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Single-Chain Flexibility and Conformation in Polyarylates[†]

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ABSTRACT: This paper describes the use of molecular modeling to study the flexibility and conformation of single-chain sections of three polyarylates based on terephthalic acid and (i) bisphenol A, (ii) bisphenol based on methyl isobutyl ketone, and (iii) phenolphthalein. Configurational entropies were calculated based on the ease of rotation of various bonds. Entropies calculated for the cooperative rotation of the bisphenol phenyl rings did not correlate with the experimentally determined glass transition temperatures. However, a correlation was found using entropies determined for the independent rotation of various bonds keeping others in their minimum-energy conformation. The relative bond flexibilities can be normalized by comparing the configurational entropy in each case against that of a hypothetical freely rotating bond. These results may be useful in interpreting the gas diffusivity and thermal and mechanical properties of these polyarylates.

I. Introduction

The diffusivity of gases in glassy polymers is controlled by polymer chain properties such as interchain distance, chain conformation, chain flexibility, etc.[1,2] It is hypothesized that increasing the intersegmental chain spacing and restricting chain mobility may simultaneously increase both gas permeability and selectivity.[3] In order to tailor-make the polymers on an a priori basis for a specific gas application, the structure property relationship needs to be elucidated.

We have synthesized several series of aromatic polyesters to study the structure permeability correlation. In our previous paper,[4] we reported the wide-angle X-ray diffraction (WAXD) data for a series of polyarylates based on modified bisphenols and phenolphthalein. A rough correlation was shown to hold between the average intersegmental chain spacing determined from WAXD and the diffusivity of the gas. The replacement of terephthalic acid by isophthalic acid resulted in a significant decrease in the average intersegmental chain spacing. It was observed that substitution on the bridge carbon of bisphenol did not affect the interchain spacing, while substitution on the phenyl ring of the bisphenol increased the interchain spacing. Both types of substitutions affected the glass transition temperature significantly. A series of polyarylates was synthesized[4] with similar intersegmental spacings but varying T_g values. The diffusivity differences in this series can be attributed to differences in chain flexibility and conformation.

In this study we use the molecular modeling technique to examine the effect of various substituents at the bridge carbon on polyarylate chain flexibility and conformation. The glass transition temperature can be considered to be a measure of chain flexibility. Additionally, other bulk polymer properties such as impact resistance,[5] chain packing, and phase transitions[6] can be explained on the basis of molecular order and their spatial conformation. Factors such as the nature and site of substitution of the functional groups, steric and electrostatic effects, intrachain and interchain interactions, the pendent chain length, etc., play a significant role in determining the conformation of the polymer chain. Conventional structure determination techniques such as X-ray diffraction are of little use in providing this detailed structural information for these amorphous polymers.

Conformational analysis of polymers was pioneered by Flory et al.[7] for vinyl polymers and was reported by Tonelli for aromatic glassy polymers like polycarbonate and poly(phenylene oxide).[8] Hummel and Flory[9] compared the structural data from X-ray crystallographic analysis in the case of *p*-phenylene polyamides and polyesters. On the basis of the empirical force field (Lennard-Jones 6–12 exponential type) approach, conformational energies were calculated for model compounds. Bond angles and bond lengths were adjusted to the values that minimize the total energy at each value of the torsion angle. They observed that the results of the crystallographic analysis agree well with the results of conformational analysis.

Extensive work on polycarbonate appears in a series of papers by Sundararajan.[10–13] In a homologous series of polycarbonates, a correlation was demonstrated between the glass transition temperature and the configurational entropy. Recently, semiempirical quantum chemical CNDO calculations on model compounds of polycarbonate have been performed, and the relative conformational energy for the rotations along various bonds has been estimated.[14] On the basis of these results, the polymer chain conformation was predicted. Hopfinger[15] has predicted the glass transition temperatures for a number of polymers by a group additivity method in which the group parameters were estimated by molecular modeling techniques.

To our knowledge, all the studies of conformational analysis to date have been restricted to either monomers or small model compounds. In this study we have considered small sections of the polymer chain (six monomer units) to also account for some intrachain interactions. Moreover, the conformation of the chain section can be directly observed, which otherwise has to be predicted from the dihedral angle configuration of either the monomer or the model compound. The interchain effects are neglected in the present study, and hence the results should be treated as only qualitative. The energy calculation have been done using the parameters for bond length, bond angle, etc., typically derived from crystal structure determinations (Table I). It is assumed that these values will not change significantly in the low-temperature range of 0–273 K.

