Supplemental Information

Reversible Colloidal Crystallization

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Some additional comments on latex particle and suspension purification are warranted. In this study, some limited purification was achieved by decanting aqueous suspensions of crystals. We illustrate how this limited purification improves crystal quality (comparing Fig. 1 with Fig. 2(left)), and we attribute this effect to lengthening of the Debye-Hückel length in the main text. This decanting decreases salt levels of indifferent salt emanating from the redox initiator components. It also decreases any unreacted monomer, mainly $VHOC_{11}ImBr$, although our own experience is that the extent of conversion of primary monomer in such systems is 97%-99%+.

Improved purification by decantation and aqueous resuspension can be done by centrifuging suspensions before decantation. More exhaustive elimination of indifferent salt can be effected by dialysis using dialysis tubing or cartridges or by equivalent ultrafiltration at constant volume.

Further studies of this monomer system should also utilize analytical determinations of unreacted monomer in the aqueous supernatant and in the polymer latexes (unreacted monomer is expected to adsorb to polymer particles). Unreacted monomer in supernatant can be determined by sequentially (1) determining salt and monomer gravimetrically by drying a gram or more of supernatant at 80°C-100°C in a drying oven and (2) determining the imidazolium bromide component content of such solids from drying by dissolving and titrating with aqueous silver nitrate to an AgBr endpoint. Similar titration analyses of dried polymer subjected to solvent extraction can be used to determine unreacted monomer associated by adsorption to and absorbtion in latex particles.

These auxiliary data complement the data presented in the main manuscript text. Figure SI-1 is an experimental thermogravimetric analysis, TGA, of the main monomer (Scheme 1), $VHOC_{11}ImBr$. It was obtained by scanning from room temperature to about 580°C at 10C/min in a purging stream of dry nitrogen gas.

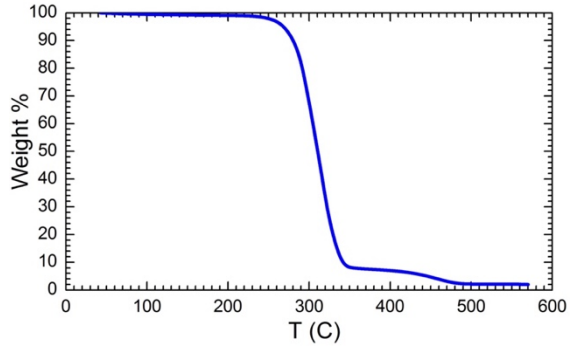

Figure SI-1. TGA of $VHOC_{11}ImBr$

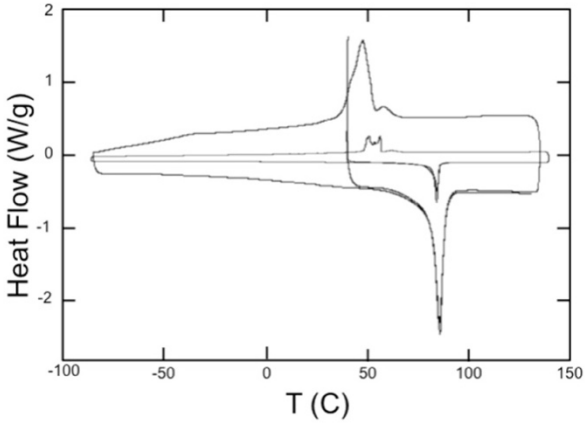

Figure SI-2. DSC analysis of monomer, $VHOC_{11}ImBr$, at two different scan rates.

Differential scanning calorimetry (DSC) analyses of the monomer $VHOC_{11}ImBr$ is illustrated in Fig. SI-2 at scan rates of 10°C/min and 2°C/min. Scans were initiated at room temperature, heated to about 135°C, held for 5 min, cooled to -85°C, held for 5 min, and heated to 135°C.

A proton NMR spectrum of the monomer, $VHOC_{11}ImBr$ in $CDCl_3$ is illustrated in Fig. SI-3 along with tentative resonance assignments. The acidic ring proton, H_a, resonance at about 11.19 ppm

