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NOTE

Copolymerization of propylene oxide and $^{13}CO_2$ to afford completely alternating regioregular ^{13}C-labeled Poly(propylene carbonate)

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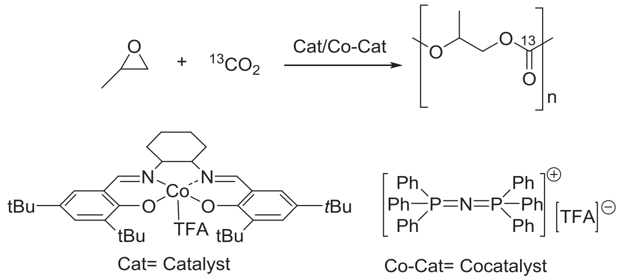
Abstract

The synthesis of poly(propylene carbonate) with 100% ^{13}C-labeled carbonate carbons is reported. The ν_{CO_3} vibration is shifted 45 cm^{-1} lower than that observed in its ^{12}C analog. This lowering of the ν_{CO_3} vibrational mode of the copolymer provides a window for observing ν_{NO} stretching motions in incorporated dinitrosyl iron complexes.

The utilization of carbon dioxide as a C1 feedstock is currently an extremely active area of interest in the chemical industry [1, 2]. One of the most successful applications of this chemistry involves the coupling of CO_2 and epoxides to produce cyclic carbonates or polycarbonates [3, 4]. Relevant to this process is the large-scale usage of carbon dioxide in the production of poly(propylene carbonate) diols for incorporation into various thermoplastic isocyanate polymers, such as polyurethanes [5, 6]. Recently, we and others have been developing the synthesis of well-defined block copolymers originating from CO_2/epoxides and their functionalization employing thiol-ene click chemistry [7–9]. In this note, we wish to report on the synthesis of poly(propylene carbonate) that is 100% ^{13}C isotopically labeled at the carbonate linkages, as well as observations on regio- and stereoregularities in the resulting polycarbonate. The motivation for preparing such a copolymer originates from our studies, which incorporate metal complexes into micelles derived from CO_2-based amphiphilic polycarbonates using chain transfer agents [10]. Some of these metal complexes possess infrared probe ligands that have vibrational modes that greatly overlap with the very intense carbonate band of the polycarbonates centered at 1750 cm^{-1}. For example, we are interested in synthesizing discrete dinitrosyl iron complexes (DNICs) contained in the hydrophobic segment of the micelle for NO drug delivery [11].

The polymerization of PO and $^{13}CO_2$ was carried out in a stainless steel reactor using an appropriate amount of the binary catalyst (salen)CoTFA/PPNTFA and PO, followed by loading the reactor with $^{13}CO_2$ at 2.5 MPa. The polymerization occurred readily at ambient temperature (Scheme 1). For comparison, two additional polymers were also synthesized under similar conditions by reacting enantiomerically pure propylene oxide (*R*-PO) with $^{13}CO_2$, as well as racemic PO with $^{12}CO_2$. All purified copolymers were characterized by ^{1}H and ^{13}C NMR spectroscopic techniques. The ^{1}H NMR spectra displayed the presence of all the peaks with matching integration, as shown in Figs. S1–S3 in the Supplementary information. Similar to earlier reports by Coates using [Co(salcy)OAc] catalysts [12], the abovementioned binary catalyst system (salen)CoTFA/PPNTFA does not produce any cyclic propylene carbonate. The expensive excess $^{13}CO_2$ can be recovered



Scheme 1 Reaction of propylene oxide and $^{13}CO_2$ to yield poly(propylene carbonate). Reaction conditions: cat/PPNTFA/PO = 1:1:1000 (TFA = $CF_3CO_2^-$), ambient temperature, 2.5 MPa, 22 h

