Block copolymers based on poly(vinylidene fluoride)
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Abstract

Poly(vinylidene fluoride) has reached the second largest production volume of fluoropolymers in recent years, and its popularity can be ascribed to high thermal stability and chemical inertness combined with its ferroelectric behavior, that arises from the strong dipole in the β-crystalline phase. Hence, this polymer can be implemented in high tech applications related to electronics and energy harvesting.

Copolymerization of vinylidene fluoride with other monomers leads to a wide variety of products, ranging from thermoplastics and elastomers to thermoplastic elastomers with modified thermal, chemical, mechanical or electrical properties. In addition to the fluorinated random copolymers manufactured by industry, well-architectured block-, graft- and alternating copolymers based on PVDF received considerable attention in recent years. In particular, PVDF-containing block copolymers can function as ordered precursors for functional nanostructured materials with ferroelectric and multiferroic (magnetoelectric) properties applicable in sensors and data storage devices.

This thesis describes the synthesis of various well-defined block copolymers containing PVDF segments and addresses their crystallization and phase behavior in detail. Additionally, the use of those block copolymers as precursors for nanoporous PVDF and PVDF-based nanocomposites is presented, and their ferroelectric and ferromagnetic behavior is discussed.

Chapter 1 comprehends a compact review of the literature based on the synthesis, self-assembly and potential applications of block copolymers containing PVDF segments.
Chapter 2 focuses on poly(L-lactide)-block-poly(vinylidene fluoride)-block-poly(L-lactide), or shortly PLLA-b-PVDF-b-PLLA, triblock copolymers. First, their synthesis route was explored, involving Cu(I)-catalyzed azide-alkyne cycloaddition of tailor-made PVDF and PLLA telechelics. Subsequently, the sequential crystallization of both blocks has been studied. The double-crystalline PLLA-b-PVDF-b-PLLA copolymers form a homogeneous melt phase, however upon cooling phase separation driven by crystallization results in an ordered lamellar nanostructure. Although the ferroelectric β-polymorph was initially observed in the solvent-cast block copolymer films, the α-phase was obtained after crystallization from the melt. The crystallization behavior of the lower temperature crystallizing PLLA segments was strongly influenced by the composition of the block copolymer. Furthermore, the PLLA blocks were found to crystallize in a confined fashion, within the interlamellar regions of the preformed PVDF spherulites.

**Impression** of the fabrication route towards lamellar PVDF/Ni nanocomposites: (1) Solvent-casting yields self-assembled crystalline-amorphous lamellar nanostructure, (2) Selective etching procedure removes amorphous PS domains leading to nanoporous PVDF template, and (3) electroless nickel plating results in PVDF/Ni nanohybrid.
A similar “click” strategy was performed to create double-crystalline triblock copolymers consisting of inner poly(vinylidene fluoride) and outer poly(3-hexylthiophene) segments. Those P3HT-b-PVDF-b-P3HT copolymers are the focus of Chapter 3. Contrary to PLLA-b-PVDF-b-PLLA, a microphase separated melt was obtained and confined crystallization of P3HT and PVDF blocks occurred within phase segregated domains. Rich phase behavior gave rise to hierarchical order at multiple length scales, involving π-π stacking between polythiophene backbones, lamellar packing of hexyl side chains, semicrystalline lamellar organization of P3HT and block copolymer microphase separation of PVDF and P3HT.

Block copolymers that contain a degradable component provide a straightforward route towards porous nanostructured materials with desired functionality and controllable pore sizes. Chapter 4 describes the fabrication of nanoporous PVDF and PVDF/nickel nanocomposites from polystyrene-block-poly(vinylidene fluoride)-block-polystyrene precursors. The developed synthesis route towards semicrystalline PS-b-PVDF-b-PS includes atom transfer radical polymerization of styrene from tailor-made chlorine-functionalized PVDF macroinitiators. The alternating crystalline-amorphous lamellar nanostructure inside a spherulitic superstructure, observed for a range of block copolymer compositions, confirmed the dominant role of crystallization during structure formation. By applying a facile chemical etching method the amorphous PS domains were selectively removed, leading to a nanoporous PVDF matrix. Subsequently, PVDF/Ni nanocomposites were fabricated via electroless Ni plating. The lamellar morphology and the PVDF β-polymorph, both originating from the block copolymer self-assembly, are preserved within the porous template and nanocomposite material.

To extend the library of well-ordered PVDF-based nanohybrids, an additional block copolymer system was developed composed of inner poly(vinylidene fluoride) and outer poly(tert-butyl methacrylate) segments: PtbMA-b-PVDF-b-PtbMA. Hence, Chapter 5 starts with discussing the synthesis route, which is based on the same strategy as adopted for PS-b-PVDF-b-PS, and the crystallization controlled self-assembly. Acidic hydrolysis of tert-butyl moieties and subsequent backfilling of the remaining polymer template through nickel plating or sol-gel synthesis generated PVDF/PMAA/Ni and PVDF/PMAA/SiO₂ nanohybrids, respectively. Both PVDF β-polymorph and lamellar morphology were conserved in all composite materials.
In order to explore the properties of the fabricated PVDF-based nanocomposites, the ferroelectric behavior of the block copolymer precursors has been examined in Chapter 6. Local hysteresis measurements for PtBMA-b-PVDF-b-PtBMA and PMAA-b-PVDF-b-PMAA confirmed polarization switching in the block copolymer films. Moreover, room temperature ferromagnetism was observed in the PVDF/PMAA/Ni nanocomposites.

To conclude, PVDF-based block copolymers can be employed as precursors for nanostructured ferroelectrics and multiferroics. Since those materials can find extensive application in information storage industry, we expect more investigations and discoveries in this field to emerge. In particular, further development of fully organic multiferroic block copolymers with ferroelectric and ferromagnetic segments will lead to a new class of fascinating materials.