high sensitivity to γ radiation. We expect to report those results in the near future.

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Registry No. (2,2-Dimethylsuccinic acid)(uranyl acetate) (copolymer), 98971-90-5; (2,2-dimethylglutaric acid)(uranyl acetate) (copolymer), 98971-91-6; (3,3-dimethylglutaric acid)(uranyl acetate) (copolymer), 98971-92-7; (2,2,6,6-tetramethylpimelic acid)(uranyl acetate) (copolymer), 98971-93-8; (thiodiglycolic acid)(uranyl acetate) (copolymer), 98971-94-9; (uranyl acetate) (maleic acid) (copolymer), 98971-95-0; (uranyl acetate)(fumaric acid) (copolymer), 98971-96-1; (uranyl acetate) (phthalic acid) (copolymer), 98971-97-2; (uranyl acetate)(isophthalic acid) (copolymer), 98987-54-3; (uranyl acetate)(terephthalic acid) (copolymer), 98987-55-4; (acetylenedicarboxylic acid)(uranyl acetate) (copolymer), 98987-56-5; (2,2-dimethylsuccinic acid disodium salt)(uranyl nitrate) (copolymer), 107985-62-6; (3,3-dimethylglutaric acid disodium salt)(uranyl nitrate) (copolymer), 107985-64-8; (2,2,6,6-tetramethylpimelic acid disodium salt) (uranyl nitrate) (copolymer), 107985-66-0; (thiodiglycolic acid disodium salt)(uranyl nitrate) (copolymer), 107985-67-1; (maleic acid disodium salt)(uranyl nitrate) (copolymer), 107985-68-2; (fumaric acid disodium salt)(uranyl nitrate) (copolymer), 107985-69-3; (acetylenedicarboxylic acid disodium salt)(uranyl nitrate) (copolymer), 107985-70-6.

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Possible Helical Shapes of the Polycarbonate Chain and Their Influence on the Unperturbed Dimensions

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ABSTRACT: The helical parameters corresponding to the various skeletal conformations of the bisphenol A polycarbonate chain have been calculated. Combining these results with the conformational energy calculations shows that both flat-helical and extended conformations are of equal energy for this chain. In addition, cyclic structures are also found to be stereochemically possible. The small values of the characteristic ratio of the unperturbed end-to-end distance and its temperature coefficient are attributed to the equal energy of the flat-helical and extended-helical, as well as the nonhelical, conformers.

Introduction

The analysis of the conformations accessible to a segment of the bisphenol A polycarbonate chain (BPAC) has been reported previously.[1,2] The schematic of the chain is shown in Figure 1. The preferred conformations of the carbonate group with respect to the contiguous phenyl moiety and those of contiguous phenyl groups with respect to each other were described.[1,2]

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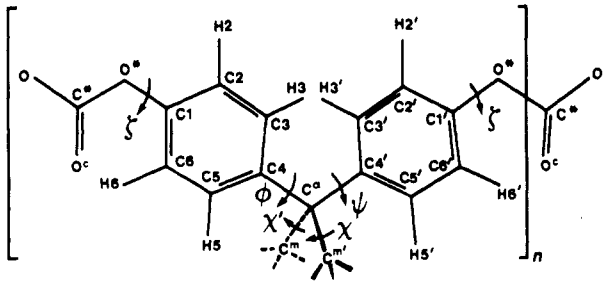

Figure 1. Schematic representation of a segment of the bisphenol A polycarbonate (BPAC) chain. The relevant torsion angles are marked.

In the literature, the BPA polycarbonate has been described as a freely rotating chain. The inability of the chain to crystallize readily and the small end-to-end distance in Θ solvents[3] ($\langle r^2\rangle_0/M = 0.87$ Å^2/(g·mol)) were taken to be indicative of this behavior. The theoretical treatment of the polycarbonate by Williams and Flory[4], as a freely rotating chain consisting of a succession of virtual bonds, led to values of $\langle r^2\rangle_0/M$, in agreement with the experimental results. The large accessible domain in the conformational map constructed in terms of ϕ and ψ (See Figure 1) substantiated the large number of rotational states available to the chain.[1,2]

It is known that if the torsion angles along the skeletal bonds, e.g., ϕ, ψ, and ζ in the case of BPAC, perpetuate over a few repeat units in the chain, the segment would take a helical shape. By use of geometrical data, the helical parameters, viz., n, the number of repeat units per turn, and h, the advance per monomer along the helix axis (pitch = nh), can be calculated in terms of the torsion angles ϕ, ψ, and ζ. The map of the helical parameters, combined with the conformational energy map, would lead to an understanding of the possible shapes of the chain. The average dimensions of the chain can also be calculated by using the conformational energy map and the transformation matrices required for the calculation of the helical parameters. Such calculations are described in this paper. A brief discussion of the possible helical shapes of the polycarbonate chain is presented.

