

# Polysaccharide Film Technologies: Interfacial Order and Chain Thermodynamic Rigidity

GEORGES M. PAVLOV\* AND ALEXEY E. GRISHCHENKO

*Department and Institute of Physics of St Petersburg University,  
Ulianovskaya str. 1, Petergof, 198904, St Petersburg, Russia*

## Introduction

The properties of various substances at or near the surface layers differ greatly from those in the bulk of the material. The contribution of surface layers to the overall characteristics of materials increases with decreasing characteristic dimensions. These effects are caused by the self-organization of molecular structures in surface layers. The results of the study of density, mechanical properties, and birefringence indicate that averaged physical characteristics of materials are profoundly affected by sample dimensions (Rostiashvili *et al.*, 1987; Grishchenko, 1996). One of the reasons for these effects is the appearance of orientational order at the interface. This is particularly pronounced in the case of chain-like linear molecules, the parts of which are characterized by high anisotropy. The published data available on these materials to date deal mainly with investigations of induced orientational order that appear under the influence of tensile stress or induced by electromagnetic fields (Hermans, 1949; Paul and Newman, 1978). There are only a relatively small number of papers that deal with the spontaneous organisation of physical properties in the vicinity of interfaces and the dependence of this organisation on the chemical structure of chain molecules (McNally and Sheppard, 1930; Cherkasov *et al.*, 1976; Grishchenko *et al.*, 1983; Grishchenko and Cherkasov, 1997). It should also be pointed out that definitive quantitative criteria for evaluating self-organization at interfaces are generally absent. In the present paper the '*orientational order parameter*' (de Gennes, 1974) is used for the quantitative characterization of chain molecular self-organization at the interface.

The idea that the orientation of polymer chains in surface layers influences the optical properties of films was first suggested by McNally and Sheppard (1930) and has been further developed by Hermans (1949), Stein and Norris (1956) and Stein (1978). Orientational order can be evaluated experimentally by using the method of an

---

\*To whom correspondence may be addressed.

inclined polarized beam in combination with sedimentation-diffusion analysis and the method of flow birefringence in solution. The present short review will attempt to establish correlations between the chemical structure and conformational characteristics of polysaccharides on the one hand and the properties of interfaces formed by them on the other, and is based mainly on work from our St. Petersburg laboratory. For this purpose, we include the results for investigations on dextran, pullulan, mannan, methylcellulose, and xanthan.

### The inclined polarized beam method

The inclined polarized beam method provides an effective way of enabling us to obtain quantitative information about the structure and orientation of anisotropic elements of polymer chains in surface layers (Cherkasov *et al.*, 1976; Grishchenko, 1996; Grishchenko and Cherkasov, 1997). This method is based on measurement of the birefringence occurring when polarized light passes through a film at an angle to the surface different from the normal angle. The appearance of birefringence in this mode of light transmission through a film has been explained in terms of the orientation of polymer chains (McNally and Sheppard, 1930). An optical method for determining the type of molecular orientation with respect to the surface has been proposed by Cherkasov *et al.* (1976). In this method, birefringence was measured at two fixed incident angles of polarized beam to the film. Cherkasov *et al.* (1976) have modified this method in such a way that it has become possible to obtain more detailed information about orientational order in polymer samples.

An equation has been derived (Cherkasov *et al.*, 1976) for relating the phase difference  $\delta$  between beams polarized in two perpendicular directions and forming an angle  $i$  with the polymer film surface

$$\delta = B(1 - \cos 2i) \quad (1)$$

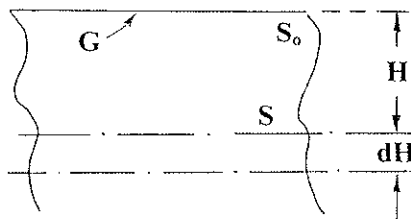
Here  $B$  is the surface birefringence given by

$$B = -\pi N_0 (\alpha_1 - \alpha_2) / n^3 \lambda \{ (n^2 + 2) / 3 \}^2 HS \quad (2)$$

and where  $N_0$  is the number of segment per unit volume,  $n$  the refractive index of the polymer,  $\lambda$  is the wavelength of the incident light,  $(\alpha_1 - \alpha_2)$  is the difference between the main polarizabilities of the anisotropic chain element,  $S = (3\langle \cos^2 \vartheta \rangle - 1) / 2$  is the factor of orientational order of molecular fragments with respect to the surface, and  $H$  is the film thickness.

It follows from equation (2) that surface birefringence  $B$  is proportional to film thickness  $H$ . This outcome of the theory is in agreement with experimental data for small values of  $H$ . However, with increasing  $H$  the experimental values of  $B$  attain a limiting value and no longer depend on film thickness (Cherkasov *et al.*, 1976; Grishchenko, 1996). This discrepancy between the theory and experiment follows from the assumption underpinning the derivation of equation (2). It was assumed that at low  $H$  the orientational order factor does not depend on film thickness and is characterized only by a certain average value of  $S$ .

In order to describe adequately the dependence of  $B$  on  $H$  over a wide range of film thickness, the dependence of the orientational order factor  $S$  on thickness should be taken into account.



**Figure 1.** Scheme for calculating the surface birefringence  $B$  versus thickness,  $H$  of a film.  $G$ : surface of film.

