Supporting Information

Core-shell particle interconversion with di-stimuli-responsive diblock copolymers†

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Methods Details

Monomers and Materials. The IL monomer, 1-(2-acryloxyundecyl)-3-methylimidazolium bromide, was synthesized according to England.[R1] The *N*-isopropylacrylamide was obtained from Acros and recrystallized from toluene:hexane (1:3 v/v). KBr was from Fisher Scientific and the thermal initiator VA-086 from Wako. All water used was distilled (PURELAB PlusTM) with a conductivity of 0.06 μS cm^{-1}.

Polymerizations. The polymerizations were done in a reaction calorimeter (CPA200, ChemiSens). The homopolymerization of the IL monomer was initiated with VA-086 in aqueous solution to produce poly(ILBr) homopolymer. After ultrafiltration of the polymerization mixture through a membrane with 5kDa cut-off the poly(ILBr) homopolymer was isolated in a lyophilizer. The poly(NIPAM) block was next grown from the poly(ILBr) block using redox initiation, where the concentration of the Ce^{4+} oxidant was chosen so that mainly one side of the homopolymer was initiated.[S1] The detailed structure of the block copolymers, whether diblocks or triblocks, cannot be specified as it depends also on the termination. The success of this comparably easy method to make block copolymers (diblock and multiblock copolymers and colloidal particles) has been repeatedly demonstrated.[R2,R3]

Dynamic Light Scattering. The thermoresponsive behavior as seen in coil length and particle size were measured using dynamic light scattering (Nicomp 380, Santa Barbara, USA equipped with a 25 mW laser).

Solids Determinations. Solids were isolated by drying and by lyophilization.

Analytical UltraCentrifugation (AUC). Poly(ILBr) homopolymer blocks were run in 0.1 M Nacl on a Beckman Optima XC-I analytical ultracentrifuge (Beckman Coulter, Palo Alto, California, USA) at 60,000 rpm and analyzed by Rayleigh interference optics.

NMR Measurements. ^{1}H NMR (Bruker-DXP 400) was used to check composition, and to measure relative peak areas of various resonances to help estimate diblock molecular weight and to evaluate whether particular blocks were condensed in the core region during particle precipitations.

Dialysis. Dialysis was done to remove the excess KBr by using 2kDa cut-off tubing (Sigma_Aldrich D2272). The water volume (1500 mL) was exchanged 3-4 times and until the conductivity of the filtrate essentially matched that of the freshly purified water.

Molecular Weight Estimations

Because this hydrophilic diblock is so amphiphilic, it was impossible to get reliable molecular weight estimates by conventional size exclusion chromatography. We used DMSO, DMF, and hexafluorylisopropanol (extensive studies in this solvent were kindly done by Dt. Thomas Mourey and Ms. Lisa Slater of the Eastman Kodak Company, Rochester, NY, USA) as carrier solvents, and we could not get reliable and sensible results. However, we were able to get self-consistent results for the PIL blocks by analytical ultracentrifugation, so we then used ^{1}H NMR to estimate the NIPAM to ILBr monomer ratios, in the diblocks, by examining the ratios of PNIPAM methyl protons to PIL undecyl protons of the central seven methylene groups. Estimates of molecular weight were obtained using size exclusion chromatography (SEC) in dimethylsulfoxide for our poly(NIPAM) comparison sample and analytical ultracentrifugation in water for diblocks **I** and **II**.

AUC measurements. Aliquots of the poly(ILBr) homopolymers used for diblocks **I** and **II** were isolated prior to adding the poly(NIPAM) blocks and analyzed by various methods for molecular weight distribution. The analytical ultracentrifugation results rest on the fewest assumptions, and were used to estimate hydrodynamic average molecular weights for these two poly(ILBr) homopolymers, **I** and **II**, respectively. The optical results from the ultracentrifugation are illustrated in Figure S1, where absorption intensity is plotted as a function of the sedimentation coefficient, S, in Svedbrgs.

