

# Poly(etherurethane) Anionomers with Azobenzene Carboxylate Groups: Synthesis and Properties

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**ABSTRACT:** A new diol with a one-sided azobenzene-carboxyl group was prepared to be used for photosensible polymers synthesis. Azobenzene carboxyl containing polyurethane based on poly(tetramethylene oxide) diol of 2000 average molecular weight, 2,4-tolylene diisocyanate, and the mentioned azo diol, was obtained and characterized. Upon neutralization the acid form with metal acetate ( $\text{Li}^{+1}$ ,  $\text{Ca}^{+2}$ ) or triethylamine azo carboxylate anionomers with an improved phase separation were obtained. Viscometric mea-

surements of diluted dimethylformamide solutions exhibited evidence of polyelectrolyte behavior. Some aspects of the *trans-cis* photoisomerization have been examined to design in future various dyed aqueous dispersions. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 577–582, 2005

**Key words:** azo polymers; ionomers; isomer/isomerization; polyurethanes

## INTRODUCTION

Polyurethane ionomers are known as one of the most complex and varied family of block copolymers, which combine the well-known properties of the parent polymers with those derived from the existence of a small number of ionic groups (usually 10 mol % or less) attached to the hydrophobic backbone. This results in the formation of aqueous dispersions with better stability and finer particle size, promoted most likely due to the ionic groups acting as internal emulsifiers.<sup>1</sup> The development of such ionic elastomers pioneered by Dietrich et al.<sup>2</sup> and Cooper et al.<sup>3</sup> continues to be of great interest for practical applications, with important advantages for air pollution reduction in UV curing industries and modern ionomer adhesive and coating materials.<sup>4</sup> Among them, the ionomers with carboxylic and sulfonic groups were considered to be more attractive since their properties can be tailored according to larger needs,<sup>5</sup> including biomedical devices, temperature-sensing elements, polymer electrolytes, and so on.<sup>6–8</sup>

For the synthesis of carboxylate anionomers, it is the conventional route to use a chain extender with performed ionic or ionogene groups, such as  $\alpha,\alpha$ -dimethylol propionic acid,<sup>9–15</sup> 2-hydroxyethyl methacrylate,<sup>16</sup> 3, 4-dihydroxycinnamic acid,<sup>17</sup> 4-hydroxycoumarin,<sup>18</sup> or phenolphthalein.<sup>19</sup> Another flexible method of controlling the ionic content in the PU backbone

was based on a two-step derivatization of a neutral polyurethane, which provides a feasible way to obtain side-chain ionic polymers.<sup>20</sup>

In our earlier articles,<sup>21–25</sup> we have dealt with the synthesis and characterization of new PU anionomers with carboxylate or sulfonated groups, and the availability of some of them to be tested in preparing composites with conductive polymers was reported.<sup>22,24,25</sup> The combination of low carboxylate content and pendant azobenzene groups introduced by means of a short diol could generate a class of photopolymers with anticipation of their improved properties. To our knowledge, the incorporation of azobenzene carboxylate units in PU anionomers by an azo carboxyl diol never was approached in the literature of ionic polyurethanes. Previously,<sup>26–29</sup> we studied PU cationomers with different chromophoric functionality as azobenzene, stilbene, and triazene to provide a good photoresponsiveness in elastomeric films, which are important in a variety of specialized applications. In this work we present the synthesis of the chain extended PU anionomers containing azobenzene carboxylate units and the effect of the structure of these building components on some physicochemical properties of the polymers. In addition, the *trans-cis* photoisomerization of the polymeric chromophore in thin film and the influence of the pendant counterion type on solution properties are addressed in this section.

## EXPERIMENTAL

### Azobenzene carboxyl diol synthesis (Az-CD)

To *para*-aminobenzoic acid (7.56 g, 55.2 mmol) dissolved in 100 mL water containing aqueous HCl (15

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mL 37%), an aqueous solution of sodium nitrite (3.8 g, 55.2 mmol) was dropped at 2–4°C for 30 min. The resulting diazonium salt was coupled with *N,N*-di( $\beta$ -hydroxyethyl)aniline (10 g, 55.2 mmol) dissolved in 150 mL methanol : water (2 : 1 v/v) at the same temperature for 50 min. In the reaction mixture sodium acetate (5 g, 60 mmol) was added, maintaining the temperature for 60 min. The reaction was stirred then at room temperature for 1 h, after which the solid was filtered. The product was recrystallized from ethanol : water (1 : 3 v/v). Yield: 15.4 g (85%), mp: 206–208°C.

