Phase Transformation of Poly(trimethylene terephthalate) in Crystalline State: An Atomistic Modeling Approach

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Abstract : The phase transformation of poly(trimethylene terephthalate) in crystalline state was simulated by atomistic modeling using molecular mechanics technique. The crystalline structure of PTT was successfully prepared using the well-defined unit cell structure of PTT and was satisfactorily verified by comparing that with the structure obtained from the x-ray diffraction experiments. The basic elastic properties were predicted in this study, showing that the crystalline structure of PTT is very pliable to the deformation at small strain. When the crystalline structure of PTT was stepwise deformed up to 50% of strain in chain direction under uniaxial extension condition, the change in dihedral angle of trimethylene unit from *gg* to *tt* conformation was accompanied with a large increase of stress, indicating that the phase transformation of PTT in crystalline state is difficult to occur.

Introduction

In recent years, poly(trimethylene terephthalate) (PTT) has attracted much interest, because it has better elastic recovery than poly(ethylene terephthalate) (PET) and poly (buthylene terephthalate) (PBT). This property may arise from the chemical structure of PTT as shown in Figure 1, i.e., the PTT has an odd number of methylene units between the terephthalate residues whereas PET and PBT have even numbers of methylene units. It is well known that, in many polycondensation polymers, an odd or even number of methylene units in their chemical structure can affect physical properties of the polymers, so-called the odd-even effect. In fact, the elastic recovery is in an order of PTT > PBT > PET[1]. However, the exact mechanism related to the above-mentioned odd-even effect has not been completely understood yet. As one of possible answers to this result, it is suggested that the crystal of PTT shows a distinct mechanical response compared to that of PET and PBT. Analysis of crystalline structures of PET[2,3], PTT[4,5], and PBT[6-11], shows that the aliphatic part of PTT takes a highly coiled structure of gauche-gauche (*gg*) conformation, whereas that of PET and PBT takes trans (*t*) and gauche-trans-gauche (*gtg*) conformation, respectively. Jakeways *et al.*[6] have stud-
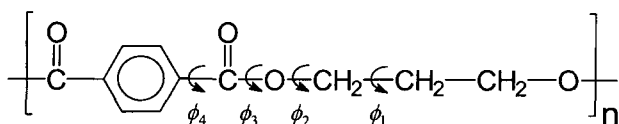

Figure 1. Chemical structure of PTT and definitions of dihedral angles in backbone chain.

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ied the deformation of crystalline structure of PTT by drawing monofilament of PTT and observed using WAXS that the crystal lattice of PTT responds immediately to the applied stress in elastic region of strain whereas the crystal lattice of PET and PBT does not change up to 4% of strain. Since the crystalline structure of PET takes trans conformation in its aliphatic part, it is not easy to deform the crystal lattice at small strain. However, the deformation behavior of PBT at small strain seems strange, because the aliphatic part in PBT crystal takes a coiled conformation as in the case of PTT.

It has been known that PBT has two distinct crystalline forms depending upon thermal and mechanical conditions. In other words, PBT shows polymorphism. An α phase was found in relaxed samples and a β phase was found in stressed samples. Crystal structures were determined for these phases by Joly[12], Mensik[13] and others[14,15] and it was agreed that in the α phase the aliphatic part of the polymer chain takes up the conformation of gauche-trans-gauche links whereas the β conformation consists of an extended all trans structure. Further confirmation of these structures was provided by infrared spectroscopy and by Raman spectroscopy[16]. The α and β transition was found by Jakeways *et al.*[6] to be completely reversible on removal of the strain and was coincident with the plateau region of the stress/strain curve. PET, however, does not show polymorphism, i.e., the crystal structure of PET is not dependent upon drawing and heat treatment conditions. Now a question arises as to whether or not PTT, the intermediate structure between PET and PBT in a series of poly(alkylene terephthalate), shows polymorphism in its crystal structure. The answer has not been reported.

