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Recent developments in polyurethane cationomers Photoisomerisation reactions in azoaromatic polycations

Emil C. Buruiana*, Tinca Buruiana

Institute of Macromolecular Chemistry "P. Poni", Romanian Academy, Aleea Gr. Ghica Voda 41 A, Iasi 6600, Romania

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1. Introduction

One of the most important groups in the class of thermoplastic elastomers is constituted of segmented polyurethanes, structured as linear block copolymers of the type (AB), with hard and soft segments, generally incompatibly [1–3]. Although, an almost unlimited variety of chemical compositions is possible, the soft segments are usually oligomeric diols of polyether or polyester type (M_w: 500–3000), while the hard segments are the result of the diisocyanate chain extended by diols of low molecular weight. An interesting development of this field, pioneered by Dieterich (1970), Cooper (1973) and Hwang (1981) was the insertion of small amount of ionic functionality into polymers to yield polyurethane ionomers [4–6]. Though the polymers contain a minority of ionic groups, below 250 meq/100 g [7] or a more constrained range between 10 and 120 meq/100 g polymer [8], their properties are strongly influenced by the presence of ionic charges which tend to aggregate via coulombic interactions into so-called "ionic domains" and thus promote phase separation and hard domain cohesion. Depending on the charge nature (positive, negative or both) placed within the chain, pendant to the chain or only at the chain ends (telechelic systems), all types of ionomers as cationomers, anionomers and zwitterionomers have received constantly much attention [9–14]. Considered now one of most fast developing and active branches of polyurethane chemistry, such polymers combine the well-known properties of the parent polymers with those derived from the existence of ionic structures in the backbone, offering an unique opportunity to form aqueous dispersions in the absence of any external emulsifier. The qualities of aqueous dispersions, notably their excellent adhesion to many polymeric and glass substrates and film-forming ability at ambient temperature, have recommended them as suitable for modern ionomer adhesive and coating applications [15,16].

Since they were first reported in 1970, a wide variety of polyurethane ionomers has been synthesized and their specific properties have been reviewed [17,18]. This paper will present a brief review on the polyurethane ionomers with cationic groups and will refer to our own work carried out in the last 10 years on cationomers bearing azoaromatic structures and, essentially for the first time, attention was drawn to the specific role of the chromophore in developing of polymer properties.

2. Polyurethane cationomers

2.1. General considerations on their synthesis and properties

Although, the most studies were focused preponderantly on the high performance anionic polyurethanes [19–22], there is still interest on the cationic ones for understanding the influence of ionic centers on the polymer properties to improve and adjust them to various technical problems including the aqueous dispersions. Based on urethane chemistry, elastomeric cationomers have been prepared by the well-known procedure of using of chain extender with tertiary amino group and subsequent modification with an ionizable component. The most common approach has been to use *N*-methyldiethanolamine [23–31] as low molecular diol with tertiary amine functionality, followed by a quaternization of the aliphatic tertiary nitrogen atoms with various acids, alkyl halides or di-Me-sulfate.

Cooper and co-workers [32,33], Varma and co-workers [34], have been synthesized new polyurethane cationomers with pendant ammonium groups using as chain extender

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* Corresponding author.
E-mail address: emilbur@ichpp.tuiasi.ro (E.C. Buruiana).

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short diols of ionic type or with trialkylamine groups, quaternized latter. Polymer morpgology and some properties were investigated as a function of ion content, neutralizing anion and alkyl group length.

Polyurethane cationomers have also been prepared by using viologen diol [35] or a soft segment based on polybutadiene carring quaternary ammonium salt [36,37].

Other ionic polymers based on ionene chemistry which allowed incorporation of the non-covalently attached cyclic species on each "paraquat" hard segment and thus preparing segmented ionic "rotaxane" [38]. Using Menschutkin reaction from di-tertiary amines and dihalides, polyetherurethane ionenes with viologen units have been prepared and examined in terms of photochromic activity [39]. Moreover, by this reaction some polyurethane ionenes with good antimicrobian response were obtained [40]. A different set of polymers containing polyurethane–polyvinylbenzylchloride blocks or pyridinium rings was also reported [41–43].

Extensive studies have been carried out on the structure-properties relationship in the polycations revealing and explaining in the same time their segmental structure and peculiarity to be utilized as coatings and adhesives in the form of water dispersions [44–46]. The effects of ionomeric architecture both on the polymer solution [47,48] and film properties [49–55] were detailed investigated. Indeed, due to the propensity of the electrostatic charges to strongly interact in polar dilute solutions, these polymers have similarities with polyelectrolytes [56]. In the same time, the ionic groups segregation into microdomains with formation of physical (Coulombic) crosslinks as well as the preparation method and thermal history influence the elastomeric characteristics of the polymers. The property profile of ionomeric films obtained from urethane–acrylate cationomer aqueous dispersions was exploited in applications including coatings, adhesives or impregnation formulations [57,58].

In contrast with the scientific and commercial interest focused on polyurethane ionomers, very little work concerning insertion of the chromophore structures in the polymeric chains, as a way to diversify the traditional applications, was reported in the literature [59–62]. Such materials include in their structure a dye [59–61] or mesogenic azobenzene moieties [62].

In the last decade, our laboratory has developed a new family of polyurethane cationomers containing quinone, anthryl, nitroaromatic and/or azoaromatic chromophores anchored to the ionomeric backbone [63–66]. Insertion of some photoactive units that elicit optical response in such polymers, could result in an enhanced knowledge of their peculiarities, opening the way to design new materials for possible practical optical devices.

Inspired by the studies performed on classical polyurethanes bearing azo chromophores and implicitly on obtaining of mecano(photo)chromic, liquid-crystal, nonlinear optical or photocleavable materials [67–70], we have considered usefully to investigate the synthesis and photo-behavior of some polyurethane cationomers with azobenzene attached to polymeric chains. As firstly demonstrated, use of photochromic azobenzene labels in the main chains of single-phase polyurethanes, as a sensitive molecular probe azoaromatic structures provided information on the aging time of the polyurethane backbone related to the loss of free volume, its distribution and its change with aging [71,72].

3. Polyurethane cationomers with pendant azobenzene chromophores

3.1. *Synthesis of azo cationomers with chromophore anchored to the hard segment*

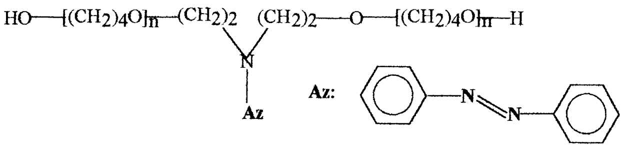
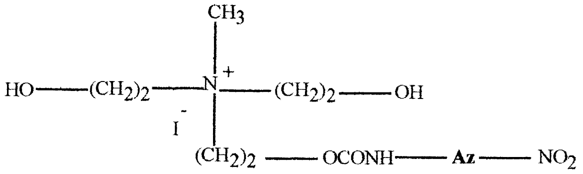
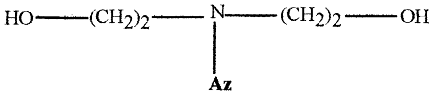
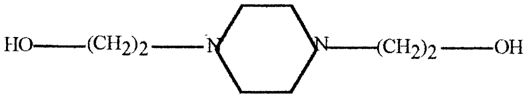
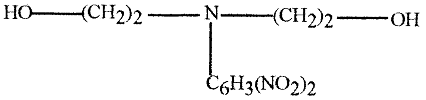
As was described in our previous papers [66,73–76], azoaromatic units containing cationomers may have a variety of chain structures introduced by means of new azo chain extenders, azo quaternizing agents or azo polyol components (Table 1). Some of the most highly investigated polymers have been elastomeric cationomers based on poly(tetramethylene glycol) of 1000 or 2000 average molecular weight (PTMG), 4,4′-dibenzyldiisocyante (4,4′-DBDI) and different chain extenders of ionic or non-ionic type (Table 2). Therefore, the use of azo ionic diol(IV) as chain extender of the prepolymer based on PTMG(II) and 4,4-DBDI(I), was a direct route to afford azo polyetherurethane cationomers (Az-PUC1) with *para*-nitroazoaromatic chromophore located in the quaternary ammonium structure, as shown in Scheme 1 [73].

Another variance widely used to introduce azo chromophore based on quaternizing tertiary amine(VI) previously introduced in polyurethanes, with azo derivative (IX, X), when the resulting polycations (Az-PUC2, Az-PUC3) contain *para*-nitroazoaromatic or azoaromatic groups attached to quaternary nitrogen atoms [74–76]. A general scheme may be described for the Az-PUC3 synthesis (Scheme 2).

In a similar manner, the use of mixture of chain extenders, such as azo-diol(V), and NMDA, followed by quaternizing with benzyl chloride led to azo cationomers (Az-PUC4, Az-PUC5), as shown in Fig. 1 [66]. Both polymers have the azoaromatic chromophore placed in the non-ionic fragment of the hard segments but differ by the concentration of ionic groups.

