

Synthesis and Properties of New Polyurethane Ionomers. I. Photosensitive Cationomers with Triazene Units

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ABSTRACT: New bifunctional triazene compounds 1-(*m*-hydroxymethyl)phenyl-3-(2-hydroxyethyl)-3-methyltriaz(1)ene and 1-*p*-nitrophenyl-3,3-di(2-hydroxyethyl)triaz(1)ene as intermediates in polyurethane synthesis were prepared. Photosensitive polyetherurethane cationomers based on poly(tetramethylene oxide) diol of 2,000 average molecular weight, tolylene-2,4-diisocyanate, and *N*-methyl-diethanolamine/triazene diols, as cochain extender, followed by a quaternization with benzyl chloride, were synthesized and characterized. Upon UV irradiation, feniltriazene chromophore in monomer and both polymers (ionomeric or nonionomeric type) is irreversibly cleaved,

as evidenced in photolytic and kinetic studies. The rate constant of photolysis in ionomer film was lower than for the corresponding nonionic film. A positive pattern can then be developed by treatment with CHCl_3 that dissolves the exposed zone, while the unexposed area remains resistant and insoluble. By incorporating side nitrofeniltriazene groups, photo-stable polyurethanes were obtained. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1203–1210, 2003

Key words: triazene diol; poly(triazene-urethane) cationomers; UV photodecomposition

INTRODUCTION

Interest in the synthesis and characterization of new photopolymers has grown in recent years due to their unusual properties and potential applications in the optic and optoelectronic field, biomedical devices, microlithography, and so on.^{1–4} In relation to polymers intended for photolithographic processes, most studies were focused primarily on microstructuring of standard polymers^{5,6} or doped systems^{7,8} by weak UV or laser irradiation. An alternative approach in the design of new photopolymers is based on the incorporation of photolabile chromophores, which are highly absorbing at the irradiation wavelength and cleaved rapidly at well-defined positions of the polymeric chains with gaseous products releasing.^{9,10} For an application of laser ablation, this preparative and analytical tool becomes one of the most actively pursued subjects in polymer photochemistry.¹¹

Much attention was paid to the polymers with triazene chromophores ($-\text{N}=\text{N}-\text{N}<$), whose structure may be conveniently adapted to the requirements for photosensitive materials such as thermostability, high photosensitivity, optical and good coating properties. So far, several triazene polymers of polyester, polyether, polysulfone, or polymethylmethacrylate type that may be structured with high resolution upon laser irradiation have been reported.^{1,12–17} It would be

of particular interest to explore the use of triazene derivatives in the preparation of photosensitive polyurethanes, unapproached in the literature, but recognized by their properties and broad-spectrum applications. Therefore, we chose first triazene functionality to introduce in the polyurethane backbone, which offers the unique opportunity of studying the structure effect on the polymer properties that can be designed for totally different purposes. Moreover, the presence of chromophoric groups in ionomeric architecture^{18–21} could be a modern alternative to diversify the conventional applications of this versatile class of polymers, predestined for coating and adhesive materials.²²

In this article, we report on the synthesis and properties of new polyurethane cationomers with polyether flexible segments and triazene units in the hard fragment, incorporated by means of diols bearing chromophore in the main or side chain and, more interestingly, the photochemical behavior of polymers in comparison with that of the parent monomers.

EXPERIMENTAL

Monomers synthesis (T-1, T-2)

A total of 5 g (40 mmol) *m*-hydroxymethylaniline dissolved in 37 mL 10% hydrochloric acid and then an aqueous solution of 2.8 g (40 mmol) of sodium nitrite was dropped at 0–3°C. The resulted diazonium salt was coupled with 3 g *N*-methylaminoethanol (40 mmol) in the presence of 5 g sodium carbonate (47 mmol) in 200 mL H_2O . After stirring at 0°C for 1 h, 5 g sodium chloride were added and the aqueous solution was extracted three times with chloroform. The

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organic layers were dried (Na_2SO_4) and the solvent was evaporated under reduced pressure to obtain 1-(*m*-hydroxymethyl)phenyl-3-(2-hydroxyethyl)-3-methyltriaz(1)ene (T-1). Data are as follows: T-1, $^1\text{H-NMR}$ (CDCl_3 , ppm): 7.1 (m, 4H, aromatic); 4.45 (s, 2H, $\text{Ph-CH}_2\text{-OH}$); 3.7 (s, 4H, $\text{HO-CH}_2\text{-CH}_2$); 3.15 (s, 3H, N-CH_3); IR (cm^{-1}): 3,350 (OH); 2,940 (CH_2); 1,600 (Ar); 1,370 (N=N-N); UV (CH_3OH), λ_{max} : 285 nm, 312 nm. Analytical calculation for $\text{C}_{10}\text{H}_{15}\text{N}_3\text{O}_2$ ($M = 209$): C, 57.41; H, 7.17; N, 20.09. Found: C, 57.29; H, 7.02; N, 19.88.

