Electronic Supplementary Information

Stimuli-Responsively Porating Gels by Condensation

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Experimental Materials

Glycerol, hexamethylene diisocyanate (HMDI), DBTL (dibutytin dilaurate), methyl imidazole, 11-bromoundecanol, methylene chloride (CH_2Cl_2)), DMF (dimethylformamde), and DMSO (dimethylsulfoxide) were obtained from Sigma-Aldrich. Water used was deionized.

The IL (ionic liquid monomer), 1-hydroxyundecyl-3-methyl-imidazolium bromide, was prepared by reacting a small excess of methyl imidazole with 11-bromoundecanol in THF.

Methods

Thermogravimetric analysis was done using a TA Instruments (New Castle, Delaware, USA) Q500 TGA. Differential scanning calorimetry (DSC) was done using a TA Instruments Q2000 differential scanning calorimeter. SEM (scanning electron microscopy) was done using a Hitachi (Pleasanton, CA, USA) S3400N scanning electron microscope. FTIR (Fourier transform infrared spectroscopy) was done using a Bruker FTIR.

IL-PU formulation and reaction

Glycerol (0.449 g, 4.87 mmol), IL (1.12 g, 3.36 mmol), HMDI (1.80 g, 10.7 mmol), and catalyst, DBTL (168 mg) were dissolved in 4:1 methylene chloride:DMF (2.7 g CH_2Cl_2, 0.67 g DMF). This reaction solution was then placed in an oven overnight at 80°C. The initial yellow-colored solution became a yellow gel after about 90 minutes. After 14 hours the gel had turned orange in color, and at 80°C there appeared to be some syneresis (layer of solvent above opaque gel). After removal from the oven and cooling to room temperature, this syneresis disappeared upon reabsobtion of the solvent. A product monolith is illustrated in Fig. S1 (left frame).

PU-control resin formulation and reaction

Glycerol (0.914 g, 9.92 mmol), HMDI (1.86 g, 11.1 mmol), and catalyst, DBTL (93 mg) were dissolved in 4:1 methylene chloride:DMF (2.2 g CH_2Cl_2, 0.55 g DMF). This colorless reaction solution was then placed in an oven overnight at 80°C. An opaque and white gel was formed overnight without syneresis. A product monolith is illustrated in Fig. S1 (right frame). This control monolith had a dense center core and a less dense, “fluffy,” shell. This difference in density was not observed in the IL-PU gel material.

Photos of the IL-PU resin and the control resins

Monoliths of resin products were removed from reaction vials by wrapping the vials in paper towel, fracturing the vials with a steel adjustable wrench, and carefully removing the glass shards. Example monoliths are illustrated in Fig. S1.

Figure S1. Photos of (left) PU-IL resin gel and (right) IL-free PU-control gel prior to removal of solvent in vacuo; (inset) photo of PU-IL resin after polymerization at room temperature; vial outer diameter is 15 mm.

Thermogravimetric Analysis (TGA) of Resins and IL Monomer

A sample of orange IL-PU and two PU-control samples, one of center-core and one of shell material) are compared in Fig. S2, along with a sample of the IL monomer. Samples were degassed *in vacuo* for a couple of hours before being analyzed under a nitrogen stream and heated at 10°C/minute. The data show that solvent has been effectively removed by the degassing treatment. The behaviors of the PU-control materials are nearly identical. The IL monomer decomposed much more steeply than the IL-PU or PU-control resins.

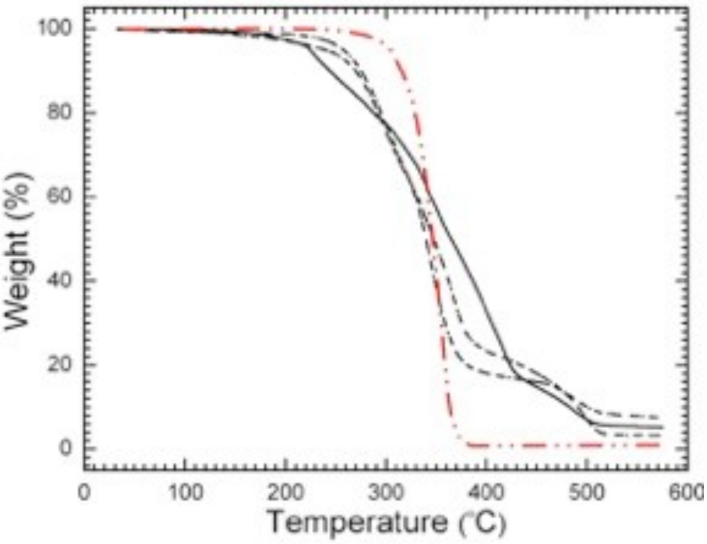


Figure S2. Thermogravimetric decompositions run in nitrogen at a heating rate of 10°C/min of IL-PU resin (——————) two samplings of no-IL PU control (—— – – —— – –; – – – – – –) and $HOC_{11}C_1ImBr$ IL (——··——··——··; red online).

