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Utilization of carbon dioxide to build a basic block for polymeric materials: an isocyanate-free route to synthesize a soluble oligourea†

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A water soluble oligourea was synthesized by an isocyanate-free route from carbon dioxide and diamine in the absence of any organic solvents or additives. The chemical structure of the product was confirmed by FTIR and ¹³C NMR analysis, and the average molecular weight was estimated with MALDI-TOF MS. The weight average molecular weight of the obtained oligourea is about 2210 Da reacting under 180 °C and 11 MPa for 12 h. Moreover, the prepared oligourea has a moderate thermo-stability, it has an initial decomposition temperature at ~220 °C and a melting temperature of 110 °C, as confirmed by TGA and DSC. As a soluble oligomer, it could be used as a building block to synthesize CO₂-based polymeric materials due to it possessing a chemically active amino end group. For example, foaming plastics, greases, spun fibers and high strength polymer materials may be fabricated by reaction of the oligomer with a chain extender like a diisocyanate, diester or diacid.

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1. Introduction

Polyureas have some special properties, like hydrolysis resistance,¹ excellent mechanical properties^{2,3} and anti-corrosion^{4,5} and thus they have wide applications in coatings,⁶ greases⁷⁻⁹ and microcapsules.^{10,11} As we know, traditional polyureas are usually produced based on the reaction of a diamine with isocyanates,¹²⁻¹⁴ urea,¹⁵⁻¹⁷ and diphenyl carbonate.¹⁸ More recently, polyureas were successfully synthesized with dimethyl carbonate and propylene carbonate as the carbonylating agents which react with the diamines. These reactions are more environmentally friendly and energy-saving as they are operated in the absence of the toxic agents phosgene and isocyanates.¹⁹ Moreover, it is possible to produce the feedstock of dimethyl carbonate and propylene carbonate from carbon dioxide with methanol and propylene glycol. These processes are important innovations as they indirectly transfer carbon dioxide, which is a global warming gas, to polymeric materials. Recently, the chemical fixation and utilization of carbon dioxide has attracted much attention in the fields of environmental protection, new

energy resources and advanced materials. Significant efforts have been devoted to exploring the methods and technologies for carbon dioxide transformation.²⁰⁻²³ Many different kinds of chemicals, polymers and fuels have been synthesized from carbon dioxide. Herein, we present a more promising process where carbon dioxide is used directly to synthesize polyurea without any solvents or additives. The use of carbon dioxide as the feedstock, instead of toxic polyisocyanates, in the production of polyurea should be an important and useful strategy. However, it has not attracted much attention up to now, as only a small number of results have been reported since the first work reported in 1947 by Gerard *et al.*²⁴ Yamazaki and his co-workers used stoichiometric amounts of diphenyl phosphate, phosphorus chlorides or *N*-acyl phosphoramidites as the catalyst for the polymerization of aromatic diamines with CO₂ in a pyridine or an acetonitrile solvent.²⁵⁻²⁷ Our previous investigation demonstrated that urea derivatives could be easily produced from alkyl amines and carbon dioxide under reaction conditions similar to those for the analogous urea.²⁸ In recent years, we have found that polyureas could be synthesized by the reaction of diamines with carbon dioxide directly. We prepared several polyureas, like polyurea-6 (from hexamethylenediamine) and polyurea-8 (from 1,8-diaminooctane), which have a high resistance to solvents such as polar solvents (H₂O, EtOH, acetone, DMF, NMP, and 5% LiCl solution), non-polar solvents (CCl₄ and C₆H₆), acids (HCl and H₂SO₄) and bases (NaOH and KOH) at room temperature.²⁹ In the present work, we prepare a water soluble oligourea by using a diamine containing ether groups and reacting it with carbon dioxide as shown in Scheme 1. Therefore, it is possible to investigate the average molecular

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weight by MALDI-TOF mass spectrometry and ^1H NMR, and the reaction conditions can be evaluated by using the average molecular weight. As a soluble oligomer, it may have wide applications in environmentally friendly coatings and hydrophilic greases without toxic organic solvents. Moreover, it could also be used as a building block to synthesize CO_2 -based polymeric materials as it has a chemically active amino end group. For example, it can be used to fabricate foaming plastics, greases, spun fibers and high strength polymer materials by reaction with a chain extender like a diisocyanate, diester or diacid, to prepare the oligourea. Therefore, the present research provides a new route for the synthesis of various polymer materials with different properties by the direct reaction of CO_2 with amines possessing different molecular structures.

