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A molecular dynamics investigation of the structural characteristics of amorphous and annealed poly(vinylidene fluoride) and vinylidene fluoride–trifluoroethylene copolymers

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Molecular dynamics (MD) computations predict that the extent of *gauche*-character for poly(vinylidene fluoride) (PVDF) is greater than that of its 50 mol% copolymer with trifluoroethylene, at both high temperatures and after annealing. PVDF is enriched in *gauche*-conformations upon cooling whereas the copolymer is enriched in *trans*-conformations. The MD results are consistent with the experimental trends observed for these polymers. Published by Elsevier Science Ltd.

(Keywords: poly(vinylidene fluoride); conformational analysis; molecular dynamics)

INTRODUCTION

When poly(vinylidene fluoride) (PVDF) is either crystallized from the melt or solvent casted, the predominant polymorph that initially forms is the α-phase. The conformation of the polymer segments within the crystalline α-phase unit cells is *tgtg'*, with the chains oriented in the cell such that no net polarization exists for the cell (*Figure 1*). On the basis of an early X-ray crystallography investigation, Hasagawa and coworkers[1] proposed that the PVDF α-phase is a distorted *tgtg'* structure, with a carbon dihedral repeating motif of 179 and 45°. Lando and coworkers[2,3] agreed with the Hasagawa conformation but also pointed out that statistical packing plays a role and proposed a more 'ideal' *tgtg'* conformation with *g* and *g'* angles of ca. 60°. When PVDF is uniaxially elongated, the α-phase undergoes polymorphism to the β-phase. Hasagawa *et al.* proposed that the β-phase conformation is a slightly distorted all-*trans* alternating planar zigzag with an alternating +172 and −172° repeating motif[1]. In the β-phase, the polymer segments are oriented such that the C–F dipoles are additive, resulting in a polar unit cell (*Figure 1*). Hence, to become piezoelectric, PVDF must be uniaxially elongated (to induce α- to β-phase polymorphism) after initial crystallization and prior to electroprocessing. In contrast, vinylidene fluoride/trifluoride copolymers (P(VDF/TrFE)) crystallize directly into a β-phase that possesses a polar unit cell. Therefore, the copolymers can be electroprocessed into a piezoelectric material immediately after crystallization.

Several theoretical investigations have confirmed the existence of polymorphism in PVDF. Karasawa and Goddard, using Hartree–Fock calculations and experimental phonon frequencies[4], recently reported that the differences in energies between four different polymorphs of PVDF (including the α- and β-phases) are within 1 kcal mol^{-1} per monomer. Farmer *et al.*, using potential energy calculations to determine the chain conformation and packing energies, confirmed that conversions between the α-phase and β-phases should be energetically feasible, but that increasing the concentration of head-to-head defects in PVDF should favour formation of the β-phase[5].

The central focus of our ongoing work deals with the structural implications of an increasing fluorine content in P(VDF/TrFE) copolymers. The fluorine content of the copolymer can be readily controlled by altering the mol% content of TrFE with respect to VDF in the generation of the copolymer. We recently reported results from molecular mechanics calculations[6] using the MM2 force field of Allinger (see ref. 7) and crystal packing simulations relating to (1) the effect of fluorine content on the intramolecular energy of PVDF and various copolymer chain segments, and (2) the relative energies of PVDF and copolymer crystallites.

The salient finding from our previous work that serves as the motivation for this present investigation is the fact that the PVDF all-*trans* conformation (which, as an

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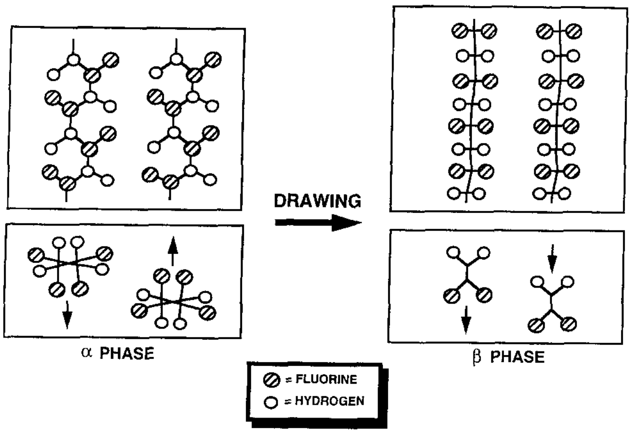

