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Effect of trifluoroethylene monomers on molecular conformation of poly (vinylidene fluoride-trifluoroethylene) copolymer*

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Hartree–Fock and density functional theory (DFT) methods were employed to study poly (vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] molecular chains with different VDF contents. The dependence of dipole moment of P(VDF-TrFE) chains on VDF content obtained from our calculation is in good agreement with the experiment. The TrFE monomer plays an important role in introducing the gauche bond into copolymer chains. A possible mechanism was interpreted.

Keywords: Hartree–Fock and B3LYP methods, P(VDF-TrFE) molecular chain, gauche bond
PACC: 3120A, 6000, 7780

1. Introduction

The research on ferroelectric materials has attracted great attention in recent years.[1,2] Poly (vinylidene fluoride) [PVDF, -(CH_2-CF_2)-] and its random copolymer with trifluoroethylene P(VDF-TrFE) [-(CH_2-CF_2)$_x$-(CHF-CF_2)$_{1-x}$] are well known ferroelectrics.[3] Extensive experiments and effort have been devoted to the study of their unique piezoelectric, pyroelectric, ferroelectric, and nonlinear optical properties.[4−7] The quasi-one-dimensional nature of PVDF and its random copolymer with TrFE has been found in both angle-resolved inverse photoemission experiment [8,9] and electronic energy band calculation.[10] PVDF does not show its Curie point, because the ferroelectric phase melts below the hypothetical Curie point. However, in copolymer with TrFE containing (50–80)mol% VDF, a clear indication of Curie point was observed.[11] Experimentally, the remnant polarization (P_r) of the copolymer as a function of composition was measured by Tajitsu *et al*,[12] as shown in Fig.1. The theoretical calculation of spontaneous polarization of β-phase PVDF has been done using iteration method by Purvis, Al-Jishi and Taylor.[13,14] They found the interesting result that the crystal electric field hardly influence the equilibrium polarization. Using the same method, Ogura and Chiba [15] calculated the equilibrium polarization of P(VDF-TrFE) at the crystal level. They found that VDF/TrFE copolymers have a large enhancement of polarization, as compared with β-phase PVDF. This is due to the effective increase in the electrostatic inter-molecular interaction in comparison with the intra-molecular interaction. Molecular dynamic simulation [16] showed that introduction of TrFE monomer units increases the instability of the copolymer system and expands the cell volume. A larger volume makes the conformation change more easily, resulting in a lower transition temperature. Despite all this, there are still open problems about the effects of TrFE on the geometrical structure and physical properties of the copolymers, e.g. what is the effect of TrFE monomers on molecular conformation of P(VDF-TrFE). A resolution of the problem is essential for a deep understanding of the physical properties of the copolymers. The purpose of our work is to try to resolve the problem.

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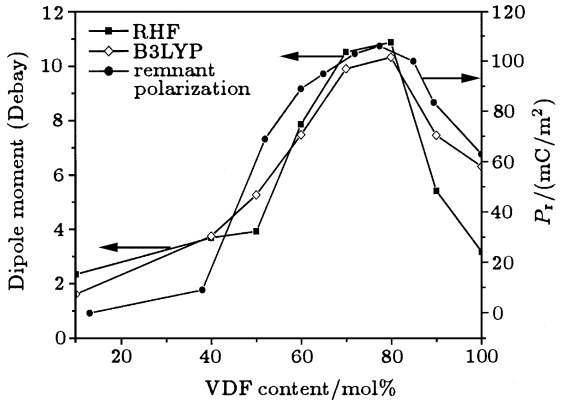


Fig.1. The calculated dependence of molecular dipole moments on VDF content. The dependence of remnant polarization on VDF content (data from Ref.[12]).

2. Computational details

For understanding the quasi-one-dimensional nature of PVDF and its copolymers P(VDF-TrFE),[8–10] it is reasonable to study the individual molecules of No.I–X shown in Fig.2. Initial optimizations were carried out at HF/3-21G level and followed by vibration analyses to determine whether each stationary point was a minimum or a transition state. Subsequent geometric refinement was carried out at B3LYP/3-21G level.[17] For the B3LYP method, the 6-31G(d) basis set was employed to perform the single point energy of the molecule II in Fig.2. All calculations were carried out using GAUSSIAN98W.[18]

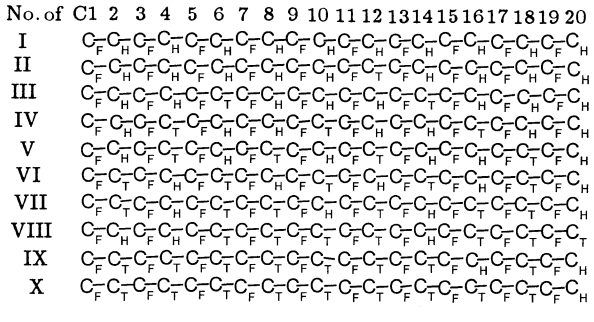


Fig.2. The molecules studied by Hartree–Fock and B3LYP methods. C_H, C_F and C_T denote CH_2, CF_2 and CHF respectively.

