

Relationship between the Absorption Spectra and Spatial Hindrance in Starch Graft Copolymers

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ABSTRACT: The photochemical trans–cis isomerization of graft copolymers of azo dyes onto starch was studied in liquids spectrophotometrically. The relationship between the absorption spectra and spatial hindrance was investigated. The experimental results showed that the structure of the graft copolymers had a marked influence on photoisomerization. The smaller the spatial hindrance was, the easier the photoisomerization was. The copolymers showed better photoisomerization than their corresponding monomers, and this showed that the backbone of starch in the

main chain influenced not the maximum-wavelength position of the copolymers but the retroactive structure of the copolymers and favored their photoisomerization. In addition, the thermal cis–trans isomerization rate of the graft copolymers was studied in various polar solvents. The results suggested that the solvent polarity had a large effect on the thermal back-isomerization. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2123–2126, 2006

Key words: azopolymers; adsorption; monomers

INTRODUCTION

The photoisomerization of azo dyes has been attracting considerable attention from interest in its photochemistry since the early part of the 20th century because of its potential applications, such as polarization holograms, the recording of wave mixing, and photon-mode optical storage, its large nonlinearity flexibility, and its cost performance.¹

As is well known, an azo dye, which has a —N=N— bond combining some benzene rings, can photoisomerize from a trans isomer to a cis isomer. Although many studies have been carried out on azo compound photoisomerization in liquid and Langmuir-Blodgett films,^{2–5} little is known about photoisomerization on starch graft copolymers. In this study, the photoisomerization of graft copolymers of azo dyes on starch was investigated. The aim of this study was to determine the relationship between the absorption spectra and spatial hindrance. In 1952, Wallace et al.⁶ investigated the relationship between the absorption spectra and solvent effect, and they suggested that, in general, hydrocarbon solvents favored isomerization, whereas ethanol appeared to suppress it. Substituent effects on the photoisomerization of substi-

tuted azobenzene were studied by Wildes et al.⁷ However, much less is known about the spatial effect of graft copolymers on the absorption spectra. Micromolecular azo compounds always have better photoisomerization than macromolecular azo compounds. However, in the laboratory, experimental results have shown that starch graft copolymers have better photoisomerization than their corresponding monomers, and this shows that the backbone of starch has a remarkable effect on azo compounds: it does not hinder the photoisomerization of copolymers but instead hinders the retroactive structure of copolymers and favors the photoisomerization of copolymers.

EXPERIMENTAL

Preparation and purification of the graft copolymers

The graft copolymers (see Scheme 1) used for this investigation were prepared by Fu et al.'s methods⁸ and were purified by recrystallization from ethanol.

Preparation of the solutions

Approximately 0.0020 g of each graft copolymer was weighed and dissolved in 80–90 mL of freshly distilled ethanol, and each mixture was diluted to 100 mL in a volumetric flask.

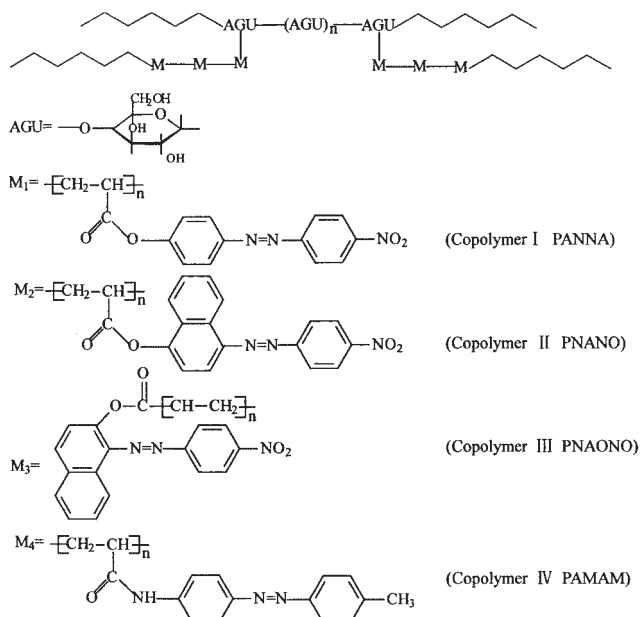
Measurement of the absorption spectra

The absorption spectra were determined with a U-3400 ultraviolet–visible spectrophotometer (Hitachi

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Scheme 1 Structures of the copolymers.

