INDOLES IN STRETCHED POLYETHYLENE AND POLYVINYL ALCOHOL FILMS

A. Suwaiyan*

Chemistry Department
King Fahd University of Petroleum & Minerals
Dhahran 31261, Saudi Arabia

الخلاصـــة :

تم وصف توجيه الإندول وخمسة من مشتقاته في نسيجين بوليمريين ممددين (بولى اثيلين وبولى ڤاينل الكحول) باستخدام نموذج TEM .
توضح النتائج في البولى اثيلين ان الإندول موجه بحيث يكون المحور الجزئي الطويل في اتجاه المد . أما في بولى ڤاينل الكحول فالتوجيه في اتجاه المحور القصير .
وقد تم شرح هذا الفرق بوجود رابطة هيدروجينيه في بولى ڤاينل الكحول .

ABSTRACT

The orientation of indole and five of its derivatives is described in two stretched polymer matrices: polyethylene (PE) and polyvinyl alcohol (PVA), using the TEM model. Results in PE show that indole is oriented with its long molecular axis in the direction of stretch. In PVA, short axis orientation is found. The difference is explained by a hydrogen bond formation in PVA.

*Address for correspondence :
KFUPM Box No. 625
King Fahd University of Petroleum & Minerals
Dhahran 31261
Saudi Arabia

INDOLES IN STRETCHED POLYETHYLENE AND POLYVINYL ALCOHOL FILMS

INTRODUCTION

The stretched polymer matrix technique has been used for some time to study the polarized spectra of solute molecules [1–4]. In this technique, solute molecules are dissolved in a polymer matrix which will then be stretched in a certain direction to orient the solute molecules. In addition to its spectroscopic applications, the orientation of these solute molecules in the polymer matrix and, in turn, the polymer solute interactions can be studied [5]. Two limiting cases are possible in this case [1]. First: the introduced molecules combine with the polymer by means of one or several active groups, e.g. covalent bonds or other fairly strong bonds. Secondly: the introduced molecules are included mechanically in the polymer matrix in the form of a solid solution. In this paper we present new studies on indole and five of its derivatives in two stretched polymer matrices. In order to examine the effect of substitution on the orientation of the indole molecules in polymer matrices, several methyl-substituted derivatives were studied where the methyl group is substituted at different positions in the ring. Two polymer matrices: polyethylene (PE) and polyvinyl alcohol (PVA), were used to study the effect of the matrix polarity.

EXPERIMENTAL

Materials

Indole and 3-methylindole were of sigma grade and were further purified by vacuum sublimation. 2-methylindole was recrystallized from petroleum ether. 3-propionic acid indole, 5-methylindole, and 7-methylindole were of sigma grade and were used as received. Polyethylene (PE) sheets (0.18 mm thickness) were kindly supplied by ICI. PVA powder was purchased from Aldrich Chemical Co.

Apparatus

A Perkin–Elmer (356) double beam spectrophotometer was used in this work. Polarization measurements were made with a 50 mm aperture, air-spaced, ultraviolet transmitting calcite, Glan–Taylor prism.

Procedure

To dissolve the indoles in PE, a piece of the film with a uniform rectangular shape was suspended in a concentrated chloroform solution for 2–3 days. The film was then washed with chloroform and dried in front of a cold stream of air from a hair dryer for 30 minutes. In the case of PVA, the indole and PVA powder were codissolved in water (about 10% hot PVA solution). Water was then evaporated by transferring the solution onto a flat surface. The resulting (PVA) film had a thickness of about 0.22 mm. The polymer films are stretched to 3 times the original length and two polarized spectra parallel $E_{\parallel}(\lambda)$ and perpendicular $E_{\perp}(\lambda)$ to the direction of stretch were obtained by rotating the polarizer. The spectra were corrected for the absorption by the film itself. The linear dichroism is given by $LD(\lambda) = E_{\parallel}(\lambda) - E_{\perp}(\lambda)$, and the reduced dichroism by: $LD_r(\lambda) = (E_{\parallel}(\lambda) - E_{\perp}(\lambda))/(E_{\parallel}(\lambda) + 2E_{\perp}(\lambda))$.

