Thermal *Cis–Trans* Isomerization of Azo Dyes in Poly(methyl methacrylate) Matrix: A Kinetic Study

Azo dyes when irradiated by visible light undergo *trans–cis* isomerization, after which the *cis* form reverts progressively to the thermodynamically more stable *trans* isomer following a photochemical or thermal path.[1–5] For a given dye, the *cis–trans* isomerization proceeds in different ways depending on the nature of the medium in which the reaction occurs. Thus, in solution as well as in molten or rubber polymers, the process follows a simple first-order kinetics; conversely, in polymeric matrices below the glass-transition temperature (T_g), the kinetics of the reaction is characterized by the occurrence of a multiplicity of simultaneous first-order processes. A decrease of the free volume extent in the amorphous regions of glassy polymeric matrices results in a lowering of the rate coefficients of the isomerization. On the other hand, no significant kinetic modifications appear to occur when the crystallinity of the sample is varied.

INTRODUCTION

The above behaviours were observed in our previous works by considering, as media, various solvents,[4–6] fluid polyethylenoxides,[7] solid poly(ethylene terephthalate),[8–10] isotactic polypropylene,[11] and polycaprolactam,[12] variously dyed. With regard to solid matrices, we used oriented and unoriented films prepared by stretching, as well as films with different degrees of crystallinity prepared by appropriate thermal treatments. As a result, the *cis–trans* isomerization of a dye coloring a given polymeric matrix proved to be a useful probe for characterizing the morphological features of such a medium.

To further confirm this capacity, in the present work we have performed a kinetic study of the *cis–trans* isomerization of two azo dyes in films of poly(methyl methacrylate) (PMMA), a completely amorphous polymer, in a temperature range below its T_g value.

EXPERIMENTAL

Materials

The azobenzene derivatives were kindly supplied by ACNA S.p.A. and purified by repeated crystallizations from 1-butanol. PMMA was a BDH product with a molecular weight of 116,000. It was a completely amorphous unoriented polymer with a T_g value of 116°C. This value was determined from differential scanning calorimetry data obtained with a Perkin–Elmer DSC-4.

The polymer films were prepared by solution casting from chloroform and drying under vacuum at 70°C for 24 h. To check the complete removal of the residual solvent, all the samples were examined by head space gas chromatography.

To dye the film samples of PMMA, the technique of sublimation transfer printing had to be used because dye uptake in water does not occur with this polymer. The dyes under investigation can sublimate and transfer into PMMA at 175–185°C.

The amount of the dye transferred into the film was evaluated from absorbance measurements. Film dye concentrations were chosen to obtain absorbances near one for isomerization measurements.

Measurements

The dyed polymer films, as described under Materials, were sandwiched between two quartz plates and exposed for 10 min in a thermostated compartment to the light of a 100 W tungsten lamp, a time long enough to reach a photostationary state. After irradiation, the film was quickly introduced into the cell compartment of a Cary 118 spectrophotometer thermostated at the same temperature of the irradiation. The thermal return was monitored as the change in absorbance (Abs) at a wavelength corresponding to the absorption maximum of the *trans* isomer.

RESULTS AND DISCUSSION

Two derivatives (I) and (II) were used:

$$X-\langle\bigcirc\rangle-N{=}N-\langle\bigcirc\rangle-N(C_2H_5)_2$$
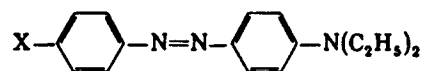
(I) X = OCH_3 and (II) X = CN. These compounds were used in dyeing the film of PMMA described in the experimental section.

The thermal *cis-trans* isomerizations of azo dyes (I) and (II) in the polymer film were kinetically followed in the temperature range 35–65°C, obtaining the time courses depicted in Figure 1. In this figure is reported, as a function of time, the reaction conversion (y), or reaction extent, defined as:

$$y = \frac{\text{Abs}_t - \text{Abs}_0}{\text{Abs}_\infty - \text{Abs}_0} \qquad (1)$$

where Abs_t, Abs_0, and Abs_∞ are the absorbance values at time t, zero, and infinity, respectively.

