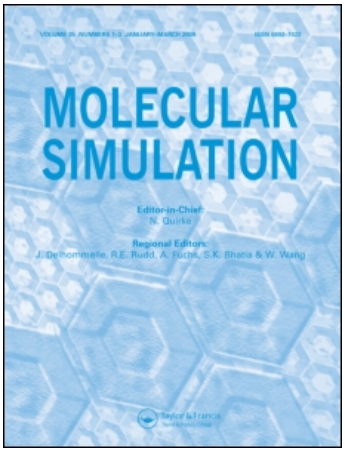

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Molecular Dynamics Studies of Amorphous Poly(Tetrafluoroethylene)

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MOLECULAR DYNAMICS STUDIES OF AMORPHOUS POLY(TETRAFLUOROETHYLENE)

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Force field parameters for amorphous poly(tetrafluoroethylene) (PTFE) and perfluoroalkanes for molecular simulations are developed using four perfluoroalkanes (C_3F_8, n-C_4F_{10}, n-C_5F_{12} and n-C_6F_{14}) as reference molecules. Molecular dynamics calculations of the amorphous PTFE are performed under constant temperature and constant pressure conditions. Surprisingly, more than 6 ns calculations are needed to equilibrate the system. The calculated density and the structure factor are in good agreement with experiment. The concentration of the trans conformation of the backbone corresponds closely to that estimated from a Boltzmann distribution. The determined force field parameters are confirmed to reproduce the realistic amorphous structure of PTFE. The molecular motions of the backbones are investigated by tracing the time evolutions of the dihedral angles and several types of the conformational changes are observed.

Keywords: Poly(tetrafluoroethylene); amorphous structure; structure factor; molecular dynamics; force field

INTRODUCTION

Poly(tetrafluoroethylene) (PTFE, Teflon) has a variety of applications in chemical, mechanical, and electrical fields due to its peculiar characteristics.

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In the xerographic technique, toner particles are heated and molten with heat rolls to fix on papers. Polymers like PTFE are used as heat roll materials with low surface energy, which enables the molten toner to detach from the heat rolls. It is difficult to form the heat rolls with only PTFE since the intermolecular interactions of PTFE are very weak. Some monomers with polar groups are usually copolymerized with perfluorocarbon monomers to increase the intermolecular interactions, which enables us to form the heat rolls. It is believed that the amorphous and crystalline phases are mixed near the surface region of the heat rolls produced with this method. One of the problems in the toner fixing process is called "off-set", where the molten toner is not fixed on the paper completely but remains partly on the heat roll to make the quality of the image poor. Many studies have been devoted to solve this problem by changing the materials for toners as well as for heat rolls. It is important for molecular design of these materials to understand the behavior of polymers at interfaces. The microscopic investigation on the behavior of polymers at the interfaces is difficult to do with experiments. In particular, the observation of the behavior of molten polymers is probably impossible, even with the recent measurement techniques. The molecular simulation is a promising method for this purpose.

It is important for the molecular simulations to employ a force field that reproduces the experimental and theoretical data as accurately as possible. The torsional potential is significant for simulations of polymers, since many characteristics come from the long backbones with a lot of dihedral angles. The torsional potential energies of perfluoro-*n*-alkanes have been investigated by using *ab initio* calculations [1–3]. The torsional potential energy in terms of the central bond of perfluoro-*n*-butane is different from that of *n*-butane in two respects. First, the dihedral angle of the backbone in trans conformation is not situated at 180° but is displaced by about ± 15°, which comes from the steric hindrance of two fluorine atoms at 1–5 position [3]. Second, the number of gauche conformations is not two but four, due to the attraction between two fluorine atoms at 1–5 position [1, 3]. It is known that the configuration interaction has to be taken into account in the *ab initio* calculations to estimate the interactions between fluorine atoms [1]. Especially, for the more stable gauche conformations the attractive interactions between two fluorine atoms are underestimated about 1.0 kcal/mol, unless the configuration interaction is taken into account. Several force field parameters for molecules with fluorine atoms have been proposed [4, 5]. These parameters were used in the molecular dynamics (MD) calculations for small fluorinated molecules such as perfluoromethane. Holt *et al.* [6] developed a force field for PTFE using semi-empirical

molecular orbital calculations. Sprik *et al.* [7] developed a force field for PTFE with *ab initio* density functional methods and performed MD calculations to investigate the structure and phase transition of PTFE crystals.