1-*p*-Nitrophenyl-3,3-di(2-hydroxyethyl)-triaz(1)ene (T-2) was prepared from 10 g (72 mmol) *p*-nitroaniline in a similar fashion to T-1, diazonium salt being coupled with 7.6 g (72 mmol) diethanolamine. After removal of the solvent, the yellow crystalline solid was recrystallized from methanol-water (1:5 v/v). Yield was 74%, mp 64–65°C. T-2, $^1\text{H-NMR}$ (CDCl_3 , ppm): 7.95 (d, 2H, aromatic CH *ortho* to NO_2); 7.15 (d, 2H, *ortho* to N=N-N); 3.85 (t, 8H, $\text{N-CH}_2\text{-CH}_2\text{-OH}$); 3.3 (s, 1H, OH); IR (cm^{-1}): 3,350 (OH); 2,950 (CH_2); 1,600 (Ar); 1,400 (-N=N-N); 1,340 (NO_2); UV (CH_3OH), $\lambda_{\text{max}} = 365$ nm, mp = 64–65°C. Analytical calculation for $\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_4$ ($M = 254$): C, 47.24; H, 5.51; N, 22.09. Found: C, 47.06; H, 5.32; N, 21.93.

Polymers synthesis

Polyurethanes (PU-T1, PU-T2) with triazene groups were synthesized by the prepolymer method under purified nitrogen using poly(tetramethylene oxide) diol (PTMO), 2,4-tolylene diisocyanate (TDI, as isomers mixture 2,4- and 2,6-TDI, 80:20 v/v), *N*-methyl-diethanolamine (NMDA), and triazene diols (1:3:1:1 molar ratio) in DMF solution. Dry PTMO ($M_w = 2,000$, 0.5 mmol) reacted with 1.5 mmol tolylene diisocyanate at 65°C for 3 h. To the prepolymer mixture dissolved in anhydrous DMF ($c = 20$ g dL^{-1}) was added 0.5 mmol triazene compound and 0.5 mmol *N*-methyl-diethanolamine, and the reaction was continued in the same conditions for 8 h. The course of these reactions was followed by IR spectroscopy until the hydroxyl and NCO—groups were reacted, as confirmed by the disappearance of the hydroxyl and the isocyanate stretching bands centered at 3,480 and 2,270 cm^{-1} . The corresponding cationomers were obtained by quaternization of the above polyurethanes with 0.52 mmol benzyl chloride in dry DMF at 60°C for 5–6 h. The resulting polymers (PUC-T-1, PUC-T-2) were precipitated with water, then washed with methanol and dried under reduced pressure for 48 h at 50–55°C.

PU-T1

$^1\text{H-NMR}$ (DMSO, δ ppm) data are as follows: 6.9 (m, 3H, aromatic); 4.1 (t, 2H, $\text{CH}_2\text{-CH}_2\text{-OCONH}$); 3.3 (t, 4H, $\text{O-CH}_2\text{-(CH}_2)_2\text{-CH}_2\text{-O}$); 2.1 (s, 3H, Ph-CH_3); 1.55 (m, 4H, $\text{CH}_2\text{-CH}_2$); IR (cm^{-1}): 3,320 (NH);

2,900 (CH_2); 1,740 (free CO); 1,710 (bonded CO); 1,620 (Ar); 1,380 (-N=N-N); UV (CH_3OH), λ_{max} : 284 nm, 315 nm; η_{red} : 0.32 dL g^{-1} ; M_w (GPC) = 47,662.

PU-T2

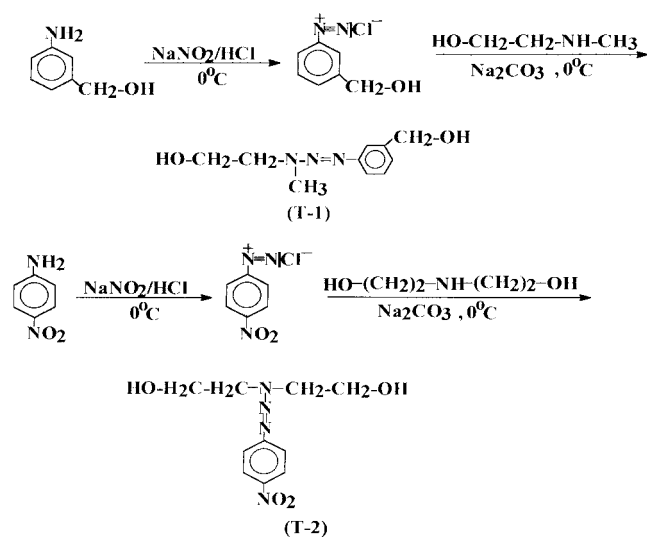
$^1\text{H-NMR}$ (DMSO, δ ppm) data are as follows: 6.95–8.1 (m, H, aromatic); 4.0 (t, 2H, $\text{CH}_2\text{-CH}_2\text{-OCONH}$); 3.3 (t, 4H, $\text{O-CH}_2\text{-(CH}_2)_2\text{-CH}_2\text{-O}$); 2.15 (s, 3H, Ph-CH_3); 1.55 (m, 4H, $\text{CH}_2\text{-CH}_2$); IR (cm^{-1}): 3,320 (NH); 2,900 (CH_2); 1,745 (free CO); 1,620 (Ar); 1,370 (-N=N-N); 1,350 (NO_2); UV (CH_3OH), λ_{max} : 375 nm; η_{red} : 0.16 dL g^{-1} ; M_w (GPC): 22,028.

