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Simulation of α - and β -PVDF melting mechanisms

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Abstract

Molecular dynamics (MD) simulations have been used to study the melting of α - and β -poly(vinylidene fluoride) (α - and β -PVDF). It is seen that melting at the ends of the polymer chains precedes melting of the bulk crystal structure. Melting of α -PVDF initially occurs via transitions between the two gauche dihedral angles ($G \leftrightarrow G'$) followed by transitions between trans and gauche dihedral angles ($T \leftrightarrow G/G'$). Melting of β -PVDF initially occurs via $T \rightarrow G/G'$ transitions and via transitions of complete β - (TTTT) to α - (TGTG') quartet. The melting point of β -PVDF is higher than that of α -PVDF, and the simulated melting points of both phases depend on the length of the polymer chains used in the simulations. Since melting starts at the chain ends, it is important to include these in the simulations, and simulations of infinitely long chains yield melting points far larger than the experimental values (at least for periodic cells of the size used in this work), especially for β -PVDF. The simulated heats of fusion are in agreement with available experimental data.

Keywords: Poly(vinylidene fluoride), melting mechanism, molecular simulation.

1 Introduction

Poly(vinylidene fluoride), PVDF, is known to exhibit good piezoelectric and pyroelectric properties[1-5]. This has attracted the attention of researchers for many years and a large number of experimental and theoretical studies on PVDF, including its crystal phases, have been made[6-11]. PVDF forms at least four crystalline phases, including the α - and β -phases. The α -phase has a TGTG' (T – *trans*, G – *gauche*⁺, G' – *gauche*[−]) dihedral conformation and β -PVDF has an all-*trans* conformation. These are the two phases that are of most interest, since α -PVDF is the thermodynamically stable phase at room temperature and pressure and β -PVDF, which is kinetically stable under these conditions, is the phase that exhibits good piezoelectric and pyroelectric properties. The γ -phase structure has the sequence TTTGTTTG' and the δ -phase is a polar polymorph of the α -phase.

Many comparative studies on the structure and piezoelectric properties of α - and β -PVDF crystals have been performed[12, 13], and most current research focuses on enhancing the β -phase in PVDF in order to achieve good piezoelectric properties. Zhu *et al.*[14] used molecular mechanics methods to study PVDF, and obtained a piezoelectric coefficient of -0.461 Å/V in β -PVDF crystals. Kim *et al.*[15] and Lund *et al.*[16] have shown the possibility of inducing the β -phase by adding carbon nanotubes to the PVDF matrix. Song *et al.*[17] and Gee *et al.*[18, 19] focused on obtaining β -phase PVDF from polymer melt by ultrafast crystallization. Results from a combined theoretical and experimental study indicate that the fraction of PVDF chains that have the TTTT conformation may be increased at temperatures near the melting point[20].

PVDF melting points are often reported as bulk melting points[18, 19, 21] or as equilibrium melting temperatures[22, 23]. The equilibrium melting temperature, T_m^0 , is estimated via extrapolation and is defined as the melting point of perfect crystals made from infinitely long polymer chains. Both of these melting points are relevant to the present study, since we simulate crystals made from finite and infinite chains. In addition, recent studies on mechanically drawn PVDF fibres by Steinmann *et al.*[24] showed that an increase in temperature converts the β -PVDF into α -PVDF, which then melts or changes into γ -PVDF. This appears to contradict data that shows that β -PVDF has a higher melting point than α -PVDF[25, 26], or that α - and β -PVDF are melting at the same temperature[27].

The present contribution uses molecular dynamics (MD) simulations to study the melting of α - and β -PVDF. The simulations are based on a force field developed specifically for PVDF,[28] and the changes in energy during $G \leftrightarrow G'$, $T \leftrightarrow G'$ and $T \leftrightarrow G$, which are expected to be very important during phase changes, are in good agreement with first principles data. As discussed below, recent first principles calculations lend further support to the validity of this force field. The simulated results, such as bulk and equilibrium melting points and heats of fusion, are compared to available literature data.

