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# PHOTOISOMERIZATION OF AZO AROMATIC CHROMOPHORES IN POLYVINYL CHLORIDE

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## ABSTRACT

The synthesis and characterization of new vinyl chloride-*p*-acryloyloxyazobenzene copolymers are reported. Kinetics of photoinduced *trans-cis* and thermal *cis-trans* isomerization of azo pendant groups in copolymer have also been investigated, and the kinetic parameters were evaluated. An azo acrylate model compound was used for comparison.

## INTRODUCTION

The incorporation of some photoisomerizable chromophores in polymers is expected to lead to changes in polymer chain conformation. These photoinduced conformational changes will modify reversibly both the physical and chemical properties of the polymer itself and the polymer solutions. Thus, chromophore photoisomerization can be utilized to study the mobility and the conformation of polymer matrix chains. The nature and the morphology of the polymer have an essential influence on the photochromism of a chromophore in a polymer matrix [1, 2]. The photochromic processes in polymers depend on the particular motions of chain segments [1, 3, 4], and the thermal recovery behavior of the photochromic units is linked to the free volume distributions [5–7].

In previous work we reported the *trans-cis* photoisomerization and the thermal *cis-trans* recovery of some polyurethane cationomers containing azo pendant groups [8]. Because the photoisomerization process is hindered in ionic polymers due to the strong ionic interactions between macromolecules, we have proposed extending

the study to copolymers of vinyl chloride with azo pendant groups. The copolymers have high  $T_g$  values, and the photoisomerization process can be followed in a wide temperature range as compared to polyurethanes having lower  $T_g$  values.

Up to now there has been very little information about the preparation of polyvinyl chloride bearing azobenzene moieties. Recently, there has been a report about obtaining PVC thin composite films containing *p,p'*-dialkylazobenzenes with liquid crystal properties [9].

The aim of this paper is to present our first results on the synthesis of some new chromophoric vinyl chloride polymers and their photoisomerization behavior.

The development of materials whose optical properties can be modified locally and in a reversible way by light is of considerable interest for optical data storage.

## EXPERIMENTAL

### Monomer Synthesis

$\beta$ -Chloropropionyloxy-*p*-azobenzene was prepared from *p*-hydroxyazobenzene and  $\beta$ -chloropropionyl chloride as previously reported [8]. *p*-Acryloyloxyazobenzene was obtained as follows. To a solution of 0.15 mol  $\beta$ -chloropropionyloxy-*p*-azobenzene in 50 mL anhydrous tetrahydrofuran was added dropwise a solution of potassium *tert*-butoxide (0.2 mol in 100 mL tetrahydrofuran) under stirring at 60°C for 1 hour. After completion of the potassium *tert*-butoxide addition, the mixture was stirred at the same temperature for 9 hours. Then the resulting mixture was poured into ice and extracted with diethyl ether. The ether layer was dried on potassium carbonate and the diethyl ether was evacuated. The resulting product was purified by recrystallization from tetrahydrofuran.

### Synthesis of Vinyl Chloride-*p*-Acryloyloxyazobenzene Copolymer

Vinyl chloride and *p*-acryloyloxyazobenzene (molar ratio 90:10) with 2,2'-azobis(isobutyronitrile) (AIBN, 1%) as initiator were introduced into glass vials. The vials were soldered under an argon atmosphere and then heated at 60°C for 48 hours. The resulting copolymer was purified by repeated precipitations from a tetrahydrofuran-water mixture and then twice from a dichloroethane-diethyl ether system. The copolymer was dried under vacuum at 60°C.

### Measurements

The electronic absorption spectra were obtained on a SPECORD M42 spectrophotometer in dichloroethane solutions using 10 mm cells or in films. NMR spectra were recorded on a JEOL-C60 HL spectrometer in  $\text{CDCl}_3$  solutions. The solvents were spectrograde and used without further purification.

The polymer films were prepared on quartz plates by casting from tetrahydrofuran solutions. After solvent evaporation, the films were dried at 40°C for 48 hours.

The sample solutions or films were irradiated by a 500-W high-pressure mercury lamp with a suitable glass filter at room temperature for measurements of the *trans* to *cis* photoisomerization of azobenzene units. The absorbance of films or solutions in the absorption band maximum of the *trans* isomer was kept between

0.8 and 1.0. The thermal *cis* to *trans* recovery was followed by UV at constant temperature.