Characterization

The structure of monomers and polymers was verified by $^1\text{H-NMR}$, IR, and UV spectroscopy by using JEOL 60 MHz, Specord M80, and Specord M42 spectrophotometers. GPC measurements were determined by a model PL 110 instrument equipped with two PL gel 5 μm mixed C-columns. The sample for measurement was 1.0 g dL^{-1} solution in DMF and the flow rate of the carrier solvent was 1 mL min^{-1} . The average molecular weight was calculated on the basis of the molecular weight versus retention volume curve of monodisperse polystyrene standard. The reduced viscosity of nonionic polymers PT-1 and PT-2 was measured in DMF ($c = 0.3$ g dL^{-1} ; $t = 25 \pm 0.2^\circ\text{C}$) using an Ubbelohde viscometer. Thermal transitions were measured on a Perkin-Elmer differential scanning calorimeter. Triazene polymers (15 ± 2 mg) were cooled to -130°C and heated at a rate of $20^\circ\text{C min}^{-1}$ up to 150°C . Thermal analysis of the polyurethanes was carried out on an MOM (Budapest) derivatograph. Thermogravimetry (TG) and TGA curves were recorded between 20 and 600°C with a heating rate of $12^\circ\text{C min}^{-1}$ under air atmosphere. UV irradiation with a 500 W high-pressure mercury lamp without wavelength selection at room temperature in methanol solution and film state was performed. The initial absorbance of the samples in the absorption band maximum was kept between 0.55 and 1.0.

RESULTS AND DISCUSSION

The synthesis of triazene diols T-1 and T-2 was performed via electrophilic coupling between an aryldiazonium salt and a secondary amine, similar to those described in the literature.¹² Reaction of diazotized 3-hydroxymethylaniline with *N*-methylaminoethanol led to 1-(*m*-hydroxymethyl)phenyl-3-(2-hydroxyethyl)-3-methyltriaz(1)ene (T-1). Another monomer, 1-*p*-nitrophenyl-3,3-di(2-hydroxyethyl)triaz(1)ene (T-2) was obtained in the same conditions starting from *p*-nitroaniline and a difunctional secondary amine as diethanolamine according to Scheme 1.



Scheme 1 Synthesis of triazene monomers.

Both compounds were characterized by $^1\text{H-NMR}$, IR, UV spectroscopy, and elemental analysis, these ones confirming the expected triazene structure. The IR spectra of monomers show typical bands corresponding to the triazene group ($-\text{N}=\text{N}-\text{N}<$) at $1,370$ (T-1) and $1,400\text{ cm}^{-1}$ (T-2), respectively. In their UV absorbance spectrum, T-1 showed two strong absorption bands centered at 285 and 312 nm, while T-2 displayed one absorption band at 365 nm, assigned to $\pi-\pi^*$ transition of the triazene units.

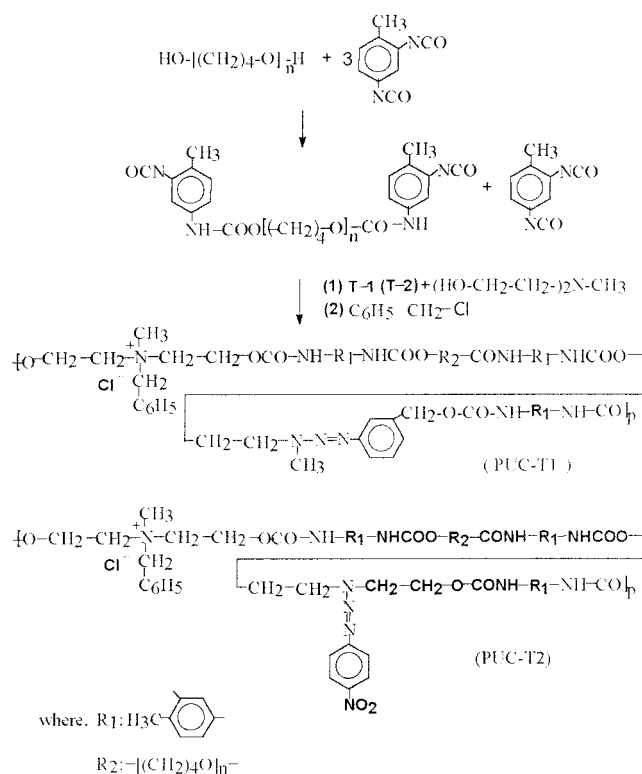
The synthesis of polyurethane cationomers involved the obtaining of precursors with triazene groups (PU-T-1, PU-T-2) using the addition reaction between PTMO and 2,4-TDI, followed by chain extending with triazene diol (T-1 or T-2) and NMDA as cochain extender, when the molar ratio between partners was $1:3:1 + 1$. Preparing the corresponding segmented cationomers assumes a quaternization of tertiary nitrogen atoms from the above precursors with benzyl chloride up to a quaternization degree of 88% (PUC-T-1) and 91% (PUC-T-2), respectively. The synthetic approach to the desired polymers is shown in Scheme 2. The polycations thus formed contain soft segments of polyether type and hard segments including the urethane and ammonium quaternary groups besides a small quantity of triazene moieties (6.95 wt %: PUC-T-1; 8.77 wt %: PUC-T-2), inserted by means of diols discussed above. Such polymers differ by the triazene structure and position of the chromophore located in the main backbone (PUC-T-1) or as pendant group (PUC-T-2). An essential feature of the polycations is that their solution in organic solvents (DMF, DMAc, DMSO, CH_3OH) could be solution-cast, giving colored ionomeric films with good optical clarity and adhesion on a variety of substrates.