Figure 1 Schematic representation of the conformational change in PVDF associated with mechanical drawing from the α- to the β-phase

isolated small polymer, is less stable than the *tgtg'* form) packs more favourably into a unit cell than the Hasagawa *tgtg'* conformation. Thus, the all-*trans* polymorph is likely the global minimum for PVDF even though the polymer is know to crystallize from the melt into a *tgtg'* repeating motif. Therefore, it is reasonable to assess whether intramolecular interactions exert kinetic control on the crystallization behaviour of the polymer. We report here the results from a molecular dynamics investigation centring upon the structures of PVDF and 50 mol% P(VDF/TrFE), when amorphous and annealed.

EXPERIMENTAL

All computations were performed on a Silicon Graphics 4D/35 IRIS workstation utilizing commercial software produced by Hypercube (HYPERCHEM) and Molecular Simulations (Cerius 3.2). The MD computations were performed at the MM2 level utilizing the force field of Allinger (see ref. 7). All structures were evaluated atomistically. Two criteria were utilized in determining the optimum temperature in the simulation of the amorphous polymers. First, the dihedral angles of the structure upon heating must not exhibit 'memory effects' with respect to the input structure (i.e. all of the dihedral angles within the structure must change from the input dihedrals as evidenced by real-time observation of the dynamic structure as it is heated. Secondly, heating the structure either slightly above or slightly below the chosen temperature must not change the distribution of dihedrals appreciably from those attained at the chosen temperature. The heating temperatures utilized do not quantitatively relate to their real-world analogues (i.e. an input temperature of 1800 K does not relate at all to a real-world temperature of 1800 K), but rather represent values utilized by the program to manipulate the extent of atom displacement per cycle. At a heating temperature of 2200 K the structure begins to distort (i.e. begins to change bond lengths and/or angles in an unrealistic fashion), while at temperatures below 1650 K memory effects seem to be present. At temperatures between 1700 and 2100 K the trends in the distribution of dihedral angles are similar, although not exact. The relative trends in structure as a function of temperature (from hot to cool), whether it be from 2000 to 270 K, or from 1750 to 270 K, are similar. The temperature chosen then for all simulations was 2000 K. The 1 ps heating time was chosen for expediency as longer heating times produced similar results. Once the polymer was heated, it was allowed to equilibrate for 3 ps. The 3 ps equilibration period was chosen because it was well into the region in which the kinetic, potential, and total energies of the system were constant (1 ps would have been sufficient based upon this criteria).

Table 1 Quantitation of the *gauche*- and *trans*-dihedrals of various 128-methylene-unit single-chain polymers

	Content (%)			
Polymer	*g/t*	*t*	*g*	Other
tt PVDF (hot)	0.73	44	32	24
tt PVDF (cold)	0.82	54	44	2
tt 50% (hot)	0.64	47	30	23
tt 50% (cold)	0.46	67	30	3
tgtg' PVDF (hot)	0.69	43	30	27
tgtg' PVDF (cold)	0.90	51	47	2

In simulating the annealing of the polymers, a 10 ps cooling time was utilized in going from 2000 to 270 K. This represents a rather slow annealing and is typical of simulations of this nature.

