polymer report

A molecular mechanics and crystal packing study of the effects of fluorine content in poly(vinylidene fluoride) and vinylidene fluoride-trifluoroethylene copolymers

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The *tgtg'* conformation of poly(vinylidene fluoride) (PVDF) is $\sim$0.5–0.7 kcal mol^{-1} monomer^{-1} more stable than the all-*trans* conformation as calculated by molecular mechanics. For vinylidene fluoride-trifluoroethylene copolymer compositions $< \sim 90$ mol% vinylidene fluoride, the all-*trans* conformation is more stable. For PVDF, crystal packing calculations support the distorted *tgtg'* conformation predicted by X-ray crystallography.

(Keywords: poly(vinylidene fluoride); VDF-TrFE copolymer; crystal packing)

Poly(vinylidene fluoride) (PVDF) and the copolymers of vinylidene fluoride (VDF) and trifluorethylene (TrFE) can be synthesized via a number of methods from simple fluorinated alkenes[1] (*Table 1*). When these materials are processed as semicrystalline polymers and then poled in the presence of a large electric field, the dipoles of the crystallites become oriented along the direction of the applied field and the material becomes piezoelectric[2–5]. That is, when mechanically deformed, the poled polymer generates an electric polarization, and conversely deforms in response to an applied electric field. These materials are potentially useful in active and passive sonar applications and in ultrasonic medical devices.

The electroprocessing conditions required to make these materials piezoelectric and the resulting piezoelectric activity of the final material are largely dictated by the polymer structures within the crystalline and amorphous regions. Therefore, an understanding of the amorphous and crystalline structures of these materials is desirable.

The central focus of our ongoing work deals with the structural implications of increasing fluorine content in P(VDF/TrFE) copolymers. The fluorine content of the copolymer can be readily controlled by altering the mole per cent of TrFE with respect to VDF in the generation of the copolymer. We report here results from molecular mechanics calculations using the MM2 force field of Allinger[6] and crystal packing simulations[7] 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.

When 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 cell 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, Hasegawa and co-workers[8] proposed that the PVDF α phase is a distorted *tgtg'* structure, with a carbon dihedral repeating motif of 179° and 45°. Doll and Lando[9,10] proposed a more 'ideal' *tgtg'* conformation with *g* and *g'* angles of $\sim$60°. When PVDF is uniaxially elongated, the α phase undergoes polymorphism to the *β* phase. Hasegawa proposed that the *β* phase conformation is a slightly distorted all-*trans* alternating planar zigzag with an alternating 172° and −172° repeating motif[8,11]. In the

Table 1 Compounds studied

Monomer	Abbreviation	Polymer
$CH_2{=}CF_2$	VDF	PVDF
$CH_2{=}CF_2$	VDF	P(VDF/TrFE)
$CFH{=}CF_2$	TrFE	PTrFE

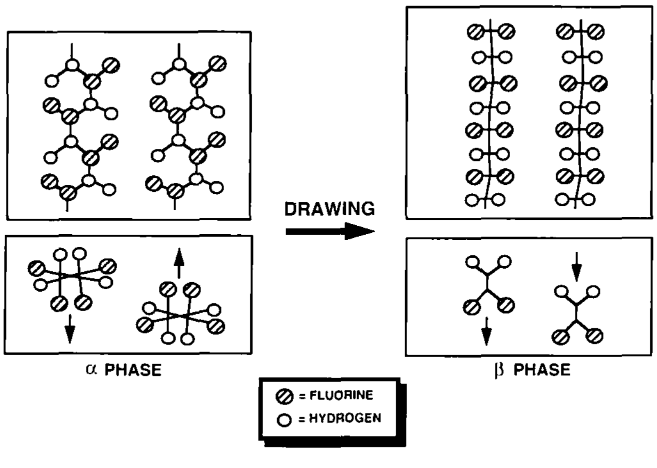

Figure 1 Views along chain direction (top) and of frontal face (bottom) of the α- and *β*-phases of PVDF (left and right, respectively)

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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, the copolymers 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. For example, according to a recent study by Karasawa and Goddard[12] using Hartree-Fock calculations and experimental phonon frequencies, the differences in energies between four polymorphs of PVDF (including the α- and β-phases) are within 1 kcal mol^{-1} monomer^{-1}. In their work, the phonon frequencies of the PVDF β-phase unit cell and polarizabilities were used to develop two new force fields for predicting the piezoelectric and mechanical properties of PVDF crystals. An earlier study by Farmer *et al.*[13] using potential energy calculations to determine the chain conformation and packing energies confirmed that conversions between the α- 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.