Let us consider the air-polymer interface (*Figure 1*). An infinitely thin layer  $dH$  parallel to film surface will be singled out. Let us assume that when the layer depth changes from  $H$  to  $H+dH$ , the order parameter decreases by  $dS$ . This decrease is proportional to  $S$  at a distance  $H$  from the surface and to layer thickness  $dH$ , i.e. we have

$$dS = -kSdH \quad (3)$$

where the minus sign shows that the order parameter *decreases* with the distance from the interface, in other words with increasing  $H$ .

Integrating equation (3) from zero

$$\int_0^H S^{-1} dS = -k \int_0^H dH$$

and assuming that at  $H=0$ ,  $S$  is equal to  $S_0$ , the following equation can easily be obtained:

$$S = S_0 e^{-kH} \quad (4)$$

It is clear that at  $H = k^{-1}$  the order parameter decreases  $e$  times. The distance from the surface  $H_0$  at which  $S$  decreases  $e$  times can be called the effective thickness of the anisotropic surface layer, i.e. we have

$$S = S_0 e^{-H/H_0} \quad (5)$$

Equation (5) makes it possible to obtain the dependence of  $B$  on  $H$  over a wide range of changes in polymer film thicknesses

$$B = -[\pi N_0 (\alpha_1 - \alpha_2) / n^3 \lambda] ((n^2 + 2)/3)^2 \int_0^H S_0 e^{H/H_0} dH = \\ -[\pi N_0 (\alpha_1 - \alpha_2) / n^3 \lambda] ((n^2 + 2)/3)^2 S_0 H_0 (1 - e^{-H/H_0}) = B_0 (1 - e^{-H/H_0}) \quad (6)$$

It can be seen that at  $H/H_0 \ll 1$  the value of  $B \sim S_0 H$  and at  $H \rightarrow \infty$  it acquires the maximum value equal to  $B = B_0 \sim S_0 H_0$ .

A comparison of the theoretical prediction (6) with experimental data makes it possible to evaluate the effective thickness of an optically anisotropic surface layer, the orientational order and of the parameter of molecular fragments near the interface.

### Examples for polysaccharide films

The films that have been investigated are based around the following polysaccharides:

1. *Dextran*: the chains in dextran consist of glucose residues linked mainly by  $\alpha(1-6)$  bonds (Yalpani, 1988; Tombs and Harding, 1998).
2. *Pullulan*: this is another microbial polysaccharide produced by *Aureobasidium pullulans*. Its chains consist of maltotriose residues linked by  $\alpha(1-6)$  links (Yalpani, 1988).
3. *Mannan* (Elinov and Vitovskaya, 1979): this is an extracellular polysaccharide produced by yeast of the *Rhodotorula rubra* strain. The repeat unit of this mannan contains  $\beta(1-3)$  and  $\beta(1-4)$  bonds in an equimolar ratio (Elinov and Vitovskaya, 1979).
4. *Methylcellulose*: this is the first member in a series of O-alkyl substituted cellulose ( $\beta(1-4)$  glucan). The mean content of  $\text{OCH}_3$  groups was 28.4%, which corresponds to the degree of substitution 1.68 (Pavlov *et al.*, 1996).
5. *Xanthan*: this is an anionic polysaccharide produced by *Xanthomonas campestris* bacteria (Yalpani, 1988). A polysaccharide of the Kelco/Keltrol company has been the subject of study with regards to film formation. Its degree of substitution with acetate groups is 0.81 and that with pyruvyl groups is 0.59.

The films investigated had been cast from aqueous solutions at different concentrations on horizontal glass surfaces. The films usually were of greater thickness on the periphery. Homogeneous central part of the films was chosen for investigations. Film thickness was measured with a micrometer. Where necessary, multi-layered 'stacks' consisting of several homogeneous films were used. Film thickness is calculated from the solution concentration  $C$  and the area  $Q$  according to the equation  $H = C \times m / Q\rho$  where  $m$  is the mass of solution distributed on the area  $Q$  and  $\rho$  is the polymer density. The assumption had been made that film thickness for a given film studied was homogeneous throughout. It should be noted that the study of birefringence of thick methyl cellulose and xanthan films ( $H > 0.1$  mm) was difficult because they were not transparent. This fact probably results from microphase segregation of the films.

### Methods for evaluating the equilibrium rigidity of polysaccharide molecules

The equilibrium chain rigidity of all polysaccharides used here was evaluated from data obtained in solution investigations by the methods of molecular hydrodynamics (Tanford, 1961; Tsvetkov *et al.*, 1970; Cantor and Schimmel, 1980). In this case, the main characteristics are the velocity sedimentation coefficient  $s_0$ , the translational diffusion coefficient  $D_0$ , and intrinsic viscosity  $[\eta]$ . Useful information about the hydrodynamic study of polysaccharides may be obtained from the articles of Pavlov (1989, 1995, 1997); Pavlov *et al.* (1997); Harding (1992, 1995). To obtain quantitative evaluations of thermodynamic rigidity (Kuhn segment length), fractions (samples) over a wide molecular weight range  $M$  have been investigated. In the case of translational friction, the most complete result taking into account the effects of intramolecular draining (percolation) and volume interaction had been obtained on the basis of the Gray, Bloomfield, Hearst theory (1967):

