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MOLECULAR MODELING STUDIES ON THE CONFORMATIONAL PROPERTIES OF POLYCARBONATES

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Abstract

This paper describes the studies on the conformations and conformational properties of bisphenol A polycarbonate (BPAPC) and structurally modified polycarbonates using Molecular Mechanics and RIS Metropolis Monte Carlo method (RMMC). Conformational analysis about the C_α atom of various polycarbonates indicated that the freedom of rotation of the backbone phenyl rings is restricted by structural modification. Conformational properties like root mean square end to end distance, root mean square radius of gyration, persistence length and characteristic ratio were derived using RMMC method. The low values of the computed characteristic ratios (2.7-3.0) indicate compact average conformations for the substituted polycarbonate chains. RMMC simulations for BPAPC were carried out in the temperature range of 300-500 K and the temperature coefficient of the mean square end to end distance was found to be - 0.415 x 10^{-3} deg $^{-1}$ which agrees with the experimental value.

Keywords

Conformational analysis, Rotational Metropolis Monte Carlo method, Polycarbonates, Substituted polycarbonates, Conformational properties.

Introduction

Polycarbonates are an extremely useful and industrially important class of engineering thermoplastics because of many desirable properties like high Tg, heat resistance, dimensional stability, toughness and transparency. The interplay between the physical properties and the molecular structure for these polymers has been the subject of several theoretical and experimental studies (Hutnik *etal.* 1991).

The chain dimensions as given by root mean square end to end distance and radius of gyration represent the most important conformational properties of a polymer chain. Experimentally, the chain dimensions are determined by dilute solution measurements involving light scattering and viscometry. Theoretically, RIS theory (Flory, 1969) has been applied widely to study the single chain conformational statistics in the unperturbed state. RIS approach involves the derivation of statistical weights for discrete rotational states for different bonds in the polymer chain. RMMC method (Honeycutt, 1998) enables the calculation of unperturbed chain dimensions of polymer chains in the melt or in theta state. It calculates the conformational properties of polymer chains from atomistic simulations.

Molecular modeling studies on the conformation of substituted polycarbonates have received little attention when compared to that of BPAPC (Sundararajan, 1989). This work is part of our efforts to elucidate the effect of structural modification on the conformational characteristics of BPAPC. The substituent effect on the conformational flexibility of the backbone phenyl rings in substituted polycarbonates was studied by Molecular Mechanics and conformational properties of the polycarbonate single chains were derived using RMMC method.

Methodology

Conformational Analysis

Figure 1 depicts the repeat unit of BPAPC and the structure of bisphenols used for the present study. Conformational analysis by force field energy minimization technique was carried out for the various polycarbonate segments.

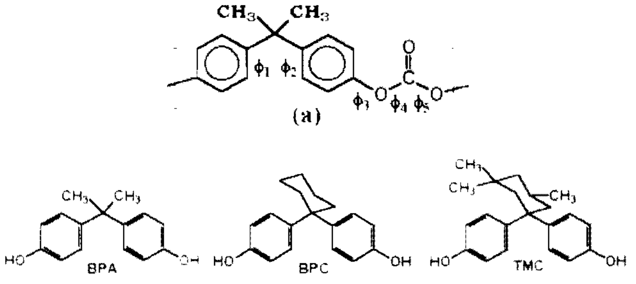

Figure 1. (a) Repeat unit of BPAPC (b) BPA and substituted bisphenols.

PCFF parameters were used to calculate the potential energy surface. Potential energy was calculated as the sum of bonded and non-bonded interactions. It included a quadratic polynomial for bond stretching and angle bending and a three term Fourier expansion series for torsional motions. Coulombic terms and a 9-6 VDW potential was used to describe the non-bonded interactions.

The potential energy surface was scanned from -180 to 180° in 5° increments. The dihedrals ϕ_1 and ϕ_2 were constrained at discrete values by applying a force constant of 1000 kcal/mol rad^2 and the rest of the molecule was allowed to relax till the gradient of energy was less than 0.001 kcal/mol Å^{-1}. For BPAPC, conformer search was also done about ϕ_4 and ϕ_5. The energy barriers were then compared with the results of *ab initio* computations reported on model compounds of BPAPC.