In our assessment of the relative energies of the various conformations as a function of fluorine content, three types of structures were considered: (1) structures with atomic coordinates corresponding to those predicted by Hasegawa *et al.*[8] from X-ray crystal studies, (2) 'ideal' all-*trans* planar zigzag and *tgtg'* structures (i.e. 180° dihedral all-*trans* and 180°, 60°, 180°, −60° *tgtg'*); and (3) structures relaxed completely by molecular mechanics. Several 16 carbon atom fluoroalkanes were considered in this study. Each model structure can be described as an idealized end-capped polymer. With the exception of PVDF (100 mol% VDF), which can exist only in a stereoregular arrangement, several arrangements of the repeat monomer units were considered for the 50 mol% and 75 mol% P(VDF/TrFE) copolymer structures to account for the possibility of tacticity. For the 75 mol% P(VDF/TrFE) copolymer, 12 structures representing several sequential arrangements and configurations were selected. In each of these structures, two TrFE monomer units are separated by three VDF monomer units. The configurations of the two chiral -CFH- centres in each structure represent isotactic and syndiotactic strucures. For the 50 mol% P(VDF/TrFE) copolymer, each structure was chosen to consist of alternating VDF and TrFE monomer units with both isotactic and syndiotactic configurations. No attempt was made to include head-to-head and tail-to-tail structures.

The molecular mechanics minimized structures generated via a complete relaxation of all bond lengths, bond angles and dihedrals, each take the form of a large helix. Thus, while these helical structures may reflect the conformations of independent polymer segments in the melt, they likely are not reflective of polymer segment conformations that are nucleated during the formation of crystallites.

Table 2 Calculated intramolecular steric energies of fluoroalkane structures[a]

VDF (mol%)	Polymorph	Hasegawa	'Ideal'	Minimized
100	all-*trans*	5.48	5.26	4.86
	tgtg'	5.14	5.63	5.09
75	all-*trans*	7.33	7.08	6.58
	tgtg'	7.26	7.85	7.05
50	all-*trans*	9.19	8.92	8.37
	tgtg'	9.24	9.92	8.87

[a] Steric energies are in kcal mol^{-1} monomer^{-1}. Molecular mechanics calculations, which were performed on all-*trans* and *tgtg'* model end-capped eight monomer polymer segments, included stretch bend stretch-bend, vdW (van der Waals), torsional and dipole–dipole interactions. In calculating the dipole–dipole interactions, the dielectric constant was assumed to be 1.5. Coulombic interactions were not considered in calculating the intramolecular steric energies. The Hasegawa and 'ideal' structures were partially minimized by allowing hydrogen and fluorine atoms to relax while maintaining a rigid carbon backbone. The 'minimized' energies represent completely relaxed helical structures. Minimizations were performed with the Allinger molecular mechanics force field (MM+) in HyperChem (Release 2 for the Silicon Graphics 4D 35 Personal Iris workstation)

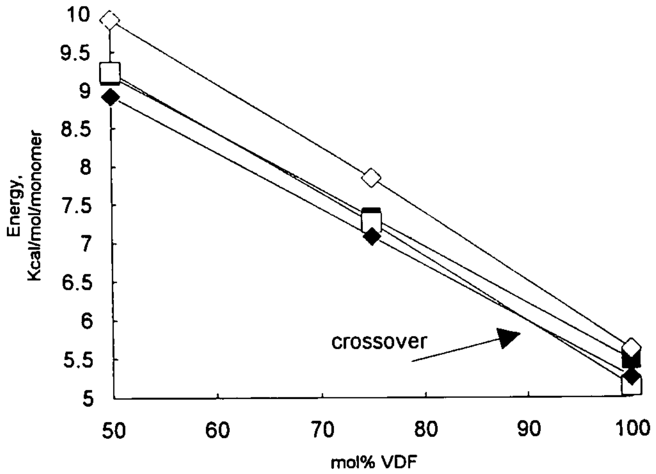


Figure 2 Steric energies of several crystal structures of PVDF and P(VDF/TrFE) copolymers: (■) Hasegawa all-*trans*; (□) Hasegawa *tgtg'*; (◆) 'ideal' all-*trans*; (◇) 'ideal' *tgtg'*