DSC of IL monomer

The IL monomer DSC is illustrated in Fig. S3. The melting endotherm peak is at about 88°C, and we can assign this relatively high melting transition to hydrogen bonding due to the undecanol hydroxyl group. These data need to be examined a bit more closely to

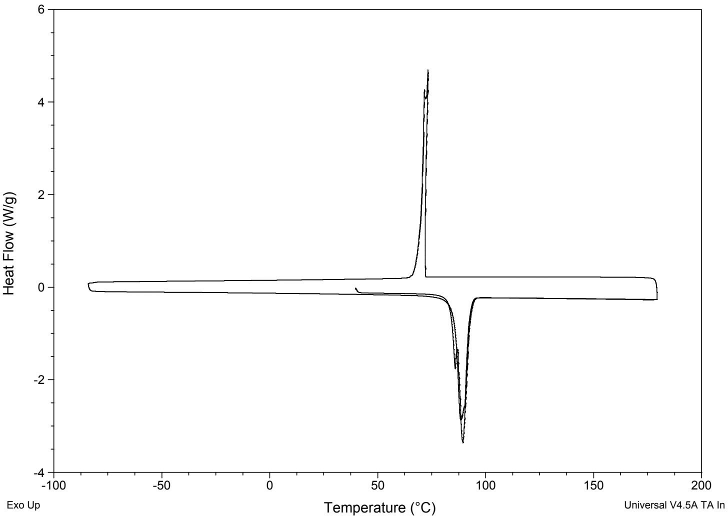


Figure S3. DSC of IL monomer, $HOC_{11}C_1ImBr$, using heating and cooling rates of 10°C/min.

identify a possible glass transition. Of particular interest, however, is that these data show unequivocally that unreacted entrapped monomer, if there were any, cannot be responsible for the melting endotherm or freezing\ exotherm observed below 0°C in the IL-PU resin DSC of Fig. 3 of the main text. This monomer melts at about 88°C when heated at 10°C/min and crystallizes at about 73°C when cooled at 10°C/min.

Melting and solidification events (T_f,T_m < T_g) due to entrapped water?

The endotherms seen on warming and the exotherms seen on cooling below the respective glass transitions in the DSC of Fig. 3 in the text are intriguing, particularly in view of their novelty. However, the possibility that these thermal events are due to entrapped water should be ruled out. Otherwise, such events cannot be considered novel. We discuss

