matic-carbon line shape as asymmetric (Figure 6), but not displaying a clear chemical shift anisotropy. Since the T_1's of the phenyl carbons can be shown to be less than a few seconds, we feel that substantial torsional motion of the phenyl side group must be occurring, although nothing like free rotation. This torsional motion results in dipolar broadening of the residual chemical shift anisotropy of the phenyl carbons as discussed above. In addition, some further dipolar broadening can be expected since the 8-G decoupling field used in these experiments is only comparable to the polystyrene proton line width.[23] Nevertheless, as seen in Figure 5, a large part of the line broadening is removed by magic-angle spinning thereby producing a spectrum with which one can readily perform T_1, $T_{1\rho}$, and cross-relaxation T_{CH} experiments.

It should be stressed, however, that a *combination* cross-relaxation and magic-angle spinning experiment could be complicated by the presence of either of two problems. First, if the static ^{13}C–^{1}H dipolar interaction is not particularly large for a given carbon (such as, for example, the nonprotonated quaternary carbon of polystyrene), and only static dipolar interactions are present (which is probably not the case for any carbon in polystyrene), magic-angle spinning at 2–4 kHz will remove all the heteronuclear dipolar interactions thereby short circuiting the spin–spin coupling necessary for the effective cross relaxation of that carbon.[2] Second, if, for some reason, the proton line width of a given polymer is not too large, say, on the order of 5–10 kHz, then magic-angle spinning at 2 kHz, while not substantially affecting the proton line width, may still make difficult establishing the Hartmann–Hahn condition. This occurs since the narrowed carbon lines cover a chemical-shift range comparable to the proton line width. Thus, a match of resonance frequencies in the rotating frame is not possible for all carbons at the same time, thereby confusing the results of a cross-polarization contact. We are presently in the process of evaluating these potential problems.

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Conformational Isomorphism. A General 2_1 Helical Conformation for Poly(β-alkanoates)

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ABSTRACT: Poly(β-hydroxyalkanoates) are found as endogenous carbon reserves in bacteria (e.g., poly(β-hydroxy butyrate, PHB) and as synthetic materials. In the former the β carbon is asymmetric due to a single substituent while in the latter (e.g., poly(pivalolactone), PVL) there are α and α' substituents. X-Ray diffraction analysis of crystalline oriented fibers of PHB and PVL has revealed near identical fiber repeats, and 2_1 chain symmetries. Conformational analysis of these two polyesters shows that of the possible conformations for each macromolecule the two of minimum energy are quasi-identical in terms of backbone dihedral angles, hence conformationally isomorphous. The general class of polyesters based on the substituted poly(β-propriolactone) backbone are predicted to have nearly identical crystalline conformations; in this respect they resemble the polypeptides which have the tendency to assume the Pauling helix in the crystalline state. In these poly(β-alkanoates) there are no intramolecular hydrogen bonds; van der Waals and electrostatic interactions are the main stabilizing forces. In the crystalline conformations the ester dipoles along a chain are perpendicular to the helix axis and contiguous dipoles are antiparallel with 3 Å between them.

From fiber diagrams it was shown that polyesters of the general formula $[\mathrm{COOR_1{-}OOCR_2}]_n$ (Carrothers' type) with alternating polarity of the ester groups present near planar conformations[1–6] in the crystalline state. Careful examination[6] of the homopolyesters based on ethylene glycol and the diacids (adipic and suberic, six and eight carbons, respectively) confirmed that the departure from planarity of the extended repeating unit was in the glycol moiety.

On the other hand a recent study[7] of the polyester based on butane-1,4-diol and adipic acid (poly(tetramethylene adipate)) showed that the skeleton was indeed completely extended in this case. It would appear that a more uniform spacing of the ester groups along the aliphatic chain, as would obtain in poly(tetramethylene adipate), removes the factor which produced the observed 0.5 Å shortening of the chain.[5]

By ring opening polymerization of lactones,[8–11] glycolides,[12,13] lactides,[14,15] and anhydro sulfites,[16,17] it is possi-

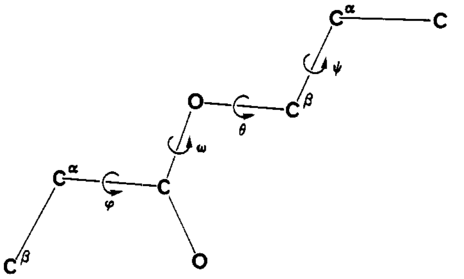


Figure 1. The standard configuration of β-lactone polyesters (ϕ = 0, Ψ = 0°, ω = 0°, and θ = 0°). The positive values of the torsion angles are obtained by taking sequences of four atoms in the backbone starting from left to right of the figure; rotation of the right-hand part of the chain counterclockwise in a Newman projection while looking from right to left causes the third bond to be superposed on the first.

ble to obtain linear polyesters with a regular "sense" of the ester groups $[\mathrm{R{-}COO}]_n$. Unlike the Carrothers type of polyesters which are nearly planar, in the crystalline state, a variety of conformations are reported for these homopolyesters. In addition to the zig-zag conformations of polyglycollide ($[\mathrm{CH_2{-}COO}]_n$),[18] poly(β-propiolactone) (PPL) ($[\mathrm{CH_2{-}CH_2{-}COO}]_n$),[19] and poly($\epsilon$-caprolactone) ($[(\mathrm{CH_2})_5{-}\mathrm{COO}]_n$),[20,21] two kinds of helical conformations are known: the 10/3 helix of the poly(L-lactide) ($[\mathrm{HC(CH_3){-}COO}]_n$)[22] and the 2_1 helix characteristic of PPL under certain conditions of crystallization.

By analysis of an X-ray fiber diagram of PPL, Wasai et al.[19] first proposed the 2_1 helix with a fiber repeat of 7 Å. Carazzolo[23] determined the crystalline structure of poly(pivalolactone) (PVL) ($[\mathrm{CH_2{-}C(CH_3)_2{-}COO}]_n$) and this polyester presents a 2_1 helix with a fiber repeat of 6 Å. These results were confirmed by Clark[24] and Perego et al.[25] Okamura and Marchessault[26] had shown that in the crystalline state poly(β-hydroxy butyrate) (PHB) ($[\mathrm{HC(CH_3){-}CH_2{-}COO}]_n$) adopts a 2_1 helical conformation with a periodicity of 6 Å, just as for PVL.[23]

It became apparent at this stage that the similarity in helix symmetry and fiber repeat for these polyesters, which are all poly(β-alkanoates) and in terms of synthesis are based on a β-propriolactone skeleton, was more than coincidental. Since the conformation of a polymer chain is de-

