Electronic Supplementary Information

## Rapid production of bicontinuous macroporous materials using intrinsically polymerizable bijels

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Supplementary Figure 1: Laser transmittance as a function of temperature of a 60/40 vol% BD/PEGDA mixture during a cloud point experiment. The horizontal line represents the 95% transmittance threshold for determining the phase separation temperature.



Supplementary Figure 2: (a-b) CLSM images of unsuccessful BD/PEGDA bijels formation using particles that are not neutrally wetting. The bright pixels correspond to the location of the fluorescently tagged silica nanoparticles. In image (a), the sample was prepared using particles that were silanized with too little HMDS. These particles preferentially wetted one phase to produce discrete droplets. To prepare the sample in image (b), a near-appropriate amount of HMDS was used to produced particles with a slight preference for one fluid phase. These particles were able to stabilize some tubular structure but failed to arrest spinodal decomposition. Yellow scale bars =  $40\mu$ m. (c) SEM image of an unsuccessful BD/PEGDA BTM that was prepared using particles with a slight preference for one fluid phase. Discrete droplets were observed throughout the porous structure. White scale bar =  $500\mu$ m.



Supplementary Figure 3: CLSM frames of PG/TMPETA phase separation evolution. Sample (ab) was quenched from 70.0 °C to 22.5 °C and sample (c-d) was quenched from 35 °C to 15.0 °C. The bright (fluorescein-tagged) fluid phase corresponds to the PG-rich phase in each image. (a-b) Droplet nucleation in a 72.0 vol% PG mixture. (c-d) Spinodal decomposition in a 58.5 vol% PG mixture. Scale bar = 40  $\mu$ m.



Supplementary Figure 4: SEM image of a BD/PEGDA BTM with a partially polymerized monomer-poor phase. Scale bar = 400  $\mu$ m. Inset provides a high magnification view. The dashed line denotes the interface between the partially polymerized monomer-poor phase (above) and the polymerized monomer-rich phase (below). Scale bar = 10  $\mu$ m.



Supplementary Figure 5: Molar extinction coefficients as a function of wavelength for fluorescein (blue) and DMPA (yellow) dissolved in the (a) BD-rich phase extracted from BD/PEGDA mixtures at 22.5 °C and the (b) PG-rich phase extracted from PG/TMPETA mixtures at 15 °C. Data points were connected to guide the eye.



Supplementary Figure 6: Concentration ( $C_{solvent}$ ) of (a) fluorescein and (b) DMPA partitioned to the BD-rich phase extracted from BD/PEGDA mixtures at 22.5 °C (blue) and the PG-rich phase extracted from PG/TMPETA mixtures at 15 °C (yellow) as a function of the initial concentration ( $C_0$ ) of fluorescein or DMPA dissolved in the pure BD and PG fluids of the BD/PEGDA and PG/TMPETA mixtures, respectively. Lines were determined via linear least squares regression.