The data for PVDF and for two copolymers of increasing fluorine content (75 mol% and 50 mol% P(VDF/TrFE) copolymers) are given in *Table 2*. As expected, the energy for each conformation (Hasegawa, 'ideal', or minimized) increases with increasing fluorine content. Interestingly, for PVDF, the Hasegawa *tgtg'* conformation is more stable than the Hasegawa and 'ideal' all-*trans* structures. In contrast, the 'ideal' all-*trans* conformations are favoured for each of the copolymers. When a portion of the data is plotted (*Figure 2*), the crossover point corresponding to the composition where the 'ideal' all-*trans* conformation becomes favoured over the *tgtg'* conformation is ~90 mol% VDF. These trends are in general agreement with (1) the experimental observation that PVDF crystallizes directly into the *tgtg'* form while the copolymers crystallize into the all-*trans* structure, (2) force field calculations on the effects of fluorine substitution and head-to-head and tail-to-tail defects in PVDF[13,14] and (3) energy calculations of the alternating planar zigzag β phase for PVDF proposed by Hasegawa *et al.*[15]. (We note that for the copolymers, an undistorted planar zigzag structure is also favoured.)

A crystal lattice consisting of an infinite array of unit cells of known symmetry was generated for each polymorph of PVDF and the P(VDF/TrFE) copolymers.

Table 3 Calculated and experimental lattice dimensions and angles of PVDF and P(VDF-TrFE)[a]

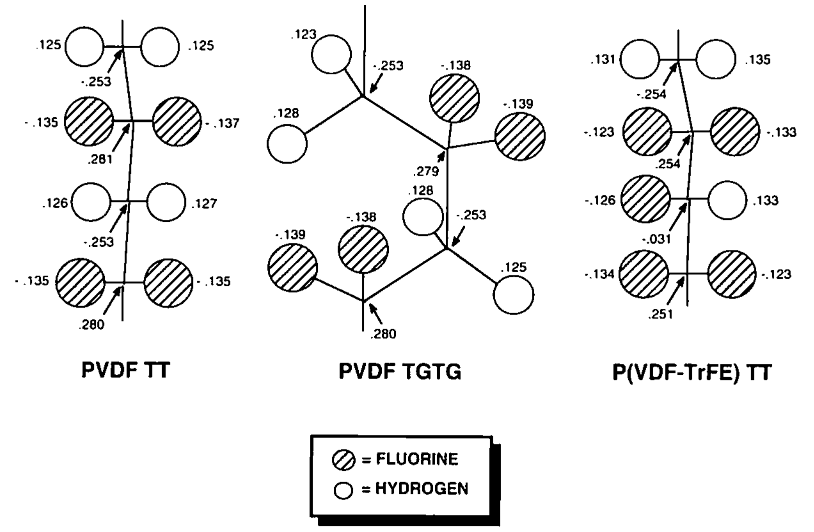
VDF (mol%)	Lattice dimensions (Å)			Lattice angles (deg)			Crystal system
	a	*b*	*c*	α	β	γ	
100	8.99	4.88	2.56	90	90	90	Orthorhombic
	(8.58[b])	(4.91[b])	(2.56[b])	(90[b])	(90[b])	(90[b])	
75	9.08)	5.11	(2.56[c])	90.01	89.9	95.2	Monoclinic
	(8.86[c])	(4.62[c], 5.12[d])		(90[c])	(90[c])	(90[c])	
50	9.10	5.27	2.56	86.6	87.5	96.3	Monoclinic
	(9.12[e])	(5.25)	(2.55)	(93)			

[a] Experimental values, where available, are shown in parentheses
[b] See ref. 8
[c] See ref. 16
[d] 78 mol% P(VDF-TrFE)[17]
[e] 55 mol% P(VDF-TrFE), low-temperature phase[18]

Table 4 Calculated crystal packing energies[a]