Generally, it is not always possible to study experimentally the mechanical behavior of polymer in the purely crystalline state, because the preparation of purely crys-

talline sample is often difficult. In this aspect, computer simulation using atomistic modeling technique has proven very useful to investigate the mechanical behavior of polymer in perfect crystalline state, because the method generates a well-defined and perfect crystal structure without any structural defect and make it possible to simulate the behavior under an ideal condition[17-24]. The mechanical behavior of PTT in amorphous state has already been investigated in our previous study[25] using the atomistic modeling technique[26,27]. In this study, the deformation of crystalline PTT is simulated using molecular mechanics in order to elucidate whether or not the phase transformation of crystalline structure is possible under extension.

Models and Simulation

Full atomistic models of PTT in crystalline state with 1600 atoms were prepared by using a unit cell of PTT shown in Figure 2. Chain conformation in unit cell and unit cell parameters were set on the basis of x-ray diffraction data[4,5]. First, a single chain of PTT was generated for trimethylene unit to have gg conformation, and then it was packed into a triclinic-type unit cell with the space group of crystalline structure of PTT, $P_{\bar{1}}$[4,5,28]. This initial structure of PTT in crystalline state was adjusted to the model proposed by x-ray diffraction study through optimization by molecular mechanics technique using the conjugate gradient algorithm until the root mean square
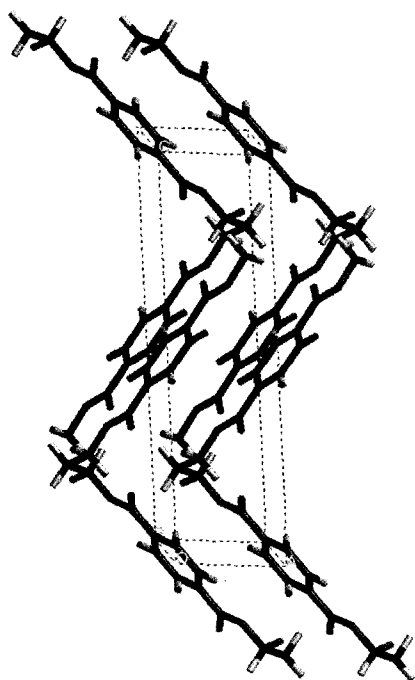
force between atoms was smaller than 0.001 kcal/(mol Å). The universal force field (UFF)[29] was used to calculate potential energies of atoms, and the charge equilibration method[30] was used to assign partial charges to every atom. The long-range interaction such as the van der Waals interaction and the Coulombic interaction was calculated by the Ewald method[31], in which real space cutoff distance, reciprocal space cutoff distance, and convergence constant were 6.0 Å, 0.5 Å^{-1} and 2.5 Å, respectively. The total potential energy (E_{total}) of system is calculated by use of eq (1):

$$E_{total} = E_b + E_\theta + E_\phi + E_{vdW} + E_{Coulomb} + E_{inversion} \quad (1)$$

where E_b is the bond stretching energy, E_θ is the valence angle bending energy, E_ϕ is the dihedral angle rotating energy, E_{vdW} is the van der Waals interaction energy, $E_{Coulomb}$ is the Coulombic interaction energy, and $E_{inversion}$ is the inversion energy. Details of the energy function are found in the literature by Rappé et al.[29].

