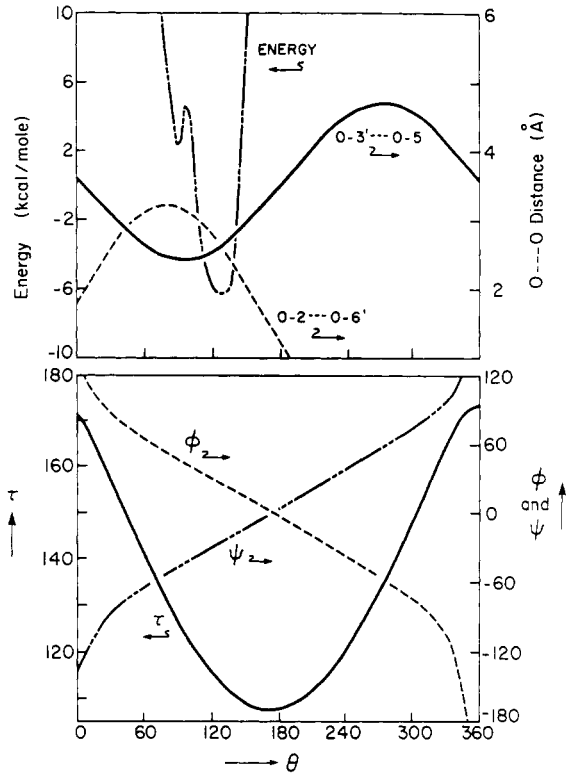

Figure 1. Results of virtual bond analysis of cellulose. The variations of τ (left ordinate), ϕ, and ψ (right ordinate) with θ are shown in the lower part. The hydrogen-bond distances (right ordinate) and the energy curve (left ordinate) are given in the upper part. The OH-6 group was placed in *tg* position in this calculation. When the C-1 atom lies in the YZ plane, $\theta = 0$.

for examining the effect of τ on the conformations of the polymer.

The Arnott–Scott parameters were used for the β-D-glucose unit, and a repeat distance of 10.3 Å was taken for the cellulose chain. The nonbonded interaction energies were estimated using the 6–12 potential function, with parameters given before.[2] The hydrogen bond energy was calculated using a simple inverse third-power expression given by Blackwell et al.[10] The strain energy due to the bond-angle deformation was calculated using an effective force constant of 80 kcal mol^{-1} for the angle ∠COC,[11] assuming the normal value for this angle to be 110°.

The results of the virtual bond analysis can be conveniently presented as shown in Figure 1. The variations in τ, ϕ, and ψ with θ are given in the lower half of the figure. The O-3′---O-5 and O-2---O-6′ hydrogen-bond distances, and the total conformational energy, are given in the upper half. The values of τ, ϕ, and ψ for any θ and the corresponding hydrogen-bond distances and energy can be read from this plot. It is seen that except for the value of τ corresponding to the minimum in the τ curve, two 2(5.15) helices are possible for a given value of τ. For example, with $\tau = 117°$, two chains, with $\theta = 115°$ and 230°, are possible. These correspond to (ϕ,ψ) values of (33°,–35°) and (–32°,31°), respectively. Although geometrically two chains can be constructed for $\tau = 117°$, the chain with $\theta = 230°$, $\phi = -32°$, and $\psi = 31°$ is ruled out since the O-3′---O-5 and O-2---O-6′ distances are 4.5 and 0.5 Å, respectively. The energy of this conformation is very high. With $\theta = 115°$, $\phi = 33°$, and $\psi = -35°$, these hydrogen-bond distances are 2.5 and 2.85° Å, respectively, and this conformation is close to the minimum in the energy curve.

The actual minimum in the energy curve corresponds to $\theta = 130°$, which leads to $\tau = 113°$. The O-3′---O-5 and O-2---O-6′ distances are 2.65 and 2.6 Å, respectively, in this case. It is interesting that the value of $\tau = 113°$, which is less than the values hitherto used in the conformational analysis of cellulose, leads to the minimum energy conformation. The "normal" value of $\tau = 110°$ was used in calculating the contribution of the energy due to bond-angle deformation. The energy minimum occurs at $\tau = 113°$ even if the bond-angle-deformation energy is omitted in the calculations. The same result was obtained when the OH-6 group was kept in the *gg* position. The repeat distance in the above calculations was taken to be 10.3 Å. With a higher value of 10.39 Å, as used by Gardner and Blackwell,[7] the energy minimum occurs at $\tau = 114.5°$. In this case also, the value of τ is less than that in the crystal structure of cellobiose.

Although $\tau = 117–117.5°$ is observed in the crystal structure of cellobiose, it is shown that a lower value of 113–114° is preferred for the polymer, from energy considerations. It is interesting to note that while $\tau = 116.8°$ in acetyl cellobiose,[12] a lower value of 115.5° occurs at one of the bridge oxygen atoms in acetyl cellotriose.[13] A significantly low value of 106° has been reported for the valence angle at one of the bridge oxygen atoms in cellotetraose.[14]

It is thus shown from energy calculations that a value of τ in the range of 113–115° is favored for cellulose. The Arnott–Scott standard geometry was used here for the glucose residue. The exact value of τ at which the minimum in energy occurs may vary depending on the geometry of the residue. Calculations may be performed using every β-D-glucose geometry available in the literature, in pursuit of the best suited one. It is beyond the scope and intent of this article, however.

