Force Field Calculations on Model Molecules Simulating Isolated Chain Segments of Poly(vinylidene halide) and Vinylidene Halide/Vinyl Halide Copolymers

Jozef Bicerano

The Dow Chemical Company, Central Research, Materials Science and Development Laboratory, 1702 Building, Midland, Michigan 48674. *Received May 16, 1988*

ABSTRACT: The results of force field calculations on isolated chain segments of PVDY and of VDY/VY copolymers are presented. (PVD denotes polyvinylidene. Y = F, Cl, or Br. VY denotes vinyl fluoride (VF for Y = F), vinyl chloride (VC for Y = Cl), or vinyl bromide (VB for Y = Br).) Force field techniques are quite adequate for studying these systems, whose preferred geometries are primarily determined by steric repulsions. A TGTG′ conformation is found for the PVDF chain segment. PVDC and PVDB have TXTX′ conformations with dihedral angles X of 48 ± 3° and 46 ± 2°, respectively. A change of torsional angle occurs around a head-to-head bonding defect site, so that the structure resembles the planar zigzag conformation of polyethylene around the defect site. Beyond it, the conformation reverts to TGTG′ or TXTX′. The helical winding direction can either remain the same or be reversed, in going through the defect site. If the defect is tail-to-tail (at two carbon atoms bonded to Y), the TGTG′ or TXTX′ general pattern is retained everywhere along the chain. Some adjustment takes place in the dihedral angles around the defect site, to reduce the Y–Y repulsions. The geometry of a VDY/VY chain segment with 10% VY is very similar to the geometry of the corresponding PVDY chain segment. A small percentage of VY comonomer should therefore not change the preferred chain conformation.

Introduction

The results of classical mechanical valence force field calculations[1] on isolated chain segments of PVDY and of VDY/VY copolymers[2] are presented. Here, PVD denotes polyvinylidene. VY denotes vinyl fluoride, VC vinyl chloride, and VB vinyl bromide. The symbol X is commonly used to denote a halogen atom; however, in this paper, X is reserved for a set of dihedral angles defining the helical conformation (see below).

The simplest types of force field calculations neglect more subtle effects, such as hydrogen bonding and other types of polar interactions. In isolated chain segments of PVDY or VDY/VY copolymers, however, the presence of the bulky Y atoms causes steric repulsions to become the most important factors in determining the molecular geometry. Force field calculations that only take steric effects into account can, therefore, give reasonable geometries and relative energies for isolated chain segments of these copolymers. Polar interactions become very important, and more sophisticated calculations have to be performed, in studying the interchain interactions.[3]

The following standard notation will be used to describe the conformations defined by the values of dihedral angles about successive C–C bonds in chains of PVDY, which contain a backbone of tetravalent carbon atoms, as well as in model molecules being used to study segments of such polymer chains: T denotes "trans", i.e., a dihedral angle of 180°; G denotes "gauche", i.e., 60°; C denotes "cis", i.e., 0°; X denotes an angle different from 0°, 60°, and 180°; and ′ denotes a negative angle, i.e., G′ implies −60° and X′ implies −X.

Calculations and Results

Computational Hardware and Software. Molecular Graphics Library (MOGLI), a sophisticated molecular graphics software package produced by the Evans & Sutherland (E & S) Corp., was used on an E & S PS330 color graphics terminal to generate molecular structures interactively, inspect them visually, and make crude initial modifications in them.

CHEMLAB-II, a general-purpose molecular modeling software package developed and owned by Chemlab, Inc., and marketed by Molecular Design Limited, was used on a VAX 8600 computer to perform most of the calculations.

The SPacFil 2 (SPF2) program, which was developed at Merck and then modified extensively by Hayden A. Clark at Dow, was used to generate and display space-filling drawings of molecular structures on a Tektronix terminal. Hard copies of these drawings were obtained by using a Hewlett-Packard plotter.

Geometry Optimization. Geometry optimization was carried out by using the molecular mechanics 2 (MM2) option in CHEMLAB-II. (CHEMLAB-II now includes, in addition to MM2, a newer molecular mechanics routine called molecular mechanics force field (MMFF); however, MM2 was used in the work reported in the present paper.) MM2 is a force field technique for calculating molecular geometries and steric energies. The most important quantity computed by MM2 is the total steric energy E of the molecule of interest. A lower E implies a thermodynamically more stable molecular structure. E is given by

$$E = \text{compression} + \text{bending} + \text{stretch/bend} + \text{van der Waals} + \text{torsional} + \text{dipole}$$

where

$$\text{van der Waals} = \text{1,4 energy} + \text{other}$$

Here, stretch/bend denotes a combined stretching and bending mode and 1,4 energy denotes the steric energy due to the interaction of all third near neighbor atom pairs in the molecule. In general, 1,n energy is the steric energy due to the interaction of all $(n-1)$st neighbor atom pairs. "Other" denotes the sum of all steric interactions with $n > 4$.

