a Thermoresponsive Shell

Yongjun Men, Markus Drechsler, Jiayin Yuan*
Supporting Information

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Experiment section

Materials

1-Vinylimidazole (Aldrich 99%), 11-Bromo-1-undecanol (Aldrich 98%), 2-Bromo-2-methylpropionyl bromide (Aldrich 98%), water-soluble nonionic azo initiator VA86 (Wake Chemicals), N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA; Aldrich 99%), Potassium bromide (Aldrich 99.95%), Copper(I) bromide (Aldrich 99.99%) were used as received without further purifications. N-Isopropylacrylamide (NIPAM; Aldrich, 97%) was recrystallized three times from a mixture of toluene/n-hexane (v/v) 1:1 prior to use. All solvents used were of analytic grade.

Synthesis of the ionic liquid monomers (ILM)

3-(11-hydroxyundecanyl)-1-vinylimidazolium bromide (ILOH): 0.1 mol of 1-vinylimidazole, 0.1 mol of 11-bromo-1-undecanol, and 40 ml of methanol were loaded into a 100 mL flask. The mixture was stirred at 60 °C for 24 h. After cooling down, the reaction mixture was added dropwise into 1L of diethyl ether. The white precipitate was filtered off, washed three times with diethyl ether, and then dried at 40°C till constant weight (yield: 80%).

3-[11-(2-bromo-2-methyl-1-oxopropoxy) undecyl]-1-vinylimidazolium bromide (ILM): 0.05 mol of ILOH, 0.1 mol K₂CO₃ were mixed with 100 mL dry dichloromethane in a 250 mL flask. The mixture was stirred in ice bath for 15 min, and then 0.1 mol 2-bromoisobutyryl bromide in 50 mL dry dichloromethane were added dropwise into the solution. The whole process was protected by argon. The reaction processed for 12 h. The mixture was filtered to
remove KBr and unreacted K$_2$CO$_3$. The filtrate was concentrated by rotary evaporation until about 50mL left, and then added dropwise into 1L of diethyl ether. Viscous light yellow liquid was precipitated at the bottom, washed three times with diethyl ether, and then dried at 40°C till constant weight (yield: 76%). The $^1$H-NMR and $^{13}$C-NMR spectra were shown in Figure 1B and Figure S1B, respectively. The thermal decomposing temperature is about 160°C (Figure S2). No melting point was observed, but a T$_g$ around -45°C was observed (Figure S3).

**Preparation of poly(ionic liquid) nanoparticle (NP-Br)**

In a typical reaction, polymerization was carried out in a 100 mL Schlenk glass. 50 ml of water containing a certain amount of ILM and VA86 (chemical structure in Figure S5) was first introduced into the reactor, and then deoxygenated by three cycles of freeze-pump-thaw procedure and was backfilled with argon. The flask was then stirred in an oil bath thermostated at 70 °C for 16 h. The formed dispersion was then cooled down to room temperature. The reaction mixture was dialyzed against Milli-Q water (molecular weight cut off at 12 000-14 000 g/mol) for 5 days (being changed 4 times per day) to remove unreacted monomer and initiator. The $^1$H-NMR spectrum of the PIL nanoparticles was shown in Figure S4.

**Grafting PNIPAM onto poly(ionic liquid) nanoparticle (NP-g-PNIPAM) by ATRP**

A suspension of NP-Br (30 mL, d=62 nm, 2.5 wt %) carrying the ATRP initiator layer was degassed for 2.5 h by argon continuous bubbling, and then transferred to the glove box. NIPAM (1.471 g, 13 mmol), PMTETA (45.1 mg, 260 μmol), and CuBr (37 mg, 258 μmol) were added into NP-Br suspension under stirring at room temperature (23 °C) in glove box. All reactions were stopped in 30 min due to extremely high reaction rate. The reaction mixture was purified though dialysis membranes with molecular weight cutoff of 12 000-14 000 g/mol. To estimate the molecular weight of the grafted PNIPAM chains (Entry 6 in Table 1), 5 mg of α-bromoisobutyric acid as co-initiator was externally added to the dispersion of PIL nanoparticles for ATRP of NIPAM. The polymerization was conducted in the same procedure as mentioned above. After the polymerization, excessive KPF$_6$ salt was added to precipitate the brush particles. After centrifugation for 10 min at 9000 rmp, the upper clear solution containing PNIPAM grown from α-bromoisobutyric acid initiator was transferred into a dialysis tube (3500 g/mol), and dialyzed for 2 days in water. The solution was then
freeze-dried to get a PNIPAM powder for GPC measurement (Eluent: NMP; Temperature: 70°C). The $M_n$ was measured to be 18,500 g/mol (DP n ~ 160, PDI ~ 1.63) against PMMA standard.

