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Optical properties of dextran in solution and in films

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Abstract

Flow birefringence of dextran solutions in dimethylsulphoxide was studied and the intrinsic optical anisotropy (α_1-α_2) of its chains was determined to be $+12.5 \times 10^{-25}$ cm^3. The dependence of birefringence in dextran films of different thickness on the angle of incidence of polarized light was then studied and the surface birefringence of the film was determined. The dependence of surface birefringence on film thickness has made it possible to determine the effective thickness of the anisotropic near-surface layer, while the comparison of the surface birefringence with the value of (α_1-α_2) enabled the estimation of the orientation of the molecular fragments with respect to the film surface.

Keywords: Birefringence; Dextran; Solution; Film

1. Introduction

Polysaccharides are one of the key components of biological structures facilitating the various functions of the living organism (Marchessault, 1984; Yalpani, 1988; Kochetkov, 1994). The complex spatial organization of biological structures cannot be completely understood without considering the behaviour of biological macromolecules at or near the interfaces near which gradients of various physical properties are formed. One of the quantitative physical characteristics of molecular structures (including biological structures) is the degree of orientational order of molecular regions or fragments near the interfaces. Consequently the degree of orientational order can be regarded as a measure of the ability of biological molecules for self-organization. Moreover, polysaccharides are natural polymers which can be recycled. Their commercial use is preferable in many cases to that of synthetic polymers because they exhibit natural affinity for the living organism and are biologically pure. The interest in both fundamental and practical investigations of polysaccharides is thus growing.

McNally and Scheppard (1930) were the first to observe that acetate cellulose and nitrate cellulose films which are optically isotropic for normal light beam incidence exhibit birefringence when incident light falls on the film at an angle to the normal. Later Stein (1959) used the tilted angle method to measure the phase difference in stretched (oriented) polymer films. Cherkasov et al. (1976) have modified the tilted film method and have also developed a theory making it possible to interpret spontaneous birefringence in polymer films at the molecular level. Grishchenko (1996) has applied this method to the study of orientation effects in surface layers of films made of various synthetic polymers.

The present work deals with the study of optical molecular properties of the neutral bacterial polysaccharide, dextran, by dynamic flow birefringence method in solution and the study of the optical properties of dextran films by a method using an inclined polarized beam.

Dextrans, polysaccharides synthesized by microorganismes, are constructed from glucose residues combined mainly by $\alpha 1 \rightarrow 6$ bonds with different degrees of branching (Yalpani, 1988). Chains of low molecular weight material are virtually linear. As the analysis of hydrodynamic data shows (Gekko, 1971; Huber, 1991; Pavlov et al., 1994; Pavlov and Korneeva, 1995), dextran is a flexible chain polymer with an equilibrium rigidity characterized by the Kuhn segment length $A = 13 \times 10^{-8}$ cm.

The conclusion that dextran chains exhibit high equilibrium flexibility is also confirmed by calculation carried out by the methods of statistical mechanics (Burton and Brant, 1983). Their high chain flexibility is due to additional possibilities of internal rotation about $\alpha 1 \rightarrow 6$ bonds as compared to those for $1 \rightarrow 4$, $1 \rightarrow 3$, $1 \rightarrow 2$ polysaccharides.

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2. Experimental

2.1. Materials

Commercial dextran from Sigma and Pharmacia Fine Chem. AB, Uppsala (Sweden) was used. The molecular weights determined by these companies as follows: $M_w =$ 2000, 500, 250, 71.4, 40, and 10.

The films were prepared from aqueous solutions of high molecular weight dextran samples. A range of solution concentrations were used in order to obtain films of different thicknesses. The solutions were cast on horizontal glass supports (without contact with vertical walls) and dried under room conditions. The drying rate per unit surface area was 3.8×10^{-6} g s^{-1} cm^2. Spontaneous macroscopic transport was observed during film formation. Its direction was opposite to that of the concentration gradient (chemical potential). Solvent evaporates from the entire solution surface in contact with the air: however, the films are formed in the region of the three-phase boundary (support–solution–air), i.e. over in the range of contact angle in which the evaporation rate of the solvent is high. Spontaneous transport of the polymer substance into this region takes place and the film formed is not of uniform thickness near the boundary. The peripheral region of the film is the region of its thickness gradient. The central part of the film — the most uniforn region of thickness — was removed and used for investigations.