We developed force field parameters for PTFE and perfluoroalkanes in the amorphous phase to use in an MD calculation package GEMS/MD (Nano-Simulation Associates). These parameters were determined using *ab initio*, MD and molecular mechanics calculations. The intermolecular interactions, especially the van der Waals interaction, are important for our simulations because the interactions with other polymers used for toner are of interest. We determined the van der Waals parameters, using the approach proposed by Jorgensen *et al.* [8], where the parameters are optimized to reproduce the experimental density and heat of vaporization using MD calculations. For the determination of the parameters for polymers, reference molecules, which are usually monomers or small units of the polymers, are employed. Perfluoroalkanes of small molecular weight can be used as the reference molecules to obtain the parameters for PTFE. The parameters for intramolecular interactions are determined using *ab initio* calculations. The procedure for the determination of the parameters, for PTFE and perfluoroalkanes, is presented in the later sections.

MD calculations of PTFE in amorphous phase were performed with the determined parameters under constant temperature and constant pressure conditions. Several physical properties and the structure of the amorphous phase were compared with experiment, and molecular motions of PTFE were investigated in this study.

THEORETICAL METHODOLOGY

Force Field Potentials

The potential energy E in the force field of GEMS/MD used in this study is represented as

$$E = E_B + E_A + E_T + E_{vdW} + E_Q + E_{1-5NB}. \tag{1}$$

Bond stretching (E_B), angle bending (E_A) and torsion (E_T) are bonded potentials. The van der Waals (E_{vdW}), electrostatic (E_Q) and 1–5 non-bonding (E_{1-5NB}) interactions are nonbonded potentials. The definitions of

the bonded potentials are as follows:

$$E_B = V_B(R - R_0)^2, \tag{2}$$

$$E_A = V_A(\theta - \theta_0)^2, \tag{3}$$

$$E_T = \sum_{k=1}^{6} V_k \cos(k\theta), \tag{4}$$

where V_B and V_A are force constants, V_k is barrier to rotation, R_0 and θ_0 are bond length and bond angle, respectively, in the energetically optimized structure and k is the periodicity. The definitions of the nonbonded potentials are

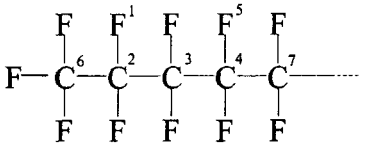
$$E_{vdW} = \left(\frac{V_{12}}{R_{ij}^{12}}\right) - \left(\frac{V_6}{R_{ij}^6}\right), \tag{5}$$

$$E_Q = \frac{1}{4\pi\varepsilon_0}\frac{q_i \cdot q_j}{R_{ij}}, \tag{6}$$

$$E_{1-5NB} = \left(\frac{V_{nb12}}{R_{ij}^{12}}\right) - \left(\frac{V_{nb6}}{R_{ij}^6}\right), \tag{7}$$

where R_{ij} is the distance of atoms i and j, V_{12} and V_6 are the van der Waals parameters for the Lennard-Jones type potential function, ε_0 is the dielectric constant of medium, q_i and q_j are the partial charges on atoms i and j, respectively, and V_{nb12} and V_{nb6} are the 1–5 nonbonding potential parameters. All the potentials except for the 1–5 nonbonding potential are commonly used in force fields for molecular simulations. The 1–5 nonbonding potential, which is an artificial potential function of the Lennard-Jones type, adjusts the potential energy between an atom and the fourth bonding atom (at 1–5 position) such as atoms F^1 and F^5 in PTFE (see Fig. 1-(a)). This potential is effectively used in case when the repulsive (the first term of the Eq. (7)) or attractive (the second term of the Eq. (7)) interaction acts between two atoms at the 1–5 position and this interaction cannot be adjusted with other potential functions. For PTFE the steric hindrance occurs between two atoms F^1 and F^5 in Figure 1-(a) when both two dihedral angles C^6-C^2-C^3-C^4 and C^2-C^3-C^4-C^7 are around 180°. The repulsion makes the angle of the backbone in trans conformation displace about ±15° from 180° [3]. Usually, it is difficult to adjust this kind of interactions acting on the atoms at 1–5 position with the torsional

(a) Molecular Structure



(b) Atom Type

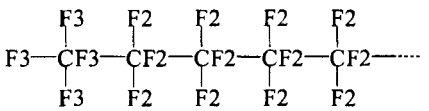


FIGURE 1 Molecular structure and atom type of PTFE.

potential, unless the coupling of two adjacent torsional potentials or the 1–5 nonbonding potential is available in the force field potential functions. That is, the torsional potential alters the barrier to rotation in terms of the bond between two atoms of 2–3 position, which means the interactions of the atoms not at 1–5 but at 1–4 position can be changed with this potential. We have employed only the first term of the 1–5 nonbonding potential in the force field for PTFE to adjust this repulsive interaction.

