



Possible reasons that piezoelectricity has not been found in bulk polymer of polyvinylidene cyanide

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ABSTRACT

The structure, energy, internal rotation, dipole moments and molecular polarizabilities of poly(vinylidene cyanide) (PVDCN) of α - and β -chain models were studied with density functional theory at B3PW91/6-31G(d) level. The effects of chain length on the polymer chain stabilities, chain conformations and electric properties were examined and compared with those of the piezoelectric PVDF in order to explore the possible reasons that the piezoelectricity has not been observed in the bulk polymer of PVDCN experimentally. The results show that the energy barriers (11.5 and 6.9 kJ/mol) of PVDCN in its α - \rightarrow β -chain and β - \rightarrow α -chain transitions are smaller than those (16.3 and 8.2 kJ/mol) of PVDF, which promises an easier transition between the two conformations. This may be one of the reasons that the preparation of the stable piezoelectric phase will be difficult. However, an extremely important feature of the ideal β -chain is that the PVDCN chain is curved with a radius of only about 8.5 Å, which is much smaller than that (30.0 Å) in PVDF and is smaller than that (12.6 Å) in polymethylvinylidenecyanide (PMVC). This suggests that the bulk polymer of PVDCN is difficult to be prepared into crystal phase, and the contribution of the dipole moment per unit to the total dipole will be cancelled if the chain is longer than 12 units (hemicycle). Therefore, the reasons that the piezoelectricity has not been found may be due to the orientation difficulties of chains and dipoles.

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1. Introduction

Ferroelectric polymers are highly attractive materials for modern technological applications due to their low weight, flexibility, and chemical inertness coupled with substantial piezoelectric and pyroelectric properties [1–5]. Especially, their low acoustic impedance matches well with water and organic tissue. Such a fortunate combination of properties allows a wide employment of ferroelectric polymers in modern industry, with applications ranging from various sensors, actuators, and transducers to ferroelectric optical memory, sonar equipment, and artificial muscles. Therefore, the discovery of the enhancement of piezoelectric

activity in poly(vinylidene fluoride) (PVDF) [6] led to the revelation and applications of pyroelectric [7,8] and ferroelectric properties [9]. Naturally, the researches have been extended to explore the chemistry, physics and technology for other classes of novel ferroelectric polymers, such as PVDF based copolymers [10–27], odd numbered polyimides [28,29], cyanopolymers [30,31] and polyurethane [32,33]. Significant progress in new materials and understanding in structure–property relationships have been reported in the last decades.

From the structure of PVDF, the ferroelectric property has been closely related to the polar β -phase to have strong piezoelectric [34] and pyroelectric properties [7,8,35]. In this phase, the large polarization value arises from a highly ordered arrangement of intrinsically polar ($-\text{CH}_2-\text{CF}_2-$) monomers, where each VDF monomer has a non-zero dipole moment directed perpendicular to the carbon backbone.

From this point of view, if it is possible to synthesize a polymer containing larger dipole moment in its monomers and to align the dipoles to form a polar crystal, the polymer may be expected to exhibit stronger piezoelectricity and pyroelectricity. Since the repeating unit of vinylidene cyanide ($-\text{CH}_2-\text{C}(\text{CN})_2-$, VDCN) has larger dipole moment (by 4.0 Debye [36] or 4.5 Debye [37]) than

Abbreviations: Vinylidene cyanide, VDCN; Poly(vinylidene cyanide), PVDCN; Polymethylvinylidenecyanide, PMVC; Polyacrylonitrile, PAN; Poly(vinylidenecyanide vinylacetate), PVDCN/Vac; Poly(vinylidene fluoride), PVDF; Poly(vinylidene fluoride-trifluoroethylene), P(VDF-TrFE); Poly(vinylidene fluoride-tetrafluoroethylene), P(VDF-TeFE); *tgtg'*, *g* refers to *gauche* and *t* refers to *trans*, and a prime in *g'* refers to the dihedral angle being opposite to the *g* conformation with respect to the reference plane *t*.

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the VDF monomer ($-\text{CH}_2-\text{CF}_2-$ by 1.96 Debye [16] or 2.0 Debye [38]), the nitrile group substituted polymers, e.g. polyacrylonitrile (PAN) [39–41], poly(vinylidene cyanide vinylacetate) (PVDCN/VAC) [42–45], polyphenylethynitrile (PPEN) [46,47] and poly(vinylidene cyanide) (PVDCN) [46], have drawn much attention because of their applications in electromechanical transducers, nonvolatile memories and biomedicine. Furthermore, polymers containing $\text{C}-\text{C}\equiv\text{N}$ groups have lower density. This results in low acoustic impedance close to the levels in water and in the human body, making them very useful in medical applications. Unfortunately, PVDCN was found thermally unstable and highly sensitive to moisture, and the piezoelectric or ferroelectric properties have not been observed so far [46,48].

