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The Effect of Substituents on the Conformational Features of Polycarbonates

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ABSTRACT: A comparison of the conformational freedom of rotation of the contiguous phenyl groups in polycarbonates, with various substituents at the C_α atom, is presented. Conformational maps were calculated for the following substituents: (i) CH_3,CH_3; (ii) H,H; (iii) H,CH_3; (iv) H,C_6H_5; (v) CH_3,C_6H_5; (vi) C_6H_5,C_6H_5; (vii) cyclohexyl; and (viii) CCl_2. Synchronous rotation of the phenyls with a low-energy barrier is possible for (i), (iv), (v), and (vii). Although the extent of freedom of rotation depends on the nature of the substituent, there is very little difference in the characteristic ratio of the unperturbed end-to-end distance for these polycarbonates, and the temperature coefficient of the characteristic ratio is extremely small. In spite of the limited conformational freedom, it is shown that the steric symmetry and the geometric asymmetry of the chain segments enable the treatment of these chains in the framework of the freely rotating chain.

Introduction

Since the theoretical work of Williams and Flory[1] on the average chain dimension of bisphenol A polycarbonate (BPAPC), several papers have been published on the conformational aspects of this polymer. Some of these efforts[2-7] were aimed at calculating the average properties and crystalline conformational features. On the other hand, the molecular motion in polycarbonate and its interpretation in terms of the π flips of the phenyl groups and the rotation of the carbonate group have been the focus of several studies[8] using NMR and dynamical mechanical spectroscopy (DMS). To this end, the purpose of a number of conformational calculations[9-13] was to estimate the barrier to the rotations of the phenyls, in order to rationalize and interpret the experimental observations. A theoretical model[14] for the local motion in BPAPC and computer simulation[15] of the ring flip have also been described.

Yee and Smith[16] studied several polycarbonates by DMS, to estimate the relative influence of the substituents at the C_α atom, at the carbonate segment as well as on the phenyl. An in-depth discussion on the phenyl motion and a comparison of the NMR and DMS results have been presented. Jones et al.,[17] from NMR studies, concluded that the phenyl motion in chloral polycarbonate is more restricted, compared to the motion in BPAPC.

In a recent paper,[6] we reported the energy calculations on BPAPC in terms of the rotations ϕ and ψ (see Figure 1) of contiguous phenyl groups. The shapes of the segments, which would result from the perpetuation of a certain (ϕ,ψ) value, were analyzed in terms of the calculation of helix parameters. The results showed that both flat-helical and extended helical shapes are of equal energy in the accessible domains of the conformational map. The small value of the characteristic ratio $\langle r^2\rangle_0/nl^2$ and its temperature coefficient were rationalized as due to the equal energy of the above conformers. Cyclic polycarbonates were also found to be stereochemically possible. In addition, the conformational map showed features which could account for the phenyl motion which has been detected by NMR and DMS studies.

In this paper, a comparison of the conformational features of polycarbonates with different substituents at the C_α atom is presented. The analysis is restricted to the relative conformation of the contiguous phenyl groups. The interaction between these substituents and the carbonate group is expected to be negligible due to the large distance of separation between them. Conformational maps were calculated for the cases of the following substituents: (i) CH_3,CH_3 (2,2-diphenylpropane); (ii) H,H (diphenylmethane); (iii) H,CH_3 (1,1-diphenylethane); (iv) H,C_6H_5 (triphenylmethane); (v) CH_3,C_6H_5 (1,1,1-triphenylethane); (vi) C_6H_5,C_6H_5 (tetraphenylethane); (vii) cyclohexyl (1,1-diphenylcyclohexane); and (viii) CCl_2 (1,1-dichloro-2,2-diphenylethylene). The relative extent of freedom of rotation of the contiguous phenyls and its bearing on the average chain dimension are examined. Analysis of the chain shapes in terms of helix parameters is also given. In addition, the concept of describing the polycarbonates as freely rotating chains is discussed.

Details of Calculations

The bond lengths and bond angles for the skeletal geometry were chosen to be the same as before[6] and were derived from the crystal structure of diphenylcarbonate.[3] A value of 109.5° was assigned for the bond angle C_4–C_α–C_4'. Bond lengths of 1.36 and 1.1 Å were used for the C–C and C–H bonds in the case of aromatic substi-