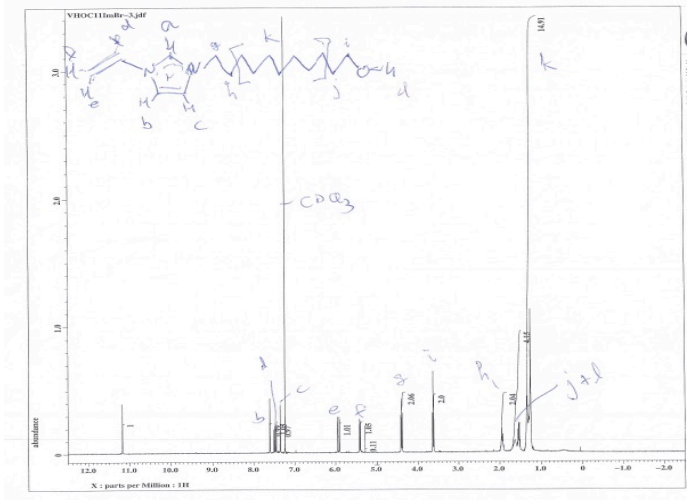

Figure SI-3. Proton 400 MHz NMR spectrum of $VHOC_{11}ImBr$ in $CDCl_3$.

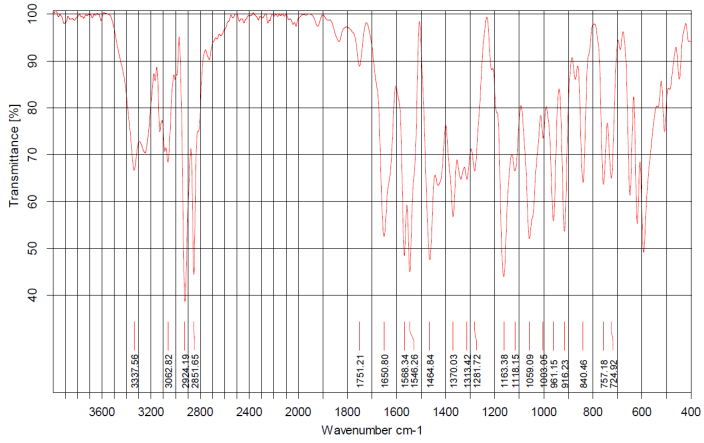

Figure SI-4. FTIR spectrum of $VHOC_{11}ImBr$ in $CDCl_3$.

FTIR spectrum of $VHOC_{11}ImBr$ dispersed in a KBr pellet is shown in Fig, SI-4.

TGA of crosslinker, BisVImBr, is illustrated in Fig. SI-5, scanned from room temperature to 590°C at 10°C/min in a dry nitrogen stream.

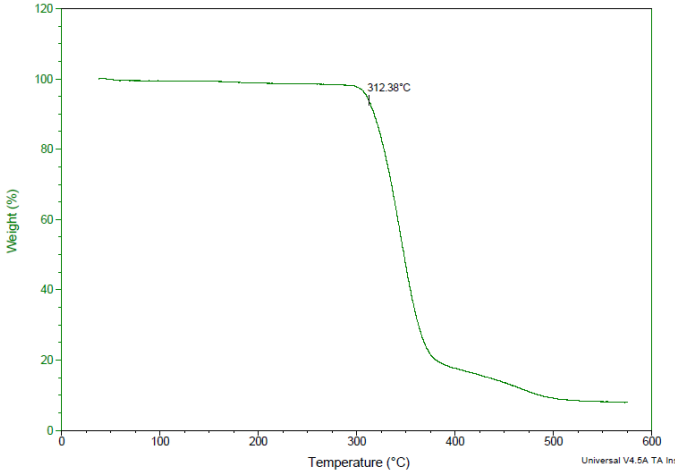

Figure SI-5. TGA of BisVImBr

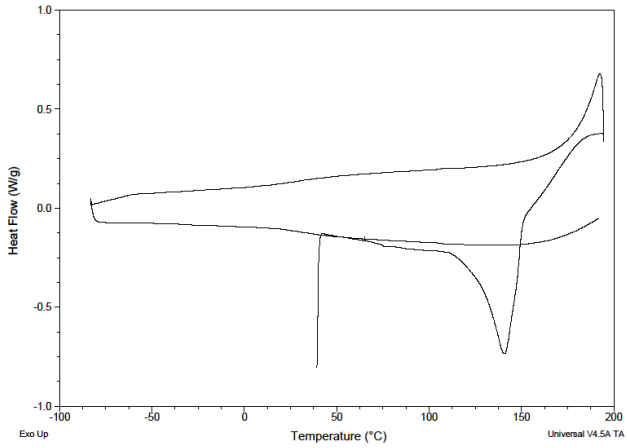

Figure SI-6. DSC of BisVImBr cross-linker.