Comparative photoreactivity of the azo chromophores in all earlier mentioned polycations exposed to UV irradiation, was explored in four studies [66,73–75]. The results indicated that the photoresponsiveness of the chromophore would be directly influenced by the structure and attachment point of the azoaromatic unit in ionomeric chains, as will be shown latterly. In the same time, another question was suggested: what happens when the chromophore is located into flexible chain of the ionomeric backbone? A concrete answer is given later.

Table 1
Chemical structures used in the synthesis of azo polyurethane cationomers

Diisocyanate	
$OCN-C_6H_4-CH_2-CH_2-C_6H_4-NCO$	I. 4,4′-Dibenzyldiisocyanate (4,4′-DBDI)
Polyols	
$HO-[(CH_2)_4O]_n-H$	II. Polytetramethylene glycol (PTMG)
	III. Azo-polytetramethylene glycol (Az-PTMG)
Chain extenders	
 $HO-(CH_2)_2-\overset{CH_3}{\underset{I^-}{N^+}}[(CH_2)_2-OCONH-Az-NO_2]-(CH_2)_2-OH$	IV. 2-Ethyl-*N*-methyldiethanolamoniu-*N*-[4(nitrophenyldiazenyl) phenyl] amino-formate iodide
 $HO-(CH_2)_2-N(Az)-(CH_2)_2-OH$	V. *N*-di-(β-Hydroxyethyl)-4-aminoazo-benzene
$HO-(CH_2)_2-N(CH_3)-(CH_2)_2-OH$	VI. *N*-Methyldiethanaolamine
	VII. *N*,*N*-di-(β-Hydroxyethyl) pipe-razine
 $HO-(CH_2)_2-N(C_6H_3(NO_2)_2)-(CH_2)_2-OH$	VIII. *N*-(2,4-Dinitrophenyl) diethanolamine
Quaternizing agents	
$I-(CH_2)_2-OCONH-Az-NO_2$	IX. 2-Iodoethyl-*N*-[4(4-nitrophenyldiazenyl) phenyl]aminoformate
$Cl-(CH_2)_2-COO-Az$	X. 4-(3-Chloropropionyloxy) azobenzene
$Cl-CH_2-C_6H_5$	XI. Benzyl chloride;
CH_3I	XII. Methyl iodide
$Cl-CH_2-CO-NH_2$	XIII. Chloroacetamide
Azo salts	
$Az-O-(CH_2)_3-SO_3^- Na^+$	XIV. 3-(*p*-Oxyazobenzene) propane sulfonic acid sodium salt
$N(CH_3)_2-Az-SO_3^- Na^+$	XV. Methyl orange sodium salt

3.2. Polyurethane cationomers with azobenzene in the soft segment

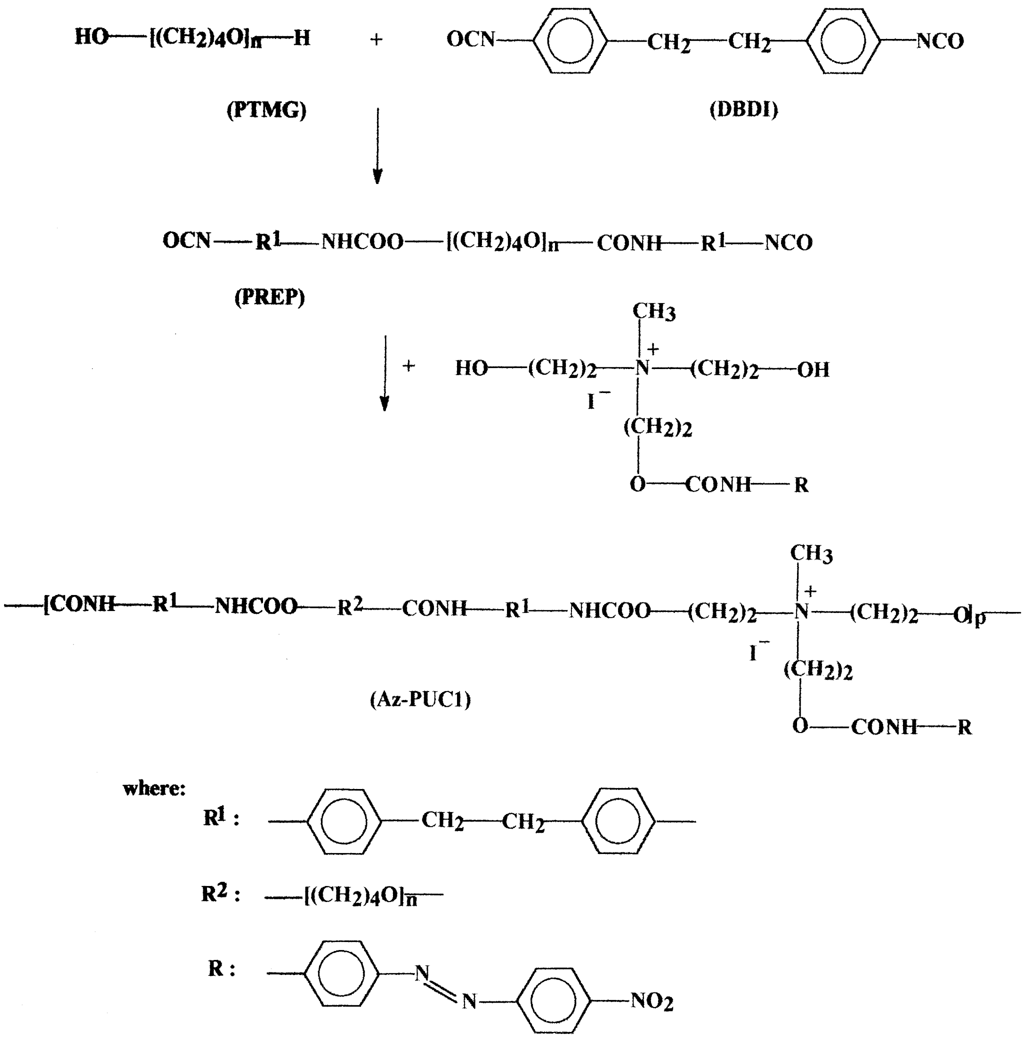
More recent study was conducted to find the appropriate conditions for incorporating azoaromatic groups into polyether component, such as PTMG, widely used in polyurethane synthesis. Attention was given to the preparing new azo PTMG containing one azobenzene side group on chain and its use as starting diol for polyurethane cationomers [77]. The key intermediate was the synthesis of 4-*N*,*N*-di(β-tosyloxyethyl)aminoazobenzene (**1**) by esterification of 4-*N*,*N*-di(β-hydroxyethyl)-aminoazobenzene with *para*-toluenesulfonyl chloride (TsCl) in the presence of pyridine. Another derivative assumed activation of the hydroxyl group of PTMG with a group susceptible to nucleophilic attack by the oxygen atom of the alcohoxyde moiety. Thus, the reaction of PTMG of 1000 average molecular weight or with shorter block length of 650 with sodium hydride, used in an appropriate amount for to transform only one hydroxyl group in alcohoxyde form, produced mainly monoalcohoxyde-PTMG (**2** or **3**). Since the above resulting ditosylate contains the tosyloxy leaving groups (TsO^-), it can serve as alkylation agent of the latter polyether with one terminal alcohoxyde functionality [78],