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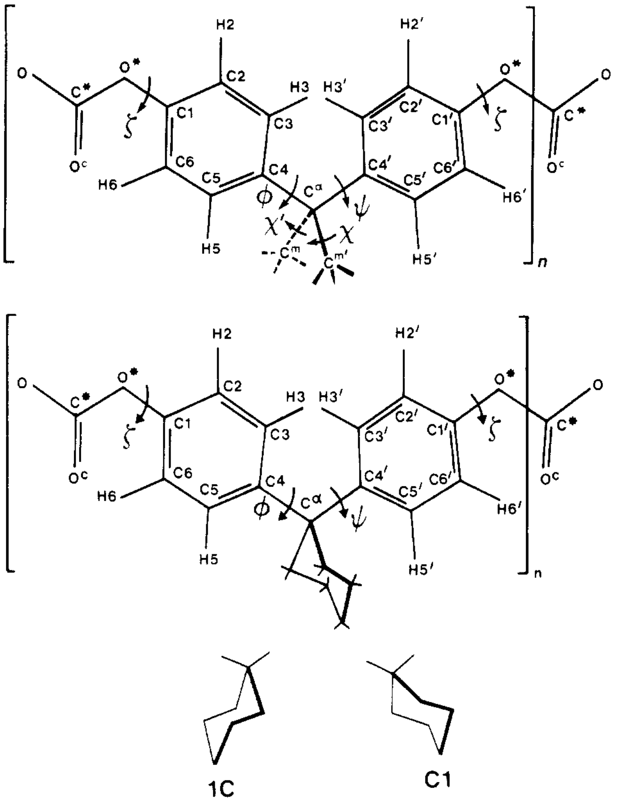

Figure 1. Schematic representation of the polycarbonate chain, with relevant torsional angles marked: (a, top) BPAPC; (b, bottom) with cyclohexyl substituent.

tution. For the CCl_2 substitution, the following parameters were used:[18] C=C, 1.38 Å; C—Cl, 1.77 Å; C_4—C_α—C_4', 108°; C_4—C=C, 126°; C_4'—C=C, 126°; C_α=C—Cl, 124°; Cl—C—Cl, 112°. A quadratic potential with a barrier of 15 kcal·mol^{-1} was used[18] for the rotation around the C_α=C bond.

The functions and parameters used for the energy calculations are the same as previously described.[6] The Lennard-Jones 6-12 function was used for calculating the nonbonded interaction energies. For the chlorine atom, values of $\alpha = 2.3$ and $N = 14$ were used.[18,19]

For the calculation of the interaction energies of the contiguous phenyl groups between themselves and with the substituents at the C_α atom, 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 (Figure 1). In the case of methyl substitution, the angle χ, defining the positions of the methyl hydrogens, was varied from 0° to 120° 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. For the phenyl substituent, the angle $\chi = 0°$ corresponds to the conformation in which the plane of the phenyl is normal to the plane defined by C_4–C_α–C_4'. For each of the (ϕ,ψ) states, the angle χ was varied from 0° to 180°, at intervals of 10°, in order to locate the phenyl side group in its minimum energy position corresponding to that (ϕ,ψ) state. A similar range was chosen for the case of the CCl_2 substitution.

In the case of the cyclohexyl substitution, the latter can be considered in two chair forms, as shown in Figure 1b. Arbitrarily denoting them as C1 and 1C forms, the two chairs are indistinguishable in the case of an isolated cyclohexane molecule. However, when appended to the C_4 and C_4' atoms as in Figure 1b, the two forms differ in their disposition relative to the adjacent skeletal bonds. In the calculation of the energies of each of the (ϕ,ψ) states, both chair forms were examined and the one which led to lower energy was taken into account. The boat or intermediate half-chair forms were not considered, due to the inherent higher energy of such conformers.

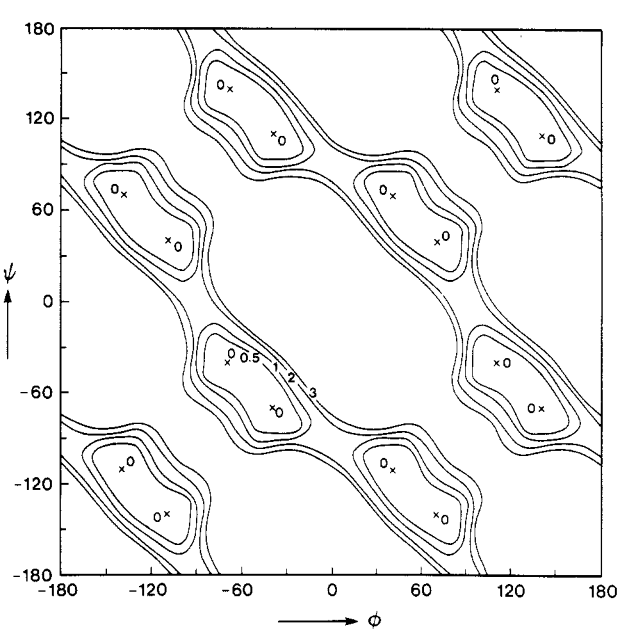

Figure 2. Conformational energy map for the BPAPC segment. Contours are drawn relative to the minima marked ×.

