

Photochromism of 6-nitrospiropyran in oriented polyethylene

P. Uznański and M. Kryszewski*

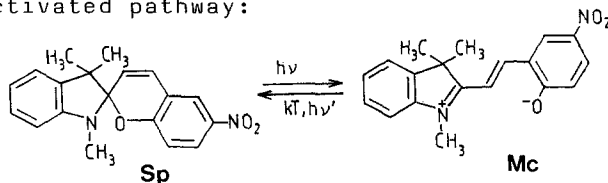
Center of Molecular and Macromolecular Studies, Polish Academy of Science, Sienkiewicza 112, PL-90-363 Łódź, Poland

SUMMARY

UV-VIS and IR dichroism spectra of 1',3',3'-trimethyl-6-nitrospiro(2H-1-benzopyran-2,2'-indoline) (6-NSP) dispersed in stretched low density poly(ethylene) (PE) films are reported. Also the kinetics of the thermally induced decay of merocyanine (Mc) form of 6-NSP was investigated in both nonoriented and oriented samples using polarized light. The analysis of experimental data reveals that decoloration process is faster in the stretched than in the nonstretched matrix. This is opposite to the photochromic phenomena occurring in stretched rubbers when the chromophores are bound chemically to the polymer.

INTRODUCTION

The phenomenon of orientation of small molecules in polymeric matrices is used in the investigation of electronic and infrared spectra of a wide group of compounds for a years (1). Their behavior and a role in semicrystalline polymers has received considerable attention also from a physical viewpoint to detect structural changes or to affect the macroproperties of the matrix. If such molecules show reversible photoisomerization reaction, they can provide a complementary technique to the studies using dielectric relaxation or electron spin resonance probes (2,3). Photochromes can be used as the probes of polymer behavior both on the scale of their molecular size and the relaxation times which extends over many orders of magnitude. One class of photochromic compounds which afforded strong photochromic effect are spiroyrans derivatives. They undergo under ultraviolet irradiation a ring opening reaction with production of strongly colored merocyanine, which can return to the colorless spiropyran in thermally or photochemically activated pathway:



In polymeric matrix, below the glass transition temperature

*To whom offprint requests should be sent

one observes a strong decrease quantum yield and a modified photostationary equilibrium of this reaction. The matrix rigidity may influence the thermal reverse reaction especially when the chromophores are bound chemically to the polymer. In this case photochromism is indeed related with the reduction of chain segment mobility. For example in stretched photochromic rubbers decoloration rate depends on their molar volume, the physical properties of the matrix and on the direction of the polarized light with respect to the stretch orientation (4). From the other hand orientation of the semicrystalline polyethylene matrix has an opposite effect on photoisomerization of molecularly dispersed azobenzene: the kinetics are faster in the stretched than in the nonstretched sample (5).

In the present paper we wish to report some spectroscopic and kinetic studies in order to learn more about the oriented environment of photochromic molecules. The research is based on earlier studies of the photochromic relaxation behavior of azobenzene molecules dissolved in low density polyethylene (5). The studies attempts to give an answer how a decay of M_c is influenced by orientation of the polymer. To our knowledge, similar studies on the response of free photochromic molecules to the orientation of the polymeric medium has not been reported in the literature.

EXPERIMENTAL

Sample preparation.

1',3',3'-trimethyl-6-nitrospiro(2H-1-benzopyran-2,2'-indoline) (6-NSP) was introduced into the low density poly(ethylene) (PE) (Lupolen 1800S, BASF) by dipping in a concentrated chloroform solution at room temperature. Evaporation of the solvent was carried out in a chamber at 35 °C under condition flow argon. Thin films were prepared by press molding at 130 °C and cooling the polymer melt in water-ice bath to diminish spherulites growth in the polymer and to improve the optical quality. The supermolecular structure formed in the samples has been characterized by values of crystallinity (43.2%), long period (103 Å) and volume average spherulite radius (1.83 μm). The PE films were oriented on an Instron tensile machine at a drawing rate of 5cm/min.

Absorption and kinetic measurements.

