

Influence of Chirality on Conformation and Aggregation Behavior of Poly(propylene oxide)-Poly(phenylene ethynylene) Copolymers

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INTRODUCTION

Block copolymers¹ represent an attractive class of macromolecules as they are joining often-contrasting properties of their individual blocks, which are well separated in space and therefore give rise to nanophase separation, representing a promising approach to generate large area functional nanostructures from the bottom-up.² We are interested in utilizing a foldamer-based block,³ i.e. a backbone capable of reversibly folding from a random coil into a helical conformation and thereby significantly changing its aspect ratio. Thus a block copolymer was targeted that in principle should allow for dynamic self-assembly leading to the design of “smart” materials. The incorporation of chirality into one block is of particular interest in order to investigate the transfer of the chiral information between both blocks,⁴ i.e. the induction of excess helicity in the single or aggregated foldamer-based block.

Here, we present our recent work on diblock and brush copolymers composed of highly isotactic, enantiopure (S)-poly(propylene oxide)s (PPOs) and poly(phenylene ethynylene)s (PPEs). It should be noted that the PPO blocks serve a dual purpose by contributing amphiphilicity to facilitate segregation and by introducing chirality to bias conformational equilibria and aggregation behavior. The influence of the chiral PPO component on the folding propensity and self-assembly of the PPE backbones will be discussed.

RESULTS AND DISCUSSION

The synthesis of the PPO-PPE diblock and brush copolymers outlined in Figure 1 starts with controlled polymerization⁶ of enantiopure (S)-propylene oxide to yield highly isotactic, enantiopure, and monofunctional PPO blocks of various molecular weights (MW = 2000-20000) and narrow dispersities (PDI < 1.1). Subsequent esterification of the PPO block's terminal hydroxyl groups provided the macromonomer for generating the PPO-*Pm*PE brushes and the macroterminator for accessing the PPO-PPE diblocks, respectively. While in the case of the diblock copolymers *meta*- or *para*-connected PPE blocks, i.e. *Pm*PEs or *Pp*PEs, were introduced, the polymer brushes were only composed of *Pm*PE backbones. The copolymers' PPE segments were synthesized using standard Pd-catalyzed polycondensation procedures.⁷ Surprisingly, our recently developed *in-situ* activation/coupling protocol to yield defect-free PPEs⁸ could not be employed successfully due to partial hydrolytic cleavage of the ester bonds linking the PPO and PPE segments.

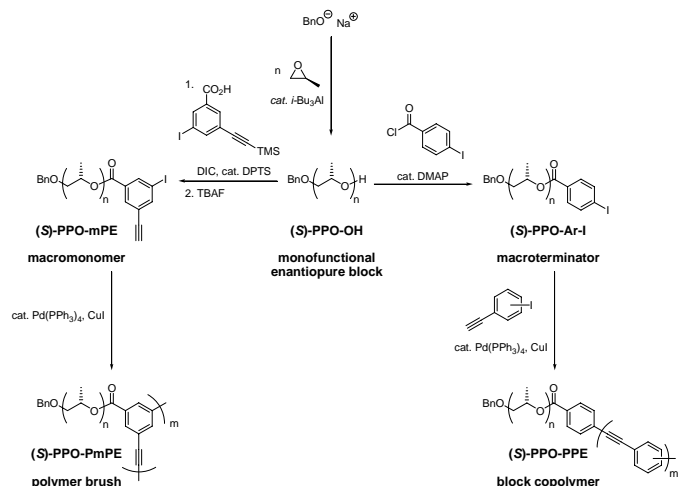


Figure 1. Synthesis of enantiopure PPO-PPE brush and diblock copolymers.

The PPO homopolymers as well as the resulting PPO-PPE copolymers were characterized by several techniques including GPC, NMR, DSC. In particular, ¹H-NMR proved very useful in determining the number average degree of polymerization of the synthesized diblock copolymers. Both folding and aggregation behavior was investigated in solution using mostly optical spectroscopy (UV/vis, fluorescence, CD). The influence of several parameters, such as concentration, solvent, temperature etc. on the polymers' hierarchical structure formation was investigated and it was shown that the chirality of the enantiopure PPO blocks can be transferred to the entire copolymer backbone or aggregate. These findings have been corroborated by comparison with racemic PPO copolymers.

CONCLUSIONS

We have successfully prepared diblock and brush copolymers composed of enantiopure (S)-PPO as well as *Pm*PE and *Pp*PE segments. The novel materials have been characterized with regard to their conformational and aggregation behavior in solution using various spectroscopic techniques. Under certain conditions, the chirality from the PPO segments can be transferred to the PPO-PPE copolymers. Work in progress involves the investigation of the prepared systems at various interfaces and in bulk.

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