2. Experimental section

Chemicals

All the chemicals were used as received from commercial sources without further purification. 4,7,10-Trioxa-1,13-tridecanediamine (E2 for short) was purchased from the Sigma-Aldrich Corporation. Carbon dioxide gas (99.5%) was purchased from the Changchun JuYang Gas Company; 1-methyl-2-pyrrolidinone (NMP), hexamethylphosphoramide (HMPA) and chloroform were purchased from the Beijing Chemical Reagent Co. Ltd.; *N,N'*-dimethylpropyleneurea (DMPU) was purchased from the Aladdin Reagent Co. Ltd.; and methanol, ethanol, acetone, dioxane, toluene, isopropanol and THF were purchased from the Xilong Chemical Reagent Co. Ltd. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) and trifluoroacetic acid (TFA) were purchased from the Merger Corporation. All water soluble diamines, except E2, (shown in the ESI†) were purchased from the Huntsman Corporation.

Synthesis of the oligomer

The typical synthesis process was as follows: 4,7,10-trioxa-1,13-tridecanediamine (E2) was selected as the reactant because it contains several ether functional groups, which will improve solubility of the oligourea in water. First of all, 40 mL of the 4,7,10-trioxa-1,13-tridecanediamine was transferred into a 100 mL autoclave. It was blown with carbon dioxide three times to remove the oxygen and then it was sealed and heated to 180 °C. Next, CO_2 was introduced into the autoclave up to 11 MPa and the reaction was then vigorously stirring for 12 h. During the reaction, the total pressure decreased slowly as the CO_2 was continuously consumed. At the end of the reaction, the

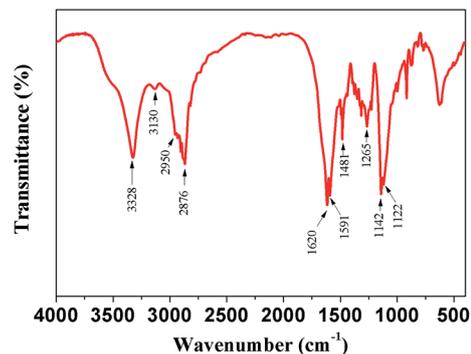


Fig. 1 FTIR-spectrum of the oligourea synthesized from E2 with CO_2 at 180 °C and 11 MPa for 12 h.

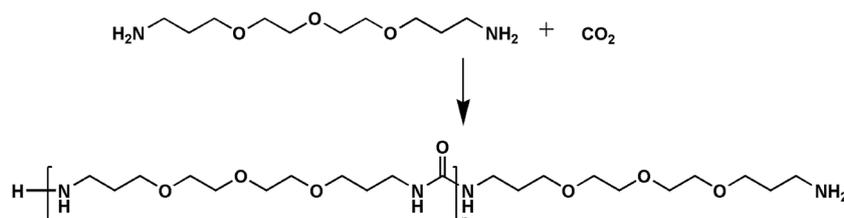
autoclave was naturally cooled down to room temperature. The product, a yellow paraffin which was wax like, was collected, dried at 50 °C for 24 h, and then stored for the following characterization.

Phase behavior observation

The phase-behavior of the reaction of 4,7,10-trioxa-1,13-tridecanediamine (E2) with CO_2 was observed using an 80 mL high pressure resistant view-cell with a magnetic stirrer. At first, 15 g of 4,7,10-trioxa-1,13-tridecanediamine (E2) was added into the view-cell at room temperature, blown with CO_2 three times, and then heated to 180 °C. After being maintained for 20 min, CO_2 was introduced into the reactor with a high-pressure liquid pump (Jasco SCF-Get) to the desired pressure, 11 MPa, then the reaction mixture was stirred vigorously for 3 h, and the phase behavior was recorded.

Characterization of the products

The CP/MAS ^{13}C NMR spectra were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CP/MAS probe head whose X channel was tuned to 100.62 MHz for the ^{13}C , using a magnetic field of 9.39 T at 297 K. All ^{13}C CP/MAS chemical shifts are referenced to the resonances of an adamantane standard ($\delta = 29.5$). Fourier-transform infrared (FTIR) spectra of the samples were recorded at room temperature with a Bruker Vertex 70 FTIR spectrometer. The measured wavenumber range was 400–4000 cm^{-1} . The MALDI-TOF MS measurements were performed using a Bruker Autoflex III smart beam MALDI-TOF mass spectrometer operated in positive ion mode; the instrument was equipped with a 355 nm



Scheme 1 Formation of the oligourea from CO_2 and diamine.