E values calculated by MM2 were minimized. No symmetry constraints were imposed on the geometries of the molecules during the energy minimizations. The full van der Waals energy calculation option was utilized. Default values were used for all computational parameters, including the equilibrium distances, bond angles, torsional angles, and force constants. Minimizations were carried out to within 0.0004 kcal/mol for the small model molecules containing only five atoms and 0.005 kcal/mol for the larger model molecules.

For a very large molecule, such as a long segment of a polymer chain, many local minima, with very similar E

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Table I
MM2 Results for CH_nY_{4-n} where n = 1, 2, or 3 and Y = F, Cl, or Br[a]

property	CH_3F	CH_2F_2	CHF_3	CH_3Cl	CH_2Cl_2	$CHCl_3$	CH_3Br	CH_2Br_2	$CHBr_3$
D_{CH}	1.103	1.097	1.093	1.108	1.105	1.103	1.111	1.110	1.109
D_{CY}	1.392	1.358	1.336	1.793	1.773	1.762	1.946	1.943	1.943
α_{HCH}	108.7	109.0		110.9	111.5		111.0	112.1	
α_{HCY}	110.3	110.2	111.4	108.0	108.2	107.0	107.9	108.5	108.3
α_{YCY}		107.0	107.5		112.4	111.8		110.6	110.6
E	0.004	0.005	0.036	0.118	0.125	0.001	0.139	0.224	0.144
comp	0.0	0.0	0.0	0.001	0.001	0.0	0.001	0.004	0.004
bend	0.004	0.005	0.036	0.118	0.127	0.001	0.141	0.229	0.148
st/be	0.0	0.0	−0.001	−0.001	−0.003	0.0	−0.003	−0.009	−0.008

[a] D_{CH} and D_{CY} denote the C–H and the C–Y bond lengths, respectively, in angstroms. α_{HCH}, α_{HCY}, and α_{YCY} denote the bond angles in degrees. comp denotes the compression energy, bend the bending energy, and st/be the stretch/bend energy. All energies are in kilocalories per mole.

values, are likely to exist on the energy surface. There is no guarantee that the particular minimum E geometry found will be the absolute minimum. This is why schemes such as rotational isomeric state (RIS) theory[4] are utilized when using information about low-energy rotational conformations to deduce the chain statistics in polymers, in cases where, as with polymer chains in solution and amorphous polymers, the chain conformation is not constrained by crystal-packing considerations.

Small Model Molecules. Results of the calculations on nine small molecules (CH_nY_{4-n}; where n = 1, 2, or 3 and Y = F, Cl, or Br) are summarized in Table I. These calculations were used to verify that MM2 gives reasonable results for molecules containing F, Cl, or Br, in addition to C and H. Bond lengths are in the expected ranges and increase slightly with increasing size of the halogen atom. Bond angles only deviate slightly from the tetrahedral angle of 109.5°. E is very small in each case, indicating that very little steric strain remains in these optimized structures. The slight differences between the E values of the nine molecules are too small to be considered meaningful. Most of the E is due to the bending energy in each case. The van der Waals 1,n energies with $n \geq 4$ and the torsional and dipole energies are all identically zero, due to the absence of third or more distant neighbor atoms.

Large Model Molecules. PVDF has more than one crystalline form (polymorph). Its chain conformation in the polymorph resembling the crystalline form of PVDC most closely is TGTG′.[2] A detail analysis,[5-8] including infrared spectroscopy, Raman spectroscopy, and force field calculations, shows that the X-ray data[9] for PVDC can be fitted well with a TXTX′ chain conformation with X corresponding to 32.5°. PVDB is isomorphous to PVDC.[2]

MM2 was used to optimize the geometry of $C_{20}H_{22}Y_{20}$, with Y = F, Cl, and Br. These model molecules are oligomers of 10 VDY units, terminated by H atoms at each end. A TXTX′ chain conformation with X corresponding to 32.5° was used as the starting geometry of $C_{20}H_{22}Cl_{20}$. The starting geometries of $C_{20}H_{22}F_{20}$ and $C_{20}H_{22}Br_{20}$ were obtained by replacing all of the Cl atoms by F or Br atoms in the optimized geometry of $C_{20}H_{22}Cl_{20}$.