Contrast to the semicrystalline PVDF, PVDCN is an amorphous polymer. The origin of the piezoelectricity in amorphous polymers has not yet become fully understood because of the lack of structural information. The piezoelectricity in amorphous polymers differs from that in semicrystalline polymers and inorganic crystals, where the polarization is not in a state of thermal equilibrium but of quasi-stable of the frozen molecular dipoles [46]. A theoretical model for the frozen dipole orientation in the amorphous polyvinyl chloride (PVC) was presented to explain piezoelectricity and pyroelectricity [49]. It is believed that the ferroelectricity of polyacrylonitrile (PAN) is related to the dipole orientation and kinking of the chain above the glass transition temperature, but the reported magnitude of the coefficients is quite small [41]. This may be from the lack of molecular orientation in the polymer. Actually, diffuse X-ray pattern shows that polymers containing nitrile group are noncrystalline or poorly crystalline [50]. Recently, Cai et al. [51] presented results of *ab initio* total energy calculations on the structure change associated with the dipole flip-flop transition in a PVDF chain and provided some detailed explanations to the previous experiments of scanning tunnel microscope (STM) [23,52]. A transient reversal of local dipole moments (polarizations) in the thin crystalline films of P(VDF-TrFE) on graphite substrate was demonstrated through the appearance of structural distortions induced by flipping the polarity of STM tip bias [23,52]. Xiao et al. [53] reported that, similar to PVDF and P(VDF-TrFE), polymethylvinylidene cyanide (PMVC, $-(\text{CH}(\text{CH}_3)-\text{C}(\text{CN})_2)_n-$) can be highly ordered when the films are prepared by the Langmuir–Blodgett (LB) technique. Their electronic structure analyses show that the samples of P(VDF-TrFE, 70:30) and PMVC are in the all-*trans* configuration with the dipoles all aligned. PVDF and its copolymers (P(VDF-TrFE), P(VDF-TeFE)) have been investigated widely [10–27], however, PVDCN (an analog of PVDF or PMVC) has not been investigated either experimentally or theoretically. Although the bulk dielectric and ferroelectric properties of a polymer can be affected by a number of external factors (e.g. water content in P(VDF-TrFE) [54] or even PVDCN being highly sensitive to moisture [48]), the orientation polarization of molecular dipoles is intrinsically responsible for piezoelectricity. Therefore, it is desirable to explore the possible reasons that piezoelectricity in the bulk polymer of PVDCN has not yet been found.

Encouraged by our previous work on PVDF [16], P(VDF-TrFE) [17] and P(VDF-TeFE) [18], this work will carry out theoretical calculations on a series properties to explore the reasons. The properties are the internal rotation potentials, geometries, vibrational spectra and electrical properties of α - and β -chain PVDCN. Energy differences, permanent average dipole moment and molecular polarizability per monomer will be obtained.

2. Theoretical method

DFT at B3PW91/6-31G(d) [55–57] level of theory is employed. The method is the same as that in the study of PVDF [16], P(VDF-

TrFE) [17] and P(VDF-TeFE) [18] for the convenience of comparisons. This level of theory is chosen because it performed systematically well [58,59] on reproducing molecular geometries. The models examined are the α - and β -chain PVDCN $\text{H}[\text{CH}_2\text{C}(\text{CN})_2]_n\text{H}$ with $n = 2$ through 15 lengths. Calculations were carried out on the internal rotation potentials (with a dimer model of $\text{H}[\text{CH}_2\text{C}(\text{CN})_2-\text{CH}_2\text{C}(\text{CN})_2]\text{H}$), geometry optimizations, vibration analyses, molecular energies and dipole moment vectors (μ_x, μ_y, μ_z). In frequency analyses, the molecular exact polarizability tensors, $\alpha_{xx}^{\text{mol}}, \alpha_{xy}^{\text{mol}}, \alpha_{yy}^{\text{mol}}, \alpha_{xz}^{\text{mol}}, \alpha_{yz}^{\text{mol}}$ and α_{zz}^{mol} , were obtained, which, e.g. α_{xy}^{mol} , is defined as the linear response to an externally applied electric field [60], $\mu_x^{\text{ind}} = \alpha_{xy}^{\text{mol}} E_y^{\text{ext}}$, where μ^{ind} is the induced molecular dipole moment, E^{ext} is the magnitude of the applied electric field and x, y, z represent the Cartesian components. In the vibrational analyses, the B3PW91/6-31G(d) frequencies were scaled by a scaling factor 0.9573 [61]. The Gaussian-03 package [62] was used for all calculations.