The isomerization was not found to follow a simple first-order rate law. A more complex kinetic behaviour was expected because the samples were tested in a temperature range below the T_g of PMMA. This is in line with our previous results[8-10] and with those of other authors in different polymeric matrices coloured with azo-compounds.[13-15] Paik and Morawetz[13] explained such a complexity as deriving from the unequal microenviron-
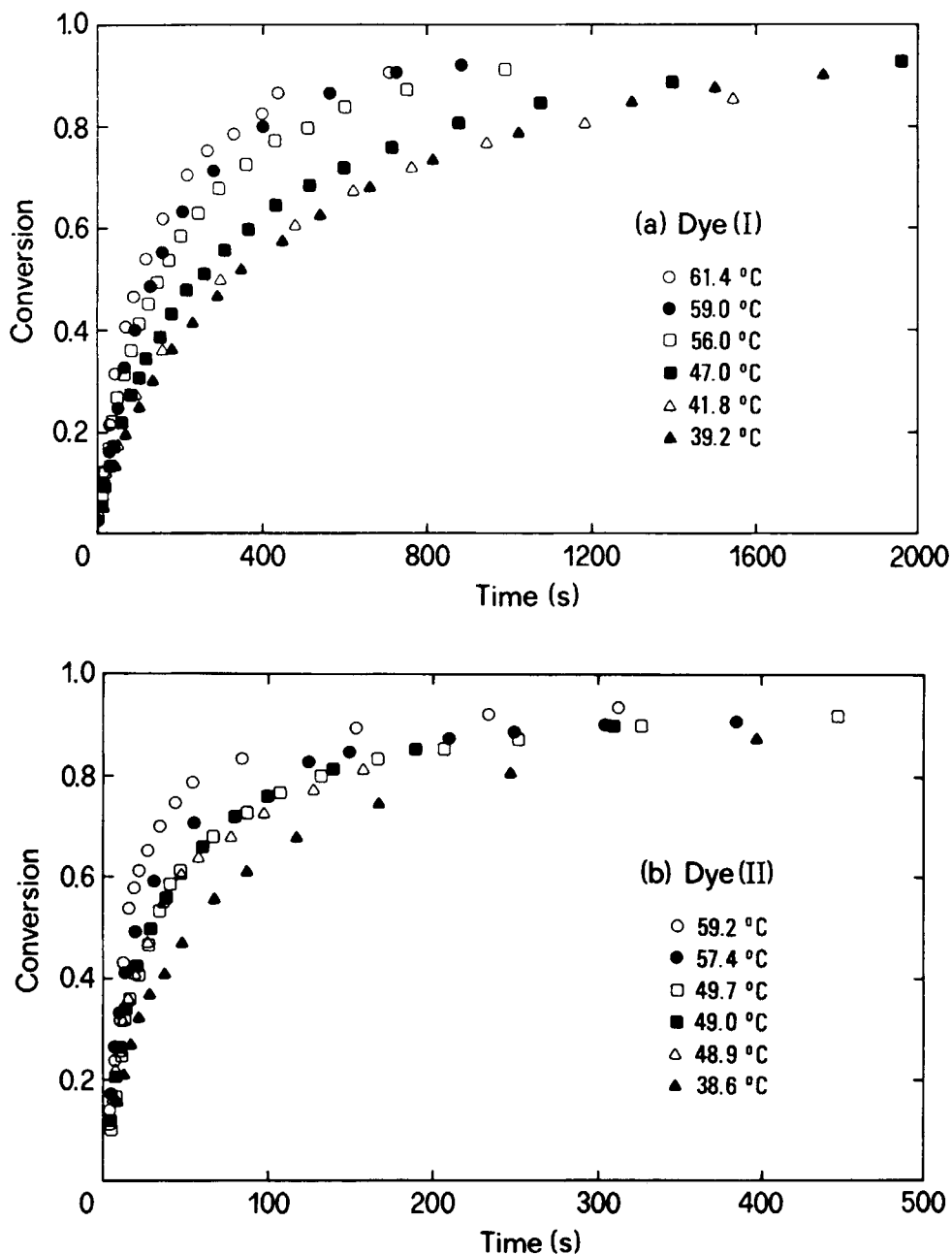

Figure 1 Time courses of the *cis-trans* isomerization of (a) dye (I) and (b) dye (II) in PMMA films at various temperatures.

ment and free volume availability of the disperse dye in the amorphous regions of the glassy polymeric matrices.

