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Molecular Modeling of Bisphenol-A Polycarbonate and Tetramethyl Bisphenol-A Polycarbonate

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Abstract : To efficiently demonstrate the molecular motion, physical properties, and mechanical properties of polycarbonates, we studied the differences between bisphenol-A polycarbonate(BPA-PC) and tetramethyl bisphenol-A polycarbonate(TMBPA-PC) using molecular modeling techniques. To investigate the conformations of BPA-PC and TMBPA-PC and the effect of the conformation on mechanical properties, we performed conformational energy calculation, molecular dynamics calculation, and stress-strain curves based on molecular mechanics method. From the results obtained from conformational energy calculations of each segment, the molecular motions of the carbonate and the phenylene group in BPA-PC were seen to be more vigorous and have lower restriction to mobility than those in TMBPA-PC, respectively. In addition, from the results of radial distribution function, velocity autocorrelation function, and power spectrum, BPA-PC appeared to have higher diffusion constant than TMBPA-PC and is easier to have various conformations because of the less severe restrictions in molecular motion. The result of stress-strain calculation for TMBPA-PC seemed to be in accordance with the experimental value of strain-to-failure ~4%. From these results of conformational energy calculations of segments, molecular dynamics, and mechanical properties, it can be concluded that TMBPA-PC has higher modulus and brittleness than BPA-PC because the former has no efficient relaxation mode against the external deformations.

Introduction

Molecular modeling is a method which can analyze the correlation of 3-dimensional structure

and physico-chemical properties of molecules and estimate molecules with desired properties.¹ At first molecular modeling techniques were applied only to the estimation of structures with geometry optimization through energy minimization and molecular dynamics methods. However, recent

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developments in calculation speed of computer and graphical technology enable complex quantum chemical calculations to make an output with accurate properties. Although there are some limits to the application, the results obtained from molecular modeling could be compared with empirical data such as NMR, X-ray, etc., and the latter can be corrected and reanalyzed by the former.^{2,3}

Polycarbonates are well known as an engineering plastic that have excellent mechanical properties in both room and low temperatures. Molecular simulations and many other investigations on the motion in polycarbonates have been made.¹⁻²⁵ It has been reported that one of the excellent mechanical properties is good impact resistance at low temperature, and it has been suggested that this toughness is related to secondary relaxation over a wide range of temperatures through the dynamic mechanical measurement and NMR studies on the secondary relaxation phenomena. Generally, the mechanical properties of polymers are closely related to the conformations of molecules, so it is useful to understand the orientation of chains and molecular motions. Yee and Jho have synthesized multiblock copolycarbonates as a model copolymer system for studying the secondary relaxation motion in bisphenol-A polycarbonate.¹⁰ They have proposed the cooperative motion of the carbonate and phenylene groups as the motions responsible for the secondary relaxation and strength, although the earlier investigations suggested the local π -flip motion of the carbonate or phenylene group as the source of the secondary relaxation.⁶ Also, in the study of a series of block copolymers, Yee and Xiao suggested that the interchain interactions are the dominant factor of cooperative relaxation of polycarbonate.⁵

To efficiently demonstrate the molecular motion, physical properties and mechanical properties of polycarbonates, we studied the difference between bisphenol-A polycarbonate (BPA-PC) and tetramethyl bisphenol-A polycarbonate (TMBPA-PC) on the molecular scale using molecular modeling techniques. TMBPA-PC has a similar structure to BPA-PC except the four methyl groups on the phenyl rings, and it shows higher T_g and strength than BPA-PC. The object of this study is to deter-

mine the conformation of BPA-PC and TMBPA-PC and the effect of the conformation on mechanical properties. Also, to investigate the relationship between physical properties and mechanical properties, the conformation and molecular motions of BPA-PC and TMBPA-PC were determined and compared.

Experimental

Force field of molecular mechanics and dynamics. A carefully chosen force field plays a significant role in the study of interaction between large molecules.² For the application to polycarbonates, previously developed force fields such as AMBER, MM2, Charm and Dreiding force field, etc., were considered.²⁷⁻²⁹ But, there were no parameters about carbonate groups in AMBER and Charm, and the calculated energies at some specific rotation angle of phenyl ring were incorrect as compared with the ab-initio calculation.²⁵ Therefore, in this study, Dreiding force field which is proper to the study of interaction between the phenyl rotation and carbonate groups was chosen for the molecular mechanical and dynamic calculations.²⁹ Here the energy is given as follows;

$$E_{total} = E_{val} + E_{nb} \quad (1)$$

$$E_{val} = E_B + E_A + E_T + E_I \quad (2)$$

$$E_{nb} = E_{vdw} + E_Q + E_{hb} \quad (3)$$

General potential energy, E_{total} (Eq. 1), consists of bonded energies (E_{val}) and nonbonded energies (E_{nb}). The first term of bonded energy is a bond stretching (E_B) which represents the energy of bond deformation from equilibrium distance. The second term, E_A , is for the angle bending which is related to the deformation of angles from the equilibrium state, and takes a second order form. The third term, E_T , is associated with the tendency of dihedral angles to have a certain n-fold symmetry and to have minimum energy for the gauche⁺-, gauche⁻-, or trans-conformation, etc. The fourth term, E_I , is the inversion term. The nonbonded energy, E_{nb} , is consisted of van der Waals interactions (E_{vdw}), electrostatic interactions (E_Q) and hydrogen bonding (E_{hb}). More information on the energy functions is found in the paper by

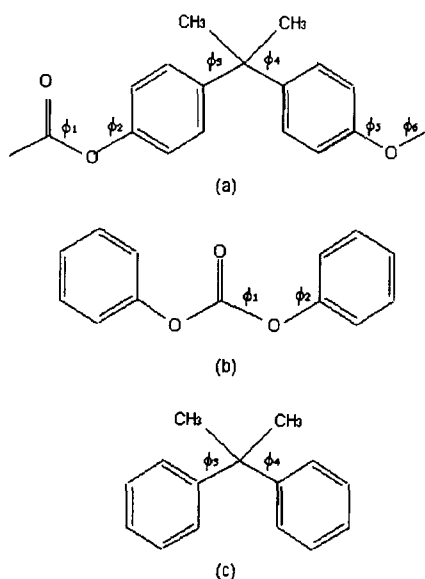


Figure 1. Definition of torsional angle parameters for schematic structures of (a) bisphenol-A polycarbonate (BPA-PC), (b) diphenyl carbonate(DPC), and (c) 2,2-diphenylpropane(DPP).

