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# Molecular Modeling of Poly(vinyl fluoride)

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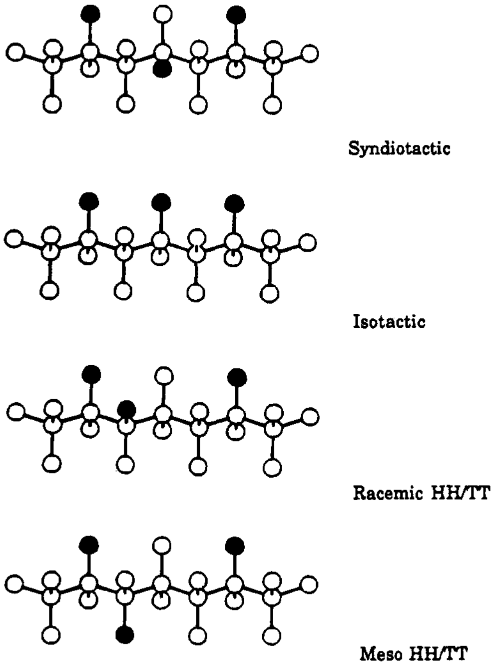
ABSTRACT: Molecular modeling techniques were used to investigate the influence of chain defects in poly(vinyl fluoride) upon the crystallization energetics. The analysis considered the presence of tacticity and regic defects in poly(vinyl fluoride) upon the crystallization energetics. The analysis considered the presence of tacticity and regic defects in both syndiotactic and isotactic chains. Calculations were performed to determine the conformational, configurational, and constitutional energies for several different isolated chains and the packing energies for various chains contained in a crystalline region. From the modeling results, inferences were drawn regarding the crystallizability of chain sequences containing the above-mentioned defects. In general, it was found that a chain sequence which contains a defect does not incur a significant energy penalty when incorporated into a crystalline region. Of the defects considered, the isotactic unit produced the least energetically favorable structure relative to any other chain defect.

## Introduction

The relationship between the structure of a polymer and its properties is of long-standing interest in the field of polymer science. This relationship is dependent not only on the chemical composition of the material but also on its configurational and/or constitutional arrangement. In the case of vinyl polymers, the possible isomeric structures include isotactic, syndiotactic, and random sequences; head-to-tail (HT) and head-to-head and tail-to-tail (HH/TT) monomer enchainment; and branch points. The presence of these structures in a polymer chain can influence the properties of a material including the mechanical, thermal, electrical, and environmental properties. Thus, to fully understand a material's behavior, the relationship between a polymer's structure and properties must be known. The present work examines both the configurational and constitutional variations in poly(vinyl fluoride).

Poly(vinyl fluoride) (PVF) presents an interesting case due to the isomorphous character of hydrogen and fluorine. The consequence of isomorphism is that there is the possibility that chains sequences which contain polymerization defects (excluding branch points) may crystallize in PVF. This would result in a fluorine occupying a lattice site normally taken by a hydrogen, while a hydrogen takes the place of the fluorine. Thus, both HH/TT defects and tacticity variations may exist in the crystalline regions. Work done on other systems have indeed shown that this is the case: HH/TT defects are known to crystallize in PVDF,[1] and Natta and coworkers[2,3] have studied several systems which exhibit isomorphous replacement of hydrogen and fluorine.

However, whereas isomorphism provides the potential that these structures could exist in the crystalline regions without perturbing the crystalline structure, it does not address whether a defect would influence the crystallizability of the chain. Additionally, hydrogen and fluorine are considered isomorphous because of similar steric size ($r_H = 1.5$ Å, $r_F = 1.65$ Å);[4] this, however, neglects the large difference in electronegativities which could, due to electrostatic considerations, perturb the crystal packing. This paper examines the effects of chain defects on both conformational stabilities and on total crystalline packing energies. The paper following this one examines the X-ray crystallographic data for PVF and the possible incorporation of structural defects in the crystalline regions.



Syndiotactic

Isotactic

Racemic HH/TT

Meso HH/TT

**Figure 1.** Trifluoroheptane structures used in the conformational calculations. (The filled atoms indicate the positions of the fluorines.)

## Conformational Analysis

The crystallization of a polymer chain usually favors the conformation of lowest energy. For PVF, the crystal structure requires that the chain be in an extended conformation.[5] The objective of this current study was to compare, for several model compounds, the energy of the trans conformation with the energy of the most stable conformation. The calculations were applied to four different trifluoroheptane structures. The four structures were chosen to simulate an isotactic, a syndiotactic, a racemic HH/TT, and a meso HH/TT sequence of the chain; see Figure 1. The length of the molecules was dictated by the desire to keep the number

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**Table 1. Parameters Used for MM2 Calculations**

Bond Length Terms

| | *k* | $l_0$ |
|---|---|---|
| C–C | 4.4 | 1.523 |
| C–H | 4.6 | 1.113 |
| C–F | 5.1 | 1.380 |

Angle Bending Terms

| | *k* | $\theta_0$ |
|---|---|---|
| C–C–C | 0.45 | 109.5 |
| C–C–H | 0.36 | 109.4 |
| H–C–H | 0.32 | 109.4 |
| C–C–F | 0.65 | 109.5 |
| H–C–F | 0.49 | 109.5 |

Stretch-Bend Terms

| | *k* |
|---|---|
| C–C–C | 0.12 |
| C–C–H | 0.09 |
| H–C–H | 0.00 |
| C–C–F | 0.00 (unspecified) |

Torsion Terms

| | V1 | V2 | V3 |
|---|---|---|---|
| C–C–C–C | 0.20 | 0.27 | 0.093 |
| C–C–C–H | 0.0 | 0.0 | 0.267 |
| H–C–C–H | 0.0 | 0.0 | 0.237 |
| C–C–C–F | 0.0 | −0.086 | 0.930 |
| H–C–C–F | 0.0 | −3.40 | 0.300 |
| F–C–C–F | 0.0 | 0.0 | 0.351 |

van der Waal Terms

| | *r** | *k* |
|---|---|---|
| C | 1.9 | 0.044 |
| H | 1.5 | 0.047 |
| F | 1.65 | 0.078 |

