



Research paper

Synthesis of polyurea from 1,6-hexanediamine with CO₂ through a two-step polymerization

Shan Jiang^{a,b,c}, Ruhui Shi^{b,c}, Haiyang Cheng^{b,c,**}, Chao Zhang^{b,c}, Fengyu Zhao^{a,b,c,*}^a School of Chemical Engineering, Changchun University of Technology, Changchun 130012, China^b State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, China^c Jilin Province Key Laboratory of Green Chemistry and Process, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

Received 28 March 2017; revised 2 May 2017; accepted 9 May 2017

Available online ■ ■ ■

Abstract

Activation and transformation of CO₂ is one of the important issues in the field of green and sustainable chemistry. Herein, CO₂ as a carbon-oxygen resource was converted to CO₂-polyurea with 1,6-hexanediamine through a two-step polymerization. The reaction parameters such as temperature, pressure and reaction time were examined; and several kinds of catalysts were screened in the absence and presence of NMP solvent. The formed oligomer and the final polyurea were characterized by FT-IR, VT-DRIFTS, NMR, XRD, AFM and their thermal properties were examined by TGA and DSC. It was confirmed that the final polyurea has a high thermal stability; the melting temperature is 269 °C and the decomposition temperature is above 300 °C. It is a brittle polymer with a tensile strength of 18.35 MPa at break length of 1.64%. The polyurea has a stronger solvent resistance due to the ordered hydrogen bond in structure. The average molecular weight should be enhanced in the post-polymerization as the appearance, hydrogen bond intensity, crystallinity, melting point and the thermal stability changed largely compared to the oligomer. The present work provides a new kind of polyurea, it is expected to have a wide application in the field of polymer materials.

© 2017, Institute of Process Engineering, Chinese Academy of Sciences. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co., Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Keywords: CO₂; Polyurea; Two-step polymerization; Catalysis

1. Introduction

As a green house gas, CO₂ is mainly emitted from the burning process of fossil fuels. The rapid increase of CO₂ in ambient air may build up an irreversible and uninhabitable earth in the near future. However, increasing the energy supply while reducing CO₂ emission simultaneously is the major

mission we are facing today. Therefore, the transformation of CO₂ to fuels, high value-added chemicals and materials is one of the important research topics from the viewpoints of environmental and green chemistry, and it has attracted more attention in this decade. Until now, some results have been achieved in the transformation of CO₂ to the high value-added chemicals such as methanol [1–4], acetic acid [5–8], alkyl carbonate [9–12], cyclic carbonate [13–15], carboxylic acid [16–19], urea derivatives [20–23], polycarbonate [24–27], polyurethane [28–31] and polyurea [32–36]. Polyurea is a useful polymer which has been widely applied in coating and adhesive in construction because of its superior mechanical properties [37]. The potent bidentate bonds in polyurea give the polymer much stronger mechanical properties than its analogs. However, the commercial polyurea is usually

* Corresponding author. School of Chemical Engineering, Changchun University of Technology, Changchun 130012, PR China. Fax: +86 431 85262410.

** Corresponding author. State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, PR China. Fax: +86 431 85262454.

E-mail addresses: hycyl@ciac.ac.cn (H. Cheng), zhaofy@ciac.ac.cn (F. Zhao).

<http://dx.doi.org/10.1016/j.gee.2017.05.001>

2468-0257/© 2017, Institute of Process Engineering, Chinese Academy of Sciences. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co., Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Please cite this article in press as: S. Jiang, et al., Synthesis of polyurea from 1,6-hexanediamine with CO₂ through a two-step polymerization, Green Energy & Environment (2017), <http://dx.doi.org/10.1016/j.gee.2017.05.001>

synthesized from diisocyanate [38], which is harmful to environment and human health. Therefore, environmental friendly method which avoids the use of toxic chemicals is very imperative. Several nonisocyanate routes to synthesize polyureas were developed [39,40]. Among them the most promising one is using CO₂ as carbonyl building block to replace isocyanate, which has attracted great attention in this decades. The transformation of CO₂ directly with diamine to polyurea was firstly reported by Yamazaki et al., and they prepared polyureas from aromatic diamines with CO₂ by using stoichiometric amount of phosphate as catalyst [41,42]. More recently, we synthesized several kinds of polyureas by polymerization of diamine with CO₂ directly in the absence of any additives, such as water soluble oligourea [33], macrocyclic oligourea [34], thermoplastic polyurethane-ureas [35], polyurea hydrophobic gel [36]. The polymerization of diamine with CO₂ is a kind of condensation polymerization, in which water will be produced as a by-product, which can retard the polymerization, leading to a relative lower molecular weight. Herein, we synthesized a new kind of polyurea with using 1,6-hexanediamine (HDA) and CO₂ through a two-step method, in which water was removed in order to increase the molecular weight. Moreover, the reaction conditions such as temperature, pressure, reaction time and catalyst, as well as solvent were discussed for the first step of oligomer preparation. The polyurea was synthesized by the post-polymerization of oligomer with CO₂. As expected, the molecular weight of the polyurea would be improved for its properties changed largely compared to the oligomer. The present synthesized polyurea is expected to have a wide application in the field of polymer materials.

