PHOTOCHROMISM OF NITRO-SUBSTITUTED SPIRONAPHTHOXAZINES
IN POLYMER FILMS


The photochromic properties of nitro-substituted spironaphthoxazines in polymer matrices of different polarity were investigated and the quantum yields of photocoloration and parameters of the dark decolorization reaction, which is a disperse process, were determined. The features of the behavior of the nitro-substituted spironaphthoxazines are determined by the more efficient reaction of the photoinduced form with the medium, which is the consequence of stabilization of the bipolar structure of the molecule of the colored form.

A new class of photochromic compounds, spironaphthoxazines (SNO), is drawing attention due to their significantly higher photostability in comparison to the well studied spirobenzopyrans (SBP) and the prospects for creation of practically important photochromic polymer materials based on them. However, the existing studies [1-5] basically concern the simplest SNO: 1',3',3'-trimethylspiro[indoline-2',3-H-naphtho[2,1-b][1,4]-oxazine] (SNO-1) and have not touched upon the study of the effect of substituents on the photochromic properties of SNO.

The effect of the NO$_2$ electron-acceptor group incorporated in different positions of SNO-1 on the photochromic properties of polymer films activated by these nitro compounds which have the following structural formula was investigated in the present study.

\[
\begin{align*}
\text{R}^1 &= \text{NO}_2, & \text{R}^4 &= \text{H(CHO-2)}; \\
\text{R}^6 &= \text{H, R}^8 &= \text{NO}_2(\text{CHO-3}).
\end{align*}
\]

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0568-5230/90/3903-0471$12.50 © 1990 Plenum Publishing Corporation
Experimental

Synthesis and purification of SNO-2 and SNO-3 were conducted according to [6] and SNO-1 was synthesized and purified according to [3]. Polyvinyl butyral (PVB), polystyrene (PS), and polymethyl methacrylate (PMMA) were used as the polymer matrices. The films were prepared by pouring a combined solution of the photochromic compound and polymer with subsequent evaporation of the solvent and vacuum drying of the films. The concentration of SNO was 1% of the weight of the polymer. The films were 30-60 µm thick. Samples of the films were irradiated with the light from a DKSSSh-200 lamp through an interference light filter with 365 nm transmission. The intensity of the exciting light measured with 2,6-di-tert-butyl-1,4-benzoquinone diazide was \((3.7-4.8) \times 10^{-6}\) einstein/(cm\(^2\)·sec\(^{-1}\)). The absorption spectra and kinetics of photocoloration and dark decolorization were recorded on a Specord UV-VIS spectrophotometer in thermostated film holders. The measurements were made in the 14-40°C region.

Results and Discussion

The polymer films containing SNO-2 and SNO-3 intensely color under the effect of UV light. The absorption spectra of the initial (A) and photoinduced (B) forms of SNO-2 and SNO-3 in a PS matrix are shown in Fig. 1. The positions of the maxima of the long-wave bands \(\lambda_{max}^B\) for forms B in different polymer matrices are reported in Table 1. The quantum yields of photocoloration, determined with the initial slope of the curve of the increase in the optical density D in recording at the wavelength \(\lambda_{max}^B\) with the following equation are shown here

\[
\varphi_B = \frac{\Delta D}{\Delta t} (t \to 0)/\varepsilon_B I_0 (1 - 10^{-D_{365}})
\]

\(\varepsilon_B\) is the extinction coefficient of form B, \(I_0\) is the intensity of the exciting light, and \(D_{365}\) is the optical density of the sample at the wavelength of 365 nm.

The \(\varepsilon_B\) for SNO-2 and SNO-3 were determined with the absorption spectrum of form B in propanol at \(-75^\circ C\), since the reverse reaction B \(\to\) A does not take place at this temperature either thermally or under the effect of light. A similar approach was used in [1] for SNO-1. In addition, it was shown in [7] that for nitro-substituted SBP, photodecolorization of the color form is also absent at low temperatures. Values of \(\varepsilon_B = 2.8 \times 10^4\) and \(5.0 \times 10^4\) liter/(mole·cm) were obtained for SNO-2 and SNO-3, respectively, and they were used for calculating \(\varphi_B\) in all of the polymer matrices.

In dark conditions, the irradiated films are thermally decolorized and the kinetics of decolorization are described by the equation

\[
D(t) = ae^{-K_d} + be^{-K_d}
\]

**Fig. 1**

Absorption spectra of SNO-2 (1, 2) and SNO-3 (3, 4) in a PS matrix before (1, 3) and after (2, 4) irradiation with UV light.

**Fig. 2**

Dependences of \(D/D_0\) on ln t (1) and ln(ln(D_0/D)) on ln t (2) for decolorization of SNO-3 in PMMA at 14°C.