Method for Determining the Potential Parameters

The procedure for determining the potential parameters employed in this study is described briefly below. Four different atom types are defined as is shown in Figure 1-(b); a carbon atom bonding with three fluorine atoms (named as CF3), a carbon atom bonding with two fluorine atoms (named as CF2), a fluorine atom bonding with CF3 carbon atom (named as F3) and a fluorine atom bonding with CF2 carbon atom (named as F2). All the *ab initio* calculations were performed with HF/6-31G level basis set using Gaussian 94(Gaussian Inc.) in this study.

At first, the partial charges on the atoms were estimated from the experimental dipole moment data. The bond stretching and the angle bending potential parameters were determined using the *ab initio* calculations of perfluoro-*n*-butane. For the determination of the torsional and 1–5 nonbonding potentials the torsional potential energy plot of perfluoro-*n*-butane in terms of the central bond is required. HF/6-31G level *ab initio* calculations of perfluoro-*n*-butane were performed changing this torsional angle from 0 to 180° at every 15° to obtain a torsional potential plot shown in Figure 2. Since the potential is symmetrical with respect to the dihedral

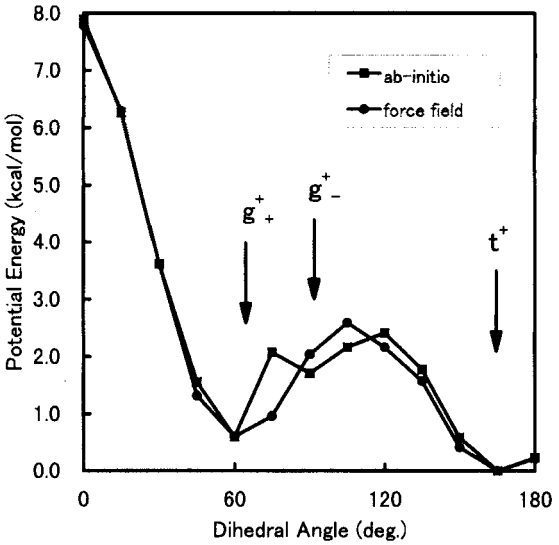


FIGURE 2 Torsional potential energy of perfluoro-*n*-butane.

angle 180°, we focused only on the dihedral angles from 0° to 180° in the discussion about the potential energy. The results of the higher level *ab initio* calculations such as MP2/D95+* have been reported in reference 1. It is said that the configuration interaction has to be taken into account in the *ab initio* calculations for molecules with two fluorine atoms located closely to each other to estimate the interactions accurately. The energy differences of the *ab initio* calculations between HF/6-31G level and MP2/D95+* [1] are not very large except for the energy of the gauche conformation at around 60°. We employed the value 0.6 kcal/mol [1] for the torsional potential energy at 60°, which is the conclusion of the reference 1. Except for this gauche conformation, the energy obtained with HF/6-31G level *ab initio* calculations were used to determine the torsional and 1−5 nonbonding potential parameters.

The same plot was obtained with the molecular mechanics calculations with temporarily assigned parameters. These temporary parameters were optimized, by trial and error, to decrease the deviation from the plot obtained by the *ab initio* calculations mentioned above. Four points were weighted to optimize the torsional and 1−5 nonbonding potential parameters; the angle of the trans conformation, the potential energy at 180°, the barrier between the trans and gauche conformations and the potential energy of the gauche conformation.

Two approaches are usually employed to determine the van der Waals parameters from the experimental data. One approach uses crystal

structural data and the other uses the density and heat of vaporization [8]. In this study we employed the second approach since we are interested not in the crystal but in the amorphous phase of PTFE. The van der Waals parameters for polymers are determined to reproduce these experimental data of reference molecules of the polymers. Perfluoroalkanes (C_3F_8, n-C_4F_{10}, n-C_5F_{12} and n-C_6F_{14}) were employed as the reference molecules for PTFE and perfluoroalkanes.

