

## Syndiotactic Isoregic 폴리비닐플로라이드 결정의 Force Fields 및 Elastic Properties

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Force Fields and Elastic Properties of Syndiotactic Isoregic Poly(vinyl fluoride) Crystal

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**초 록** 6-31G\*\* basis set을 이용한 ab initio 양자역학적 방법에 의하여 2,4,6-trifluoroheptane 구조를 구함으로서 syndiotactic isoregic PVF 결정의 force field를 유도하였다. 또 그 결과를 PVF의 structure parameter 및 elastic constant를 계산하는데 응용하였다. 그 결과 cell parameter는 각각 a (5.205 Å : chain axis), b(8.457 Å), 및 c(4.621 Å)로 나타났으며 X-ray data(5.04 Å, 8.57 Å, 및 4.95 Å) 결과와 비교적 잘 일치함을 알 수 있었다. Defect 비존재하에서의 syndiotactic PVF 결정의 Young's 모듈러스 계산값은 267GPa로 나타났으며, polyvinylidene fluoride(277-293 GPa) 및 polyethylene(264-337 GPa) 결정의 경우와 비슷한 수준으로 나타났다. 또한 optimum geometry에서 얻어진 bulk modulus값은 experimental geometry에서 얻어진 값보다 두배의 차이를 보였으며, 이것은 geometry에 따른 elastic compliance constant(특히 S<sub>33</sub>인자)가 크게 달라지기 때문인 것으로 나타났다.

**Abstract** Force fields of syndiotactic isoregic PVF crystal have been extracted by optimizing a structure of 2,4,6-trifluoroheptane with *ab initio* Quantum mechanical method with 6-31G\*\* basis set, and applied to calculate the structure parameters and elastic constants of the material. The cell parameters turned out to be 5.205 Å of a axis(chain axis), 8.457 Å of b axis and 4.621 Å of c axis. These parameters are in fair agreement with those of the atactic X-ray structure(5.04 Å, 8.57 Å, and 4.95 Å, respectively). The young's modulus of defect free syndiotactic PVF crystal was computed to be 267 GPa comparable to those of polyvinylidene fluoride(277-293 GPa) and polyethylene(264-337 GPa) crystals. Bulk modulus value obtained at optimum geometry is more than twice greater than that obtained at experimental geometry due to large difference of elastic compliance constant (especially S<sub>33</sub> element) at these two different geometries.

### I. Introduction

Due to the excellent chemical and physical properties, there has been a growing interest in the structure-property relations of fluorine-polymers. This is primarily related to the fact that fluorine polymers such as polytetra fluoroethylene (PTFE), polyvinylidene fluoride (PVDF), and polyvinyl fluoride (PVF) can

serve in a wide range of applications from surface coatings to engineering materials as it exhibits superior thermal, chemical, mechanical, electrical, and barrier properties. Recently, the isoregic(perfect head-to-tail) PVF has been synthesized by the reductive dechlorination of appropriate precursor polymer where head-to-head addition is sterically blocked by chlorine substituents<sup>1)</sup>. Furthermore, the result of fluo-

rine 19nmr study shows that the isoregic PVF produced by reductive dechlorination method has no branching defect in the material<sup>2</sup>). With this defect free structures, the new version of PVF materials is expected to be used more than ever in many applications due to its improved processibility resulting from broadened gap between its melting temperature and degradation temperature.

Since the mechanical properties of the new PVF has not been addressed yet, an examination of key properties such as elastic modulus of this material is necessary. There are various experimental techniques to evaluate elastic modulus of polymers ranging from stress-strain measurement, X-ray diffraction, and inelastic neutron scattering method to Raman studies of longitudinal acoustic vibrational mode<sup>3-7</sup>). Since PVF is semicrystalline polymer, however, the elastic constant derived from the above method is affected by the morphology of the material. Therefore the true response of the crystalline phase, which is important in practical and academic points of view, is difficult to be obtained. In this study, force field parameters of syndiotactic isoregic PVF crystal have been derived by *ab initio* Quantum Mechanical method and used to calculate the structure and some elastic properties.