Note that this conformational search procedure is quite limited. It was *not* intended to be a full conformational analysis, including a search for the many possible minima with similar energies. Instead, it was to be a set of specific calculations of those conformations of fully extended chains resembling most closely the chain conformations obtained[5-8] by analyzing the crystallographic results.[9] Furthermore, the physical state being modeled formally corresponds to a gaseous molecule at a temperature of 0 K and not to Θ conditions.

The treatment being presented here is, therefore, simpler and less ambitious than, for example, the "polymer reduced interaction matrix method" developed by Orchard et al.[10] for the correct and efficient enumeration of the intrachain conformational energetics of very long chains. These authors based their method on symmetry considerations and molecular mechanics energetics. They employed calculations on relatively short chain sequences and used isotactic polystyrene as an example of the application of their technique.[10]

Calculations such as those presented in this paper are, nevertheless, useful as starting points for more detailed analysis of chain conformations or the physical properties of polymers. For example, Hutnik and Suter[11] are using the results obtained in a similar study[12,13] on bisphenol-A polycarbonate to parametrize an RIS-type[4] model for this polymer. Such an extension can result in the development of a detailed atomistic model of the structure,[14] elastic constants,[15] and molecular level mechanisms of response to small-strain elastic deformation[16] of a glassy polymer, as illustrated by Theodorou and Suter[14-16] for atactic polypropylene. With some caution, similar techniques should also be applicable to amorphous phases of semicrystalline polymers.

In addition, the molecular geometries resulting from the present calculations can be used to generate starting coordinates for assemblies of large numbers of chain segments by using the polymer chain packing routine in CHEMLAB-II. Such assemblies could be used as starting points in (i) studies of chain packing in the desired crystalline phase of the polymer and (ii) molecular dynamics simulations of time-dependent behavior.

$C_{20}H_{22}Y_{20}$ molecules with one head-to-head or tail-to-tail bonding defect site were used to study these major types of defects. (If two carbon atoms, both bonded to H, are bonded to one another along the chain, the defect is said to be head-to-head. If two carbon atoms, both bonded to Y, are bonded to one another along the chain, the defect is said to be tail-to-tail.) A separate model molecule was used to represent each of these configurations.

A $C_{20}H_{23}Y_{19}$ molecule, i.e., an oligomer of nine VDY units and one VY unit, terminated by H atoms at each end, was used to represent a VDY/VY copolymer with 10% VY. The starting geometry of $C_{20}H_{23}Cl_{19}$ was obtained by replacing one of the two Cl atoms bonded to the 11th carbon atom in $C_{20}H_{22}Cl_{20}$ by an H. The starting geometries of $C_{20}H_{23}F_{19}$ and $C_{20}H_{23}Br_{19}$ were obtained by replacing all of the Cl atoms in $C_{20}H_{23}Cl_{19}$ by F or Br atoms.

The results of these calculations are summarized in Table II. The optimized molecular geometries are shown in space-filling illustrations in Figures 1 and 2, for Y = F and Cl, respectively. The geometries for the structures with Y = Br are very similar to the geometries with Y = Cl, and they are therefore not shown. To avoid confusion, it should be noted that some atoms are hidden from view. The E values of the four types of model molecules are

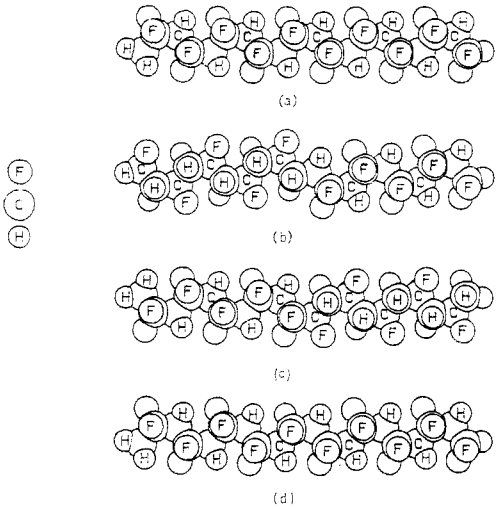

Figure 1. Space-filling illustrations: (a) standard geometry for $C_{20}H_{22}F_{20}$; (b) $C_{20}H_{22}F_{20}$ with head-to-head bond at the 10th and 11th carbon atoms; (c) $C_{20}H_{22}F_{20}$ with tail-to-tail bond at the 10th and 11th carbon atoms; and (d) $C_{20}H_{23}F_{19}$, where the 11th carbon atom from the left is bonded to both an H and an F.

