Synthesis of micron-sized, highly crosslinked polystyrene particles via dispersion polymerization

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The synthesis of monodisperse, highly crosslinked polystyrene (PS) particles with a radius of about 500 nm and larger is a challenging research in molecular chemistry. The most reliable synthesis route for this is dispersion polymerization and different groups are currently active in this field [1, 2]. They all have in common the use of divinylbenzene as a cross-linking agent. However, this choice creates problems when aiming for high degree of crosslinking due to the difference in the copolymerization parameters, since the reaction mechanism is similar to bulk or solution polymerization. To overcome these drawbacks we present a different approach. By using diisopropenylbenzene, which provides better copolymerization parameters [3], as a cross-linking agent a more homogeneous polymerization and network building of the resulting particles could be obtained for crosslink densities up to 1:50 (one crosslink per 50 monomer units).

Here, we investigated the influence of different solvent mixtures on the final particles. The procedure for the reaction was motivated by systematic studies of dispersion polymerization of styrene by Zhang et al. [4]. Using a modified procedure a 99:1 (w/w) mixture of styrene and diisopropenylbenzene was polymerized in different solvent mixtures of isopropylalcohol (iPrOH) and water. In this way the solution quality for PS in the solvent was gradually lowered with increasing content of water. A positive influence on the particle morphology and the degree of polymerization was observed when the polarity of the solvent was slightly increased. The obvious difference in the morphology is shown in fig. 1.



Figure 1: SEM-pictures of highly crosslinked PS particles synthesized via dispersion polymerization. On the left hand side the particles resulting of a polymerization in pure iPrOH can be seen. The sample consist to equal parts of small round particles and hollow hemispherical particles. On the right hand side the resulting particles for a polymerization in a solvent mixture of iPrOH/H₂O (80/20) are shown. Here the particles are clearly spherical and mostly within a radius of around 500 nm.

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