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Carbon dioxide as a sustainable resource for macrocyclic oligourea

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Z. Ying^{a,b,c}, Y. Dong^d, J. Wang^e, Y. Yu^{a,b,c}, Y. Zhou^{e*}, Y. Sun^e, C. Zhang^{a,b}, H. Cheng^{a,b}, F. Zhao^{a,b*}

Carbon dioxide as an inexpensive, abundant, sustainable and green carbonyl resource, its utilization to produce value-added chemicals and polymeric materials has attracted much more attention. In this work, novel macrocyclic oligourea oligomers were synthesized and it is the first time to produce macrocyclic oligourea from a sustainable substrate of CO₂. The chemical composition and molecular structure of oligourea has been confirmed by FTIR, MALDI-TOF and tandem mass spectrometry. The formation of macrocyclic polyurea largely depends on the kind of solvent chosen and the reaction duration, which has been discussed according to the reaction phase behavior observation. The synthesized novel macrocyclic oligourea is expected to have important and special applications in pharmaceuticals industry. The present work provides a green and renewable process for synthesis of macrocyclic oligomer, which opens a new route for the carbon dioxide utilization.

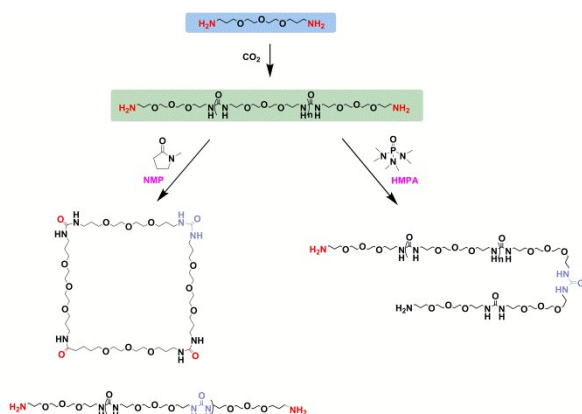
Introduction

Carbon dioxide as a green feedstock is non-toxic, non-flammable, abundant and renewable, it has attracted a number of attentions in synthesis of value-added chemicals and polymers.^[1] Especially, utilization of CO₂ to build new C-N, C-O bonds is of great importance in academia and industry because of its economic and environmental merits.^[2] Recently, Some progresses have been obtained in transformation of CO₂ to valuable chemicals, like urea, salicylic acid, synthesis gas, carbonates and urea derivatives.^[3] For example, Kleij et al. synthesized several cyclic carbonates from carbon dioxide and epoxide by using a homogeneous metal complexes as a catalyst.^[4] While, cyclic carbonate and its derivatives has much application attempt in the research of lithium battery as an electrolyte.^[5] Besides, several kinds of novel polymeric materials have been manufactured based on carbon dioxide; Such as poly-(propylene carbonate), a bio-degradable polymer, has been prepared from carbon dioxide and propylene epoxide catalyzed by several kinds of homogeneous catalysts.^[6] Nowadays, Darensbourg et al. reported a new one-pot synthesis method of a novel poly-(lactide-b-propylene carbonate-b-lactide) triblock copolymers, this method connects the two famous bio-degradable polymer (the PPC and the PLA), which offers an efficient and straightforward route for the synthesis of model ABA triblock copolymers.^[6c] Besides, the industrial production of poly-(propylene carbonate) has been realized and widely used as plastic wrapper, agricultural plastic, mulching film and biomedical material.^[7] The synthesis of polyurea usually needs highly toxic polyisocyanates, which is produced from even more toxic