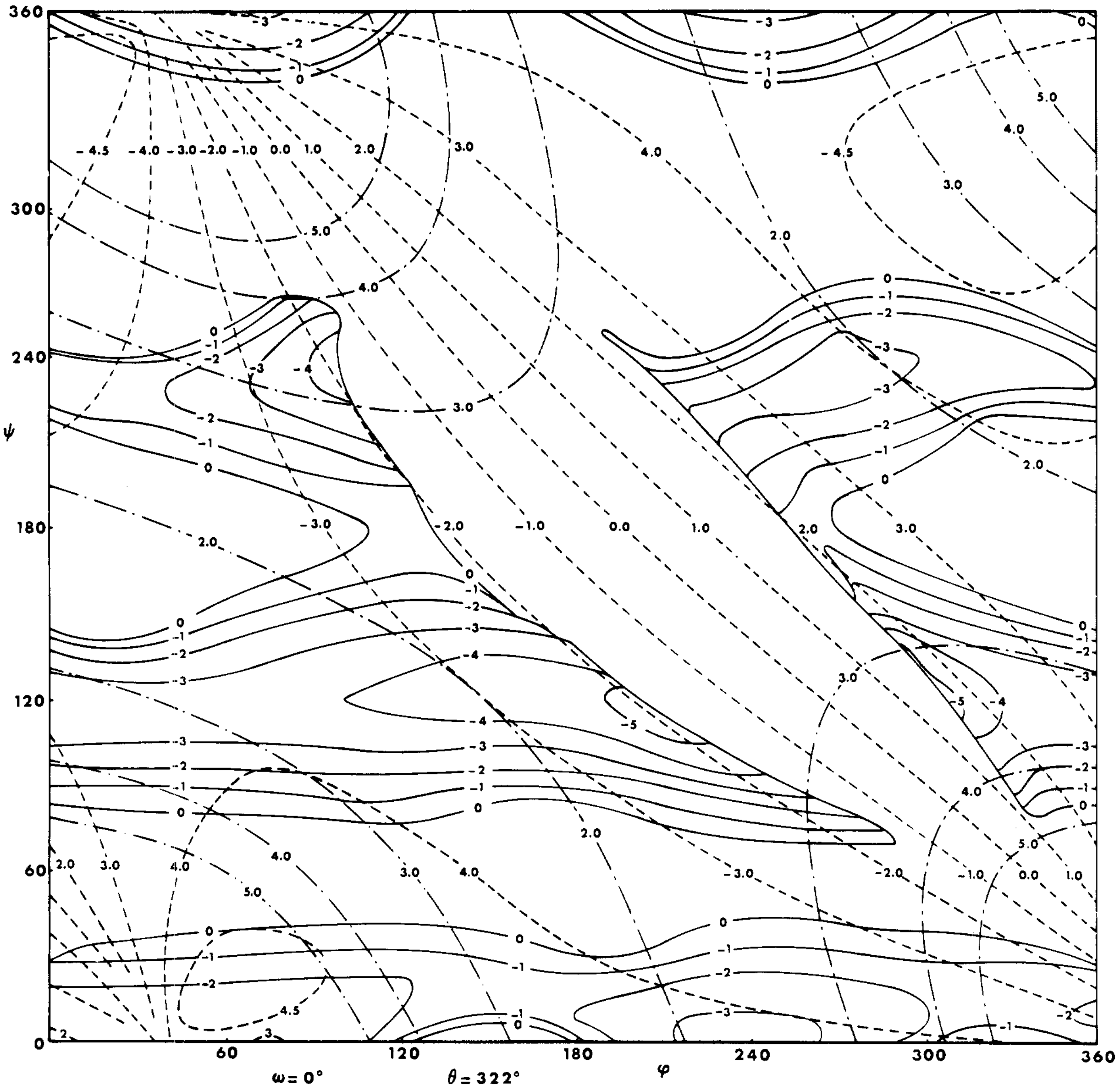
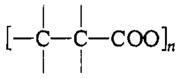


Figure 2. Poly(β-hydroxy butyrate): potential energy contours for ω = 0° and θ = 322° in kcal mol^{-1}. The curves of constant n (number of monomers per turn, -·-) and h, in Å (advance per monomer, - - -), are superimposed on the energy contours (—). Signs + or − on the h curves represent right- or left-handed helix regions, respectively.

Table I
Torsional Angles in Degrees and Contributions from Nonbonded Energies (U_{NB}), Electrostatic Interactions (U_E), and Torsional Energy (U_T) to the Total Potential Energy (U) (kcal/mole of residue) for Each "Trial" Crystalline Model of Poly(β-hydroxy butyrate)

Model	1	2	3
ω	0	4	36
θ	322	240	318
ϕ	149	41	247
ψ	123	211	220
Chirality	Left	Right	Right
U_{NB}	−2.43	−1.93	−3.06
U_E	−2.15	−2.20	−2.13
U_T	0.11	1.52	3.73
$U = U_{NB} + U_E + U_T$	−4.47	−2.61	−1.46

termined by the torsional angles of the backbone bonds, Natta's[27] minimum energy postulate to predict the crystalline conformation allows one to select that particular conformation by comparison of the internal energy of all possible regular conformations. This method was used for various polypeptides,[28,29] polysaccharides[30] and synthetic polymers.[31] We have applied it to the β-lactone polyesters whose backbones have the common sequence



$$[-\mathrm{C}-\mathrm{C}-\mathrm{COO}]_n$$

in order to understand what energetic factors encourage different macromolecules with this common backbone to adopt similar conformations in the crystalline state.

Methods

For monomer building, we have used bond lengths and bond angles[32,33] obtained from simple esters such as methyl formate, methyl acetate, and ethyl formate using electron diffraction[34] and microwave spectrometry[35] or from standard data of organic molecules.[36]

The helical main chains of these homopolyesters are described by four torsional angles ϕ, ψ, θ, and ω (Figure 1). The latter takes account of the possible departure from planarity of the usual "trans" ester group.[26] The three former bonds are varied over 0° → 360° but because of the high torsional barrier of ω (vide infra) a range of ±40° is quite sufficient for this angle. The four torsional angles are measured from the fully extended conformation depicted in Figure 1.

We considered the total intramolecular potential energy, U, as the sum of the following contributions: the torsional energy, U_T, around the four torsional angles, the nonbonded energy, U_{NB}, and the electrostatic energy, U_E, for the polar interactions of the ester groups. The interactions were calculated for a chain of ten residues; the electrostatic energy between the first and tenth residues for each model discussed is in the order of −0.01 kcal/mol of residue.

For the torsional energies we used the Pitzer type of equation proposed by Scott and Scheraga[37]

$$U_T(\chi) = (U_\chi/2)(1 - \cos n\chi)$$

where U_χ is the potential barrier of the torsional angle χ and n, the symmetry, is equal to 3 (except for ω where $n = 2$). The parameters used[32] are from the conformational analysis of the polyacids based on L-aspartic and L-glutamic acids.[38] The potential barrier U_ω for the departure of the ester group from planarity is rather large (8.75 kcal/mol of residue) and rejects deformations greater than 40°.