Rotational Metropolis Monte Carlo Method

In an RMMC calculation, the first step involves the geometry optimization of the single chain allowing the variation of bond lengths, bond angles and torsional angles. The second step involves the Monte Carlo simulation of the minimized chains, where only the torsional angles are allowed to vary. Bond lengths and bond angles are held constant. Torsional angles are varied continuously. To determine the interaction range of the potential either a bond-based cutoff or a distance-based cutoff is used. The Monte Carlo simulation is performed in two substages. First, the starting conformation is equilibrated and then the production stage is carried out with a large number of Monte Carlo steps. The polymer chain properties are averaged during the production stage specifying a fixed interval. A description of the method in detail can be found elsewhere (Honeycutt, 1998).

Monte Carlo simulations were done for preminimized single chains of BPAPC and substituted polycarbonates with 21 repeat units at 300K. A bond-based cutoff was used to determine the interaction range of the potential. The values assigned for the present simulations were 3 and 6 respectively for n_{min} and n_{max} and 2 for the dielectric constant. The number of equilibration and simulation steps was 500,000 and 2,000,000 steps, respectively. Data collection during simulation was carried out after every 200 steps. For BPAPC, calculations were also carried out at 400 and 500K to determine the temperature coefficient of the mean square end to end distance. There was no evidence of any long-term drift of energy during the simulation, which indicated that the chains were fully equilibrated.

The calculations were performed using the InsightII Polymer 4.00 molecular modeling package from MSI and a Silicon Graphics O2 workstation.

Results and Discussion

Conformational Studies

Iso-energy contours about ϕ_1 vs ϕ_2 and ϕ_4 vs ϕ_5 for BPAPC are given in Fig. 2. The iso-energy contours are drawn at intervals of 1 kcal/mol from the global minima. In all the iso-energy contour maps, the conformations having energy ≥ 10 kcal/mol were ignored. It is assumed that all such conformations are not statistically feasible under equilibrium conditions.

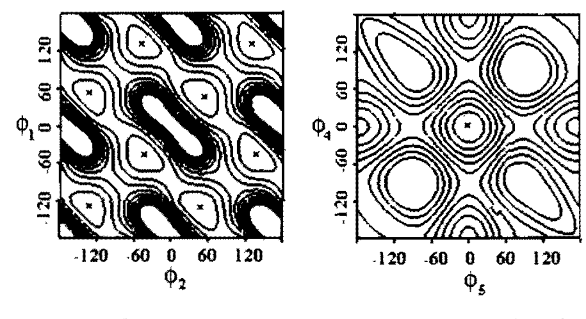

Figure 2. Iso-energy contours for various bond pairs in BPAPC. The minima are marked as 'x'.

8 equivalent minimum energy conformations are possible due to rotation about ϕ_1 and ϕ_2 for BPAPC, where the phenyl rings are twisted out of the plane by 50°. The 4 local minima 0,±90 and ±90,0 (Morino conformation) are at a saddle point between equivalent global minima and the energy barrier for the transformation is 1.7 kcal/mol. The interconversion is also possible *via* the intermediate ±90, ±90 (Butterfly conformation) states and the energy barrier is 3.5 kcal/mol. As shown in Table 1, the energy barriers match well with the results of quantum chemical calculations reported on model compounds of BPAPC (Sun *etal*, 1995; Laskowski *etal*, 1988).

Table 1. Comparison of Conformational Energies (in Kcal/mol).

	HF-6-31G*	STO-3G	PCFF
(ϕ_1, ϕ_2)			
Optimized (50, 50)	0.0	0.0	0.0
Morino (0, 90)	2.17	1.9	1.7
Butterfly (90, 90)	3.93	-	3.5
(0, 0)	17.21	-	19.8
(ϕ_4, ϕ_5)			
trans, trans (0, 0)	-	0.0	0.0
trans, cis (0,180)	-	1.68	1.61

Iso-energy contours evaluated about ϕ_4 and ϕ_5 for BPAPC clearly indicates the preference for the *trans, trans* conformation of the carbonate group (0,0) over the *trans, cis* (0,180) conformation by 1.61 kcal/mol of energy. This agrees well with the value 1.68 kcal/mol obtained from *ab initio* computations on DPC (Laskowski *etal*, 1988). Thus it can be concluded that minimum energy conformations and torsional energy barriers obtained from PCFF are in agreement with the quantum chemical calculations and hence this force field is well suited for the simulation for polycarbonates.