If the same values of the torsion angles ϕ, ψ, and ζ perpetuate over a few repeat units in the chain, the segment would take a regular helical shape. The calculation of the helix parameters n, the number of repeat units per turn of the helix, and h, the advance per repeat unit parallel to the helix axis (pitch = nh), has been described before.[6] Based on the previous results,[4,6] a value of $\zeta = 60°$ was used for these calculations.

The characteristic ratio $\langle r^2\rangle_0/nl^2$ was calculated by using eq 5–7 in ref 6. The partition function Z was calculated in the usual manner, after locating the side groups in their minimum energy positions as described above. The value of Z_f, corresponding to free rotation, is 36^2. In addition, a partition function Z' was calculated so as to include each one of the combinations of the skeletal and side group conformations. With this scheme, for BPAPC, for example, Z' would include the energies of 36 × 36 × 12 × 12 states. The Z'_f corresponding to free rotation is simply the total number of states: 186 624.

Results and Discussion

The conformational map for BPAPC and the map of helix parameters are shown in Figures 2 and 3, respectively. Although these two figures have been published in part before,[6] they are included here for the purpose of comparison and discussion.

The energy map in Figure 2 shows that the contours for 2 and 3 kcal·mol^{-1} envelope a continuous range of conformations. Interconversions between conformations can occur by synchronized variations in ϕ and ψ. Such a synchronization of conformational movement is indicated in the work of Tonelli[2] and Bicerano and Clark.[13] The energy is high in the vicinity of conformations with ϕ = 0° or 180° and ψ = 0° or 180°. This is due to the strong repulsive interaction between the ortho hydrogens. Bicerano and Clark,[13] using quantum mechanical methods, calculated the minimum in energy to occur at $\phi = \psi = 48.1°$. This conformation is within 0.5 kcal·mol^{-1} from the minimum in Figure 2. The energy at (ϕ,ψ) = (90°,90°) is

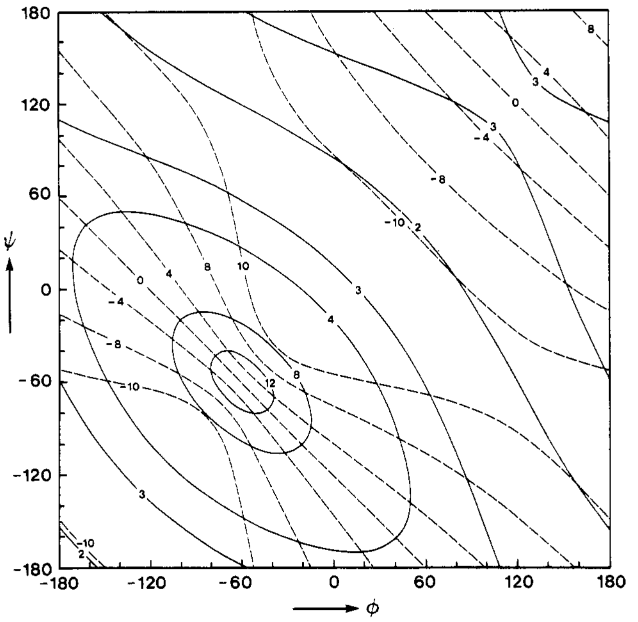

Figure 3. Isocontours of helix parameters n (solid lines) and h (dashed lines) shown as a function of ϕ and ψ. The negative values of h denote left-handed helices.

Table I
Results of the Conformational Analysis of the Various Polycarbonates

substituent at the C_α atom	E_0, kcal·mol^{-1} [a]	partition function Z[b]	partition function Z'	C_∞
H,H	-4.92	84.5	84.5	1.797
H,CH_3	-3.03	41.1	75.2	1.787
CH_3,CH_3	0	179.3	410.6	1.789
H,C_6H_5	1.81	70.6	118.8	1.779
CH_3,C_6H_5	3.74	41.7	133.9	1.769
cyclohexyl	5.26	40.1	40.1	1.738
C_6H_5,C_6H_5	19.66	62.1	94.4	1.743
C,Cl_2	-8.12	64.5	200.6	1.730

[a] Energies at the minima, relative to the CH_3,CH_3 case. [b] For free rotation, Z = 1296 and C_∞ = 1.736.

7.5 kcal·mol^{-1}, which, along with a torsional energy contribution (neglected in the present calculations as insignificant[2-4]) of about 1 kcal·mol^{-1}, is close to the value of 9.0 kcal·mol^{-1} deduced by Bicerano and Clark. However, with conformations such as (ϕ,ψ) = (70°,-80°), (80°,110°), (-110°,-80°), and (-100°,110°) which constitute the least energy path, the barrier is 3.8 kcal·mol^{-1}. This is similar to the value of 3.1 kcal·mol^{-1} obtained by Jones et al.[17] using the MNDO method. Thus, in spite of the limitations of the semiempirical method of the type used here, the similarity of the present results to those using the quantum mechanical methods is encouraging. It was discussed before that the π flip of one phenyl, accompanied by a small rotation of the contiguous unit, does not involve high energy. For example, consider two conformations with (ϕ,ψ) = (-120°,90°) and (-60°,-90°). If a straight path is drawn between them, all the intermediate conformations are within 2 kcal·mol^{-1}. Thus, a 180° change in ψ is accomplished, with only a 60° change in ϕ.