Co., Japan) with matching quartz absorption cells and with the solvent as the reference standard.

Irradiation of the solutions

The sample solutions were irradiated with 365-nm light from a high-pressure mercury lamp (450w). The rotating shutter was then placed in position, and intermittent irradiation was continued until the equilibrium was reached, that is, until no further changes in the absorption spectra occurred.

Kinetic analysis

All measurements were performed at room temperature. The thermal back-isomerization rate constant $k(T_{\text{isom}})$ was determined with UV measurements as a function of time. The amount of trans was assumed to be linearly related to its absorbance at the maximum wavelength at time t [$\lambda_{\text{max}}(t)$] because during the whole process the absorbance was less than 1. Furthermore, the thermal cis-trans back-isomerization was an irreversible process. With eq. (1), $k(T_{\text{isom}})$ was computed; $k(T_{\text{isom}})$ was plotted versus time t to obtain a curve with slope $k(T_{\text{isom}})$:⁹

$$k(T_{\text{isom}})t = \ln\left(\frac{A_{\text{trans}} - A_{\text{cis}}}{A_{\text{trans}} - A_t}\right) \quad (1)$$

where A_{trans} is the absorbance reached at infinite time, which is (normally) also the starting situation after storage in the dark before irradiation with UV light, A_t is the absorbance during the time at t , and A_{cis} is the

absorbance at time t after irradiation. The value for the absorbance was taken at $\lambda_{\text{max}}(t)$.

RESULTS AND DISCUSSION

Effect of the backbone of starch in the main chain on the absorption spectra

As indicated in Figure 1, copolymer I poly-azobenzene-nitro-acrylate (PANNA) and its azo dyes monomer have the same UV absorption band at 361 nm, and this is consistent with previous work: the backbone of starch has a slight influence on UV spectroscopy.¹⁰ It is well known that the factors affecting the position of absorption are the conjugative effect, the auxochromic domino effect, and the solvent effect. The backbone of starch is a saturated system; that is, copolymer I and its monomer have the same conjugative effect and auxochromic domino effect in the same solvent. Therefore, their λ_{max} position does not change. The absorption spectra of a series of starch graft copolymers and their corresponding monomers were investigated, and they had the same λ_{max} position.

Effect of spatial hindrance on the absorption spectra

The changes induced in the absorption spectra of azo compounds in ethanol solutions by irradiation from a high-pressure mercury lamp were found to be invertible and dependent on the structures of the graft copolymers. Figures 2 and 3 illustrate the behavior of photoisomerization with 365-nm light for two graft copolymers in ethanol at room temperature. As shown in Figure 2, copolymer II poly-nitro-azobenzene-naphthyl-oxo-acrylate (PNANO) in an ethanol solution undergoes trans-cis photoisomerization until a photostationary state is eventually reached. The existence of isobestic points at 420 and 485 nm is characteristic for the existence of two distinct absorbing species in equilibrium with each other and at the same time

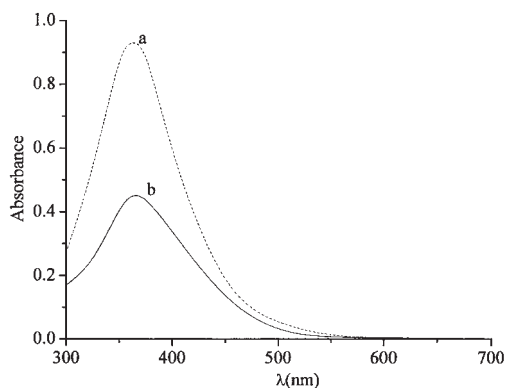


Figure 1 UV absorption of (a) monomer I and (b) copolymer I.

