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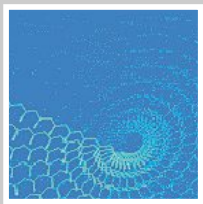

Polymer and Colloid Highlights

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Non-aggregating Poly(*p*-benzamide)s

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Oligo(*p*-benzamide)s have a similar chemical structure as Kevlar® and hence exhibit exceptional chain-stiffness and shape-persistence due to their ability of hydrogen bond formation. The latter, however, leads to strong aggregation and low solubility in organic solvents, which complicates the synthesis in solution. Our research deals with overcoming this disadvantage and investigating the aggregation behavior in organic solvents.

Unsubstituted oligo(*p*-benzamide)s longer than the trimer are virtually insoluble in organic solvents and can only be solubilized in concentrated sulfuric acid or hydrogen bond-breaking solvents such as mixtures of dimethylacetamide and lithium chloride. This emphasizes the forces arising from intermolecular hydrogen bonds between the oligomer chains, mimicking β-sheets in peptides (Fig. 1A).[1] To suppress intermolecular hydrogen bond formation, flexible triethylene glycol (TEG) and hexyloxy-side chains were attached to the oligoaramide backbone using *p*-aminosalicylic acid as the monomer. TEG-grafted oligomers and polymers are soluble in organic solvents, but still show a strong aggregation tendency,[2] whereas hepta(2-hexyloxy-*p*-benzamide) is insoluble in all common organic solvents.

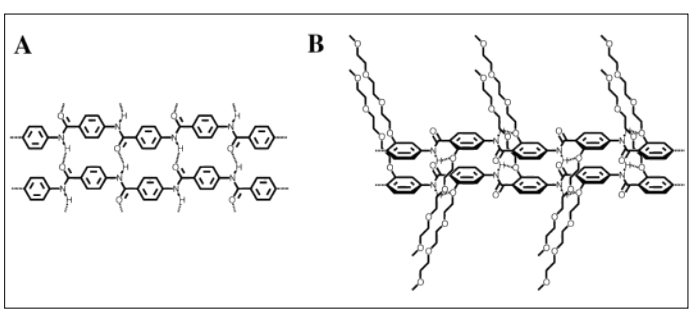

Fig. 1. A. H-bonding between poly(*p*-benzamide) chains; B. π-π stacking between TEG-grafted poly(*p*-benzamide) chains.

This can be explained by the coplanarity of the phenyl rings triggered by intramolecular hydrogen bond formation between the amide N-H and the ether oxygen. This effectively results in a flattening and rigidification of the corresponding oligomers and polymers. With all hydrogen bond donors saturated π-π interactions become the favored binding motif between these flat oligomers (Fig. 1B). In contrast to hexyloxy-groups, triethylene glycol side chains balance the loss in conformational freedom with an entropic gain due to their flexibility and high organo-solubility.

These assumptions led us to the synthesis of dendronized oligo(*p*-benzamide)s with the aim of obtaining organo-soluble oligomers and polymers. To suppress aggregation *via* stacking interactions, Fréchet dendrons[3] of first (G1) and second (G2) generation were attached to the aromatic backbone using *p*-aminosalicylic acid derivatives (Fig. 2),[4] following up on a very successful strategy previously exploited by the Schlüter group.[5] Indeed, G2 Fréchet dendrons are bulky and flexible enough to prevent π-interactions while maintaining good solubility. Interestingly, alternating co-polymers from dendron (G1)- and triethylene glycol-substituted *p*-aminosalicylic acid did not show aggregation in organic solvents either, although one edge of the polymer was not shielded by sterically demanding groups. This shows the solubility-mediating effect of triethylene glycol side chains once more.

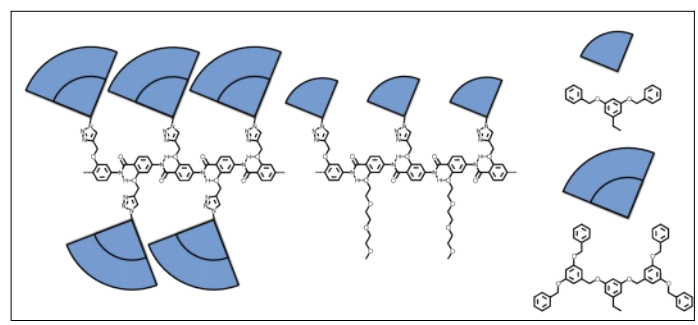

Fig. 2. Non-aggregating dendronized poly(*p*-benzamide)s.

On the basis of our latest achievements in the field of substituted oligo- and poly(*p*-benzamide)s we gained access to non-aggregating, shape-persistent rods for the construction of nanoscopic objects. Combining sequence control through automated peptide synthesis[6] with the rigidifying, solubility-mediating behavior of Fréchet dendrons and triethylene glycol side chains[4] we are now able to build linear arrays in which functionalities can be placed at specific distances from each other. In addition, the use of different side groups (sterically demanding, hydrophilic, lipophilic) will provide us with shape persistent scaffolds in which amphiphilicity patterns can be designed to create exciting new self-assembling structures.

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