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CONFORMATIONAL PROPERTIES OF HYDROXYPROPYLCELLULOSE—II. FLOW BIREFRINGENCE AND OPTICAL ANISOTROPY OF HYDROXYPROPYLCELLULOSE MACROMOLECULES

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Abstract—The flow birefringence of solutions of hydroxypropylcellulose (HPC) in dimethylacetamide and tetrachloroethane has been investigated over a wide range of molecular weights. Comparison of the experimental dependence of shear optical coefficient $[n]/[\eta]$ on molecular weight with the theoretical dependence for rigid wormlike chains made it possible to determine the equilibrium rigidity of HPC molecules. The segment length thus determined is in good agreement with the evaluation of rigidity from viscometry and diffusion data. The optical anisotropy of HPC molecules, $(\alpha_1 - \alpha_2) = 500 \times 10^{-25}$ cm^3 and the degree of their intramolecular orientational-axial order were determined.

INTRODUCTION

The investigation of hydrodynamic parameters of hydroxypropylcellulose (HPC) solutions has established [1] that the macromolecules of HPC adopt the conformation of a Gaussian coil characterized by a considerable degree of draining and high equilibrium rigidity. Study of flow birefringence and the dependence of optical properties of molecules on their molecular weight makes it possible to obtain important information on the optical and structural features of macromolecules, in particular the information about the orientational order of structural elements of the macromolecule [2]. In the present paper, the method of flow birefringence was applied to the analysis of optical properties of HPC molecules in various solvents.

EXPERIMENTAL PROCEDURES

The investigations were carried out on solutions of HPC samples and fractions characterized previously [1]. Flow birefringence was measured with a visual method described previously [2] by using a dynamo-optimeter 4 cm high at a gap width between the rotor and the stator of 0.031 cm. These parameters of the instrument made it possible to make reliable measurements of flow birefringence Δn and orientation angles of the optical axis of the anisotropic solution with respect to the flow φ in the concentration range of solutions $c \leqslant (1 - 0.1) \times 10^{-2}$ g/cm^3 and flow rate gradients $g \leqslant 2000$ sec^{-1} with maintenance of laminar flow.

The orientation angle φ virtually did not differ from 45° for most fractions over the investigated range of rate gradients. For samples of highest molecular weight, the angle φ decreased with increasing g and solution concentration (Fig. 1). This change was taken into account in the measurement of Δn.

The character of the dependences $\Delta n = f(g)$ and $\varphi = f(g)$ (for high molecular weight fractions) indicates that these solutions are molecular ones. The intrinsic value of flow birefringence

$$[n] \equiv \lim_{g \to 0,\, c \to 0} \Delta n / g c \eta_0$$

(η_0 is the solvent viscosity) was obtained by extrapolation of the experimental dependences $\Delta n / g c \eta_0 = f(g, c)$ to zero rate gradient and zero solution concentration. Shear optical coefficients $[n]/[\eta] \equiv \Delta n / g(\eta - \eta_0)$ are given in Table 1. This table also lists the molecular weights M and intrinsic viscosities of HPC in DMAA and tetrachloroethane (TChE). η is the solution viscosity. Table 1 also gives the molar degrees of substitution MS of fractions and samples and the degrees of polymerization, z, corresponding to molecular weight (see part I [1]).

RESULTS AND DISCUSSION

In both solvents, positive birefringence is observed in HPC solutions; the value of shear optical coefficient $[n]/[\eta]$ is relatively high and comparable to the values for a number of cellulose ethers [3].