Substituted Polycarbonates

Figure 3 shows the iso-energy contours about ϕ_1 and ϕ_2 for BPCPC and TMCPC. The global minima correspond to the conformations in which the phenyl rings are twisted out of the plane by 55-70 degrees. The butterfly (±90,±90) and the two of the morino (±90,0) conformations represent the local minima which are at 1.7 and 0.8 kcal/mol above the global minima. The 0,±90 conformers were of higher energy about 4.6 kcal/mol above the global minima. This difference in energy of the otherwise equivalent 'morino' conformations was studied and it was found that the iso-energy contours depended on the disposition of the cyclohexyl group in the starting model compound.

The cyclohexyl group can have two configurations as shown in Fig. 3c, which are equivalent in energy (global minimum). But for BPC1, 0,±90 are preferred over ±90,0 conformation and for BPC2 the reverse holds true. In each case, the preference for one conformation over the other was found to be due to the VDW interaction energy. In the model compound studied the cyclohexyl group was in BPC2 configuration.

For TMCPC, rotation about ϕ_1 and ϕ_2 leads to 4 minima at -70,-60; -70,120; 110,-60 and 110,120. Local minima are at ±90, 0 and ±90, ±90 conformations, which are 1.6 and 2.1 kcal/mol respectively above the global minima.

For both BPCPC and TMCPC, the iso-energy contours shows that a series of continuous lower energy conformations are accessible provided one of the phenyl rings is constrained at a dihedral angle of 90°. But in both cases the mobility of the backbone phenyl rings is restricted by substitution of the cyclohexyl group at the C atom.

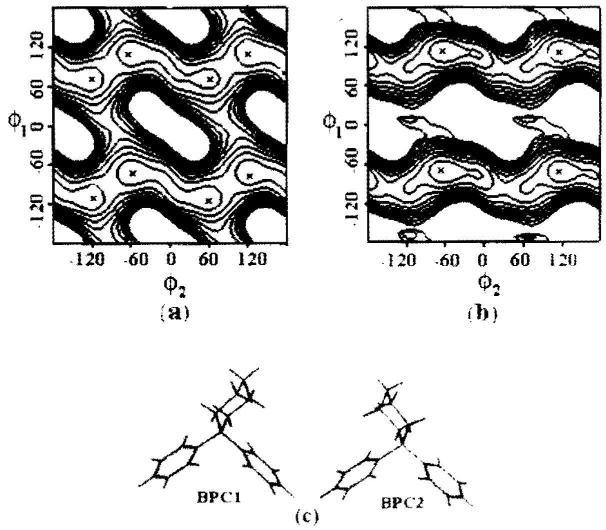

Figure 3. Iso-energy contours for (a) BPCPC and (b) TMCPC for the bond pair ϕ_1 and ϕ_2 (c) Two different configurations of the cyclohexyl group.

RMMC Simulations

The probability distribution of the end to end vector obtained from the single chain simulation of various polycarbonates was found to obey the gaussian chain statistics, typical of polymer chains in the θ state. Distributions of the various dihedrals as obtained from RMMC simulations of single chain polycarbonates are given in Fig. 4. For BPAPC, the distribution of ϕ_1 and ϕ_2 shows two states at -55 and 145 degrees for each. The two angles ϕ_1 and ϕ_2 are strongly coupled, which leads to the possible conformations as −55,-55; -55,145; 145,-55 and 145,145. Distribution about ϕ_3 shows 4 minima at -130, 50, 50 and 130 degrees, where as ϕ_4 shows single state corresponding to the *trans, trans* conformation of the carbonate group in the polycarbonate chain. These dihedral distributions are consistent with the results obtained from conformational analysis on BPAPC segment.

