

# New Polyurethane Cationomers with Naphthyl and Phenyltriazene Pendants: Synthesis and Properties

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**ABSTRACT:** Two new diols bearing triazene moiety, 1-( $\alpha$ -naphthyl)-3,3-di(2-hydroxyethyl) triazene-1 (NT-D) and 1-phenyl-3,3-di(2-hydroxyethyl) triazene-1 (PT-D), were synthesized from aromatic amines and diethanolamine. These monomers were used as chain coextenders in the two-step addition reaction between poly(tetramethylene oxide) diol, 2,4-tolylene diisocyanate, and *N*-methyldiethanolamine to obtain photosensitive polyurethanes of elastomer type. Triazene polyurethane cationomers with chlorine counterions were prepared via a quaternization reaction of the above polymers with benzyl chloride. All polyurethanes had a quantity of triazene units between 7.02 and 8.93 wt % polymer, and the content of ammonium quaternary groups in the cationic ones was of 30.56 meq/100 g naphthyl triazene polyurethane cationomer (PUC-NT) and 30.19 meq/100 g phenyl triazene polyurethane cationomer (PUC-PT), respectively. Photobehavior of the triazene units in all poly-

mers under continuous Hg-lamp irradiation was similar to that found for monomers, when both chromophores were transformed during UV irradiation. It is concluded that the PT-D acts as a more efficient sensitizer in the UV light-induced reaction but the photolysis in elastomeric films was lower than that observed in solution. The presence of quaternary ammonium structure on the same polymer backbone decreases the constant rates of photolysis. Because the triazene polyurethanes become crosslinked during UV irradiation could be assessed as potential negative-resist polymers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2599–2605, 2004

**Key words:** triazene diols; photoreactive polyetherurethanes; triazene cationomers; Hg-lamp irradiation; synthesis; kinetics; thin films

## INTRODUCTION

Polymers with photosensitive structures in the main backbone or as pendant groups have become an attractive research area for materials processing with unique properties tailor-made for an ever-increasing number of applications.<sup>1,2</sup> Among these, the triazene-sensitized polymers were the subject of extensive investigations because the triazene bond through its high photosensitivity and spontaneous fragmentation into gaseous products is considered one promising candidate for excimer laser ablation lithography.<sup>3–5</sup> Therefore, various classes of polymers containing photolabile triazene groups (Ph—N=N—N—) in the main or side chain, such as polyesters, polyethers, poly(methyl methacrylates), polysulfones, or polytriazenes, with high thermal stability and favorable photolytic sensitivity, have been described in the literature.<sup>6–11</sup> Starting from the efforts made with the above-mentioned polymers in excimer laser ablation and the increasing demand for high-performance new polymers, another route to tailored photopolymers should

be developed. One such versatile way of recent interest to us was to synthesize new monomers that impart the desired properties to the polymeric chains. This provided an opportunity to evaluate triazene polyurethanes on the basis of triazene diols, unreported yet to data, for an understanding of structure/property/photoreactivity relationships of great importance in extending possible applications for such versatile polymers.

As a part of our work in the synthesis of new ionomeric polyurethanes with different chromophores (stilbene, azoaromatic, quinone) located in both constituent segments of the polymer backbone,<sup>12–16</sup> a compilation of polyurethane cationomers with triazene moieties in the hard fragment was previously reported.<sup>17</sup> Specifically, polyurethane with phenyltriazene in the main chain as a predictable breaking point that released nitrogen afforded the advantage of high photolytic sensitivity for UV irradiation at around 365 nm. By contrast, the polyurethane with *para*-nitrophenyltriazene as pendant unit showed a better photochemical stability as related to the structural and electronic properties. Because the effect of substitution of the aromatic system adjacent to the triazene group seems to control the decomposition characteristics of the chromophore, we chose to quantify the dependence of photolytic decay on the polymer structure in polyurethanes with naphthyltriazene and phenyltriazene.

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zene pendant groups. In this article, we present the synthesis, characterization, and properties of the triazene monomers and their corresponding poly(ether urethane) cationomers bearing chromophores inserted on the polymer backbone by means of 1-( $\alpha$ -naphthyl)-3,3-di(2-hydroxyethyl) triazene-1 (NT-D) and 1-phenyl-3,3-di(2-hydroxyethyl) triazene-1 (PT-D).

