the absorption at 7.83 ppm can be assigned to this proton. Rather, we feel that it is more likely attributable to either the N^{ϵ} NH or the carbobenzoxy N–H protons. Since it was not possible to assign the peak positions of the backbone resonances with any confidence, the nmr studies could not be used to differentiate between the relative helicity of the various blocked polymers. They were useful in assigning peak positions which were applied in the analysis of the corresponding hydrobromide salts.

Broadening of backbone protons can arise from any structural feature which will inhibit rotational motion of the molecule. Certainly helicity causes such an effect. We therefore use our nmr results as supporting evidence for the helicity in the glycyl and other blocked polylysines. However, the primary support for our contention is based on our CD results.

The conformational analysis on the free poly-L-lysine compounds suggests that amino acid branches can have an important influence on the backbone conformation of proteins. In our simple model systems, we observed that significant stereochemical differences existed among the various polylysines.

The effect of moving the charge on a polyelectrolyte away from the backbone is to lower the excess electrostatic repulsive energy, thus stabilizing the less expanded conformation. Since it is such electrostatic repulsion which is mainly responsible for destabilizing the helical form of poly-L-lysine, this effect is primarily responsible for the differences between the substituted and unsubstituted polylysines. It was also observed, however, that significant conformational differences exist between poly(N^{ϵ}-glycyl-L-lysine) on one hand and the phenylalanyl and leucyl analogs on the other. These differences indicate that the effect of these substituents is not solely to remove the charge from the peptide backbone. The stereochemical variations among the substituted polylysines could be due to changes in solvation because of the nature of the side chain or interactions between side chains which stabilize less expanded forms. These are especially prevalent when the solvent is polar and the side chains are hydrocarbon-like in nature. The hydrocarbon nature of the phenylalanyl and leucyl derivatives is expected to have a much different effect on the solvation of the peptide than that of the glycyl or unsubstituted polylysines. It is also known that the presence of aliphatic and aromatic groupings can affect the local dielectric constant in an aquous solution. The effect of such groups is to lower the dielectric constant in their immediate environment. According to Coulomb's law, such a decrease in dielectric constant would be expected to increase the interaction between neighboring charges, thereby leading to a more expanded conformation. We observe, however, helical structures for the leucyl- and phenylalanyl-substituted polylysines. The existence of these compact species suggests that the hydrophobic side chains may be attracting each other in these aqueous solutions. Such interactions are apparently sufficient to overcome any increase in the electrostatic repulsion and thus result in the stabilization of helical species.

Finally, it should be noted that interactions between bulky hydrocarbon side chains can result in opposite effects in organic and aqueous media. In the latter, "hydrophobic bonding" of these groups prevents the expansion of the polymer and stabilizes helical species. In the former, however, steric interactions between these same groupings can result in destabilization of the helical conformation.

Acknowledgment. We wish to thank the Kurtz-Deknatel Foundation and the National Institutes of Health (Grant No. GM08974) for their generous support of this research. This research was also supported by the National Science Foundation (Grant No. GB 7558) and a grant from the Research Corporation and the Sloan Foundation to a Consortium at the Rockefeller University for the 220-MHz nuclear magnetic resonance facility.

Unperturbed Dimensions of Some 1–4-Linked Homopolysaccharides

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ABSTRACT: The characteristic ratios of a number of 1–4-linked homopolysaccharides are calculated using the methods developed by Flory and coworkers. It appears that the characteristic ratio is related to the freedom of rotation about the glycosidic bonds but also to the type of bonding (*e.g.*, axial–axial, equatorial–axial, etc.) between the monomers.

In recent years a number of calculations have been made of the characteristic ratios of polysaccharides such as amylose,[1] cellulose,[2] and alginic acid.[3] However, no serious attempt has been made to investigate the characteristic ratios of a series of such polysaccharides in order to draw general conclusions on the influence of types of bonding or positions of substituents on the characteristic ratios. In this paper characteristic ratios are calculated for a number of 1–4-linked polysaccharides with the sugar rings in the pyranose form. In practice, the details of the ring geometry and the bridge parameters will vary with the different polymers, and it has been shown[2] that the calculated value of the characteristic ratio is quite sensitive to the assumed bridge parameters. However, at least the general qualitative findings of this paper should not be influenced by small changes in these parameters or in the potential function and, at this stage, it appears to

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(2) N. Yathindra and V. S. R. Rao, *ibid.*, **9**, 783 (1970).

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be more important to use a consistent series of such parameters than to attempt accurate and detailed calculations in specific cases.

