The Stretching Effect on the Anisotropy of Poly (Vinyl) Alcohol (PVA) Foils

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The polymer foils, obtained from pure and coloured (with cycloimmonium ylids) poly (vinyl) alcohol (PVA) gel, are studied from the optical anisotropy point of view. The dried foils were stretched under heating and their optical birefringence was measured for different degrees of stretching. The changes in the birefringence were correlated with the stretching degree of the polymer foils. The influence of the cycloimmonium ylid structural peculiarities on the coloured foils' anisotropy is also discussed.

Keywords: cycloimmonium benzoyl anilido-benzoyl methylids, optical birefringence, stretched coloured and pure PVA foils

Poly (vinyl) alcohol (PVA) is a polymer obtained from vinyl polyacetate or vinyl polyformiate. The transformation of vinyl polyacetate in poly (vinyl) alcohol was firstly realized by W.O. Hermann and W. Hacchel in 1924 by introducing the polyacetate powder in an alcohol solution of KOH. H. Standinger obtained PVA by esterification of vinyl polyacetate in 1926. The PVA can be obtained from its esters in anhydrous alcohols (methanol, ethanol and glycohols) heated with catalytic quantities of alkane alcoholates.

The PVA foils cast from water solutions are transparent, have high tensile and tear resistance and also are of low costs [1]. Today, PVA is an important material used in biomedicine, as biosensors, electrochemical sensors, or as biomembranes with selective permeability [1, 2]. Transparent matrices for the visible range [4-6] are also obtained from PVA.

The PVA foils possess an intrinsic anisotropy due to the interactions between the dipolar polymer chains. In the stretching process a supplementary induced anisotropy is added to the initial one. The birefringence of the polymer foils increases with the degree of stretching [3-5].

The PVA foils are usually uniax materials with their optical axis oriented parallel to the stretching direction [3, 4].

Cycloimmonium ylids [7] are zwitterionic molecules which can be oriented by stretching in polymer foils [4]. Having a dipolar character, cycloimmonium ylids can interact with polymer chains by orientation-induction forces, increasing the anisotropy of the stretched polymer foils.

Cycloimmonium ylids are coloured molecules with a visible electronic absorption band due to an intramolecular charge transfer (ICT) [8-10]. This band is characterized by small intensity and by a high sensitivity to the solvent nature [7-10]. The ICT is oriented from the carbanion (negatively charged) towards the heterocycle (positively charged).

When the PVA foil containing a cycloimmonium ylid is illuminated by linearly polarized monochromatic light [11], the absorption will depend on the reciprocal orientation of the ylid N^+ - C^- bond and the electric field of the incident polarized light. The maximum of the optical density was obtained for the polarizer transmission direction parallel to the polymer stretching direction, while the minimum corresponds to perpendicular directions. The predominant orientation of the ylid bonds is parallel to the stretching direction.

The absorption measurements [12-15] in linearly polarized monochromatic light can offer information about the ylid orientation in a stretched polymer foil and about the influence of the dye structure on the foil anisotropy

The aim of this study is to establish correlations between the birefringence (as a measure of the PVA foils' anisotropy) and the degree of stretching of the pure and coloured foils. The dependence of the PVA foils birefringence on the cycloimmonium benzoyl anilido-benzoyl methylids 'heterocycle is also established in this paper.

Experimental part

Cycloimmonium benzoyl anilido-benzoyl methylids were obtained in our labs by known methods [7]. The purity of these compounds was tested by spectral and elemental analyses. The structure of the studied ylids is given in figure 1. The studied cycloimmonium ylids have common carbanion (with benzoyl and anilido-benzoyl substitutes to the negative carbon) and different heterocycles, as it results from figure 1. The heterocycles are: 3-(p-phenyl)-pyridazinium; 3-(p-cumyl)-pyridazinium and benzo-[f][-quinolinium.

The phase difference was measured with a Babinet compensator standardized with yellow radiation of a sodium lamp [3-5]. The thickness of the foil was estimated by using a micrometer.

