

# Synthesis and Properties of New Polyurethanes with Triazene Moieties in the Main Chain

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Received 18 May 2004; accepted 10 October 2004

DOI 10.1002/app.21441

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A new diol with bistriazene groups, 1,1' [4,4'-diphenylether]-3,3'-di( $\beta$ -hydroxyethyl methyl)-bistriazene (BTD), was synthesized and characterized. BTD, along with *N*-methyldiethanolamine as a chain extender, was used to prepare a segmented polyurethane based on poly(tetramethylene oxide) diol (weight-average molecular weight = 2000) and 2,4-tolylene diisocyanate (80:20 v/v 2,4-/2,6-isomer mixture). Subsequent quaternization of the amine with benzyl chloride formed the cationomer. The structure-property relationships, including the photochemical behavior of the triazene linkage in these polymers, were investi-

gated with respect to another polyurethane prepared from 4,4'-diphenylmethane diisocyanate and a bistriazene compound. Photolysis experiments were carried out in polymer solutions and in the film state, and the reduction of the  $\pi$ - $\pi^*$  absorption band, characteristic of the triazene chromophore in ultraviolet spectra, was followed. A kinetic evaluation revealed a first-order photoprocess. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 385–391, 2005

**Key words:** adsorption; polyurethanes; synthesis; UV-vis spectroscopy

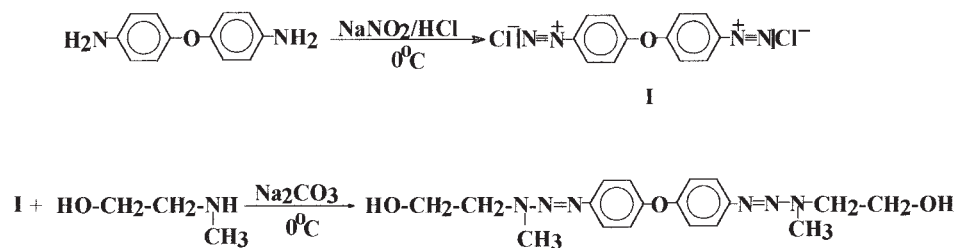
## INTRODUCTION

The design of specialized photosensitive polymers for the development of recording materials,<sup>1,2</sup> liquid crystals,<sup>3,4</sup> nonlinear optics,<sup>5,6</sup> and photoresists applied to microlithography<sup>7–9</sup> has become one of the great challenges of the last years. A valid alternative to doping with low-molecular-weight chromophores<sup>10,11</sup> is the incorporation of photochemically active units into the polymeric backbone to obtain photoreactive materials able to interact with light and provide a variety of interesting physical and optical properties. Among them, polymers with triazene moieties (Ph—N=N—NR<sub>2</sub>) have been successfully used and tested in the structuring of photopolymers for laser ablation, a powerful technique in photolithography. In this context, the ablative photodecomposition of polymers with high sensitivity has become one of the most actively pursued subjects in photochemistry. Many reports on polymers with triazene linkages in the main chain or as a pendant (polyesters, polyethers, polytriazenes, and polysulfides) have been published.<sup>12–16</sup>

Polyurethanes, which generally show a wide range of properties<sup>17–19</sup> and implicit applications, are also accessible to structuring through the choice of the appropriate triazene monomers and an optimum composition of the polymers. With respect to the design of new photopolymers, our interest in studying the addition of various chromophore functionalities along the ionomer backbone<sup>20,21</sup> led to an investigation of polyurethanes with a triazene structure in the main or side chain. Additionally, there is a lack of reference data for ionomers with N=N—N bonds, which could extend the range of materials that could be structured. Recently, we reported the synthesis and properties of some triazene derivatives incorporated into polyurethanes<sup>22,23</sup> and cationomers; the idea of existing photosensitive breaking points into such polymer chains, with preferred positions of bond breaking, was demonstrated. From ultraviolet–visible (UV–vis) spectra of triazene polymers, a pronounced modification of their structure after irradiation was identified. As expected, the photochemistry of this chromophore is strongly influenced by the monomer structure and especially by the aromatic ring substituents binding to the —N=N=N— groups. In this article, we present a new type of polymer with bistriazene linkages in the main chain in addition to polyether sequences and a polyurethane cationomer derived from the former, as well as their photolytic behavior under ultraviolet (UV) irradiation. In parallel, another hard triazene polyurethane was studied for the purpose of creating highly photosensitive materials.