Electrostactic Terms

| | *a* | *b* | *c* |
|---|---|---|---|
| C | 7.98 | 9.18 | 1.88 |
| H | 7.17 | 6.24 | −0.56 |
| F | 14.66 | 13.85 | 2.31 |

of possible conformations to the reasonable number. The conformational space was sampled by rotating the four interior backbone torsion angles through all possible combinations of trans, gauche plus, and gauche minus. The energy of each conformation was minimized using the MM2 program developed by Allinger[6] and the conformational state rechecked to ensure the molecule was still in the desired conformation. The parameters used are listed in Table 1.

The results of the conformational calculations of the four structures are tabulated in Table 2. There are a total of 81 possible conformations for each structure. However, some are prohibited for steric reasons or generated unreasonably large energies (there are indicated by an asterisk in the energy column). Table 3 lists the five lowest energy conformations for the four structures. As can be seen from the torsion angles, no conformational rearrangements occurred although there was limited distortion from the ideal values.

The important conformations are the minimum-energy structures and the all-trans structures. For the syndiotactic configuration, the trans was the lowest energy conformation. For the isotactic chain, the minimum-energy conformation was tggt with a relative energy of +4.75 kcal/mol for the all-trans conformation. The HH meso structure had a minimum-energy conformation of gttt (the gauche rotation is about the HH bond); the all-trans conformation had a relative energy of +0.381 kcal/mol. Last, the HH racemic structure had a minimum-energy conformation of ttg$^{-}$t (the gauche rotation is about the TT bond) and a relative energy of +0.492 kcal/mol for the all-trans conformation.

The minimum-energy conformation for the syndiotactic structure of tttt is expected and is in agreement with work on other syndiotactic polymers. It is also supported by calculations by Carballeira et al.,[7] Tonelli,[8] and Allegra and Meille[9] predicting an extended conformation as preferred. This conformation is preferred as a result of maximizing the favorable F–H electrostatic interactions while reducing the adverse F–F electrostatic interactions.

The fluorine interactions that favor the trans conformation in a syndiotactic structure are reversed for the isotactic configuration. Hence, the all-trans conformation shows a large energy handicap. A 2-fold helix (tggt) followed by a 3-fold helix (tgtg) is predicted to be most stable. Carballeira et al. also predict a helical chain conformation as the most stable. However, they calculated the 3-fold helix to be the minimum-energy structure ($\Delta E_{(3\text{-fold}\ -\ 2\text{-fold})} = +0.215$ kcal/mol). Although they did not report the energy of the all-trans conformation, it is implied that the relative energy is at least +2.6 kcal/mol. Tonelli[8] also indicates a helical conformation is preferred but that the relative energy of the trans conformation is only +0.4 kcal/mol. Allegra and Meille[9] indicate there is not a significant energy difference between the trans conformation and a 3-fold helix. Although the analyses by Tonelli and Allegra and Meille indicate little or no energy difference for an isotactic structure in an extended conformation relative to a 3-fold helix, their analyses were based on rotational isomeric state models which do not afford as complete an analysis, due to the neglect of valence terms, as using the molecular mechanics approach of the MM2 program.

The HH/TT structures present interesting results. Although the preferred conformation for both is a 3-fold helix, the all-trans conformation is highly favored with a relative energy of less than +0.5 kcal/mol in both cases. The trans conformation of the meso structure has a favorable energy since it places the fluorines in the HH unit at their maximum possible distance, 3.33 Å. The all-trans racemic structure has a favorable energy as a result of placing the fluorines gauche to each other. The gauche state is the preferred conformation for 1,2-difluoro compounds and is based on experimental studies of the conformation of 1,2-difluoroethane.[10-12] This is known as the "gauche effect" and has been observed with other systems.[13,14] Tonelli[8] also performed calculations on HH structures and reported approximately the same result, although he predicted that for the meso HH structure the all-trans conformation was almost identical energetically to the 3-fold helix.

Additional information can be obtained by examining a breakdown of the energies into its component parts. Table 4 contains a listing for the all-trans conformations. This table shows that thae electrostatic contribution is the determining factor in the energies of the systems. With this the case, the relative order is somewhat surprising. To a first approximation, it could be assumed that the electrostatic energy would be dominated by the F–F separation distance (see Figure 2), and hence the electrostatic energy would have the same relative order as the F–F separation distances. However, this is not what is observed. The F–F separation distances indicate the isotactic structure should have the highest energy due to the fact that it has the shortest F–F distance, 2.52 Å. Likewise, the meso HH structure should have the highest energy due