RESULTS AND DISCUSSION

The absorption spectra of these indoles in PE and PVA resemble those in n-hexane (a non-polar medium) and water (a polar medium), respectively. Figures 1 and 2 present the LD spectra in PE and the $LD_r(\lambda)$ in PVA, respectively. In PE, the LD spectrum shows a clear resolution of the peaks. This is not the case in PVA so the LD_r is chosen for this purpose. The Thulstrup, Eggers, and Michl (TEM) model [2, 6, 7] is used to interpret the results obtained. In the TEM model the dimensionless reduction parameters $d_{\parallel}$ and $d_{\perp}$ are obtained using the reduction procedure [2]. Linear combinations of the polarized absorption spectra $E_{\parallel}(\lambda)$ and $E_{\perp}(\lambda)$ such as $E_{\parallel}(\lambda) - d_{\parallel} E_{\perp}(\lambda)$ and $E_{\perp}(\lambda) - d_{\perp} E_{\parallel}(\lambda)$ are plotted as a function of the wavelength. By computer stepwise reduction of these functions, $d_{\parallel}$ and $d_{\perp}$ are determined such that some spectral feature would just disappear from the spectrum. In the case of the indoles studied in this work, $d_{\parallel}$ is chosen so that the O–O ^1L_b disappears and $d_{\perp}$ is chosen at the other end of the absorption band (at about 245 mm) where it is believed to have minimum ^1L_b contribution. The orientation parameters K_1 and K_2 are given by: $K_1 = 1/(2d_{\perp}+1)$, $K_2 = d_{\parallel}/(d_{\parallel}+2)$.

Saupe orientation parameters [5] are given by: $S_{zz} = (3K_1 - 1)/2$, $S_{yy} = (3K_2 - 1)/2$, and $S_{xx} = S_{zz} - S_{yy}$. The orienting power (O.P.) of a polymer [5] is given by: $\text{O.P.} = |S_{zz}| + |S_{yy}| + |S_{xx}|$.