IR (KBr,  $\text{cm}^{-1}$ ): 3400, 3200 (OH), 1690 (CO), 1600 (aromatic CH), 1370 and 1150 (N=N), 820 (1,4- $\text{C}_6\text{H}_4$ ). Anal. Calcd for  $\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_4$ : C, 62; H, 5.77; N, 12.76%. Found: C, 61.99; H 5.75; N, 12.73%.

### Polymer synthesis

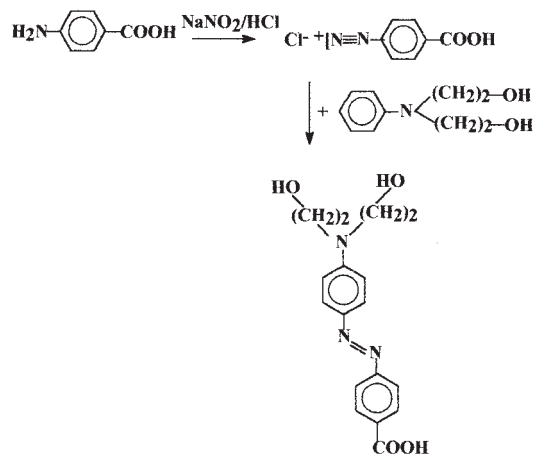
Polyurethane anionomer (Az-PUA1) was synthesized by the prepolymer method under purified nitrogen, using poly(tetramethylene oxide) diol of average molecular weight of 2000 (PTMO), 2,4-tolylene diisocyanate (2,4-TDI as mixture 2,4- and 2,6- isomers 80 : 20 v/v), the above diol (Az-CD) in a molar ratio of 1/2/1 (Az-PUA1). Dry PTMO (0.5 mmol) was reacted with 1 mmol TDI under purified nitrogen atmosphere at 70°C for 4 h. To the prepolymer mixture dissolved in anhydrous DMF ( $c = 20 \text{ g dl}^{-1}$ ) was then added 0.5 mmol azo diol, and the reaction was continued for 10 h at 65°C. The evolution of these reactions was monitored by IR spectroscopy until the end hydroxyl and isocyanate groups were reacted, as confirmed by the disappearance of their stretching bands centered at 3480 and 2260  $\text{cm}^{-1}$ , respectively. Carboxylated anionomers (Az-PUA2–4) were prepared by neutralization of carboxylic groups in DMF solution of Az-PUA1 ( $c = 10 \text{ wt } \%$ ) with a stoichiometric amount of metal acetates or triethylamine, so that the molar ratio of carboxylic to acetate was 1 : 1. The temperature was increased at 70°C, where it was maintained for 4 h (Az-PUA2,3) or 30 min (Az-PUA4). All polymers were isolated by precipitation from DMF solutions with diethyl ether washed with water, and dried under reduced pressure at 50–55°C for 48 h.

$^1\text{H-NMR}$  for Az-PUA1 (DMSO- $d_6$ , ppm,  $\delta$ )  $\mu$  9.5, 8.8–9 (NHCOO), 8.07 (d, CH *ortho* to COOH), 7.83 (d, CH *ortho* to N=N), 6.95–7.2 (m, CH *ortho* to N and aromatic protons from TDI), 4.28, 4.06 (s,  $\text{CH}_2\text{-OCONH}$ ), 3.3 (m,  $\text{CH}_2\text{-O}$  from PTMO), 2.2, 2.1 (s,  $\text{CH}_3$  from TDI), 1.49 (m,  $\text{CH}_2\text{-CH}_2$  from PTMO).

Anal.(%) Calcd for Az-PUA1: C, 65.04; H, 9.60; N, 3.66; Found: C, 65.0, H, 9.57; N, 3.60.