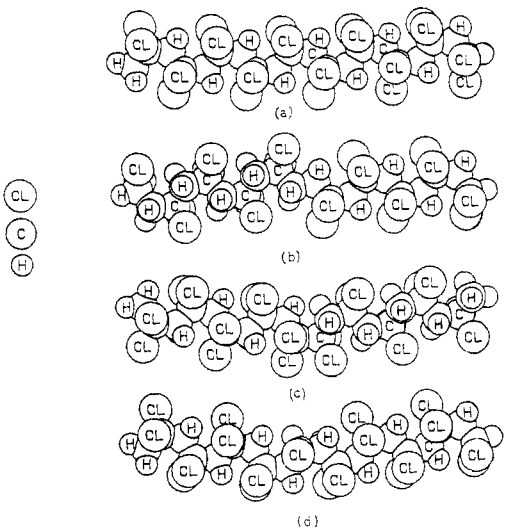

Figure 2. Space-filling illustrations: (a) standard geometry for $C_{20}H_{22}Cl_{20}$; (b) $C_{20}H_{22}Cl_{20}$ with head-to-head bond at the 10th and 11th carbon atoms; (c) $C_{20}H_{22}Cl_{20}$ with tail-to-tail bond at the 10th and 11th carbon atoms; and (d) $C_{20}H_{23}Cl_{19}$, where the 11th carbon atom from the left is bonded to both an H and a Cl.

shown as a function of the halogen atom in Figure 3.

Discussion

Standard Geometries of $C_{20}H_{22}Y_{20}$. The TTTT (planar zigzag) conformation, which is the preferred crystalline conformation in polyethylene (PE),[17] is disfavored in PVDC and PVDB, because of large van der Waals 1,5 steric repulsions between the halogen atoms. The TGTG′, TXTX′, and TCTC conformations all have smaller steric repulsions than the TTTT conformation.

The optimized geometry of $C_{20}H_{22}F_{20}$ was very close to having TGTG′ symmetry, as found in the structure of one of the crystalline polymorphs of PVDF. The dihedral angles corresponding to X were in the range of 60.5 ± 2.5°.

A geometry very similar to TXTX′ was obtained for $C_{20}H_{22}Cl_{20}$. Since the molecule was not constrained to remain at a symmetry of TXTX′, the dihedral angles varied somewhat from the standard T value of 180° and from a single X value. The dihedral angles corresponding to T were in the range of 180 ± 10°. The dihedral angles corresponding to X were in the range of 48 ± 3°. C–Cl bond lengths in interior sites were in the range of 1.797 ± 0.008 Å. The optimized geometry computed for $C_{20}H_{22}Br_{20}$ was isomorphous to the geometry computed for $C_{20}H_{22}Cl_{20}$, with X in the range of 46 ± 2°.

E increases with increasing size of the halogen atom in the series Y = F, Cl, and Br. This increase is much larger between Y = F and Y = Cl than between Y = Cl and Y = Br. This result is consistent with the fact that the

Table II
MM2 Results for $C_{20}H_{22}Y_{20}$ and $C_{20}H_{23}Y_{19}$ [a]

energy	$C_{20}H_{22}Y_{20}$ standard	$C_{20}H_{22}Y_{20}$ head-to-head	$C_{20}H_{22}Y_{20}$ tail-to-tail	$C_{20}H_{23}Y_{19}$ standard
		Y = F		
total steric	64.979	59.454	69.801	62.417
compression	3.857	3.690	4.794	3.705
bending	15.651	14.064	13.929	14.867
stretch/bend	1.542	1.463	1.512	1.512
vdW (1,4 energy)	15.433	15.564	15.004	15.383
vdW (other)	1.566	0.919	1.273	0.979
torsional	2.596	2.255	−1.895	2.720
dipole	24.335	21.500	35.185	23.252
		Y = Cl		
total steric	113.141	102.414	123.624	105.899
compression	10.495	9.466	13.249	9.439
bending	35.554	32.367	31.662	33.274
stretch/bend	3.073	2.921	3.145	2.944
vdW (1,4 energy)	31.043	28.820	32.224	28.970
vdW (other)	3.711	2.944	4.157	3.541
torsional	3.977	2.767	5.117	3.919
dipole	25.287	23.130	34.069	23.812
		Y = Br		
total steric	126.901	114.447	135.943	119.107
compression	13.663	12.070	17.211	12.139
bending	46.547	42.639	41.590	43.929
stretch/bend	3.550	3.400	3.689	3.437
vdW (1,4 energy)	34.221	31.527	36.220	31.971
vdW (other)	2.875	2.326	4.059	3.247
torsional	4.716	2.922	5.174	4.493
dipole	21.329	19.563	28.001	19.892

[a] vdW denotes van der Waals.

