(11) (a) C. C. Han and B. Mozer, *Macromolecules*, **10**, 44 (1977). (b) In ref 11a, neutron and light scattering are made on a PS–PM diblock copolymer (with a deuterated PS block) and the relevant homopolymers in tolune. The authors conclude that $\gamma_{\mathrm{PS}} \simeq 1$ and $\gamma_{\mathrm{PM}} \ll 1$, according to which they propose a "partially segregated core-in-shell model". Since this is directly in opposition to our basic assumption that $\gamma_{\mathrm{K}} = 1$, it is felt necessary to comment on their results in some detail. First, the neutron scattering measurements seem to be made in a range of Q (momentum transfer) apparently too high to correctly estimate $\langle S^2 \rangle$ and the second virial coefficient A_2 of those samples. This must be true especially for the block copolymer in the one-component-invisible system.[12] Second, the molecular weights of the PS and the PS block seem to be too low ($M < 10^5$) for light scattering to provide reliable data. In fact, some questions arise as to the reported data with regard to the previously published data on high molecular weight samples.[3,12,13] Third, their interpretation on the $\langle S^2 \rangle$ data for the block copolymer seems erroneous: As to the neutron experiments, for example, they remark that the scattering from the PS block is so small that $\langle S^2 \rangle_{\mathrm{app}}$ is very close to $\langle S^2 \rangle_{\mathrm{PM}}$. This certainly is not the case. With the numerical data presented therein, we have $\mu_{\mathrm{PS}} = 1 - \mu_{\mathrm{PM}} = -0.08$. Putting these and the measured values of $\langle S^2 \rangle_{\mathrm{app}}{}^{1/2} = 85$ Å and $\langle S^2 \rangle_{\mathrm{PS}}{}^{1/2} = 225$ Å into eq 11 of ref 3, we find $\langle S^2 \rangle_{\mathrm{PM}}{}^{1/2} = 140$ to 170 Å corresponding to the assumption of $\sigma' = 1.0$ to 1.5 (see ref 3).

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(31) Rahlwes and Kirste (*Makromol. Chem.*, 178, 1793 (1977)) have reported light-scattering results on PS–poly(α-methylstyrene) (PMS) diblock copolymers with high homogeneity. The conclusion they reached is essentially the same as ours, i.e., the PS–PMS conformation in TOL corresponds very closely to that of PS and PMS. Since the PS/PMS pair is known as a fairly compatible one (see, e.g., D. G. H. Ballard, M. G. Rayner, and J. Shelten, *Polymer*, 17, 640 (1976)), their conclusion and ours here for the two rather typically different polymer pairs certainly reinforces the conformational picture obtained from the Monte-Carlo calculations.[3,5]

Notes

The Valence Angle at the Bridge Oxygen Atom in Cellulose

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The results of the stereochemical analysis of polysaccharides depend significantly on the geometrical parameters used for the repeat unit.[1-3] Inherent in these calculations is the assumption that the geometry of the residue in the crystal structures of the mono- and disaccharides would remain the same when incorporated in the polymer. Using the geometries derived from various crystal structure reports on small molecules containing the β-D-glucose moiety, French and Murphy[3] found differences in the results of the structure analysis of cellulose.

In addition to the geometry of the monomer unit, the valence angle ∠COC (denoted here by τ) at the bridge oxygen atom is also an important parameter. In methyl glycosides it is of the order of 113°, whereas it increases to 116–118° in disaccharides.[2,4-6] It would thus seem that the angle τ increases with the size of the substituent on the sugar residues, as well as on the type of linkage between the units, in the crystal structure of the small molecules. Conventionally, values in the range of 116.5 to 117.5° (similar to those in disaccharides) have been used in the conformational calculations on cellulose. However, using the Arnott–Scott geometry for the residue,[6] Gardner and Blackwell[7] concluded that a lower value of 114.8° should be used for τ to achieve a distance of 2.75 Å for the O-3′---O-5 hydrogen bond. Use of $\tau = 117°$ leads to a shorter hydrogen bond distance. The calculations of French and Murphy[3] also led to similar results and they observed that neither a small glycosidic angle nor a short hydrogen bond distance should be considered improbable in cellulose structure.

In view of the preference shown in the above work for a lower value of τ, it is appropriate to examine the effect of the variation of τ in the conformational energies of the cellulose chain. The results of such an analysis are presented here.

When the repeat distance and the screw symmetry are known from diffraction data, the virtual bond method has proved useful for rapid analysis of the conformations of a polymer. The description of the virtual bond method was given before.[1,8,9] Essentially, it involves a rotation θ of the residue about its virtual bond or the end-to-end vector, thereby varying the disposition of the atoms of the residue with respect to the helix axis. In this process, the angle at the bridge atom varies with θ. For each value of θ, contiguous residues may be generated and the energy of interaction between contiguous residues or between remote residues can be calculated. From the coordinates of the residues along the helix thus generated, the angle τ as well as the torsion angles ϕ and ψ around the glycosidic bonds can be evaluated. It is thus a convenient method

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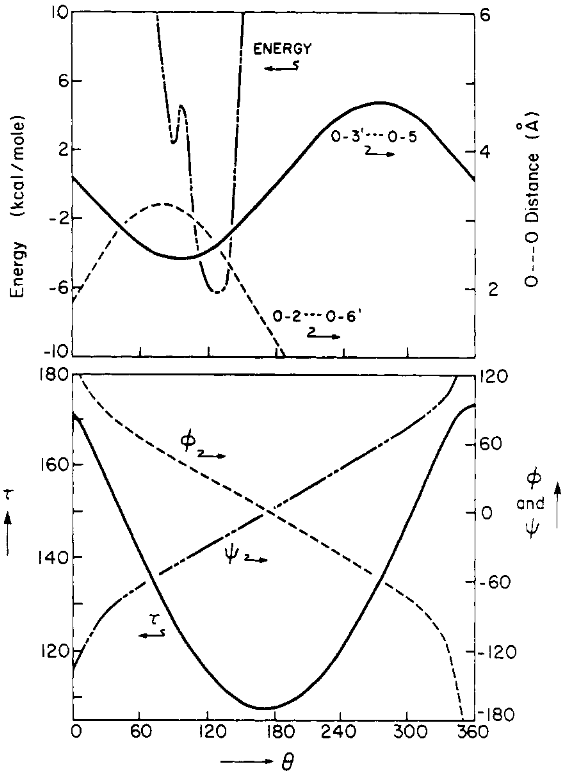

Figure 1. Results of virtual bond analysis of cellulose. The variations of τ (left ordinate), ϕ, and ψ (right ordinate) with θ are shown in the lower part. The hydrogen-bond distances (right ordinate) and the energy curve (left ordinate) are given in the upper part. The OH-6 group was placed in *tg* 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 $\angle$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 τ = 117°, two chains, with θ = 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 τ = 117°, the chain with θ = 230°, ϕ = −32°, and ψ = 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 θ = 115°, ϕ = 33°, and ψ = −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 θ = 130°, which leads to τ = 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 τ = 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 τ = 110° was used in calculating the contribution of the energy due to bond-angle deformation. The energy minimum occurs at τ = 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 τ = 114.5°. In this case also, the value of τ is less than that in the crystal structure of cellobiose.

Although τ = 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 τ = 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-