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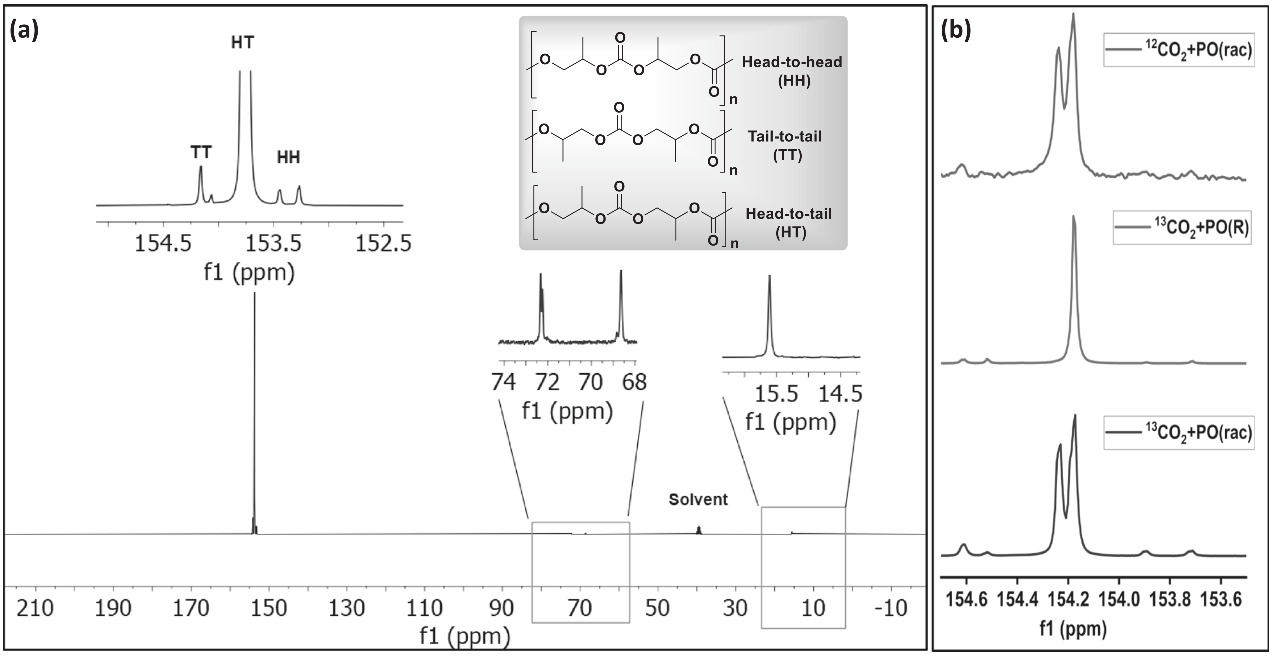

Fig. 1 **a** ^{13}C-NMR spectrum of poly(propylene carbonate) produced by coupling racemic PO and $^{13}CO_2$ using the binary catalyst (salen)CoTFA/PPNTFA. **b** Comparison of the carbonyl region in the ^{13}C-NMR spectra of all three copolymers

using a MOF-filled stainless steel column as described previously [13].

Regarding the regioregularity of the afforded copolymers, it has been reported earlier that [Co(salcy_**3**)OAc], [Co(salcy_**1**)OAc], [Co(salcy_**2**)OAc], where the 3-positions of the salcy ligands are **1** = Br, **2** = H and **3** = ^{t}Bu, and [Zn(BDI)OAc] were found to have regioregularities of 80%, 70%, 75%, and 60%, respectively [12, 14, 15]. Coates and coworkers later investigated [(salcy)CoX] (where X = either a halide or acetate anion) along with ionic cocatalysts, which yielded highly regioregular polycarbonates having up to 99% carbonate linkages with 94% head-to-tail connectivity [16]. A poly(propylene carbonate) with high regio- and stereo-selectivity has also been reported by Lu and coworkers from racemic propylene oxide using unsymmetrical chiral (salen) Co(III) complexes [17]. The ^{13}C-NMR spectra of the polymers we report here revealed preferential formation of head-to-tail regioisomers with very small proportions of the other linkages, such as HH (head-to-head) and TT (tail-to-tail) linkages, as shown in Fig. 1 and Supplementary information.

The formation of these copolymers was further confirmed by recording their FT-IR spectra in dichloromethane. The infrared spectra revealed that the carbonyl absorption peak, which generally occurs at ~1750 cm^{-1} in the case of polycarbonates, as expected, shifted to lower wavenumbers upon using $^{13}CO_2$ instead of $^{12}CO_2$ during the copolymerization reaction (Fig. 2). The carbonate absorption occurred at 1706 cm^{-1}, which is ~45 cm^{-1} lower than that in $^{12}CO_2$-derived polycarbonates. The main advantage of this shift can be exploited to observe different functional groups in functionalized polycarbonates that exhibit absorbances in this region. This is illustrated in Fig. 3 for the nitrosyl stretches in a typical DNIC complex. The molecular weights of these