Table 2
Structural characteristics of azo polyetherurethane cationomers

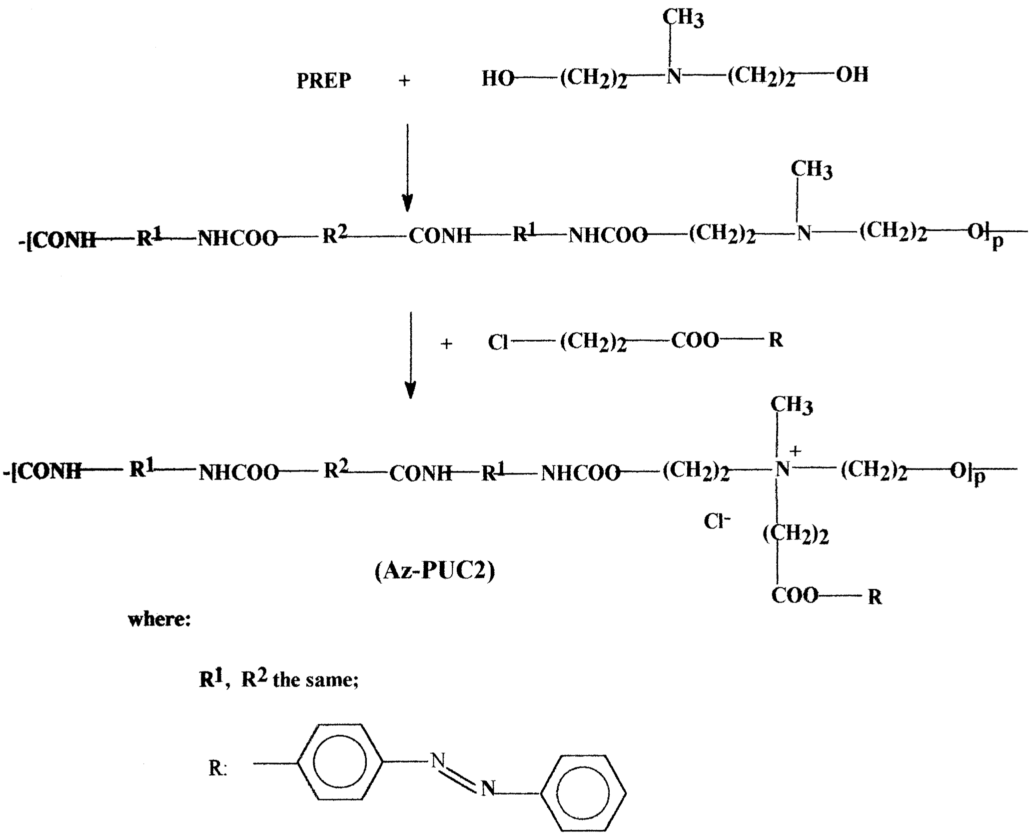
Polymer	Azo-derivative (cf. Table 1)	Molar ratio (polyol/NCO/OH)	Ionic halogen content (meq/100 g)	Azo content[a] (wt.%)	λ_{max} (nm)		Reference
					DMF	Film	
Az-PUC1	IV	1/3/2	49.23	28.59	452	440.0	[73]
Az-PUC2	IX	1/3/2	48.35	28.08	450	440.5	[74,75]
Az-PUC3	X	1/3/2	50.35	13.92	451	440.5	[76]
Az-PUC4	V	1/3/2	28.56	8.50	415.0	412.5	[66]
Az-PUC5	V	1/2/1	16.42	5.00	408.0	406.0	[66]
Az-PUC6	III	1/3/2	51.93	7.24	410	405.5	[77]
Az-PUC7	III	1/3/2	65.52	9.13	–	407	[77]
Az-PUC8	XIV	1/2/1	33.57	9.29	351	345	[79]
Az-PUC9	XIV	1/2/1	4.95	15.79	350	347	[79]
Az-PUC10	XV	1/3/2	47.09	23.50	423	434.5	[80]

[a] Calculated from the ionic halogen content.

so that coupling can occurs only at one end of the PTMG molecule. Therefore, using the coupling reaction between the active ester (**1**) and monoalcohoxyde-PTMG (**2** or **3**), two blocks of polyether were connected by means of azo aromatic derivative. It assumed that the formation of the dialcohoxyde derivate in a small amount would be also possible and allowed for multiple azo units to be incorporated within the soft segment. Obviously the subsequent purification provided the azo diol with one azo chromophore, whose structure was further confirmed. By this simple



Scheme 1. Synthesis of Az-PUC1.



Scheme 2. Synthesis of Az-PUC2.

procedure, two azo polyether diols of average molecular weight 2239 (Az-PTMG1) and 1542 (Az-PTMG2), respectively bearing one azobenzene side group as coupling moiety between two symmetric flexible segments were firstly synthesized. The synthetic approach to Az-PTMGl is sketched in Scheme 3.

Synthesis of azo polyurethane cationomers (Az-PUC6, Az-PUC7) developed by us, was similar to the formation of other polymers, differing only by the starting polyol, which contains one azoaromatic side group between two flexible blocks of the same length and composition. One of polyurethane cationomers (Az-PUC6) based on Az-PTMGl, 4,4′-DBDI and NMDA, further quaternized with chloroacetamide, whose structure in idealized form is outlined in Fig. 2. Under such circumstances, polycations with azobenzene in the soft segment and quaternary ammonium groups in the hard block might be obtained as thin films with good optical qualities.

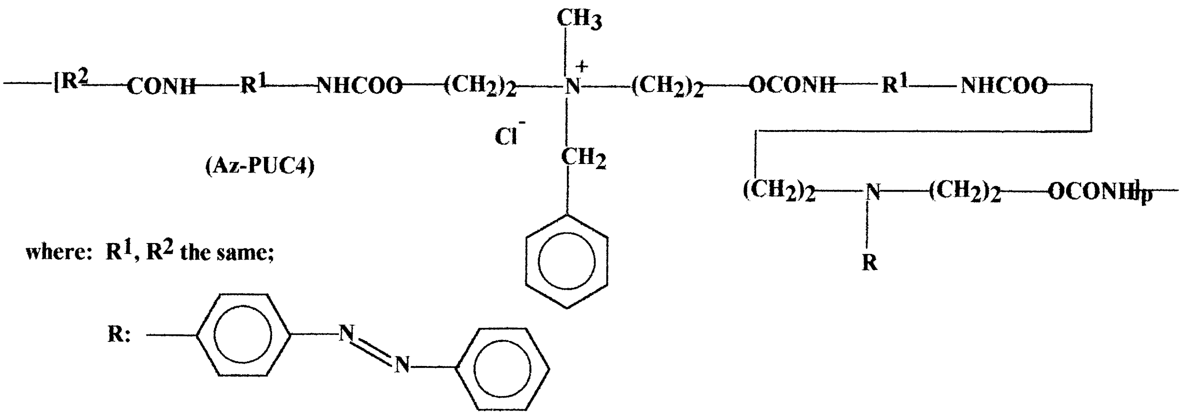
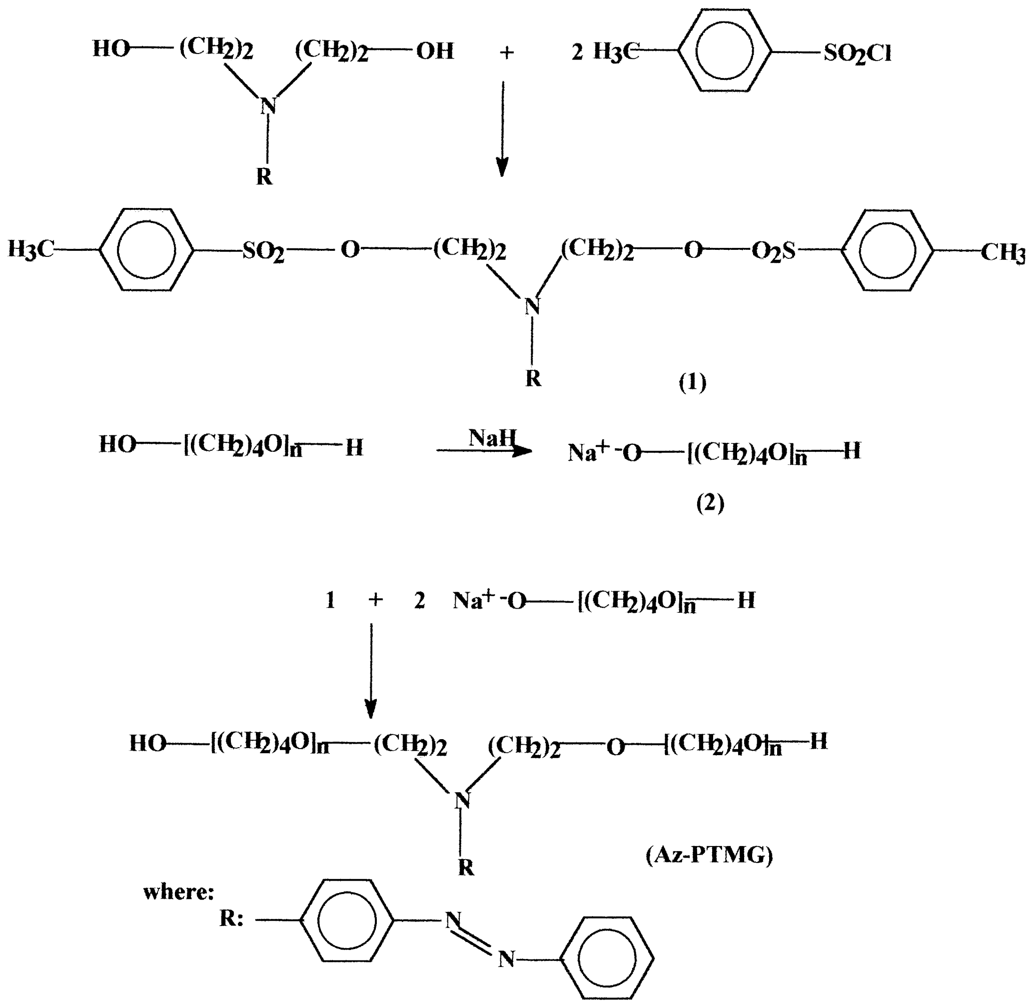


Fig. 1. Schematic representations of Az-PUCs.



Scheme 3. Synthesis of Az-PTMG.

