

# Ionomeric Polyurethanes of Pyridinium Type with Side Azobenzene Groups

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**ABSTRACT:** New polyurethane cationomers synthesized by a two-step substitution postreaction of urethane hydrogen atoms with nitroazobenzene groups were studied. As a starting polymer, a polyurethane based on poly(tetramethylene oxide)diol, isophorone diisocyanate, and 2,6-bis(hydroxymethyl)pyridine was used. After a preliminary metalation of the above polymer with sodium hydride, by reaction of polyurethane *N*-sodate with 4-nitro-4'( $\beta$ -iodoethylurethane)azobenzene, chromophoric groups between 2.85 and 10.53 wt % could be incorporated instead of hydrogen. Such polymers partially functionalized with azobenzene and further quaternized with methyl iodide led to the formation of pyridinium polyurethane

cationomers *N*-modified with nitroazo groups. The photosensitive properties of the azobenzene chromophore in a polymer solution and film state indicated important differences in their photoresponse. In the polymer solution, the *trans-cis* photoisomerization of the chromophore is accompanied by an irreversible photobleaching effect, while under the same UV irradiation conditions, the ionomeric films exhibited an enhanced photostability. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1240–1247, 2002

**Key words:** azo polymers; functionalization of polymers; polyurethane ionomers; elastomers; photo

## INTRODUCTION

Polymers with azoaromatic groups have attracted the strong interest of chemists for many years and numerous articles have been published on the synthesis and their specific behavior.<sup>1</sup> Given the great versatility of polyurethanes and their special properties, various monomeric and polymeric materials carrying azoaromatic chromophores were prepared and studied, taking into account the development of new nonlinear optical, liquid crystal, photochromic, or photodegradable systems.<sup>2–5</sup> Despite research efforts focused on azoaromatic polyurethanes, there are few examples in the literature describing ionic polyurethanes with chromophore structures in polymeric chains.<sup>6–9</sup> Such materials include those that contain a dye or azobenzene moieties introduced by the quaternizing of tertiary amine from the polyurethane precursor with a mesogenic agent. In the latter polycation, a nematic phase and a smectic mesophase were evidenced.

Our program concerning the synthesis and characterization of new polyurethane ionomers with a chromophoric functionality (quinone, anthryl, nitroaromatic)<sup>10–13</sup> has been directed toward insertion of azoaromatic groups into an ionomeric architecture, which

combine the well-known properties of polyurethanes with those derived from the coexistence of a minority of ionic groups, usually 1 meq/g polymer or less. The unique properties of these polymers to form aqueous dispersions and the film-forming ability at ambient temperature recommend them for applications as modern ionomer adhesives and coating materials.<sup>14,15</sup>

In previous articles,<sup>16–19</sup> a series of polyurethane cationomers bearing different azobenzene chromophores anchored to the hard or soft segments of the polymer chains were prepared and studied with respect to some of their some photophysical properties. The results evidenced the structural changes that take place during UV irradiation and established that the photobehavior of the polymers is a function of the nature, location, and content of the chromophore attached on the ionomeric backbone. A better photochromic response of the elastomeric films based on polyurethane cationomers containing a side azobenzene group in the flexible component<sup>20</sup> or as an anion of quaternized piperazine rings<sup>21</sup> was also noticed.

To achieve a greater influence of ionic groups on the photoreactivity of chromophores related to the chemical composition of the polymers, our strategy was to obtain functionalized polyurethane cationomers by a two-step substitution of urethane hydrogen atoms with azo groups. Previously, we synthesized some polyester polyurethane anionomers with carboxylate or sulfonate groups on urethane nitrogen atoms by the same procedure and some properties of these poly-

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mers were reported.<sup>22,23</sup> In this article, we describe the synthesis and characterization of polyurethane cationomers with pyridinium rings, *N*-modified with nitroazobenzene groups.