## EXPERIMENTAL

### Monomers synthesis (NT-D, PT-D)

#### NT-D

A stirred solution of  $\alpha$ -naphthylamine (10 g, 70 mmol) in HCl 10% (64 mL) was cooled to 0°C and diazotized with an aqueous solution of sodium nitrite (4.8 g, 70 mmol). The reaction mixture was added dropwise to a solution of 7.35 g diethanolamine (70 mmol) and 9.2 g sodium carbonate (87 mmol) in 250 mL water at 0°C over 1 h. Then, 10 g sodium chloride was added and the resulting mixture was extracted three times with Et<sub>2</sub>O. The organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated under reduced pressure. The crude oil was chromatographed through basic aluminum oxide in a glass column, using THF/(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O (1 : 3 v/v) as mobile phase. The triazene derivative was obtained as a brown viscous oil.

Yield: 13.8 g (76.2%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 7.1–7.65 (7H, m, aromatic); 3.8 (8H, s, HO-CH<sub>2</sub>-CH<sub>2</sub>). UV (CH<sub>3</sub>OH),  $\lambda_{\max}$  = 225, 330, and 343 nm;  $M_w$  = 259.31. Analytical calculation for C<sub>14</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>: C, 64.84; H, 6.62; N, 16.19. Found: C, 64.59; H, 6.61; N, 16.02.

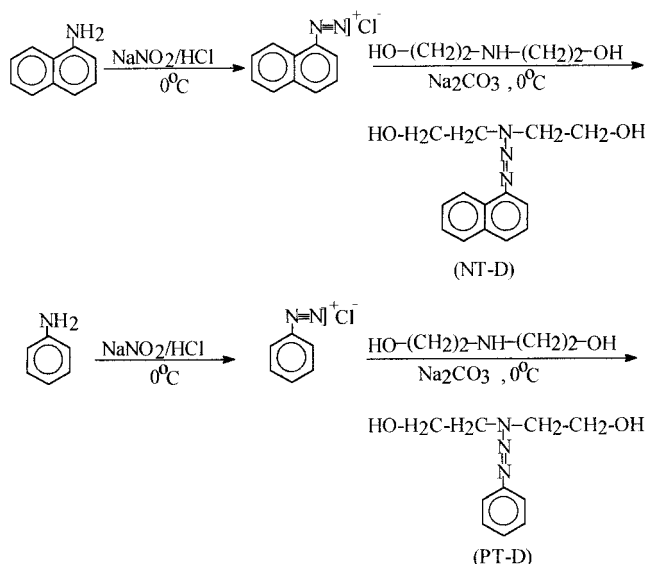
#### PT-D

Monomer was prepared as described above from 10 g aniline (0.1 mol), further diazotized, and then coupled with 11.3 g diethanolamine (0.1 mol). After solvent removal and aluminum column chromatography of the crude oil with THF/(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O (1 : 3 v/v) as eluant, a brownish viscous compound was obtained.

Yield: 12 g (53%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 6.95 (5H, m, aromatic), 3.65 (8H, s, HO-CH<sub>2</sub>-CH<sub>2</sub>); UV (CH<sub>3</sub>OH),  $\lambda_{\max}$  = 220, 283, and 309 nm;  $M_w$  = 209.25. Analytical calculation for C<sub>10</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>: C, 57.39; H, 7.24; N, 20.07. Found: C, 57.23; H, 7.15; N, 19.86.

### Polymer synthesis

Polyurethanes [naphthyl triazene (PU-NT), phenyl triazene (PU-PT)] were prepared by the prepolymer method, using poly(tetramethylene oxide) diol (PTMO,  $M_w$  = 2000), 2,4-tolylene diisocyanate (as 2,4-, 2,6-TDI, 80 : 20 v/v), *N*-methyl-diethanolamine (NMDA), and triazene diol (1 : 3 : 1 : 1M ratio). Dry PTMO (0.5 mmol) was reacted with 1.5 mmol TDI at 60–65°C for 3 h under purified nitrogen. Extending of



Scheme 1 Synthesis of triazene monomers.

prepolymer was performed by using NMDA (0.5 mmol) and triazene compound (0.5 mmol) in anhydrous DMF (c: 20 g dL<sup>-1</sup>) at the same temperature for 6 h. The change in the isocyanate (NCO) value during the reaction was monitored with IR spectral data after the disappearance of the absorption band from 2260 cm<sup>-1</sup>, which is characteristic of NCO group absorption. The quaternization of tertiary nitrogen atoms from NMDA with benzyl chloride (0.51 mmol) was carried out in dry DMF at 60°C for 8 h. The resulting polycations (PUC-NT, PUC-PT) were precipitated with water, washed with methanol, and dried for 48 h at 50–55°C under reduced pressure.