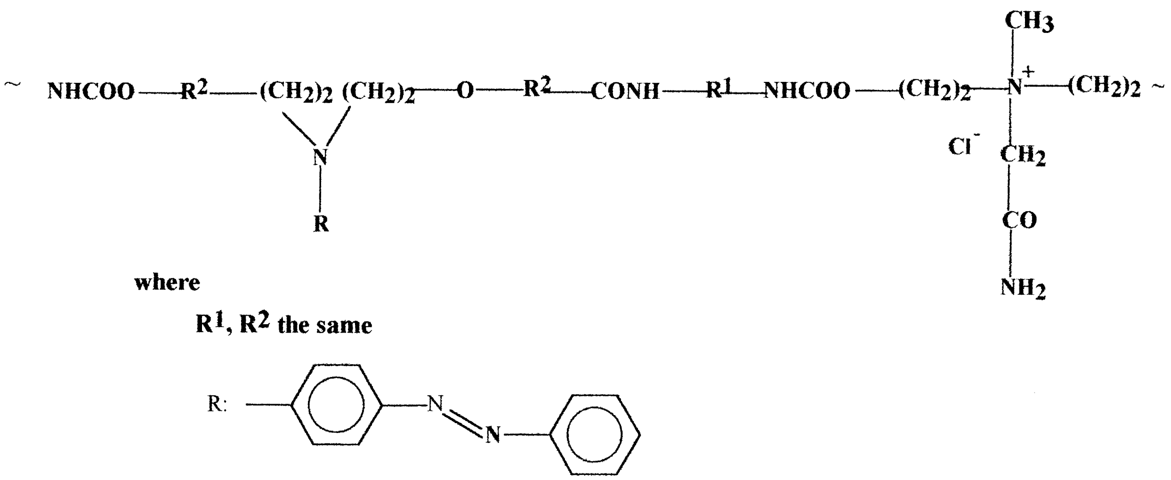


Fig. 2. Schematic representations of Az-PUCs.

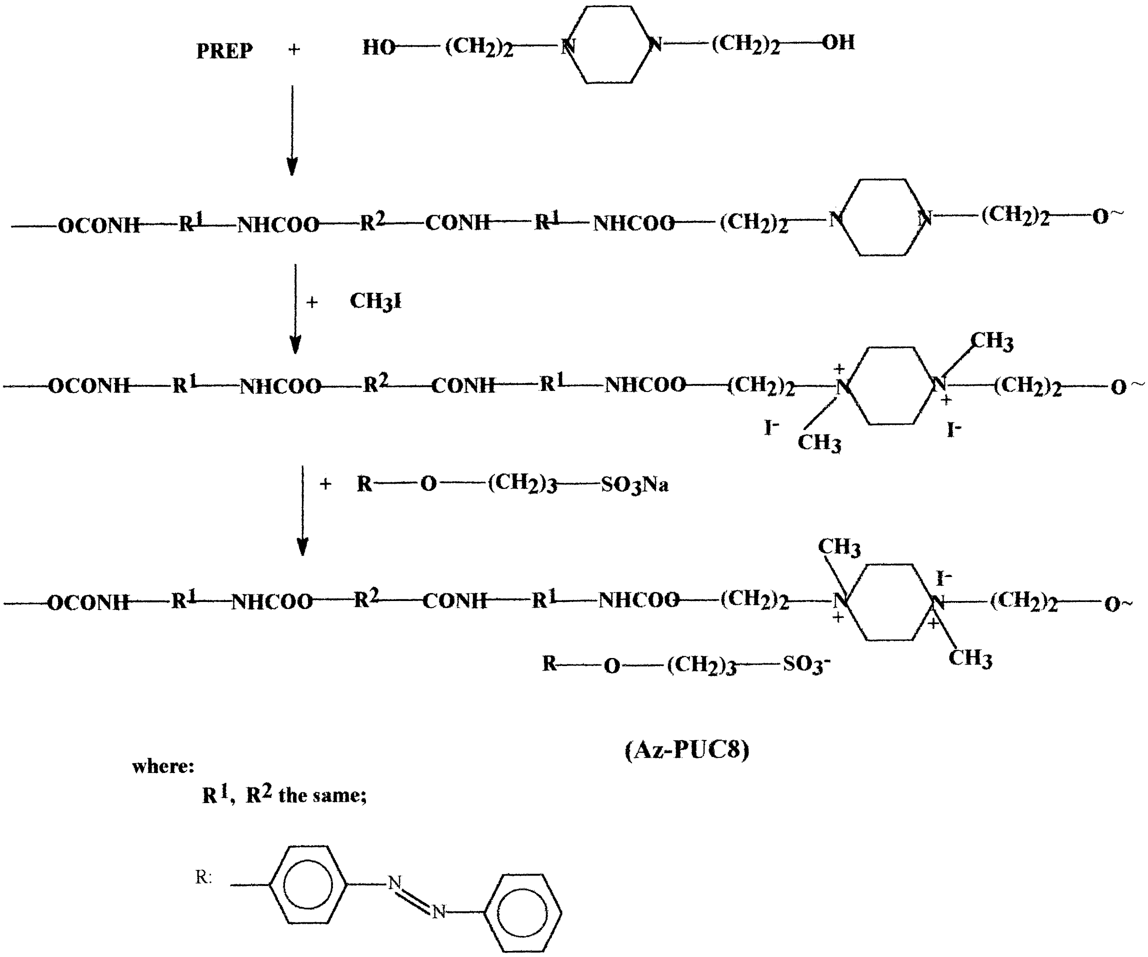
3.3. Polyurethane cationomers with azobenzene in the field of ionic structure

In order to investigate more close influence of the ionic groups on photoreactivity of the chromophore, azo cationomers bearing piperazine ring and azoaromatic units as counterions of the ammonium quaternary structure were prepared with the aspiration that they may have a better chance of being photochromic materials [79]. Synthesis of these polymers implied the use of *N*,*N*′-bis (β-hydroxyethyl)piperazine as chain extender and its quaternization with methyl iodide. Based on the polycation ability in complexing of the chromophore, by a simple route, such as the ionic exchange reaction between polymer and 3(*p*-oxyazobenzenc)propane sulfonic acid sodium salt, the electrostatic incorporation of different concentration of azo groups was possible (Scheme 4).

This facile reaction which generates azo functionality in the field of quaternary structure was suggested by decreasing of ionic iodine content from the starting polycation up to a certain value, simultaneously with increasing of the sulfur content. Polycations thus formed differ from the pure cationomer only by inclusion of the azoaromatic ionic groups instead of the commonly used anion (iodine). Two different azo polymers (Az-PUC8, Az-PUC9) with an ionic exchange degree of 52.7 and 92.31 wt.%, respectively, were synthesized in order to study the effect of chromophore content on the photophysical properties related to chemical composition of the polymers.

In the same connection, by using methyl orange (as sodium salt) in this ionic exchange reaction, polyurethane cationomers with azo-dye as counterions of quaternary ammonium groups were prepared too [80]. Structure of azo-dye polycation (Az-PUC10) is presented in Fig. 3.

All resulting azo polyetherurethane cationomers (Az-PUC1–10) were found to be soluble in common solvents like THF, CH_3OH, DMF, DMAc and DMSO. Solutions from these red polymers, as resulted from reaction, were coated onto a glass substrate and dried to form colored and flexible polymeric films with typical elastomeric characteristics of the conventional polyurethanes. Moreover, the optical clarity of these films is suitable for various applications. Structure of all polymers was determined by elemental analysis, IR and UV–VIS absorption



Scheme 4. Synthesis of Az-PUC8.

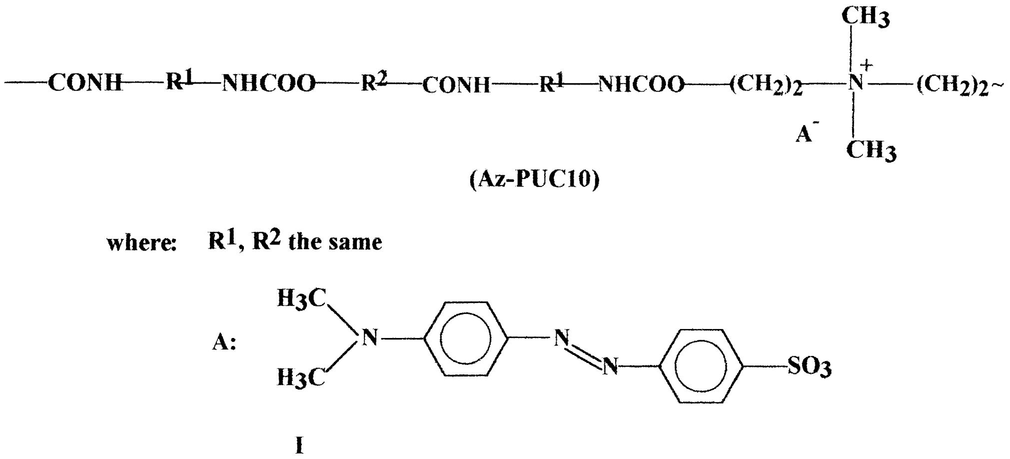


Fig. 3. Schematic representations of Az-PUCs.

spectroscopy. The results of elemental analysis were in good agreement with those calculated values of the expected structure of polymers. From the ionic halogen content the amount of ionic groups was estimated. GPC analysis performed on some precursors indicated the absence of low or high molecular weight tails and reasonable number-average molecular weights. Such polymers have a variety of interesting features worthily of study. First, they contain different azobenzene groups in varying compositions which provide an unusual opportunity to approach photobehavior of these chromophores in solution and in film state. Part of the difficulty in treating azo polymers derived from the interchain interactions of polyurethane ionomers via Coulombic forces. In the following, we are concerned with photoresponsive properties of the azo polycations investigated by photoirradiation with UV light.