Triazene polymers were characterized by $^1\text{H-NMR}$, IR, and UV spectroscopy, GPC and TGA techniques, elemental analysis data, and viscometric measure-

ments. The results of elemental analysis were in good agreement with the calculated ones (Table I). The ionic chlorine content of the polymers shows that the polycations have a small concentration of ammonium quaternary groups (PUC-T-1: 29.56 mequiv./100 g polymer; PUC-T-2: 30.11 mequiv./100 g polymer), specifically to the ionomeric field.²³ This provides an interesting system to study the formation of aqueous dispersions with film-forming ability, which makes them suitable as special adhesive and coating materials.²⁴ Experiments addressing this aspect are in process.

The IR spectrum of PUC-T-1 (Fig. 1) exhibited characteristic bands to the common polyetherurethanes, e.g., the NH and CH_2 asymmetrical stretching vibration in the $3,300$ and $2,960\text{ cm}^{-1}$ region, the urethane carbonyl stretching band at $1,740\text{ cm}^{-1}$ (hydrogen unbounded component), and the CH-aromatic stretching at $1,620\text{ cm}^{-1}$. To the triazene chromophore corresponds an absorption band centered at $1,380\text{ cm}^{-1}$, while the quaternary structure ($^+\text{N}-\text{C}$) is characterized by the absorption band at around $1,050\text{ cm}^{-1}$. Additionally, in PUC-T-2 a small peak positioned at $1,350\text{ nm}$ assigned to the NO_2 substituent was noticed, too. The chemical composition of the triazene polyurethanes was also confirmed in $^1\text{H-NMR}$ spectra.

The study of thermal transition behavior by DSC has been important to understand the morphology and intermolecular bondings in these segmented polyetherurethanes. The variation of the glass-transition



Scheme 2 Synthesis of triazene polyurethane cationomers.

TABLE I
Characteristics of Polyetherurethanes with Triazene Chromophores

Polymer	Elemental analysis (%)			Triazene content ^a (wt %)	Ionic chlorine content (meq/100 g)	T_g (°C)
	C	H	N			
PU-T-1	Calculated	64.04	9.41	7.33		-34
	Found	63.98	9.38			
PUC-T-1	Calculated	64.14	9.24	6.95	29.56	-48
	Found	64.00	9.22			
PU-T-2	Calculated	63.05	9.23	8.77		-30
	Found	62.95	9.20			
PUC-T-2	Calculated	63.20	9.10	8.32	30.14	-45
	Found	63.14	9.00			

^a Calculated value.

temperature (T_g) of the flexible segment, as a function of segmental chemical structure, has been used as an indicator of the degree of microphase separation of those two constituent segments. Table I summarizes the soft-segment T_g of triazene polyurethanes. There were differences in the T_g values of polyurethane cationomers when compared to nonionic polymers. The decrease in soft-segment T_g of the ionomeric form (PUC-T-1, PUC-T-2) indicated an improvement of phase separation with incorporating cationic groups in polymers. On the other hand, all the polymers showed a soft segment-rich phase with a T_g greater than that for the polyether component,²⁵ suggesting a solubilization to a certain extent of the hard segments into the soft segments (phase mixing). Therefore, the increase in soft-segment T_g in triazene polyurethanes can be explained by the reduction in ability of the hard segments to form hydrogen bonds with itself, resulting in increased hard-segment solubility into soft-segment phase. Additionally, high-temperature melting endotherms, associated with crystalline and semicrystalline hard-segment domains, were not observed in the above polymers, since the asymmetric 2,4- and

2,6-isomer of the urethane group is enables to prevent hard-segment crystallization.

The thermal behavior of the polyurethanes with triazene groups was also studied in air by thermogravimetric analysis. The thermal stability data are listed in Table II. An examination of the results reveals that the nonionic polyurethanes (PU-T-1 and PU-T-2) were decomposed in four stages, while in the case of polycations (PUC-T-1, PUC-T-2), the decomposition took place in three well-defined steps. The polymers sustained a 10% weight loss around 150–260°C and on the further decomposition of these polymers, a higher residue content was obtained for PU-T-1 and PUC-T-1 (12–13%) as compared to PU-T-2 and PUC-T-2 (7–8%).

To investigate the photolability of the triazene structure, the progress of the photodecomposition reaction of the monomers and polymers by an exhaustive irradiation with a high-pressure mercury lamp was monitored via UV/vis spectroscopy. As mentioned above, depending on the substituent nature attached to the aromatic ring, triazene monomers T-1 and T-2 showed different absorption peaks in UV/vis spectra. Following the UVvis absorption of the triazene chromophore as a function of irradiation time, it is observed that the photolysis does not proceed in each monomer. Figure 2 displayed the changes of the UV absorption spectrum for T-1 monomer in methanol solution, exposed to direct UV light. After distinct irradiation intervals, a gradual decrease of the absorptions corresponding to the triazene group from 285 and 312 nm is a clear indicator for the irreversible photodecomposition of this chromophore. The determined over half-life for its decomposition was about 16 min.