DSC analysis of crosslinker, BisVImBr, scanned at 10°C/min from room temperature to about 185°C, held for 5 min, cooled to – 85°C, held for 5 min, and heated to 185°C. A glass transition is seen on cooling over 35°C to 20°C and on warming over 25°C to 48°C. After melting in the first heating scan over 115°C to 150°C, subsequent crystallization and re-melting are not observed.

FTIR of BisImBr in a KBr pellet is illustrated in Fig. SI-7.

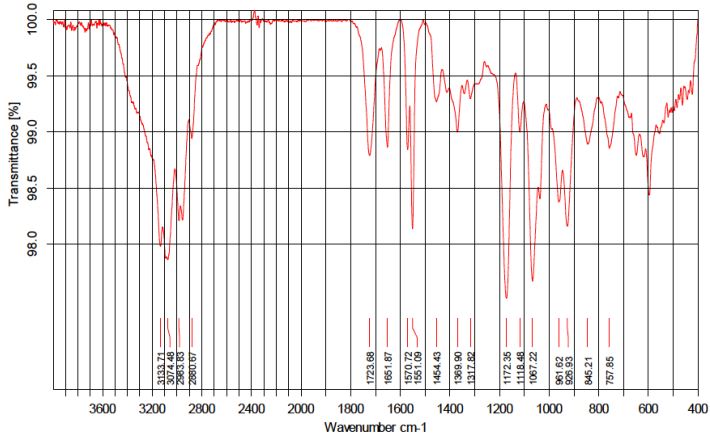

Figure SI-7. FTIR of BisVImBr cross-linker.

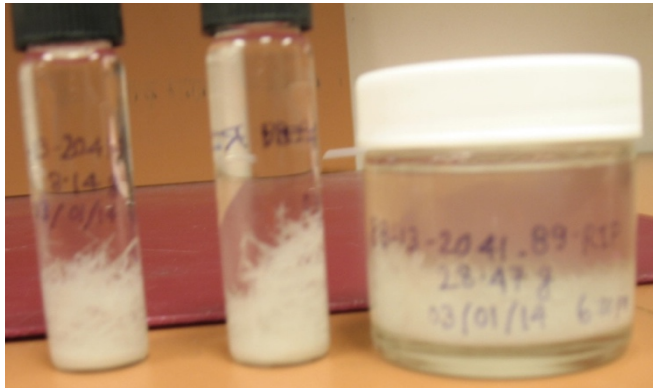

Figure SI-8. Photograph of reaction products decanted into these vials and chilled overnight in a refrigerator at 4°C.

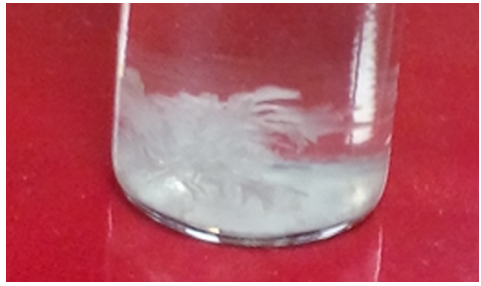

Figure SI-9. Photograph of crystals formed from supernatant S1 after refrigerating at 4°C.

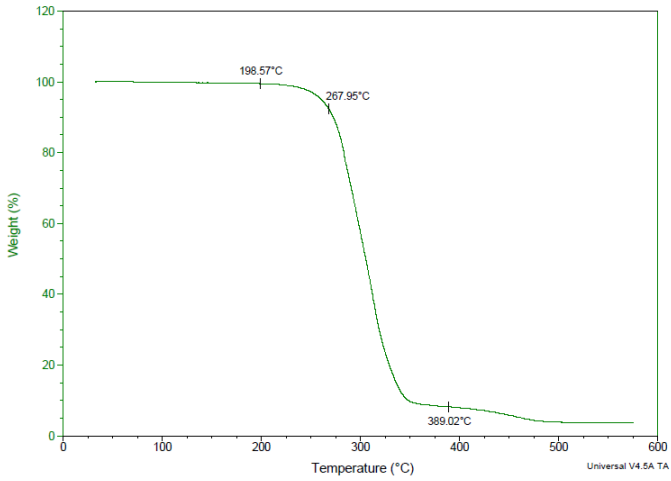

Figure SI-10. TGA of polymer

TGA of polymer is illustrated in Fig. SI-10, scanned from room temperature to 590°C at 10°C/min in a dry nitrogen stream.

DSC analysis of polymer, scanned at 10°C/min from room temperature to about 130°C, held for 5 min, cooled to – 85°C, held for 5 min, and heated to 130°C. A glass transition is seen on warming over -75°C to -50°C. Endothermic peaks are visible over 75°C to 85°C and an exothermic peak is seen on cooling from 55°C to 30°C.