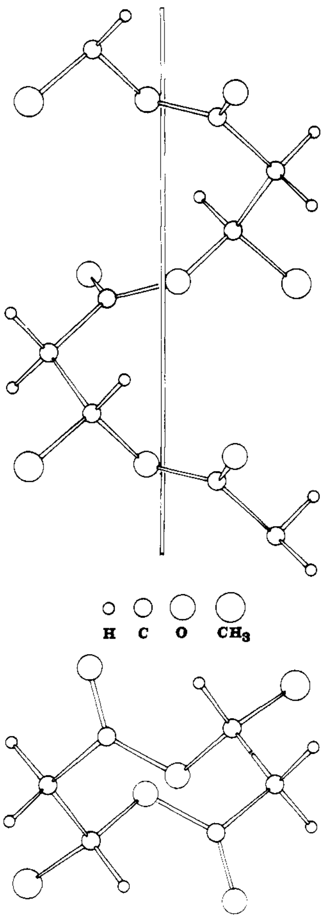


Figure 3. Poly(β-hydroxy butyrate): molecular model ($\omega = 0°$, $\theta = 322°$, $\phi = 149°$, $\Psi = 123°$) with the lowest energy. Above, the model is viewed from a direction normal to the helix axis and, below, along the helix axis.

To compute the non-bonded energies $U_{NB,ij}$ between atoms i and j, we used the classical "6–12" Lennard-Jones relation[28]

$$U_{NB,ij} = (d_{ij}/r_{ij}^{12}) - (e_{ij}/r_{ij}^{6})$$

This equation is used for all interatomic distances r_{ij} which are functions of the torsional angles but a limiting factor of $r_{ij} \leq 7.0$ Å[28] was introduced. A set of interaction parameters, d_{ij} and e_{ij},[32] from studies of Yan et al.[38] was used. To reduce the computation time, we did not consider the internal rotations around the C–CH$_3$ bond for PHB and PVL. Following a suggestion of Gibson and Scheraga,[39] the hydrogen atoms of the methyl groups were incorporated into an enlarged carbon atom.

To represent the dipole moment of the ester group, we used the partial charge concept[28] and the data used[32] introduced a dipole moment of 1.50 D nearly parallel to the carbonyl bond. The dipole–dipole interactions are calculated by Coulomb's law

$$U_{E,ij} = 332.0(q_i q_j/D r_{ij})$$

where the factor 332.0 gives the energy in kcal/mol for distances expressed in ångström units and partial charges in fractions of electronic charges; $U_{E,ij}$ is the electrostatic energy between two charges q_i and q_j separated by the distance r_{ij}. For the dielectric constant D, we used the value of 3.0 which is commonly used in the conformational analysis of polypeptides[28] and poly-L-lactic acid.[40]

Because of the four rotation angles, conformational maps

Table II
Torsional Angles in Degrees and Contributions from Nonbonded Energies (U_{NB}), Electrostatic Interactions (U_E), and Torsional Energy (U_T) to the Total Potential Energy (U) (kcal/mole of residue) for Each 2_1 Molecular Model of Poly(pivalolactone)

Model	1	2
ω	0.0	5.0
θ	331.9	258.1
ϕ	145.6	43.7
ψ	120.5	198.1
Chirality	Left	Right
U_{NB}	−0.40	3.53
U_E	−2.15	−2.10
U_T	0.08	2.45
$U = U_{NB} + U_E + U_T$	−2.47	3.88

Table III
Torsional Angles in Degrees and Contributions from Nonbonded Energies (U_{NB}), Electrostatic Interactions (U_E), and Torsional Energy (U_T) to the Total Potential Energy (U) (kcal/mole of residue) for Each 2_1 Molecular Model of Poly(β-propiolactone)

Model	1	2
ω	−2.5	1.9
θ	355.6	250.6
ϕ	119.9	1.0
ψ	121.3	231.3
Chirality	Left	Right
U_{NB}	−2.85	−2.25
U_E	−2.17	−2.17
U_T	0.02	0.15
$U = U_{NB} + U_E + U_T$	−4.99	−4.27

(Figure 2) are in four dimensions, i.e., a chart for each ω and θ. Lines of constant energy, of constant advance per monomer, h, and of constant number of monomers per turn of helix, n, are plotted as functions of ϕ and ψ (e.g., in Figure 2). Different maps are obtained as ω and θ change. By inspection, when an area of correct helical parameters and of low energy is recognized, another computation program[41] is used for the refined search for the minimum energy. A detailed explanation of our search strategy of ϕ, ψ, θ, and ω space is contained in ref 32.