**Table 2. Conformational Energies for Configurations of Trifluoroheptane**

| | energy (kcal/mol) | | | | | energy (kcal/mol) | | | |
|---|---|---|---|---|---|---|---|---|---|
| conformation | syndiotactic | isotactic | racemic | meso | conformation | syndiotactic | isotactic | racemic | meso |
| tttt | −7.737 | −2.067 | 1.331 | 1.164 | g$^-$ggg | −1.279 | 0.452 | 6.555 | 4.914 |
| gttt | −4.525 | −3.919 | 2.082 | 0.783 | tg$^-$gg | −2.166 | −1.249 | 6.170 | 6.572 |
| g$^-$ttt | −6.309 | −4.169 | 1.695 | 0.875 | gg$^-$gg | * | * | * | * |
| tgtt | −4.626 | −4.144 | 1.549 | 2.226 | g$^-$g$^-$gg | −0.299 | −0.501 | 6.496 | 6.127 |
| ggtt | −5.950 | −3.128 | 2.860 | 2.743 | ttg$^-$g | −3.948 | −0.391 | 4.380 | 5.297 |
| g$^-$gtt | −3.985 | −0.380 | 4.700 | 4.692 | gtg$^-$g | −0.287 | −2.324 | 5.322 | 5.359 |
| tg$^-$tt | −6.499 | −4.406 | 1.728 | 2.611 | gtg$^-$g | −2.207 | −2.071 | 5.567 | 5.311 |
| gg$^-$tt | −3.613 | 1.594 | 4.667 | 4.817 | tgg$^-$g | * | * | * | * |
| g$^-$g$^-$tt | −5.531 | −2.876 | 1.479 | 2.424 | ggg$^-$g | * | * | * | * |
| ttgt | −6.495 | −4.412 | 3.308 | 2.477 | g$^-$gg$^-$g | * | * | * | * |
| gtgt | −2.917 | −5.864 | 4.660 | 2.088 | tg$^-$g$^-$g | −1.998 | −1.752 | 5.884 | * |
| g$^-$tgt | −3.964 | −5.135 | 5.451 | 2.946 | gg$^-$g$^-$g | * | 3.798 | 7.688 | * |
| tggt | −3.900 | −6.823 | 0.978 | 4.285 | g$^-$g$^-$g$^-$g | −1.364 | −0.237 | 6.559 | 6.123 |
| gggt | −2.858 | −3.388 | 4.555 | 7.280 | tttg$^-$ | −4.521 | −3.915 | 1.088 | 2.260 |
| g$^-$ggt | −1.979 | −1.756 | 5.650 | 4.026 | gttg$^-$ | −0.311 | −4.729 | 2.790 | 2.801 |
| tg$^-$gt | −6.418 | −0.415 | * | 6.131 | g$^-$ttg$^-$ | −2.562 | −5.587 | 1.972 | 2.396 |
| gg$^-$gt | * | * | * | * | tgtg$^-$ | −0.118 | −4.567 | 3.297 | 3.204 |
| g$^-$g$^-$gt | −0.831 | −1.277 | 4.913 | 4.334 | ggtg$^-$ | −2.150 | −4.239 | 3.813 | 3.194 |
| ttg$^-$t | −4.618 | −4.132 | 0.839 | 2.731 | g$^-$gtg$^-$ | −0.493 | −2.312 | 4.930 | 4.829 |
| gtg$^-$t | −0.099 | −4.572 | 2.912 | 3.220 | tg$^-$tg$^-$ | −2.913 | −5.870 | 3.049 | 3.391 |
| g$^-$tg$^-$t | −2.714 | −5.953 | 1.658 | 2.724 | gg$^-$tg$^-$ | −0.058 | −0.597 | 5.743 | 4.086 |
| tgg$^-$t | * | * | * | * | g$^-$g$^-$tg$^-$ | −1.500 | −4.119 | 3.279 | 3.519 |
| ggg$^-$t | −0.460 | −3.007 | 5.038 | 3.965 | ttgg$^-$ | −3.618 | 1.589 | 4.493 | 4.389 |
| g$^-$gg$^-$t | * | * | * | * | gtgg$^-$ | 0.192 | −0.184 | 5.496 | 4.142 |
| tg$^-$g$^-$t | −3.900 | −6.822 | 3.114 | 2.826 | g$^-$tgg$^-$ | −2.095 | −0.393 | 7.966 | 4.145 |
| gg$^-$g$^-$t | −1.110 | −0.379 | 5.992 | 4.259 | tggg$^-$ | −1.115 | 0.422 | 5.004 | 7.437 |
| g$^-$g$^-$g$^-$t | −1.791 | −4.532 | 3.888 | 3.488 | gggg$^-$ | −2.145 | * | 7.434 | 7.565 |
| tttg | −6.310 | −4.170 | 1.794 | 2.272 | g$^-$ggg$^-$ | −0.005 | * | * | 8.619 |
| gttg | −2.562 | −5.583 | 3.046 | 2.281 | tg$^-$gg$^-$ | * | * | * | * |
| g$^-$ttg | −4.158 | −5.571 | 3.015 | 2.670 | gg$^-$gg$^-$ | * | * | * | * |
| tgtg | −2.701 | −5.954 | 2.284 | 3.053 | g$^-$g$^-$gg$^-$ | 4.212 | * | * | * |
| ggtg | −3.635 | −4.519 | 3.968 | 3.992 | ttg$^-$g$^-$ | −5.953 | −3.118 | 2.548 | 5.106 |
| g$^-$gtg | −1.708 | −1.608 | 5.322 | 4.606 | gtg$^-$g$^-$ | −2.141 | −4.237 | 4.083 | 5.011 |
| tg$^-$tg | −3.976 | −5.125 | 3.916 | 4.084 | g$^-$tg$^-$g$^-$ | −3.633 | −4.520 | 4.032 | 5.579 |
| gg$^-$tg | −2.093 | −0.354 | 5.895 | 5.211 | tgg$^-$g$^-$ | −0.456 | −3.007 | 4.340 | 6.444 |
| g$^-$g$^-$tg | −3.234 | −4.097 | 3.366 | 3.616 | ggg$^-$g$^-$ | * | * | * | * |
| ttgg | −5.531 | −2.877 | 2.195 | 3.072 | g$^-$gg$^-$g$^-$ | * | * | * | * |
| gtgg | −1.502 | −4.108 | 3.564 | 3.296 | tg$^-$g$^-$g$^-$ | −2.862 | −3.398 | 7.630 | 4.830 |
| g$^-$tgg | −3.234 | −4.106 | 3.629 | 3.534 | gg$^-$g$^-$g$^-$ | −1.932 | 0.356 | 6.276 | 4.144 |
| tggg | −1.788 | −4.532 | 3.452 | 3.582 | g$^-$g$^-$g$^-$g$^-$ | −3.030 | −3.441 | 6.109 | 3.462 |
| gggg | −3.032 | −3.444 | 4.753 | 4.051 | | | | | |

