

SALT EXCHANGE REACTIONS – A VERSATILE DETOUR TO OTHERWISE HARDLY ACCESSIBLE MONOMER SALTS

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Aromatic polyimides (PIs) are a class of advanced polymers that possess outstanding thermal, mechanical and electrical properties, as well as excellent chemical resistance. Therefore, PIs are being widely used in the microelectronics and aerospace industries as materials for electronic packaging and electrical insulation, respectively. Unfortunately, PIs are commonly synthesized via harsh and toxic routes. We could recently develop a novel, ‘green’ polymerization technique (*Hydrothermal polymerization, HTP*) that aside using nothing but water and the monomers additionally generates outstanding crystallinities.[1-3] In HTP of PIs, monomer salts form upon first contact of the diamine and dianhydride comonomers.[1] These species have been identified as crucial intermediates for HTP, as they impart (i) a defined stoichiometry of the comonomers and (ii) a preorganization of the comonomers in close proximity.[2,3] However, generating monomer salts of the desired 1:1 ratios (with respect to condensing functions) can be a challenging task in some cases. The ΔpK_a between the free acid and the diamine comonomers plays a crucial role in this respect. It is generally accepted that reaction of an acid with a base will be expected to form a salt if the $\Delta pK_a > 2-3$. [4] That parameter, however, is not always appropriate to accurately predict salt formation.

With this contribution, we present a novel route towards otherwise hardly accessible monomer salts: salt exchange reactions. Moreover, several new monomer salts including their detailed structural characterization.

[1] B. Baumgartner, M. J. Bojdys, M. M. Unterlass*, Polym. Chem. 2014, 5, 3771-3776. “Geomimetics for Green Polymer Synthesis: Highly Ordered Polyimides via Hydrothermal Techniques”

[2] B. Baumgartner, M. Puchberger, M. M. Unterlass*, Polym. Chem. 2015, 6, 5773-5781. “Towards a General Understanding of Hydrothermal Polymerization of Polyimides”

[3] B. Baumgartner, M. J. Bojdys, P. Skrinjar and M. M. Unterlass*, Macromol. Chem. Phys. 2016, 217, 485-500. “Design Strategies in Hydrothermal Polymerization of Polyimides”

[4] S. L. Childs, G. P. Stahly, A. Park, Mol. Pharm. 2007, 4, 323-338. “The Salt-Cocrystal Continuum: The Influence of Crystal Structure on Ionization State”