Order Degree of Polyvinyl Alcohol (PVA) Films, Estimated by a Spectral Method

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Poly-(vinyl alcohol) (PVA) films, colored with pyridinium ylids and dried by water evaporation, become stretched under the heating influence. The visible electronic spectra of the stretched films were measured for linearly polarized visible radiations having their electric field intensity parallel and perpendicular on the stretching direction. The dichroism of the colored PVA films depends on the stretching degree. The birefringence of each film was estimated by using a polarizing microscope with compensatory wedge.

Keywords: stretched PVA films, pyridinium ylids, dichroism, birefringence

The isotropic substances can become anisotropic under the action of external fields of forces. The remanent anisotropy can be characterized by optical birefringence Δn.

$$\Delta n = n_e - n_o \quad (1)$$

n_e and n_o are the extraordinary and the ordinary refractive indices of the material measured for stretching optical radiations having their electric field parallel, perpendicular to the external field direction, respectively.

The birefringence induced by mechanical and magnetic fields is directly proportional with the strength of the field, while the electrically induced birefringence is proportional to the square of the field.

The induced anisotropy offers information about the distribution of tensions in the mechanisms working in mechanical fields of forces. Models at reduced scales are made from transparent resins; their optical aspect between crossed polarizers is studied and photo elasticity is measured and discussed.

Intense magnetic and electric fields can be measured based on the birefringence dependence on their intensity [1]. The polymer films become anisotropic by stretching under uniform heating [1, 2]; so, the polymer long chains are ordered along the etiration direction. The external electric fields can increase the anisotropy of the liquid crystalline layers [3-5] by dipolar interactions.

An etired polymer film is equivalent to a uniax anisotropic crystalline layer. When the polymer does not absorb in the searched optical range, the magnitudes of the ordinary and extraordinary radiations do not change their values in the propagation process, but changes in the radiation polarization state become possible due to the phase difference $\Delta\psi$ introduced between the two components:

$$\Delta\Psi = 2\pi\bar{\nu}_0(n_e - n_o)L \quad (2)$$

In relation (2) $\bar{\nu}_0$(cm^{-1}) is the wavenumber of the monochromatic radiation used in measurements and L is the thickness of the anisotropic layer.

Observed at a polarizing microscope, the stretched film has a colored image which can become black only when the phase differences introduced by the stretched film between the ordinary and extraordinary components and by a compensatory wedge are equal and of opposite sign.

If the polymer film are absorbent (colored with substances absorbing the visible radiations), the dichroism can be also measured. For the oriented absorbent molecules the directions parallel and perpendicular to the stretching directions are not equivalent and, consequently, the components acting parallel to these directions are absorbed in different portions. The higher the degree of order of the colored small molecules, the higher the difference between the two absorptions is.

The dichroism can be estimated by the following relation [6]:

$$D = \frac{E_p - E_n}{E_p + E_n} \quad (3)$$

In relation (3) D is the dichroism, E is the extinction in the maximum of the absorption electronic band for the parallel (p) and perpendicular (n) orientations of the electric field intensity related to the stretching direction.

The degree of orientation of the absorbent molecules in the stretched films [6] can be expressed by the relation (4):

$$g = \frac{C_o}{C} = \frac{2D}{3 - D} \quad (4)$$

In relation (4) C_o denotes the concentration of molecules oriented with their long axis parallel to the stretching direction and C is the overall concentration, respectively. The polarization state of the emergent radiations can be easily established by using special anisotropic plates [7].

Poly-(vinyl alcohol) [2] is a very good solvent for rod-like dipolar molecules such as pyridinium ylids. So, these molecules can be aligned in the polymeric matrix. By stretching, the rod-like molecules become parallel with the polymeric chains. These molecules are colored (spectrally active in the visible range) and the stretched polymer films are also dichroic in visible range. Their spectral extinction differs for linearly polarized radiations having their electric field intensity parallel and perpendicular to the stretching direction. The difference between the corresponding values of absorbance determines the linear dichroism (3).

Pyridinium ylids (fig.1) are stable, colored cycloimmonium ylids [8-11]. Pyridinium ylids are zwitterionic substances with an electronic absorption band in the visible range [1, 12] that appears by the electron transfer from the carbanion towards the heterocycle (fig.2).

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Table 1

CARBANION CHEMICAL STRUCTURE OF THE STUDIED PYRIDINIUM YLIDS, THEIR DENOMINATION AND THE WAVENUMBER IN THE MAXIMUM OF THE VISIBLE ABSORPTION BAND IN PVA

Ylid	R_1	R_2	Denomination	$\bar{\nu}(cm^{-1})$
Y_1	$-CO_2C_2H_5$	$-CO_2C_2H_5$	Dicarbo ethoxy-pyridiniym methylid	25600
Y_2	$-CO_2C_2H_5$	$-CONHC_6H_5$	Anilido-ethoxy-pyridinium ylid	24750
Y_3	$-COCH_3$	$-COC_6H_5$	Acetyl-benzoyl pyridinium methylid	27060

The intramolecular charge transfer is realized along the long molecular axis. So, the pyridinium ylid alignment in the PVA film stretching process can be evidenced by its dichroism.

