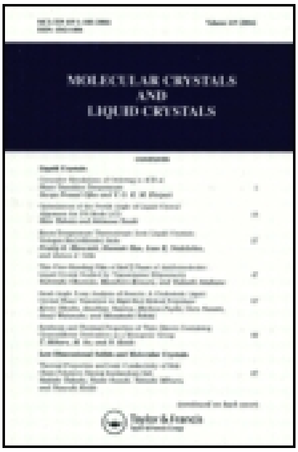

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The Influence of Anisotropic Polymeric Solids on Dopant Orientation and Reactivity: Azobenzene in Low Density Polyethylene

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THE INFLUENCE OF ANISOTROPIC POLYMERIC SOLIDS ON DOPANT ORIENTATION AND REACTIVITY: AZOBENZENE IN LOW DENSITY POLYETHYLENE.

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Abstract The conformational studies of the title compound, both trans and photogenerated cis form, were carried out in oriented polyethylene (PE) by linear dichroism (LD) method in UV/Vis and IR region. The observed orientation factors for the vibrational and electronic transition moment direction are consistent with the assumption of a rigid planar structure for trans form, whereas cis form attain globular conformation with the phenyl rings twisted perpendicular to the -N=N- plane. The trans-cis photoisomerization is also measured in polarized light with electric vector parallel and perpendicular to the uniaxially stretched polyethylene sample. Although the macroscopic stretching of the PE film altered the distribution of the site size the rate of phototransformation is faster in the stretched than in unstretched sample.

INTRODUCTION

Numerous investigations have been carried out on trans-cis photoisomerization of azobenzene molecule and its derivatives. This interest is both for fundamental questions in basic research[1,2] and for its importance in view of possible application in optical data storage systems[3]. In particular covalently linked azobenzene unit, undergoing photoisomerization, can control the orientation within the liquid-crystalline polymeric phase or induce changes between different mesophases. For example the change in orientation of a functional part of a photoresponsive polymer is possible because the photochromic unit is immobilized in a matrix that has macroscopic order. So that the change of dye orientation may induce a change in optical properties such as linear dichroism[4].

On the other hand, molecular conformation of azobenzene isomers as well as the mechanism for trans-cis isomerization are still a matter of debated problem in the field of matrix-dependent photophysical and photochemical processes[5]. trans-Azobenzene (t-Ab) and cis-azobenzene (c-Ab) can belong to point group C_{2h}, C_2 or C_i depending on the phenyl twisting angle. Also two basic mechanism for isomerization are considered viz. rotation or inversion with respect the azo linkage. In the present paper we wish to summarize the results of our studies on orientation of photochromic azobenzene molecules in anisotropic polyethylene (PE). This problem is important because these photochromes embedded in polymers are often used for determination of local mobility and heterogeneity of polymeric systems[6].

EXPERIMENTAL

Samples used for this study were sheets of low density polyethylene. Uniaxially oriented films had draw ratios $\lambda=8$ (strained samples at constant elongation) or $\lambda=6$ (stretching tension was released). Azobenzene was introduced into the PE matrix by sublimation at room temperature. Preparation of oriented PE/Ab samples is described in detail in our previous papers[7,8]. IR and UV/VIS LD-spectra were recorded at room temperature on a spectrophotometers equipped with polarizes. We recorded two separate dichroic absorption spectra of the dopant molecules. In the first case the electric vector of linearly polarized analyzing light was parallel ($E_Z(\tilde{\nu})$) to the stretching direction Z of the PE samples and in the second case it was perpendicular ($E_Y(\tilde{\nu})$) to Z. Kinetic measurements of trans-cis photoisomerization were carried out using 337 nm nonpolarized nitrogen laser light. Changes in absorbance as a function of time irradiation were recorded for components parallel and perpendicular to the stretch direction Z.

RESULTS AND DISCUSSION

The polarized IR and UV/VIS spectra $E_Z(\tilde{\nu})$ and $E_Y(\tilde{\nu})$ of t-Ab before (pure trans-) and after illumination at photo-equilibrium (mixture of cis- and trans- content) in stretched PE sheet are shown in FIG. 1 and FIG. 2. These absorbance spectra demonstrate that the alignment of t-Ab is much better than that of the globular cis form.