Under the same irradiation conditions, the *para*-nitrofeniltriazeno monomer (T-2) exhibited almost no changes in the UV spectra, revealing that the photodecomposition of the chromophore is not feasible even after long periods (over 1 h). Such behavior could be explained by the effect of the nitro aromatic substituent on the triazene group. Previous studies on the photolability of some triazene model compounds¹¹

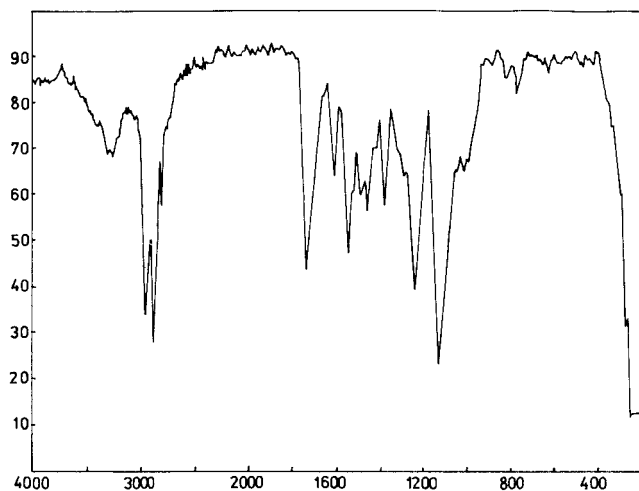


Figure 1 IR spectrum of triazene polyurethane cationomer (PUC-T-1) in film.

TABLE II
Thermal-Behavior of Triazene Polyetherurethanes

Sample	Stage 1			Stage 2			Stage 3		
	T_i-T_f	T_{max}	Weight loss (%)	T_i-T_f	T_{max}	Weight loss (%)	T_i-T_f	T_{max}	Weight loss (%)
PU-T-1	150-250	230	10	250-370	360	30	370-450	410	43
PUC-T-1	155-255	230	10	255-380	350	58	390-590	360	20
PU-T-2	130-250		7	230-300	265	10	300-365	360	20
PUC-T-2	150-260	240	10	260-395	360	66	390-450	420	20

T_i , initial decomposition temperature; T_f , final decomposition temperature; °C.

demonstrated that the presence of electro-donating groups (alkyl, ether, etc.) at the aromatic ring has a major effect on the photolytic decay, whereas the electron-withdrawing groups, such as nitro, cyano, and halides, increase the photochemical stability.

To assess the influence of polymer architecture on the photolabile character of the triazene groups from polyurethanes, we set about to follow the photosensitivity of the chromophores both in polymer solutions and films. For this purpose, we initially compared the photobehavior of the triazene polyurethanes with that of the corresponding ionic polymers through exposure to UV irradiation in methanol solution. Like starting monomers, in the electronic absorption spectra the $-N=N-N<$ groups from polymers have two absorption maximum around 284 nm (315 nm in PU-T-1) and at 282 nm (318 nm in PUC-T-1), respectively, whereas only the strong $\pi-\pi^*$ band of PUC-T-2 was observed with a bathochromic shift of about 10 nm. After irradiation of the polymer solutions, in the case of PU-T-1 and PUC-T-1 (Fig. 3), a pronounced decreasing of the absorption bands mentioned above could be seen, whereas by irradiation of PUC-T-2, no changes of its spectral characteristic could be detected.

Therefore, the distinctive change of triazene structure in monomers and thus the accompanying changes of polymer photodecomposition must be the reason for this behavior. It also appeared that the intensity of the band assigned to the triazene chromophores in methanolic solution of PUC-T-1 decreased less than in the case of PU-T-1 [Fig. 3, (b)]. Thus, after 30-min photolysis time, absorption is reduced to about 28% in PUC-T-1, compared to PU-T-1, which showed a photolysis degree of 52%. As result, we tentatively conclude that the ionic polyurethane is slowly cleaved upon irradiation with UV light due to the lower photosensitivity of the triazene groups inserted into complex polymer structure governed by structural and electrostatic factors. Obviously, the ionic backbone exerts influence on the decomposition properties of the feniltriazenes moieties in polymer solutions.

From a possible application standpoint, a photolysis process in the elastomeric films would be most desirable. For this reason, thin films based on both polymers were tested to UV irradiation. Figures 4 and 5 reveal the behavior of PU-T-1 and PUC-T-1 films when in the UV-exposed area a photochemically induced decomposition can be tailored. As expected, the