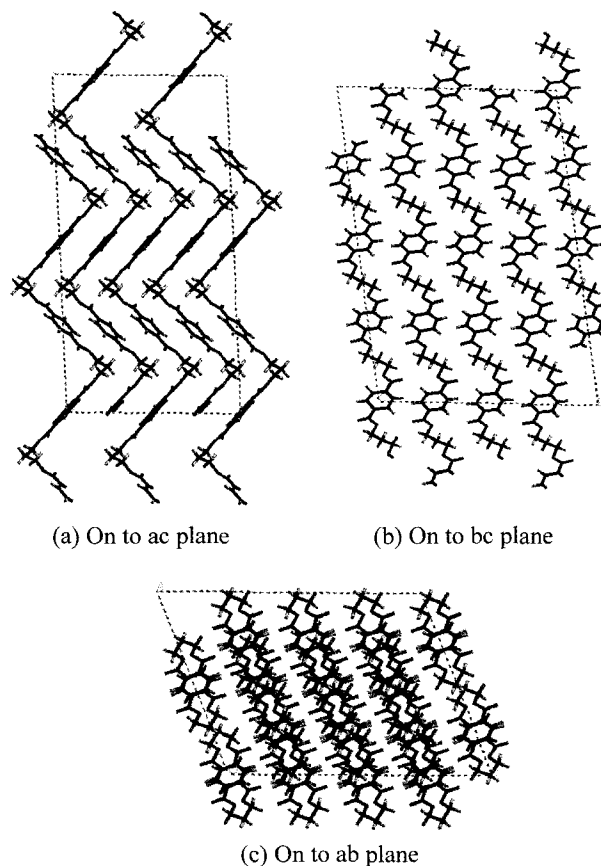In order to confirm whether the simulated unit cell corresponds to the real unit cell of PTT, x-ray diffraction pat-

(a) On to ac plane   (b) On to bc plane

(c) On to ab plane

Figure 3. Projection of crystalline structure of PTT on ac-, bc-, and ab-plane.

Figure 2. Simulated unit cell of PTT.

tern was calculated by

$$F(hkl)= \sum_{j=1}^{n} f_j(\sin\theta/\lambda)\exp[2\pi i(h, k, l)\cdot(x_j, y_j, z_j)] \quad (2)$$

where n is the number of atoms in the unit cell, h, k, and l are the indices defining the crystallographic planes, and f_j is the atomic scattering factor expressed as a function of the Bragg angle (θ) and the wavelength of radiation (λ) for atom j located at the fractional coordinate position (x_j, y_j, z_j). In this calculation, the polarization factor was assumed to be 0.5 and the effect of Lorentz scattering and thermal motion on the diffraction was not taken into account. The x-ray source was CuKα whose wavelength is 1.542 Å.

By accumulating 32 unit cells, the model of PTT in crystalline state was generated and then was optimized by molecular mechanics. A typical model of PTT in crystalline state is shown in Figure 3. The periodic boundary conditions were imposed to the three directions to simulate the perfect crystalline structure with infinite size.

In order to simulate the deformation of crystalline structure of PTT, the cell was extended in the chain direction (c-axis) by 0.2% of the initial cell dimension and then was relaxed by molecular mechanics until the root mean square force between the atoms was smaller than 0.001 kcal/(mol Å). This procedure was repeated until the strain reached 50%. In order to improve the statistics, nine structures were simulated independently and their properties were averaged. In this study, the commercial modeling software, *Cerius²* of Molecular Simulation Inc., was used.

Results and Discussion

Validation of Simulation

It is important to verify whether the simulated unit cell structure of PTT in crystalline state is properly constructed or not. For this purpose, the unit cell parameters obtained in this simulation are compared with those

Table 1. Observed and simulated unit cell parameters of crystalline structure of PTT

Cell parameters	Observed			Simulated
	I[a]	II[b]	III[c]	
a (Å)	4.64	4.60	4.58	4.56 ± 0.08
b (Å)	6.23	6.20	6.22	6.22 ± 0.07
c (Å)	18.65	18.30	18.12	18.48 ± 0.64
α (deg)	98.5	98.0	96.9	98.21 ± 2.49
β (deg)	93.0	90.0	89.4	90.54 ± 0.99
γ (deg)	111.1	112.0	111.0	111.37 ± 1.17

[a]Data taken from ref. 4.
[b]Data taken from ref. 5.
[c]Data taken from ref. 29.

