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

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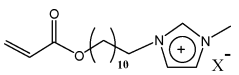
Core–shell reversible particle precipitation from aqueous di-stimuli-responsive diblocks is demonstrated as also is the interconversion from one core–shell combination to the other.

Ionic liquids (ILs; organic salts with melting points less than 100 °C)[1] and polymers of ionic liquid monomers (PIL)[2] are exhibiting diverse uses in various types of chemical synthesis,[3,4] electrochemical applications requiring high polarization,[5] and alternative solvation[6] while exhibiting high chemical and thermal stability and virtually no vapor pressure. The combination of such polymerized ILs with other monomers and materials[7,8] is providing diverse porous materials[9,10] including polyelectrolyte membranes suitable for fuel cells and fast ion batteries,[11] super-stable latexes[12] for new classes of organic coatings and composite films of nanocarbon,[13] and diverse nanoparticle suspensions. The anion and solvent stimuli responsiveness[14,15] of such IL-based materials provide chemical and physical switches around which new materials and processes may be designed. Many amphiphilic diblock copolymers have been synthesized,[16] but their condensation from solution usually results in macroscopic phase separation into amorphous domains or into mesophases of diverse types.[17] We show herein that di-stimuli responsive diblock copolymers incorporating an anion sensitive PIL block and a thermoreversible block provide tunable new materials. We use this tunability by design to demonstrate core–shell particle formation on submicron length scales and the *interconversion* of one core–shell multiphase domain into the other. While such amphiphilicity has been shown to provide micellar inversion using solvent responsiveness,[18,19] the materials we derive show how such materials may be used to construct ultrastable dispersions and switchable core–shell inversion. We expect that these dispersions will provide new approaches to chemical delivery and alternative pathways to the synthesis of hydrogel particles and phases and will broaden the types of stimuli responsive sensors that can be fabricated.

Diblocks were synthesized by free radical chain polymerization. We first synthesized poly(ILBr) blocks using a thermal initiator (2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide]), which was done at 70 °C and at 90 °C to produce short and longer poly(ILBr) blocks, respectively, keeping the respective monomer amounts the same. We next used a redox initiator comprising Ce^{4+} that produces a radical on the α-methylene group adjacent to the hydroxyl group in the presence of *N*-isopropylacrylamide (NIPAM) to grow the poly(NIPAM) block.[20,21] We denote the diblock with the shorter poly(ILBr) block **I** and the one with a longer poly(ILBr) block as **II**. Analytical ultracentrifugation indicated hydrodynamic molecular weights of 60 kDa and 250 kDa, respectively, for the poly(ILBr) blocks in **I** and **II**. From ^{1}H NMR, the number ratio of NIPAM to ILBr units was about 1.8 for **I** and about 2.6 for **II**. We estimate total molecular weights of approximately 93 kDa for **I** and 450 kDa for **II** (see ESI†).



ILBr ($X^- = Br^-$)

In Fig. 1 we summarize the effects of temperature on the particle size of aqueous solutions of **I** and **II** and a poly(NIPAM) comparison sample (SEC $M_w \approx 600$ kDa in DMSO). We see that as the LCST (lower critical solution temperature)[22] of poly(NIPAM) is approached, the diblock solutions begin to condense and transform from 30 to 50 nm extended coils in solution to 1–2 μm diameter particles based on intensity weighted photon correlation data; most of the particles are submicron in size, as seen by the relatively low turbidity their suspensions exhibit. We see that the thermoreversible LCSTs for the diblocks are essentially the same as that for the poly(NIPAM) control. For both the diblocks, we see that the condensation of the poly(NIPAM) blocks leads to condensation and aggregation, but instead of obtaining macrophase separation, we obtain colloidally stable particles, having poly(NIPAM) cores and stabilizing poly(ILBr) corona from the diblocks.

The significance of this poly(ILBr) block stabilization can be better appreciated by the sequence illustrated in Fig. 2. There we see that with heating the solution turns highly turbid, but the particles formed remain colloidally stable, even while

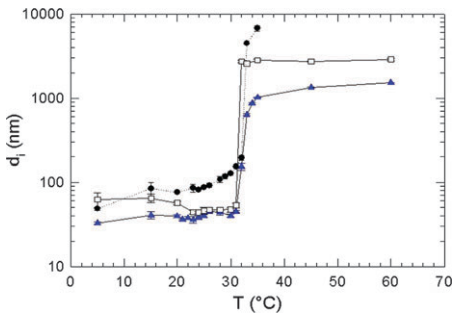


Fig. 1 Intensity weighted diameters of extended coil and condensed particle size evolution of poly(ILBr-*b*-NIPAM) **I** (□) and **II** (blue triangle) solutions and suspensions and of comparison poly(NIPAM) homopolymer (●) solutions and suspensions, all at 1.9% (w/w) solids, upon heating.

