

# A new amino-alcohol originated from carbon dioxide and its application as chain extender in the preparation of polyurethane

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## ARTICLE INFO

### Keywords:

CO<sub>2</sub>  
Five-membered cyclocarbonate  
Polyurethane urea  
Chain extender  
Water/solvents resistance

## ABSTRACT

In this work, CO<sub>2</sub> was chemically fixed by reacting with 1, 4-butanediol diglycidyl ether in the presence of a basic polystyrene resin catalyst. Under the 100% conversion of 1, 4-butanediol diglycidyl ether, five-membered cyclocarbonate with a selectivity of 98.5% was obtained. The cyclocarbonate was then reacted with an excess of 1, 2-ethylenediamine and the product was characterized by Fourier transform infrared spectrometer and nuclear magnetic resonance spectrometer. The results confirmed the successful synthesis of –NH<sub>2</sub> terminated product with a selectivity of 98.9%, accompanied by the formation of hydroxyls on β-C to the carbonyl groups, which can be regarded as a new amino-alcohol. Further, the obtained amino-alcohol was applied for the preparation of polyurethane urea as chain extender in a prepolymer way. Since the reactivity of isocyanate with –NH<sub>2</sub> is much faster than that with –OH, the –OH groups can be maintained in the system and hence strengthen the hydrogen bonding in polyurethane urea, which endows the materials with some unique properties. Comparing with the polyurethanes yielded from 1, 6-hexanediamine and 1, 6-hexanediol, polyurethane urea synthesized from the new amino-alcohol possessed better water/solvents resistance, considerable mechanical and thermal properties.

## 1. Introduction

As one of the most abundant greenhouse gases, the increasing amount of CO<sub>2</sub> in our atmosphere may not only result in serious environmental problems, but also lead to a pronounced change in our ecosystem because some plant species are sensitive to CO<sub>2</sub> concentration [1]. Therefore, urgent actions are required to control and minimize the emission of CO<sub>2</sub>. However, on the other hand, CO<sub>2</sub> has various advantages such as nontoxic, cheap, abundant, reproducible and non-flammable [2,3]. The effective utilization of CO<sub>2</sub> could alleviate problems mentioned above to some extent. Several fixation ways of CO<sub>2</sub> have been explored in the fields of solar fuel, mineralization, polymer synthesis, biological utilization and so on [4].

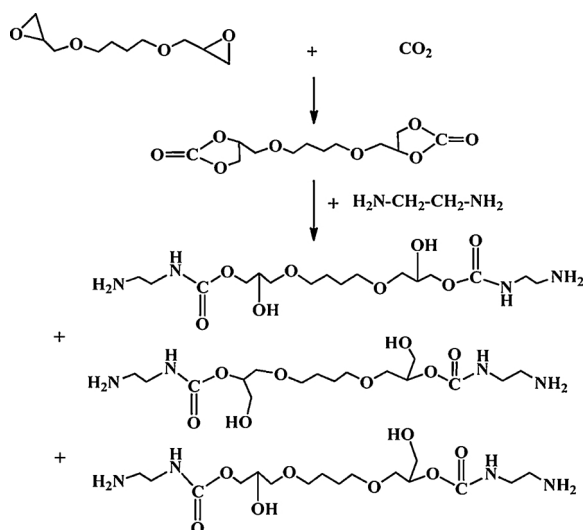
One strategy for CO<sub>2</sub> usage is the synthesis of polymers. The introduction of CO<sub>2</sub> into polymer molecular structures to increase their added value is an attractive topic. Poly(propylene carbonate), fundamental polymer-poly(1, 2-glycerol carbonate) and some other polymers were successfully synthesized from CO<sub>2</sub> [5–7]. Particularly, the usage of CO<sub>2</sub> in synthesizing polyurethanes (PUs), as a material with excellent performances, has recently arisen as an active field. Prakash Alagi, for

instance, reported a carbon dioxide-based polyol as a sustainable feedstock of thermoplastic polyurethane for corrosion-resistant metal coating [8]. Wang Jin presented a superior oxidation and hydrolysis-resistant waterborne PU synthesized from CO<sub>2</sub>-based polyols, and compared it with the common used polyether and polyester based polyols [9].