Polymer foils were obtained [3-5,14] from PVA (molecular mass of about 85000) 20% solution in distilled and deionised water (Loba Feinchenius-Austria). A viscous and transparent PVA aqueous solution has been obtained
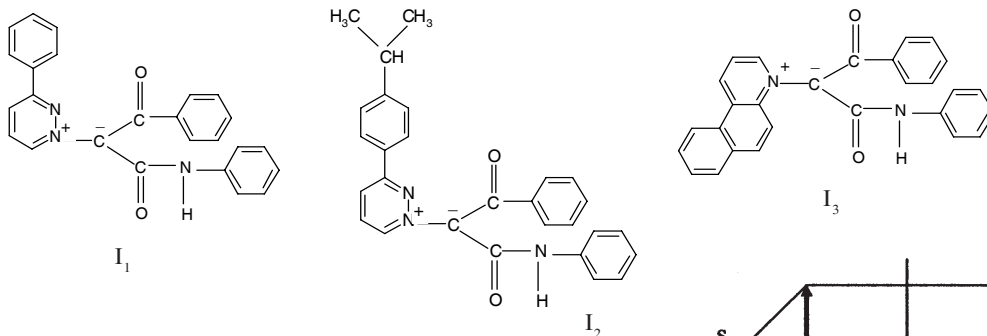
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Fig. 1. Structure of the studied cycloimmonium ylids I_1, I_2 and I_3

Fig. 2 Device for birefringence measurements

after stirring the mixture for about 6h, at temperature 353-363K. The solution was separated in four parts. Three of the parts of solution were mixed by stirring with one of the studied ylid (in concentrations of about 10^{-2} mol/L, at room temperature (293K) for 4h. Two kinds of gel were obtained: one uncoloured, pure PVA and one containing an ylid. The gels were cast on glasses by means of a doctor blade with a slit of 0.6mm. The foils were dried by water evaporation at low pressure for 48h.The dried foils were stretched under heating.

The degree of stretching of the polymer foils was estimated by the ratio of the semi-axes a and b of an ellipse in which a circle drawn on the foil degenerated in the stretching process.

$$\gamma = \frac{a}{b} \tag{1}$$

The device used for the measurements of birefringence is drawn in figure 2.

In figure 2 S is the source (a Natrium lamp or a filament bulb source), L-is a lens with small focal distance; P and A are identical polarizing filters used with crossed transmission directions; AL is the PVA foil; BC is the Babinet compensator standardized for yellow radiation of a Natrium lamp (λ = 596.3 nm) and the screen E. The measurements were made in natural light.

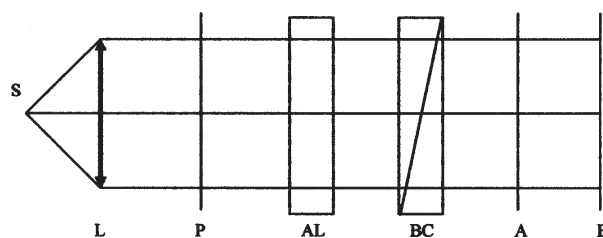The incident light becomes linearly polarized after the polarizer P. Because the polarizers are crossed, in the absence of AL and BC, light does not pass through the second polarizer, after which the flux density is null. When AL is introduced in the device from figure 2, the flux density after the second polarizer becomes different of zero, due to the phase difference introduced by AL between the ordinary and extraordinary components of the linearly polarized light. When BC is introduced in the device illuminated at a filament bulb source, the central fringe (corresponding to zero phase difference) is shifted from its initial zero position. Babinet compensator is used to measure the phase difference introduced by LA, between the two light components, by shifting the central fringe at its initial position [3, 5].

Results and discussions

The birefringence of the pure and coloured PVA foils at different stretching degrees are given in table 1.

As it results from table 1, the birefringence of the pure (uncoloured) PVA foil increases with the degree of stretching (fig. 3a, b, c, d). A saturation of the optical birefringence for the degrees of stretching higher than 2.5 is also evidenced in figures 3.

Foil	$\gamma = \dfrac{a}{b}$								
	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
PVA	2.6	6.5	9.4	13.2	17.2	21.1	24.0	25.0	26.1
PVA +I_1	4.0	9.6	14.2	19.3	23.7	26.6	27.2	28.0	28.5
PVA +I_2	3.8	7.8	13.0	17.5	21.1	24.9	26.1	27.0	27.5
PVA +I_3	3.0	6.9	10.8	15.2	19.3	22.8	24.8	26.1	26.7

