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Synthesis of polyureas with CO_2 as carbonyl building block and their high performances

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ABSTRACT

A series of polyureas were synthesized with CO_2 as the carbonyl building block, which consist of a hard segment of CO_2-based oligourea and a soft segment of soluble polyether diamine. The hard segment was formed from 1,3-bis(3-aminopropyl) tetramethyl disiloxane with CO_2, and the soft segment was obtained through polyaddition of polyether diamine with an extender agent. The Number-average Molecular Weight (Mn) and Weight-average Molecular Weight (Mw) were estimated by Gel permeation chromatography (GPC). The properties of the synthesized polyureas such as thermo-stability and the tensile strength were examined, and these properties could be adjusted by varying the molecular weight of polyether diamine and oligourea segments. The synthesized polyureas have an amorphous structure and presented satisfied thermo-stability (~250 °C) and the high tensile strength (22.4 MPa).

1. Introduction

The climate anomaly and the global temperature increase have drawn an abundant attention to reduce the emission of carbon dioxide. Therefore, the carbon dioxide capture and utilization is of great significant mission for the researchers in the fields of environmental, green chemistry and chemical engineering [1–4]. Under the view of environment and sustainable developments, CO_2 as a green chemical feedstock is of significance in the synthesis of value-added chemicals [5,6]. Especially, CO_2 has been used widely as a monomer in synthesizing useful CO_2-based polymeric materials [7,8]. For instance, poly (propylene carbonate), a famous bio-degradable polymer has been produced commercially and widely used as environmental protecting package and medical materials [9,10].

As a linear polymer, polyurea consists of 'hard' and 'soft' segments. The chemical structure and intermolecular interaction of the polyurea endow the highly elastic, weather resistance, mechanical stabilities and resistant to abrasion. Therefore, polyurea is widely used in many different commercial applications such as coating, grease, catalyst carrier and microcapsule. Recently, the polyureas with special function and properties have been developed, for example, Cheng et al. synthesized a kind of polyurea with self-healing function based on the reversible reaction of diisocyanate and diamine with alkyl group steric hindrance [11]. In addition, we have synthesized several kinds of polyureas based on carbon dioxide route, such as the water soluble polyurea [12], macrocyclic polyurea [13], water phobic polyurea [14] and the polyurethane oligomer [15]. Comparing to polycarbonate [16–18], the polyurea is a kind of polar polymeric materials.

In this work, a series of polyureas were synthesized by the reaction of a hard segment prepared by polycondensation using CO_2 as carbonyl synthon and 1,3-bis(3-aminopropyl) tetramethyl disiloxane with a soft segment formed through a polyaddition of polyether diamine and extender agent. A series of polymeric materials at a molecular weight around 40,000–60,000 Da with varied properties were obtained by adjusting the molecular weight of polyether diamine and oligourea segments. It is the first report for the CO_2-based polyureas to have satisfied properties such as thermo-stability (~250 °C) and the high tensile strength (22.4 MPa).

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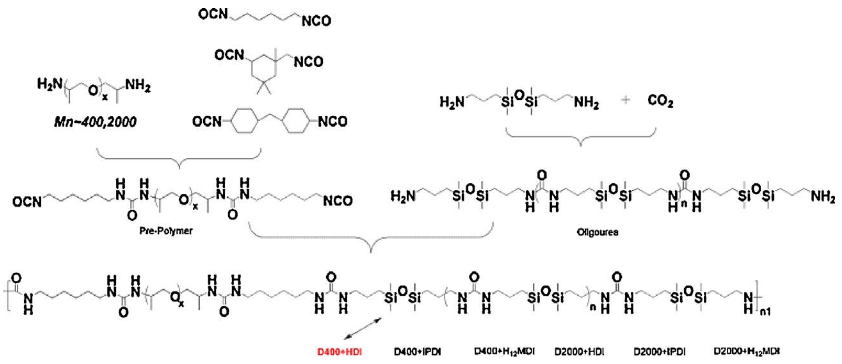

Scheme 1. Synthesis route of a series of polyureas.

2. Experimental section

2.1. Chemicals

All the chemicals were used as received from commercial sources without further purification. 1,3-bis(3-aminopropyl)tetramethyl disiloxane (short for BAS) was purchased from Alfa Asear Corporation. Gas of carbon dioxide (99.5%) was purchased from Changchun JuYang Gas Company; 1-methyl-2-pyrrolidinone (NMP), *N,N′*-dimethylacetamide (DMAc), m-cresol, Dioxane and *N,N′*-Dimethylformamide (DMF) were purchased from Beijing Chemical Reagent Co., Ltd.; methanol, toluene, chloroform, acetone, diethyl ether, ethanol were purchased from Xilong Chemical Reagent Co. Ltd. Isophorone diisocyanate, hexamethylene diisocyanate and hexamethylene diisocyanate were purchased from Aladdin reagent Corporation. Polyether diamine, both D400 and D2000 were purchased from Hunstman Corporation. All the substrtes are used directly without purification.

