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POLYURETHANE CATIONOMERS CONTAINING NITROAROMATIC AND AZO CHROMOPHORES. EFFECT OF UV IRRADIATION ON POLYMER PROPERTIES

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ABSTRACT

Polyurethane cationomers containing azoaromatic dyes and *o,p*-nitroaromatic photoactive groups, covalently or electrostatically incorporated, have been synthesized. The photobehavior of polymer solutions and films was studied by electronic absorption spectra. It was found that a bleaching process occurs in these polymers by UV irradiation.

INTRODUCTION

Synthesis of some polymers as polyamides, polyimides, polyethers, or polyacrylates containing *o*-nitroaromatic photoactive groups in the polymer chain was described in recent papers [1–4].

The feature of these polymers consists in the possibility of inducing some photoprocesses on the polymer backbone by UV irradiation, with a direct effect on the structural properties of the polymer materials and consequently on their use in electronic and optical devices.

Recently, we reported on a preliminary investigation of some elastomer polyurethanes with *o,p*-nitroaromatic photosensitive groups [5] and compared them with a monomer model. By extending the study to polyurethane cationomers [6] bearing the same chromophores, we provided new data showing that the photobleaching effects always take place faster in solutions than in polymer films during UV irradiation.

A similar experiment was carried out on polyurethane cationomers with azoaromatic chromophores covalently [7] or electrostatically [8] bound in polymer, and by taking into account the structure of the azo moiety, photoisomerization or photobleaching processes were evidenced. The above experimental results suggested that UV irradiation induced structural modifications of macromolecules, accompanied by reversible or irreversible variations of the polymer properties.

The major aim of the present work was the synthesis of some polyurethane cationomers containing both *o,p*-nitroaromatic photoactive groups and azoaromatic dyes, covalently or electrostatically included in polymer chain, in order to show the possible involvement of photosensible groups in obtaining photodegradable polyurethanes.

EXPERIMENTAL

Polyurethane precursors were obtained by the prepolymer method, using poly(tetramethylene oxide) (PTMO, M_n = 2000, 0.01 mol), 4,4′-dibenzyldiisocyanate (4,4′-DBDI, 0.03 mol), and *N*-methyldiethanolamine (NMDA, 0.02 mol), which were then quaternized at tertiary nitrogen atoms with methyl iodide to polyurethane cationomers (PUC).

Synthesis of polyurethane nitrocationomer (PUC-N) was performed using a mixture of diols [NMDA and *N*-(2,4-dinitrobenzene)-diethanolamine, 1:1 molar ratio] as a chain extender, and subsequent quaternization of aliphatic nitrogen with methyl iodide [6].

Polymer solutions in DMF (10% w/v) were treated with methyl orange (10% excess versus ionic groups) by mixing at 50–55°C for 2–3 hours before standing overnight at the same temperature. The polycations (PUC-A, PUC-A-N) were precipitated and thoroughly washed with water, then washed with CH_3OH, and then dried under reduced pressure for 48 hours at 50–55°C.

The ionic iodine content was determined tritrimetrically.

Reduced viscosity measurements were performed with an OA Ubbelohde viscometer using DMF polymer solutions (c = 0.4 g/100 mL).

Ultraviolet and visible absorption spectra were recorded with a Specord M42 spectrophotometer.

Irradiations were carried out by using a 500-W high-pressure lamp at room temperature. The absorbance of the samples under study in the absorption band maximum was kept between ~0.8–1.0.

The polymer films were prepared by casting the polymer solutions in DMF or THF (1%) onto quartz plates and then allowed to dry at 50–55°C under reduced pressure.

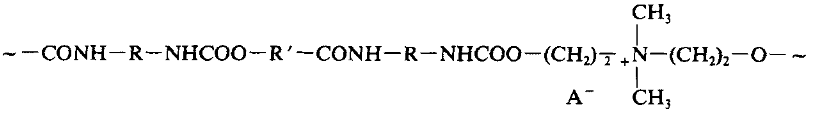
RESULTS AND DISCUSSION

Polyurethane cationomers (PUC) were prepared by the polyaddition reaction between PTMO, 4,4′-DBDI and NMDA, followed by the quaternization reaction of tertiary nitrogen with methyl iodide. These polyurethanes have the ability to interact electrostatically with azoaromatic compounds which are dyes. Thus, the polycation was treated with methyl orange in DMF solution and it was found that the quaternary structure underwent an exchange of the counteranion due to interaction with the azo dye. In this case the ionic iodine content of the polyurethane cationomer will decrease by the ionic exchange reaction (Table 1). Different concentrations of azoaromatic groups as anions were electrostatically incorporated by this method in the ammonium quaternary structure in the polyurethane chain (PUC-A_1, PUC-A_2).