### Characterization

The structure of monomer and polymers was verified by  $^1\text{H-NMR}$ , and IR spectroscopy, using a Bruker 300

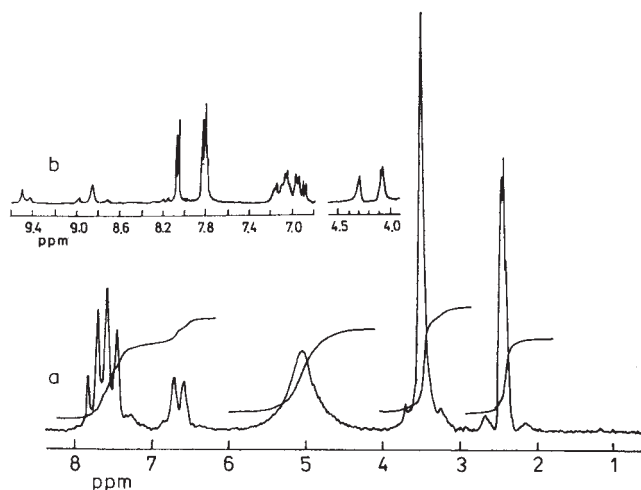


**Scheme 1** Synthesis of azobenzene diol with carboxyl group (Az-CD).

MHz or a Specord M80 spectrophotometer. Thermal transitions were measured on a Perkin–Elmer differential scanning calorimeter. Polymers ( $15 \pm 2 \text{ mg}$ ) were cooled to  $-130^\circ\text{C}$  and heated at a rate of  $20^\circ\text{C min}^{-1}$  up to  $230^\circ\text{C}$ . GPC measurements were performed with a PL MD-950 apparatus (Polymer Laboratories) equipped with an evaporative mass detector and two PL gel  $5 \mu\text{m}$  columns. The sample for measurement was  $1.0 \text{ g dl}^{-1}$  solution of Az-PUA1 in DMF, and the flow rate of the carrier solvent was  $1 \text{ mL min}^{-1}$ . The average molecular weight was calculated on the basis of the molecular weight versus retention volume curve of monodisperse polystyrene standard. The reduced viscosity of anionomer solutions in DMF was measured with an Ubbelohde viscometer with a 0A capillary in a temperature-controlled water bath ( $25.0 \pm 0.2^\circ\text{C}$ ). Irradiations were carried out using a 500 W high pressure mercury lamp at room temperature in 10 mm path length quartz cells, when the initial absorbance of the samples was maintained between 0.9 and 1.0. The polymer film was deposited on a quartz plate by casting from DMF solution ( $c = 1 \text{ g dl}^{-1}$ ) and then allowed to dry at  $55\text{--}60^\circ\text{C}$  under reduced pressure for 48 h.

## RESULTS AND DISCUSSION

Synthesis of the chromophoric diol incorporating azobenzene carboxyl acid group assumed preparing diazonium salt of the *p*-aminobenzoic acid followed by a coupling reaction of the resultant intermediate with *N,N*-di- $\beta$ -hydroxyethylaniline, according to Scheme 1. The new diol (Az-CD) with azobenzene carboxyl pendant was characterized with spectral and analytical methods. The elemental analysis data given in the experimental part were in agreement with those calculated values for the expected structure.



**Figure 1**  $^1\text{H-NMR}$  spectra of (a) the azobenzene diol (Az-CD) with carboxyl group, and (b) the hard segments of azobenzene polyurethane (Az-PUA1) with carboxylic groups.