## EXPERIMENTAL

A polyurethane precursor was synthesized by a two-step condensation reaction, using a prepolymer technique from poly(tetramethylene oxide) (PTMO, 0.01 mol,  $M_n$ : 2000) with isophorone diisocyanate (IPD, 0.03 mol) and 2,6-bis(hydroxymethyl)pyridine (0.02 mol). A NCO prepolymer was first prepared by reacting PTMO with IPD in the presence of dibutyltin dilaurate (0.03 wt % in toluene, based on total solids), under a nitrogen atmosphere at 85–90°C, for 4–5 h. A solution of 2,6-bis(hydroxymethyl)pyridine (5 wt % in anhydrous DMF) was then added to the prepolymer dissolved in the same solvent ( $c = 10 \text{ g dL}^{-1}$ ). The reaction was continued for about 6 h. The change of the NCO value during the reaction was monitored by the IR spectral data, following the disappearance of the absorption band centered at  $2260 \text{ cm}^{-1}$ , characteristic of NCO-group absorption.<sup>24</sup> The resulting polymer was purified by precipitation into diethyl ether and then dried under reduced pressure. The polymers with azo groups were obtained as previously described,<sup>22</sup> by a two-step modification of the above polyurethane. In the first step, the reaction of the polymer with sodium hydride in DMF was performed. In the second step, the solution of sodium-substituted polyurethane was reacted with an equivalent quantity of 4-nitro-4'( $\beta$ -iodoethylurethane)azobenzene. To obtain a certain content of chromophoric groups, stoichiometric quantities of a hydride and, respectively, a nitroazobenzene derivative were used, based on the urethane group content. The azo polymers were precipitated with diethyl ether and washed many times with the same nonsolvent. The dried polymers were redissolved in DMF and the solution was stirred with an excess of methyl iodide at room temperature for 15 h to allow quaternization of the pyridine rings. To further purify the azo polycations, they were precipitated again in diethyl ether, collected by filtration, and then dried under reduced pressure.

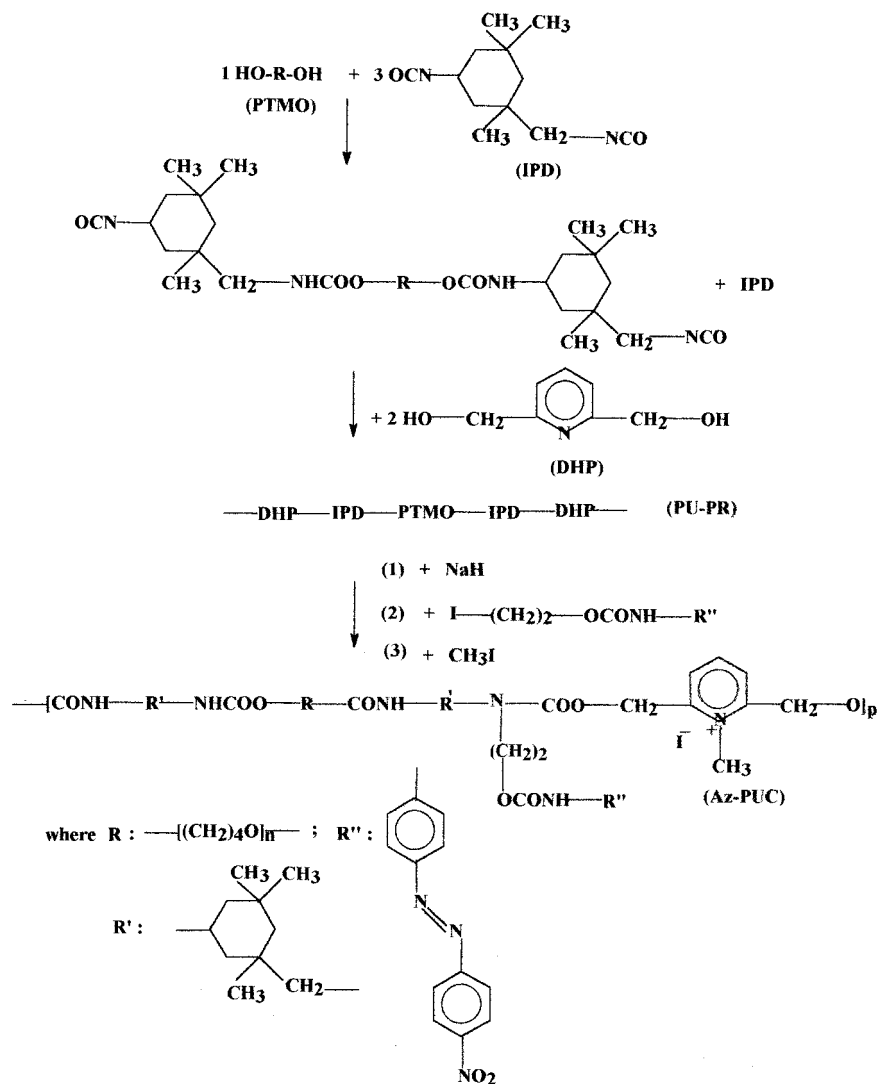
The molecular weight distribution of the pyridine polyurethane (PU-PR) was measured by a PLEMD 950 apparatus equipped with two PL gel mixed columns at 120°C. The sample for measurement was a  $1\text{-g dL}^{-1}$  solution in DMF and the flow rate of the carrier solvent was  $0.7 \text{ mL min}^{-1}$ . The average molecular weight was calculated on the basis of the molecular weight versus the retention volume curve of the monodisperse polystyrene standard. The reduced viscosity of PU-PR was measured with an Ubbelohde viscometer at  $25 \pm 0.2^\circ\text{C}$  in a DMF solution ( $c = 0.4 \text{ g dL}^{-1}$ ). The ionic iodine content was determined tritrimetrically.

