Polymer Degradation and Stability 149 (2018) 45–51

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Comments on the depolymerization of polycarbonates derived from epoxides and carbon dioxide: A mini review

Donald J. Darensbourg*

Department of Chemistry, Texas A&M University, College Station, TX, 77843, United States

ARTICLE INFO

Keywords:
Depolymerization
Carbon dioxide
Epoxides
Degradation
Recyclable

ABSTRACT

There are in general few examples where polymers can be effectively recycled to their monomers. If this situation exists, the recycling of these monomers to polymeric materials which possess identical properties and applications of their virgin monomer derived counterparts is possible. In this brief review we have examined the degradation of polycarbonates derived from carbon dioxide and epoxides to provide either their thermodynamically more stable product, the corresponding cyclic five-membered carbonate, or in special instances their return to starting monomers. A mechanistic understanding of these pathways allows for the synthesis of polymers that will favor the latter pathway.

1. Introduction

The depolymerization of polymeric materials to selectively produce their corresponding monomers is highly desirable, nevertheless generally not likely. Recently, it has been demonstrated for various polycarbonates produced *via* the coupling of CO_2 and epoxides that this is possible, thereby, showing high levels of reversible polymerization reactions under rather mild reaction conditions. Since the copolymerization of CO_2 and epoxides is emerging as a viable and potentially significant utilization of carbon dioxide, it seems appropriate to analyze current achievements in depolymerization pathways of these polymers [1–14]. Thereby, this analysis might lead to the design of polymers having the ability to be converted into their starting monomers. Consequently, this will allow for recycling of these monomers to materials possessing identical properties and uses of their virgin polymeric materials.

Our initial studies of the depolymerization of a variety of copolymers produced from CO_2 and epoxides revealed the process to proceed *via* a backbiting pathway leading to the corresponding cyclic carbonate following deprotonation of a hydroxyl end group by base (Scheme 1a) [15]. Alternatively, under special circumstances, the fate of the boxed intermediate in Scheme 1a can lead to reformation of the corresponding monomers (Scheme 1b) [16].

Prior to discussing the depolymerization pathways for copolymers produced from CO_2 and epoxides, it is useful to review the catalytic mechanism for the metal catalyzed formation of these polycarbonates. Scheme 2 depicts the commonly accepted series of steps relevant to copolymer production, where, the rds is the displaced of the growing polymer carbonate chain end by epoxide and subsequent ring-opening by anionic carbonate [17]. The living polymerization process is generally quenched by the addition of acidic methanol resulting in a hydroxyl end group. The chain growth process is explicitly described in Scheme 3, where the free polymer chain has been shown to rapidly undergo depolymerization *via* a backbiting process. The development of second-generation bifunctional (salen)MX catalysts (Fig. 1), where the salen ligand bears a covalently tethered onium salt which supplies the nucleophile for epoxide ring-opening, aids in retarding this backbiting process [18,19]. In this instance, the dissociated anionic copolymer chain maintains close contact with the metal complex *via* electrostatic interaction with the positive charge of the onium salt.

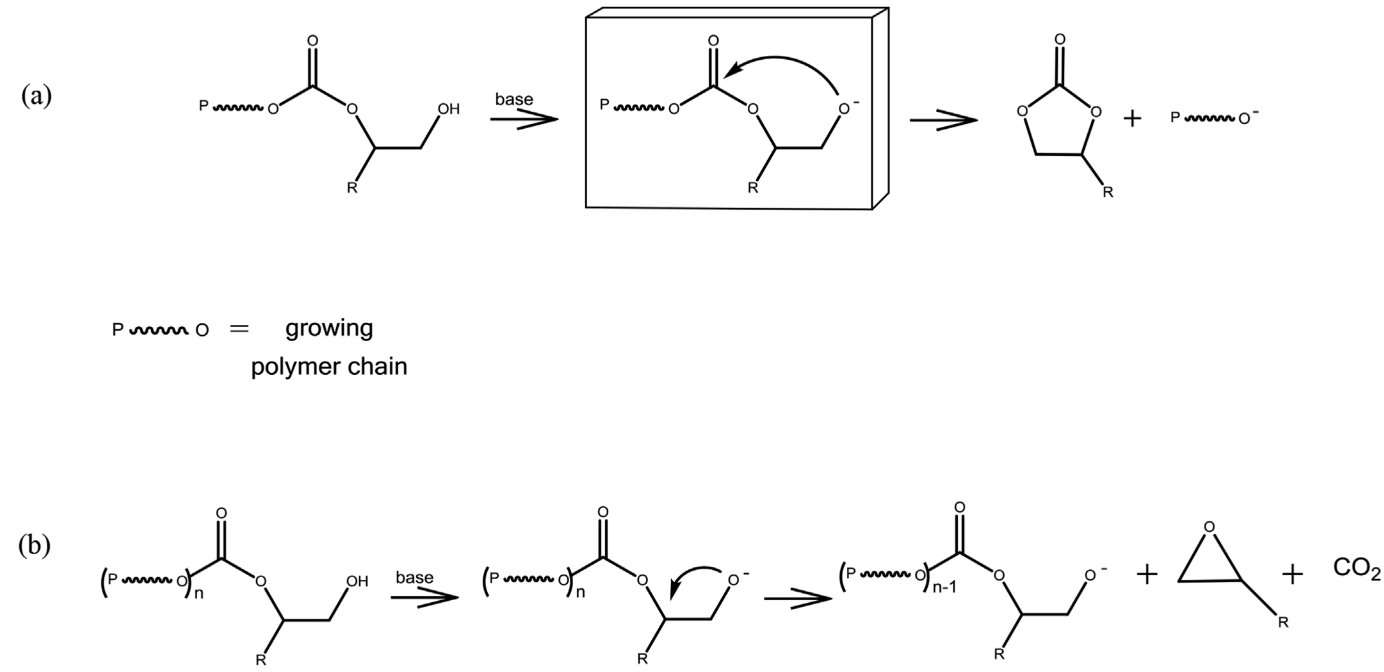
Backbiting of the metal-free anionic copolymer chain has been shown to undergo cyclic carbonate formation much faster than the metal-bound copolymer (Scheme 4). Based on computational studies, the transition state for proceeding from the open polymer chain to the tetrahedral intermediate is generally rather small, however, going from the intermediate to cyclic carbonate and the corresponding anionic polymer chain represents the activation barrier for cyclic carbonate formation (Scheme 5) [20].

