

Synthesis of polyureas with CO₂ as carbonyl building block and their high performances



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ABSTRACT

A series of polyureas were synthesized with CO₂ as the carbonyl building block, which consist of a hard segment of CO₂-based oligourea and a soft segment of soluble polyether diamine. The hard segment was formed from 1,3-bis(3-aminopropyl) tetramethyl disiloxane with CO₂, 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, CO₂ as a green chemical feedstock is of significance in the synthesis of value-added chemicals [5,6]. Especially, CO₂ has been used widely as a monomer in synthesizing useful CO₂-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

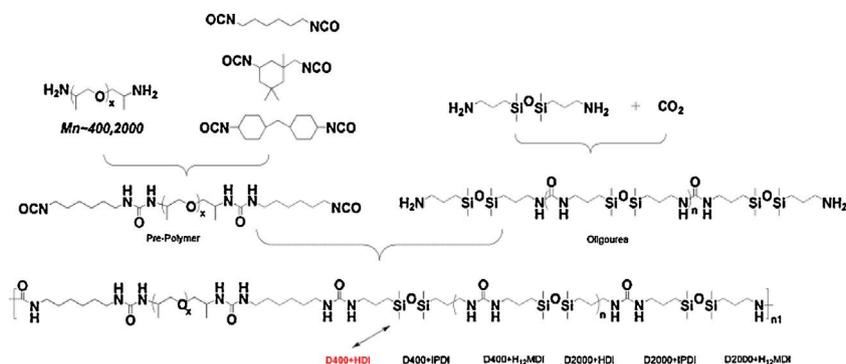
and properties have been developed, for example, Cheng et al. synthesized a kind of polyurea with self-healing function based on the reversible reaction of diisocyanate and diamine with alkyl group steric hindrance [11]. In addition, we have synthesized several kinds of polyureas based on carbon dioxide 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 CO₂ 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 CO₂-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 Aesar 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 substrates are used directly without purification.

2.2. Synthesis of the oligourea

First of all, 40 mL of the 1,3-bis(3-aminopropyl)tetramethyl disiloxane was transferred into an 100 mL autoclave, blown it with carbon dioxide for three times to remove the oxygen and then sealed it and heated to 180 °C. Next, CO₂ 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 CO₂ 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 product 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 beaker and ADI as extender reagent dissolved 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/NH₂ 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 N₂ 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 N₂ 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 CO₂ 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 CO₂ 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

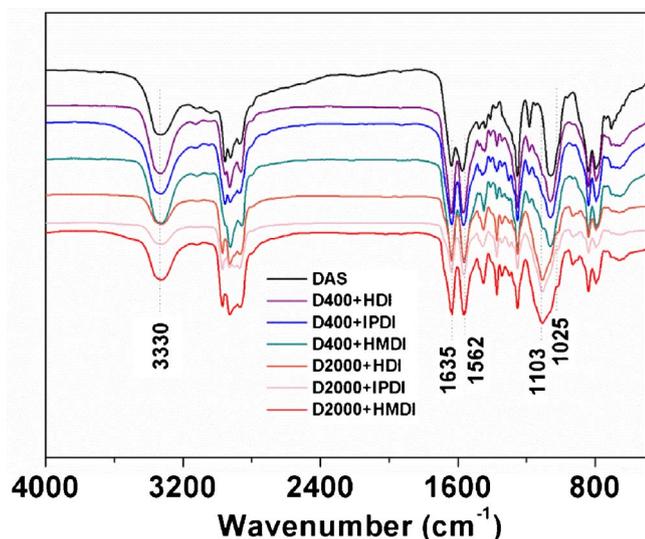


Fig. 1. FT-IR spectra of the prepared polyureas.

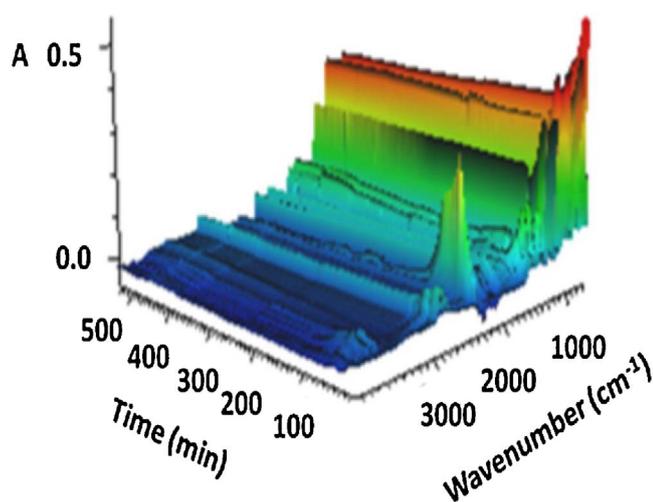


Fig. 2. In-situ FTIR spectra for the formation of oligourea from CO₂.