Energy Calculations

Method of Calculation. The bond lengths and bond angles derived from the crystal structure[5] of diphenyl carbonate were used for the carbonate and phenyl groups. This was referred to as "Set II geometry" in the previous paper.[2] A value of 109.5° was used for the bond angle C_4–C^α–$C_{4'}$. The methyl groups were appended to the C^α atom, with bond lengths of 1.53 and 1.1 Å for the C–C and C–H bonds, respectively. Tetrahedral values were used for all the bond angles involving the methyl groups.

The functions and parameters used for the energy calculations are the same as previously described.[2] The Lennard-Jones 6-12 function was used for calculating the nonbonded interaction energies.

Based on the results and discussion given before,[2] the conformation of the carbonate group with respect to the contiguous phenyl was taken to be defined by $\zeta = 60°$. For the calculation of the interaction energies between two contiguous phenyl groups, the conformations were varied in terms of the torsion angles ϕ and ψ, at intervals of 10° each. The eclipsed conformation of the C_4–C_3 and C^α–$C_{4'}$ bonds defines $\phi = 0°$. Likewise, for $\psi = 0°$, the C_4–C^α bond eclipses the $C_{4'}$–$C_{3'}$ bond (see Figure 1). The angles χ and χ', defining the positions of the methyl hydrogens, were varied at intervals of 10°, for each of the ϕ,ψ states in order to locate the hydrogen atoms in the least energy conformation corresponding to that ϕ,ψ state.

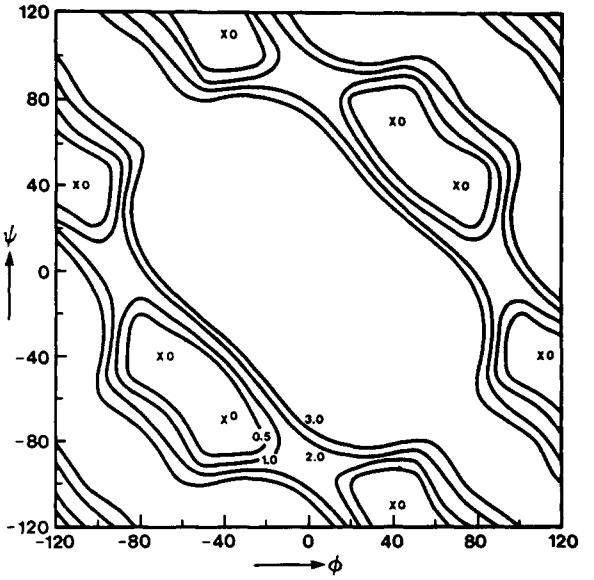

Figure 2. Energy contours in terms of the torsion angles ϕ and ψ shown for the segment of the BPAC chain. Contours are drawn relative to the minima marked by ×.

Following the calculation of the conformational energies $E(\phi,\psi)$ for the ϕ,ψ states, the partition function was calculated according to

$$z = \sum_{\phi}\sum_{\psi} \exp(-E(\phi,\psi)/RT) \tag{1}$$

The average energy is given by

$$\langle E\rangle = z^{-1}\sum_{\phi}\sum_{\psi} E(\phi,\psi)\exp(-E(\phi,\psi)/RT) \tag{2}$$

Results and Discussion of Energy Calculations

Although the conformational map of the diphenylpropane segment of the BPAC chain has been discussed before,[2] the features will be described here briefly for the purpose of the discussion of helix parameters.

