



Reversibly photo-crosslinkable aliphatic polycarbonates functionalized with coumarin

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ABSTRACT

Cinnamoyl and coumarin groups can be used to introduce photo-responsive behaviour to polymer systems, but they have never been directly compared within the same polymer system. Thus, this study examined cinnamoyl and coumarin functionalized aliphatic polycarbonate copolymers to determine their relative suitability for use as biomaterials. Coumarin functionalized polycarbonates photo-crosslinked significantly faster and resulted in networks with high crosslink density when irradiated with UVA radiation. Real-time tracking using rheometry showed that increasing the degree of coumarin functionalization on the aliphatic polycarbonate copolymers resulted in quicker gelation and higher final storage modulus. In addition, decreasing the UV intensity and increasing the sample thickness also increased the final storage modulus. Although no appreciable reversibility was detected for solvent-free or solvent-swelled crosslinked polymer networks, rapid reversibility upon exposure to 254 nm light was observed in dilute solutions. The kinetics of photo-dimerization were third order while the photo-cleavage reaction kinetics were second order with respect to the concentration of the photoactive group. Overall, the photo-reversible crosslinking of coumarin functionalized aliphatic polycarbonates was demonstrated. These polymers have potential for use in photo-crosslinking or photo-reversible biomaterials applications.

1. Introduction

The preparation of polymers that can respond to external stimuli such as light or pH is a growing research area with biomedical applications including responsive drug delivery systems and intraocular lenses [1–3]. Many of these systems employ functional groups that can either undergo a reversible isomerization [4,5] or form or cleave bonds [6–10] when photo-irradiated. The reversibility of these bonds is dependent on the functional group used, with acrylates [11,12] and *o*-nitrobenzyl [6,7,13,14] resulting in irreversible bond formation or cleavage respectively, while anthracene [1,8], cinnamoyl [9,15,16], and coumarin [10,17–20], are capable of photo-reversible bonding. These functional groups can be incorporated into polymer backbones [14,15,18], conjugated to the end of polymer chains [1,6,8], or incorporated as pendant crosslinking nodes along the polymer backbone [16,17]. By exposing these materials to the appropriate wavelength of light, the disintegration of the polymer backbone, crosslinked hydrogel, or unswollen polymer network can be induced. The incorporation of these compounds as pendant groups results in polymer matrices wherein the degree of crosslinking is dependent on their density along

the polymer backbone and can be altered using light [9,16,17]. The most convenient way to prepare these materials is through copolymerization of functionalized and non-functionalized monomers. In particular, a wide variety of functionalized carbonate monomers have been synthesized, including ones with pendant cinnamoyl or coumarin groups [9,21]. These monomers have been successfully copolymerized with commercially available non-functionalized monomers such as trimethylene carbonate (TMC) and lactide, both of which have been used extensively in biomaterials applications [11,22–28].

Cinnamoyl and coumarin are both capable of reversible photo-dimerization through [2 + 2] cycloaddition, with dimerization occurring when irradiated with UV wavelengths of 300–380 nm, and dimer cleavage occurring when irradiated with UV wavelengths of 250–280 nm (Fig. 1) [15,29–31]. Consequently, polycarbonate copolymers with these compounds as pendant groups should be capable of photo-reversible network formation, which could be used to prepare photo-triggerable materials. However, there are no reports of a systematic comparison between cinnamoyl and coumarin functionalized polymers. In this study, the UV–Vis absorbance profiles of aliphatic polycarbonate copolymers functionalized with either pendant

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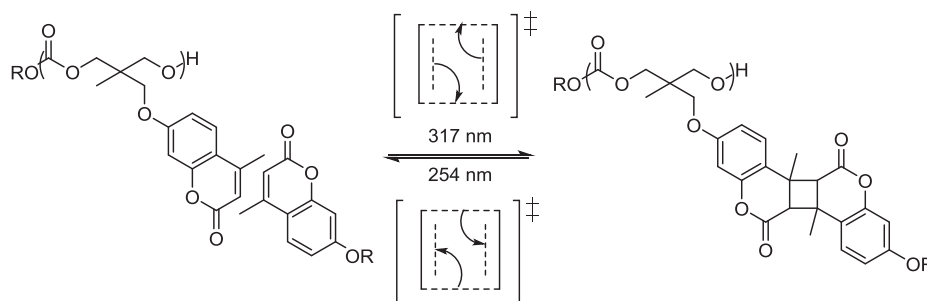


Fig. 1. Schematic of the reversible [2 + 2] photo-cycloaddition reaction for an aliphatic polycarbonate with a pendant coumarin group.

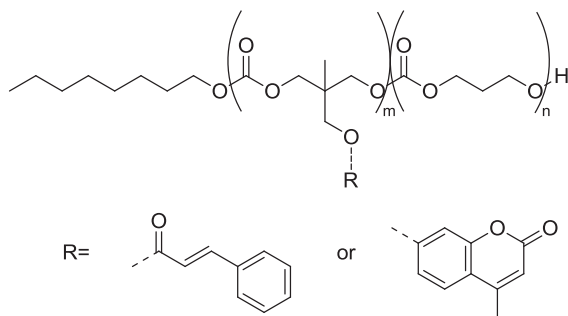


Fig. 2. Cinnamoyl or coumarin functionalized aliphatic polycarbonate copolymers initiated with 1-octanol.

cinnamoyl or coumarin groups (Fig. 2) were examined.