$$[s]P_0N_A = [3/(1-\epsilon)(3-\epsilon)]M_L^{(1-\epsilon)^{3/2}} A^{-(1-\epsilon)^{3/2}} M^{(1-\epsilon)^{3/2}} + (M_L P_0 / 3\pi)$$

$$[\ln(A/d) - (1/3)(A/d)^{-1} - \varphi(\epsilon)]$$

where  $[s] = s_0 \eta_0 (1 - \nu \rho_0)^{-1}$ ,  $\eta_0$  is the viscosity of solvent and  $(1 - \nu \rho_0)$  is the buoyancy factor or density increment;  $M_l = M_0 / \lambda'$  is the mass of the unit length of macromolecules,  $M_0$  is the molecular weight of the repeating unit,  $\lambda'$  is the projection of the unit in the chain direction;  $A$  is the Kuhn segment length,  $d$  is the hydrodynamic chain diameter;  $P_0 = 5.11$  is the Flory hydrodynamic parameter,  $N_A$  is Avogadro's number;  $\epsilon$  is the parameter characterizing the volume effects where  $\langle h^2 \rangle \sim M^{1+\epsilon}$  and  $\langle h^2 \rangle$  is the mean-square end-to-end distance of the chain and  $\varphi(\epsilon)$  is the function that can be tabulated utilizing the theory of Gray, Bloomfield, Hearst (1967).

Viscometric data is usually interpreted on the basis of an assumption that chain dimensions in phenomena of translational and rotational friction are equivalent. In the analytical form, the relationship between hydrodynamic parameters is expressed by the following equation (Pavlov *et al.*, 1990; 1992)

$$[s] P_0 N_A = (M^2 \Phi / [\eta])^{1/3}$$

where  $\Phi$  is the Flory hydrodynamic parameter, and  $[\eta]$  is the intrinsic viscosity.

### The determination of segmental optical anisotropy

The intrinsic segmental anisotropy ( $\alpha_1 - \alpha_2$ ) is a fundamental characteristic necessary for interpreting the results of birefringence in films. The principal method for its determination is flow birefringence (the 'Maxwell effect') of macromolecules in solutions when the contour length of macromolecules  $L$  greatly exceeds the Kuhn segment length,  $A$  (so that  $L/A > 15$ ). Under these circumstances, the dependence on molecular parameters is given by the following expression (Tsvetkov and Andreeva, 1981; Tsvetkov, 1989)

$$[\eta] / [\eta] \{ 45kTn_0 / 4\pi(n^2 + 2)^2 \} = \{ (\alpha_1 - \alpha_2) + (\Delta n / \Delta c)^2 M_s / 2\pi\nu N_A + (2.61\Phi(\Delta n / \Delta c)^2 / \pi^2 N_A^2) (M / [\eta]) \} \quad (7)$$

where  $(\alpha_1 - \alpha_2)$  is the intrinsic segmental anisotropy of optical polarizabilities,  $M_s$  is the molar weight of the segment,  $n_0$  is the refractive index of the solvent,  $\nu$  is the partial specific volume of the polymer,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature.

The first term in equation (7) reflects the contribution of intrinsic polarizability anisotropy to the birefringence effect, the second one corresponds to the microform effect, and the third term corresponds to the effect of the form of random coil in solution. If refractive indices of the polymer and the solvent coincide, birefringence is determined only by the difference between main polarizabilities of a statistical segment ( $\alpha_1 - \alpha_2$ ). If the refractive index increment of the polymer-solvent system  $\Delta n / \Delta c$  is non-zero, then to determine the value of  $(\alpha_1 - \alpha_2)$ , the effects of macro- and microform should be taken into account. As can be seen from equation (7), the extrapolation of the dependence of  $[\eta] / [\eta]$  on  $M / [\eta]$  to the zero value of the parameter  $M / [\eta]$  makes it possible to take into account the contribution of the macroform effect to the total birefringence value. The values of  $\lim_{M / [\eta] \rightarrow 0} [\eta] / [\eta]$  have in this way been determined for pullulan in water and DMSO.

The second extrapolation of the values of  $\lim_{M / [\eta] \rightarrow 0} [\eta] / [\eta]$  at  $M / [\eta] = 0$  to the zero value of

refractive index increment ( $\Delta n/\Delta c \rightarrow 0$ ) enable us to exclude from consideration the microform effect as well, which follows from equation (7):

$$\lim_{M \rightarrow 0; \Delta n/\Delta c \rightarrow 0} [n]/[\eta] = \{4\pi(n^2+2)^2/45 kTn_s\}(\alpha_1 - \alpha_2)$$

The above procedure has made it possible to estimate the intrinsic optical segmental anisotropy of pullulan ( $\alpha_1 - \alpha_2$ ) to be  $+33 \times 10^{-25} \text{ cm}^3$  (Pavlov *et al.*, 1998a). The intrinsic optical anisotropy of a dextran segment has also been obtained in an analogous way ( $\alpha_1 - \alpha_2$ ) =  $+12.5 \times 10^{-25} \text{ cm}^3$  (Pavlov *et al.*, 1998b). The results from these studies have in this way shown that the polarizabilities of pullulan and dextran in the main chain direction slightly exceed those in the transverse direction, which is in good agreement with the chemical structure of their monomer units.