The conformational energy map for the segment of BPAC, in terms of ϕ and ψ, is shown in Figure 2. Contours are drawn relative to the minimum marked by × in the figure. It is seen that several minima occur, in symmetrically related positions. Within each domain enveloped by the contour for 1 kcal·mol^{-1}, two minima occur, for example, at $(\phi,\psi) = (-40°,-70°)$ and $(-70°,-40°)$. The barrier between them is 0.5 kcal·mol^{-1}, occurring at $(\phi,\psi) = (-55°,-55°)$. Conformations close to the diagonal spanning from $\psi = 120°$ to $\phi = 120°$ are high in energy. The contours for 2 and 3 kcal·mol^{-1} envelope a wide range of conformations.

A number of studies on the molecular motion in BPAC, using solid-state NMR methods and mechanical relaxation measurements, have been reported.[6-14] Although it is not our intention here to interpret these data in terms of the energy maps, some comments can be made based on the results shown in Figure 2. As mentioned above, the contour for 3 kcal·mol^{-1} spans a wide area of the (ϕ,ψ) domain. Interconversion between conformations within this region can occur by synchronized variations in ϕ and ψ. However, the phenyl groups themselves cannot be considered independent of the carbonate group during such a motion. As seen from Figure 1, the rotations ϕ and ζ or ψ and ζ' share the same axis. A rotation ϕ of the phenyl group about the C_4–C^α axis affects not only its disposition with respect to the contiguous phenyl but the carbonate group as well.

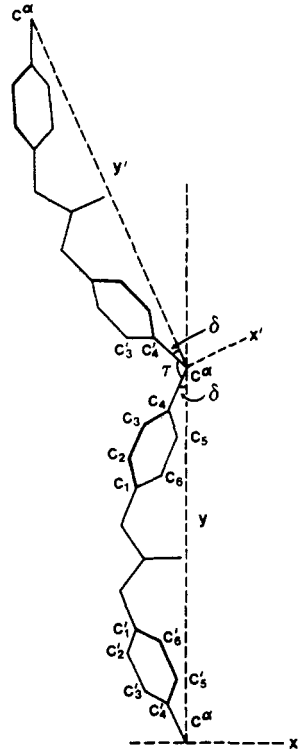

Figure 3. Coordinate system used for calculating the transformation matrices.

Interdependence of the conformation of the phenyl group on the carbonate group on one side and the contiguous phenyl on the other would suggest that the mobility of the segment would be cooperative. The positions of the methyl hydrogens play a role as well. Such a cooperativity has been suggested by NMR studies cited above.

The π-flip model has been discussed in the literature, to describe the motion in BPAC. It is seen from Figure 2 that when ϕ is held constant, say at -40°, a π flip of ψ from -70° to 110° involves the phenyl group traversing the region near the diagonal of the map, which entails very high energy. The same holds for changing ϕ by 180° when ψ is held invariant. A variation of the π-flip model can, however, be conceived by examining the energy contours in Figure 2. Consider, for example, the two conformations, with (ϕ,ψ) = (-120°,90°) and (-60°,-90°). If a straight path is drawn between these two conformations, all the intermediate conformers are within 2 kcal·mol^{-1}. Thus, a 180° change in ψ can be accomplished, with only a 60° change in ϕ, and the π flip of one phenyl accompanied by a small rotation of the contiguous unit does not involve high energy. Similar conclusion was reached by Spiess based on solid-state NMR studies.[11]

Helix Parameters

The values of n, the number of repeat units per turn of the helix, and h, the advance per repeat unit parallel to helix axis (h = pitch/n), were calculated by using the method described before.[15,16] The value of ζ was taken to be 60°, and n and h were calculated as a function of ϕ and ψ. Extrapolation of the results to any other value of ζ is simple, as explained below. The carbonate group was kept in the trans configuration.

In order to calculate n and h, two contiguous repeat units are defined in a coordinate system shown in Figure 3 and a virtual bond is drawn from C^{α}_{i-1} to C^{α}_{i}. The atom C^{α}_{i-1} is at the origin with the virtual bond C^{α}_{i-1}–C^{α}_{i} along the Y axis and the atom C_4 in the XY plane. The coordinate system corresponding to the second unit is also

