

Polyurethane Cationomers with Azobenzene Side Groups in the Flexible Component. Synthesis, Characterization, and Properties

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ABSTRACT: Azo poly(tetramethylene oxide) diols containing one azobenzene side unit on the chain are proposed as intermediates for chromophoric polyurethanes, to avoid difficulties linked with the photochromic behavior of some azo polyurethane cationomers in the film state. Starting from the azo diols of different molecular weight, 4,4'-dibenzyl-diisocyanate and *N*-methyldiethanolamine, followed by a quaternization with chloroacetamide, two polyurethane cationomers with azobenzene in the soft segment were synthesized and characterized. As a reference polymer, the azo non-ionomeric polyurethanes were also synthesized and characterized. Indeed, it evidenced that under UV irradiation, the polymeric films exhibited photochromic behavior, explained by the molecular mobility of the azo chromophore inserted in the polyether component but controlled of the electrostatic interactions between neighboring chains, specifically to the ionomeric matrix. These polymers are known for their elastomeric nature and is assumed to be of interest in some future applications.

KEY WORDS Azo Polyether / Polyurethane Cationomer / Photobehavior /

For over a decade, incorporation of the chromophore structures into polymeric thin films has become an important means of obtaining desired properties in materials intended for optical technologies.¹ One of the most common chromophore for these materials is the azo aromatic based derivative, whose fast photoisomerization between the generally more stable *trans* isomer and the less stable *cis* form, is seeing widespread use in the performing of practical devices.^{2–5} Among currently used polymers, polyurethane systems offer a number of advantages such as facile synthesis, optical quality thin films, good stability, and solvent resistance.⁶ By tailoring the molecular structure of the polyurethane backbone and azo aromatic group, a variety of azo-based polyurethanes have been studied and developed for applications in liquid crystal displays, photochromic systems, non-linear optical or photodegradable materials.^{7–10} As first demonstrated in the literature, use of photochromic azobenzene labels in the chains of some polyurethanes, as a sensitive molecular probe of physical aging in amorphous polymers, provided information on the aging time of the polymeric backbone related to the loss of free volume, its distribution and its change with aging.¹¹

Our interest has been directed toward segmented polyurethane ionomers, whose interesting applications are generally related to the ability of polymers to form aqueous dispersions, widely utilized as film and coating materials.^{12–14} The insertion of some photoactive moieties that elicit optical response in such polymers, can be particularly challenging owing to the inherent reactivity of many of these groups located into very

complex ionomeric architecture, whose properties are at least in part, governed by electrostatic considerations.^{15–17} In contrast with the scientific and commercial interest focused on polyurethane cationomers, very little work concerning the insertion of chromophore structures in polymeric chains, as a way to diversify the traditional applications, was reported in literature.^{18,19}

In previous papers,^{20–24} several polyetherurethane cationomers with azo aromatic units bound to the hard segments of the polymer chains were synthesized and studied. Characterization of the azo polycations has shown that the structural changes induced by UV irradiation depend on the structure of the azo derivative, polymer matrix, and the content of chromophore covalently or electrostatically attached to the polymer chains. It reasonable to conclude that the mobility of azo aromatic moieties is primarily responsible for the differences observed in photoresponsiveness of the azo polycations with the same chromophore and composition. To further probe the photochromic properties of the elastomeric ionomer films, azobenzene groups could be inserted into the low- T_g segment of the polyurethane chain. This allow for the determination of molecular mobility of the chromophore within the soft segment of the polymeric backbone. The approach chosen in this study was to introduce an azobenzene side-group between two flexible blocks of the same length and composition in poly(tetramethylene oxide) diols used as intermediates for polyurethanes. The synthesis and characterization of these new azo diols and the corresponding polyurethane cationomers are presented below in order to study the structure-property

relationship required for the development of novel photochromic elastomeric materials.

EXPERIMENTAL

Materials

Poly(tetramethylene oxide) diols of 1000 and 650 average molecular weight (PTMO, BASF comp.) were dried and degassed at 100–110°C and 1–2 mmHg for 2 h before utilization. 4,4'-Dibenzylideneisocyanate (DBDI) was synthesized in our laboratory and freshly distilled before use.²⁵ *N*-Methyldiethanolamine (NMDA) (Aldrich Chem. Comp.) was used as received. Dimethylformamide (DMF) and the solvents used in the synthesis were dried over 5A molecular sieves.

Synthesis of Azo-Polyether Diols

A solution of *para*-toluenesulfonyl chloride (4.5 g, 0.0224 mol, TsCl) in anhydrous THF (20 mL) was dropped into a solution of 4-*N,N*-di(β -hydroxyethyl)-azobenzene (3.19 g, 0.0112 mol) in THF (20 mL) and pyridine (3 mL). The reaction mixture was stirred at 5°C for 30 min and then at room temperature for 3 h. After the solvent removal by distillation, the compound was dissolved in chloroform and washed several times with a solution of potassium hydrogen carbonate ($c = 10 \text{ g dL}^{-1}$). The chloroform phase was collected and dried over anhydrous sodium sulfate. The solvent was removed by distillation and the 4-*N,N*-di(β -tosyloxyethyl)aminoazobenzene (I) was recrystallized from a mixture of ethyl alcohol and water (95:5 v/v). Yield 6.2 g, (93.3%).

¹H NMR (CDCl₃): (ppm) 2.35 (3 H, s, CH₃-C₆H₄); 3.60 (4 H, m, CH₂-N-C₆H₄); 4.05 (4 H, m, CH₂-OTs); 6.75 (2 H, m, aromatic protons ortho to N-CH₂); 7.25 (3 H, m, aromatic protons meta and para); 7.75 (4 H, aromatic protons ortho to N=N); 7.8–8 (aromatic protons of Ts).