#### PU-NT

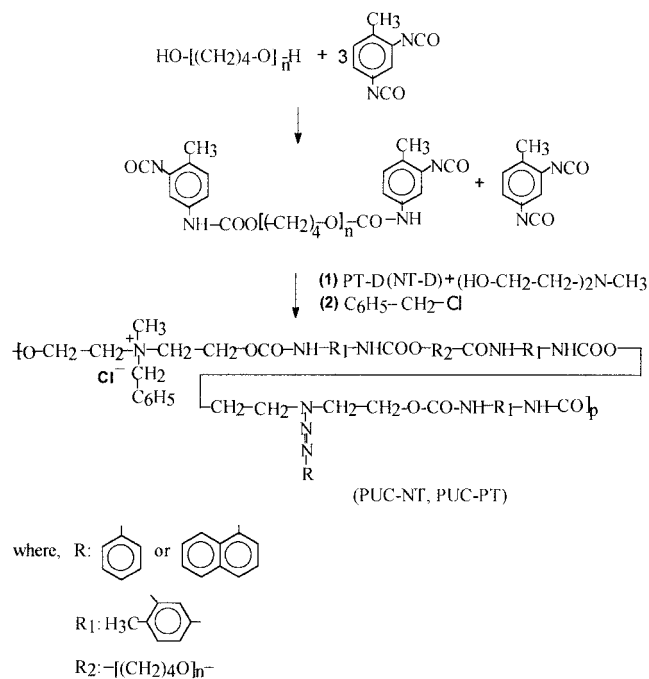
<sup>1</sup>H-NMR (DMSO,  $\delta$  ppm): 7.25–7.65 (H, m, naphthalene); 6.85 (H, m, TDI); 4.1 (H, m, —CH<sub>2</sub>—CH<sub>2</sub>—OCONH); 3.35 (H, t, —O—CH<sub>2</sub>—(CH<sub>2</sub>)<sub>2</sub>—CH<sub>2</sub>—O—); 2.2 (H, s, Ph-CH<sub>3</sub>); 1.5 [H, m, CH<sub>2</sub>—CH<sub>2</sub> from poly(ether diol)]. UV (CH<sub>3</sub>OH),  $\lambda_{\max}$ : 346 nm;  $\eta_{\text{red}}$ : 0.31 dLg<sup>-1</sup>;  $M_w$  (GPC): 30,465; polydispersity: 1.32.

#### PU-PT

<sup>1</sup>H-NMR (DMSO,  $\delta$  ppm): 7.2–7.6 (aromatic protons); 4.1 (H, m, —CH<sub>2</sub>—CH<sub>2</sub>—OCONH); 3.35 (H, s, —O—CH<sub>2</sub>—(CH<sub>2</sub>)<sub>2</sub>—CH<sub>2</sub>—O—); 2.2 (H, s, Ph-CH<sub>3</sub>); 1.5 [H, s, CH<sub>2</sub>—CH<sub>2</sub> from poly(ether diol)]. UV (CH<sub>3</sub>OH),  $\lambda_{\max}$ : 287 and 316 nm;  $\eta_{\text{red}}$ : 0.3 dLg<sup>-1</sup>;  $M_w$  (GPC): 29,738; polydispersity: 1.25.

### Characterization

The infrared spectra were recorded on a Specord M80 spectrophotometer. The proton NMR spectra were recorded on a JEOL 60 MHz spectrophotometer with TMS as an internal standard. The UV absorption spec-



**Scheme 2** Synthesis of triazene polyurethane cationomers.

tra were measured with a Specord M42 spectrophotometer in methanol or DMF solutions and thin films. Molecular weight distributions of the polymers were determined by a model PL 100 instrument equipped with two PL gel 5- $\mu\text{m}$  mixed-C columns. The sample for measurement was 1.0  $\text{g dL}^{-1}$  solution in DMF and the flow rate of the carrier solvent was 1  $\text{mL min}^{-1}$ . The reduced viscosity of the polyurethanes PU-NT and PU-PT were measured with a Ubbelohde viscometer thermostated at  $25 \pm 0.2^\circ\text{C}$  at 0.3  $\text{g dL}^{-1}$  concentration in DMF. Thermogravimetric analyses (TGA) were conducted in air on a MOM (Budapest) derivatograph by using a heating rate of  $12^\circ\text{C min}^{-1}$ . For UV spectroscopic investigations, the samples were ex-

posed to UV irradiation in methanol or DMF solution and film state by using a high-pressure mercury lamp without wavelength selection, at room temperature.

