



*Dedicated to Professor Victor-Emanuel Sahini
on the occasion of his 85th anniversary*

2D IR DICHROISM SPECTRA OF POLY(VINYL ALCOHOL)

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Fourier transform-infrared (FTIR) spectroscopy and two-dimensional infrared (2D IR) correlation spectroscopy were used to measure the linear dichroism and to probe the submolecular dynamics of poly(vinyl alcohol) films. 2D IR is a powerful analytical technique especially suited for the elucidation of localized motions of polymer segments. Infrared linear dichroism has been a useful tool for studying the conformation and orientation of polymer molecules in deformed samples. When a polymer film is stretched, the macromolecular chains tend to align in a specific direction. The oriented film may then absorb, to different extents, incident infrared radiation polarized parallel and perpendicular to a reference direction usually defined as the stretch direction. This study shows how useful information can be effectively extracted by applying 2D correlation spectroscopy to the linear dichroism investigation of polymers.

INTRODUCTION

The properties of polymeric materials strongly depend on the degree of alignment or orientation of their constituent molecules. Oriented samples absorbing in the infrared (IR) wavenumber range exhibit vibrational linear dichroism (VLD), *i.e.* differential absorption between orthogonal states of linearly polarized IR light. Therefore, polarized Fourier transform infrared (FTIR) spectroscopy and VLD can be used to characterize molecular orientation and to quantify anisotropy, order and disorder of molecules.^{1,2}

Infrared absorption bands arise from the vibration of different functional groups and depend on physical factors such as molecular orientation and crystallinity. FTIR spectroscopy is a powerful tool to evaluate the dynamics of polymers and it has been frequently used to study stress-induced molecular orientation in polymeric systems. Two approaches are used, depending on the time-dependent nature of

the perturbation. The first one, in the static mode – no time-dependence is involved, the experiment for studying the molecular response to a static or a step-wise strain is called an infrared linear dichroism experiment¹. The second one consists in the investigation of the molecular response to an externally applied perturbation strain. In this case, the method is referred to as a dynamic linear dichroism experiment.

Two-dimensional infrared correlation spectroscopy (2D IR), pioneered by Noda,³ has been proven very valuable in studies of polymer reorientation as a response to applied perturbations. This technique was used by Gregoriou *et al.*⁴ to evaluate the reorientation kinetics of a uniaxially aligned nematic liquid crystal (4-pentyl-4'-cyanobiphenyl) under the influence of an external electric field, and to evidence the viscoelastic behavior of liquid crystalline polyurethanes using static and dynamic FTIR spectroscopy,⁵ and by Czarnecki *et al.*⁶ who

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studied the segmental mobility of a ferroelectric liquid-crystalline polymer (FLCP) in the Sc* phase under the influence of an electric field.

Poly(vinyl alcohol) (PVA) is a hydrophilic biodegradable polymer, mainly composed of C-C bonds,⁷ a material with a high technological potential since it can be easily modified in aqueous solution or in the melting state. Its water solubility is related to its degree of hydrolysis, molecular weight, and the modification while blended with processing additives.⁸

PVA is an excellent film forming material, acts as an emulsifier and has outstanding adhesive properties. It is resistant to oil, grease and solvents, odourless and nontoxic. It possesses high tensile strength and flexibility, as well as high oxygen and aroma barrier properties.

In this study, static linear dichroism and 2D IR correlation spectroscopy were used for optical characterization of PVA films.

MATERIALS AND METHODS

Sample preparation

Three commercial types of polyvinyl alcohol (PVA) with 88, 98, 99 % hydrolysis degrees were used. To obtain films with anisotropic properties, PVA was dissolved in hot water. The obtained solution was moulded as thin layers on glass plates. After solution casting, optically isotropic films with different thicknesses were obtained. The anisotropy was induced by local heating and stretching. The experiments were performed using a static stretcher (designed and machined for this purpose) which allows elongation of the sample up to 450% of its initial length.