It follows from experimental data (Table 1) that, in the investigated range of the molecular weights, the value of the shear optical coefficient $[n]/[\eta]$ is not constant: when molecular weight increases by a factor of 65, this value increases three times in TChE and twice in DMAA. This dependence of $[n]/[\eta]$ on degree of polymerization shown in Fig. 2 is the most characteristic feature of optical properties of rigid-chain polymers. It indicates that the conformation of HPC molecules and, hence, their properties vary from those of a weakly bending rod (at low z) to those of Gaussian chains (in the range of $z > 4\ 10^2$). The experimental change in the ratio $[n]/[\eta]$ with molecular weight correlated with the theoretical dependence of optical properties of a kinetically rigid wormlike chain [4]: the relative value of

$$\Delta(x) = ([n]/[\eta])/([n]/[\eta])_\infty = f(x)$$

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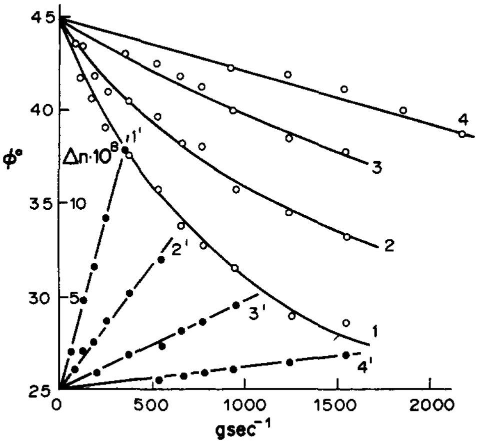

Fig. 1. Angles φ (1–4) and flow birefringence Δn (1'–4') vs rate gradient of the flow g for sample 1 of HPC in DMAA. The numbers on the lines correspond to solution concentrations: (1) $C_1 = 0.45 \times 10^{-2}$, (2) $C_2 = 0.264 \times 10^{-2}$, (3) $C_3 = 0.128 \times 10^{-2}$, (4) $C_4 = 0.051 \times 10^{-2}$ g/cm³.

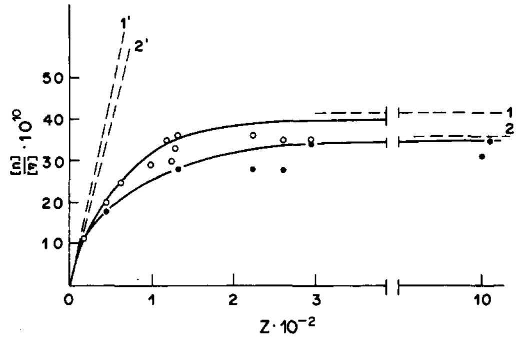

Fig. 2. Shear optical coefficient $[n]/[\eta]$ vs degree of polymerization for HPC samples and fractions in (1) TChE, ○ and (2) DMAA, ●.

$[([n]/[\eta])_\infty$ is the limiting value of $[n]/[\eta]$ in the range of $M \to \infty]$ is a function of the reduced chain length $x = 2\,L/A$ (A is the length of the statistical segment and L is the total hydrodynamic length of the molecule). The function $\Delta(x)$ has been tabulated [4] over the entire range of x. At limiting low x (rodlike conformation) the value of

$$[n]/[\eta] = B\Delta a \cdot z. \qquad (1)$$

In other words, the value of $[n]/[\eta]$ increases linearly with z (this is shown in Fig. 2 by straight lines 1' for TChE and 2' for DMAA). The following designations are used in equation (1): Δa is the optical anisotropy of the monomer unit, B is the optical coefficient $B = (4\pi/45\,kT)\,(n^2+2)^2/n$, n is the refractive index of the solvent, k is Boltzmann's constant, T is the absolute temperature. In the Gaussian range of conformations, the limiting value of

$$([n]/[\eta])_\infty = B \cdot \Delta a \cdot S \qquad (2)$$

(S is the number of monomer units in a segment, $S = A/\lambda$ and λ is the projection of the length of the monomer unit on the main direction of the molecule; for cellulose ethers, $\lambda = 5.15$ Å) which is independent of molecular weight and is determined by the optical anisotropy of the segment $\alpha_1 - \alpha_2 = \Delta a \cdot S$. In Fig. 2, this range independence of the value of $[n]/[\eta]$ of z is denoted by straight lines 1 for TChE and 2 for DMAA. Comparison of the theoretical dependence $\Delta(x)$ with experimental data allows determination of such parameters of the molecules as equilibrium rigidity A (or S) and Δa.