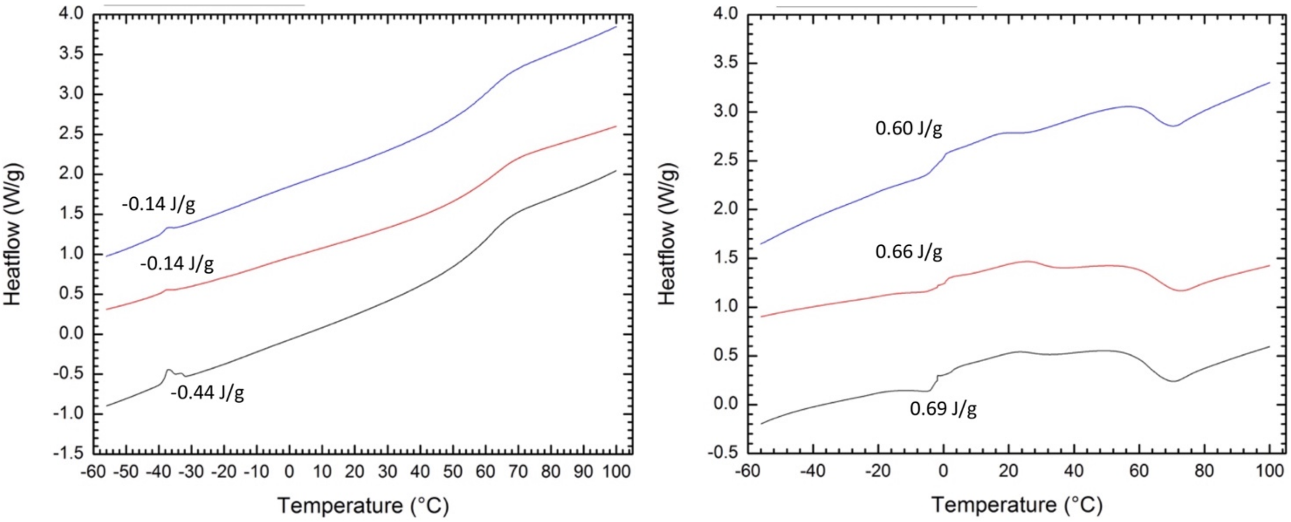


Figure S4. DSC of resin control shell materials (no-ILPU control) using cooling (left) and heating (right) rates of 10°C/min. The royal blue curve had been exposed to ambient laboratory air for 22 months. The red curve is for this same material after it had been heated in vacuo at 120°C for two hours. The black curve is for the material of the red curve after being heated an additional two hours in vacuo at 120°C.

several experiments in this section that support a conclusion that such events cannot be reliably attributed to entrapped water.

In Fig. S4 we compare DSC of the shell control material discussed in the text that has been subjected to various treatments. We see that the shell material illustrated there (royal blue colored line) that had been exposed to laboratory ambient for almost two years only exhibits minor features corresponding to an exothermic solidification at about -37°C and similarly a broad endotherm on heating at -5°C. The enthalpies for these events are -0.14 J/g and 0.60 J/g, respectively, on cooling and heating. This sample also exhibits a T_g over 60°C to 50°C on cooling and over 55°C to 60°C on heating. After treating this same material in vacuo for 2 hours at 120°C and obtaining a weight loss of 6.04% (w/w), the DSC (red curve in Fig. S4) now appears very similar to the “untreated” curve (royal blue) with respect to these exotherms and endotherms and T_g transitions. However, the integral enthalpies of the freezing exotherm (-0.14 J/g) and of the melting endotherm (0.66 J/g) are *slightly higher* than observed prior to heating in vacuo. This vacuum heat treated sample was then heated for another two hours at 120°C to yield a weight loss of 5.81% (w/w). This activated sample was examined by DSC (black curve in Fig. S4). We see an additional small increase in the magnitude of these enthalpies as a result of further activated vacuum treatment, with integral enthalpies of -0.44 J/g and 0.69 J/g, respectively, for freezing and melting.

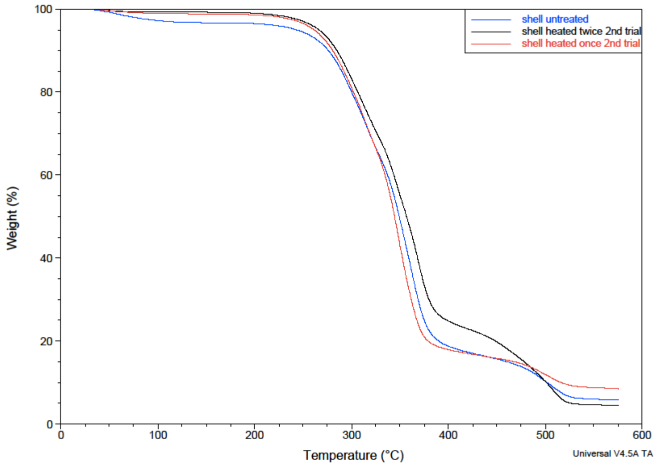


Figure S5. TGA of resin control shell materials (no-ILPU control) discussed in Fig. S4. Samples were heated from room temperature to 580°C at 10°C/min in a nitrogen stream. The royal blue curve had been exposed to ambient laboratory air for 22 months. The red curve is for this same material after it had been heated in vacuo at 120°C for two hours. The black curve is for the material of the red curve after being heated an additional two hours in vacuo at 120°C.

TGA of the samples discussed in Fig. S4 are illustrated in Fig. S5. These analyses show that the material exposed to ambient atmosphere for almost two years loses about 3.2% (w/w) solvent (DMA, CH_2Cl_2) on heating to about 160°C and then begins to lose more weight at about 175°C. Heating this sample in vacuo for two hours at 120°C produces a 6.04% weight loss, and a sample that only loses about 1.2% (w/w) up to 140°C. An additional 120°C treatment in vacuo for two hours an additional 5.81% weight loss. This activated sample yields only a small amount of additional weight loss, 0.75% (w/w) at up to 133°C.