Ultraviolet-visible and IR absorption spectra were recorded with Specord M42 and Specord M80 spectrophotometers. Thermal analysis was performed using a Perkin–Elmer differential scanning calorimeter. The polymers ( $15 \pm 2 \text{ mg}$ ) were cooled to  $-130^\circ\text{C}$  and heated at a rate of  $20^\circ\text{C min}^{-1}$  to  $230^\circ\text{C}$ . Transparent films for further testing were prepared by DMF solution casting ( $c = 10 \text{ g dL}^{-1}$ ) at  $60^\circ\text{C}$  on a Teflon plate. Films were allowed to dry at  $50\text{--}55^\circ\text{C}$  for 24 h and vacuum-dried at  $60^\circ\text{C}$  for 48 h to remove any residual solvent. The tensile properties of the azo polycations were measured at room temperature on 0.2–0.4-mm film samples. The measurement was carried out using an universal testing machine Model 500. Irradiations were carried out 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 film was prepared by casting the polymer solution in DMF (1%) onto quartz plates and then allowed to dry at  $50\text{--}55^\circ\text{C}$  under reduced pressure.

## RESULTS AND DISCUSSION

Preparing segmented polyurethane (PU-PR), used as the matrix for ionomer synthesis, involved an addition reaction of a typical oligomeric diol, such as polyether (PTMO,  $M_n$ : 2000) with isophorone diisocyanate, followed by chain extending with 2,6-bis(hydroxymethyl)pyridine, when the molar ratio between the partners was 1/3/2. The synthesis of azo polymers is based on the ability of the polyurethanes to be chemically modified by reactions at amidic nitrogen atoms.<sup>25</sup> Using a two-step procedure, the polyurethane, obtained as above, was derivatized by partial deprotonation of nitrogen atoms from urethane groups to form a sodate compound. The sodium-substituted polymer was then treated with 4-nitro-4'( $\beta$ -iodoethylurethane)azobenzene when nitroazobenzene side groups were introduced. The desired proportion of chromophores inserted onto the polymeric backbone (Az-PU-1-3) can be rigorously controlled by the ratio between the reagent quantity and the urethane nitrogen content, as shown in Table I. As a result, the transformation degree with respect to the content of the azo units incorporated in the polymeric chains was limited to a low level so as to avoid chromophore–chromophore interactions that often lead to complexity in photobehavior. Classical preparation of polyurethane cationomers (Az-PUC-1-3) involved a subsequent quaternization of pyridine rings from the azo support polymers with methyl iodide. The synthetic route for polyurethane cationomers *N*-modified with nitroazobenzene groups is summarized in Scheme 1.