observed in x-ray diffraction experiments[4,5,28], as shown in Table 1. Although the experimental data show some scattering according to the authors, it is obvious that the agreement between simulation and experiment is satisfactory. The simulated density of PTT in crystalline state was 1.410 ± 0.002 (g/cm³). This value is comparable to those calculated from x-ray diffraction (1.387~1.430 (g/cm³))[4,5,28]. When the simulated values of dihedral angle defined in Figure 1 were compared with those observed from experiments, it is revealed that the simulated chain conformation in crystalline structure agrees well with those observed in experiments, as shown in Table 2. The x-ray diffraction pattern calculated from the simulated unit cell structure of PTT successfully reproduced the one obtained experimentally[4,5], as shown in Figure 4. The values of d-spacing and scattered intensity were obtained from this calculation and compared with the experimental values in Table 3. The measure of agreement between the observed intensity and the simulated intensity is expressed by the reliability index, R, defined as

$$R = \frac{\sum||F_0| - |F_s||}{\sum|F_0|} \quad (3)$$

where F_o and F_s denote the observed structure factor in

Table 2. Comparison between the observed and the simulated dihedral angles of PTT chain in crystalline state

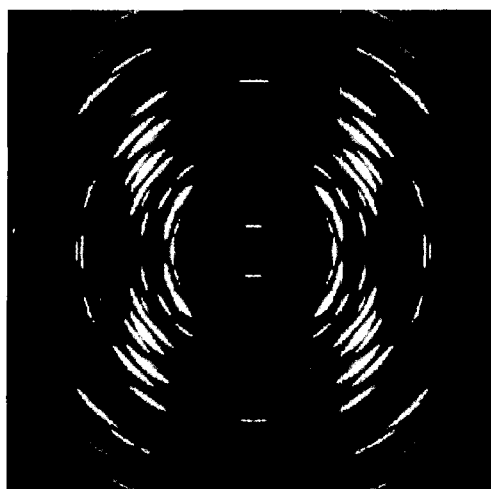| Dihedral angles(deg)	Observed[a]	Simulated
ϕ_1	67.8	67.9 ± 5.0
ϕ_2	160.1	175.2 ± 1.0
ϕ_3	173.2	170.2 ± 3.4
ϕ_4	168.3	173.9 ± 5.2

[a]Data taken from ref. 5.

Figure 4. X-ray diffraction pattern simulated for highly oriented PTT fibers. The tilted angle from perfect orientation is about 5°.

Table 3. Comparison between the observed and the simulated d-spacings and scattered intensities of crystal structure of PTT

h	k	l	d-spacing(Å)		Intensity (arbitrary unit)	
			Observed[a]	Simulated	Observed[a]	Simulated
0	1	0	5.682	5.705	11.16	10.65
1	0	0	4.628	4.258	2.90	2.05
-1	0	0	4.268	4.259	2.90	2.05
-1	1	0	4.268	4.259	2.90	2.23
2	0	0	2.112	2.129	2.79	2.05
-2	2	0	2.112	2.129	2.79	2.60
0	3	0	1.899	1.902	6.06	4.80
0	4	0	1.420	1.408	2.64	1.83
-3	3	0	1.420	1.412	2.64	1.95

[a]Data taken from ref. 4.

experiments and the simulated structure factor in this study, respectively. The value of R calculated from Table 3 is 0.179. Usually, the crystalline structure of polymers is accepted when the value of R is equal to or less than 0.20[32,33]. Therefore, it is concluded that the crystalline structure of PTT obtained in this simulation is in good agreement with the real crystalline structure.