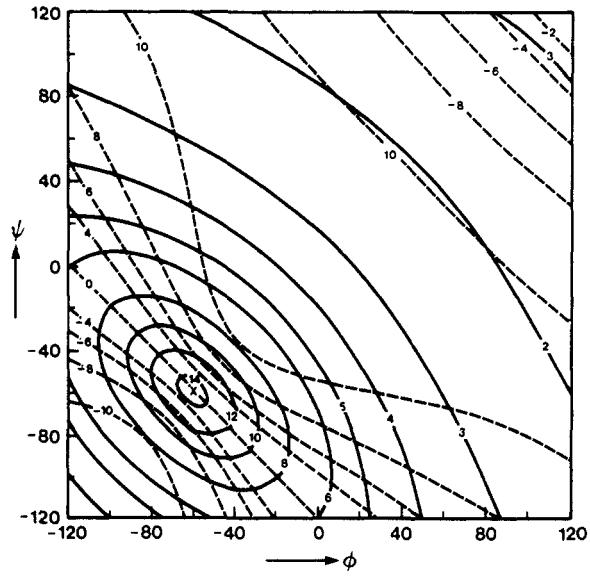

Figure 4. Isocontours of the helical parameters n (solid lines) and h (dashed lines) shown in terms of ϕ and ψ for the polycarbonate chain. A value of ζ = 60° was used here.

shown in Figure 3. The matrix which transforms the coordinate system associated with the first repeat unit to that of the second is given by

$$\mathbf{T} = \mathbf{T}_{\psi}\mathbf{T}_{\theta}\mathbf{T}_{\phi} \tag{3}$$

where

$$\theta = 180 - (\tau + 2\delta) \tag{4}$$

The angles τ and δ are defined in Figure 3. With the geometrical parameters used, the angle δ between C_4–C^{α} and the virtual bond is 23° and the length of the virtual bond is 12.63 Å. The matrices in eq 3 are of the general form described before.[15,16] Note that in the system defined in Figure 3, since ζ = 60°, the angles $\phi = C_3$–C_4–C^{α}–$C_{4'}$ and $\psi = C_4$–C^{α}–$C_{4'}$–$C_{3'}$ are 60°. The angle τ = 109.5° was chosen for the calculations. Following the calculation of the matrices $\mathbf{T}$ for the various values of ϕ and ψ, the helix parameters n and h were evaluated as described before.[15,16]

Explicit inclusion of the values of ζ can be taken into account by following the method of Erman et al.[17] In this case, seven matrices (instead of the three in eq 3) would be required to transform the coordinate system of one repeat unit to that of the next.

The isocontours of n and h are shown in Figure 4. The negative values of h denote left-handed helices. As mentioned above, this figure corresponds to ζ = 60°. If any other value of ζ is used, this figure can be easily adapted. For example, for a value of ζ = 40°, add 20° to the values of ϕ and ψ marked on the axes of Figure 4, such that the map will read from ϕ = -100° to 140° and ψ = -100° to 140°. Thus, the map can be transposed to any value of ζ.

Figure 4 shows that the value of n ranges from 2 to 14.69. The maximum of 14.69 occurs at (ϕ,ψ) = (60,-60°). The value of $|h|$ varies from 0 to 11.2 Å, the latter occurring at (ϕ,ψ) = (-10°,-10°). An interesting aspect is that corresponding to the maximum of h = 11.2 Å (maximum extension of projection of the repeat unit on the helix axis), the value of n is not 2 as is usually the case with most polymers. Instead, the value of n corresponding to (ϕ,ψ) = (-10°,-10°) is 4.01. Thus, a near 4-fold helix, with h = 11.2 Å, leads to a fully extended chain, with a pitch of 44.8 Å. However, if Figure 4 is compared with Figure 2, this conformation is of very high energy.

Superposition of Figures 2 and 4 shows that in the accessible regions of ϕ and ψ, various helical shapes are possible for the BPAC chain. The values of n and h, corresponding to the minimum energy positions, are listed in Table I. Some of these helical shapes are shown in Figure 5. Although these helices are all nonintegral, a small change in ϕ and ψ values close to the energy minima would, of course, lead to integral helices. Another interesting aspect is that both extended- and flat-helical structures are of equal intramolecular energy, which is rarely the case with most polymers.