The samples were excited at 365 nm with HBO 50 high pressure mercury lamp as UV source equipped with Wood filter transmitting light from 300 to 410 nm. Specimens were irradiated to photoequilibrium for 15 s. The ultraviolet-visible dichroism spectra of dyed samples were measured on a Shimadzu MPS-2000 spectrophotometer equipped with a Glan-Thomson prism. The polarized infrared spectra were measured using Perkin Elmer 1700 FTIR instrument, equipped with a wire grid polarizer. In the oriented samples containing spiropyran the solute molecules tend to be aligned with their long axes parallel to the direction of the orientation. Thus two linearly independent spectra named $E_z(\bar{\nu})$ and $E_y(\bar{\nu})$, respectively, were recorded. The orientation distribution for the nonoriented samples is isotropic. All spectra recorded were corrected for PE absorption. Absorption measurements and kinetics runs of

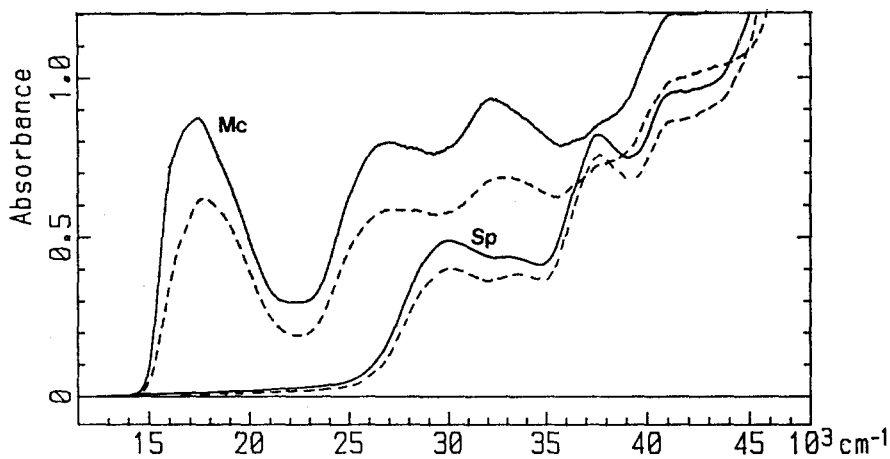


Fig.1 UV-VIS linear dichroism spectra of Sp and Mc form of 6-nitro-spiropyran in stretched PE. Polarization of the analyzing light was parallel (solid line) and perpendicular (broken line) to the stretching direction.

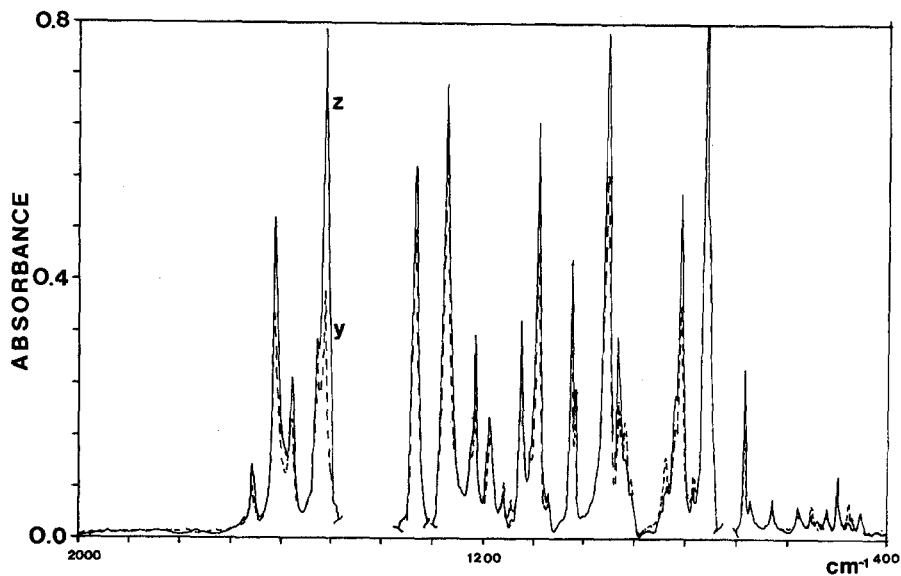


Fig.2 Polarized Fourier-transform IR spectra of 6-nitrospiropyran in oriented PE. The light polarization was parallel (Z) or perpendicular (Y) to the stretching direction.

thermal back reaction of 6-NSP were performed at ambient temperature.

