Creating Honeycomb Structures in Macroporous Polymers by Solvent-Driven Phase Separation

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ABSTRACT

After polymerization of the continuous phase of a monodisperse, hexagonally close-packed water-in-monomer *high internal phase emulsion* (HIPE) with a water-soluble initiator and removal of the water by drying, one obtains a monodisperse, macroporous polymer with an intriguing morphology. In scanning election microscopy (SEM) analysis, the pore cross-sections of these materials are closed hexagons and the pore wall is composed of three distinctive layers (see Figure 1). Though already observed for two different monomer systems [1,2], the mechanism behind this intriguing morphology has not been identified yet. A hypothesis presented by *Quell et al.* [1] that relies on the presence of two monomers (styrene and divinylbenzene DVB) cannot explain the results of *Dabrowski et al.* [2] who obtained similar shapes while using only one monomer. After thorough variation of a range of system parameters we show here that Quell's hypothesis cannot be validated [3]. New experimental results led us to propose a new surfactant-driven mechanism: Excess surfactant is dissolved in the continuous phase where it emulsifies water from the large emulsion droplets. When the polymerization is initiated from the interface, the continuous phase becomes a poor solvent for the surfactant and the emulsified water which react by "fleeing" from the site of the polymerization (1) towards the water/monomer interface or (2) into the yet unpolymerized inside of the continuous phase. The first process may cause the emulsion droplets to change their shape from spherical to polyhedral and the second process may be responsible for the formation of the three observed layers in the pore wall. We will discuss both processes in detail and present the experimental results that clearly support them.

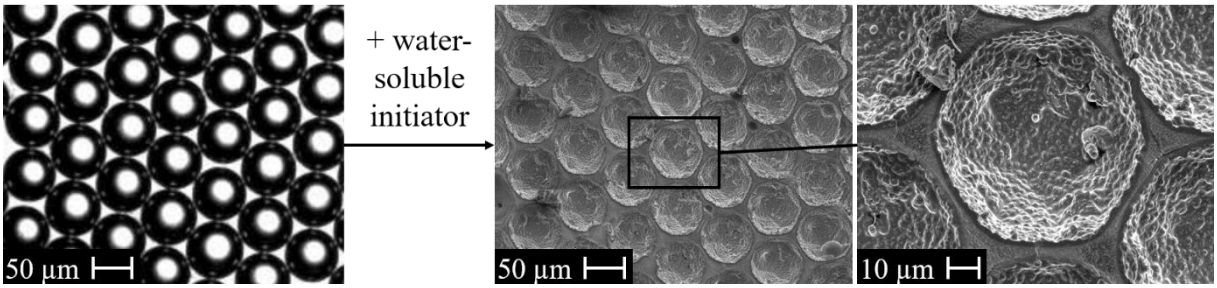

Figure 1: A monodisperse water-in-styrene/DVB emulsion template (left) is polymerized with a water-soluble initiator and dried leading to monodisperse macroporous polystyrene/poly-DVB with hexagonal, closed pore cross-sections and three-layered pore walls (right).

[1] A. Quell et al. ChemPhysChem 18:451-454, 2017., [2] M. Dabrowski et al. Phys. Chem. Chem. Phys. 22:155-168, 2020., [3] L. Koch et al., submitted 2020.