

Structure, phase transition and electric properties of poly(vinylidene fluoride-trifluoroethylene) copolymer studied with density functional theory

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Abstract

The geometry, energy, internal rotation, vibrational spectra, dipole moments and molecular polarizabilities of poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) of α - and β -chain models were studied with density functional theory at B3PW91/6-31G(d) level and compared with those of the poly(vinylidene fluoride) (PVDF) homopolymer. The chain length and the trifluoroethylene (TrFE) concentration were examined to discuss the copolymer chain stabilities, chain conformations and electric properties. The asymmetrical internal-rotation potential energy curve shows that the angles for the g and g' conformations in the α -chain (tg and tg') models are 53° and -70° , respectively, and the β -chain (ttt) conformation is a slightly distorted *all-trans* plane with dihedral angle at 177° . The energy differences, $E_\beta - E_{\alpha(g)}$ and $E_\beta - E_{\alpha(g')}$, between the β - and the α -conformation are 2.1 and 7.8 kJ/mol, respectively. These values are smaller than that in PVDF (8.4 kJ/mol), suggesting that the β -conformation in the copolymer will be more stable than in PVDF. The energy barriers for $\beta \rightarrow \alpha(g)$ and $\beta \rightarrow \alpha(g')$ transitions are 16.2 and 5.8 kJ/mol, respectively. The former is almost twice of the energy barrier in PVDF by 8.2 kJ/mol and the latter is slightly smaller (by 2.4 kJ/mol) than that in PVDF. The respective energy barriers for $\alpha(g) \rightarrow \beta$ and $\alpha(g') \rightarrow \beta$ transitions are 18.3 and 13.6 kJ/mol compared with the value 16.3 kJ/mol in PVDF. The asymmetrical energy barriers may be one of the reasons for the copolymers with 0.5–0.6 (mole fraction) VDF exhibiting complicated phase transition behavior. The conformation of α -chain P(VDF-TrFE) exhibits from a *helical* (containing higher TrFE) to a nearly beeline (containing lower TrFE). This behavior is different from that in the PVDF and the nearly beeline conformation might be responsible for the increasing crystallizability. The *helical* might also be associated with the complicated phase transition behavior and the larger lattice strain in the P(VDF-TrFE)s with higher TrFE concentration. The energy difference per monomer unit between the β - and α -chain decreases with increasing TrFE content. The ideal β -chain is curved with a radius of about 30 Å, which is similar to that in PVDF. The chain curvature and the TrFE content will affect the dipole moment contribution per monomer. The chain length and TrFE content will not significantly affect the mean polarizability. The calculations indicated that there are some additional characteristic vibrational modes that may be used in identification of the α - or β -phase P(VDF-TrFE)s with different TrFE contents.

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1. Introduction

The discovery of the enhancement of piezoelectric activity in poly(vinylidene fluoride) (PVDF) by Kawai [1] led to the revelations of other properties, e.g., pyroelectricity [2,3] and ferroelectricity [4]. The exploration of the chemistry, physics, and technology of PVDF led to the search for other classes of novel ferroelectric polymers, such as its copolymers [5–8],

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odd numbered polyimides [9,10], cyanopolymers [11,12], polyurethane [13,14], etc. Significant progresses in new materials and the understanding of structure–property relationships have been reported in the last decades.

Although PVDF possesses strong piezoelectric and pyroelectric properties, it is necessary that the polymer film be subjected to mechanical stretching and electrical poling to obtain the polar β -phase with the extended planar zigzag (*all-trans*) conformation. Such procedures include, for example, subjecting ferroelectric polymer to mechanical deformation [15,16], electron irradiation [17], uniaxial drawing [18], crystallization under high pressure [19] and crystallization under high electric field [20,21]. It is desirable to obtain a polymer with piezoelectric phase by simple treatment. Some improvements have been achieved by synthesizing copolymers of vinylidene fluoride (VDF) with trifluoroethylene (TrFE) [7,22–25], tetrafluoroethylene (TeFE) [23,26,27], vinyl fluoride (VF), or VDF/TrFE/chloro-containing terpolymers [28]. The copolymers were demonstrated to possess ferroelectricity over a wide composition range [29,30].