## RESULTS AND DISCUSSION

The triazene unit-containing monomer, NT-D, was prepared by a coupling reaction of diazotized  $\alpha$ -naphthylamine with diethanolamine in a basic medium, as shown in Scheme 1. In the case of PT-D, aniline was used as a parent component. The chemical structure of the synthesized triazene diols was confirmed by elemental analysis, IR/UV, and  $^1\text{H-NMR}$  spectroscopic techniques. The determined values of elemental analysis are very close to the theoretical ones. The IR spectra of monomers showed strong absorption at about  $3340\text{ cm}^{-1}$ , corresponding to OH group, at  $2950\text{ cm}^{-1}$  for aliphatic  $-\text{CH}$  linkages, at  $1590$ ,  $1460$ , and  $775\text{ cm}^{-1}$  due to the naphthalene and at  $1600$ ,  $1460\text{ cm}^{-1}$  for benzene ring. The characteristic IR absorption band to the triazene group appeared at  $1350\text{ cm}^{-1}$  in the case of both compounds. The structure of triazene diols was determined by  $^1\text{H-NMR}$  spectra. The vanish of triplets characteristic for  $\text{CH}_2$  protons from the vicinity of OH or N in diethanolamine (3.7 and 2.7 ppm, respectively) and the concomitant formation of new singlet at 3.8 (NT-D) or at 3.65 ppm (PT-D) together with the signals due to the aromatic protons (7.1–7.65 ppm for NT-D; 6.95 ppm for PT-D) confirmed that indeed the coupling reaction occurred. In the UV spectra, the  $\pi-\pi^*$  transition of the naphthyl-triazene chromophore is centered around 343 nm for the NT-D monomer, whereas the same transition of phenyltriazene in PT-D is revealed by two characteristic bands at 283 and 309 nm.

Segmented polyetherurethanes with triazene pendant groups (PU-NT, PU-PT) were obtained by two-step addition reaction from poly(tetramethylene oxide) diol of average molecular weight of 2000, 2,4-

**TABLE I**  
Characteristics of Polyurethanes with Triazene Chromophores

Polymer	Elemental analysis (%)				Triazene content (wt %)	Ionic chlorine content (mequiv/100 g polymer)
	C	H	N	Cl		
PU-NT						
Calc:	64.58	9.10	4.82		8.93	
Found:	64.53	9.02	4.78			
PU-PT						
Calc:	64.03	9.19	4.91		7.33	
Found:	64.01	9.14	4.86			
PUC-NT						
Calc:	64.66	8.89	4.62	1.17	8.55	30.56
Found:	64.63	8.85	4.58	1.06		
PUC-PT						
Calc:	64.13	9.04	4.70	1.19	7.02	30.19
Found:	64.11	9.02	4.68	1.08		

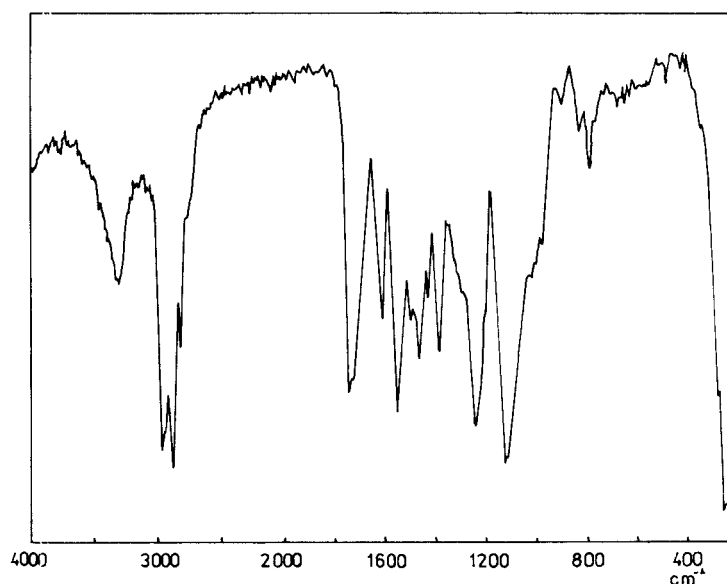


Figure 1 IR spectrum of triazene polyurethane cationomer (PUC-NT) in film.

