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Conformational Characteristics of the Polycarbonate of 4,4′-Isopropylidenediphenol

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ABSTRACT: A classical force field has been developed to represent the conformational characteristics of the polycarbonate of 4,4′-isopropylidenediphenol (Bisphenol A polycarbonate (PC)) based upon recent experimental and quantum mechanical data reported for diphenyl carbonate and diphenylpropane. This force field is an improvement upon previously published molecular mechanics force fields because it allows for rotation about all the single bonds in the PC repeat unit. A rotational isomeric state model of PC has been obtained using the force field results; the computed unperturbed chain dimensions of $\langle r^2\rangle_0/M = 1.03$ (Å^2 mol g^{-1}) agree well with reported experimental values.

I. Introduction and Previous Work

In order to simulate dense structures of glassy polymers, an essential requirement is detailed knowledge of both the short-range and long-range interactions between atoms in the system. In the following we develop the necessary atom–atom force field of poly(oxycarbonyloxy-1,4-phenyleneisopropylidene-1,4-phenylene) (Bisphenol A polycarbonate (PC)) and explore the effects of the short-range (intramolecular) interactions along the molecule by investigating the conformational characteristics of the fragment molecules diphenyl carbonate (DPC) and 2,2-diphenylpropane (DPP). These molecules were chosen to represent the conformational characteristics of the PC repeat unit. In a companion paper to this one we report on a simulation of the dense structure of PC performed in collaboration with Gentile and Ludovice which in the remainder of the present paper will be referred to as II.[1]

The conformational characteristics of DPC and DPP have been the subject of several detailed studies involving molecular mechanics[2-9] and quantum mechanics methods.[10-18] Previous work on molecular mechanics could not benefit from the recent, detailed experimental results and quantum calculations and therefore does not accurately describe the conformations of the fragments of PC. One of the earliest works published on the conformational analysis of DPC and DPP using molecular mechanics is that by Williams and Flory.[2] Their approach is based on structural data from tables of interatomic distances[19] and a 6–12 power-law potential energy function for the nonbonded interactions between pairs of atoms. Despite the simplicity of the approach, the resulting conformational analysis was quite accurate; however, rotational barriers and electrostatic interactions were neglected in these calculations. The later work by Tonelli,[3] Erman et al.,[4,5] and Sundararajan[6] is based on the same experimental data, with additional information on DPC from crystal structure analysis.[20] The nonbonded interactions used in these calculations have employed Lennard-Jones 6–12 and Hill's functions. Although these studies go into more detail than the earliest work, such as including some single-bond torsional energy functions, no electrostatic interactions are included, and for DPC the carbonate group is considered rigidly fixed in the all-trans conformation. Recent experimental and theoretical data clearly indicate that this assumption is invalid. Tekely and Turska[7] have attempted to rectify this problem, but at the time did not have available sufficient data to obtain values for all the relevant force field parameters.

Recently, Perez and Scaringe presented results utilizing single-crystal X-ray diffraction data on the dicarbonate 4,4′-isopropylidenediphenylbis(phenyl carbonate) (DBPC).[8] Henrichs, Luss, and Scaringe have further studied the crystalline structure of DBPC, identifying a second crystal structure.[9] The results of the two studies are very informative.

Considerable research has been reported applying quantum mechanics to the conformational and structural analysis of DPC and DPP. Among the several semiempirical methods used on DPC and DPP are CNDO (complete neglect of differential overlap), MNDO (modified neglect of differential overlap), and AM1 (Austin model 1).[10-14] Bicerano and Clark[13,14] have published two very detailed studies which include results obtained not only with MNDO and AM1 but also with PRDDO (partial retention of diatomic differential overlap) calculations, an approximate ab initio method, on DPC, DPP, and the dicarbonate of 4,4′-isopropylidenediphenol and two methanols. Of the ab initio methods, STO-3G-level[21,22] Hartree–Fock calculations have been the most widely employed.[15-18] Laskowski et al.[17] and Jaffe[18] have also reported the results of calculations on DPC, DPP, and smaller model compounds at the STO-3G, 4-31G,[21,23] and 6-31G* levels.[21,23]

On the whole, there exist consistent experimental data and reliable theoretical calculations on DPC and DPP. On the basis of these studies, a new molecular mechanics method can now be developed.