This paper reports the conformational studies for three aromatic polyester chains derived from terephthalic acid and different bisphenols, viz., bisphenol A (Bis-A/TPC),

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Table I
Significant Force Field Parameters Used for Bond Length, Bond Angle, and Dihedral Angle Functions[a]

(a) Bond Length Function: $E_{\text{bond}} = K_b(r - r_0)^2$

bond	K_b, kcal/mol·Å^2	r_0, Å
C1–C2	345.0	1.470
C1–C3	386.0	1.444
C1–O1	365.0	1.460
C3–O1	375.0	1.350
C3–O2	640.0	1.230

(b) Bond Angle Function: $E_\theta = K_\theta(\theta - \theta_0)^2$

bond	K_θ, kcal/mol·deg^2	θ_0, deg
C1–C1–C1	70.0	120.0
C2–C2–C2	50.0	112.5
C1–C1–C2	70.0	120.0
C1–C2–C2	70.0	113.0
O1–C1–C1	65.0	120.0
O2–C3–C1	86.0	125.3
C3–O1–C1	116.0	125.3
O2–C3–O1	81.0	123.5

(c) Dihedral Angle Function: $E_\phi = K_\phi[1 + \cos(n\phi_0 - \delta)]$

notation	bond	K_ϕ, kcal/mol	ϕ_0, deg	n
θ	C2–C2–C1–C1	2.0	0.0	3
ϕ	O2–C3–C2–C2	1.0	0.0	3
τ	C1–C1–O1–C3	3.0	180.0	2
χ	X–C2–C2–X	1.6	0.0	3

[a] Abbreviations: C1 = aromatic carbon, C2 = sp^3 aliphatic carbon, C3 = carbonyl carbon, O1 = carboxyl oxygen, O2 = carbonyl oxygen.

Table II
Configurational Entropies Calculated for Independent Rotations of Dihedral Angles

(A) Angles with Significant Rotational Barriers

	configurational entropy, kcal/mol·K						
polymer	χ_1	χ_2	av χ	θ_1	θ_2	av θ	T_g, °C
Bis-A/TPC	5.61	5.55	5.58	4.73	4.78	4.76	210
Bis-MIBK/TPC	1.04	4.83	2.94	3.93	5.26	4.60	235
PPha/TPC				4.54	4.18	4.36	300

(B) Angles with Small Rotational Barriers

dihedral angle	configurational entropy,[a] kcal/mol·K
ϕ_1,ϕ_2 ($B = 0$)	7.04
($B = 3$)	5.99
τ_1,τ_2 ($B = 0$)	6.64
($B = 3$)	5.81
($B = 7$)	4.12

[a] Entropy values are the same for all three polyarylates.

bisphenol based on methyl isobutyl ketone (Bis-MIBK/TPC), and phenolphthalein (PPha/TPC). On the basis of the ease of rotation of the different bonds, configurational entropies were calculated. The configurational entropies calculated for the independent rotations of various bonds were found to correlate with the experimentally determined T_g values.

II. Experimental Section

The polyesters used in the present study were synthesized as described earlier.[4] The glass transition temperatures were measured on the Rheometrics dynamic mechanical spectrometer Model 7700. The measurements were made on polymer strips prepared by either compression molding or solution casting. A uniform strain of 5 rad/s was used for all samples. The glass transition temperatures (T_g) are shown in Table II.

III. Method and Model

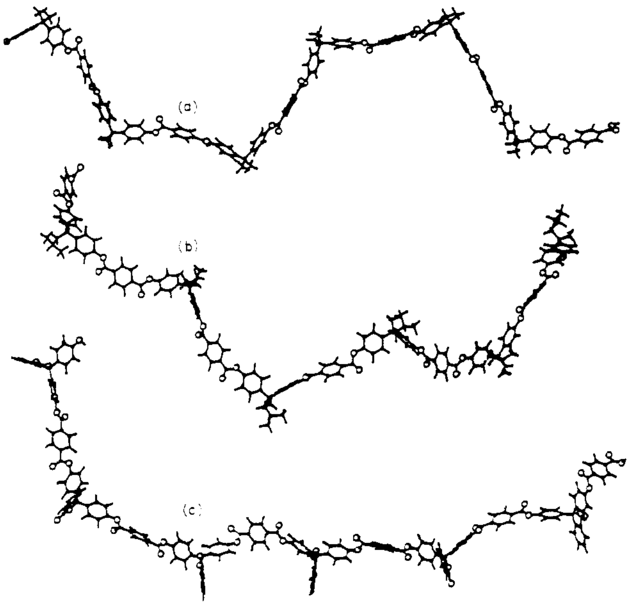

Figure 1. Minimum-energy conformation of three chain sections each comprised of six polyarylate monomer units: (a) Bis-A/TPC, (b) Bis-MIBK/TPC, and (c) PPha/TPC. The middle four units have the same dihedral angle configurations for (a) and (c) while (b) has an alternating sequence.