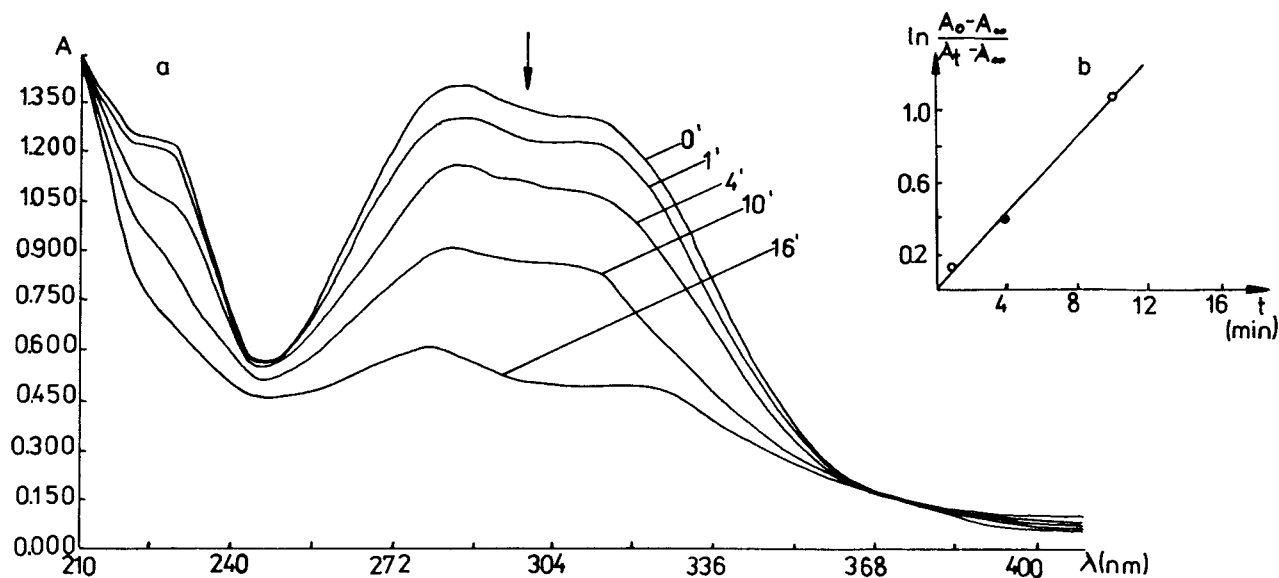


Figure 2 Changes in UVvis absorption spectra of triazene chromophore for T-1 monomer in methanol solution upon UV light exposure (a) and kinetic evaluation of its photolysis (b) at 298°C.

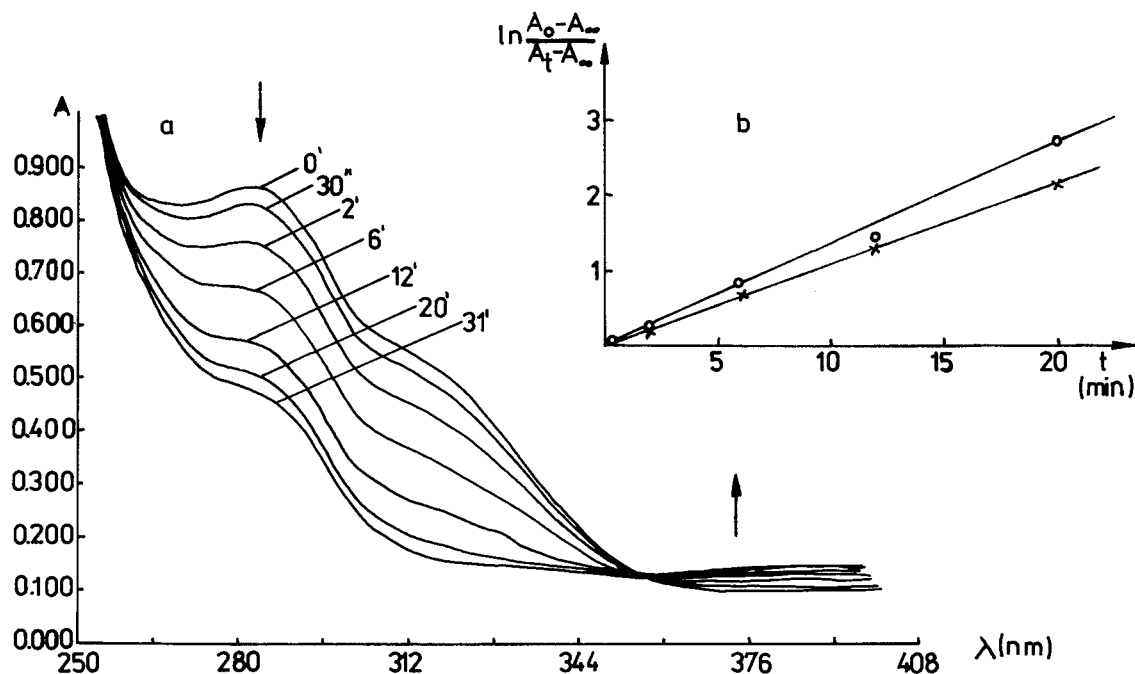


Figure 3 UV absorption spectra monitoring the phototransformation of triazene chromophore during UV irradiation of nonionic polyurethane (PU-T-1) in methanolic solution (a) and kinetic evaluation of the photolysis (b) in PU-T-1 (o) and PUC-T-1 (×).

polymeric films showed the same following trend as solutions, but were less photosensitive to irradiation. Thus, the photolytic fragmentation of PUC-T-1 occurs up to about 22% photolysis degree after defined time intervals (25 min) and is lower than for film based on PU-T-1 (37% phototransformation).