RESULTS AND DISCUSSION

Molecular dynamics of related dimers

As a preamble to evaluating polymers, a molecular dynamics investigation of the dimers of vinylidene fluoride and vinylidene fluoride/trifluoroethylene was undertaken. Each dimer initially possessed a 180° C–C–C–C dihedral angle. The input structures were heated to 2000 K over a 1 ps time-frame and allowed to equilibrate at that temperature for an additional 3 ps, at which point the dihedral angle was evaluated. Then the structure was allowed to anneal over a 10 ps time-frame to 300 K, and again the dihedral angle was evaluated. The hot vinylidene fluoride dimer initially is of *gauche*-nature (−68°), which upon annealing remains *gauche* (−51°), whereas the hot vinylidene fluoride/trifluoroethylene dimer, which initially possesses *gauche*-nature (68°), upon cooling becomes *trans* (172°).

Molecular dynamics of single-chain polymers

In an effort to model a small PVDF polymer whose structure is representative of the amorphous polymer (i.e. from the melt), a 128-methylene-unit long end-capped polymer was generated (initially with an all-*trans* structure) and heated to 2000 K over a 1 ps time-frame and allowed to equilibrate at that temperature for an additional 3 ps. In the evaluation of the resulting structure, each of the C–C–C–C dihedral angles were analysed (as absolute values, such that both −45° and +45° are reported as 45°, and +170° and −170° reported as 170°, etc.). The results (*Table 1*) reveal that a preference for *trans*-like dihedrals (between 145 and 180°) exists, although the structure is also rich in *gauche*-like bonds (dihedrals between 37 and 90°). The *gauche/trans*, or *g/t* ratio for the amorphous polymer is 0.73, suggesting that the polymer at high temperature has substantial *gauche*-character.

