Thermal decomposition of poly(propylene carbonate): End-capping, additives, and solvent effects

Oluwadamilola Phillips, Jared M. Schwartz, Paul A. Kohl[*]

School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA, 30332-0100, USA

ABSTRACT

Two routes to the thermal decomposition of poly(propylene carbonate) (PPC) have been considered-polymer chain-end unzipping and random chain scission. The inhibition and catalysis of each mechanism has been studied. End-capping of low molecular weight (2 kDa) PPC has been achieved and confirmed with NMR analysis resulting in stabilization from unzipping. Citric acid was used as an additive and shown to stabilize the PPC backbone from random chain scission. The combination of both stabilizing agents (i.e. unzipping and ransom chain scission) results in the highest thermal stability. Photo-acid and base generators were incorporated into films and used to catalyze decomposition pathways of PPC. Residual solvent effects in PPC, such as methanol used in its purification, have been shown to affect the thermal stability through interactions with the backbone of PPC. This study demonstrates a widened thermal stability window for PPC, such as when used as a sacrificial material.

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1. Introduction

Poly(propylene carbonate) (PPC) is an amorphous, aliphatic polymer synthesized by the copolymerization of propylene oxide and carbon dioxide with an organometallic catalyst, typically zinc glutarate [1–7]. The polymer is attractive because it is made by the fixation of CO_2, and it is biodegradable and biocompatibile [8]. The low glass transition temperature makes PPC suitable for low-temperature packaging applications. The glass transition temperature of PPC can range from 25 °C to 45 °C depending on molecular weight and regioregularity of the polymer. Molecular weights ranging from 15 kDa to 200 kDa have previously been produced in commercial quantities. Recently lower molecular weight of 2 kDa PPC Polyol has been synthesized [9].

PPC has a relatively low onset temperature for decomposition, widely reported in the range from 180 °C to 240 °C depending on heating rates [5,10–13]. The low decomposition temperature makes it ideal for specific sacrificial polymer applications in microelectronics, especially those involving solder, epoxy, and movable components such as microelectromechanical systems (MEMS). The movable MEMS component can be encapsulated by a sacrificial polymer and a photo-definable dielectric as the overcoat

in order to protect the movable component during processing. Later, a thermal treatment can be used to decompose the PPC and volatize the products, which diffuse through the overcoat, freeing the movable component in an air-cavity [14–17].

A critical step in the fabrication process is controlling the thermal decomposition of PPC, so that the MEMS device is released at the desired point in the fabrication sequence. The thermal behavior of PPC has been studied; however, conflicting reports have led to an inadequate understanding of the thermal degradation process for PPC. A better understanding of the PPC decomposition process can lead to modification and control of the rate and temperature of polymer decomposition making for a better match of the sacrificial polymer to the overcoat material. For example, benzoyclobutene (BCB) has been used by Uzunlar et Al. as an overcoat material in the air-cavity process [17]. A thermal treatment of the polymer/BCB structure at 190 °C is done to cure the BCB and make it a mechanically stable overcoat before significant decomposition of PPC occurs. Afterwards, the temperature is increased to 240 °C to quickly decompose PPC. At 190 °C BCB needs 1.3 h to cure to 70% cross-linking density. A modest increase of 20 °C in the sacrificial polymer decomposition temperature can lower the curing time of BCB by a factor of 20 to just 4 min.

Desirable thermal properties of the sacrificial polymer that are needed for the process include: (i) thermal stability of the polymer during overcoat curing, (ii) rapid speed of decomposition at the degradation temperature, and (iii) minimal residue after

decomposition. In this paper, the mechanisms for PPC decomposition have been studied and the means for altering the PPC decomposition temperature investigated. The results are compared to previous studies to shed light on the conflicting results.

2. Background

Modifying the thermal properties requires a fundamental understanding of PPC degradation pathways. The thermal decomposition mechanisms of PPC have been previously proposed [2,8,18,19]. The polymer can be modified and additives can be added to the PPC polymer to inhibit or facilitate the decomposition. The thermal decomposition occurs via two mechanisms: (i) polymer unzipping (i.e. decomposition from the ends of the polymer chain with the reaction proceeding inward), and (ii) random chain scission (i.e. internal repeat units of the polymer randomly undergo reaction), as shown in Fig. 1a and b respectively.