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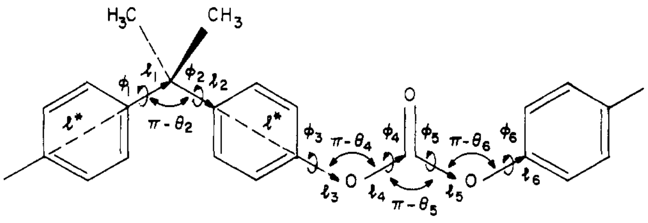

Figure 1. Repeat unit of PC. In the given planar reference conformation all torsion angles assume a value of zero.

Table I
Geometrical Data of the PC Repeat Unit

Data of Relevance for the Rotational Isomeric State Scheme			
Bond Lengths, Å			
l_1	1.54	l_4	1.33
l_2	1.54	l_5	1.33
l^*	2.76	l_6	1.41
l_3	1.41		
Bond Angles, deg			
$\pi-\theta_2$	109.5	$\pi-\theta_5$	109.0
$\pi-\theta_4$	124.0	$\pi-\theta_6$	124.0
Details of the Molecular Geometry			
Bond Lengths, Å			
$C^{ar}-C^{ar}$	1.38	$C^{C=O}-O^{C=O}$	1.21
$C^{al}-$methyl	1.53	$C^{ar}-H$	1.10
Bond Angles, deg			
$C^{ar}-C^{ar}-C^{ar}$			120.0
$O-C^{C=O}-O^{C=O}$			125.5
$C^{ar}-C^{al}-$methyl			109.0

II. Energy Representation

The molecular structure, i.e., the bond lengths and bond angles, was chosen based upon the experimental and theoretical data available in the literature. A Lennard-Jones potential energy function was selected to represent the van der Waals interactions,[24] and a Coulombic potential with a distance-dependent dielectric constant was used to represent the electrostatic interactions.[25] Structure-specific intrinsic torsional potential energy functions have been included to represent the bonded interactions (see below). Since the purpose of this force field was primarily for its use in the generation of dense, glassy microstructures of PC (described in II), the assumptions of fixed bond angles and bond lengths and the representation of the methyl groups as spherical pseudoatoms were made for computational expedience. The choice of the intrinsic torsional energy functions is strongly dependent on these assumptions.

Figure 1 shows the fragment from a PC structure in the conformation where all torsion angles are zero. The geometric parameters used are described in Figure 1 and in Table I. They are based upon the X-ray diffraction experiments on DBPC by Perez and Scaringe[8] and by Henrichs et al.,[9] the diffraction experiments by Yoon and Flory on DPC,[20] and the quantum mechanical calculations of Bicerano and Clark.[13] Because the model developed here does not allow for any bond angle opening or changes in the bond length, some adjustments needed to be made if realistic torsional barriers were to be obtained: The bond angles of the carbonate group were chosen to be slightly larger than the experimental values. The numbering scheme for the bonds and torsion angles described in Figure 1 will be used throughout this paper.

The nonbonded forces include van der Waals and electrostatic interactions. The parameters for the nonbonded potential energy functions representing these interactions are listed in Table II.

