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Synthesis and characterization of a photo-crosslinkable polyurethane based on a coumarin-containing polycaprolactone diol

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ABSTRACT

A new coumarin diol was designed and used as initiator for the ring opening polymerization of ε-caprolactone. A photo-reactive polyurethane based on the resulting polycaprolactone diol with pendant coumarin moieties was synthesized. Photo-dimerization/photocleavage reactions were studied by UV and Raman. The linear non-irradiated soft polyurethane transformed into a tough elastomeric crosslinked material. DQ-NMR measurements showed that conversion of the photo-reaction was not directly related to relative amount of crosslinking but provided complementary information. Crosslinking reduced the crystallinity of the polycaprolactone segments and the melting point of the crystals.

1. Introduction

Recently, much research has been devoted to the development of self-healing polymers [1–4], which are able to autonomously repair damage inflicted on them. Some of these polymers can self-repair by surface contact [5,6], but most need different external stimulus as a trigger, such as heat or light. There are many studies in which light has been utilized as a trigger for these kind of materials [7–10]. The most important advantage of using light is that light-triggered processes can be halted and resumed "on demad" by turning off and on the excitation light [11]. Several light-sensitive groups or chromophores that can undergo a reversible photo-induced reaction can be used in these materials such as antracenes [12,13], coumarins [14], or cinnamic acid derivatives [12,15]. These light-sensitive materials have been proposed for shape memory polymers [15,16], hydrogels [13], surface patterning [17], drug release [18–21], light stabilization and surface sizing of paper [22], cellular imaging [23], photovoltaics [24], oil recovery [25], micro-phase stabilization of block copolymers [26] and intraocular lenses [27].

Coumarin was first reported and isolated in 1820s, recognized as the hay-like sweet aroma of the tonka bean [28]. The uses for coumarins are as diverse as the structures of over 1000 different derivatives in the coumarin family [29]. Coumarin molecules can undergo reversible photo-induced reactions; thus, when irradiated at >300 nm a [2+2] cycloaddition reaction

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to give rise to a cyclobutane ring takes place, and when irradiated at 254 nm a photo-scission reaction renders the original coumarin structures as seen in Fig. 1 [14,30–32].

Coumarin monomers have been included in the backbone of different types of polymers, including polyethers [30], poly (meth)acrylates [32,33], polyesters [34], silicones [35,36] and polyurethanes [37]. When incorporated in a polyurethane chain, the coumarin monomer was introduced as a chain end [38–40] or as a chain extender [37]. In both cases coumarin monomer was linked to the isocyanate monomer by a polar urethane group, and when introduced as a chain extender, coumarin units were situated within the hard segments.

In this work we report a coumarin-based photo-reative polyurethane based on a new coumarin diol. It is known that in solid state, the rate and degree of dimerization depend on the mobility of the chain to which the coumarin molecule is attached, and therefore, rubbery domains are necessary for the photo-reaction with high efficiency [37]. This new monomer was designed to have the coumarin moiety separated from the main chain in order to be more mobile. Importantly enough, the coumarin diol was used for the first time, to our knowledge, as initiator for the ring opening polymerization of ε-caprolactone to give polycaprolactone diols that were reacted with hexamethylene diisocyanate to produce a polyurethane with the coumarin moiety within the soft segment. Furthermore, we report the evaluation of photochemical and mechanical properties of this polyurethane.

2. Materials and methods

2.1. Materials

2.2-Bis(hydroxymethyl)propionic acid, 2.2-dimethoxypropane, p-toluenesulfonic acid monohydrate (PTSA), 1.3-dicyclohexylcarbodiimide (DCC), resorcinol, ethyl acetoacetate, 2-bromoethanol (BrEtOH), anhydrous pyridine, dowex H+ resin, ε-caprolactone, stannous octoate ($SnOct_2$) and hexamethylenediisocyanate (HDI) were supplied by Sigma–Aldrich and used as received. Acetone, dichloromethane, 1,4-dioxane, concentrated sulphuric acid, ethyl acetate, ethanol, N,N-dimethylformamide (DMF), pyridine, potassium carbonate, sodium bisulfite, magnesium sulfate and dichloroethane were supplied by Scharlau and used as received.

2.2. Experimental techniques

Solution 1H NMR spectra were recorded at room temperature in a Varian Unity Plus 400 instrument using deuterated chloroform (CDCl3) or deuterated dimethylsulfoxide (DMSO-d6) as solvent. Spectra were referenced to the residual solvent protons at 7.26 or 2.50 ppm respectively.

Irradiations were carried out in an ultraviolet crosslinker supplied by Ultra-Violet Products equipped with two set of 5×8 W lamps for 354 nm or 254 nm irradiations (354 and 254 nm are the wavelengths on the maxima of the irradiation spectra of the lamps respectively).

UV experiments were performed in a Perkin Elmer Lambda 35 UV/Vis spectrometer. Absorbance of the thin film was measured from 450 to 210 nm.

Raman spectroscopy measurements were carried out by a Renishaw in Via (UK) Laser micro-Raman Spectrometer. A laser beam with wavelength of 785 nm served as the excitation light. The testing area on the film was about 1 μm^2.

The thermal transitions of the samples were analyzed by differential scanning calorimetry (DSC) on a Mettler Toledo (DSC 822e) calorimeter equipped with a liquid nitrogen accessory. Disc samples cut from films weighing approximately 6 mg were sealed in aluminium pans. Samples were heated, from −90 °C to 100 °C at a rate of 10 °C min^{-1}, cooled at 10 °C min^{-1} to −90 °C, maintained for 7 min at this temperature and re-heated from −90 °C to 100 °C at a rate of 10 °C min^{-1}. Data on Table 1 have been taken from the second scan. Melting temperatures, Tm, were taken as the maximum of the endothermic transition, and glass transition temperatures, Tg, were taken as the midpoint of the transition

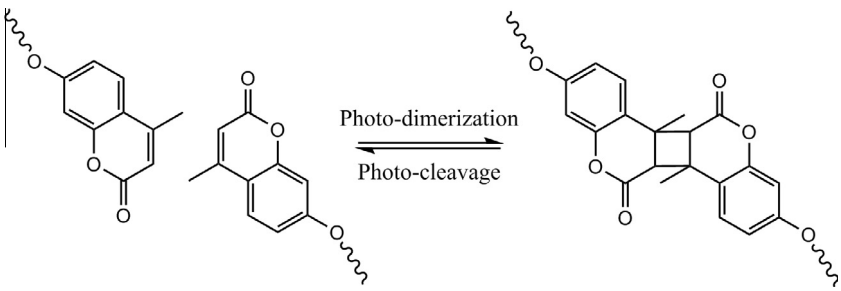

Fig. 1. Photo-dimerization/photo-cleavage reactions of coumarin molecules.