2 Materials and Methods

2.1 Force Field

The force field of Byutner and Smith that was developed for PVDF has been used in this study[28]. The potential energy is the sum of bond stretching (V_B), angle bending (V_A), torsional rotation (V_T), electrostatic (V_{el}) and van der Waals interaction (V_{vdW}) interactions:

$$V_{tot} = V_B + V_A + V_T + V_{el} + V_{vdW} \quad (1)$$

$$V_B = \sum_{i,j} \frac{1}{2} K_{ij}^B (r_{ij} - r_{ij}^0)^2 \quad (2)$$

$$V_A = \sum_{i,j,k} \frac{1}{2} K_{ijk}^A (\theta_{ijk} - \theta_{ijk}^0)^2 \quad (3)$$

$$V_T = \sum_{i,j,k,l} \sum_{n=1}^6 K(n)_{ijkl}^T (1 + \cos(n\phi_{ijkl} - 180)) \quad (4)$$

$$V_{el} = \sum_{i>j} \frac{q_i q_j}{4\pi\epsilon_0\epsilon_r r_{ij}} \quad (5)$$

$$V_{vdW} = \sum_{i>j} A_{ij} e^{-B_{ij}r_{ij}} - \frac{C_{ij}}{r_{ij}^6} \quad (6)$$

where r_{ij} , θ_{ijk} and ϕ_{ijkl} are the distance, angle and torsional angle between the bonded atoms i and j ; i, j and k , and i, j, k and l , respectively. q_i and q_j are charges of atom i and j , respectively. ϵ_0 is the permittivity of vacuum ($8.85419 \times 10^{-12} \text{ J}^{-1}\text{C}^2\text{m}^{-1}$) and ϵ_r is the relative dielectric constant and is set to 1. The constants K^X , r_{ij}^0 , θ_{ijk}^0 , A_{ij} , B_{ij} and C_{ij} are given in Table 1.

Table 1: Force field parameters

Bonds^a	r_{ij}^0 (nm)	K^B (kJ mol⁻¹ nm⁻²)				
CH-H^b	0.1085	274135.68				
CF-F	0.1357	417814.24				
CF-CH	0.1534	258487.52				

Angles^a	θ_{ijk}^0 (deg)	K^A (kJ mol⁻¹ rad⁻²)				
F-CF-F	105.27	1004.1600				
F-CF-CH^c	107.74	753.1200				
CH-CF-CH	118.24	671.9504				
H-CH-H	109.27	322.1680				
H-CH-CF^d	108.45	358.9872				
CF-CH-CF	118.24	671.9504				

Torsions^a (kJ mol⁻¹)	$K(1)^T$	$K(2)^T$	$K(3)^T$	$K(4)^T$	$K(5)^T$	$K(6)^T$
CF-CH-CF-CH	1.65268	3.01248	-1.58992	-0.85772	1.77820	-0.10460
F-CF-CH-CF	1.48532	1.44348	-1.58992	0.58576	0.60668	-0.10460

Charges	q_i	Van der Waals	A_{ij} (kJ mol⁻¹)	B_{ij} (nm)	C_{ij} (nm⁶ kJ mol⁻¹)
H	0.18070	C-C	62659.5840	30.900	2.68111E-03
F	-0.22660	H-H	11085.9264	37.400	1.14474E-04
CH2^e	-0.52020	F-F	568111.8880	45.461	4.44006E-04
CF2^e	0.61200	C-H	18074.8800	34.150	5.78396E-04
CH3^e	-0.62150	C-F	188673.2960	38.181	1.09106E-03
CF3^e	0.75920	H-F	51463.2000	41.431	2.25434E-04

^aCF refers to the carbon atoms in CF2 and CF3 groups and CH refers to the carbon atoms in CH2 and CH3 groups. ^{b-d}These parameters are also used for ^b the terminal H-C bond, ^c the H-C-F angle and ^d the H-C-C angle in the terminal -CF2H group.