Comparison of Figures 2 and 3 shows that both flat-helical and extended helical conformations are possible in the accessible domains and that these are equal in energy. In addition, macrocyclic polycarbonates are also stereochemically feasible. These features were discussed in detail before.[6] The calculated values of the partition functions Z and Z' and C_∞ are given in Table I. The latter is in good agreement with the experimental values of ~1.9.[20-22]

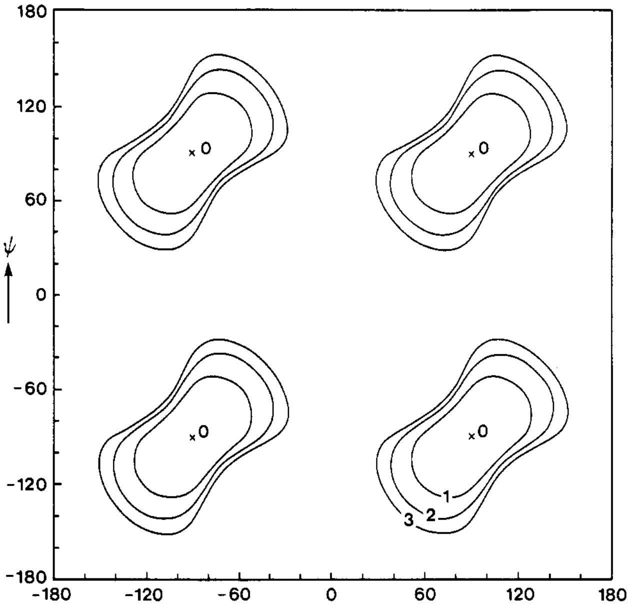

Figure 4. Conformational energy map for the polycarbonate chain segment with H,H substitution at the C_α atom.

H,H Substitution. The energy map for the case of H,H substitution at the C_α atom is shown in Figure 4. Compared with Figure 2, the notable difference is that the continuous range of accessible conformations seen in Figure 2 is not available for this case. The minima in Figure 4 occur at positions which are of high energy for the BPAPC chain. For example, the minimum in Figure 4 at (ϕ,ψ) = (90°,90°) falls in the high energy region of the map shown in Figure 2. The energy E_0 at the minimum for the H,H substitution case is about 4.9 kcal·mol^{-1} less than that for the case of BPAPC. The calculated barrier between the symmetrically related minima is 5.6 kcal·mol^{-1}. Surrounding each minimum in Figure 4, the contour for 3 kcal·mol^{-1} spans a range of about 100° in ϕ and ψ. Hence, local large-scale oscillation of the phenyls is possible. Although the size of the atoms appended to C_α is smaller than in the case of BPAPC, the conformational partition function Z (Table I) is about half that of the latter. When the side group rotations are considered, the value of Z' is about one-fifth of that of BPAPC.

Superposition of Figures 2 and 4 shows that each of the domains within 3 kcal·mol^{-1} in the latter bridges two similar domains in Figure 2. For example, the domain in the vicinity of the minimum at (ϕ,ψ) = (-90°,-90°) in Figure 4 bridges the two domains in Figure 2 centered around (ϕ,ψ) = (-120°,-120°) and (-60°,-60°).

Superposition of Figures 3 and 4 shows that in the accessible domains, both flat-helical and extended helical conformations are possible. Corresponding to the minima at (ϕ,ψ) = (-90°,-90°), (90°,-90°), (90°,90°), and (-90°,90°), the helix parameters (n, h) are (6.26, -10.7 Å), (2.65, 9.6 Å), (2.78, -5.7 Å), and (2.65, 9.6 Å), respectively. Within the contour of 3 kcal·mol^{-1}, around the minimum at (-90°,-90°), large flat-helical conformations with n ranging from 4 to 12 and h from 0 to 10 Å occur. In the same region, macrocyclic structures, with n = 10–14, are possible. Likewise, close to the minimum at (90°,90°), cyclic structures with n = 3 are stereochemically possible.