Method of Calculation

The ring geometry was derived from the idealized xylose coordinates of Settineri and Marchessault[4] and was assumed to be fixed in each calculation. The bridge parameters used were those obtained for cellobiose by Chu and Jeffrey,[5] *i.e.*, the Cl–O bond length was 1.397 Å, the O–C4′ bond length was 1.446 Å, and the bridge valence angle was 116°. With a fixed ring geometry, so that the only variables are the dihedral angles about the glycosidic bonds, it is convenient to define a sequence of virtual bonds, $\mathbf{l}_i$, between adjacent bridge oxygens. The unperturbed mean-square length of a polymer of degree of polymerization n is then given by

$$\langle r_n{}^2\rangle_0 = nl^2 + 2\sum_{i<j}\langle \mathbf{l}_i \cdot \mathbf{l}_j\rangle \qquad (1)$$

where $l = |\mathbf{l}_i|$. We set up coordinate systems on each monomer so that the x coordinate is directed along the virtual bond and define the matrix $\mathbf{T}_i$ as that matrix which, apart from translation, transforms from the coordinate system on monomer i to that on monomer $(i + 1)$. Then

$$\langle \mathbf{l}_i \cdot \mathbf{l}_j\rangle = l^2[\langle \mathbf{T}_i\mathbf{T}_{i+1}\ldots\mathbf{T}_{j-1}\rangle]_{11} \qquad (2)$$

For 1–4-linked polysaccharides it has been found that, to a good approximation, these **T** matrices are independently distributed[1–3] so that, for homopolymers, the above expression reduces to

$$\langle \mathbf{l}_i \cdot \mathbf{l}_j\rangle = l^2[\langle \mathbf{T}\rangle^{j-i}]_{11} \qquad (3)$$

If we define the characteristic ratio C_∞ by the limit

$$C_\infty = \lim_{n\to\infty}[\langle r_n{}^2\rangle_0/nl^2] \qquad (4)$$

then performing the summations and taking the limit yields[6]

$$C_\infty = \{[\mathbf{I} + \langle\mathbf{T}\rangle][\mathbf{I} - \langle\mathbf{T}\rangle]^{-1}\}_{11} \qquad (5)$$

In order to calculate $\langle\mathbf{T}\rangle$ it is necessary to calculate $\mathbf{T}(\phi, \psi)$ for a number of values of the dihedral angles ϕ and ψ about the glycosidic bonds and to calculate the conformational energy $V(\phi, \psi)$ of the dimer in each conformation. Then $\langle\mathbf{T}\rangle$ is given by

$$\langle\mathbf{T}\rangle = \frac{\iint \mathbf{T}(\theta, \psi)\exp(-V(\phi, \psi)/RT)\mathrm{d}\phi\mathrm{d}\psi}{\iint \exp(-V(\phi, \psi)/RT)\mathrm{d}\phi\mathrm{d}\psi} \qquad (6)$$

The potential function used in the calculation of $V(\phi, \psi)$ was the Kitaygorodsky[7] function

$$V = 3.5(-0.04/Z^6 - 8.6 \times 10^3\exp(-13Z))\ \text{kcal/mol} \qquad (7)$$

where $Z = r/r_0$, r is the interatomic distance, and r_0 is a parameter dependent on the nature of the atoms. The values of r_0 used were mainly those used by Rao, *et al.*,[1] and are given in Table I.

In the estimation of $\langle\mathbf{T}\rangle$ the integrals over ϕ and ψ were approximated by summing over 10° intervals of the dihedral angles.

TABLE I
PARAMETERS USED FOR KITAYGORODSKY POTENTIAL

Atom pair	Kitaygorodsky parameter, r_0
C···C	3.80
C···O(H)	3.55
C···H	3.15
O(H)···O(H)	3.33
O(H)···H	3.00
H···H	2.60
C···CH$_2$OH	4.45
O(H)···CH$_2$OH	4.215
H···CH$_2$OH	3.85
CH$_2$OH···CH$_2$OH	5.1

TABLE II

Monomer	Ring conformation	Bonding	C_∞	No. of "allowed" conformations[a]
β-D-Xylose	C1	e–e	31	75
α-D-Xylose	C1	a–e	1	52
β-D-Glucose	C1	e–e	154	46
α-D-Glucose	C1	a–e	10	23
β-D-Mannose	C1	e–e	96	62
α-D-Mannose	C1	a–e	2	38
β-D-Galactose	C1	e–a	56	32
α-D-Galactose	C1	a–a	358	28
α-D-Galactose	1C	e–e	24	
α-L-Gulose	1C	a–a	354	
α-L-Arbinose	C1	e–a	2	51

[a] Possible total = 36^2. These values are taken from ref 8.

Results and Discussion

The characteristic ratios, calculated using the above Kitaygorodsky function for a series of 1–4-linked homopolysaccharides are shown in Table II.

It is interesting to compare the results for amylose and cellulose with those calculated by Rao and coworkers.[1,2] Rao's results are marginally lower than ours for amylose and considerably lower than ours for cellulose. This arises, not primarily as a result of our use of slightly different geometrical parameters, but because we treat the –CH$_2$OH group as a single bulky group (see Table I) while Rao treats this as a single carbon atom. Although his results are closer to the experimental values, we do not regard his neglect of the substituents on C6 as being entirely justified.