Table II
Values of the Parameters for the Potential Energy Functions

i	atom or group[a]	r_i°,[b] Å	α_i,[c] Å^3	$N_{e,i}$[d]	q_i[e]
1	C^{al}	1.70	0.93	5.0	0.00
2	C^{ar}, H subst	1.85	1.23	5.0	−0.14
3	C^{ar}, C subst	1.85	1.23	5.0	0.00
4	C^{ar}, O subst	1.85	1.23	5.0	0.08
5	$C^{C=O}$	1.70	1.23	5.0	0.50
6	H	1.20	0.42	0.9	0.14
7	O	1.50	0.70	7.0	−0.18
8	methyl	1.90	1.77	7.0	0.00
9	$O^{C=O}$	1.50	0.84	7.0	−0.30

[a] C^{al} identifies an aliphatic carbon, and C^{ar} an aromatic carbon; the superscript "C=O" indicates atoms that are part of the carbonyl group. [b] r_i° = van der Waals radius.[26] [c] α_i = polarizability.[27] [d] N_e = effective number of electrons.[28] [e] q_i = partial electrostatic point charge.[29]

A Lennard-Jones function is used to represent the van der Waals interactions:

$$U^{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1}$$

where U^{LJ} is the pairwise van der Waals interaction between atoms i and j and σ is the fundamental length measure of the potential where the interaction vanishes and is obtained using the Slater–Kirkwood equation.[28]

The electrostatic nonbonded interactions are represented by the following Coulomb potential:

$$U^C{}_{ij}(r) = \frac{1}{4\pi D(r)\epsilon_0}\left(\frac{q_i q_j}{r}\right) \tag{2}$$

where $U^C{}_{ij}$ is the electrostatic pairwise interaction potential, ϵ_0 is the permittivity in a vacuum, $D(r)$ is the effective dielectric constant, and the q's are the partial charges on atoms i and j. At atomic-level dimensions, the dielectric constant is strongly dependent on the interatomic separation, and therefore a distance-dependent dielectric constant $D(r)$ is used, based on an approximation first introduced by Block and Walker:[25]

$$D(r) = 1 \qquad \text{for } r < a \tag{3a}$$

$$D(r) = \epsilon_B \exp(-\kappa/r) \qquad \text{for } r > a \tag{3b}$$

$$\kappa = a \ln(\epsilon_B) \tag{3c}$$

where ϵ_B is the dielectric constant of the bulk polymer, which for these calculations was taken to be 3.07.[30] The value a of r at which D switches from unity to an exponentially decaying function was chosen to be the same for all atom pairs, i.e., a = 3.05 Å. This value is the sum of the smallest and the largest van der Waals radii for the charged atoms. The choice of a made here differs from that made in the calculations of Ludovice and Suter,[31] where a was allowed to vary according to the sum of the van der Waals radii of atoms i and j. The Coulombic potential including the Block–Walker approximation for two hydrogens is shown in Figure 2. The partial point charges, q_i, shown in Table II, are based upon MNDO and AM1 calculations[29] and were chosen so that the PC repeat unit is electrically neutral. A rough test for the partial charges can be obtained by comparing computed and experimental values for the considerable dipole moment of DPC. The estimated value from the force field (keeping DPC electrically neutral) is 0.97 D and shows good

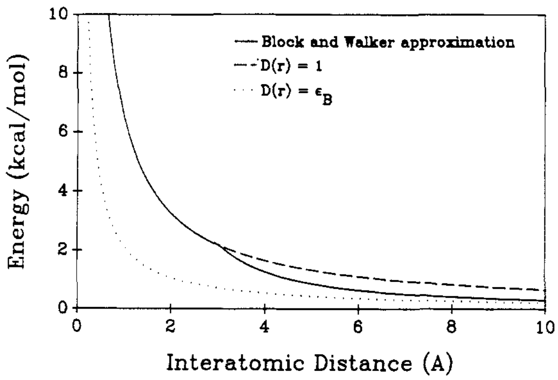

Figure 2. Potential energy of electrostatic interactions for two hydrogen atoms and the Block and Walker interpolation approximation.