2.2. Synthesis of the oligurea

First of all, 40 mL of the 1,3-bis(3-aminopropyl)tetramethyl disiloxane was transferred into an 100 mL autoclave, blowed it with carbon dioxide for three times to remove the oxygen and then sealed it and heated to 180 °C. Next, CO_2 was introduced into the autoclave up to 7.5 MPa and the reaction was started with vigorously stirring for 6 h. During reaction, the total pressure decreased slowly as the CO_2 was consumed continuously. Until to the end of reaction, the autoclave was naturally cooled down to room temperature. The product, a light yellow wax, was collected and dried in a protecting gas of nitrogen at 50 °C for 24 h, then the produt was stored, for the use of characterization and post-polymerization.

2.3. Pre-polymerization

The polyureas were synthesized in a 100 mL flask equipped with a magnetic stirrer in a water bath at 0–4 °C. Firstly, a certain amount of polyether diamine dissolved in DMAc in a breaker and ADI as extender reagent dissoved in DMAc in another beaker at room temperature. The ADI/DMAc solution was added into the polyether diamine/DMAc solution gradually to form a pre-polymer with a mole ratio of NCO/NH_2 as 2. After reaction performed the product was still stirred for 30 min at 0–4 °C.

2.4. Post-polymerization

A certain amount of the prepared oligourea (947 g/mol by titration, the ratio of the NCO group in pre-polymer to the amino group was 1:1) was dissolved in the DMAc in a beaker at 0 °C, and then which was added with the polyether diamine (end group was isocyanate) into a flask and reacted for about 30 min. The termination of reaction was judged by the disappearance of NCO group with FT-IR analysis.

2.5. Characterization of the products

Fourier-transform infrared (FTIR) spectra of the samples were recorded at room temperature with a Bruker Vertex 70 FTIR spectrometer at a wavenumber range of 400–4000 cm^{-1}. Gel permeation chromatography (GPC) measurement was conducted on a Waters 410 GPC equipment. DMF was used as eluent with a flow rate of 1.0 mL/min at 35 °C, and PS was used as standards for calibration. Thermal gravimetric analysis (TGA) experiments were performed by using a PerkinElmer Thermal Analysis at a temperature range of 50–600 °C with raising rate of 10 °C min^{-1} in N_2 flow. Differential scanning calorimetry (DSC) experiments were carried out on a PerkinElmer apparatus with heating and cooling-rates of 10 °C min^{-1} from −70 °C up to 140 °C in an N_2 flow. The first heating run was used to remove the effects due to thermal history of the sample and the second heating run was recorded. Wide-angle X-ray diffraction (WAXD) was carried out with a Bruker D8, the scan velocity was 4 °C/min at a range of 5–50°. The static mechanical properties were measured with an Instron 1121 tensile testing machine, and the crosshead rate was set at 50 mm/min. For each data point, five samples were tested, and the average value was collected. In-situ IR spectra was collected with a Nicolet iS50 infrared spectrometer at a region of 400–4000 cm^{-1} by using a 22 mL high-pressure cell equipped with a transparent window and a mechanical stirrer, the spectra were collected at 7.5 MPa, 180 °C with an interval of 12 s.

3. Results and discussion

3.1. Synthesis of polyureas

A series of polyureas were synthesized by the reaction of a hard segment with a soft segment. As shown in Scheme 1, the hard segment was prepared by polycondensation of 1,3-bis(3-aminopropyl) tetramethyl disiloxane with CO_2 as carbonyl building block, and the soft segment was synthesized through a polyaddition of polyether diamine and extender agent. In the typical synthesis, 1,3-bis(3-aminopropyl) tetramethyl disiloxane was selected as reactant because it contains Si—O—Si functional group, which can improve the solubility of oligourea in organic solvents. The chemical structure of the final polyurea synthesized was characterized and confirmed by using FTIR spectroscopic analysis, and the spectra are shown in Fig. 1. The functional groups in the final product were identified for all the obtained samples. For example, the absorbance peaks at 1103 cm^{-1} and 1025 cm^{-1} with relatively high intensity are the characteristic of Si—O—Si stretching vibration, and the urea functional groups was confirmed according to the peaks at 1635 cm^{-1} (C=O stretching vibration), 1562 cm^{-1} (N—H bending vibration) and 3330 cm^{-1} (stretching vibration for N—H in the urea functional group).

The forming process of oligourea from CO_2 and siloxane was monitored and confirmed by the *in situ* high −pressure FTIR spectra, as shown in Fig. 2. It is clear that the carbamates were quickly formed