at the beginning of reaction as soon as introducing CO₂, then the urea linkage was formed slowly with the disappearance of the carbamates and finally the reaction attained the equilibrium after reacting for 6 h, forming the hard segment.

The solubility of the synthesized a series of polyureas are list in Table 1. It is clear that all the polyureas synthesized have good solubility in ethanol, DMF isopropanol, and DMAC, the solubility parameter (δ) of these solvents is at a range of 11–13. But they are

Table 1

The dissolution behavior of the polyureas and the oligoureas.

Solvent	δ	Samples						
		DAS	D400 + HDI	D400 + IPDI	D400 + HMDI	D2000 + HDI	D2000 + IPDI	D2000 + HMDI
H ₂ O	23.2	–	–	–	–	–	–	–
Acetone	10.0	–	–	–	–	–	–	–
Diethyl ether	7.4	–	–	–	–	–	–	–
DMF	12.1	+	+	+	+	+	+	+
DMAC	11.1	+	+	+	+	+	+	+
Ethanol	12.7	+	+	+	+	+	+	+
Isopropanol	11.5	+	+	+	+	+	+	+
THF	9.9	+	+	–	–	+	+	+
NMP	11.0	+	–	+	+	–	–	–

“+” soluble; “–” insoluble.

Table 2

The molecular weight of the polyureas.

Sample	M _n ($\times 10^4$)	M _w ($\times 10^4$)	PDI
D400 + HDI	1.64	4.02	2.45
D400 + IPDI	1.82	4.26	2.35
D400 + HMDI	1.40	3.34	2.39
D2000 + HDI	1.79	5.26	2.94
D2000 + IPDI	2.49	6.44	2.59
D2000 + HMDI	2.40	6.72	2.80

not soluble in water, acetone and diethyl ether these with a deviation in δ , and some of the polyureas dissolve in THF, NMP. The solubility of the final polyureas should depend on the molecular weight of polyether diamine and the extender agent used.

3.2. Properties of polyureas

As shown in Table 2, the average molecular weights of the **D2000** series are higher than the corresponding **D400** ones due to their larger soft segments. In comparison with the traditional polyurethane, the molecular weights of these formed polyureas are relative lower. This phenomenon is similar to the case of the non-isocyanate polyurethane (NIPU), which is due to the ratio of the two kinds of functional groups are hard to control to 1:1 strictly. And so, the molecular weight distribution of the final polyurea is somewhat wide, because of the wide poly-dispersity index of the oligourea formed from polycondensation.

CO₂-based polyurea can be used as membrane or plate in the architecture and construction. Considering the membrane processing, the heat resistance of polyurea is a key indicator. The thermal stabilities of the synthesized polyurea characterized are shown in Fig. 3, the weight of polyurea can retain more than 95% at high temperature of 300 °C and maintained at 100% basically at 250 °C. Moreover, the difference in the chemical structure of the isocyanate did not influence the decomposing behaviour of the final polyureas. The thermo-stability of the final polyurea depends strongly on the chemical structure of the soft segment. As a result, the prepared polyurea has a wide processing temperature range; it can endure the heat generated in the process and resist the special conditions encountered.

The molecular weight of polyether diamine and the kind of ADI will lead to a difference in glass transition temperature (T_g). With the same thermal history, the curves of polyureas with different components at the second heating run were recorded, as shown in Fig. 4, it was found that all the samples have only one glass transition temperature (T_g) in their DSC curves, and interestingly, the T_g depends largely on the size of polyether diamine, and it decreases with increasing of the molecular weight of polyether diamine. For the same polyether diamine, the sort of ADI also affect the T_g, HMDI series has the highest T_g than the others, which can be explained by the chemical structure of ADI, that