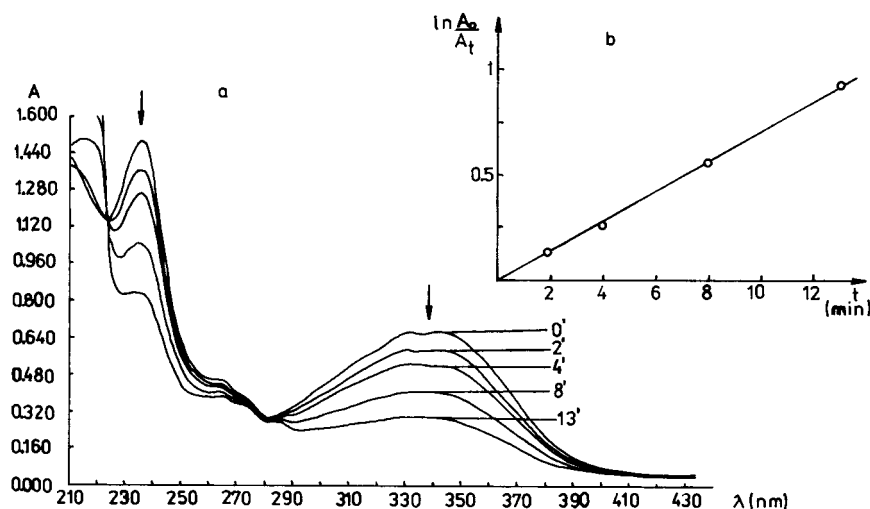
tolylene diisocyanate, and a diol mixture, as *N*-methyldiethanolamine/triazene diol (NT-D or PT-D), into molar ratio of the partners of 1/3/1/1. Convertibility of the nonionic polyurethanes in ionomeric structure (PUC-NT, PUC-PT) implied the quaternization reaction of aliphatic tertiary amino functionality from the aforementioned polymers with benzyl chloride, performing in this way a quaternization degree around 91% (Scheme 2). Under such conditions, polyurethane cationomers with long flexible segments of polyether-type and short, hard blocks including the urethane and quaternary ammonium moieties along the polymer chain besides fragments bearing naphthyl(phenyl)triazene pendants were synthesized. As seen in Table I, through the concentration of ionic groups these polymers belong to the ionomer class. The distinguishing feature of these polymers, in comparison with other polyurethane cationomers prepared by us, is sustained by the presence of a relatively small content of naphthyl(phenyl)triazene chromophore (PUC-NT: 8.55 wt %; PUC-PT: 7.02 wt %) anchored to the ionomeric backbone, whose properties are generally governed by the contribution of structural factors and

electrostatic interactions. Because of these specific groups, all polymers have an intensive brown-red color, indicative of triazene chromophore, and are soluble in common polar solvents such as DMF, DMSO, and CH<sub>3</sub>OH. The peculiar property of the triazene polymers is that their solutions could be solution cast, giving colored films with a microstructure typically to the urethane elastomers, a good adhesion on a variety of substrates and optical quality. Polyurethanes were characterized by elemental analysis, IR, <sup>1</sup>H-NMR and UV spectroscopy, thermogravimetric analysis, GPC, and viscosity measurements. The elemental analysis results agree well with the expected structure of the polymers.

The structure of triazene polymers was elucidated by IR and UV spectroscopy. IR spectra of PUC-NT (Fig. 1) displayed its bonded —NH stretching vibration located at 3300 cm<sup>-1</sup>, CH<sub>2</sub> asymmetrical stretching vibration at 2800–2960 cm<sup>-1</sup>, as well as the free and bonded urethane carbonyl absorption at 1740 and 1720 cm<sup>-1</sup>, respectively. The presence of the bonded carbonyl indicates the extent of hard-segment rich, hard domain formation, encountered in the common polyurethanes. Absorption bands due to C—O—C

TABLE II  
Thermal Behavior of Triazene Polymers

Sample	Stage I			Stage II			Stage III			
	$T_i - T_r$ (°C)	$T_{max}$ (°C)	Weight loss (%)	$T_i - T_r$ (°C)	$T_{max}$ (°C)	Weight loss (%)	$T_{10\%}$ (°C)	$T_i - T_r$ (°C)	$T_{max}$ (°C)	Weight loss (%)
PU-NT	205–290	250	7	290–465	420	71	310	465–580	530	11
PU-PT	200–270	235	8	280–440	390	71	250	440–540	490	10
PUC-NT	200–300	230	12	300–445	395	68	290	445–545	520	10
PUC-PT	190–275	240	11	275–450	410	73	270	450–560	520	11