Table III

$E_{\text{bond length}} = K_b(r - r_0)^2$	(a)[a]
$E_{\text{bond angle}} = K_\theta(\theta - \theta_0)^2$	(b)[b]
$E_{\text{dihedral angle}} = K_\phi[1 + \cos(n\phi - \delta)]$	(c)[c]
$E_{\text{improper torsion}} = K_l(l - l_0)^2$	(d)[d]
$E_{\text{electrostatic}} = (q_i q_j / 4\pi\epsilon_0 r_{ij})$	(e)[e]
$E_{\text{van der Waals}} = (A_{ij}/r_{ij}{}^{12} - B_{ij}/r_{ij}{}^{6})$	(f)[f]
$E_{\text{delocalization}} = -B\cos^2\phi$ or $-B\cos^2\tau$	(g)[g]

[a] K_b = force constant; r_0 = equilibrium bond length. [b] K_θ = force constant; θ_0 = equilibrium bond angle. [c] K_ϕ = force constant; ϕ = equilibrium dihedral angle; δ = deviation from the equilibrium dihedral angle; n = periodicity. [d] K_l = force constant; l_0 = equilibrium improper angle. [e] $q_i q_j$ = atomic charges; ϵ_0 = dielectric constant; r_{ij} = interatomic distance. [f] r_{ij} = radius computed from Cartesian coordinates; A_{ij} and B_{ij} = empirical parameters derived from atom polarizability and valence electrons. [g] B is a parameter in kcal/mol. ϕ and τ are dihedral angles.

III.A. Method. The conformation of polyarylate chains shown in Figure 1 was obtained using the molecular force field method developed by Gelin and Karplus.[16] The total energy for the polyester chains is expressed by the following equation.

$$E_{\text{total}} = E_{\text{bond length}} + E_{\text{bond angle}} + E_{\text{dihedral angle}} + E_{\text{improper torsion}} + E_{\text{electrostatic}} + E_{\text{van der Waals}} + E_{\text{delocalization}} \quad (1)$$

The corresponding equations for the calculation of the individual energy terms are shown in Table III. These equations except for the electron delocalization term are described by Gelin and Karplus.[16] The software used was QUANTA/CHARMm developed by Polygen Corp. The software was validated by modeling a few small compounds such as isophthalic acid, the crystal structure of which had been earlier determined by X-ray diffraction.[17] Predicted geometric parameters like bond angles, bond lengths, and dihedral angles were found to agree with the experimental results within ±0.5%.

The total energy of the polyester chains was minimized first by the steepest descent method to eliminate initial bad contacts and then later by the modified Newton–Raphson method. A thermodynamically stable conformation corresponds to the minimum free energy with respect to the energy functions described above. However,

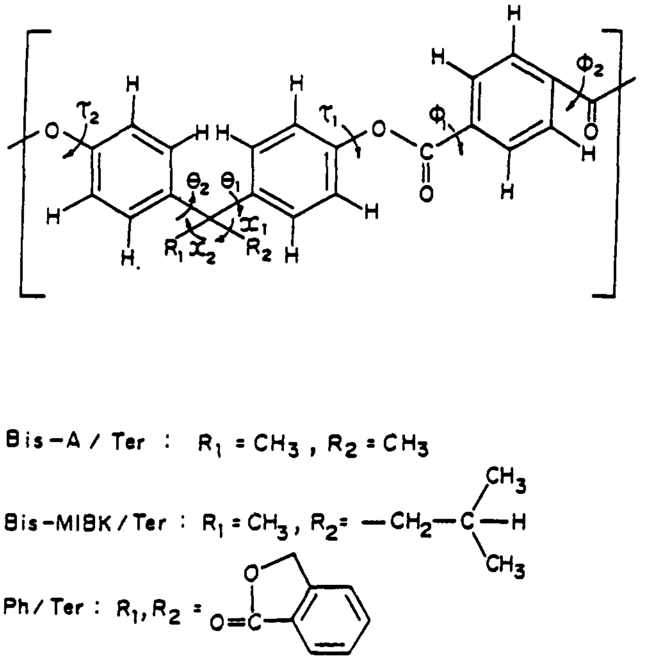

Figure 2. Monomer units of (a) Bis-A/TPC, (b) Bis-MIBK/TPC, and (c) PPha/TPC showing identification of the eight dihedral angles. The arrow direction indicates the increasing value of the dihedral angle.

macromolecules are known to have multiple minima in addition to the global minimum.[13,14] Therefore, in addition to the above minimization techniques, a conformational search analysis was performed to identify all possible minimum-energy conformations of a polymer chain and to select the globally optimized structure.