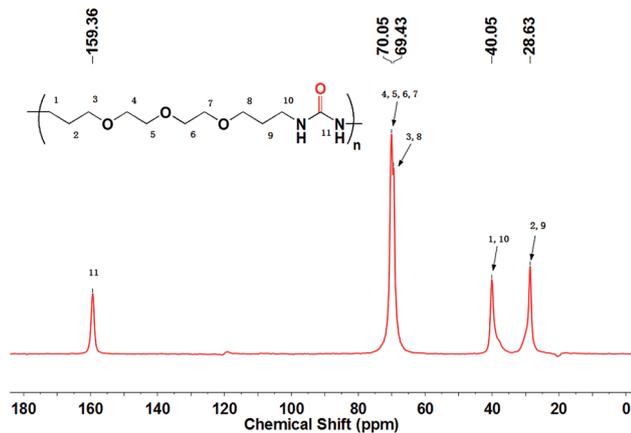


Fig. 2 ^{13}C -NMR of the oligourea synthesized from E2 with CO_2 at 180 $^\circ\text{C}$ and 11 MPa for 12 h.

Table 1 Comparison of the dissolving capacity of several solvents for the prepared oligourea^a

Solvent	Solubility	Solvent	Solubility
Water	+	Methanol	–
HMPA	+	Ethanol	–
DMPU	+	Isopropanol	–
NMP	+	Dioxane	–
HFIP	+	THF	–
TFA	+	Chloroform	–
Acetone	–	Toluene	–

^a “+” soluble at room temperature; “–” insoluble.

nitrogen laser with a pulse duration of 5 ns. The accelerating voltage and delay time were maintained at 20 kV and 200 ns, respectively, for all experiments. We obtained all of the mass spectra in the reflector mode by summing the spectra from 100 selected laser shots and used standard peptides of known masses for calibration. Matrices of 2,5-dihydroxybenzoic acid (DHB), obtained from Aldrich, were used in this study. Matrix solutions were freshly prepared in water at a concentration of approximately 20 mg mL^{-1} . Thermal gravimetric analysis (TGA) experiments were performed using a Perkin-Elmer Thermal Analysis system at a temperature rate of 10 $^\circ\text{C min}^{-1}$ from room

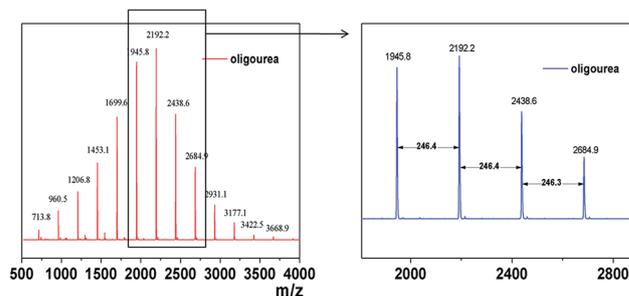


Fig. 4 MALDI-TOF MS spectrum of the oligourea synthesized at 180 $^\circ\text{C}$ and 11 MPa for 12 h.

temperature up to 800 $^\circ\text{C}$ in an N_2 flow. Differential scanning calorimetry (DSC) experiments were carried out on a Perkin-Elmer apparatus with heating and cooling rates of 10 $^\circ\text{C min}^{-1}$ from -50 $^\circ\text{C}$ up to 180 $^\circ\text{C}$ in an N_2 flow. The first heating run was used to remove all effects due to the thermal history of the sample and only the second heating runs were used.

3. Results and discussion

In order to prepare the water soluble polyurea, several kinds of water soluble diamines were selected as starting substrates and tested. The 4,7,10-trioxa-1,13-tridecanediamine presented the best comprehensive performance and it showed a good water solubility (Table S1[†]), which is important and a prerequisite for the following research, such as the examination of the molecular weight and the evaluation of the synthesis parameters. Thus, 4,7,10-trioxa-1,13-tridecanediamine was selected as the starting material for this study.