To a solution of poly(tetramethylene oxide) diol of 1000 average molecular weight (24.95 g, 0.02495 mol) in anhydrous dioxane (75 mL), sodium hydride (1.2 g, 0.025 mol, 50% in oil) was added under agitation at 5°C. The mixture was maintained at this temperature for 30 min and then a solution of 4-*N,N*-di(β -tosyloxyethyl)aminoazobenzene (7.42 g, 0.01247 mol) in a mixture of anhydrous dioxane (25 mL) and DMF (3 mL) was added dropwise for 1 h. The solution was then heated at 60–65°C for 8 h. The reaction was stopped with a mixture of dioxane and water (5:0.5 v/v) and then with 1 mL acetic acid. After removal of the solvent by distillation, the product was dissolved in ethyl ether, washed with water and then dried

over CaCl₂. The azo polyether diol (Az-PTMO-1) was isolated after ether removal and dried under vacuum for at least 48 h. Yield: 23.7 g, (85%). In the same way, using poly(tetramethylene oxide) diol of 650 average molecular weight (16.21 g, 0.02495 mol), Az-PTMO-2 was obtained too.

Anal.(%), Calc.: Az-PTMO-1: C, 66.75; H, 10.54; N, 1.86; Found: C, 66.71; H, 10.52; N, 1.85. Calc.: Az-PTMO-2: C, 66.79; H, 10.29; N, 2.71; Found: C, 66.75; H, 10.27; N, 2.70.

Synthesis of Azo Cationomers

Polyurethane precursors (PR-1, PR-2) were prepared by a typical two-step addition reaction. NCO-terminated prepolymers were obtained reacting 1 mol azo polyether (Az-PTMO-1 or Az-PTMO-2) with 3 mol 4,4'-DBDI at 60–65°C under nitrogen atmosphere. After about 6 h, the resulting prepolymers were dissolved in anhydrous DMF (20 wt%) and then 2 mol NMDA in anhydrous acetone (30% w/v) was added slowly at 50°C. To ensure a complete reaction, the mixture was stirred for 5 h at 60–65°C. The course of these reactions was followed by IR spectroscopy until the hydroxyl and NCO groups respectively were consumed, as confirmed by the disappearance of the hydroxyl band of poly(tetramethylene oxide) at 3480 cm⁻¹ and isocyanate stretching band centered at 2270 cm⁻¹. Using then 2.01 mol chloroacetamide in DMF solution at 70°C for 25 h the quaternization reaction occurred. The polyurethane cationomers were precipitated in diethyl ether and dried under reduced pressure at 55–60°C for 48 h.

Measurements

NMR spectra were obtained on a GE NMR QE-300 MHz spectrometer in CDCl₃ at room temperature. IR and electronic absorption spectra were measured on SPECORD-M80 and SPECORD M42 spectrophotometer. GPC measurements were determined by a model PL 110 instrument equipped with two PL gel 5 μm mixed-C columns at 120°C. The sample for measurement was 1.0 g dL⁻¹ solution in THF (azo diol) or DMF (PU-PR) and the flow rate of the carrier solvent was 1 mL min⁻¹. The average molecular weights were calculated on the basis of the molecular weight vs. retention volume curve of monodisperse polystyrene standards. The pure azo polyether diols were chromatographically separated on a silica gel column using methyl alcohol - diethyl ether (8:2 v/v) as mobile phase. The content of ionic chlorine as anion of the quaternary ammonium structure was determined titrimetrically. Reduced viscosity of non-ionic polyurethanes was measured at 25 \pm 0.2°C in DMF solution ($c = 0.3 \text{ g}$

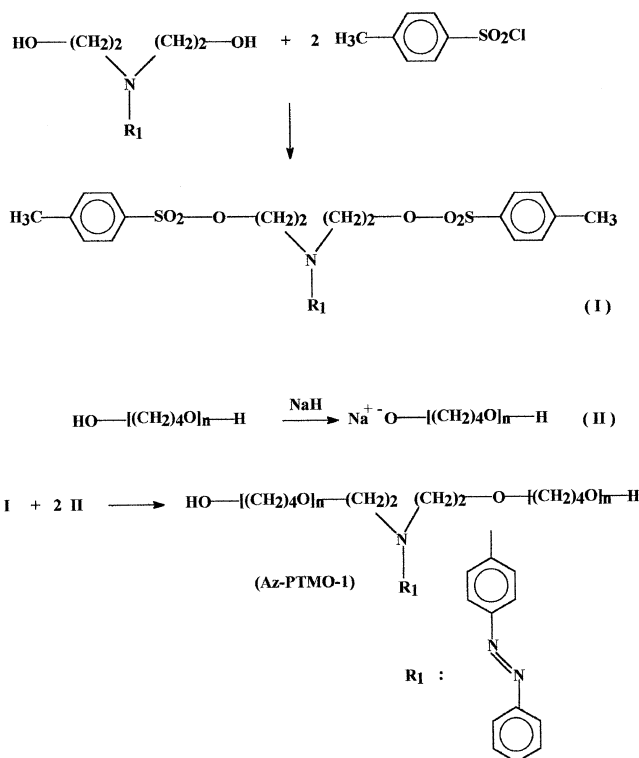
dL⁻¹) using an Ubbelohde viscometer. Thermal analysis was performed using a Perkin–Elmer differential scanning calorimeter. Azo polymers (15 ± 2 mg) were cooled to -130°C and heated at a rate of 20°C min⁻¹ up to 230°C. Irradiation was carried out using a 500 W high pressure mercury lamp at room temperature in argon atmosphere. The polymer films were deposited on quartz plates by casting from DMF solution (1 g dL⁻¹) and then allowed to dry at 50–55°C under reduced pressure for 2–3 days.