From the potential energy calculations mentioned above the enthalpy difference between various conformations was computed. Entropy effects may also play a significant role in deciding the final conformation of the polymer chain. The configurational entropy was calculated for the variation of all dihedral angles from 0° to 350° with a step size of 10°. Configurational entropies were calculated[13] using the equations

$$S = -R\sum P \ln P \tag{2}$$

$$P = \exp(-\Delta E/RT)/Z \tag{3}$$

where ΔE is the energy difference between a specific conformation and the global minimum and the partition function Z is given by

$$Z = \sum \exp(-\Delta E/RT) \tag{4}$$

The correlation of T_g with the entropies calculated using the above equation was done in two different ways. In the first method the energies were calculated for the cooperative rotation of the main-chain phenyl rings around the bridge carbon of bisphenol (angles θ_1 and θ_2 in Figure 2). The energy map was constructed, and configurational entropies were calculated. In the second approach the entropies were calculated for the independent rotations of each dihedral angle, keeping all the other dihedral angles constant as in their minimum-energy conformation.

III.B. Model. The monomer units of the three polyarylate chains modeled in the present study are shown in Figure 2. The conformational analysis was performed on the eight dihedral angles identified in Figure 2. The dihedral angles θ_1, θ_2, χ_1, and χ_2 for the minimum-energy conformation are listed in Table IV. The other four dihedral angles ϕ_1, ϕ_2, τ_1, and τ_2, are close to 180° in this conformation. The polymer chains consisting of six monomer units in their minimized energy conformation are shown in Figure 1. The choice of building a chain of six monomer units is explained below. The number of monomer units in the Bis-A/TPC chain was varied from three to eight, and the total energy of the chain was minimized. For this polyarylate it was observed that except for the terminal units the conformational parameters, viz, bond lengths, bond angles, and dihedral angles, remained constant for the remaining nonterminal monomer units. Thus the middle four units in the chain containing six monomer units are thought to represent the minimized conformation of the longer chains. A common feature observed in all three chains is that the substituents on the bridge carbon tend to lie outside the axis of the main chain. The kinks in the chain occur at the bridge carbon of the bisphenol, while the chain is linear along the ester linkage.

Table IV
Average Dihedral Angles (deg) at the Minimum-Energy Configuration of Polyarylate Chains[a]

polymer		θ_1	θ_2	χ_1	χ_2
Bis-A/TPC		130	130	−62	−61
Bis-MIBK/TPC[b]	i	90	180	−71	−67
	ii	101	125	−75	−66
PPha/TPC		170	120		

[a] ϕ_1, ϕ_2, τ_1, and τ_2 are close to 180° for all three polyarylates. [b] In the case of Bis-MIBK/TPC, two values of dihedral angles were observed.

Table V
Components of Total Energy (kcal/mol) for Minimized Chain Structures (Six Monomer Units)

polymer	E_{elec}	E_{vdw}	E_{angl}	E_{bond}	E_{impr}	E_{total}[a]
Bis-A/TPC	−72.7	72.7	30.4	7.2	1.5	39.1
Bis-MIBK/TPC	−115.3	73.1	39.9	9.2	2.0	8.9
PPha/TPC	−71.7	69.7	95.4	9.4	3.3	106.7

[a] Calculated neglecting electron delocalization energy, i.e., $B = 0$ in eq g, Table III.

The Bis-A/TPC chain has a regular arrangement of monomer units and a crankshaft-type conformation. All the dihedral angles are identical for the four monomer units in the center. In the Bis-MIBK/TPC chain an alternating arrangement of the monomer units is observed and the overall conformation is of a zigzag type. In the Bis-MIBK/TPC chain, the dihedral angles repeat alternately. This could be due to the necessity of finding a conformation in which the van der Waals interactions of the bulky isobutyl and the main-chain phenyl rings are minimized. The PPha/TPC chain has the most regular conformation, which may be due to its high rigidity. All the phthalide rings lie on the same side of the chain and tend to be perpendicular to the main-chain axis.

IV. Results and Discussion

The contributions from the individual terms given in eq 1 to the total energy (defined in Table III) of the minimized conformation for the three polyarylates are listed in Table V. In all cases, electrostatic and van der Waals energy terms are important factors determining the optimum conformation. Bis-MIBK/TPC has particularly significant electrostatic interactions. The large angular energy value for PPha/TPC polyarylate is reasonable considering the large angular strain involved in this chain.