Experimental part

Three colored pyridinium ylids [8, 12] having the formulae given in figure 1 were used in this study. They were prepared in our laboratory after the methods described in [8]. Chemical and physical analyses demonstrated the high degree of purity of the obtained compounds. The studied ylids differ by the chemical structure of the cation substituents. The carbanion substituents are listed in table 1.

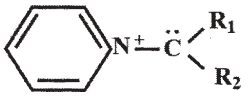

Fig. 1. Studied pyridinium ylids structure

They have a visible band which appears by an intramolecular electronic charge transfer from the carbanion towards the heterocycle. This transition takes place along the ylid bond in the case of the symmetrically substituted pyridinium ylids [8], such as Y_1, and near the ylid bond when the ylid posses a non-symmetrical substituted carbanion, like Y_2 and Y_3.

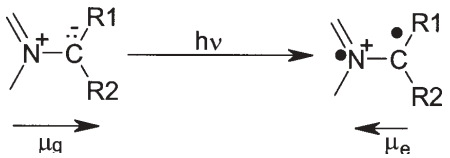

Fig. 2. Intramolecular charge transfer for visible absorption band of cycloimmonium ylids

Pyridinium ylids were solved in the PVA aqueous solutions and then a thin layer of solution has been deposited on a glass plate. Foils were prepared by the known procedure [2]. They were dried and stretched under heating. The degree of stretching has been estimated from the ratio of the ellipse axis derived from a circle initially drawn on the polymer film.

The electronic spectra of the stretched films were recorded by a UV VIS Specord Carl Zeiss Jena spectrophotometer having in the measure beam a polarizer oriented with its transmission direction parallel and, respectively, perpendicular on the stretching direction of PVA films. An identical polarizer has been introduced for compensation reasons in the comparison beam. The transmission direction of the polarizer from the measure beam was oriented parallel and perpendicular to the preferential direction.

The birefringence was estimated by using a polarizing microscope with a compensatory wedge [2, 13].

Results and discussions

The spectra of the stretched polymer films containing 10^{-2} mol/L pyridinium ylids are given in figures 3 a, b and c for the highest degree of stretching.

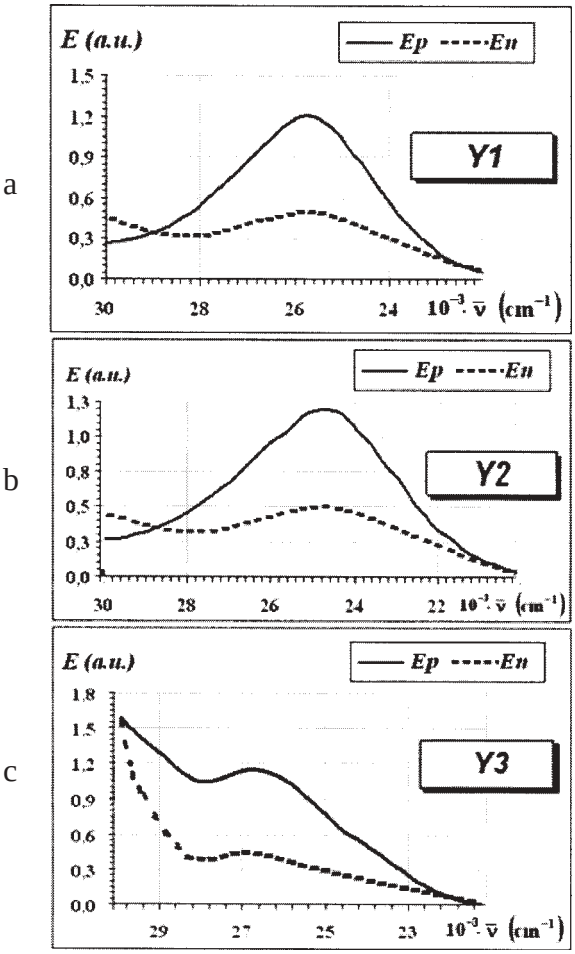

Fig. 3. Electronic spectra of pyridinium ylids oriented in PVA stretched films registered in linearly polarized radiations with electric field intensity parallel (p) and perpendicular (n) to the stretching direction for Y_1, Y_2 and Y_3

The linear dichroism is plotted against the degree of stretching in figures 4 a, b and c for Y_1, Y_2 and Y_3, respectively. From these figures it results a tendency of dichroism increasing when the stretching degree of the films increases. The measurements are affected by errors induced by the decrease of the spectrally active molecule's concentration in the light beam and also by the non-uniform deformation of the film in the high mechanical fields.