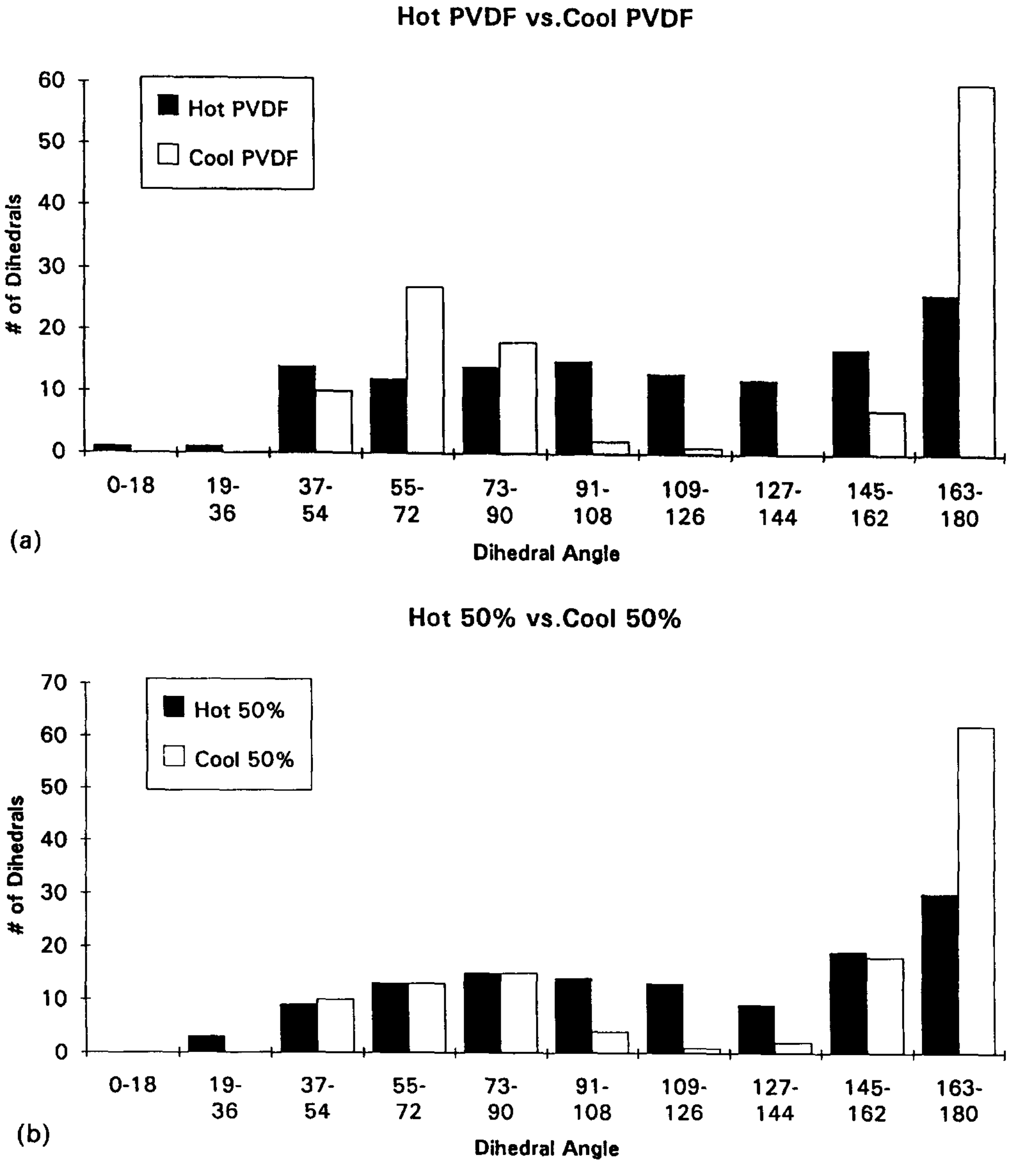

Figure 2 (a) Hot PVDF vs cool PVDF; (b) hot 50% vs cool 50%

When the above PVDF polymer is allowed to anneal over a long time-frame (10 ps), it takes upon itself a new conformational structure. The analysis of the dihedrals indicate that the polymer becomes more ordered upon cooling in that the percentage of dihedrals other than those that are either *trans*- or *gauche*-like is reduced (from 24 to 2%). The percentage contributions from both *trans*- and *gauche*-like bonds increase with cooling, although the magnitude of the increase for *gauche*-like bonds is greater (*Table 1*). As such, the g/t ratio of the annealed structure is increased upon cooling ($g/t = 0.82$ for the annealed and 0.73 for the hot polymer). In *Figure 2a*, which shows a histogram comparing the dihedrals associated with both the hot and cool PVDF, the trends leading to greater order and enrichment in *gauche*-character with cooling are graphically represented.

An identical approach was used in the analysis of 50 mol% P(VDF/TrFE), the results of which are shown in *Figure 2b* and *Table 1*. Once again, the polymer becomes much more ordered upon cooling. However, unlike PVDF, the percentage *trans*-character increases dramatically upon cooling but the percentage *gauche*-character remains constant (*Table 1*). The resulting g/t ratios indicate that the copolymer is enriched in *trans*-character upon cooling (g/t for the amorphous structure is 0.64 while that for the annealed structure is 0.46).

In comparing hot PVDF to hot P(VDF/TrFE), the PVDF is richer in *gauche*-character (*Figure 3a*). Similarly, in *Figure 3b*, the comparison between the two polymers after annealing reveals the same trend (that PVDF is richer in *gauche*-character). Moreover, the homopolymer is enriched in *gauche*-character upon cooling whereas the copolymer is enriched in *trans*-character. These results are in accord with the experimental trends observed for the cooling of both PVDF and 50 mol% P(VDF/TrFE).

Molecular dynamics of modified single-chain polymers

A modified starting structure for PVDF, one with a *tgtg'* repeating motif, was utilized in order to compare with the results from the earlier all-*trans* PVDF. This structure was chosen for investigation because the *tgtg'* polymorph for PVDF is well known. When the *tgtg'* PVDF structure is first heated and then annealed under