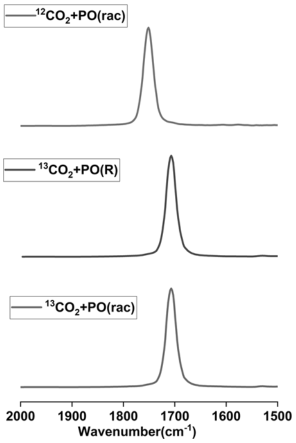

Fig. 2 FT-IR spectra of copolymers produced by the coupling of PO and carbon dioxide

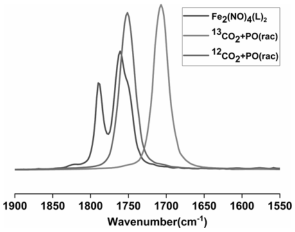

Fig. 3 Comparison of FT-IR spectra of copolymers in the carbonate region and the nitrosyl region of a typical DNIC complex

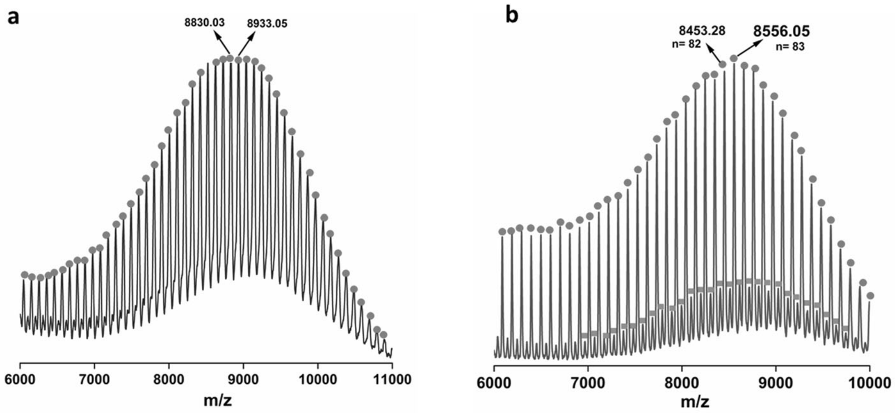

Fig. 4 MALDI-ToF spectrum of a copolymer produced by coupling of (**a**) *rac*-PO with $^{13}CO_2$ and (**b**) *R*(+) PO with $^{13}CO_2$. Both spectra show a separation of 103, characteristic for the incorporation of labeled $^{13}CO_2$. The major signals are assigned to the copolymer initiated by $CF_3CO_2^-$, with the minor peaks being due to the presence of water as the chain-transfer agent

Table 1 Polymers obtained during the copolymerization of PO, R(+) PO and $^{13}CO_2$

Polymer	Mn	Mw	PDI	FT-IR CO ν values
Racemic PO and $^{13}CO_2$	38,100	51,400	1.34	1706
R(+)PO and $^{13}CO_2$	13,500	14,600	1.07	1706
Racemic PO and $^{12}CO_2$	35,000	40,800	1.20	1751

copolymers were obtained by gel permeation chromatography, and the results of these GPC traces (Fig. S6) are summarized in Table 1.

To better understand the structure of the polymers produced during this polymerization, copolymer samples were subjected to MALDI-ToF analysis. The MALDI-ToF spectrum (Fig. 4) of the copolymers produced during coupling of racemic PO and *R*(+)PO with $^{13}CO_2$ shows a separation of 103, which corresponds to the repeating unit of these polymers. In addition, it is of interest to note that the T_g of isotactic poly(propylene carbonate) is 3 °C lower than its stereoirregular analog (Fig. S7 in Supplementary information).

In summary, we successfully synthesized polypropylene carbonates by coupling PO with $^{13}CO_2$ instead of $^{12}CO_2$ for the first time and characterized these polymers by different spectroscopic techniques. The binary catalyst system (salen) CoTFA/PPNTFA selectively formed regioregular polycarbonates with no cyclic byproducts. ^{13}C-NMR studies revealed that the polymers formed were regioselective with preferential head-to-tail connectivity. We further demonstrated how the carbonyl absorptions in the FT-IR spectra of these polycarbonates can be shifted to lower wavenumbers using $^{13}CO_2$ instead of the routinely used $^{12}CO_2$. This concept can be exploited to visualize the functional groups in functional polycarbonates with infrared absorbance in this region.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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