3. Results and discussion

For the molecules shown in Fig.2, full optimization was performed using HF/3-21G and B3LYP/3-21G, respectively. The optimized structure data are listed in Table 1, along with the x-ray crystal structure.[19] For bond angles, the results of B3LYP/3-21G agree better with experiment than that of HF/3-21G. However, both bond lengths and angles calculated at the two levels agree well with the results of the x-ray diffraction.[19] From Table 1, we find that there exist two different values of bond length for C—C and C—F in our calculation, which are still not found in previous experiments. C_H^F—C_F of TrFE monomer is larger than C_H—C_F of VDF monomer, and C_H^F—F of CHF is larger than C_F-F of CF_2, which is consistent with the result of molecular dynamics.[16] Our calculation showed that the C_F—C_H^F—C_F is larger than C_H—C_F—C_H and C_F—C_H—C_F; this has not been previously reported in the literature, and may be helpful for future experiments.

Table 1. Average value of bond length and bond angle. C_H and C_F denote the C atoms bonding with H and F atoms, respectively. C_H^F denotes the C atoms bonding with F and H atoms.

	HF	B3LYP	EXP
Bond length/nm			
C_H—C_F	0.151	0.152	0.154
C_H^F—C_F	0.151	0.152	
C_H—F	0.137	0.137	0.134
C_H^F—F	0.140	0.142	
C_H—H	0.108	0.108	0.109
Bond angle/(°)			
F-C_F—F	107.6	107.9	108.0
H-C_F—H	109.8	110.1	112.0
F-C_H^F—H	109.6	110.3	
C_H—C_F—C_H	112.0	111.8	112.0
C_F—C_H—C_F	113.0	113.3	114.0
C_F—C_H^F—C_F	114.3	114.1	

The molecules of I–X denote those of the random copolymer with different VDF contents,100, 90, 80, 70, 60, 50, 40, 30, 20 and 10mol%, respectively. Their dipole moments are obtained from our calculation and plotted against VDF content in Fig.1. From this figure, we can see that the dependence of dipole moment on VDF content agrees well with the dependence of P_r on VDF contents.[12] Since the spontaneous polarization results from the alignment of dipole moments, it is reasonable that our calculation is in good agreement with the experiment.[12] Firstly, the experimental maximum value of the remnant polarization lies in the range of 70–80mol% VDF. In the same range, the calculated maximum values of dipole moments of the copolymer molecules are found in both HF/3-21 and B3LYP/3-21 results. Secondly, the rapid decrease of P_r for the copolymer containing less than 50mol% VDF was found experimentally, and the same decreasing tendency of dipole moments in the range of 10–50mol% VDF appeared in both HF/3-21G and

B3LYP/3-21G results. Thirdly, as the VDF content exceeds 80mol%, P_r decreases with the increase of VDF content;[12] this kind of decrease is also found in our calculation. The agreement between our calculation and the experiment [12] reflects the quasi-one-dimensional nature of the copolymers to some extent.

Table 2. Torsion angles of molecules I–X gauche torsion angles. The number of C atoms corresponds to that in Fig.2.

Torsion angles	I	II	III	IV	V	VI	VII	VIII	IX	X
1, 2, 3, 4	163.2	–163.0	158.9	161.4	–161.9	–81.6*	151.9	162.5	64.1*	–159.2
2, 3, 4, 5	159.1	–158.3	160.0	160.9	159.8	160.8	161.0	159.5	153.3	–159.6
3, 4, 5, 6	164.7	–164.8	159.7	–81.5*	–81.6*	–161.4	–161.5	166.3	155.2	–164.4
4, 5, 6, 7	162.5	162.4	–161.0	166.7	166.4	161.6	153.8	–80.8*	–179.0	–119.6
5, 6, 7, 8	–157.6	157.6	80.6*	157.2	159.6	81.0*	168.1	162.1	–61.1*	67.0*
6, 7, 8, 9	–158.8	158.4	–168.5	161.3	–159.2	153.5	111.5	–176.1	–157.0	–144.0
7, 8, 9, 10	–158.9	158.8	–158.5	159.1	81.2*	–163.9	–61.3*	–157.9	–172.6	–162.6
8,9,10,11	–157.7	160.2	–161.3	160.3	–166.5	–115.0	157.0	–160.8	–159.2	175.4
9,10,11,12	–163.4	158.1	–160.3	80.7*	–154.8	68.6*	153.9	77.6*	158.1	143.9
10,11,12,13	163.4	–161.6	–158.8	–167.4	–76.0*	–161.5	–76.2*	157.1	160.1	–176.3
11,12,13,14	158.3	81.0*	–160.0	–159.7	156.9	160.6	156.2	166.5	163.5	–157.2
12,13,14,15	158.6	–165.7	80.8*	–161.2	–159.6	159.4	–157.0	–81.0*	115.9	–166.2
13,14,15,16	162.8	–164.2	–159.6	–161.2	161.2	–80.8*	167.2	–163.5	68.4*	139.7
14,15,16,17	–163.6	164.0	159.6	159.5	–154.8	167.4	81.8*	163.8	154.2	–72.6*
15,16,17,18	–157.8	157.7	160.8	–81.1*	–168.1	155.3	–163.9	142.9	169.1	166.3
16,17,18,19,	–158.5	159.7	159.7	–166.7	81.2*	77.0*	–161.6	70.9*	–80.8*	161.4
17,18,19,20,	–161.3	161.3	161.3	160.8	–159.8	–155.9	81.0*	–169.8	159.8	–81.3*