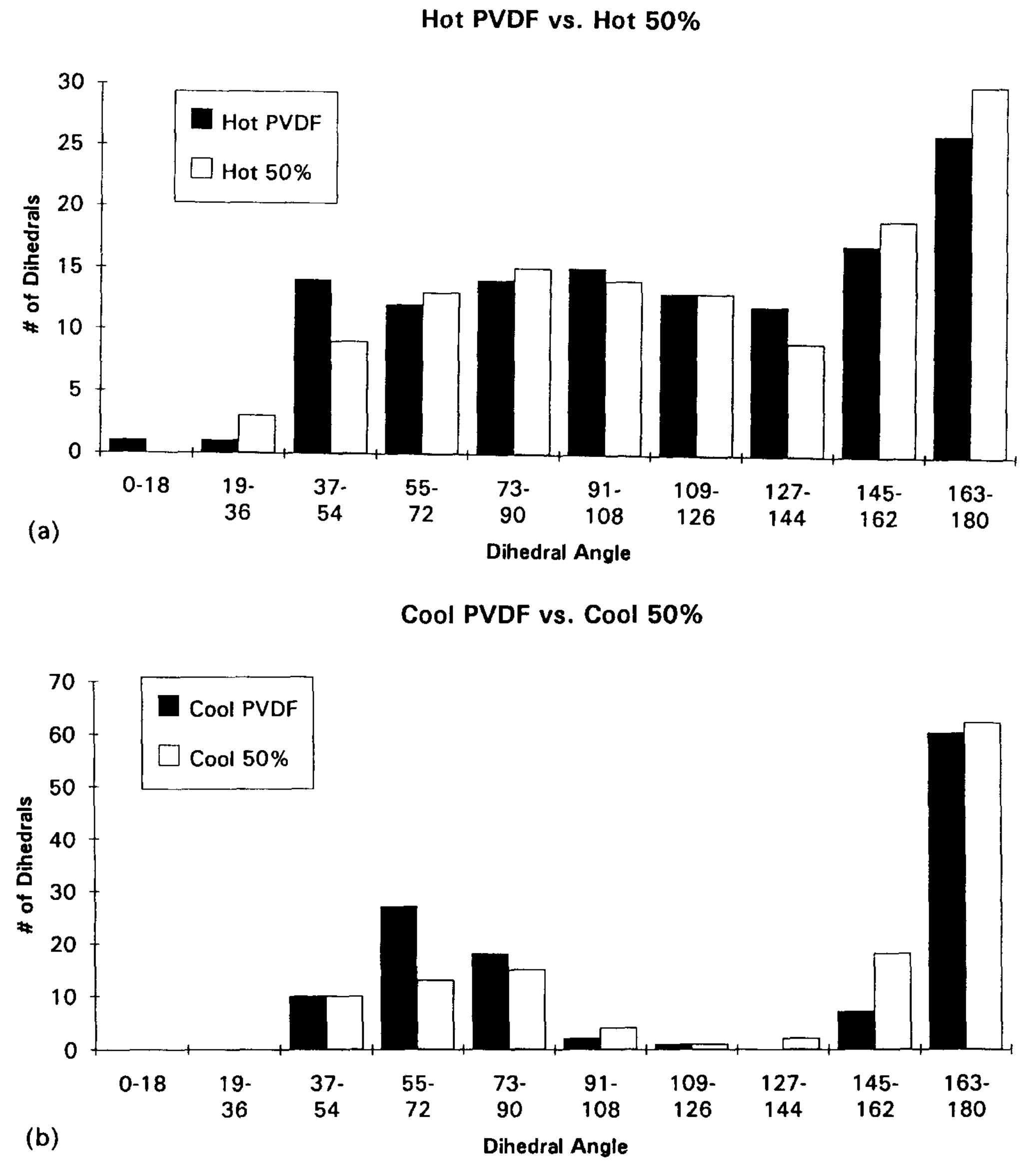

Figure 3 (a) Hot PVDF vs hot 50%; (b) cool PVDF vs cool 50%

identical conditions to those stated earlier, the g/t ratio changes from 0.69 to 0.90 (amorphous and annealed, respectively). Both the magnitude of the g/t ratio and the trends in the g/t ratio upon cooling agree with results from the earlier experiment utilizing the all-*trans* PVDF input structure.