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Contract grant sponsor: National University Research Council; contract grant number: 32952/2004.



Scheme 1 Synthesis of BTD.

## EXPERIMENTAL

### Monomer synthesis: 1,1'[4,4'-diphenylether]-3,3'-di( $\beta$ -hydroxyethyl methyl)-bistriazene (BTD)

The bistriazene diol was synthesized in two steps, as shown in Scheme 1. A stirred solution of 4,4'-diaminodiphenyl ether (10 g, 0.05 mol) in 10 wt % HCl (91 mL) was cooled to 0°C and diazotized with an aqueous solution of sodium nitrite (6.9 g, 0.1 mol). The reaction mixture was added dropwise to a solution of *N*-methylaminoethanol (7.5 g, 0.1 mol) and sodium carbonate (16 g, 0.15 mol) in 250 mL of water at 0°C over 1 h. Then, 10 g of sodium chloride was added, and the resulting mixture was extracted three times with Et<sub>2</sub>O. The organic layers were dried onto Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. After the removal of the solvent, the monomer was recrystallized from methanol and water (1:5 v/v), and this led to a brown, crystalline compound (14.5 g, 78% yield).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 7.5–6.92 (8H, q, aromatic protons), 3.9 (8H, s, —N—CH<sub>2</sub>—CH<sub>2</sub>—OH), 3.3 (6H, s, N—CH<sub>3</sub>). UV  $\lambda_{\max}$  (CH<sub>3</sub>OH): 296, 324 nm.

### Polymer synthesis

The elastomeric polyurethane (PUE-T) was synthesized by the prepolymer method from 10 g (5 mmol) of poly(tetramethylene oxide) diol (PTMO; weight-average molecular weight = 2000) and 2.15 mL (15 mmol) of tolylene diisocyanate (TDI; 80:20 v/v 2,4-/2,6-isomer mixture). The reaction was carried out in dimethylformamide (DMF; concentration = 20 g dL<sup>-1</sup>) at 60°C under purified nitrogen for 3 h. The prepolymer with isocyanate end groups was reacted with 1.86 g (5 mmol) of bistriazene diol and 0.595 g (5 mmol) of *N*-methyl-diethanolamine (NMDA) at 60°C for 12 h. The evolution of this reaction was monitored by IR spectroscopy, which was used to follow the disappearance of the isocyanate stretching band at 2260 cm<sup>-1</sup>. The corresponding bistriazene poly(ether urethane) cationomer (PUE-CT) was prepared by the quaternization of this polymer (2 g) with benzyl chloride (7 mg, 0.05 mmol) in dry DMF at 60°C for 8 h. The hard bistriazene polyurethane (PU-T) was obtained by a polyaddition reaction between 4,4'-diphenylmeth-

ane diisocyanate (MDI; 5 g, 0.013 mol) and a bistriazene derivative (3.36 g, 0.013 mol). The synthesis was performed in dry DMF under purified nitrogen at 65°C for 15 h. The resulting polymers were precipitated in methanol, washed with methanol, and dried for 48 h at 60°C under reduced pressure.