Vibrational linear dichroism

The static infrared spectroscopic data were collected using a FT-IR Bomem MB-104 Canada Spectrometer, with a spectral resolution of 4 cm⁻¹. A Harrick infrared polarizer was placed into the infrared beam to allow plane polarized light to reach the sample.

2D correlation spectroscopy

Two-dimensional correlation spectroscopy enables cross-correlation analysis of spectral series of systems which change with a modulation variable.⁹ Two-dimensional wavenumber–

wavenumber correlation analysis provides two different correlation maps. The synchronous map displays correlations between all spectral bands changing in phase during the experiment and shows whether they increase or decrease relative to each other. In contrast, the asynchronous correlation map relates spectral bands that change at different rates and also contains information about the sequence of the occurring events.

RESULTS AND DISCUSSION

Linear dichroism is the phenomenon of the anisotropic absorption of light. It is observed in materials containing oriented molecules for which the absorption varies with the direction of the orientation plane. The absorption intensity is proportional to the square of the scalar product between the electric field vector of the light and a molecule-characteristic transition moment vector. The absorption reaches the maximum value when the light vector is parallel polarized to the transition moment and is zero when it is perpendicular to it. Linear dichroism can therefore provide directions of transition moments when the molecule orientation is known (spectroscopic application), or information on molecular orientation when the transition moments are known (structural application).

The reorientability of chemical functional groups is strongly influenced by the presence of the various inter- and intramolecular interactions. The reorientation rate of electric dipole transition moments provides valuable information on the local chemical environment, as well as on the structure of functional groups contributing to the molecular vibration detected by IR spectroscopy.

To evidence the variation of the spectral bands intensities with incident linear polarised light, FTIR spectra of PVA films of different orientations of transmission direction of the polarizer were recorded. The IR band intensities depend on the θ angle between the transmission direction of polarizer and the stretching direction (Fig. 1).

With increasing the degree of hydrolysis, differences were observed in the 1800-800 cm⁻¹ region of the IR spectra. Thus, the band at 1330 cm⁻¹, assigned to the deformation vibration of C-H and O-H groups, shows significant spectral changes, the 1720 cm⁻¹ and 1268 cm⁻¹ bands intensities decrease, while the 1820 cm⁻¹ and 1240 cm⁻¹ bands intensities increase. The appearance of a band with a maximum at 1142 cm⁻¹, assigned to the stretching vibration of C-C and C-O bonds can be also observed.

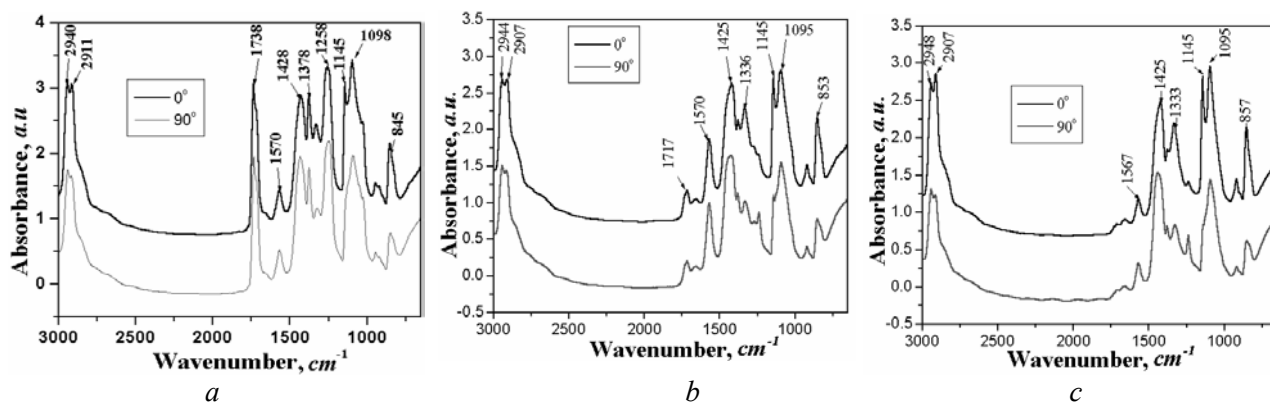


Fig. 1 – FTIR spectra for two directions of the polariser and difference spectra of uniaxially oriented PVA with 88 (a), 98 (b) and 99 % (c) hydrolysis degree.

