



Anthracene-based polyurethane networks: Tunable thermal degradation, photochemical cure and stress-relaxation

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ABSTRACT

Anthracene dimer diols having very different thermal stabilities have been incorporated in polyurethane networks. The thermal de-crosslinking of these networks was shown to be dependent on the anthracene dimer used, allowing tunable thermal degradation. This scission was studied using (HR-MAS) NMR, DSC and rheometry. The tunable thermal decrosslinking was validated as a technique to easily remove the coatings at their end-of-life. The UV irradiation of the thermally degraded materials allows for recuring the coatings to materials having similar properties. By simultaneous irradiation and heating of (partially) reversibly cross-linked networks, the networks were able to relief internal stress and adopt a new permanent shape.

1. Introduction

Within polymer material science, polyurethanes (PUs) play an important role. They are commonly used for making foams, elastomers, adhesives and coatings. Their unique properties are a result of hydrogen bridge formation between the repeating carbamate groups. Short repeating units result in hard, crystalline domains which act as physical cross-links. Most often, PU networks are made by polyaddition of polyols with diisocyanates, while the use of polyisocyanates to achieve a cross-linked material is also applied in industrial context. However, isocyanates have harmful effects on human and environment and are progressively banned by Europe (REACH) [1]. Attractive alternatives are curing chemistries that form urethanes without using (toxic) isocyanates. For example, polyhydroxyurethanes can be formed by the polyaddition of cyclic carbonates and amines [2]. The urethane bonds can also be made beforehand in precursor molecules, followed by cross-linking using a different chemistry such as acrylate polymerization [3] or thiol-ene addition [4].

Additionally, the increasing demand on the performance and sustainability of polymer materials, as well as the request for adaptability and additional functionalities, has inspired scientists to incorporate reversible bonds to develop covalently adaptable networks [5]. Depending on the chemistry involved, these reversible bonds may lead to bond exchange while maintaining a constant connectivity (vitrimers) [6] or to a (temporary) change in connectivity.

Self-healing polyurethanes have been developed by incorporating thermoreversible bonds such as Diels-Alder cycloadducts [7] and triazolinedione-ene adducts [8]. Raising the temperature of these materials leads to bond scission and thus a lower connectivity, which is restored upon cooling. This temporary decrease and increase in connectivity allows the formation of new bonds across a damaged area, resulting in a (partial) recuperation of the original properties and longer lifetimes.

Photoreversible bonds formed by coumarin dimerization, have also been incorporated in polyurethane materials [9]. The [2+2] cycloaddition of the pending coumarin groups requires irradiation above 270 nm (e.g. 350 nm), while scission of the formed dimers requires irradiation below 270 nm (e.g. 254 nm). Photochemical scission of the coumarin bonds at cut surfaces, followed by photostimulated cross-linking while pressing the cut surfaces together, led to reattachment with partial restoration of the mechanical properties.

Very recently, Fang and coworkers developed thin self-healing polyurethanes using anthracene dimers as reversible cross-links [10]. For this, they started from prepolymers having pendent anthracene groups, followed by photochemical cure (anthracene dimerization) during 20 min. Cracked materials were repaired by heating to 130 °C for 1 h, which cleaves the dianthracene bonds, followed by anthracene dimerization by 10 min irradiation using UVA light.

The synthesis of novel functional anthracene derivatives [11] and the incorporation thereof in materials using thiol-ene reactions [12] has been studied by our group. It was shown that the thermal scission of the

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model dimers is highly tunable by altering the 9-substituent. Additionally, the thermal stability of similar dimers can be raised by the occurrence of melting points at or above the thermal scission temperature region. The thermal scission behavior of the studied derivative was similar when incorporated in cross-linked materials, and thus thermally cleavable materials with a designed scission behavior could be made. More information on anthracene-containing polymers can be found in our very recent review [13].