**Solution behavior of NP-Br and NP-g-PNIPAM at different ionic strength**

KBr were added slowly to a 10 g/L of aqueous NP-Br and NP-g-PNIPAM solution, respectively, under vigorous stirring. The size evolution of the nanoparticles at different salts concentrations were monitored by dynamic light scattering.

**Characterization Methods**

The average particle size (intensity-weighted) and the standard deviation was determined by dynamic light scattering (DLS) at 90° with a NICOMP particle sizer (model 370, NICOMP particle sizing systems, Santa Barbara, CA).

Transmission electron microscopy (TEM) was performed with a Zeiss EM 912 Omega microscope operating at 120 kV. The TEM samples were prepared by placing one drop of the diluted dispersion of PIL nanoparticles on a 200 mesh carbon-coated copper grid and left in air to dry.

Cryogenic transmission electron microscopy (cryo-TEM) characterization was carried out on a Zeiss EM922 OMEGA EFTEM instrument. For the sample preparation, a drop of the sample solution (c ~0.1 g/L) was placed on a lacey carbon-coated copper TEM grid (200 mesh, Science Services, München, Germany), where most of the liquid was removed with blotting paper, leaving a thin film stretched over the grid holes. The specimens were shock vitrified by rapid immersion into liquid ethane in a temperature controlled freezing unit (Zeiss Cryobox, Zeiss NTS GmbH, Oberkochen, Germany) and cooled to approximately 90 K. The temperature was monitored and kept constant in the chamber during all the preparation steps. After freezing the specimens, they were inserted into a cryo-transfer holder (CT3500, Gatan, München, Germany) and transferred to the TEM instrument. Examinations were carried out at temperatures around 90 K. The transmission electron microscope was operated at an acceleration voltage of 200 kV. Zero-loss filtered images ($\Delta E \sim 0$ eV) were taken under reduced dose conditions (100–1000 e/nm2). All images were registered digitally by a bottom mounted CCD camera system (Ultrascan 1000, Gatan), combined and processed with a digital imaging processing system (Gatan Digital Micrograph 3.9 for GMS 1.82).
Proton nuclear magnetic resonance (\(^{1}H\)-NMR) and \(^{13}C\)-NMR spectra were recorded at ambient temperature using a Bruker DPX-400 spectrometer operating at 400.1 MHz and 100.6 MHz, respectively. D\(_2\)O, DMSO-\(d_6\) and CDCl\(_3\) were used as solvents.

Elemental analysis was accomplished as combustion analysis using a Vario Micro device. TGA experiments were accomplished on a Netzsch TG209-F1 apparatus at a heating rate of 10 K min\(^{-1}\) under nitrogen. SEM images were obtained on a LEO 1550-Gemini instrument after sputtering with platinum. FT-IR spectra were collected with a Varian 1000 FT-IR (scimitar series) spectrometer, equipped with an attenuated total reflection (ATR) setup.

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\frac{N_{\text{NP-g-PNIPAM}} - N_{\text{NP-g-PNIPAM}}} {M_{\text{NP-g-PNIPAM}}} = \frac{C}{N} 
\]

Equation (S1)

Scheme S1. Schematic illustration of the temperature and ionic strength responsive NP-g-PNIPAM.

Figure S1. \(^{13}C\)-NMR spectra of 3-(11-hydroxyundecanyl)-1-vinylimidazalium bromide (A) and the ILM with ATRP terminus (B). All chemical shifts can be assigned to the chemical structures.
Figure S2. TGA curve of the ILM with an ATRP terminus.

Figure S3. DSC curve of the ILM with an ATRP terminus. The ILM has no apparent melting point but a low glass transition temperature at -45°C.

Figure S4. $^1$H-NMR spectra of NP-Br in CDCl$_3$ (black line) and in DMSO-d$_6$ (red line, peaks at 2.5 ppm and 3.3 ppm are due to the residue DMSO and water peaks, respectively).
Figure S5. Chemical structure of the water soluble non-ionic thermal initiator VA86.