RESULTS AND DISCUSSION

Azo Polyether Diol Synthesis (Az-PTMO)

The synthetic approach to Az-PTMO appears in Scheme 1. The key intermediate is the preparation of 4-*N,N*-di(β -tosyloxyethyl)aminoazobenzene (I) by esterification reaction of 4-*N,N*-di(β -hydroxyethyl)-aminoazobenzene with TsCl in the presence of pyridine. Another key intermediate is based on the ability of polyether diols to be modified by metallation reactions at one hydroxyl end group.²⁶ Thus, the reaction of poly(tetramethylene oxide) diol of average molecular weight 1000 or 650 with sodium hydride (2 equiv. OH groups to 1 equiv. NaH), produces mainly polyethers with alkoxide and hydroxyl functionality as end groups. Since the above resulting ditosylate contains the tosyloxy leaving groups (TsO⁻), it can serve as alkylation agent of the latter polyethers so that coupling can occur only at the alkoxide unit of the oligomeric chain. Therefore, using the coupling reaction between the active ester (I) and alkoxide-polyether, two flexible blocks with molecular weight 1000 (II) or shorter block of 650 (III) were connected by one azo aromatic derivative. It is assumed that the formation of small amount of polyether with two alkoxide end groups would be possible, when a couple of azo units would be incorporated within the soft segment and an azo polyether of higher molecular weight is expected. But the chromatographic separation of the synthesized derivatives provided the azo polyether diols with one azo chromophore whose structure was further confirmed. By this simple procedure, two azo polyether diols with average molecular weight of 2239 (Az-PTMO-1) and 1542 (Az-PTMO-2), respectively, bearing one azobenzene side group as coupling moiety between two symmetric flexible segments were synthesized.

¹H NMR spectroscopy was used to characterize the azo polyether diols. As inferred from the NMR spectrum of Az-PTMO-1, shown in Figure 1, the resonances at 7.9, 7.47, 6.9 ppm correspond to the chemical shifts of aromatic protons at *ortho* (to -N=N-



Scheme 1. Synthesis of Az-PTMO

4 H), *meta* and *para* (3 H), and *ortho* positions (to -N-CH₂, 2 H, d) of the azo aromatic chromophore. The aliphatic protons exhibited chemical shifts at 3.63 ppm and 3.4 ppm, assigned to CH₂-O (4 H, t) and CH₂-N (4 H) of diethylaminoazobenzene fragment. The last signal overlaps with the resonance of protons CH₂-O from azo polyether diol in the region 3.39–3.44 ppm. The chemical shifts of the methylene protons CH₂-CH₂ and hydroxyl group from poly(tetramethylene oxide) appeared at 1.6 ppm and 3.7 ppm, respectively. An additional proof in the favor of the expected structure was the absence of the signals at 2.35, 4.0, and 7.8–8.0 ppm characteristic of the aromatic - Ts protons from ditosylate (I), whose spectral characterization is given in the experimental part. According to the integral ratio of protons CH₂-O at 3.6 ppm and CH₂-CH₂ at 1.63 ppm, a polymerization degree of approximately 27.4 was determined. This result was in good agreement with average molecular weight expected from the molecular formula.

As Figure 2 shows, purity of the azo polyether diols was checked by GPC measurements. Initially, difficulties with incomplete coupling of the azo derivative were encountered, when about 15% 4-*N,N*-di(β -hydroxyethyl)aminoazobenzene was produced by the tosyl derivate (I) hydrolysis during processing azo diols was found (Figure 2, curve a). To ensure the total removal of this impurity, chromatography on silica gel column, using a mixture of methanol and diethyl

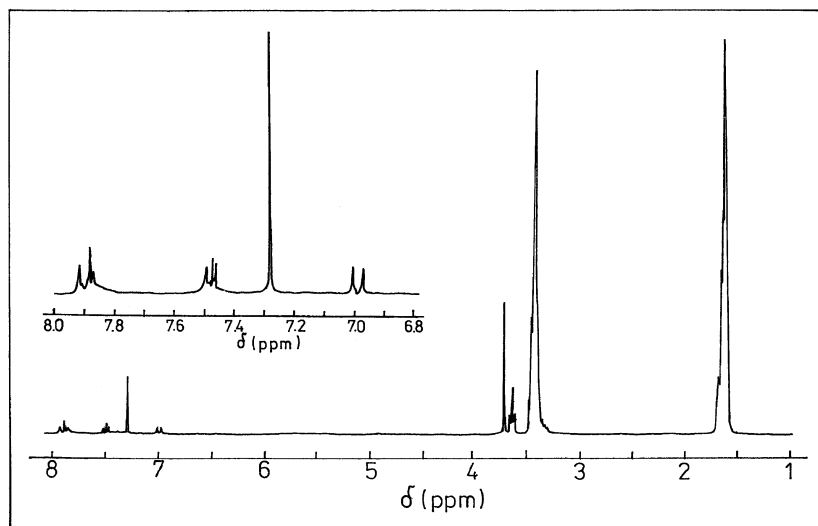


Figure 1. ^1H NMR spectrum of azo poly(tetramethylene oxide) diol (Az-PTMO1).