reagent of phosgene^[8,9]. Therefore, using the cheap, renewable and nontoxic carbon dioxide to replace toxic reagents is more desirable and significant from the view point of sustainable development. A variety of functional polymeric materials can be prepared with carbon dioxide as the renewable carbonyl source to react with different chemical substrates. Recently, we have successfully synthesized the urea derivatives and polyureas from amines with CO₂ directly.^[3b, 10, 11] Herein, a kind of novel macrocyclic oligourea has been synthesized based on carbon dioxide in NMP solvent. As we know, the properties of polymer do not only depend on the chemical structure, but also rely on the molecule structure. For instance, the linear, branch and macrocyclic polymers show different properties, even though they have the same chemical structure and similar average molecular weight. The macrocyclic polymer has shown a great advantage in some properties, such as low viscosity, high thermo-stability and the good solubility due to its unique molecular structure and none end groups in its molecule. The macrocyclic polymer may have different applications comparing to the corresponding linear polymer, like the macrocyclic polyether is a kind of useful ionophore antibiotics,^[12] while the linear polyether is a useful material in the polyurethane industry.^[13] The macrocyclic polyamide is a promising antimicrobial agent candidate,^[14] but the linear polyamide is an ideal ingredient for thermoplastic polymeric materials and fibers.

In this work, a novel macrocyclic oligourea was derived from carbon dioxide and polyether amine as shown in Scheme 1. The chemical structure of the formed oligomers was ascertained by using FTIR, MALDI-TOF (Matrix-Assisted Laser Desorption Ionization-Time of Flight) and tandem mass

spectrometry. Typically, MALDI-TOF and tandem mass spectrometry were usually used to deduce the structure preliminary. [15-18] The formation of macrocyclic polyurea oligomer was discussed with varying solvent and reaction time. The present synthesis strategy is a green and sustainable process, it is expected that the synthesized macrocyclic polyurea oligomer will find potential applications in some special materials.



Scheme 1. The synthesis route of the oligoureia in different solvents

Experimental section

Chemicals

All the chemicals were used as received from commercial sources without any further purification. A linear polyether diamine of 4,7,10-trioxa-1,13-tridecanediamine (short for E2) was purchased from Sigma-Aldrich Corporation. N-Methyl-2-pyrrolidinone (NMP) and acetone were bought from XiLong chemical co., LTD. And Hexamethyl phosphoramide (HMPA) was obtained from QingPu Synthesis Reagent Company. Gas of carbon dioxide (99.5%) was purchased from Changchun JuYang Gas Company and used as delivered.

Synthesis of polyurea oligomer

The reaction was performed in an 80 ml high-pressure reactor. Firstly, charged 20 g of 4,7,10-trioxa-1,13-tridecanediamine to the reactor, flushed with CO₂ for three times, then placed the reactor into an oil bath. After the reactor was heated to 180 °C, about warming for 20 min, carbon dioxide was pumped to reactor to the desired pressure 11 MPa by means of a high-pressure liquid pump (Jasco SCF-Get). The reaction was recorded at starting the vigorously stirrer. After reaction, the reactor was cooled to room temperature gradually and then depressurized carefully. Yellow solid product was collected and dried at 50 °C for 12 h, then the sample was collected and marked as oligomer-1, the yield is above 95%.

Post-polymerization in solvents

The post-polymerization was started in 80 ml high-pressure reactor with organic solvents of N-Methyl-2-pyrrolidinone (NMP)

and Hexamethyl phosphoramide (HMPA), respectively. The reactor was firstly charged with 2 g of prepared oligomer-1 and 20 ml solvent, flushed with CO₂ for three times, then placed into an oil bath. After heating to 180 °C, keep warming for 20 min, carbon dioxide was pumped to the pressure 11 MPa. Finish reaction, the reactor was cooled to room temperature and then depressurized carefully. For the case of HMPA solvent, a transparent yellow solution with some precipitates was obtained on the wall reactor. The products were collected by dissolving them with distilled water and then precipitated by using diethyl ether, finally dried at 50 °C for 12 h. The sample was collected and marked as oligomer-2, the yield is above 80%. In the case of NMP solvent, a transparent orange solution was obtained; the product was extracted or precipitated by using diethyl ether. The precipitates were dried at 50 °C for 12 h, after that the sample was collected and marked as oligomer-3, the yield is above 80%.