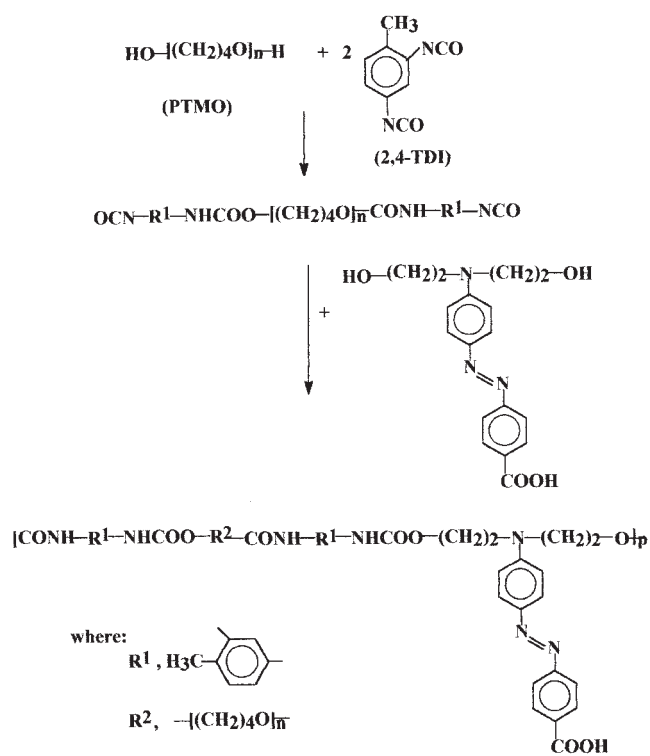
In the  $^1\text{H-NMR}$  spectrum of Az-CD (Fig. 1a) were found the signals of  $\text{CH}_2\text{-CH}_2$  protons at 3.5 ppm (s, 8H) and at 5.1 ppm (m, 2H) corresponding to OH protons. The other three signals at 6.6 (d, 2H), 7.6 (d, 2H), and 7.75 ppm (d, 2H) were assigned to aromatic protons in *ortho* position to N,  $\text{N}=\text{N}$ , and  $\text{COOH}$ , respectively.

Using this azo diol as a chain extender in the polyaddition reaction, one side chain of azobenzene carboxylic acid groups-bearing polyurethane was prepared from a PTMO diol with an average molecular weight of 2000, 2,4-TDI, and the above diol, in which the molar ratio of the partners was 1/2/1 (Az-PUA1). The molecular architecture of the azocarboxyl polyurethane is shown in Scheme 2. The carboxyl groups within a linear polymer chain were further neutralized with lithium and calcium acetates or triethylamine to form azo anionomers (Az-PUA2, Az-PUA3, and Az-PUA4). The azo anionomers so formed differ by the kind of neutralizing cation ( $\text{Li}^+$ ,  $\text{Ca}^{2+}$ ,  $^+\text{NHR}_3$ ), and it is reasonable to suppose that the interactions between ions and their counterions are responsible mainly for the physical properties of the polymers. These polymers exhibited excellent film-forming properties so that thin films of optical quality could be easily obtained by casting the filtered polymer solutions in DMF.

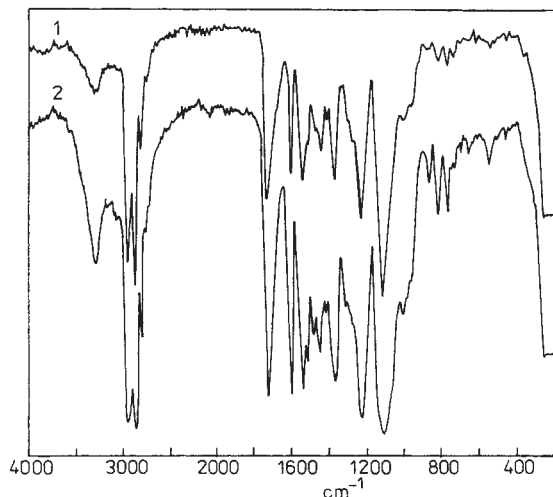
The structure of the polymers was confirmed by  $^1\text{H-NMR}$ , IR, UV spectral data, GPC, and elemental analysis. For Az-PUA1 a molecular weight of 28,300 determined by GPC supports the formation of the block copolymer with long flexible polyether segments and short hard segments including urethane structure joining the azobenzene carboxyl chromophore to the polymer chain. In the NMR spectrum

of Az-PUA1 (Fig. 1b) a shifting of peaks towards the lower field with about 0.25 ppm was observed for the aromatic protons to azo group. The integral values of these protons (8.07, 7.95 ppm) and the aromatic protons from TDI (6.95–7.2 ppm) as well as of the methylene protons from urethane groups (4.06, 4.28 ppm) indicates that the molar composition ratio of the azo polyurethane determined by the peak areas is in concordance with the feed ratio of the components employed for polymerization. From these observations, it is considered that Az-PUA1 contains around 73 meq. carboxyl groups/100 g polymer.