### Experimental evaluation of orientational order

Orientalional order of polysaccharide chain fragments in surface layers has indeed been successfully probed by the inclined polarized beam method, and a standard optical scheme with a visual system of birefringence recording has been used to obtain this information.

To achieve this, the optical phase difference, or 'optical retardation'  $\delta$  induced by the polymer film is determined with the aid of a penumbral Brace compensator,  $\delta = \delta_0 \sin 2\Delta\varphi$  (Tsvetkov *et al.*, 1970). Here  $\Delta\varphi = \varphi - \varphi_0$  is the difference between compensator readings when the film forms an angle with the optical axis and when the polarized beam is normal to the film and  $\delta_0$  is the phase difference induced by the mica plate of the compensator ( $\delta_0 = 0.076$  radians).

Figure 2 shows as an example the dependence of  $\Delta\varphi$  on the incidence angle  $i$  of the

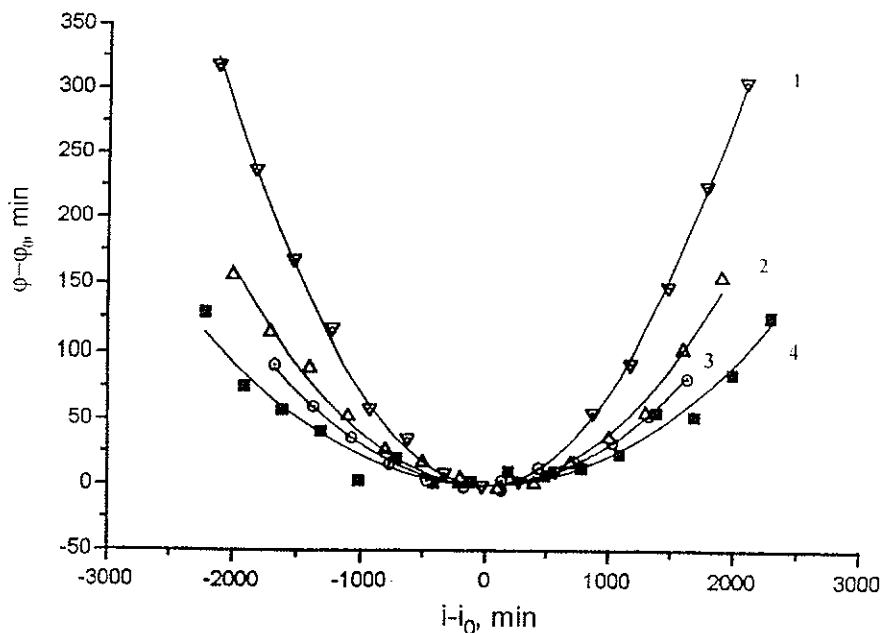
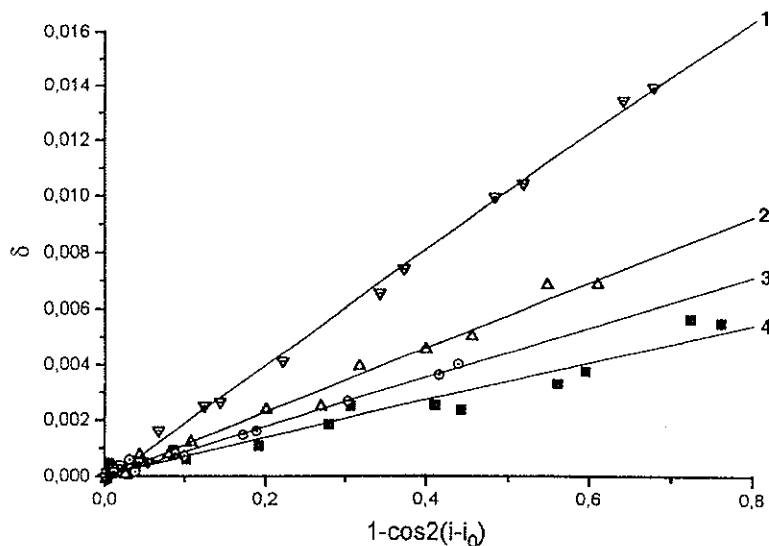
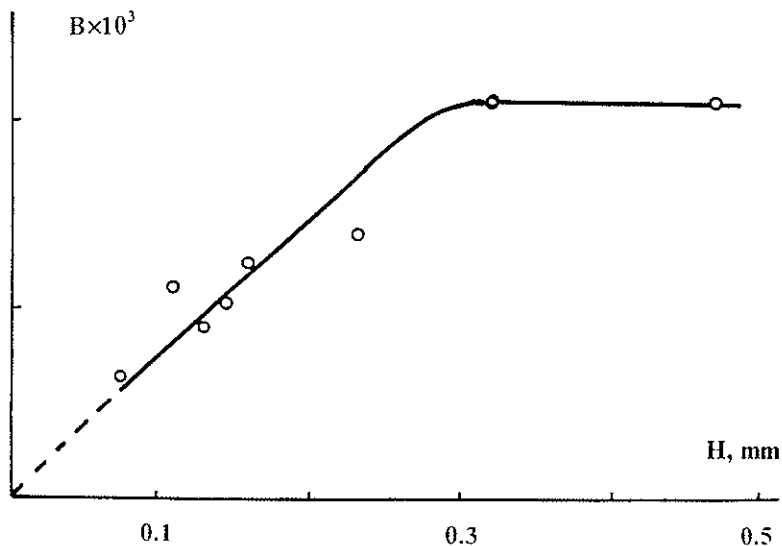


Figure 2. Plot of  $\Delta\varphi$  (see text) versus angle  $i$  between the beam and normal to the film for dextran films of different thickness  $H$ . 1 -  $H=0.47$  mm, 2 -  $0.23$  mm, 3 -  $0.13$  mm, 4 -  $0.075$  mm.