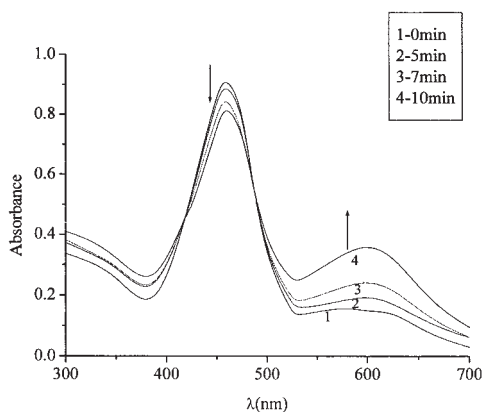


Figure 2 UV spectra of copolymer II (PNANO) samples for different irradiation times in ethanol solutions at 25°C.

proves that no side reaction takes place during the photoisomerization process in the range studied.¹¹ The two isobestic points at 420 and 485 nm indicate that only trans and cis isomers are present. Figure 3 shows that the curve of copolymer III poly-nitro-azo-benzene-ortho-naphthoxy-acrylate (PNAONO) has no equi-absorption point in its absorption spectra by UV exposure, and the copolymer does not undergo trans-cis photoisomerization. As the solution is irradiated, the intensity of absorption at λ_{\max} increases for both isomers, and this shows that for graft copolymer III (PNAONO), photochromic hindrance occurs. Upon a comparison of Figures 2 and 3, we find that copolymer II (PNANO) manifests good photoisomerization, whereas copolymer III (PNAONO) experiences photochromic hindrance. Therefore, the spatial hindrance must be taken into consideration. A large difference in the effects of 2- and 4-acroloyloxy groups for the two copolymers seems to indicate that distinctly different behaviors of photoisomerization. For copolymer II (PNANO) and copolymer III (PNAONO), the 4-acroloyloxy group facilitates photoisomerization, whereas the 2-acroloyloxy group re-

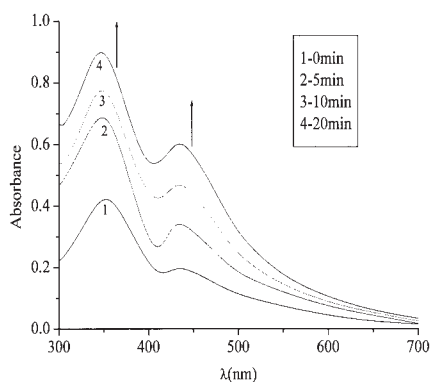


Figure 3 UV spectra of copolymer III (PNAONO) samples for different irradiation times in ethanol solutions at 25°C.

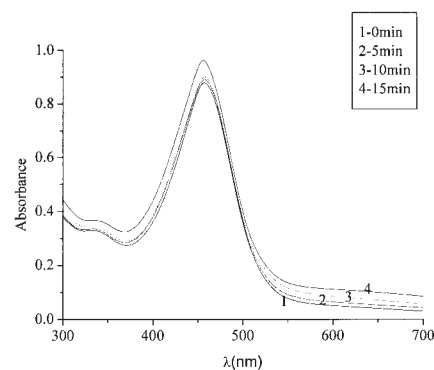


Figure 4 UV spectra of monomer II samples for different irradiation times in ethanol solutions at 25°C (the UV spectra of monomer III are similar to the UV spectra of monomer II).

tards photoisomerization and facilitates photochromic hindrance. To some extent, the molecular structure of 4-acroloyloxy-substituted PNANO can provide enough free volume to allow the trans-cis photochromic reactions to occur in an ethanol solution at room temperature and reduce the activation energy (E_a).¹² However, 2-acroloyloxy-substituted PNAONO (copolymer III) has a stronger steric interaction between the oxyacroyloxy group and nitro-substitution benzene ring. As a result, when $-\text{N}=\text{N}-$ is rotated or inverted around substituted benzene rings, the repulsive force among them becomes so severe that the 2-acroloyloxy group hinders rotation or inversion, that is, enhances E_a 's. Therefore, the experimental results show that *para*-acroloyloxy-substituted PNAONO (copolymer II) is easier to photoisomerize from trans to cis than *ortho*-acroloyloxy substitution (copolymer III).