In the lower left part of Figure 4, the curve for $h = 0$ passes through the area of low energy conformations, with n ranging from 6 to 14.69. This would imply that it should be possible to synthesize low molecular weight, cyclopolycarbonates, with $n \geq 8$. This region also gives rise to flat helices, with a large diameter. It is seen that helices with n ranging from 8 to 14, with h up to ~8 Å, are possible. In addition, both left- and right-handed helices are also likely. In certain areas of the conformational map, small changes in ϕ and ψ lead from a right-handed to a left-handed helix. For example, with $(\phi,\psi) = (-40°,-70°)$, the helix parameters are $n = 12.14$ and $h = 3.51$ Å. This conformation corresponds to one of the minima. If ϕ and ψ change by 10° each, i.e., $(\phi,\psi) = (-50°,-80°)$, the helix becomes left-handed, with $n = 12.14$ and $h = -3.51$ Å. These two helices are shown in parts c and d of Figures 5. Although these helical conformations are theoretically possible, they have not been detected hitherto in the crystalline state of BPAC.

In the top right-hand portion of Figure 4, the value of n is close to 2 in the accessible regions and h varies from 8 to 10 Å. Thus, these conformations of ϕ and ψ lead to zigzag-type helices. In this case also, in certain regions, a small variation in ϕ and ψ results in a change in the helix sense. For example, with $(\phi,\psi) = (-40°,110°)$, the helix parameters are $n = 2.01$ and $h = 10.27$ Å, whereas with $(\phi,\psi) = (-30°,110°)$, the helix is left-handed, with $n = 2.07$ and $h = -10.17$ Å. According to the analysis of Bonart,[18] the BPA polycarbonate crystallizes in a monoclinic unit cell, with $a = 12.3$ Å, $b = 10.1$ Å, c (chain direction) = 20.8 Å, and $\gamma = 84°$. Two monomers are contained in the repeat distance of 20.8 Å (i.e., $n = 2$, $h = 10.4$ Å). Analysis of Figure 4 shows that the curves for $n = 2$ and $h = 10.4$ Å do not intersect. This means that with the geometrical parameters used here, a chain with a 2-fold screw axis and 20.8 Å repeat distance cannot be constructed. However, calculations based on a "virtual bond method"[19] show that such a helix can be constructed by enlarging the value of τ at the C^α atom to 110.9° and with $(\phi,\psi) = (-60°,120°)$.

Calculation of the Unperturbed End-to-End Dimension

The theoretical treatment of BPAC chain by Williams and Flory,[4] as a freely rotating chain consisting of a succession of virtual bonds, essentially assumes a hypothetical chain in which all the rotational conformers are of equal energy. Rigorous calculation of the average dimensions is possible by taking into account the relative energies of the conformations. The transformation matrix which establishes the correlation between successive units in the chain is weighted according to the relative energy of the conformation. With the energy map presented in Figure 2 and the transformation matrices (eq 3), the characteristic ratio ($C_x = \langle r^2\rangle_0/xl^2$) can be calculated according to[20]

$$\langle r^2\rangle_0/xl^2 = \{(\mathbf{E} + \langle\mathbf{T}\rangle)(\mathbf{E} - \langle\mathbf{T}\rangle)^{-1} - (2/x)(\langle\mathbf{T}\rangle) \times (\mathbf{E} - \langle\mathbf{T}\rangle^x)(\mathbf{E} - \langle\mathbf{T}\rangle)^{-2}\}_{2,2} \quad (5)$$

where x is the number of repeat units in the chain, l is the length of the virtual bond C^α_{i-1}–C^α_i, $\mathbf{E}$ is the identity matrix of order 3, and $\langle\mathbf{T}\rangle$ is the matrix constructed with the Boltzmann-averaged elements of the transformation ma-

