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Modification of the Benoit model for β1-4 glucans

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Abstract

The Benoit model for β1-4 glucans is considered taking into account intrachain hydrogen bonds. This model is basis for calculation of equilibrium rigidity of chains with completely free rotation. Analysis of the experimental value of equilibrium rigidity is carried out and the fraction of hinge C(1)OC(4) bonds about which rotation is free is evaluated.

Keywords: Benoit model; β1-4 glucans; Equilibrium rigidity

1. Introduction

The information about the equilibrium properties of macromolecules related to their size may be obtained by studying the scattering of electromagnetic radiation or by studying the movement (translational and rotational) of the macromolecules in a solvent. The behaviour of linear macromolecules is described by the behaviour of different kinds of model chains, for instance: the chain of Kuhn statistical segments or, the persistent chains of different kind (Tanford, 1961; Tsvetkov et al., 1970; Cantor et al., 1980). The quantitative characteristic of the unperturbed (by thermodynamic interaction with solvent) dimension of a macromolecule is the Kuhn statistical segment length (A) (or persistence length $a = A/2$). This value (Kuhn segment length) permits us to compare polymers of different structure and to establish the correlation with the chemical structure of the repeat unit of the polymer (Tsvetkov et al., 1970; Munk, 1989; Fujita, 1990).

The flexibility of polymer chains may be realized by different mechanisms. One of the most important is the rotation about the bonds of a polymer chain, which may more or less be restricted. The measure of rotational restriction is the value $\sigma^2 \equiv A/A_f$, where A_f is the Kuhn segment length of an infinitely long (or long enough to be Gaussian) chain with completely free rotation. This value (A_f) can be calculated using the methods of statistical mechanics for different model chains (Tanford, 1961). The dimensions of a chain constructed with identical bonds connected through the same valency angle was first calculated by Eyring (1932). This model was generalized for the case of different bond lengths connected through different angles by Birshtein (1977). These models were utilized for the interpretation of unperturbed dimensions of flexible polymers (Tsvetkov et al., 1970) and rigid-chain macromolecules (aromatic polyamides and polyheteroamides) (Tsvetkov, 1989). The degree of restriction of rotation (σ^2) for the flexible vinyl polymers is about $\sigma^2 = 5$; while for the rigid-chain polymer this value is in the range 1–2 (Tsvetkov et al., 1970, Tsvetkov, 1989; Birshtein, 1977). This means that the rotation in rigid-chain polymers of this kind is less restricted in comparison with the flexible vinyl polymers. The considerably higher A values for rigid-chain polymers is possible only with the long rigid bond of these chains.

2. Results and discussion

The cellulosic chain was one of the first for which the value A_f was calculated by Benoit (1948). The cellulose chain was modelled by a rigid zigzag connected under the tetrahedral angles. Fig. 1 gives the conformation of the repeat unit of the cellulose chain. The real chain is replaced by a virtual chain with each repeat unit constructed by two parallel bonds b_1 about which rotation is free and one bond d_1 which is perpendicular to b_1 and about which rotation is completely hindered. Benoit obtained for a long-enough chain the square average of the end-to-end distance as:

$$\langle h^2 \rangle_f = A_f L = A_f \lambda Z = Z\{d_1^2 + (2b_1)^2[(1+\cos\theta)/(1-\cos\theta)]\}$$

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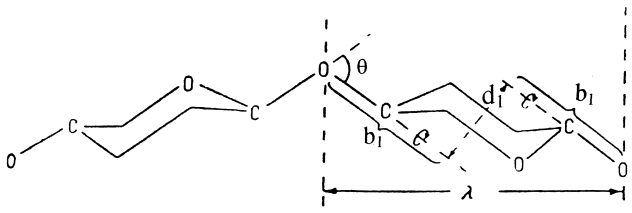

Fig. 1. Conformation of the repeat unit of a cellulose chain.

where L is the contour length of the chain; Z the degree of polymerization; λ the length of the projection of the repeat chain unit on its main direction. For the cellulose chain we have: $\lambda = 5.15 \times 10^{-8}$ cm; $(\pi - \theta) = 109.5°$ and $2b_1 = 5.3 \times 10^{-8}$ cm; $d_1 = 1.42 \times 10^{-8}$ cm; $A_f = 11.3 \times 10^{-8}$ cm.