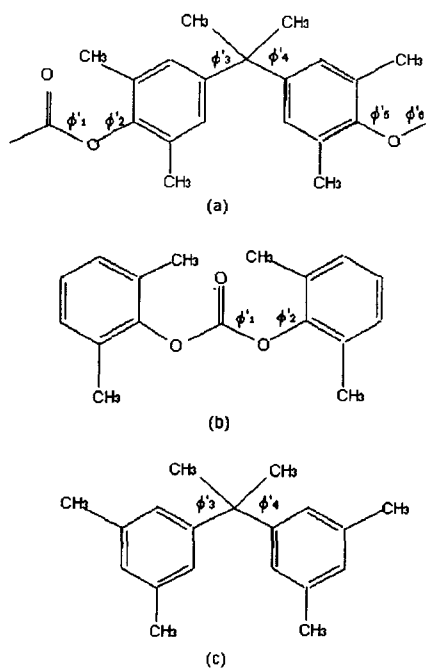


Figure 2. Definition of torsional angle parameters for schematic structures of (a) tetramethylbisphenol-A polycarbonate(TMBPA-PC), (b) 3,3',5,5'-tetramethyldiphenyl carbonate(TMDPC), and (c) 2,2',6,6'-tetramethyl-4,4'-diphenylpropane(TMDPP).

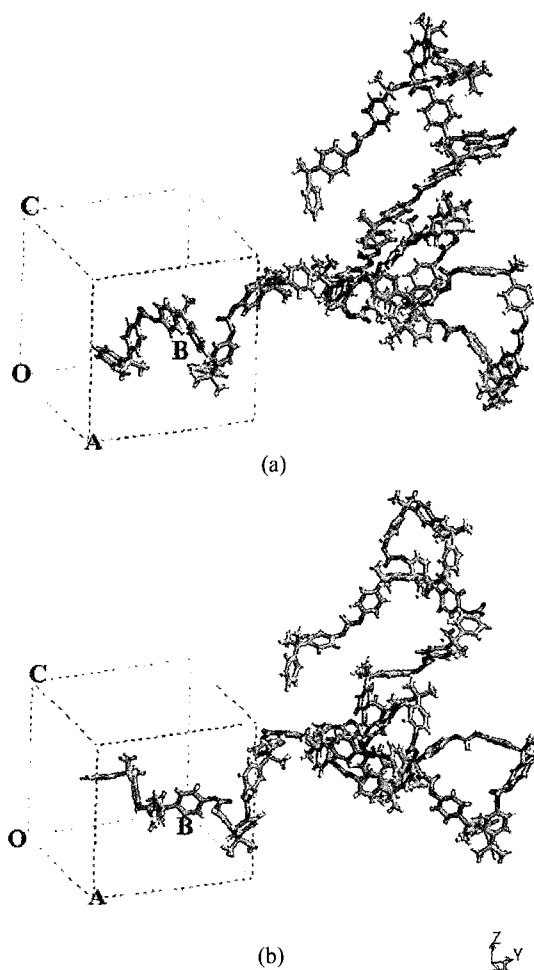


Figure 3. A typical model structure of amorphous BPA-PC; (a) as generated and (b) after equilibration process.

Goodard *et al.*²⁹

Model System.

Segment Model : The segments shown in Figures 1 and 2 were used to identify the most stable conformation of BPA-PC and TMBPA-PC and verify the feasibility of the force field.

Preparation of Amorphous Sample : All the calculation processes were carried out with IRIX 6.3 workstation and, to deal effectively with polymer system, Cerius² 3.5 package. Cerius² was appropriate for this study concerning its outstanding function for the estimation of molecular structure, molecular motions, various properties, and empirical data.

Preparing the initial amorphous polymer sam-

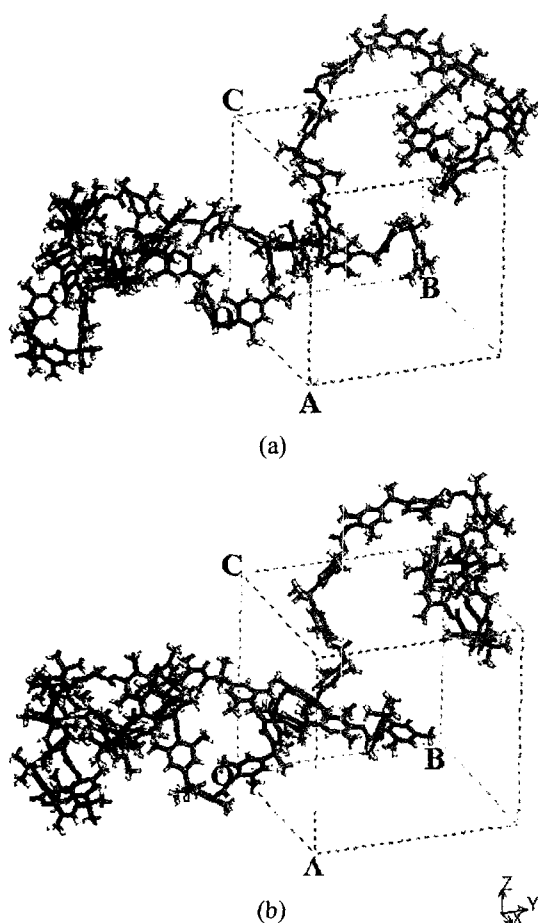


Figure 4. A typical model structure of amorphous TMBPA-PC; (a) as generated and (b) after equilibration process.

ple is similar to that proposed by Fan and Hsu.^{30,31} The initial amorphous polymer sample for the measurements of molecular dynamics was prepared with repeated energy minimization and molecular dynamics simulation under the periodic boundary condition and NVT ensemble at 500 K and then 300 K. In molecular dynamics process, the total time was 300 ps at 500 K and 150 ps at 300 K at an interval of 0.001 ps. After the molecular dynamics process, energy minimization was carried out with energy convergence of 0.01 kcal/mol for the stable condition.

Flory's rotational isomeric state(RIS) method based on the conformational energy calculation of dimer was adopted for the initial configuration of the amorphous sample.^{23,32} Figures 3 and 4

Table I. Cell parameters of BPA-PC and TMBPA-PC

Sample	BPA-PC		TMBPA-PC	
	Before	After	Before	After
Equilibration				
a(Å)	19.516	20.015	21.589	22.252
b(Å)	19.516	19.767	21.589	22.123
c(Å)	19.516	19.952	21.589	21.46
α (degree)	90	91.10	90	90.29
β (degree)	90	88.84	90	88.56
γ (degree)	90	88.4	90	90.49
density(g/cm ³)	1.2	1.14	1.08	1.04

show typical model structures of amorphous samples initially generated and after the equilibrium process, respectively. Table I summarizes the cell parameters of BPA-PC and TMBPA-PC.