**Figure 3.** The optical retardation  $\delta$  vs  $(1-\cos^2 i)$  for dextran films of different thickness: 1 –  $H=0.47$  mm, 2 –  $0.23$  mm, 3 –  $0.13$  mm, 4 –  $0.075$  mm.

polarized beam for dextran films of different thicknesses (Pavlov *et al.*, 1998b). *Figure 3* shows the dependence of  $\delta$  on  $(1-\cos^2 i)$  for the same films. According to equation (1), the tangents to the slopes of such plots make it possible for us to evaluate the coefficients of surface birefringence  $B$  for all dextran films. Plots similar to those in *Figures 2* and *3* have also been constructed for other polysaccharides, and such plots have enabled the determination of the surface birefringence  $B$  for films of different thicknesses for all polysaccharides investigated. The dependences of  $B$  on  $H$  for these



**Figure 4.** Dependence of surface birefringence  $B$  on thickness  $H$  of dextran films.

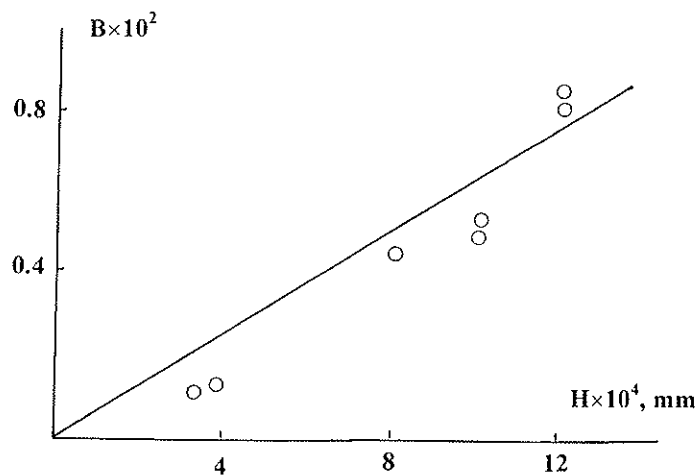


Figure 5. Dependence of surface birefringence  $B$  on thickness  $H$  of xanthan films.

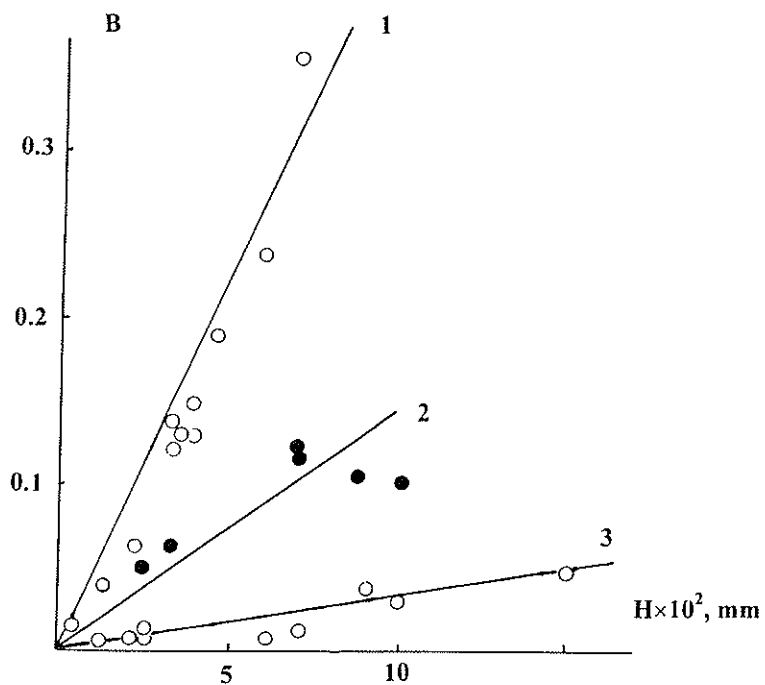


Figure 6. Dependence of surface birefringence  $B$  on thickness  $H$  of methylcellulose (1), mannan (2) and pullulan (3) films.



**Table 1.** The film birefringence, orientational order parameter and equilibrium rigidity of some polysaccharide molecules

Polysaccharide	Structural type	$dB/dH \times 100 \text{ mm}^{-1}$	S	$A \times 10^8 \text{ cm}$	Reference
dextran	$\alpha(1-6)$	7.2	-0.007	13	Gekko (1971); Huber (1991)
pullulan	$\alpha(1-6)$ , $\alpha(1-6)$	33	-0.012	21	Kawahara (1984); Pavlov (1994)
mannan	$\beta(1-3)$ , $\beta(1-4)$	167	-(0.06-0.16)	51	Pavlov (1992)
methyl cellulose	$\beta(1-4)$	463	-(0.17-0.45)	155	Pavlov (1995)
xanthan	double helix	650	-(0.24-0.5)	2400	Sato (1984)

polysaccharides are shown in *Figures 4-6*: all these data are recent work from our St. Petersburg laboratory.