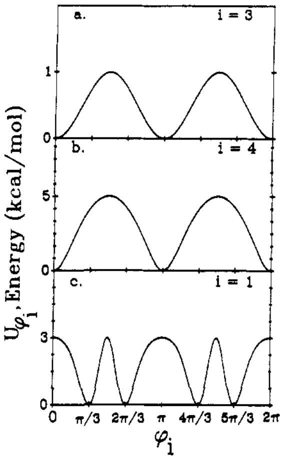

Figure 3. Dependence of intrinsic torsional potential energy functions on specific torsion angles: (a) dependence of U_{φ_3} on φ_3, corresponding to the C^{ar}–O bond in DPC; (b) dependence of U_{φ_4} on φ_4, referring to the O–$C^{C=O}$ bond on DPC; (c) dependence of U_{φ_1} on φ_1, describing the situation for the C^{ar}–C^{al} bond in DPP.

agreement with the experimental value of 0.87 ± 0.05 D.[4] Similarly, the charges in the phenylene rings can be used to obtain an estimate of the quadrupole moment of benzene; the calculated value is -29.0×10^{-40} C m^2, which compares favorably with the experimental value of $-(29.0 \pm 1.7) \times 10^{-40}$ C m^2.[32]

In addition to the nonbonded interactions, intrinsic torsional potentials must be included to complete the description of the interactions along the molecule. Such bonded interactions are typically represented by trigonometric functions and are chosen so that the bond rotation barriers and the conformational minima determined with the force field closely resemble experimental or theoretical values. In the cases of DPC and DPP, the trigonometric functions chosen were of somewhat unusual form.

For DPC, the intrinsic torsional energy function about the C^{ar}–O bond (a carbonate flanking bond) is a simple squared sinusoidal function, often used to represent the effect of π-orbital overlap on conformation, and is shown in Figure 3a:

$$U_{\varphi_3}(\varphi) = B_{\varphi_3} \sin^2 \varphi \tag{4}$$

$$\frac{\mathrm{d}(U_{\varphi_3})}{\mathrm{d}\varphi} = B_{\varphi_3} \sin 2\varphi \tag{5}$$

where U_{φ_3} is the intrinsic torsional energy, B_{φ_3} is the barrier height and is 1 kcal/mol, and φ is the rotational angle measured from the datum plane of the molecule as depicted in Figure 1.

For rotation in the carbonate group about the O–$C^{C=O}$ bond, it was necessary to devise a more complex function, implicit in the dummy variable τ:

$$\varphi = {}^1/_2(\tau - \lambda \sin \tau) \tag{6a}$$

$$U_{\varphi_4} = \frac{B_{\varphi_4}}{2}(1 - \cos \tau) \tag{6b}$$

$$\frac{\mathrm{d}(U_{\varphi_4})}{\mathrm{d}\varphi} = \frac{B_{\varphi_4} \sin \tau}{1 - \lambda \cos \tau} \tag{7}$$

where U_{φ_4} is the intrinsic torsional energy, B_{φ_4} is again the barrier height and in this case is 5 kcal/mol, and φ is the rotational angle. The parameter λ controls the width of the energy well (if $\lambda = 0$, the function is a simple sinusoidal, and if $\lambda = 1$, the function is a cycloid). Here, λ was chosen to be 0.3. The intrinsic torsional energy function is shown in Figure 3b. The need for such a torsional energy function arose from the desire to keep the minimum-energy conformations planar while at the same time keeping the total rotational energy barrier about the bond low (see below).

For the rotation about the C^{ar}–C^{al} bonds (the bonds joined to the isopropylidene group) it was again necessary to devise a particular functional form for the energy minima to be correctly located:

$$U_{\varphi_1} = \frac{B_{\varphi_1}}{2}[1 + \cos\{4(\varphi - \nu \sin 2\varphi)\}] \tag{8}$$

$$\frac{\mathrm{d}(U_{\varphi_1})}{\mathrm{d}\varphi} = -2B_{\varphi_1} \sin\{4(\varphi - \nu \sin 2\varphi)\}(1 - 2\nu \cos 2\varphi) \tag{9}$$

where U_{φ_1} is the intrinsic torsional energy, B_{φ_1} is the barrier height and is 3 kcal/mol, and ν is a parameter which changes the location of the energy minima. This function, where ν was set to 0.3, is shown in Figure 3c.