It is clear that activated vacuum treatment at 120°C causes significant loss of solvent in this “original” sample. Degassing in a vacuum oven at 120°C removes much more solvent at that temperature than does rapid heating at atmospheric pressure, as illustrated in these TGA data. The magnitude and clarity of the DSC freezing and melting peaks grow in size and become more significant with maximum sample activation. Such behavior is inconsistent with these exotherms and endotherms being attributed to water.

A separate control resin sample was synthesized for analysis, but in this case a more precise balance of stoichiometry was used, although the preparation was essentially identical to that of the no-ILPU control described in the “PU-control resin formulation and reaction” section above. Glycerol (0.402 g, 4.38 mmol), HMDI (1.10 g, 6.60 mmol), and catalyst, DBTL (160 mg) were dissolved in 6.1:1 methylene chloride:DMF (5.0 g CH_2Cl_2, 0.82 g DMF). This colorless reaction solution was then placed in an oven for 24 hours at 80°C. A gel formed in about five minutes. The NCO/OH mole ratio was 1.004.

DSC analyses of this material are illustrated in Fig. S6. This material had been heated in vacuo to remove solvent in March of 2017 (approximately seven months ago), shortly after synthesis, and then stored in a closed vial in a desiccator. Results for this material are illustrated by the blue curves in Fig. S6. The exotherm (-2.00 J/g) and endotherm (1.50 J/g) corresponding to freezing and melting, respectively, are clearly developed, with a broader endotherm than exotherm in Fig. S6, as was also illustrated in Fig. S4. Further heating at 120°C for two hours in vacuo produced (red curves) a slightly increased set of enthalpies for both freezing (-2.36 J/g) and melting (1.79 J/g). This vacuum heating process resulted in a weight loss of 7.08% (w/w). Further heating in vacuo at 120°C for two hours (black curves) yielded slightly increased enthalpies for freezing (-2.62 J/g) and melting (2.01 J/g), and yielded a further weight loss of 5.42% (w/w).

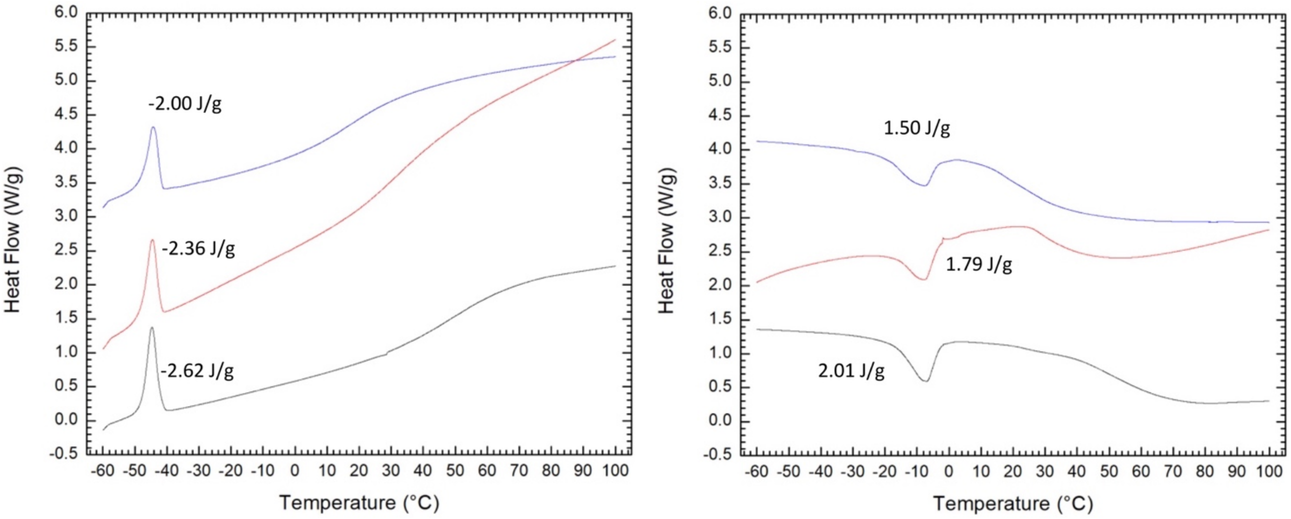
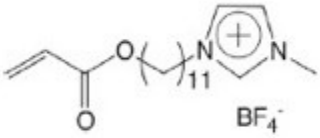


Figure S6. DSC of no-IL resin materials prepared with stoichiometric combinations of glycerol and hexamethylene diisocyanates. Cooling (left) and heating (right) rates of 10°C/min were used. The royal blue curve had been heated in vacuo once, about seven months ago and stored in a desiccator. The red curve is for this same material after it had been heated in vacuo at 120°C for two hours. The black curve is for the material of the red curve after being heated an additional two hours in vacuo at 120°C.