IV.A. Configurational Entropy from the Cooperative Rotation of the Bisphenol Phenyl Rings. Con-

Table VI
Energy Barrier along the Minimum-Energy Path for the 180° Cooperative Rotation of Bisphenol Phenyl Rings

polymer	180° rotation barrier (kcal/mol) assuming cooperative motion of dihedral angles θ_1	θ_2
Bis-A/TPC	4.3	4.3
Bis-MIBK/TPC	>100.0	4.5
PPha/TPC	5.3	5.1

formational energies were calculated for the dihedral angles θ_1 and θ_2 for each of the polyarylate chains. The isoenergy contour diagrams for the three polyarylate chains are shown in Figure 3a–c. The isoenergy contour diagrams also show the minimum-energy paths for the phenyl ring flips. The highest rotational barriers along these minimum-energy paths are listed in Table VI. Some of the features common to all three plots are as follows:

(i) The two bisphenol phenyl rings never lie in the same plane as depicted by the high-energy values for θ_1 and θ_2 = 0 and 0° or 0 and 180°. This high energy arises from the repulsion between the ortho hydrogens of the two phenyl rings.

(ii) The rotation of the phenyl rings over 180° (180° phenyl ring flip) is possible at relatively low energies through the cooperative motion of both the rings. This is similar to the results of Sung et al.,[14] who worked with model compounds of polycarbonate.

As mentioned before, the Bis-MIBK/TPC chain shows an alternating arrangement of monomer units corresponding to two sets of θ_1 and θ_2 values (Table IV). Bond rotation along θ_1 and θ_2, for either set, gives identical final values of the configurational entropy. The calculations are reported for the set $\theta_1 = 90°$ and $\theta_2 = 180°$ (see Figure 3b), and this set was used in all further rotational energy barrier calculations. The energy path for θ_1 involves an extremely high energy barrier. The phenyl ring rotation is significantly hindered by the presence of the bulky isobutyl group. During the variation of θ_1, many situations also arise involving high energy due to the repulsions between the ortho hydrogens of the two phenyl rings.

The entropies calculated using eq 2 for the isoenergy contour plots for the three polyarylates, viz., Bis-A/TPC, Bis-MIBK/TPC, and PPha/TPC, are 7.2, 6.9, and 8.4 cal/mol·K, respectively. This would imply that PPha/TPC is more flexible than Bis-A/TPC. This erroneous result shows that the glass transition temperature is not determined by the ease of phenyl ring flips alone but is also affected by the motion of other groups in the polymer chain. Results from DMA studies[18] indicate that the configurational entropies calculated in the above manner do not correlate with the T_γ transition temperatures measured in this polymer. However, considering the inherent broadness of the T_γ peaks, it appears that further study (e.g., NMR) would be worthwhile. In the following sections we discuss results of conformational analysis carried out by performing rotations along each bond, keeping all the other bonds in their minimum-energy conformation.

IV.B. Configurational Entropy from the Independent Rotation along Various Bonds. Among the various dihedral angles it was found that the four angles ϕ_1, ϕ_2, τ_1, and τ_2, are very flexible, involving very low rotational energy barriers, whereas the other four angles θ_1, θ_2, χ_1, and χ_2 are more rigid, involving significant rotational energy barriers. The results of studies involving rotation along each class of bonds are discussed separately below.

a. Rotation around Rigid Bonds. i. Bis-A/TPC Polyarylate. A plot of ΔE versus θ_1,θ_2 and χ_1,χ_2 is shown