^eRefers only to the carbon atom, e.g. CH2 refers to the carbon atom in the CH2 group.

The particle mesh Ewald method was used to calculate the electrostatic Coulombic interactions. The radial cut-off for non-bonded interactions was set to 10.5 Å, which is the same value used by Bytner and Smith[28]. The non-bonded interactions were included for all atom pairs except between atoms separated by one or two bonds.

2.2 Molecular dynamics

The simulation package GROMACS version 4.5[29, 30] was used for the MD studies presented here. The studies were based on short PVDF molecules with α - and β -conformations (used for comparison with first principles calculations) as well as α - and β -PVDF crystals containing infinite or finite length chains. Previous simulations of polymer phase transitions have used periodic boundary conditions with infinite chains[31, 32], and the importance of using finite length chains when studying the melting of PVDF crystals is discussed below.

All molecular and crystal structures were based on the experimentally determined geometries. The α -PVDF unit cell is monoclinic with a P21/C space group and dimensions $a \approx 4.96$ Å, $b \approx 9.64$ Å and $c \approx 4.62$ Å as reported by Hasegawa et al.[11] and Doll et al.[33]. This unit cell contains two *anti* parallel chains with two monomer ($-\text{CH}_2\text{F}_2-$) units in each chain as shown in Figure 1A. The β -PVDF unit cell is orthorhombic with a Cm2m space group and cell dimensions $a \approx 8.47$ Å, $b \approx 4.9$ Å and $c \approx 2.56$ Å[11, 34]. This unit cell has two planar zigzag chains with one monomer unit in each chain (i.e., half the number of atoms as in the α -PVDF unit cell), and is shown in Figure 1B.

Figure 1

Short α - and β -PVDF chains were generated from the unit cells. The chains contained four monomer units truncated by hydrogen atoms (IUPAC name: 1,1,3,3,5,5,7,7-octafluorooctane).

These length chains were selected in order to compare with first principles data obtained in a previous study.[20] Steepest descent geometry optimizations were performed to obtain the minimum energies of α - and β -PVDF chains according to the force field used here.

The crystal systems were also built from the unit cells. The α -PVDF unit cell was replicated 6, 3 and 6 times in the x-, y- and z-directions, respectively. This resulted in a supercell containing 36 periodic chains (6 in each of the x- and y-directions) with each chain consisting of 12 monomer units. The finite chains of PVDF, were obtained by truncating the 12 monomer chains with hydrogen atoms. In addition to this, crystals of chains comprised of 24 monomer units were generated by doubling the supercell in the z-direction. Periodic boundary conditions were applied in all three dimensions in both the infinite and finite chain systems.

The β -PVDF unit cell was replicated 3, 6 and 12 times in the x-, y- and z-directions, respectively, to obtain a supercell that, similarly to the α -PVDF supercell, contained 36 periodic chains, each with 12 monomer units per chain. Supercells containing infinitely long chains or chains with 12 or 24 monomer units were generated in the same way as described above.

The initial structure for the MD simulations of the crystal structures were obtained by geometry optimisation with the steepest decent method. These structures were subsequently equilibrated for 1 ns at 300 K in the NVT ensemble (for the 24 monomer long chains the starting temperature was chosen to be just below melting point of the 12 monomer systems). The system was considered to be equilibrated once the total energy remained constant over time. These equilibrated structures were then used as initial structures for NpT ($p = 1$ bar) MD simulations of 3 ns at 300 K to equilibrate the volume of the system. The final structures of these NpT simulations were then used to prepare an initial structure for NpT simulations at the next temperature (i.e. 325 K) by propagating the crystal for 3 ns at 325 K and 1 bar. This procedure was then repeated for all temperatures (i.e., up to 900 K in steps of 25 K).