These separate IL-free control resin samples both show that the intensities of the enthalpies associated with the T_f and T_m events below T_g increase with increasing vacuum activation. Such behavior is inconsistent with these events emanating from any molecular water condensed in pores of these materials, and we conclude that these events are not associated with condensed water. We also mention that when we equilibrate these resin controls at 100% relative humidity at room temperature overnight, condensed water becomes visible via the water bending mode at 1649 cm^{-1} in the FTIR. Shoulders or peaks at this frequency are not evident in the FTIR spectra of Fig. 2.

Solvent-responsive co-polymeric gels

A microemulsion with water:1-propanol:$ILBF_4$:MMA (35:35:15:15 wt.%) was prepared having ethylene glycol dimethylacrylate (EGDMA 2 wt% with respect to monomers) as a cross-linker.[S1,S2] This microemulsion was prepared in a 25 mm inner-diameter vial. After bubbling nitrogen about 20 min, the microemulsion was polymerized at 60°C for 8 h resulting in a transparent gel 2-3 mm in thickness. This gel is illustrated in Fig. S7(a). This gel was removed from its synthesis vial and subjected to anion exchange in aqueous 0.1 M KPF_6. This process induced local phase separation to form an open-cell opaque material (Fig. S7(b)). This material was then placed in DMSO, that solvates imidazolium-PF_6 in pairs, as well as the polymer backbone, to produce a transparent gel, shown in Fig. S7(c). Soaking this disc in water results in re-poration and desolvation of the imidazolium-PF_6 ion pairs (Fig. S7(d)). Fig. S7(e) and Fig. S7(f) show a repeat cycle of this solvent responsiveness.



Scheme S1. $ILBF_4$, 1-(11-acryloyloxyundecyl)-3-methyl imidazolium tetrafluoroborate.

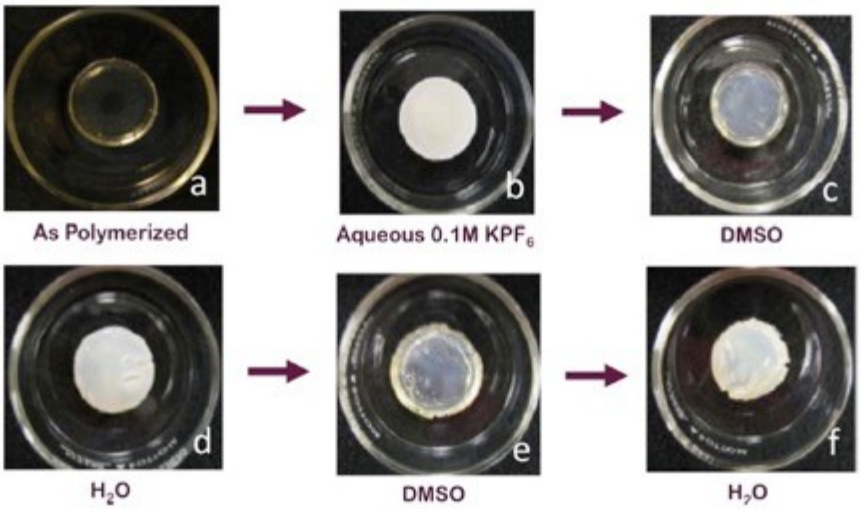


Figure S7. Photographs of gel emanating from microemulsion polymerization of 0.70/0.15/0.15 aqueous propanol (50:50)/$ILBF_4$/MMA composition (a) as polymerized after removal from sacrificial vial; (b) after immersion in 0.1 M KPF_6; (c) after immersion in DMSO; (d) after immersion in H_2O; (e) after immersion in DMSO; (f) after immersion in H_2O. ©2014 Elsevier; reproduced by permission from Ref. [S1], ©2014 Elsevier.

References

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[S2] F. Yan and J. Texter, *Angew. Chem. Int. Ed*. 2007, **46**, 2440-2443.