RESULTS AND DISCUSSION

The polarized UV-VIS spectra $E_z(\bar{\nu})$ and $E_y(\bar{\nu})$ of parent spiropyran (Sp) and merocyanine (Mc) form of 6-NSP in stretched PE are shown in Fig.1. The dichroic spectra demonstrated that alignment of Sp isomer is small and much lower than that of colored Mc form. Thus the information obtained from UV spectra did not allow determination of the long orientation axis of the Sp molecule. More pronounced changes are observed in the IR region (see Fig.2). The peak at $\bar{\nu}_f = 1511 \text{ cm}^{-1}$ with the largest dichroic ratio $d=2.1$ ($d=E_z/E_y$) is connected with $C_{ar}-NO_2$ stretching and is higher than for absorption band of the Mc isomer ($d=1.43$ at 18.0 kK at $t=0$). We conclude that the long orientation axis of Sp isomer is parallel to the stretching vibration of NO_2 group and its alignment in oriented PE is higher than Mc isomer. The kinetics of the thermally induced ring closure reaction $Mc \rightarrow Sp$ in the uniaxially oriented PE as well as in nonoriented sample are non-exponential. They are presented in Fig.3. The plots connected with nonoriented PE samples can be fitted with a function being a sum of two exponential:

$$Mc(t)/Mc(0) = \alpha \cdot \exp(-k_1 \cdot t) + (1-\alpha) \cdot \exp(-k_2 \cdot t) \quad (1)$$

where α is the fraction of the fast process, and k_1 and k_2 the rate constants for the fast and slow processes. In oriented PE films equation 1 does not describe kinetics patterns. In these case we were succeed to fit experimental kinetic data with KWW stretched exponential function given by

$$Mc(t)/Mc(0) = \exp(-(k \cdot t)^\beta) \quad (2)$$

where β expresses the dispersion of the process i.e. the deviation from first order kinetics and k characterizes the spread of the rate coefficients of the reaction (6). The rate of photochromic isomerization measured in polarized light with the electric vector parallel to the orientation of PE matrix are slightly higher than that measured with perpendicular polarization. The narrowest distribution of relaxation times occur perpendicular to the orientation direction (higher β - values). Characteristic kinetic parameters based on equation (1) and (2) are collected in Table I.

Table I. Characteristics kinetic parameters for $Mc \rightarrow Sp$ thermal reaction in PE measured at 18.0 kK based on equations (1) and (2). In oriented matrix the electric vector of the analyzing light was parallel (||) or perpendicular (\perp) to the stretching direction or a beam was nonpolarized (\circ).

specimen	$k_1(s^{-1})$	$k_2(s^{-1})$	$k(s^{-1})$	β
nonoriented PE	$7.7 \cdot 10^{-4}$	$3.3 \cdot 10^{-3}$	-	-
oriented PE	-	-	$3.4 \cdot 10^{-3}$	0.65
oriented PE \circ	-	-	$3.0 \cdot 10^{-3}$	0.63
oriented PE \perp	-	-	$2.6 \cdot 10^{-3}$	0.70

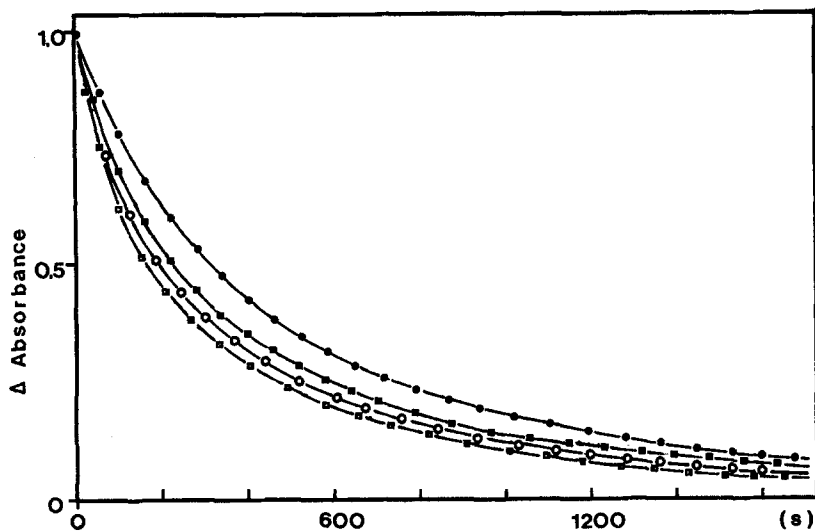


Fig.3 The representative normalized plots for Mc \rightarrow Sp thermal decoloration of 6-NSP in nonoriented (\bullet) and in oriented PE. The analyzing light was nonpolarized (\circ) and polarized parallel (\square) or perpendicular (\blacksquare) to the stretching direction.