Modification of oligomers

The reaction was performed in a 50 ml flask connected with a condenser. The reactor was firstly charged with 5 g powder of oligomer-1 and 20 ml acetone as the solvent, 5 mg of acetic acid as a catalyst was added. Then the reactor was flushed with N₂ for three times, and then placed into water bath and heated to 50 °C. The reaction was conducted for 5 h while the reactant was stirred vigorously with a magnetic stirrer. After reaction, a yellow powder product precipitated on the bottom of the flask, the products were collected by dissolving them with distilled water and then precipitated by using diethyl ether, finally dried at 50 °C for 12 h. The sample was stored and marked as oligomer-4, the yield is about 26%.

Phase behavior observation

The phase behavior of the oligomer-1 react with CO₂ was observed in an 80 ml high pressure resistant view-cell with a magnetic stirrer. At first, 4 g of oligomer and 40 ml of the solvent (NMP or HMPA) were added into the view-cell at room temperature, Then operating procedure is similar to the polymerization reaction as described above, besides the phase behavior was interval recorded by a digital camera during the reaction.

Characterization and analysis

Fourier-transform infrared (FTIR) spectra of the samples were recorded at room temperature with a Bruker Vertex 70 FTIR spectrometer. The measured wave number range was 400-4000 cm⁻¹. Mass spectrometric and tandem mass spectrometric analysis were performed on a Bruker Autoflex III MALDI-TOF/TOF mass spectrometer (Bruker Daltonics, Billerica, MA, USA) equipped with a 355 nm Nd:YAG laser. DHB (20 mg/ml stock solution in 0.1% of TFA/ACN (50:50, vol/vol)) was used as the matrix, and the polymer samples were prepared by diluting to a 2 mg/ml concentration in the ultrapure water contains 0.1% of TFA. The matrix and polymer solutions were mixed in equal ratio, and 1.0 μL of the final mixture solution was deposited onto the MALDI target plate and allowed to dry at ambient conditions via the dried droplet method.

Results

Structure of the oligoureas

Firstly, we prepared oligomer-1 with using 4,7,10-trioxa-1,13-tridecanediamine and carbon dioxide in the absence of solvent, and then oligomer-1 was used to prepare oligomer-2 in the HMPA and oligomer-3 in NMP, respectively. The average molecular weight of oligomer was calculated with the mass spectrum similar to our previous work^[11], because that the GPC cannot give helpful information (Figure S5, S6). Figure 1 shows the MALDI-TOF mass spectra of the synthesized oligomers, the polyurea oligomer-2 (obtained in HMPA) has the similar single molecular distribution with a repetitive unit of 246.4 Da to the polyurea oligomer-1. As seen in Figure 1, oligomer-2 has the highest number average molecular weight and the highest corresponding average degree of polymerization among the three samples. Besides, oligomer-1 and oligomer-2 have the same end groups although there are some satellite peaks in the oligomer-2 which ascribed to the sodium or potassium ion brought in the characterization process. By comparison, the polyurea oligomer-3 obtained in NMP solvent shows a double molecular distribution. One is similar with the oligomer-1 and oligomer-2 containing the same repetitive unit of 246.4 Da as well as the same end groups. While, the other (1478.9, 1232.9, 986.3 Da) has the same repetitive

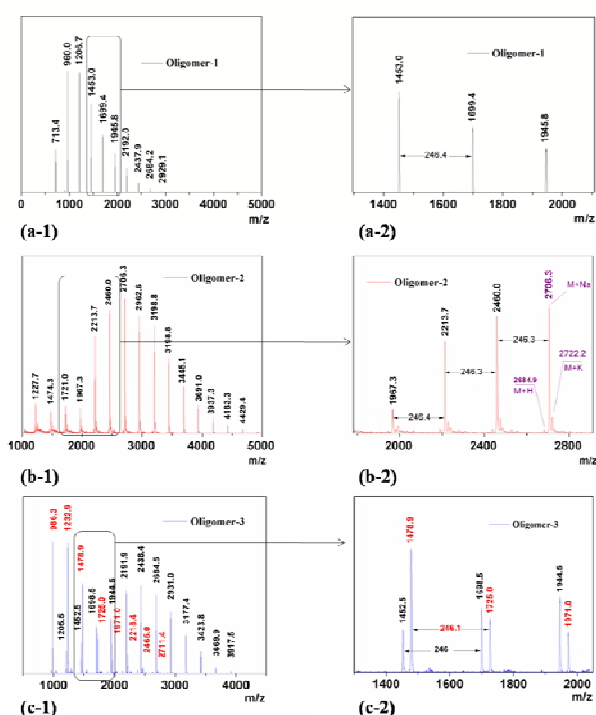


Figure 1 The MALDI-TOF spectra of the oligourea (a) oligomer-1, (b) oligomer-2 and (c) oligomer-3