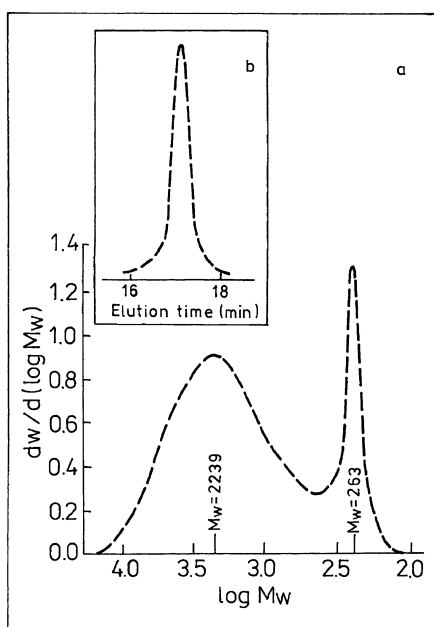


Figure 2. GPC analysis of Az-PTMO1.

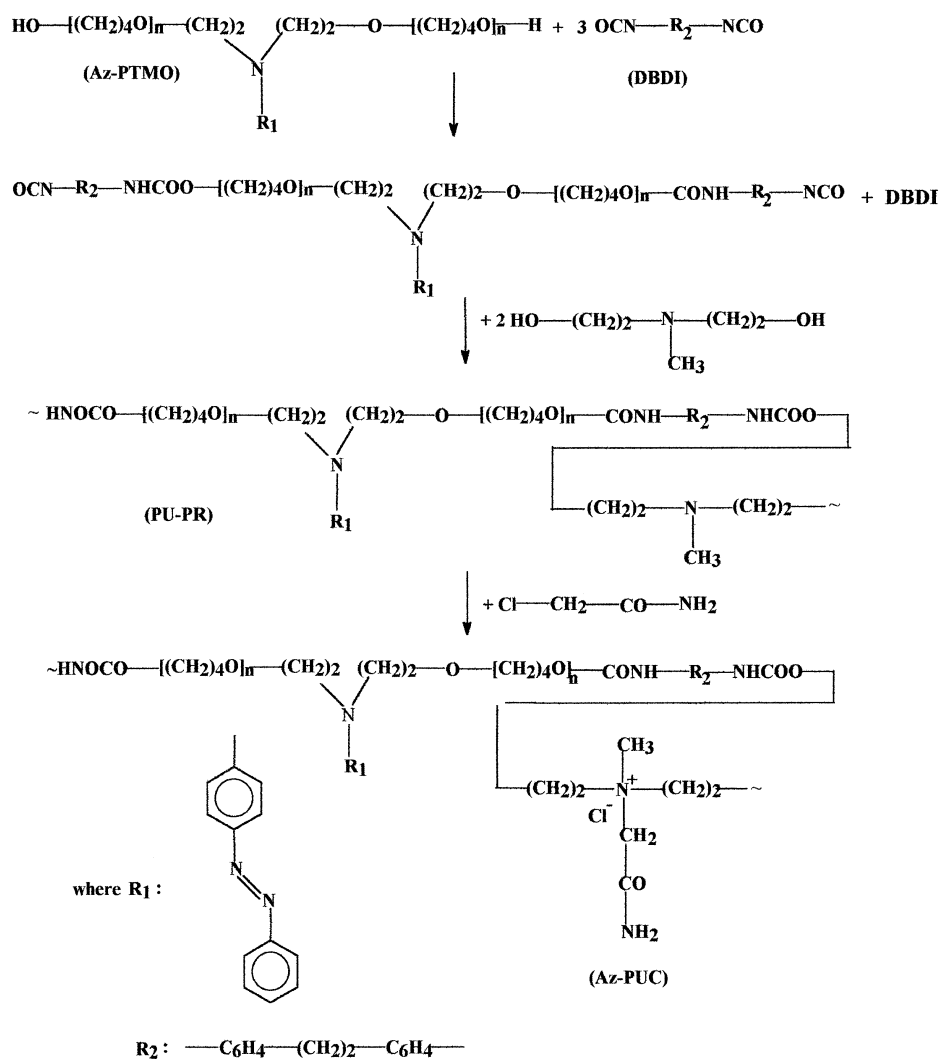
ether, as mobile phase was carried out. GPC measurement of the pure products indicated a weight-average molecular weight of 2239 and 1542 with polydispersity of about 1.09, closely of that theoretically calculated (M_w : 2249/Az-PTMO-1; 1549/Az-PTMO-2), which indirectly supports the azo polyether diols structure (Figure 2, curve b).

Polymer Synthesis

The synthesis of segmented polyetherurethanes (PR-1, PR-2) involved the polyaddition reaction of azo oligomeric diols, namely, Az-PTMO-1 or Az-PTMO-2 with 4,4'-dibenzyl diisocyanate, followed by chain extending with *N*-methyldiethanolamine, when the molar ratio of the reactive compounds is 1:3:2. Preparing polyurethane cationomers (Az-PUC-1, Az-PUC-2)

implies quaternization of the tertiary nitrogen atoms from the above precursors with chloroacetamide. In ideal form, the preparative method is summarized in Scheme 2.