FT-IR spectroscopic analysis was used to characterize and confirm the structure of the sample prepared from the reaction of 4,7,10-trioxa-1,13-tridecanediamine (E2) with CO_2 as described above. As shown in Fig. 1, the formation of the urea functional group was confirmed in the synthesized sample according to the peaks at 1620 cm^{-1} (C=O stretching vibration), 1591 cm^{-1} (N–H bending vibration) and 3328 cm^{-1} (stretching vibration for N–H in the urea functional group).^{30,31} In addition, the signal peaks at 1142 cm^{-1} and 1122 cm^{-1} demonstrated the existence of an ether bond. The existence of

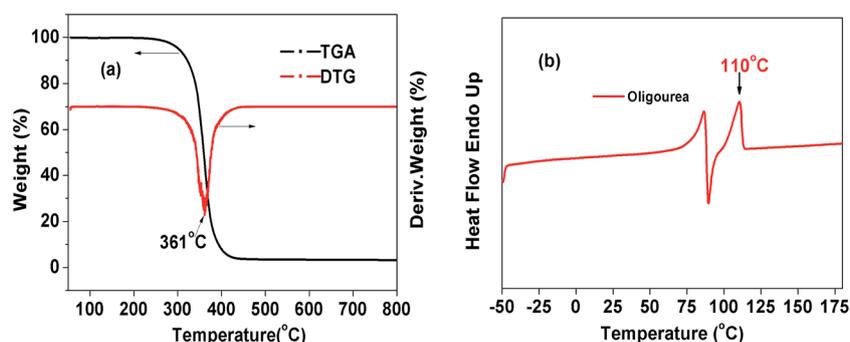


Fig. 3 TGA (a) and DSC (b) analysis for the oligourea synthesized at 180 $^\circ\text{C}$ and 11 MPa for 12 h.

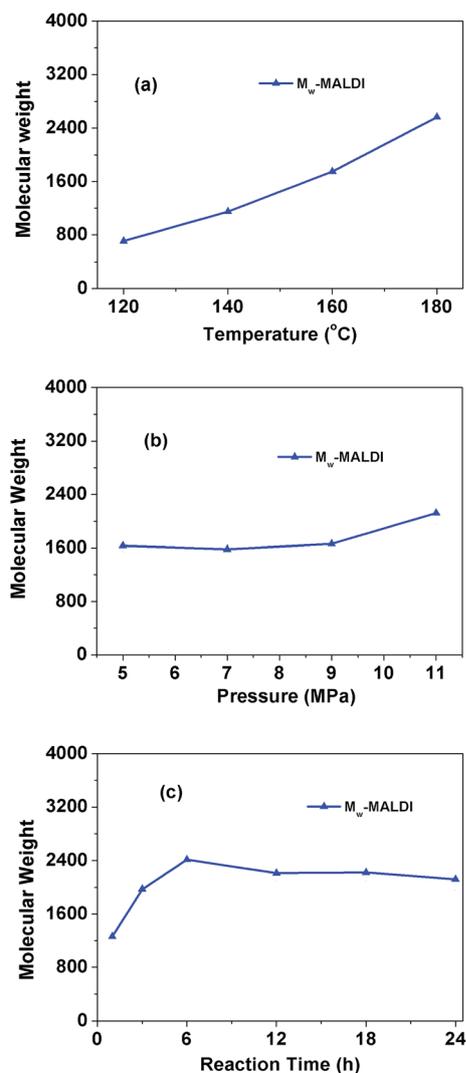


Fig. 5 The relationship of the parameters with the average molecular weight.

urea groups in the oligourea was also supported by the results of the CP/MAS ^{13}C NMR (Fig. 2). For the sample prepared from the reaction of 4,7,10-trioxa-1,13-tridecanediamine (E2) with CO_2 , a new peak was present at 160.0 ppm, which clearly indicates the formation of the carbonyl group in the urea linkage. The other peaks at 70.0 ppm, 69.4 ppm, 40.1 ppm and 28.6 ppm are ascribed to the corresponding methylenes of the substrate.

In addition, the solubility of the prepared polyurea oligomer was checked. As shown in Table 1, it is soluble in water and it is also soluble in some organic solvents, such as the polar aprotic solvents hexamethylphosphoramide (HMPA), *N,N'*-dimethylpropyleneurea (DMPU) and 1-methyl-2-pyrrolidinone (NMP), and the polar protic solvents trifluoroacetic acid (TFA) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). However, it is not soluble in the conventional solvents acetone, ethanol, methanol, isopropanol, THF, dioxane and toluene.