In the unzipping reaction, chain ends become "active" via thermal energy and initiate a reaction with specific carbon sites across the polymer backbone, leading to degradation. Cyclic propylene carbonate is the typical product that is formed from this degradation mechanism [7,8,20]. It has been widely understood that the unzipping reaction proceeds by either an alkoxide or carbonate backbiting reaction, depending on how the polymer chain is terminated (i.e. terminated in a hydroxyl propyl or carbonate moiety). In alkoxide backbiting, a carboxylate nucleophile attacks a carbonyl carbon atom. In carbonate backbiting, the weaker nucleophile of the alcohol end-group attacks an electrophilic carbon atom from the polymer backbone. It is believed that carbonate backbiting is the most common route due to its lower activation energy [4]. Reactive hydroxyl chain ends can be rendered "inactive" in the unzipping reaction by terminating the polymer chain (i.e. "end-capping" the polymer chain) with a less reactive moiety. Dixon et al. first showed the end-capping of PPC with a variety of electrophilic organic compounds [21]. The end-cap kinetically stabilizes the polymer ends so that chain unzipping is inhibited. Although reports of PPC end-capping have appeared in the literature [10,22,23], characterization of end-capped PPC has not been well-studied because the density of polymer ends is small for high molecular weight polymers. Analysis has been mostly limited to dynamic thermogravimetric analysis (TGA). In this study, lower molecular weight PPC with a higher density of end-groups has been used to characterize the end-groups.

Chain scission is the second thermal decomposition pathway for PPC. It has higher activation energy than chain unzipping and is not very sensitive to the type of polymer end-group. Chain scission occurs through the random, thermally-induced cleavage of C–O bonds within the backbone of the polymer, generally creating
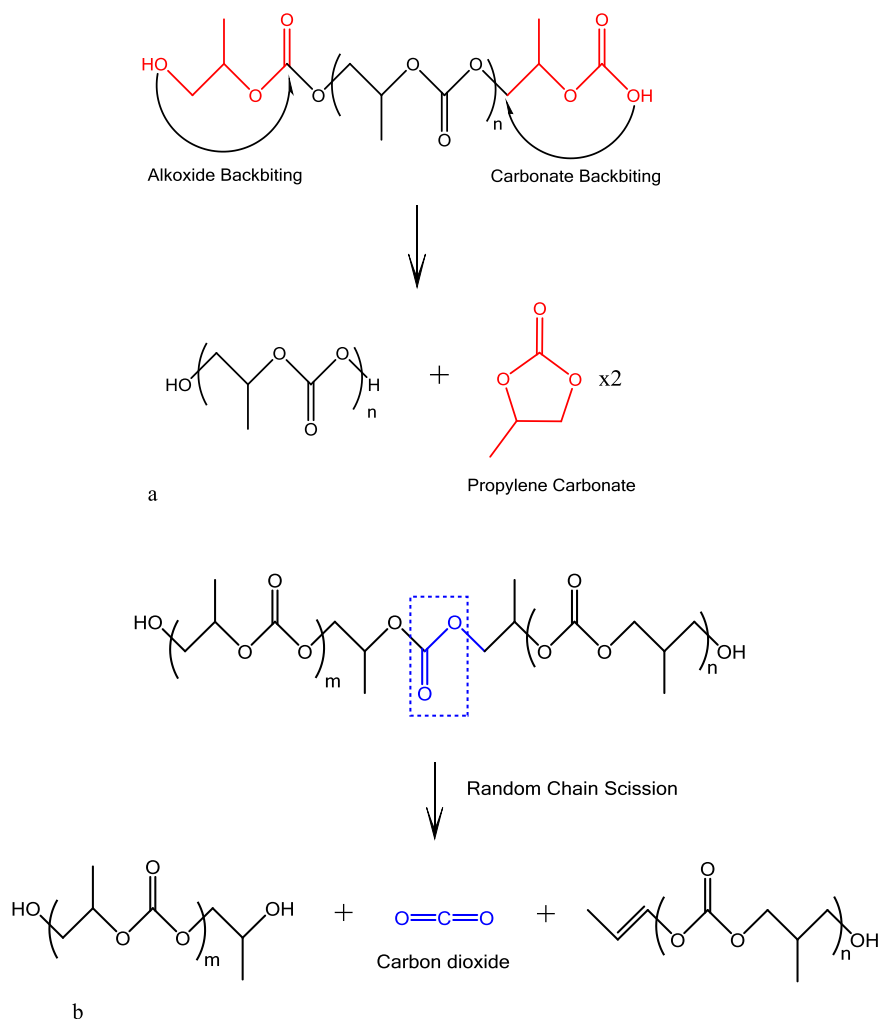
Fig. 1. a Chain unzipping reaction in PPC occurring via an alkoxide or carbonate backbiting pathway creating the cyclic propylene carbonate as the product. b Chain scission reaction in PPC via thermally induced cleavage of C–O bonds creating carbon dioxide as one of the products.