3. Results and discussion

3.1. Internal rotation of related dimer model

In order to emphasize the intramolecular rotation interactions, the dimer model of PVDCN, $\text{H}[\text{CH}_2\text{C}(\text{CN})_2-\text{CH}_2\text{C}(\text{CN})_2]\text{H}$, is employed, although the rotation of the monomer unit in the polymer chain is much more complex than that in the dimer model. The potential curve (lower panel) is plotted in Fig. 1(a) and compared with that of PVDF [16] (Fig. 1(b)). The rotation angle starts and terminates at $\text{C}-\text{C}-\text{C}-\text{C}$ eclipsed-conformation (denoted as 0° and 360° for the $\text{C}-\text{C}-\text{C}-\text{C}$ dihedral angle). Newman projections of the eclipsed, *gauche* and *trans*-conformations in PVDCN and PVDF dimer models are shown in the upper panel of Fig. 1.

Fig. 1(a) shows that the α -conformation (*tggt'*) angles for *g* and *g'* are about $\pm 47^\circ$. It is interesting that this angle is 8° smaller than that in the PVDF [16]. The β -conformation (*ttt*) is a distorted all-*trans* plane with dihedral angles at $\pm 164^\circ$. This is even 11° smaller

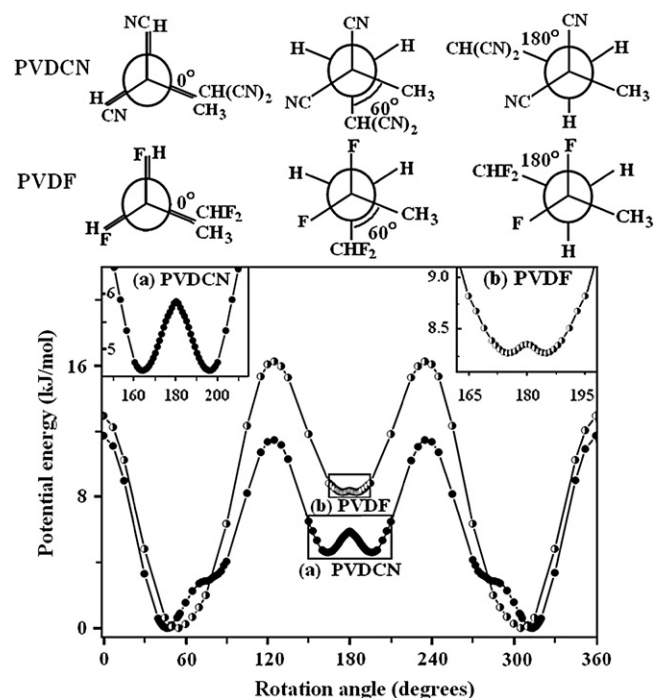


Fig. 1. Newman projections of eclipsed, *gauche* and *trans*-conformations (upper panel) and internal rotation potential energy curves (lower panel) of PVDCN and PVDF [16] chain units in the $\text{H}[(\text{CH}_2\text{C}(\text{CN})_2)_2]\text{H}$ and $\text{H}[(\text{CH}_2\text{CF}_2)_2]\text{H}$ models obtained from B3PW91/6-31G(d) calculations.

than that in PVDF [16]. The smaller angle illustrates that the structure departs much more from the ideal (the chain being assumed to have the local dipole moments parallel to each other, i.e. C–C–C dihedral angle being 180°) β -conformation. Another feature in the curve of PVDCN is that a slow change of potential energies occurs in the range of $\pm 70^\circ$ to $\pm 82^\circ$, which implies that there exists a more complicated electrostatic interaction. As shown in Fig. 1, the all-*trans* “ideal β -chain conformation” of PVDCN is also a transition state (having sole imaginary frequency) in the path of internal rotation, which is similar to that of PVDF [16]. The energy barrier is about 1.3 kJ/mol, which is larger than the negligible value of about 0.1 kJ/mol in PVDF [16]. Nevertheless, the value is still quite small, e.g. much smaller than the zero-point vibration energy of a (even a diatomic) molecule. This indicates that the carbon dihedral angle in the repeating motif of β -chain conformation in PVDCN would also be an arbitrary angle around 180° . The difference is that the angle would be in a larger region than that of PVDF.

