



Synthesis of oligo(carbon dioxide)

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ARTICLE INFO

Keywords:

Carbon dioxide
Oligomerization
Synergetic catalysis
Mild conditions

ABSTRACT

For the first time, we reported the preparation of the oligomer of carbon dioxide. The oligomerization of carbon dioxide was carried out with the aid of the synergetic catalysis of 1,8-diazabicyclo(5, 4, 0)undec-7-ene (DBU) and quaternary salt of water-soluble chitosan (QWSC), which was conducted at 75 °C for 24 h by using petroleum ether as dispersing medium. The product was separated and purified through repeated dissolution-precipitation by using dichloromethane, petroleum ether and distilled water as solvents and precipitant respectively. Fourier transform infrared spectroscopy (FTIR), fluorescence spectroscopy, carbon nuclear magnetic resonance (¹³CNMR), and MALDI-TOF spectrometry (MS) was applied to characterize the product. The results confirmed that the obtained product was the expected oligomer of CO₂, linear H-(O-CO)₁₇-H and cyclic (O-CO)₁₃ containing DBU-like group.

1. Introduction

Recently, much attention has been paid to employ carbon dioxide as C1 source to synthesize chemical substances [1–3]. To this end, various catalysts, active reagents and energy-consuming conditions are the common adopted means. So far, most of the reported CO₂-based polymers are the copolymers derived from carbon dioxide and epoxide and prepared in the presence of catalysts [4].

In fact, carbon dioxide is an unsaturated compound. It may polymerize under suitable conditions. Iota and his cooperators have reported a quartzlike solid generated from CO₂. However, its preparation conditions are as extreme as the pressure and temperature are 40 GPa and 1800 K respectively [5]. Rodig et al. have synthesized a cyclic trimer of CO₂ through four-step synthesis, but its starting material is not carbon dioxide at all. Besides, the trimer only exists at the temperature lower than –40 °C [6]. To our best knowledge, no other research about the oligomerization or polymerization of CO₂ has been reported until now. CO₂ is so inert that it is hard to be polymerized. As well known, suitable catalyst is useful to overcome the barrier. For instance, Tsutsumi et al. have applied a bifunctional catalyst to activate the coupling of carbon dioxide with epoxide. As a result, the reaction can be performed under 1 MPa [7]. Herein, we present a facile approach to carry out the oligomerization of carbon dioxide, which is attributed to taking advantage of a synergetic catalyst.

2. Experimental section

2.1. Materials

Water-soluble chitosan was obtained through physically treating chitosan [8]. Quaternary salt of water-soluble chitosan (QWSC) was prepared by reacting 1% WSC aqueous solution with 20 mL 2,3-epoxypropyltrimethylammonium chloride (weight ratio between WSC and salt is 1:3) at 75 °C for 48 h. QWSC was harvested by precipitating the reaction mixture from ethanol, filtered and dried. The quaternary-group amount of QWSC equaled to 2.84 mmol/g, which was determined by conductometric titration. Carbon dioxide gas (99.9%), 1,8-diazabicyclo(5, 4, 0)undec-7-ene (DBU, analytical grade), petroleum ether (60–90 °C, 90–120 °C, analytical grade) and dichloromethane (analytical grade) were all purchased domestically and used as received.