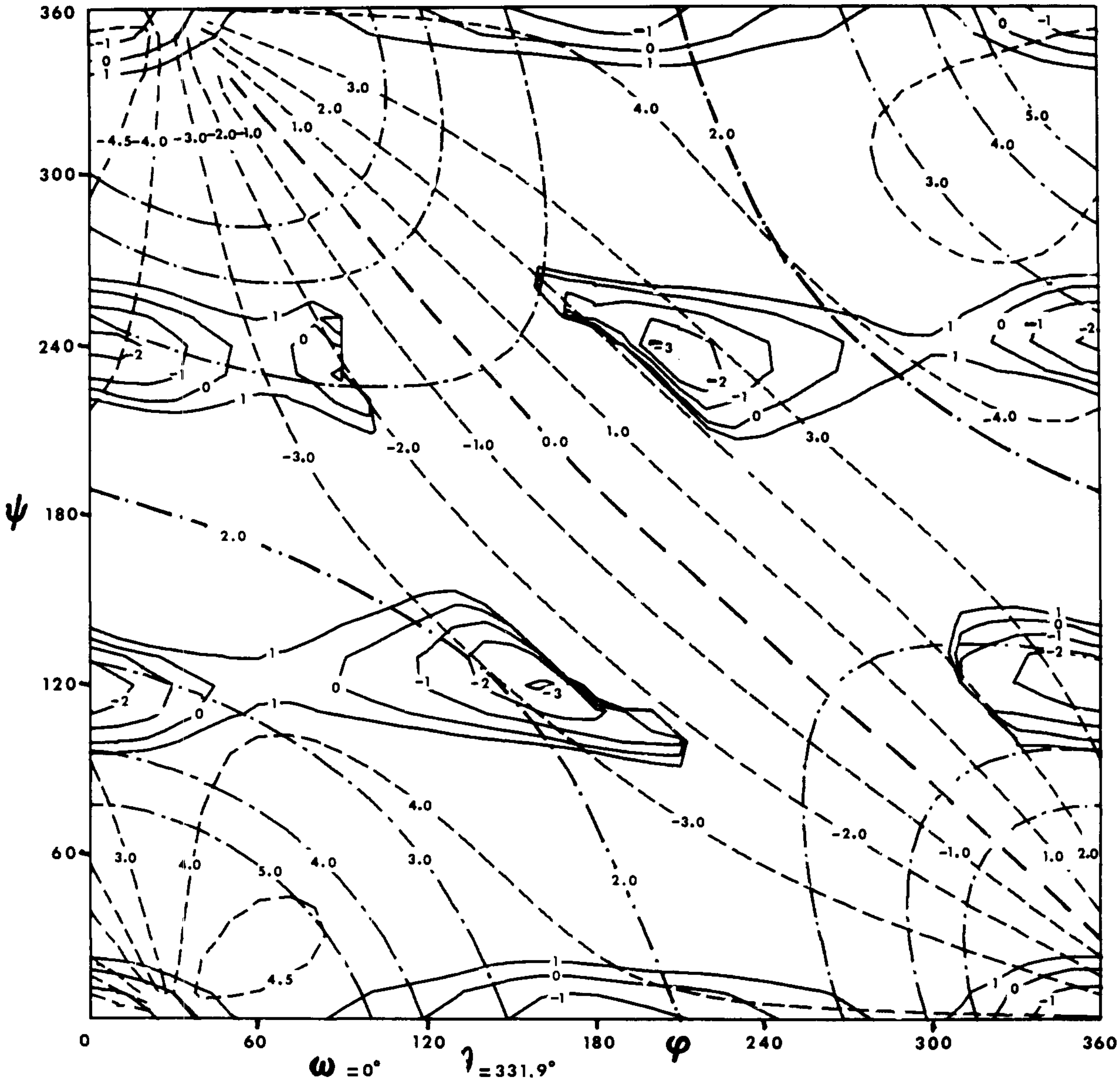


Figure 4. Poly(pivalolactone): potential energy contours for ω = 0° and θ = 331.9° in kcal mol^{-1}. The curves of constant n (–·–) and h, in Å (- - -), are superimposed on the energy contours (—).

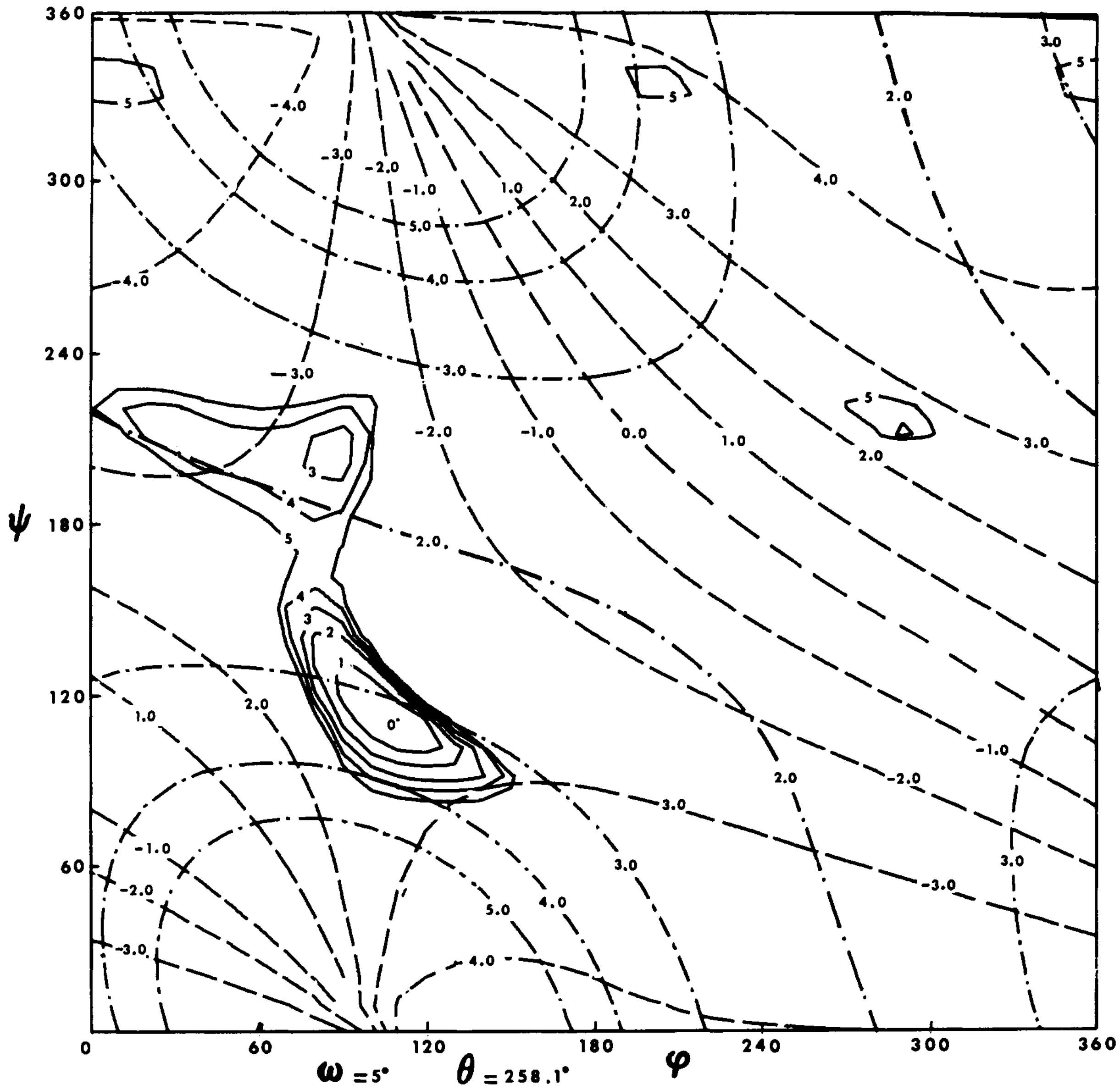


Figure 5. Poly(pivalolactone): potential energy contours for ω = 5° and θ = 258.1° in kcal mol^{-1}. The curves of constant *n* (—·—) and *h*, in Å (- - -), are superimposed on the energy contours (—).

Results

Poly(β-hydroxy butyrate). Without departing too much from the planarity of the ester group, trial crystalline conformations (h = 2.98 Å n = 2.0) coinciding with low energy regions in the (ϕ,ψ) maps are shown for the area which is shown in Figure 2 and in Figure 4 of ref 32: area I with $\theta \simeq 322°$, $\phi \simeq 150°$, and $\psi \simeq 120°$; area II near $\theta \simeq 240°$, $\phi \simeq 40°$, and $\psi \simeq 210°$. When deformations from planarity are allowed, i.e., $\omega > 30°$, a new area appears. Figure 5 of ref 32: area III with $\theta \simeq 318°$, $\phi \simeq 250°$, and $\psi \simeq 220°$. In each area, the positions corresponding to the n and h of the crystalline conformation for PHB are a function of the two angles ω and θ; hence we have searched for the conformations with the lowest energies in terms of the parameters ϕ, ψ, θ, and ω. The chirality and the contributions U_{NB}, U_{T}, and U_{E} to the total potential energy U are collected in Table I for the trial crystalline models h = 2.98 Å and n = 2, corresponding to these three areas. (Based purely on a symmetry operation definition a 2_1 helix cannot have a chirality but the progression of bonds which provide the continuity from atom to atom in linear chains does define a chirality which can be either right or left handed (cf. Figures 3, 6, and 9.)