The overlapped bands were deconvoluted and the integral absorption, spectral width and band position were evaluated using the Grams 32 program. It appeared that the integral absorption of some spectral bands increases with the angle between the transmission direction of the polarizer and the stretching direction of the sample (θ angle), and for others decreases. Fig. 2 shows the dependence of the 1450 and 1415 cm^{-1} bands on θ angle.

To study the dependence of the stretching degree on the dichroic ratios, FT-IR spectra of PVA samples with 180, 240, 270, 350, 410, 440% stretching degrees with parallel and perpendicular orientations to the direction of the incident electric field were recorded.

The dichroic ratio is defined by $D = A_0/A_{90}$, where A_0 is the intensity of spectral bands for $\theta=0^\circ$ and A_{90} is the intensity of spectral bands for $\theta=90^\circ$ in the 2990-2860 cm^{-1} , 1770-1670 cm^{-1} , 1620-1525 cm^{-1} , 1515-1390 cm^{-1} , 1390-1355 cm^{-1} , 1355-1297 cm^{-1} , 1290-1200 cm^{-1} , 1170-975 cm^{-1} , 965-877 cm^{-1} and 875-790 cm^{-1} spectral regions.

When a film absorbs more light in parallel direction than in the perpendicular one, the dichroic difference is positive and the dichroic ratio is higher than unit. The dichroic ratio has traditionally been used in the assigning of infrared bands to specific vibrational modes and to help determine the molecular chain orientation.

Most of the bands have a positive dichroism (or Dichroism- π), however the bands located at 1450 cm^{-1} and 1240 cm^{-1} show negative dichroism (Dichroism- σ).

For some spectral intervals, one can observe that the values of dichroic ratios increase with increasing the stretching of the films, while for others they decrease. The dichroic ratios show a rapid increase with increasing the stretching degree up to 250% and then remain approximately constant.

The dichroic ratio values of different types of PVA are given in Table 2.

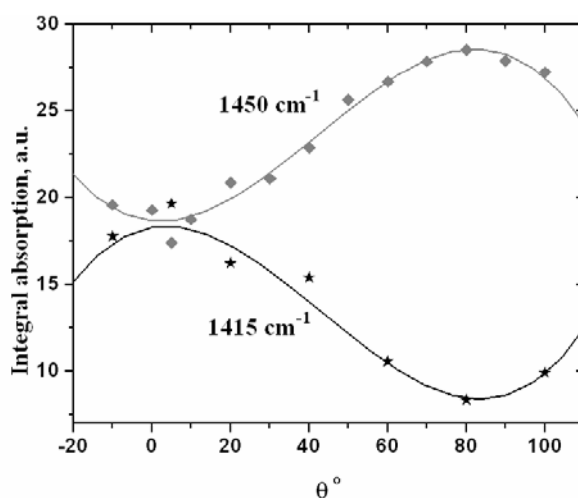


Fig. 2 – Integral absorption at different polarising angles.

Table 1

Dichroic ratios corresponding to the absorption bands of PVA

Elongation degree %	Dichroic ratio				
	2990-2860	1770-1670	1620-1525	1515-1390	1390-1355
180	1.55	1.28	0.93	1.01	1.06
240	1.66	1.27	0.96	0.96	1.04
270	1.74	1.30	0.88	0.93	1.06
350	1.95	1.38	0.89	0.91	1.09
410	1.92	1.39	0.99	0.89	1.11
440	2.02	1.40	0.88	0.89	1.29
	Dichroism- π	Dichroism- π	Dichroism- σ	Dichroism- σ	Dichroism- π
Elongation degree %	Dichroic ratio				
	1355-1297	1290-1200	1170-975	965-880	875-790
180	1.79	1.05	1.35	1.84	1.84
240	1.97	1.03	1.37	2.65	2.07
270	2.28	0.98	1.45	1.91	2.24
350	2.28	1.02	1.49	2.65	2.55
410	2.59	1.02	1.50	2.96	2.49
440	2.25	1.05	1.62	3.50	2.49
	Dichroism- π	Dichroism- σ	Dichroism- π	Dichroism- π	Dichroism- π

