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Flow birefringence of pullulan molecules in solutions*

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Flow birefringence (FB) of polymaltotriose (pullulan) in water and in dimethylsulfoxide (DMSO) has been studied. Pullulan has a high refractive index increment ($\Delta n/\Delta c$) in water but in DMSO it is low. Accordingly, in water the FB of molecules is mainly determined by the macroform effect and in DMSO by the intrinsic anisotropy of polarizabilities of the polysaccharide chain. The analysis of the dependencies of reduced FB values $[n]/[\eta]$ on molecular weight and on $\Delta n/\Delta c$ makes it possible to determine quantitatively the value of intrinsic segmental anisotropy of pullulan molecules: $(\alpha_1 - \alpha_2) = +33 \times 10^{-25}\,\mathrm{cm}^3$. On the basis of this value the optical anisotropy of the glucopyranose ring was determined. © 1997 Published by Elsevier Science Ltd.

(Keywords: flow birefringence; linear polysaccharide; optical anisotropy)

INTRODUCTION

Polysaccharides (PS) are natural polymers having various biological functions in the living organism. The spectrum of molecular structures of PS chains is very large. These structures can be varied depending on the types of monosugars, the character of ring bonding into the chain, the location of OH– groups in the glucopyranose ring, and the nature of OH– substituents[1-7].

The variations in the PS structure should affect profoundly the flow birefringence (FB) in a polymer solution. The standing liquid (solution) is isotropic because the individual molecules of the solvent and the solute are randomly oriented. A flowing solution of asymmetric macromolecules shows birefringence, which can be measured by appropriate methods. The value of the birefringence depends on the intrinsic optical anisotropy of the macromolecular chain, the asymmetry of the coil, the difference between the refractive indexes of the solvent and solute, and on the flow rate gradient. The principles of this phenomenon are given in a monograph[5]. The theories and much of the experimental data, with the interpretation of flow birefringence of polymer solutions, are given by Tsvetkov and other authors[6-9]. Flow birefringence (Maxwell effect) in a polymer solution is determined by the optical, geometrical and mechanical properties of the dissolved macromolecules.

The Maxwell effect in PS solutions has not been studied in detail. The only exception is the investigation of cellulose derivatives in which the value and sign of the FB effect are entirely determined by the nature of OH– substituents in β-1 → 4- glucan[10]. The value and even the sign of this effect, related to the optical anisotropy of cellulose proper and, hence, of the glucopyranose ring itself, remains open to question[11]. This is explained by the fact that cellulose is soluble only in multicomponent complex-forming solvents. Cellulose is dissolved as a result of the interaction between solvent components and OH– groups of the glucopyranose ring. This interaction may be regarded as the partial substitution on these rings[12].

The present work deals with the study of FB of some pullulan samples. Pullulan (polymaltotriose) is one of the virtually linear neutral polysaccharides which is formed from yeast-like *Aureobasidium* pullulan microorganisms. It consists of maltotriose units (α- D-glucopyranosyl-(1 → 4)-α-D-glucopyranosyl-(1 → 4)-α-D glucose) linked by α-1 → 6 bonds (*Figure 1*)[13].

The molecular characteristics of pullulan and the dimensions of its molecules have been investigated and discussed in a number of papers[14-20]. The character of molecular weight dependencies of hydrodynamic values and the estimation of the Kuhn segment length A for pullulan in water ($A = (21 \pm 3) \times 10^{-8}$ cm) indicate that pullulan molecules are flexible-chain molecules. The length of the Kuhn segment (persistent length) of linear chain representing the pullulan molecule was evaluated[20] on the basis of data on translational and rotational friction by using the length of repeat unit per glucopyranose ring in pullulan as calculated by Buliga and Brant[18]. The theoretical calculations of pullulan chains have been carried out and the conformational features of its chains and their unperturbed dimensions have been discussed[20-22].

EXPERIMENTAL

Materials

Some of the pullulan samples manufactured by Showa Denko K. K. and g.p.c. standards were studied. The

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* This paper is dedicated to the memory of Professor Emiliya V. Frisman

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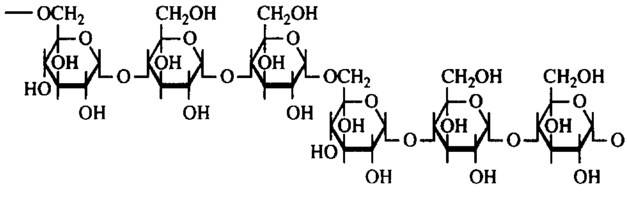

Figure 1 Molecular structure of pullulan

nomenclature and weight-average molecular weights assigned by the manufacturer to the samples are as follows: P-800 ($8.53 \times 10^5\,\mathrm{g\,mol^{-1}}$); P-400 ($3.80 \times 10^5$); P-200 ($1.86 \times 10^5$); and P-100 ($1.00 \times 10^5$).