**Table 3. Conformational Energy of Four Configurations of Trifluoroheptane**

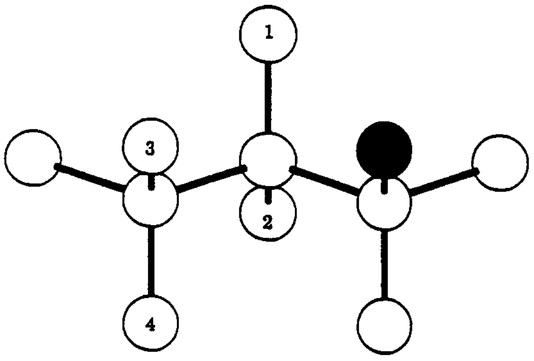
| system conformation | energy (kcal/mol) | torsion angles | | | |
|---|---|---|---|---|---|
| | | $\omega_1$ | $\omega_2$ | $\omega_3$ | $\omega_4$ |
| | | Syndiotactic | | | |
| **tttt** | **−7.74** | **−175.7** | **−176.9** | **−176.6** | **175.8** |
| ttgt | −6.50 | −177.9 | 177.9 | 64.3 | 169.7 |
| tg$^-$gt | −6.42 | −169.0 | −69.0 | 176.8 | 176.0 |
| tttg | −6.31 | −176.3 | −176.8 | 171.8 | 65.5 |
| ggtt | −5.95 | 55.5 | 56.4 | 171.6 | 177.1 |
| | | Isotactic | | | |
| tggt | −6.82 | 176.2 | 57.7 | 59.5 | 169.6 |
| tgtg | −5.95 | 174.0 | 62.0 | 174.7 | 63.0 |
| gtgt | −5.87 | 62.0 | 165.5 | 61.8 | 169.5 |
| gttg | −5.59 | 62.1 | 169.2 | 177.0 | 63.2 |
| g−ttg | −5.57 | −60.9 | −176.8 | 176.8 | 61.3 |
| **tttt** | **−2.07** | **−174.0** | **174.1** | **−174.7** | **173.2** |
| | | Racemic HH/TT | | | |
| ttg−t | 0.839 | 176.1 | −178.2 | −57.2 | −174.0 |
| tggt | 0.978 | 172.9 | 56.1 | 62.3 | 172.1 |
| tttg$^-$ | 1.09 | 175.4 | 176.9 | −174.8 | −61.5 |
| **tttt** | **1.33** | **176.0** | **177.0** | **−176.6** | **179.8** |
| g$^-$g$^-$tt | 1.48 | −50.1 | −60.8 | −179.0 | 177.9 |
| | | Meso HH/TT | | | |
| gttt | 0.783 | 71.3 | −179.5 | 176.7 | 176.7 |
| g$^-$ttt | 0.875 | −70.9 | −175.0 | −177.9 | 179.1 |
| **tttt** | **1.16** | **−179.7** | **−178.6** | **−180.0** | **178.1** |
| gtgt | 2.09 | 73.1 | −177.0 | 78.7 | 176.2 |
| tgtt | 2.23 | 173.9 | 62.5 | 178.3 | 178.5 |

**Table 4. Breakdown of Energies of Four Isomers of Trifluoroheptane**

| energy term (kcal/mol) | syndiotactic | isotactic | meso | racemic |
|---|---|---|---|---|
| compression | 0.35 | 0.41 | 0.40 | 0.40 |
| bend | 0.56 | 0.88 | 0.62 | 0.84 |
| stretch−bend | 0.09 | 0.13 | 0.11 | 0.13 |
| van der Waals | | | | |
| 1,4 | 3.90 | 3.70 | 3.81 | 3.79 |
| other | −0.85 | −0.88 | −0.84 | −0.88 |
| torsion | −0.37 | −0.26 | −0.45 | −3.29 |
| charge | −11.43 | −6.05 | −2.48 | 0.33 |

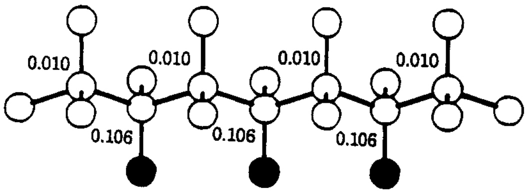
to the fact that it has the shortest F−F distance, 2.52 Å. Likewise, the meso HH structure should have the lowest energy since it has the larges F−F distance, 3.33 Å. What was actually found, however, was that the HT structures had lower energies than the HH structures, with the relative order of the two HT and two HH structures apparently correct.

The explanation for this result can be found by looking at the partial charges induced on the backbone; see Figure 3. For a HT structure, the large electronegativity of the fluorine induces a significant positive partial charge of +0.11 on the carbon to which it is attached. The carbon with no fluorine, however, develops only a slightly positive charge of +0.01, reuslting in only the fluorine atoms possessing a partial negative charge. On the other hand, when fluorines are placed on adjacent carbons, as occurs in a HH structure, both carbons have an increased partial positive charge to +0.13. This increase is large enough to cause the carbons in the TT region to develop a slightly negative partial charge of −0.02. The resultant polarization of the backbone is

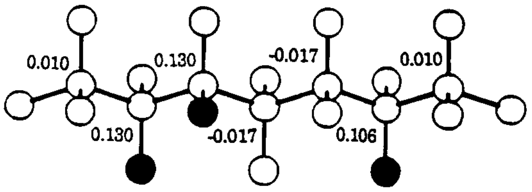


| Structure | Distance (Å) |
|---|---|
| • 3 Head-to-tail isotactic: | 2.52 |
| • 1 Head-to-head racemic: | 2.77 |
| • 4 Head-to-tail syndiotactic: | 3.25 |
| • 2 Head-to-head meso: | 3.33 |

**Figure 2.** Fluorine–fluorine separation distances for different chain isomers.



Head-to-tail structure



Head-to-head structure

**Figure 3.** Partial charges produced on the backbone of a HT and HH/TT chain. (The filled atoms indicate the positions of the fluorines.)

energetically unfavorable and results in the HH/TT structures having energies higher than the HT structures. This behavior has been observed independent of the chain length and for HH/TT structures placed in the middle of long HT sequences.