It is preferable to determine the parameters for the torsional, 1–5 nonbonding and van der Waals potentials at the same time, if possible. However, it is difficult to determine the inter- and intra-molecular potentials at the same time, since the optimization methods are different from each other. At first, the torsional and 1–5 nonbonding potential parameters for perfluoro-n-butane were temporarily determined by using the roughly estimated van der Waals parameters for perfluoropropane, which does not have a dihedral angle composed of four carbons. Then, by using the determined torsional and 1–5 nonbonding potentials, the van der Waals potential parameters were optimized by MD calculations to reproduce the experimental densities and heats of vaporization of the four perfluoroalkanes. After that, the torsional and 1–5 nonbonding potential parameters for perfluoro-n-butane were re-optimized. Preferably these procedures should be iterated until the theoretical and experimental values are well reproduced. However, since the errors of the obtained values from theoretical and experimental ones were small at the first iteration, we finished the optimization of the potential parameters at this point.

Molecular Dynamics Calculations

All the MD calculations were performed under constant pressure and constant temperature conditions with GEMS/MD. The pressures of all the MD systems were kept at 1.0×10^5 Pa. The temperatures of the systems with the four perfluoroalkanes are listed in Table I. The temperature of the PTFE system was set at 300 K. The methods proposed by Nosé [14, 15], Hoover [16] and co-workers to control temperature and by Andersen [17] to control pressure were employed. The three angles of the MD cell with the periodic boundary conditions were fixed at 90°, while the lengths of the MD cell were allowed to change after the systems were equilibrated. A timestep of 2 fs (1 fs = 10^{-15} s) was chosen to conserve the total energies of the MD systems. A cut-off radius of the van der Waals potential of 10 Å was used. The spherical Ewald truncation method [18, 19] was employed to evaluate electrostatic interactions.

TABLE I Heats of vaporization and densities of perfluoro-*n*-alkanes

	ΔHv (*calc.*) *kcal/mol*	ΔHv (*exp.*) *kcal/mol*	*density* (*calc.*) g/cm^3	*density* (*exp.*) g/cm^3
C_3F_8 236 K	4.67 (−0.4%)	4.69 [9]	1.65 (+3.4%)	1.60 [9]
n-C_4F_{10} 273 K	5.54 (+1.5%)	5.46 [10]	1.60 (+0.8%)	1.59 [10]
n-C_5F_{12} 298 K	6.37 (+0.5%)	6.34 [11]	1.60 (0.0%)	1.60 [12]
n-C_6F_{14} 298 K	7.65 (+1.9%)	7.51 [11]	1.62 (−2.9%)	1.67 [13]

Preparation of Samples

Four perfluoroalkane systems were prepared to evaluate the densities and heats of vaporization for the optimization of the van der Waals parameters. Each homogeneous system contained 216 molecules for perfluoropropane and perfluoro-*n*-butane, 125 for perfluoro-*n*-pentane and perfluoro-*n*-hexane. The concentrations of the conformations estimated from the Boltzmann distribution were used to create the initial systems.

To produce the amorphous phases of polymers, two promising methods have been proposed. In one method atoms of the polymers are supposed to have smaller radii than van der Waals radii. Polymer chains are put in an MD box preventing the overlapping of atoms, where the size of the box is estimated from the given density beforehand. The dihedral angles of the backbones are assigned to follow the Boltzmann distribution. In the other method polymers are at first put in a large MD box to make a "gas" phase and then slowly compressed with MD calculations at a given temperature [20]. The concentration of the conformations following a Boltzmann distribution is achieved spontaneously with this method.

One PTFE molecule was composed of 602 atoms whose degree of polymerization was 100 with a molecular weight of about 1.0×10^4. Four PTFE molecules were put into the MD cell to obtain the "gas" phase. Then, the system was equilibrated after the gradual compression using MD calculations.

RESULTS AND DISCUSSION

All the force field parameters for the molecular simulations of PTFE and perfluoroalkanes determined in this study are listed in Table II. The atom

TABLE II Force field parameters for PTFE

Bond Stretching

Atom A	*Atom B*	R_0 (Å)	V_B (*kcal/mol/Å*^{2})
CF3	CF2	1.5304	357.0
CF2	CF2	1.5302	344.0
CF3	F3	1.3494	508.0
CF2	F2	1.3653	391.0

Angle Bending

Atom A	*Atom B*	*Atom C*	θ_0(*rad*)	V_A(*kcal/mol/rad*^{2})
F3	CF3	F3	108.79	104.4
F3	CF3	CF2	110.14	80.2
F2	CF2	CF3	107.20	84.7
F2	CF2	F2	108.84	106.3
F2	CF2	CF3	108.45	79.5
CF2	CF2	CF3	116.51	97.9
CF2	CF2	CF2	116.51	97.9