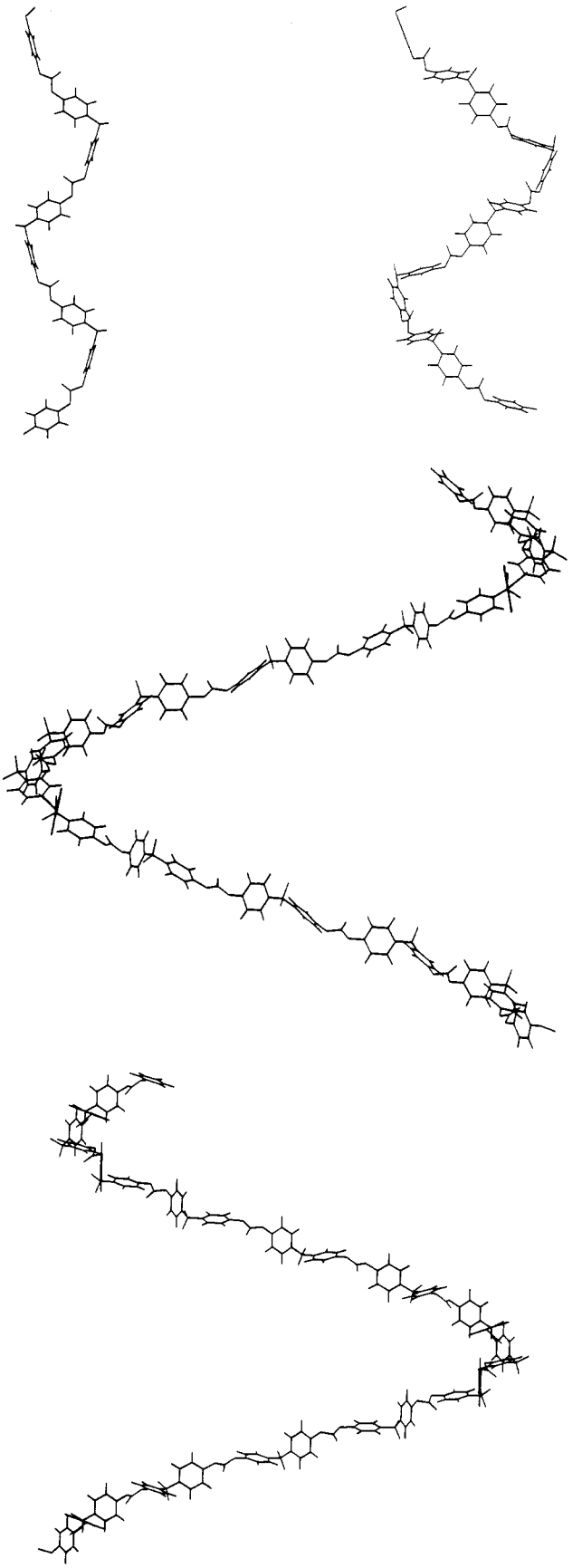

Figure 5. Some of the possible helical conformations of the BPAC chain: (a, top left) $n = 2.01$, $h = 10.27$ Å; (b, top right) $n = 4.26$, $h = 6.48$ Å; (c, middle) $n = 12.14$, $h = 3.51$ Å; (d, bottom) $n = 12.14$, $h = -3.51$ Å.

Table I
Helical Conformations Corresponding to the Minima in the Energy Surface for BPA Polycarbonate

ϕ,ψ	n	h
70,40 40,70	2.14	−9.39
−40,−70 −70,−40	12.14	3.51
−50,−80[a] −80,−50	12.14	−3.51
−40,110 110,−40	2.01	10.27
−110,40 40,−110	4.26	6.48

[a] Position close to the minimum; see text.

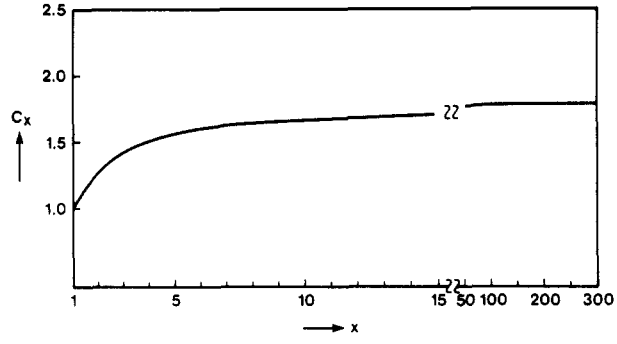

Figure 6. Characteristic ratio C_x plotted as a function of x (the degree of polymerization) for BPA polycarbonate.

trix **T**. The subscript refers to the 2,2 element. The matrix $\langle \mathbf{T} \rangle$ is given by

$$\langle \mathbf{T} \rangle_{ij} = z^{-1} \sum_{\phi} \sum_{\psi} \mathbf{T}_{ij} \exp(-\mathbf{E}(\phi,\psi)/RT) \qquad (6)$$

with z defined according to eq 1. In the limit of an infinite chain, eq 5 reduces to

$$C_\infty = (\langle r^2 \rangle_0 / x l^2)_\infty = (\mathbf{E} + \langle \mathbf{T} \rangle)(\mathbf{E} - \langle \mathbf{T} \rangle)^{-1} \qquad (7)$$

In this case, the values of C_∞ and $(\langle r^2 \rangle_0/M)_\infty$ are related by

$$(\langle r^2 \rangle_0/M)_\infty = C_\infty l^2 / M_b \qquad (8)$$

Here, M_b is the molecular weight of one repeat unit. In the calculations which follow, $M_b = 254$ and $l = 12.63$ Å were used.