unit of 246.3 Da, but its average molecular weight varied to the former one (1453.0, 1206.7, 960.0 Da) with a deviation of 26 Da at the same polymerization degree. Based on these analyses, the polyurea oligomer-3 should contain two kinds of the molecular structures. Furthermore, FTIR was used to confirm the structure of

the oligomers. As shown in Figure 2, All of these samples have the similar characteristic peaks of urea groups at 1620 cm^{-1} (amide I), 1591 cm^{-1} (amide II) and 3328 cm^{-1} (N-H) similar to the previous work,^[11] indicating the formation of urea functional groups and the CO_2 molecules were successfully inserted into the polyether amines. The absorbance peaks at 1142 cm^{-1} and 1122 cm^{-1} belong to the ether bonds brought by the initial substrate of diamine. The FTIR analysis could not give sufficient information for the new molecular structure formed in polyurea oligomer-3. Besides, we also failed to get valuable information from NMR. In order to confirm and identify the new molecular structure formed in the polyurea oligomer-3, tandem mass spectrometric was used to analyze the structure of the oligomer-3 based on their tetramers (986.3, 960.0 Da). The analysis procedure is as follows, firstly detect the molecular ion peaks by using MALDI-TOF, then impact the 986.3, 960.0 Da peaks and analyze their corresponding trimer fragments. The results show that signal at 960.0 only have two kinds of main trimer fragments (713.2, 739.6 Da), due to the tetramer molecule is a linear symmetric structure. To check the difference between 986.3 and 960.0 ion peaks is coming from variation of the end groups or not, we have prepared a linear polyurea oligomer-4 based on the reaction of acetone and oligomer-1 (described in the experimental section, Scheme S1 and Figure S1), in which both the

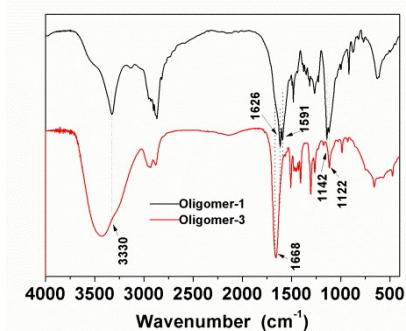


Figure 2 The FT-IR-spectra of the corresponding oligourea

molecules with unilateral end group (999.7 Da) and double end groups (1039.8 Da) modified by acetone were obtained. We chose the molecule unilateral side modified with acetone to analyze and compare with the peaks of oligomer-3. The oligomer-4 at 999.7 Da presents four kinds of fragments (713.8, 740.4, 753.7, 780.0 Da), which is different to the oligomer-3 at 986.3 Da (713.8, 739.6, 765.6 Da). In addition, the formation of the trimer fragment ion experiences the similar proton transfer process^[19,20] as the same with polyamide, and the chemical structure was shown in the Figure S2. Considering these oligomers, they all have three main clusters with the similar fragments and the same repetitive unit. But at the same polymerization degree, there is a 26 Da difference in the molecular weight between 986.3 Da and 960.0 Da. Similar to the fragmentation pattern of polyamides, each urea linkage has two adjacent cleavage sites with a 26.0 deviation between two kinds of fragments which is aroused by the cleavage in the neighboring N-C and C-N bonds.

