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Optical activity anisotropy in thin films of chitosan L- and D-ascorbate

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Abstract. The specific optical rotation $[\alpha]$ of thin films of chitosan L- and D-ascorbate was studied. It was found that optical activity anisotropy occurs in the systems analyzed and $[\alpha]$ depends on the orientation angle θ of the film sample relative to the direction of the polarization vector of the incident light beam in the plane perpendicular to this beam. The angular dependences $[\alpha] = f(\theta)$ (indicatrices) were processed to extract the constant term $[\alpha]_0$ and four harmonics ($[\alpha]_1$, Fourier's series) determined by structure elements with the corresponding symmetry, namely: the amorphous (isotropic) chitosan phase ($[\alpha]_0$), irregular-shaped structures ($[\alpha]_1$), rod-shaped ones in the film plane ($[\alpha]_2$), helical ones located perpendicular to the film surface ($[\alpha]_3$), and crystalline structures ($[\alpha]_4$).

Keywords: chitosan, L- and D-ascorbic acid, films, optical activity, anisotropy

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Анизотропия оптической активности тонких пленок L- и D-аскорбата хитозана

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Аннотация. Исследовано удельное оптическое вращение $[\alpha]$ тонких пленок хитозана L- и D-аскорбата. Установлено, что в анализируемых системах имеет место анизотропия оптической активности и $[\alpha]$ зависит от угла ориентации θ образца пленки относительно направления вектора поляризации падающего пучка света в плоскости, перпендикулярной этому пучку. Угловые зависимости $[\alpha] = f(\theta)$ (индикатрисы) были обработаны для извлечения постоянного члена $[\alpha]_0$ и четырех гармоник ($[\alpha]_1$, ряд Фурье), определяемых элементами структуры с соответствующей симметрией, а именно: аморфная (изотропная) фаза хитозана ($[\alpha]_0$), структуры неправильной формы ($[\alpha]_1$), стержнеобразные в плоскости пленки ($[\alpha]_2$), спиралевидные, расположенные перпендикулярно поверхности пленки ($[\alpha]_3$), и кристаллические структуры ($[\alpha]_4$).

Ключевые слова: хитозан, L- и D-аскорбиновая кислота, пленки, оптическая активность, анизотропия

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Introduction

Optical activity anisotropy is a vivid example of self-organization in chiral polymer systems. This property was first discovered for lyotropic LC phases of acetic cellulose esters [1] and subsequently found in oriented films of both acetic and basic chitosan [2]. This phenomenon consists in the manifestation of a clear functional dependence of the specific optical rotation $[\alpha]$ on the samples orientation angle θ relative to the direction of the polarization vector of the incident light beam in the plane perpendicular to this beam. Decomposition of the indicatrices $[\alpha] = f(\theta)$ into individual sinusoids (harmonics) allows drawing some conclusions about the supramolecular optically active structures formed in the polymer material during its preparation.

For example, by comparing the harmonic components $[\alpha]_i$ with the axisymmetric elements, the contribution of individual supramolecular structures (anisotropic subsystems) to the total optical activity of chitosan was estimated: crystalline and rod-shaped (in the film plane) structures predominate for freshly formed films of the salt form, while crystalline ones predominate for the basic form [2]. The conditioning of chitosan films of both chemical forms is accompanied by spontaneous water removal, increases the absolute value of $[\alpha]$ and enhances the harmonics corresponding to crystallites. At the same time, the results of our numerical decomposition of the $[\alpha]$ indicatrices are in satisfactory agreement with the X-ray diffractometry data of chitosan films.

Nonlinear optical activity effects have also been found for biological macromolecules and biological microstructures built therefrom, in particular, collagen fibers and multilayer vesicles, considered from the standpoint of complex anisotropic 3D media [3]. It was noted that studying of optical anisotropy and optical activity is very promising for assessing the orientation of protein macromolecules and their supramolecular aggregates in anisotropic collagen membranes used in tissue engineering [4]. These optical quantities play an important role in the comparative analysis of the complex degree of mutual anisotropy of birefringent structures in biological tissues with benign and malignant changes [5].

The optical activity of chitosan predetermines the possibility of obtaining smart materials based thereon, performing the function of a “chemical plug” or “chemical corkscrew”, a depot of genetic material or biologically significant compounds with their subsequent release after volume reduction in the planned localization zone [6]. Recent publications have reported on chitosan-containing chiro-optic switches responding to the acid–base properties of a liquid medium [7], imprinted materials for the enantioselective separation of racemic drug mixtures [8], hydrogels with supramolecular chiral architecture [9], as well as non-invasive measuring instruments based on linear and non-linear optical effects [10].