## Configurational and Constitutional Analysis

The next set of calculations investigated the effect of placing a defect in a chain sequence. Eight different chains were considered, each composed of 12 monomers in ann all-trans conformation. The chain structures studied were a pure syndiotactic chain and a syndiotactic chain with the center monomer replaced with an isotactic unit, a meso HH/TT unit, and a racemic HH/TT unit. The four corresponding isotactic chains were also studied. The purpose of these calculations were to determine how structural irregularities influenced the energy of the chain.

**Table 5. Change in Energy of an Ideal Chain Due to the Presence of an Isolated Defect**

| structure chain | defect | energy |
|---|---|---|
| syndiotactic | none | −32.47 |
| | isotactic | −27.17 |
| | racemic | −25.91 |
| | meso | −25.24 |
| isotactic | none | 3.32 |
| | syndiotactic | −5.41 |
| | racemic | 3.52 |
| | meso | 2.10 |

**Table 6. Torsion Angles Following Energy Minimization for Chains with Isolated Defects**[a]

| | iso/ iso | iso/ syn | iso/ rac | iso/ meso | syn/ syn | syn/ iso | syn/ rac | syn/ meso |
|---|---|---|---|---|---|---|---|---|
| $\omega_1$ | −173.7 | −173.9 | −173.4 | −173.7 | 176.6 | 176.2 | 175.5 | 177.0 |
| $\omega_2$ | 175.9 | 175.8 | 176.7 | 176.2 | 177.6 | 177.3 | 176.1 | 177.4 |
| $\omega_3$ | −173.9 | −174.7 | −173.5 | −174.3 | −177.1 | −176.7 | −176.2 | −177.1 |
| $\omega_4$ | 178.5 | 177.3 | 179.3 | 178.0 | −176.6 | −176.5 | −176.3 | −176.9 |
| $\omega_5$ | −176.3 | −177.4 | −176.6 | −177.3 | 176.8 | 176.8 | 175.7 | 177.4 |
| $\omega_6$ | 179.8 | 177.3 | 178.7 | 177.7 | 176.7 | 174.6 | 174.8 | 177.0 |
| $\omega_7$ | −177.8 | −177.0 | 178.7 | −178.6 | −176.6 | −173.9 | −176.6 | −177.8 |
| $\omega_8$ | −178.5 | 179.8 | 173.5 | 177.6 | −176.7 | −177.9 | −173.9 | −177.0 |
| $\omega_9$ | 179.3 | −178.4 | 171.3 | 178.0 | 176.8 | 177.4 | −174.7 | 179.1 |
| $\omega_{10}$ | −179.5 | −171.0 | **−178.7** | **−175.0** | 176.5 | −178.0 | **−178.7** | **178.1** |
| $\omega_{11}$ | 179.5 | 170.8 | **179.5** | **174.2** | −176.6 | 178.0 | **177.1** | **−179.0** |
| $\omega_{12}$ | −179.1 | **178.5** | **−175.5** | **−178.3** | −176.6 | **−177.4** | **179.4** | **−178.2** |
| $\omega_{13}$ | 178.4 | 180.0 | **−176.4** | **−178.2** | 176.7 | 177.6 | **175.3** | **177.2** |
| $\omega_{14}$ | 178.6 | 177.4 | −179.3 | 179.0 | 176.5 | 174.0 | 175.4 | 176.9 |
| $\omega_{15}$ | 179.7 | −177.6 | −177.3 | −177.6 | −176.8 | −174.7 | −175.4 | −176.7 |
| $\omega_{16}$ | 177.4 | 178.4 | 179.4 | 178.6 | −176.5 | −177.1 | −176.1 | −176.6 |
| $\omega_{17}$ | −179.4 | −178.1 | −179.0 | −178.7 | 176.8 | 177.0 | 176.0 | 177.4 |
| $\omega_{18}$ | 174.9 | 175.8 | 175.9 | 175.6 | 176.6 | 176.6 | 175.8 | 177.0 |
| $\omega_{19}$ | −176.8 | −176.8 | −177.6 | −177.2 | −176.6 | −176.7 | −175.4 | −177.0 |
| $\omega_{20}$ | 173.6 | 174.0 | 173.9 | 173.8 | −177.2 | −176.0 | −176.0 | −176.9 |
| $\omega_{21}$ | −175.8 | −176.1 | −176.4 | −176.2 | 177.8 | 176.8 | 176.6 | 177.6 |

[a] The torsion angles for the atoms associated with the defects are indicated in boldface.

The results of the energy calculation using the MM2 program are shown in Table 5. The energies are from the minimized structures and, as with the conformational calculations, the final structures were inspected to ensure they were still in an extended conformation; see Table 6. As expected, the syndiotactic chains have a lower energy than the isotactic chains. For a syndiotactic chain, the addition of any of the three defects provides an energetically less favorable chain. The syndiotactic chain has an energy of −32.47 kcal/mol which with the addition of an isotactic defect increases the energy by +5.3 kcal/mol, with the addition of a racemic HH/TT unit increases the energy by +6.56 kcal/mol, and with the addition of the meso HH/TT unit increases the energy by +7.23 kcal/mol. For the isotactic chain the energy was calculated to be +3.32 kcal/mol, with the incorporation of a syndiotactic defect lowering the energy by −8.73 kcal/mol, the addition of a racemic defect increasing the energy by +0.20 kcal/mol, and the addition of a meso defect improving the energy by −1.22 kcal/mol.

