Synthesis of Cinnamoyl and Coumarin Functionalized Polycarbonates

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Introduction

Polycarbonates

Aliphatic polycarbonates are promising biomaterials due to their nonacidity, degradability and tunable properties. By combining specific monomers, the hydrophobicity, degradability, viscoelasticity, and other properties can be easily tailored. Commercially available monomers include trimethylene carbonate (TMC) and a wide variety of carbonate monomers (>30) have been synthesized for use in specific applications. The relative simplicity of preparing custom carbonate monomers makes them attractive candidates for introducing specific functionality into polycarbonates and polymer networks. For example, carbonate monomers have been synthesized to introduce pendant protected hydroxyls, azides, and halides.

Triggers Properties

Polymers that can respond to external stimuli such as light or pH are of growing research interest. In particular, photo-responsive materials have been extensively explored using groups such as 2-nitrobenzyl, anthracene, cinnamoyl and coumarin. These groups are often incorporated along polymer backbones, so that exposure to an appropriate wavelength of light causes the polymer to disintegrate. However, the incorporation of cinnamoyl and coumarin moieties as pendant groups would result in polymers where the crosslinking can be reversibly modified as shown in Figure 1.

Experimental

All reagents were obtained from commercial suppliers and used as received, except triethylamine (TEA) and tetrahydrofuran (THF) which were stored over 4 Å molecular sieves prior to use. Polymerization kinetics were studied by monitoring the polymerization in real-time using a 500 MHz Bruker NMR spectrometer. Differential scanning calorimetry (DSC) was conducted using a Mettler Toledo DSC1 System and the samples were monitored through two heating cycles (-40°C to 120°C) at 10°C/min. The glass transition temperature was determined from the second heating cycle. A Cary 50 Bio UV-Vis spectrophotometer (Varian) was used for UV-Vis absorbance studies.

Results

Synthesis

In this study, several cinnamoyl and coumarin functionalized cyclic carbonate monomers were prepared utilizing various functional groups as linkages as they can affect the ease of monomer preparation, the stability of the monomers and resulting polymers, and the photochemistry of the photoactive groups. With the exception of 1, this is the first reported synthesis of each monomer. The synthesis of 1 was previously reported with an overall yield of 33%, which was nearly doubled to 65% in this study (Figure 2).

Polymerization Kinetics

Next, the polymerization kinetics of the monomers were examined. It was hypothesized that the bulky cinnamoyl and coumarin groups would slow the polymerization rate relative to TMC by stabilizing the carbonate ring as had previously been reported for large alkyl substituents. Surprisingly, 1 and 3 polymerized significantly faster than TMC (Figure 7).

Conclusions

In this study, several cinnamoyl and coumarin functionalized cyclic carbonate monomers were synthesized. Polymerization studies on these monomers identified that the functional groups present have a more significant impact on the polymerization kinetics than the size of the pendant group. The size of the alkyl substituent is only relevant when comparing the kinetics of monomers with equivalent functionality. In addition, the reversibility of the photo-crosslinking was examined under various conditions.

References