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Enhanced Stability of Piezoelectric Crystalline Phase of Poly(Vinylidene Fluoride) (PVDF) and Its Copolymer upon Epitaxial Relationships

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Abstract : As an approach to manipulate the performance of polymer thin film, epitaxy crystallization within polymer blends of poly(vinylidene fluoride) (PVDF) and its copolymer poly(vinylidene fluoride-trifluoroethylene) P(VDF-TrFE) was studied in this research, which involves the competition between phase separation and crystal growth of constitutive semicrystalline polymers. The unique piezoelectric feature of poly(vinylidene fluoride) crystalline phase is derived from the packing of molecular chains in all-trans conformation, which spatially arranges all the substituted fluorene atoms on one side of the molecular chain and hydrogen atoms on the other side. Therefore, the net dipole moment is induced across the lateral packing of molecular chains. Nevertheless, due to the mutual repulsion among fluorene atoms, this all-trans molecular conformation is not stable, and ready to change above curie temperature, where thermal energy is sufficient to cause segmental rotation. This research attempts to explore whether the epitaxial interactions between piezoelectric crystals and crystal lattice of hexamethylbenzene (HMB) crystalline platelet is able to stabilize this metastable all-trans molecular conformation or not. As an aromatic crystalline compound, the melt of HMB was surprisingly found able to dissolve the poly(vinylidene fluoride), resulting in homogeneous eutectic solution. Thus, after quenching this binary eutectic mixture to room temperature, subsequent heating or annealing processes were designed to explore the involve phase separation and crystallization behavior. The phase transition behaviors were observed in-situ by X-ray diffraction and differential scanning calorimetry (DSC). The molecular packing was observed via transmission electron microscope (TEM) and the principles of electron diffraction were brought to study the internal crystal structure epitaxially developed within thin films. Obtained results clearly indicated the occurrence of heteroepitaxy of PVDF/PVDF-TrFE on HMB crystalline platelet. Both the concentration of poly(vinylidene fluoride) and the mixing ratios of these two constitutive polymers have been adopted as the influential factors for studying the competition between the epitaxial crystallization of PVDF and P(VDF-TrFE) on HMB crystalline. Furthermore, the involved epitaxial relationship is to be deciphered and studied as a potential factor capable of guiding the wide spread of piezoelectric crystalline form.

Keywords : epitaxy, crystallization, crystalline platelet, thin film and mixing ratio
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