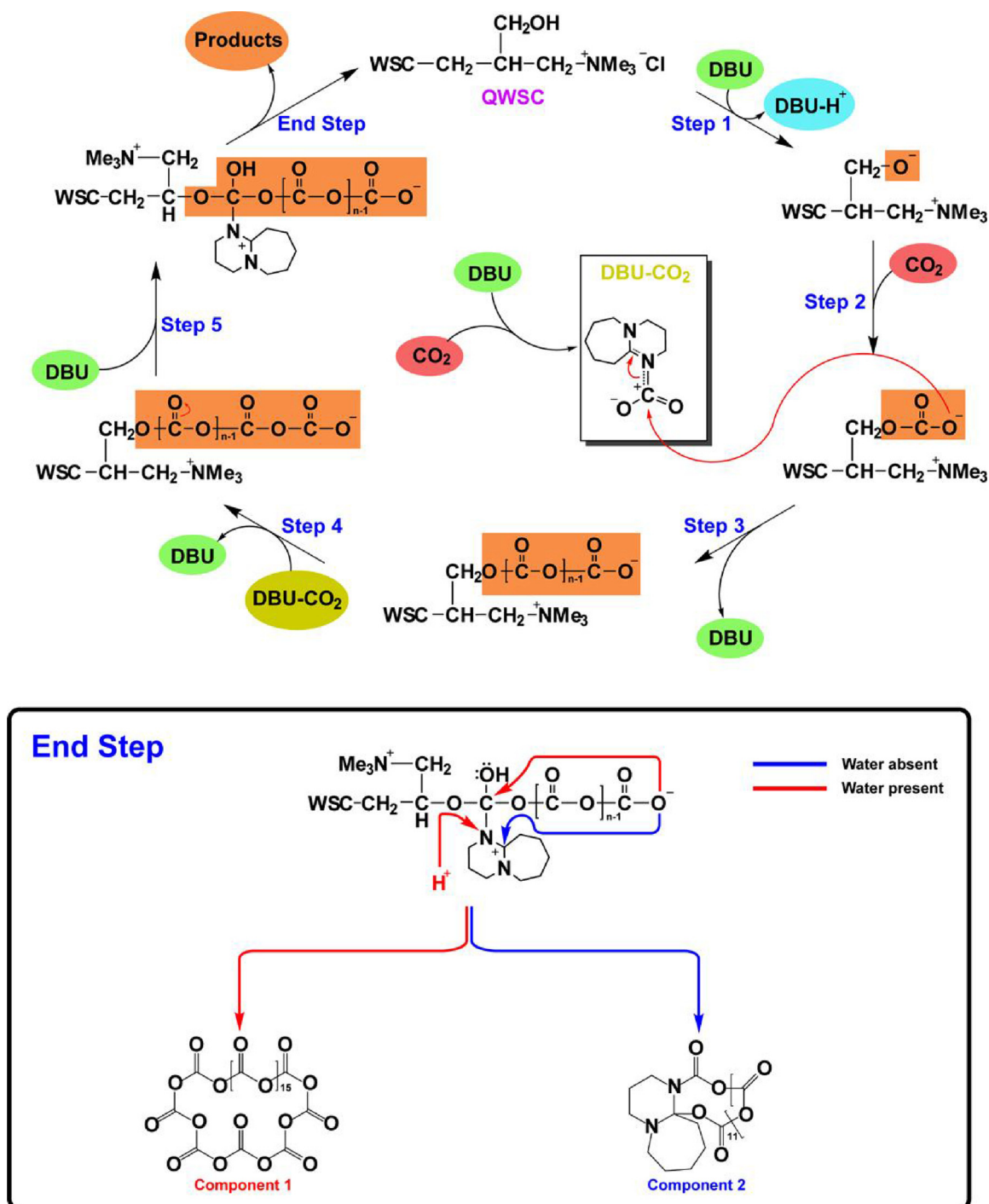
2.2. Synthesis of oligomer of CO₂

The oligomer was prepared in the following process. Five millilitres DBU, 0.1 mL water and 50 mL petroleum ether (90–120 °C) was mixed in a three-neck bottle with magnetic stirring. CO₂ gas was introduced and the mixture was kept at room temperature for 2 h. Another 1 mL DBU and 0.5 g QWSC was added and the bottle was filled with the gas again. Then, the mixture was kept at 75 °C under stirring for 24 h.

The solid phase of the mixture was separated and washed with petroleum ether (60–90 °C) to remove most of DBU. The raw product was dissolved with 10 mL dichloromethane from the solid phase. Most

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Scheme 1. Designed polymerization route of carbon dioxide.

of dichloromethane and a little petroleum ether were removed by distilling at 60 °C. The remained petroleum ether was removed and blew with CO₂ gas to examine whether it became turbid or not. The raw product was dissolved with 5 mL dichloromethane, precipitated from 20 mL petroleum ether (60–90 °C) and separated out as mentioned above. This purification process was repeated for 5 times. In order to completely purify the product, the obtained raw product was dissolved in dichloromethane and extracted with distilled water. The dichloromethane-phase was subjected to distilling for removal of the solvent, the purified product was dried in vacuum and its yield was 98.47 mg. The control experiment was performed by replacing CO₂ gas with N₂ under the same conditions.

2.3. Characterizations

Fluorescence profiles of the solutions of the product and DBU were recorded using a HITACHI F-7000 FL Spectrophotometer. The excitation wavelength was 300–600 nm and the emission wavelength was between 300 and 800 nm at a scan speed of 1200 nm/min. Fourier transform infrared (FTIR) spectroscopy of the product was recorded using a Nicolet iS50 FTIR spectrometer. MALDI-TOF mass spectrometry of the product was analyzed with a Bruker AutoHex III instrument in reflecting positive ion mode by using alpha-cyano-4-hydroxycinnamic acid (CHCA) as matrix. The outlet and detection voltages were 19 and 1.7 kV respectively, and the wavelength of the nitrogen laser was

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