The degree of substitution of the urethane hydrogen atoms with nitroazobenzene groups was obtained from elemental analysis (Table I), by determining the



Scheme 1 Synthesis of azo pyridinium polyurethane cationomers.

increase of the nitrogen content in the nonionic polymers (Az-PU-1-3). On the other hand, the amount of the remaining iodine in the polymers is effectively zero, indicating that the azo chromophore is covalently bound to the polyurethane backbone. This finding argues that the polyurethane precursor was indeed modified by chromophoric groups. Upon quaternization of the pyridine rings with methyl iodide, the formation of pyridinium rings with iodine as the anion (Az-PUC1-3) was evident. From the determination of the ionic iodine content, the quaternization degree of pyridine rings at 82–85% was estimated. By its concentration of ionic groups, of about 50 meq ionic moieties/100 g polymer, the polymers belong to the ionomer class. The data of elemental analysis were in agreement with those of the calculated values of the structure of the polymers. It should be expected that the presence of the nitroazoaromatic chromophore between 2.85 and 10.53 wt % beside the pyridinium moieties extends some traditional properties of the

polyurethane ionomers. Moreover, it is assumed that the structural changes produced by partial functionalization of the polyurethane chains with chromophoric groups does not affect significantly the physicochemical and physicomechanical properties of the corresponding polymeric films.

The basic structure of these azo polymers is of the block copolymer type,<sup>26,27</sup> with alternating soft polyether segments and hard segments composing the *N*-modified and urethane groups beside pyridinium/pyridine rings, where, usually, a microphase separation results. IR and UV absorption spectroscopy confirmed the expected chemical structure of the polymers. In the IR spectrum of Az-PUC-3 (Fig. 1), the hydrogen-bonded NH stretching vibration appeared around 3380 cm<sup>-1</sup> with a relatively weak free NH stretching vibration at 3430 cm<sup>-1</sup>, while the carbonyl stretching band occurred as a doublet with one component at 1745 cm<sup>-1</sup> (free carbonyl) and the other at 1710 cm<sup>-1</sup> (hydrogen-bonded component). Conse-

TABLE I  
Characteristics of Azo-functionalized Pyridinium Polyurethane Ionomers

Polymer	U/A* molar ratio	Azo groups (wt %)	Quaternary degree (%)	Ionic groups <sup>b</sup> (meq/100 g)	Elemental analysis (%)		
					C	H	N
PU-PR <sup>c</sup>	—	—	—	—	Calcd: 65.26 Found: 65.22	9.99 9.97	3.80 3.78
Az-PU-1	1/0.05	2.86	—	—	Calcd: 65.02 Found: 65.04	9.81 9.82	4.23 4.22
Az-PUC-1	1/0.05	2.85	85	51.84	Calcd: 62.50 Found: 62.84	9.52 9.53	3.95 3.92
Az-PU-2	1/0.1	5.58	—	—	Calcd: 64.80 Found: 64.83	9.64 9.66	4.65 4.59
Az-PUC-2	1/0.1	5.56	82	48.90	Calcd: 62.81 Found: 62.80	9.37 9.39	4.53 4.51
Az-PU-3	1/0.2	10.55	—	—	Calcd: 64.38 Found: 64.47	9.33 9.38	5.40 5.27
Az-PUC-3	1/0.2	10.53	83	46.80	Calcd: 62.15 Found: 62.53	9.12 9.13	5.08 5.04

<sup>a</sup> Urethane groups/nitroazobenzene groups.

<sup>b</sup> Determined from ionic iodine content.

<sup>c</sup> Molecular weight of 28,000 determined by GPC;  $\eta_{red} = 0.35$  dL g<sup>-1</sup>.

quently, a part of the carbonyl groups may interact by hydrogen bonding and the intensity of the bonded carbonyl band is a direct measure of the extent of hard-domain formation, typically to polyurethanes. That the "free bond" effect is more pronounced in these polymers compared to other chromophoric polycations<sup>16</sup> is reasonable considering the way of introduction of nitroazoaromatic units into the polymeric chains, as suggested by the IR measurement. Evidence of the incorporating azobenzene is seen in the peaks corresponding to this structure, whose absorptions around 1600 cm<sup>-1</sup> (aromatic —C—H), 1350 and 1540 cm<sup>-1</sup> (symmetric and asymmetric stretching) for —NO<sub>2</sub>, and 1070 cm<sup>-1</sup> for —N=N— appeared. Absorption bands due to CH<sub>2</sub> stretching at 2875–2950

cm<sup>-1</sup> and C—O—C stretching at 1175 and 1250 cm<sup>-1</sup> were also observed.