## II. Computational Method

### 1. Force Field

Potential energy or force field used in this paper consists of three parts (electrostatic, van der Waals, and valence terms). The total electrostatic energy can be written as

$$E_{coul} = \sum_{i>j} \frac{Q_i Q_j}{\epsilon R_{ij}} \quad (1)$$

where  $Q_i$  and  $Q_j$  are the net atomic charges in electron units,  $R_{ij}$  is the distance in Å, and  $\epsilon$  is the dielectric constant ( $\epsilon=1$  for vacuum), and the conversion factor  $C_0 (=332.0637)$  takes care of the units, giving  $E_{coul}$  in kcal/mol. The van der Waals energy is expressed as in an ex-

ponential-6 form :

$$E_{vdw}(R) = A e^{-cR} - BR^{-6} \quad (2)$$

$$= D_0 \left( \frac{6}{\zeta - 6} \right) \exp^{\zeta \left( 1 - \frac{R}{R_0} \right)} - D_0 \left( \frac{\zeta}{\zeta - 6} \right) \left( \frac{R_0}{R} \right)^6$$

where  $D_0$  is the well depth in kcal/mol,  $R_0$  the equilibrium bond length, and  $\zeta$  the scaling factor.

The valence potential energy includes bond stretching(morse-type), bond angle bending (cosine stretch-type), torsional terms, etc. (the details of valence terms are given in reference 8 of Polyvinylidene Fluoride force field). We employed the force field parameters used in reference 8 except for atomic charges and some of the valence terms. The valence force constants of PVF (which were not defined in PVDF) were arbitrarily set because force constants do not affect final ground-state geometry.

In order to calculate the atomic charges of PVF, we extracted the net atomic charges of 2,4,6-trifluoroheptane,  $\text{CH}_3\text{CHFCH}_2\text{CHFCH}_2\text{CHFCH}_3$  (we call this TFH) as shown in Figure 1. First, the optimum geometry of TFH was computed by the GAUSSIAN92 *ab initio* Quantum Mechanical program<sup>9</sup>) with 6-31G\* \* basis set. The number of basis functions is then 215. Since the Mulliken population does not give correct atomic charges, we calculated potential derived atomic charges by the PS-GVB(PseudoSpectral Generalized Valence Bond) *ab initio* program<sup>10</sup>) at the optimum geometry using the same basis set. Note that the

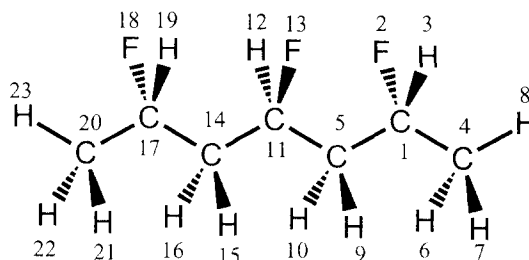


Fig. 1. 2,4,6-trifluoroheptane.

PS-GVB program can calculate physical properties such as atomic charges with much shorter cpu time than the GAUSSIAN92 program can.

## 2. Modulus calculations

From the force field obtained above, Young's modulus and bulk modulus of PVF were calculated at both experimental and optimum geometries using a material simulation package, POLYGRAF by Molecular Simulation Inc. The Young's modulus in the chain direction ( $E_c$ ) is defined by

$$E_c = \sigma_c / e_c \quad (3)$$

where  $e_c$  and  $\sigma_c$  are strain and stress in the chain direction. Components of strain and stress are related each other by

$$\sigma_i = C_{ij} e_j \quad (4)$$

$$e_j = S_{ij} \sigma_i \quad (5)$$

where  $C_{ij}$  and  $S_{ij}$  are the elastic stiffness constants and compliance constants, and  $i, j = 1, 2, \dots, 6$  denotes  $xx, yy, zz, yz, zx,$  and  $xy,$  respectively.

The bulk modulus ( $\beta$ ) is given by

$$\beta^{-1} = \sum_{i,j=1}^3 S_{ij} \quad (6)$$

## III. Results and Discussion

The full geometry (Z-matrix form) of TFH is given in Table 1. The atom numbers appeared in Table 1 are shown in Figure 1. After the computation of potential derived atomic charges of the monomer form, TFH, the net atomic charges of PVF are assigned as

$$Q(\text{C of CH}_2) = -0.24$$

$$Q(\text{C of CHF}) = 0.33$$

$$Q(\text{H of CH}_2) = 0.09$$

$$Q(\text{F of CHF}) = -0.30$$

Table 1. Z-Matrix of 2,4,6-trifluoroheptane (Angstroms and Degrees)