The orientation parameters S_{zz} and S_{yy} and the

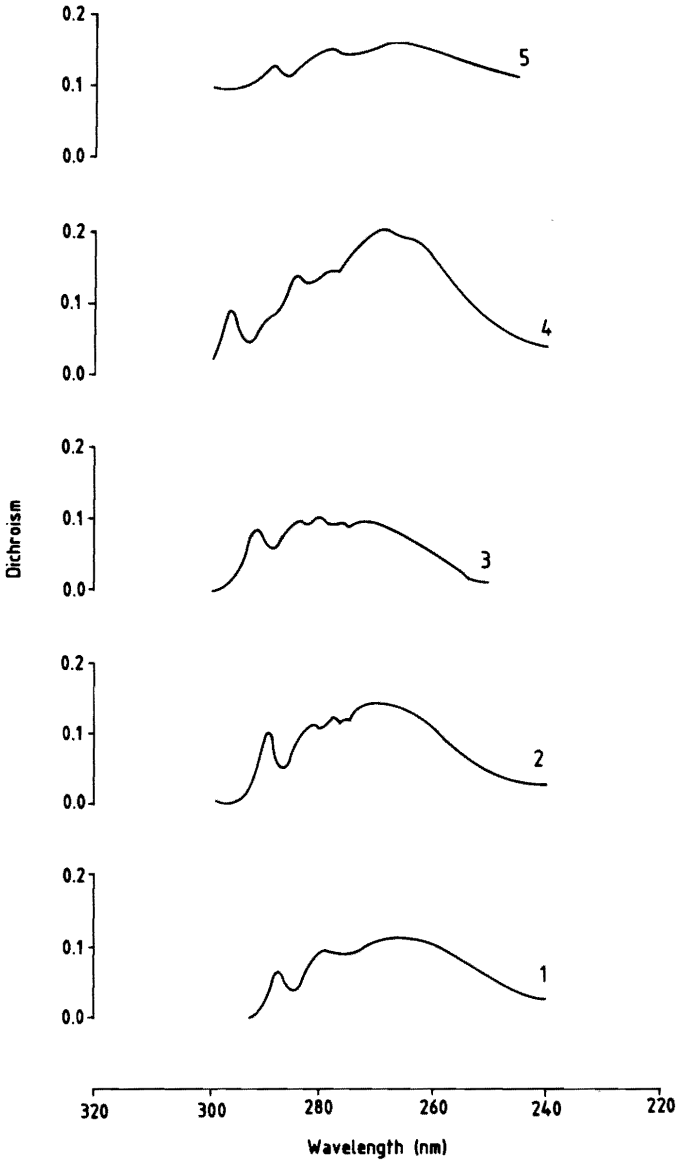

Figure 1. The LD *spectra in PE. (1) Indole; (2) 2-Methylindole; (3) 3-Methylindole; (4) 5-Methylindole; (5) 7-Methylindole.*

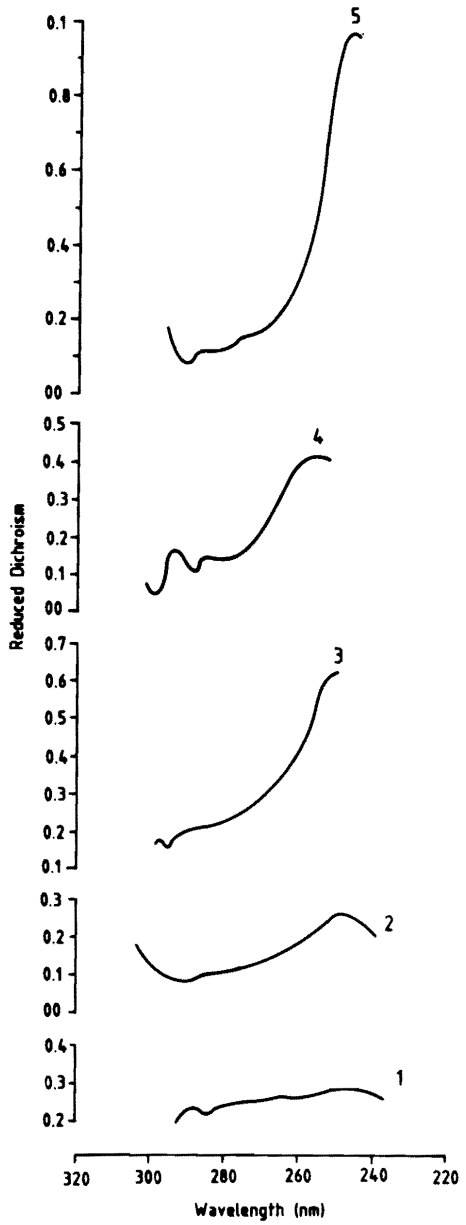

Figure 2. The LD_r *spectra in PVA. (1) Indole; (2) 2-Methylindole; (3) 3-Propionic Acid Indole; (4) 5-Methylindole; (5) 7-Methylindole.*

orienting power (O.P.) in PE and PVA are presented in Table 1. 3-propionic acid indole was used in PVA because the solubility of the 3-methylindole in PVA was very low (less than 0.001 mole/liter). The solubility of 3-propionic acid indole in PE is also very low. The O.P. is a measure of the degree of orientation of the solute molecules in the polymer matrix. The unsubstituted solute molecule will be oriented with a certain molecular axis parallel to the direction of stretch. If, upon substitution, the O.P. decreases then this means the orientation is becoming more effective in the perpendicular direction. When the O.P. increases upon substitution then this means that the orientation in the same direction is enhanced. The orienting power in PE shows that maximum orientation is obtained in the case of the 5-methylindole and minimum for the 7-methylindole with a gradual change as the position of the substituent is moved. This is a clear indication that these indoles are oriented with the longest molecular axis in the direction of stretch. In contrast, the orienting power in PVA is maximum for the 7-methylindole with the minimum for the 2-methylindole; an indication for a short axis orientation. The fact that indole is oriented with its longest