Since the properties of polyurethane ionomers are due mainly to the phase behavior of the two constituent segments, itself governed by the architectural characteristics and the electrostatic contributions of the ionic species involved, some tensile measurements of the solution-cast films were made (Table II). The tensile response of the azo polyurethanes and the initial nonionic precursor used in this investigation indicated that the polymeric films exhibited a typical elastomeric quality of the normal polyurethanes, with elongation-at-break values reaching over 400%. For the above-mentioned polymers, characterized by a relatively small fraction of repeat hard segments, all

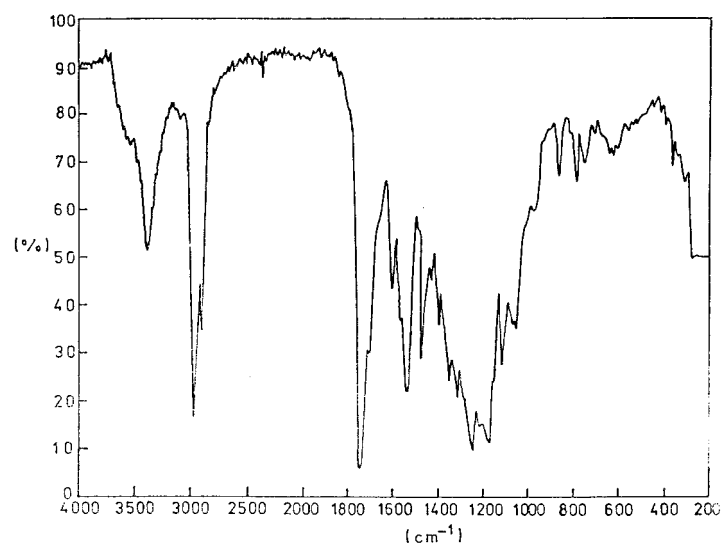


Figure 1 IR spectrum of pyridinium polyurethane cationomer (Az-PUC-3) with nitroazobenzene chromophore in film.

TABLE II  
Tensile and Thermal Properties of the Polyetherurethane Precursor (PU-PR) and Azo Polyurethane Cationomers

Polymer	Tensile strength (MPa)	Elastic modulus		Elongation at break (%)	$T^*$ (°C)	$T_g$ (°C)
		$M_{100}$ (MPa)	$M_{300}$ (MPa)			
PU-PR	3.40	1.15	1.30	450	215	-30
Az-PUC-1	3.90	1.95	1.50	650	210	-52
Az-PUC-2	3.60	1.80	1.46	600	212	-48
Az-PUC-3	3.30	1.68	1.40	500	220	-40

<sup>a</sup> Temperature of 5% weight loss, determined by thermogravimetric analysis.

films showed a good combination of strength and flexibility. Such properties should be attributed to the formation of a hard-segment-rich- and a soft-segment-rich domain structure, further strengthened by electrostatic interactions between ionic groups.

Evidence for microphase separation of these pyridinium polycations can be observed in the DSC thermograms (Fig. 2). According to the DSC results, the azo cationomers showed glass transition temperature values between  $-52^\circ\text{C}$  (Az-PUC-1) and  $-40^\circ\text{C}$  (Az-PUC-3), attributed to the soft-segment-rich phase, in agreement with the data found for other cationomers.<sup>27</sup> As a result of the imperfect phase separation of the flexible and hard segments, these values are greater than those measured for the pure polyether component.<sup>28</sup> Compared to the ionic polymers, the DSC results for the starting polyurethane given in the same figure indicate an increase in the glass transition temperature at a higher value to around  $-30^\circ\text{C}$  (PU-PR), reflecting a increased hard-segment solubility into the soft-segment phase. Furthermore, the  $T_g$  variation is more pronounced for polycations, where aggregation of ionic groups by Coulombic interactions constitutes the primary driving force for an enhanced biphasic separation, as clearly evidenced in ionomers.<sup>29</sup>