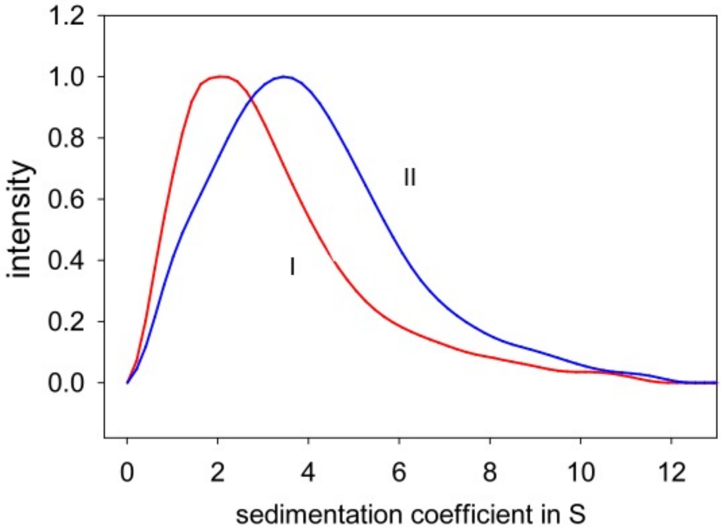

Figure S1. "Intensity" as a function of sedimentation coefficient (S, Svedbergs) for the poly(ILBr) homopolymers used for preparing diblocks I and II, respectively. This "Intensity" is the least squares direct boundary modeling of fringe shifts in the 100 repeat sedimentation scans.

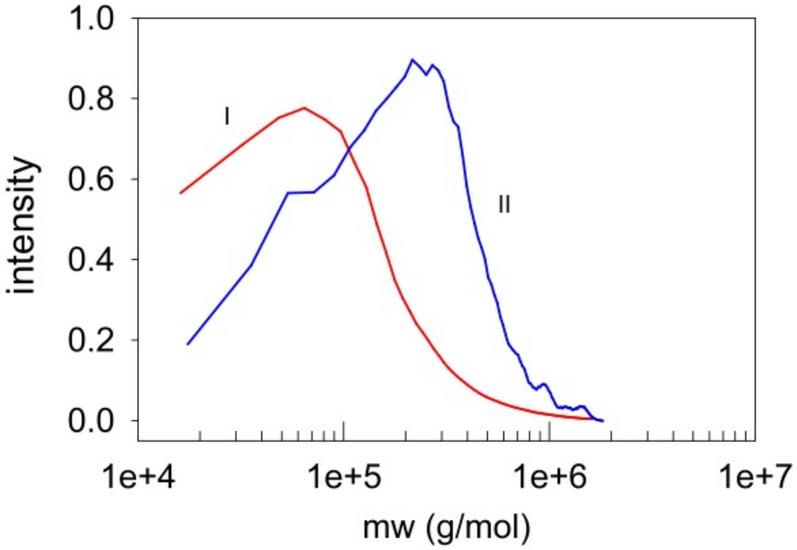

Figure S2. Calculated molar mass distributions of hydrodynamic molecular weights for diffusion corrected sedimentation coefficient distribution s fo Lamm equation solutions[R4] for the poly(ILBr) homopolymers used for preparing diblocks I and II, respectively.

These sedimentation data were then transformed into the hydrodynamic equivalent molecular weight distributions illustrated in Fig. S2. Here the relative mass is plotted as a funcitn of hydrodynamic molecular weight. The maxima of these distributions occur at 60kDa and 250kDa, respectively, for homopolymer blocks **I** and **II**.

NMR analysis of monomer ratios.

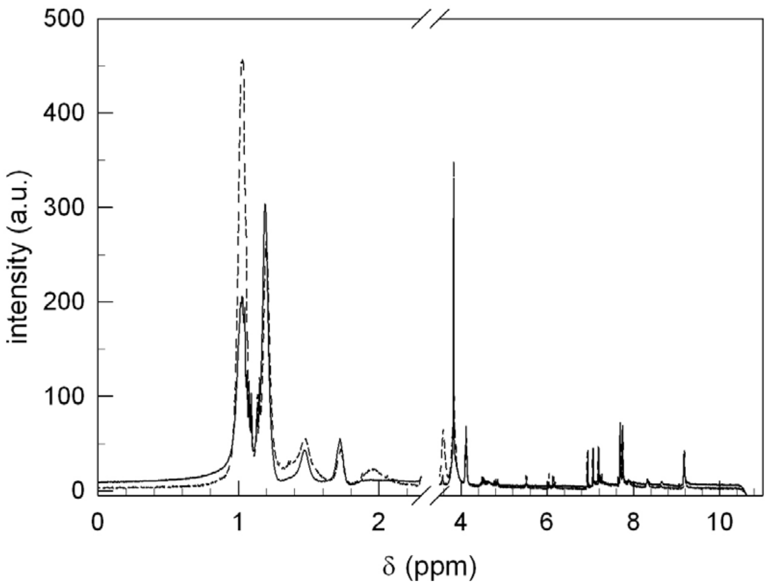

Figure S3. ^iH NMR spectra of the diblocks I (——) and II (– – –), respectively.