Another effective way of utilizing CO<sub>2</sub> in PU preparation is the polymerization between amines and cyclocarbonates. The latter can be obtained through the cycloaddition between CO<sub>2</sub> and epoxides. Since no isocyanate was used during the whole process, this method was regarded as a non-isocyanate route for PU preparation. However, the products polyhydroxylurethanes (PHU) exhibited poor mechanical properties because of fairly low molecular weight and cross-linking degree among the main chain [10]. Various modifications have been adopted to improve the mechanical performances of PHU. For instance, Figovsky and his coworkers brought bisphenol resins to react with several aliphatic and aromatic cyclocarbonates, obtaining PHU hybrid coating with better performances [11,12].

Besides issues mentioned above for the utilization of CO<sub>2</sub> in PU synthesis, CO<sub>2</sub> can also be fixed in PU as chain extender. Enlightened by

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**Scheme 1.** Scheme of preparation of amino-alcohol chain extender from 1, 4-butanediol diglycidyl ether, carbon dioxide and 1, 2-ethylenediamine.

the PHU preparation method, we speculated that the reaction between cyclocarbonate and excessive diamines could result in  $\text{-NH}_2$  terminated compound accompanied with the formation of hydroxyl on  $\beta\text{-C}$  atom, which might be used as chain extender in PU preparation like the commonly used 1,4-butanediol or 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) [13–15]. Because of the faster reaction rate between isocyanate and  $\text{-NH}_2$  than that with  $\text{-OH}$ , the  $\text{-OH}$  can be maintained in polyurethane urea (PUU) and strengthen the hydrogen bonding interaction. In addition, the hydroxyl groups can also react with some residual isocyanate and increase the cross-linking density of PUU correspondingly. All above mentioned aspects are helpful for the improvement of mechanical or other properties of formed PUU material.

Herein, 1, 4-butanediol diglycidyl ether (BDODGE) was reacted with  $\text{CO}_2$  and transformed into five-membered cyclocarbonate (BDODGE-5CC) as shown in Scheme 1. Then BDODGE-5CC was reacted with an excessive amount of 1, 2-ethylenediamine (EDA) and converted to  $\text{-NH}_2$  terminated amino-alcohol compound. Finally, the amino-alcohol was reacted with  $\text{-NCO}$  terminated prepolymer and produced the PUU materials. Structures of BDODGE-5CC and amino-alcohol were confirmed by FT-IR,  $^1\text{H}$  NMR and elemental analysis. Performances of the acquired PUU were investigated by mechanical test, water and solvents resistance test, thermogravimetry (TG), dynamic mechanical analysis (DMA), contacting angles and so on. Moreover, 1, 6-hexanediamine (HDA) and 1, 6-hexanediol (HDO), the typical  $\text{-NH}_2$  and  $\text{-OH}$  terminated chain extenders, were used for PUU and PU preparation. The compared results showed that the novel amino-alcohol could endow the PUU with better water and solvents resistance, considerable mechanical and thermal properties.

## 2. Experimental

### 2.1. Materials

1, 2-ethylenediamine (EDA), *N,N*-dimethyl formamide (DMF), 1,6-hexanediol (HDO) and 1,6-hexanediamine (HDA) were purchased from Aladdin Chemistry Co., Ltd. 1, 4-butanediol diglycidyl ether (BDODGE) was supplied by Wuhan Yuanchen technology Co., Ltd. 4, 4-diphenylmethane diisocyanate (MDI) was prepared by Yantai Wan Hua Co., Ltd. Polytetramethylene ether glycol (PTMG) with molecular weight of 1000 g/mol was supplied by Yantai Huada chemical industry Co., Ltd. The basic polystyrene resin (D296) was purchased from Tianjin Resin Technology Co., Ltd. Carbon dioxide ( $\text{CO}_2$ ) was supplied by Chinese

Academy of Sciences. All the raw materials were used as received without further purification.