From Table I, it appears that the electrostatic energies are nearly equivalent for the three models. There are two important factors for the choice of the molecular models, namely the nonbonded and the torsional potential energies. Although model 3 has the lowest nonbonded energy, this model has a high torsional energy because it involves an energetically costly departure from the trans planarity of the ester group and it seems that this model is the least probable. Model 1 is the most likely, based on potential energy considerations.

Since the original crystalline structure proposed for PHB[26] was similar to model 3, which seems unlikely based on energy considerations, we have reexamined the crystalline structure in relation to these three molecular models obtained by conformational analysis.[32]

From a fiber diagram of PHB, analysis of the diffracted intensities showed that model 1 (lowest intramolecular potential energy) gives the best agreement between the calculated and measured intensities.[32] Using the equatorial reflections, the factor $R_I = \Sigma|I_c - I_o|/\Sigma I_o$ with the calculated

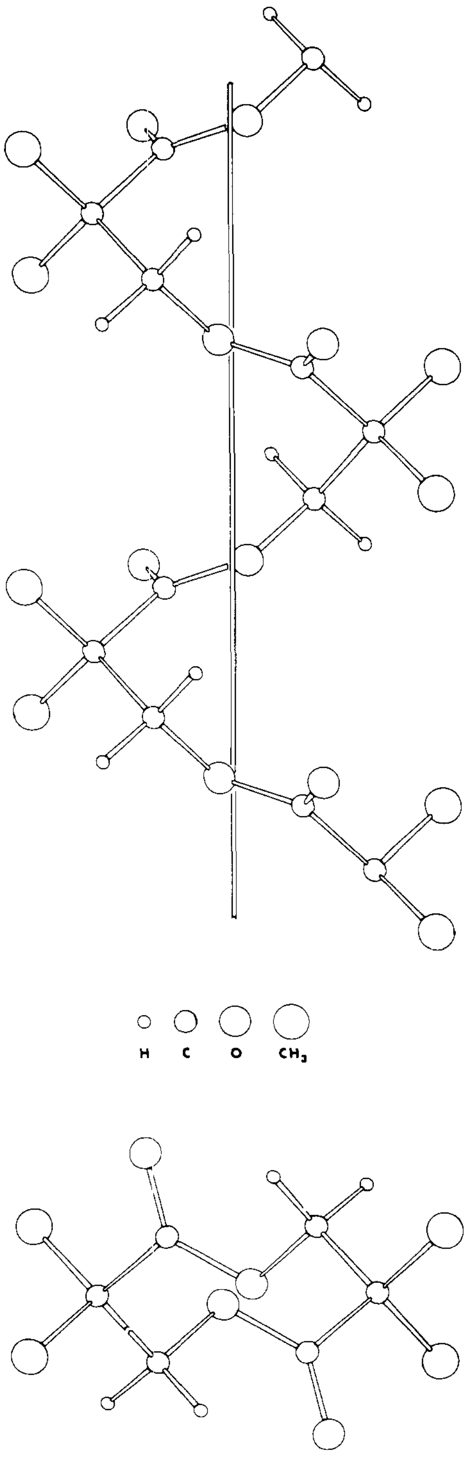


Figure 6. Poly(pivalolactone): molecular model (ω = 0°, θ = 331.9°, θ = 145.6°, and ψ = 120.5°) with the lowest energy. Above, the model is viewed from a direction normal to the helix axis and, below, along the helix axis.

and measured intensities, I_c and I_o, gives as minimum R_I for the three molecular models of Table I: 0.19, 0.42, and 0.43, respectively.

On this basis only model 1 (Figure 3) was considered for the final refinement using all observed intensities to obtain a new crystalline conformation[32] characterized by an R_I factor of 0.24. This new crystalline conformation which fits into the unit cell proposed by Okamura and Marchessault[26] is almost identical to the poly(pivalolactone) conformation.[23]

Poly(pivalolactone). Conformations of PVL with a 2_1 axis coincide with low energy valleys of (ϕ,Ψ) maps only for two areas (Figures 4 and 5): area I near $\theta \simeq 330$, $\phi \simeq 145$, and $\Psi \simeq 120$; area II with $\theta \simeq 260$, $\phi \simeq 45$, and $\Psi \simeq 200$. These two areas are very similar to the two allowed areas for PHB (cf. above) but the energy levels are higher because of increased nonbonded effects due to the α and α' methyl groups of PVL. Using the same method as for PHB, 2_1 molecular type models corresponding to these two areas were found; chirality and energy contributions (U_{NB}, U_T, U_E, and U) are gathered in Table II.

As for PHB, U_{NB} and U_T are the most important factors in the total energy of the molecular models. The energy difference of 6.35 kcal/mol of residue between models 1 and 2 is rather large. Model 2 possesses unfavorable methyl–carbonyl interactions. On an energy basis we reject model 2 and retain only 1 as the crystalline model for PVL.[33]

Two X-ray studies of poly(pivalolactone) are reported: Carrazolo proposed a conformation similar to model 1 (Figure 6) while a more refined analysis of the X-ray fiber data by Perego et al. yielded a crystalline conformation which is slightly different from model 1 (specifically the chain atoms of the ester group are no longer in the planar trans conformations (ω = 16°) such as is usually the case in the crystalline conformation of low molecular weight esters[33]). Our calculations based strictly on energy considerations show that so high a deviation from the ideal trans conformation of the ester group would be energetically costly and it is noteworthy that the conformation of Perego et al.[25] does not coincide with the minimum energy crystalline conformation[33] predicted by our calculations. In conclusion, we believe that model 1 is the more probable structure for this polyester although differences between this model and that proposed by Perego et al. are of a quantitative and not of a qualitative nature.

Poly(β-propiolactone). Again, there were two areas where 2_1 type conformations coincide with low energy valleys in the (ϕ,ψ) map (Figures 7 and 8). These areas are slightly different from those of PHB and PVL because of the increased fiber repeat of PPL (7.02 Å): area I with $\theta \simeq$ 335.6°, $\phi \simeq$ 120°, and $\psi \simeq$ 120°; area II near $\theta \simeq$ 251°, $\phi \simeq$ 1.0°, and $\psi \simeq$ 230°. It appears that the energy wells of the maps are less deep than those of PHB because the absence of lateral groups decreases the number of favorable nonbonded interactions. The 2_1 type molecular models corresponding to these two areas, the chiralities, and the contributions U_{NB}, U_E, and U_T to the total energy U are gathered in Table III.