For this purpose, it is necessary to select from the experimental dependence of $[n]/[\eta]$ on z two molecular parameters: $([n]/[\eta])_\infty$ and Δa (or S), i.e. to determine reliably both the initial slope of the curve $[n]/[\eta] = f(z)$ and its limiting value. It is clear from the data shown in Fig. 2 that this choice is not

Table 1. Optical and hydrodynamic characteristics of samples and fractions of HPC

				DMAA			TChE		
N	MS	$M\,10^{-5}$	$Z\,10^{-3}$	$[\eta]\,10^{-2}$	$\frac{[n]}{[\eta]}\,10^{10}$	x	$[\eta]\,10^{-2}$	$\frac{[n]}{[\eta]}\,10^{10}$	x
1*	3.80	4.15	1.082	6.0	35	47.4			
2*	2.90	3.29	0.997	5.4	31	43.7			
3	2.71	0.94	0.294	1.40	34	12.88		35	13.17
4	2.46	0.79	0.259	1.13	28	11.35	2.20	35	11.6
5	3.17	0.77	0.222	1.10	28	9.73	1.20	36	9.94
6*	3.38	0.53	0.147				1.38	32.6	6.58
7	3.58	0.53	0.143	1.10		6.27		30	6.40
8*	3.26	0.44	0.130	1.10	28	5.70	1.25	38	5.82
9	3.43	0.42	0.117	0.90			0.67	35	5.24
10	3.50	0.36	0.097	0.70			0.58	29	4.34
11	3.76	0.244	0.062	0.40			0.44	25	2.78
12	3.20	0.17	0.044	0.26	17.7	1.95	0.20	20	1.99
13		0.064	0.016	0.10			0.09	11	0.71

*Unfractionated samples.

Table 2. Optical parameters of HPC and polypropylene macromolecules

Polymer	Solvent	$\frac{[n]}{[\eta]}\,10^{10}$	$(\alpha_1 - \alpha_2)\,10^{25}$	S	$\Delta a\,10^{25}$	Ref.
HPC	DMAA	35.7	450	46	9.9	This paper
	TChE	41.7	505	45	11.3	
Polypropylene (for comparison)	TChE		30		3.5	[8]

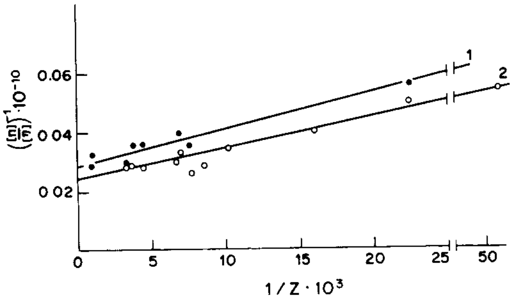

Fig. 3. Value of $([n]/[\eta])^{-1}$ vs z^{-1} for HPC in (1) DMAA and (2) TChE.

unequivocal. It has been shown [3, 4] that, in order to determine the values of $([n]/[\eta])_\infty$ and S, it is desirable to construct the following plot:

$$([n]/[\eta])^{-1} = (B\Delta a\cdot S)^{-1} + (B\cdot\Delta a)^{-1}\cdot z^{-1}. \quad (3)$$

This linear dependence makes it possible to determine the value of $([n]/[\eta])_\infty$ from the intercept with the ordinate, and the slope allows determination of the optical anisotropy of the monomer unit Δa; the ratio of the intercept to the slope gives the value of S. This plot is constructed from the experimental data in Table 3 (Fig. 3). It is clear that this linearization of data presentation makes it possible to determine reliably the values of $([n]/[\eta])_\infty$ and Δa for the entire range of the investigated degrees of polymerization. Straight lines 1 and 2 corresponding to the two solvents give values of (1) $([n]/[\eta])_\infty = 41.7\times10^{-10}$ in TChE and (2) 35.7×10^{-10} in DMAA. The slopes of straight lines in Fig. 3 equal to $(B\cdot\Delta a)^{-1} = 1.07\times10^{10}$ (in TChE) and 1.275×10^{10} (in DMAA) correspond to values of $\Delta a = 11.3\times10^{-25}\,\mathrm{cm}^3$ in TChE and $\Delta a = 9.9\times10^{-25}\,\mathrm{cm}^3$ in DMAA. The use of these values of Δa and the limiting values $([n]/[\eta])_\infty$ gives the values of $S = 46$ in DMAA ($A = 235$ Å) and $S = 45$ ($A = 230$ Å) in TChE.