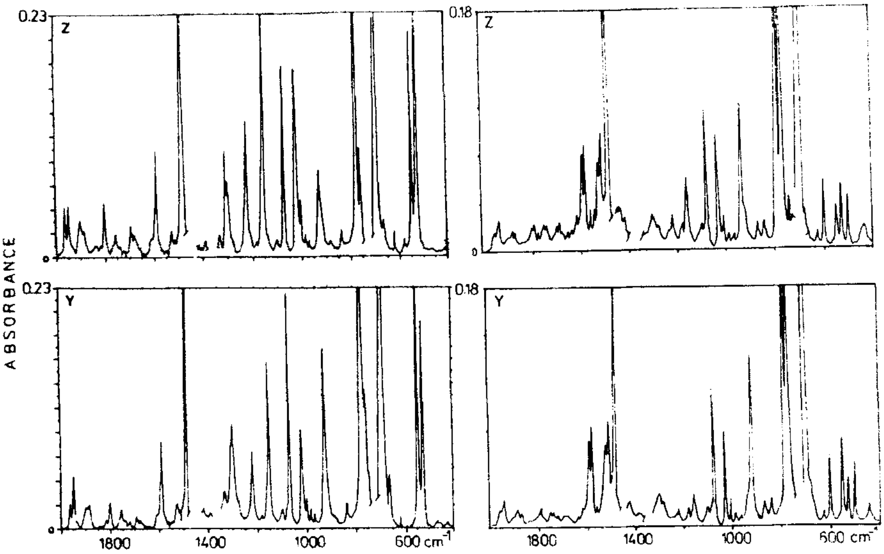

FIGURE 1 Dichroic FT-IR spectra of t-Ab (left) and the mixture of trans and cis contents after illumination at photo-equilibrium (right) in oriented PE.

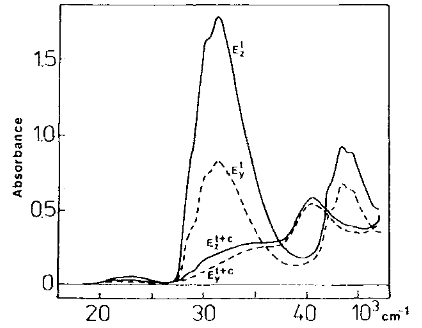

FIGURE 2 Dichroic UV/VIS spectra of t-Ab (E^t) before and after illumination at photo-equilibrium (E^{t+c}) in oriented PE sheet. Polarization of analyzing light was parallel (———) or perpendicular (----) to the stretch direction Z.

LD-spectroscopy provides quantitative information on molecular alignment of azobenzene molecules in stretched PE and allows conclusions concerning their molecular symmetry[9] from the measured K_f-values of spectroscopic transition moments. The orientation factor $K_f=<\cos^2(Z,\underline{M}_f)>$ is defined as the average square of the direction cosine of the transition moment $\underline{M}_f$ with respect to the macroscopic orientation direction Z of the matrix. K_f is related to the dichroic ratio $d_f = E_Z(\bar{\nu}_f)/E_Y(\bar{\nu}_f)$ through the equation $K_f = d_f/(2+d_f)$. The observed K_f values must fulfil the condition $K_x \leq K_f \leq K_z$ for any transition, both in the UV/VIS and IR regions, where $K_u (u=x,y,z)$ are orientation parameters of the orientation axes of the solute (by definition $K_z \geq K_y \geq K_x$ and $K_z + K_y + K_x = 1$). If we look at FIG.1, we can see that the peaks for t-Ab associated with out-of-plane vibration i.e. the peaks at 545, 669, 690, 774, 925 and 983 cm^{-1} have a common K_f values equal to 0.18. We are therefore led to the conclusion that t-Ab molecule is planar with C_{2h} geometry and the three orientation factors are $K_x=0.18$, $K_y=0.27$ and $K_z=0.55$.