The introduction of *o,p*-nitroaromatic photosensitive chromophores in the polyurethane chain was carried out by the same polyaddition reaction by using a diols mixture [NMDA and *n*-(2,4-dinitrobenzene)-diethanolamine] as a chain extender, followed by quaternization of the aliphatic tertiary nitrogen with methyl iodide (PUC-N).

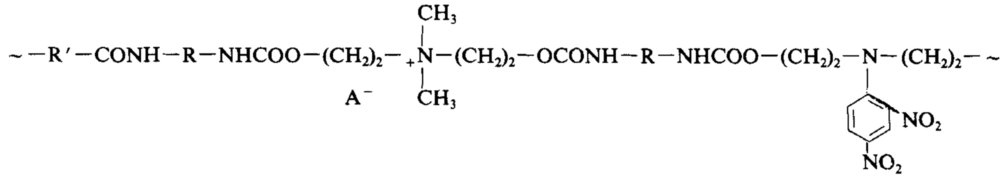
By using the same ionic exchange reaction between anions, azoaromatic chromophores other than *o,p*-nitroaromatic moieties have been introduced (PUC-A-N).

The idealized structures of polyurethane cationomers containing photosensitive groups are the following:

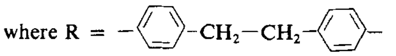


$$\sim\!-CONH-R-NHCOO-R'-CONH-R-NHCOO-(CH_2)_2-\underset{A^-}{}\,{}^{+}\overset{CH_3}{\underset{CH_3}{N}}-(CH_2)_2-O-\!\sim$$

PUC-A



PUC-A-N



where R =

$R' = -[(CH_2)_4O]_n-$

$A = (H_3C)_2N-C_6H_4-N{=}N-C_6H_4-SO_3^-;\ I^-$

TABLE 1. Structural Characteristics of Polyurethane Cationomers

Sample	Ionic iodine content, meq/100 g	Azo group content,[a] meq/100 g	λ_{max}, nm			t,[b] min		
			THF	DMF	Film	THF	DMF	Film
PUC-A_1	47.09	23.50	419	423	434	12	30	110
PUC-A_2	16.59	54.00	419	423	428.5	20	75	150
PUC-N	33.21	—	368	380	—	88	90	—
PUC-A-N	12.96	20.25	415.5	416.5	428	30	40	225
PUC	70.59	—	365.5	364	366			

[a] Calculated from the ionic iodine content.
[b] Photobleaching time.

The polymers were characterized by IR and UV absorption spectroscopy and elemental analysis (Table 1).

In order to understand the photobehavior of azo dye chromophores and those of the *o,p*-nitroaromatic type in terms of their environment, we first studied the polymer solutions in solvents with different electric permittivities (THF, DMF) and then as polymer films.

The photosensible properties of chromophores were followed by photochemical reactions of polymer solutions and films occurring by UV irradiation, and measuring the changes appearing in the electronic absorption spectra before and after irradiation. If the polymer solutions were excited by UV light source, the chromophores underwent structural modifications marked by a significant decrease of absorbance compared with their initial absorbance.

In our experiment the THF and DMF polymer solutions of PUC-A_1 were irradiated with the light of a Hg high-pressure lamp for different times, leading to a progressive decrease of absorbance at 419 and 423 nm, respectively (Fig. 1). These absorption bands correspond to π-π^* transition of the azobenzene chromophores in the two solvents [9].

The decrease in intensity of these absorption bands and their disappearance suggests that photobleaching effects occur in these systems (Table 1). The photobleaching process takes place more rapidly in THF than in DMF because the interactions of the excited species with the polar medium retards the photoprocess evolution.

The same progressive tendency decrease during irradiation of the absorbance at 423 nm also appears in the case of a DMF solution (PUC-A_2) containing a higher concentration of azoaromatic chromophores (Fig. 2) but at a much smaller rate.

In the first step of the photoprocess a photoisomerization of azo chromophores was observed only for DMF solutions, with a tendency to return to the initial state occurring when irradiation was interrupted.

In THF the azo anion is in close contact with the positive charged polymer, and so the flexibility of the bonds is restricted. Thus, irradiation has only a small influence.

