Summary

Nowadays, ferroelectric polymers are essential elements for future flexible organic devices due to their light weight, flexibility and processability. Poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (P(VDF-TrFE)), which exhibit a large polarization, high dielectric constant, good thermal and chemical stability, are the most used ferroelectric polymers. Introduction of extra functionalities into the structure of ferroelectric polymers can further widen their application in related fields, as it delivers additional benefits to the material, such as improved dispersion of nano-objects or any other functional component, better adhesion to the electrodes or preparation of nonporous ferroelectric materials. In addition, the response of PVDF-based polymers to an applied electric field can be altered from ferroelectric to relaxor or even linear dielectric by the adjustment of the crystalline domain size or by screening the nominal electric field values inside the crystalline ferroelectric phase. Thus, it is highly beneficial to develop a simple method that can simultaneously tailor the hysteresis shape while adding new functionalities.

Self-assembly processes are one of the possibilities in this respect, as they emerge as one of the most effective means to construct functional nanomaterials that combine properties of all constituent components, readily tailored by either changing molecular characteristics of a material or under external stimuli. In polymers, one of the simplest ways to accomplish improved tunable functionalities is by the preparation of block copolymers. By adjusting the block length, the ratio between the blocks and the temperature, it is possible to obtain lamellar, cylindrical, spherical or gyroid structures in the range between 10 and 100 nm. The preparation of block copolymers based on ferroelectric PVDF and the addition of the insulating functional component to the ferroelectric polymer can significantly modify the coupling forces between dipoles and can alter the ferroelectric switching behavior. However, due to the absence of synthetic procedures that grant the successful preparation of high molecular weight block copolymers that demonstrate strong phase separation, the ferroelectric properties of PVDF-based block copolymers have not yet been investigated.

Chapter 1 gives an overview of the properties and application of the PVDF and its copolymers. In addition, the so far developed synthetic procedures for the preparation of PVDF-based block copolymers and their phase separation are described. Finally, the factors that are influencing dipole switching mechanism of the ferroelectric polymers are explained in detail.
Chapter 2 is focused on the development of a versatile synthetic procedure for the preparation of relatively high molecular weight PVDF-based block copolymers. The use of alkyne/chlorine functionalized benzoyl peroxide initiators in the polymerization of vinylidene fluoride allowed the preparation of tailor-made PVDF telechelics with high end group fidelity. The obtained polymers were further used for the synthesis of various semi-crystalline triblock copolymers using a copper(I)-catalyzed azide-alkyne cycloaddition reaction. Subsequently, the crystallization behavior of block copolymers has been examined. Depending on the molecular characteristics of the amorphous block, block copolymers demonstrated either phase segregation or mixing in the melt, which substantially influenced their crystallization behavior. The block copolymer that forms a homogeneous melt demonstrated complete disruption of the crystallization, while the outcome of the crystallization for the phase separated block copolymers was dependent on the glass transition temperature ($T_g$) of the non-crystalline block. For example, the high $T_g$ of polystyrene (PS) in PS-$b$-PVDF-$b$-PS block copolymers induced crystallization inside spherical domains preformed in the melt, whereas break-out crystallization occurred for block copolymer with low $T_g$ poly(tert-butyl acrylate).

The incorporation of insulating polymer chains in the structure of ferroelectric polymers can form a good electric shield around ferroelectric crystals that can alter the dipole switching behavior inside polymer. Therefore, the ferroelectric characteristics of PVDF-block copolymers are elucidated in Chapter 3. The main factor that affects the shape of hysteresis loops of block copolymers is the dielectric constant of the amorphous block attached at both ends of the ferroelectric P(VDF-TrFE). The use of polar poly (2-vinyl pyridine) (P2VP) and its phase separation from P(VDF-TrFE) forming lamellar morphology caused preservation of the ferroelectricity inside block copolymers. On the contrary, the addition of the non-polar PS into the structure of P(VDF-TrFE) lead to the absence of dipole switching and linear dielectric properties with almost zero remanent polarization were demonstrated. In addition, the incorporation of extra TrFE units inside P2VP-$b$-P(VDF-TrFE)-$b$-P2VP block copolymer resulted in formation of a mixture of paraelectric and ferroelectric phases and a double loop antiferroelectric-like behavior was obtained. The decrease in the dielectric constant of the components at the crystalline-amorphous phase boundary caused the reduction of the compensational polarization that is responsible for dipole switching, and therefore alters the shape of the hysteresis loops.