At low values for the ratio  $H/H_0 \ll 1$ , equation (6) becomes

$$B = -[\pi N_0(\alpha_1 - \alpha_2)/n^3 \lambda]((n^2 + 2)/3)^2 S_0 H \quad (8)$$

It is clear that the slope of the plot of B against H in the region of low H makes it possible to evaluate the orientational order parameter near the interface  $S_0 = (dB/dH)_{H \rightarrow 0}$ . Taking into account that  $N_0 = \rho N_A / M_s$  and using values for the optical anisotropy of unit mass of polysaccharide chains  $\beta = (\alpha_1 - \alpha_2)/M_s$ , it is easy to estimate  $S_0$ .

*Table 1* gives the values of orientational order parameter  $S_0$  for dextran and pullulan. No reliable data are unfortunately available on intrinsic optical anisotropy of mannan, methyl cellulose, and xanthan. Therefore, the parameter  $S_0$  for these polymers has been evaluated by proceeding from the assumption that the specific optical anisotropy values,  $\beta = (\alpha_1 - \alpha_2)/M_s$ , differ only slightly from those for dextran and pullulan. The  $S_0$  values for mannan, methyl cellulose, and xanthan have thus been evaluated in this way (*Table 1*). The analysis of equation for the orientational order factor  $S = (3\langle \cos^2 \vartheta \rangle - 1)/2$  shows that when the chains are oriented in the plane of film surface, i.e.  $125.3^\circ > \vartheta > 54.7^\circ$ , then we have  $S < 0$  ( $S = 0.5$  at complete planar order). In the case when the chains are largely arranged normally to the surface ( $54.7^\circ > \vartheta > -54.7^\circ$ ), the orientational order parameter  $S > 0$  and attains a value of unity ( $S = +1$ ) at complete normal order ( $90^\circ$ ).

Analysis of the experimental data in this way thus shows that fragments of chain molecules of at least all the polysaccharides investigated so far are oriented at the interface mainly *parallel to the film surface*.

As follows from theoretical equation (6), the dependence of B on H makes it possible for us to determine the effective value of the thickness of the optically anisotropic surface layer. This evaluation has thus become possible for films made of dextran for which the dependence of B on H was investigated over a wide range of film thicknesses (Pavlov *et al.*, 1999).

*Figure 4* shows that at low H value, B value is proportional to H. However, with increasing film thickness, B attains the limiting value. The experimental dependence of B on H for dextran is best described by the theoretical dependence (equation (6)) when the effective value of surface layer thickness  $H_0 = 0.14 \text{ mm}$ . The comparison of the value for  $H_0$  with segment length A for dextran shows that  $H_0$  exceeds A by five order of magnitude.

#### ORIENTATIONAL ORDER AND THERMODYNAMIC RIGIDITY

Let us consider the problem of the relationship between the capacity of polysaccharide

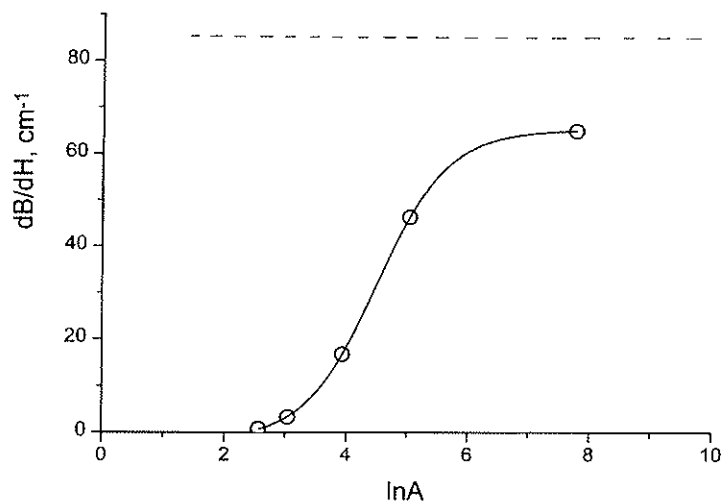


Figure 7. Plot of  $(dB/dH)$  versus  $\ln A$ . A: Kuhn segment length.

molecules to form orientational order in surface layers and the thermodynamic rigidity of molecules.

The surface birefringence from a film reflects the ability of polysaccharide chains to undergo self-organization at the interface or to form molecular orientational order. The value of  $dB/dH$  depends on specific optical anisotropy  $\beta = (\alpha_1 - \alpha_2)/M_s$  (a value characterizing the structure of the polymer repeat unit; it is effectively a *structural factor* of the surface birefringence) and on the orientational order parameter of molecules in surface layers at the interface  $S_0$  (orientational factor of the surface birefringence).

To a first approximation the value of  $\beta = (\alpha_1 - \alpha_2)/M_s$  may be considered to depend slightly on the molecular structure of the polysaccharides investigated. Therefore, the value of  $dB/dH$  can serve as a quantitative measure of molecular orientational order of fragments of polysaccharide chains in surface layers.