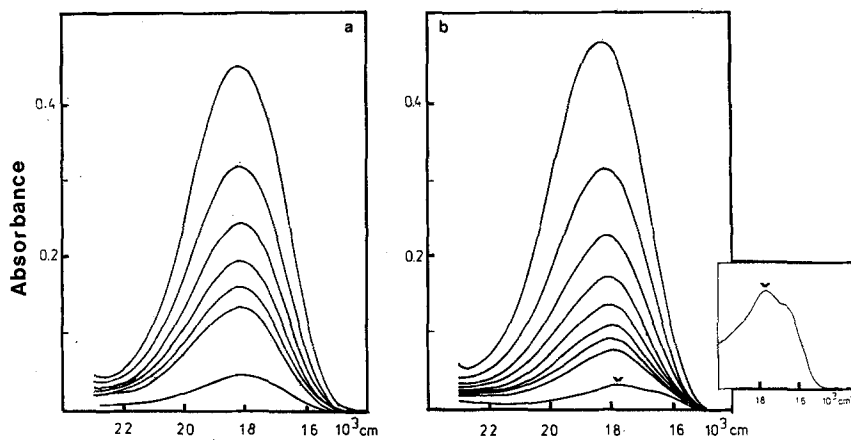


Fig.4 Spectral changes of Mc isomer as a function of time in oriented (a) and (b) nonoriented PE.

The results of kinetic studies can be correlated with the changes in absorption spectra of merocyanine form as a function of time (see Fig.4). One can note that the shape and position of the absorption band in oriented samples is the same as the decoloration proceeded. In nonoriented films, the maximum of the absorption band shifted from 18.2 kK at the beginning of the process to 17.5 kK. These data clearly indicate that the behavior of Mc form should be results from the appearance of several trans-species of Mc with different absorption maxima.

In nonoriented PE there are three potential sites for location of solutes: in amorphous phase, on a lateral and on a folded surface of the crystal. Yielding process transforms the morphology, based on spherulite lamellae, into microfibrils and gives rise to an additional potential location in the interfibrillar amorphous phase. In spherulitic low-density PE the Mc conformers can be in different equilibria due to interaction with different sites available within the amorphous phase. Orientation induced by stretching, produces only a "cages" in which relaxation of Mc form manifests itself by continuous bleaching of absorption band with maximum at 18.2 kK. This may be a reflection of one type of Mc transient species involved to photochromic process. The influence of stretching the polymer matrix on the decoloration process of molecularly dispersed photochromic molecules has an opposite effect as in the case of photochromic rubbers where orientation suppress color fading (4).

The kinetic data for PE samples are not so strongly affected by stretching. It is the same situation as in the case of azobenzene molecules where trans \rightarrow cis photoisomerization is slightly influenced by stretching while their orientation is affected significantly (5). This can provide strong evidence that oriented solubilization sites do not prevent the transformation. Therefore it would appears that aromatic molecules are located in a fairly "roomy" environments. Alternatively, faster rate of thermal ring closure reaction of 6-NSP in oriented PE films than the rates in original nonstretched samples might reflect the existence of some portion of Mc isomers in strain conformation. This observation may correspond to previous results on anomalous behavior of azobenzene cis \rightarrow trans transformation in amorphous polycarbonate (7). It is not possible to distinguish between these two mechanism at the present time.

CONCLUSION

No attempt has been made to generate a model of the mechanism of orientation quest molecules in polyethylene; rather we have been content to discuss only some aspects of behavior of photochromes. It is clear, that the introduced molecules are placed in different environments depending on the morphology of the matrix. It appears that in oriented polyethylene there is more room for reorganization of photochromes than in nonoriented one. It can be another explanation: a strained PE environment produces unstable configurations of

Mc isomer which relax faster than more stable configurations present in nonoriented state. The phenomenon of orientation of small molecules in semicrystalline PE matrix and its influence on relaxation of embedded molecules is fascinating but it still remains a matter for more extensive investigations.

ACKNOWLEDGEMENT

This work was supported by CPBP 01.19 Project. We are grateful to Dr. A.M. Wrobel for critical reading of the manuscript.

REFERENCES

1. Michl J, Thulstrup E-W (1986) "Spectroscopy with polarized light. Solute Alignment by Photoselection in Liquid Crystals, Polymers and Membranes". VCH Publishers, Deerfield Beach, Fl.
2. Jang Y-T, Phillips P-J (1986) J. Polym. Sci. Polym. Phys. Ed. 24: 1259.
3. Parikh D, Phillips P-J, Jang Y-T (1989) J. Polym. Sci. Polym. Phys. Ed. 27: 1333
4. Smets G (1983) Adv. in Polymer Sci. 50: 17
5. Uznanski P, Kryszewski M, Thulstrup E-W (1991) Eur. Polym. J. 27: 41
6. Uznanski P, Kryszewski M (1990) Eur. Polym. J. 26: 141
7. Mita I, Horie K, Hirao K (1989) Macromolecules 22: 558

Accepted April 2, 1991 C