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Calculation of the Fundamental Elongational Relaxation Time for a Slightly Flexible Rodlike Molecule

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Many polymer molecules of both natural and synthetic origin are thought to be rodlike. The solution dynamics of such molecules are well characterized, for many purposes, by a single relaxation time corresponding to end-

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over-end rotation. However, recent measurements of viscoelastic properties of dilute solutions have shown that some of these rodlike macromolecules exhibit additional relaxation processes corresponding to internal modes of motion.[2-4] Wada and collaborators have used an elastic cylinder model to investigate this phenomenon theoretically, and have calculated the fundamental relaxation time for flexure, which has been assumed to correspond to the slowest internal mode of motion. In the present report an analogous method has been used to calculate the relaxation time for the fundamental elongational, or accordion-like, mode.

Consider an elastic cylinder of equilibrium length L, diameter d, and Young's modulus E. A Cartesian coordinate system is placed at the center of the cylinder with the x axis directed along its length. External forces acting in the axial direction result in a deformation $2\Delta L$; each half is stretched ΔL with respect to the origin of the coordinate system. The external forces will be balanced by the internal elastic forces, F_{el}. Assuming $\Delta L \ll L/2$, these forces are given by

$$F_{el} = (\pi d^2/4)E[\Delta L/(L/2)] \quad (1)$$

Upon removal or relaxation of the external forces, the cylinder will return to its rest length, driven by F_{el} and opposed by viscous forces, F_V. The latter, neglecting end effects, will be:

$$F_V = \int_0^{L/2} \zeta V_x(x)\, dx \quad (2)$$

where ζ is the friction coefficient per unit length of cylinder and $V_x(x)$ is the velocity of the cylinder wall as a function of position relative to the origin. Assuming uniform deformation,

$$V_x(x) = [x/(L/2)]\ [d(\Delta L)/dt] \quad (3)$$

Inserting eq 3 into 2 and integrating yields

$$F_V = [\zeta L/4]\ [d(\Delta L)/dt] \quad (4)$$

As the cylinder retracts, $F_{el} + F_V = 0$; combination of eq 1 and 4 followed by integration shows that there is an exponential decay of ΔL with a characteristic relaxation time, τ_L:

$$\tau_L = \zeta L^2/2\pi d^2 E \quad (5)$$

The friction coefficient may be obtained from Broersma's[6] analysis of lengthwise motion of a rigid rod through a medium of viscosity η_s. Neglecting end effects again, the approximate result is:

$$\zeta = 2\pi\eta_s/\ln (L/d) \quad (6)$$

and thus

$$\tau_L = \eta_s L^2/d^2 E \ln (L/d) \quad (7)$$

which is then the relaxation time for the fundamental accordion-like elongational mode.

This result can be compared to the results of previous analyses for rotation[7] and flexure[5] which also neglect end effects. There are, respectively

$$\tau_R = \pi\eta_s L^3/18kT \ln (L/d) \quad (8)$$

$$\tau_F = (5.53 \times 10^{-3})\pi\eta_s L^4/B \ln (L/d) \quad (9)$$

where k is Boltzmann's constant, T is the absolute temperature and B ($=\pi d^4 E/64$) is the flexural rigidity of the cylinder. It is interesting to note the different L dependencies of eq 7–9 and the ratios τ_L/τ_F and τ_L/τ_R

$$\tau_L/\tau_F = 2.8(d/L)^2 \quad (10)$$

$$\tau_L/\tau_R = (9/2)(kT/VE) \quad (11)$$

where V is the cylinder volume.

For typical molecules, (L/d) may be 10 to 100 and hence elongational relaxation will occur on a time scale 2–4 orders of magnitude faster than flexure. This is consistent with flexural mode interpretations of the longest internal relaxation time which have yielded values of B and E for several molecules. For instance, for paramyosin in water at 20 °C, τ_R and τ_F were experimentally determined to be 23 μ and 2.7 μs, respectively. From these results E was calculated to be 1.2×10^{10} dyn/cm^2.[3] From eq 10 or 11, then, τ_L can be estimated to be about 1×10^{-3} μs.

Finally it should be noted that the above analysis, derived to describe macromolecules in solution, is not applicable to the solid state where viscous forces no longer dominate. For such systems other analyses must be applied.[8]

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Carbon-13 Nuclear Magnetic Resonance Analysis of Model Compounds of Saturated End Groups in Polypropylene

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Macromolecular structure is a valuable source of information on the stereochemical polymerization mechanism. Actually, in previous papers, we have been able to contribute to the elucidation of the mechanism of the steric control and the regiospecificity in propylene polymerization by comparing the ^{13}C NMR spectra of polypropylene and of ethylene–propylene copolymers with the spectra of suitable model compounds for methylene and methyl carbons of monomeric units in different sterochemical sequences, as well as in different chemical arrangements.[1-3]

As several other details of the macromolecular structure do, also the end groups can reveal important features of the polymerization mechanism, especially if their sterochemistry is considered. In the next paper[4] it is shown how the sterochemistry of chain initiation and propagation is related to the stereochemical structure of some saturated end groups (isopropyl, 2-butyl, and 2-pentyl) of isotactic, syndiotactic, and atactic polypropylene.

In view of the ^{13}C NMR analysis of the just mentioned saturated end groups, we report in this paper the ^{13}C-NMR spectra of three methyl branched hydrocarbons chosen as reasonable model compounds (see Figure 1): (a) (2*R*,-

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