Compared with the energy difference, $E_\beta - E_\alpha = 8.4$ kJ/mol in PVDF [16], the value is 5.9 kJ/mol in PVDCN. This suggests that the β -chain PVDCN is also an unstable conformation (with respect to the α -conformation) but will be slightly more stable than the β -chain PVDF thermodynamically. Since the α -phase PVDF can form β -phase by mechanical drawing and electric poling in the bulk thick film [6] or by LB technique or by electric poling in the ultrathin film [23,52,53], we can expect that PVDCN (similar to PMVC [53]) might be higher ordered when the material is prepared by some proper techniques. However, the existence of such higher ordered β -PVDCN will be associated with the molecular chain structure, the interaction with the substrate and the strain effects, which need to be further investigated experimentally.

The transition energy barriers of the $\alpha \rightarrow \beta$ -conformation and the $\beta \rightarrow \alpha$ -conformation are 11.47 and 6.86 kJ/mol, respectively. Both of them are smaller compared with 16.3 and 8.2 kJ/mol in PVDF [16] dimer. Although the magnitude is only -4.8 or -1.3 kJ/mol, the influence on the stability of β -conformation is even important since amorphous PVDCN has different polarization mechanism (where the polarization is not in a state of thermal equilibrium but of quasi-stable of the frozen molecular dipoles [46]). This implies that the transitions are easier and it would be more difficult to obtain stable β -conformation either in bulk or in thin film of PVDCN. This may be one of the reasons that piezoelectricity has not been found in bulk polymer of PVDCN.

3.2. Structure and stability

For the PVDCN polymer with different chain lengths, structures of α - (or *tg'tg'*, where *g* refers to *gauche* and *t* refers to *trans*, and a prime in *g'* refers to the dihedral angle being opposite to the *g* conformation with respect to the reference plane *t*) and ideal β -chains (or *ttt*, where *t* also refers *trans*, see Fig. 2 upper panel) within $2-n$ ($n = 15$) monomer units in the models of $\text{H}[(\text{CH}_2\text{C}(\text{CN})_2)_n\text{H}]$ were optimized and compared with PVDF [16]. The corresponding β -chain is for the ideal conformation (the dihedral angle for all of the backbone carbons is 180°). The optimized structures from B3PW91/6-31G(d) for the 15-unit PVDCN and the 20-unit PVDF [16] are shown in Fig. 2 (lower panel).

Fig. 2(a) and (b) are the β - and α -chain PVDCN with 15 monomers in $\text{H}[(\text{CH}_2\text{C}(\text{CN})_2)_n\text{H}]$; (c) and (d) are the β - and α -chain PVDF with 20 monomers in $\text{H}[(\text{CH}_2\text{CF}_2)_n\text{H}]$ [16] for comparison. Similar to the α -chain PVDF homopolymer (Fig. 2(d)), the α -chain PVDCN is also curved (Fig. 2(b)). For both PVDCN and PVDF in β -conformation, the chains are also curved mainly due to electrostatic repulsion between $-\text{CN}$ groups and $-\text{F}$ atoms on one side of the backbone chain. It should be noted that the $-\text{CCN}$ structure is in a straight line and perpendicular to the backbone chain, the steric hindrance that lead to the chain bend would be less important. All the values of the curvature radii are about 8.5 Å for the ideal β -chain PVDCN containing 6–15 monomer units. It is quite interesting that this value is much smaller than that, 30 Å, found in either PVDF [16] or its copolymer P(VDF-TrFE) [17] or P(VDF-TeFE) [18]. As a comparison, we have calculated (with the same theoretical method) the ideal β -PMVC (its LB ultrathin films with highly ordered chain have been deposited on substrates of freshly cleaved pyrolytic graphite wafers [53]) chain containing 8 monomer units with the methyl group alternatively beside the chain. The result shows that the chain is also curved to the same direction with a curvature radius of 12.6 Å. Compared with PVDCN, the increase of the radius is due to the steric hindrance of the methyl group on the inner side of the chain, but the magnitude, 12.6 Å, is still quite small compared with 30 Å in PVDF and its copolymers. Therefore, PVDCN in bulk would not be able to align orderly (to have ferroelectricity) in the relatively longer chains or to form a crystal as presented by Ree et al. [41] that the poor ferroelectricity of PAN is due to lacking of molecular orientation in the bulk of polymer. It has also been examined that the curvature radius is about 15.3 Å in the distortion