In figures 5 a, b and c, the birefringence is plotted versus the degree of stretching. The birefringence increases when the degree of stretching increases. A linear dependence between the film birefringence and its degree of stretching

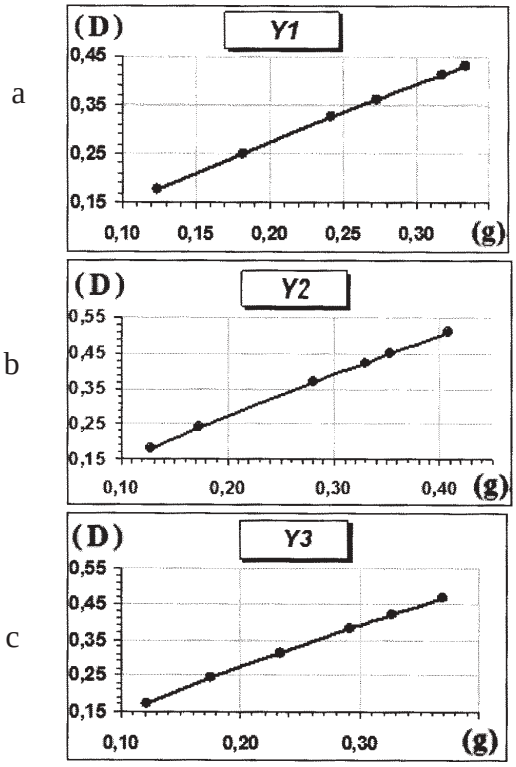

Fig. 4. Linear dichroism versus degree of stretching for PVA films

results from figure 5.

The degree of order of the spectrally active molecules in the stretched films was estimated by using formula (4). The dependence of the degree of order of the spectrally active molecules on the film birefringence is illustrated in figure 6 a, b and c.

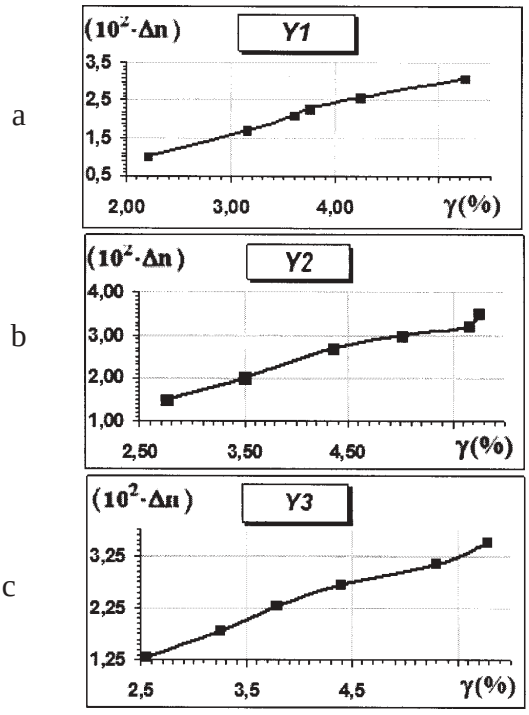

Fig. 6. Birefringence for PVA films containing a) Y_1 ; b) Y_2 and c) Y_3 versus degree of order of the spectrally active molecules

As it results from figures 4, 5, and 6, the birefringence, the dichroism and the degree of order of the spectrally active molecules increase when the stretching degree of the polymer foils increases.

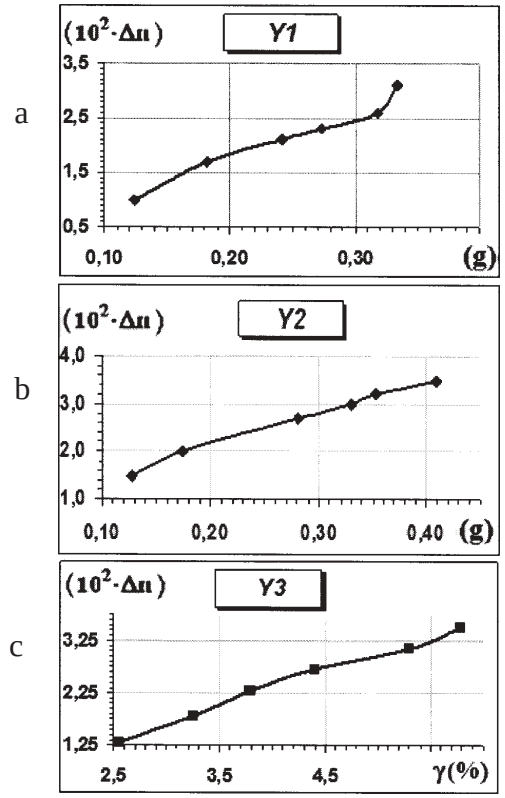

Fig. 5. Birefringence versus degree of stretching for PVA films containing a) Y_1 ; b) Y_2 and c) Y_3 .

Conclusions

The linear dichroism of the stretched colored films offers information on the percent γ(%) of the rod like molecules aligned along the stretching direction. There is a linear dependence between the foil birefringence and the degree of order of the small molecules. In this way the percent of the aligned rod-like molecules could be directly estimated.

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