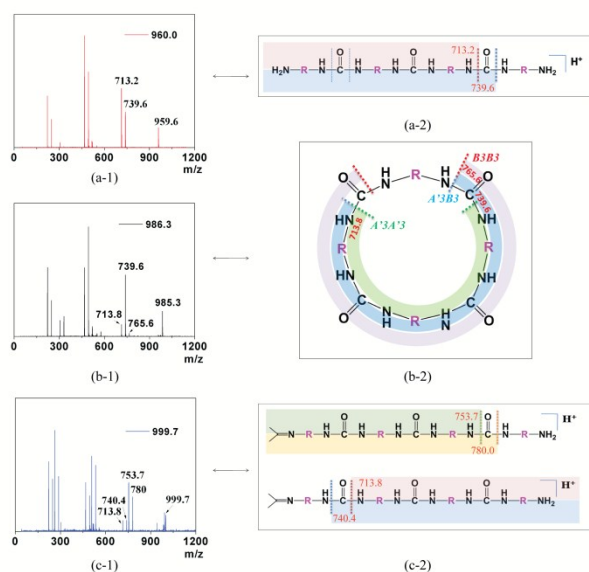


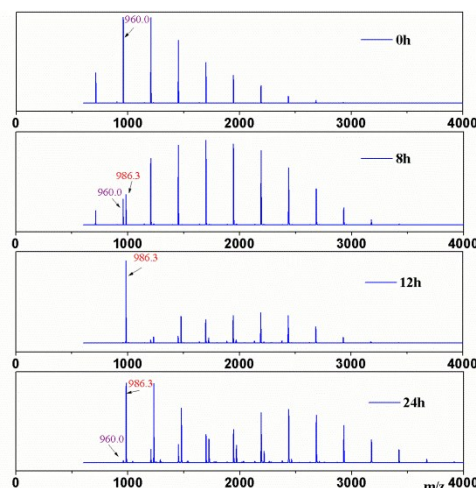
Figure 3 Fragments formation analysis of (a) oligomer-1, (b) oligomer-3, and (c) oligomer-4.

For further analysis, the fragments were named according to their end groups, for example, the fragment ion containing amino end group was named as A_n , in which the primary amino as A_n and secondary amino group as A'_n . The fragment ion containing carbonyl end group was termed as B_n , and the fragment ion with the end groups neither amino group nor carbonyl group was termed as C_n , (n is corresponding to the polymerization degree of the fragment ion). As to the trimer fragments ion of oligomer-1 of 959.7 Da, two types of fragments were derived from the symmetric amino end group (Figure 3a-2). While, for the trimer fragment ion of oligomer-4 (999.7 Da), four types of fragments were derived from the asymmetric end group (Figure 3c-2). In which, two fragments contain the imine end group (753.7, 780.0 Da), and the other two contain amino end group (713.8, 740.4 Da). However, for the trimer fragment ion of oligomer-3 at 986.6 Da, three types of fragments are obtained as seen in Figure 3b-2, indicating the oligomer-3 is not the linear molecule with the same or different end groups. Therefore, a macrocyclic structure was speculated and further analyzed. The trimer fragments of oligomer-3 at 986.6 Da may be formed via two C-N bonds in macrocyclic molecule rupture to three types of trimer fragments ($A'_3A'_3$, $2A'_3B_3$, B_3B_3) as seen in Figure 3b-2. For the cleavage of macrocyclic polyurea molecule there are two features: One is that three adjacent peaks have a 26

Table 1 Comparison of the theory and experimental results of mass spectrometry for the polyurea oligomer-3.

$[M_n+1]^+$	Tetramer	Pentamer		
Theory	959.6598	986.6391	1205.8178	1231.7971
Experimental	959.6579	986.6415	1205.8149	1231.7995

Da consecutive difference in each cluster, and the number of clusters is related to the degree of the polymerization. The other is that the signal intensity of the middle fragment (A'_3B_3 -739.6) in each cluster should be the strongest due to the superposition of A'_3B_3 and $B_3A'_3$ fragments because of its symmetric ring structure. These features have been clearly illustrated in the Figure 3b, and that can also explain the characteristics of dimer fragments in oligomer-3 (Figure S3). Moreover, the formation of the macrocyclic structure was further certified by high resolution mass spectrometry, it is an effective method for accurate measurement of the molecular weight of polymer.^[21-23] Internal standard calibration method is used to improve the precision of mass. We have compared theory and experimental molecular weights for the tetramer and pentamer calculated directly according to the deduced chemical structure. As shown in Table 1, the experimental data are well in agreement with the theory results and the repeat unit 246.157 matches the theoretical one of 246.158 exactly of polyurea oligomer-3 (Figure S4). The theory data of mass as 246.158 for this component further shows it is a polyurea repetitive unit. In addition, at the polymerization degree of 4 or 5, the theoretical mass of macrocyclic oligourea is 986.6391 and 1231.7971, respectively, which is about 2.4 ppm and 1.9 ppm error to the experimental results. Therefore, the high resolution mass spectrometry results further proved the formation of the



macrocyclic structure.