A second type of modified input structure was also utilized. In each of the single-chain structures investigated, the polymer chains undergo folding and hence bend back upon themselves a number of times. As such, small regions of the chain are interacting with other folded-over regions of the same chain. The extent of folding over is small and difficult to quantitate for 128-methylene-unit polymers. However, if much longer polymers were to be evaluated, it is likely that the effect would be more pronounced (however, due to limited computational times available to us, such an investigation would not be feasible). So as to be efficient with regard to time of computation, an alternative input structure was utilized. The structure possesses two parallel dynamic chain segments (ca. 7 Å apart) where one end of each chain segment is tethered to a common fixed U-shaped link. This structure makes possible a simulation with enhanced intermolecular interaction because the two chain segments are parallel, in close proximity to one another, and dynamic.

Table 2 Quantitation of the *gauche*- and *trans*-dihedrals of various U-shaped polymers

	Content (%)			
Polymer	g/t	t	g	Other
tt PVDF (hot)	0.64	47	30	23
tt PVDF (cold)	0.65	58	38	4
tt 50% (hot)	0.53	51	27	22
tt 50% (cold)	0.53	63	34	3

As expected, the analysis of the U-shaped PVDF polymer reveals that the structure becomes more ordered upon cooling, with an increase in both the percentage contribution from the *trans*- and *gauche*-like bonds (*Table 2*). The g/t ratio for amorphous 'folded-over' U-shaped PVDF is 0.64, which, upon annealing, remains relatively constant (changing only slightly to 0.65). The

Table 3 Elongation of an initial *tgtg*′ PVDF tetramer

	C–C–C–C dihedral angle (degree)				
End-to-end distance (Å)	1	2	3	4	5
9.252	45	180	−45	180	45
9.502	83	175	−84	−174	83
9.752	98	173	−91	−172	89
10.002	154	171	−97	−168	124
10.252	170	169	−168	−166	176

analysis of the U-shaped 50 mol% copolymer again reveals increased order upon cooling, with the g/t ratio remaining constant at 0.53. (The structures themselves change, although the statistical ratio remains the same.) That PVDF retains greater *gauche*-character in both the amorphous and annealed structures than does the copolymer is consistent with the single-chain computations and the experimental behaviour of the true polymers.

Elongation of tgtg′ *PVDF*

It is known that when PVDF is cast as a thin film it initially possesses a *tgtg*′ repeating motif, which is consistent with both the results of our earlier investigation[6] regarding crystal packing and the MD results obtained in this study. When the thin film is mechanically stretched, the initial *tgtg*′ structure undergoes polymorphism to an all-*trans* structure. To model such a phenomenon, a *tgtg*′ PVDF tetramer was constructed with initial dihedral angles at 45, 180, −45 and 180° (corresponding to the Hasagawa distorted *tgtg*′ geometry experimentally observed for PVDF crystallites[1], based upon X-ray diffraction and consistent with our earlier crystal packing computations)[6]. All bond angles and distances were then allowed to relax via MM2 geometry optimization (with fixed dihedrals). The resulting structure possessed an end-to-end distance of 9.252 Å. This initial structure was then incrementally elongated in 0.25 Å steps to an ultimate end-to-end distance of 10.252 Å. With each elongation, the complete structure was allowed to relax (with end-to-end distance fixed), thus mimicking the elongation of the crystallite. Throughout the elongation, all the C–C–C–C dihedral angles were monitored. From *Table 3*, a clear and systematic polymorphism from the *tgtg*′ structure to an all-*trans*-like structure is evident as each *gauche*-bond smoothly converts to a *trans*-bond upon elongation.

CONCLUSIONS

Molecular dynamics (MD) computations predict that the extent of *gauche*-character for poly(vinylidene fluoride) is greater than that of its 50 mol% copolymer with trifluoroethylene, at both high temperatures and after annealing. PVDF is enriched in *gauche*-conformations upon cooling, whereas the copolymer is enriched in *trans*-conformations. The MD results are consistent with the experimental trends observed for these polymers.

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