Flow birefringence

Birefringence in pullulan solutions was measured using a mica plate compensator with a phase difference $\delta = (0.04 \pm 0.002)2\pi$ and a photoelectric recording technique[23,24]. A He–Ne laser was used as the light source ($\lambda = 6328 \times 10^{-8}$ cm). FB was investigated in a thermostatted titanium dynamooptimeter with an inner rotor 3 cm long along the path of the light beam[24]. The gap between the rotor and the stator was 1.6×10^{-2} cm. A condition of non-turbulence is provided by Taylor's formula[25]:

$$G_{cr} = \pi^2 \eta R^{0.5}/(A^{0.5}\rho\Delta R^{5/2})$$

where G_{cr} is the critical velocity gradient below which the flow is laminar (in water $G_{cr} = 17 \times 10^3\,\mathrm{s^{-1}}$; in DMSO $G_{cr} = 40 \times 10^3\,\mathrm{s^{-1}}$), $A = 0.057$, R = radius of rotor, ΔR = value of the gap, and η and ρ are the values of the viscosity and density of the liquid. Thermostatting was carried out to within 0.1°C at 21°C.

Positive FB proportional to flow rate gradient G was observed in pullulan solutions in water and DMSO (*Figure 2*). The character of the dependence of orientational angles (*Figure 3*) and Δn (*Figure 2*) on G indicates that the solutions under investigation are molecular. Reduced FB values $[n]/[\eta]$ were calculated from the ratios of intrinsic FB values $[n] = \lim_{g,\ c\to 0}(\Delta n/g\eta_0 c)$ to intrinsic viscosities $[\eta]$. For the cases of measurable values of relative viscosity $\eta_r = \eta/\eta_0$, the values of reduced FB were also calculated according to Peterlin[6] from $\Delta n/g(\eta - \eta_0)$ where η and η_0 are the viscosities of solvent and solution, respectively. The values of $[n]/[\eta]$ and $\Delta n/g(\eta - \eta_0)$ coincide within experimental error (*Table 1*). They were determined to within 7–10%.

Intrinsic viscosity

Intrinsic viscosities were determined by plotting η_{sp}/c vs c, where $\eta_{sp} = \eta_r - 1$. Relative viscosities η_r were calculated from $\eta_r = \tau/\tau_0$, where τ and τ_0 are the flow times of the same volumes of solution and solvent in Ostwald viscosimeters.

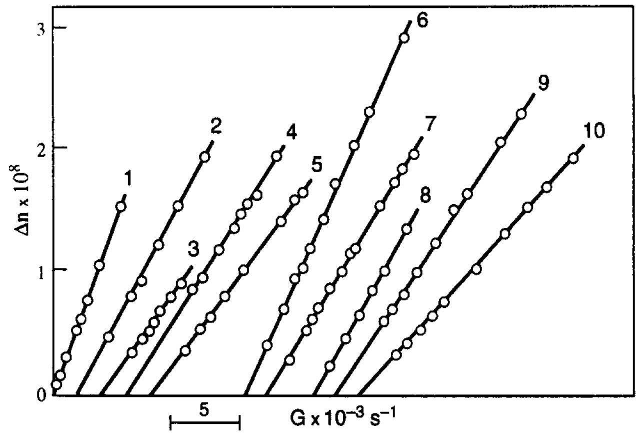

Figure 2 Flow birefringence Δn vs velocity gradient G for solutions of pullulan samples in water (1–7) and in DMSO (8–10). 1-1-0.114; 2-1-0.077; 3-2-0.110; 4-3-0.218; 5-3-0.175; 6-4-0.571; 7-4-0.421; 8-1-0.064; 9-2-0.094; 10-3-0.119. Here the first figure is the curve number; second, the sample number according to *Table 1*; third, the concentration in $10^{-2}\,\mathrm{g\,cm^{-3}}$