Table 1
BIREFRINGENCE ($10^3 \cdot \Delta$n) OF THE PURE AND COLOURED PVA FOILS AT DIFFERENT DEGREES OF STRETCHING
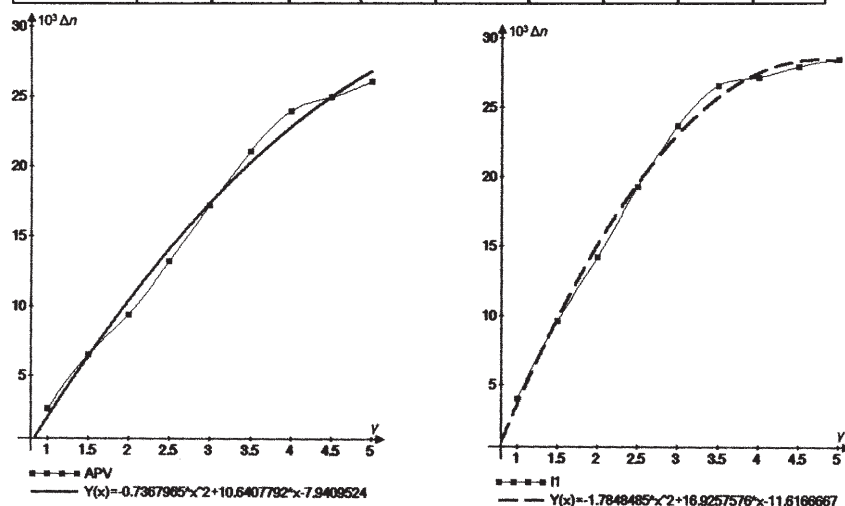

a

b

Fig. 3 –Birefringence ($10^3 \cdot \Delta$n) vs. the stretching degree(γ): *a*) pure PVA; b) PVA + I_1;
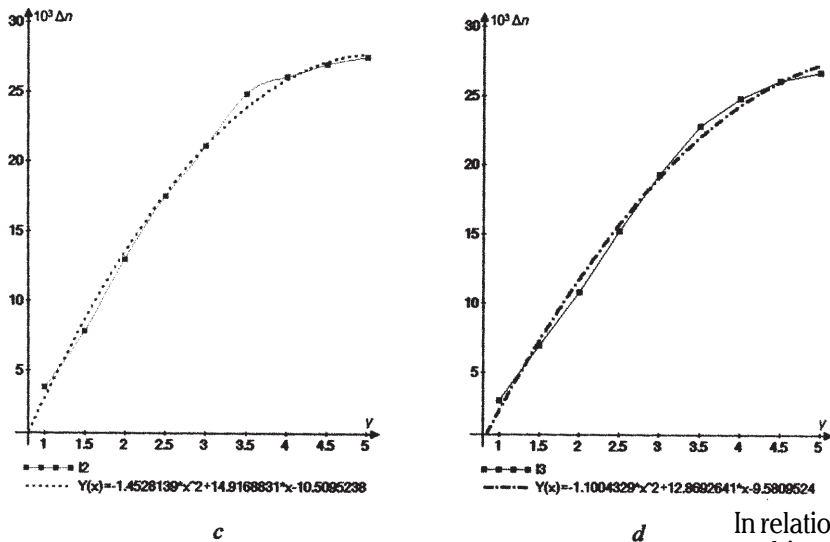
Fig. 3 –Birefringence (10^3 . Δn) vs. the
stretching degree (γ):
c) PVA + I_2; d) PVA + I_3

The birefringence of the PVA coloured foils is higher than the birefringence of the pure APV foil (fig. 3a). This is an experimental evidence of the orientation action of the ylid dipolar molecules. In figures 3*b, c* and *d* the birefringence of the coloured PVA foils as function of stretching is illustrated.

The birefringence dependence on the degree of stretching can be expressed by relation (2).

$$\Delta n = \Delta n(1) + A\gamma + B\gamma^2 \qquad (2)$$

In relation (2), Δn is the birefringence, γ is the degree of stretching, and Δn(1), A and B are the polynomial regression coefficients. The coefficient Δn(1) has the significance of the birefringence of the un-stretched PVA foil.