In our previous works, analogous cases were kinetically resolved by the procedure reported by Frost and Pearson,[16] considering the process as the result of two or three simultaneous first-order reactions. According to this procedure, for each kinetic run, at a given temperature, the process was split in two or three reactions by consecutive extrapolations of the absorbance trends versus time. However, this approach is not completely satisfactory because it can lead to a certain unreliability of the results; this was revealed in some cases by a lack of linearity in the Arrhenius (or Eyring) plots where the kinetic coefficients determined at various temperatures are considered all together.

Thus, in the present study we have used a mathematical approach that allows one to consider at the same time all the experimental data at the various couples time/temperature, having the activation parameters as the main unknowns to be determined. This approach conforms to the Arrhenius law and to the hypothesis of the multiplicity of simultaneous independent first-order reactions:

$$C_1 \xrightarrow{k_1}$$
$$C_2 \xrightarrow{k_2}$$
$$C_3 \xrightarrow{k_3} T$$
$$\cdots \xrightarrow{k_i}$$
$$C_i$$
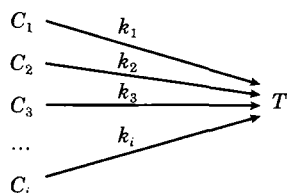
where C_i is the *cis*-isomer, in a microenvironment i, that

thermally reverts to the *trans* form T with a rate constant k_i.

Using the reaction conversion (y), the following equation can be derived:[17]

$$y = 1 - \sum_i w_i \cdot \exp(-t \cdot k_i) \qquad (2a)$$

or:

$$y = 1 - \sum_i w_i \cdot \exp[-t \cdot A_i \cdot \exp(-E_i/RT)] \qquad (2b)$$

where A_i and E_i are the frequency factor, or pre-exponential factor, and the activation energy, respectively, of the i-th reaction, and w_i its relative weight, namely its relative importance. On the basis of the last equation, an optimization treatment employing all the conversion degrees $y(t, T)$ as input data can give the best set of w_i, A_i, and E_i values.

In this work, the value of the frequency factor A_i was assumed to be the same for all the independent first-order reactions, that is, it was assumed that the different microenvironments that surround the azo dye and that are responsible for the multiplicity of reactions mainly affect the energy barriers of the process. Thus, the optimization procedure gave a single frequency factor and a set of activation energies. The spreading of such a set is a good measure of the morphological complexity of the amorphous regions of the polymeric matrix. The more complex the structure of the medium, the more spread is to be expected for the spectrum of the activation energies.
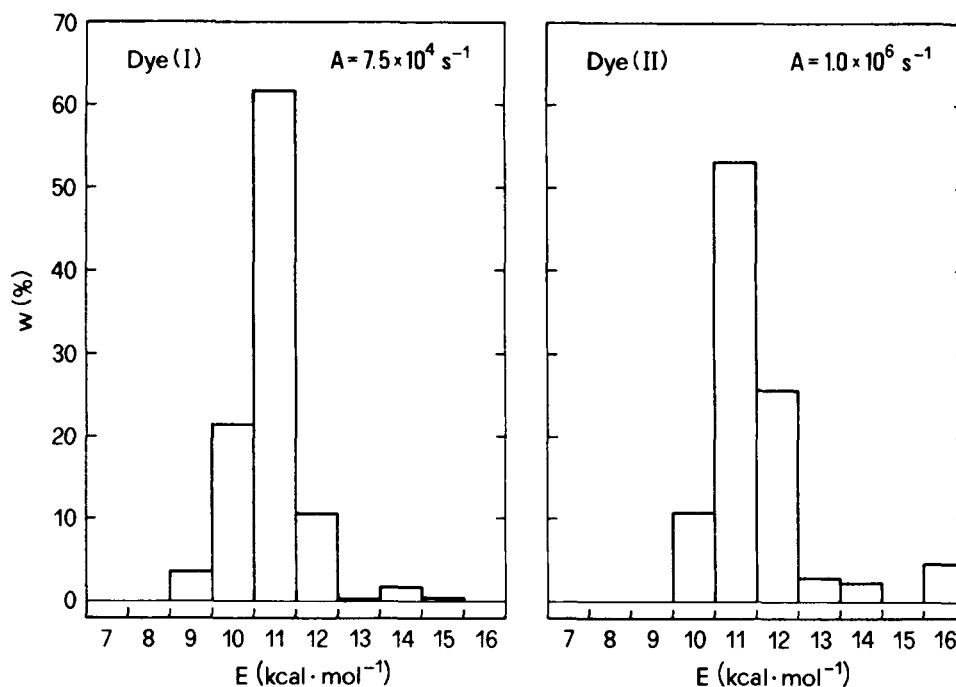

