
Benzene-1,3,5-tricarboxamides: versatile building blocks for supramolecular materials and single chain polymeric nanoparticles

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Benzene-1,3,5-tricarboxamides (BTAs) cooperatively self-assemble into helical supramolecular polymers in apolar alkane solvents.¹ The monomers are held together by 3 intermolecular hydrogen bonds between the amides of consecutive molecules and when chiral information is embedded in the alkyl side chains, one helical conformation, P or M, is preferred in the supramolecular polymer.³ The supramolecular polymerization is highly sensitive to the length of the alkane solvents and to the polarity of the solvent (Fig 1A).

In the first part, we focus on the self-assembly properties of BTAs and how this understanding can be used in a variety of applications. The self-assembly of BTAs is highly cooperative in alkane solvents and, if properly designed, BTAs also show cooperative self-assembly in water. In addition, end-functionalization of telechelic hydrophobic (e.g. Kraton)² or hydrophilic polymers (eg pEG), results in thermoplastic elastomeric materials or hydrogelators, respectively. Solid state IR studies, DSC and AFM revealed that the material properties can be ascribed to phase segregation of the hard BTA based nanorods and the soft polymeric matrix. A systematic investigation showed that telechelics containing prepolymers of increasing polarity resulted in a decrease of the stability of the nanorods in the solid state and this eventually resulted in the loss of material properties (Fig 1, left).^{2b} In water, the hydrophobic effect ensures phase segregation of the BTA nanorods and this induces the formation of elastic and reversible hydrogels.

In the second part, we describe the copolymerization of BTA based methacrylates with hydrophilic PEG methacrylate using controlled radical polymerization techniques. The copolymers obtained fold in water. Elaborate characterisation of the polymers in water with UV and CD spectroscopy, DLS, SAXS and cryo-TEM indicated that one particle contains one polymeric chain only. The thermal folding and unfolding of the single chain polymeric nanoparticles can be described by a two state model, which is characteristic for protein folding. By embedding a catalytically active site in the interior of the nanoparticle, efficient catalysis in water is achieved (Figure 1, right).³

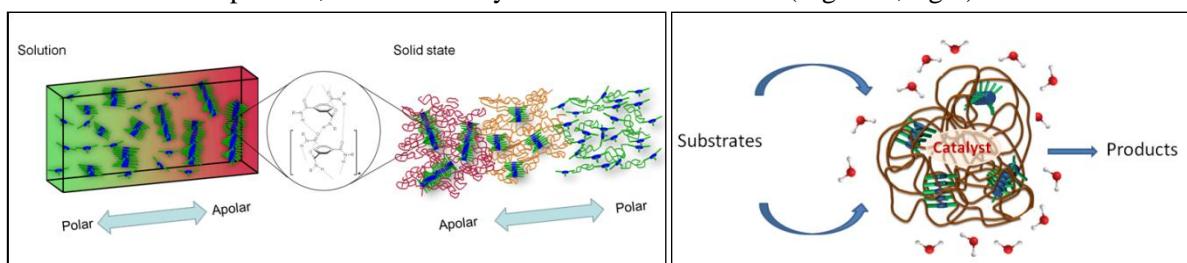


Figure 1.

References

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