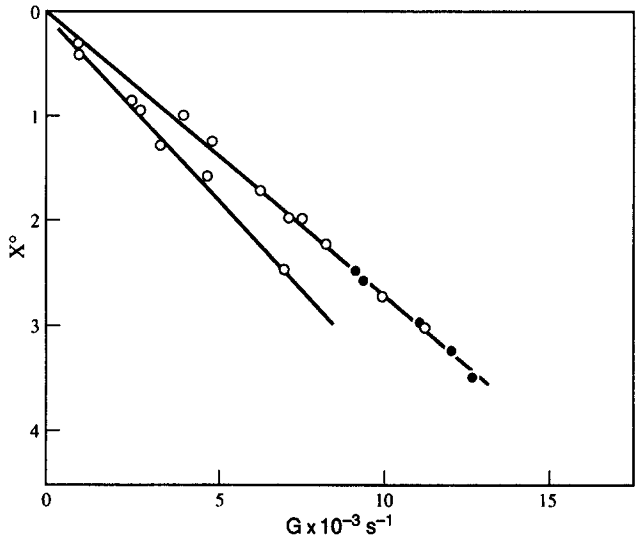

Figure 3 Orientation angle χ vs velocity gradient G for aqueous pullulan solutions. 1: sample 1 ($c = 0.114 \times 10^{-2}\,\mathrm{g\,cm^{-3}}$); 2: sample 3 ($c = 0.218 \times 10^{-2}$—open circles; $c = 0.175 \times 10^{-2}$—filled circles). Orientation angle $\chi = 45° - \varphi$, where φ is the angle between the direction of flow and the optical axis of the flowing solution. Orientation angles are very sensitive to the presence of molecular associations, i.e. to the nonmolecularity of the solution. This figure shows a good linear dependence, $\chi = f(G)$, which is evidence of good quality of the solution and FB measurements

Refractive index increments

Refractive index increments $\Delta n/\Delta c$ were determined at room temperature with the aid of a differential refractometer based on Lebedev's polarizing interferometer[26,27]. A pair of identical 'Iceland spar' plates each 3 cm thick was used. The greatest divergence between ordinary and extraordinary beams at the beam's exit from the spar plates (spar twinning a) is $a = 0.11d$[26], where d is the spar thickness. This divergence greatly exceeds the thickness of the partition separating the two cell sectors occupied by the solution and the solvent. Three systems of interference bands are observed in the field of vision: the two side bands are formed as the result of interference of beams that passed either only through the solvent sector or only through the solution sector. The central band system is formed by the interference of beams one of which passed through the solution sector and other through the solvent sector. The interferometer and the cell are arranged in such a way that the central band system is displaced with respect to the side system along the vertical axis by the distance H, related to the optical difference Δ between the path of beams that passed through the solution and the solvent by the simple ratio

$$\Delta = \frac{H}{b_\lambda} \cdot \lambda = l \cdot \Delta n$$

Table 1 Molecular weights M_{SD}, Kuhn segment number L/A of modelling polymer chain, intrinsic viscosities $[\eta]$, reduced FB $[n]/[\eta]$ and shear rate coefficients $\Delta n/\Delta\tau$ of pullulan samples in water and in DMSO

No.	Sample	$M_{SD} \times 10^{-3}$ [a]	L/A [a]	H_2O $[\eta]$ ($cm^3\,g^{-1}$)	H_2O $[n]/[\eta] \times 10^{10}$ ($cm\,g^{-1}\,s^2$)	H_2O $\Delta n/\Delta\tau \times 10^{10}$ ($cm\,g^{-1}\,s^2$)	DMSO $[\eta]$ ($cm^3\,g^{-1}$)	DMSO $[n]/[\eta] \times 10^{10}$ ($cm\,g^{-1}\,s^2$)	DMSO $\Delta n/\Delta\tau \times 10^{10}$ ($cm\,g^{-1}\,s^2$)
1	P-800	644	910	164	13.0	13.7	350	3.2	3.1
2	P-400	340	480	107	12.4	12.7	210	2.9	2.9
3	P-200	171	240	63	11.0	10.0	130	2.7	2.6
4	P-100	87	120	45	8.0	8.1	—	—	—

[a] Data from ref. 20

where b_λ is the constant of the Babinet compensator, λ is the wavelength of light, l is the cell length along the beam path and Δn is the difference between refractive indices. Hence, $\Delta n/\Delta c$ is calculated according to the equation

$$\Delta n/\Delta c = \frac{(H/l)\cdot\lambda}{\Delta c\cdot b_\lambda}$$

Figure 4 shows the results that make it possible to determine $\Delta n/\Delta c$. Consequently, for pullulan in water we have $(\Delta n/\Delta c)_1 = (0.166 \pm 0.009)\,cm^3\,g^{-1}$ and in DMSO $(\Delta n/\Delta c)_2 = (0.043 \pm 0.005)\,cm^3\,g^{-1}$.