The resulting polycations contain alternate ionic hard segments and polyether soft segments including azobenzene side-chromophore as well as the urethane hydrogen bonds formed by interactions between the hard segment-hard segment or soft segment-hard segment. The azo polymers are able to form homogeneous solutions in organic solvents such as THF, DMF, *N,N'*-Dimethylacetamide (DMA), and DMSO. Polymers solutions coated onto a glass or teflon substrate and dried yield transparent and flexible optical quality films, which exhibit typical elastomeric properties. Characterization data of all polymers are given in Table I. The results of elemental analysis were in excellent agreement with those of calculated values for the azo polymers structure. According to the quaternization characteristics described below only aliphatic tertiary amino functionality can be considered as source of ionic groups. The amount of quaternary groups quaternized by chloroacetamide at 90% degree of quaternization was estimated from the ionic chlorine content and the found values harmonized with the ionomer field.¹² As shown in this table, the ionic groups content from the polymer backbone may be easily increased by changing the molecular weight of the azo polyether component, owing to decreasing molecular chain length between the urethane groups and tertiary nitrogen atoms. Consequently, the ionic crosslinking density from opposite charge moieties and the coulombic interactions were increased and they markedly affected the ionomer properties. This is the reason why only the parent polyurethanes were characterized by reduced viscosity measurements and gel permeation



Scheme 2. Synthesis of azo PU cationomer

Table I. Characteristics of azo polyurethanes

Polymer	Mol. weight	Azo cont. %		Elem. anal			Ionic chlorine (mequiv/100 g polymer)	UV nm
	Az-PTMO M_w			C	H	N		
Az-PUC-1	2239	7.24	Calc.	64.64	7.48	5.17	51.93	405
			Found:	64.60	7.45	5.14		
Az-PUC-2	1542	9.13	Calc.	64.57	8.32	5.50	65.52	407
			Found:	64.54	8.31	5.49		
PR-1	2239	7.65	Calc.	67.01	7.69	4.67	—	403
			Found:	66.99	7.68	4.65		
PR-2	1542	9.73	Calc.	67.10	8.58	5.97	—	403.5
			Found:	67.02	8.56	5.96		

chromatography (GPC). The reduced viscosity values (PR-1: 0.45 dL g⁻¹; PR-2: 0.39 dL g⁻¹) suggested that the synthesized azo precursors had relatively high molecular weight, further proved by the elastomeric nature of the corresponding ionomeric films. GPC results indicated values of the molecular weight of 56240 (PR-1) and 42380 (PR-2) with polydispersity index of 1.3 and 1.4, respectively. In addition, GPC investigation showed that there are no irregularities such as low or

high molecular weight tails, including azo derivative susceptible to induce photochromism to the polymeric backbone. However, it is reasonable to suppose that the polycations containing a small fraction of ionic repeat units are not expected to possess no more different results than those of the precursors with the same molecular weight. Certainly the electrostatic interactions between hard segments have a major effect on the mechanical properties of the cationomer films but these

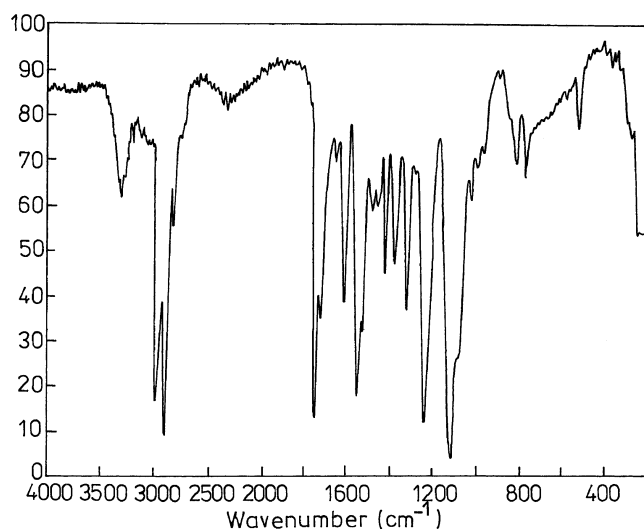


Figure 3. IR spectrum of Az-PUC1 film.

will be reported further.

The structures of the azo polymers were determined by IR spectroscopy. The IR spectrum of AZ-PUC-1 (Figure 3) showed characteristic absorptions of the NH stretching vibrations at 3300 cm^{-1} (hydrogen bonded), CH_2 stretchings at $2800\text{--}2875\text{ cm}^{-1}$ (sym) and 2950 cm^{-1} (asym), urethane carbonyl stretchings at 1730 cm^{-1} (hydrogen unbonded) and 1705 cm^{-1} (hydrogen bonded), benzene C=C stretching at 1600 cm^{-1} , azo stretching at 1370 cm^{-1} , C–O–C stretching at 1225 and 1110 cm^{-1} . The presence of the bonded carbonyl manifested by intensity of the 1705 cm^{-1} band is a direct measure of the extent of hard domain formation characteristic to the common polyurethanes. Comparison of this spectrum with that of the non-ionic precursor indicated an increase of the ratio of hydrogen bonded carbonyl groups as quaternization occurred, suggesting a better-defined microphase separation in ionic polymers.

Evidence for microphase separation of these polymers is seen in the DSC thermograms (Figure 4). Consistent with DSC results, every azo polycation exhibited only a well-defined glass transition (T_g) near -60°C (Az-PUC-1) and -54°C (Az-PUC-2), greater than that obtained for pure polyether segment.²⁷ Observed changes in the shift of T_g toward a higher value with decreasing molecular weight of Az-PTMO, may be accounted for by an imperfect phase separation of the soft and hard segments, due to their high degree of chemical incompatibility. The former azo cationomer exhibits a higher degree of phase separation than the 1542 molecular weight polyol-based ionic polymer because the longer soft segments possess a higher driving force for phase separation. T_g s obtained from the DSC were ascribed to the soft segment rich phase glass transition temperature in agreement with those evidenced

