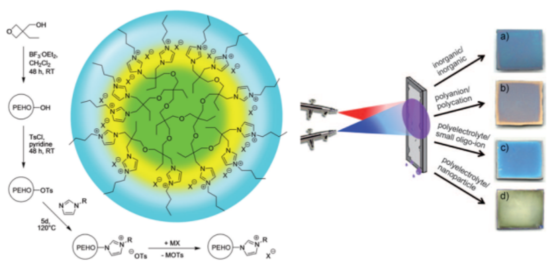
Project B5: Compartmentalized smart polymer ionic liquids for responsive systems

Principal investigators: R. Mülhaupt (Freiburg) / J.-F. Lutz (Strasbourg)
Collaborators: G. Decher (Strasbourg)

Current state of the research. Polymer ionic liquids (PILs) combine properties typical of low molecular weight ionic liquids (ILs), e.g., high ion conductivity or negligible vapour pressure, with facile processing, durability and low toxicity typical of polymers. Tailored PILs enable the fabrication of functional coatings and 3D printed multifunctional systems. Going beyond molecular design, the PIL functions are governed by controlling PIL nanostructures. Nanostructured and compartmentalized PILs hold the promise of playing a prominent role in the development of new responsive ("smart") materials. For example, PILs with integrated 3D-ordered pores are employed as tunable photonic crystals or electro-optical switches. State-of-the-art thermoresponsive PIL block copolymers are obtained by controlled radical polymerization linking linear poly(N-vinylimidazolium) PIL and PNIPAM segments. Yet, the conformations of most linear PILs are sensitive to shear forces and changes of pH or temperature. Thus, we plan to create novel conformationally and chemically stable hyperbranched PILs ("hyperPILs") as a molecular tool box for compartmentalized thermoresponsive PIL systems, which can be deployed in layer-by-layer (LbL) assembly to obtain artificial smart skin surfaces (see Figure).



Contributions of the principal investigators. The project joins complementary expertise in PIL design (Mülhaupt), thermoresponsive system formation (Lutz) and LbL assembly (Decher). The Mülhaupt group has developed a versatile strategy for tailoring micelle-like hyperPILs which assemble as nanodroplets in nonaqueous medium and polymer melts. Going beyond PNIPAM chemistry, the Lutz group conducts leading research on thermoresponsive polyethers. The Decher group has pioneered the LbL assembly of polyelectrolytes. Their spraying technology holds very promising potential for hyperPIL processing.

Research project and collaborations. First, imidazole-terminated thermoresponsive polyethers are tailored by the Lutz group and alkylated with tosylated polyoxteanes from Freiburg to render hyperPIL thermoresponsive (see Figure). Tuning of the hyperPIL structure aims at nanophase separation to thermally reversibly produce compartments for nanoparticle synthesis and dispersion. In the Decher group, hyperPIL and their nanoparticle dispersions will be sprayed to produce multilayer coatings. Variations of chemistry and processing aim at creating multifunctional coatings with thermoresponsive color formation, moisture permeation, or wetting/dewetting.

Work plan. The PhD project has three work packages. *WP1. Preparation thermo-responsive hyperPIL:* Preparation of tosylated polyoxetan cores (Mülhaupt) and of imidazole-terminated polyethers (Lutz). Preparation and characterization of thermoresponsive hyperPIL (Lutz). *WP2. Self-assembly and nanostructure formation:* Systematic variations of hyperPIL architectures (Lutz). Nanostructure analysis by cryo-TEM and SEM (Mülhaupt) and light scattering (ICS). Tuned hyperPILs as compartments for TiO_2 nanoparticle synthesis (Mülhaupt). LbL assembly of hyperPILs by spraying (Decher). 3D printing of hyperPIL (Mülhaupt). *WP3. Smart functional coatings (Decher, Lutz, Mülhaupt):* Thermoresponsive color formation. Wetting/dewetting by thermoresponsive wrinkling. Temperature-induced water absorption/desorption. Investigation of film formation and tribology (with Project C3).