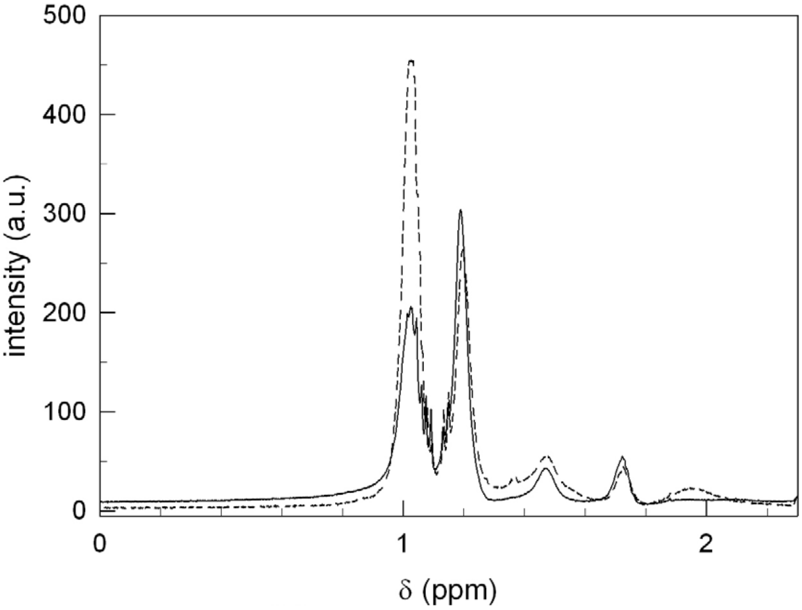

Figure S4. Expanded view of the 0 to 2.3 chemical shift region of the ^iH NMR spectra of the diblocks I (——) and II (– – –), respectively. The poly(NIPAM) methyl group resonances are just slightly above 1 ppm and the next peek just above 1.2 ppm corresponds to the central 7 methylene protons of the undecy group in the ILBr monomer groups.

The area ratios of the poly(NIPAM) methyl group protons just above 1 ppm relative to the undecyl methylene protons (for the central 7 methylene groups) at about 1.2 ppm were used to estimate the ratio of NIPAM and ILBr monomers incorporated into the respective diblocks **I** and **II**. From repeat runs and determinations using spectra such as those in Figs. S3 and S4, we obtained estimated of 1.8 and 2.6, respective ely, for the number ration of NIPAM to ILBr units in diblocks **I** and **II**. The total diblock hydrodynamic molecular weights were then estimated as 93kDa and 450kDa, respectively, for diblocks **I** and **II**.

Auxiliary Results

Assignments of Core-Shell Components. Our initial assignments of the core-shell chemical components was based on our designed model of heat condensing poly(NIPAM) in the core and high bromide induced precipitation condensing poly(ILBr) in the core, with the remaining block staying predominately in a hydrated corona region providing steric stabilization. However, such presumption is not an adequate substitute for concrete physical proof. When the poly(ILBr) blocks are condensed in high bromide and the resulting particles are being stabilized by a corona of hydrated poly(NIPAM) blocks, it was our presumption that heating such suspensions above the poly(NIPAM) LCST would result in macroscopic phase separation by coagulation of the particles, due to unstabilzied aggregation of the poly(NIPAM) corona. In initial experiments where we precipitated the poly(ILBr) blocks with KPF_6 and with NaBF, and we then heated the stabile dispersions, we in fact observed the expected results. We then centrifuged the mixtures to remove the phase separated material for further experiments in studying the redispersion of such material in deionized water at room temperatures and above.

In the case addressed in this paper, where condensation to produce a nominally poly(ILBr) core was achieved by adding excess bromide anion, we recorded the heating process photographically. This sequence of photographs is illustrated in Fig. S5.

