



Photo-induced crosslinking and thermal de-crosslinking in polynorbornenes bearing pendant anthracene groups

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ABSTRACT

Functional polynorbornenes bearing anthracene molecules in their side chain were synthesized by ring opening metathesis polymerization (ROMP). The pendant anthracene molecules undergo a $[4\pi + 4\pi]$ cycloaddition upon irradiation with UV-light, which was studied by means of UV-Vis spectroscopy in thin films of these polymers. This photodimerization reaction also leads to a crosslinking of the macromolecules due to the photodimer formation, resulting in a decrease in solubility of the UV illuminated areas. A thermally induced de-crosslinking could be obtained, revealing the reversibility of this photoreaction. The influence of the flexibility of the macromolecules, i.e. the mobility of the anthracene groups in the polymeric material, on the conversion rate, reversibility and the crosslinking behavior was studied by means of spectroscopy and sol-gel analysis. Furthermore, photo-patterned films were obtained by structured illumination and subsequent development with dichloromethane revealing a negative resist behavior.

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1. Introduction

Already in the 19th century, Fritzsche and co-workers reported on the reversible photochromism of anthracene crystals [1,2]. They discovered that an exposure of a saturated solution of anthracene to sunlight yields a colorless crystalline precipitate, which regenerates anthracene upon melting. A great number of studies were carried out on this photoinduced dimerization reaction, revealing a mechanism based on a $[4\pi + 4\pi]$ cycloaddition of the central ring of the anthracene π -system [3–6]. A reversion of this reaction can be achieved either thermally or by irradiation with deep UV-light (<300 nm) as shown in Scheme 1. It has to

be noted, that the photodimerization reaction takes only place in the absolute absence of oxygen. otherwise the formation of endoperoxides occurs [7,8].

In addition to a great number of investigations performed with anthracene derivatives in solution, the photodimerization reaction in the solid state has drawn great interest in material science. In particular, anthracene dissolved in polymeric materials induces considerable changes in their optical properties [9,10]. This fact has been exploited for the realization and development of photo-chromic devices [11]. In recent polymer related studies, anthracene units have been covalently attached to the polymer backbone. These polymeric materials have the advantage that a high anthracene concentration can be incorporated without crystallization, phase separation, or the formation of concentration gradients.

Over the past few years, reactions of macromolecular anthracene derivatives have undergone a great revival

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due to their orthogonal “click” like behavior. Besides the photo-induced dimerization also the Diels–Alder reaction with maleimide groups has been used for the creation of highly defined polymer architectures [12,13]. Moreover, the photodimerization reaction has already been applied for a selective crosslinking of macromolecules, leading to changes in solubility [14,15] as well as in refractive index [16].

Very recent endeavors focus on the reversible photoreaction between polymer based anthracene-derivatives and singlet oxygen to give endoperoxides, which significantly alters the surface potential [17]. This interesting material property can be used for the realization of photochromic storage devices that can be read out by Kelvin probe force microscopy.

Apart from polymeric materials, this photoreaction has also been exploited for the fabrication and crosslinking of nanoparticles, respectively [18,19]. A very important aspect of this photodimerisation reaction in the solid state is the required steric arrangement of the anthracene moieties. While the 9- and 9,10- substituted anthracene derivatives generate these arrangement very easily in solution and yield tail–tail and/or tail–head photoproducts [20], in polymeric materials the mobility and diffusion are restricted, which can prevent the required arrangement and thus photodimerization. Many studies pointed out that the anthracene mobility in the polymer chain is more important for the successful photodimerization than the density of anthracene moieties [21,22].

Several investigations are related to this specific feature in different classes of polymeric materials. Tazuke et al. explored the influence of the glass transition temperature of polyesters and polyurethanes bearing anthracene units in the side chain on the conversion, rate and reversibility of the photodimerization reaction [23]. It turned out that the mobility of the anthracene units in the polymeric material mainly determines the efficiency of the photoreaction, which is in good accordance with theoretical considerations of an appropriate alignment. Moreover, also an efficient cleavage of the dimers needs a certain degree of flexibility [7].