The final structures for each temperature were subsequently used for further equilibration using the NpT ensemble at 1 bar. The system was considered to be equilibrated once the average density and total energy remained constant over time. This required between 20 and 45 ns for

each crystal and at each temperature. This was followed by a production simulation of 20 ns to obtain average densities and enthalpies curves for each crystal structure.

The Berendsen thermostat and barostat[35] were used to control the temperature and pressure in the NpT simulations, with scaling parameters $\tau_T = 0.2$ ps and $\tau_p = 10$ ps. The compressibility was chosen as $1.2 \times 10^{-5} \text{ bar}^{-1}$, which is the average compressibilities of α - and β -PVDF [36].

Integration was performed using a 1 fs time step and the Verlet integration algorithm. This algorithm is computationally inexpensive at the same time as being formally time reversible[37].

3 Results and Discussion

3.1 Short PVDF chains.

As mentioned in the introduction, the force field used here yields changes in energy during $G \leftrightarrow G'$, $T \leftrightarrow G'$ and $T \leftrightarrow G$ which are in good agreement with first principles data.[28, 38] This is significant for the present work since the torsion dynamics are expected to be important during phase changes such as those studied here. The relative melting points of the α - and β -crystals may also be affected by the relative potential energies of the α - and β -conformers (both as molecular structures and in the crystal). A previous study used first principles calculations[20] to determine the energy difference between α - and β -conformers ($\Delta E = E_{\beta\text{-PVDF}} - E_{\alpha\text{-PVDF}}$) for chains that contained four monomer units. This energy difference was $\Delta E = 8.08$ kcal/mol when using HF / 6-311++G(2d,2p), $\Delta E = 8.85$ kcal/mol using MP2 / 6-311++G(2d,2p) and $\Delta E = 8.33$ kcal/mol when using the B3LYP / 6-311++G(2d,2p) method. The energy difference obtained using geometries optimized with the force field used here is 9.5 kcal/mol, which is in good agreement with the first principles results. This lends further support to the validity of this force field to study the melting of α - and β -PVDF.

Figure 2

3.2 α - and β -PVDF crystals with infinitely long molecular chains

The average densities of the α - and β -PVDF as a function of temperature are shown in Figure 2 by thick solid blue and red lines, respectively. The melting point, which is observed by a sudden decrease in the density, is 550-575 K for α -PVDF and 825-850 K for β -PVDF. As discussed in detail below, there are actually three steps in the conversion from α -PVDF crystal to liquid densities, and it is assumed that the first large decrease in density is associated with melting since the change in enthalpy during this decrease is far larger than the enthalpy change at the last two decreases in density. For simplicity, the discussion below will consider the melting point as the lowest temperature where the density shows a liquid phase, e.g., 575 and 850 K for the α - and β -PVDF crystals discussed here, respectively. Hence, the melting point of β -PVDF is larger than that of α -PVDF which, as shown in Table 2, is in agreement with experiments performed on bulk materials[25] (but as discussed in the introduction, this is in disagreement with experiments performed on mechanically drawn fibres). Table 2 also shows that both melting points are larger than the experimental values[22, 23, 25, 39]. For example, the bulk melting point of α -PVDF is

449 K[25], which is more than 100 K below the simulated value. The equilibrium melting temperature, which may be more relevant for the crystals with infinite chains studied here is 483 K[39]. In addition, Nandi and Mandelkern calculated the equilibrium melting temperature by extrapolation to no head-to-head impurities (i.e. the melting point for an infinite perfect head-to-tail α -PVDF polymer), and obtained a value of 532.5 K[23]. These values are in better agreement with the simulated value of 575 K. The situation is worse for β -PVDF where the bulk melting point of 463 K[25] is almost 400 K below the simulated value. Unfortunately, there are no equilibrium melting temperatures for β -PVDF available in the literature.

Table 2. Melting points and heats of fusion.