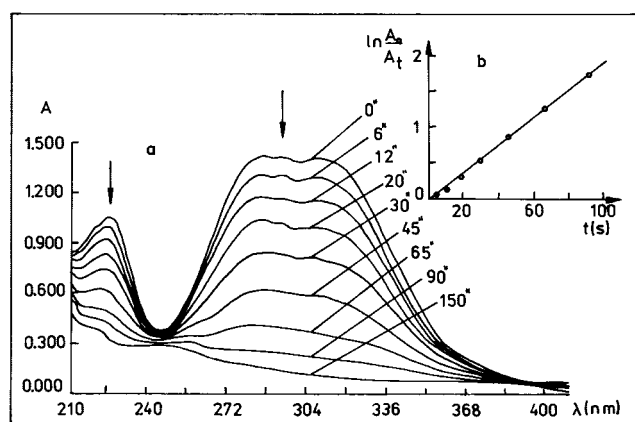
**Figure 2** Changes in UV-Vis absorption spectra of naphthyltriazene monomer in methanol solution upon UV light exposure (plot a) and kinetic evaluation of its photolysis (plot b) at 298 K.

stretching vibration at  $1240$ ,  $1130$   $\text{cm}^{-1}$  and CH aromatic stretching at  $1610$   $\text{cm}^{-1}$  were also observed. Characteristic of the triazene structure chemically connected to the polymer chain is the absorption at  $1375$   $\text{cm}^{-1}$ . The chemical shifts of the protons in the  $^1\text{H-NMR}$  spectra given in Experimental confirmed, once again, the polyether (triazene-urethane) structure.

The effect of chromophore structure on thermal stability in all polymers was followed by thermogravimetric analysis. The temperature of different weight losses and initial and final decomposition temperature were determined from the original TGA curves. The thermal decomposition temperature (TDT) was defined as the temperature of 10% weight loss. As can be seen in Table II, the polymer decomposition occurred in three well-defined steps for all polyether (triazene-urethanes) prepared. TDT values were somewhat higher for polyurethanes with naphthyltriazene groups ( $310^\circ\text{C}$ ) than in the case of the polymers bearing phenyltriazene ( $250^\circ\text{C}$ ). As assumed, the weight losses corresponding to the first stage of the thermal decomposition (7% for PU-NT, 8% for PU-PT) can be caused by a loss of the pendant groups, namely naphthalene and nitrogen or benzene and nitrogen. Compared to these polymers, the ionic forms showed higher losses due to the thermal decomposition of the quaternary ammonium structure.

Because most triazene polymers are expected to be used in microlithography, it is desired that the photodecomposition of the triazene moiety in the synthesized naphthyl(phenyl)triazene monomers be studied comparatively to that of polyurethanes. Photobehavior of both monomers was followed by visualizing the change of the  $\pi-\pi^*$  transition of the triazene unit during the illumination with a high-pressure mercury lamp. Figure 2(a) illustrates UV absorption spectral changes of the naphthyltriazene monomer in methanol solution, over

various irradiation times. It is worth noting that the absorption maximum around  $343$  nm decreased gradually and exhaustive irradiation of the solution causes the disappearance of this peak, suggesting an irreversible cleavage of the naphthyltriazene chromophore. As reported in the literature,<sup>5</sup> the molecular species formed upon irradiation of the triazene units are the aminyl and naphthyl radical pair and gas nitrogen. Further, the photoproduct radical fragments can undergo changes with their passing into more stable forms by a hydrogen abstraction or through other pathways. Thus, the photodecomposition of naphthyltriazene in methanol was completed within about 13 min, much longer than in the case of phenyltriazene diol when the same process took place in only 2.5 min [Fig. 3(a)]. Moreover, the existence of isosbestic points at  $392$  nm in NT-D and at  $285$  and  $410$  nm for PT-D indicates clearly that the photoreaction



**Figure 3** Changes in UV-Vis absorption spectra of phenyltriazene monomer in methanol solution upon UV light exposure (plot a) and kinetic evaluation of its photolysis (plot b) at 298 K.