The differences between the structures (see Table 7) are again due primarily to the electrostatic term. However, the racemic defect does improve the torsion interaction by about +2.7 kcal/mol.

In an extended conformation, the syndiotactic chain produces the most favorable electrostatic term and any change in the structure increases the energy. Of the defects that are introduced, the isotactic unit is most favorable. This is due primarily to the advantage HT structures have over HH structures in regard to the induced partial charges on the backbone. For the HH defects it is somewhat surprising that the racemic unit has a lightly more favorable energy than the meso unit. As would be expected from the fluorine separation distances, the meso defect provides, overall, more favorable electrostatics. However, the difference is not as

**Table 7. Breakdown of Energies for Chains Containing an Isolated Defect**

| | syndiotactic chain | | | |
|---|---|---|---|---|
| energy term (kcal/mol) | pure | isotactic defect | meso defect | racemic defect |
| compression | 1.41 | 1.56 | 1.51 | 1.51 |
| bending | 1.94 | 2.30 | 2.24 | 2.05 |
| stretch−bend | 0.32 | 0.39 | 0.39 | 0.36 |
| torsion | −2.15 | −2.07 | −4.85 | −2.26 |
| van der Waals | | | | |
| 1,4 | 15.96 | 15.56 | 15.67 | 15.72 |
| other | −3.44 | −3.28 | −3.60 | −3.44 |
| charge | −46.50 | −41.63 | −37.27 | −39.15 |

| | isotactic chain | | | |
|---|---|---|---|---|
| energy term (kcal/mol) | pure | syndiotactic defect | meso defect | racemic defect |
| compression | 2.19 | 2.08 | 2.18 | 2.15 |
| bending | 3.69 | 3.56 | 3.80 | 3.59 |
| stretch−bend | 0.66 | 0.61 | 0.67 | 0.64 |
| torsion | −2.11 | −1.93 | −4.80 | −2.10 |
| van der Waals | | | | |
| 1,4 | 14.0 | 14.27 | 14.16 | 14.10 |
| other | −2.16 | −2.97 | −2.83 | −2.90 |
| charge | −12.98 | −21.03 | −9.67 | −13.38 |

**Table 8. Parameters Used for the Maximin2 Program**

Bond Length Terms

| | $k$ | $l_0$ |
|---|---|---|
| C−C | 633.6 | 1.54 |
| C−H | 662.4 | 1.10 |
| C−F | 600.0 | 1.36 |

Angle Bending Terms

| | $k$ | $q_0$ |
|---|---|---|
| C−C−C | 0.024 | 109.5 |
| C−C−H | 0.016 | 109.5 |
| H−C−H | 0.024 | 109.5 |
| C−C−F | 0.036[a] | 109.5 |
| H−C−F | 0.025[a] | 109.5 |

Torsion Terms

| | $k$ |
|---|---|
| C−C−C−C | 0.50 |
| C−C−C−H | 0.32 |
| H−C−C−H | 0.32 |
| C−C−C−F | 0.20 |
| H−C−C−F | 0.32 |
| F−C−C−F | 0.20 |

van der Waal Terms

| | $r^*$ | $k$ |
|---|---|---|
| C | 1.7 | 0.107 |
| H | 1.2 | 0.042 |
| F | 1.47 | 0.109 |

Electrostactic Terms

| | $a$ | $b$ | $c$ |
|---|---|---|---|
| C | 7.98 | 9.18 | 1.88 |
| H | 7.17 | 6.24 | −0.56 |
| F | 14.66 | 13.85 | 2.31 |

[a] These terms default to 0.02; therefore, they were estimated from the MM2 values.

great as might be expected. This results from the fact that the electrostatic interaction is a long-range force, in our case dropping off with distance as $r^{-2}$, and thus, whereas the primary fluorine interaction in the HH region favors the meso placement, the secondary interactions favor a racemic structure. The racemic structure is also favored by the torsion term.

The isotactic chains show a behavior opposite to the syndiotactic chains. In this case all of the defects lower the energy except the racemic defect. The syndiotactic defect is energetically most favored owing to the decreased F−F interaction and increased F−H interaction. The meso HH defect also has a lower energy than the pure isotactic chain. This is again a result of improved electrostatic interactions since the meso placement of the fluorine positions it at the maximum distance to the other fluorines on the chain. The improvement in the electrostatics is sufficient to compensate for the unfavorable energy associated with the backbone in the HH/TT region.

The racemic defect, however, has a less favorable energy than the other structures. The torsion term is still very favorable, but the electrostatic term is less favorable than for the pure isotactic chain. The racemic placement of the fluorine, unlike the meso placement, is not sufficient to compensate for this energy penalty associated with the backbone in the region of the HH/TT unit.

An examination of the torsion angles in Table 6 reveals that there is a small conformational variation along the backbone of the chains. In all cases there is an oscillation of the torsion angle resulting in an average torsion angle of 180°. It is interesting to note that, whereas the syndiotactic chains oscillate between values of +177° and −177°, the isotactic chains do not have as regular an oscillation. Also, it appears that the addition of a defect to either the syndiotactic or isotactic chain has little effect on the conformational state. The one possible exception to this is the isotactic system with the syndiotactic defect. However, even for this chain the average torsion angle is still 180°.

## Calculation of Packed Chains

The final question that was addressed pertains to the packing energy. In this set of calculations eight different systems were analyzed. Each system was composed of 48 chains and each chain consisted of 12 monomers. Periodic boundary conditions were used to simulate the crystalline lattice. The chains were packed together in a manner consistent with the unit cell that had previously been determined for PVF.[15] This resulted in a system of 4 unit cells by 6 unit cells by 12 unit cells. The system contained approximately 3500 atoms and as a result MM2 was no longer practical for these calculations. Thus the energy of each system was calculated using the Maximin2 program which is part of the SYBYL molecular modeling package from Tripos Associates.[16] Maximin2 uses a simplified force field and is able to perform calculations on large systems in a reasonable time frame. See Table 8 for a summary of the parameters used.