Elastic Properties and Finite Deformation of Crystalline structure of PTT

The elastic properties of PTT in crystalline state were calculated from the stiffness matrix. The components of the stiffness matrix are defined as

$$C_{ij} = \frac{1}{V}\left(\frac{\partial U^2}{\partial \varepsilon_i \partial \varepsilon_j}\right) = \frac{\partial \sigma_i}{\partial \varepsilon_j} = \frac{\sigma_{i+} - \sigma_{i-}}{2\varepsilon_j} \quad (4)$$

where U is the total potential energy, V is the cell volume, ε_i and ε_j are the ith and jth component of the strain tensor, respectively, σ_i is the ith component of the stress tensor, and σ_{i+} and σ_{i-} are the components associated with the stress tensor under extension and compression, respectively. In this study, the components of the stiffness matrix were calculated at an applied strain of 5.0×10^{-4} (0.05% of the initial dimension). For the convenience of calculating elastic constants, the stiffness matrix (C_{ij}) was converted into the compliance matrix (S_{ij}). The compliance matrix averaged for nine independent structures is

$$S_{ij} = \begin{bmatrix} 0.1702 & -0.0836 & -0.0533 & 0.0220 & 0.0134 & 0.0955 \\ -0.0836 & 0.1081 & 0.0130 & 0.0094 & 0.0079 & -0.1208 \\ -0.0533 & 0.0130 & 0.0817 & 0.0128 & 0.0082 & 0.0406 \\ 0.0220 & 0.0094 & 0.0128 & 0.2466 & 0.0980 & 0.0159 \\ 0.0134 & 0.0079 & 0.0082 & 0.0980 & 0.1000 & 0.0114 \\ 0.0955 & -0.1208 & 0.0406 & 0.0159 & 0.0114 & 0.2770 \end{bmatrix} (\text{GPa}^{-1})$$

$$(5)$$

Because the PTT crystal is a triclinic system having only a center of symmetry, the compliance matrix con-

Table 4. Elastic constants calculated from the averaged compliance matrix for PTT in crystalline state

Elastic constants	Simulated value
Young's modulus (GPa)	
E_{xx}	5.876 ± 0.002
E_{yy}	9.249 ± 0.001
E_{zz}	12.246 ± 0.004
Linear compressibility (GPa^{-1})	
β_{xx}	0.03331
β_{yy}	0.01157
β_{zz}	0.01535
Volume compressibility (GPa^{-1})	
Δ	0.06023

sists of 21 independent constants, whereas the matrix of isotropic system has only 2 independent constants[34,35]. Young's modulus and linear and volume compressibility were calculated from elements of the compliance matrix by the following relations:

$$E_{xx} = S_{11}^{-1}(\text{GPa}) \quad (6a)$$

$$E_{yy} = S_{22}^{-1}(\text{GPa}) \quad (6b)$$

$$E_{zz} = S_{33}^{-1}(\text{GPa}) \quad (6c)$$

$$\beta_{xx} = S_{11} + S_{12} + S_{13} \quad (7a)$$

$$\beta_{yy} = S_{12} + S_{22} + S_{23} \quad (7b)$$

$$\beta_{zz} = S_{13} + S_{23} + S_{33} \quad (7c)$$

$$\Delta = S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{23} + S_{13}) \quad (8)$$

where E_{ii} and β_{ii} ($i = x, y$, and z) represents Young's modulus and linear compressibility in the direction of each axis, respectively, and Δ denotes volume compressibility. The results are listed in Table 4. It is interesting that the value of E_{zz}, i.e., the modulus in the chain direction, is very small compared to that of perfect crystal for other polymers which is determined in theory or in experiments using x-ray diffraction and Raman spectroscopy[36], indicating that the PTT crystal is very pliable to the external stress. These simulation results for the elastic properties of PTT crystal may explain the experimental observation that the crystal lattice of PTT is easily deformed at small stress[6].

