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KINETICS OF THE PHOTOCHROMIC REACTION IN A POLYMER CONTAINING AZOBENZENE GROUPS

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Thermal *trans-cis* isomerization of photochromic 4-[4-(6-hydroxy-hexyloxy)phenylazo] benzonitrile chromophore copolymerised with methylmethacrylate was investigated by isothermal kinetic measurements. A non-exponential relaxation in the solid phase was found, related to a distribution of the constants of the process, while the relaxation in solution followed an exponential decay. The activation energy E_a = 89 kJ/mol and frequency factor $\nu_0 = 1 \times 10^{11}$ Hz were determined from the experimental data.

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1. Introduction

Photochromic materials have potential applications in optoelectonics as optical storage media, holographic diffraction gratings and optical switches. They are also promising materials for 'smart' windows and information display panels. Among them, azobenzene-containing side chain polymers (ASCPs) have been recently investigated due to their low cost, easy processing and environmentally friendly behaviour. It has been reported [1, 2] that a surface relieved grating in ASCP thin films could be formed by laser irradiation.

When ASCP is exposed to UV light with a specific wavelength, an anisotropic *trans-cis* isomerization occurs. It is associated with orientational redistributution of side group chromophores [1]. This results in a change in the absorption spectrum. The initial state can be recovered thermally, or by exposure with light of another wavelength.

In this work, we present the results of optical measurements of the kinetic process of the *trans-cis* isomerization of ASCP. A novel derivative method consisting of data processing based on cubic splines is utilized.

2. Outline of the theory

The isomerization of azobenzene and its derivatives in solutions is known to follow the first-order kinetics, with the rate constant k_R obeying the Arrhenius equation:

$$k_R = \nu_0 \exp\left(\frac{E_a}{RT}\right), \tag{1}$$

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where ν_0 is a frequency factor, E_a is the activation energy, R is the universal gas constant and T is the temperature. However, the kinetics of the *cis* (R - reactant) to *trans* (P - product) relaxation:

$$R \overset{k_R(E)}{\rightarrow} P \tag{2}$$

in azobenzene containing polymers often differs from the first order process. This feature can be attributed to a distribution of the rate constants $k_R = k_R(E)$ in energy, associated with a distribution of microenvironments of reacting species [3, 4]. Thus, the momentary concentration of the reacting species $n_R(t)$ can be obtained from a modified first order kinetic equation:

$$n_R(t) = \int n_R(0,E)\exp(-k_R(E)t)dE \,. \tag{3}$$

The isomerization kinetics can be investigated by monitoring the absorbance of the *trans* form of azobenzene [5]. For a 'standard' first-order kinetics, the following equation is fulfilled:

$$\frac{t}{\tau} = -\ln\left(\frac{n_R(t)}{n_R(0)}\right) = -\ln\left(\frac{A(\infty)-A(t)}{A(\infty)-A(0)}\right). \tag{4}$$

Here, the time-constant (τ) is defined as $\tau = k_R^{-1}$, $A(0)$, $A(t)$ and $A(\infty)$ are the initial, momentary and final values of the absorbance, respectively. Sometime it is difficult to determine $A(\infty)$, especially in the case of long time relaxation processes where an instability in the measurement could play an essential role, and in the case of some UV degradation of the material. To overcome the problem, a derivative method has been introduced [6]. Upon differentiating Eq. (1) one gets:

$$\frac{t}{\tau} \propto \ln\frac{dn}{dt} \propto \ln\frac{dA}{dt} \,. \tag{5}$$

Both methods (Eq. (4) and Eq. (5)) give similar results for τ.

3. Experimental details

The 4-[4-(6- hydroxy-hexyloxy) phenylazo] benzonitrile chromophore monomer was polymerized by a radical reaction with methylmethacrylate in dioxane solution. The formula of the obtained copolymer (denoted here as PB-MMA) with a concentration of the chromophore of 23 mol% is shown in Fig. 1.