The experimental dependence of $[n]/[\eta]$ on z may be correlated with the theoretical dependence of dynamo-optical properties of an assembly of rigid-chain wormlike molecules [4] shown in Fig. 4 in a system of coordinates $\Delta = ([n]/[\eta])/([n]/[\eta])_\infty$ and $x = 2\ L/A$. The experimental points are in good agreement with this theoretical dependence at the values of $([n]/[\eta])_\infty = 41.7\times10^{-10}$ and $S = 45$ in TChE (points 1 in Fig. 4) and at $([n]/[\eta])_\infty = 35.7\times10^{-10}$ and $S = 46$ in DMAA (points 2), i.e. by using the molecular parameters determined for HPC from the experimental data in Fig. 3. This plot shows that the observed molecular weight dependence of the shear optical coefficient of HPC molecules in the two solvents is adequately described by the theory of dynamo-optical properties of kinetically rigid wormlike chains. The value of the equilibrium rigidity of HPC molecules determined from optical data $A = (230–235)$ Å in both solvents is in good agreement with the rigidity parameters determined from viscometry and translational diffusion [$A_\eta = (210\pm10)$ Å and $A_D = (240\pm30)$ Å] of HPC macromolecules [1] and also confirms the quantitative coincidence of A values determined in these two solvents.

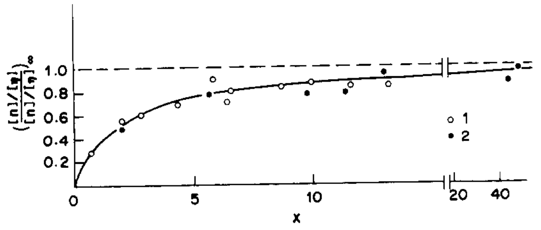

Fig. 4. Relative value of the shear optical coefficient $([n]/[\eta])/([n]/[\eta])_\infty$ vs relative length of molecules for HPC fractions in (1) TChE and (2) DMAA. The curve describes the theoretical dependence $\Delta(x)$ [4].

Experimental data show (Fig. 2) that, at high molecular weights, the HPC molecule may be represented in its optical properties as a Gaussian coil. In this case the main condition of the Gaussian statistics $L \gg A$ of macromolecules is fulfilled, and the value of the ratio $[n]/[\eta]$ attaining its limit is independent of molecular weight. Hence, according to Kuhn's equation [5, 3], the shear optical coefficient of the Gaussian coil is determined by the optical anisotropy of the segment of the molecule $\alpha_1 - \alpha_2$

$$\left(\frac{[n]}{[\eta]}\right)_\infty = B(\alpha_1-\alpha_2)$$

$$= [4\pi(n^2+2)^2/45k\,Tn]\,(\alpha_1-\alpha_2). \quad (4)$$

The value of $\alpha_1 - \alpha_2$ calculated from the limiting value of $([n]/[\eta])_\infty$ according to equation (4) is $505\times10^{-25}\,\mathrm{cm}^3$ in TChE and $450\times10^{-25}\,\mathrm{cm}^3$ in DMAA. The segmental anisotropy of the molecule $\alpha_1 - \alpha_2$ is determined by the degree of order of its structural elements (in this case of monomer units) and by the chemical structure of the monomer unit, which determines its optical anisotropy $\Delta a = (\alpha_1 - \alpha_2)/S$. The values of $\alpha_1 - \alpha_2$ of HPC molecules close to each other in the two solvents are sufficiently high compared with the corresponding values for flexible-chain polymers and are comparable to those for cellulose esters which do not contain strongly anisotropic side groups, e.g. phenyl or nitrogroups [2, 3].