TABLE III  
Physical and Photolysis Data of the Triazene Monomers and Polymers

Sample	NT-D	PT-D	PU-NT		PU-PT		PUC-NT	PUC-PT
			solution	film	solution	film	film	film
$\lambda_{\max}$ (nm)	330, 343	283, 309	346	348	284, 316	287, 318	343	284, 315
$\epsilon$ ( $1 \text{ mol}^{-1} \text{ cm}^{-1}$ )	11785	14105						
$k \cdot 10^{-3}$ ( $\text{s}^{-1}$ )	1.06	16.9	0.41	0.29	12.2/6.2	5.4	0.23	4.3

proceeds uniformly. Its kinetic evaluation (Table III) may be expressed by the first-order rate equation:  $\ln(A_0/A_t) = kt$ , where  $A_0$  and  $A_t$  are values of the absorbance at time  $t_0$  and  $t$ , respectively, and  $k$  is rate constant. Comparing the rate value calculated for naphthyl monomer ( $k_{\text{NT-D}} = 1.06 \times 10^{-3} \text{ s}^{-1}$ ) with the one corresponding to the phenyltriazene moiety ( $k_{\text{PT-D}} = 1.69 \times 10^{-2} \text{ s}^{-1}$ ), it can be seen that there is a significant difference in the rate constant of photolysis [Figs. 2 and 3(b)] for the triazene monomers selected. Such values can be interpreted as arising from the structure difference, which differently influenced the course of reaction. Therefore, an extended conjugation of the triazene group with naphthyl ring induced a good stabilization effect and consequently, a better photostability in the former monomer under illumination with unfiltered light of the Hg lamp.

To probe the photoreactivity of triazene polyurethanes, UV-Vis spectroscopic assessment of structural changes caused by irradiation in solutions was first performed. Our results suggest that the polyurethane with naphthyltriazene was decomposed in DMF within 16 min, whereas that with phenyltriazene polymer was decomposed in about 5.5 min. Although the triazene polymers are expected to behave quite similarly to those of low molecular weight compounds with the same sequence, their photolysis was much slower and after irradiation, only PU-NT exhibited

one isosbestic point at 322 nm. Comparing the kinetic plots [Figs. 4(b) and 5(b)], it was obvious that this reaction in DMF solution took place faster for PU-PT ( $k = 6.2 \times 10^{-3} \text{ s}^{-1}$ , 72% photolysis degree/6 min) than for PU-NT ( $k = 0.41 \times 10^{-3} \text{ s}^{-1}$ , 20% photolysis degree/6 min). Monitoring PU-PT in methanol solution [Fig. 4(b)], its decomposition ( $k = 12.2 \times 10^{-3} \text{ s}^{-1}$ , 90% photolysis degree/5.5 min) was twice as fast as that in DMF, owing to the methanol quality of good chain-transfer agent.

Of practical interest are the spectral changes induced by UV light to the thin polymer films. In this case, the rates of photolysis were lower compared with the polymeric solutions because of the more restricted mobility of the chromophore moieties inserted in a complex polymer matrix [Figs. 4 and 5(a)]. An examination of the rate constant [Figs. 4 and 5(b)] in film based on phenyltriazene polymer ( $k = 5.4 \times 10^{-3} \text{ s}^{-1}$ , 26% photolysis degree/7 min) revealed that this one is about 18 times higher than that for polyurethane film with naphthyltriazene ( $k = 0.29 \times 10^{-3} \text{ s}^{-1}$ , 11% phototransformation/7 min). The spectral changes observed in both films support the view that the triazene units are also transformed during irradiation and the formation of isosbestic points at 300 and 392 nm only in PU-NT indicates homogeneity of the photoprocess. It is appropriate to compare the UV spectra of these polymers with those of polyurethane