The calculated value of the characteristic ratio C_∞ is given in Table I. In spite of the lower partition function as compared to the BPAPC chain, the value of C_∞ does not differ drastically. This can be rationalized on the basis of the contributions to the chain shape from the flat-helical

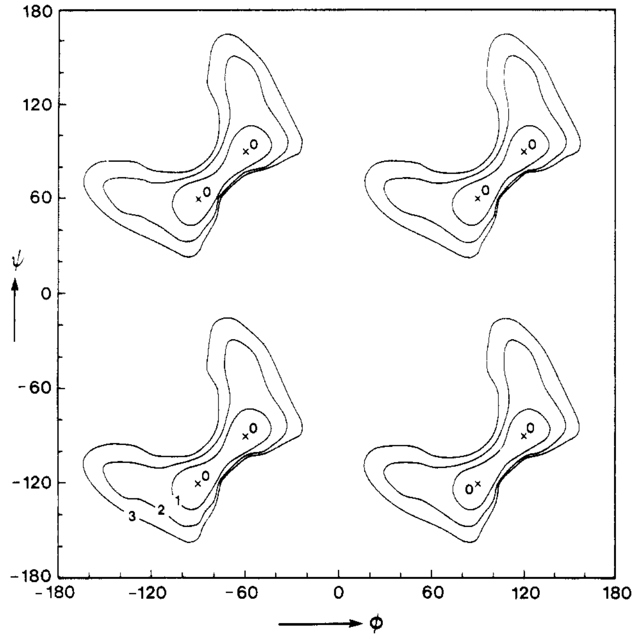

Figure 5. Conformational energy map for the polycarbonate chain segment with H,CH_3 substitution at the C_α atom.

and extended helical conformers, which are of equal energy.

H,CH_3 Substitution. The conformational map is shown in Figure 5. In terms of the overall features, it is similar to the case of the H,H substitution shown in Figure 4. However, the locations of the minima are shifted, and the energy (E_0) corresponding to the minimum is approximately 1.9 kcal·mol^{-1} higher than for the H,H substitution. Similar to the map in Figure 4, the minima are localized. The extent of local oscillation available to the phenyls is less than the case of the H,H substitution. This is reflected in the conformational partition function, Z (Table I), which is about half of that of the H,H case. Comparison of Figures 2 (BPAPC) and 5 shows that each of the domains within 3 kcal·mol^{-1} in the latter bridges two similar domains in Figure 2, as discussed above for Figure 4.

Comparison of Figures 3 and 5 shows that in this case, also, helices of different shapes are stereochemically possible. The calculated value of the characteristic ratio (Table I) differs very little from either that of the BPAPC or the H,H substitution.

H,Phenyl Substitution. The energy map for this case is shown in Figure 6. The striking feature is its overall resemblance to the map shown in Figure 2 for BPAPC. Several minima occur, at symmetrically related positions. The location of the minima differ drastically from the case of the H,H substitution. The contours for 2 and 3 kcal·mol^{-1} span a wide, continuous range of conformations similar to the case of BPAPC, although the width of the band of accessible conformations is less in this case. Hence, it is possible that π flips similar to the case of BPAPC occur with H,phenyl substitution, with a synchronization of the rotations of the contiguous phenyl groups.

The conformational partition functions, Z and Z', are less than those of BPAPC but higher than the value for the case of H,CH_3 substitution. The calculated value of the characteristic ratio is small in this case as well and differs very little from that of BPAPC or the other polycarbonates discussed above. This can be again traced to the equal energies of the extended and helical conformational shapes of the chain in the accessible domains.

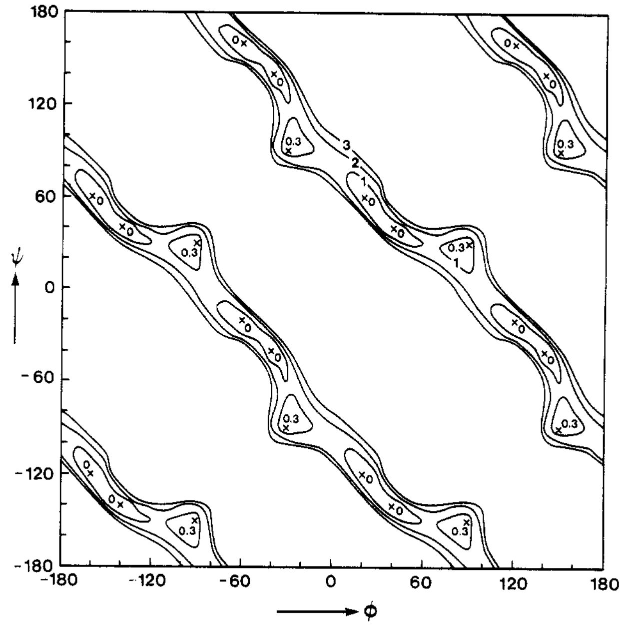

Figure 6. Conformational energy map for the polycarbonate chain segment with H,C_6H_5 substitution at the C_α atom.