By using the value of equilibrium rigidity of HPC molecules determined from both optical and hydrodynamic data, it is possible to evaluate such an important characteristic of the conformation of the molecule as the optical anisotropy of the monomer unit, Δa: $\Delta a = (\alpha_1 - \alpha_2)/S = 11.3\times10^{-25}$ cm in TChE and 9.9×10^{-25} cm in DMAA. All these characteristics of HPC molecules are given in Table 2.

Both the value of $\alpha_1 - \alpha_2$ and that of Δa contain not only the intrinsic anisotropy of the molecule but also that of the microform [3] since the refractive indices of the solvent n_S and that of HPC, n_K, for the solvents used in flow birefrengence measurements do not coincide.

According to the theory [3], the microform effect may be evaluated from the equation

$$\Delta a_{fS} = (\mathrm{d}n/\mathrm{d}c)^2\cdot M_0/2\pi N_A\cdot\bar{v} \quad (5)$$

where $\bar{v}$ is the partial specific volume of the polymer, N_A is Avogadro's number and M_0 is the molecular weight of the monomer unit.

The degree of molar substitution of HPC fraction varies somewhat, and the average values of $M_0 = 354$,

$dn/dc = 0.0423$ in DMAA and $dn/dc = 0.019$ in TCE are used in equation (5). Since the refractive index increments for the polymer and the solvents are low, the values of Δa_{fS} are $\Delta a_{fS} = 2 \times 10^{-25}$ cm^3 in DMAA and 0.4×10^{-25} cm^3 in TChE. The low value of Δa_{fS} implies that the segmental optical anisotropy $\alpha_1 - \alpha_2$ and the anisotropy of the monomer unit Δa for HPC in TCE are determined by the intrinsic anisotropy of the molecules which is not high, $\sim 10 \times 10^{-25}$ cm^3, and is positive. The latter fact implies that it is determined by the optical anisotropy of the main chain, in this case by that of the glucose ring $(a_\parallel - a_\perp)_{gl} \approx 12 \times 10^{-25}$ cm^3 [6]. In fact, this is the value that coincides with the experimental Δa value for HPC, and the corresponding value for side substituents with low optical anisotropy is small. The optical anisotropy of the monomer unit of polypropylene, close in chemical structure to that of the side groups of HPC, is only $+3.5 \times 10^{-25}$ cm^3. Hence, even when the side groups are normal to the main chain, their contribution might decrease the anisotropy of the monomer unit of the molecule by not $> 5 \times 10^{-25}$ cm^3. However, since the location of the side groups differs from normal as a result of some freedom of rotation, their contribution to the anisotropy of the monomer unit is even lower.

The fact that although the optical anisotropy of the monomer unit is low, the segmental anisotropy of the molecule, $\alpha_1 - \alpha_2$, and the observed birefringence, $[n]/[\eta]$, of HPC molecules are relatively high, is a direct reflection of the high degree of order of the monomer units with respect to the axis of the greatest asymmetry of the molecule with regard to the end-to-end vector h.

Tsvetkov has introduced for macromolecules the definition of the function characterizing the degree of intramolecular order, $Q(x)$ [7]. This function depends on the parameter $x = 2\,L/A$ and reflects the orientational-axial order of the arrangement of chain elements. For HPC molecules, this function, $Q(x)$, in the range of lengths of molecules from 80 to 5000 Å represented here, varies from 0.7 to 0.2. In the same range of lengths of molecules, this degree of intramolecular order is comparable to the degree of order in ladder polymers, for example, and is higher by an order of magnitude than in the molecules of flexible-chain polymers [7].

Hence, the investigation of the optical anisotropy of HPC molecules made it possible to show the change in the conformation of the molecule with increasing molecular weight from that of a weakly bending rod to that of a draining wormlike Gaussian coil, to evaluate the equilibrium rigidity of molecules from optical data and to demonstrate the high degree of orientational-axial order in the HPC molecule, which determines its mesomorphic properties.

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