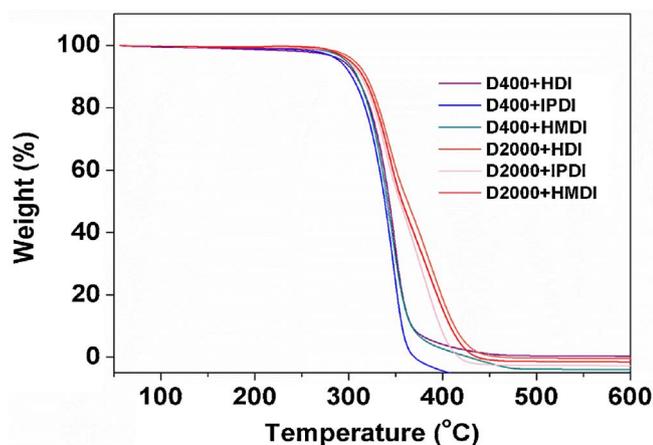


Fig. 3. TGA results of the final polyureas.

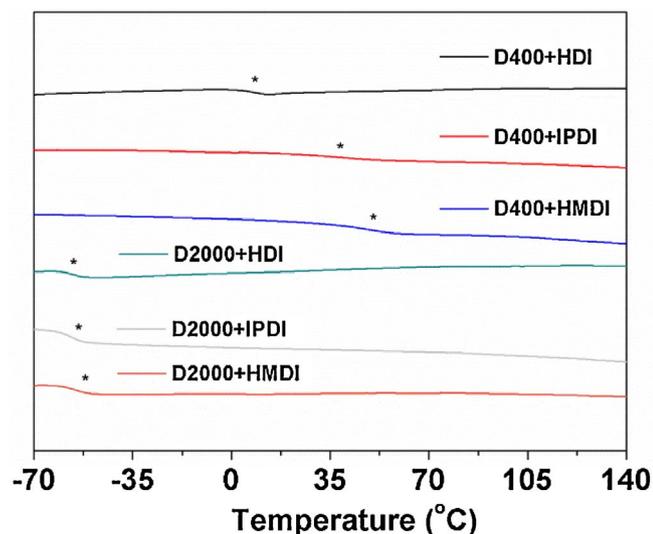


Fig. 4. DSC curve of the final synthesized polyureas.

the HMDI is much more rigid than the IPDI and HDI. While, the results in this work are different from the situation for the double carbon dioxide route polyurethane-urea reported previous [11]. It can be explained by the weaker interaction between the soft and hard segments in the polyether diamine materials compared to that in the polyurethane-urea. As a new kind of polyurea/polyurethane-urea material, the glass transition temperature of CO₂-based polyurethane materials is decided by the interaction between the soft and hard segments. For the strong interaction system, such as the polyurethane-urea, the glass transition temperature increases with increasing of the length of soft segment [11]. On the contrary, it decreases for the weak interaction system such as the present polyether-oligourea. The freedom degree of the chain segment is a key factor for this issue.

Moreover, the tensile property of the polyureas was checked, the results are shown in Fig. 5. It is clearly that the tensile property is also depending on the molecular structure, the higher tensile property presented in the polyureas with a short soft segment compared to those with a long soft segment, such as D400 + HMDI and D2000 + HMDI, although they contain the same hard segment and the same diisocyanate. The tensile strength is up to 22.4 MPa and the ultimate elongation is nearly 500% for the sample of D400-HMDI, but the tensile strength for D2000 + HMDI is just 0.1 MPa. Not only the length of the soft segment is important factor to the tensile property, the structure of the diisocyanate used also influence the tensile property extremely. The ultimate elongation and the modulus is in an order of HDI < IPDI < HMDI, increased with diisocyanate rigidity. There is an apparent yield

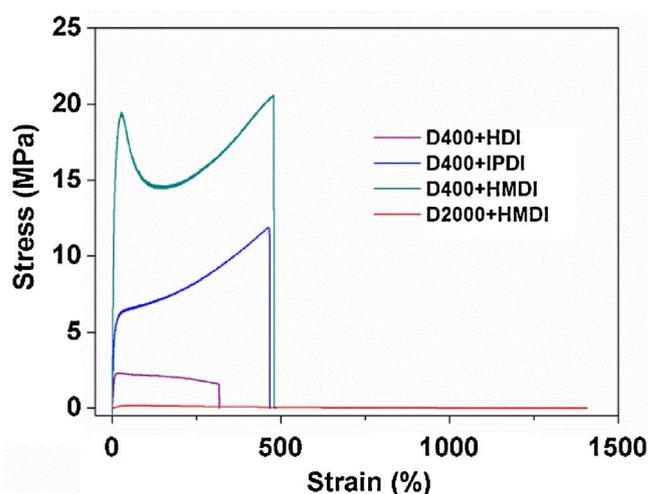


Fig. 5. The tensile properties of the final polyurea.