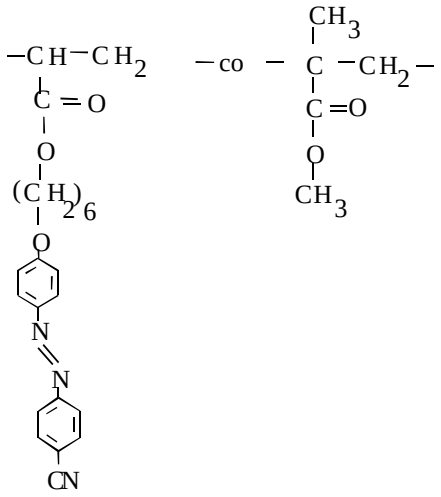

Fig. 1. Chemical formula of the azobenzene-containing polymer studied in this work.

Solid films were deposited from chloroform solution by spin-coating (at 1100 rpm) onto quartz substrates. Another set of experiments was carried out on PB-MMA dioxane solution.

The measurements of UV-VIS absorption spectra and the kinetics were performed with a Perkin Elmer Lambda 950 spectrophotometer. The samples were irradiated for 1 min with UV light (a mercury lamp, combined with appropriate band and thermal filters). The *cis-trans* relaxation was monitored as the absorption changes at 360 nm as the function of time at different temperatures in the range of 303 - 323 K.

Before the derivative calculations at least the second order polynomial interpolation was applied to reduce noise. For the data smoothing and derivative calculation the method of cubic splines was used. τ was determined from the plots $t \times n(t)$ vs. ln t or $t \times |dn/dt|$ vs. ln t. It was demonstrated [6], that the maximum of the resulting bell-shaped curve appears at $t_{max} = \tau$. Finally E_a and ν_0 were calculated from the slope and intercept of the Arrhenius plot (Eq. (1)).

4. Results and discussion

In Fig. 2a, the absorption spectra of PB-MMA before (Curve 1) and after the UV irradiation (Curve 2) are presented. The *cis* to *trans* relaxation as a function of the time is plotted in Fig. 2b, Squares 1. The maximum of the t x dA/dt vs. ln t dependence was determined after the second order polynomial fit (Curve 3) and after the smoothing by cubic splines (Curve 4).

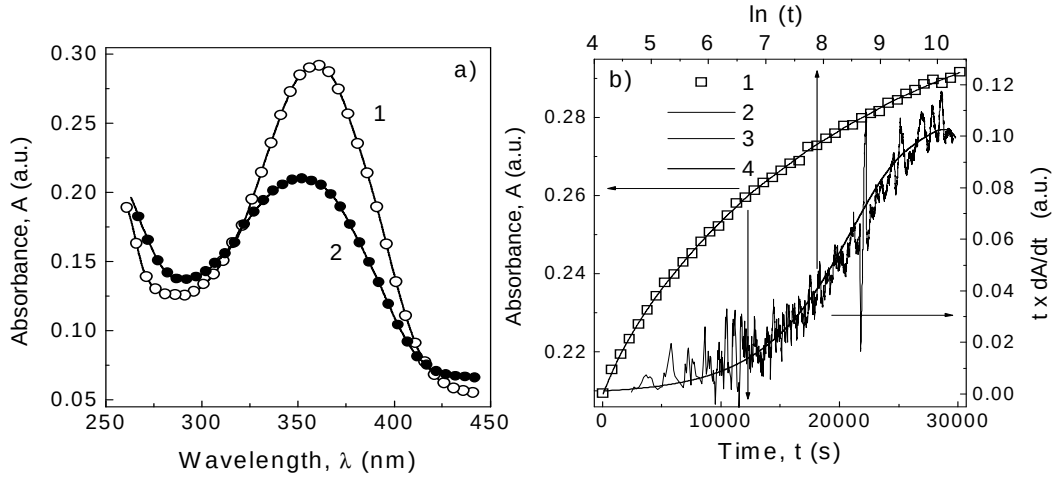

Fig. 2. a) – Absorption spectra of a PB-MMA film before (1) and after (2) UV irradiation; b) – relaxation curve - measured absorbance (Squares 1) and spline fitting (Curve 2); t x dA/dt vs. ln t calculated after the second order polynomial fit (Scattered curve 3) and smoothed by cubic splines (Curve 4).

