

Scanning Transmission X-ray Microscopy (STXM) of Onion-type Polymer Microspheres

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Polymer microspheres consisting of concentric layers with different chemical compositions and physical properties may be useful as 3D-phonic bandgap devices and as catalyst supports. They are prepared here for the first time by precipitation polymerization of crosslinking monomers under conditions where thermal or chemical perturbations of the polymerization conditions are used to write concentric patterns into the growing microspheres. STXM at ALS beamline 5.3.2 is then used to map the compositions of the resulting onion-type microspheres with high spatial and chemical resolution. For these samples we use the $C1s \rightarrow \pi^*$ transitions for divinylbenzene (DVB) at 285.2 eV and for the phenylmaleimide carbonyl at 288.4eV. The microsphere formation involves polymerizing crosslinking monomers including DVB in marginal solvents such as acetonitrile, such that the forming polymers aggregate in controlled fashion to form mono-disperse microspheres of about 3 micron diameter. Under certain conditions, this aggregation becomes sensitive to thermal fluctuations of the polymerization, permitting rings of lower crosslink density to be inscribed into the growing microspheres by imposing a thermal profile on the polymerization.

Fig. 1 shows one possible thermal profile imposed during a 20 hour polymerization, the corresponding internal ring structure as seen by TEM, the quantitative DVB map of one quadrant of a sphere, and a radial line profile. This line profile can be used to calculate the refractive index profile of these microspheres, and hence evaluate potential use as photonic band gap materials. In analogy, doping with carefully

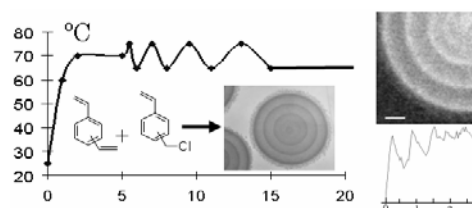


Fig. 1 Thermally generated polymer onions. (left) T(reaction) vs. time (hr) and TEM. (right) STXM-derived DVB map, and radial profile.

selected comonomers such as phenylmaleimide at, for example, 4 and 8 hours into a similar precipitation polymerization gives rise to the corresponding poly(DVB-co-PMI) layers. **Fig. 2** compares a TEM image (mapping electron density) with a $C1s$ STXM derived quantitative map of the PMI component. Use of chemically reactive comonomers such as itaconic anhydride (IA) instead of PMI permits subsequent layer-specific chemical modification of the onion microspheres. Experiments are in progress to trap organometallic catalysts at specific layers for subsequent catalytic reactions.

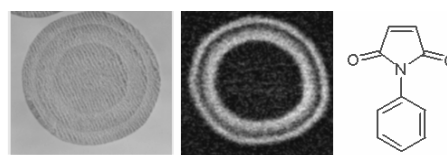


Fig. 2 TEM image, STXM-derived PMI map of DVB-PMI onion; PMI structure.

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