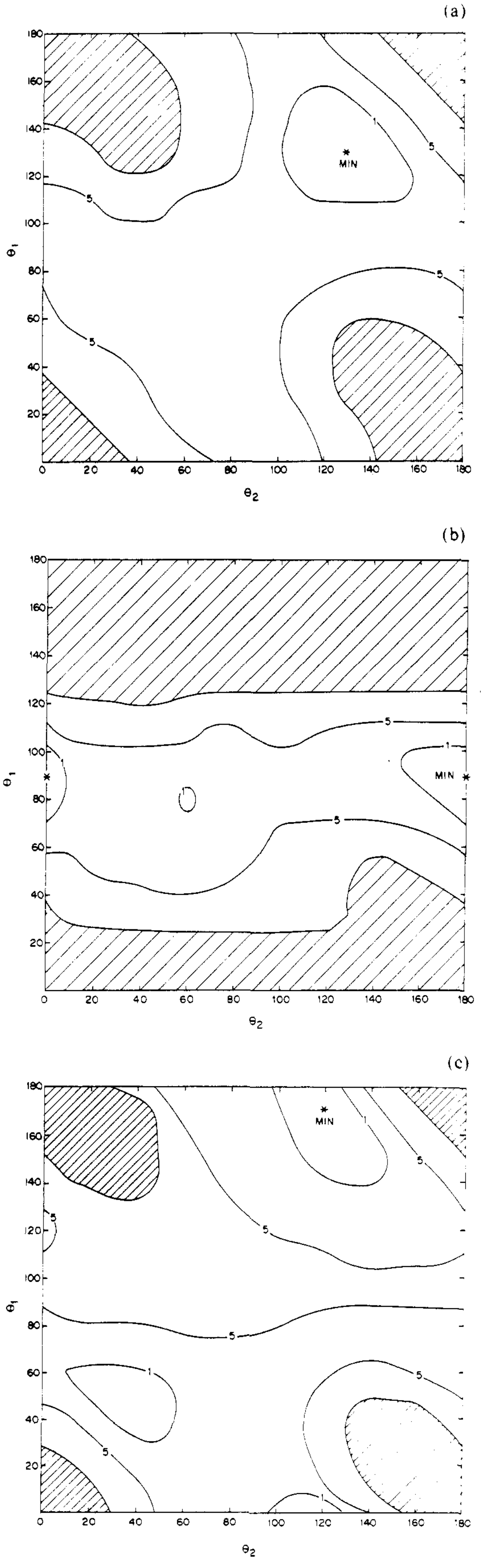

Figure 3. Isoenergy contour diagrams for the cooperative rotation of the bisphenol phenyl rings (defined by dihedral angles θ_1 and θ_2) for (a) Bis-A/TPC, (b) Bis-MIBK/TPC, and (c) PPha/TPC. Energy units ΔE are in kilocalories per mole. Shaded areas indicate relatively inaccessible regions (>10 kcal/mol).

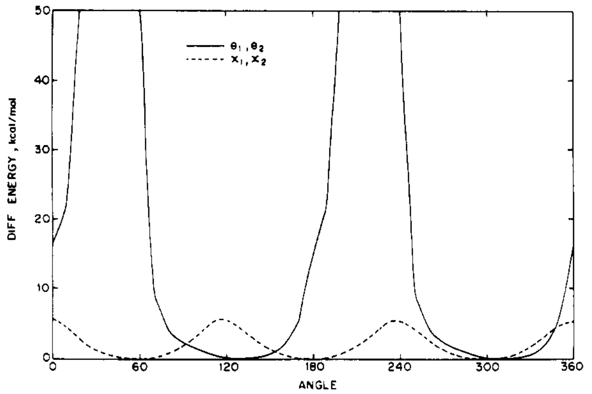

Figure 4. Energy (ΔE, kcal/mol) for the independent rotation of bisphenol phenyl rings θ_1 and θ_2 and methyl groups χ_1 and χ_2 in Bis-A/TPC. The energy contours for θ_1 and θ_2 and for χ_1 and χ_2 overlap.

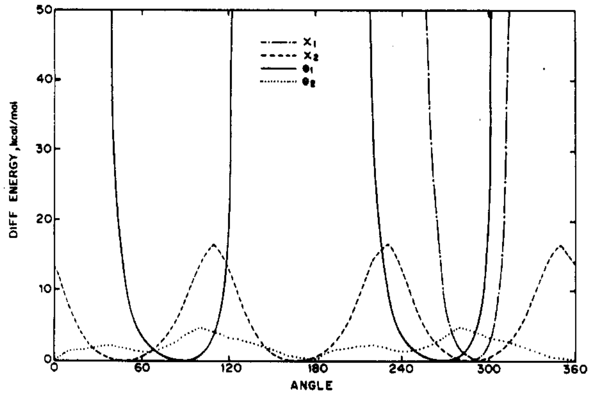

Figure 5. Energy (ΔE, kcal/mol) for the independent rotation of bisphenol phenyl rings θ_1 and θ_2, isobutyl group χ_1, and methyl group χ_2 in Bis-MIBK/TPC.

in Figure 4. The energies involved in the phenyl group rotation are symmetric about 180°, and the methyl group rotation is symmetric about 120°. Because of symmetry, the energy profile of θ_1 is identical to that of θ_2 and that of χ_1 is identical to that of χ_2.

It is observed that the independent rotation of θ_1 or θ_2 over 180° is energetically unfavorable. Analysis of the individual energy contribution shows that the main contribution to the strain energy is from the nonbonding van der Waals interaction arising from the interaction between ortho hydrogens of the two phenyl rings. In the highest energy conformation the ortho hydrogens of the two separate phenyl rings are only 1 Å apart.