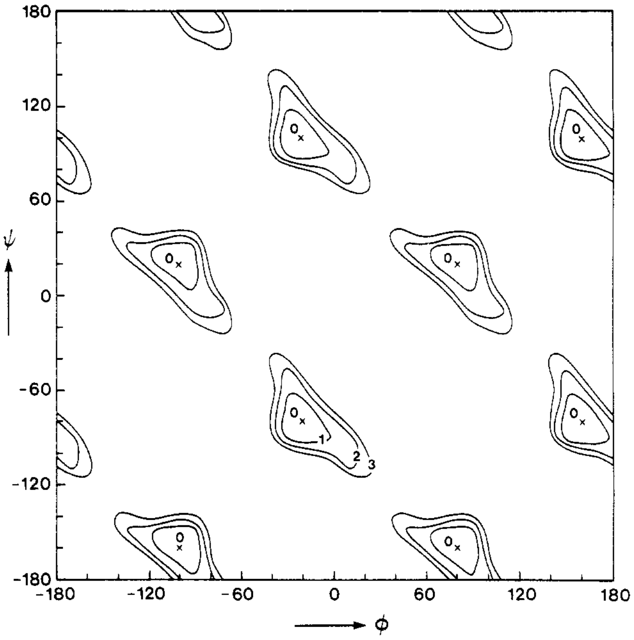

Figure 7. Conformational energy map for the polycarbonate chain segment with CH_3,C_6H_5 substitution at the C_α atom.

CH_3,Phenyl Substitution. The conformational map is shown in Figure 7. In contrast to the case of H,phenyl substitution (Figure 6) or BPAPC (Figure 2), the minima are localized. Compared to the map in Figure 4 for H,H substitution, the oscillation of the phenyl around each of the minimum is also more restricted. This is reflected in the partition function, Z, which is less than that for the cases of BPAPC, H,H, or H,phenyl substitution. However, because of the additional states afforded by the CH_3 group, the value of Z' is slightly higher than the H,phenyl case. Comparison of Figures 6 and 7 shows that the minima in the latter occur close to the secondary minima (of relative energy 0.3 kcal·mol^{-1}) in Figure 6. The value of the characteristic ratio is 1.77, which is again similar to the cases discussed above.

Phenyl,Phenyl Substitution. The energy map for this case is not shown here, due to the very small area in each domain within the contour of 1 kcal·mol^{-1}. The energy

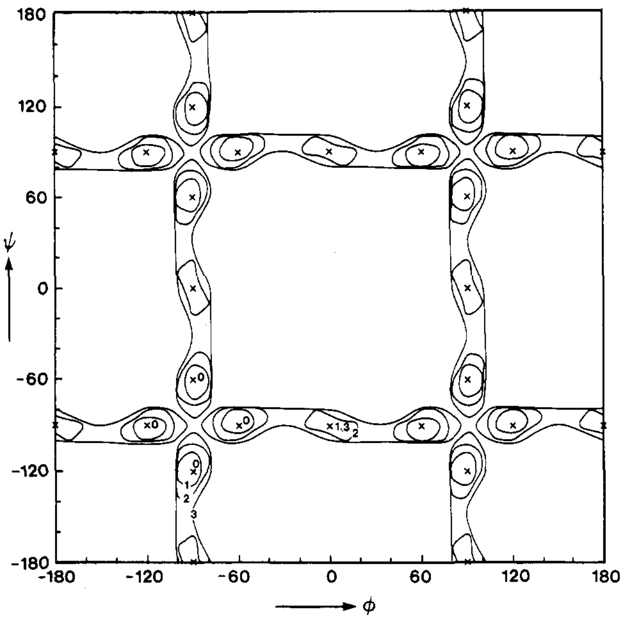

Figure 8. Conformational energy map for the polycarbonate chain segment with cyclohexyl substitution at the C_α atom.

increases rapidly around each of the principal minima, which occur at $(\phi,\psi) = (\pm 90°,\pm 160°)$ and $(\pm 160°,\pm 90°)$. The energy, E_0, corresponding to the minima is also high compared to the other cases listed in Table I. The partition function is, however, comparable to that of the H,phenyl substitution, and the value of C_∞ is also small.

Cyclohexyl Substitution. The energy map for the 1,1-diphenylcyclohexane segment is shown in Figure 8. As mentioned above, the two dispositions of the cyclohexyl moiety, C1 and 1C, were examined at each of the ϕ,ψ conformations. Comparison with Figure 2 shows that the rotation of the phenyls is much more restricted in this case. In Figures 2 (BPAPC) and 6 (H,phenyl substitution), the contour for 2 kcal·mol^{-1} spans a band of conformations. In contrast, in Figure 8 for the cyclohexyl substitution, the contour for 2 kcal·mol^{-1} envelopes a small domain. The partition function (Table I) is smaller than that of BPAPC by a factor of 4.