Polymer		Chain length (number of monomers)	T_m (K)	ΔH_{fus} (J/g)
α-PVDF	This work	Infinite	575	96
		12	475	141
		24	525	150
	Experimental		449 ^a	
			532.5 ^b	
			483 ^c	104.6 [39]
β-PVDF	This work	Infinite	850	187
		12	525	147
		24	650	161
	Experimental		463 ^a	

^aThe bulk melting temperature, ref. [25]. ^bThe equilibrium melting temperature compensated for chain length and head-head impurities, ref. [23]. ^cEquilibrium melting temperature only compensated for chain length, ref. [39].

The overestimation of the melting point, especially for β -PVDF, may be due to the fact that the experimental measurements are performed on systems with a lower degree of crystallization and where impurities may be present. However, it is unlikely that these effects would lead to the large differences discussed above, and it is also unlikely that they would affect β -PVDF far more than α -PVDF. It is more probable that the large discrepancies are due to the simulation method. In particular, the flexibility of the polymer chains may be limited by the periodic boundary conditions. That is, $G \leftrightarrow G'$, $T \leftrightarrow G'$ and $T \leftrightarrow G$ changes, which are required for melting, can only occur if they do not disrupt the periodicity. This is more likely to affect β -PVDF which initially requires $T \rightarrow G'$ and $T \rightarrow G$ changes, and where the molecules are more closely packed than in α -PVDF (see Figure 1).

Figure 3

This is illustrated in Figure 3, which shows typical structures of α - and β -PVDF below their melting points (550 K for α - and β -PVDF in panels A and C, respectively) and above their melting points (750 and 850 K for α - and β -PVDF in panels B and D, respectively). It can be seen that melting, due to $G \leftrightarrow G'$, $T \leftrightarrow G'$ and $T \leftrightarrow G$ transformations, leads to large changes in the molecular structure. This can only occur under these simulation conditions if the molecular geometries at the edge of the simulation box fit with the geometries of the periodic image. In addition, it is clear (and will be quantified later) that the dimension of the box in the molecular

axis direction changes during melting, and that this is larger for β -PVDF than α -PVDF. This can only occur if all 36 molecules undergo the same change. This inflexibility, which may hinder the melting of the crystal structures in the simulation time, may be alleviated by using a much larger simulation box. This was not investigated here since, as discussed below, it is important to include the ends of the polymer chains in the simulation in order to obtain the correct melting mechanisms for PVDF.

The reason for the step-like changes in the density of α -PVDF, seen in Figure 2, and which is not observed for any of the other crystal transformations, is not completely understood but may be due to limitations in the flexibility imposed by the periodic boundary conditions. Figure 4 shows the distribution of torsion angles for α - and β -PVDF at different temperatures (300 – 550 K in red, 575 – 650 K blue, 675 – 725 K black, 750 – 825 K green and 850 – 875 K magenta). These temperature ranges correspond to the step-like changes in α -PVDF density seen in Figure 2. The relative ratios of T:G:G' torsions can be obtained by integrating the areas of the peaks at $\pm 180^\circ$, 60° and -60° , respectively. The ratio from 300 – 550 K is 2:1:1 (as it should be for α -PVDF), between 575 and 650 K the percentage of T torsions is 54 % and above 675 K it is lower than 50 %, which is also the composition in the melt. The fact that the α -PVDF torsion ratio cannot change completely to the ratio of the melt at 575 K may be due to the periodic boundary conditions. This is supported by the fact that these step-like changes in densities are not seen for the crystals comprised of finite length chains. It can also be noted that these step-like changes remain even when we perform very long simulations.

Figure 4

As discussed above with reference to Figure 3, there is a large change in the dimensions of the simulation box during melting, and all chains must undergo this change at the same time. As shown in Figure 5, the α -PVDF box length in the x-direction extends by 10 % at the melting point, the y-dimension by 2.4 % and the z-dimension, which is the direction of the polymer chains contracts by 1.5 %. The changes are much larger for β -PVDF. The x- and y-dimensions increase by 37 % and 57 % respectively, and the z-direction decreases by 24 %.

