Microporous polymer particles via phase inversion in microfluidics: impact of non-solvent quality on microstructure

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We report the controlled formation of internally porous polyelectrolyte particles with diameters ranging from tens to hundreds of micrometers through selective solvent extraction of polymer solution droplets by an external solvent. Microfluidic devices fabricated by frontal photopolymerisation are employed to produce monodisperse polymer (P)/solvent (S) droplets, with low polydispersity and well-defined radii, suspended in a carrier (C) phase. The suspension is then brought into contact with a selective extraction solvent (NS) that is miscible with C and S but not P, leading to the solvent extraction of S from the droplets. The ensuing phase inversion yields polymer capsules with a smooth surface but highly porous internal structure. We find that ternary phase behavior impacts the microstructure of the porous polymer particles and demonstrate how to design the internal structure of the capsules, with pore sizes from 1-100 um, by tuning the timescales of the directional solidificiation process and coarsening of the phase-separated structures. pore sizes.

Model systems of sodium poly(styrenesulfonate) (P), water (S), hexadecane (C), and either methyl ethyl ketone (MEK) or ethyl acetate (EA) as NS, are selected. . The ternary phase diagrams are measured by turbidimetry and the kinetics of phase separation estimated by stopped-flow small-angle neutron scattering. We extract kinetic data by tracking the radius of a polymer drop during solvent extraction and show scanning electron microscope images of the internal structure of formed particles. We provide tentative phase inversion pathways for particle extraction along the ternary phase diagrams and show that by simply changing the non-solvent quality (NS) we are able to predict and tune particle porosity, extraction time and microcapsule shell thickness. We therefore demonstrate a versatile route to porous particle or capsule formation based on ternary solution thermodynamics and interdiffusion at a moving liquid-to-solid boundary. The effects of droplet size, polymer content and non-solvent quality provide comprehensive insight into porous particle and capsule formation by phase inversion, with a range of practical applications.

Acknowledgements The financial support from the Department of Chemical Engineering, Imperial College London.

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