## RESULTS AND DISCUSSION

The acrylate monomer containing azo groups (*p*-acryloyloxyazobenzene) was characterized by <sup>1</sup>H-NMR and electronic absorption spectra. The NMR signals of the aromatic protons were observed in the expected area between 7.25 and 8.05 ppm. In the aromatic region a signal assigned to protons in the *o,o'*-position of the ester oxygen appears as a doublet at 7.0 ppm. The protons of unsaturated groups give a signal between 5.9 and 6.6 ppm.

In the electronic absorption spectrum recorded in dichloroethane, an absorption band at about 334 nm was observed; it is in agreement with the *trans* isomer of the azo unit [10, 11].

The composition of the copolymer was estimated by integration of <sup>1</sup>H-NMR signals and elemental analysis. The NMR spectrum shows the chemical shifts of methylene protons and -CHCl groups from polyvinyl chloride at 1.8–2.0 and 4.2–5.0 ppm, respectively. The aromatic protons of the acrylate monomer are observed at 7.3–8.0 ppm. Elemental analysis gave the following composition for the copolymer: N, 1.37%; Cl, 50.12%. This is consistent with the structure established from NMR data. The absorption bands at around 327 and 425 nm are associated with the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions of the azo aromatic units.

The effect of polymer matrix on the photoisomerization of the azobenzene moiety in a pendant position has been studied by comparing the isomerization rates of copolymers with those of the corresponding low molecular weight model compound (*p*-acryloyloxyazobenzene).

The copolymer containing azo units exhibits reversible photochromic properties (Scheme 1).

Upon irradiation at about 330 nm, the isomerization to *cis* azobenzene units occurs as shown in Fig. 1.

As the irradiation time increased, more *trans* isomer changed to the *cis* form, and the *trans* band intensity decreased progressively. At the same time, this absorption band shifts to shorter wavelengths until a photostationary state is eventually reached. The presence of the isosbestic points at 380 and 288 nm in the electronic absorption spectra of the copolymer indicates that only two absorbing species are present in the system.

As compared with the low molecular weight azo model, the electronic absorption spectra of the copolymer exhibit a hypsochromic shift. A similar behavior has been observed in other polymers containing aromatic chromophores [12, 13], and it can be attributed to electronic interactions between neighboring chromophores [14].

The thermal recovery at 60°C restores the absorption band at  $\lambda_{\max} = 325$  nm and depletes the band at  $\lambda_{\max} = 425$  nm, implying that the *trans* form of the azo pendant of polymers is regenerated and the sample exhibits reversible photochromic properties. After four cycles of irradiation–thermal recovery, the electronic absorption spectra of the *trans* form are practically identical, the recovery taking place at almost the same value as the absorbance.

The  $A_{\infty}/A_0$  ratio is of the same order of magnitude for all samples. This ratio has the smallest value for the solution of Polymer B. We conclude that the



TABLE 1. UV Absorption Properties and Photochromism of Azobenzene Derivatives

Sample	$\lambda_{\max}$ , nm	<i>Cis</i>		
		fraction	$k \times 10^2, \text{s}^{-1}$	$t$ , s
A. Azo acrylate model	334	0.42	8.3	120
B. Copolymer solution	327	0.51	15.8	35
C. Copolymer film	327	0.39	4.8	1100

where  $A_0$ ,  $A_t$ , and  $A_\infty$  are the sample absorbances at times zero,  $t$ , and  $\infty$ , respectively, and  $k$  is the rate constant.

Plots of  $\ln [(A_0 - A_\infty)/(A_t - A_\infty)]$  versus irradiation time ( $t$ ) were linear when the model and polymer samples were studied in solution. In contrast to the behavior in solution, the photochemical behavior in solid films deviates from first-order kinetics at high irradiation times (Fig. 2).

It is known that azobenzene undergoes a reversible photochemical isomerization reaction. This reaction generally has high quantum yields, and there are no competing reactions of significance. These systems have another advantage; namely, there is no known evidence of emission from the excited state of azobenzene in the *cis* form or in the *trans* form [15].