The experimental values of A for some β1-4 glucans are presented in Table 1. These values were obtained from the hydrodynamic study of cellulose and its derivatives (Lujbuna et al., 1977, Valtassaari, 1971, Pavlov et al., 1988; Pavlov, 1995; Kamide et al., 1986; Saito, 1989; McCormik et al., 1985; Pavlov et al., 1995; Pavlov et al., 1982; Bushin et al., 1983) and chitin and its derivatives (Terbojevich et al., 1988; Pavlov et al., 1986a,b). Table 1 also contains for comparison, the corresponding values for one flexible (Brandrup et al., 1989) and one rigid-chain (Pavlov et al., 1985) synthetic polymer.

The values of A were obtained by comparison of the sedimentation coefficients (s_0) and/or intrinsic viscosity ([η]) with the molecular weight following the theories of Hearst et al. (1962); Yamakawa et al. (1973) (s_0) and Bushin's plot $[(M^2/[\eta])^{1/3}]$ (Bushin et al., 1981):

$$[S]N_A P_0 = (M^2\Phi_0/[\eta])^{1/3} = (M_L/A)^{1/2}M^{1/2} + (P_0 M_L/3\pi)[\ln A/d - \varphi(0)]$$

where $[S] \equiv s_0\eta_0/(1 - \upsilon\rho_0)$, η_0 is the solvent viscosity, $(1 - \upsilon\rho_0)$ is the buoyancy factor, P_0, Φ_0 are Flory hydrodynamic parameters; N_A is Avogadro's number; $M_L = M_0/\lambda$; M_0 is the molecular weight of the repeat unit, d the hydrodynamic diameter of the chain; $\varphi(0) = 1.43$ (Hearst et al., 1962) or 1.056 (Yamakawa et al., 1973).

Table 1 contains also the values of degree of restriction of rotation (σ^2) calculated by utilizing the value $A_f = 11.3 \times 10^{-8}$ cm. which is obtained with the assumption of complete rotational freedom about OC(1) and OC(4) bonds based on the Benoit model (Fig. 1) (Benoit, 1948; Tanford, 1961). This factor greatly exceeds the values of σ^2 for all other linear polymers (Tsvetkov et al., 1970; Tsvetkov, 1989). The high values of σ^2 can be due to the fact that the initial Benoit model does not take into account intramolecular hydrogen bonds in polyglucoside chains.

It is known from results of IR and NMR spectroscopy and X-ray scattering that intramolecular hydrogen bonds are formed between the hydrogen of OH group at C(3) and the oxygen of the neighbouring pyranose ring (Jbankov et al., 1983; Kennedy et al., 1985). The maintenance of these hydrogen bonds in a cellulose molecule in solution leads to the formation of a ladder structure for fragments of the chain (Burchard, 1965). Moreover, the existence of another intramolecular bond between the OH groups at C(2) and C(6) is also possible (Jbankov et al., 1983). This bond also favours ladder structure formation. Intrachain hydrogen bonds are shown by broken lines in Fig. 2a.

In completely substituted derivatives of β1-4 glucans other interactions instead of hydrogen bonds are formed between side groups of glucopyranose rings in particular electrostatic interactions. As a result, for instance, in cellulose trinitrate and triacetate molecules the conformational mobility of monomer units is relatively limited (Panov et al., 1988). Hence, the macromolecules of completely substituted derivatives of β1-4 glucans in solution are relatively rigid. This fact can also be interpreted in terms of rotation hindrance about the glucoside bonds, although this hindrance is not caused by the formation of a system of intrachain hydrogen bonds.

The existence of ladder-structure fragments of the cellulose chain implies that the rigid part between two hinge points can contain several glucopyranose rings. This part can also, like Benoit's original model, be represented by three virtual bonds: two $\mathbf{b}_n$ bonds about which rotation is free and the $\mathbf{d}_n$ bond about which rotation is completely hindered.