2. Experimental section

2.1. Materials

All of the chemicals were used as received without further purification. HDA was purchased from Aladdin Reagent Co. Ltd.; CsOH and Bu₄P·Br were purchased from Macklin Biochemical Co. Ltd.; CeO₂ was purchased from Sinopharm Chemical Reagent Co. Ltd.; NaOH and 1-Methyl-2-pyrrolidinone (NMP) were purchased from Beijing Chemical Reagent Co. Ltd.; ZnO was purchased from Huadong Reagent Co. Ltd.; Cs₂CO₃ was purchased from Wako Pure Chemical Industries. Ltd.; and Carbon dioxide (CO₂) and N₂ gas were purchased from Changchun Juyang Gas Company.

2.2. Synthesis of oligomer

For the synthesis of oligomer, a 100 mL stainless steel autoclave with mechanical stirrer was used. In a typical experiment, 40 g HDA was introduced into 100 mL autoclave, flushed with N₂ three times to remove the air, then CO₂ was introduced into the autoclave up to 11.5 MPa when it was heated to 180 °C. The reaction was proceeded for 6 h under strong stirring. After that, the autoclave was cooled down to room temperature, the products were collected and washed by

water to remove the intermediate of carbamate, the solid samples were dried at 80 °C for 12 h and then stored in a dryer. The yield was calculated based on the weight of product formed divided by initial weight of 1,6-hexanediamine charged.

2.3. Synthesis of polyurea

The post-polymerization process was carried out in a 250 mL three-necked flask. 20 g oligomer was added and then purged by CO₂ gas continuously. The reaction was carried out at 250 °C for 1 h under stronger stirring, then the reaction product was cooled down to room temperature naturally and collected.

2.4. Product characterization

Fourier-transform infrared (FT-IR) spectra of the sample were measured and recorded with a Nicolet iS50 FT-IR spectrometer with a DTGS-KBr detector and a wavenumber range of 400–4000 cm⁻¹ at room temperature. Variable temperature diffuse reflection infrared Fourier transform spectroscopy (VT-DRIFTS) was measured by Nicolet iS50 FT-IR spectrometer with a MCT/A detector. KBr was purged by helium (70 ml/min) for 10 min at 25 °C, and a background spectrum was collected, then the sample was replaced KBr and put onto the chamber, then purged by helium (70 ml/min) and heated in sequence to the desired temperature of 25, 80, 140, 200, 220, and 240 °C and recorded the corresponding spectra based on the above background spectra. The ¹³C NMR spectrum was made on a Bruker AV-400 with tetramethylsilane as the internal label. Oligomer was dissolved in CF₃COOD for the ¹³C NMR measurement. X-ray diffraction (XRD) measurements were conducted with a Bruker D8 advance instrument. Thermal gravimetric analysis (TGA) was carried out using a Perkin–Elmer Thermal Analysis at a heating rate of 10 °C/min from 50 to 500 °C in a N₂ flow. Differential scanning calorimetry (DSC) curves of the polyureas were measured on a Perkin–Elmer apparatus with a heating or cooling rate of 10 °C/min between 0 and 300 °C in a N₂ flow. Tapping mode atomic force microscope (AFM) image was acquired on a MultiMode V atomic force microscope. The sample of polyurea bars for tensile examination were prepared by melt-press method with a size of 25 mm × 10 mm × 1 mm. Mechanical analysis was conducted on an Instron-1121 tensile testing machine with a crosshead speed of 5 mm/min at 20 °C. But the sample bar could not be prepared due to the oligomer is too crisp.

3. Results and discussion

3.1. Preparation and identification of oligomer

3.1.1. Identification of oligomer

The oligomer was synthesized via the polymerization of HDA with CO₂ directly as described above. At first, the product (purified by washing with water and dried at 80 °C for 12 h) was analyzed and identified by using FTIR and NMR.

Download English Version:

<https://daneshyari.com/en/article/8089100>

Download Persian Version:

<https://daneshyari.com/article/8089100>

[Daneshyari.com](https://daneshyari.com)