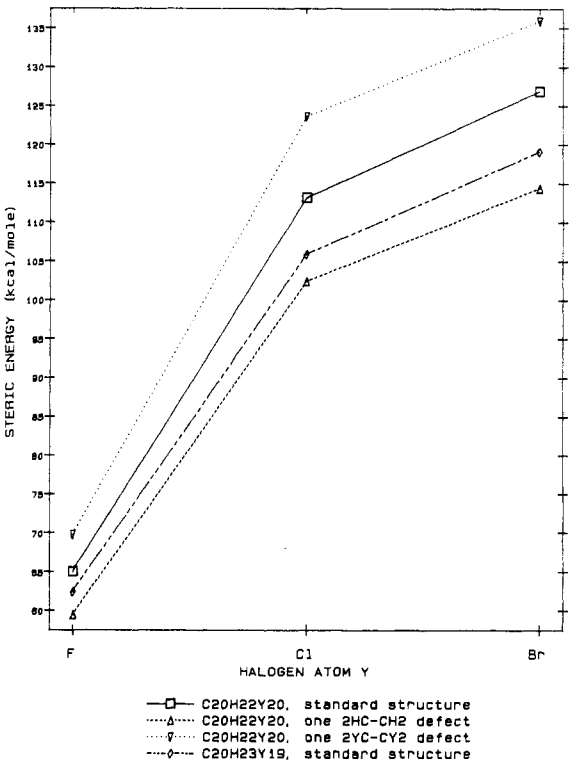

Figure 3. MM2 steric energy as a function of the halogen atom.

percent difference between atomic volumes is much larger between F and Cl than between Cl and Br. Each individual component of E increases, paralleling the increase in E itself. The largest proportional increase occurs for the compression energy. The largest increase in terms of amount occurs for the bending and the van der Waals 1,4 energies. The smallest increase occurs for the dipole energy.

PVDB has the most sterically hindered vinylidene-type chain for which a TGTG′ or TXTX′ conformation does not have prohibitively large steric repulsions. If the halogen atom is replaced by a methyl group, as in poly(1,1-dimethylene) (commonly referred to as polyisobutylene, PIB), the crystalline conformation becomes[2] an 8_3 helix, with an expanded C–CH_2–C bond angle of 123°. The repeat distance of a PIB chain is 18.6 Å, a much larger value than the chain repeat distances in PVDF (4.62 Å), PVDC (4.68 Å), and PVDB (4.77 Å).

The conformational characteristics of PIB chains have been studied by Suter et al.[18] utilizing a combination of (i) a Lennard-Jones force field, (ii) an iterative scheme using the results computed for a series of model molecules of different lengths to eliminate effects due to chain ends and correctly estimate the effects of steric strain, and (iii) a four-state RIS scheme with only one adjustable statistical weight parameter. These calculations[18] result in an 8_3 helical conformation with helix parameters in excellent agreement with the conformation observed by X-ray crystallography in crystalline PIB.

$C_{20}H_{22}Y_{20}$ with Head-to-Head Bonding. The defective structure has a lower E than the standard structure, which only has head-to-tail bonding. This effect becomes much more pronounced with increasing size of the halogen atom in the series Y = F, Cl, and Br.

If a polymer chain has this type of defect site, its thermodynamic energy in the amorphous phase can be expected to remain lower than in the standard structure with only head-to-tail bonding sites. In the crystalline regions, however, periodicity would be disrupted and the energy would go up. This defect would, therefore, be especially unlikely to be incorporated in the crystallites of PVDC and PVDB, where there is a large disparity between the sizes of H and the halogen atom. One of its preferred locations might be the boundary between a crystallite and the amorphous region surrounding it, especially when the percent crystallinity is high.

Because of the very strong kinetic preference for head-to-tail bonding during synthesis,[2] very few (if any) such head-to-head bonding defect sites will occur in PVDC and PVDB, in spite of their low steric energies. Once such a defect is incorporated in a chain, the occurrence of a second such defect in the same chain would be even more unlikely. An even less favored tail-to-tail bonding defect would first be required to create a chain end with H attached to the terminal C. Consequently, at most one such defect is likely to occur per chain of PVDC or PVDB.