phenomenon for the polyureas D400 + HMDI as the rigidity of the diisocyanate and the relatively strong interaction between the soft and hard segments. In comparison with the tensile strength (22.4 MPa) of the sample of D400 + HMDI, it decreased to 4.48 MPa for D400 + HDI and decreased to 13.67 MPa for D400 + IPDI. For the elongation at break, it decreased from 500% of D400 + HMDI to 490% and 355% for D400 + HDI and D400 + IPDI, respectively. For the tensile strength, generally, the series of D400 is stronger than the series of D2000, which is aroused by the percentage decrease of the hard segment and the reduction of the interaction between soft and hard segments. So that, the D400 + HMDI containing short soft segment and rigid extender agent (HMDI) showed satisfactory tensile strength. It was found that D400 ± HDI was different from those of the D400 ± IPDI and D400 ± HMD. It is because that HDI as an extender it is more flexible than IPDI and HMDI, and the interaction between the polymer linkage of the D400 ± HDI was weaker, which leads the responding D400 ± HDI polymers to have the smaller Young modulus and small ultimate elongation.

Comparing with the traditional spray polyurea, the CO₂ based polyurea is more like a plastic with an apparent yield behaviour and an elastic modulus of 0.5 GPa, by contrast, the traditional polyurea is more like a rubber without yield phenomenon but having a low elastic modulus. The morphological structure of the polyureas was analysed by wide-angle X-ray diffraction analysis at 2θ ranging of 5–50°, as shown in Fig. 6. It is clear that the polyureas are amorphous, which is attributed to the loosening chain packing of the polymer with incorporation of flexible siloxane structure and the twisting polymer backbone with conducting of urea linkage units. Therefore, the synthesized polyureas are transparent and colourless, no melting point, and soluble in a number of solvents, thus they have a wide processing temperature compared to the conventional polyurethane. For the polyurethane, the hard segment usually aggregates to form a crystalline region and leads to the microphase separation. For the polyureas, however, the segment contains some methyl which hinders the formation of crystalline region.

4. Conclusions

We have successfully synthesized a series of polyureas with a CO₂-based oligourea, which contain both the hard and soft segments in the molecule. The synthesized polyureas have an average molecular weight at a range of 40,000–60,000 Da, and have good solubility in the solvents of ethanol, isopropanol, THF, and DMF, DMAC, but they did not dissolve in water, acetone and diethyl ether. The synthesized polyureas have an amorphous structure, and they presented a satisfac-

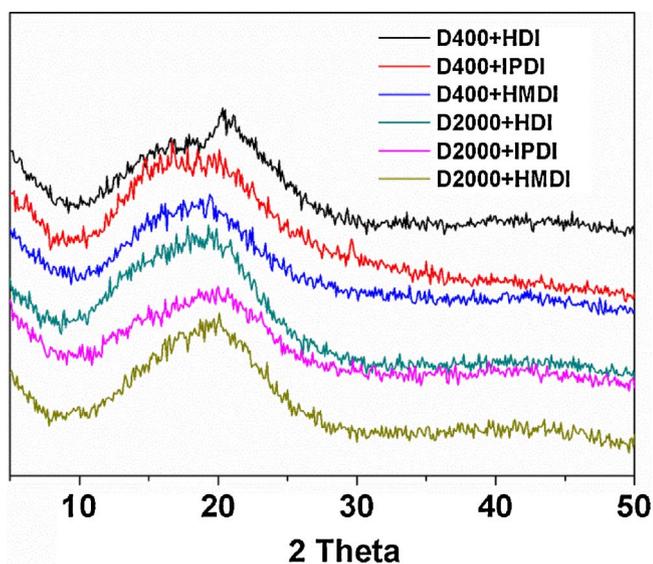


Fig. 6. XRD patterns of the final polyureas.

tory thermo-stability and the higher tensile strength, these properties depend on the molecular weight of the substrate used of polyether diamine and extender agent. The present work provides a new route for the synthesis of novel polyureas with some satisfactory properties, which we hope will have a wide application in biomaterials, transparent film and plastic materials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcou.2017.04.001>.

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