2.2. Methods

The orientational order of anisotropic regions or 'fragments' of molecules in the surface layers of dextran films was evaluated by measuring the birefringence when polarized light passes at different angles to the film surface. This method is based on the measurement of the phase differences δ which appear between two light components polarized in perpendicular directions on passing through a film by the incident angle i (Stein, 1959; Cherkasov et al., 1976; Grishchenko, 1996).

The optical phase difference or 'optical retardation' δ induced by the film was determined on special device for observing birefringence. The film was placed between two crossed polarizing prisms. The δ value was measured visually by a Brace penumbral elliptic compensator. In this case we have $\delta = \delta_0 \sin 2\Delta\varphi$ ($\delta_0 = 0.076$ is the phase difference induced by the compensator) and $\Delta\varphi = \varphi - \varphi_0$ is the difference between compensator counts when the light passes at an arbitrary angle and at $i = 0$. Fig. 1 shows the dependences of $\varphi - \varphi_0$ on i for dextran films of different thickness.

The difference between main polarizabilities of the statistical segments of dextran chains was evaluated by flow birefringence in dextran solution in DMSO. The FB effect was detected by photoelectric recording of light flux (Pen'kov and Stepanenko, 1963; Tsvetkov, 1989). A mica compensator ($\delta_0 = 0.0078$) was used for compensating FB, Δn, induced by the shear field. Flow birefringence was measured in a thermostatted ($T = 21.0$°C) titanium dynamooptimeter with an inner rotor 3 cm long along the light beam path. Samples with the molecular weight $M_w =$ 10, 40, and 71.4 were investigated. Flow birefringence values for solutions in DMSO were positive and proportional to rate gradient, which made it possible to determine the 'reduced birefringence' $\Delta n/\Delta\tau = \Delta n/G\,(\eta - \eta_0) = +1.35 \times 10^{-10}$ (Fig. 2). Here η and η_0 are dynamic viscosities of solution and the solvent, respectively, G is the rate gradient, and $\Delta\tau$ is the flow shear stress. The refractive

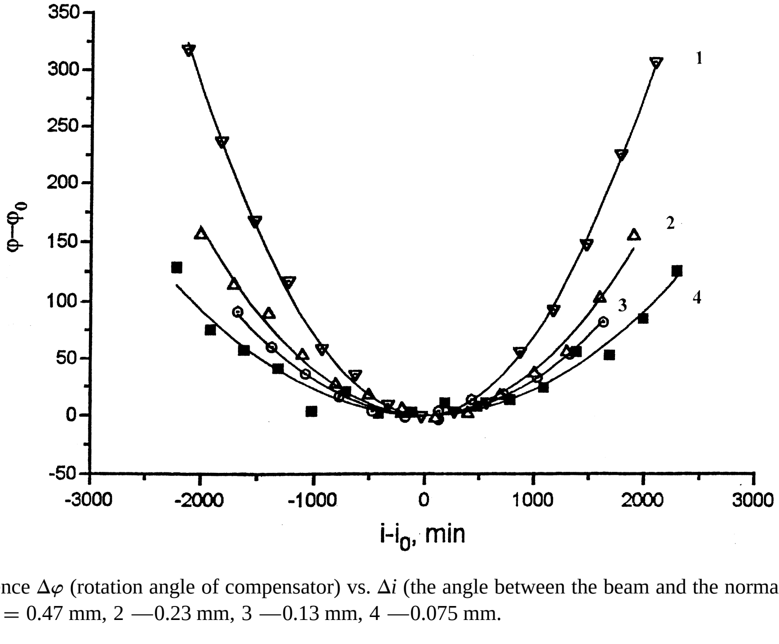

Fig. 1. Dependence of birefringence $\Delta\varphi$ (rotation angle of compensator) vs. Δi (the angle between the beam and the normal to the film) for dextran films of different thickness H: 1 —— $H = 0.47$ mm, 2 —0.23 mm, 3 —0.13 mm, 4 —0.075 mm.

index increment $\Delta n/\Delta c$ for dextran solutions in DMSO was measured by a differential refractometer based on Lebedev polarizing interferometer (Pavlov, 1988). An Ostwald viscometer was used for viscometric measurements.