2. Experimental

2.1. Materials

All reagents were obtained from commercial suppliers and used as received unless otherwise noted. Dimethylsulfoxide- d_6 , chloroform- d (99.8%D) (CDCl_3), anhydrous dimethylformamide (DMF) (99.8%), liquid chromatography (LC)-grade acetonitrile, dioxane, 1,1,1-tris(hydroxymethyl)ethane (99%), cinnamoyl chloride (98%), 4-methylumbelliferone (98%), *p*-toluenesulfonic acid monohydrate (98%), sodium hydrogen sulfate monohydrate (99%), anhydrous 1-octanol (99%), and methyl *tert*-butyl ether (98%) were obtained from Sigma-Aldrich (Oakville, Canada). Toluene (99.85%, Extra Dry over molecular sieves), 2,2-dimethoxypropane (98%), ethyl chloroformate (99%), sodium bicarbonate (99.7%), and anhydrous 2-methyltetrahydrofuran were obtained from Acros Organics (New Jersey, USA). Acetonitrile, dichloromethane (DCM), tetrahydrofuran (THF), isopropanol, anhydrous diethyl ether, toluene, acetone, methanol, ethyl acetate, hexanes, potassium carbonate (99%), sodium chloride (99%), sodium hydroxide (97%), anhydrous magnesium sulfate (97%), 48% hydrobromic acid (HBr), concentrated hydrochloric acid (HCl), 85% phosphoric acid, and triethylamine (TEA) (99%) were obtained from Fisher Scientific (Ottawa, Canada) and the THF and TEA were stored over 4 Å molecular sieves. 3-methyl-3-oxetanemethanol (97%) was obtained from Alfa-Aesar (Ward Hill, USA). Trimethylene carbonate (99%) was purchased from Leapchem (Hangzhou, China) and purified by recrystallization from ethyl acetate (3 mL/g). The cinnamoyl functionalized monomer, 5-cinnamoyloxymethyl-5-methyl-1,3-dioxan-2-one (COM), and the coumarin functionalized monomer, 5-(4-methylumbelliferyloxymethyl)-5-methyl-1,3-dioxan-2-one (MUM), were synthesized as previously described [21].

2.2. Polymerization

COM and MUM were copolymerized with TMC by catalyst-free melt

polymerization and characterized as previously described [21]. Briefly, TMC (1.53 g, 15.0 mmol, 22.5 eq) and either COM (1.52 g, 5.0 mmol, 7.5 eq) or MUM (1.38 g, 5.0 mmol, 7.5 eq) were combined in a flame-dried ampule and 1-octanol diluted in anhydrous toluene (87 mg, 0.67 mmol, 1 eq, 20% w/w) was added as an initiator. The ampule was purged with argon, evacuated at a reduced pressure of 28 kPa for 30 s, and flame-sealed. The ampules were then placed in an oil bath thermostat-controlled at 120 °C and allowed to polymerize for 18 h. The copolymers were purified by precipitation from 20:1 methanol:DCM. Purified polymers were characterized by ^1H NMR spectroscopy in CDCl_3 using a Bruker 500 MHz NMR spectrometer with peak shifts referenced to an internal tetramethylsilane standard. In addition, the glass transition temperature (T_g) of the polymers was assessed by differential scanning calorimetry (DSC). DSC was conducted using a Mettler Toledo DSC1 System and the samples were monitored through two heating cycles from -60 °C to 105 °C at a 10 °C min^{-1} heating rate. The glass transition temperature was determined from the second heating cycle.

2.3. Photo-crosslinking and photo-cleavage

The photo-crosslinking of various copolymers either solvent-free or as a concentrated solution in dioxane (50 mass% polymer) was conducted using an EXFO Acticure 4000 light source with a mercury bulb and a 320–500 nm filter via a liquid light-guide at 1.4 W cm^{-2} (measured at 365 nm) and the photo-cleavage was examined using a UVP Pen-Ray 11SC-1 with an unfiltered/uncoated mercury bulb at 0.3 mW/cm^2 (measured at 254 nm). Changes in the polymer properties were monitored in real-time using a ARES rheometer (TA Instruments, USA) with parallel plate geometry and a 0.3 mm gap. The top plate was a 20 mm quartz plate with a Peltier plate on the bottom. The photo-crosslinking was conducted at 25 °C using an oscillatory frequency of 10 rad s^{-1} and a strain of 1%.

2.4. Photo-kinetics

The reversible photo-crosslinking of various copolymers in a very dilute solution in LC-grade acetonitrile (15–40 mg L^{-1}) was monitored in real-time using a UV–Vis spectrophotometer to determine the photo-crosslinking and photo-de-crosslinking kinetics. A Cary 50-Bio UV–Vis spectrophotometer (Varian) was modified to allow irradiation of samples perpendicular to the instrument beam, thereby allowing real-time tracking of changes in the UV–Vis absorbance of the samples as they were irradiated using either an EXFO Acticure 4000 light source via a liquid light-guide attenuated to 83 mW/cm^2 (measured at 365 nm) for crosslinking or a UVP Pen-Ray at 0.3 mW/cm^2 (measured at 254 nm) for de-crosslinking.

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