



Physical Aspects of Polymer Science

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Microporous polymer particles via phase inversion of a ternary polymer solution in microfluidics

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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 using microfluidics. Binary polymer (P)/solvent (S1) mixtures are encapsulated by a carrier solvent phase (C) to form plugs with well-defined radii and low polydispersity. The suspension is then brought into contact with a selective extraction solvent (S2) that is miscible with C and S1 but not P, leading to the solvent extraction of S1 from the droplets. The ensuing phase inversion yields polymer capsules with a smooth surface but highly porous internal structure. Tuning the timescales of the directional solidification process and the coarsening of the phase-separated structure enables fine tuning of the internal structure. The extraction time required to form particles from liquid droplets was found not to depend on the initial polymer concentration. The resulting particle size followed a linear relationship with the initial droplet size for all polymer concentrations, albeit with different internal porosities, which ranged from 10 to 50% at the polymer concentrations studied.

Further, we map the ternary phase diagrams varying non-solvent quality and quench depth, in order to optimize relative time scales for phase separation and glass formation. The latter is the dominant mechanism for solidification, i.e. when the polymer concentration in solution is sufficiently high to cross the glass transition temperature at ambient conditions. Specifically, we form sodium poly(styrenesulfonate) (P) particles using water (S1), hexadecane (C), and methyl ethyl ketone (S2) or ethyl acetate (S2). Varying the water concentration in the S2 phase also allows us to access different tie lines, and thus particle composition, in the phase diagram. We extract kinetic data by tracking the radius of a polymer drop during solvent extraction. We show scanning electron microscope images of the internal structure of formed particles and provide tentative phase inversion pathways for particle extraction along the ternary phase diagrams. We show that by simply changing the non-solvent quality (S2) we are able to predict and tune particle porosity (by 50 percent), 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.