Table 2

Dichroic ratios for PVA films with 88, 98, 99 (% mol) hydrolysis degree for a 250% stretching degree and film thickness of 27 μm

Spectral region (cm^{-1})	Dichroic ratio	Hydrolysis degree (% mol)		
		88	98	99
2990-2860		1.38	1.35	1.62
1770-1680		1.13	1.30	1.00
1680-1625		-	0.95	-
1620-1520		0.95	0.94	0.87
1510-1180		1.02	1.05	0.97
1170-975		1.24	1.28	1.40
960-880		1.62	1.99	2.54
875-790		1.74	2.73	2.16

For all studied PVA samples, the dichroic ratio is greater than one for almost all spectral bands, except the band at 1620-1520 cm^{-1} , which implies an orientation of transition dipole moments in an almost parallel direction to the stretching direction. In the case of 1620-1520 cm^{-1} band, the dipole moment of transition is perpendicular to the stretching direction.

The specific reorientation rates of individual dipole transition moments, which are determined by the type and local environment of functional groups contributing to the molecular vibrations, can be used as convenient spectroscopic labels to differentiate highly overlapped IR bands. Wavenumber dependent variation of static dichroism intensities reflects the non-uniformity of reorientation rates among various dipole transition moments and are analysed quite effectively by 2D correlation method.

The spectra defined by two independent wavenumber axes are constructed by applying a correlation analysis to such signals.¹⁰ The 2D spectra

provide detailed information about the local dynamics of submolecular constituents of the system.

2D correlation spectra were generated for infrared spectra recorded at different angles between the transmission direction of polarizer and stretching direction of PVA films (from 0 to 90 degrees). The correlation spectra were generated in the 3700-2700 and 1800-900 cm^{-1} regions.

The synchronous spectra in the region of 3700-2700 cm^{-1} are similar for the PVA samples with different degrees of hydrolysis. The synchronous correlation spectrum offers an indication of simultaneous spectral intensity changes as a result of the perturbation.

Three auto-peaks at 3149, 2939 and 2910 cm^{-1} were evidenced for PVA of 88% hydrolysis degree, while for PVA of 98% hydrolysis degree they appeared at 3209, 2939 and 2908 cm^{-1} and for PVA of 99% hydrolysis degree at 3251, 2941 and 2908 cm^{-1} . These auto-peaks indicate that the transition dipoles and thus the functional groups associated to the spectral bands have an orientational response to the perturbation.