Next, a finite deformation was stepwise imposed to the crystalline structure of PTT up to 50% of strain. When the model was extended under uniaxial extension condition, a stress-strain curve was obtained as shown in Figure 5. The three regions showing a feature of elastic response are observed. The components of elastic moduli in the
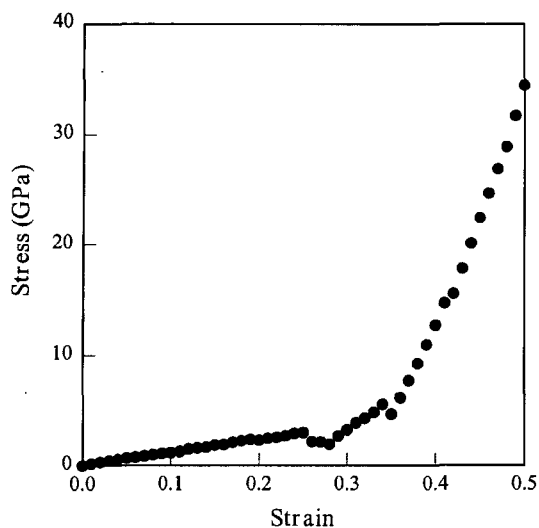
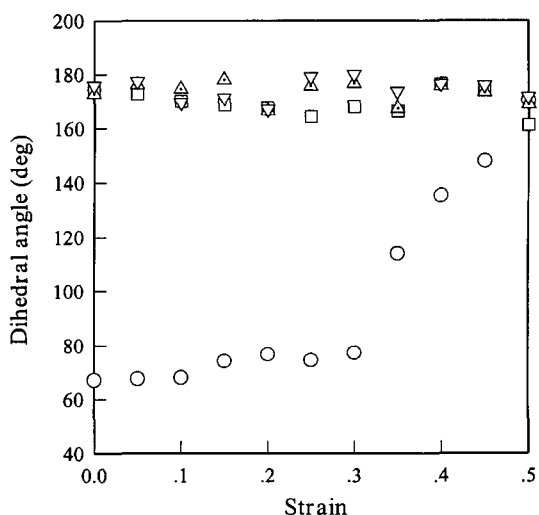**Figure 5.** Stress-strain curve of crystalline structure of PTT.

Figure 6. Change in dihedral angles with strain: ($\bigcirc$), ϕ_1; ($\square$), ϕ_2; ($\triangle$), ϕ_3; (∇), ϕ_4.

first region (0-25% strain) is listed in Table 1. The zz components of elastic moduli in the second (28-34%) and in the third (34-50%) region are 57.723 ± 0.006 (GPa) and 217.415 ± 0.007 (GPa), respectively. In transient regions between the elastic regions, the stress does not increase and rather decreases, indicating that the plastic deformation occurs in these transient regions. The feature of the stress-strain curve in Figure 5 is quite different from that of polymer in amorphous state[25]. In other words, the stress-strain curve of PTT in crystalline state consists of elastic deformation regions except for the narrow transient regions between the elastic regions, whereas the stress-strain curve of PTT in amorphous state shows the plastic deformation following the elastic deformation.

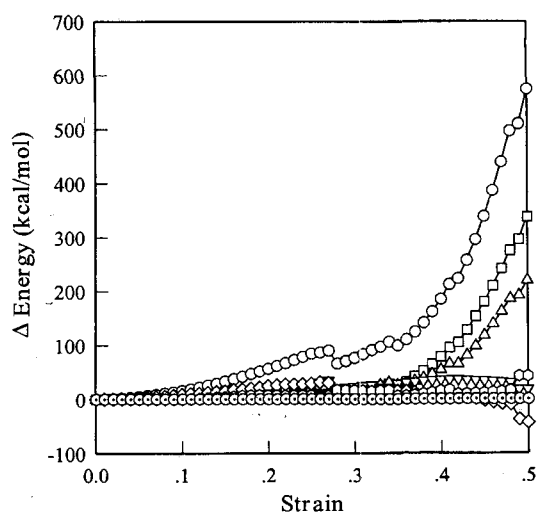During the extension of crystalline structure of PTT, the

Figure 7. Change in energy components with strain: ($\bigcirc$), E_{total}; ($\square$), E_b; ($\triangle$), E_θ; (∇), E_ϕ; ($\diamondsuit$), E_{vdW}; ($\bigcirc$), $E_{Coulomb}$; ($\odot$), $E_{inversion}$.

