Bringing Hydrothermal Polymerization to Broader Applicability

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In 2014, we have reported a novel synthetic approach towards polyimides (PIs): *Hydrothermal Polymerization (HTP)*.[1][2] This geomimetic technique is inspired by natural mineral formation in hydrothermal veins and generates PIs in solely H_2O under high-temperature and high-pressure conditions. Due to the absence of toxic and harmful catalysts and solvents (conventional PI syntheses employ e.g. isoquinoline as catalyst and DMF or NMP as solvent), HTP is an environmentally friendly polymerization technique. In a typical HTP experiment (Figure 1), the comonomers are simply brought in contact in H_2O at 80 °C to form a monomer salt (MS) dispersion of ideal 1:1 stoichiometry in a first reaction step. This dispersion is subsequently heated to elevated temperatures (> 180 °C) in a closed vessel aka autoclave for the desired reaction time. Alternatively, the MS can be isolated, washed and dried, then redispersed in H_2O, and subsequently heated to the hydrothermal regime.

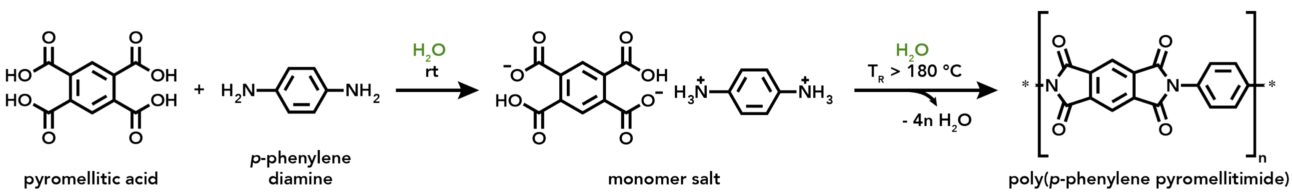

Figure 1: HTP of the PI poly(*p*-phenylene pyromellitimide) from its monomers *via* a MS intermediate. Both reaction steps are carried out in solely H_2O.

HTP yields solid PI microparticles as product. The generated microparticles do not only show full crystallinity, but also unique morphologies. Typically, the majority of obtained particles consists of intergrown and highly decorated microsheets (Figure 2A). In addition to that, usually also a second PI phase can be found comprising flower-like microstructures (Figure 2B). The feature of full crystallinity is extremely promising: It enhances the chemical and thermal stability of these polymers. Hence, the properties that are most important for PIs' applications benefit from their preparation *via* HTP.

However, tuning the morphology of the obtained microparticles while maintaining the promising property of fully crystallinity would be a truly crucial step for bringing PI particles from HTP closer to real-life applications. Two recently developed strategies for morphological tuning of PI particles are: (*i*) Applying a H_2O-soluble additive (*e.g.* PEG) during HTP that significantly influences the growth of PI crystallites during the reported dissolution-polymerization-crystallization mechanism for the transformation of the MS to the PI.[4] The resulting changes in morphology (see Figure 2C) are attributed to the adhesion of additive onto the growing crystallite facets and the subsequent induction of split growth to yield densely packed microflowers of partially oriented petals. (*ii*) Adjusting the solvent's physico-chemical properties by adding alcohols as co-solvents which affects the rates of MS dissolution, diffusion, polymerization and crystallization.[5] Thereby, it is even possible to generate a plethora of further microstructures – including even nanostructured microparticles (Figure 2D).

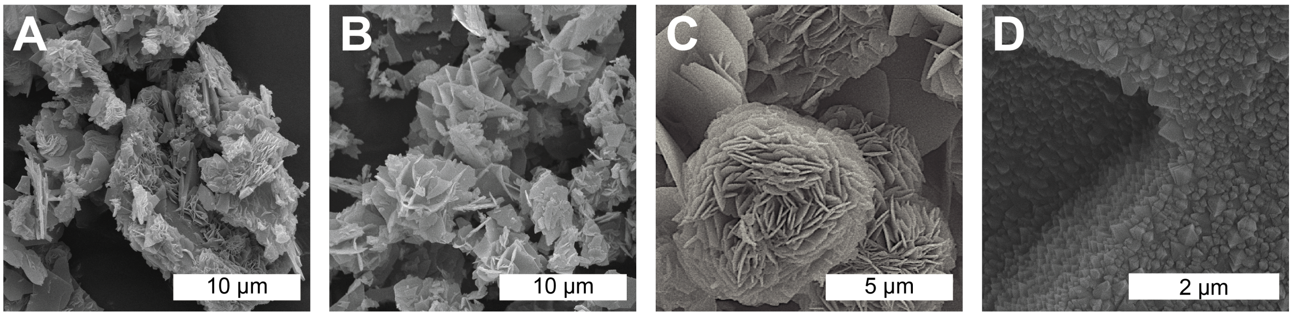

Figure 2: SEM micrographs of hydrothermally synthesized PI: A, B – intergrown and decorated PI microsheets as well as flower-like structures obtained using solely H_2O; C – densely packed PI microflower generated in the presence of an additive; D – nanostructured PI microparticle synthesized by applying an alcohol as co-solvent.

Such particles of different size, shape and morphology have different surface areas and show different degrees of anisotropy regarding various physical properties such as thermal conductivity and mechanical strength. By using such microparticles as light-weight organic fillers in high-performance polymer matrices, composite materials with various properties can be obtained. We are currently using different processing techniques as well as different matrices to generate a wide array of advanced, purely organic, light-weight high-performance composites.

With this contribution, we present our recent studies on altering the morphology of hydrothermally generated PI particles. In addition to that, we will also present our first results of the fabrication and characterization of composite materials using highly crystalline PI particles as filler.

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[5] M. J. Taublaender, M. Reiter, M. M. Unterlass, *submitted,* **2019**.