The aim of this work was to study the chiro-optic properties of chitosan salt films obtained from solutions in L- and D-ascorbic acid in order to reveal and quantitatively describe optical activity anisotropy.

Materials and Methods

Powdered chitosan (CS) with an average-viscosity molecular weight of 200 kDa and a deacetylation degree of 82 ± 2 mol% (Bioprogress LLC, RF); L-ascorbic acid (L-AscA) with 99% of the main substance (Glenvitol LLC, RF) and D-ascorbic acid (D-AscA) with 98% of the main substance (CJSC Khimreaktiv, RF) were used. Films were cast by pouring a 2 g/dL CS solution, prepared at an equimolar CS : AscA ratio, onto a polyethylene terephthalate substrate, followed by drying in the absence of natural light at room temperature and under atmospheric pressure for 3–4 days. The film thickness was 802 μm .



Optical activity was recorded on a PolAAR 3001 automatic spectropolarimeter (Optical Activity Ltd, England) in the wavelength range $\lambda = 405\text{--}589$ nm at 25 ± 0.5 °C. A 20 W tungsten-halogen lamp was the light source. The experimental conditions were standard, the measurement error of rotation angles did not exceed ± 0.001 deg. Spectra $[\alpha] = f(\theta)$ (where θ is the rotation angle of the sample in the plane perpendicular to the direction of the incident light beam, with respect to an arbitrarily chosen initial position) were recorded using a specially designed cuvette with a thermal chamber and a cell rotating around its horizontal axis and having a circular scale calibrated from 0 to 360° with a 5° step relative to an arbitrarily chosen reading direction. At least 10 film samples were used for each measurement. Three replicate experiments were carried out at each orientation angle.

The specific optical rotation $[\alpha]$ (deg mL dm⁻¹ g⁻¹) of films was calculated by the formula:

$$[\alpha]_{\lambda, \text{nm}}^{20^\circ\text{C}} = \frac{\alpha}{\ell \cdot \rho},$$

where α is the measured angle of optical rotation of the film sample, deg; ℓ the length of the optical path, dm; and ρ the density of the film material, g·cm⁻³. Graphic dependences $[\alpha] = f(\theta)$ in polar and Cartesian coordinates were plotted in the Microcal Origin Pro software.

The algorithm for processing indicatrices consisted of extracting the constant term and several harmonics (Fourier's series) from the $[\alpha] = f(\theta)$ dependence, which were given a certain physical meaning. It is described in detail elsewhere [2]. The general approximating formula was:

$$[\alpha] = [\alpha]_0 + \sum_{i=1}^4 [\alpha]_i \cos[i(\theta - \Delta_i)],$$

where $[\alpha]_0$ and $[\alpha]_i$ are the components of specific optical rotation corresponding to the isotropic and anisotropic subsystems; Δ_i is the phase shift (specific for each harmonic). Since the average cosine over an integer number of periods is zero, $[\alpha]_0$ is actually the average value of $[\alpha]$ over all orientation angles, i.e., the angle-average specific optical rotation.

Results and Discussion

The optical rotary dispersion curves (ORD) of thin films of CS L- and D-ascorbate were established to be of the normal type and characterized by $[\alpha]$ values close in absolute value, but opposite in sign, namely: negative for CS·L-AscA and positive for CS·D-AscA. It was found that $[\alpha]$ depended on the orientation angle θ of the film sample relative to the direction of the polarization vector of the incident light beam in the plane perpendicular to this beam. The indicatrices, as can be seen, have a complex, irregular shape. For CS·L-AscA films, the values of specific optical rotation range from +18 to -62 deg·mL·dm⁻¹·g⁻¹ (Fig. 1, *a, b*). CS·D-AscA film samples are characterized by more positive $[\alpha]$ values: from +40 to -5 deg·mL·dm⁻¹·g⁻¹ (Fig. 1, *c, d*).