change in dihedral angles was monitored as shown in Figure 6. The value of dihedral angles such as ϕ_2, ϕ_3, and ϕ_4 remains unchanged in trans state. On the other hand, the value of ϕ_1 slowly increases up to 30% of strain and then rapidly increases. At a glance, the result of Figure 6 indicates that the phase transformation of crystalline structure of PTT can occur after about 30% of strain. The change in dihedral angle of PTT is very different from the change in dihedral angle during the phase transformation of PBT [10]. Furthermore, the stress of PTT strikingly increases as the value of ϕ_1 changes from gauche state to trans state after 30% of strain, as shown in Figure 5, whereas the stress of PBT remains unchanged when the phase transformation from α- to β-phase takes place. This result indicates that the phase transformation of crystalline structure of PTT is very difficult to occur because it accompany with a large increase of stress. In Figure 7, the change in energetic state of PTT in crystalline state is plotted against strain. The total energy remarkably increases after about 35% of strain, which is dominated by two components, i.e., the bond stretching and the valence angle bending. Such a high energy state after 35% of strain may not allow PTT to be in the crystalline state, but may rather cause dislocation of crystalline structure[37,38]. Therefore, it is concluded that the gg conformation in aliphatic part of PTT in crystalline state may not be converted into the tt conformation before dislocation under uniaxial extension condition.

Figure 8 shows the change in angles of unit cell parameter with strain. It is observed that the value of the angles β and γ discontinuously changes at about 28% and 34% of strain where the plastic response appears as shown in Figure 5. Although the phase transformation as occurring
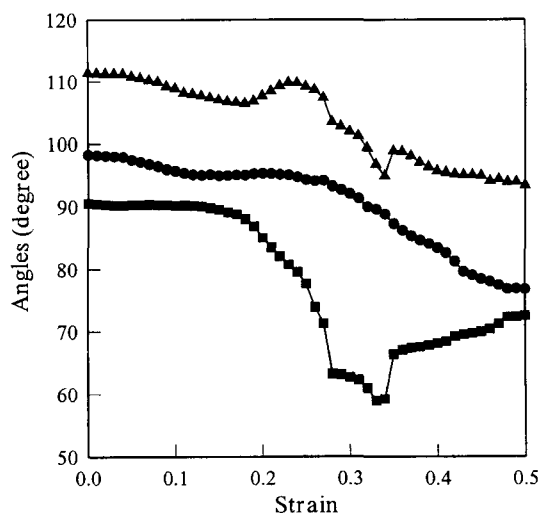
Figure 8. Change in angles of unit cell with strain: ($\bullet$), α; ($\blacksquare$), β; ($\blacktriangle$), γ.

in PBT may not be observed in PTT, the result of Figure 8 indicates that the crystalline structure of PTT is adjusted to the increasing strain through changing the angles of its unit cell. It is concluded that PTT in crystalline state undergoes the plastic deformation under uniaxial extension condition through changing the angles of unit cell parameters instead of the phase transformation from *gg* to *tt* conformation.

Conclusions

The crystalline structure of PTT was successfully prepared by molecular modeling, and its structure was verified by comparing with the structure obtained from the x-ray diffraction experiments. The elastic properties predicted from this simulated structure shows that PTT in crystalline structure is very readily deformed at small strain, as observed in experiment. The dihedral angle of aliphatic part of PTT was changed from *gg* to *tt* conformation after about 30% of strain. Nevertheless, the phase transformation of PTT in crystalline state seems to be very difficult to occur because the energetic state of the simulated structure after 30% of strain is unrealistically high. Such high energy may induce dislocation of crystalline structure rather than phase transformation. It is observed that the plastic deformation of crystalline structure of PTT observed at about 28% and 34% of strain can occur through changing the angles of unit cell.

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