III. Conformational Analysis of the Model Compounds

1. DPC. DPC has two sets of conformations of low energy, the more favored one occurring when the O–$C^{C=O}$ bonds of the carbonate group are in their trans,trans conformation. At the secondary set of minima the carbonate group is in its cis,trans or its trans,cis conformation and has a slightly higher energy. The carbonate group itself is planar due to electron delocalization. The phenyl rings are rotated out of the plane of the carbonate group because of opposing forces. Electron delocalization between the carbonate group and the phenyl rings favors an all-planar conformation, whereas the steric hindrance between the ortho hydrogen on the phenyl ring and the carbonate oxygen favor a perpendicular arrangement of the phenyl rings and the carbonate group. The rotation of the C^{ar}–O bonds is not coupled; all the combinations of either positive rotations or negative rotations have approximately the same energy.

In Table III the force field results developed here are compared with the published experimental and theoretical values. The location of the minima refers to the dihedral angles of the phenyl rings, where all the angles are zero in the all-planar conformation shown in Figure 1. The values of $\Delta E = E_{cis} - E_{trans}$ in kcal/mol refer to the difference in the energy between the trans,trans conformation and the cis,trans or the trans,cis conformation. The achieved agreement between our adjusted force field results and the corresponding theoretical and the experimental values from the literature is satisfactory.

Table III
Comparison of Energy Minima in DPC

method	principal minima (φ_3,φ_6), deg	ΔE,[a] kcal/mol
X-ray[20]	(48,48)	
AM1[13]	(44,44)	
PRDDO[13]	(44,44)	1.1
STO-3G[17]	(57,57)	1.68
6-31G*[b]		2.74 (2.21)
this force field	(47,47)	1.7

[a] $\Delta E = E_{cis} - E_{trans}$. [b] The 6-31G* calculations are from ref 18 and were done for methyl phenyl carbonate using two different methods.

Table IV
Total Rotational Energy Barriers in DPC

method	barrier C^{ar}–O,[a] kcal/mol	barrier O–$C^{C=O}$,[b] kcal/mol
PRDDO[13]	0.6	4.0
STO-3G[17]	1.23	4.5
this force field	3.3 (0.86)	4.0

[a] Barrier for the rotation of the C^{ar}–O bond, all other bonds being continuously adjusted to give minimum-energy conformations. [b] Barrier for the rotation of the O–$C^{C=O}$ bond, all other bonds being continuously adjusted to give minimum-energy conformations.

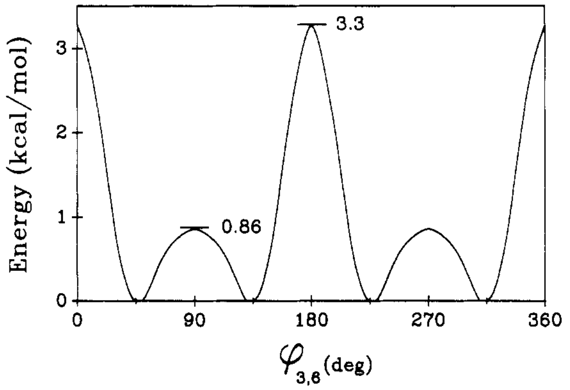

Figure 4. Total rotational energy barrier about the C^{ar}–O bond in DPC. The values of all other torsion angles are continuously adjusted to give minimum-energy conformations.

Furthermore, the energy barriers to rotation were considered. In Table IV the values calculated from the developed force field are compared with available theoretical values. The bond energy barrier for the C^{ar}–O bond is plotted in Figure 4 and shows two energy barriers to rotation: the smaller barrier at (90°,270°) is usually attributed to the breaking up of the electron delocalization between the phenyl ring and the carbonate group,[4] while the larger barrier at (0°,180°) is due to the steric hindrance between the ortho hydrogen and the carbonate oxygen. The contour map shown in Figure 5 displays the energy as a function of the two O–$C^{C=O}$ bonds (angles φ_4 and φ_5) in the carbonate group. The map clearly illustrates that the carbonate group, being much "softer" than previously assumed, must be represented with a higher degree of flexibility than was done in earlier force fields. The force field results agree with the theoretical values, except that the larger barrier of the C^{ar}–O bond is slightly higher than the theoretical results.