2.3. Results and discussion

The orientational order of anisotropic chain fragments with respect to polymer film surface may be characterised by the orientational order parameter (de Gennes, 1974; Grishchenko, 1996; Grishchenko and Cherkasov, 1997)

$$S \equiv 1/2(3\langle\cos^2\theta\rangle - 1)$$

where θ is the angle formed by the segment (an anisotropic element) axis and the normal to the film surface and $\langle\,\rangle$ means an averaging of $\cos^2\theta$ value. If $\cos^2\theta$ is 1/3, than S is equal to zero, which shows that predominant orientation of chain fragments relative the surface does not exist. When orientational order exists in surface layers ($S \neq 0$), the film exhibits optical anisotropy when the polarized light beam passes through the film obliquely. The birefringence in films is caused by different polarizabilities of anisotropic chain elements along vertical and horizontal axes in the plane normal to the beam (Cherkasov et al., 1976; Grishchenko and Cherkasov, 1997). This difference in polarizabilities is a function of the polar angle θ and the azimuthal angle γ of the orientation of chain elements counted from axes Z and X, respectively. When the film is optically isotropic at a normal incident angle, the difference distribution of polarizabilities with respect to γ is regular, and in this case the phase difference will depend only on the angle θ. Using the Lorentz–Lorenz ratio for experimentally observed phase difference δ, the following equation was obtained (Cherkasov et al., 1976):

$$\delta = -(2\pi/\lambda n^3)[(n^2+2)/3]^2 N_0(\alpha_1-\alpha_2)\sin^2 i \times \int_0^\pi\int_0^H (3\cos^2\theta - 1)/2\mathrm{f}_H(\theta)\mathrm{d}\theta\mathrm{d}H$$

where $f_H(\theta)$ is the density of orientation distribution of anisotropic elements on angle θ in the layer of thickness dH; (α_1-α_2) is the difference between the main polarizabilities of a statistical chain segment; N_0 is the number of anisotropic elements in unit volume; H is the film thickness; n is the average refractive index, and θ is the wavelength of light.

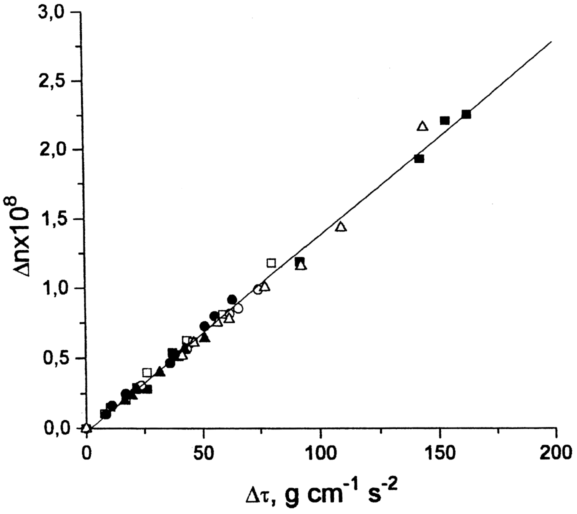

Fig. 2. Dependence of the flow birefringence value Δn vs. shear rate tension $\Delta\tau = G(\eta - \eta_0)$ for three dextran samples of different molecular weights (kDa ≡ kg/mol) at different solute concentrations, (g cm^{-3}). $M = 71.4$, $c = 1.851$ (▲); 0.536 (△); $M = 40$, $c = 2.945$ (■); 1.763 (□); 1.142 (●); $M = 10$, $c = 4.347 \times 10^{-2}$ g cm^{-3} (○).

Using the following expression for the orientational order parameter S:

$$\mathrm{S} \equiv 1/2(\langle 3\cos^2\theta\rangle\cos^2\theta - 1) = 1/H\int_0^\pi\int_0^H (3\cos^2\theta - 1)/2 f_H(\theta)\mathrm{d}\theta\mathrm{d}H$$

and bearing in mind that $N_0 = N_A\rho/M_S$ we obtain

$$\delta = -N_A\pi\rho/\lambda n^3((n^2+2)/3)^2[(\alpha_1-\alpha_2)/M_S]SH(1-\cos 2i)$$

where M_S is the molecular weight of statistical segment and ρ is the average polymer density in bulk.