With $\zeta = 60°$ and if ϕ and ψ are varied from 0° to 360° each at intervals of 10°, the average matrix for BPAC is given by

$$\langle \mathbf{T} \rangle = \begin{bmatrix} -0.0390 & -0.1093 & -0.0019 \\ 0.1090 & 0.2943 & 0.0048 \\ 0.0020 & 0.0052 & 0.0012 \end{bmatrix} \qquad (9)$$

The plot of C_x for BPAC, as a function of x, is shown in Figure 6. It is seen that C_x increases slightly up to $x \approx 15$, and thereafter the increase is negligible. The value of C_∞ is 1.789. This translates to $\langle r^2 \rangle_0/M = 1.12$. The calculated values of C_∞ for the BPAC chain with $\zeta = 40°$ and 80° are 1.780 and 1.792, respectively. Thus, the effect of varying ζ seems to be insignificant.

It was discussed above that both extended and flat-helical types of conformations are equally probable for the BPAC chain. The effect of these conformations on C_∞ can be discerned by considering only parts of the (ϕ,ψ) map. In Figure 4, in the range of $\phi = 0$–120° and $\psi = 0$–120°, the extended type of conformations occur, and n varies between 2 and ~4. If the calculation is performed within this range, a value of 8.3 is obtained for C_∞, which is far greater than the value of 1.789 obtained by averaging over the entire (ϕ,ψ) domain. On the other hand, in the range of $\phi = -120°$ to 0° and $\psi = -120°$ to 0°, flat-helical conformations occur. Restricting the calculation of C_∞ to this range leads to $C_\infty = 1.39$. Thus, in actuality, the BPAC chain can be described as consisting of segments of flat-helical and extended-helical conformations, as well as the nonhelical conformers.

The value of $\langle r^2 \rangle_0/M = 1.12$ derived here is higher than the experimental value[3] of 0.87 Å^2/(g·mol). However, it compares well with the more recent experimental and theoretical results.[21,22] In the present calculations, the carbonate group was confined to the trans configuration. The occurrence of the cis form has been shown[4] to cause a small but significant reduction in the value of $\langle r^2 \rangle_0/M$. These calculations are not attempted here. The purpose of this work was to show that the equal energies and hence the equal population of the extended- and flat-helical conformations of the BPAC chain contribute to the small value of $\langle r^2 \rangle_0/M$.

The temperature coefficient of the characteristic ratio, $d[\ln (C_\infty)]/dT$, calculated at 300 K, with $\zeta = 60°$ leads to a value of 9.78×10^{-5}. Such a small value for the temperature coefficient has been indicated from experiments. The measurements of Berry et al.[3] show that the characteristic ratio is essentially independent of temperature. The small value of the temperature coefficient can be attributed to the equal energy of the flat- and extended-helical, as well as the nonhelical, conformations.

Conclusions

For the bisphenol A polycarbonate, both helical and extended types of conformations are of equal energy and the resulting equal population of these conformers contribute to a small value of the characteristic ratio of the unperturbed end-to-end distance and its temperature coefficient. Although the flat-helical conformations have not hitherto been observed in the crystalline state of BPAC, complexation with suitable small molecules could lead to the crystallization of such conformations. The calculations also show that cyclic conformers are possible energetically for BPAC oligomers.

Registry No. BPAC (SRU), 24936-68-3; BPAC (copolymer), 25037-45-0.