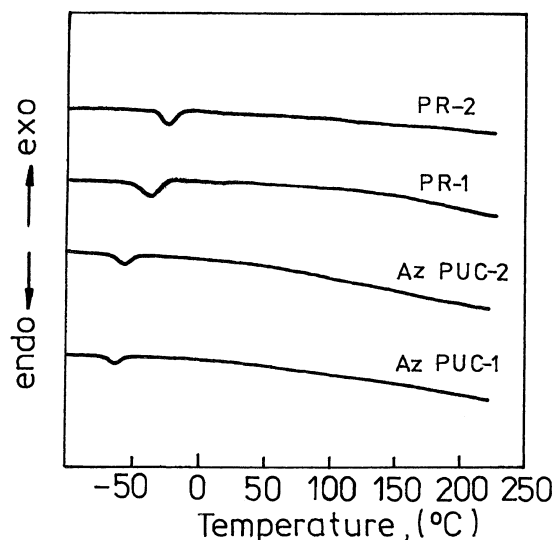


Figure 4. DSC thermograms of the azo polyurethanes.

on other polyurethane cationomers.^{28,29} Compared to the ionic polyurethanes, DSC results for their precursors given in the same figure indicate also an increase in the glass transition temperature at higher values up to -35°C (PR-1) and -31°C (PR-2), respectively. Thus, the soft segment domain in both polymers appears to have a fair degree of phase mixing, where a higher concentration of urethane segment is solubilized in the soft segment matrix with effect on the raise its T_g . In azo polycations, as evidenced by slight increase in values for the soft segment T_g , the bulk of the soft segment domains seems relatively pure indicating an enhanced biphasic morphology by coulombic interactions. The absence of the high temperature melting endotherms in any of the above azo polymers may be the result of the indiscernible crystallinity of the hard segment phase. This behavior is surprisingly because in preparation of the hard segment was used a diisocyanate more crystallizable. Earlier interpretations of such trends found in amorphous ionic or non-ionic polyurethanes, where a hard segment T_g was seldom measured in DSC thermograms, have sustained that domain perfection is controlled by several factors including the preparation and characterization method.^{28,30–32}

Photochromic Activity

Since we initially assumed that the incorporation of an azobenzene chromophore into the polyether segment of the polyurethane cationomers, may induce photochromism to the ionic films, the main object of this study was investigation of the photoreactivity of the polycations in comparison with the non-ionic precursors films. In order to examine the *trans*–*cis* photoisomerization of azo chromophore, the UV irradiation of the polymer films was carried out with a high pressure Hg lamp using a cut-off filter ($\lambda = 365\text{ nm}$), to exclude

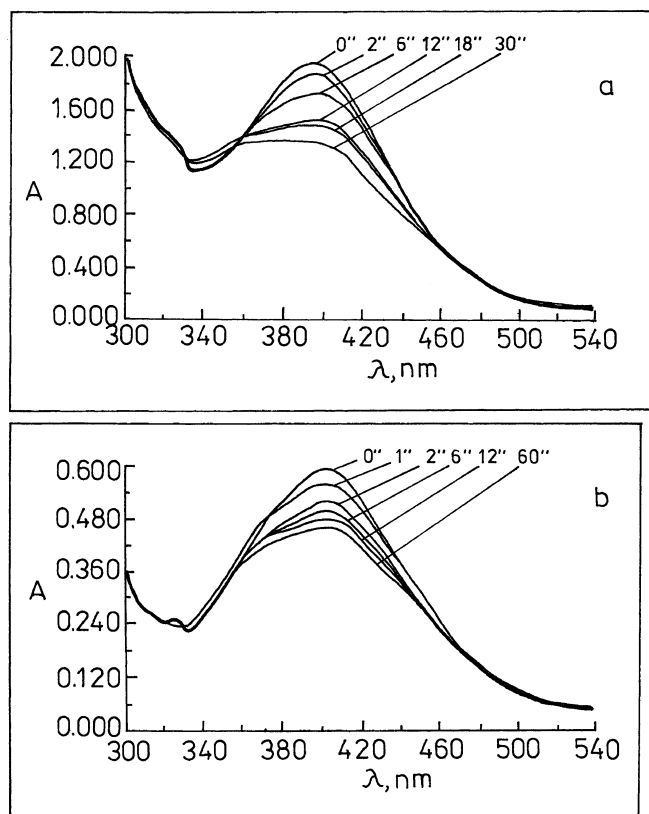


Figure 5. Changes in UV-vis absorption spectra of Az-PUC1 polyurethane cationomer in film (plot a) and its PR1 azo precursor (plot b) upon UV light exposure.

short wavelength UV light which causes side reactions. Every azo polymeric film showed a strong absorption band centered at about 405 nm attributed to the $\pi - \pi^*$ electronic transition of the azo *trans* configuration. In these experiments, the changes appearing in the electronic absorption spectra during UV irradiation were monitored by UV-vis spectroscopy. The progress of the *trans-cis* photoisomerization of azo aromatic groups in polyurethane cationomer (Az-PUC-1) with irradiation time is shown in Figure 5 (plot a).