Molecular Dynamics. Compared with the energy minimization process, molecular dynamics simulation can raise the probability of access to the lowest energy state by overcoming the energy barrier which may be a restriction in the energy minimization. Also, it may provide informations about solvent-effect and molecular motions in real time.³³⁻³⁶

In this study, to consider the state of each repeating unit and molecular motions of BPA-PC and TMBPA-PC, molecular dynamics were performed at 300 K for 100 ps. Spline switching function with cutoff distance of 8.0 Å was employed in non-bonded interaction under constant temperature and constant volume(NVT) at time step of 0.001 ps.³³

Mechanical Properties. To obtain the calculated stress-strain curve of BPA-PC and TMBPA-PC, the strain ϵ was applied to the sample in each case. In this method, a strain was imposed by fixing the c axis at a value corresponding to this strain, and the other cell parameters as well as the coordinates are optimized. The stress is obtained from the corresponding component of the internal stress tensor.^{15,20}

Initial structure of each sample for the measurement of mechanical properties was prepared from initial amorphous structure with NPT ensemble at 300 K, total 100 ps. The stress of the prepared sample was measured up to 10% of strain along

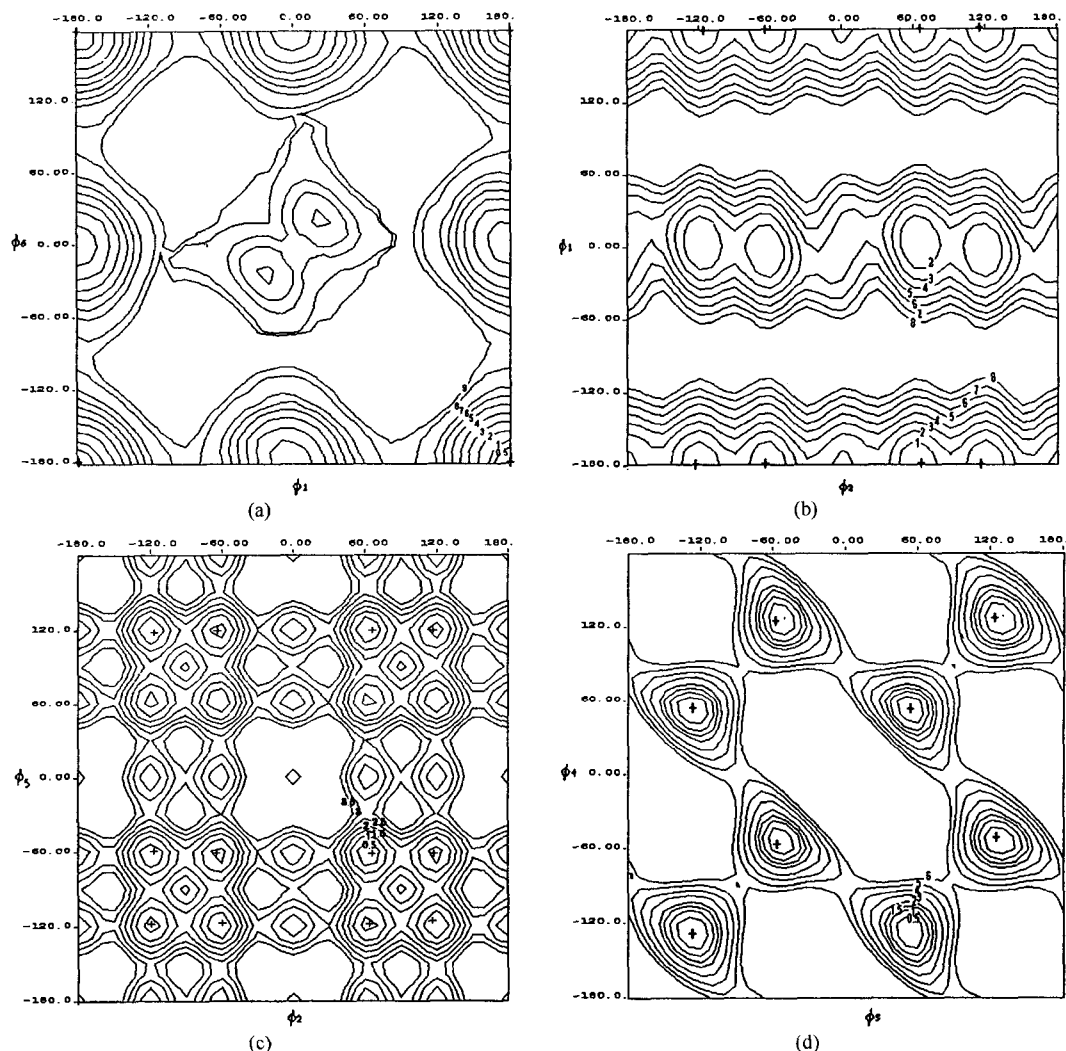


Figure 5. Conformational energy contours in BPA-PC. Local minima are marked as +, and the unit for the energy lines kcal/mol. (a) ϕ_1 vs ϕ_6 , (b) ϕ_1 vs ϕ_2 , (c) ϕ_2 vs ϕ_5 , and (d) ϕ_3 vs ϕ_4 .

the c axis.

Results and Discussion

Conformational Energy Calculation. To obtain the most probable conformations of BPA-PC and TMBPA-PC, conformational energy calculation was carried out at all the defined torsions. Generally, the results of conformational energy calculation may provide useful information about conformation of the whole chain as well as its segments.