Calculations were performed on eight different chemical systems. The systems were composed of two pure systems and six systems with defects. For the two pure systems, one contained syndiotactic chains and one isotactic chains. For the syndiotactic system, the possibility of varying the handedness of the chains was not considered. The six systems containing defects were a syndiotactic system with approximately 8% isotactic defects, a syndiotactic system with approximately 8% meso HH/TT defects, a syndiotactic system with approximately 8% racemic HH/TT defects, and the corresponding isotactic systems. The defect level equates to one per chain and is in the range of commercial PVF.

The results of the calculations are shown in Table 9. The energy values listed for the eight systems are the total energies. Thus it is a combination of both the intramolecular energy and the intermolecular energy.

**Table 9. Total Energies for Systems of 48 Packed Chains**

| system | total energy (kcal/mol) |
|---|---|
| syndiotactic | −3717 |
| syndiotactic with isotactic defects | −3486 |
| syndiotactic with racemic HH/TT defects | −3340 |
| syndiotactic with meso HH/TT defects | −3429 |
| isotactic | −2824 |
| isotactic with syndiotactic defects | −2921 |
| isotactic with racemic HH/TT defects | −2708 |
| isotactic with meso HH/TT defects | −2600 |

**Table 10. Packing Energies for Different Systems Containing 48 Chains**

| system | packing energy (kcal/mol) |
|---|---|
| syndiotactic | −2092 |
| syndiotactic with isotactic defects | −2059 |
| syndiotactic with racemic HH/TT defects | −1942 |
| syndiotactic with meso HH/TT defects | −1954 |
| isotactic | −2344 |
| isotactic with syndiotactic defects | −2207 |
| isotactic with racemic HH/TT defects | −2219 |
| isotactic with meso HH/TT defects | −2037 |

The results indicate that in general the syndiotactic systems are energetically more favorable than the isotactic systems. Also, the addition of HH/TT units always results in systems that are less favored energetically. The pure syndiotactic system resulted in an energy of −3717 kcal/mol, whereas the addition of isotactic defects increased the energy by +231 kcal/mol. Addition of the racemic HH/TT units increased the energy by +377 kcal/mol, and the incorporation of the meso HH/TT units increased the energy by +288 kcal/mol. The energy of the pure isotactic system was higher than that for the syndiotactic system and had a total energy of −2824 kcal/mol. The addition of the defects changed the energy by −97 kcal/mol for the syndiotactic defects, by +116 for the racemic HH/TT defect, and by +224 kcal/mol for the meso HH/TT unit.

In order to more clearly distinguish the influence of the defects on the crystal, the packing energies were determined; see Table 10. The packing energies were calculated by subtracting from the total energy of each system the energy associated with 48 isolated chains of corresponding average configuration. What is most apparent is that the isotactic systems have more favorable packing energies than the syndiotactic systems. The packing energy for the pure syndiotactic system is −2092 kcal/mol and increases slightly by +33 kcal/mol with the addition of isotactic defects. The incorporation of racemic HH/TT defects increases the energy by +150 kcal/mol, whereas for meso HH/TT defects the energy increases by +138 kcal/mol. For the pure isotactic system, the packing energy is −2344 kcal/mol and increases by +137 kcal/mol with the addition of syndiotactic defects. The addition of either HH/TT defect increases the packing energy of the isotactic system, with the energy increasing +125 kcal/mol for the racemic HH/TT units and +307 kcal/mol for the meso units.

The packing energies can be explained by the fact that the structures differ simply by the location of the fluorines. This has little impact on the van der Waals energy, since it is a short-range force, but affects the electrostatic contribution. The systems that maximize the intermolecular F−F distance are favored. Hence, the isotactic chain is favored over the syndiotactic chain by allowing the fluorines to pack at the maximum possible distance from each other within the constraints of the unit cell. This has the added advantage of maximizing the intermolecular H−F contact. This optimum placement of the fluorines can be visualized by examining an *a*−*b* projection of a packed isotactic system as shown in Figure 4. This can be contrasted with the less optimal placement of the fluorines for packed syndiotactic chains as shown in Figure 5. (The half-shaded atoms indicate the statistical placement of the fluorine atoms.) For the syndiotactic system, the minimum intermolecular F−F distance is 4.04 Å compared with 4.96 Å for the isotactic system.

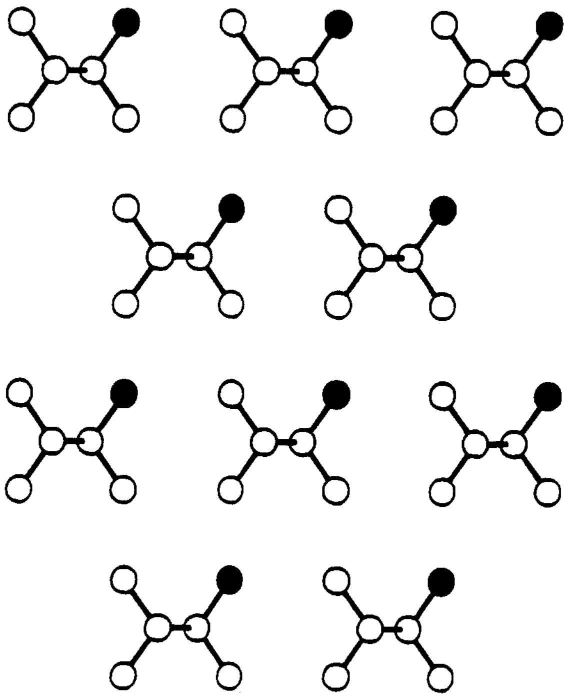


**Figure 4.** Packed array of isotactic chains showing placement of fluorines. (The fluorines are indicated by the filled atoms.)