The photolysis process of the triazene chromophore, as measured at the absorbance maximum, can be described by the relation: $\ln A_0/A = kt$, where A is the

absorbance, k is the rate constant of photolysis, and t is time. The parameters calculated from the fits are listed in Table III. Comparing the values of the photolysis rate, it can be seen that the photochemical decomposition of the triazene polymers in solution occurs at a lower rate (PUC-T-1: $k = 2.5 \times 10^{-4} \text{ s}^{-1}$; PU-T-1: $k = 3.5 \times 10^{-4} \text{ s}^{-1}$) than for the corresponding monomer (T-1: $k = 7.74 \times 10^{-4} \text{ s}^{-1}$). These data may be explained in terms of steric effects inside the polymeric chains,

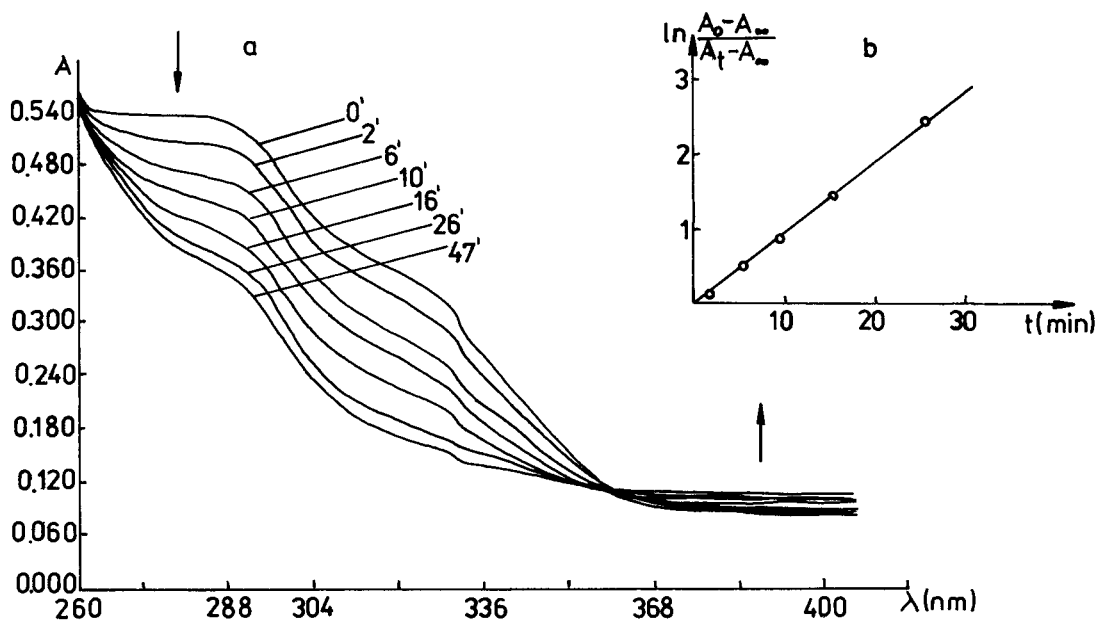


Figure 4 Changes in UVvis spectra of nonionic polyurethane (PU-T-1) in thin film (a) with irradiation times and kinetic evaluation of its photolysis (b) at 298°C.

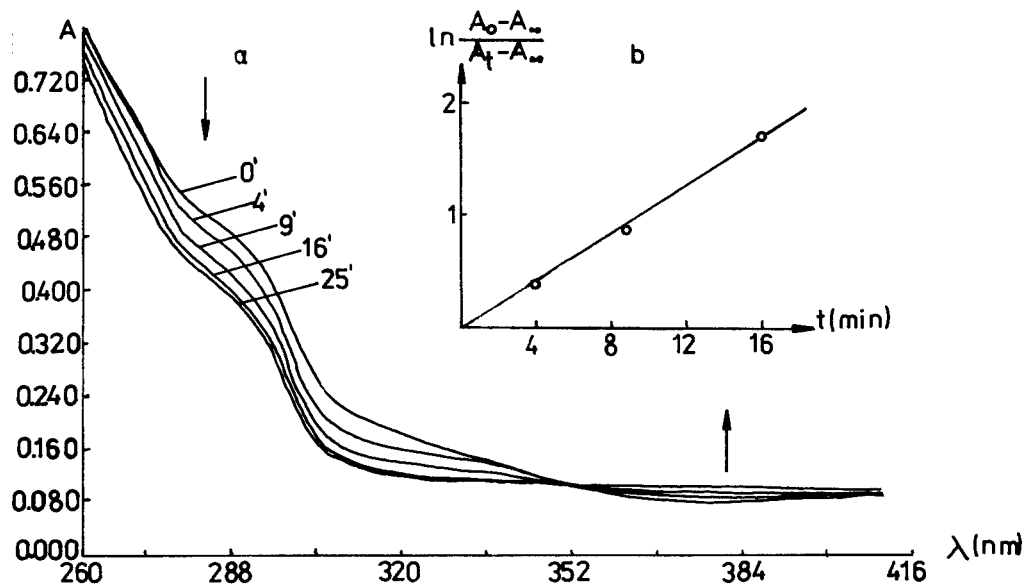


Figure 5 UVvis spectra of polyurethane cationomer film (PUC-T-1) during UV progressive irradiation (a) and kinetic evaluation of its photolysis (b) at 298°C.

which diminished the chromophore mobility to isomerize first. As expected, we have found that in the polymer films the rate constant (PUC-T-1: $k = 2.18 \times 10^{-4} \text{ s}^{-1}$; PU-T-1: $k = 3.14 \times 10^{-4} \text{ s}^{-1}$) continues to decrease slightly with a significant difference between the ionic and nonionic form. Such finding suggests that the triazene groups in polyurethane matrix become increasingly hindered owing to the elastomeric nature of these polymers, and consequently with lower mobility to orient them in a manner favorable for *cis*-formation. An important feature of the photoprocess discussed in the above polymers and T-1 monomer is that invariably, the photodecomposition of the feniltriazeno chromophore follows a first-order kinetics [Fig. 2-4 (b)].