| CD | Cent | Atom | N1 | Length/X     | N2 | Alpha/Y     | N3 | Beta/Z       | J |
|----|------|------|----|--------------|----|-------------|----|--------------|---|
| 1  | 1    | C    |    |              |    |             |    |              |   |
| 2  | 2    | F    | 1  | 1.382800( 1) |    |             |    |              |   |
| 3  | 3    | H    | 1  | 1.082700( 2) | 2  | 106.653(23) |    |              |   |
| 4  | 4    | C    | 1  | 1.514400( 3) | 2  | 108.017(24) | 3  | -118.886(44) | 0 |
| 5  | 5    | C    | 1  | 1.519100( 4) | 2  | 107.710(25) | 3  | 117.894(45)  | 0 |
| 6  | 6    | H    | 4  | 1.085100( 5) | 1  | 110.623(26) | 2  | -62.559(46)  | 0 |
| 7  | 7    | H    | 4  | 1.085200( 6) | 1  | 110.630(27) | 6  | -120.445(47) | 0 |
| 8  | 8    | H    | 4  | 1.083800( 7) | 1  | 110.074(28) | 6  | 119.718(48)  | 0 |
| 9  | 9    | H    | 5  | 1.086900( 8) | 1  | 109.143(29) | 2  | -182.732(49) | 0 |
| 10 | 10   | H    | 5  | 1.086700( 9) | 1  | 108.802(30) | 9  | -117.309(50) | 0 |
| 11 | 11   | C    | 5  | 1.518200(10) | 1  | 112.793(31) | 9  | 121.392(51)  | 0 |
| 12 | 12   | H    | 11 | 1.080700(11) | 5  | 110.429(32) | 1  | 54.743(52)   | 0 |
| 13 | 13   | F    | 11 | 1.386700(12) | 5  | 107.709(33) | 12 | -116.217(53) | 0 |
| 14 | 14   | C    | 11 | 1.518200(13) | 5  | 113.517(34) | 12 | 124.628(54)  | 0 |
| 15 | 15   | H    | 14 | 1.086900(14) | 11 | 109.066(35) | 5  | 59.226(55)   | 0 |
| 16 | 16   | H    | 14 | 1.086700(15) | 11 | 109.181(36) | 15 | -117.480(56) | 0 |
| 17 | 17   | C    | 14 | 1.519100(16) | 11 | 112.791(37) | 15 | 121.445(57)  | 0 |
| 18 | 18   | F    | 17 | 1.382800(17) | 14 | 107.706(38) | 11 | 61.356(58)   | 0 |
| 19 | 19   | H    | 17 | 1.082700(18) | 14 | 109.867(39) | 18 | -115.798(59) | 0 |
| 20 | 20   | C    | 17 | 1.514300(19) | 14 | 113.721(40) | 18 | 119.667(60)  | 0 |
| 21 | 21   | H    | 20 | 1.085200(20) | 17 | 110.627(41) | 14 | 63.553(61)   | 0 |
| 22 | 22   | H    | 20 | 1.085100(21) | 17 | 110.625(42) | 21 | -120.439(62) | 0 |
| 23 | 23   | H    | 20 | 1.083800(22) | 17 | 110.073(43) | 21 | 119.836(63)  | 0 |

$$Q(\text{H of CHF}) = 0.03$$

From the force field derived above, the geometry of PVF is calculated. The optimum geometry of PVF is shown in Table 2 where the experimental geometry of PVF and the optimum value of TFH are also listed. The X-ray structure of PVF is not easily compared to the calculated value of syndiotactic PVF since PVF used in the X-ray analysis<sup>11)</sup> has the following complex structures, i.e., (1) syndiotactic and isotactic mixture, (2) head to head defect, and (3) possible branching. Nevertheless, the agreement between the experimental and optimum bond lengths of PVF is excellent. On the other hand, the bond angles of PVF are slightly different from the optimum values of PVF. Note that the experimental bond angles

Table 2. Comparison of Geometries<sup>a</sup>

|                          | Polymer(PVF) |         | TFH                       |
|--------------------------|--------------|---------|---------------------------|
|                          | Expt.        | Optimum | Optimum                   |
| <b>Bond Length</b>       |              |         |                           |
| C-C                      | 1.54         | 1.547   | 1.518                     |
| C-H(in CHF)              | 1.09         | 1.097   | 1.084                     |
| C-F(in CHF)              | 1.36         | 1.367   | 1.384                     |
| C-H(in CH <sub>2</sub> ) | 1.09         | 1.089   | 1.087                     |
| <b>Bond Angle</b>        |              |         |                           |
| C-C-C                    | 109.5        | 114.6   | 112.8, 113.6 <sup>b</sup> |
| H-C-H                    | 109.5        | 106.5   | 108.4                     |
| H-C-F                    | 109.5        | 102.3   | 106.7                     |

a Bond lengths is Å and bond angles in degrees.

b Bond angles depend on carbon centers, i.e., 112.8° when

C center is attached by two hydrogens and 113.6° when

C center is attached by one hydrogen and one fluorine.