2D energy contour maps derived from the defined torsions of BPA-PC are shown in Figure 5. In each calculation, the specified pair of dihedrals are constrained at the desired values and the rest of the structure is allowed to move freely to minimize the energy.¹⁵ As shown in Figures 5a and 5b, the carbonate group of diphenyl carbonate (DPC) predominantly assumes trans-trans and trans-cis conformations but avoids cis-cis conformation. Also, the carbonate groups of BPA-PC mostly exist in trans-trans conformation, because it is more stable than cis-cis conformation. Figure 5c

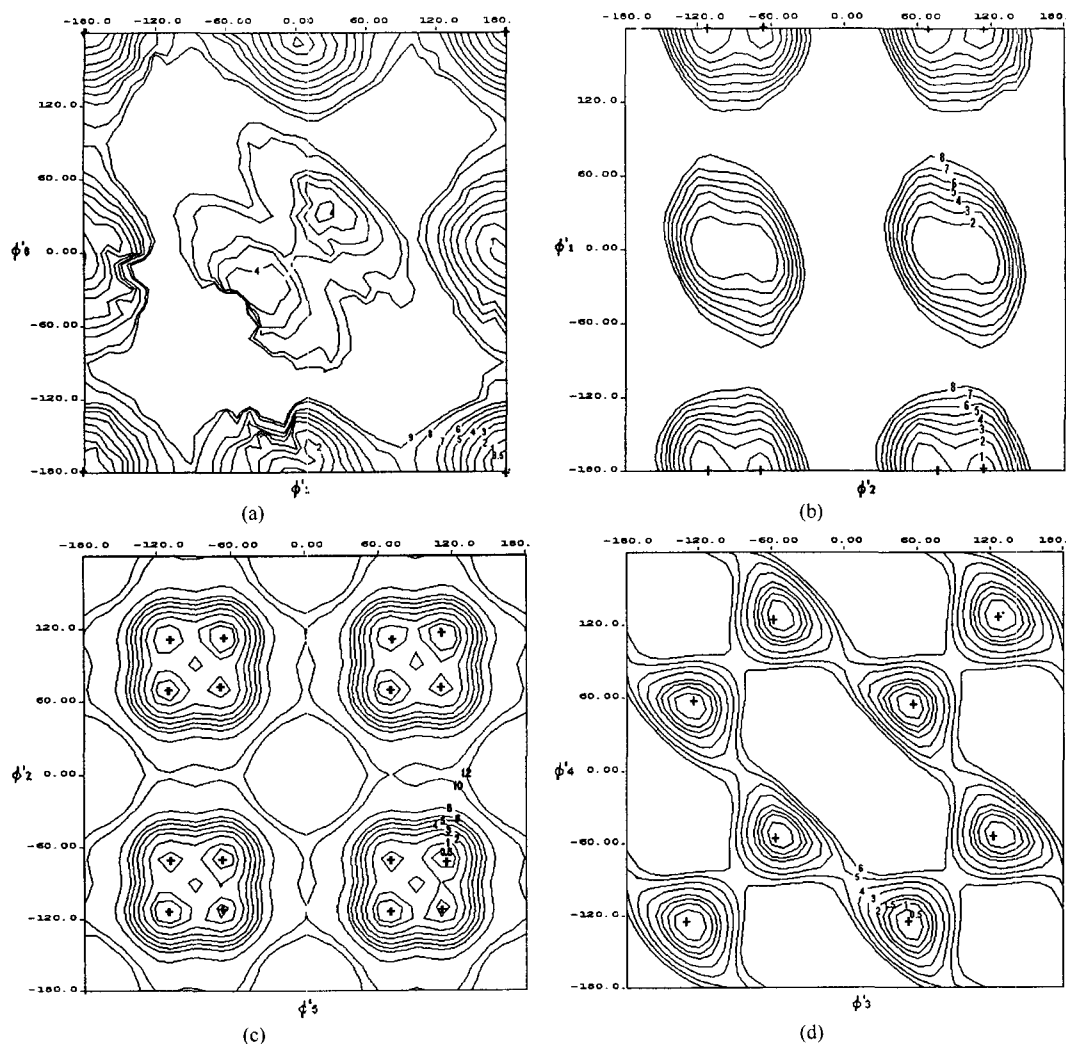


Figure 6. Conformational energy contours in TMBPA-PC. Local minima are marked as +, and the unit for the energy lines kcal/mol. (a) ϕ_1' vs ϕ_6' , (b) ϕ_1' vs ϕ_2' , (c) ϕ_2' vs ϕ_5' , and (d) ϕ_3' vs ϕ_4' .

shows the energy contour map of the two phenylene groups of DPC. It can be pointed out that the local minima of phenylene groups exist around $\pm 70^\circ$ and $\pm 110^\circ$, and the phenylene group is tilted against the main chain because the energy is larger by about 2 kcal/mol. As shown in Figure 5d, the result of energy contour map of the two phenylene groups of 2,2-diphenylpropane (DPP) reveals the conformation of phenylene. The local minima of phenylene groups exist around $\pm 60^\circ$ and $\pm 120^\circ$ and it is the same as phenylene groups of DPC. These results show that the carbonate group exists in the trans and

cis states, while the trans state is dominant, and the phenylene groups are tilted around $\pm 70^\circ$ and $\pm 110^\circ$ against the main chain.

Energy contour maps from the conformational results calculated from TMBPA-PC are shown in Figure 6. Figure 6a shows the conformational energy contour of ϕ_1' and ϕ_6' in TMBPA-PC. The carbonate groups of BPA-PC mostly exist in trans-trans conformation because it is more stable than cis-cis conformation which is in accordance with the result of DPC.

On the other hand, for the carbonate group, comparing Figure 5b and Figure 6b, the local