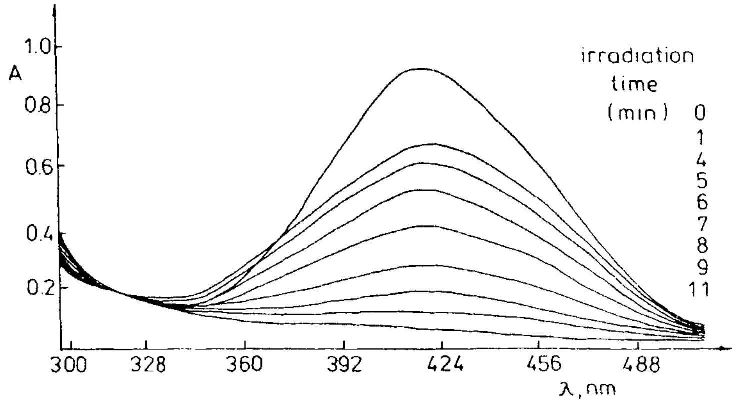


FIG. 1. Electronic absorption spectra monitoring the photobleaching of PUC-A_1 in THF.

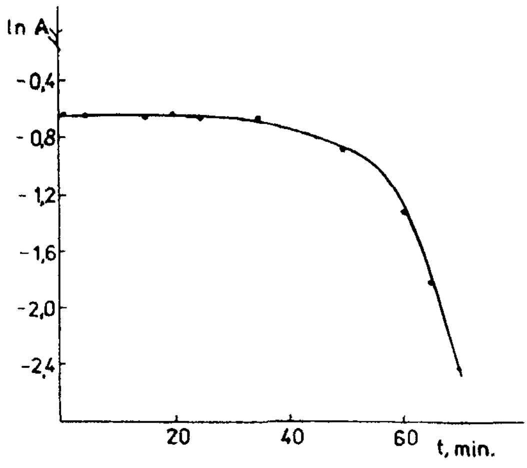


FIG. 2. Absorbance decay at 424 nm for PUC-A_2 in DMF.

In DMF the cationomer can dissociate, so the azo anion can be free in solution, thus supporting rapid changes in configuration by UV irradiation. By using a pH in the acid range, the effect of dissociation is suppressed, and the same behavior as in the THF solution is observed. An increase of ionic concentration in the environment determines the shielding of positive charges from the polymer chain and consequently decreases electrostatic repulsions between quaternary nitrogen atoms. The macromolecules adopted a less extended conformation, and by incorporating azo chromophores they limited the possibilities of responding to irradiation.

An increase of azo chromophores concentration leads to a slower evolution of the photoprocess because the complete disappearance of the π-π^* absorption band occurs after about 75 minutes. This finding can be ascribed to a further increase of polarity due to the presence of azo anions in the vicinity of quaternary cations from the hard segments of the polyurethane elastomer.

During irradiation the azoaromatic chromophores pass to photoexcited states due to a photobleaching effect and finally to scission of the polymer chain. In order to verify if UV irradiation can induce some scissions of macromolecular chains, measurements of reduced viscosity were performed. These very sensitive indicators of photoprocess evolution showed that the PUC-A_1 DMF solutions underwent some viscosity modifications with increasing irradiation times (Fig. 3).

The variation of the viscosity with irradiation time suggests photodegradation of polyurethane cationomers having azo dyes moieties.

By also taking into account that *o,p*-nitroaromatic groups from a polyurethane chain subject to UV irradiation induce irreversible modifications of the polymer chain [6], it is expected that a similar photobehavior will take place in the case of polyurethane cationomers containing nitroaromatic chromophores.

Moreover, the electrostatic incorporation of azoaromatic dyes should enhance photochemical transformations, finally leading to stable photoproducts.

The changes in the electronic absorption spectra of a polyurethane cationomer having two chromophores in THF solution are shown in Fig. 4.

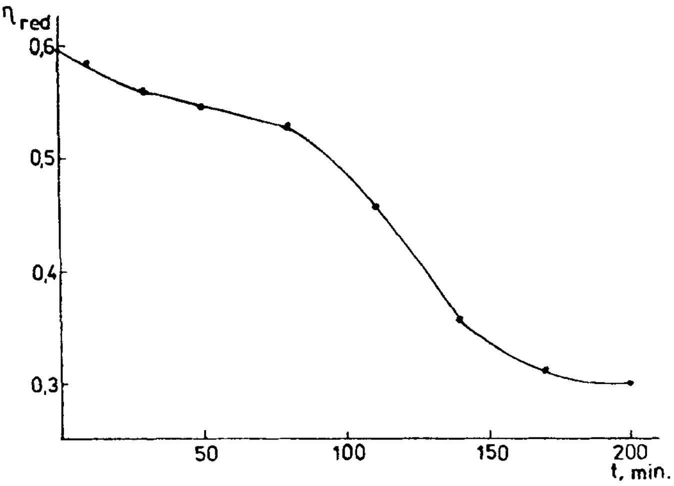


FIG. 3. Reduced viscosity of PUC-A_I in DMF versus irradiation time.