Figure 7 shows the dependence of  $dB/dH$  on the logarithm of length of polysaccharide statistical segments. It is clear that for dextran and pullulan, the molecules of which are characterized by high flexibility, the value of surface birefringence is not high. However, with increasing thermodynamic rigidity of polysaccharides, the value of  $dB/dH$  increases abruptly, tending to the limiting value. The experimental values of  $dB/dH$  and  $S_0$  (Table 1) enable us to evaluate the limiting value of  $dB/dH$  for dextran and pullulan proceeding from the assumption that the orientational order parameter of these polysaccharides is characterized by the theoretical maximum value  $S_{\max} = -0.5$ .

$$\lim_{S \rightarrow S_{\max}} (dB/dH) = (dB/dH)(S_{\max}/S_0)$$

The average limiting value  $\lim (dB/dH)$  calculated for dextran and pullulan was found to be  $85 \text{ cm}^{-1}$ . This limiting value is designated by a broken line in Figure 7. It can be seen that the  $dB/dH$  values found in this work for five polysaccharides are characterized by the common dependence on  $\ln A$  and have the same limiting value of  $dB/dH$  corresponding to the maximum value of the orientational order parameter of chain fragments with respect to the surface  $S_{\max} = 0.5$ .

Consequently, the results of this work confirm the concept that the tendency to form ordered structures, i.e. the liquid crystalline phase is most pronounced in macromolecular substances which have an elongated shape. All these observations make it possible for us to estimate quantitatively the geometric parameters of molecules, which correspond to the conditions of orientational order formation. As indeed can be seen in *Figure 7*, the formation of orientational order already begins for chain molecules with segment length  $A=1$  nm. The most abrupt change in this parameter takes place at segment length  $A=10$  nm. The results of this work show unequivocally that *chain thermodynamic rigidity is the determining parameter in the formation of orientational order* and can serve as the principal quantitative criterion for molecular self-organization on the interface.

### Final remarks

It is interesting to mention that the relationship between orientational order and thermodynamic flexibility was first pointed out in the interpretation of data on flow birefringence of comb-like polymer solutions (Tsvetkov and Andreeva, 1981). To explain adequately the values of optical anisotropy, it was necessary to assume that steric interactions of regularly spaced side chains result in an orientational order which corresponds to increasing equilibrium rigidity of these chains.

It should be also noted that quantitative evaluations of equilibrium polysaccharide rigidity that correspond to a transition to a maximum degree of self-organization in surface layers are in agreement with the understanding that the equilibrium rigidity plays an important role in the formation of lyotropic mesophase (Flory, 1956; Khokhlov, 1988).

### References

- BOGDANOVA, L.M., GRISHCHENKO, A.E., IRZHAK, V.I. AND ROSENBERG, B.A. (1987). Mechanooptical properties and structure of surface layers of epoxide network polymers. *Vysokomol Soedin* **29**, 1588–1592.
- CANTOR, C.R. AND SCHIMMEL, P.R. (1980). *Biophysical Chemistry, Part 2*. San Francisco: W.H. Freeman.
- CHERKASOV, A.N., VITOVSKAYA, M.G. AND BUSHIN, S.V. (1976). Preferential orientation of macromolecules in the surface layers of polymer blends. *Vysokomol Soedin* **18**, 1628–1635.
- DE GENNES, P.-J. (1974). *The Physics of Liquid Crystals*. Oxford, UK: Clarendon Press.
- ELINOV, N.P. AND VITOVSKAYA, G.A. (1979). Mannan produced by *Rhodotoruoa rubra* strain 14. *Carbohydrate Research* **75**, 185–193.
- FLORY, P.J. (1956). Phase equilibria in solutions of rod-like particles. *Proceedings of the Royal Society of London* **234A**, 73–89.
- GEKKO, K. (1971). Physicochemical studies of oligodextran. Intrinsic viscosity molecular weight relations. *Makromol Chem* **148**, 229–238.
- GRAY, H.B., BLOOMFIELD, V.A. AND HEARST, J.E. (1967). Sedimentation coefficients of linear and cyclic wormlike coils with excluded-volume effects. *Journal of Chemical Physics* **46**, 1493–1499.
- GRISHCHENKO, A.E., RUCHIN, A.E., KOROLIOVA, S.G., SKAZKA, V.S., IRZHAK, V.I., ROSENBERG, B.A. AND ENIKOLOPIAN, N.S. (1983). Study of structure of surface layers of epoxide networks. *Doklady Akademii Nauk SSSR* **269**, 1384–1387.
- GRISHCHENKO, A.E. (1996). *Mechanooptics of Polymers*. St. Petersburg: St. Petersburg University.