The resulting phase difference depends on the incident angle i as follows:

$$\delta = B(1-\cos 2i) \tag{1}$$

$$B = -\pi N_0 H(n^2+2)^2[(\alpha_1-\alpha_2)/9n^3\lambda]S \tag{2}$$

According to Eq. (1), the experimental dependences of δ on $(1 - \cos 2i)$ for all dextran films were found to be linear regardless of H (Fig. 3). Hence, in each case, it was possible to determine the value of surface birefringence B. Fig. 4 shows the dependence of B on H. It can be seen that B for thin films is proportional to their thickness H, but for thick films ($H > 0.3$ mm) B becomes independent of film thickness. This dependence can be interpreted by using a three-layer model for polymer films (Grishchenko, 1996; Grishchenko and Cherkasov, 1997). This model assumes that the film consists of three-layers: two optically anisotropic surface layers with thickness H_a (to the first approximation these layers are assumed to be identical) and an optically isotropic layer with a thickness $H_i = (H - 2H_a)$ located between them. It is assumed that surface layers are characterised by predominant orientation of chain fragments, whereas the fragment in the intermediate layer are arranged chaotically.

Therefore, it is possible to evaluate the thickness of the anisotropic surface layer of dextran films from the analysis of the experimental dependence of B on H. It can be seen that for dextran this dependence reaches a plateau region at $H > 0.28$ mm. Hence $H_a = H/2 = 0.14$ mm.

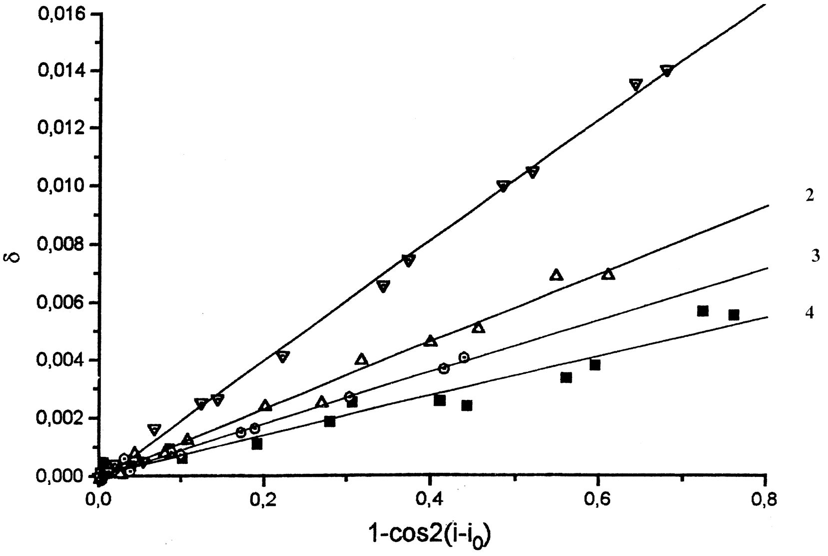

Fig. 3. The optical phase difference (optical retardation) δ vs. $[1 - \cos 2(i - i_0)]$ for dextran films of different thickness H: 1 — $H = 0.47$ mm, 2 — 0.23 mm, 3 — 0.13 mm, 4 — 0.075 mm.

Eq. (2) makes it possible to determine the orientational order parameter S. For this purpose the intrinsic optical anisotropy (α_1-α_2) of dextran molecules contained in Eq. (2) will be evaluated. The following relationship will be used in which the value of reduced birefringence (shear optical coefficient) $[n]/[\eta] = \Delta n/\Delta\tau$(Fig. 2) is related to the value of (α_1-α_2) and other dextran molecular parameters (Tsvetkov, 1989):