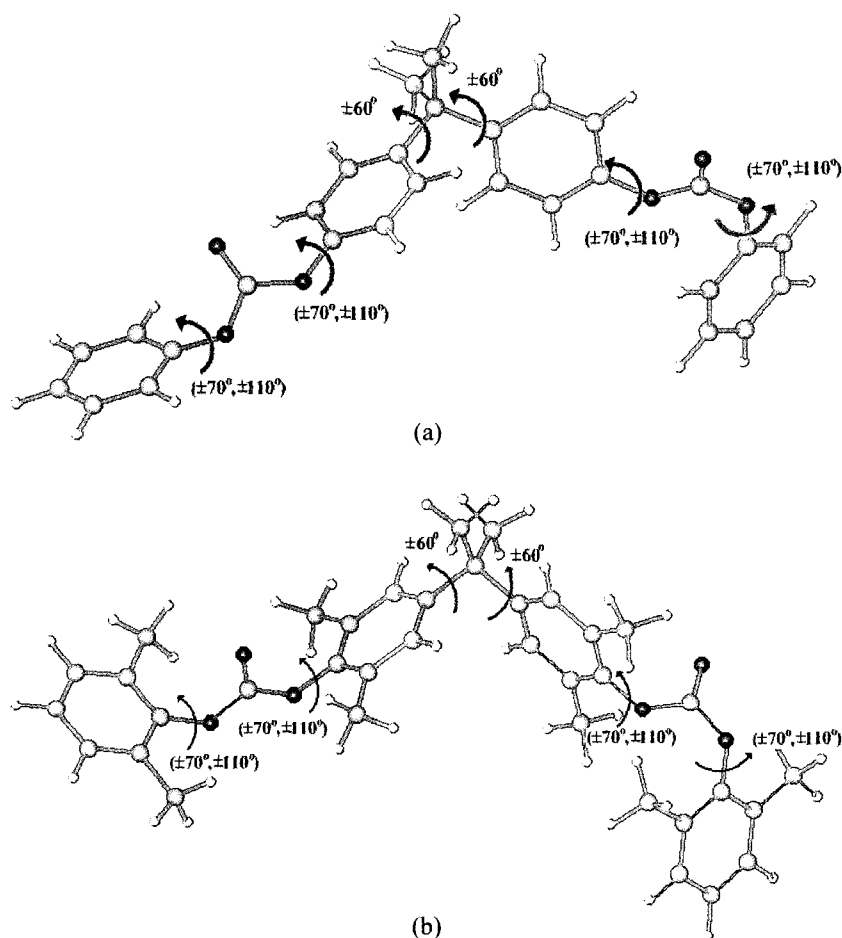


Figure 7. Three dimensional structures of BPA-PC(a) and TMBPA-PC(b) constructed based on the results of conformational energy calculation of segments.

minima appear to be located at similar positions, but the distributions are quite different. That is, while ϕ_2' of DPC is widely distributed around $\pm 180^\circ$ and $\pm 0^\circ$, ϕ_2' of TMDPC is more restricted around $\pm 110^\circ$ and $\pm 70^\circ$. From the conformational energy calculation of phenylene group of TMDPC (Figure 6c), it has been found that the local minima are located near $\pm 110^\circ$ and $\pm 70^\circ$ as in DPC. But the energy distribution of the phenylene group of TMDPC is more restricted than DPC. Because the methylene groups substituted on the phenylene group of TMDPC affect the rotation of phenylene group, TMDPC appears to have more restricted conformation than DPC.

In the case of the rotation of the phenylene groups, 2,2',6,6'-tetramethyl-4,4'-diphenylpropane

(TMDPP) shows similar behavior to DPP. The methylene groups attached to the phenylene rings in TMDPP were seen to have little effect on the rotation of phenylene group around ϕ_3' and ϕ_4' .

The conformational energy calculation for the segment of BPA-PC and TMBPA-PC showed good agreement with the results from previously reported ab-initio method.²⁵ Putting together these results of conformational energy calculations, the most probable conformations of BPA-PC and TMBPA-PC are shown in Figure 7.

Molecular Dynamics (MD). Figures 8~12 show the results which have been obtained from the trajectory of MD runs. To track qualitatively and quantitatively the motions of polymer chains at molecular level, the analysis was made separat-

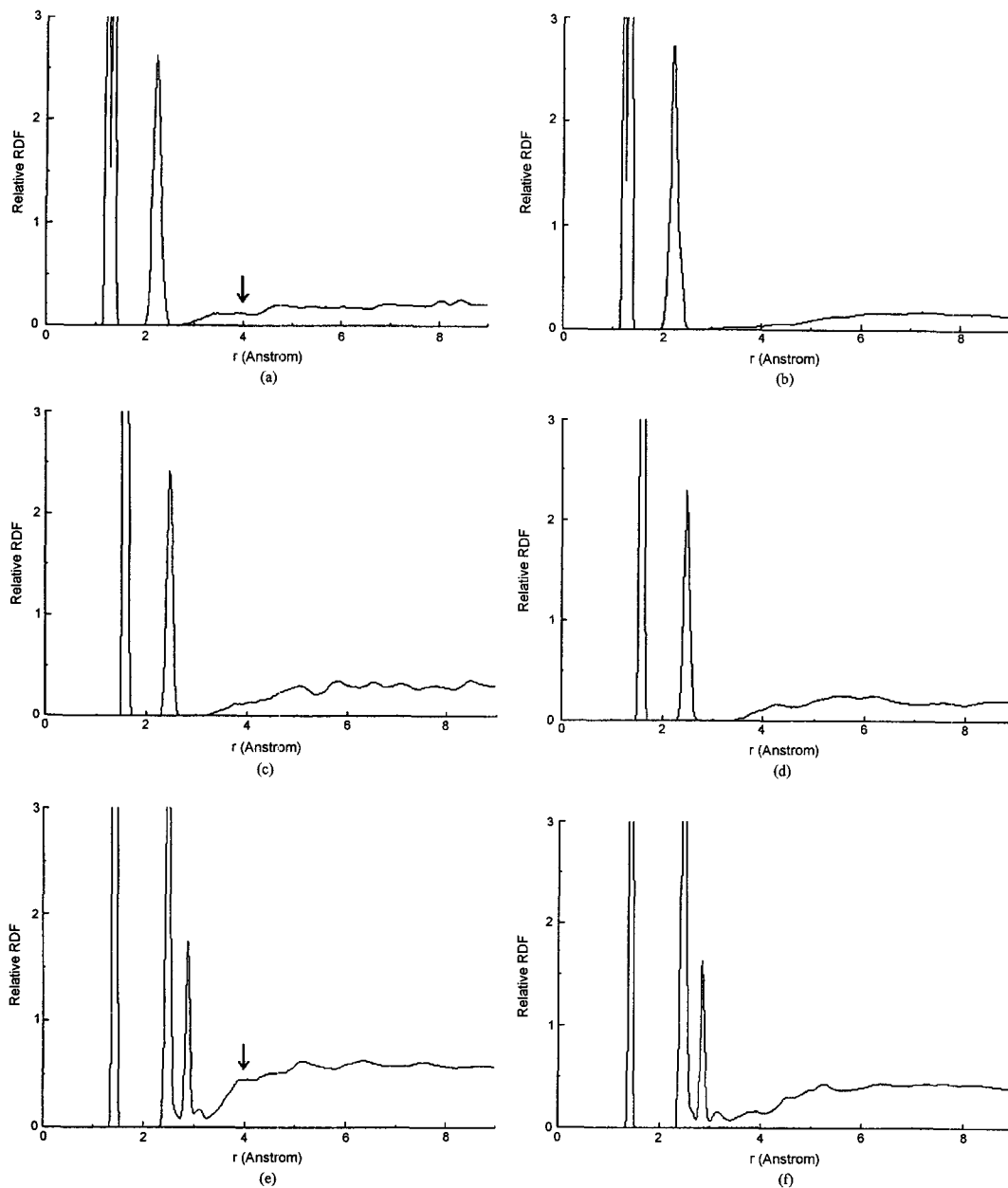


Figure 8. Radial distribution function(RDF) for BPA-PC and TMBPA-PC. (a) the carbonate groups in BPA-PC, (b) the carbonate groups in TMBPA-PC, (c) the methyl groups in BPA-PC, (d) the methyl groups in TMBPA-PC, (e) the phenylene groups in BPA-PC, and (f) the phenylene groups in TMBPA-PC.

edly on the carbonate group, methyl group, and phenylene group.

