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Synthesis and photochemical investigations of novel bistriazene polyurethanes

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Abstract

Two bistriazene monomers, 1,1′[4,4′-diphenyl]-3,3′-di(β-hydroxyethyl, methyl)-bistriazene (T1) and 1,1′[4,4′-diphenylsulfone]-3,3′-di(β-hydroxyethyl, methyl)-bistriazene (T2) were prepared by an electrophilic *N*–*N* coupling of substituted aryldiazonium salts with *N*-methyl-aminoethanol, and further employed as reaction partners for 2,4-toluene diisocyanate (2,4- and 2,6-TDI isomer mixture, 80:20, v/v) or 4,4′ methylene bis(phenylisocyanate) to achieve hard type bistriazene polyurethanes. The synthesized monomers and polymers were characterized by analytical and spectroscopic methods, while the surface morphology of polymers was visualized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Photochemical assessment of the triazene moieties in monomers and polymers was carried out in solution (methanol, DMF) and film state, following the decreasing under UV irradiation of the π–π^* absorption band in the corresponding UV spectra, the kinetic evaluation indicating a first order photoprocess. Laser ablation experiments performed at an irradiation wavelength of $\lambda = 308$ nm illustrate that bistriazene polyurethanes have a high potential to furnish good quality surfaces intended for microlithography.

Keywords: Bistriazene diol; Hard triazene polyurethanes; Photolysis; UV irradiation; Laser ablation

1. Introduction

Research on photopolymers in which photosensitive moieties are chemically incorporated has been motivated by various intriguing potential applications, the foremost of these including devices for optical data storage [1–3], photoresists [4–6] and photolithographic assemblies [7–9]. Such materials must be highly sensitive to light processing and should exhibit mechanical, thermal and chemical stability for all additional manufacturing steps. In this field, one of the most interesting topics in the recent years is the fabrication of artificial surface relief structures in triazene functionalized polymer films by their exposure to UV/laser irradiation, particularly attractive as dry etching of resists in microlithography [10–13]. Triazene polymers are suitable candidates for this type of applications owing to their high photosensitivity and especially spontaneous fragmentation into low molecular gaseous products upon irradiation [14]. Until now, a variety of triazene polymers, for instance polyesters [15], polytriazenes [16], polysulfides [17], have been obtained by different preparation methods and investigated from the point of view of the ablation properties.

Taking into account the broad spectrum of properties of the polyurethanes combined with a superior photosensitivity of triazene units, our group designed and synthesized a series of poly(ether urethanes) with such chromophore structures in the main backbone or as side chains introduced by means of new triazene monomers [18,19]. Studies performed on these systems revealed that materials photosensitivity increased with an increase of the triazene content in the polymers [20]. For this reason, new hard type triazene polyurethanes that include photolabile triazene units in every repeating segment were developed [21]. Excimer laser ablation experiments carried out on polyurethane films obtained from the latter polymers suggested a reduced quality of the ablation patterns as compared to other

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triazene polymers reported in the literature [22]. Therefore, the location of triazene units in the side chain of the polymeric backbone had a pronounced effect on the ablation parameters [23]. To surmount these limitations, a class of new hard triazene polyurethanes in which the photolabile units of bistriazene type are positioned in the polymer main chain was considered. This paper presents the synthesis, characterization and photochemical behaviour of these novel polymeric materials with a special emphasis on the photochemical and ablation properties.

2. Experimental

2.1. Materials

4,4′-Diaminodiphenyl, 4,4′-diaminodiphenyl sulfone, *N*-methyl-aminoethanol, toluene diisocyanate (2,4- and 2,6-TDI isomer mixture, 80:20, v/v) and 4,4′ methylene bis (phenylisocyanate) (Aldrich) were used as received. Dimethylformamide (DMF) wad dried over 5 Å molecular sieves.

