ORGANIC HIGH-PERFORMANCE MATERIALS VIA HYDROTHERMAL SYNTHESIS

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INTRODUCTION

We recently established a novel synthetic preparation method for various organic high-performance materials which solely employs water under high-temperature and high-pressure conditions as reaction medium. While classical protocols for generating the substances we are interested in require toxic solvents and often yield harmful reaction byproducts, our strategy does not pose any risk for environment and health. In fact, our technique can be considered as inherently "green", since water is the only solvent used as well as the only reaction byproduct formed. Hence, handling and disposal of harmful substances can be completely avoided just by replacing the usual synthetic methods by ours based on high-temperature water.

THEORETICAL BACKGROUND

These so-called hydrothermal (HT) preparation techniques are inspired by natural mineral formation processes taking place in the earth's crust. There, it can occur that subterranean, entrapped water in close proximity to magma chambers is heated to elevated temperatures ($T > 100$ °C). Due to the constraint space, the resulting hot steam cannot evaporate and consequently autogenous pressure ($p > 1$ bar) arises – similar to what happens in an ordinary pressure cooker some of us frequently use for cooking. Under HT conditions certain physico-chemical properties of water change, allowing for dissolution of a plethora of compounds that are virtually insoluble in water at ambient conditions. In addition to that, HT water can also facilitate certain types of chemical reactions – among others condensations. In nature, this enables the formation of various highly crystalline minerals. By using autoclaves, which are basically high-end pressure cookers, we can mimic such HT systems in our laboratory and take advantage of the altered properties of water in order to prepare advanced organic high-performance materials.

RESULTS AND DISCUSSION

We have already successfully demonstrated that HT conditions are perfectly suitable for not only synthesizing, but also crystallizing highly aromatic, low-molecular weight compounds.[1] Interestingly, HT conditions are also nicely suitable for generating polymers, *i.e.* high-molecular weight compounds. If our synthetic approach is applied to synthesize polymers, it is generally termed hydrothermal polymerization (HTP). Besides other types of polymers, HTP is especially well-known for generating various polyimides. By carefully choosing monomers as well as optimizing reaction conditions, it has been shown that even highly crystalline polyimide microparticles can be synthesized in solely HT water (see Figure 1).[2,3]

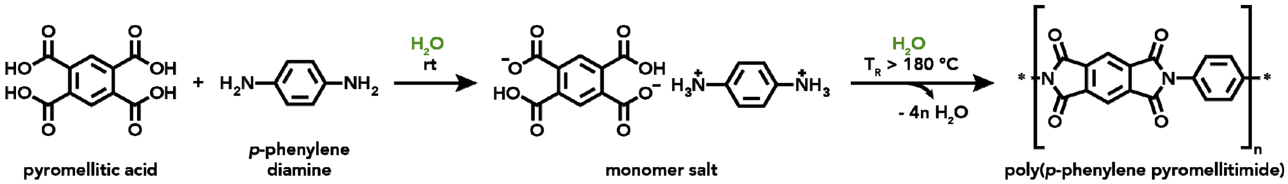

Figure 1: HTP of the polyimide poly(*p*-phenylene pyromellitimide) from its monomers *via* a monomer salt intermediate. Both reaction steps are carried out in solely H_2O.

This is a truly startling finding considering the polymeric nature of these material. The obtained high crystallinities are a significant advantage compared to classical polyimides prepared in toxic, harmful solvents which only show low degrees of crystallinity. It is a well-known fact that with increasing crystallinity several materials properties such as mechanical, chemical and thermal stability improve.

Furthermore, it has also been shown that by applying environmentally benign additives and co-solvents during HTP polyimide microparticles of different morphologies can be obtained while maintaining the highly promising feature of extraordinarily high crystallinity. The morphological possibilities include microsheets, various types of magnificent flower-like structures as well as nano-structured microparticles (see Figure 2).[4,5] 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 for high performance matrices, composite materials with various properties can be obtained.

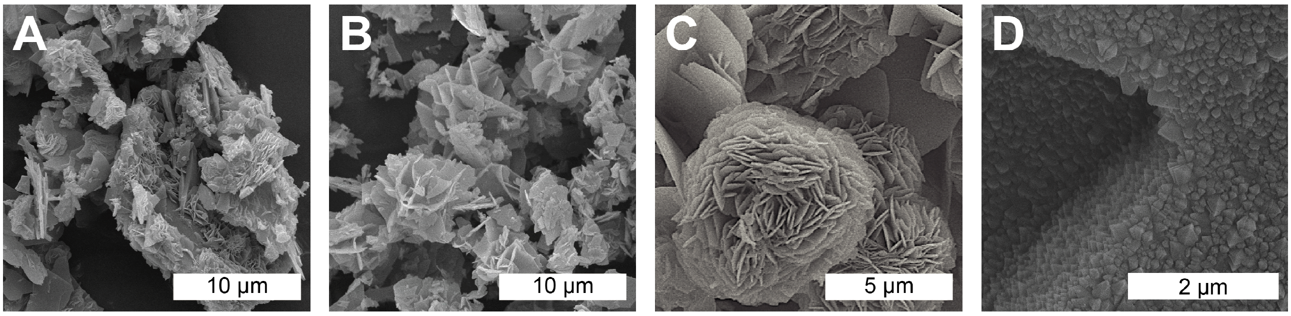

Figure 2: SEM micrographs of hydrothermally synthesized polyimides: A, B – intergrown and decorated polyimide microsheets as well as flower-like structures obtained using solely H_2O; C – densely packed polyimide microflower generated in the presence of an additive; D – nanostructured PI microparticle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

CONCLUSION

Together with their environmentally benign origin the enhanced properties as well as the simplicity of morphological tuning are most important for the future perspective of HTP as synthetic approach since only such novel and green processes have realistic chances to replace existing methods if they yield products of at least equal or even improved quality.

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