### PUE-T

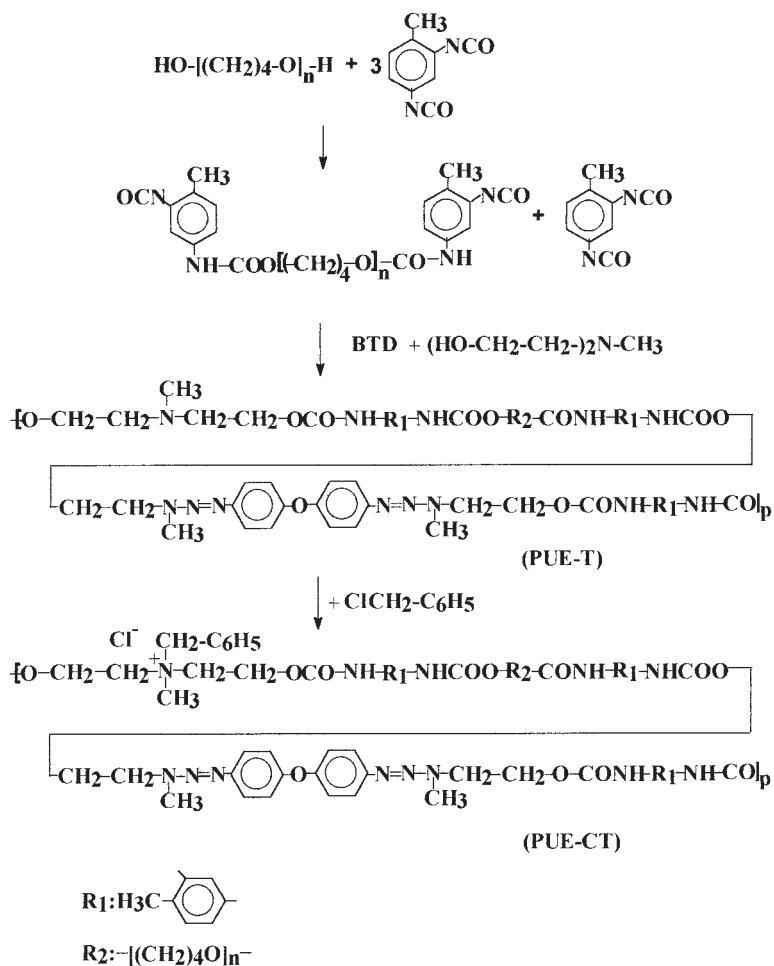
<sup>1</sup>H-NMR [deuterated dimethyl sulfoxide (DMSO-*d*<sub>6</sub>),  $\delta$ , ppm]: 6.75–7.6 (m, aromatic protons from TDI and BTD), 4.33 (m, methylene protons from ester-urethane triazene), 4.03 (m, methylene protons of the ester-urethane type from PTMO), 3.85 [m, NHCOO—CH<sub>2</sub>—CH<sub>2</sub>—N(CH<sub>3</sub>)—N=N], 3.67 (t, N=N—N—CH<sub>3</sub>), 3.44 [m, —O—CH<sub>2</sub>—(CH<sub>2</sub>)<sub>2</sub>—CH<sub>2</sub>—O—], 2.19, 2.09 (s, Ph—CH<sub>3</sub>), 1.49 (m, —O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—O—). UV (DMF)  $\lambda_{\max}$ : 290, 330 nm. Hard-segment content: 43.9 wt %.

### PU-T

<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 8.65, 7.96 (NH—COO), 7.34 (m, aromatic protons from MDI and BTD in the ortho position to urethane and triazene groups), 7.11–6.9 (m, aromatic protons from MDI and BTD in the meta position to urethane and triazene groups), 4.35 (m, NHCOO—CH<sub>2</sub>—CH<sub>2</sub>), 4 [m, NHCOO—CH<sub>2</sub>—CH<sub>2</sub>—N(CH<sub>3</sub>)—N=N], 3.8 (m, Ph—CH<sub>2</sub>—Ph), 3.66 (s, N=N—N—CH<sub>3</sub>). UV (DMF)  $\lambda_{\max}$ : 328 nm. Hard-segment content: 100 wt %.