The IR spectra of Az-PUA1 film (Fig. 2) showed characteristic bands to the common polyetherurethanes, for example, the NH and  $\text{CH}_2$  asymmetrical stretching vibration in the 3300 (H-bonded component) and 2850–2950  $\text{cm}^{-1}$  region, the urethane carbonyl stretching band at 1720  $\text{cm}^{-1}$ , and the CH-aromatic stretching at 1600  $\text{cm}^{-1}$ . To the polyether structure corresponds an absorption band positioned at 1100, 1220  $\text{cm}^{-1}$ , whereas the *p*-phenylene is characterized by the absorption band at around 820  $\text{cm}^{-1}$ . Vibration bands in the 1400–1500 zone and 1500–1650  $\text{cm}^{-1}$  were not distinguished due to the overlapping of CO absorption bands and bands of the aromatic rings from isocyanate, one of which is connected with the asymmetric deformational vibrations of carboxylate anions. After the ionization of  $-\text{COOH}$  to  $-\text{COO}^-$   $\text{Ca}^{+2}$  (Fig. 2), some changes take place at 1600 and



**Scheme 2** Synthesis of azobenzene polyurethane with carboxylic groups (Az-PUA1).



**Figure 2** IR spectra of (1) the azobenzene polyurethane with carboxylate groups (Az-PUA3, 1) and (2) azobenzene polyurethane with carboxylic groups (Az-PUA1).

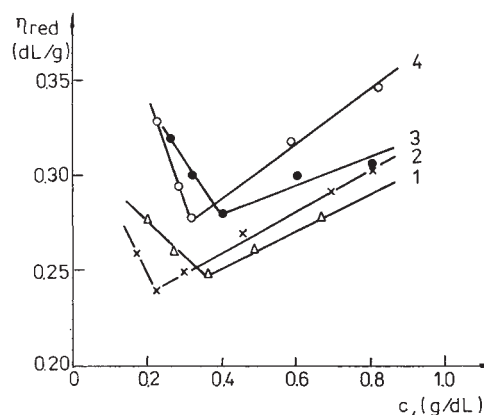
$1220\text{ cm}^{-1}$ , in which the intensity of the absorption bands decreased compared to Az-PUA1. The N=N stretching from the azobenzene trans configuration was also observed as a band at  $1370\text{ cm}^{-1}$ .

Since it has been recognized that segregation of the ionic groups into microdomains, forming coulombic crosslinks, gives rise to many of the unique properties of ionomers, glass transition temperatures of all anionomers were measured using DSC. Excepting Az-PUA2, each polymer showed evidence of a single well defined glass transition attributed to the soft-phase transition as a sensitive indicator of order within a PU backbone.<sup>30</sup> Az-PUA2 exhibited a small melting endotherm near  $-10^\circ\text{C}$ . Because the distance between the Tg of the pure polyether (Tg, PTMO:  $-84^\circ\text{C}$ )<sup>31</sup> and that of synthesized polyanions increased, a certain degree of hard-soft segment mixing occurred. Examining the obtained values (Tg, Az-PUA: 1,  $-28^\circ\text{C}$ ; 2,  $-40^\circ\text{C}$ ; 3,  $-32^\circ\text{C}$ ; 4,  $-36^\circ\text{C}$ ), it is clear that these differences are the consequence of the increased number of hard-segment interactions resulting from the structure of the carboxyl chain extender and from the interaction of ions between different polymer chains, where may exist the association of ions groups, the crosslinking of polymer chains, and coordination effects. As expected, the weaker acid strength of the carboxylate group led to formation of weaker physical crosslinks in the carboxylate anionomers and resulted in less phase-separated structures.