Figures 8 and 9 show the radial distribution function(RDF) and structural factor(STF) of carbonate, dimethyl, and phenyl groups in the DPP

and TMDPP. The RDF measures how atoms organize themselves around one another, so called "local structure". It plays a central role in statistical mechanical theories of dense substances, it can be extracted from X-ray and neutron diffraction

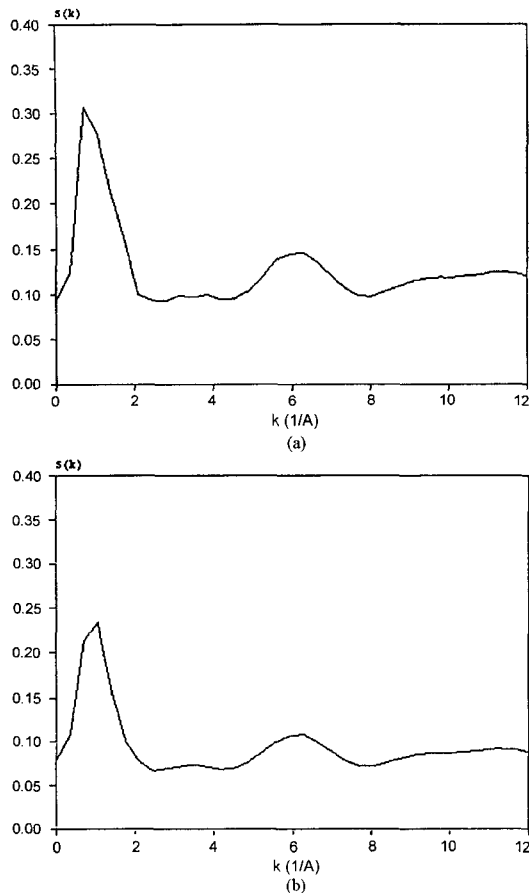


Figure 9. Structural factor(STF) for the carbonate groups. (a) STF of BPA-PC and (b) STF of TMBAP-PC.

experiments. The RDF is defined by

$$\rho g(r) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \delta[r - r_{ij}] \right\rangle \quad (4)$$

Here N is the total number of atoms, ρ is the number density, r_{ij} is the vector between centers of atoms i and j , and the angular brackets represent a time average.³⁴

The STF provides some information on the whole structural properties such as packing, ordering, compressibility and phase transition. It is calculated from the radial distribution function through the following equation.

$$S(k) = 1 + (4\pi\rho/k) \int_0^{\infty} dr \sin(kr) r [g(r) - 1] \quad (5)$$

Here k is the wave vector and ρ is the atom density.³⁴

Figures 8a and 8b show the RDF for carbonate groups in BPA-PC and TMBPA-PC, respectively. The peaks observed at 1.3 and 2.2 Å respectively represent the distance between atoms one bond and two bonds apart in the carbonate group. It can be seen that the RDF in Figure 8a is distributed more wider and stronger around 3~4 Å than that in Figure 8b. This can be interpreted as that BPA-PC has greater chain mobility and flexibility, so there are higher probability for the neighboring carbonate groups to come closer compared with TMBPA-PC.

The RDF results for the methyl groups are shown in Figures 8c and 8d. The peaks around 1.3 and 2.5 Å appear from within the methyl group itself and the broad peaks above 4 Å are similar in shape and amplitude for BPA-PC and TMBAP-PC. It suggests that the effect of the methyl groups on the chain mobility and conformation is respectively small. This tendency was also clearly observed in the conformational energy calculations(Figures 5d and 6d).

In Figures 8e and 8f for the phenylene groups of BPA-PC and TMBPA-PC, the peaks around 1.4~2.8 Å arise from within the phenylene groups. This can be shown that the distance between the first atom and the second atom($r_{1,2}$) is 1.4 Å, that for the first and third ones($r_{1,3}$) is 2.4 Å, and that for the first and fourth ones($r_{1,4}$) is 2.8 Å. From the peaks above ~4 Å, one can see that BPA-PC has more intense RDF values. This result may be interpreted as that BPA-PC has the higher possibility of neighboring of phenylene groups in the chain.

Also, the STF results for the carbonate, phenylene, and methylene groups were seen to agree well with the above interpretation(Figure 9). Though computer simulation experiments can effectively deal with the phenomena for short duration of nano scale, and as a result there are some limitations on quantitative analysis of the whole polymer chain,⁶ these analyses of the distributions of each portion of the polymer could provide us useful informations on the local chain mobility.