Figure 5

The enthalpies of α - and β -PVDF as a function of temperature are shown in Figure 6. The change in enthalpy at the melting point, which is the heat of fusion (ΔH_{fus}), is 96 J/g for α -PVDF and 187 J/g for β -PVDF. The available experimental value is for α -PVDF and is 104.6 J/g[22]. These results are also shown in Table 2. There is therefore good agreement between the simulated and experimental heats of fusion for α -PVDF, in spite of the limitations mentioned above. The simulated value for β -PVDF may not be as accurate since, as described above, this crystal structure was affected more by the periodic boundary conditions than α -PVDF.

Figure 6

3.3 α - and β -PVDF crystals with chains containing 12 and 24 monomer units

As shown in Figure 2, the melting point of the α - and β -PVDF crystals containing 12 monomer units in each chain are 475 and 525 K, respectively and for the crystals containing 24 monomer units in each chain the melting points are 525 and 650 K, respectively. The increase in melting point with increased chain length is expected[24] and is partially due to the increased density. It is also consistent with the fact that the α - and β -PVDF crystals with infinite chains gave the

highest melting points. It is also noteworthy, and consistent with the results from crystals with infinite chains, that the difference between α - and β -PVDF melting points is larger for the longer chains. As shown in Table 2, the melting points of the α - and β -PVDF crystals containing 12 and 24 monomer units in each chain is larger than the experimental bulk values (449 and 463 K for the α - and β -PVDF, respectively). However, as was the case with crystals with infinitely long chains, one obtains the same trends that β -PVDF melts at a higher temperature than α -PVDF.

As discussed above with reference to Figures 3 and 5, the dimensions of the simulation box in the molecular axis direction decreases during melting. This was investigated for the finite chain crystals by following the average monomer length at each temperature. This was calculated as a time average of the distance between the ends of the chains divided by the number of monomers in the chains. The results were also averaged over the 36 chains in the simulation box. Increasing the temperature of α - and β -PVDF crystals leads to a decrease in the average monomer length just before the melting point, i.e. the thermal expansion coefficient is negative. This has also been observed in recent experiments,[24] where the relative average monomer lengths are measured as lattice parameter c . As shown in Figure 7, the simulated data obtained from the crystals containing 12 monomer units in each chain is in good agreement with the experimental data. Similar trends are seen with the crystals containing 24 monomer units. Linear regression of the α -crystal c parameter from 300-350 K gives a thermal expansion coefficient of $-13 \times 10^{-6} \text{ K}^{-1}$, and between 400 K and 450 K the coefficient $-49 \times 10^{-6} \text{ K}^{-1}$. These values are in very good agreement with experiment, which are $-12.6 \pm 0.8 \times 10^{-6} \text{ K}^{-1}$ up to 401 K and $-75 \pm 0.8 \times 10^{-6} \text{ K}^{-1}$ between 401 and 433 K.[24] The β -crystal thermal expansion coefficient is $-33 \times 10^{-6} \text{ K}^{-1}$ from 300K to 450 K, which is close to the experimental coefficient of $-38 \pm 10 \times 10^{-6} \text{ K}^{-1}$ between 405 and 433 K.

Figure 7

The melting mechanism was analysed by following the change in torsion angles, either as individual torsions (i.e., $G \leftrightarrow G'$, $T \leftrightarrow G'$ and $T \leftrightarrow G$), as changes in quartets (e.g., change in the number of α - (TGTG') or β - (TTTT) quartets) or as changes in octets (e.g., change in number of γ - (TTTGTTTG') octets). A trans (T) dihedral is here an angle in the interval between 110° and 250° , a gauche⁺ (G) dihedral between 0° and 110° , and gauche⁻ (G') between -110° to 0° . The border at 110° was chosen due to the minimum in the dihedral distribution (Figure 4).