### Characterization

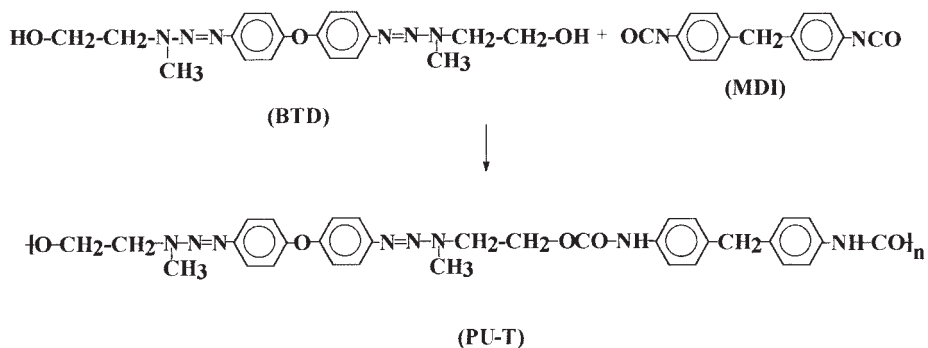
The structures of the monomer and polymers were verified with <sup>1</sup>H-NMR, IR, and UV spectroscopy with Bruker 400-MHz, Specord M80, and Specord M42 spectrophotometers, respectively. Gel permeation chromatography (GPC) measurements were taken with a PL MD-950 apparatus (Polymer Laboratories) equipped with an evaporative mass detector and two PLgel 5- $\mu$ m columns. The sample for measurement was a 1.0 g dL<sup>-1</sup> solution in DMF, and the flow rate of



Scheme 2 Synthesis of PUE-CT.

the carrier solvent was  $1 \text{ mL min}^{-1}$ . The average molecular weight was calculated on the basis of a molecular-weight/retention-volume curve of a monodisperse polystyrene standard. The thermal stability of the polyurethanes was analyzed by thermogravimetry (TG) with a derivatograph (MOM, Budapest, Hungary). TG and thermogravimetric analysis (TGA) curves were recorded between 20 and  $600^\circ\text{C}$  at a heat-

ing rate of  $12^\circ\text{C min}^{-1}$  in air. UV irradiation was performed in methanol and DMF and in the thin-film state with a 500-W high-pressure mercury lamp without wavelength selection at room temperature. The lamp intensity was  $0.6 \text{ mW/cm}^2$ , and the distance between the sample and the irradiation slot was 5 cm. The initial absorbance of the samples in the absorption band maximum was kept between 0.9 and 1.0.



Scheme 3 Synthesis of PU-T.

**TABLE I**  
**Elemental Analysis of the Monomer and Polymers with**  
**Triazene Chromophores**

Sample	Calcd (%)			Found (%)			Triazene content (wt %)
	C	H	N	C	H	N	
BTD	58.02	6.51	22.56	57.93	6.49	22.03	
PUE-T	63.75	9.13	6.04	63.68	9.09	6.01	12.34
PUE-CT	63.67	8.98	5.79	63.71	9.02	5.42	11.84
PU-T	63.63	5.51	17.99	63.52	5.53	17.87	59.80

## RESULTS AND DISCUSSION

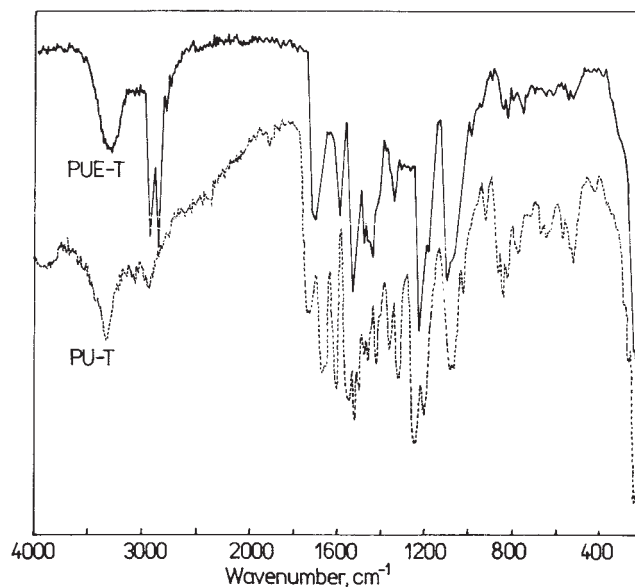
The bistriazene diol used in this investigation was prepared through an electrophilic N—N coupling between the bisdiazonium salt and *N*-methylaminoethanol, the desired compound being obtained in a good yield. The monomer was characterized with IR, <sup>1</sup>H-NMR, and UV spectroscopy, as well as elemental analysis, to confirm its structure and purity. The IR spectrum showed a characteristic band at 1350 cm<sup>-1</sup> assigned to the triazene moiety (—N—N=N—) and another band at 3360 cm<sup>-1</sup> due to terminal hydroxyl groups. The absorption bands corresponding to the aromatic structure appeared at 1590, 1500, and 840 cm<sup>-1</sup>, whereas the C—O—C linkages revealed strong absorptions at 1240, 1200, and 1075 cm<sup>-1</sup>. The photolytic behavior of the bistriazene monomer was investigated with UV-vis irradiation in a methanol solution: the changes in the absorption bands centered at 296 and 324 nm were observed.

