

An Improved Method for the Preparation of Polyethylene Oriented Matrices Suitable for Linear Dichroism Studies

B. Nadolski, P. Uznański, A. M. Wróbel and M. Kryszewski

Department of Polymer Physics, Centre of Molecular and Macromolecular Studies,
Polish Academy of Sciences, Boczna 5, 90-362 Łódź Poland

SUMMARY

A method is presented of improving the optical behaviour of stretched Polyethylene (PE) matrices suitable in linear dichroism studies. It is based on the modification of the drawn PE matrices by filling microcracks (the light scattering centers) with Poly(vinyl alcohol). Absorption spectra of modified and unmodified matrices show enhancement of light transmission in uv-visible range for modified matrices. Suggestions on the influence of the crystallinity degree and drawing conditions of PE matrices, used as anisotropic solvent, are given.

INTRODUCTION

Since the pioneer works of Jabłonski (JABŁONSKI, 1935) the uniaxially oriented polymer/solute matrices have been widely used in the linear dichroism (LD) studies in connection with determination of the transition moment directions of the elongated solute molecules. Among the numerous polymer films, drawn PE seems to be the most suitable as a highly oriented medium, interacting weakly with the solute molecules and almost nonabsorbing within a whole uv-range. Unfortunately, most of the apparent absorption of PE oriented films in the uv-visible region is due to light scattering and depends on the polarization direction as well as on the wavelength of the incident light. Depolarization effects caused by the light scattering and a matrix baseline problem, however, are a source of serious error in LD studies (THULSTRUP, 1980).

It is well known that light scattering results from the presence of microcracks which are aligned in oriented PE films mostly along the drawing direction. The aim of our work was to propose a novel method of preparing anisotropic PE matrices with considerably improved optical behaviour. This method comprises a pretreatment of matrix surface in low-temperature plasma of air and filling the microcracks up with

poly(vinyl alcohol). Moreover, the effect of different conditions of polymer drawing process on its orientation is reported.

EXPERIMENTAL

Polymers. Poly(vinyl alcohol) (PVA) was obtained by alkaline hydrolysis of poly(vinyl acetate) (BDH) of average molecular mass $M_v = 8.2 \times 10^4$, carried out according to (SACURADA and FUJIKAWA, 1945). PE, Lupolen 1800S (BASF), with the density of 0.918 g/cm^3 , $M_v = 2.8 \times 10^4$, m.p. of 112°C , and containing 35 methyl groups per 10^3 carbon atoms was purified by dissolution in hot toluene and precipitation after cooling the solution down to room temperature. Two dissolution-precipitation cycles were carried out to obtain high purity of the polymer.

Preparation of PE films. PE films ca. $100 \mu\text{m}$ thick were prepared according to the following methods:

(i) casting of 5% hot PE/toluene solution onto the heated quartz plate. The initial temperature of the solution/plate was kept at about 80°C and was then raised up to 130°C with a constant heating rate of ca. 4 deg/min . Such heat-treatment conditions prevented PE gelation during solvent evaporation. To prevent thermal oxidation process in PE, evaporation of the solvent was carried out in a chamber under continuous flow of argon. The molten PE on a quartz substrate was then cooled down by immersion in ice water bath to diminish spherulites growth in the polymer;

(ii) compressing of the molten PE in argon atmosphere between stainless steel plates which were first heated initially at 130°C and then cooled down in ice water bath.

The uv spectroscopic examination of the PE films prepared by the above methods proved that they were free of residual solvent and did not display any oxidative destruction.

Crystallinity measurements. The crystallinity degree of the unoriented PE films was determined by wide angle x-ray scattering according to the method of Hermans and Weidinger. The diffraction patterns were recorded on DRON 2.0 diffractometer for scatter angles within the range of $2\theta = 6 - 30^\circ$.

Drawing experiments. The PE films prepared according to the methods (i) and (ii) were oriented in Instron apparatus using two different drawing procedures: a/ drawing with necking at various drawing rates of 1, 5 and 20 cm/min ;
b/ drawing through a die (PAKUŁA and FISCHER, 1981) at drawing rate of 0.5 cm/min .

Birefringence measurements. The optical anisotropy in the oriented PE films was estimated from birefringence measurements according to a standard interference-

polarization method using an interference-polarization microscope.