As for PHB and PVL, the two most important factors which decide between possible models are U_{NB} and U_T. Model 1 has the lowest energy but the energy difference between 1 and 2, 0.6 kcal/mol of residue, is rather minor. Thus on energetical grounds these two models are equally probable with a slight preference for model 1. This result is quite different from the two preceding cases, PHB and PVL, where energy considerations allowed a clear choice in favor of one conformation.

If we compare Tables I and III, it appears that the two proposed models of the 2_1 helix of PPL are closely related to models 1 and 2 of PHB. The exchange of the β-methyl group for a hydrogen atom encourages two small rotations of θ and ϕ torsional angles to extend the chain to a greater fiber repeat of 7.02 Å.

Curiously, the reported fiber diagram of the 2_1 helical form of PPL is not well defined although the sample used seemed to be pure and of high molecular weight.[19] To date, it has been impossible to analyze the fiber diagram in detail in order to reject one or the other model, drawn in projection in Figures 9 and 10, in Table III.

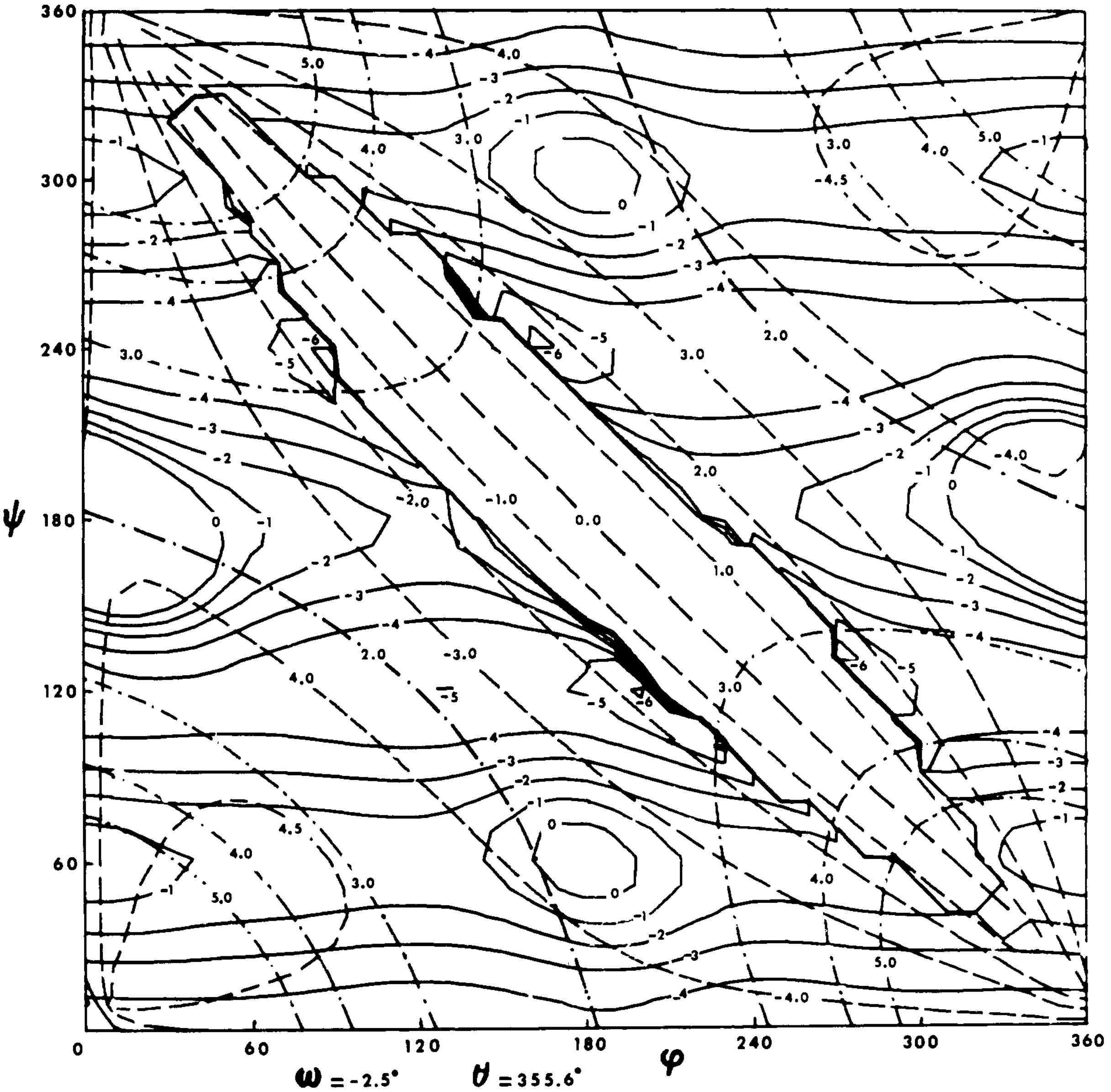
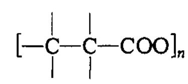


Figure 7. Poly(β-propiolactone): potential energy contours for $\omega = -2.5°$ and $\theta = 355.6°$ in kcal mol^{-1}. The curves of constant n (-·-) and h, in Å (- - -), are superimposed on the energy contours (—).

General 2_1 Helical Conformation. These three polyesters, PHB, PVL, and PPL, have the same main chain



$$[\text{—}\underset{|}{\overset{|}{\text{C}}}\text{—}\underset{|}{\overset{|}{\text{C}}}\text{—COO}]_n$$

but different lateral groups. The 2_1 helical models (Tables I-III and Figures 3, 6, and 9) with the lowest energies are similar, especially PHB and PVL where we have only an exchange of methyl groups and hydrogen atoms (Figures 3 and 6) between the α and β carbons.

In these models the ester groups have the same orientation in relation to the helical axis. It is noteworthy that this orientation has the plane of the ester group nearly perpendicular to the chain axis which is in direct contrast to the disposition of the amide group in the α helix of polypeptides.[42] In the α helix, the amide planes are parallel to the helix axis and form intramolecular hydrogen bonds. This particular ester group orientation does not seem related to the length of the residue because this same kind of disposition is found in the 10/3 helix of poly(L-lactide) ($[\text{HCCH}_3\text{-COO}]_n$).[41] The reason for this orientation is that it permits the most favorable intramolecular dipolar interaction between neighboring residues. It is noteworthy also that even in the conformations of the higher energy forms for PHB, PVL, and PPL (model 2 in Tables I, II, and III), the disposition of the ester groups is the same.

