Supplementary Information:  
Microporous polymer particles via phase inversion in microfluidics: impact of non-solvent quality

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Microfluidic device fabrication

Microfluidic devices were fabricated by frontal photopolymerization of a negative epoxy photoresist, using a procedure previously reported.1,2 Thiolene is a curable prepolymer with long shelf life and good adhesion to glass, metal and polymer surfaces. Its photopolymerization nature allows for the patterning of optically clear 3-D structures with dimensions easily tunable by exposure to light. Photomasks were first designed using AutoCAD and printed on a high resolution photographic film with commercial 40,000 dpi resolution page setter (microlithography services, UK). Glass slides (corning, (75 x 25 x 1) mm³) were first cleaned with acetone and allowed to dry. Holes, corresponding to inlets and outlet, were cored in glass slides using a drill press fitted with a carbide tipped drill bit. Glass slide is placed on the glass workspace and thin strips of acetate sheet (100 μm) was placed at its corners. The acetate sheet serve as spacers which determine microdevice channel depth. For deeper channels, silicon wafer (360 μm) can be used as spacers. Thiolene was poured into
the well created by the spacers and a second glass slide placed over it carefully to prevent the formation of bubbles (a glass workspace is needed to protect work benches from the photoresist). Previously printed photomask was placed on the glass sandwich and cured under UV-A source at 0.7 W/cm² for 20 s. During exposure, microchannels were protected from UV waves whilst other areas were polymerized. The uncured photoresist was washed out using ethanol and acetone leaving behind clear microchannels for operation. The device was postcured for 30 mins without the photomask. Channels were rendered hydrophobic by treating with 10 wt% octadecytrichlorosilane in toluene for one hour after which the device was placed in a convection oven for 24 hours at 110 °C. Finally, nanoports (N-333, Upchurch) were attached to the device using an epoxy adhesive (Araldite, Huntsman).

Optical microscopy movies: droplet extraction kinetics

Two videos detail the extraction droplet process of representative polymer solutions in MEK and EA (rate increased 32 times).

- Movie S1: Video depicting the mechanism and kinetics of solvent extraction of 1.0 wt% NaPSS/H₂O in neat MEK over a timescale of 80 s
- Movie S2: Video depicting the mechanism and kinetics of solvent extraction of 1.0 wt% NaPSS/H₂O in neat EA over a timescale of 290 s
Droplet extraction with MEK

Figure S1: Representative time series of polymer solution droplet extraction and demixing with neat MEK as non-solvent. Images were obtained by reflection optical microscopy. The concentration of the NaPSS/H$_2$O solution and the initial droplet radius were 2.5 wt %, and 225 µm respectively. Internal cloudiness is first observed at droplet interface suggesting that solvent/non-solvent concentration gradients are significant during extraction. Demixing and coarsening is visible and polymer particle is formed after 100 s.
Droplet extraction with H₂O diluted MEK

Figure S2: Representative time series of polymer solution droplet extraction and demixing with non-solvent composition 0.025H₂O/0.975MEK (top row) and 0.05H₂O/0.95MEK (bottom row). Images were obtained by reflection optical microscopy. The concentration of the NaPSS/H₂O solution was 2.5 wt %, and the initial droplet radius was 220 µm. Demixing is visible in both series, but particles are formed only for the system with 0.025H₂O/0.975MEK as non-solvent. After 600 s, drops placed in 0.05H₂O/0.95MEK remain as viscous drops with no visible change in radius. When allowed to dry in ambient air, the viscous drops solidify.
Additional SEM images of MEK-extracted particles

Figure S3: SEM micrographs of final polymer particles obtained by extraction in MEK with initial polymer concentration, $C_{NaPSS,t=0}$, 1.0 wt% (A), 2.5 wt% (B), 3.5 wt% (C) and 10 wt% (D). At low initial polymer concentration (low viscosity), final particles exhibit heterogeneities in microstructure as seen for particles A, B and C. Particle outer shell show thin and thick regions depending on the extent of coarsening. (C), for initial polymer concentration 10 wt%, particle outer shells are found to exhibit uniform thickness of $\sim7 \mu$m (D).
Additional data analysis on droplet kinetics

In Figure S4, we compare ‘best fits’ to representative datasets $R(t)$ with ‘ensemble’ calculations, using our semi-empirical model (eq. (2)) and based on the overall correlations shown in Figures 4e, 5a,b (main paper) and S4c,d (Supplementary Information). We select illustrative datasets whose parameters ($R_{inf}$), extraction time ($\tau$) and alpha ($\alpha$) deviate the most from the ensemble trendlines. We find that the profiles of the ‘ensemble fit’ generally capture the experimental extraction data and that deviations are likely caused by an inaccurate estimation of the initial time ($t = 0$) and droplet size ($R_0$) for the extraction process, as well as effects associated to droplet crowding and dissolution of carrier phase. Overall we conclude that our semi-empirical model and ensemble parameters provide a good description of all data.
Figure S4: Comparative analysis of fits of data with large standard deviation to semi-empirical model (eq. (2)) for (A-C) MEK and (G-F) EA, and calculated dependence of droplet radius on extraction time using constitutive predictions of final droplet radius ($R_{inf}$), extraction time ($\tau$) and alpha ($\alpha$) from linear fits for (D-F) MEK and (J-K) EA.
References