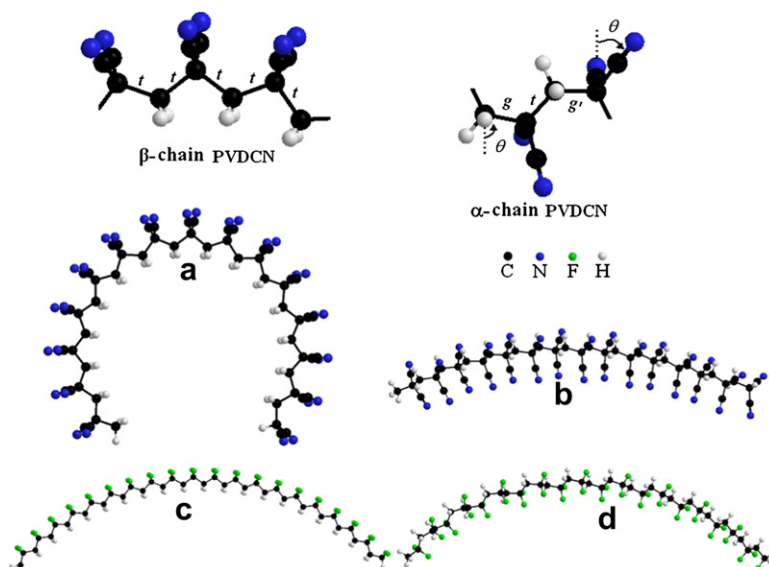


Fig. 2. Structural model of β - and α -chain PVDCN and B3PW91/6-31G(d) optimized structures of PVDCN and PVDF [16]: (a) and (b) are β - and α -chain of 15-monomer PVDCN; (c) and (d) are β - and α -chain of 20-monomer PVDF.

β -PVDCN chain with the dihedral angles (at about $\pm 164^\circ$ as shown in Fig. 1) determined without any restriction. The value is still quite small but slightly larger than that in PMVC. Therefore, the attempt to prepare ultrathin film of PVDCN is suggested with some proper methods, e.g. LB technique as will be discussed in the next paragraph. Actually, we have calculated the model that the ideal β -chain is forced unbent (similar to the unbent polymer chain arranged on the planar substrate orderly). The additional energy per monomer unit is 32.0 kJ/mol, which, for example, is much higher than the internal rotation barrier. Such high energy suggests that the unbent β -chain as well as the crystal phase can hardly be formed by mechanical drawing and be kept stable in the bulk polymer. Therefore, the extremely bent structure might be the second and the main reason that the piezoelectricity in the bulk film of PVDCN has not been observed. This is because the chains must be arranged on substrate orderly in the polymer film to have piezoelectricity or ferroelectricity. Clearly, the chains with smaller curvature (or larger curvature radius) will be easier to arrange orderly on substrate with smaller internal strain. Therefore, the magnitude of the curvature radius of the polymer chain is one of the most important measurements of the interactions between the polymer chains and the substrate. Actually, the interactions should also include other factors, for example, lattice mismatches and different adsorption sites on the substrate. These factors need further study.

Choi et al. [63,64] suggested that the differences between the surface and bulk ferroelectric phase transitions would be related to a reconstructed surface that differs from the bulk with lower coordination and different electronic structure. Since most of the molecules are in the surface in the very thin polymer film, PVDCN ultrathin film may have different electronic structure and be more stable. From this point of view, we suggest that similar to PVDF and PMVC [53], piezoelectric ultrathin polymer film of PVDCN, in which the chains are in partial-*trans* configurations (or the dipoles align in partial orders), may be fabricated by the LB technique combined with the mechanism of the polarization manipulations (STM tip bias [23,52]). The strong strain (due to the polymer chain inherent steric hindrance and to the mismatching in the interchain spacing with substrate) in the film is expected to be released through the introduction of defects and disorder [65,66]. For example, it is seen that the PVDF chains may adopt a canted phase with a small amount of C–C bond twisting [67], and the all-*trans* P(VDF-TrFE) in the surface is a distorted 'zigzag' structure caused by steric hindrance between fluorines [26,68].