2. DPP. The DPP molecule has one symmetrically unique conformational energy minimum, where the phenyl rings rotate out of the plane in a propeller-like conformation. This rotation is due to the steric hindrance between the ortho hydrogens on different phenyl rings. In Table V the force field results devised here are compared with available experimental and theoretical values. The minimum refers to the dihedral angle of the phenyl rings, where the all-planar conformation is defined as (0°,0°). The energy barrier refers to the bond total rotational energy barrier to phenyl ring rotation about the C^{ar}–C^{al} bond. The optimal path for rotation is when the phenyl rings move simultaneously through a saddle point at (0°,90°) or (90°,0°). In Figure 6 the force field results (a) are compared with the STO-3G-level results of Laskowski et al.[17] The energetically preferred path of rotation is indicated by the dotted line.

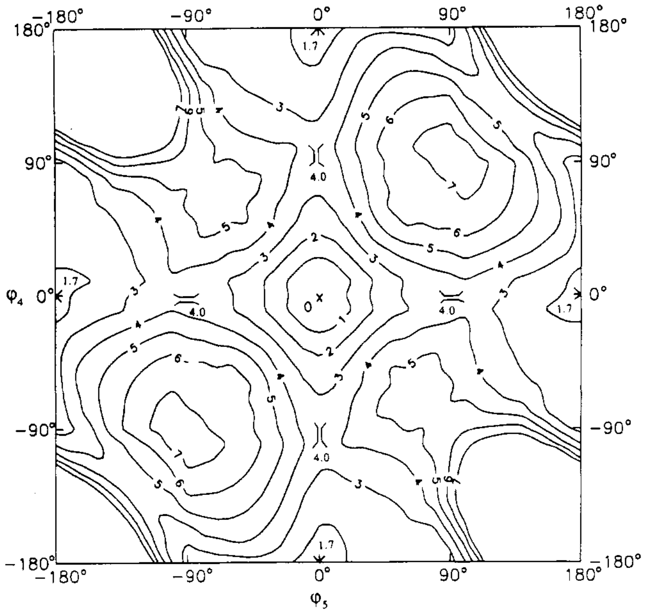

Figure 5. Calculated total rotational energy for DPC as a function of the torsion angles φ_4 and φ_5 labeled in Figure 1. The values of all other torsion angles are continuously adjusted to give minimum-energy conformations. Contours are drawn with respect to the absolute minima at φ_4 = φ_5 = 0° (trans,trans conformation) with intervals of 1 kcal/mol. × denotes minima, and)(denotes columns between troughs.

Table V
Energy Minima and Total Rotational Energy Barrier in DPP

method	minima (φ_1,φ_2), deg	barrier C^{ar}–C^{al},[a] kcal/mol
X-ray[20]	(55,55)	
AM1[13]	(53,53)	
PRDDO[13]	(48,48)	
STO-3G[17]	(51,51)	1.9
this force field	(45,45)	2.7

[a] Barrier for the rotation of the C^{ar}–C^{al} bond, all other bonds being continuously adjusted to give minimum-energy conformations.

IV. Rotational Isomeric State Model

From the results obtained from the fine-tuned force field described above, a rotational isomeric state (RIS) model was deduced.[33] The statistical weight matrices thus obtained are shown in Table VI, where the bond numbering refers to the scheme used in Figure 1. The parameter γ gives the fractional concentration of the cis,trans or trans,cis states as a function of ΔE, the difference in energy between the cis,trans or the trans,cis state and the energy of the trans,trans state, $\Delta E = E_{cis} - E_{trans}$, as

$$\gamma = \exp(-\Delta E/RT) \qquad (10)$$

(The value for γ considered here is slightly different from the one reported by us earlier.[34]) The cis,cis conformation brings the two phenylene rings into very close proximity, and the concomitant excess energy makes this conformation inaccessible.