Table 1
Equilibrium rigidity of some β1-4 glucans and the parameters characterizing polysaccharide chains

	Solvent	A (10^{-8}) cm	$\sigma_1^2 = A/A_{f1}$	L_{max} (10^{-8})	δ%	Refs.
Cellulose	Cadoxen	100	8.8	58	9.7	Lujbuna et al., 1977
Cellulose	FeTNa	140;	12.4;	82;	6.7	Valtassaari, 1971; Pavlov et al., 1988; Pavlov et al., 1995
Cellulose	6% LiOH	70	6	40	14.6	Kamide et al., 1986; Saito, 1989
Cellulose	DMAA + LiCl	500	44.2	298	1.8	McCormik et al., 1985
Methylcellulose (1.68)	H_2O	160	14.1	94	5.8	Pavlov et al., 1995
Chitin	DMAA + LiCl	230	20.3	136	3.9	Terbojevich et al., 1988
Chitosane (0.8)	0.33 M CH_3COOH + 0.3 M NaCl	240	21.2	142	3.8	Pavlov et al., 1986a, b
Nitrate cellulose (1.1)	DMAA + LiCl	130	11.5	76	7.2	Bushin et al., 1983
Chitine nitrate (1.75)	DMFA	230	20.3	136	3.9	Pavlov et al., 1986a, b
Nitrate cellulose (2.7)	Ethyl acetate	390	34.5	232	2.3	Pavlov et al., 1989
Polystyrene		25	5			Brandrup et al., 1989
Polyamide–parabenzimidazol		250	1.6			Pavlov et al., 1985; Tsvetkov, 1989

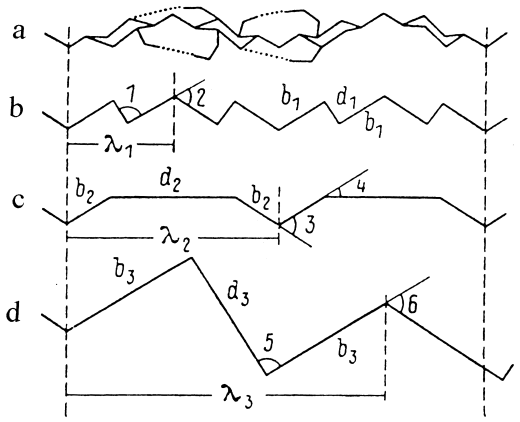

Fig. 2. Cellulose chain (a) and its corresponding chains of virtual bonds (b-d). a-cellulose chain fragment. Intramolecular hydrogen bonds between three glucopyranose rings are shown by broken lines. b-Benoit model (n = 1, angle 1 = 90°, angle 2 = θ); c-n = 2, angle 3 = θ, angle 4 = $\theta/2$; d-n = 3, angle 5 = 90°, angle 6 = θ.

We suppose to a first approximation that the rotation about the OC(1) and OC(4) bonds between two neighbouring glucopyranose rings which are not included into the system of intrachain hydrogen bonds is free. It is also assumed that the chain consists of identical fragments joined at an angle of ($\pi - \theta$).

Let us consider the case of different numbers **n** of glucopyranose rings (Fig. 2) contained in the rigid part and calculate $\boldsymbol{A}_{\mathrm{fh}}$. For even $\boldsymbol{n}$ values it is convenient in calculating ($\boldsymbol{A}_{fn}\lambda_n$) to use the virtual bonds shown in Fig. 2(c) (Tanford, 1961) where

$$\begin{aligned} b_n &= b_1, \text{Angle4} = \theta/2 \\ d_n &= 2(n-1)b_1\cos(\theta/2) + nd_1\sin(\theta/2) \\ A_{fn}\lambda_n &= (d_n\sin(\theta/2))^2 \\ &\quad + (2b_n + d_n\cos(\theta/2))^2[(1+\cos\theta)/(1-\cos\theta)] \end{aligned} \tag{1}$$

and λ_n is the length of the projection of the repeat chain unit on its main direction.