On the other hand, it seems that the primary cause of the differing Tg's must be ascribed to anion type. For Az-PUA3 a greater interaction between the  $\text{Ca}^{+2}$  anion and polymer chains led to an increase in Tg. Similar thermal behavior has been observed on model systems of carboxylate PU ionomers and other carboxylate polyurethanes.<sup>32,33</sup>

Previously, studies on ionomer solutions by viscometry, static and dynamic light scattering, small-angle neutron scattering, or conductometry evidenced the modification of chain conformation and dimensions of the anionomers in solution.<sup>23,33</sup> Experimental results have established that in the nonpolar or low polarity solvents, intramolecular and intermolecular aggregation due to the dipolar attractions between chain segments predominates,<sup>34,35</sup> whereas in high-polarity solvents the repulsive electrostatic interactions between like charges on the same backbone lead to a chain expansion, known as the polyelectrolyte effect.<sup>36</sup> Although these aspects have been extensively studied, the interpretation of polymer-solvent interactions and the ionic content of the polymer in determining the solution structure of ionomers is not clear yet.

From this point of view, our data regarding viscometric measurements of the synthesized azo polymers illustrated also a polyelectrolyte behavior in DMF. In Figure 3 is displayed the reduced viscosity evolution as a function of polymer concentration. At high dilution (below  $0.2\text{ g dL}^{-1}$ ), both the carboxyl and carboxylate polymer solutions showed a slight increase in the value of reduced viscosity with decreasing polymer concentration, comporting similarly to that of PU anionomers bearing carboxylate groups.<sup>21,37-39</sup> The obtained values can be attributed to the ionization process of the carboxyl groups and appearance of repulsive electrostatic interactions between identical charges of the same macromolecule. This is the typical electrostatic expansion behavior of weak polyacids. In the same concentration range, reduced viscosity decreased when the carboxyl groups were neutralized with  $\text{Li}^+$ ,  $\text{Ca}^{+2}$ , and  $^+\text{NHR}_3$  cations. Like polyelectrolyte solution<sup>15,16</sup> in a higher polarity medium that dissolves both the hydrophobic and hydrophilic segments, dissociable groups on the polyurethane undergo a state change from the polarized residue to free



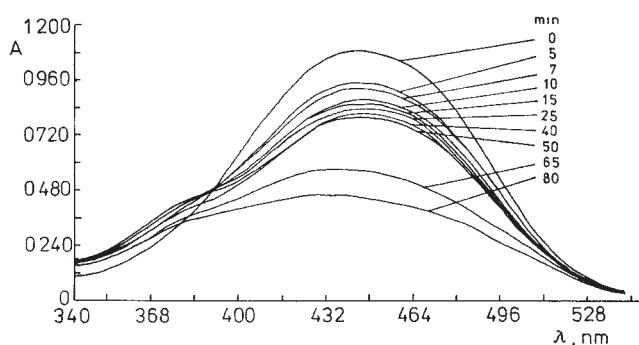
**Figure 3** Reduced viscosity ( $\eta_{red}$ ) versus concentration for azobenzene polyurethane with (1)  $-\text{COO}^- \text{Li}^+$ , (2)  $-\text{COO}^- \text{N}^+\text{HR}_3$ , and (4)  $-\text{COO}^- \text{Ca}^{+2}$ ; and (3) azobenzene polyurethane with  $-\text{COOH}$  in DMF.

ions via tightly and loose bound ion pairs with increasing distance between the centers of positive and negative charges. Ion pairs are forming on account of anions anchored on the polymer side chain and counterions, with the appearance of dipole-dipole attraction between these. The existence of the associated species in tandem with free polyions in dilute solution of ionomers and in a polar medium has been proved by Cooper et al.<sup>34</sup> using the dynamic light scattering method. For a concentration higher of  $0.4 \text{ g dL}^{-1}$  (Az-PUA1) and  $0.2 \text{ g dL}^{-1}$  (Az-PUA2-4), these azo PUs showed a Huggins constant near to that of a nonionic polymer, suggesting that the shape of the chain segments of the polyanions is similar.