Next, the thermal stability of the polyurea oligomer was examined by thermogravimetric analysis (TGA) in nitrogen (Fig. 3a). The initial decomposition temperature of the polyurea was near 220 °C, the maximum decomposition temperature was around 361 °C, and the 5% weight lost occurs around 303 °C. The thermogravimetric analysis indicates that the prepared polyurea oligomer has a moderate thermal stability. Moreover, the DSC curves showed that its highest melting temperature was about 110 °C (Fig. 3b). Compared to aliphatic oligoureas, the prepared oligourea has a lower melting point as the ether functional groups give the chain more spin conformations and make the structure of the polyurea oligomer more flexible. In addition, imperfections or different degrees for crystallization of the prepared oligourea may lead to multiple melting phenomena. Both of the ether carbon group chains and the urea functional group will affect the crystallization. Based on the thermal stability, melting behavior and water solubility, the prepared oligomer is an environmentally benign material as it could be processed under a wide range of processing temperatures without organic solvents.

The average molecular weight of the obtained water soluble oligomer was detected by a MALDI-TOF mass spectrometer. The

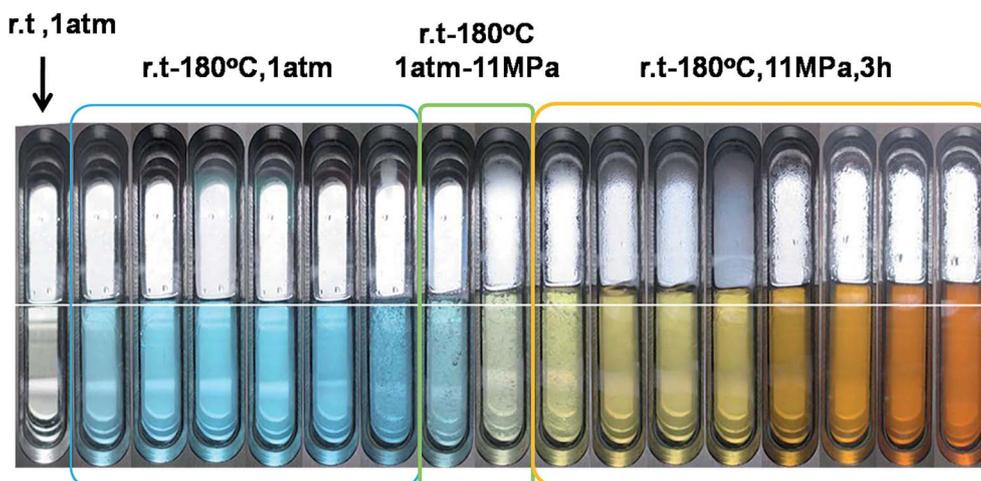
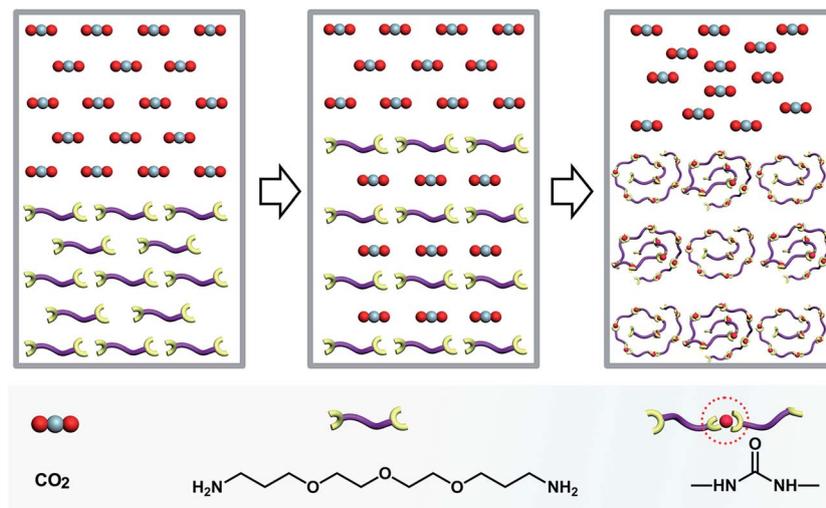


Fig. 6 Phase behavior of the reaction of E2 with CO_2 at 180 °C and 11 MPa for 3 h.