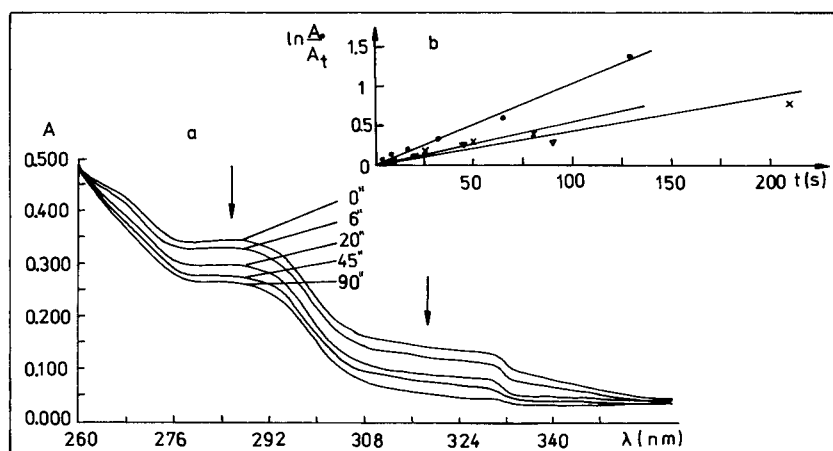
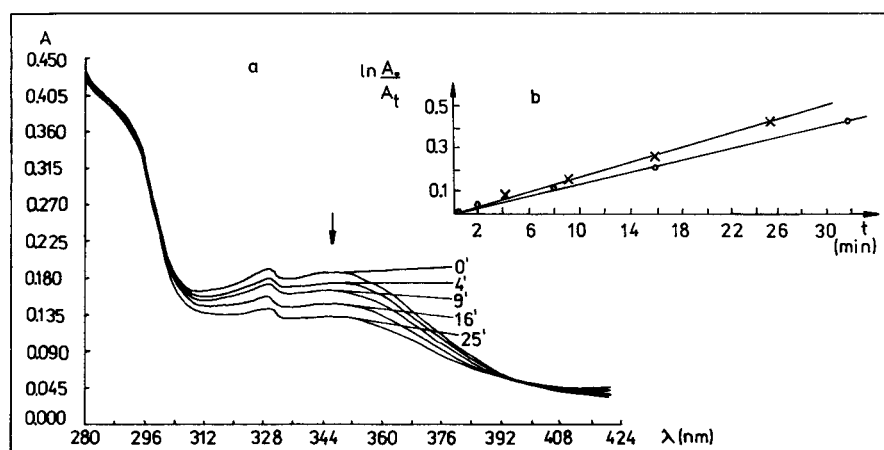


Figure 4 Changes in UV-Vis spectra of phenyltriazene polymer (PU-PT) in film state (plot a) with irradiation times and kinetic evaluation of its photolysis (plot b) in methanol (O) and DMF (x) solution, and in film (∇).



**Figure 5** UV absorption spectra monitoring the phototransformation of triazene chromophore during UV irradiation of nonionic naphthyl polyurethane (PU-NT) in film (plot a) and kinetic evaluation of the photolysis (plot b) in DMF solution (○) and in film state (×).

cationomers. Under continuous Hg-lamp exposure, the photodecomposition of the polycations in films occurred more slowly (PUC-NT:  $k = 0.23 \times 10^{-3} \text{ s}^{-1}$ ; PUC-PT:  $4.3 \times 10^{-3} \text{ s}^{-1}$ ) than in the parent nonionic polymers, maintaining the same structure effect discussed above. This variation is consistent with the idea that the electrostatic interactions between the polymer chains are principally responsible for the difference observed in polymer photolysis caused by UV light in the triazene polyurethanes of ionic type. From the above examples, it can be seen that for all polymers this photoprocess follows a first-order kinetic.

To demonstrate that the fragmentation of triazene pendants via photolysis with unfiltered UV light is accompanied by a crosslinking effect, some preliminary experiments on polyurethane films irradiated and subsequently developed in methanol were performed. A decrease of solubility with increasing irradiation time (1 h) indicates the irreversible decomposition of chromophore and photocrosslinking all polymer films. Further investigations on the photolability of these polymers are in progress in our laboratory.

## CONCLUSION

Novel poly(ether urethane) cationomers with pendant triazene groups were synthesized by using NT-D or PT-D as chain coextenders in two-step addition reaction between poly(tetramethylene oxide) diol of 2000 average molecular weight, 2,4-tolylene diisocyanate, and *N*-methyl-diethanolamine, further quaternized with benzyl chloride. The photoreactivity of all studied polyurethanes under Hg-lamp irradiation was found to be more reduced in thin polymer films than in solution and is dependent on the structure of the starting monomer. Phenyltriazene leads to polymers with a higher photosensitivity to UV irradiation, in comparison with those of naphthyltriazene, and the

presence of quaternary ammonium structure on the same backbone induces a slight decrease in the constant rate of photolysis. Therefore, when using triazene chromophores with photolabile groups, a smaller amount of comonomer was necessary to obtain polyurethanes with desired properties. It appears promising to investigate further the photobehavior of elastomeric polymers bearing such groups under laser irradiation.

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