Modification of drawn PE films. To improve the adhesion of the PVA filler to highly hydrophobic PE, the oriented films were subjected to treatment in low-temperature plasma generated in air using the electrode system described elsewhere (WRÓBEL et.al., 1976). Film samples fixed between stainless steel electrodes spaced 3 cm apart were treated at the following plasma parameters: current frequency, 20 kHz, current density, 1 mA/cm²; pressure, 0.1 and 0.3 Torr; treatment duration, 60 s. The extent of PE surface modification resulting from plasma treatment was examined by the measurements of the advancing contact angle of distilled water and freshly prepared PVA water solutions.

Plasma treated PE films were then modified with PVA by their threefold soaking in PVA water solution and subsequent evaporation of water.

RESULTS AND DISCUSSION

Effect of purification on the crystallinity degree of casted and compressed PE matrix. The data in Table 1 clearly show that purification of commercial PE decreases markedly its crystallinity degree.

TABLE 1

Crystallinity degree of nonpurified (NP) and purified (P) PE matrices prepared by casting and compressing techniques

PE Matrix	Degree of Crystallinity (%)
Casted	
NP	42
P	27
Compressed	
NP	43
P	25

Presumably this results from the elimination of easily crystallized linear macromolecules of low molecular mass and of some additives as optical stabilizers, antioxidants and residual catalyst which can create heterogenous nucleation centers.

In general, the presence of the crystalline phase in the matrix is disadvantageous, since the investigated molecules introduced into the matrix are located in the amorphous phase only. The presence of the crystalline phase involves a decrease of the "effective

volume" that can be occupied by the molecules introduced to the matrix. This consequently leads to nonuniform concentration of the molecules throughout the matrix and under such conditions undesirable aggregates can be formed. It is also known, that the microcracks appearing in PE during drawing originate from the transformation of the spherulites into the fibrils. Thus, the light scattering on the microcracks strongly depends on the crystallinity degree and on the spherulite size in the initial matrix, and therefore the low-crystallinity PE such as Lupolen 1800S is the most suitable for optical studies.

In the widely used procedure for the preparation of PE matrices to LD studies the organic molecules are introduced into the matrix by diffusion (THULSTRUP, 1980). It is a highly time-consuming process that enables to introduce a relatively small amount of the molecules, in fact, without any possibility of controlling their concentration in the matrix. It seems that most of the organic molecules can be introduced into the matrix by casting technique using toluene as a solvent. The evaporation conditions of toluene specified in the experimental section prevent the polymer from undergoing gelation and prepared PE matrices were found to be of uniform structure. It also seems that evaporation of the solvent at elevated temperature should markedly reduce aggregation of the solute molecules. The casted matrices were slightly rough and additional compression of the molded films was needed to smooth their surface. As can be seen from Table 1 the method of matrix preparation does not influence its crystallinity.

Effect of drawing conditions on optical properties of oriented matrices. It can be seen from the data in Table 2 that birefringence of PE matrices drawn with necking increases with drawing rate. Since birefringence reflects the orientation of the polymer chains in the amorphous and crystalline phases so the same rate dependent effectiveness of the orientation should be observed for elongated solute molecules in PE.

The matrices drawn through a die exhibit higher orientation than those drawn with necking as it was already observed for various polymer materials (PAKUŁA and FISCHER, 1981; ZACHARIADES et.al., 1978). Unfortunately, this drawing procedure requires the polymer film to be enough thick (at least 1 mm) to avoid its rupture during deformation, so its application for preparation of PE matrices for optical studies is rather limited. The matrices prepared according to the mentioned procedures contain microcracks (Fig.1) although drawing through a die yields a medium with slightly less light scattering (Fig.2).

TABLE 2
Birefringence (Δn) of PE matrices drawn with necking and through a die at various drawing rate

Drawing rate (cm/min)	Birefringence, Δn^x	
	Drawn with necking	Drawn through a die
0.5	0.1189	0.1705
1	0.1293	-
5	0.1308	-
20	0.1608	-

^{x/} $\Delta n = n_{\parallel} - n_{\perp}$, where n_{\parallel} and n_{\perp} are the refractive indices along and perpendicular to the drawing direction, respectively, as viewed through cross-polarized light.



Fig.1. Micrograph of PE drawn film, immersed in silicon oil, taken at crossed polarizers.