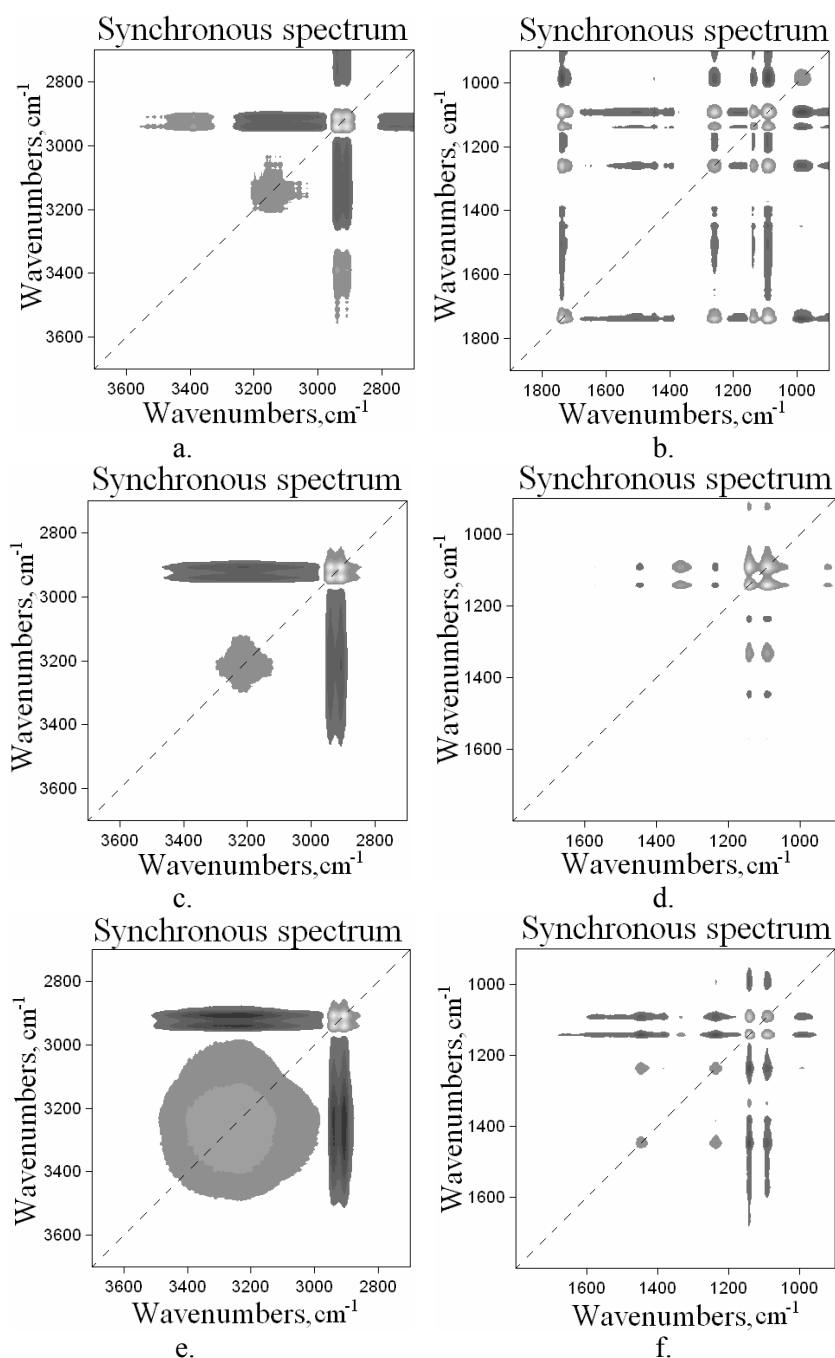


Fig. 3 – 2D correlation spectra of PVA samples in the 3700–2700 and 1800–900 cm^{-1} regions: 88% (a, b), 98% (c, d) and 99% (e, f) hydrolysis degree.

All auto-peaks form negative cross-peaks. The cross-peaks illustrate the degree the dipoles respond in phase with each other and, from their signs, the relative reorientation of these dipoles. A negative cross-peak indicates that the two corresponding dipole moments reorient perpendicular to each other. In the present case, the appearance of negative cross-peaks indicates that the dipole moments of OH groups vary in opposite direction with those of CH_3 and CH_2 groups.

Numerous correlation peaks are evidenced in the fingerprint region (1800–900 cm^{-1}). For the PVA sample of 88% hydrolysis degree, the auto-peaks are observed at around 1737, 1259, 1139, 1091 and 985 cm^{-1} , positive cross-peaks at 1739 vs. 1259, 1139 and 1091 cm^{-1} , 1259 vs. 1139 and 1091 cm^{-1} , 1139 vs. 1091 cm^{-1} and negative cross-peaks at 1737 vs. 1496, 1450, 1392, 1188 and 985 cm^{-1} , 1496 vs. 1259, 1139 and 1091 cm^{-1} , 1450 vs. 1259, 1139 and 1091 cm^{-1} , 1392 vs. 1259, 1139

and 1091 cm^{-1} , 1259 vs. 1188 and 985 cm^{-1} , 1188 vs. 1139 and 1091 cm^{-1} , 1139 vs. 985 cm^{-1} and 1091 vs. 985 cm^{-1} .

