

DESIGN OF NON-SPHERICAL COLLOIDAL POLYMER PARTICLES FOR SELF-ASSEMBLED MATERIALS

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INTRODUCTION

Self-assembly (SA) is the process by which complex aggregates are generated from the non-covalent interplay of their building blocks without any human intervention. From DNA, micelles, liquid crystalline phases or nanoparticle assemblies, a plethora of structures is generated by SA. Therefore, SA constitutes a most useful tool for synthesizing new and intriguing functional materials across various size scales. By exploiting SA, one can obtain properties that are yet to be achieved by conventional top-down or bottom-up approaches [1].

EXPERIMENTAL PART

Research aiming at generating new materials has until recently mainly been dominated by materials design on the molecular level, *i.e.* by using tailor-made molecular building blocks. One recent and highly promising route towards new materials, and therefore also novel materials properties, is to use building blocks that are bigger than molecules, *i.e.* colloidal particles, for obtaining nano- and micro-structured materials. The generation of such materials is often achieved by bringing the colloidal particles together by means of SA. Generally, SA depends on three main factors (Fig. 1A), namely: (i) shape, (ii) dimension, and (iii) chemical composition of the building blocks.

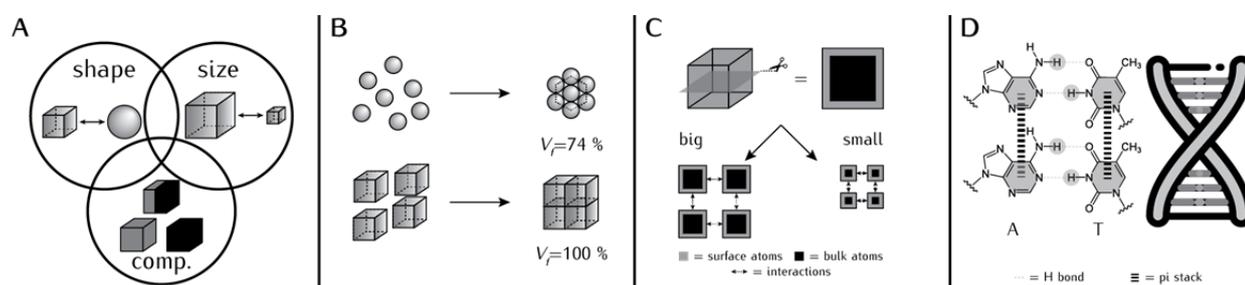


Figure 1: A - The three key parameters driving SA: shape, size and chemical composition. B - Shape determines the packing efficiency: Cubes ($V_f = 100\%$) can fill space more efficiently than spheres ($V_f = 74\%$). C - Interparticle forces scale with particle size: Smaller particles have a higher surface atom/bulk atom ratio than bigger particles, leading to higher G_i . D - The DNA double helix structure arises from the interplay of π -stacking and H-bonding between nucleobases.

Shape affects the packing efficiency. For instance, spheres are able to fill up a given volume to a maximum of 74 % (closest packing), whereas cubes can fill up to 100 % of the volume (Fig. 1B). The size of the building blocks dictates their total interface free energy (G_i), therefore determining the strength of interparticle interactions (Fig. 1C). Finally, the chemical composition is responsible for the nature of cooperative interactions of the assembly. For example, H-bonding and π -stacking between nucleobases determine the double-helix structure of DNA (Fig. 1D).

Our group has recently introduced a new method towards the synthesis of anisotropic angular polyimide (PI) particles by means of solid-state polymerization (SSP) [2]. SSP is a solvent-free polymerization technique that involves heat treatment of monomer salts at temperatures below their melting point. Such monomer salts are obtained by a simple acid-base reaction between the co-

monomers diamine and tetracarboxylic acid (Fig. 2). Using monomer salts as starting materials presents some advantages over monomers used in classical syntheses: (i) they are single-source precursors providing ideal stoichiometry; (ii) they show high reactivity for the proximity of reacting groups within the salt structure; and (iii) they show better stability and therefore storability than the pristine co-monomers. Interestingly, for the vast majority of reported examples, SSP of monomer salts results in PI particles that retain the morphology of the initial monomer salt. Therefore, the reaction provides a promising route towards non-spherical PI particles. This project aims at modifying the dimensions and crystal habit of monomer salts in order to generate arrays of colloidal PI particles with different non-spherical shapes, and study their SA.

RESULTS AND DISCUSSION

In order to modify their crystal habit, monomer salt precipitation has been performed in presence of additives. This technique is well known in the field of crystal growth, and relies on the interaction of additives with crystal facets. By attaching to facets with higher G_i , *i.e.* with higher growth rates, additives inhibit the growth in certain directions, thus generating crystals with altered habit. With this contribution we present our investigation of (i) the influence of additives and (ii) the effect of various parameters, *e.g.* temperature or concentration, on the monomer salt formation. Specifically, we studied the monomer salt $[\text{H}_2\text{PDA}^{2+}\text{PMA}^{2-}]$, obtained by acid-base reaction of *p*-phenylene diamine (PDA) and pyromellitic acid (PMA). All studied systems were characterized using optical microscopy, scanning electron microscopy (SEM), infrared (IR) spectroscopy, and powder X-Ray diffraction (PXRD). Our studies show, that it is indeed possible to alter the crystal habit of the prototypical monomer salt $[\text{H}_2\text{PDA}^{2+}\text{PMA}^{2-}]$.

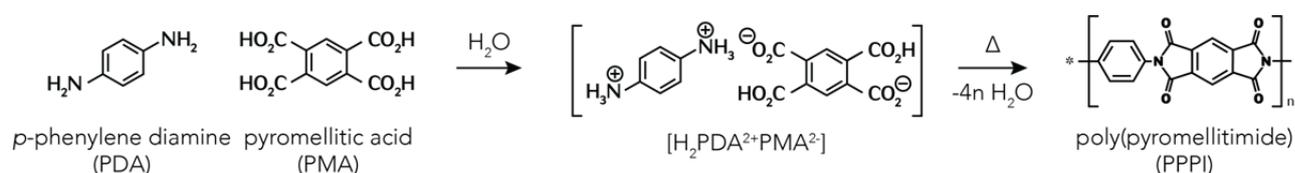


Figure 2: Acid-base reaction between pyromellitic acid (PMA) and *p*-phenylenediamine (PDA) in aqueous solution generates the monomer salt $[\text{H}_2\text{PDA}^{2+}\text{PMA}^{2-}]$, which is then converted to poly(*p*-phenylene pyromellitimide) (PPPI) by SSP.

CONCLUSION

Solid-state polymerization of the monomer salt $[\text{H}_2\text{PDA}^{2+}\text{PMA}^{2-}]$ is a promising route towards non-spherical polymer particles. These particles are intended to be used as particle building blocks for novel nano- and microstructured materials. In order to generate such materials and comprehensively study their formation, we aim at accessing different particle shapes and sizes at same chemical composition. For obtaining PI particles of different shape and size, we target morphology alterations at the monomer salt level. Therefore, the effect of several parameters on the obtained monomer salt form and size has been studied. Overall, it can be stated that materials generated from self-assembled particles are likely to exhibit intriguing novel properties. As PIs intrinsically display properties such as high thermal and chemical resistance, SA products of PI particles bear the potential to be promising colloidal structured high-performance materials.

REFERENCES

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- [2] Kriechbaum, K.; Cerrón-Infantes, D. A.; Stöger, B.; Unterlass, M. M., *Macromolecules* **2015**, 48, 8773.