A much larger percentage of head-to-head defect sites, as much as 10–20%, is found in PVDF, where both steric effects and the resonance stabilization of the macroradical growing by polymerization are much smaller.[17]

The conformations of model molecules incorporating this defect resembled the conformations of the standard structures. The only exception occurred in the vicinity of the two carbon atoms, 10th and 11th along the chain, where the defect was incorporated. The bonding around the defect site became trans, interrupting the normal TGTG′ or TXTX′ pattern. A succession of three trans torsional angles (TTT) resulted, as in the preferred TTTT conformation of PE. The bonding pattern then returned to TGTG′ or TXTX′.

In the model molecules illustrated as examples of this type of defect in Figures 1 and 2, the "handedness" of the helix is reversed in going through the defect region. In each case, there is also a corresponding structure (not shown) which has the same handedness before and after the defect region and an E almost identical with the E of the structure displayed. A head-to-head bonding defect might therefore also serve as a site where the helix loses all "memory" of its direction of winding and can either continue in the same direction or reverse directions, with almost equal likelihood.

Gaining a full understanding of the role of head-to-head bonding defects is much more crucial in studying PVDF than in studying PVDC and PVDB, because, as mentioned above, crystalline PVDF (i) displays polymorphism and (ii) has a much larger percentage of such defects. In order to provide a more complete perspective, some of the previous work on these defects is reviewed below.

Farmer et al.[19] studied the effects of head-to-head bonding defects on the chain conformation and packing of PVDF. They showed[19] that the presence of such defects can (i) cause an isolated all-trans (TTTT) chain of PVDF to become lower in energy than the TGTG′ form, (ii) play an important role in the polymorphism exhibited by the crystalline domains of PVDF, and (iii) change the most favored polymorph when present in sufficient concentrations.

Farmer et al. also showed[19] that the calculated results were only in good agreement with the experimentally observed polymorphic behavior of PVDF if intramolecular and intermolecular calculations were combined. This result underscores the interdependence of chain conformation and chain packing and demonstrates that calculations (such as those being reported here) which treat these factors independently must be interpreted with caution.

Farmer and Lando[20] also carried out a conformational and packing analysis of the alternating copolymer of ethylene and tetrafluoroethylene. This copolymer represents a chain of PVDF polymerized entirely as an alternating succession of head-to-head and tail-to-tail defects. They showed[20] that the conformation and packing of this copolymer are quite different from those of PVDF, with three possible low-lying packing modes of very similar energies.

Tonelli[21] utilized approximate conformational energy estimates to evaluate the RIS model of PVDF. He included occasional head-to-head and tail-to-tail defect pairs in his calculations. He found[21] that, within the framework of an RIS treatment of isolated unperturbed chains, the conformational properties of PVDF chains were, in general, relatively insensitive to the amount of such defects added but were instead markedly dependent upon the value of the dielectric constant (ϵ) selected to mediate the electrostatic interactions encountered along a PVDF chain. The range $4 \leq \epsilon \leq 6$ gave the best agreement with experimental results on PVDF dissolved in benzophenone (a very polar molecule which is a Θ solvent for PVDF).[21]

Tonelli also studied[22] head-to-head and tail-to-tail defects in PVF, poly(fluoromethylene) (PFM), and poly(trifluoroethylene) (PF_3E), again using RIS models. When considered together with the results on PE, PVDF, and poly(tetrafluoroethylene) (PTFE), these calculations provide a detailed picture of the effects of increasing fluorination. With the exceptions of PTFE and isotactic PFM, all members of this polymer series are found[22] to have chain dimensions which are remarkably similar. The

conformations of the isolated chains are relatively insensitive to the defects in PVF and PF_3E but rather sensitive to them in PFM.

Unfortunately, much fewer computational data are available on the role of such defects in chlorinated and brominated polymers. Tonelli[23] has carried out an RIS study of PVB and ethylene–VB copolymers; however, this calculation did not include head-to-head or tail-to-tail defects.

$C_{20}H_{22}Y_{20}$ with Tail-to-Tail Bonding. Note that some of the discussion of tail-to-tail defects has been included in the preceding subsection, within the context of the calculations of Farmer et al.[19,20] and Tonelli.[21-23]

Y–Y 1,4 interactions, which can only be alleviated by distortions away from the ideal chain conformation, cause E to become higher than in the standard structure. This effect also becomes much more pronounced with increasing size of the halogen atom in the series Y = F, Cl, and Br. This type of defect site is therefore much less likely to occur than the one with the head-to-head bonding. It is thermodynamically much less stable and also kinetically even less favored during synthesis, since its formation requires the bonding of two carbon atoms hindered by the bulky Y's.