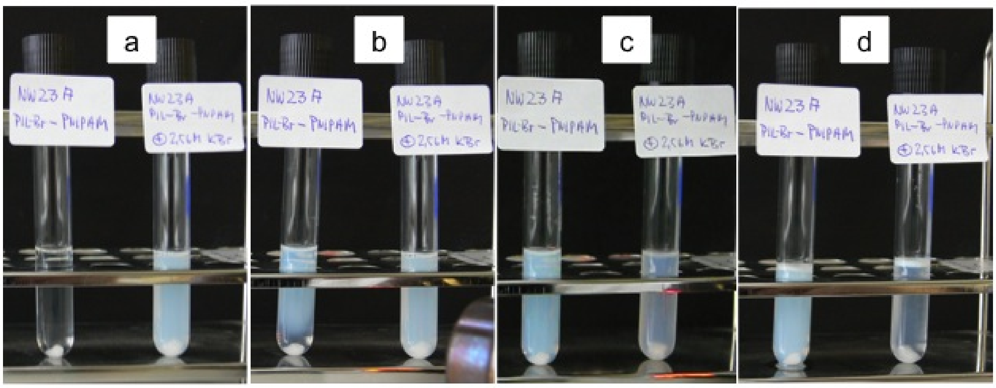

Figure S5. In each from we have on the left a solutin of diblock II in water and on the right the same solution of diblock II after adding and excess of KBr (2.56 M KBr net) to precipitate poly(NIPAM) corona stabilized particles. The white objects at the bottom of each tube is a boiling stone. (a) The starting solution and dispersion. (b) After beginning to heat the solution on the left and the dispersion on the right, we see condensation of poly(NIPAM) core particles stabilized by poly(ILBr) blocks by the advancing (desending) turbidity on the left, and not much change on the right. (c) After more extensive heating we see increased turbidity on the left, and an apparent decrease in turbidity on the right, indicating coagulation of small particles into larger particles. (d) After further heating we see higher turbidity on the left, and further lessening of turbidity on the right. In addition on the right, a layer of coagulum, indicating macroscopic phase separation, has collected at the upper fluid/air interface in the tube on the right.

The heating sequence in Fig S5 shows a repeat of the thermal condensation of poly(NIPAM) blocks to form super stable core shell particles, stabilized by a corona of poly(ILBr) blocks. In addition, the heating of the tubes on the right of each frame shows the conversion of a stable poly(ILBr) core – poly(NIPAM) shell particle dispersion into a macroscopically phase separate system with coagulum creaming to the fluid-air interface and the overall turbidity decreasing as small particles coalesce to larger particles and on to phase separated coagulum.

We also examined analogous solution and dispersion pairs, such as the one illustrated in Fig. S5(a), except instead of water we used D_2O, the diblock **II** concentration was 2.5% w/w in the solution and about 1.25% in the KBr precipitated case (where a volume of 2.5% w/w diblock **II** was mixed with an equal volume of 15% KBr in D_2O). We measured both of these systems at 26°C by ^{1}H NMR, and a substantial portion of the NMR spectra are illustrated in Fig. S6. Here we see on going from the black to green spectrum as substantial drop in the signal heights due to dilution by the KBr solution addition. However, a substantial decrease in the relative methylene proton resonance area at about 1.4 ppm relative to the poly(NIPAM) methyl resonance is seen, and quantitatively this change in proton peak area ratio, methyl/methylene, goes from about 1.95 to 2.6. This change very strongly supports our assignment of a poly(ILBr) core and a poly(NIPAM) corona upon precipitation by excess bromide.

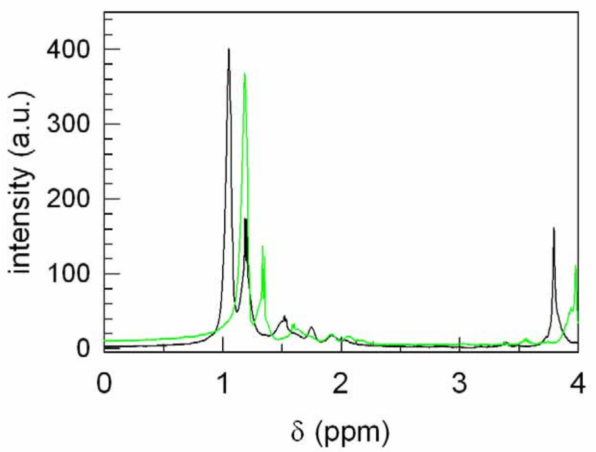

Figure S6. ^{1}H NMR spectra at 26°C for diblock II (——) at 2.5% w/w in D_2O and (———) at 1.25% w/w in D_2O after addition of an equal volume of 15% w/w KBr in D_2O.