Additionally, in the DSC curves of the polycations, a small endotherm appeared about  $80^\circ\text{C}$ , but its origin remains unclear. This could be related to a possible rearrangement of the pyridinium groups and hydro-

gen bondings accompanying the polymer *N*-modification with the azo chromophore, as stored at room ambient. For other polyurethane ionomers, the peak temperature around  $70$ – $90^\circ\text{C}$  was assigned to the dissociation temperature of the short-range ordering in the hard domain of the elastomers, water desorption, or as an "annealing" endotherm.<sup>24,27,30</sup> Studies on the morphology of some polyionenes reported the second relaxation temperature as caused by the glass transition of the polycation segments.<sup>31</sup> But this endotherm was not observed in the DSC curve of PU-PR, sustaining, rather, the above explanation. Unlike common polyurethanes, in all azo polymers, higher-temperature melting endotherms were not evidenced, possibly due to the unsizable crystallinity of the hard-segment phase, generated by an asymmetric isocyanate and voluminous chromophore. Such behavior is in agreement with the results found on some amorphous polyurethanes of ionic or nonionic type, according to that a hard-segment  $T_g$  was seldom measured in the DSC thermograms.<sup>27</sup>

The thermal stability of the azo polycations was determined by thermogravimetric analysis under nitrogen with a scan rate of  $10^\circ\text{C}/\text{min}$ . All the polymers presented a decomposition temperature in the range of  $210$ – $220^\circ\text{C}$ , indicating a good thermal stability, similarly to the most classical polyurethanes (Table II).

One of the new properties introduced by the presence of photoisomerizable chromophores may be the geometrical structure changes of azobenzene from the *trans* configuration to the *cis* form, useful to control the chain conformations in the polymer backbone. To examine the effect of hindered motions of azo units on their behavior, the photosensitivity of the azo polymers in solution and film was studied, following the changes that appeared in the electronic absorption spectra during UV irradiation.

In Figure 3 is shown UV spectra for Az-PUC-3 in a DMF solution before and after UV irradiation. As seen, the azo polymer displays a strong absorption band centered at  $428\text{ nm}$  assigned to the  $\pi$ – $\pi$  electronic transition of the *trans* isomer. The intensity of the  $\pi$ – $\pi^*$  absorption band decreased slowly but gradually with the irradiation time, reaching a phototransformation degree of about 20% after 30-min irradiation.

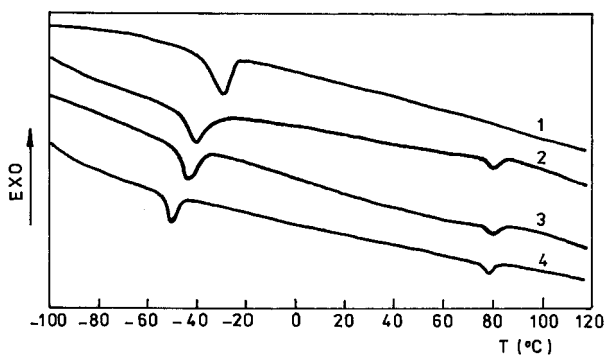
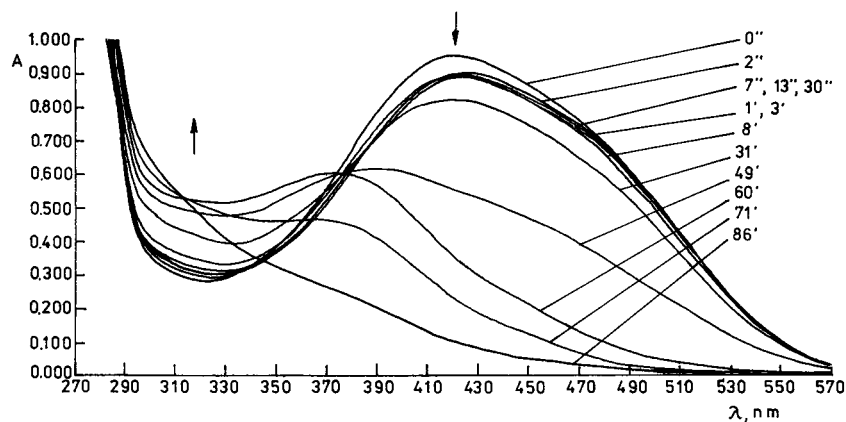


Figure 2 DSC thermograms of polymers: (1) PU-PR; (2) Az-PUC-3; (3) Az-PUC-2; (4) Az-PUC-1.