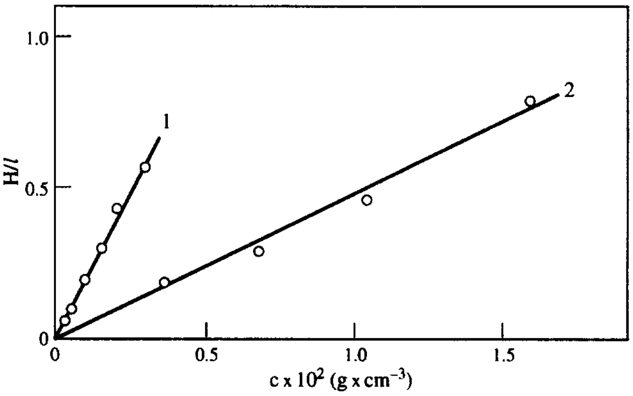

Figure 4 Plot of H/l (see text) vs concentration of pullulan in water (1) and in DMSO (2)

RESULTS AND DISCUSSION

The experimental results refer to the range of relatively high M. The number of Kuhn segments N in the molecules of the samples being investigated ($N = L/A$, where L is the length of chain that is completely extended with retention of the valence angles) in all cases greatly exceeds the number N at which reduced FB determined by intrinsic optical anisotropy (and microform effect) virtually attains the limiting value ($N = 15$)[24]. If volume effects are absent, linear molecules behave as Gaussian coils. For this molecular weight range in the general case ($\Delta n/\Delta c \neq 0$) reduced FB may be expressed by the equation[5,6,24]

$$\frac{[n]}{[\eta]}\cdot\frac{45kTn_s}{4\pi(n_s^2+2)^2} = \left\{(\alpha_1-\alpha_2) + \frac{(\Delta n/\Delta c)^2 M_s}{2\pi\nu N_A} + \frac{2.61\cdot\Phi(\Delta n/\Delta c)^2}{\pi^2 N_A^2}\cdot\frac{M}{[\eta]}\right\} \qquad (1)$$

where $(\alpha_1 - \alpha_2)$ is the anisotropy of the optical polarizability of the segment, M_s is its molecular weight, Φ is the Flory viscous hydrodynamic parameter, n_s is the refractive index of the solvent, ν is the partial specific volume of the polymer, k is the Boltzmann constant, N_A is Avogadro's number, and T is the temperature in K.

The first term of equation (1) determines the contribution to FB provided by the intrinsic anisotropy of the polymer chain part $(\alpha_1 - \alpha_2)^{28}$. The second term is provided by the anisotropy of the segment shape (microform effect of FB)[29], and the third is provided by that of the macromolecule as a whole (macroform effect of FB)[30–32]. The last term determines the dependence of $[n]/[\eta]$ on the molecular characteristics of the polymer and on the $M/[\eta]$ ratio when the refractive indices of polymer and solvent are different.

The sign of the contribution of intrinsic anisotropy to the value of FB is determined by the orientation of optical anisotropic bonds (or bond groups) with respect to the main chain direction. The sign of the contribution of the microform effect is usually positive. However, for polymers with a large tranverse chain (segment) dimension it can be negative[33,34]. The sign of the macroform effect is always positive because, in flow, the axes of spherically asymmetric macromolecules are predominantly oriented along the flow (at low angles to it).

The concept of the microform effect has been introduced by Tsvetkov[6,29] into the FB theory to explain the value of the Maxwell effect in solutions of cellulose derivatives and also for other rigid-chain polymers when $\Delta n/\Delta c \neq 0$. For these systems at relatively high M and at $\Delta n/\Delta c \neq 0$ the $[n]/[\eta]$ ratio does not depend on $M/[\eta]$, whereas for flexible-chain polymers this dependence is observed.

The dependence of $[n]/[\eta]$ on $M/[\eta]$ for pullulan in two solvents, taking into account the factor in equation (1) $K = 45kTn_s/4\pi(n_s^2+2)^2$ (in water $K = 1.36 \times 10^{-14}\,g\,cm\,s^{-2}$ and in DMSO $K = 1.22 \times 10^{-14}$), is shown in *Figure 5*. The type of dependence of $[n]/[\eta]$ on $M/[\eta]$ for pullulan in water is analogous to that for typical flexible-chain polymers[6,32]. Hence dynamooptical investigations, like hydrodynamic investigations, make it possible to assign pullulan to the class of flexible chain polymers.