Compared with VDF, TrFE has lower polarity and TeFE does not have. However, the P(VDF-TrFE) and P(VDF-TeFE) copolymer systems can be grown with 90% or higher crystallinity [31–35], which results in stronger polarization and piezoelectric responses than those of the 50% crystalline PVDF. In addition, these structures can be grown in the form of ultrathin films [36,37] and have other important electromechanical properties, e.g., giant electrostriction [38,39]. Among these copolymers, the mostly studied system is the copolymer, poly(vinylidene fluoride-trifluoroethylene), obtained by random copolymerization of VDF and TrFE. This is also the best known and the most widely used ferroelectric polymer [40,41]. The randomly distributed VDF and TrFE units form the co-crystalline phase in the whole composition range. The larger proportion of bulky trifluorine atoms in the PVDF prevents the molecular chains from accommodating the α -chain (or *tgtg'*, where *g* refers *gauche* and *t* refers *trans*, and a prime (') in *g* refers the dihedral angle being opposite to the *g* conformation with respect to the reference plane *t*) conformation. Therefore, the copolymer crystallizes directly at room temperature into a ferroelectric β -phase (or *ttt*, where *t* also refers *trans*) [42,43] that possesses a polar unit cell (similar to the β -phase of PVDF homopolymer), and the copolymer can be electroprocessed into a piezoelectric material immediately after crystallization.

The ferroelectric regions, with crystalline order, in the copolymer are embedded in an amorphous matrix. A number of experimental techniques and theoretical methods, such as differential scanning calorimetry, dielectric constant, ferroelectric measurement, X-ray diffraction, molecular dynamic (MD) simulation and *ab initio* technique, have been employed to investigate the electrical properties and structure changes during the phase transition of P(VDF-TrFE) to clarify the essential features of the transition mechanisms [23,24,44–47] and the origin of ferroelectric properties. The transition is associated with three types of crystalline phases, namely, the low-temperature (*LT*) phase, high-temperature (*HT*) phase

and the cooled (*CL*) phase [40,44–51] and will be mainly affected by several factors, e.g., the composition of copolymer, history of heating, distribution of molecular weights and preparation conditions. Among those, the VDF content is especially important [40,50,52]. For instance, a copolymer sample with 0.7–0.8 (mole fraction) of VDF shows a clear and discontinuous first-order transition between the *LT* and *HT* phases at temperature close to the melting point [49,53]. A sample with 0.5–0.6 (mole fraction) of VDF, however, shows more complicated transition behavior [30,40,45,49,50,52,54]. In addition, experimental results show that the diffuse phase transition of copolymer from the ferroelectric into the paraelectric phase is also associated with the statistical variation of the VDF content of the crystallites [55]. Interestingly, there is a large strain change associated with the phase transformation. For example, for a copolymer with VDF/TrFE of 65/35 (mole ratio), the lattice strain as high as 10% has been detected during the phase transition [54].

In understanding the structure–property relationship of P(VDF-TrFE), Holman and Kavarnos [56] investigated the structural characteristics of amorphous and annealed P(VDF-TrFE) copolymers with VDF/TrFE of 50/50 (mole ratio) by molecular dynamics. Their MD computations predicted that the extent of *gauche*-character for PVDF is greater than that of its copolymer with 0.5 (mole fraction) of TrFE, at both high temperatures and after annealing. PVDF is enriched in *gauche*-conformations upon cooling, whereas the copolymer is enriched in *trans*-conformations. Farmer et al. [6], using potential energy calculations to determine the chain conformation and packing energies, confirmed that conversion between the α - and β -phase should be energetically feasible, and that increased concentration of head-to-head defects ($-\text{CH}_2$ refer to head and $-\text{CF}_2$ refer to tail) or TeFE co-monomer can cause the β -phase to become the favored structure for PVDF. From intermolecular potential investigations of P(VDF-TrFE), Lando and Doll [5] concluded that the isomorphous replacement of fluorine atoms by hydrogen atoms, which occurs in the head–head units in the homopolymer, strongly influences the polymorphism displayed by PVDF. Abe et al. [24] studied the phase transition of copolymer P(VDF-TrFE)s (with 0.5 and 0.7 mole fraction of VDF) by MD simulations. They predicted that the copolymer with higher VDF content exhibits the transition at higher temperature, and the molecular conformation in the high-temperature phase was a statistical combination of *tg*, *tg'*, *tttg* and *tttg'* sequences, in which the population of *tg* and *tg'* was higher and that of *tttg* and *tttg'* was lower for the copolymer with higher VDF content. Nakhmanson et al. [23] investigated the polar properties of the β -phase of PVDF and its copolymers with TrFE and TeFE using an *ab initio* multigrid-based total-energy method. Their calculations show that polarization in such polymers is described by cooperative, quantum-mechanical interactions between polymer chains, which cannot be viewed as a superposition of rigid dipoles. For β -PVDF, the monomer dipole moment is increased by 50% (from 2 to 3 Debye) as the isolated chains are brought together to form a crystal. In PVDF crystals containing copolymers, they observed a weakly parabolic

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