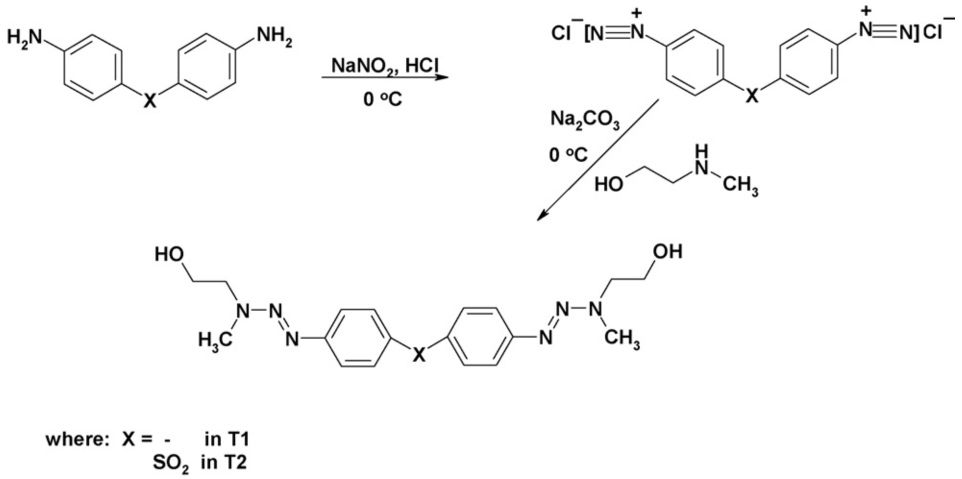
2.2. Synthetic procedures

The bistriazene diols 1,1′[4,4′-diphenyl]-3,3′-di(β-hydroxyethyl, methyl)-bistriazene (T1) and 1,1′[4,4′-diphenylsulfone]-3,3′-di(β-hydroxyethyl, methyl)-bistriazene (T2) were synthesized in a two step procedure, as shown in Scheme 1. As an example, the synthetic pathway used to obtain the T1 monomer is described. A stirred solution of 4,4′-diamino-diphenyl (10 g, 0.054 mol) in HCl 10 wt.% (84 mL) was cooled to 0 °C and diazotized with an aqueous solution of sodium nitrite (7.5 g, 0.1 mol). The reaction mixture was dropwise added to a solution of N-methyl-aminoethanol (8.15 g, 0.1 mol) and sodium carbonate (9.1 g, 0.085 mol) 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_2O. The organic layers were dried onto Na_2SO_4 and concentrated under reduced pressure. After removal of the solvent, the monomer was separated as a brown crystalline solid.

The hard type polyurethanes (PUH-T1 and PUH-T2) were obtained by polyaddition carried out in dry DMF starting from 5 g triazene diols and a corresponding stoichiometric amount of toluene diisocyanate (2,4- and 2,6-TDI isomer mixture, 80:20, v/v) (PUH-T1) or 4,4′ methylene bis(phenylisocyanate) (PUH-T2). The reactions were performed under purified nitrogen at 65 °C for 15 h. The triazene polyurethanes were precipitated in methanol and dried for 48 h at 60 °C under reduced pressure.

2.3. Equipment

The polymer structures were verified by ^{1}H NMR, IR and UV spectroscopy using a Bruker 400 MHz spectrometer, a Specord M80 and a Specord M42 spectrophotometer, respectively. Gel permeation chromatography (GPC) measurements were determined with a PL MD-950 instrument (Polymer Laboratories) equipped with an evaporative mass detector and two PL gel 5 μm 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 thermal stability of the polyurethanes was analyzed through thermogravimetry using a MOM Budapest derivatograph. TG and TGA curves were recorded between 20 and 600 °C with a heating rate of 12 °C min^{-1} in air. UV irradiations were performed in DMF solutions and for thin films, using a 500 W high-pressure mercury lamp without wavelength selection, at room temperature. The initial absorbance of the samples in the absorption band maximum was kept between 0.9 and 1.0. For the irradiation at 308 nm a Complex 205 XeCl excimer laser from Lambda Physik ($\tau = 30$ ns) was used. The samples for the laser ablation experiments were prepared by solvent casting from a 15 wt.% DMF solution on glass substrates. SEM analyses were made through polymer film deposition on aluminum plates and subsequent metallization with gold layer. AFM measurements of the samples were achieved in air at room temperature, using a PicoScan (Molecular Imaging) system, with a scanning area of 30 μm.



Scheme 1. Synthesis of bistriazene monomers (T1 and T2).