Fig. 3(a) plotted the energy difference per monomer unit between the α - and the β -chain PVDCN, i.e. $(E_\beta - E_\alpha)/n$ vs. chain

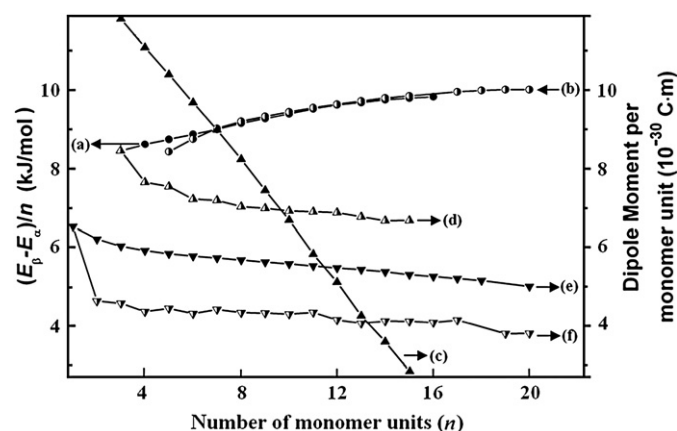


Fig. 3. Energy difference per monomer unit between α - and β -chain $(E_\beta - E_\alpha)/n$, vs. chain length (left-hand axis): (a) PVDCN; (b) PVDF [16]. Dipole moment per monomer unit vs. polymer chain length (right-hand axis): (c) β -chain; (d) α -chain PVDCN; (e) β -chain and (f) α -chain PVDF [16].

length. The curve of PVDF (Fig. 3(b)) [16] is also plotted for comparisons. It shows that the energy difference increases with increasing chain length and converges to a nearly constant value of 9.8 kJ/mol. This is very similar to that of PVDF (about 10 kJ/mol) [16]. The result again suggests that the stability of the α -chain is higher than the corresponding β -chain either in PVDCN or PVDF polymer.

3.3. Dipole moment and mean polarizability

The electric dipole moment and polarizability are of fundamental importance in piezoelectric polymers. In order to examine the effect of chain length on the electric properties of PVDCN, the average permanent dipole moment per monomer unit $\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}/n$ (Fig. 3(c) and (d)) and the mean polarizabilities per monomer unit $\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3n$ (Fig. 4(a) and (b)) [58] for different chain lengths (n units) were calculated. These results as well as those of PVDF [16] for the β - and α -chain are plotted in Fig. 3(e) and (f) and Fig. 4(c) and (d), respectively.

It is shown that the over-all average dipole moment contribution per monomer unit decreases with increasing chain lengths for the α - and β -chain PVDCN and PVDF [16]. Compared with the β -chain PVDF, however, the contribution in PVDCN decreases very rapidly with increasing chain length. This is because the curvature radius of the β -chain PVDCN is much smaller than the β -chain PVDF. It is also the small curvature radius of β -chain PVDCN that leads to the contribution of the average dipole moment per monomer even much smaller than PVDF if $n > 12$ in spite of the individual dipole moment of C–C \equiv N is larger than that of the C–F. This is obvious since the dipole moment is in an opposite direction and it will cancel the contribution if the chain is longer than a hemicycle as shown in Fig. 2(a). This result suggests that the β -chain PVDCN in the bulk is unable to exhibit significant spontaneous polarization in a crystal with longer chains even if it is prepared.

Fig. 4(a) and (b) shows that the mean polarizability per monomer unit in the β -chain PVDCN is slightly higher than that in the α -chain. This behavior is similar to that of PVDF [16] (Fig. 4(c) and (d)). However, the magnitude in PVDCN (i.e. $7.27\text{--}7.29 \times 10^{-40} \text{ C m}^2 \text{ V}^{-1}$) is larger than that in PVDF (i.e. $3.84\text{--}3.63 \times 10^{-40} \text{ C m}^2 \text{ V}^{-1}$). The extremely high value may promise its potential applications. Similar to PVDF [16], the chain length in PVDCN does not produce a significant change on the mean polarizability for either α - or β -chain.

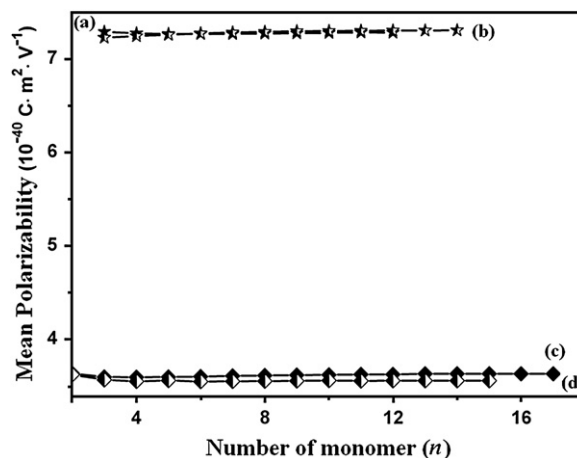


Fig. 4. Mean polarizability per monomer unit vs. polymer chain length: (a) β -chain; (b) α -chain PVDCN; (c) β -chain and (d) α -chain PVDF [16]. All data are obtained from B3PW91/6-31G(d).