PUE-T was synthesized by a well-known pathway in a two-step process, with a prepolymer method consisting of PTMO and 2,4-TDI, followed by chain extension with a bistriazene diol used in tandem with NMDA. For comparison with the nonionic polymer, a transformation into a cationomer form (PUE-CT) was performed via the quaternization of aliphatic tertiary nitrogen atoms with benzyl chloride. Because of the concentration of the ammonium quaternary structure, about 33 mequiv of ionic groups/100 g of polymer, this polymer belonged to the ionomer class. The synthetic approach to bistriazene polymers is shown in Scheme 2. Both chromophoric polyurethanes possessed an alternating structure of flexible polyether segments and hard segments, including bistriazene (12.34 wt %) and urethane groups (11.74 wt %). The main difference between the two polymers used in this study was that the latter contained ionic groups. To investigate the influence of the chromophore content on polymer photolability, we also prepared PU-T (59.81 wt % bistriazene), which was based on MDI and bistriazene diol. The structural formula of the polymer is given in Scheme 3. All polymers possessing a common bistriazene photolabile chromophore in the main chain were characterized with IR, UV, and <sup>1</sup>H-NMR

spectroscopy, GPC and TGA techniques, and elemental analysis. An examination of the elemental analysis data allowed a comparison of the theoretical values with the real compositions of the triazene polymers (Table I).

IR analyses of PUE-T (Fig. 1) confirmed the formation of the urethane groups (NHCOO) by the presence of the characteristic functionalities, CO and NH, at 1720 and 3360 cm<sup>-1</sup>, respectively. Other important absorption peaks were due to the alkyl stretching vibration (CH<sub>2</sub>) at about 2955 and 2880 cm<sup>-1</sup>. The peaks at 1240 and 1110 cm<sup>-1</sup> were assigned to the C—O—C bond from the polyether soft segment. In the PU-T IR spectrum (Fig. 1), the main absorption peaks were assigned to the vibration associated with the NH stretching at 3325 cm<sup>-1</sup>, the amide I (C=O stretch) and amide II (NH deformation) bands around 1675 and 1525 cm<sup>-1</sup>, respectively, and the CH aromatic stretching band at 1600 cm<sup>-1</sup>, whereas the triazene vibration band was observed at 1360 cm<sup>-1</sup>. The synthesized polyurethanes had good solubility in common polyurethane solvents such as DMF, DMSO, and dimethylacetamide and excellent film-forming properties. Consequently, homogeneous and transparent yellow films were easily prepared by solvent casting with subsequent drying at a moderate temperature, and so two of them (PUE-T and PUE-CT) suggested possible applications as soft, photodegradable membranes. The molecular weights of the polymers, determined by GPC, were 22,300 (PUE-T) and less than 10,000 (PU-T).

Because photochemical reactions are more suitable for triazene polymers than thermal and photothermal reactions, the thermal stability of the polymers in air was examined with TGA. The original TGA curves revealed a three-step decomposition process for the triazene polyurethanes (Table II). Just as for all previ-



**Figure 1** IR spectra of PUE-T and PU-T.

TABLE II  
Thermal Behavior of Bistriazene Polyurethanes

Sample	Stage I			$T_{10\%}$ (°C)	Stage II			Stage III		
	$T_r - T_f$ (°C)	$T_{\max}$ (°C)	Weight loss (%)		$T_r - T_f$ (°C)	$T_{\max}$ (°C)	Weight loss (%)	$T_r - T_f$ (°C)	$T_{\max}$ (°C)	Weight loss (%)
PUE-T	140–250	170	8	270	250–340	335	19	340–425	380	49
PUE-CT	155–250	220	8	275	250–350	345	20	350–420	385	34
PU-T	80–170	140	16	140	170–230	195	7	230–360	315	16