Table 1. Orientation Parameters and Orienting Power in PE and PVA

SOLUTE	PE			PVA		
	S_{zz}	S_{yy}	O.P.	S_{zz}	S_{yy}	O.P.
Indole	0.133	0.112	0.492	0.100	0.065	0.331
2-Methylindole	0.196	0.032	0.455	0.115	0.020	0.269
3-Methylindole	0.215	0.007	0.443	—	—	—
3-Propionic acid indole	—	—	—	0.250	0.032	0.565
5-Methylindole	0.228	0.130	0.717	0.152	0.020	0.344
7-Methylindole	0.091	0.064	0.310	0.449	0.017	0.899

axis parallel to the direction of stretch is the normal behavior [8]. However, the result of short axis orientation in PVA is unexpected because solute molecules are usually oriented with their longest axis parallel to the direction of stretch. Our results which show anamolous orientation behavior of indole in PVA are in agreement with the findings of other research groups [9, 10].

The difference in behavior between the two polymers might be due to the existence of hydrogen bonding between the indoles and the PVA chains.

This result shows very clearly that the shape of the solute molecule cannot be used alone to describe the orientation in different polymers. It also shows that the nature of the solvent polymer matrix plays an important role in determining the orientation of the solute molecules. Interactions between the polymer matrix and the solute molecules such as hydrogen bonding or the polymer chain conformation [5] might alter the orientation behavior from that otherwise expected.

REFERENCES

[1] K. R. Popov, "Dichroism of the Absorption Bands of Planar Molecules Oriented in Films of Transparent Polymers. I. Orientation Model: Derivation of General Equations", *Optical Spectroscopy,* **39** (1975), p. 142.

[2] J. Michl, E. W. Thulstrup, and J. H. Eggers, "Polarization Spectra in Stretched Polymer Sheets. III. Physical Significance of the Orientation Factors and Determination of $\pi-\pi^*$ Transition Moment Directions in Molecules of Low Symmetry", *Journal of Physical Chemistry,* **74** (1970), p. 3868.

[3] Y. Matsuoka and B. Norden, "Linear Dichroism Study of 9-Substituted Acridines in Stretched Polyvinyl Alcohol Film", *Chemical Physics Letters,* **85** (1982), p. 302.

[4] Y. Matsuoka and Yamaoka, "Film Dichroism. I. The Method of Measurement and Analyses and the Application to Polymer–Dye Systems", *Journal of Science, Hiroshima University, Series A,* **40** (1976), p. 105.

[5] A. Davidsson and B. Norden, "New Details in the Polarized Spectrum of Naphthalene by Means of Linear Dichroism Studies in Oriented Polymer Matrices", *Chemical Physics Letters,* **28** (1974), p. 221.

[6] E. W. Thulstrup, "A Critical Comparison of Methods for Analyses of Linear Dichroism of Solutes in Stretched Polymers", *Journal of Physical Chemistry,* **84** (1980), p. 82.

[7] E. W. Thulstrup and J. Michl, "Orientation and Linear Dichroism of Symmetrical Aromatic Molecules Imbedded in Stretched Polyethylene", *Journal of the American Chemical Society,* **104** (1982), p. 5594.

[8] V. N. Umetskaya and K. K. Turoverov, "Study of the Excited State of Indole. Dichroism Spectrum of Stretched Polyethylene Films Activated with Indole", *Optical Spectroscopy,* **44** (1978), p. 637.

[9] K. R. Popov, N. V. Platonva, S. I. Khorunzhina, and S. P. Maiburov, "Spectral Course of Dichroism, Direction of the Electron Transitions and Orientations of the Molecules of Indole and Tryptophan in Stretched Films of Polyvinyl Alcohol", *Biofizika,* **24** (1979), p. 565; *VINITI,* No. 647-79, 20 February 1979.

[10] I. Maki, K. Nishimoto, M. Sugiyama, H. Hiratsuka, and Y. Tanizaki, "Polarized Absorption Spectra of Indole and Benzimidazole", *Bulletin of the Chemical Society of Japan,* **54** (1981), p. 8.

Paper Received 4 November 1985; Revised 21 January 1986.