For BPCPC and TMCPC, ϕ_1 and ϕ_2 can take values of -70 and 110 degrees, the dihedrals being coupled similar to BPAPC. The various conformations possible are -70,-70; -70,110; 110,-70 and 110,110. The probability distribution about ϕ_3 shows 4 minima at -130, -50, 50 and 130. Distribution about ϕ_4 confirms *trans, trans* as the preferred conformation about the carbonate group. The substituted polycarbonate single chains also [illegible] interaction between the substituents on the C [illegible] the carbonate group is expected to be negligible due to the large distance of separation between them. Hence the conformation about Ph-O bond and the carbonate group remains the same as in BPAPC.

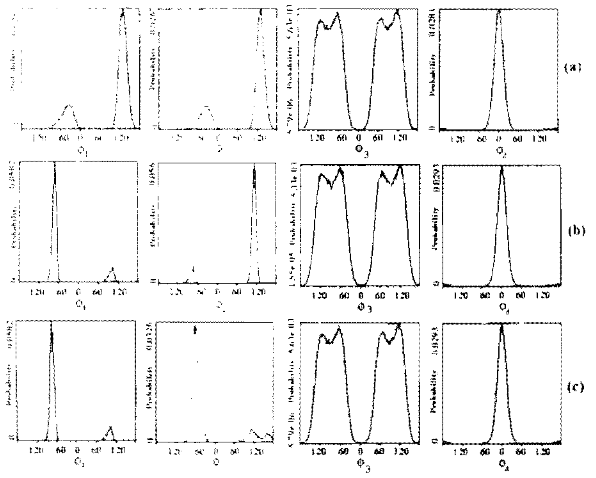

Figure 4. Probability distributions of the various dihedrals in (a)BPAPC, (b)BPCPC and (c)TMCPC from RMMC simulations.

The various conformational properties calculated for polycarbonates are given in Table 2. For BPAPC, reasonable agreement is found for the calculated and the experimental values (Brandrup, 1975; Anwer *etal*, 1991). C_n was calculated from the mean square end to end distance of the single chains (Flory, 1969). For the substituted polycarbonates, no experimental values are available for comparison. To the best of our knowledge these properties are reported for the first time from our studies on substituted polycarbonates.

The simulations done for BPAPC alone at 400 and 500K gave interesting insights into the effect of temperature on conformation. It was observed that the unperturbed dimensions decreased with increase in temperature. No significant changes in the distribution of the dihedrals ϕ_1, ϕ_2 and ϕ_3 were noted at 400 and 500K. But, the distribution about ϕ_4 showed that the population of the *trans*, *cis* conformations increases with temperature. This can be explained on the basis that at lower temperatures, chains prefer the more expanded *trans,trans* conformations of the carbonate group. Increasing the temperature facilitates the polymer to have conformations of higher energy namely the contracted *trans,cis* states. This results in dimensional contraction of the chains in response to the increased temperature, and hence the reduction in the unperturbed dimensions with increase in temperature. A slightly negative temperature coefficient was obtained for the mean square end to end distance, the value being -0.415×10^{-3} deg^{-1}. Experimentally, this was found to be between zero and -0.6×10^{-3} deg^{-1} (Reddy *etal*, 1988). Thus, the predicted value comes well within the experimentally reported value.

Table 2. Conformational Properties of Polycarbonates from RMMC Simulations at 300K.

Polymer	$(\langle r^2\rangle/M)^{1/2}$ $(A^{o2}mol/g)^{1/2}$	$(\langle s^2\rangle/M)^{1/2}$ $(A^{o2}mol/g)^{1/2}$	C_n	A (A^{o})
BPAPC	0.983	0.392	2.7	12.7
	(0.87-1.28)	(0.45)	(2.4)	(11.3)
BPCPC	0.925	0.371	2.9	12.9
TMCPC	0.884	0.353	3.0	13.3

Conclusions

Conformational analysis about the C_α atom for various polycarbonates were carried out and it was observed that substitution by the cyclohexyl group reduces the conformational flexibility of the backbone phenyl rings. The single chains were simulated using RMMC method to derive various conformational properties. The unperturbed dimensions are not drastically effected by substitution. The computed values of characteristic ratios are in the range of 2.7-3.0. The low values of the unperturbed dimensions and characteristic ratios could be an indication of compact average conformations of the substituted polycarbonate chains.

Acknowledgement

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