Scheme 2 Illustration of the phase behavior for the reaction of E2 with CO₂.

MALDI-TOF MS spectrum of the oligourea synthesized at 180 °C and 11 MPa for 12 h showed a symmetric distribution of molecular weight (Fig. 4). The weight average molecular weight is 2210 Da, for which the degree of polymerization is near 8–9. In addition, the repetitive unit is 246.4 Da, which is equal to the formula weight of the chemical repeat unit, as shown in the Scheme 1. The end group is 221.5 Da but the molecular weight of the E2 is 220 Da, indicating that the end group of the oligourea is an amino group which maybe contain one hydrogen. These amino groups at the ends are chemically active, and so, as a building block, the oligourea can be widely utilized in the synthesis of various polymeric materials.

The effect of the reaction parameters such as temperature, pressure and reaction time was evaluated by considering the molecular weight. The designed temperature was selected according to the melting point and initial decomposition temperature. The relationship of the reaction conditions with the molecular weight are shown in Fig. 5. The molecular weight increases linearly with the reaction temperature from 120 °C to 180 °C (Fig. 5a), but it changes less under a pressure of around 5–11 MPa (Fig. 5b). Moreover, the reaction time was evaluated with the reaction at 180 °C and 11 MPa. The molecular weight of the oligourea increased quickly within the initial 6 h and then it tended to remain constant around 2210, in which eight or nine repeat units may be contained. This means that a chemical equilibrium has been established after reaction for 3 h (Fig. 5c). On the basis of polycondensation theory, the chemical equilibrium constant is near 49–64, calculated by the relationship between the polymerization degree and the chemical equilibrium constant in the closed reaction system ($\bar{X}_n = \sqrt{K} + 1$, X_n : the degree of polymerization, K : the chemical equilibrium constant).³²

The phase-behavior of the reaction of 4,7,10-trioxa-1,13-tridecanediamine (E2) with CO₂ was observed using a high pressure view-cell (Fig. 6). 15 mL of E2 was transferred into an 80 mL view-cell at room temperature, then the view-cell was heated to 180 °C and CO₂ was introduced to the view-cell with

continuous stirring. It was found that the volume of liquid phase increased with the introduction of 11 MPa CO₂ because the CO₂ could dissolve into the liquid phase of the reactant, and thus the volume was expanded. It is clear that the color of the reaction mixture turns from transparent to light blue with the increasing temperature, and then it turns to a light yellow after 11 MPa CO₂ is introduced. Finally it turns to yellow after being maintained at 180 °C and 11 MPa for 3 h. These color changes may be caused by the following reactions: the reactant polyether diamine reacting with carbon dioxide to form a carbamate, and the polycondensation of the carbamate with diamine to form the polyurea shown in Scheme 2.

Overall, we have successfully prepared a water soluble polyurea oligomer using CO₂ as the carbon–oxygen resource directly. The prepared oligourea can be used as a building block to synthesize various polymers through post-polymerization. For example, by reacting with a chain extender like a diisocyanate, diester or diacid, the prepared oligourea could be used to make foaming plastics, greases, spun fibers and high strength polymer materials.

4. Conclusion

In conclusion, we have prepared a new kind of water soluble oligourea with a direct reaction between CO₂ and polyether diamine without any solvents or additives. The produced oligomer has an initial decomposition temperature of 220 °C and a melting temperature of around 110 °C. At 180 °C and 11 MPa, reacting for 12 h, the weight average molecular weight of the oligourea is near 2100 Da, as detected by MALDI-TOF mass spectrometry. The relationship between the reaction parameters and the average molecular weight shows that the effect of temperature is more significant than that of the reaction pressure. A higher temperature can lead to a higher polymerization degree after reaching equilibrium. Therefore, as the prepared oligourea has an initial decomposition temperature around 220 °C and a melting temperature about 110 °C, the suitable

reaction temperature in this work was selected as the range of 120–180 °C. The reaction attains a chemical equilibrium after reaction for 6 h at 180 °C and 11 MPa. In addition, due to the end group being a chemically active amino group, the oligourethane fabricated directly from carbon dioxide can be used as a building block to synthesize various polymeric materials. Therefore, the present work opens a new route for transforming CO₂ into useful and value-added polymeric materials.

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