Under copolymerization reaction conditions, where the CO_2 pressure is significant, the backbiting process proceeding *via* either process, i.e., metal-bound or metal-free, would be expected to occur by way of a carbonate end group. However, in the case of the degradation of an isolated copolymer with a hydroxyl end group, following deprotonation, backbiting would follow the alkoxide pathway as illustrated in Scheme 5.

Scheme 2 represents an idealized presentation of the pathway for copolymer formation in the absence of trace water or other protic

* Corresponding author.
E-mail address: djdarens@chem.tamu.edu.

https://doi.org/10.1016/j.polymdegradstab.2018.01.019
Received 18 December 2017; Accepted 18 January 2018

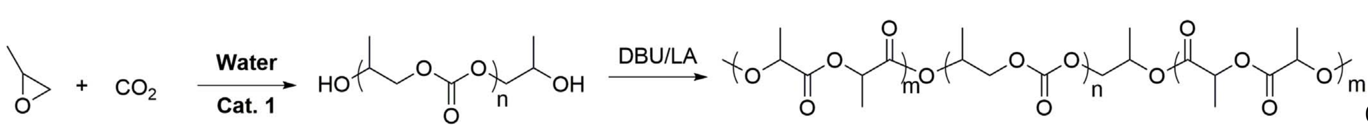


Scheme 1.

sources, where in this instance the thus formed polycarbonate is of the composition Nuc∿∿∿OH. In the presence of adventitious or added water, the copolymer consists of a bimodal distribution of Nuc∿∿∿OH and HO∿∿∿OH polymer chains due to rapid and reversible chain transfer processes, or exclusively HO∿∿∿OH depending on the quantity of added water and the nature of the initiating nucleophile. It should be noted here that the hydroxyl end groups of these copolymers can serve as macro-initiators for ring-opening polymerization (ROP) reactions with other cyclic monomers. For example, see equation (1) for the formation of a block copolymer between polypropylene carbonate and polylactide. These processes can be carried out in a two-step, one-pot process, and clearly demonstrate from the lack of any cyclic carbonate production that initiation of lactide polymerization is faster than backbiting. We have summarized our efforts in this general area for formation of a variety of block polymers employing this technique [21–23].

process monitored by *in situ* infrared spectroscopy, the depolymerization process exhibited an induction period of 10min reaction period (Fig. 2). The induction period and rate of depolymerization were observed to be highly dependent on the nature and concentration of the anion, suggestive of an equilibrium process between protonated and deprotonated polymer chains (equation (2)). Indeed, in the presence of a stong base such as sodium *bis*(trimethylsilyl)amide (NaHMDS), these depolymerization reactions exhibit *no* induction period.

In order to better define the mechanism of the depolymerization process, the molecular weight of the copolymer, along with its polydispersity were monitored as a function of time. As illustrated in Fig. 3, where the azide concentration has been greatly reduced relative to that in Fig. 2 in order to slow down the rate of depolymerization, sequential loss of cyclic carbonate was observed with little increase in molecular weight distribution which is indicative of a stepwise process as shown in Scheme 6.



(1)

The generally observed pathway for the depolymerization of polycarbonates derived from CO_2 and epoxides is formation of the thermodynamically more stable product of CO_2/epoxide coupling, the cyclic carbonate. Previously, we have examined several of these processes by way of infrared spectroscopy and size exclusion chromatography which I will describe in detail below.

Our initial study involved the depolymerization of a purified sample of well-characterized poly(styrene carbonate) which contained 99% carbonate linkages [15]. Of importance, the copolymer's molecular weight distribution was monomodal and narrow, i.e., deprotonation of the hydroxyl end groups of the copolymer chain was carried out using anions similar to those employed in the polymerization reactions. For example, in the presence of [nBu$_4$N][N$_3$] in toluene at 70 °C for a

The energy of activation barrier (E_a) for the depolymerization of poly(styrene carbonate) to styrene carbonate for reactions carried out in the presence of azide anion was determined to be 46.7 ± 2.2 (kJ/mol). This is similar to the activation barrier noted for the formation of styrene carbonate during the copolymerization of styrene oxide and CO_2 catalyzed by (salen)CoX complexes in the presence of initiating anions (50.7 kJ/mol). On the other hand, depolymerization of a pure poly(styrene carbonate) sample in the presence of n-Bu$_4$NN$_3$ and (salen)CrCl displayed a much higher E_a value of 141.2 kJ/mol. These observations taken together indicate that production of cyclic carbonates during copolymerization reactions originates from the free anionic copolymer chains as previously described.

The depolymerization of other aliphatic polycarbonates were shown