Rees and Scott[8] have carried out hard-sphere calculations on a number of homopolysaccharides and have calculated the helix parameters as well as the fraction of conformations of the dimer which are "allowed" according to hard-sphere criteria. From these calculations they have classified the polysaccharides according to their regular conformations. The only two of their categories which concern us here are A, extended and ribbon-like with about two residues per turn, and B, flexible and helical with, typically, three or four residues per turn. All the 1–4-equatorial–equatorial-linked polysaccharides and all the 1–4-axial–axial-linked polysaccharides are of type A, while all 1–4-linked axial–equatorial or equatorial–axial-linked polysaccharides are of type B. Our calculations indicate that, in general, the characteristic ratios of type A polysaccharides are greater than those of type B polysaccharides. However, the rule is not inviolable

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in that the characteristic ratio of poly(β-D-galactan) is greater than that of poly(β-D-xylan).

Two interesting points emerge from the results shown in Table II. The first is that, for a given bonding geometry (*e.g.*, e–e, a–e, etc.) the characteristic ratio is negatively correlated with the number of conformations of the dimer which are allowed according to the hard-sphere criteria of Rees and Scott.[8] This number of "allowed" conformations is clearly related (albeit somewhat crudely) to the degree of rotational freedom about the glycosidic bonds. The second point is that, for a given number of allowed conformations of the dimer, the characteristic ratio decreases as the bonding changes in the order a–a, e–e, e–a, a–e. It is important to notice that the characteristic ratio of a given polysaccharide depends both on the type of bonding and on the degree of rotational freedom about the glycosidic bonds.

Rees and Scott[8] have pointed out the correlation between the degree of rotational freedom and the number of substituents which are equatorial, and the above results indicate that, for a fixed bonding geometry, the characteristic ratio increases as the number and size of the equatorial groups increase.

It is unfortunate that numbers of "allowed" conformations are not available for α-D-galactose (1C) or α-L-gulose. In the former case, it is easy to rationalize the rather low characteristic ratio for an equatorial–equatorial-linked system in that both hydroxyls, as well as the $-CH_2OH$, are axial and we would therefore expect there to be many dimer conformations which are allowed.

Although the number of "allowed" conformations is not known for the α-L-gulose dimer, we would expect this number to be greater than for the α-L-galactose (C1) dimer, since the hydroxyl on C2 of gulose is axial while all other substituents are equatorial, as in the galactose case. However, the calculated values of the characteristic ratios are almost equal for these polymers.

In conclusion, it appears that the characterstic ratios of 1–4-linked polysaccharides are very dependent on the geometry of the bonding in the polysaccharide and are closely correlated with the degree of rotational freedom about the glycosidic bonds (or the fraction of conformations which are "allowed" according to the hard-sphere criteria of Rees and Scott).

Acknowledgments. The author wishes to acknowledge helpful correspondence with D. A. Rees and O. Smidsrød and the financial assistance of the National Research Council of Canada.

Infrared Spectra of Poly(*trans*-1,4-butadiene) Single-Crystal Mats

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ABSTRACT: High-resolution infrared spectra have been obtained in the 1000–1400-cm^{-1} region for crystal mats of poly(*trans*-1,4-butadiene) grown from six different solvents or solvent mixtures. It was found that the ratio of the ir band at 1350 cm^{-1}, an amorphous band, to that at 1335 cm^{-1}, a regularity band, varied with the solvent used and with thermal history. For selected preparations the fraction of monomer units at the crystal surfaces, α, was determined using an epoxidation reaction. A comparison of $\alpha/(1-\alpha)$ and I_{1350}/I_{1335} is used to provide information about the amorphous fraction in the various crystal preparations.

Infrared spectroscopy has been employed to study the nature of chain folding at the surfaces of crystals prepared from various polymers.[1–5] In particular, Koenig and coworkers have identified infrared bands due to unique fold conformations in poly(ethylene terephthalate)[1] and in poly(hexamethyleneadipamide).[3] However, all of the previous work was carried out on specimens for which no independent method was used to determine the amount of chain folding. One polymer for which such independent information is now available is poly(*trans*-1,4-butadiene), PTBD.[6,7] For this polymer the number of double bonds available for epoxidation has been determined for crystals grown from various solvents. The average number of monomer units per fold has been estimated from the epoxidation data, the crystal thickness, and the cell repeat distance. Although infrared spectra have been given for solvent cast samples of PTBD and a number of the infrared bands have been assigned,[8,9] spectra from single-crystal mats have not been reported to date.

In the present study the high-resolution infrared spectra in the 1000–1400-cm^{-1} region have been obtained for: (1) mats of poly(*trans*-1,4-butadiene) crystals prepared from dilute solutions of various solvents and solvent combinations, (2) mats annealed near to or above the crystal transition temperature,[10,11] (3) melt-cooled samples, and (4) a sample cast from solution. It is seen that by comparison of the relative intensities of certain ir bands with results for the epoxidation of the surface double bonds, the location of the amorphous fraction can be determined.

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