Figure 8A shows the number of α -quartets during melting of α -PVDF at 475 K, and Figure 8B shows the number of β -quartets during melting of β -PVDF at 525 K. Crystals with 12 monomer units in each chain are used to plot the figure, and the number of quartets are given as a function

of the position along the chain, where 1 and 18 are the outermost quartets. It is apparent that the initial decrease in α - or β -quartets is at chain ends, and that melting proceeds from the outer quartets to the bulk of the crystal.

Figure 8

The melting of α -PVDF initially occurs via $G \leftrightarrow G'$ transitions. This is expected since, in agreement with first principles calculations,[38] the force field used here has a lower energy barrier for $G \leftrightarrow G'$ transitions than for $T \leftrightarrow G'$ and $T \leftrightarrow G$ transitions. Each quartet undergoes up to 40 transitions per nanosecond (averaged over all 36 chains), first at the extremities of the chains and then in the bulk. This is followed by $T \leftrightarrow G/G'$ transitions, but at a lower rate (up to 15 transitions per nanosecond). These transitions also start at the extremities of the chains and then occur in the bulk.

Figure 9 shows the percent of α -quartets (TGTG', GTG'T, TG'TG and G'TGT), β -quartets (TTTT), γ -quartets (TTTG, TTGT, TGTT, GTTT, TTTG', TTG'T, TG'TT and G'TTT) and other quartets (the remaining combinations) during melting of α -PVDF (Panel A) and β -PVDF (Panel B). The data are for the same crystals and conditions used for Figure 8. Figure 10 shows the same data but for octets, defined in the figure legend. When α -PVDF starts to melt there is an increase in the number of γ -quartets, such that the percentage of these quartets almost equals that of the α -quartets. However, data in Figure 10A shows that this occurs at the same time that there are on average less than half the number of γ -octets as α -octets. In the melt, the total percentage of α -, β - and γ - dihedral octets is very small (on average $< 0.7\%$). In the liquid phase the rates of transitions between dihedrals is very similar, and are 7.6 transitions per ns for $T \leftrightarrow G$, 7.8 transitions per ns for $T \leftrightarrow G'$ and 7.4 transitions per ns for $G \leftrightarrow G'$.

Figure 9

Figure 10

As can be seen in Figure 9B, there is an increase in α - and γ -quartets during the melting of β -PVDF. This occurs during the melting of the entire crystal at about 33 ns as well as at 32.4 ns. Transition from β - to γ -quartets occurs from the TTTT quartet to any of the γ -quartets by a single $T \rightarrow G$ or $T \rightarrow G'$ transition, and hence a large percentage of γ -quartets can be formed as intermediate structures during melting. Of interest is that α -quartets also have small peaks, just before melting and during melting, showing that these quartets can also be formed as intermediate structures. A detailed analysis revealed that β - to α -quartet transitions occur mainly in the middle of the chains, via a simultaneous transition of $T \rightarrow G$ and $T \rightarrow G'$ at two positions separated by one dihedral angle, i.e. the dihedral sequence of TTTT is converted into TGTG' in a single step. These transitions do not affect the orientation of the chain, but the crystal lattice is distorted by the lower density α -quartet structure. Hence, α - and γ -quartets are formed as intermediates during melting of β -PVDF. Figure 10B shows that, similarly to what was observed for α -PVDF, the percentage of crystal phase dihedral octets is very small when the crystal has melted.

The heats of fusion for α - and β -PVDF crystals containing 12 and 24 monomer units in each chain are shown in Table 2. The heat of fusion for β -PVDF is larger than that for α -PVDF (for both chain lengths) which is also in agreement with the trend seen for the infinite chain crystals. There is also an increase in heat of fusion (for both α - and β -PVDF) which is expected since, as was discussed above with respect to melting points, longer chain systems are denser than systems with shorter chains. Similarly to the discussion on the melting points, one cannot expect quantitative agreement between the simulated and experimental data, and the simulated heats of fusion are larger than the experimental values.