Figure 4 MLADI-TOF of the oligomer-3 formed at different reaction time

Furthermore, the formation and distribution of the molecular weight with the reaction proceeding have been discussed. As shown in Figure 4 and table 2, it is clearly that the average molecular weight increased with prolonging the reaction time and the cyclic molecule was gradually formed after reaction for 8 hrs. Moreover, the cyclic oligomer presented to compete with the linear one with further extension of the reaction time, and it presented two kinds of distribution apparently. The left imperfect distribution was ascribed to the macrocyclic molecules, and the right normal distribution is assigned to linear molecules, and they have the same repetitive unit of 246.3 Da. It was found that the formation of the cyclic oligomer becomes the competitive advantage step. The

reaction of low molecular weight oligomer occurring in NMP system may go through the following two ways: one is the reaction

Table 2 The relationship between reaction time and cyclic percentage

Reaction Time (h)	Linear Polymer		Cyclic Polymer		Cyclic (%)
	M_n	M_w	M_n	M_w	
0	1389.43	1514.33	--	--	--
8	1918.61	2066.50	986.63	--	3.9
12	2184.41	2253.89	1195.40	1271.64	40.2
24	2284.26	2441.12	1392.75	1481.88	52.0

between two end amino groups in an oligomer with a CO₂ molecule to form a macrocyclic oligomer; the other is the reaction between amino groups in two oligomers with a CO₂ molecule to form a larger linear oligomer. The molecular weight was calculated by using PolyTools 1.0, the distribution or the percentage of macrocyclic oligourea was estimated by relative peak intensity of one series to another. Based on the above results, the solvent has a significant effect on the post-polymerization. The macrocyclic oligomer was formed in NMP system, while large linear oligomer with high molecular weight was produced in the HMPA.

The phase behavior

Herein, the reaction phase behaviors were observed and analyzed for both the NMP and HMPA solvents polymerizing system. As seen in Figure 5, the oligomer-1 is not soluble at room temperature, while it could dissolve in them with increasing temperature up to 180 °C. With introducing CO₂ to 11 MPa, the desired reaction pressure, a homogeneous solution was formed. The NMP solution was expanded largely due to its high CO₂-philicity^[24] resulting in large amount of CO₂ dissolved in it. By contrast, the HMPA system was seldom expanded as its CO₂-phobicity. During the reaction, all the products were completely dissolved and the phase behavior kept no change in NMP system. However, some precipitates were found to form at the interface of HMPA and CO₂ phase during the reaction, indicating that the large oligomers were formed and could not dissolve in the HMPA. In comparison, in the NMP system the reaction occurred in a homogeneous CO₂ expanded NMP phase, as the concentration of the oligomer was lower, which will reduce the probability of the reaction between intermolecular of oligomers, but benefit for the reactions of intramolecular amino groups with a CO₂ molecule to form a ring molecule. However, in the HMPA system the reaction occurred on the interface, the molecules of oligomer-1 (end groups like double amino groups, double carbamate groups, a amino group-a carbamate group) and CO₂ concentrated on the inter-phase resulted in a probability increase of the intermolecular reaction between two or three oligomer molecules in the interface. Thus, the larger linear oligomers were formed in the HMPA systems. However, there may be other reasons except for the phase

behavior as the formation of cyclic product may be complicated, both the intermolecular and intramolecular hydrogen bonding exist in oligomers and solvent. The hydrogen bonding in HMPA would be stronger than that in NMP solvent, which may affect the polymerization.