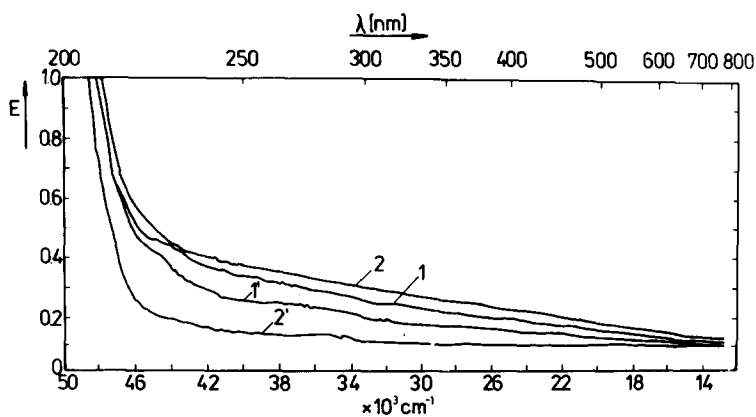


Fig.2. Absorption spectra of PE films: drawn through, a die, before (1) and after plasma/PVA modification (1'); drawn with necking, before (2) and after plasma/PVA modification (2').

Effect of plasma and PVA water solution treatments on optical behaviour of PE matrix. The low-temperature air plasma treatment of the drawn matrices increases their wettability to water and PVA water solutions as is seen from the contact angle values presented in Table 3.

TABLE 3

Contact angles for water and PVA water solutions on the surface of PE oriented matrices untreated and treated in plasma generated in air at various pressures. Other glow discharge parameters: current frequency = 20kHz, current density = 1mA/cm², and discharge duration=60s.

Concentration of PVA in Water (%)	Contact Angle, θ (deg)		
	Untreated PE	Plasma Treated PE	
		0.1 Torr	0.3 Torr
0	96	34	24
0.6	74	25	17
1.2	73	24	16
1.8	72	23	13
2.4	69	22	10
3.0	68	23	12

A better hydrophilicity of PE matrices is observed for plasma treatment at air pressure of 0.3 Torr as compared to those treated at 0.1 Torr. Wettability of plasma treated PE matrices for PVA water solutions does not change within the concentration range of 1.8-3.0% and further PE modification was carried out using 3% PVA solution.

The advantage of modification of PE matrices appears as one compares the absorption spectra of the modified (1',2') and unmodified (1,2) matrices which are presented in Fig.2. The improvement in optical behaviour of the modified matrices is magnified when linearly polarized light is used for the recording of their absorption spectra (Fig.3). Moreover, it is manifested not only as a lowering of the scattered light but also as a convenient linear apparent absorption/wavelength characteristic.

Finally, we tested application of the modified matrices in the low-temperature spectroscopy, down to liquid nitrogen temperature, and no breaking and delaminating of the samples was observed.

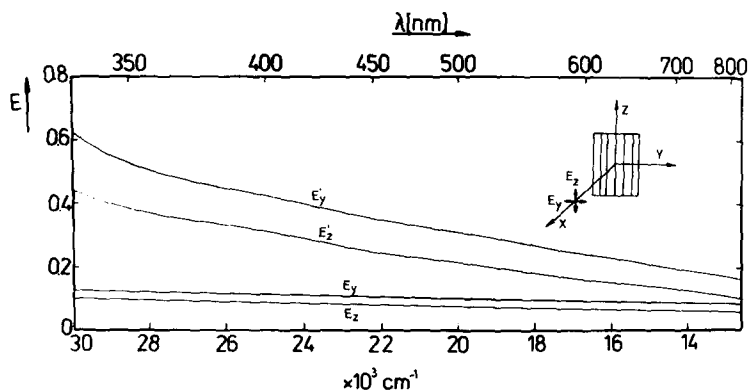


Fig.3. Polarized absorption spectra of PE matrices drawn with necking at the rate of 20 cm/min., before (E_z', E_y') and after plasma/PVA modification (E_z, E_y). E_z', E_y' and E_z, E_y denote optical densities for light polarized parallel and perpendicular to the drawing direction, respectively.

REFERENCES

- JABŁONSKI, A.: Acta Phys.Polonica, 4, 371 /1935/
 THULSTRUP, E.W.: Linear and Magnetic Circular Dichroism of Planar Organic Molecules, Lecture Notes in Chemistry, Springer-Verlag, Berlin, 1980.
 SAKURADA, I. and FUJIKAWA, N.: Kobunshi Kagaku, 2, 143 /1945/; C.A.; 44, 5148c /1950/
 PAKUŁA, T. and FISCHER, E.W.: J.Polym. Sci.Polym. Phys.Ed., 19, 1705 /1981/
 WRÓBEL, A.M., KRYSZEWSKI, M. and GAZICKI, M.: Polymer, 17, 673 /1976/
 ZACHARIADES, A.E., KANAMOTO, T. and PORTER, R.S.: paper presented at the Meeting of the American Phys.Soc.and Biophys.Soc. Washington, D.C., 27-30 March 1978.

Accepted August 22, 1983