The optimized result of B3LYP/3-21G agrees better with the experiment than that of HF/3-21G, so the torsion angles of the copolymer molecular chains obtained at the B3LYP/3-21G level were used to study the molecular conformation, as listed in Table 2, in which we find that all the torsion angles can be divided into two groups. Group one is about 160°, group two is in the range of 61°–83°. With the increase of TrFE content, the value of some torsion angles belonging to group two drops to about 61°. The torsion angle of gauche bond obtained from x-ray diffraction is 57°,[19] which is consistent with group two of our calculation. From Table 1, we see that the gauche bonds always occur in the position of TrFE monomers. In order to study the mechanism of introduction of gauche bond by TrFE monomer, we have conducted the following calculation for molecule II in Fig.2. All the bond lengths and bond angles are fixed except for the dihedral angle 11, 12, 13, 14 listed in Table 2. The dependence of molecular energy on dihedral angle has been obtained from our calculation, as shown in Fig.3. It is easy to find that only one minimum of energy is obtained for the torsion angle of about 81°. This indicates that the value of about 81° is only one stable conformation for dihedral angle 11, 12, 13, 14 including the TrFE monomer. In addition, the possible mechanism of introducing gauche bond by TrFE monomer can also be explained by force balance. It is well known that the diameter of a fluorine atom is 0.27nm, which is slightly larger than the space (0.255±0.0001nm) between fluorine pairs. If the torsion angle of the PVDF molecule is 180°, the neighbouring fluorine atoms will overlap each other. In order to diminish the overlap of neighbouring fluorine atoms, the CF group is deflected slightly to the right or left of the plane of zigzag in all-trans segment.[11]

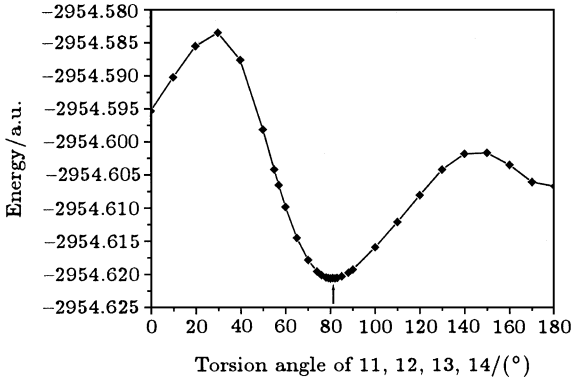


Fig.3. The potential energy surface of molecule II.

From Table 1, we find the torsion angle of group one is about 161, which is consistent with previous calculation of small (about 15°) dihedral deflections.[19] So the conformation of PVDF chain (No. I of Fig.2) is not absolute all-trans (torsion angle =180°) but semi-all-trans conformation (torsion angle ≈161°). Our calculation shows that, in the semi-all-trans conformation, the distance between the fluorine atom and the nearest hydrogen atom (e.g. 1F and 1H in Fig.4) is 0.24nm. From our calculation, we find that the charges of the fluorine and hydrogen atoms are –0.38e and 0.28e, respectively. So the Coulomb attractive force between the two atoms calculated from these data is 2.49×10^{-10}N. Provided that a hydrogen atom is replaced by a fluorine atom, i.e. a TrFE monomer is introduced in the molecule, the attraction between the fluorine and hydrogen atoms is replaced by a larger Coulomb repulsive force (2.92×10^{-10}N). Thus the force balance of the molecular chain is broken, and the CHF group is deflected from the former equilibrium position and stays in a new equilibrium position. As a result, the value of rotation angle of adjacent carbon atoms in the position of TrFE monomer lies in the range of 61–83°, rather than about 165°. So the gauche bond is formed, because the VDF monomer is replaced by a TrFE monomer in the copolymer molecules.

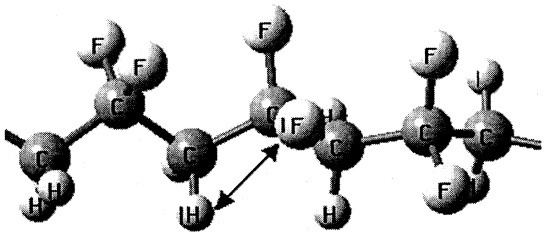


Fig.4. Schematic diagram of the shortest distance between F and H atoms.

4. Conclusions

In summary, P(VDF-TrFE) molecules containing different VDF content have been studied in detail using Hartree–Fock and DFT methods. The dependence of dipole moment of the molecules on VDF content agrees well with that of the remnant polarization.[12] Our calculation shows that the TrFE monomer plays an important role in the introduction of the gauche bond into copolymer chains. This may be helpful for a deep understanding of the ferroelectric property of the P(VDF-TrFE) molecules.

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