4. Photobehavior of azo polyurethane cationomers in dilute solutions

4.1. *Trans–cis photoisomerization of the azo chromophore in DMF polymer solution*

It is well known that a large number of chromophores used in polymer synthesis may undergo different photochemical reactions when irradiated by UV light [81]. Since we had considered that the insertion of photosensitive chromophores into ionomeric chains might be a very useful and versatile technique for modification of the polymer structure, it was interesting to follow if some polymer properties may be controlled by means of photoirradiation. In order to enlighten these processes, photochemical experiments on all azoaromatic chromophores covalently or electrostatically bound to polymeric chains were done using as irradiation source, a high pressure Hg lamp equipped with a proper filter. The photoresponse of the azo chromophores was investigated by electronic absorption spectroscopy and evaluated comparatively with the corresponding azo models. In general, no large difference observed between the photobehavior of azo polymers and analogous low molecular weight derivatives, excepting the isomerization rates, always higher in the latter.

Normally, in every derivative the azoaromatic chromophores are in the thermodynamically more stable *trans* configuration. Photoexcitation of this structure induces a structural change of the *trans* conformer to *cis* isomer [82]. Once the molecule is in the *cis* form, it often recovers to the initial *trans* configuration by either the back thermal reaction or inverse photoisomerization cycle.

In our case, the main feature of the azo polycations arises from the photoprocesses induced by UV irradiation, with major influence on the structural properties of the materials, accompanied by reversible or irreversible modification of the polyurethane properties, as we will see later. Thus, depending on the chromophore nature, its location and content, the determination of the isomerization characteristics of azo moieties indicated significant differences in the rate of isomerization and photoprocess evolution. These factors were studied by the UV–VIS spectral changes of azo chromophores under different exposure times, as shown in the next figures. In each azo polycation, upon UV exposure of DMF polymer solution , the intensity of long wavelength absorption band characteristic of the *trans* isomer decreased gradually with irradiation times and only in some cases a photostationary state is possible to reach [73–76]. The changes in the electronic absorption spectra were utilized to examine the kinetics involved. The ratios of absorbances of irradiated sample (A_t) to the non-irradiated one (A_0) are given in Fig. 4 (plot a) as a function of irradiation time for Az-PUC1, Az-PUC2 and Az-PUC3 in DMF solutions. As can be seen from these plots, the *trans–cis* photoisomerization of *para*-nitroazoaromatic or azoaromatic groups covalently attached at the quaternary structure of polymeric chains involves long times of irradiation. This was caused by steric restrictions imposed to the photochrom by the rigid

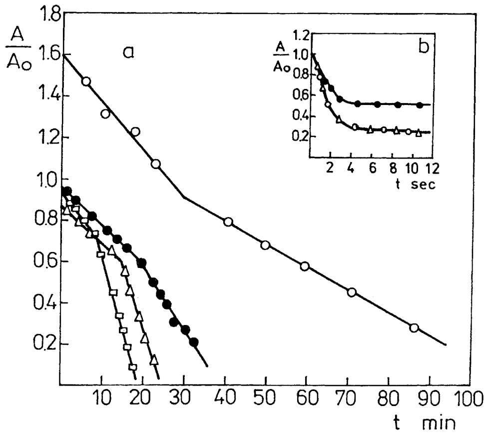


Fig. 4. Decrease of relative absorbance (A/A_0) as a function of irradiation time for *trans–cis* photoisomerization in DMF solution at 298 °K. Plot a: Az-PUC1(●), Az-PUC2 (□), Az-PUC3 (○), Az-PUC10 (△); plot b: Az-PUC4 (○), Az-PUC5 (△), Az-PR4 (●).

spacer groups and the inter- and intra-chain electrostatic interactions of the charged polymers. Cooperative effects involved in strong interactions, generated by the nature of the disubstituted azo chromophore with electron-withdrawing and electron-relasing group (Az-PUC1, Az-PUC2) led to a *trans–cis* isomerization in the first stage of the photoprocess. The occurrence of the isosbestic points in this first stage suggested that only the *trans–cis* photoisomerization is the photochemical change and no side reactions are produced.

One consequence of the irradiation is occurring photobleaching effect in the second stage but the question of the exact structure of the resulting products, remain open. Evolution of the photoprocess may be considered as a two step process in which the exposure to UV irradiation first excites a ground state of chromophore to an excited *trans* isomer, accompanying its relaxation to a stable *cis* state. Reactions between species can further lead to an irreversible photobleaching. A similar photobehavior was also evidenced for some NLO polyurethanes and urethane–urea copolymers [83].

Unlike *para*-nitroazo chromophore, the *trans–cis* photoisomerization of azoaromatic groups placed in the same quaternary structure (Az-PUC3) with attainment of the photostationary state after 120 min of irradiation was evidenced. Thus, in this state, the molar fraction of *cis* isomer was about 0.78. From these observations one can easily see a strong tendency for favorable interactions of these latter groups that are brought into neighboring positions which facilitates the *cis* isomer formation even when the azo groups are irradiated at longer time. Such behavior of the azo derivative provided information about the intrachain interactions between azo ammonium quaternary groups and the local environments around the chromophores, which, in turn, can be related to polymer structure in solution.

Comparatively with the above polycation, a synthetic mixture based on polyurethane cationomer and azobenzene (1:1 azo/tertiary amine groups) reached the photostationary state in shorter times (about 20 s). In their pioneering work on azo polyurethanes, Sung et al. [71,72] and Eisenbach [84] investigating the kinetics of the *trans–cis* photoisomerization and the thermal *cis–trans* isomerization of the azobenzene labels containing hard segments revealed that the relatively facile photoprocess reflected the structure, morphology and segmental mobility of the surrounding polyether(ester)urethanes in dilute solution. They reported that for more than 75% of the course of the reaction there is no difference in the photobehavior of the dilute solution and polymeric film. As the reaction approaches the photostationary state, its composition in *cis* conformer is higher in solution (0.8 *cis* isomer) than in film (0.62 *cis* isomer).

The difference in the isomerization of azo derivative as ammonium group into the ionomeric architecture, whose properties are at least in part, governed by electrostatic considerations is illustrated by the photoprocess dynamics influenced by the strong interaction between polycation having a local charge density and counterion around it.

One of the ways to overcome a part of this drawback affected mainly by restrictive mobility of the azo chromophore may be the photoisomerization of azoaromatic groups placed in the non-ionic fragment of the hard segments (Az-PUC4, Az-PUC5) [66]. Indeed, during careful irradiation of the polymer solutions the *trans–cis* photoisomerization of azo chromophore occurred and the time required for attaining photostationary state considerably decreased at about 30 s (Fig. 4, plot b). Under these conditions, the molar fractions of *cis* isomer in the equilibrium state was of 0.55. At first glance, one might think that increased sensitivity to UV irradiation of this last polycation is a direct consequence of the higher conformational mobility of the polymeric chains with azo groups as non-ionic fragment of the hard segments. Comparison of the photobehavior of Az-PUC4 with that of non-ionic polyurethane precursor showed that the presence of ammonium quaternary structure besides chromophoric groups on the same polymer chain retards slightly the attaining of photostationary state. It is logically to expect that the *trans–cis* photoisomerization of azoaromatic chromophore located in the polyether flexible segment to be a faster process than in the case of the chromophores placed in the hard segment. Consequently, upon UV irradiation of the Az-PUC6 and Az-PUC7 solutions, the *trans–cis* photoisomerization of azoaromatic groups, after about 5 s, was interpreted as arising from the specific polymer structure [77]. The effect of higher mobility of the azo chromophore controlled by both local chain stiffens imposed by pendant inserted azobenzene and overall chain length on the macromolecular conformations are well reflected in the isomerization behavior in part, due to the more efficient incorporation of the azo groups within the soft microdomains.