**Figure 3** Changes in electronic absorption spectra of Az-PUC-3 in DMF solution during UV irradiation at 298 K. The irradiation times are indicated in the figure.

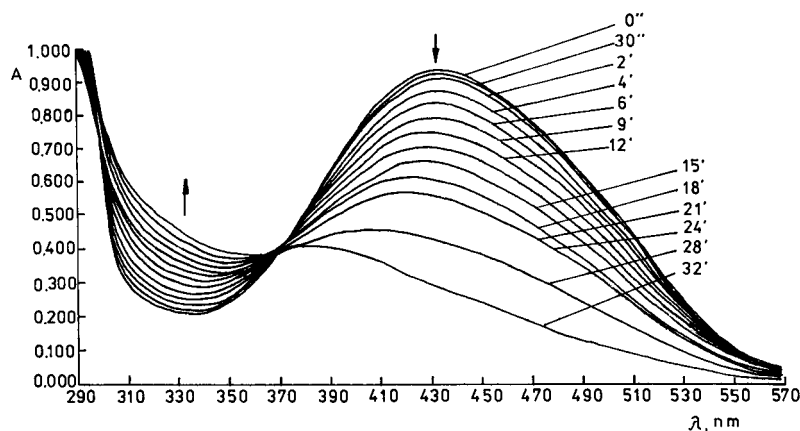
tion. The presence of the isobestic point at 370 nm in the first stage of this photoprocess indicates that the *trans-cis* photoisomerization is only a chemical transformation suffered by the chromophore. As the irradiation time increased to 86 min, the absorption band completely disappeared as result of an irreversible photobleaching reaction which accompanied the chromophore. Such behavior may be the effect of complex photoreduction pathways of nitroazobenzene groups at colorless hydrazobenzene structures.<sup>32</sup>

On studying the corresponding neutral azo precursor (Az-PU-3), an increased sensitivity to UV irradiation comparatively with its ionomeric form was observed. Thus, the absorption maximum at 430 nm ascribed to the *trans* isomer decreased more rapidly as the exposure time increased (Fig. 4). In this respect, it can yield about 58% phototransformation of the chromophore on 25-min irradiation. This difference of the photoresponse between nonionic and ionic polymers may be related to the lower mobility of the chromophore in the azo cationomer, as a result of the association of ionic groups achieved in polar solvents

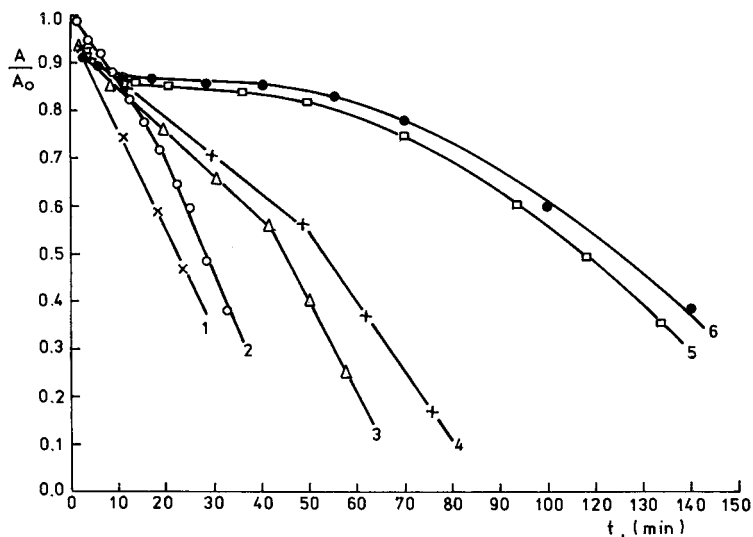
and interactions between the solvent and the ionomeric backbone.