3.4. Vibrational spectra

Vibrational spectrum is one of the most useful tools to examine polymer chain conformation changes. Unfortunately, we have not found any reported experimental spectra for the pure PVDCN polymer so far. Therefore, vibrational spectra for both α - and β -chain PVDCN (with 2–12 monomer units) were calculated. The results within the wavenumber 400–2500 cm^{-1} (IR spectra) and 400–3500 cm^{-1} (Raman spectra) are shown in Figs. 5 and 6. Fig. 5(a) and (b) are simulated IR spectra of the β - and α -chain PVDCN with 12 monomer units, Fig. 6(a) and (b) are Raman spectra of the β - and α -chain PVDCN with 12 monomer units.

In Fig. 5(a), the peak at 2286 cm^{-1} is from the C \equiv N stretching with medium IR intensity. Comparing this mode of the β -chain PVDCN with that of the α -chain (Fig. 5(b)), the peak position shifts to the lower value (from 2286 to 2162 cm^{-1}). This is consistent with the observed C \equiv N stretching, 2240 cm^{-1} , in the copolymer poly(vinylidene cyanide-vinyl acetate) (PVDCN-VAc) [42]. The peak at 1434 cm^{-1} (Fig. 5(a)) with medium intensity corresponds to the mode of the CH₂ in-plane scissoring. Comparing this mode of the β -chain PVDCN with that of the α -chain (Fig. 5(b)), the peak intensity increases and becomes the strongest while the position shifts to a lower wavenumber (from 1434 to 1419 cm^{-1}). The peak at 1334 cm^{-1} with medium intensity corresponds to the in-plane rocking of all the H atoms in –CH₂. This can be recognized as a characteristic frequency since the peak is not found in the α -chain. The band of frequencies within 1122–1199 cm^{-1} corresponds to the modes that half of the C atoms in –CH₂ groups collectively moving in-plane and perpendicular to the polymer chain axes, and the –CH₂ rocking. Comparing these modes of the β -chain PVDCN with those of the α -chain (Fig. 5(b)), the intensities decreased and the position shifted to lower frequencies (i.e. from 1122–1199 cm^{-1} to 1109–1168 cm^{-1}). The peak at 515 cm^{-1} with relatively higher intensity is another characteristic frequency of β -chain PVDCN, and comes from the mode that of the –C(CN)₂ wagging out-of-plane. Another medium intense peak at 982 cm^{-1} is also a characteristic mode corresponding to all the –CH₂ groups rocking.

Similar to IR, the most intense Raman peak (2286 cm^{-1} , Fig. 6(a)) comes from the C \equiv N stretching in the β -chain and shifts to a lower frequency (2162 cm^{-1} , Fig. 6(b)) in the α -chains. It is interesting that the band of frequencies within 2907–3051 cm^{-1} comes from C–H stretching mode with weak or medium Raman activity in the β -chain, but the band becomes the most intense in the α -chain, especially the peak at 3052 cm^{-1} . The Raman peak at 982 cm^{-1} with weak intensity corresponds to the backbone C-chain

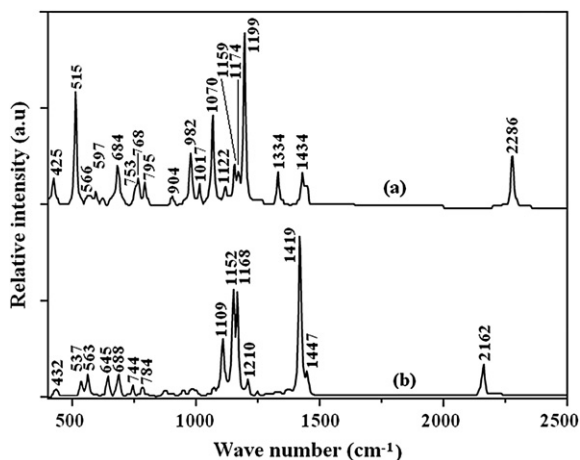


Fig. 5. Calculated vibrational spectra of β - and α -chain PVDCN with 12 monomer unit by B3PW91/6-31G(d): (a) IR of β -PVDCN; (b) IR of α -PVDCN. All of the theoretical frequencies were scaled by the scaling factor 0.9573 [61].