Photobehavior of 3(*p*-oxyazobenzene)propane sulfonate electrostatically incorporated as anion around the quaternary structure from ionomeric backbone was relatively simple [79]. From the comparison of the data concerning evolution

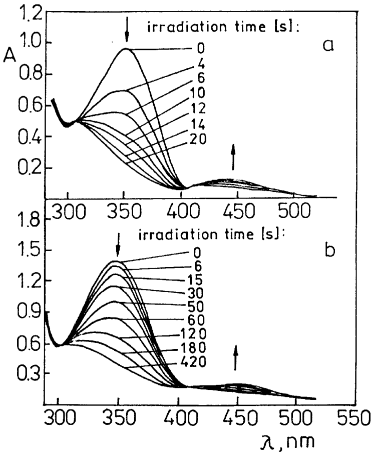


Fig. 5. UV–VIS absorption spectra monitoring the *trans–cis* photoisomerization of azo chromophores in polycations. Plot a: Az-PUC8 in DMF solution; plot b: Az-PUC8 in film.

of the photoprocess, the notable difference in the photoresponse of polymeric solutions may be mainly attributed to the chromophore structure and its ionic bonding. Following the progress of the *trans–cis* photoisomerization of azoaromatic group in the polyurethane cationomer (Az-PUC8) with irradiation time (Fig. 5, plot a), a rapid reaction with reaching a photostationary state in only 20 s was observed. In the equilibrium state, the value of *cis* isomer estimated at 0.8. Well defined isosbestic points (308 and 415 nm) confirmed the presence of *cis* and *trans* isomers resulted by a single chemical phototransformation of the azo chromophore. The increase of photoisomerizable structure content in polymer chains (Az-PUC9) has not been favorably to a faster *trans–cis* photoisomerization in polymer solution.

By contrast, a significant difference in the photobehavior of azo cationomer prepared by using methyl orange as photoactive chromophoric agent capable of interacting electrostatically with ammonium groups was noticed (Fig. 4, plot a) [80]. As a consequence of azo-dye structure, photoisomerization of the dye-polycation (Az-PUC10) was observed only in the first step of the photoprocess, with a tendency to return to the initial state when irradiation was interrupted. On continued irradiation (over 20 min), colorless polymer solutions were obtained and the photobleaching effect was accompanied by the photodecomposition reaction of polyurethane cationomers. An important cause of this photobehavior may arise from the chromophore nature, dissociated in polar solvent, its distribution and its orientation on the ionomeric chains. By using a pH in the acid range, the effect of dissociation is suppressed and so the sulfobetaine structure of azo chromophore formed is more favorable to the responding at irradiation. The rather peculiar viscosity behavior of Az-PUC10 in DMF solution may be mentioned at this point. Measurement of the reduced viscosity as sensitive indicator of photoprocess evolution, showed that the polymer solution underwent viscosity modifications with the irradiation time, suggesting photodegradation of the polycation with azo-dye chromophore. This seems to be a feature for ionomeric backbone with an azo-dye electrostatically loaded. It was also remarked that the systematic shifts of the absorption maxim towards longer wavelengths for all chromophoric polymers, are apparently due to a microenvironmental polarity effect of the surrounding azoaromatic groups.

4.2. *Cis–trans* back reaction of the azo chromophore in DMF polymer solution

The kinetics of *cis–trans* relaxation process of all azo chromophores in polymer solution was monitored by the changes of specific absorbances to the *trans* configuration, of the irradiated samples. A better understanding of the important factors affecting this process is essential for the development of new photochromic systems. One of the parameters that affected the rate of *cis–trans* isomerization was temperature. For this reason, the back isomerization of *cis* isomers was studied by recovery at room temperature in dark or at temperatures between 50 and 90 °C, and by irradiation with 365 nm. In some cases (Az-PUC3; Az-PUC4, Az-PUC5, Az-PUC6, Az-PUC8, Az-PUC9), the return to the initial *trans* configuration state occurred but with different rates.

The thermal *cis–trans* isomerization was expressed by a first order rate equation:

$$\ln\left(\frac{A_\infty - A_0}{A_\infty - A_t}\right) = kt$$

where A_0, A_∞, A_t are values of the absorbance at times t_0, t_∞ and t, respectively and k is the rate constant of *cis–trans* isomerization [85]. Apparently, the differentiation between the photoresponse of above azo polycations may be due to the different incorporation of the azoaromatic chromophore in polymeric chains. In spite of strong interactions exercised by the quaternary ammonium structure bearing azoaromatic side group on the *cis* isomer once formed (Az-PUC3), the thermal recovery (68 °C) in DMF solution becomes possible but requires high times, over 120 h [76]. At lower temperatures, the same reaction necessitates more and more time. For example, after a standing at room temperature of about 200 h, only 10% *cis* form was capable to return in *trans* configuration. This is not surprising because the relaxation process assumes the reorientation of azobenzene molecules in various constrained environment of the ionic matrix. The understanding of the time dependence of this photoprocess is more difficult because several structural factors including a few highly polar ionic sites in an organic hydrophobic neighborhood may perturb the reorientation of azobenzene units. In contrast with these structures, the return of the earlier mentioned synthetic mixture (at 68 °C) with a complete transformation of the *cis* isomer to initial *trans* form takes place within 48 h. This is obviously due to the weak chromophore–polycation interactions leading to *trans* isomer reformation. In this way, the physical incorporation of

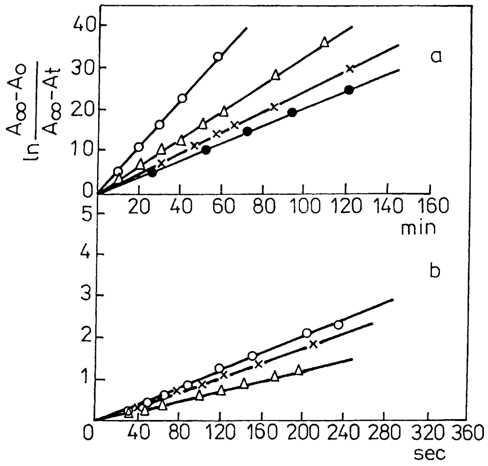


Fig. 6. Plots for *cis–trans* isomerization of azo polyurethanes. Plot a: Az-PUC8 (×), Az-PUC9 (●) in DMF solution; Az-PUC8 (○) and Az-PUC9 (△) in film; plot b: Az-PUC4 (△), Az-PUC5 (×) and Az-PR4 (○) in DMF solution.

the azo chromophore in the polyurethane ionomer matrix does not offer information on the ionomeric chain mobility.

An important difference in the return of *cis* isomer located far away from the ionic vicinity of the polymer chain, namely in the non-ionic fragment of hard segments (Az-PUC4, Az-PUC5), was evidenced. In both azo polycations as well as in their precursors was clearly observed an enhancement of the thermal recovery at higher temperature (relaxation time is about 7 min at 90 °C), suggesting a considerable mobility of the azo chromophore in solution (Fig. 6, plots b). A quite comparable situation was also found and in Az-PUC6 and Az-PUC7 containing lateral azobenzene unit in the polyether segments of the ionomeric chains.

Following the back isomerization process of Az-PUC8 and Az-PUC9 in DMF solution, the return of *cis* azo chromophore to the starting *trans* form was noted in both polymers, but the thermal recovery required higher times (over 180 min at 72 °C). An increase of the azo photochromic groups concentration as anions around the quaternary structure (Az-PUC9) led to a decrease in the *cis–trans* isomerization rate (Fig. 6, plot a). On the other hand, although they are in intimate contact into polar medium, the effect of ionic groups on the isomerization of azo chromophore is significantly smaller than those observed in the case of polycation (Az-PUC3) possessing azoaromatic unit covalently bound to the ammonium quaternary structure. In fact, an improvement of the return efficiency of the azoaromatic groups upon changing incorporation from covalently to electrostatically really occurs for this reason, due to a higher local mobility of the chromophores in the latter. It is reasonable to believe that besides the size of the azo moiety and the free volume around the azobenzene, the local mobility is controlled and by the ionic strength of the coupling interaction between the azo moiety and the polymeric backbone.

5. Photobehavior of azo polyurethane cationomers in thin films

5.1. *Trans–cis photoisomerization of the azobenene in polymeric films*

The photophysical properties of the chromophores are more complex when the azoaromatic groups are studied in polymeric films. It is well known that the isomerization reactions of the azo chromophores are substantially slow-down in polymer films than in solutions, as a direct consequence of their reactivity sensitively to the local mobility of reactants and heterogeneity of reaction sites in solid state [86]. The same rule also applies when the substrate itself is a polyurethane. As mentioned, the earlier work of Sung et al. [71,72] and Eisenbach et al. [84] based on the molecular labeling techniques of polymer chains studied the *trans–cis–trans* photoisomerization of azobenzene attached to the hard segment of the amorphous, single-phase polyether(ester)urethanes. Their results showed that in the polymer films the reaction was completely reversible but the quantum yield was reduced to about 30%, as compared to the analogous process occurring in solution. In contrast to this, distinct differences were observed in the case of two-phase polyurethanes containing the same chromophore in the hard segment or in the soft segment. Direct evidence of the reversible isomerization of the azo chromophore in the soft segment has been obtained. The ability to differentiate the photobehavior of the flexible and rigid portions of the polymeric films, and the effects of molecular mobility, widely suppressed within hard domain, on the isomerization process were demonstrated. The authors have also sustained as possible the *cis–trans* isomerization of azobenzene placed in hard segments explained in terms of no phase separation occurred.