Tonelli et al.[24,25] performed nuclear magnetic resonance (NMR) studies on PVDF, PFM, PVF, and PF_3E. They compared observed ^{13}C chemical shifts[24] and ^{19}F chemical shifts[25] to those calculated as functions of stereoregularity and/or defect structure. Since each head-to-head defect was assumed to be followed by a tail-to-tail defect in a defect pair in these studies, they cannot be used to evaluate the assertion made in the preceding paragraph concerning the relative abundance of head-to-head and tail-to-tail defects. It is quite encouraging, nevertheless, that the ^{13}C and ^{19}F studies agree in giving 3.2–3.4 mol % of defects in PVDF and 10.6–11.6 mol % in PVF.

Unlike the situation prevailing in head-to-head bonding, the TGTG′ or TXTX′ general pattern is retained everywhere along the chain. The dihedral angle corresponding to X becomes somewhat larger around the defect site, compared to the range observed for X in the standard structures. This defect site angle is 70° for Y = F, in comparison with the range of 60.5 ± 2.5°; 68° for Y = Cl, in comparison with the range of 48 ± 3°; and 67° for Y = Br, in comparison with the range of 46 ± 2°. This increase in X at the defect site enables some reduction of the Y–Y 1,4 interactions.

$C_{20}H_{23}Y_{19}$. For each Y, the optimized geometry of $C_{20}H_{23}Y_{19}$ was very similar to the optimized geometry of the standard structure for $C_{20}H_{22}Y_{20}$. There were no significant differences, even in the configuration around the 11th carbon atom, where a Y had been replaced by an H. The largest change was observed for Y = Br; however, even with this largest halogen atom, the dihedral angle corresponding to X, at the 11th carbon atom along the chain, which is bonded to both an H and a Br, only increases to 52.5°, i.e., very slightly above the range of 46 ± 2° calculated for $C_{20}H_{22}Br_{20}$.

Adding a small percentage of VY comonomer should therefore not change the preferred chain conformation. A small number of VY units should be able to enter the crystallites, without destabilization effects caused specifically by distortions away from the preferred chain conformations. Such defective crystallites would, however, still have lower cohesive energies than perfect crystallites of PVDY.[3] Some of the polar interchain interactions between the H and Y atoms would be lost. In addition, the packing would be imperfect, creating extra hole volume.

The effects of adding a large percentage of VY comonomer can, however, be expected to be more pronounced, especially when Y = Cl or Br (one of the bulkier types of halogen atoms). As the percentage of VY is increased, the loss of stabilization resulting from the loss of polar interactions, as well as the increasingly imperfect packing, should, at some composition, cause a transition from a predominantly PVDY-like structure with VY defect sites to a PVY-type structure with VDY defect sites.

Electrostatic Effects. Electrostatic (Coulombic) effects were *not* explicitly included in the present calculations on *isolated* chain segments. Only the steric energy terms of MM2 were utilized. Electrostatic interactions *were* explicitly included in later calculations on *pairs* of chain segments and turned out to have a very small effect.[3]

Farmer et al. showed,[19] in their crystal-type calculations, that electrostatic effects are quite important in determining the preferred crystalline polymorph of PVDF. Nevertheless, as discussed below, neither the neglect of electrostatic interactions for isolated chain segments (present paper) nor the fact that they are quite small for pairs of chain segments[3] implies any inconsistency or discrepancy with the results obtained by Farmer et al.[19]

Electrostatic effects are much larger in a periodic crystalline structure than in an isolated chain, because of the Madelung-type stabilization induced by the addition of partial charges over a crystalline lattice.[26] (The term "Madelung-type" was used instead of simply "Madelung" because the lattice sum techniques by means of which the Madelung constant can be calculated for a particular type of crystal structure were developed for ionic crystals. They have to be extended to molecular crystals, where each atom only has a partial charge, in order to apply the same ideas in the present context.) The neglect of electrostatic interactions for the particular problem at hand, namely, for studying the fully extended TGTG′ conformation of an isolated gaseous PVDF chain segment and the TXTX′ conformation of an isolated gaseous PVDC or PVDB chain segment, is therefore an acceptable approximation.

Furthermore, a pair of polymer chain segments is also quite far from being truly representative of a crystallite, and it can also only be expected to have a very small fraction of the Madelung-type electrostatic stabilization of a crystalline lattice. The smallness of the electrostatic energy when only a pair of chain segments is considered is therefore a consequence of the incompleteness of a pair of chain segments as a representative model for a periodic crystalline structure.

Finally, it should also be kept in mind that, whether the physical system being studied is an isolated chain, a pair of chain segments, or a crystal, electrostatic effects become increasingly less important and steric effects become increasingly more important as (i) the size of the halogen atom increases and (ii) simultaneously its electronegativity decreases, in the series Y = F, Cl, or Br. The importance of steric effects in determining the chain conformation can also be seen from the calculations of Suter et al.[18] on PIB.