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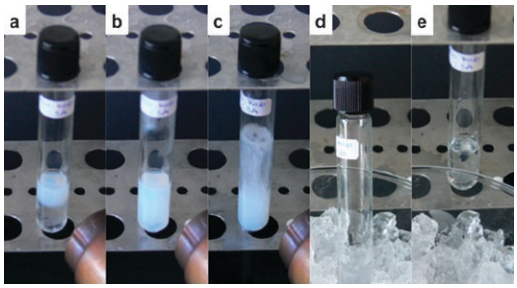

Fig. 2 Heating–cooling cycle showing the transformation of aqueous poly(ILBr-*b*-NIPAM) to the formation of poly(NIPAM) core particles, very well stabilized by corona-forming poly(ILBr) blocks: (a) initial condensation as solution warms; (b) the whole solution has warmed; (c) the suspension is actively boiling; (d) the suspension is being cooled in ice; (e) clear solution after re-dissolution of poly(NIPAM) cores following cooling in (d).

boiling (Fig. 2c). After boiling and after the suspension is cooled in ice, we see that an optically clear solution of the diblock is reversibly recovered (Fig. 2e).

The anion sensitivity of the poly(ILBr) blocks[9] suggested we investigate whether high bromide induces condensation. Earlier it was found that poly(ILBr-*co*-MMA) nanolatexes were precipitated by Br^-, BF_4^-, PF_6^-, and S^{2-},[9,12] by a mechanism based on imidazolium–anion condensation, rather than a Debye–Hückel screening effect. We found such an effect in this aqueous diblock system as well. In Fig. 3 we illustrate the effect of increasing Br^- concentration on particle size, and it appears that at a starting diblock **II** concentration of 1.9% (w/w), the diblock condenses above a Br^- concentration of 1.5 M. Note that the intensity weighted particle size remains relatively small, in the range of 300–400 nm, even at 2.3 M Br^-! In this system, while the poly(ILBr) block is condensed, the colloidal stability appears provided by a corona of poly(NIPAM).

This anion–imidazolium based condensation cycle is illustrated in Fig. 4, where we see the onset of colloidal particle formation in Fig. 4b at about 0.3 M KBr. A turbidity is just visible and a previously formed hard foam (indicating the diblock has become essentially nonionic) is evident. As the Br^- concentration is increased to 2.56 M in Fig. 4c the turbidity increases as shown. We then see that this stable colloid in high Br^- can be dialyzed, resulting in dissolution of the particles to form an aqueous solution of the diblock **II**. In this experiment the KBr was added as a powder to the solution/suspension, so

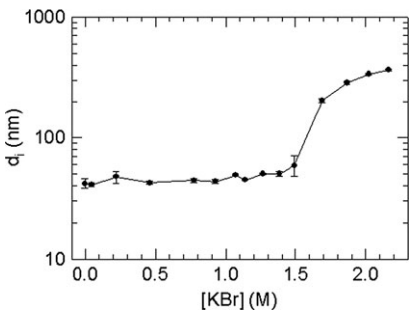

Fig. 3 Evolution of intensity weighted diameters of extended coils and condensed particle sizes for poly(ILBr-*b*-NIPAM) diblock **II** solutions and suspensions upon addition of 4.64 M aqueous KBr solution to a 1.9% (w/w) solution of **II**.

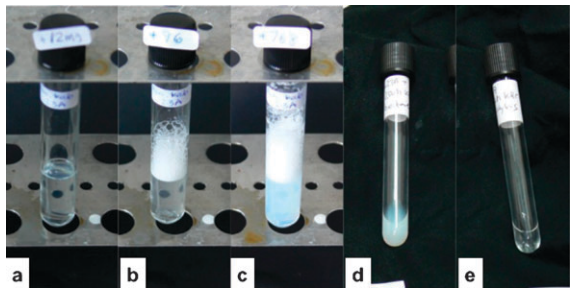

Fig. 4 KBr addition–removal cycle showing the transformation of aqueous poly(ILBr-*b*-NIPAM) diblock **II** to the formation of poly(ILBr) core particles, very well stabilized by the poly(NIPAM) blocks: (a) starting 1.9% (w/w) solution of **II**; (b) just noticeable turbidity at about 0.3 M KBr and "hard foam" due to diblock becoming essentially a nonionic surfactant due to high bromide binding; (c) highly turbid condensation product at 2.56 M KBr; (d) same as in (c) but in smaller culture tube; (e) after extensive dialysis (18 h) to remove excess KBr illustrating complete dissolution of the poly(ILBr) core particles.

that the concentration of **II** was hardly diminished as the Br^- concentration was increased. In the experiment illustrated in Fig. 3, the onset at 1.5 M KBr illustrates the concentration dependence of the condensation of **II**. Similar effects were seen in precipitating latexes of poly(ILBr-*co*-MMA).[12]

The ratio of ^{1}H resonance areas of poly(NIPAM) isopropyl methyl protons to poly(ILBr) undecyl methylene protons is plotted in Fig. 5 for diblock **II** as a function of increasing temperature, and at 26 °C after addition of high KBr. As the blocks condense in the core we expect their proton mobilities to slow and the intensity of their proton resonances to decrease. We see that as the diblock solution is heated above the poly(NIPAM) LCST, this ratio steadily decreases, consistent with the isopropyl methyl proton signals decreasing in relative area by 30%; this decrease results from a decrease in the relative mobility of these methyl protons. In addition, this ratio increases by 33% upon addition of high amounts of KBr; this change is consistent with the core condensation of the poly(ILBr) undecyl methylene groups, and a concomitant decrease in the mobility of these protons. See the ESI† for the corresponding NMR spectra.