- GRISHCHENKO, A.E. AND CHERKASOV, A.N. (1997). Orientational order in surface layers of polymers. *Advances in Physical Science (Russian)* **167**, 269–285.
- HARDING, S.E. (1992). Sedimentation analysis of polysaccharides. In *Analytical Ultracentrifugation in Biochemistry and Polymer Science*. Eds. S.E. Harding, A.J. Rowe and J.C. Horton, pp 495–516. Cambridge: Royal Society of Chemistry.
- HARDING, S.E. (1995). On the hydrodynamic analysis of macromolecular conformation. *Biophysical Chemistry* **55**, 69–93.
- HERMANS, P.H. (1949). *Physics and Chemistry of Cellulose fibres*. New York: Elsevier.
- HUBER, A. (1991). Characterization of branched and linear polysaccharides by size-exclusion chromatography/low-angle laser light scattering. *Journal of Applied Polymer Science Applied Polymer Symposium* **48**, 95–102.
- KAWAHARA, K., OHTA, K., MIYAMOTO, H. AND NAKAMURA, S. (1984). Preparation and solution properties of pullulan fractions as standard samples for water-soluble polymers. *Carbohydrate Polymers* **4**, 335–346.
- KHOKHLOV, A.R. (1988). Statistical physics of liquid crystal ordering in polymer systems. In *Liquidcrystal Polymers*. Ed. N.A. Plate, pp 98–137. Moscow: Khimia.
- MCNALLY, J.G. AND SHEPPARD, S.E. (1930). Double refraction in cellulose acetate and nitrate films. *Journal of Physical Chemistry* **34**, 165–177.
- PAVLOV, G.M. (1989). Sedimentation parameter of cellulose, cellulose derivatives and some other polysaccharides. *Khimia Drevesiny (Wood Chem)* **4**, 3–13.
- PAVLOV, G.M., PANARIN, E.F., KORNEEVA, E.V., KUROCHKIN, C.V., BAIKOV, V.E. AND USHAKOVA, V.N. (1990). Hydrodynamic properties of poly(1-vinyl-2-pyrrolidone) molecules in dilute solution. *Makromol Chem* **191**, 2889–2899.
- PAVLOV, G.M., KORNEEVA, E.V., MICHAILOVA, N.A. AND ANANYEVA, E.P. (1992). Hydrodynamic properties of the fraction of mannan formed by *Rhodotorula rubra* yeast. *Carbohydr Polymers* **19**, 243–248.
- PAVLOV, G.M. (1995). Investigations of cellulose and lignins by molecular hydrodynamic methods. In *Cellulose and cellulose derivatives*. Eds. J.F. Kennedy, G.O. Phillips, P.O. Williams and L. Piculell, pp 541–546. Cambridge: Woodhead Publishers Limited.
- PAVLOV, G.M., MICHAILOVA, N.A., TARABUKINA, E.B. AND KORNEEVA, E.V. (1995). Velocity sedimentation of water soluble methyl cellulose. *Progr Colloid Polym Sci* **99**, 109–113.
- PAVLOV, G.M., MICHAILOVA, N.A., KORNEEVA, E.V. AND SMIRNOVA, G.N. (1996). Hydrodynamic and molecular characteristics of water-soluble methylcellulose. *Vysokomol Soedin* **38A**, 1582–1586
- PAVLOV, G.M. (1997). The concentration dependence of sedimentation for polysaccharides. *European Biophysical Journal* **25**, 385–397.
- PAVLOV, G.M., ROWE, A.J. AND HARDING, S.E. (1997). Conformational zoning of large molecules using the analytical ultracentrifuge. *Trends in Analytical Chemistry* **16**, 401–405.
- PAVLOV, G.M., YEVLAMPIEVA, N.P. AND KORNEEVA, E.V. (1998). Flow birefringence of pullulan molecules in solution. *Polymer* **39**, 235–240.
- PAVLOV, G.M., GRISHCHENKO, A.E., RUMTSEV, E.I. AND YEVLAMPIEVA, N.P. (1999). Optical properties of dextran in solution and films. *Carbohydrate Polymers* **38**, 267–271.
- PAUL, D.R. AND NEWMAN, S. (Eds.) (1978). *Polymer Blends*. Orlando: Academic Press.
- SATO, T., NORISUYE, T. AND FUJITA, H. (1984.) Double-stranded helix of xanthan. Dimensional and hydrodynamic properties in 0.1 M aqueous sodium chloride. *Macromolecules* **17**, 2696–2703.
- STEIN, R.S. AND NORRIS, F.H. (1956). The X-ray diffraction, birefringence, and infra-red dichroism of stretched polyethylene. *Journal of Polymer Science* **21**, 381–396.
- STEIN, R.S. (1978). Optical behavior of polymer blends. In *Polymer Blends*. Eds. D.R. Paul and S. Newman, pp 393–444. Orlando: Academic Press.
- ROSTIASHVILI, V.G., IRZHAK, V.I. AND ROSENBERG, B.A. (1987). Glass-transition in polymers. Leningrad: Chimiya.
- TANFORD, C. (1961). *Physical Chemistry of Macromolecules*. New York: J. Wiley and Sons.
- TOMBS, M.P. AND HARDING, S.E. (1999). *An Introduction to Polysaccharide Biotechnology*. London: Taylor and Francis.

- TSVETKOV, V.N. AND ANDREEVA, L.N. (1981.) Flow and electric Birefringence in rigid-chain polymer solutions. *Advances in Polymer Science* **39**, 96–205.
- TSVETKOV, V.N. (1989). *Rigid-chain polymers. Hydrodynamic and Optical Properties in Solution*. New York and London: Consultant Bureau.
- TSVETKOV, V.N., ESKIN, V.E. AND FRENKEL, S.YA. (1970). *Structure of Macromolecules in Solutions*. London: Butterworths.
- TURKOV, V.K. AND GRISHCHENKO, A.E. (1990). Properties and structure of surface layers of polyesterureurethanes. *Vysokomol Soedin* **32**, 1032–1035.
- YALPANI, M. (1988). *Polysaccharides*. Amsterdam: Elsevier.