Table 3. Cell Parameters of PVF Crystal

|                         | Expt.    | Optimum  |
|-------------------------|----------|----------|
| a(Å)                    | 5.0400   | 5.2045   |
| b(Å)                    | 8.5700   | 8.4572   |
| c(Å)                    | 4.9500   | 4.6207   |
| Volume(Å <sup>3</sup> ) | 213.8043 | 203.3827 |
| Density(g/cc)           | 1.4305   | 1.5038   |

of PVF are assumed to be tetrahedral around the Carbon atoms. Therefore, the optimum bond angles of PVF are expected to be closer to the real values. Table 3 shows the result of cell parameters. The X-ray cell parameters along the chain axis (a axis) is almost half compared with the optimum value (experimental unit cell is shown in Figure 2). This is because fluorine atoms were assumed to be displaced statistically with respect to the carbon atoms without changing either the planar conformation of the chain or the regularity of the chain packing between the different chains. It is reasonable that the optimum cell parameters along the chain direction are slightly longer than the experimental ones since the optimum C-C-C angle is larger than the experimental one. Table 4 presents the results of the elastic properties calculated from the above force field. Data show that Young's modulus of syndio-

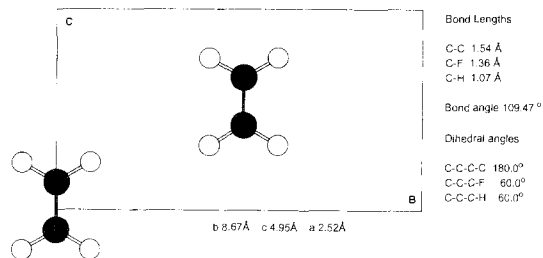


Fig. 2. Unit Cell of PVF

Table 4. Elastic Properties of PVF Crystal

|  | Experimental<br>Geometry | Optimum<br>Geometry |
|--|--------------------------|---------------------|
| Young's Modulus(GPa)                       | 254.33                   | 267.77              |
| Bulk Modulus(GPa)                          | 4.20                     | 10.44               |
| Compressibility(1/GPa)                     | 0.2379                   | 0.0958              |
| <b>Elastic Compliance Constants(1/GPa)</b> |                          |                     |
| S <sub>11</sub>                            | 0.003932                 | 0.003735            |
| S <sub>12</sub>                            | -0.001000                | -0.000922           |
| S <sub>13</sub>                            | -0.000954                | -0.000814           |
| S <sub>22</sub>                            | 0.068946                 | 0.059768            |
| S <sub>23</sub>                            | -0.007738                | -0.006975           |
| S <sub>33</sub>                            | 0.153492                 | 0.049740            |

tactic isoregic PVF crystal is 267 GPa which is comparable to those of PVDF crystal(277–293 GPa)<sup>8)</sup> and PE crystal(264–337 GPa)<sup>12)</sup>. To our knowledge, experimental Young's modulus of the PVF crystal in the chain direction is not available yet, thus calculated modulus can not be compared directly with experimental one. Young's modulus of commercial PVF obtained from stress-strain measurement is 1.79 GPa<sup>13)</sup> which is much lower than defect free PVF crystal by 265 GPa. Obviously, it is due to the fact that the measured modulus not only depends on the degree of crystallinity but also on the test conditions. Commercial PVF has defect structures such as branching and head-to-head defects as described earlier, thus the degree of crystallinity drops to around 50%. Another factor to be considered is the temperature effect. Since semicrystalline PVF has two glass transition temperatures one around 65°C due to the tie molecules and the loose loops and the other around -30°C due to the cilia,<sup>14)</sup> part of commercial PVF material is in rubbery state at the room temperatures. Thus, factors mentioned above must be considered when interpreting the modulus data. The relation<sup>15-16)</sup> between the crystallinity and elastic constant of the semicrystalline polymer above glass transition temperature may be written as

$$E^{1/5} = (k 10^5)^{1/5} w_a + (k 10^9)^{1/5} w_c$$

where E is the Young's modulus in the pascal,

k is a constant,

$w_a$  and  $w_c$  are weight fraction of amorphous and crystal.