Leung *et al.*[23] reported core–shell particle formation from poly(NIPAM-*g*-ethyleneimine) and poly(NIPAM-*g*-chitosan) di-stimuli responsive (temperature and pH) copolymers. In these systems poly(NIPAM) was grafted off of amine groups in the hydrophilic polymer above the LCST and pH was used to vary the thickness of the outer charged shell. The NIPAM core

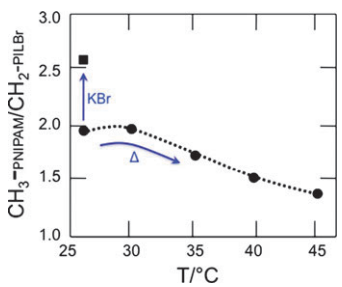

Fig. 5 Methyl to methylene proton resonance area ratio for diblock **II** at 2.5% (w/w) in D_2O as a function of temperature (●) and the same ratio at 26 °C (■) after mixing with an equal volume of 15% KBr in D_2O.

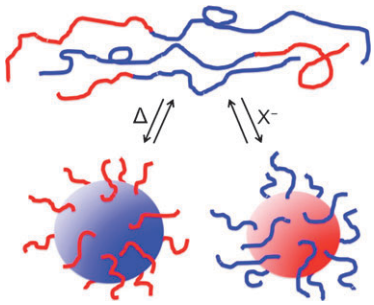

Fig. 6 Cartoon illustrating reversible condensation of particles from di-stimuli responsive diblocks to produce (left) poly(NIPAM) core nanoparticles on heating or (right) poly(ILBr) core nanoparticles on addition of excess bromide.

was crosslinked with *N*,*N*-methylenebisacrylamide. Aqueous diblock solutions of poly(2-[dimethylamino]ethyl methacrylate-*b*-methacrylic acid),[24] of poly(methylmethacrylic acid-*b*-IL),[25] and of poly(acrylamide-*b*-IL)[25] (different IL monomer than ours) were utilized to form vesicles, setting a precedent for reversibly traversing a first order phase boundary in colloidally stable particle formation from aqueous diblock solutions.

We believe that this system, shown schematically in Fig. 6, illustrates the first core–shell particle interconversion where first order boundaries are traversed in each condensation and dissolution step. This thermodynamic constraint distinguishes this system from homologous interconversions achieved in *de facto* micellar systems,[18,19] where the only phase transitions are continuous or second order. Amphiphilic diblock copolymers of every charge type are expected to exhibit such regular and inverse micelles for the same solvent interaction reasons as "regular surfactants", and in every such micellar or microemulsion case, these core–shell micelles or reverse micelles are manifestations of exotic complexes of thermodynamically single phase solutions.[26]

These second order processes will be studied and reported upon subsequently once a more systematic phase study can be executed in detail. However, of greater importance is achieving an understanding of the microphase separation processes exhibited herein to result in highly stable dispersions and the details of the longer length scale aggregation of diblocks to form much larger particles. While solvent shifting is a well known and industrially very important process for dispersing chemicals in an immiscible fluid, usually water, additional stabilizing components (surfactants, polymers) are always necessary to provide kinetic stabilization (colloid stability) against macrophase separation.[27]

The primary factor making this core–shell interconversion possible, we believe, is that both hydrophilic blocks are good stabilizers in water. The basic diblock can be taken into aqueous solution at the conclusion of its polymerization, when the reaction mixture is cooled to room temperature, or after being isolated in the solid state following lyophilization. Then, core–shell particles can be formed by condensation, either thermally or by mass action with bromide condensation of the imidazolium groups. In each case the phase separation is nanoscopic, owing undoubtedly to micellar seeding and a water-loving corona provided by the block not being condensed. This stabilization is remarkable, particularly in the case of the thermal condensation, where stabilization persists to boiling! The dissolution of each type of particle is achieved by either lowering the temperature or by lowering the bromide chemical potential (*via* dialysis). When poly(ILBr) core particles stabilized by poly(NIPAM) corona are heated, macroscopic phase separation results (see ESI†).

This superstabilization by the PIL corona is one of the new and exciting features of ionic liquid stabilizers, and represents a truly expanded potential for the use of diblocks in advanced materials synthesis and particle stabilization. We expect triblock (our diblocks illustrated here further incorporating hydrophobic blocks) and surface grafted or surface polymerized analogues of these di-stimuli responsive diblocks to revolutionize dispersion stabilization and processing.

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