Torsion

				V_k (*kcal/mol*)					
Atom A	*Atom B*	*Atom C*	*Atom D*	V_1	V_2	V_3	V_4	V_5	V_6
CF2	CF2	CF3	F3	0.0	0.0	0.5908	0.0	0.0	0.0
CF2	CF2	CF2	CF3	17.70	3.253	1.748	0.525	−0.020	−0.462
CF2	CF2	CF2	CF2	17.70	3.253	1.748	0.525	−0.020	−0.462

van der Waals

Atom A	*Atom B*	V_{12} (*kcal/mol/Å*^{12})	V_6 (*kcal/mol/Å*^{6})
CF2	CF2	83394	230.00
CF3	CF3	39955	56.64
F2	F2	50487	138.51
F3	F3	54473	179.45

1–5 Nonbonding

Atom A	*Atom B*	V_{nb12} (*kcal/mol/Å*^{12})	V_{nb6} (*kcal/mol/Å*^{6})
F2	F3	1300000	0
F2	F2	1300000	0

Partial Charges and Masses

Atom	*Charge* (*e*)	*Mass* (*a.u.*)
CF2	0.48	12.0
CF3	0.63	12.0
F2	−0.24	19.0
F3	−0.21	19.0

types used in Table II correspond to those shown in Figure 1-(b). Parameters for some dihedral angles are not listed in Table II, since their torsional potentials are incorporated in other ones and set to zero.

Torsional Potential

The torsional potential energy of the backbone is important for simulations of polymers since some characteristics such as the transition temperature and the tensile strength are closely related to the barrier to rotation of the backbone. The torsional energy of the main chain of PTFE is assumed to be same as that of perfluoro-*n*-butane in this study. The torsional potential energy plots of perfluoro-*n*-butane in terms of the central two carbon atoms obtained from *ab initio* calculations and estimated with the determined parameters are shown in Figure 2. The potential energies of all the points in Figure 2 except for one at 60° are calculated in this study. The potential energy at 60° assigned by Smith *et al.*, is used by the reason explained in the introduction section. They have assigned the potential energy of g_+^+ conformation of PTFE to 0.6 kcal/mol from MP2/D95+* level *ab initio* calculations of perfluoro-*n*-butane, perfluoro-*n*-pentane, and perfluoro-*n*-hexane [1]. The potential energies of trans and gauche conformations and the barriers to rotation are listed in Table III. The energy minimum of perfluoro-*n*-butane is not at 180° like n-alkanes but is displaced by about $\pm 15°$ (t^+ and t^- conformations). Smith *et al.* [1] and Sprik *et al.* [3] have attributed these displacements to the repulsive forces between fluorine atoms at 1 – 5 position. The potential energy at 180°, that is a saddle point between t^+ and t^- conformations, is in good agreement with the theoretical calculation result listed in Table III, although the barrier to rotation is very small and it will not be important for the MD calculations at high temperature. Two gauche conformations are observed in the plot obtained from the theoretical calculations between 0° and 180° (g_+^+ and g_-^+ conformations) as shown in Figure 2. The same result has been reported in reference 1. The g_-^+ conformation could not be reproduced in the potential energy plot obtained with the determined parameters. As the depth of the well of the g_-^+ conformation is very shallow and the energy is much higher than those of t^+ and g_+^+ conformations, it will not be significant for the MD calculations of the systems in the amorphous phases at high temperature. The potential energy of the g_+^+ conformation estimated with the determined parameters is in good agreement with the value assigned by Simth *et al.* [1]. The barrier to rotation from t^+ to g_+^+ conformations corresponds closely to the theoretically calculated value.

TABLE III Potential energies of perfluoro-*n*-butane

	*Potential Energy** *at* 180°	*Potential Energy of* $g_{\pm}^{\pm}$	*Barrier to Rotation from trans* (t^{+}) *to gauche* ($g_{\pm}^{\pm}$)
HF/4-31G [1]	0.15	1.73	
MP2/4-31G [1]	0.27	1.15	
HF/D95+* [1]	0.11	1.02	
MP2/D95+* [1]	0.23	0.47	
HF/6-31G (this work)	0.17	1.62	2.51
Force Field (this work)	0.22	0.60	2.59

* kcal/mol.