Figure 8 shows that, for discrete values of $\phi \approx \pm 90°$, the value of ψ can vary from -80 to $+80°$ within a barrier of less than 3 kcal·mol^{-1} and from -180 to $+180°$ within a barrier of 3.5 kcal·mol^{-1}. In all these conformations, the preferred disposition of the side group remains 1C chair form. In this conformation of the cyclohexyl moiety, severe steric repulsions between the atoms of the side group and the atoms of the unprimed phenyl (Figure 1) restrict the conformation of the latter to $\phi \approx \pm 90°$. However, the primed phenyl group is virtually free of any interaction with the side group. Similarly, with $\psi = \pm 90°$, the value of ϕ can vary over the entire range of -180 to $+180°$, within a barrier of 3.5 kcal·mol^{-1}. In all these conformations, the C1 chair form of the side group is preferred. Thus, for select dispositions of one of the phenyls, the contiguous moiety can enjoy a wide range of accessible conformations. Hence, heterogeneity of phenyl motion is indicated in this case. The flip motion of the cyclohexyl group is also a possibility.

As in the other cases discussed above, the characteristic ratio is small and differs very little from the value for polycarbonates with other substituents at the C_α atom.

CCl_2 Substitution. The conformational map is shown in Figure 9. The features of the map are similar to that shown in Figure 4 for the case of H,H substitution. The minima occur at identical locations, although the energy,

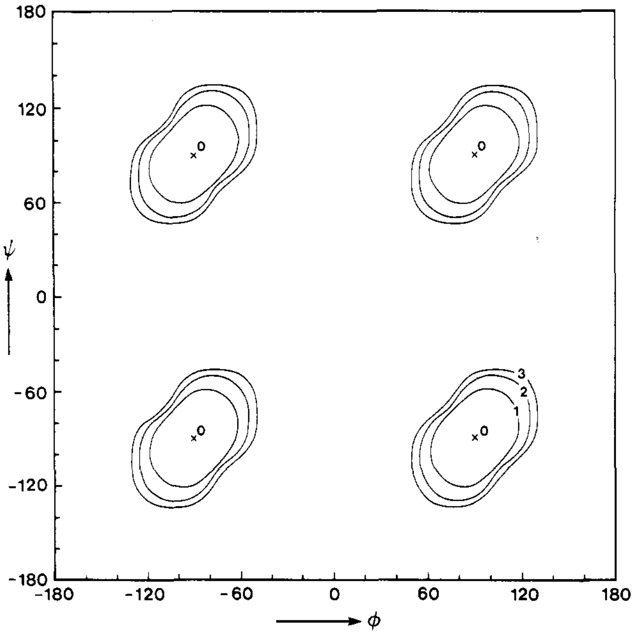

Figure 9. Conformational energy map for the polycarbonate chain segment with CCl_2 substitution at the C_α atom.

E_0, corresponding to the minima is about 3 kcal·mol^{-1} less in the present case (Table I). Around each of the minima, the range of conformations, within the contours for 1, 2, and 3 kcal·mol^{-1}, is small compared to that in Figure 4. The calculated barrier between the domains is about 14 kcal·mol^{-1}, which is similar to the value of 10 kcal·mol^{-1} from the MNDO results of Jones et al.[17] Comparing Figures 2 and 9, it is evident that the band of accessible conformation, which would facilitate synchronous rotation of the phenyls, does not exist in the case of the CCl_2 substitution. This agrees with the NMR observation[17] that the phenyl motion in this case is more restricted compared to that in BPAPC. Figure 9 shows that oscillation of the phenyls of about ±60° is possible around the minima. The value of the characteristic ratio is small and is similar to that of the other polycarbonates discussed above.

Conclusions

The above calculations show that although the extent of freedom of rotation depends on the nature of the substituent, the value of C_∞ does not differ appreciably between all these types of polycarbonates. Williams and Flory[1] and Tonelli[2] treated the BPAPC as freely rotating chain. This has been questioned by Bicerano and Clark.[13] As seen from Figure 2, while synchronized rotations of the phenyls are possible, the range of accessible conformations is indeed limited. With the interval of 10° in ϕ and ψ used for the above calculations, only 38% of the conformations in Figure 2 is within 3 kcal·mol^{-1}. Similarly, for the H,H substitution (Figure 4), only 27% of the conformations is within 3 kcal·mol^{-1}. On this basis, the polycarbonate is not a freely rotating chain. However, the conformational features of the chain lend themselves to be treated under the framework of the freely rotating chain concept. The figures presented in this paper show that the conformational energy maps are symmetric, and in each map the symmetrically related positions are of equal energy. In geometric terms, these conformers which are sterically symmetric, when perpetuated, lead to flat-helical or extended helical type of shapes. Thus, both types of helical shapes are of equal energies. This is not usually the case for other polymers; i.e., the flat and extended helices are not of equal energy. The conformations which promote flat-helical or macrocyclic shapes reduce the average end-to-end distance. Because of this feature, i.e., the energetic symmetry and the geometric asymmetry of the conformational map, the value of C_∞ is close to that of a freely rotating chain. The value of $(C_\infty)_f$ corresponding to free rotation, with the geometry used here, is 1.736, which leads to $\langle r^2\rangle_0/\langle r^2\rangle_{0,f} = 1.03$. Thus, the symmetry of the energy surface permits treatment of the BPAPC and the other polycarbonates discussed above, as freely rotating chains, with each repeat unit segment represented by a virtual bond.[1,2] The calculated values of the temperature coefficient, $d(\ln C_\infty)/dT$ (in the range of 10×10^{-5} deg^{-1}), are also extremely small in these cases, indistinguishable from zero, i.e., that of the freely rotating chain.