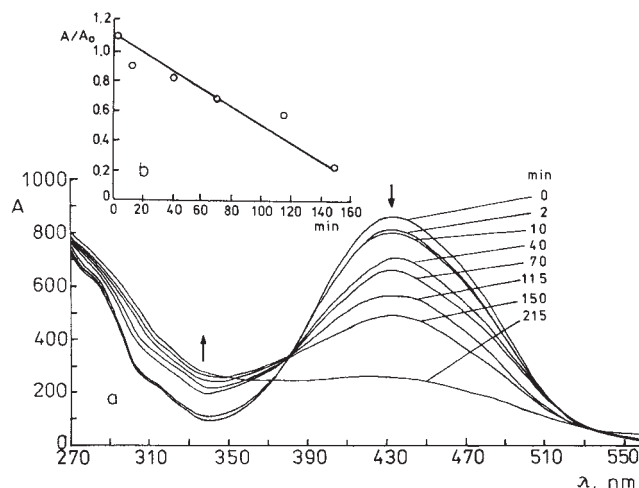
Such results demonstrate the importance of poly-anion-solvent interactions and the nature of neutralizing cation from the polyurethane chain in determining the solution properties of carboxylate azo ionomers.

Noticing the chromophoric and amphiphilic nature of the anionomers, it is of interest to check whether the azobenzene chromophores in the side chains of the polymers act as photoresponsive sites under particular conditions. Thus, within the classic scheme of isomerization of the azo carboxyl groups, the photobehavior of the polymeric chromophore (Az-PUA1) was compared with that of the starting diol. In Figure 4 is shown the UV spectra for Az-CD in a DMF solution prior to and after UV irradiation. As can be seen, the azo diol displays a strong absorption band centered at  $447 \text{ nm}$  ascribed to the  $\pi-\pi^*$  electronic transition of the *trans* isomer. The photoisomerization from the *trans* to the *cis* azobenzene isomer was followed by decreasing the intensity of this band with irradiation time, when a phototransformation degree of about 80% after 70 min irradiation was found. In this case the appearance of two isosbestic points at 390 and 540 nm suggests purity of the photoisomerization process.

Under the same irradiation conditions, the *trans-cis* photoisomerization of azobenzene groups in the thin film of Az-PUC1 exhibited a similar photobehavior to that observed for the above described azobenzene



**Figure 4** Changes in UV-Vis spectra of azobenzene diol (Az-CD) with carboxyl group in a DMF solution during UV irradiation times.



**Figure 5** (a) Changes in the electronic absorption spectra of the azobenzene polyurethane with carboxylic groups (Az-PUA1) in film during irradiation times and (b) the dependence of the relative absorbance on the irradiation time of the Az-PUA1 film.

diol. From the results presented in Figure 5 (plots a,b), it was observed that the photoisomerization required high times of irradiation for reaching an equilibrium state. As a consequence of a lower mobility of chromophore moieties in the polymer film, the intensity of the absorption band at  $435 \text{ nm}$  decreased much more slowly during irradiation, the molar fraction of *cis* isomer after 215 min of irradiation being 0.85. The presence of two isosbestic points at 380 and 530 nm indicated the photoisomerization as the most important photochemical change of the azobenzene carboxyl chromophore without involving side reactions of photodegradation. Comparing the photobehavior of the Az-PUC1 film with that of the azo diol, it can be seen that the photoreaction needs longer times of irradiation in the former than in the monomer solution. Therefore, the *trans-cis* photoisomerization is sensitive to the competitive interactions with other segments of the polymeric backbone, and as a result a difference in the photoisomerization rate of the azobenzene in film ( $k = 1.6 \times 10^{-4} \text{ s}^{-1}$ ) and in the starting diol ( $k = 4.5 \times 10^{-4} \text{ s}^{-1}$ ) was determined. Studies regarding other properties including the formation of dyed aqueous anionomer dispersions based on azobenzene carboxylate PUs with or without additives are in progress now in our laboratory.

## CONCLUSIONS

Novel polyurethane anionomers with azobenzene carboxylate groups were synthesized using an azo carboxyl diol as the chromophoric chain extender. Anionomers with  $\text{Li}^+$ ,  $\text{Ca}^{2+}$ , and  $^+\text{NHR}_3$  cations were prepared from carboxyl-containing polymers via neu-

tralizing with acetates or triethylamine. The morphology and their behavior in dilute solution were investigated as a function of the neutralizing anion. Consequently, the phase separation between hard and soft segments improved as evidenced by an increase in  $T_g$ , while the ionic interactions are responsible for the polyelectrolyte effect present in a polar solvent. In thin films the *trans-cis* isomerization can be photochemically induced to a high level as the UV light exposure time increased.

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