Density, Heat of Vaporization and Order Parameter

The systems with perfluoropropane, perfluoro-*n*-alkanes and PTFE took a surprisingly long time to be equilibrated. The reason why the long time calculations are needed is that the interatomic interactions of the fluorine atoms in perfluoropropane, perfluoro-*n*-alkanes and PTFE are weak. In addition to this it usually takes a long time to equilibrate the polymer systems using MD calculations since the relaxation of polymers is slow because of the long backbone chains. The calculated and experimental densities and heats of vaporization for perfluoro-*n*-alkanes are listed in Table I. The deviations of the calculated values from experiments are also listed in the parentheses in Table I. The heat of vaporization is defined as the sum of the difference of internal energy of the liquid and gas phases and the work done by the volume change. In this study the difference of the internal potential energy of the liquid and gas phases is supposed to be nearly equal to the cohesive energy of the liquid phase. That is, the sum of the cohesive energy of the liquid phase and the work done by the volume change is assumed to be the same as the heat of vaporization. The calculated values are in excellent agreement with experiment within the differences of 4%. The time evolution of the density of PTFE is shown in Figure 3. After 6 ns MD calculations the density of the system started to fluctuate at around its average value and we confirmed that the system was equilibrated at this point. The obtained average density of PTFE 1.9 g/cm^3 is also in good agreement with the experimental value of 2.0 g/cm^3 [21]. Since PTFE is a crystalline polymer, a completely amorphous PTFE cannot be obtained experimentally. This experimental density of its amorphous phase is derived from the extrapolation of the densities of samples composed of both crystalline and amorphous phases. From the experimental densities of perfluoro-*n*-pentane, perfluoro-*n*-hexane and PTFE at room temperature

the density of perfluoroalkane becomes higher as the number of the carbon atoms in a molecule increases. The same trend was observed in this study.

As PTFE is a crystalline polymer, the growth of crystalline is expected below the melting point 600 K [22]. As shown in Figure 3, the density of the MD system increased gradually. The slow increase of the density might come from the creation of the crystalline phase whose density is higher than that of the amorphous phase. The creation of the crystalline was investigated with both graphical tools and the order parameter. No large structural order was found out in the equilibrated PTFE structure visualized with a molecular modeling software. The time evolution of the order parameter was calculated. The order parameter is defined as

$$S = \sum_{i,j>i} \frac{1}{2} \left(3\langle \cos^2 \theta_{ij} \rangle - 1\right), \tag{8}$$

where θ_{ij} is the angle between two vectors defined with two every other carbon atoms such as C^2 and C^4 or C^3 and C^7 in Figure 1-(a). All the pairs of the vectors are taken into account in the summation. The structural order was kept at about zero during 10 ns MD calculations, which shows that the large scale order of segments such as the crystalline phase is not contained in the equilibrated amorphous PTFE. The reasons why the crystalline was not obtained in this calculation are that the temperature was much lower than the melting point and the equilibration time was too short. The molecular motion might not be active at 300 K and the nucleation and growth of the crystalline did not occur during the calculation time range. Moreover, we have not confirmed that the developed force field parameters can reproduce

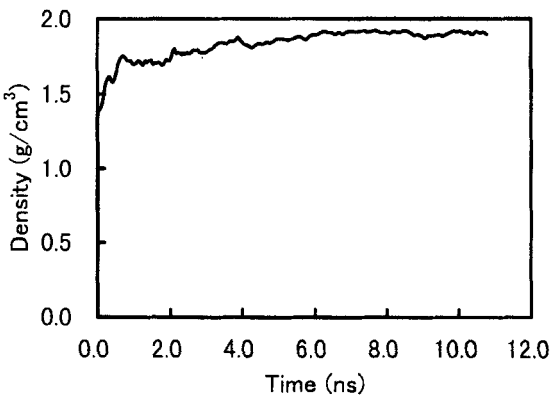


FIGURE 3 Time evolution of density of PTFE.

the crystalline PTFE properties since the parameters were determined for PTFE in the amorphous phase. Further investigation is required for the discussion of the creation of the crystalline phase.

Structure of Amorphous PTFE

The radial distribution function (Fig. 4) and the structure factor (Fig. 5) are calculated with the equilibrated amorphous PTFE. Xu [23] reported that the amorphous peaks are observed at about $2\theta = 17°$ and 40° with X-ray diffraction measurement with Cu-Kα radiation. These peaks correspond to the peaks in radial distribution function at 6.4 Å and 2.7 Å, respectively. In the calculated radial distribution function peaks at 2.7 Å, 3.1 Å and between 5.2 Å and 6.9 Å correspond to the experimental values. In the calculated structure factor four large peaks observed at $k = 0.35$, 1.14, 2.73 and 6.13 that correspond to $2\theta = 4.95°$, 16.1°, 39.1° and 97.3° of the X-ray diffraction measurement with Cu-Kα radiation, respectively. The first peak, that corresponds to the distance of about 22 Å, is an error for some reason since the radial distribution function is calculated up to 15 Å. The peak at 97.3° was out of the range of the experimental data in the literature 23. The rest of the two calculated peaks are in good agreement with experiment [23]. The distribution of the conformations in terms of the dihedral angles of the backbones is shown in Figure 6. As expected, t^+ and t^- conformations could not be observed clearly because the barrier to rotation between them is subtle. The obtained concentration of the trans conformer is 64.4%. This is in good agreement with the concentration of 58.1% calculated with the difference of energy by following a Boltzmann distribution. The agreement of the calculated properties with experiment implies that the amorphous structure obtained with the parameters is realistic.