For odd $\boldsymbol{n}$ values it is more convenient to use Fig. 2(d) where

$$\begin{aligned} 2b_n &= (n-1)b_1 + [(n-1)/2](2b_1\cos\theta + d_1\sin\theta) \\ d_n &= [(n+1)/2]d_1 + [(n-1)/2](2b_1\sin\theta - d_1\cos\theta) \\ A_{fn}\lambda_n &= d_n^2 + (2b_n)^2[(1+\cos\theta)/(1-\cos\theta)] \end{aligned} \tag{2}$$

At all $\boldsymbol{n}$ values we have $\lambda_n = \boldsymbol{n} \times \lambda_1$, where $\lambda_1 = 0.515$ nm, $(\pi - \theta) = 109.5°$, $\boldsymbol{d}_1 = 0.142$ nm, $\boldsymbol{b}_1 = 0.265$ nm.

Eqs. (1) and (2) give the single linear dependence (nm) represented by Fig. 3.

$$A_{fn} = 0.278 + 0.858\boldsymbol{n} \tag{3}$$

with the coefficient of correlation $r = 1$.

On the basis of Eq. (3) it is possible to determine the maximal number of glucopyranose rings contained in a rigid fragment of a cellulose chain and its maximum length $\boldsymbol{L}_{\max} = \boldsymbol{n}\lambda$ (see Table 1). For this purpose it is necessary to assume that $\sigma^2 = 1$ (it is known that for rigid-chain polymers $1 < \sigma^2 < 2$ (Tsvetkov, 1989)). Using $\boldsymbol{n}$ it is also possible to determine the order of the value of bond fraction δ of C(1)OC(4) about which rotation is free and which provide the flexibility of β1-4 glucans:

$$\delta = \boldsymbol{1}/(\boldsymbol{n} - \boldsymbol{1})$$

These estimations are presented in the 6th column of Table 1. The glucopyranose rings adjacent to these bonds are included only partially in the system of intrachain OH bonds.

The system of intrachain hydrogen bonds in β1-4 glucan (cellulose) and in its structural model in bulk is virtually perfect (Gessler et al., 1994; Saenger, 1996). During the

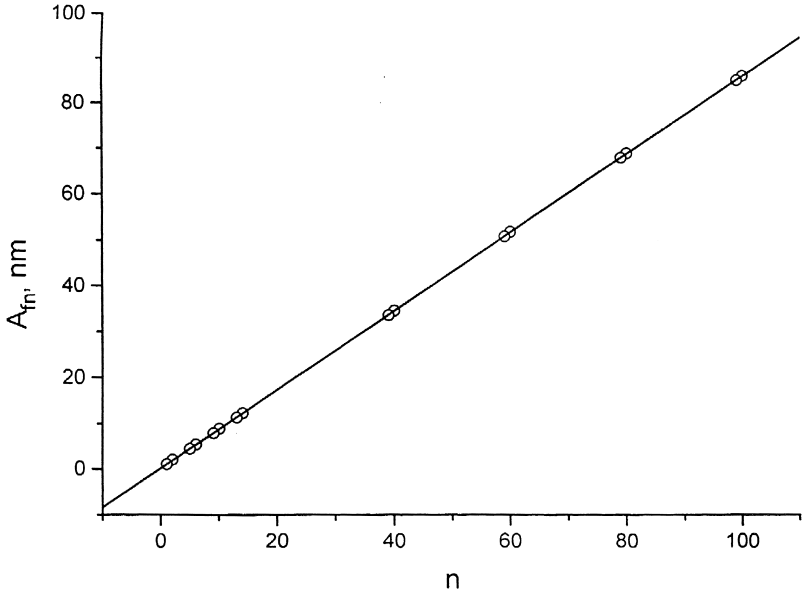

Fig. 3. Dependence of the Kuhn segment length A_f on the number of glucopyranose rings n in the rigid fragments.

molecular dissolution, the destruction of not only all interchain but also some of intrachain hydrogen bonds occurs.

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