### 2.2. Preparation of 1, 4-butanediol diglycidyl ether cyclic carbonate from carbon dioxide and 1, 4-butanediol diglycidyl ether

The five membered bis(cyclic carbonate) BDODGE-5CC was prepared by cycloaddition reaction between  $\text{CO}_2$  and BDODGE. A portion of BDODGE (100.00 g, 0.50 mol), basic polystyrene resin catalyst D296 (10.00 g) was charged into a high pressure autoclave. After purging by  $\text{N}_2$  for 10 min and heating to  $120^\circ\text{C}$ ,  $\text{CO}_2$  was pressurized into the autoclave and maintained at 10 bar for 30 h under stirring. Then, the reaction mixture was filtrated to separate the catalyst and the formed BDODGE-5CC. Structure of the product was confirmed by FT-IR and  $^1\text{H}$  NMR spectroscopy. Conversion of BDODGE was determined by chemical titration of the epoxy group and further confirmed by  $^1\text{H}$  NMR. Selectivity of the reaction was confirmed based on  $^1\text{H}$  NMR spectra of BDODGE and BDODGE-5CC, too.

### 2.3. Preparation of the amino-alcohol from 1, 4-butanediol diglycidyl ether cyclic carbonate and 1, 2-ethylenediamine

BDODGE-5CC (50.00 g, 0.17 mol) and EDA (41.38 g, 0.69 mol) were added into a four-necked round-bottom flask equipped with thermometer, mechanical stirrer, refluxing condenser and feeding inlets. In order to ensure the thorough conversion of BDODGE-5CC, twice as theoretical necessitated EDA was added and the reaction was performed at  $90^\circ\text{C}$  for 6 h. After that, the reaction system was cooled to  $70^\circ\text{C}$  and maintained for 8 h under vacuum to remove the unreacted EDA. The synthesized  $\text{NH}_2$ -terminated chain-extender (BDAMAL) was characterized by  $^1\text{H}$  NMR and FT-IR. The preparation of chain extender from BDODGE,  $\text{CO}_2$  and EDA can be seen in Scheme 1.

### 2.4. Preparation of polyurethane urea films

The PUU and PU films were formulated from PU prepolymer (S1) cured with different kinds of chain-extenders as shown in Scheme S1 [16]. Stoichiometric amount of prepolymer with chain-extender was calculated as Eq. (1). DMF was used as solvent to dilute the reactants and prohibit the system from gelation during reaction process. Subsequently, the liquid reaction mixture was poured into polytetrafluoroethylene mold, and then the solvent DMF was evaporated under infrared light for 2 h. Finally, after above synthesis, the completely cured and uniform PUU and PU film were obtained.

$$m_{\text{BDAMAL}} = \frac{m_{\text{p}} \times (\text{-NCO})\%}{42} \times 0.9 \times M_{\text{BDAMAL}} \quad (1)$$

\*In Eq. (1),  $m_{\text{BDAMAL}}$ ,  $m_{\text{p}}$ ,  $M_{\text{BDAMAL}}$  are the mass of chain extenders, the weight of prepolymers and the molecular weight of chain extenders, respectively.

### 2.5. Characterization and analysis

FT-IR spectra of raw materials and products were obtained with an NICOLET-380 Fourier transform infrared instrument (Thermo Electron Co., Ltd. Massachusetts, USA) and their molecular structures were further confirmed on a Bruker Avance 400 MHz spectrometer and Bruker AVANCE III 600 MHz Wide Bore spectrometer (Bruker Spectrospin, Rheinstetten, Germany).

Resistance to chemical solvents and water absorption were evaluated by the soaking method. Approximately 0.20 g films were immersed in different organic solvents and water solutions of 5.0 wt% HCl and 5.0 wt% NaOH until equilibrium was attained at  $25^\circ\text{C}$ , respectively.

The contact angles (CAs) were measured at  $25.0 \pm 0.1^\circ\text{C}$  using a DSA25 drop shape analyzer (KRÜSS GmbH, Hamburg, Germany) and

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