Molecular Motion

The glass transition temperature of the amorphous PTFE is reported as 200K [24]. Since the calculations are performed at room temperature, the molecular motion of backbone is expected to be observed in the MD calculations. The time evolutions of the dihedral angles of the backbone are calculated for 100 ps MD calculations. Most of the dihedral angles stayed and fluctuated in the gauche or trans conformations. Some of them showed large dihedral angle changes shown in Figure 7, where 180° is trans, whereas 60° and 300° are gauche conformations. The dihedral angle shown in

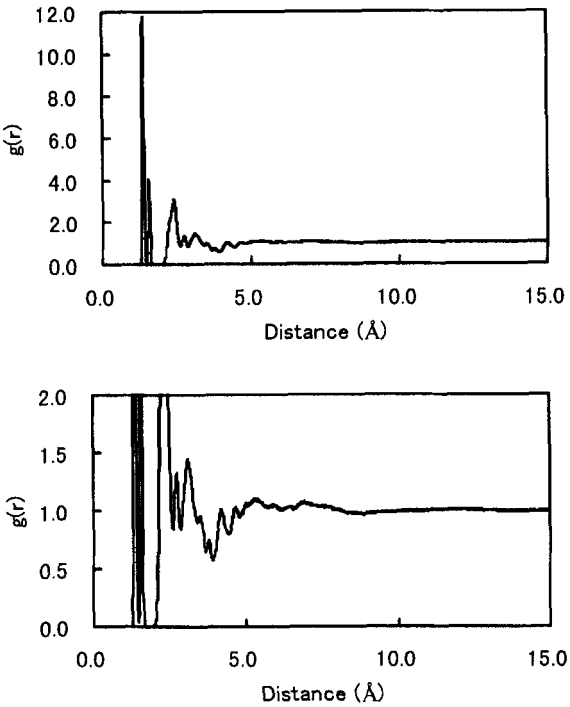


FIGURE 4 Radial distribution functions of PTFE.

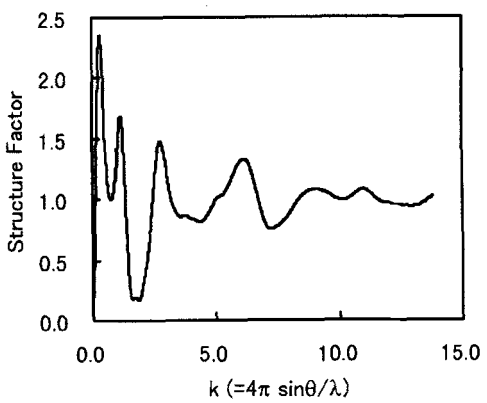


FIGURE 5 Structure factor of PTFE.

Figure 7-A was fluctuated from trans toward gauche frequently. The dihedral angle shown in Figure 7-B changed the conformation from gauche to trans. Figures 7-C, D, E, and F show the angle changes of the successive

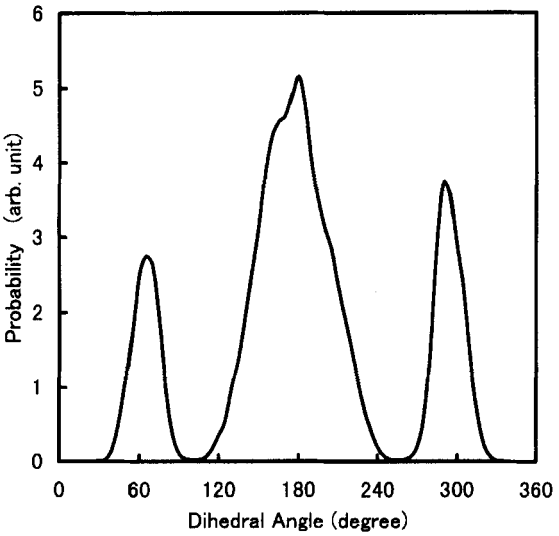


FIGURE 6 Distribution of dihedral angles of PTFE.