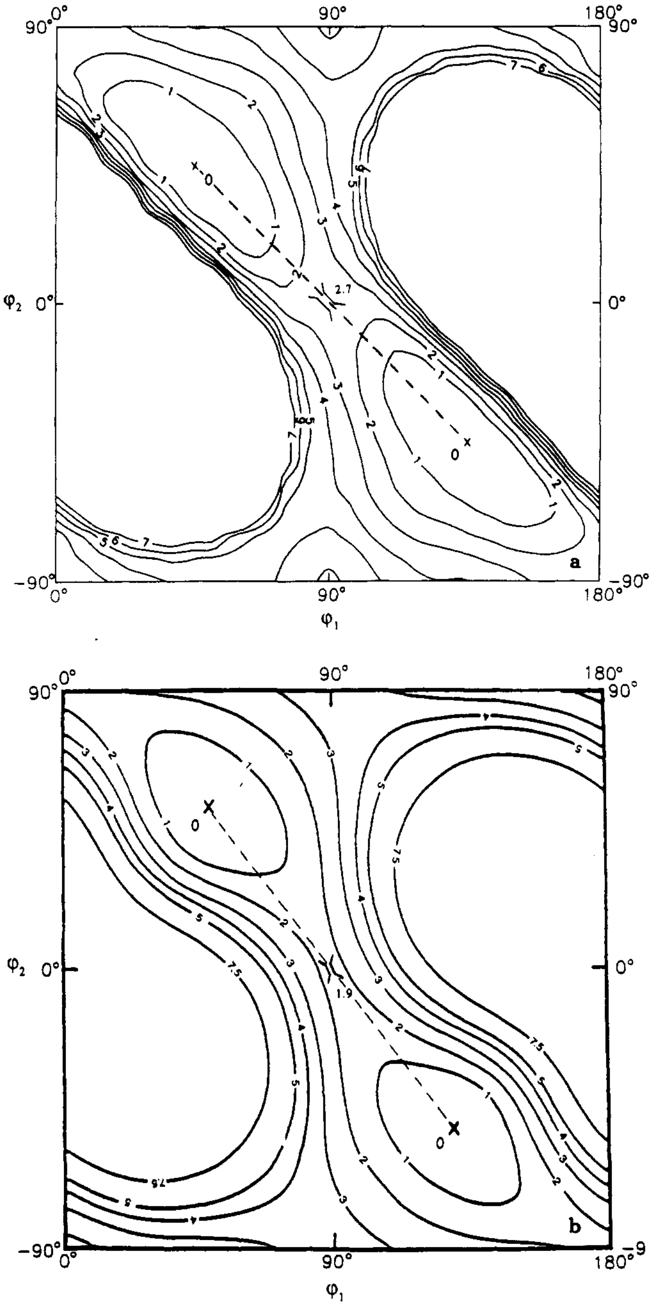

Figure 6. Energy contour maps of DPP as a function of the torsion angles φ_1 and φ_2 shown in Figure 1: (a) results from the force field devised here compared with (b) that calculated by Laskowski et al.[17] For details see legend to Figure 5.

Previous research that utilized the RIS method for PC includes work by Williams and Flory[2] and by Laskowski et al.[17] Both groups of researchers employed the same RIS scheme, a model with significantly fewer states and fewer explicitly considered bonds than the one presented here. Our RIS scheme differs from that of Williams and Flory in that we describe the conformations of the repeat unit with six statistical weight matrices, whereas Williams and Flory use only four. Also, we include a four-state model which explicitly represents the symmetrically equivalent positions of the phenylene ring conformations about the carbonate group and about the isopropylidene group.

The conformations of the phenylene rings about the carbonate group are mutually independent and have a 4-fold symmetry, resulting in four equivalent states (see U_3 and U_6 in Table VI). All first-order interactions are identical, and no second-order parameter is required.