In this paper, we introduce several alcohol-functionalized anthracene dimers and discuss their thermal stabilities in polyurethane materials. These anthracene dimer building blocks and the polyurethane materials are industrially more relevant, as polyurethanes are more widely spread than thiol-ene cured materials. Additionally, the hydrogen bridges in the polyurethanes may influence the mobility of the (di)anthracene groups and therefore alter the thermal behavior [14]. By using pre-dimerized anthracenes, the derivatives can easily be implemented in existing PU-formulations. It eliminates the necessity of an – often slow and incomplete – photochemical curing step, which limits the material dimensions to thin films and coatings. The mechanical and thermal properties of the synthesized polyurethanes were studied for different types and quantities of reversible bonds. The thermal scission of these materials was evaluated as a method to easily remove coatings. Also, proof of concept trials for stress-relaxation by simultaneous dimerization and dimer scission were performed.

2. Experimental

2.1. Materials

Chloroform ($\geq 99.8\%$), zirconium (IV) acetylacetonate (97%), methanol (99.9%), diethyl ether ($\geq 94.8\%$), ethyl acetate ($\geq 99.7\%$), poly(tetramethylene oxide) ($M_n \sim 650$ and $M_n \sim 2900$ g/mol), polycaprolactone diol ($M_n \sim 530$ and $M_n \sim 2000$ g/mol), hexamethylene diisocyanate ($\geq 98\%$), acetone ($\geq 99.8\%$), 2,2-bis(hydroxyl)methylpropionic acid (98%) and dibutyltin dilaurate (95%) were purchased via Sigma-Aldrich. Toluene (99.9%), 1,12-dodecanediol (99%), methanesulfonyl chloride (99.5%), triethyl amine (99%) and methanesulfonyl chloride (99.5%) were purchased via Acros Organics. Sodium hydrogen carbonate ($\geq 99.5\%$), sodium chloride ($\geq 99\%$), magnesium sulfate hydrate ($\geq 99\%$) and potassium carbonate ($\geq 99\%$) were purchased via Carl Roth. Silica 60 Å (99.5%) was purchased via ROCC. Hexamethylene diisocyanate trimer (Desmodur N-3300) was provided by Covestro. Toluene was dried by distillation over sodium prior to use. Anhydrous dimethylformamide, tetrahydrofuran and triethylamine were purchased from Acros Organics and used as such.

2.2. Instruments

IR spectra were recorded with a Perkin Elmer FTIR SPECTRUM 1000 and a PIKE Miracle ATR unit. NMR spectra were recorded with Bruker AVANCE 300 (300 MHz) and Bruker DRX500 (500 MHz) NMR spectrometers. HR-MAS NMR spectroscopy was performed using a Bruker Avance II 700 (700.13 MHz) spectrometer equipped with a HR-MAS probe. Sample materials were cut to small pieces, brought into a 4 mm rotor (50 μ L) and deuterated chloroform was added to swell the sample. ^1H NMR spectra were measured at rotational frequency of 6 kHz. LC-MS analyses were performed on an Agilent Technologies 1100 series LC/MSD system with a diode array detector (DAD) and single quad MS. Analytical reversed phase HPLC-analyses were performed with a Phenomenex Luna C18 (2) column (5 μ m, 250 mm \times 4.6 mm) and a solvent gradient (0 or 75–100% acetonitrile in H_2O in 15 min), the eluted compounds were analyzed via UV detection (214 nm). Unless mentioned otherwise, photoirradiation occurred under inert atmosphere in a Metalight Classic from Primotec, with 12 double 365 nm or 254 nm UV lamps of 9 W each (intensity measured in the middle $\sim 5 \text{ mW cm}^{-2}$). Differential scanning