To process the angular dependences $[\alpha] = f(\theta)$, an algorithm was used with the isolation of a constant term ($[\alpha]_0$) and four harmonics ($[\alpha]_i$, Fourier's series) determined by the structure elements with the corresponding symmetry, namely: $[\alpha]_1$ corresponds to irregular shaped structures, $[\alpha]_2$ to rod-shaped ones in the plane of the film, $[\alpha]_3$ to helical ones, located perpendicular to the surface of the film, and $[\alpha]_4$ to crystalline ones. The results of the numerical decomposition of the $[\alpha] = f(\theta)$ indicatrices into harmonics are given in Table. The graphic dependences $[\alpha]_i = f(\theta)$ at $\lambda = 436$ nm are shown in Fig. 2. For clarity, the origin of coordinates is chosen so that the value of the specific optical rotation is $[\alpha]_0$ at the point $\theta = 0$ deg. The value of the argument of the function $[\alpha] = f(\theta)$ was chosen so that it coincided with the beginning of the period of the corresponding sinusoid.

It is shown that the mean-angle specific optical rotation $[\alpha]_0$ reflects the optical activity of the amorphous phase of the sample, is characterized by simple dispersion and satisfactory agreement with the experimental ORD curves. For CS·L-AscA films, the fourth harmonic $[\alpha]_4$ had the highest amplitude, followed by $[\alpha]_2$ and $[\alpha]_3$. For CS·D-AscA film samples, $[\alpha]_4$ and $[\alpha]_2$ predominated, followed by $[\alpha]_1$ as the intensity decreases. The intensity of these harmonics for CS·L-AscA films was significantly higher compared to CS·D-AscA ones.

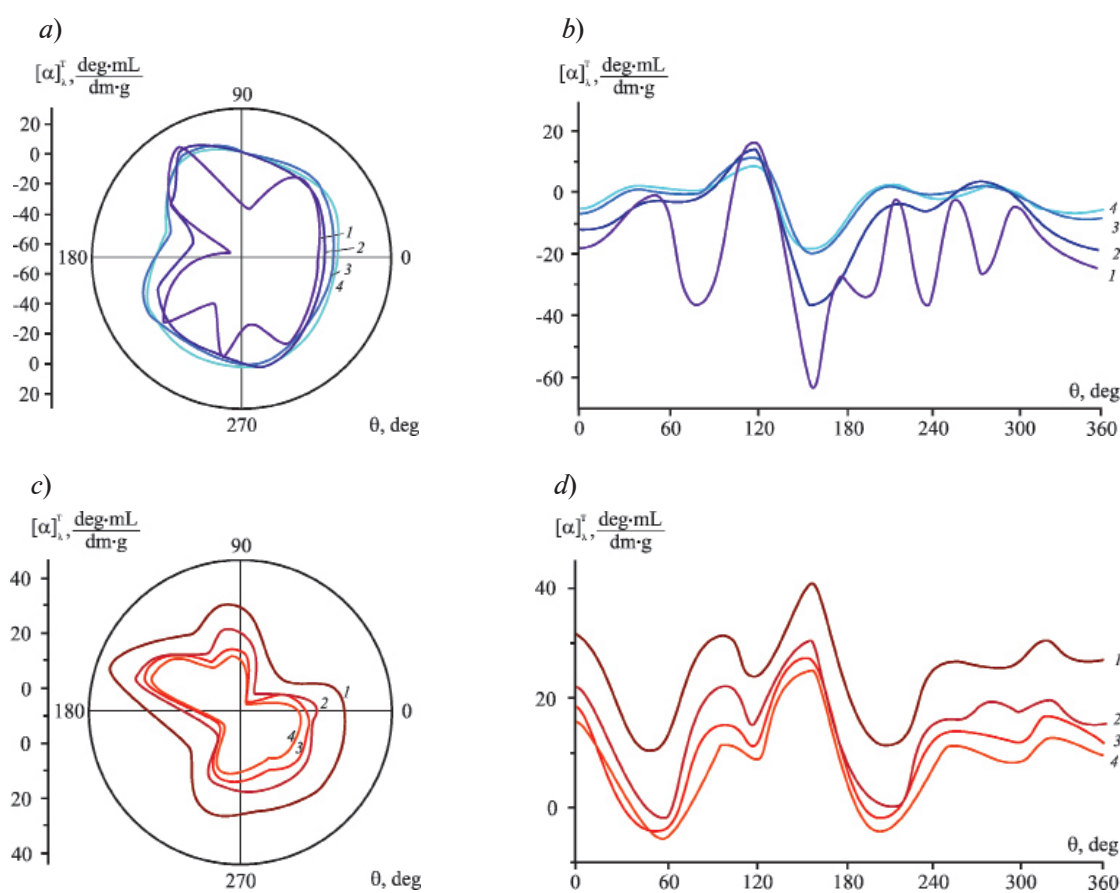


Fig. 1. Dependence of the specific optical rotation $[\alpha]$ of CS·L-AscA (*a, b*) and CS·D-AscA (*c, d*) films on the sample rotation angle θ in polar (*a, c*) and Cartesian (*b, d*) coordinates; $\lambda = 405$ (1), 436 (2), 546 (3), and 589 nm (4)

Thus, the numerical processing of the indicatrices $[\alpha] = f(\theta)$ showed that the optical activity of the films analyzed is due not only to the molecular chirality of the elementary macromolecular chains, but also to the supramolecular chirality of the supramolecular structures of CS L- and D-ascorbates.