$$[n]/[\eta] \times (45kTn_s/4\pi(n_s^2+2)^2) = \qquad (3)$$

$$= (\alpha_1 - \alpha_2) + [(\Delta n/\Delta c)^2 M_S/2\pi\bar{\nu}N_A]$$

$$+ (2.61\Phi(\Delta n/\Delta c)^2/(^2N_A^2) \times (M/[\eta])$$

where $\Delta n/\Delta c = 0.034\ \mathrm{cm^3/g}$ is the refractive index increment measured in DMSO, $n_s = 1.477$ is the refractive index in DMSO, $M_S = 369.5$ is the molecular weight of a dextran segment, $\bar{\nu} = 0.61\ \mathrm{cm^3/g}$ is the specific partial volume, Φ is the Flory hydrodynamic parameter, M and $[\eta]$ are the molecular weight and intrinsic viscosity of dextran samples. To minimize the contribution of form effects deriving (mainly from the macroform effect for flexible chain dextran) the solvent, DMSO was chosen in which the form effects are about twenty times lower than those in water [in water we have for dextran $\Delta n/\Delta c = 0.15\ \mathrm{cm^3/g}$ (Huglin, 1975)]. Moreover, samples with low molecular weights ($M = 10$, 40, and 71.4) were investigated for reducing the contribution of the macroform effect. In the molecular weight range investigated the $\Delta n/\Delta\tau$ ratio is virtually independent of M (Fig. 2). The number of Kuhn segments in dextran chains (M/M_S) is sufficiently great, so that the chains behave as Gaussian chains in the absence of volume effects, and Eq. (3) enabling us to determine the intrinsic optical anisotropy of a statistic segment (α_1-α_2) is obeyed.

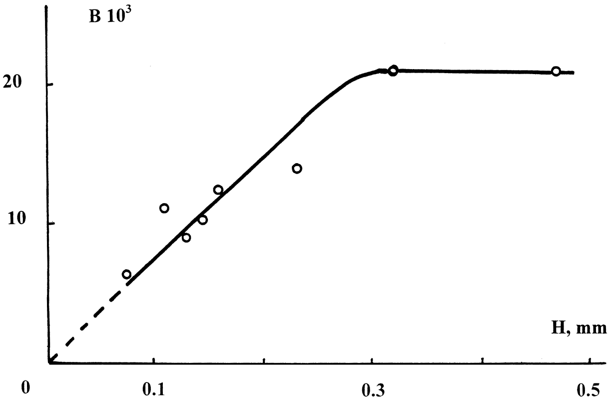

Fig. 4. Dependence of surface birefringence B on thickness H of dextran films.

As a result it was possible to obtain for (α_1-α_2) $= +12.5 \times 10^{-25}\ \mathrm{cm^3}$. This value is in reasonable agreement with the value of (α_1-α_2) $= +33.0 \times 10^{-25}\ \mathrm{cm^3}$ obtained previously for pullulan molecules (Pavlov and Yevlampieva, 1995; Pavlov et al., 1998). The different values of (α_1-α_2) for dextran and pullulan are probably a consequence of glucopyranose rings in their macromolecules being oriented differently with respect to the main chain. In order to determine the parameter S, Eq. (2) is rearranged as follows:

$$S = -(3/(n^2+2))^2[n^3(\lambda/\pi N_0(\alpha_1 - \alpha_2))](dB/dH) \qquad (4)$$

where $dB/dH = 0.72\ \mathrm{cm^{-1}}$ is the tangent of the slope of B vs. H (Fig. 4) at low H.

It follows from Eq. (4) that $S = -0.007$. The negative sign of S shows that the mean orientation angle of anisotropic dextran chain fragments to the normal to the film surface is $\theta > 54.7°$. In other words, anisotropic chain fragments are predominantly parallel with respect to the surface. It must be noted that the value of thickness of an optically anisotropic surface layer for dextran films coincides with that for poly-bis-trifluoroethoxyphosphasene (PTFP) a polymer with a tendency to adopt orientational order (Schneider, 1978), and is seven times that for polystyrene (a classical representative of amorphous synthetic polymers). This fact, without doubt, indicates that dextran chains have a high ability to form orientational order. At the same time the parameter $S = -0.007$ for dextran is 26 times smaller in absolute value than that for PTFAP (Grishchenko et al., 1996; Grishchenko et al., 1997). Whether or not these values are peculiar for dextran molecules or not, could, we believe, established after films of polysaccharides with other chain structures have been investigated.

3. Conclusion

Flow birefringence of dextran solutions and birefringence in surface layers of dextran films by the method of tilted polarized beam have been studied. Effects related to spontaneous orientation of dextran chain fragments or regions with respect to film surface were determined. A three-layer model for dextran films was discussed. This model has enabled us to determine the thickness of the effective optically anisotropic layer ($H = 0.14$ mm). The orientational order parameter of dextran chains in surface layers was negative ($S = -0.007$), which indicates that molecular fragments are oriented predominantly parallel with respect to film surface. The discrepancy between the relatively large surface layer thickness and the small value of the parameter S is probably related to considerable thermodynamic flexibility of dextran chains and some peculiarities of their structure (branching of macromolecules).

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