The normalized ratios $[n_R(t)/n_R(0)]$ calculated by Eq. (4) for different temperatures are shown in Fig. 3a for a solid sample and in Fig. 3b for a PB-MMA solution. The relaxation curves of the solid samples differ from straight lines which indicates a distribution of the rate constants in energy. The straight lines obtained from the solution measurement suggest a pure first-order process. Similar shapes of the curves were obtained using the derivative method (Eq. (5)).

After the calculations of the concentrations by Eqs. (4) and (5), τ was determined from the $t \times n(t)$ vs. ln t and $t \times |dn/dt|$ vs. ln t dependencies. The temperature dependencies of τ calculated from the results for the solid state and solution are plotted in Figs. 4a and 4b, respectively. All dependencies could be well fitted by straight lines; thus E_a and ν_0 could be determined. The data were processed by the standard procedure (circles) and by the derivative method (squares). For the solid state case, both methods yielded similar results. For solutions, both methods gave the same E_a values but different values of ν_0. The values E_a and ν_0 are close for the solid state and solution.

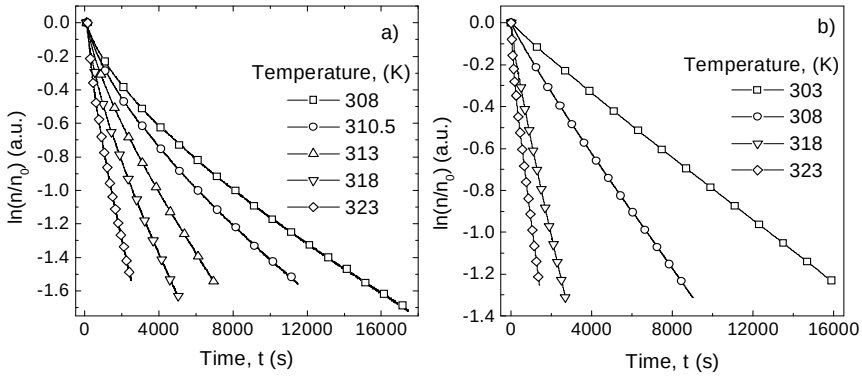

Fig. 3. Kinetics of the thermal isomerization of PB-MMA in: a) – the solid state, b) - solution in dioxane.

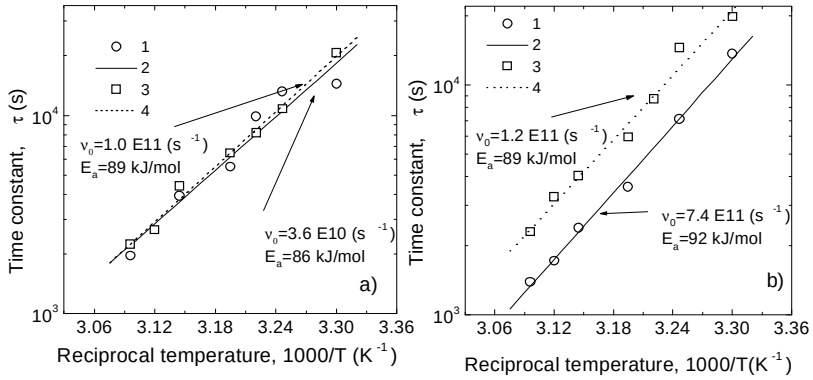

Fig. 4. Temperature dependencies of the time constant of the *cis-trans* relaxation process in PB-MMA: a) – in the solid state, b) – in solution; Circles 1 – data calculated by the standard (Eq. (4)) and Squares 3 – by the derivative (Eq. (5)) methods; Lines 2 and 4 are the corresponding linear fits to the data.

5. Conclusions

The measurement of the *cis-trans* relaxation in solid PB-MMA show a distribution of the rate constants, while the relaxation process in solution follows the pure first order kinetics. The typical values of the activation energy and frequency factor are E_a = 90 kJ/mol and $\nu_0 = 5 \times 10^{11}$ s^{-1}.

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