Table VI
Rotational Isomeric State Parameters for PC

bond no. i	θ_i	$\{\varphi_i\}$, deg	U_i[a]
1	0	45,135,225,315	$\begin{bmatrix}1&1&1&1\\1&1&1&1\\1&1&1&1\\1&1&1&1\end{bmatrix}$
2	70.5	45,135,225,315	$\begin{bmatrix}1&0&1&0\\0&1&0&1\\1&0&1&0\\0&1&0&1\end{bmatrix}$
3	0	45,135,225,315	$\begin{bmatrix}1&1&1&1\\1&1&1&1\\1&1&1&1\\1&1&1&1\end{bmatrix}$
4	56.0	0,180	$\begin{bmatrix}1&\gamma\\1&\gamma\\1&\gamma\\1&\gamma\end{bmatrix}$
5	71.0	0,180	$\begin{bmatrix}1&\gamma\\1&0\end{bmatrix}$
6	56.0	45,135,225,315	$\begin{bmatrix}1&1&1&1\\1&1&1&1\end{bmatrix}$

[a] $\gamma = \exp(-900/T)$, with T in K, at room temperature; $\gamma \approx 0.05$.

Table VII
Limiting, Unperturbed Mean-Square End-to-End Distance

method	$\lim_{M\to\infty} \langle r^2\rangle_0/M$, Å^2 mol g^{-1}
this RIS model	1.03
light scattering	0.75[a]
	0.98[b]
$[\eta]$	0.87[a]
SANS	1.25[c]
	1.28[d]

[a] Reference 37. [b] Reference 38. [c] Reference 39. [d] Reference 40.

Two matrices are used to represent the conformations of the phenylene rings about the isopropylidene group. The first matrix, U_1, encompasses four equivalent states representing the rotational minima found in DPP which are independent of the previous bond. The second matrix, U_2, comprises four states which are dependent on the state chosen for the previous bond so that only the "propeller-like" conformations of the rings (i.e., ring rotations of (+45°,+45°)) are allowed, whereas ring rotations of (+45°,+135°) are not.

Although our scheme and that of Williams and Flory differ formally, using equivalent conformational parameters the two schemes yield identical results. The RIS scheme presented here, even though it is of lesser elegance, has the major advantage that it can be easily modified to allow for simple substitution, extending its use to other polycarbonates and to other structurally similar polymers.[35] Our RIS scheme representation can also be used without modification for the construction of initial chain conformations used for the generation of dense, amorphous microstructures as we demonstrate in II.

Values calculated for the limiting, unperturbed mean-square end-to-end distance for PC by standard generator matrix techniques[36] are compared with experimental values in Table VII. The value of 1.03 (Å^2 mol g^{-1}) deduced from the above-described force field compares very favorably with experimental data.

V. Conclusions

A classical force field has been developed for the PC repeat unit based upon the experimental and theoretical data that have recently become available. The inclusion of electrostatic charges and structure-specific torsional potentials creates a force field more detailed than those previously published. The principal difference between this force field and earlier ones is that torsion around all single bonds is considered. Earlier molecular mechanics models had fixed the carbonate group in its all-planar conformation or did not allow for full rotation about the O-$C^{C=O}$ bonds.[2–6,8]

The results show that there is good agreement between the experimental and the quantum mechanical data. There is also good agreement between results obtained with this force field and quantum mechanical data with respect to the location of the energy minima and their relative energies and also with respect to the energy barriers to rotation. The potential weakness of the force field is the use of fixed bond angles, fixed bond lengths, and the representation of the methyl groups as spherical pseudoatoms. These adjustments are computational expedients, implemented with regards to the intended use of this force field in dense packing simulation (see II), and have been taken into consideration when the geometrical parameters were chosen. The intrinsic torsion potentials were selected to compensate as far as possible for these shortcomings.

A new, and very flexible, RIS model was thus deduced from the results of the force field computations. Computed values for the characteristic ratio of the unperturbed chain dimensions compare very well with experimental values in the literature.

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