Figure 2   Distribution of activation energies involved in the *cis–trans* isomerization of dyes (I) and (II) in PMMA films with the corresponding frequency factors (A).
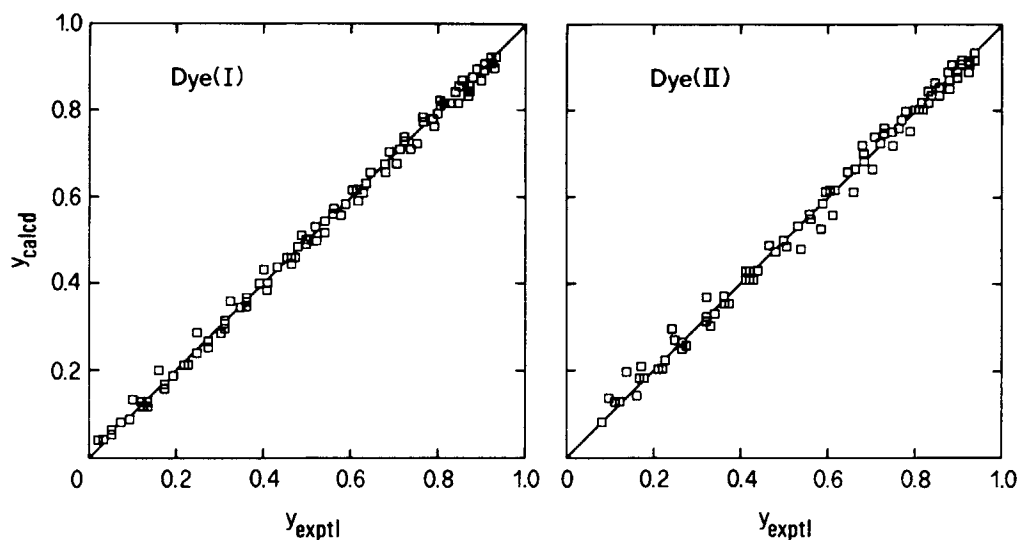
Figure 3   Comparison between the experimental extents of the *cis-trans* isomerization of dyes (I) and (II) in PMMA films and the corresponding values calculated from the optimized parameters in eq. (2b).

The optimizations were carried out considering the following objective function to be minimized:

$$\varepsilon = \left[\sum_{0}^{n} (y_{\text{calcd},i} - y_{\text{exptl},i})^2 / (n - f) \right]^{1/2} \quad (3)$$

where n is the total number of observations, f the number of parameters to be optimized, $y_{\text{expt},i}$ the experimental value of the conversion at a given time and temperature, and $y_{\text{calcd},i}$ the corresponding value calculated by eq. (2b), which gives the conversion as a function of time and temperature.

The results for dyes (I) and (II) are shown in Figure 2. Apart from the different values of the frequency factors that mostly characterize the two different dyes, the spectrum distribution of the activation energies appears to be rather similar. However, it can be appreciated that for dye (II) the importance of reactions with higher activation energies is somewhat greater than for dye (I).

Figure 3 shows the comparison between the experimental and the calculated data at the various times and temperatures considered. The fit is rather good.

As regards the dye-substituent effect on the reaction rate, in our previous works on poly(ethylene terephthalate)[9] and polypropylene,[11] we determined the order of reactivity H < OCH_3 < CN, from the values of mean relaxation time:[18]

$$\bar{\tau} = \int_{0}^{\infty} dt \cdot \sum_i w_i \cdot \exp(-k_i t) = \sum_i (w_i / k_i). \quad (4)$$

This revealed a V-shaped Hammett plot that is typical for the *cis-trans* isomerization of these dyes in liquid solution and in other media.[4,9,19] To also check the occurrence of such a trend in the present case, some kinetic measurements were performed at 50°C on the isomerization

of unsubstituted 4-diethylaminoazobenzene in PMMA film. The following relative rate ratios have been obtained:

$$H : OCH_3 : CN = 1 : 2.8 : 18.$$

Besides confirming the V-shaped Hammett plot, these ratios evidence a substituent effect much more marked than that previously observed.[9,11]

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