The self-diffusion constant which is calculated

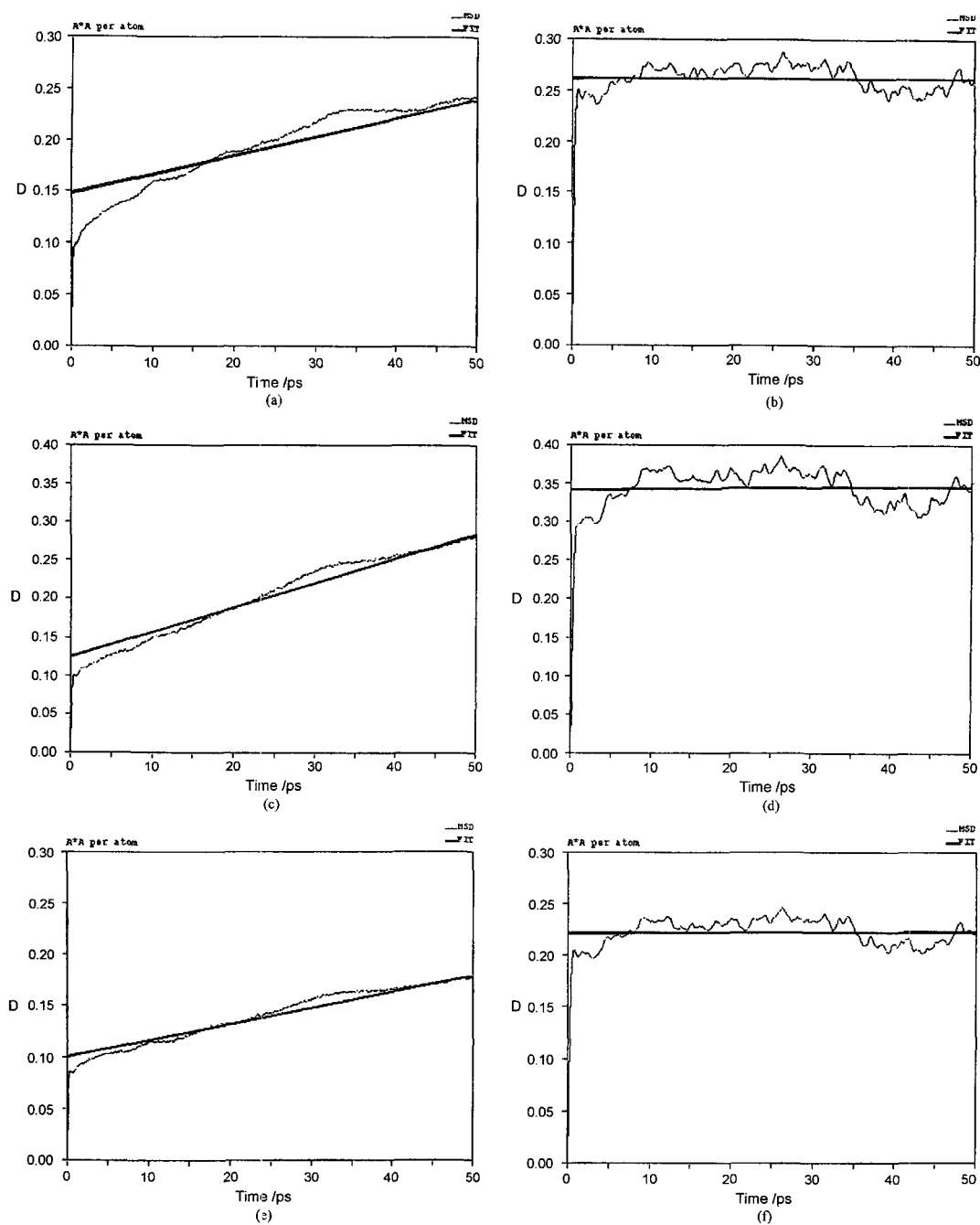


Figure 10. Mean square displacements(MSD) for BPA-PC and TMBPA-PC. The solid line is the result of fitting to calculate the self diffusion constants. (a) the carbonate groups in BPA-PC, (b) the carbonate groups in TMBPA-PC, (c) the methyl groups in BPA-PC, (d) the methyl groups in TMBPA-PC, (e) the phenylene groups in BPA-PC, and (f) the phenylene groups in TMBPA-PC.

from the mean-square displacement(MSD) can be defined by

$$D = \frac{1}{6N} \lim_{t \rightarrow \infty} \frac{d}{dt} \left\langle \sum_i^N [r_i(t) - r_i(0)]^2 \right\rangle \quad (6)$$

Table II. Diffusion Constants of BPA-PC and TMBPA-PC.(unit : $10^{-3}\text{\AA}^2/\text{ps}\cdot\text{atom}$)

Group	BPA-PC	TMBPA-PC
Carbonate	0.30	~0
Methyl	0.54	~0
Phenyl	0.26	~0

Here N is the number of atoms, r is the position of particle and t is the time.^{34,39} Figure 10 shows the MSD of the carbonate, phenylene, and methylene groups. These results indicate that the self-diffusion constants(SDC) of BPA-PC is larger than TMBPA-PC in all of the portions considered.

The SDC of BPA-PC and TMBPA-PC are reproduced in Table II. From this result, one can see that the atomic motions of the TMBPA-PC chains are restricted to small scales because of the methylene groups substituted on the phenylene. These limited atomic motions of TMBPA-PC can be considered to be closely related to its hard but brittle mechanical properties. It is to be noted from Table II that, in the case of BPA-PC, the methyl group has the highest mobility, followed by the carbonate and the phenylene group. Generally, it is easy to introduce the concept of correlation time as in NMR (nuclear magnetic resonance) for the evaluation of the molecular motion. One NMR study for a polyester copolymer showed that the methylene group undergoes the fastest movement, followed by the phenylene, and the carbonyl group.³⁸ In our case of polycarbonates, however, because of the single bonded O which increases the chain mobility between phenylene and carbonyl groups, the carbonate group shows faster movements than the phenylene group. Similarly, the diffusion constants of the carbonate and the phenylene groups are on the same order while that of the methylene group is larger than them. Apparently this indicates that the phenylene and the carbonate groups move relatively slowly along with the whole chain, and the methyl group moves more flexibly than the phenylene and the carbonate groups.

Velocity autocorrelation function(VACF) and power spectrum allow informations about dynamical, vibrational, and thermal properties at a given temperature. VACF is defined by the fol-

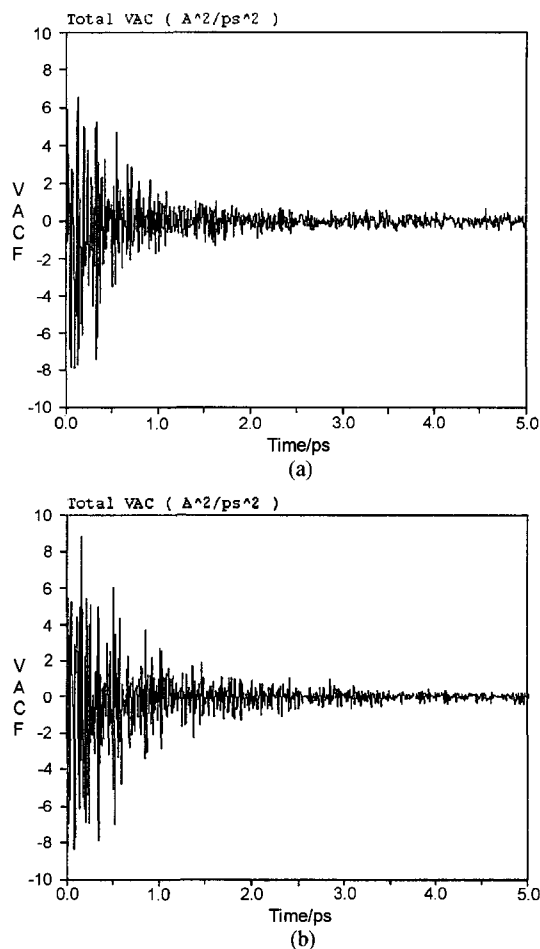


Figure 11. Velocity autocorrelation function(VACF) of the phenylene groups. (a) BPA-PC and (b) TMBPA-PC.

lowing equation.