The photobehavior of the PUC-N-A solution is similar to that of azo cationomer PUC-A in THF; however, the rate of the photobleaching process is lower (Table 1) when both photosensitive groups are present in the polymer.

A new absorption maximum appears in a DMF solution of PUC-A-N after some tens of seconds at about 380 nm, and the intensities of the two absorption bands are almost equal. Further, a photobleaching effect takes place.

We observed that both chromophores easily pass to the excited state, thereby inducing the irreversible chemical transformations. However, the nature of the various excited state interactions occurring in the system makes it difficult to evaluate the activity of each photoactive group separately.

Although it is known that the interaction of chromophores with other structural units is more restrictive in a polymer matrix than in a polymer solution, the good-forming properties of the film as well as the potential applications of these

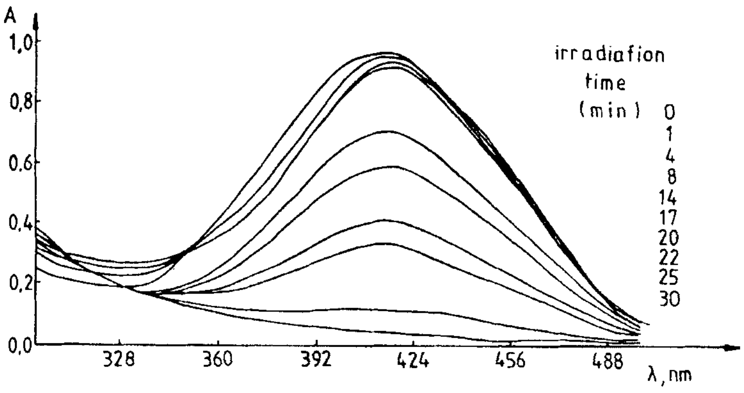


FIG. 4. Variation of absorption spectrum of PUC-A-N in DMF with irradiation time.

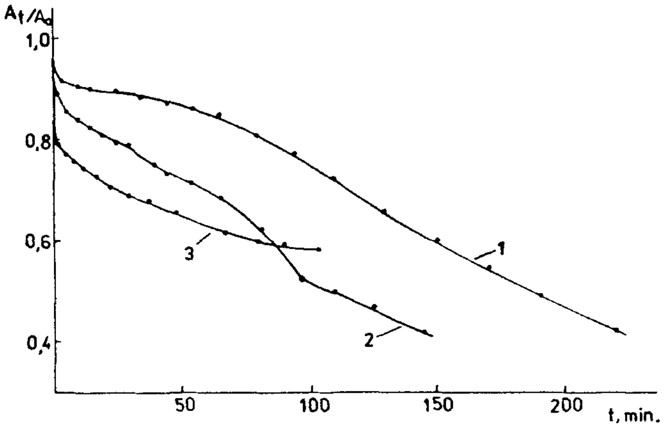


FIG. 5. Dependence of relative absorption on irradiation time for polymer films: PUC-A-N (1); PUC-A_2 (2); PUC-A_1 (3).

polymers necessitate study of the possible modifications occurring in ionomer films.

The electronic absorption spectra of some polymer films subjected to different irradiation times are presented in Fig. 5. By following the photoprocess evolution, it can be seen that the relative absorption (A/A_0) for PUC-A-N films is much slower than that of PUC-A_1 and PUC-A_2 films, probably due to a hindered trans-cis isomerization in the first stages of the reaction.

The presence of a second absorption maximum was not found in PUC-A-N films as it was in polymer solutions during irradiation. The photobleaching process is accompanied by a hypsochromic shift of the absorption band at 428 nm.

CONCLUSIONS

Azoaromatic moieties of the dye type were electrostatically introduced in polymers by the ionic exchange reaction between anions from polyurethane cationomers.

The photobehavior of polymer solutions shows a photobleaching effect which depends on the nature of the solvent. This process is accompanied by photodecomposition of the polymer.

The evolution of the photoprocess is much slower in polymer films than in solution, and the presence of both chromophores on the polymer chain does not enhance photobleaching.

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