calorimetry (DSC) was performed under nitrogen atmosphere using a DSC1/700 Mettler-Toledo apparatus. The used heating rate was 10 K min^{-1} . Thermogravimetric analyses (TGA) were performed on a Mettler-Toledo TGA/SDTA 851e under nitrogen atmosphere. Samples were heated from 25 to 600 $^\circ\text{C}$, at rate of 10 K min^{-1} . Dynamic mechanical thermal analysis (DMTA) was performed on a Mettler-Toledo DMA/SDTA 861e in shear mode using a force of 5 N, temperature sweep from -50 $^\circ\text{C}$ to 50 $^\circ\text{C}$ and a frequency of 1 Hz. The data from TGA, DSC and DMTA measurements were analyzed using the STARe software from Mettler-Toledo. Size exclusion chromatography (SEC) was performed on three sequential polymer standards services SEC columns (1x GRAM Analytics 30 Å, 10 μ m and 2 \times GRAM Analytical 1000 Å, 10 μ m) at 35 $^\circ\text{C}$. N,N-Dimethylacetamide containing 0.42 mg L^{-1} LiBr was used as eluent (1 ml min^{-1}). The system was calibrated using PMMA standards (690 g mol^{-1} and 1,944,000 g mol^{-1}) with a narrow dispersity. A Hitachi Column Oven L-7300, a Waters 2414 Refractive index Detector, a Waters 610 Fluid Unit and a Waters 600 controller were used. Mechanical properties were determined using a Tinius Olsen H10KT tensile machine. The dogbone shaped samples with a width of 2 mm were pressed out of films prior to use. The length of the samples in between the clamps was 12–14 mm and the elongation speed was 0.5 mm s^{-1} . Solvent rub tests were performed using a cheese cloth drenched in butanone (and refreshed every 20 rubs). Approximately 100 N force was applied on a surface of 1 cm^2 . Steel substrates were washed with soap, followed by rinsing with water and acetone and drying before use. The coating resins were doctor bladed, with a gap of 100 μ m. Rheology experiments were performed using an Anton Paar MRC 302. For UV-curing and stress-relaxation experiments (on 100 μ m thick samples), a 25 mm peltier plate was used and an Omnicure S2000 with mercury lamp of 13.23 W/cm^2 maximum intensity was used with a light guide to the rheometer. In other rheometry measurements, a 8 mm peltier plate was used with samples of 2 mm thickness, using a normal force of 2 N, a frequency of 1 Hz and 1% deformation. Pencil hardness was determined using an Elcometer 3086 motorized pencil hardness tester in a forward fashion (chip method) with a force of 7.5 N.

2.3. Synthesis of anthracene mesylate 6

Dry triethylamine (3.7 ml, 26 mmol, 2 equiv.) was added to a solution of anthracene ether 5 (5 g, 13 mmol, 1 equiv.) in anhydrous tetrahydrofuran (50 ml). After cooling in an ice bath, methanesulfonyl chloride (1.5 ml, 20 mmol, 1.5 equiv.) was slowly added. The solution was stirred for 3 h until full conversion as confirmed via thin layer chromatography. The solution was washed with water (30 ml). This separated aqueous phase was extracted with ether (3 \times 30 ml). The combined organic phases were washed with a saturated bicarbonate solution (30 ml) and brine (30 ml). The organic phase solution was dried with magnesium sulfate. Concentration *in vacuo* yielded the mesylate 6 as a brown oil (5.69 g, 12.5 mmol, 94%). ^1H NMR (300 MHz, CDCl_3): δ (ppm) = 1.06–1.85 (m, 18H, CH_2), 1.98 (m, 2H, CH_2 - CH_2 -OMs), 2.92 (s, 3H, CH_3), 4.14 (m, 4H, CH_2 -OMs + CH_2 -OAntr), 7.39 (m, 4H, CH-CH-CH-CH), 7.91 (m, 2H, CH-C-CH-CH), 8.13 (s, 1H, C- CH-C), 8.22 (m, 2H, C-C- CH-CH).

2.4. Synthesis of anthracene diol 7

A solution of mesylate 6 (5.96 g, 12.5 mmol, 1 equiv.) in anhydrous dimethylformamide (15 ml) was slowly added to an ice-cooled mixture of 2,2-bis(hydroxyl)methylpropionic acid (1.65 g, 12.5 mmol, 1 equiv.), potassium carbonate (1.89 g, 13.8 mmol, 1.1 equiv.) and anhydrous dimethylformamide (15 ml). The mixture was stirred overnight at 80 $^\circ\text{C}$. After cooling to room temperature, the salts were filtered off and the filtrate was concentrated *in vacuo*. The resulting orange-brown oil was diluted to 10 w%, using 5% triethylamine in ethyl acetate. After 10 min of ultrasonication, the salts were filtered off and the filtrate was concentrated *in vacuo* to yield anthracene diol 7 as a yellow oil (4.89 g,

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