The energy barrier for the independent rotation of the methyl groups over 180° is 5 kcal/mol. The relatively low energy barrier for both χ_1 and χ_2 suggests that both the methyl–phenyl and the methyl–methyl interactions are weak.

ii. Bis-MIBK/TPC Polyarylate. In Figure 5 Bis-MIBK/TPC shows an extremely high energy barrier for the 180° independent variation of θ_1 and χ_1 and low energy barriers for that of θ_2 and χ_2. The reason for the high energy barrier for the rotation of θ_1 and χ_1 is the significant phenyl–isobutyl interactions plus the ortho hydrogen repulsions. At the highest energy conformation the ortho hydrogens of the two phenyl rings of the Bis-MIBK are only 0.7 Å apart. The rotational energy barrier for θ_2 is even lower than that in the case of Bis-A/TPC polyarylate. The reason for this could be that during the 180° rotation of θ_2 the distance of closest approach for the ortho hydrogens is greater than 4 Å. The energy barrier for the rotation of χ_2 is higher than that in the case of Bis-A/TPC, and this difference is attributed to the moderate amount of the methyl–isobutyl interactions during the rotation of the methyl group.

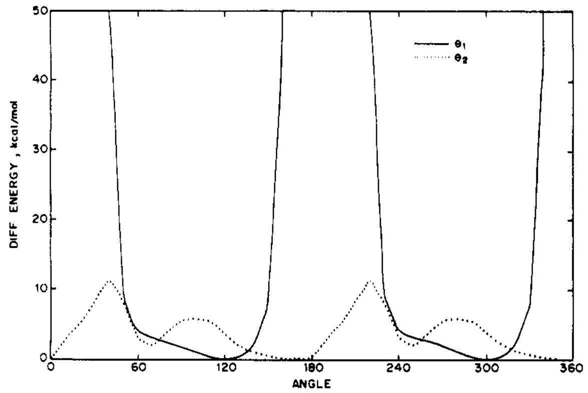

Figure 6. Energy (ΔE, kcal/mol) for the independent rotation of bisphenol phenyl rings θ_1 and θ_2 in PPha/TPC.

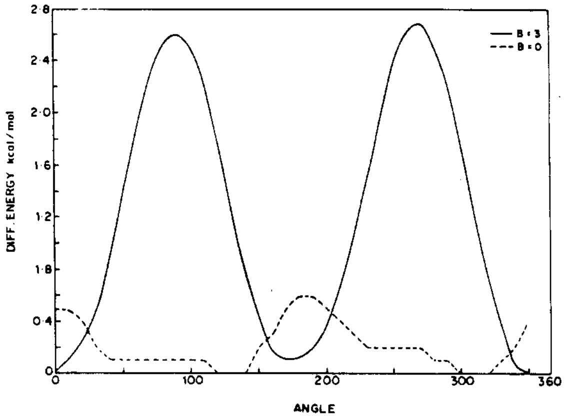

Figure 7. Energy (ΔE, kcal/mol) for the independent rotation of the relatively flexible bonds around the ester linkages ϕ_1 (defined in Figure 2) for the values of $B = 0$ and $B = 3$ in the term $E_{\text{delocalization}}$ as defined in Table III. The energy profile for ϕ_2 is the same as that for ϕ_1. Energy contours overlap for all three polyarylate chain sections.

iii. PPha/TPC Polyarylate. In Figure 6 ΔE is plotted against the independent 180° variation of θ_1 and θ_2. In the minimum-energy conformation of the PPha/TPC polyarylate chain, $\theta_1 = 170°$ and $\theta_2 = 120°$. The high energy barrier for the rotation of θ_2 and the low energy barrier for that of θ_1 could be explained as due to phthalide–phenyl ring interactions by a similar logic as in the case of Bis-MIBK/TPC.

b. Configurational Entropy for the Rotation around Flexible Bonds. The plots of ΔE versus ϕ_1 and τ_1 are shown in Figures 7 and 8. The energy profiles for ϕ_2 and τ_2 are the same as those for ϕ_1 and τ_1, respectively. The plots for these flexible bonds are the same for all three polymer chains. The flexibility around these bonds is clearly seen from the generally lower values of the rotational energy barriers. The exact value of the energy depends on the choice of the parameter B in the electron delocalization term ($E_{\text{delocalization}} = -B\cos^2\phi$ or $-B\cos^2\tau$). Literature indicates values of B from 3 to 7 kcal/mol.[9] The relatively flexible nature of these bonds is in agreement with Sung et al.,[14] who have also observed free rotation of the phenyl rings in diphenyl carbonate. The coplanarity of the carbonate group with the phenyl ring is opposed by the nonbonded interaction of the ortho hydrogen of the acid phenyl ring and the oxygen of the carbonyl group. On the other hand, the preference for the coplanar conformation is favored by electron delocalization. It is observed