$T_i$  = initial decomposition temperature;  $T_f$  = final decomposition temperature;  $T_{\max}$  = decomposition temperature at which the weight loss is maximum;  $T_{10\%}$  = temperature at 10% weight loss.

ously reported triazene poly(ether urethane)s,<sup>22,23</sup> the dominating thermal process was assigned to bistriazene group decomposition followed by additional degradation of the polymers. The PUE-T and PUE-CT polymers were more stable, their thermal decomposition starting at 140 and 155°C, respectively. Despite the photolabile character of the bistriazene group, these polymers presented a weight loss of 10% up to 270°C, and this corresponded to the breakage of the triazene linkage with the release of gaseous nitrogen and small aromatic fragments during this fragmentation. At 425°C, the total weight loss of the process was about 76% for PUE-T, with a relatively small amount of residue. PU-T behaved somewhat differently, probably because of the greater number of labile units. Although its thermal decomposition onset was observed at 80°C, there was not a distinct correlation between the weight loss and the bistriazene content in this polyurethane. Theoretically, the amount of triazene diol in the polymer structure was about 60%, but the total weight loss during the TG investigation until 360°C was about 39 wt %. Therefore, the presence of bistriazene units represented a restrictive element for the low thermal stability of the synthesized polyurethane.

UV-vis spectroscopy was appropriate for studying the bistriazene photochemistry; the vanishing of the UV absorption maximum of the triazene linkage after certain irradiation periods was monitored. For photolysis experiments, a high-pressure mercury lamp was used as the irradiation source. It was interesting to compare the photosensitivity of the bistriazene polymers to that of the corresponding monomer. When a methanol solution of the bistriazene monomer (BTD) was subjected to progressive photolysis, a fast reduction of the absorption maximum close to 324 nm, assigned to intense decomposition, was observed. A typical profile of such a process is shown in Figure 2(a). Accordingly, the almost complete decay of the strong  $\pi-\pi^*$  transition at 324 nm within 2 min demonstrated that the fragmentation of the bistriazene moieties upon irradiation with unfiltered UV light occurred. The rate constant ( $k$ ) of this photoprocess can be expressed as follows:

$$k = \ln\left(\frac{A_0 - A_\infty}{A_t - A_\infty}\right) \times \frac{1}{t}$$

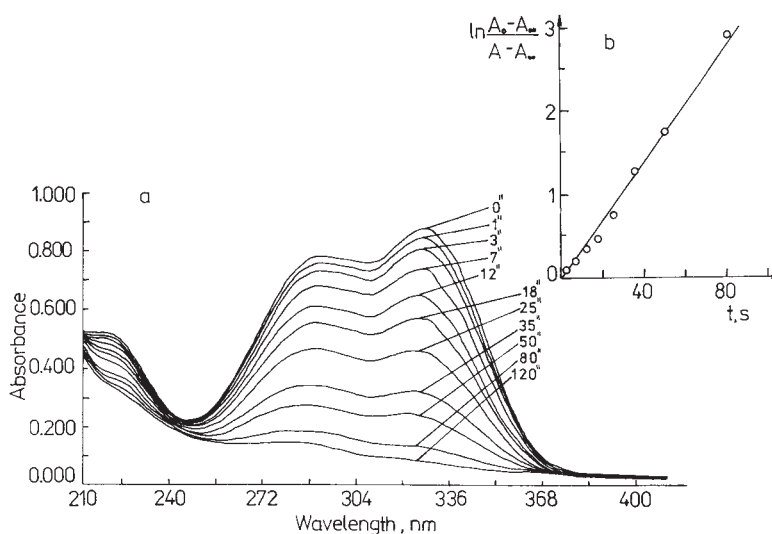
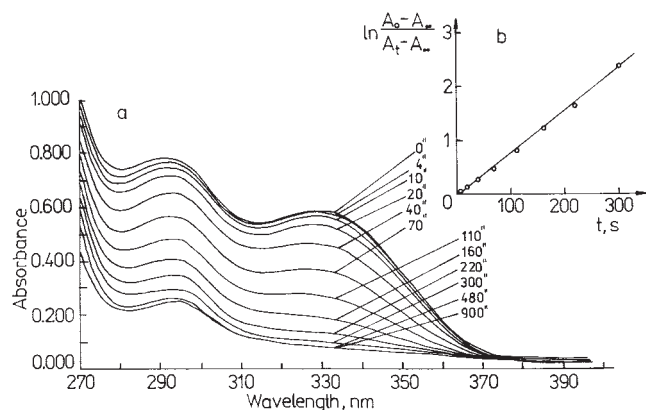