From figures 3*a, b, c, d* and table 1 it results that the birefringence of the pure PVA foil is smaller than the birefringence of the coloured PVA foils. For comparison, in figure 4 all dependences of the type (2) are plotted in the same graph. The quadratic term of relation (2) written for pure PVA is very small, so the dependence (2) seems to be

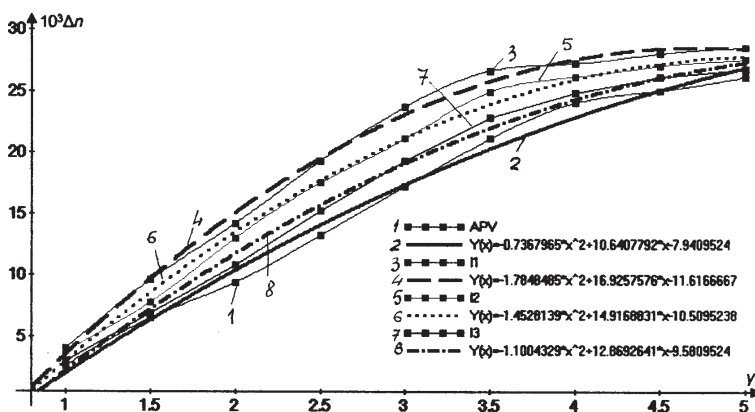| Coefficient	Pure PVA	PVA + I_1	PVA + I_2	PVA + I_3
$\Delta n(1)$	-0.0079410	-0.0116167	-0.0105095	-0.0095810
A	0.0106408	0.0169258	0.0149169	0.0128693
B	-0.0007367	-0.0017848	-0.0014528	-0.0011004

Table 2
REGRESSION COEFFICIENTS IN RELATION (2)

Fig. 4. 10^3 . Δn vs. γ from experiment and computed
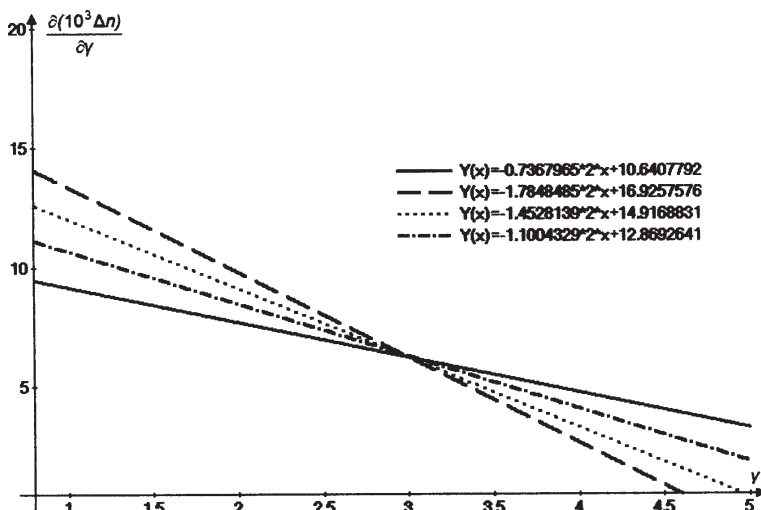using formulae (2)

Fig. 5. $\dfrac{\partial\left(10^3 \Delta n\right)}{\partial \gamma}$ vs. γ

a linear dependence, compared with the dependences obtained for the coloured foils.

Consequently, one can estimate that the dipolar molecules of cycloimmonium ylids facilitate the orientation of the polymer side-chains. The ordering ability of ylid I_1 is higher than the ordering capability of ylid I_2, probably because the cumyl substitute of pyridazinium in the case of I_2 has a steric influence.

The saturation of the orientation effect is illustrated in our experimental data by the appropriate values of Δn for all studied foils (coloured and uncoloured) at high degrees of stretching (figs. 3 and 4).

The velocity of the birefringence variation with the stretching degree, $\frac{\partial(\Delta n)}{\partial \gamma}$, linearly depends on the degree of stretching, as it results from figure 5. This parameter was obtained by deriving relation (2):

$$\frac{\partial(\Delta n)}{\partial \gamma} = A + 2B\gamma \qquad (3)$$

The slopes of the lines (3) in the case of coloured PVL foils depend on the cycloimmonium ylid structure, as it results from figure 5 and table 2. The smallest velocity for the birefringence variation with the degree of stretching was obtained for the pure PVA foil, while the highest was obtained for the PVA foil coloured by Y_1.

Conclusions

The birefringence of the pure (uncoloured) PVA foil increases with the degree of stretching. A saturation of the optical birefringence is observed for the degrees of stretching higher than 2.5.

An experimental result of the orientation action of the ylid dipolar molecules is that the birefringence of the coloured foils is higher than the birefringence of the pure APV foil.

The highest birefringence is obtained for the 3-(*p*-phenyl)-pyridazinium ylid the molecule with the smallest spatial distribution of its atoms.

The velocity of the birefringence variation with the stretching degree linearly depends on the degree of stretching.

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