In these polyester systems U_{NB} and U_{E} are of comparable magnitude which is not the case with the α-helix polypeptides where U_{NB} is the dominant factor.[46] In fact the orientation of the ester dipoles in this helical polyester series is more comparable to what is found in the β form of polypeptides.

The molecular models shown in Figures 3, 6, and 9 show that the lateral alkyl groups are directed outside of the main chain of the helix. This kind of disposition is very similar to the orientation of lateral groups of the α helix of polypeptides[42] and for that matter of most poly(α-olefins).[27]

For each polyester which we have studied, the "global minimum" on the energy surface is always in the same area as the 2_1 helical models but generally is different by a small ψ rotation. In our calculation we do not consider crystal packing interactions which could be the "driving force" for

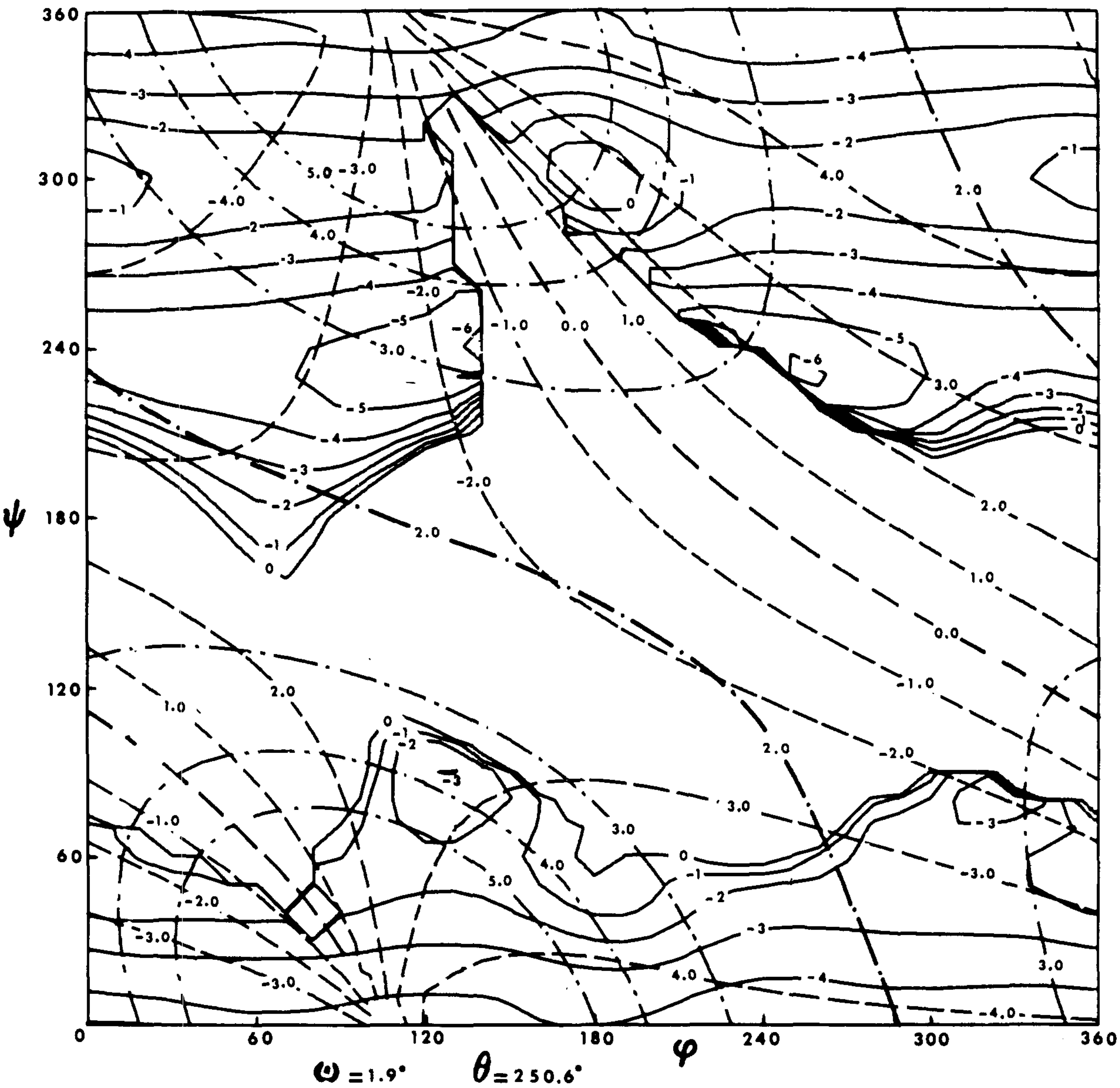


Figure 8. Poly(β-propiolactone): potential energy contours for $\omega = 1.9°$ and $\theta = 250.6°$ in kcal mol^{-1}. The curves of constant n (-·-) and h, in Å (- - -), are superimposed on the energy contours (—).

the choice of the 2_1 helix in the crystalline state rather than the "global minimum" helix.

Based on the foregoing observations, we formulate the following proposition; polyesters of the type $[HCR_1{-}CR_2R_3{-}COO]_n$ generally adopt a 2_1 conformation in the crystalline state similar to the crystalline molecular model of PHB. In other words, the same molecular conformation can accomodate quite different lateral chains R_1, R_2, and R_3, i.e., they exhibit conformational isomorphism. This general rule includes the case where R_2 and R_3 are different,[10,44] but the rule has not been tested up to now for the case where R_1, R_2, and R_3 are simultaneously other than hydrogen.

Discussion

This general 2_1 helical conformation for poly(β-alkanoates) is only stabilized by nonbonded energies and polar interactions. Because there are no hydrogen bonds to rigidify the structure, the size of lateral chains can induce slight deformations of the main chain. As a consequence, the fiber repeat can vary in a narrow range from one derivative to another.

For example, the poly(D,L-β-isopropyl-β-propriolactone) adopts a 2_1 helical conformation in the crystalline state with a fiber repeat of 6.49 Å,[43] slightly greater than for PHB, because interactions of the β-isopropyl group are more important compared to the methyl group of PHB. The crystalline structure is being analyzed but the fiber diagram of this polyester[43] is very similar to the fiber diagram of PHB.[26] We believe that the main chain conformation of this β-lactone will be found to correspond to the proposed general conformation.

Poly(D,L-α-methyl-α-n-propyl-β-propiolactone) exhibits dimorphism[44] similar to what was found for PPL[19] and PVL.[45,47] When films of this polymer were stretched, the predominant crystalline form was the planar zig-zag conformation with a fiber repeat of 4.74 Å, very similar to the ones reported for the zig-zag conformation of PPL and PVL, respectively 4.74 and 4.76 Å. In the unstressed state only a helical conformation with a fiber repeat distance of 5.9 Å was found. Although the corresponding fiber diagram is not well defined it is to be associated with the general 2_1 helical conformation because of the similarity of the fiber repeat compared to PVL.