Figure 2 (a) UV-vis spectra of BTD in methanol solutions, showing the vanishing of the UV absorption maximum of the triazene linkage after different irradiation periods, and (b) a kinetic evaluation of its photolysis at 298 K.



**Figure 3** (a) Changes in UV-vis absorption spectra of PUE-T in DMF solutions upon UV light exposure and (b) a kinetic evaluation of its photolysis at 298 K.

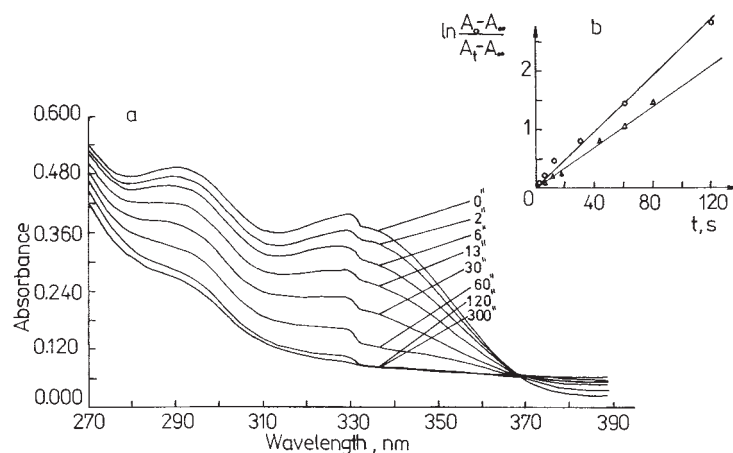
where  $A_0$  and  $A_t$  are the values of the absorbance at time  $t_0$  and  $t$ , respectively.  $k$  of the bistriazene diol ( $2.65 \times 10^{-2} \text{ s}^{-1}$ ) is an expression of a fast photodecomposition induced by the presence of double labile breaking points in every molecule. To compare the rate constants of the different compounds, we plotted the logarithm of the reduced absorption against the time, the bistriazene monomer following first-order kinetics, as shown in Figure 2(b).

To further investigate this reaction associated with the photolytic degradation of the bistriazene polyurethanes, we performed irradiation experiments in DMF solutions and thin films in the same way described previously. Figure 3(a) illustrates the irradiation time-dependent photobehavior of the absorption at  $\lambda_{\text{max}}$  for PUE-T in a DMF solution. After the irradiation of the polymer solution, the absorptions at 290 and 328 nm decreased monotonically up to the final value, with a minor redshift of the position. Notably, the photolysis of the investigated polyurethane required a longer time (15 min) than that of the starting monomer.