Comparatively with Az-PUC-3, where the photoprocess dynamics can be considered as a two-step process, the decrease of the absorption band in its precursor occurred almost linearly (Fig. 5). A decrease of the azobenzene content in polymeric chains (Az-PUC-1) has a favorable effect on the *trans-cis* photoisomerization of the chromophore in the first stage of UV irradiation. In each case, the formation of isobestic points argued the presence of two spectrophotometrically distinguishable species in such azo polymers.

Following the evolution of the photoprocess in thin films (Az-PUC-3), under the same irradiation conditions, it was found that the absorption maximum at 430 nm, corresponding to the  $\pi-\pi^*$  transition decreased much more slowly as the UV exposure time increased (Fig. 6). Comparison of the data for Az-PUC-3 in solution and the film state indicated an enhanced photostability of the chromophore in the latter, even under long irradiation times. Thus, after



**Figure 4** UV absorption spectra monitoring the phototransformation of nitroazobenzene chromophore from nonionic precursor (Az-PU-3) in DMF solution at 298 K.



**Figure 5** Dependence of relative absorbance on irradiation time of azo polyurethane in solution and the film state during UV irradiation at 298 K, in DMF: (1) Az-PU-1; (2) Az-PU-3; (3) Az-PUC-1; (4) Az-PUC-3; in film: (5) Az-PU-3L; (6) Az-PUC-3.

about 30 min of irradiation time, a transformation degree of about 10% was estimated. It can be clearly seen that there is a reduced movement of the nitroazobenzene groups in the polymer matrix, limited probably by their location in the nonionic hard fragment of the polyurethane backbone, on the one hand, and by physical crosslinking of ionic structures, on the other hand.

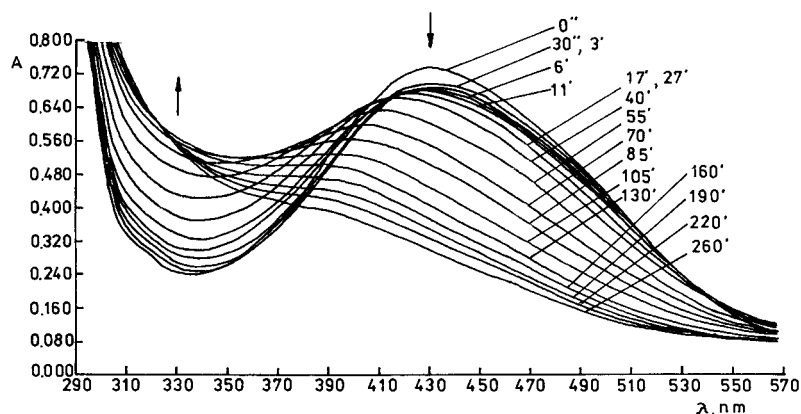
Therefore, the main factor responsible for the photobehavior of the polymer films is the local mobility of the chromophore, controlled by its size, the free volume around the azo units, and the hydrophobic-hydrophilic interactions typical to the ionomer systems. In the neutral polymer, the distribution of the relative absorption on the irradiation time indicated that the photosensitivity is slightly higher than that for the ionic azo polymer (Fig. 5). These characteristics, together with a higher concentration of azo chromophores regularly placed at the urethane linkages of

these ionomers as pendant-azo types, may be an advantage for optical applications.

One might expect that investigation of these polymers by other methods would provide useful data about their properties and application potential. Further experiments on the chromophoric polyurethanes of the ionomer type are in progress in our laboratory.

## CONCLUSIONS

A novel series of chromophoric polyurethane cationomers of the pyridinium type with nitroazobenzene incorporated on urethane hydrogen atoms was synthesized and their properties were characterized. The new ionomeric polymers exhibit good film-forming ability and typical elastomeric behavior. A more accentuated sensitivity of polymers in solution than in the film state was evidenced when the samples were exposed to UV irradiation.



**Figure 6** Changes in UV-vis absorption spectra of Az-PUC-3 in film upon UV light exposure.

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