The bands located at 1737 , 1259 , 1139 and 1091 cm^{-1} , assigned to stretching vibrations of C=O, CH₃, C–O and C–C groups, vary in the same direction and can be assigned to polymeric side chains, while the bands located at 1496 , 1450 , 1392 , 1188 and 985 cm^{-1} , assigned to deformation vibration of CH₂, C–H, C–O–C and C–C groups from backbone, vary in opposite direction.

For PVA with 98% hydrolysis degree, two auto-peaks at 1141 and 1091 cm^{-1} , positive cross-peaks at 1334 vs. 1141 and 1091 cm^{-1} , 1141 vs. 1091 cm^{-1} and 1141 vs. 921 cm^{-1} and negative cross-peaks at 1446 vs. 1141 and 1091 cm^{-1} , 1236 vs. 1141 and 1091 cm^{-1} are observed. The bands at 1446 and 1236 cm^{-1} , assigned to deformation vibration of C–O and C–H groups, vary in the same direction and in opposite direction with the vibration bands located at 1334 , 1141 , 1091 and 921 cm^{-1} , assigned to stretching vibration of C–C and C–H from backbone.

For PVA with 99% hydrolysis degree, the synchronous spectrum generated from 1800 – 900 cm^{-1} spectral region contains four auto-peaks at 1446 , 1236 , 1141 and 1091 cm^{-1} . Positive cross-peaks appear at 1446 vs. 1236 cm^{-1} , 1334 vs. 1141 and 1091 cm^{-1} , 1141 vs. 1091 cm^{-1} and negative cross-peaks at 1446 vs. 1141 and 1091 cm^{-1} , 1236 vs. 1141 and 1091 cm^{-1} , 1141 vs. 992 cm^{-1} and 1091 vs. 992 cm^{-1} . According to spectral interpretation, the bands located at 1334 , 1141 and 1091 cm^{-1} , assigned to deformation vibration of C–O and C–H groups, vary in the same direction and in opposite direction with the bands located at 1446 , 1236 and 992 cm^{-1} which are assigned to the stretching vibration of C–O–C, C–C and C–H groups from backbone.

It can be concluded that the auto-peaks represent the re-orientation of transition dipole moments assigned to asymmetric and symmetric stretching vibrations and deformation vibrations of C–H groups. The appearance of cross-peaks indicates that the transition dipole moments of these bands vary with the same rate. The positive sign of cross-peaks suggests that the transition moments of spectral bands are oriented in the same direction, i.e. perpendicular to the direction of applied stretching perturbation. Since it is known that the transition dipole moments are perpendicular to polymer backbone, one can conclude that PVA chains are aligned to the

applied stretching direction. The dynamic reorientation of lateral groups is more complex, suggesting that the reorientation motion of these groups under the applied perturbation is different.

CONCLUSIONS

FT-IR linear dichroism studies represent a powerful tool in exploring polymeric deformations caused by unidirectional stretching. The dependence of dichroic ratio on the stretching degree of PVA samples indicates that it increases almost linearly up to 250% stretching, and then remains almost constant. The dichroic ratios depend on the thickness of the polymeric film.

For all studied samples, the dichroic ratio increases with increasing the hydrolysis degree for most spectral regions, this indicating an increased orientation of the macromolecules.

The 2D IR dichroism spectroscopy based on the correlation analysis of localised reorientation motions of various submolecular moieties constituting a system proves to be a very powerful tool for the investigation of complex molecules such as polymers.

2D synchronous correlation spectra evidence the spectral bands associated with the chemical groups in the backbone and in the side chain and point out their orientation.

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