The ferroelectric properties of block copolymer systems are further investigated in Chapter 4. Here, a detailed study of the microphase separation of P2VP-$b$-P(VDF-TrFE)-$b$-P2VP block copolymer system is reported and the influence of the structural characteristics of block copolymers on the shape of the hysteresis loops are explored. By simple changes of the ratio between the blocks, different morphologies, lamellar, cylindrical and spherical were
readily achieved. The overall crystallinity of block copolymers and the size of the crystalline domains were significantly affected by the dimensionality of the formed nanodomains. The increase of the confinement level induced a decrease in the size of the formed crystals and also a reduction in the coupling forces between the ferroelectric nanodomains, which induced a change in the ferroelectric properties of block copolymers. All samples with lamellar morphology demonstrated ferroelectric switching behavior with a coercive field close to the pristine P(VDF-TrFE), whereas the block copolymers with cylindrical or spherical morphology were characterized with a delayed spontaneous polarization or even linear dielectric behavior.

The presence of P2VP blocks, that act as hydrogen bond acceptors, in the structure of block copolymers, provides a straightforward route for the selective and improved dispersion of nano-objects inside the ferroelectric polymer matrix and preparation of nanocomposites with additional value. In this perspective, Chapter 5 deals with the development of multiferroic polymer-based nanocomposites by directing the dispersion of the functionalized magnetic cobalt ferrite nanoparticles in the ferroelectric P2VP-b-P(VDF-TrFE)-b-P2VP block copolymer. The modification of the nanoparticles’ surface with gallic acid and a hydrogen bond formation between hydroxyl groups of gallic acid with 2VP units grants the selective dispersion of the nanoparticles inside the insulating P2VP layers of the lamellar block copolymer. The selective dispersion of nanoparticles is proven to be beneficial for the preservation of the ferroelectric crystalline phase and the improvement of the crystallinity of the obtained nanocomposites. The nanocomposites prepared using this approach demonstrated both ferroelectric behavior and strong interaction with the magnetic field with zero coercive field.

The same approach was used in Chapter 6 to prepare ferroelectric polymer-based nanocomposites with improved dielectric properties. Here, ultra-small gallic acid modified hafnium oxide nanorods were selectively dispersed in a P2VP-b-P(VDF-TrFE)-b-P2VP block copolymer with relaxor ferroelectric characteristics. The selective incorporation of the medium dielectric constant hafnium oxide inside P2VP layers induced the formation of physical crosslinking and consequently deeper charge traps as compared to the pristine block copolymer. In addition, a more rigid structure of the amorphous polymer matrix after the incorporation of nanorods is responsible for a more pronounced stretching of the P(VDF-TrFE) chains at the interface and an increased content of the paraelectric phase. Thus, the reduction in both conductive and ferroelectric losses after the addition of nanorods presents the main reason for distinctly slimmer hysteresis loops with a reduced remanent displacement and consequently improved energy density and charge-discharge efficiency of nanocomposites.
In conclusion, this thesis contributes to a deeper understanding of the self-assembly behavior of ferroelectric block copolymers, their dipole switching characteristics and possible application for the preparation of advanced highly defined nanocomposites. A deeper understanding of the physical phenomena that contribute to the change in ferroelectric behavior of PVDF-based block copolymers enables the establishment of the design rules to reach desired properties necessary to obtain more advanced materials. Given the simplicity of the molecular structure adjustment and simplicity of material preparation, this approach shows immense potential to be applied in various fields.