Considering the previous results on triazene derivatives,¹⁴ a photolysis mechanism for feniltriazeno polymers could be proposed (Scheme 3). It can be assumed that in the first step of the photoprocess, the *trans-cis* (E-Z) isomerization of the $N=N$ double bond with the formation of more unstable thermodynamically *cis*-isomer occurred. Once formed, this can be

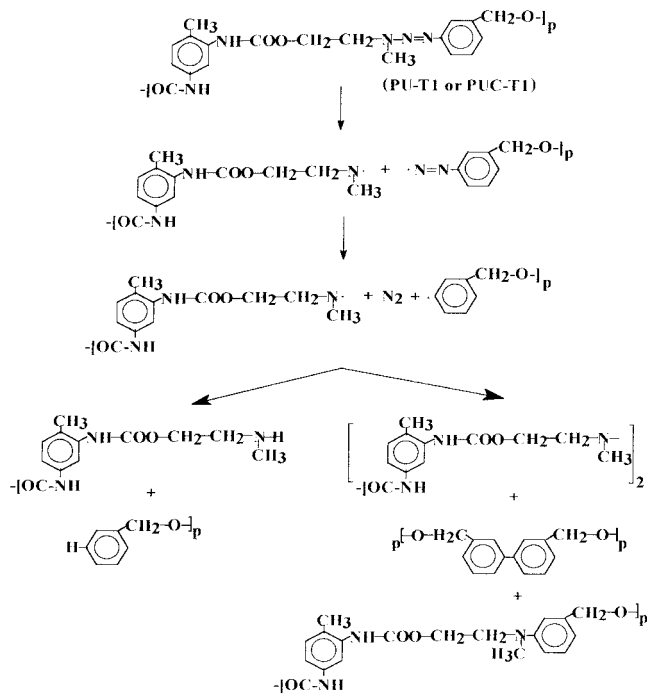
decomposed photochemically much easier than the polymers without this group, leading to aminyl and phenyldiazenyl macroradicals capable of generating phenyl radical and molecular nitrogen by a β -scission of the last. Thus, one would expect that the radical species formed would be stabilized by a pathway of hydrogen atom extraction or recombination with different consequences on the polymeric chains length. If the wavelength used in UV is sufficiently high to induce chain scission, the polymer viscosity and solubility must be altered. Indeed, when a nonionic polymer solution in DMF (20 ml PU-T-1; $c = 0.3 \text{ g dL}^{-1}$) was irradiated for 10 h, the reduced viscosity is lowered from 0.32 to 0.24 dL g^{-1} , indicating that the polyurethane chains were cleaved by UV light. In comparison to the polymer response evidenced by UV measurements, when a photolysis degree of 52% was attained after 30 min, the same process of polymer degradation has to last much longer. At first glance, such a result is most probably due to the enormous difference between those two concentrations of polymer taken in the study. A preliminary experiment has

TABLE III
Physical and Photolysis Data of Triazene Monomers and Polyurethanes

Sample	T1-diol	T2-diol	PU-T-1	PUC-T-1
λ_{max} (nm)	285; 312 (CH ₃ OH)	365 (CH ₃ OH)	284; 315 (CH ₃ OH) 288; 324 (film)	282, 318 (CH ₃ OH) 285; 312 (film)
ϵ (l mol ⁻¹ cm ⁻¹)	10,715.5	20,314		
k (s ⁻¹) ^a	7.74×10^{-4} (CH ₃ OH)		3.5×10^{-4} (CH ₃ OH) 3.14×10^{-4} (film)	2.5×10^{-4} (CH ₃ OH) 2.18×10^{-4} (film)
t (min) ^b	16		30 (CH ₃ OH) 25 (film)	30 (CH ₃ OH) 25 (film)

^a The rate constant of photolysis.

^b Photolysis time.



Scheme 3 Decomposition mechanism of triazeno polymer after UV irradiation.

been performed with DMF casting thin films on a quartz plates and then subjected to UV source ($\lambda = 365$ nm) through a mask pattern for 60 min and at a power of 60 mW cm^{-2} . A positive photoresist can be developed by treatment with CHCl_3 of the exposed region that dissolves rapidly in comparison to the unexposed zone insoluble.

For a latter application of these new polymers as possible candidates with adequate sensitivity to the UV radiation, control of the molecular weight GPC measurements during irradiation and other representative parameters should be determined. Moreover, variability of the polyurethanes topology can be used in preparing polymers with high glass transition and improved film-forming properties for development of new photolithographic materials. Additional work is needed to study the influence of triazene functionality on the ablation behavior.

CONCLUSIONS

We are exploring the use of triazene diols in obtaining of polyetherurethane of elastomer type. Polyurethane cationomers with triazene groups in the backbone or as a side chain were also synthesized and characterized. The photobehavior of the monomers and polymers exposed to UV irradiation, generated by a conventional radiation from a high-pressure mercury lamp, evidenced important differences between two

triazene structures. It has been found that the polymers with feniltriazene in their main chains can be converted into positive photoresists sensitive to UV irradiation, owing to the susceptibility of the triazene structure to induce chain scission and its degradation. By contrast, polyurethanes based on nitrofeniltriazene group located as lateral chain showed a high photostability.

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