Table

Harmonic amplitudes at several wavelengths for CS·L-AscA and CS·D-AscA films

Film	Wavelength λ , nm	Harmonics (Fourier's series) $[\alpha]_i$, deg·mL·dm ⁻¹ ·g ⁻¹				
		$i = 0$	$i = 1$	$i = 2$	$i = 3$	$i = 4$
CS·L-AscA	405	-17.5	7.03	6.51	5.48	13.9
	436	-7.62	3.15	12.9	4.99	7.89
	546	-1.96	1.26	6.93	3.11	5.64
	589	-2.07	1.87	5.77	2.71	4.94
CS·D-AscA	405	42.9	3.42	6.06	2.25	7.21
	436	41.9	3.70	2.22	1.30	4.42
	546	21.7	1.57	1.34	0.94	2.74
	589	16.4	2.4	1.47	0.93	2.38

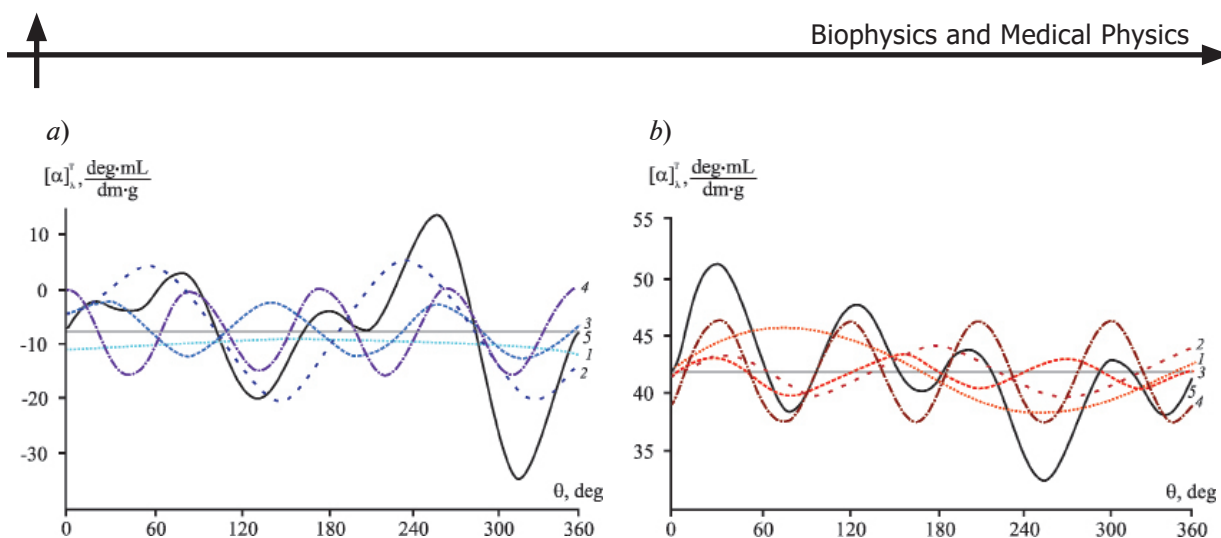


Fig. 2. Angular dependence of the specific optical rotation $[\alpha]$ at $\lambda = 436$ nm and its decomposition into harmonics for CS·L-AscA (a) and CS·D-AscA (b) films; 1–4 are the numbers of harmonics $[\alpha]_1 - [\alpha]_4$, 5 the total curve. The horizontal line corresponds to the constant term $[\alpha]_0$

Conclusion

As a result of our studies, it was found that CS L- and D-ascorbate films selectively rotate the polarization plane of polarized light passing through them, depending on the sample orientation angle relative to the direction of the polarization vector of the incident light beam in the plane perpendicular to this beam. The discovered regularities predetermine the prospects for obtaining film thermal indicators, optical filters, chiral planar waveguides, and chiro-optic sensors with novel functional properties based on these systems.

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