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Configurational Statistics of C(4)–C(8) Linked Homopolymers of (+)-Catechin or (−)-Epicatechin

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ABSTRACT: Configuration-dependent physical properties of homopolymers of (+)-catechin and (−)-epicatechin, linked from C(4) of one monomer to C(8) of the next, have been investigated by using rotational isomeric state theory. The characteristic ratios and components of the persistence vector have been evaluated for these polymers using structural information obtained from MM2 calculations for dimers of (+)-catechin and (−)-epicatechin. There are two rotational isomers at the interflavan bond between monomer units. Helices are formed if one rotational isomer is populated to the exclusion of the other. The chirality of the helix is determined solely by the selection of the rotational isomer. It is independent of the stereochemistry at C(3) and C(4). The polymers form random coils with unperturbed dimensions smaller than those of atactic polystyrene with the same molecular weight if the relative population of the two rotational isomers is assigned in the manner required by recent time-resolved fluorescence measurements and the rotational isomers are randomly distributed along the chain.

Polymers of (+)-catechin and (−)-epicatechin are abundant in the plant kingdom.[1-4] The structure of the monomers and the numbering scheme for atoms in the fused ring system are depicted in Figure 1. The older literature refers to these polymers as condensed tannins. The structure of (−)-epicatechin has been firmly established by X-ray crystallography.[5,6] In contrast, the free phenol form of (+)-catechin has thus far resisted crystallization in a form suitable for a structure determination. Nevertheless, the combination of crystal structures for several derivatives of (+)-catechin and (−)-epicatechin,[7-11] detailed analysis of coupling constants measured by high-resolution NMR,[11] theoretical conformational analysis,[12,13] and time-resolved fluorescence[14-16] has produced a good picture of the conformational behavior of the monomers and several dimers. This information provides an adequate basis for the construction of a realistic rotational isomeric state treatment of the higher polymers and a determination of the relationship between the conformational properties of a long chain and the type of linkage used for connection of the monomers.

The development of a realistic rotational isomeric state model for these polymers is a matter of some urgency because their conformational behavior in solution is controversial. The most common linkage is from C(4) of one monomer to C(8) of its neighbor.[17,18] Haslam[1] suggested that polymers with this type of linkage would form helices. Furthermore, the handedness of the helix was believed to be determined by the stereochemistry at C(3). The helices would be right-handed if the monomer units were (+)-catechin and left-handed if the polymer was formed from (−)-epicatechin.[1] Minimization of the conformational energy has been used for identification of helices of low energy for several types of oligomers.[19]

Two lines of experimental evidence are not easily reconciled with the proposition that the polymers are helical or rodlike. The overall dimensions, as measured by the behavior of peracetylated polymers upon gel permeation chromatography, are more compact than polystyrene of the same molecular weight.[2] Furthermore, there are two rotational isomers at the interflavan bond, and both rotational isomers are populated to a significant extent at ambient temperature in the free phenol forms of 4–6 and 4–8 linked dimers.[15,16] Interconversion of these rotational isomers is fast on the NMR time scale, but it is slow on the fluorescence time scale. A helix would be formed if one rotational isomer were populated to the exclusion of the other, but population of both rotational isomers should disrupt the helix and produce a random coil.

A rotational isomeric state model is described here for $4\alpha \rightarrow 8$ and $4\beta \rightarrow 8$ linked homopolymers of (+)-catechin and (−)-epicatechin. The required geometry and heterocyclic ring conformations used in the present analysis are based on MM2 calculations for the monomers[11] and dimers.[12,13] The MM2 algorithm provides excellent agreement with the crystal structure conformation of (+)-catechin–($4\alpha \rightarrow 2$)-phloroglucinol heptamethyl ether,[11] and also correctly predicts the preferred conformation of free (−)-epicatechin, as determined by the crystal structure. In this crystal structure (as well as in most other derivatives), the dihydroxyphenyl substituent at C(2) is placed in a pseudoequatorial position. An exception is provided by the crystal structure of penta-*O*-acetyl-(+)-catechin, where a pseudoaxial orientation is observed,[8] but MM2 calculation predicts a pseudoequatorial orientation.[11] This unusual conformation may arise from crystal packing forces (of intermolecular origin) not considered in the MM2 algorithm. Support for this contention is provided by the observation that the NMR coupling constants measured in solution are incompatible with the conformation adopted by penta-*O*-acetyl-(+)-catechin in the crystalline state.[11] Conformational analysis of the dimers of (+)-catechin and (−)-epicatechin using the MM2 algorithm has been performed for both axial and equatorial orientation of the C(2) substituent.[12,13] However, since the equatorial conformers are more frequently observed in solution[11] and

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