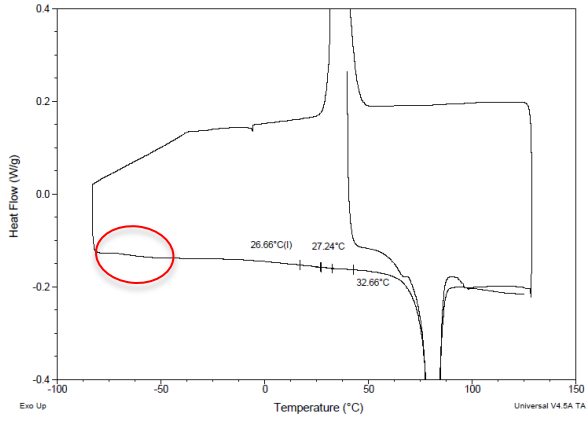

Figure SI-11. Expanded scale DSC of polymer.

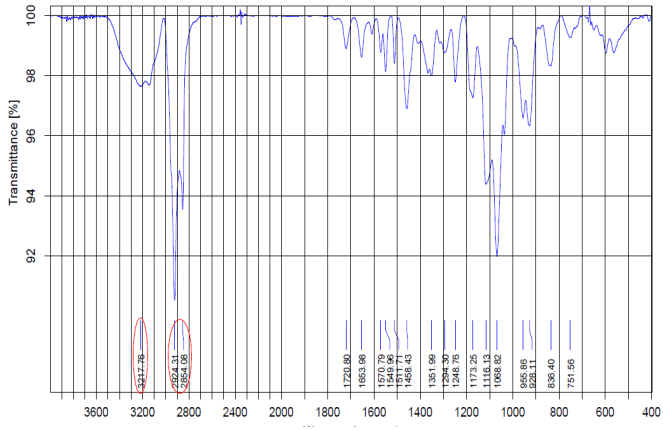

Figure SI-12. FTIR of polymer.

FTIR of polymer dispersed in a KBr pellet is illustrated in Fig. SI-12

Photograph of polymer after extensive drying of crystal aggregates illustrated in Fig. 4(right).

Figure SI-13. Powdered polymer product after extensive drying.

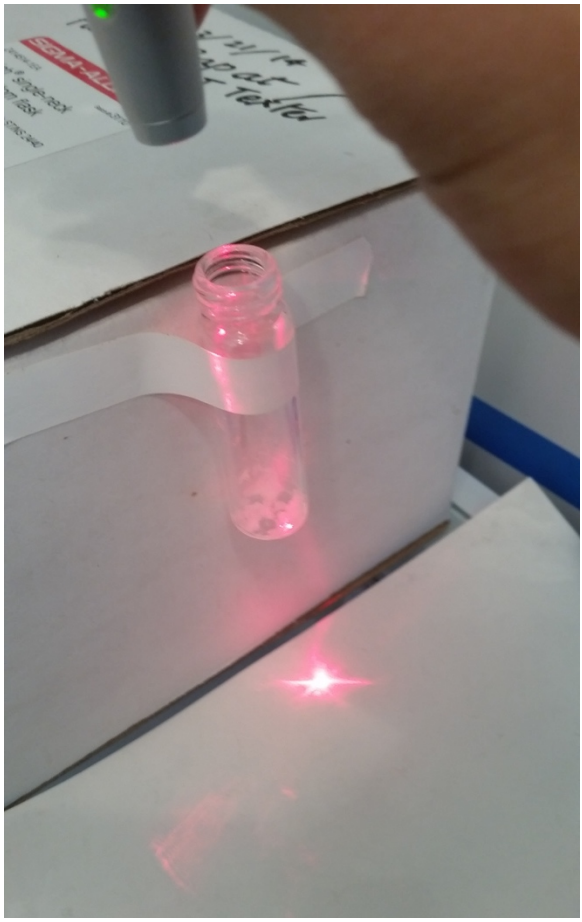

Figure SI-14. Light diffraction experiment using a red laser pointer. A vrtical side of a cardboard box is used to mount a vial containing substantially dried crystals (see Fig. 4(right)). The zero angle scattering and diffracted beams are imaged on a white cardboard perpendicular to the incident laser beam.

An experimental arrangement for laser pointer irradiation of partially dried colloidal crystals is illustrated in Fig. SI-14. The sample vial is attached with tape in a vertical orientation on the side of a cardboard box. The diffraction image is diffracted onto a piece of card stock.