$$C(m) = \frac{1}{n} \sum_{i=1}^n V(m+i) \times V(i) \quad (7)$$

Here m is the maximum data points allowed in the VACF calculation, n is the data number, i is the interval of calculation and V is the velocity. Power spectrum is obtained from the Fourier transform of VACF.^{34,39}

The power spectra and VACF of the phenylene groups in BPA-PC and TMBPA-PC are shown in Figures 11 and 12. The carbonyl and methyl groups gave similar results. It can be seen that the VACF of BPA-PC (Figure 11a) converges relatively

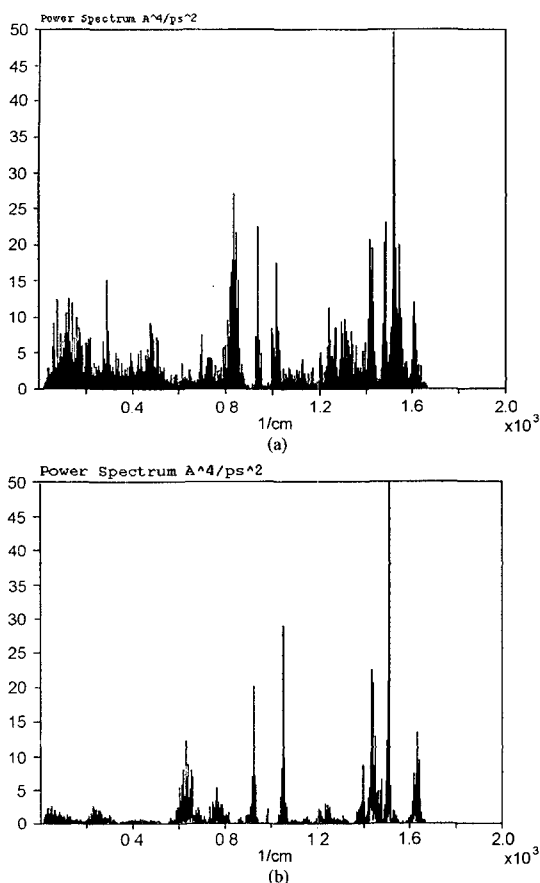


Figure 12. Power spectrum(POWS) of the phenylene groups. (a) BPA-PC and (b) TMBPA-PC.

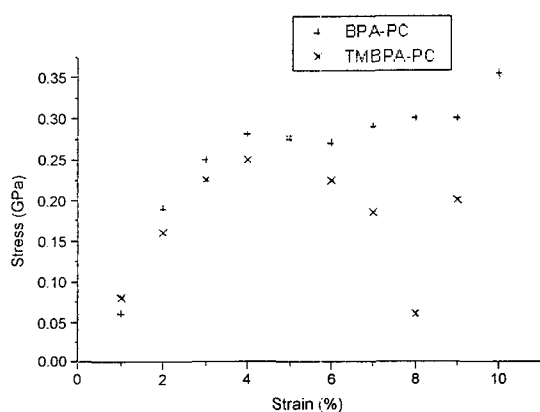


Figure 13. The calculated stress-strain curves of BPA-PC and TMBPA-PC.

more rapidly. Considering this result of VACF, it is obvious that the groups of BPA-PC move more

rapidly than those of TMBPA-PC. This apparently indicates that the molecular motion of BPA-PC is more vigorous and diffusive than TMBPA-PC. It was observed from the rate of convergence that the methylene group underwent the fastest movement, followed by the phenylene and the carbonyl groups. This is in agreement with the results of RDF and STF. From the results of the power spectrum, it is apparent that the intensities for BPA-PC are more sharp and dense while these for TMBPA-PC appear scattered at the low frequency region. This series of experiments, then, show clearly that the molecular motion of BPA-PC has higher diffusion constant than TMBPA-PC and BPA-PC is easier to have various conformations because of low restrictions in molecular motion.

Mechanical Properties. The stress-strain curves of BPA-PC and TMBPA-PC calculated by the molecular mechanics method are shown in Figure 13, indicating the mechanical property and yielding behaviour.

In the case of BPA-PC, the calculated stress increases up to 4% strain and then levels off. On the other hand, in the case of TMBPA-PC, it seemed to follow a similar curve up to 4% strain, but then it exhibits irregular stress-strain behavior. In actual samples of TMBPA-PC, they are generally broken at 4% strain because of the high modulus and brittleness.³⁷ But, it is usually impossible to show a rupture of specimen in molecular modeling, so we consider that the irregular behavior after 5% strain under consideration may be closely related to the physical rupture of TMBPA-PC.

Conclusion

To elucidate the dependency of properties on the conformations of BPA-PC and TMBPA-PC on the molecular level, we performed conformational energy calculation and molecular dynamics calculation based on molecular mechanics method.

From the results obtained from the conformational energy calculation of each segment, one may conclude that the molecular motions of the carbonate and the phenylene groups in BPA-PC are more vigorous and have lower restriction to mobility than those in TMBPA-PC. Both the carbonate groups of BPA-PC and TMBPA-PC mostly

exist in trans-trans conformation, but those of BPA-PC has lower energy than those of TMBPA-PC. Also, the phenylene groups of BPA-PC and TMBPA-PC whose motion is considered as one of the dominant molecular motions in polycarbonates have the local minima around $\pm 110^\circ$ and $\pm 70^\circ$, but TMBPA-PC is seen to have more restricted conformation than BPA-PC because the methylene groups substituted on the phenylene groups of TMDPC affect the rotation of the phenylene group.

The results of molecular dynamics effectively corroborate the conformational energy calculation of segments. The radial distribution function shows that BPA-PC has higher chain mobility and flexibility, so it has more possibility of the carbonate groups being in the neighbor than TMBPA-PC. In addition, the results of the mean-square displacement and self-diffusion constant calculation show that the atomic motions of the TMBPA-PC chains are restricted to small scale because of the methylene groups substituted on phenylene, and the phenylene and the carbonate groups move more slowly along with the whole chain. From the results of velocity autocorrelation function and power spectrum, we found out that the molecular motions of BPA-PC show higher diffusion constants than TMBPA-PC and that BPA-PC is easier to have various conformations because of low restrictions in molecular motion.

The result of stress-strain curve calculations which can explain the mechanical properties was in accordance with the general behavior of rupturing of TMBPA-PC at $\sim 4\%$ strain. From these results of conformational energy calculations of segments, molecular dynamics and mechanical properties, it has been found that TMBPA-PC has higher modulus and brittleness than BPA-PC because it has no efficient relaxation mode against the external deformations.

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