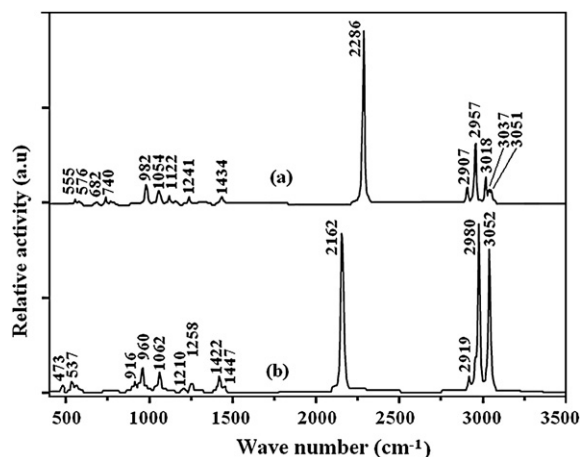


Fig. 6. Calculated vibrational spectra of β - and α -chain PVDCN with 12 monomer unit by B3PW91/6-31G(d): (a) Raman of β -PVDCN and (b) Raman of α -PVDCN. All the theoretical frequencies were scaled by the scaling factor 0.9573 [61].

bending in β -PVDCN. The position of this frequency shifts to a lower value and splits into two peaks (i.e. 916 and 960 cm^{-1}). These results might be very useful predictions for the identifications of PVDCN polymer and of α - or β -configuration.

4. Conclusions

DFT-B3PW91/6-31G(d) has been employed to investigate the internal rotation potentials, geometries, relative stabilities, vibrational spectra, dipole moments and polarizabilities of the α - and β -chain PVDCN. In the study of chain structure and the electric properties, the possible reason(s) that the piezoelectricity in the bulk of polymer has not been found are examined. The following conclusions are drawn.

1. The internal rotation potential of the H(CH₂C(CN)₂)₂H dimer model shows that the g and g' conformation angles in the α -chain $tg'tg'$ are about $\pm 47^\circ$. The β -conformation is a distorted all-*trans* plane with dihedral angles at $\pm 164^\circ$. These values are smaller than those, $\pm 55^\circ$ and $\pm 175^\circ$, in the H(CH₂CF₂)₂H dimer model. The $\alpha \rightarrow \beta$ -chain and $\beta \rightarrow \alpha$ -chain transition energy barriers are 11.47 and 6.86 kJ/mol for the PVDCN dimer model, respectively. These barriers are also smaller than those, 16.3 and 8.2 kJ/mol, in the PVDF dimer model, representing that the transitions are easier and it would be more difficult to obtain stable β -chain PVDCN. This may be one of the reasons that the piezoelectricity in the bulk of polymer has not been found.
2. Both of the α - and the ideal β -chain PVDCNs are curved, which is similar to PVDFs. However, the curvature radius of the ideal β -chain PVDCN with 6–15 monomer units is only 8.5 Å, which is much smaller than that of the ideal β -chain PVDF (about 30.3 Å) and is smaller than that of the ideal β -chain PMVC (about 12.6 Å). This may be the main reason that β -PVDCN in the bulk would neither be able to align orderly in the longer chains to form a crystal phase, nor to exhibit piezoelectricity.
3. The energy difference per monomer unit of PVDCN; $(E_\beta - E_\alpha)/n$, increases with increasing chain length and converges to a nearly constant value (about 9.8 kJ/mol). The value is almost identical to that of PVDF (about 10 kJ/mol).
4. For the ideal β -chain PVDCN, the magnitude of average dipole moment contribution per monomer unit decreases rapidly with increasing the length of chain, which results in the contribution much smaller than that of PVDF if $n > 12$, even if the dipole moment of C–CN is higher than that of the C–F. This result suggests that β -PVDCN is unable to exhibit significantly

spontaneous polarization in the bulk (if it can be prepared) with longer chains. Similar to PVDF, the chain lengths do not produce significant impacts on mean polarizability for the α - and β -chain PVDCN. The mean polarizability per monomer unit in the β -chain is slightly higher than that in the α -chain. However, the mean polarizability in PVDCN is almost twice of the value in PVDF.

5. Compared with PMVC, PVDF and P(VDF-TrFE), the piezoelectric ultrathin film of PVDCN is predicted to be prepared possibly by the LB technique. However, a certain extent of defects and disorders would exist to release the steric hindrance (mainly due to the very small curvature radius of the β -chain).
6. By comparing the calculated IR and Raman spectra of the α - and β -chain PVDCNs, characteristic vibrational frequencies in identifications of the PVDCN polymer and of the α - or β -chain were predicted.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2008.03.043.

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