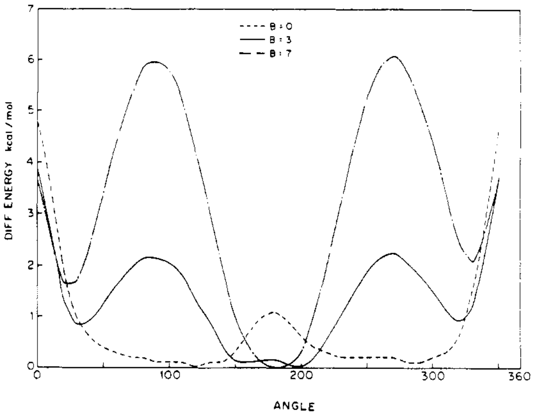

Figure 8. Energy (ΔE, kcal/mol) for the independent rotation of the relatively flexible bonds around the ester linkages τ_1 (defined in Figure 2) for the values of $B = 0$, $B = 3$, and $B = 7$ in the term $E_{\text{delocalization}}$ as defined in Table III. The energy profile for τ_2 is the same as that for τ_1. Energy contours overlap for all three polyarylate chain sections.

Table VII
Relative Approach of Various Dihedral Angles to Complete Flexibility

(A) Angles with Significant Rotational Barriers

	relative flexibility					
polymer	χ_1	χ_2	av χ	θ_1	θ_2	av θ
Bis-A/TPC	79	78	78.5	66	67	66.5
Bis-MIBK/TPC	15	68	41.5	55	74	64.5
PPha/TPC				64	59	61.5

(B) Angles with Small Rotational Barriers

dihedral angles	relative flexibility,[a] %
ϕ_1,ϕ_2 ($B = 0$)	99
($B = 3$)	84
τ_1,τ_2 ($B = 0$)	93
($B = 3$)	82
($B = 7$)	58

[a] Values of the relative flexibility are the same for all three polyarylates.

that for values of $B = 3$ kcal/mol the electron delocalization term dominates and the preferred conformation is close to the planar one (i.e., ϕ and $\tau = 180°$).

IV.C. Correlation of the Configurational Entropy with T_g. The entropies for the independent rotation of all dihedral angles along with the glass transition temperatures determined by dynamic mechanical analysis (DMA) are listed in Table II. An inverse correlation is observed between the calculated entropy and the experimental glass transition temperatures. This correlation holds both for the main-chain bonds θ_1 and θ_2 and for the side chain bonds χ_1 and χ_2.

IV.D. Relative Stiffness of the Chains. On the basis of the different entropy values for the rotation of different groups, a bond flexibility parameter $R(F)$ can be calculated:

$$R(F) = S_G/S_0 \times 100 \qquad (5)$$

where S_G is the entropy for rotation around a particular bond and S_0 is the entropy for rotation of a hypothetical bond with a zero energy barrier. The relative flexibilities of the various bonds are listed in Table VII.

V. Conclusions

In the case of the three polyarylates in this study, chain sections with six monomer units appear to satisfactorily represent chain conformation. The chain conformation can be directly observed.

T_g has a poor correlation with the entropies calculated for the cooperative rotation of the phenyl rings or with the rotation barriers along the minimum-energy paths obtained from the corresponding isoenergy contour diagrams. However, T_g correlates with the entropies for the independent rotation of each bond. While this correlation is valid using the configurational entropies calculated from independent rotation of the main-chain bonds alone, it is strengthened by also considering the side-chain contribution as proposed by Hopfinger.[15]

It was found that the bond rotations corresponding to θ_1, θ_2, χ_1, and χ_2 involved high energy barriers whereas ϕ_1, ϕ_2, τ_1, and τ_2 were relatively flexible. The ortho hydrogens in the phenyl rings play a significant role in restricting the rotation of the phenyl rings and thereby increasing the T_g of the polymer. Thus, it would be interesting to study the effects of bulkier substituents at the ortho position of bisphenol phenyl rings on the configurational entropy. Substitution on the acid phenyl ring may also have a significant effect on chain flexibility. Studies in this direction are currently underway.

It is useful to define a bond flexibility parameter R_F (eq 5) for bonds in these polymers by normalizing the configurational entropy with respect to a hypothetical bond with zero energy barrier.

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Registry No. Bis-A/Ter (copolymer), 26659-86-9; bis-A/Ter (SRU), 26659-32-5; bis-MIBK/TER (copolymer), 123203-71-4; bis-MIBK/TER (SRU), 123203-73-6; Ph/Ter (copolymer), 25777-12-2; Ph/Ter (SRU), 24938-86-1.