4 Conclusion

The simulations presented here show that α -PVDF has a lower melting point than β -PVDF irrespective of the model used to describe the crystal. This agrees with experimental findings[22, 23, 25]. The simulations also show that melting initiates at the ends of PVDF chains in the crystal structure, and proceeds in to the middle of the crystal. It is therefore important to include the ends of the chains in the simulation when studying the melting mechanism. Melting of α -PVDF initially occurs via transitions between the two gauche dihedral angles ($G \leftrightarrow G'$) followed

by transitions between trans and gauche dihedral angles ($T \leftrightarrow G/G'$). Melting of β -PVDF initially occurs via $T \rightarrow G/G'$ transitions, and transitions of β - (TTTT) to α - (TGTG') quartets occurs in a single step (i.e. simultaneous transition from $T \rightarrow G$ and $T \rightarrow G'$) at two positions separated by one dihedral angle.

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Figure captions:

Figure 1. A) Projection of the b-c and a-b planes of the α -PVDF monoclinic unit cell, containing two monomer units in each of the two PVDF chains. B) Projection of the a-c and a-b planes of the β -PVDF orthorhombic unit cell, which contains one monomer in each chain. Colours (online): carbon atoms in gray, hydrogen in white and fluorine in cyan.

Figure 2. Changes in density of α - (blue, filled symbols) and β - (red, open symbols) PVDF crystals as a function of temperature. The crystals contain infinitely long chains (thick solid lines) or finite chains of 12 (dotted lines and diamonds) or 24 (dashed lines and triangles) monomer units. The density is the average value over the 20 ns MD-simulation and standard deviations are smaller than the symbols.

Figure 3. Snapshots from the simulation of α -PVDF at A) 550 K and B) 750 K and β -PVDF at C) 550 K and D) 850 K. Same colours (online) as Figure 1. Only one of the 36 polymer chains is shown by large balls-and-sticks for clarity.

Figure 4. Torsion angle distribution for different temperature ranges (colour online). 300 – 550 K in red, 575 – 650 K blue, 675 – 725 K black, 750 – 825 K green and 850 – 875 K magenta.

Figure 5. Simulation box dimensions during α - (blue filled symbols) and β -PVDF (red open symbols) melting as a function of temperature. Standard deviation errors are smaller than the symbols.

Figure 6. Enthalpies of α -PVDF (blue circles) and β -PVDF (red diamonds) as a function of temperature (colour online). Standard deviation errors are smaller than the symbols.

Figure 7. Experimental [24](dashed black line) and simulated lattice parameter c in percent of c parameter at 300 K, plotted against temperature for α - (blue circles) and β -PVDF (red diamonds).

Figure 8. Number of α - (TGTG' – Panel A) and β - (TTTT – Panel B) dihedral quartets during the melting of A) α -PVDF at 475 K and B) β -PVDF at 525 K. The number of α and β quartets is given as a function of the position along the chain, where 1 and 18 are the outermost quartets. Coloured by number of quartets (online).

Figure 9. Number of dihedral quartets during the melting of A) α -PVDF at 475 K and B) β -PVDF at 525 K. (colour online) *Black*: α -quartet (TGTG', GTG'T, TG'TG or G'TGT), *red*: β -quartet (TTTT), green: γ -quartet (TTTG, TTGT, TGTT, GTTT, TTTG', TTG'T, TG'TT or G'TTT) and *purple*: the remaining combinations.

Figure 10. The same as Figure 9 but for octets. (colour online) *Black*: α -octet (TGTG'TGTG', GTG'TGTG'T, TG'TGTG'TG or G'TGTG'TGT), *red*: β -octet (TTTTTTTT), green: γ -octet (TTTGTTTG', TTGTTTG'T, TGTTTG'TT, GTTTG'TTT, TTTG'TTTG, TTG'TTTGT, TG'TTTGTT or G'TTTGTTT) and *purple*: the remaining combinations.