The small values of the characteristic ratio and its temperature coefficient has been interpreted as due to the equal energy of the flat-helical and extended helical conformers.[6] In the crystalline state, the BPAPC assumes an extended 2-fold helical conformation.[23] An indirect evidence for the flat-helical conformations in polycarbonate is derived from the recent experimental observation[24] of a helix–coil transition in the mixed solvent system of 1,1,2,2-tetrachloroethane and n-propyl alcohol. The energies included in the partition function, Z', involve all the rotational states of both the skeletal and side group atoms. These energies could be used to calculate the conformational entropies in the manner described recently by Hopfinger et al.[25] to rationalize the differences in the glass transition temperatures of these polycarbonates.

Registry No. $(4,4'\text{-}HOC_6H_4C(CH_3)_2C_6H_4OH)(HOCO_2H)$ (copolymer), 25037-45-0; $(4,4'\text{-}HOC_6H_4C(CH_3)_2C_6H_4OH)(HOCO_2H)$ (SRU), 24936-68-3; $(4,4'\text{-}HOC_6H_4CH_2C_6H_4OH)(HOCO_2H)$ (copolymer), 29832-46-0; $(4,4'\text{-}HOC_6H_4CH_2C_6H_4OH)(HOCO_2H)$ (SRU), 28935-53-7; $(4,4'\text{-}HOC_6H_4CH(CH_3)C_6H_4OH)(HOCO_2H)$ (copolymer), 27815-48-1; $(4,4'\text{-}HOC_6H_4CH(CH_3)C_6H_4OH)(HOCO_2H)$ (SRU), 28774-91-6; $(4,4'\text{-}HOC_6H_4CHPhC_6H_4OH)(HOCO_2H)$ (copolymer), 29250-89-3; $(4,4'\text{-}HOC_6H_4CHPhC_6H_4OH)(HOCO_2H)$ (SRU), 31694-37-8; $(4,4'\text{-}HOC_6H_4CPh(CH_3)C_6H_4OH)(HOCO_2H)$ (copolymer), 29250-91-7; $(4,4'\text{-}HOC_6H_4CPh(CH_3)C_6H_4OH)(HOCO_2H)$ (SRU), 26985-42-2; $(4,4'\text{-}HOC_6H_4CPh_2C_6H_4OH)(HOCO_2H)$ (copolymer), 118631-41-7; $(4,4'\text{-}HOC_6H_4CPh_2C_6H_4OH)(HOCO_2H)$ (SRU), 28934-44-3; $(4,4'\text{-}HOC_6H_4C_6H_{10}C_6H_4OH)(HOCO_2H)$ (copolymer), 26471-16-9; $(4,4'\text{-}HOC_6H_4C_6H_{10}C_6H_4OH)(HOCO_2H)$ (SRU), 25135-52-8; $(4,4'\text{-}HOC_6H_4C{=}CCl_2C_6H_4OH)(HOCO_2H)$ (copolymer), 29057-43-0; $(4,4'\text{-}HOC_6H_4C{=}CCl_2C_6H_4OH)(HOCO_2H)$ (SRU), 31546-39-1.

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Long-Range Reading of Polypropylene Stereosequences: Undecad Assignment in Proton Spectrum by Two-Dimensional NMR Spectroscopy

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ABSTRACT: Application of 2D NMR spectroscopy to hemiisotactic polypropylene allowed us to resolve the proton methyl resonances of polypropylene at the nonad and undecad level. From the proton homonuclear J-resolved experiment, after strong digital filtering, the ^{1}H NMR spectrum devoid of homonuclear couplings was obtained at high resolution as a cross section of the 2D matrix at $^3J(CH_3\text{–}CH)/2$. Similarly, the $^{13}C\text{–}^1H$ correlated spectrum shows an unprecedented resolution, mainly in the methyl region. Thus, the assignment of the ^{1}H NMR spectrum was possible starting from ^{13}C resonances previously identified on the basis of a known stereosequence distribution.

Two-dimensional NMR spectroscopy has proved to be a useful tool for increasing resolution, achieved by spreading the spectrum along a second dimension. The best results have been obtained for biological macromolecules, for which overcrowding of resonances entirely precludes the analysis of certain spectral regions.[1,2] In the field of synthetic polymers a number of applications of 2D NMR have appeared in the past few years.[3-8]

Two-dimensional studies of polypropylene tacticity have

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