

4 Summary and Outlook

Summary

A series of amphiphilic *ortho*-phenylene ethynylene oligomers has been synthesized from a tetramer to a hexadecamer. Several synthetic approaches have been investigated including (i) a classic iterative convergent/divergent synthesis, (ii) a stepwise synthesis on a soluble support resembling Merrifield's solid-support methodology, and (iii) the controlled oligomerization of a suitable shorter oligomer to access longer oligomers and their subsequent isolation from the reaction mixture. The oligomers were designed with suitable side chains contributing amphiphilicity as well as chirality and enabling folding among these oligomers. The numerous optical spectra recorded in different solvents point to changing backbone conformations depending on the nature of the solvent. The spectral features were assigned to helical and extended conformations and particularly CD spectroscopy demonstrated changes in optical activity arising from helical folding. The huge CD differences between tetramer and octamer proved chiral amplification via adoption of helical secondary structures while for higher oligomers an additional alternative conformational and aggregational mode was presented.

A novel π -conjugated polymer based on an *ortho*-alternating-*para*-phenylene ethynylene backbone was designed, successfully synthesized, and spectroscopically analyzed. An adequate multi-purpose side chain based on a natural amino acid was synthesized fulfilling the requirements of polarity, chirality, and branched structure. The results from absorbance and emission spectroscopy strongly point towards helical folding in polar solvents. The corresponding CD spectra were more complex than spectra of purely *ortho*-PEs and support the postulation of solvophobic induced conformational changes. Unfortunately, the changes in optical activity were only moderate, probably arising from inefficient chirality transfer.

The initial exploratory work on a supported oligomer synthesis led to the successful construction of a series of amphiphilic block copolymers based on a flexible PPO segment and an aromatic PE segment. The PPO segment was polymerized from enantiopure propylene oxide and optimization of reaction conditions yielded highly isotactic, non-racemic and thus optically active polymeric material of controlled length and low polydispersity. *Para*-PE and *meta*-PE monomers were successfully grafted from PPO segments of different lengths generating block copolymers of distinct architectures, i. e. rod-coil copolymers with π -

conjugated aromatic blocks in the case of *p*PE repeat units and switchable segments of differing aspect ratios in the case of *m*PE repeat units undergoing helix-coil transitions. The influence of the connectivity among the aromatic segments as well as the influence of the length of the PPO segment on the block copolymers' solution properties was analyzed in extensive spectroscopic studies.

Finally, the architectural modification of attaching PPO segments on trifunctional PE monomers and their subsequent polymerization lead to graft copolymers of respectable molecular weight. Spectroscopic characterization demonstrated the ability of the PE-backbone to fold although water as strong polar co-solvent was needed to overcome the activation barrier of folding due to the large steric demand of the long PPO side chains. Here, shorter PPO segments should facilitate the helix-coil transition while maintaining the advantages of such hybrid macromolecular materials.

Outlook

The work described in this thesis contributes to the continuing trend of merging classical disciplines namely organic synthesis and polymer chemistry. Meshing the characteristics of these often-complementary fields helps to surpass limitations and greatly expands the freedom of designing custom-tailored *de novo* hybrid materials. But what are the field's unsolved problems and future challenges?

Increasing and controlling the length accessible in the polymerization of phenylene ethylenes. While the polydispersity is governed by the limitations of polycondensation reactions that will be hard to overcome, the access to longer *ortho*-connected PEs still suffers from low conversions.

Controlling self-assembly of macromolecules into tubular or rod-like objects of defined finite dimensions is still an unconquered territory.

Controlling the functionalization of the interior and exterior surfaces of self-assembled structures. In particular, peripheral modification of helices with polymers as exemplified by our graft copolymers represents an attractive route to tune materials properties and control pattern formation at the nanometer scale.

Finally, improving systems discovered in the laboratory and incorporating them into real-world applications is the ultimate driving-force for chemical and materials advances, while curiosity-driven research will continue to unravel Nature's most exquisite mysteries at the chemical boundary of both life and materials science.