As can be seen in the above equation, crystallinity can change the modulus of semicrystalline polymer by a factor of 10,000<sup>17)</sup>. Therefore, our calculated data of the elastic constants are not unreasonable. The similar results have been observed in the polyethylene case where Young's modulus of crystal and the semicrystalline material are 280 GPa and 0.13 GPa (low density polyethylene), res-

pectively<sup>18)</sup>. On the other hand, the bulk modulus obtained at optimum geometry of PVF crystal is more than twice greater than that obtained at experimental geometry. This is because of large difference of the elastic compliance constants, especially,  $S_{33}$  element between these two geometries. Note that the inverse of the bulk modulus can be expressed by the summation of elastic compliance constants shown in Table 4.

Force fields have been derived for syndiotactic isoregic PVF crystal and applied to calculate the elastic constants of the material. In order to investigate the effects of the defect structures such as tacticity and regioirregularity (degree of head-to-head defect concentration), the calculations of the isotactic and atactic structures and the aregic (imperfect head-to-tail) structure are necessary. In the next paper, molecular dynamics calculations will be applied to address the above effects at different temperatures.

#### IV. Conclusion

Structures and some elastic properties of PVF were calculated with newly defined force-field parameters which were estimated by *ab initio* Quantum Mechanical method. Young's modulus of defect free syndiotactic PVF crystal turned out to be 267 GPa which is comparable to those of PVDF and PE crystals. We believe that the force field and elastic constants of defect free syndiotactic PVF crystal represent a starting point to build the various defect structures and our results should be capable of lending insight to the interpretation of the structure-property correlation of PVF materials.

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### References

1. R. E. Cais, J. M. Kometani, in J. C. Randall (Ed.), *NMR and Macromolecules*, Am. Chem. Soc. Symp. ser., 247 (1984) 153.
2. J. W. Hong, Ph. D. Thesis, Case Western Reserve University, Cleveland, OH, (1991).
3. K. Akagi, M. Suezaki, H. Shirakawa, H. Kyotani, M. Shimomura, and Y. Tanabe, *Synth. Met.* 28, D1 (1989).
4. J. Clements, R. Jakeways, and I. M. Ward, *Polymer* 19, 639 (1978).
5. R. P. Wool and R. H. Boyd, *J. Appl. Phys.*, 51, 5116 (1980).
6. R. A. Feldkamp, G. Venkaterman, and J. S. King, *Neutron Inelastic Scattering* (IAEA, Vienna, 1968), Vol. II, p.159.
7. J. R. Rabolt and B. Fanconi, *J. Polym. Sci. B* 15, 12 (1977).
8. N. Karasawa and William A. Goddard III, *Macromolecules*, 25, 7268 (1992).
9. M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gompers, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople. *Gaussian 92*, Inc., Pittsburgh, PA, 1992.
10. J. M. Langlois, R. P. Muller, T. R. Coley, W. A. Goddard III, M. N. Ringnalda, Y. Won, R. A. Friesner, *J. Chem. Phys.*, 92, 7488 (1990).
11. G. Natta, I. W. Bassi, and G. Allegra, *Atti. Accad. Naz. Lincei Cl. Sci. Fis. Mat. Nat. Rend.*, 31, 350 (1961).
12. N. Karasawa, S. Dasgupta, and W. A. Goddard, III, *J. Phys. Chem.*, 95, 2260 (1991).
13. V. L. Simril and B. A. Curry, *J. Appl. Polymer Sci.*, 4(10), 62 (1960).
14. R. F. Boyer, *Encyclopedia of Polymer Sci. and Tech. Supplement Vol. II*, p.749, John Wiley & Son, Inc., New York, NY (1973).
15. L. E. Nielsen, *J. Appl. Polymer Sci.*, 19, 1485 (1975).
16. W. E. A. Davies, *J. Phys.*, D4, 318, 1176, 1325 (1971).
17. L. E. Nielsen and R. F. Landel, *Mechanical Properties of Polymer and Composites*, 2nd Ed., Chapter 4, p.177, Marcel Dekker, Inc., New York (1994).
18. C. R. Barrett, W. D. Nix, and A. S. Tetelman, *The Principles of Engineering Materials*, Chapter 6, p.197, Prentice-Hall, Inc. Englewood Cliffs, New Jersey (1973).