A straightforward extension of the earlier results can be made for the polyurethane cationomers containing different azo chromophores in order to detect possible photochromic properties of some ionomeric films of elastomer type. Although, still in their infancy, our current work has revealed some possibilities in the structural tailoring of such ionomers capable to assure good photoresponse of the azo chromophores in thin films.

Therefore, azo polycations are expected to behave somehow differently compared with non-ionic polymers with the same azo sequence unit. Consequently, it was confirmed that in thin films the isomerization rate and phototransformation degree of the azobenzene groups were affected by restrictions in movement of the chromophores, imposed to the molecular chains by steric and shielding effects. Moreover, these are considered to be due to the electrostatic perturbation of the ammonium quatemary groups exerted by the charge distribution on polymer backbone. Data for the azo polymers, showed that the attainable level of *cis* isomerization was primarily affected on the attachment point of the azoaromatic derivative in polymeric chains, content and the incorporation way, covalently or electrostaticaly. This was implicitly observed when one compares the *trans–cis* photoisomerization for Az-PUC3 with that of the polymers series, Az-PUC4, Az-PUC5, Az-PUC6-7 and Az-PUC8-9. Following evolution of the photoprocess in every thin polymeric film subjected under the same irradiation conditions, it was found that the absorption maximum corresponding to π–π* transition, decreased much more slowly as the UV light exposure time increased. This decreased tendency is the result of slower *trans–cis* photoisomerization of the azo chromophores in film state with or without attainment of an equilibrium state. Therefore, the difference in the *trans–cis* photoisomerization of the azo chromophores in azo polycations based films may be reasonably explained not only by the structure variance of azobenzene moiety but also by the different mobility of the polymeric chains assisted by ionic interactions and hydrogen bonds.

When the photobehavior of Az-PUC3 film was compared with that of Az-PUC4 and Az-PUC5 films, it observed that photoreaction required longer times of irradiation then those in solutions, and only the polymers Az-PUC4, Az-PUC5 (Fig. 7, plot a) reached the photostationary state. For example, the measurement of the relative absorbance A/A_0 indicated a value of 0.63 after 240 min of irradiation for PUC4 film, while in DMF, the same parameter was 0.45, after only 10 s. As in the case of non-ionomeric precursors, the first photoprocess was attributed to the photoisomerization of azoaromatic groups, proved by the presence of two isosbestic points at 364 and 497 nm, respectively. Under these UV irradiation conditions, a photobleaching process starts in the polymer film after 150 min and it takes place very slowly as the reaction goes on. By contrast, in the case of Az-PUC3, the strong electrostatic interactions of azo chromophores covalently attached to quaternary structure greatly reduced the *trans–cis* photoisomerization of azo derivative in film state. The increase in the irradiation time up to 5 h, led to a transformation degree of the *trans* isomer of only 10%, suggesting a very limited mobility of the chromophore in thin film.

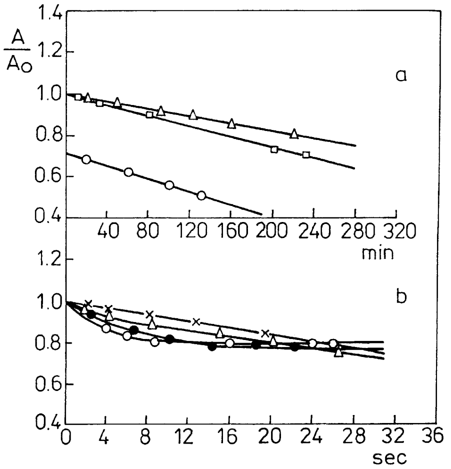


Fig. 7. Dependence of relative absorbance of azo polymeric films on irradiation time. Plot a: Az-PUC4 (□), Az-PUC5 (○), Az-PR4 (△); plot b: Az-PUC6 (×), Az-PUC7 (□), Az-PR6 (●), Az-PR7 (○).

At less content of azoaromatic groups, the changes appeared in the electronic absorption spectra are much more pronounced for Az-PUCS film (Fig. 7, plot a). In this case, the intensity of absorption band at 406 nm decreases faster during irradiation reaching a molar fraction of *cis* isomer of about 0.24 after 50 min irradiation. For the same irradiation time, in the Az-PUC4 film approximately 0.09 *cis* form was measured. In the first polycation, the chromophore loading on the ionomeric chains was limited to a low level to avoid chromophore-chromophore interactions that often lead to a complex photobehavior. The process is dynamic in nature with a photobleaching effect observed in the time-dependent phototransformation data. The electronic absorption spectra of Az-PUC5 film exhibited no modifications by its standing at 120 °C for 405 min, the photobleaching process being irreversible in these conditions.

Azoaromatic chromophores located in the soft segment of polyurethane chain are assumed to have an interesting photobehavior [77] In the following, we first studied some properties of the corresponding polymers of ionomeric (Az-PUC6, Az-PUC-7) or non-ionomeric type in thin films. Accordingly, one might reasonably expect that the *trans–cis* photoisomerization of the azo chromophore to be a faster reaction comparatively with the earlier discussed azo polycations. Indeed, as can be seen from the Fig. 7 (plot b), in the ionomer film the photostationary state is reached in only 30 s of UV irradiation with a molar fraction of *cis* isomer of about 0.34. In the analogous non-ionic polyurethane film, it was found that absorption maximum corresponding to π–π* transition decreased more quickly as the UV light exposure time increased. This decrease was the result of the same *trans–cis* photoisomerization of azo unit, with attainment of an equilibrium state in 12 s, when the molar fraction of *cis* form was about 0.25. Although, the polyether matrix in which the azobenzene was incorporated can provide a better 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. As assumed, the *trans–cis* photoisomerization was particularly sensitive to the competitive interactions with other portions of the polymer chains, namely at the ionic interactions within the hard segment dispersed in the polyether phase. As a result, a difference in the photoisomerization rate of the azo aromatic chromophore in the ionic film (Az-PUC6, $k = 7.7 \times 10^{-1}\,\mathrm{s}^{-1}$) and in the analogous non-ionic film (PR, $k = 35.5 \times 10^{-1}\,\mathrm{s}^{-1}$) was found. The general photobehavior of the Az-PUC7 corresponds to that previously seen for Az-PUC6, with a small decrease in the photoisomerization rate of ionomeric film (Az-PUC7, $k = 7.2 \times 10^{-2}\,\mathrm{s}^{-1}$) as well as in its corresponding precursor of identical soft chain (PR, $k = 33.8 \times 10^{-2}\,\mathrm{s}^{-1}$). As the data show, it should be noted that the observed deference between Az-PUC6 and Az-PUC7 could result from changes in the content of ionic groups and implicitly the extent of physical crosslinking. So it can speculated that the activity of precursor is a reflection of matrix polarity which allowed a more efficient arrangement of the chromophore units because of the lack of electrostatic interactions within the polymer. In fact, the enhancement of photoisomerization efficiency of the azo moieties by providing a lower barrier to photoreaction occurred for this reason. From the presence of the isosbestic points at 362 and 470 nm, one can draw the conclusion that the photoisomerization is the only chemical phototransformation suffered by polymeric chains.

Similar results were also reported on Az-PUC8 and Az-PUC9 with azobenzene attached as anion to the piperazine rings of ionomeric backbone. In thin film, the rapid *trans–cis* photoisomerization of azoaromatic chromophore from Az-PUC8 (Fig. 5, plot b) with reaching of equilibrium state in about 60 s irradiation occurred, too. The molar fraction of *cis* isomer in the photostationary state was approximately 0.56. At a higher content of azobenzene chromophore (Az-PUC9) the isomerization reaction has not favored. In the isomerization rate determination from *trans* to *cis* isomer in the thin film, a decreasing in the rate value ($k = 10.8 \times 10^{-3}\,\mathrm{s}^{-1}$) as the chromophore concentration increased in this latter polymer comparatively with Az-PUC8 ($k = 12.4 \times 10^{-2}\,\mathrm{s}^{-1}$) was found. It is also evident that the difference in the photoisomerization rate of chromophore in thin film comparatively with that found in solution, is primarily due to the mobility of the itself photochrom, more restricted in polymer film than in solution.

Studies reported so far have mostly concentrated on the *cis–trans* isomerization of azobenzene chromophore in polymer films based on all earlier described polyurethane cationomers. In general, the direct detection and characterization of the polymer photosensibility by UV measurements depend on the different local environments of the chromophores inserted in the polyurethane ionomer which give rise to different photobehavior. With few exceptions, the thermal recovery of azo chromophore in the cationomer matrix was not evidenced. This aspiration is important in connection with photochromic phenomena which may be induced in ionomeric films of elastomer type, which are assumed to be of great interest in versatile applications. The principal driving force for the chromophores relaxation is a large increase in mobility and free volume, sufficiently to promote the return of the *cis* azobenzene structure to the initial *trans* form. These conditions are satisfied by a small number of polymers such as those containing azo chromophore in the soft segment of the ionomeric chains (Az-PUC6, Az-PUC7) or as anion in the field of ammonium quatemary structure (Az-PUC8, Az-PUC9). Evidence for this claim is that the spectral changes during the return of the chromophore can be easily observed within the thin polymeric films.