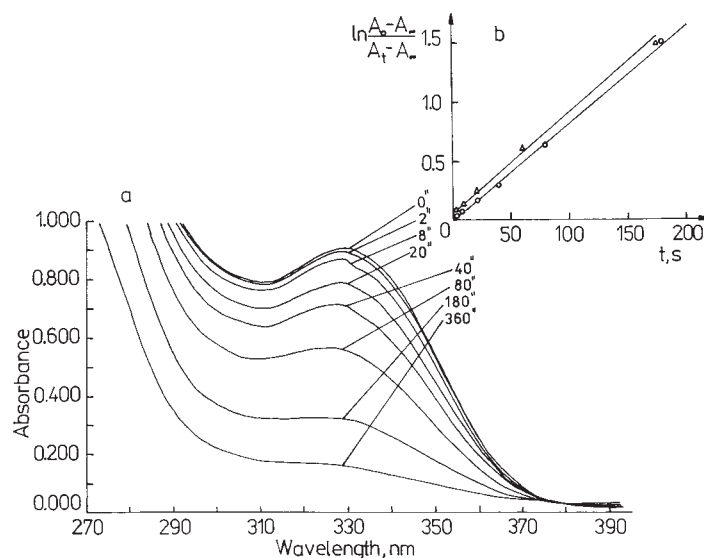
The kinetic analysis [Fig. 3(b)] revealed the first-order kinetics of the photolysis for PUE-T, and a generally lower decomposition rate for the polymer ( $k_{\text{sol}} = 3.09 \times 10^{-3} \text{ s}^{-1}$ ) was found. In comparison with the polymer solution, a significant difference in the photolytic behavior of the PUE-T polymer in the film state was observed [Fig. 4(a,b)]. Thus, a surprising increase in the photosensitivity was detected in the PUE-T film, for which a complete disappearance of the absorption band at 330 nm proceeded in only 5 min of irradiation. Additionally, the rate of film photolysis ( $k_{\text{film}}$ ) was  $2.03 \times 10^{-2} \text{ s}^{-1}$ . A possible explanation could arise from the appearance of the cage effect in the polymer solution exposed to irradiation, by which a recombination of the formed radicals was favored, without the release of gaseous nitrogen to enhance the radical lifetime. A similar reduction of the photosensitivity was encountered (not shown) for PUE-CT. As shown in Figure 4(b), the rate of photolysis was slightly lower than that of its corresponding nonionomeric polymer. Such photosensitivity of the ionomer chain could be ascribed to the conformational restrictions determined by the coupling of structural factors and electrostatic interactions.

Along this line, the photolysis of pure PU-T revealed greater photosensitivity than that of PUE-T, with the same difference in the photobehavior in solution and in the film state. Figure 5(a) depicts the changes in the UV spectra of the hard polymer solution in DMF with the irradiation time. After distinct irradiation intervals, a continuous reduction in the absorption band assigned to the triazene chromophore at 328 nm was a clear indicator of the irreversible photodecomposition of the bistriazene linkage. The solution photolysis was completed in about 6 min, with a rate constant value of  $k_{\text{sol}} = 6.21 \times 10^{-3} \text{ s}^{-1}$ , whereas the photolability in the film state exhibited a slightly higher value of  $k_{\text{film}} = 9.18 \times 10^{-3} \text{ s}^{-1}$  [Fig. 5(b)].

These results may be understood mainly through the topology of the polymer backbone: the bistriazene



**Figure 4** (a) Photolytic behavior of PUE-T in the film state and (b) a kinetic evaluation of (○) its photolysis and (△) the photolysis of a PUE-CT polyurethane film.



**Figure 5** (a) Changes in the UV spectra of PU-T in DMF solutions with the irradiation time in the film state and (b) a kinetic evaluation of its photolysis (○) in a DMF solution and (△) in the film state.

content and consequently a more restricted mobility of the chromophore in PUE-T favored a lower photolysis rate than that of PU-T.

From a chemical standpoint, we anticipated that the electron-donating or electron-withdrawing character of the bridging substituent between the phenyl rings in the bistriazene monomers would profoundly influence the absorption maximum and rate constants of photolysis. Further experiments will determine the origin of the described differences in the decomposition behavior observed between the two types of polyurethanes as well as their photolysis rate data recorded in solution and in the film state.

## CONCLUSIONS

A new triazene diol with two photolabile units in the structure was synthesized and characterized. This monomer was further used in the synthesis of hard and elastomeric polyurethanes to design polymers with various amounts of chromophores. PU-T showed a higher photosensitivity to UV irradiation than the elastomeric polymer, but its thermal stability was relatively poor because of its high triazene content. The photoreactivity of all the studied polyurethanes under mercury-lamp irradiation was more reduced in solution than in thin polymer films. A possible reason for this may be the appearance of the cage effect in the polymer solutions exposed to irradiation, by which a recombination of the radicals created inside was favored, without the release of gaseous nitrogen to enhance the radical lifetime.

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