As seen from this figure, the intensity of $\pi - \pi^*$ absorption band decreased gradually with irradiation time reaching a photostationary state in only 30 sec, when the molar fraction of *cis* isomer is about 0.35. Following the evolution of the photoprocess in the non-ionic film (PR-1), subjected under the same irradiation conditions, it was found that the absorption maximum corresponding to $\pi - \pi^*$ transition (407 nm) decreased more quickly as the UV light exposure time increased (Figure 5, plot b). This decrease tendency is the result of the same elementary process of *trans-cis* photoisomerization of the azobenzene, with attainment of an equilibrium state in 12 sec. in which the molar fraction of *cis* form is approximately 0.30. It appears that although the polyether matrix bearing azobenzene can provide a greater mobility to the chromophore, the composition

of the photostationary state indicates that a high portion of *trans* isomer is unable to isomerize to the *cis* form, probably due to the energetically unfavorable local environments. This means that the *trans-cis* photoisomerization of azobenzene depends on the architecture of polymers and is difficult to predict it due to various interactions of interchain that include a few highly polar ionic sites in a relatively non-polar matrix, with tendency to decrease the overall chain mobility. As result, a difference in the photoisomerization rate of the azo aromatic chromophore in the ionic film (Az-PUC-1, $k = 7.7 \times 10^{-2} \text{s}^{-1}$) and in the analogous non-ionic film (PR-1, $k = 35.5 \times 10^{-2} \text{s}^{-1}$) was found. The general photobehavior of the Az-PUC-2 corresponds to that previously seen for Az-PUC-1, with a small decrease in the photoisomerization rate of the ionomeric film ($k = 7.2 \times 10^{-2} \text{s}^{-1}$) as well as of its corresponding precursor of identical soft chain (PR-2, $k = 33.8 \times 10^{-2} \text{s}^{-1}$). As the data show, it should be noted that some of the observed difference between Az-PUC-1 and Az-PUC-2 could result from changes in the content of ionic groups and implicitly the extent of phase mixing. Based on this argument, smaller values of the photoisomerization rate in non-ionic films were expected. In contrast, the precursors with a lower degree of the phase separation displayed a higher photoisomerization rate than that of the ionomeric films, suggesting that the phase purity is not solely responsible for the increased rate of this photoreaction. As the soft/hard segment interaction increases in addition to the temporary changes of the geometrical shape and of the azobenzene polarity, the microstructure and molecular dynamics are influenced by the photoreaction. Thus, possibly, the precursors activity is a reflection of matrix polarity which provides a lower barrier to photoisomerization upon the action of the hydrogen bonds which allows for more efficient arrangement of the chromophore units than in the presence of the electrostatic interactions. During the spectral measurements, the occurrence of the isosbestic points at about 362 nm and 470 nm indicates that the photoisomerization reaction is only the chemical transformation suffered by polymer chains without other side reactions, such as photodegradation.

The kinetics of the thermal *cis-trans* relaxation process of azo chromophore in the irradiated films, were followed by monitoring the changes of absorbances at about 405 nm, specific to the *trans* isomer at 80°C and at ambient temperature. The thermal *cis-trans* isomerization can be expressed by a first-order rate equation: $\ln(A_\infty - A_0)/(A_\infty - A_t) = kt$, where A_0 , A_∞ , and A_t are values of the absorbances at time t_0 , t_∞ , and t , respectively. The first order plot for the thermal *cis-trans* isomerization of azo chromophore in films based on

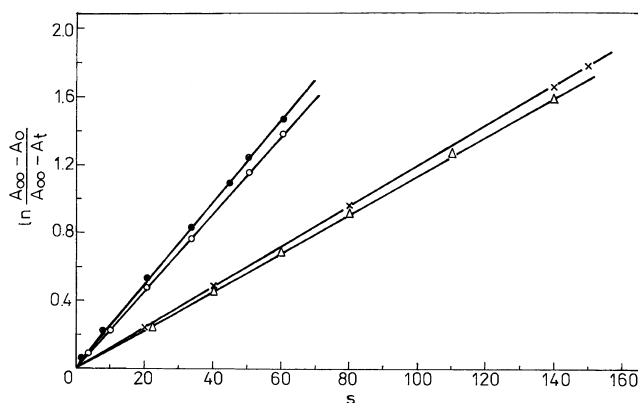


Figure 6. Plots for *cis*–*trans* isomerization of Az-PUC1 (x), Az-PUC2 (Δ), PR1 (●), and PR2 (○) in film state.

cationomer and non-ionomer polymer is shown in Figure 6.

In all cases, a sufficient molecular mobility of the chromophore exists to allow for the return of the *cis* azobenzene structure to the initial *trans* configuration, however at a different rate. Comparing the rate values found in ionomeric films (Az-PUC-1: $k = 29.19 \times 10^{-3} \text{ s}^{-1}$; Az-PUC-2: $k = 25.5 \times 10^{-3} \text{ s}^{-1}$) with that of the non-ionomeric films (PR-1: $k = 59.3 \times 10^{-3} \text{ s}^{-1}$; PR-2: $k = 57.8 \times 10^{-3} \text{ s}^{-1}$), is clear that the thermal recovery of the *cis* isomer to the *trans* form is also strongly influenced by specific effects such as ionic interactions and hydrogen bondings encountered in ionomeric systems. In contrast to the non-ionic film, whose *cis*–*trans* isomerization required around 60 sec, the same reaction required about 155 sec in the ionomeric film. Additionally, a slower recovery of the chromophore in all films at ambient temperature (over 200 in) was also noticed. This behavior is a clear indication of the photochromic nature of polymer films containing azobenzene within the polyether soft domains as continuous phase in which are dispersed the hard domains. Since the fatigue behavior of these films can be quite important, five cycles of *trans*–*cis* and *cis*–*trans* isomerization were followed, but in the electronic absorption spectra no modifications were observed.

Finally, for a complete understanding of the relationship of dynamics and photochemical behavior in thin elastomeric films based on ionomeric polyurethanes containing photoisomerizable azobenzene additional investigations need to be combined.