A comparison of Figures 2 and 3 shows that the trans isomer for 4-acroloyloxy substitution has a much stronger conjugative united effect than 2-acroloyloxy substitution, and this results in a remarkable bathochromic shift in the absorption spectra of the trans isomer for 4-acroloyloxy substitution. In addition, as the solutions of monomers II and III are irradiated, their absorption spectra only appear at 459 (Fig. 4) and 351 nm, respectively (the absorption spectra of monomer III are similar to those of monomer II). With the time of irradiation increasing, their λ_{\max} position does not shift, and their cis isomers cannot be observed. This shows that the photoisomerization of the mono-

TABLE I
Absorption of Copolymer IV in Different Solvents

	DMF	Ethanol	1,2-Dichloroethanol	Benzene
n	1.4269	1.3614	1.4449	1.5011
λ_{\max}	359	346	355	384

DMF, dimethyl formamide.

mers does not take place. Fu et al.⁸ investigated the relationship between the grafting efficiency and monomer structure in graft copolymerization onto potato starch, and they emphasized that spatial hindrance is an important factor influencing the grafting efficiency. Our experimental results have shown that the spatial hindrance of the macromolecular backbone has a positive effect on photoisomerization. In most cases, the photoisomerization of a monomer is superior to the photoisomerization of a copolymer, although the experimental results show that copolymers have much better photoisomerization behavior than their corresponding monomers. That is, monomers II and III do not manifest photoisomerization in ethanol solutions, and copolymer II (PNANO) manifests good photoisomerization. However, copolymer III (PNAONO) displays photochromic hindrance. On the basis of these studies, the backbone of starch in the main chain should be taken into consideration; the structure of starch is a saturated system, which does not affect the λ_{\max} position, and so the effect of spatial hindrance must be the factor influencing the transplantation of λ_{\max} . In summary, macromolecular spatial hindrance has two effects, one positive and the other negative. The negative effect always impairs and even balances out completely the appearance of absorption spectra and displacement. Most macromolecular spatial hindrance shows this negative effect. On the contrary, the positive effect strengthens and even prompts the appearance of absorption spectra and displacement. This interesting phenomenon is being studied in the laboratory, and further study is being developed.

Effect of the solvent on thermal back-isomerization

As shown in Table I, the absorption spectra of copolymer IV are different in different polar solvents. In general, in various solvents, increasing the solvent refractive index (n) results in a bathochromic shift in the absorption spectra. To discuss such a solvent effect on the UV spectra, the solvent polarity changers must be taken into consideration. The interaction between a solute's inherent dipole and a solvent's induced dipole, as well as the interaction of the solute and solvent's inherent dipole, results in a bathochromic shift in the UV spectra.

In addition, the solvent polarity influences $k(T_{\text{isom}})t$ of the thermal back-isomerization. As indicated in Figure 5, the $k(T_{\text{isom}})t-t$ relation is nearly linear, as expected for first-order kinetics. The solvent polarity has a large effect on the rate of thermal back-isomerization. The rate of thermal back-isomerization increases as the solvent polarity increases, and this is probably due to E_a being different in different polar solvents. The free energy of activation for thermal back-isomerization in polar solvents is much lower than that in nonpolar solvents.⁷

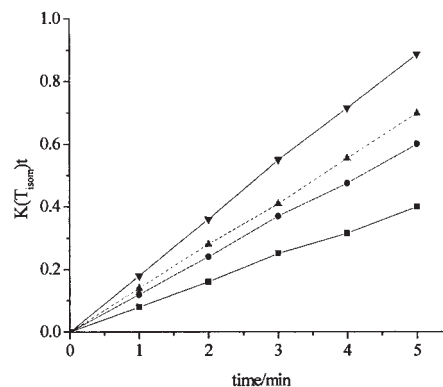


Figure 5 Plots of $k(T_{\text{isom}})t$ versus time t for copolymer IV in different solvents: (▲) dimethylformamide, (▼) ethanol, (●) 1,2-dichloroethanol, and (■) benzene.

CONCLUSIONS

As the experimental results suggest, the structures of graft copolymers remarkably influence the behavior of photoisomerization; spatial hindrance is especially an important factor. Macromolecular spatial hindrance has a positive effect and a negative effect. The negative effect is well known. However, people have rarely paid attention to the positive effect. A deep investigation of the positive effect not only can make people understand better the effect of spatial hindrance but also can favor its use in the future. In addition, the solvent polarity influences the rate of thermal back-isomerization: the larger the solvent polarity is, the lower the free energy of activation is for thermal back-isomerization. This research not only overcomes the limitations of micromolecular azo compounds in practical applications but also provides an approach for making the most of starch.

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