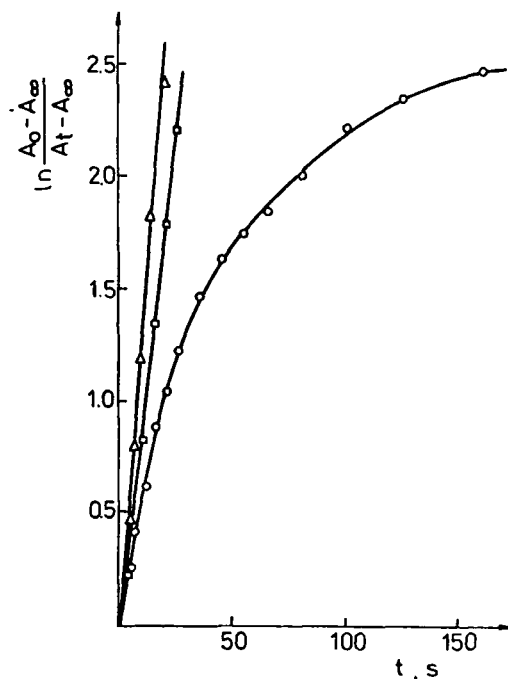


FIG. 2. Kinetics of *trans-cis* photoisomerization of azobenzene units in polymer film (O), in polymer solution (DCE) ( $\Delta$ ), and in azo acrylate model ( $\square$ ).

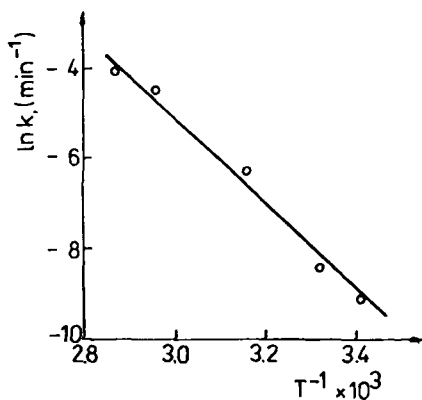


FIG. 3. Arrhenius plot for the thermal *cis-trans* isomerization rate constants of azo polymer film.

In our case, in contrast to literature data on the *trans-cis* photoisomerization process of azobenzenes in a polymer matrix [7], the isomerization rate is not identical in solution and in film, even at the beginning (Fig. 2). The isomerization rate is much higher in solution than in polymer film; the highest value is found for the azo copolymer in dichloroethane (Table 1). In the first part of the plot the sample can freely isomerize, while in the second part the rate is controlled by the polymer matrix. The deviation from first-order kinetics can be due to the mobility restrictions of the polymer chain and to the heterogeneity of the free volume distribution in the reaction sites [5, 16, 17]. This deviation is a characteristic phenomenon of the isomerization reaction in an amorphous solid polymer below  $T_g$ , and here it appears even at room temperature, which is far below  $T_g$ .

Thermal *cis-trans* isomerization follows a linear dependence of  $\ln [(A_\infty - A_0)/(A_\infty - A_t)]$  vs recovery time for all samples, similar to other azo chromophores.

An Arrhenius plot of the rate constants of thermal recovery gives a straight line (Fig. 3).

The activation energy ( $E_a$ ) and the preexponential factor ( $Z$ ) of the thermal *cis-trans* isomerization can be evaluated from the Arrhenius plot:  $E_a = 78.2$  kJ/mol and  $Z = 1.82 \times 10^8$  s $^{-1}$ . This activation energy value is almost of the same order of magnitude as that of azobenzene [6, 16], which suggests that thermal isomerization can only take place by an inversion mechanism; namely, through a change in the hybrid orbital of nitrogen from  $sp^2$  to  $sp$  and then to  $sp^2$  again [18], although the mechanism of thermal *cis-trans* isomerization of azo species is still a controversial problem [18, 19].

There is no significant difference in the rate constants between the polymer and its low molecular weight model. In this case the relaxation of polymer conformation is rapid enough to follow thermal isomerization. The decrease in *cis* content of the polymer film can be due to decreasing possibilities of local mobility in the polymer matrix.

## CONCLUSIONS

Photoinduced *trans-cis* and thermal *cis-trans* isomerization of vinyl chloride copolymer bearing azo pendant groups was studied both in film and in solution, and compared with a low molecular weight compound.

The activation energy of the thermal *cis-trans* isomerization process of azo pendants is similar to that of azobenzene, suggesting that thermal isomerization can take place by an inversion mechanism.

The deviation from first-order kinetics of *trans-cis* photoisomerization is related to the influence of free volume distribution on the reactive sites.

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