CONCLUSIONS

New azo poly(tetramethylene oxide) diols with one azo aromatic chromophore incorporated as a side group between two symmetric polyether blocks were successfully synthesized and characterized. The new

polyurethane cationomers based on azo polyether diol, 4,4-dibenzoyldiisocyanate and *N*-methyldiethanolamine quaternized with chloroacetamide, showed in film state photochromic activity as result of the capability of the polymer chains to allow for movement of the azo moiety induced by the photoisomerization reaction.

In contrast to the non-ionomeric film, whose isomerization shows a higher sensitivity to UV irradiation, the presence of ammonium quaternary groups beside the chromophoric ones, can influence structural features and therefore potentially play an important role in controlling photochemical properties. Owing to the location of azo chromophore in the soft segment of ionomeric matrix, the azo cationomer exhibited considerable difference in photochemical properties in comparison with another polycations involving the same chromophore in the hard segment.

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REFERENCES

- O. Nuyken, C. Scherer, A. Baidl, A. R. Brenner, U. Dahn, R. Gartner, S. K. Rohrich, R. Kollefrath, P. Matusche, and B. Voit, *Prog. Polym. Sci.*, **22**, 93 (1997).
- H. Knobloch, H. Orendi, M. Buchel, T. Seki, S. Ito, and W. Knoll, *J. Appl. Phys.*, **77**, 481 (1995).
- G. S. Kumar and D. C. Neckers, *Chem. Rev.*, **89**, 1915 (1989).
- S. Xie, A. Natansohn, and P. Rochon, *Chem. Mater.*, **5**, 403 (1993).
- R. Ruhman, *Polym. Int.*, **43**, 103 (1997).
- D. Dieterich, "Polyurethane in Houben-Weyl", 4th ed, 1987, p 1561.
- N. Tsutsumi, S. Yoshizaki, W. Sakai, and T. Kiyotsukuri, *Macromolecules*, **28**, 6437 (1995).
- O. Watanabe, M. Tsuchimori, and A. Okada, *J. Mater. Sci.*, **6**, 1487 (1996).
- M. Chen, L. R. Dalton, L. P. Yu, Y. Q. Shi, and W. M. Steier, *Macromolecules*, **25**, 4032 (1992).
- O. Nuyken, J. Stebani, and A. Long, *Angew. Makromol. Chem.*, **226**, 143 (1995).
- C. S. P. Sung, L. Lamarre, and K. H. Chung, *Macromolecules*, **12**, 666 (1979).
- X. Yu, B. P. Grady, R. S. Reiner, and S. L. Cooper, *J. Appl. Polym. Sci.*, **47**, 1673 (1993).
- H. Reiff and D. Dieterich, "Urethane Based Ionomer Dispersions in Ionomers", M. R. Tant, K. A. Mauritz, and G. L. Wilkes, Ed., Blakie, London, 1997, p 444.
- D. Dieterich, W. Keberle, and H. Witt, *Angew. Makromol. Chem. Int. Ed. Engl.*, **9**, 40 (1970).
- R. W. Seymour and S. L. Cooper, *Macromolecules*, **6**, 48 (1973).
- T. R. Hesketh, J. W. C. Van Bogart, and S. L. Cooper, *Polym. Eng. Sci.*, **20**, 190 (1980).

17. B. K. Kim, J. C. Lee, and K. H. Lee, *J. Macromol. Sci., Pure Appl. Chem.*, **A31**, 1241 (1994).
18. Y. M. Kuo, K. Y. Ku, H. C. Lin, N. H. Wang, C. P. Chwang, and D. Y. Chao, *J. Appl. Polym. Sci.*, **69**, 2097 (1998).
19. H. A. Al-Salah, *Acta Polymerica*, **49**, 465 (1998).
20. T. Buruiana, A. Airinei, E. C. Buruiana, and I. Bestiuc, *Angew. Makromol. Chem.*, **258**, 39 (1998).
21. E. C. Buruiana, T. Buruiana, A. Airinei, and G. Robila, *Angew. Makromol. Chem.*, **206**, 87 (1993).
22. T. Buruiana, A. Airinei, E. C. Buruiana, and G. Robila, *J. Macromol. Sci., Pure Appl. Chem.*, **A32**, 1397 (1995).
23. E. C. Buruiana, T. Buruiana, A. Airinei, G. Robila, and I. Grecu, *Polym. J.*, **31**, 510 (1999).
24. T. Buruiana, E. C. Buruiana, A. Airinei, and I. Grecu, *Eur. Polym. J.*, **37**, 343 (2001).
25. I. Bestiuc, A. Caraculacu, S. Idriceanu, and T. Buruiana, *Romania Patent*, 104 788 (Sep. 20, 1994).
26. S. Kinugasa, S. Hattori, and H. Hayashi, *Polym. Prepr. Jpn. (Engl. Ed.)*, **40**, 5 (1991).
27. J. A. Faucher and J. V. Kolesche, *Polymer*, **9**, 44 (1968).
28. R. J. Goddard and S. L. Cooper, *J. Polym. Sci., Polym. Phys. Ed.*, **32**, 1557 (1994).
29. H. A. Al-Salah, H. X. Xiao, J. A. McLean, and K. C. Frisch, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 1609 (1988).
30. S. A. Chen and W. C. Chan, *J. Polym. Sci., Polym. Phys. Ed.*, **28**, 1499 (1990).
31. M. Watanabe, N. Toneaki, Y. Takizawa, and I. Shinohara, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 2669 (1982).
32. L. Irusta and M. J. F. Berridi, *Polymer*, **40**, 4821 (1999).