The difference between $[n]/[\eta]$ ratios in two solvents is due to different refractive index increments of pullulan in these solvents. Our estimation of $\Delta n/\Delta c$ shows that the form effects in DMSO are approximately 15 times smaller than those in water. Hence, in water the FB of pullulan molecules is determined mainly by the macroform effect and that in DMSO by the intrinsic anisotropy of polarizabilities of the polysaccharide chain.

The slope of the dependence plotted in *Figure 5* (curve 1) makes it possible to evaluate the Flory viscous hydrodynamic parameter Φ: $\Phi = (1.9 \pm 0.2) \times 10^{23}\,mol^{-1}$.

These evaluations of Φ have been carried out previously for carbon chain synthetic polymers[6]. The value of Φ obtained will be compared with that calculated on the basis of results of the theory[35] expressing the dependence of Φ on the thermodynamic quality of the solvent, which is characterized by the parameter $\varepsilon(\langle h^2\rangle \simeq M^{1+\varepsilon}$, where $\langle h^2\rangle$ is the mean-square end-to-end distance)

$$\Phi = 2.86 \times 10^{23}(1 - 2.6\varepsilon + 2.86\varepsilon^2) \qquad (2)$$

The estimate of ε has been obtained[17] from data on translational and rotational friction: $0.084 \leq \varepsilon \leq 0.112$. This leads to the following range of Φ values: $2.12 \leq \Phi \times 10^{-23} \leq 2.29$. Consequently, the values of Φ based on plot (1) (*Figure 5*) and equation (2) are in agreement.

The value of the equilibrium rigidity of the pullulan chain A was determined in water. It follows from the results given in *Table 1* that intrinsic viscosities in DMSO are approximately twice as high as those in water. This may be associated with higher excluded volume effects of pullulan molecules in DMSO than those in water. Assuming that the molecular weight of molecules is the same in water and DMSO, we will analyse viscometric data in DMSO similarly to the procedure used by us[20]. In this case $[\eta] \simeq M^{0.76}$, $\varepsilon = 0.18$ are obtained and the plot of $(M^2/[\eta])^{1/3} = f(M^{(1-\varepsilon)/2})$ gives the equilibrium rigidity of polymaltotrose molecules in DMSO, $A = 20\times 10^{-8}$ cm, which virtually coincides with the value obtained in water.

Since the values of A in water and DMSO are identical, it is possible to extrapolate the values of $(\alpha_1 - \alpha_2)$ to conditions $(\Delta n/\Delta c)^2 \rightarrow 0$ (*Figure 6*). In the case of considerable difference between A values in different solvents, it is the value of Δa (anisotropy of the repeat unit of the polymer chain or the main anisotropical part of the repeat unit) or β (anisotropy per unit of polymer chain length) that should be extrapolated to this condition. The intercept on the ordinate corresponds to the condition $\Delta n/\Delta c = 0$ and is the quantitative value of intrinsic segmental anisotropy of pullulan. Hence, the anisotropy of optical polarizability of the pullulan molecule segment was estimated as:

$$(\alpha_1 - \alpha_2) = +33 \times 10^{-25}\,\mathrm{cm}^3$$

On the basis of this value the anisotropy of the unit length of the pullulan chain can be calculated: $\beta = (\alpha_1 - \alpha_2)/A = +1.65 \times 10^{-17}\,\mathrm{cm}^2$. The positive sign $(\alpha_1 - \alpha_2)$ (or β) indicates that the optical polarizability of the pullulan chain is greater in the main chain direction and smaller in the orthogonal directions. This fact is in qualitative agreement with the β values obtained by extrapolating the FB data for cellulose nitrates with different degrees of substitution (y) to the condition $y \rightarrow 0$, as well as with the data obtained in the FB study of β- $\rightarrow$ 4-glucane containing weakly anisotropic substituents (triacetatemethylolcellulose and chitosane)[36].