dihedral angles. The dihedral angle in Figure 7-D changed from the stable gauche conformation to 240°, that is energetically unstable in a short period of time between $t = 60$ and 70 ps. To the contrary, the dihedral angle in Figure 7-E, which is the next to the dihedral angle in Figure 7-D, changed from an unstable angle of 120° to the stable gauche conformation at the same period of time. The adjacent dihedral angles shown in Figures 7-C and 7-F are affected by the conformational change. The dihedral angle in Figure 7-C stayed in the trans conformation most of the time except for a short period of time when the dihedral angles in Figures 7-D and 7-E changed. After that, the dihedral angle in Figure 7-C went back to the trans conformation. On the other hand, the dihedral angle in Figure 7-F stayed at around 180° before that period and then the dihedral angle changed to t^- conformation with the average dihedral angle of 193°. This dihedral angle is probably forced to stay in the t^- conformation by the surrounding atoms in PTFE. These molecular motions might be processes of the equilibration of polymers, or these kinds of discrepancies might exist in the amorphous polymers at room temperature.

The molecular motions of the backbone of PTFE are observed in the MD calculations. Probably the reason why PTFE has a relatively low glass temperature is that the barrier to rotation of the backbone is small and the intermolecular interaction is weak. As the glass transition temperature of polymers is said to be related with the motion of the backbone, the small

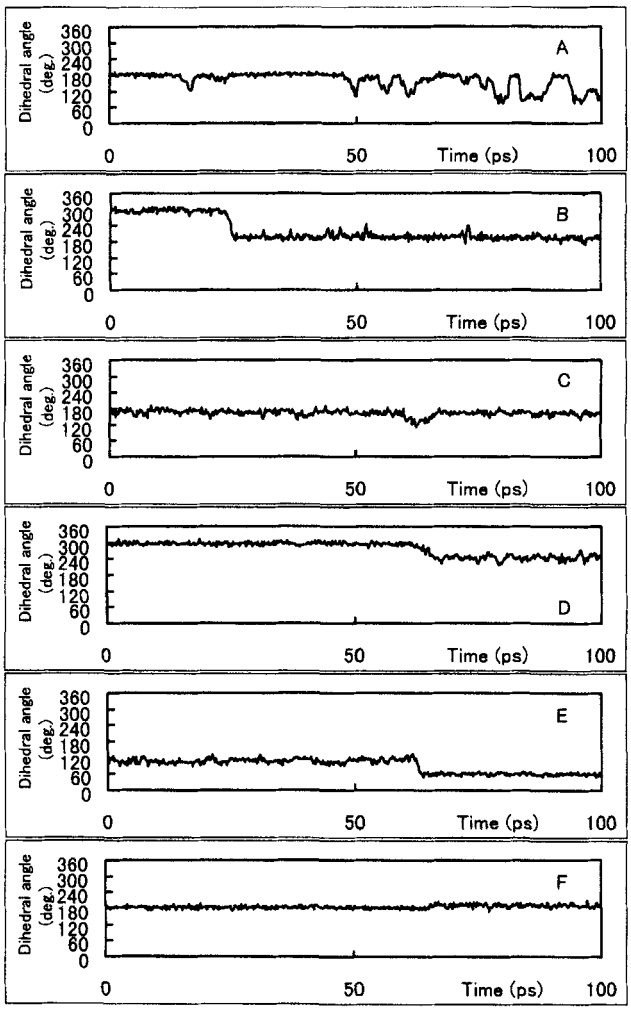


FIGURE 7 Time evolutions of dihedral angles of PTFE.

barrier to rotation of the backbone causes the conformational changes at low temperature.

CONCLUSION

Force field parameters for poly(tetrafluoroethylene) and perfluoroalkanes to be used in molecular simulations are developed. MD calculations of PTFE

and perfluoroalkanes are performed under constant temperature and constant pressure conditions. The densities and heats of vaporization of four perfluoroalkanes (C_3F_8, n-C_4F_{10}, n-C_5F_{12} and n-C_6F_{14}), which are used as reference molecules for PTFE to determine the parameters, are in excellent agreement with experiment. The creation of the crystalline is not observed in 10 ns equilibration time. The density and structure factor of the amorphous PTFE are in good agreement with experiment. We confirmed that the determined force field parameters reproduced the realistic amorphous structure of PTFE. The molecular motions of the backbones are observed, such as the gauche to trans conformational changes and the stable to unstable angle changes. During the conformational changes the affection to the adjacent dihedral angles is also observed.

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