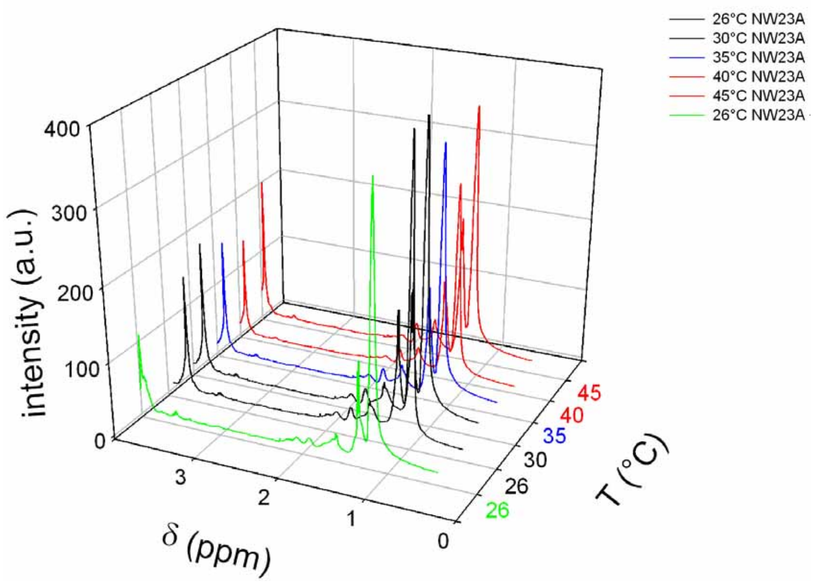

Figure S7. ^{1}H NMR spectra at 26 (——), 30 (——), 35 (——), 40 (——), and 45°C (——) for diblock II at 2.5% w/w in D_2O as the solution is heated; the 26C green curve (——) is the same as that shown if Fig. S6 after addition of KBr.

The data of Fig. S6 are also depected in the perspective Fig. S7, as are a series of spectra for the 2.5% w/w diblock II solution as the temperature is increased from 26 to 30 to 35 to 40 to 45°C. These spectra do not change much on going from 26 to 30°C, but above the LCST of poly(NIPAM) at 35°C, the intensity of the poly(NIPAM) methyl proton resonance decreases and continues to decrease with increasing temperature. While the resoance at 45C appears to have increased again, the methyl/methylene ratio steadily decreases above the LCST as illustrated in Fig. 5 of the manuscript. Again, these NMR data nicely corroborate our assignment of a poly(NIPAM) core as the temperature is raised above the LCST at 32°C.

TEM of diblock II. While our TEM capability ruled out capturing the PNIPAM-core-PIL-shell particles (dissolve on cooling) or the conjugate PIL-core-PNIPAM-shell particles (dissolve on dilution), we were able to image the diblock **I** materials by drying a solution on a TEM grid, as illustrated in Fig. Sx. There we see a fairly dispersed set of deposits illustrating phase separation of the blocks, wherein the darker phase is attributed to the PIL blocks.

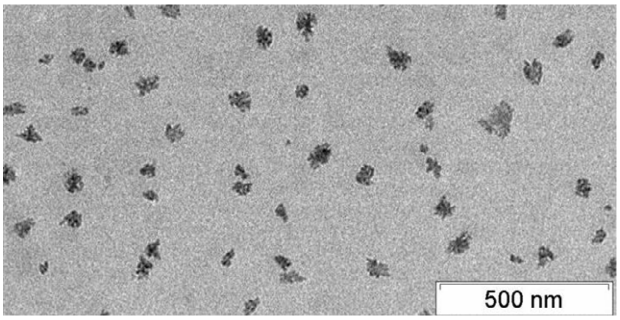

Figure S8. TEM of diblock **I** prepared by drying a solution of **I** on the TEM grid.

Supplementary References

R1 England, D. MS Thesis. Eastern Michigan University (2008).

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