For irradiated samples the LD spectra are the mixture of vibrations of trans and cis form and we can take into consideration the K_f values of new peaks, which have appeared in the spectrum after trans-cis photoisomerization i.e. at 495, 701, 759 cm^{-1}, with $K_f=0.29$ and at 593, 860, 1587, 1591 cm^{-1} with $K_f=0.33$. The orientation factor for the electronic $\pi\pi^*$ transition is $K_f=0.33$, for the $n\pi^*$ it is $K_f=0.37$. Now if we combine K_f values from UV/VIS and IR region we note that they add up quite accurately to unity and they can be refereed to orientation factors K_u with $K_x=0.29$, $K_y=0.33$, $K_z=0.37$. The present results suggests that we can assume a C_{2v} symmetry for c-Ab with nonplanar geometry rather.

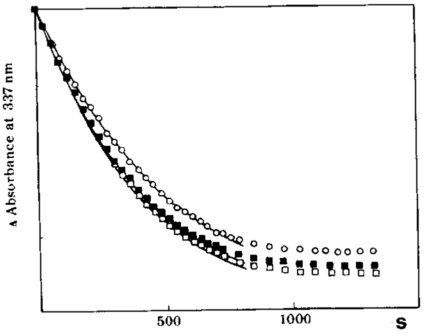

FIGURE 3 Changes of absorbance at 337 nm due to the irradiation of t-Ab in unoriented (○) and in stretched PE. Electric vector of analyzing light parallel (□) or perpendicular (■) to the stretching direction Z.

The dichroic spectra of the mixture of both isomers give also information on the extent of photoisomerization of azobenzene in stretched PE matrix. It equals to 95% for molecules both oriented parallel and perpendicular to the stretching. FIG. 3 shows kinetic data of trans-cis photoisomerization at 337 nm of unstretched sample, stretched to λ=6 and strained sample at constant elongation. The analysis of the kinetics data reveals that photoisomerization process is purely exponential vs. time up to 83% conversion and than it deviates from first order kinetics. TABLE I collects the kinetic constants and trans fraction at photo-equilibrium measured with light polarization parallel or perpendicular to the stretch direction Z and alignment (dichroic ratio d) for specimens being studied here.

TABLE I The dichroic ratios (d) for t-Ab at 337 nm, first order kinetic constants (k) and trans fraction content (t) at photoequilibrium in PE measured parallel (Z) and perpendicular (Y) to the stretch direction Z.

matrix	d	k_Z[1/s]	k_Y[1/s]	t_Z	t_Y
unoriented	1.0	0.00193	0.00193	0.175	0.175
stretched λ=6	2.5	0.00249	0.00231	0.105	0.146
strained λ=8	3.45	0.00218	0.00197	0.105	0.146

The presented data show that the magnitudes of kinetic constants k_Z and k_Y are not affected by stretching while d is affected significantly. It may therefore be inferred that the transformation of azobenzene molecules is not influenced by stretching and their orientation is affected significantly. When the polymer is stretched to λ=6 the kinetic become a little faster and the extent of photoisomerization decrease. Further stretching caused very small opposite effect. We can therefore state that for the oriented PE the photoisomerization is not affected by the presence of the applied stress. The most striking observation is the small change of equilibrium trans-cis izomerization as a function of stretching and the lack of significant changes in k associated with molecules oriented parallel (k_Z) or perpendicular (k_Y) to deformation. It appears that in oriented PE there is more room for isomerization than in nonoriented one. Probably there is a difference between solubilization sites for molecules before and after stretching of the matrix.

A similar studies for molecules that show reversible photochromic reaction in unstretched and stretched PE has been made by us earlier[10]. Also the kinetic of the thermally induced decay a merocyanine form of spiropyran reveals that decoloration process is a little faster in oriented PE sample. Our results are also consistent with the measurements of the activation energy for diffusion of dopant molecules[11]. It also changes a little with a stretching of PE.

CONCLUSIONS

Results for t-Ab is consistent with the assumption of a planar C_{2h} geometry while the results for c-Ab suggests the C_{2v} symmetry with the phenyl rings twisted perpendicular to the plane determined by the -N=N- . The rate of trans-cis photoisomerization is scarcely affected by the stretching. The data indicates that although trapping sites are anisotropic in shape and show an orientation they not provide anisotropy for isomerization of azobenzene molecules.

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