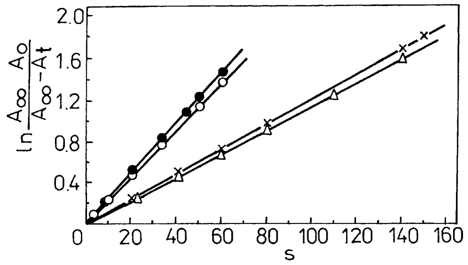


Fig. 8. Plots for *cis-irans* isomerization of azo polyurethane films: Az-PUC6 (×), Az-PUC7 (△), Az-PR6 (●), Az-PR7 (○).

5.2. *Cis–trans isomerization of the azobenzene in polymeric films*

The kinetics of *cis–trans* relaxation process of azobenzene in the irradiated films, was followed by monitoring the changes of absorbances specific to the *trans* isomer, appeared by standing of films at 80 °C or at ambient temperature. In both cases, the return of the chromophores to the initial *trans* configuration occurred, but with various rates. The first order plot for thermal *cis–trans* isomerization of azo chromophore in Az-PUC6 and Az-PUC7 films are shown in Fig. 8. Although, the Az-PUC6 and Az-PUC7 films contain azobenzene in the flexible segment, comparing the rate value found in ionomeric films (Az-PUC6: $k = 29.17 \times 10^{-3}\,\mathrm{s}^{-1}$; Az-PUC7: $k = 25.9 \times 10^{-3}\,\mathrm{s}^{-1}$) with that of the non-ionornenc films (PR6: $k = 59.3 \times 10^{-3}\,\mathrm{s}^{-1}$; PR7: $k = 57.8 \times 10^{-3}\,\mathrm{s}^{-1}$), 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 from the hard domains whose microphase separation is not very well delimited. In contrast with the ionomeric films, whose *cis–trans* isomerization necessitated 300 s, the same back reaction required about 60 s in the non-ionic films. Additionally, a slower recovery of the chromophores in both films at ambient temperature, over 200 min, was noticed too. The thermal recovery data indicated the role of the structural and steric environments surrounding the azo groups inserted in the polymeric backbone. Since the fatigue behavior of these films can be quite important, five cycles of *trans–cis* and *cis–trans* isomerization were followed, but no modifications were observed in the electronic absorption spectra.

The same trend of chromophores to relax has been observed and in the case of polycations with azobenzene as counterions of piperazine rings (Az-PUC8, Az-PUC9). Comparing the rate value of Az-PUC8 film ($k = 8.46 \times 10^{-4}\,\mathrm{s}^{-1}$) with that found in solution ($k = 3.81 \times 10^{-4}\,\mathrm{s}^{-1}$), is obviously that the thermal recovery of the *cis* form to *trans* isomer is much faster (about 70 min) in polymer film (Fig. 6, plot a). Such result suggested that in film state, the *cis* configuration of azobenzene structure there is in a very constrained state. On the other hand, as result of increasing the azo chromophore concentration in Az-PUC9 film, the return to the initial *trans* state is a slower process, which needs over 100 min. Data for the rate value found in the latter polycation containing film ($k = 5.2 \times 10^{-4}\,\mathrm{s}^{-1}$) reflected the temperature-induced slower back reaction, comparatively with Az-PUC8 film. These results confirmed photochromic nature of the thin elastomeric films prepared from azo cationomers with photoisomerizable azobenzene chromophore placed as anion around ionic groups. Hence, working with a certain azo counterion in the field of ammonium quaternary structure may result in a better *cis–trans* isomerization, while working with an azo-dye (methyl orange) the photodegradation reaction might appear.

Our findings sustain that the covalent introduction of the azobenzene chromophore as side group in the polyether segments of the polyurethane backbone seems to be a decisive factor of the reversible photo(thermo)reactions. An alternative approach should be the electrostatic incorporation of photoisomerizable azoaromatic structures into polyurethane cationomers as a convenient way for inducing photochromic properties in polymeric films, intended for special applications. We expect that in the near future these polymers to be developed and characterized in many other aspects of the polyurethane photochemistry. By selecting the measurement conditions and instrumentation, it is possible to investigate selectively the chemical structure, molecular dynamics and the orientation of a specific chromophore in polymer films. Correlation of some photoinduced chain motions with mechanical properties should improve understanding of the polymer behavior at macroscopic level.

5.3. *Effect of some additives on the isomerization of the azo chromophore in the films*

In terms of *trans–cis* isomerization and *cis–trans* relaxation of the azobenzene chromophore in film state, one can not always explicitly interpret the relative small content of *cis* isomer from the equilibrium state or inability of the *cis* isomer to return to the *trans* form. One of the unanswered questions is how the photoreactivity of azo groups in ionomeric chains would be influenced by the presence of small amount of photosensitive derivative. A convenient means to enhance the photostimulated activity of the polymer chains was the incorporation of sensitizers in polymer films, such as benzophenone or iodine vapors [66]. In a previous investigation, we reported that the nitropolyurethane with 2,4-nitroaromatic groups in polymer chains was sensitively to UV irradiations [87]. Based on this finding, to improve the isomerization of azobenzene by means of physical interactions between an azo polycation and nitropolyurethane in polymer film, we choose as sensitizer 2,4-dinitro-polyurethane. Following the evolution of the photoprocess in Az-PUC5 films, it was found that the presence of both sensitizers, either nitropolyurethane or benzophenone does not enhance the dynamics of the photoprocess. Moreover, the photoprocess rate in azo cationomer-nitropolyurethane based film was reduced comparatively with that found in the absence of the sensitizer. Therefore, the adding of these sensitizers had a negligible effect on the photosensibility of azo cationomers. A somewhat different behavior was evidenced to the exposure of the irradiated films at iodine vapors (for low exposure times, of only 1–2 min), known as catalyst of the *cis–trans* isomerization of the monomeric azobenzenes. The origin of this property of the *cis* isomer may be explained by the photochemical formation of the iodine atoms, capable to lead to a radical intermediate, whose free rotation is possible. In Fig. 9, is depicted the effect of the iodine vapors on the behavior of Az-PUC5 film, irradiated 170 min, when the ratio between A/A_0 is 0.54. Note that it is here a fast increase of the absorbance at 405 nm, with reaching almost the starting absorbance value after about 265 s. In the same time, a common polyurethane film based on PTMO, 4,4′-DBDI and NMDA, treated with iodine vapors exhibited an absorption band at 357 nm, assigned to some complexes between iodine and the aromatic structure. Such behavior confirms that the *cis–trans* isomerization of Az-PUC5 film obviously proceeded. By reirradiation of the azo polycation films exposed to iodine vapors, the *trans* to *cis* isomerization takes place but with a slower rate and finally a photobleaching effect was evidenced, too. It is reasonable to assume that the combinative effect of this treatment may affect the stability of the polymer. So, the data analysis led to some preliminary conclusions regarding the role played by sensitizer present into azo ionomer matrix. Clearly, it is not as easy to predict how specific structure of the sensitizer will influence the isomerization reaction of the azobenzene. To examine a variety of sensitizers and methods might led to correlations that are less subject to the bias due to the specific probe dependent interactions and interpretation of such results based upon insufficient knowledge of the molecular architecture of ionomer films.

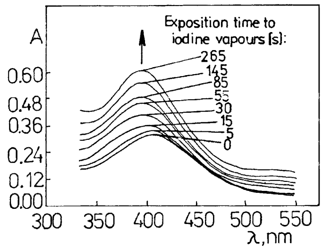


Fig. 9. Influence of iodine vapors on the electronic spectra of UV irradiated thin film Az-PUC5. The exposition times to iodine are given in figure.

6. Applications of the polyurethane cationomers

As described in Section 1, the most important property of the polyurethane ionomers from a technical point of view is their strong interaction with water that makes them suitable especially for applications as aqueous dispersions for coating and adhesive materials [15,40,41,88]. The development of aqueous polyurethane applications continues to be motivated by environmental considerations pursuing in particular, solvent emission reduction in atmosphere. Besides these classical encouraging developments, further specific properties of the cationomers could be used for developing biocidal coatings with high activity against Gram-positive and Gram-negative bacteria [40,41,89]. Also, promising is the use of the polyurethane ionomers as membrane for gas permeability or mixture separation by pervaporation [27,34,90]. A number of these uses that would satisfy various needs of the industry could also include many chromophoric polyurethane ionomers as polymeric colorants. This would result in major advances by working with colored aqueous dispersions. Moreover, some polymeric films of elastomer type could find applications as photochromic materials [35,77,79].

Our approach in the field of azo cationomers has been shown clearly to be flexible and adaptable to a variety of azo coupling agents and attachment methods of the chromophore. General properties of the azo cationomers described earlier should be just a starting point for their own area of interest as polyurethane elastomers. In summary, it can be said that already this field was marked by an enormous progress stimulated of environmental reasons and a current wide diversity of applications, new polyurethane ionomers are expected to be developed, as we improve overall properties and structural design.

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