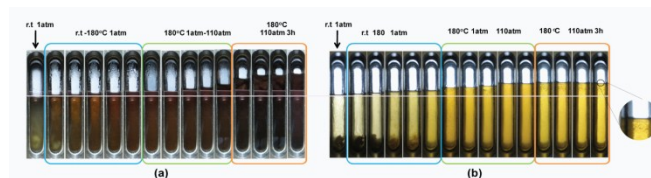


Figure 5 The phase behaviour of the reaction process in NMP (a) and HMPA (b)

Conclusion

In summary, a new kind of macrocyclic polyurea oligomer has been successfully synthesized by an environmental benign and green process, with using carbon dioxide as carbonyl resource to react with polyether diamine directly. The molecular weight and structure of the formed polyurea were identified by using Tandem mass spectrometry. The molecular weights and structure were largely related to the solvent used, the oligomers formed in HMPA were much larger compared to that in NMP. Moreover, a kind of novel macrocyclic polyurea oligomer was formed in NMP except for the sort of linear one, and the ratio of the macrocyclic to linear oligomers increased with prolonging the reaction time. The phase observation shows that the reaction occurred on the interface and the product precipitated out during the reaction in HMPA. However, the reaction occurred in the expanded homogeneous liquid NMP phase as large amount of CO₂ dissolved into the CO₂-philic NMP solvent, which may contribute to the formation of macrocyclic oligourea. It is a green and sustainable chemical process as carbon dioxide was used as carbonyl group. We hope the synthesized macrocyclic polyurea oligomer would have a special application as an additive or pharmaceutical intermediate.

Acknowledgements

We gratefully acknowledge the financial support from the National Natural Science Foundation of China (21273222) and NSFC-JSPS international cooperation project (2131140166).

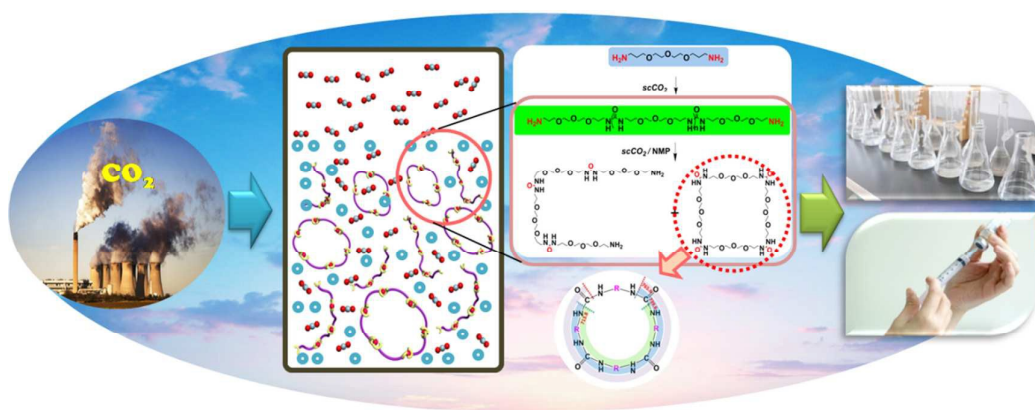
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- a, State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (CAS), Changchun 130022 (P.R. China) corresponding authors, E-mail: fyzhao@ciac.ac.cn; yhzhou@ciac.ac.cn
 b, Laboratory of Green Chemistry and Process, Changchun Institute of Applied Chemistry, CAS, Changchun 130022 (P.R. China)
 c, University of Chinese Academy of Sciences, Beijing 100049c,
 d, National Analytical Research Center of Electrochemistry and Spectroscopy, Changchun Institute of Applied Chemistry, CAS, Changchun 130022 (P.R. China)
 e, Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, CAS
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Carbon dioxide as a sustainable resource for macrocyclic oligourea

Zhong Ying, Yanlei Dong, Jianwei Wang, Yancun Yu, Yihan Zhou, Yuequan Sun, Chao Zhang, Haiyang Cheng, Fengyu Zhao



A macrocyclic polyurea oligomer was synthesized from a sustainable CO₂ route. MALDI-TOF and tandem mass spectrometry were used to confirm the formation of macrocyclic via fragment analysis.