In the present contribution, we focus on the preparation of anthracene containing polymers via ring opening metathesis polymerization (ROMP). ROMP is a versatile technique for the preparation of highly defined functional polymers. In particular, polynorbornenes have been intensively used as polymeric model compounds for the investigation of several photo-induced reactions due to their good film forming- and optical-properties [24–27].

In order to provide a better mobility of the anthracene moieties, also copolymers with oligoethyleneglycol groups were prepared in order to lower the glass transition temperature. The photochromism will be utilized for a selective crosslinking of the macromolecules, leading to changes in the solubility, which is exploited for a photolithographic patterning of thin films of the obtained functional (co)polymers. A particular focus of this study is the influence of the glass transition temperature, i.e. the mobility of the pendant anthracene groups, on the conversion rate and reversibility of the photoreaction as well as on the crosslinking behavior. The thermally

induced reversion of the photodimerization is evaluated as a way to de-crosslink polymeric materials.

2. Experimental

2.1. Materials preparation

All chemicals were purchased from commercial sources and were used without further purification. All experiments were carried out under inert atmosphere using Schlenk technique or a glove box. Endo,exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, bis[2-[2-(2-ethoxyethoxy)ethoxy]ethyl] ester (mono-2) was synthesized as previously reported [28]. For the ROM polymerization [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-(3-phenyl-1H-inden-1-ylidene) (pyridyl)ruthenium(II) (Umicore M31) purchased from Umicore AG & Co. KG was used. *Caution: For preparative work, hazardous chemicals and solvents were used. Reactions must be carried out in a fume hood and protective clothes and goggles must be used!*

2.2. Endo, exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, bis(anthracen-9-ylmethyl) ester (mono-1)

(9-Anthracenyl)methanol (1.05 g; 5 mmol) was added to a stirred solution of bicyclo[2.2.1]hept-5-ene-2,3-dicarbonyl dichloride (0.372 mL; 2.3 mmol) and pyridine (0.405 mL; 5 mmol) in dichloromethane. The solution was stirred for 48 h at ambient temperature. The reaction mixture was then filtered to remove the pyridinium salt and extracted with dichloromethane. The organic layer was extracted with 3 × 20 mL of 5% hydrochloric acid solution to remove excess pyridine, and with 20 mL of saturated sodium bicarbonate solution, and then dried over sodium sulfate. The solvent was removed in vacuo and subsequently a column separation using cyclohexane/ethyl acetate (20:1) for product purification was performed. Yield: 1.12 g of a white solid (87% of theoretical yield). ¹H NMR: (δ, 400 MHz, 20 °C, CDCl₃): 8.51 (d, 2H an10), 8.26 (vt, 4H an1,8), 8.03 (d, 2H an5), 7.50 (m, 8H an2,3,6,7), 6.20–6.00 (m, 5H, O—CH₂, nb6), 5.83 (m, 1H, nb5), 3.47 (t, 1H nb3), 3.11 (s, 1H, nb4), 3.01 (s, 1H, nb1), 2.77 (dd, 1H, nb2), 1.54, 1.32 (d, 2H, nb7); ¹³C NMR: (δ, 125 MHz, 20 °C, CDCl₃): 174.5, 173.3 (2C, C=O), 137.63, 134.94 (2C, nb5,6), 131.35 (1C, an9), 131.03, 130.98 (2C, an8a,9a), 129.18 (2C, an4a,4b), 129.07 (2C, an4,5), 126.62 (1C, an10), 126.54 (2C, an2,7), 125.09 (2C, an3,6), 123.92, 123.87 (2C, an1,8), 59.44, 59.13 (2C, O—CH₂), 47.91 (1C, nb1,3), 47.28 (1C, nb7), 47.23 (1C, nb2), 45.86 (1C, nb4); IR-Data (CaF₂, cm⁻¹): 2854, 1722, 1448, 1305, 1262, 1161, 1111, 985, 889, 739.

Polymerization of mono-1 to give poly(bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, bis(anthracen-9-ylmethyl) ester) (poly-1): a solution of mono-1 (200 mg, 0.355 mmol) in 2.5 mL of dichloromethane was added to a solution of Umicore M31 (1.78 mg, 2.38 μmol) in 1 mL of CH₂Cl₂ and was stirred at ambient temperature for 12 h. Afterwards, the reaction was stopped by adding 0.10 mL of ethylvinylether. The polymer was precipitated

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