Summary

The results of force field calculations on isolated chain segments of PVDY and VDY/VY copolymers are presented. Here, PVD denotes polyvinylidene and Y = F, Cl, or Br. The simplest types of force field calculations are quite adequate for studying these systems, whose preferred geometries are primarily determined by steric repulsions. Polar interactions become very important in studying interchain interactions.

A TGTG′ conformation is found for the PVDF chain segment. PVDC and PVDB have TXTX′ conformations

with a dihedral angle X corresponding to 48 ± 3° and 46 ± 2°, respectively.

A change of torsional angle occurs around a head-to-head bonding defect site, so that the structure resembles the planar zigzag conformation of PE around the defect site. Beyond it, the conformation reverts to TGTG′ or TXTX′. The helical winding direction can either remain the same or be reversed, in going through the defect site. If the defect is tail-to-tail, the TGTG′ or TXTX′ general pattern is retained everywhere along the chain. Some adjustment of the dihedral angles around the defect site takes place, to reduce the Y–Y repulsions.

The geometry of a VDY/VY chain segment with 10% VY is very similar to the geometry of the corresponding PVDY chain segment. A small percentage of VY comonomer should therefore not change the preferred chain conformation.

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Registry No. PVDCl, 9002-85-1; PVDF, 24937-79-9; PVDBr, 51736-72-2; (VC)(VDCl) (copolymer), 9011-06-7; (VF)(VDF) (copolymer), 25101-40-0; (VB)(VBBr) (copolymer), 117828-31-6; CH_3F, 593-53-3; CH_2F_2, 75-10-5; CH_3Cl, 74-87-3; CH_2Cl_2, 75-09-2; $CHCl_3$, 67-66-3; CH_3Br, 74-83-9; CH_2Br_2, 74-95-3; $CHBr_3$, 75-25-2; CHF_3, 75-46-7.

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Semiempirical Calculations Simulating Interacting Pairs of Chain Segments of Poly(vinylidene halide) and Vinylidene Halide/Vinyl Halide Copolymers

Jozef Bicerano

The Dow Chemical Company, Central Research, Materials Science and Development Laboratory, 1702 Building, Midland, Michigan 48674. *Received May 16, 1988*

ABSTRACT: As a continuation of previous work on isolated chain segments of PVDY and VDY/VY copolymers, the results of calculations on interacting pairs of chain segments are presented. Here, PVD denotes polyvinylidene and Y = F, Cl, or Br. The semiempirical AM1 technique was used first, to determine the heats of formation of individual chain segments and the charges on atoms occupying different types of valence environments. The stability of the isolated chain segments was found to decrease in the order Y = F ≫ Cl > Br. The model molecules with Y = Br had positive heats of formation. Replacement of one Y atom by H resulted in a slight decrease in stability for Y = F and a slight increase in stability for Y = Cl or Br. The intermolecular energies of pairs of rigid molecules were then minimized, by optimizing the distance between them and their relative orientations. A force field Hamiltonian with Lennard-Jones (6–12 potential) and electrostatic (Coulombic) energy terms was used for this purpose. The pairs of molecules were found to be antiparallel and perfectly aligned for Y = F and antiparallel but at a slight oblique angle for Y = Cl or Br. The intermolecular energy was attractive and comparable (−26 to −28 kcal/mol) for all three $C_{20}H_{22}Y_{20}$–$C_{20}H_{22}Y_{20}$ pairs. The intermolecular energy of $C_{20}H_{22}Y_{20}$–$C_{20}H_{23}Y_{19}$ was slightly lower (more attractive) for Y = F and considerably higher (less attractive) for Y = Cl or Br, compared to the corresponding $C_{20}H_{22}Y_{20}$–$C_{20}H_{22}Y_{20}$ pair. The Lennard-Jones energy was always at least 97% of the total intermolecular energy. The Coulombic energy can be expected to increase significantly in larger ordered assemblies of chains.

Introduction

The results of force field calculations on isolated chain segments of PVDY and of VDY/VY copolymers[1] were reported in the preceding paper.[2] The results of semiempirical quantum mechanical calculations on isolated chain segments, and valence force field calculations[3] on interacting pairs of chain segments, are presented in this manuscript. Here, PVD denotes polyvinylidene and Y is a halogen atom. PVDC denotes Y = Cl, and PVDB denotes Y = Br.

Simple force field calculations neglect subtle effects, such as hydrogen bonding and other types of polar interactions.

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