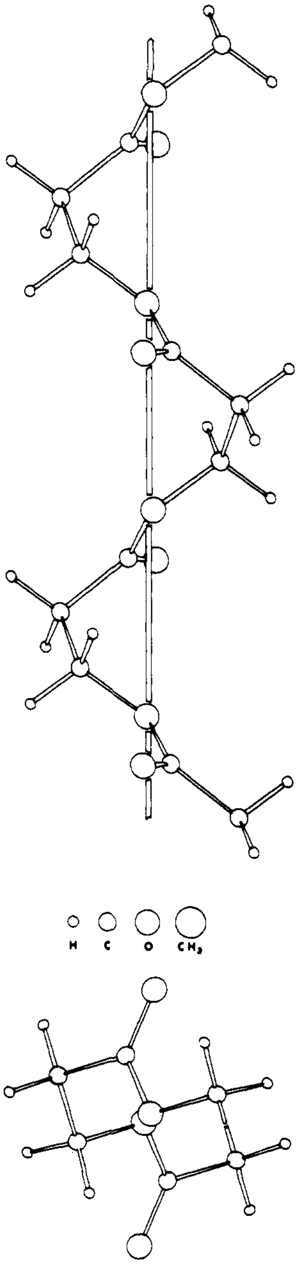


Figure 9. Poly(β-propiolactone): molecular model (ω = −2.5°, θ = 355.6°, ϕ = 119.9°, and ψ = 121.3°).

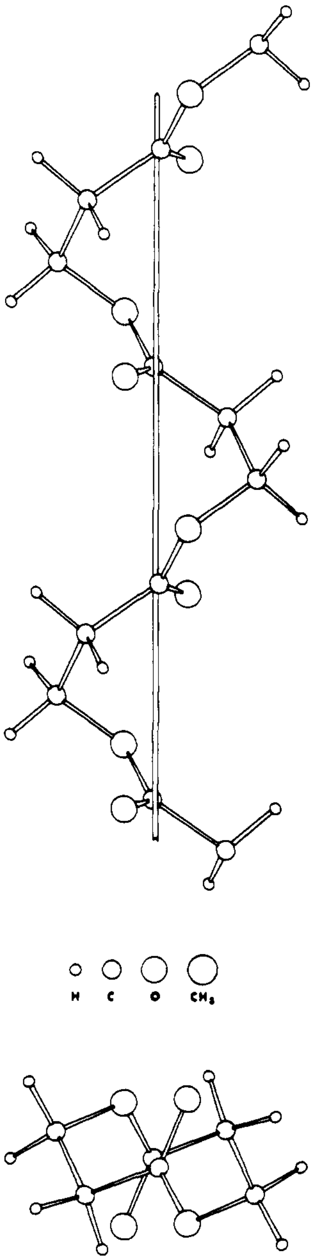


Figure 10. Poly(β-propiolactone): molecular model (ω = 1.9°, θ = 250.6°, ϕ = 1.0°, and ψ = 231.3°).

Many polyesters of type $[HCR_1-CR_2R_3-COO]_n$ can be prepared by ring opening polymerization . of lactones.[48] Most of them are crystalline[48] and in relation to this general conformation it will be interesting to examine the spectrum of crystalline structures of these polyesters with different substituents at R_1, R_2, and R_3. Proper testing of the above "general proposition" will frequently demand preparation of optically active polyesters.[49]

In terms of the number of backbone atoms, polyesters of the $[HCR-COO]_n$ series are more analogous to polypeptides hence their investigation might a priori be of greater interest. So far, only poly(L-lactide) has been thoroughly stidied and while there is some controversy concerning the exact conformation, it seems that a 10/3 helix is the most likely interpretation.[41] Geometrically speaking, this is close to the Pauling helix; however, our calculations based on energy considerations again show the ester groups in a planar conformation with the planes nearly perpendicular to the helix axis.

There is not sufficient data to generalize as to whether or not polyesters of the $[HCR-COO]_n$ class will always adopt a 10/3 helix in the crystalline state. Information is starting to appear on the preparation of suitable polymers to settle this question.[50]

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Observation of Relaxation Processes Near the Glass Transition by Means of Excimer Fluorescence[1]

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ABSTRACT: Excimer fluorescence of a guest aromatic vinyl polymer dissolved at low concentration in a polymer host matrix has been used to monitor relaxation processes near the glass transition region. Suitable intramolecular excimer forming sites in the guest result from specific chain conformational states. The concentration of these sites, while initially fixed by the temperature at which the film is cast, will change as a function of time due to molecular motion in the relaxation region of the host. The change in site distribution is reflected in the fluorescence, thus allowing the molecular rearrangement to be followed. Fluorescence results for 0.20% poly(2-vinylnaphthalene) in polystyrene are shown to correlate quite well with mechanical dilatometric data. Consideration is given to both kinetic and thermodynamic aspects of the process.

In a recent series of papers,[2,3] excimer formation has been examined in fluid and rigid solutions of poly(2-vinylnaphthalene) (P2VN), polystyrene (PS), and poly(4-vinylbiphenyl) (PVBP). An excimer is an electronically excited molecular complex formed between two aromatic chromophores in a coplanar sandwich arrangement. Excimer formation in aromatic vinyl polymers may result from both intermolecular and intramolecular interaction, particularly at high concentrations. However, the latter situation predominates in sufficiently dilute systems formed by placing the polymer under study in a suitable fluid solvent ($\sim 10^{-4}$ *M*) or in a rigid polymer matrix ($\sim$0.20 wt %), as used in this work. Furthermore, it has been shown that the intramolecular interaction in the vinyl polymers considered in this study is between adjacent chromophores.[2b]

Photophysical sampling of excimer sites consists of excitation of a pendent chromophore followed by random exciton migration along the chain until competitive trapping and fluorescence occurs from a suitable excimer chain conformation. In fluid solution interconversion of chain conformations proceeds rapidly with the lifetime of a particular conformation limited by collision with solvent molecules. As a result of free rotation, thermodynamic equilibrium of chain conformations will be maintained as the temperature is varied. However, the situation is quite different for rigid cast films. With the evaporation of the casting solvent below the glass transition temperature of the guest–host system, a chain conformation distribution will be frozen in which is characteristic of the casting temperature. To be sure, some molecular motion will be present on a limited scale below T_g, as evidenced by the various suborder transitions. However, the skeletal rotations necessary for excimer site formation will be severely restricted, thus fixing the site concentration.

It was shown previously that the distribution of excimer forming chain conformations which allow interaction of adjacent chromophores on the same polymer chain may be predicted by a simple statistical model.[2b] In this model, the rotational isomeric state approximation is used to enumerate nine possible chain conformations for a three-skeletal