VDF (mol%)	Polymorph	Hasegawa			'Ideal'		
		vdW	Coul.[b]	Total energy	vdW	Coul.	Total energy
100	all-*trans*[c]	−4.77	−2.41	−7.19	−5.04	−2.47	−7.51
	tgtg'[d]	−4.21	−0.11	−4.32	−3.82	0.36	−3.47
75	all-*trans*[e]	−4.73	−1.78	−6.44	−4.85	−1.75	−6.60
	all-*trans*[c]	−4.62	−1.72	−6.34	−4.83	−1.75	−6.58
	tgtg'[d]	−4.33	−0.47	−4.80	−3.92	−0.12	−4.04
50	all-*trans*[e]	−4.63	−1.07	−5.70	−4.85	−1.10	−5.96
	all-*trans*[c]	−4.59	−1.04	−5.64	−4.82	−1.14	−5.94
	tgtg'[d]	−4.28	0.88	−3.40	−3.67	0.89	−2.78

[a] Energies are in kcal mol^{-1} monomer^{-1}. Crystal packing simulations on α- and β-phase superlattice cells were performed with Cerius Version 3.1 Software for the Silicon Graphics 4D/35 Personal Iris workstation
[b] Coulombic interactions were calculated using the Ewald summation technique
[c] The symmetry was assumed to be orthorhombic for planar zigzag ('ideal') and alternatively deflected (Hasegawa) structures. During crystal packing, the *a* and *b* unit cell dimensions and the setting angles were allowed to relax. Symmetry remained orthorhombic during crystal packing when α, β and γ cell angles are allowed to relax
[d] Structure of *tgtg'* unit cell was assumed to be monoclinic. Crystal packing energies were determined by relaxing *a* and *b* unit cell dimensions and the setting angles
[e] Monoclinic symmetry. *a* and *b* dimensions, α, β and γ cell angles, and the setting angles were allowed to relax



PVDF TT **PVDF TGTG** **P(VDF-TrFE) TT**

Figure 3 AM1 calculated charges for the atoms within the two polymorphs of PVDF and for all-trans P(VDF-TrFE) (left and right, respectively)

The lattice unit cell dimensions and crystal types for each of the polymers are listed in *Table 3*. As expected, the *a* and *b* crystal dimensions increase with increasing fluorine substitution in accord with experimental findings. The atomic charges within the polymer chain segments, as calculated by semi-empirical AM1 methodology[19], are found in *Figure 3*. An internal comparison of crystal packing energies (*Table 4*) reveals several insights. In comparing the Hasegawa and 'ideal' *tgtg'* crystal structures, the Hasegawa polymorphs are favoured for all compositions. The extent to which the Hasegawa *tgtg'* is preferred decreases somewhat with increasing fluorine content. In PVDF, coulombic interactions appear to be important in stabilizing the Hasegawa *tgtg'* over the 'ideal' *tgtg'* crystal structure. That the Hasegawa *tgtg'* crystal structure is more stable than the 'ideal' *tgtg'* is especially significant for PVDF, because the initial polymorph which crystallizes from the melt is known to possess a *tgtg'* motif.

Because the relative crystal packing energies reported here pertain to true polymer chains within a crystal lattice and the aforementioned relative intramolecular energies pertain to independent end-capped small polymers, it is not reasonable to add the two values together so as to arrive at a total energy. It nevertheless should be noted that the PVDF all-*trans* conformation (which, as an isolated small polymer, is less stable than the *tgtg'*) packs more favourably into a unit cell than the Hasegawa *tgtg'* conformation. Thus, it is conceivable that the all-*trans* polymorph is the global minimum for PVDF, but intramolecular interactions may exert kinetic control on the crystallization behaviour for this polymer. The crystal packing energies for the copolymers also favour the all-*trans* over the *tgtg'* conformation, but given their relative intramolecular energies (which also favour all-*trans*), it is not surprising that the copolymers crystallize into an all-*trans* polymorph.

In conclusion, the calculations of intramolecular energies using the MM2 force field, when used in combination with calculations of long-range intermolecular van der Waals and electrostatic interactions, are consistent with the crystallization behaviour of PVDF and P(VDF/TrFE) polymers from the melt. The small differences in energy between the all-*trans* and *tgtg'* polymorphs of PVDF are in general agreement with the conclusions of other studies suggesting easy interconversions between these forms[12,13]. Also, in agreement with the calculations of Farmer *et al.*[13] we find, using the MM2 force field, that increasing fluorine substitution favours the β-phase in P(VDF/TrFE).

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