The value of $(\alpha_1 - \alpha_2)$ obtained here makes it possible to evaluate to the first approximation the anisotropy of optical polarizability of the glucopyranose ring Δa in a system of coordinates of statistical segment which contains m glucopyranose rings

$$(\alpha_1 - \alpha_2) = \beta A \cong \Delta a \cdot m = \Delta a (A/\lambda)$$

where $\lambda = 4.79 \times 10^{-8}$ cm is the mean value of projection of one glucopyranose ring in pullulan on the main chain direction[18]. The following value of Δa was obtained on the basis of FB of pullulan molecules in water and DMSO: $\Delta a = +7 \times 10^{-25}\,\mathrm{cm}^3$. This value is one order of magnitude smaller than that of the phenyl ring ($\Delta a_{\mathrm{ph}} = +60 \times 10^{-25}\,\mathrm{cm}^3$)[37]. We do not know any data on the optical anisotropy of the glucopyranose ring. In this sense cyclohexane is the most similar compound to it. The optical anisotropy of cyclohexane was determined from its electric birefringence (Kerr effect) in the gas phase $\Delta a_{\mathrm{ch}} = +9.8 \times 10^{-25}\,\mathrm{cm}^3$ [37]. The value of optical anisotropy obtained by us for the glucopyranose ring is in agreement, in the order of magnitude, with that for cyclohexane.

The anisotropy of optical polarizability per glucopyranose ring is determined by (1) the anisotropy of optical polarizability of ring-forming bonds, (2) ring-conformation ((1) and (2) determine the optical

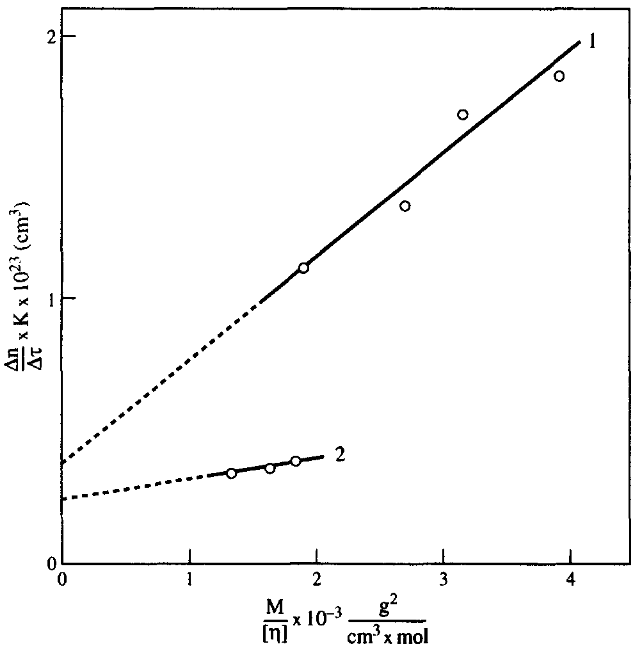

Figure 5 Plot of $K[n]/[\eta] \equiv K(\Delta n/\Delta\tau)$ vs $M/[\eta]$. 1: pullulan in water; 2: pullulan in DMSO

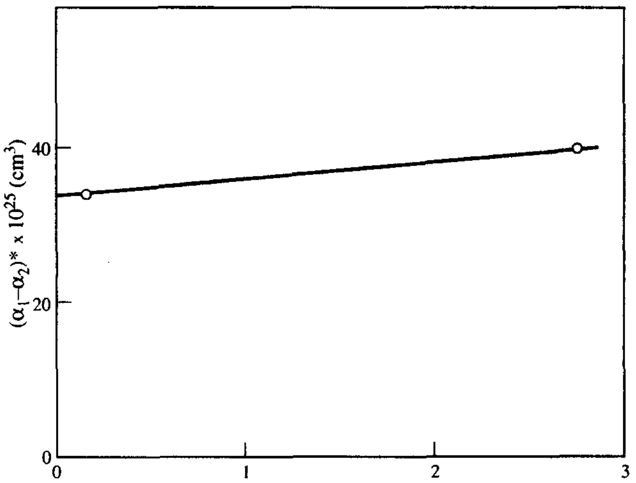

Figure 6 Plot of effective value of segmental anisotropy $(\alpha_1 - \alpha_2)^*$ vs $(\Delta n/\Delta c)^2$, where $(\alpha_1 - \alpha_2)^* = (\alpha_1 - \alpha_2) + [(\Delta n/\Delta c)^2 M_s]/2\pi\nu N_A$

polarizability of the glucopyranose ring in the ring's axes and, in principle, may be estimated by using the valence–optical scheme[38]) and (3) ring orientation with respect to the axis of the polysaccharide chain.

In order to determine the anisotropy of optical polarizability of the glucopyranose ring in its axes, it is necessary to carry out further investigation of the Maxwell effect for solutions of linear polysaccharides with another type of bonding of glucopyranose rings into the polymer chain.

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