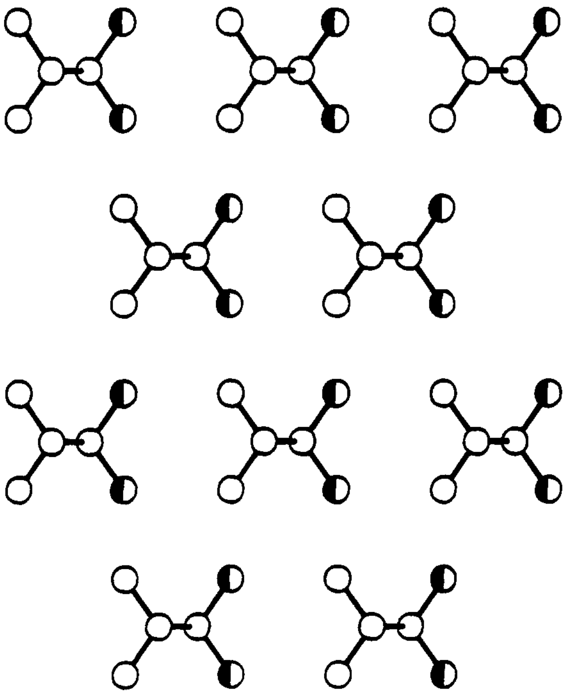


**Figure 5.** Packed array of syndiotactic chains showing placement of fluorines. (The half-filled atoms indicate the average weighting of the fluorines.)

The minimum F−F distances can also be used to explain packing energies of the defect systems. The introduction of HH defects in the crystalline region always produces shorter F−F distances, and thus HH defects always increase the packing energy. For the syndiotactic system, the addition of racemic HH units produces a minimum distance of 2.38 Å, whereas the meso HH unit generates a minimum distance of 2.44 Å. For the isotactic system, the minimum distances are 2.77 and 2.38 Å, respectively. The relative order of the minimum distances corresponds well with the calculated packing energies. The two systems that contain tacticity defects both generate minimum F−F distances of 3.22 Å, and the packing energy for both is less favorable than for the corresponding pure systems.

The one apparent contradiction in these results is the relative order of the isotactic system with syndiotactic defects and racemic HH defects. It appears that, although the racemic HH sequences produce a smaller F−F distance, they are compensated by the presence of the TT units by improving the H−F interactions relative to the HT chain, thus compensating for the smaller F−F distance.

The energies of the packed systems were determined by a direct calculation of the energy. To a first approximation, this was considered satisfactory since the crystal structure is known and the objective was simply to determine how different chain isomers affect the energy of the system. However, it would be preferable to use a minimized energy for each system in order to relieve any local energy maxima in the system. Although this was attempted, the results were unreliable. Only the pure syndiotactic system was stable during the minimization process and it converged quickly to a minimum energy. By visual inspection little movement had occurred in the minimized structure, resulting in the total energy of the syndiotactic system decreasing by 3.4% to −3845 kcal/mol. However, when a minimization was performed for the isotactic system and for the systems containing defectes, the minimization was unstable and a minimum was never reached. Visual inspection of the resultant systems revealed noticeable conformational distortion of some chains and rotation of some chains about their axes.

There are several possible reasons for this. First, it is not known how the local packing would be influenced by defects. Although it is possible that chain defects would crystallize in a completely random fashion, as has been assumed, it is also possible that on a local level there would be some ordering. However, the instability of the isotactic system cannot be explained by this reasoning.

Second, it is possible that the equation parameters used by Maximin2 are not appropriate for a crystalline system. This is supported by the behavior of a system when boundary conditions are not applied. Other force fields which work well with isolated chains have occasionally been shown to be inappropriate for crystalline systems. This is usually related to the van der Waals interaction parameters being "too soft". In addition, the incomplete parametrization of the valence terms in Maximin2 could be a contributing factor. However, the fact that the syndiotactic system is stable indicates that at best this is an incomplete answer.

Last, it is possible that the minimized structures which were obtained correspond, at least in part, to the crystalline structure of PVF. If this is the case, it would imply the possibility of conformational distortion and a statistical packing within the crystalline regions. Recent X-ray work that we have performed on PVF supports the possibility of statistical packing occurring in PVF. These results are presented in the following paper.

## Conclusions

The purpose of the modeling calculations was to determine how the crystallization process was influenced by the different structures possible in PVF. From the work, several conclusions can be reached. First, the syndiotactic structures have the largest driving force to crystallize. This is due to the trans conformation being the minimum-energy conformation and possessing a negative packing energy, both of which favor crystallization of the chains.

Likewise, the HH/TT units should freely participate in the crystallization process. Although the all-trans conformation is not the most favored, the energy difference is small. In addition, the HH/TT units, if incorporated into the crystalline ring, only modestly affect the packing energy of the chains, and in all cases the packing energy is favorable.

For the cases considered, crystallization of isotactic sequences is the most energetically unfavored. However, from this work it is not possible to establish the position of equilibrium between the crystalline and amorphous phases for these chain sequences. The packing energy indicates that there is a large favorable driving force for the isotactic sequences to exist in the crystalline region: although there is a rather significant energy penalty to constrain the chain to a trans conformatiom. Therefore, the extent to which the sequences crystallize may depend on the details of the crystallization process. Specifically, it may depend on the number of repeating units that must be all-trans in order to crystallize. It the crystal growth process proceeds by the addition of one repeat at a time to the growing crystal face, then the isotactic sequences would have simply a torsional energy barrier to overcome in order to crystallize. However, if the crystallization process requires a coordinated conformational state, the barrier to crystallization will quickly increase with the number of repeats that must be in coordination. Unfortunately this is not a question that can be answered from this work. The conclusion that can be drawn is that the chain configurations most likely to be excluded from the crystalline regions are the isotactic sequences.

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