RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

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

Zhong Ying [a,b,c], Lijun Zhao[d], Chao Zhang [a,b], Yancun Yu [a,b], Tong Liu[a,b,c], Haiyang Cheng[a,b], Fengyu Zhao [a,b*]

[a] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China

[b] Laboratory of Green Chemistry and Process, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China

[c] University of Chinese Academy of Sciences, Beijing 100049, PR China

[d] Department of Chemical Engineering, Changchun University of Technology, Changchun 130012, P R China

*Corresponding author, Tel:+86-431-85262410; zhaofy@ciac.ac.cn

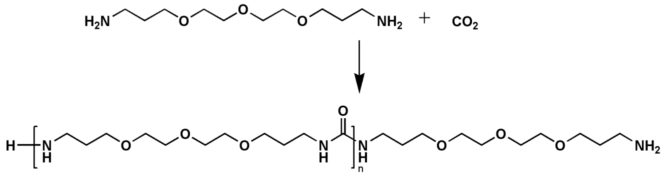
Abstract

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 the ^{13}C NMR analysis, and the average molecular weight was estimated with MALDI-TOF MS spectrum. The weight average molecular weight of the obtained oligourea is about 2210 Da under 180 ^oC and 11 MPa reacting for 12 hrs. Moreover, the prepared oligourea has a moderate thermo-stability, it has an initial decomposition temperature at ~220 ^oC and the melting temperature of 110 ^oC as confirmed by TGA and DSC. As a soluble oligomer, it could be used as a building block to synthesize CO_2-based polymeric materials for that it possesses chemical active end group of amino. For example, the foaming plastic, greases, spun fiber and high strength polymer materials may be fabricated by reaction of oligomer with a chain extender like diisocyanate, diester or diacid.

Keywords: CO_2 utilization; polyurea; oligomer; green synthesis;

1. Introduction

Polyureas have some special properties like hydrolysis resistance[1], excellent mechanical property[2, 3] and anti-corrosion[4, 5,] thus they have wide applications in coating[6], grease[7-9] and microcapsule[10, 11]. As we known, tranditional polyurea is usually produced base on the reaction of diamine with isocyanates[12-14], urea[15-17], and diphenyl carbonate[18]. More recently, the polyureas were successfully synthesized with the dimethyl carbonate and propylene carbonate as carbonylating agents to react with diamines, those reaction are more environmental friendly, energy-saving as they are operated in the absence of toxic agents of phosgene and isocyanate. [19] Moreover, the feedstock of dimethyl carbonate and propylene carbonate are possible produced from carbon dioxide with methanol and propylene glycol. These processes are of important innovation as they indirect transfer carbon dioxide which is the global warming gas to polymeric materials. Recently, the chemical fixation and utilization of carbon dioxide has attracted much attention in the field of environment protection, new energy resources and advanced material. Significant efforts have been devoted to exploring 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 that carbon dioxide was used directly to synthesize polyurea without any solvents or additives. Use of carbon dioxide as the feedstock instead of the toxic polyisocyanates in production of polyurea should be a terrific and appreciated strategy. But it has not attracted enough attention up to now, only several results were reported since the first work reported in 1947 by Gerard et al.[24] Yamazaki and his co-workers used stoichiometric amount of diphenyl phosphate, phosphorus chlorides or N-acyl phosphoramidites as catalyst to catalyze the polymerization of aromatic diamine with CO_2 in pyridine or acetonitrile solvent. [25-27] Our previous investigation demonstrated that urea derivates could also be easily produced from alkyl amines and carbon dioxide at the reaction conditions similar to its analogous urea.[28] In recent years, we found that polyurea could be synthesized by the reaction of diamines with carbon dioxide directly. The prepared several polyureas like polyurea-6 (from the hexamethylenediamine) and polyurea-8 (from the 1,8-Diaminooctane), which are high resistance to the solvents such as polar solvent (H_2O, EtOH, Actone, DMF, NMP, 5% LiCl solution), non-polar solvent (CCl_4, C_6H_6), acid (HCl, H_2SO_4) and base (NaOH or KOH) at the room temperature[29]. In the present work, we prepare a water soluble oligourea by using diamine containing ether groups reacting with carbon dioxide as shown in scheme 1. Therefore, it is possible to investigate the average molecular weight by MALDI-TOF mass spectrometer and ^{1}H NMR, and the reaction conditions could be evaluated by using average molecular weight. As a soluble oligomer, it may have wide applications in the environment friendly coating and hydrophilic grease without the toxic organic solvents. Moreover, it could be also used as a building block to synthesize CO_2-based polymeric materials as it has chemical active end group of amino. For example, it can be used to fabricate the foaming plastic, greases, spun fiber and high strength polymer materials by reaction with a chain extender like diisocyanate, diester or diacid, the prepared oligourea. And so, the present research provides a new route for synthesis of various polymer materials with different properties by direct reaction of CO_2 with the amines having different molecular structures.



Scheme 1 Formation of oligourea from CO_2 and diamine

2. Experimental Section

Chemicals

All the chemicals were used as received from commercial sources without further purification. 4,7,10-Trioxa-1,13-tridecanediamine (short for E2) was purchased from Sigma-Aldrich Corporation. Gas of carbon dioxide (99.5%) was purchased from Changchun JuYang Gas Company; 1-Methyl-2-pyrrolidinone (NMP), hexamethylphosphoramide (HMPA) and chloroform were purchased from Beijing Chemical Reagent Co. Ltd. ; N,N'-Dimethylpropyleneurea (DMPU) from Aladdin Reagent Co. Ltd.; and methanol,ethanol, acetone,dioxane, toluene, isopropanol and THF were purchased from Xilong Chemical Reagent Co. Ltd. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) and trifluoroacetic acid (TFA) were purchased from Meryer Corporation. All kinds of water soluble dimines except E2 (shown in the supporting imformation) were purchased from Hunstman Corporation.

Synthesis of the oligomer

The typical synthesis process is as follows: 4, 7, 10-trioxa-1,13-tridecanediamine (E2) was selected as reactant because it contains several ether functional groups. And the ether functional groups 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 an 100 mL autoclave. And blew carbon dioxide for three times to remove the oxygen and then sealed and heated to 180 ^{o}C. In the next moment, CO_2 was introduced into the autoclave up to 11 MPa and the reaction was started with vigorously stirring for 12 hrs. 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 yellow paraffin wax like, was collected and dried at 50 ^{o}C for 24 hrs, 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, blew with CO_2 for three times, and then heated to 180 ^{o}C. After maintaining 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 kept for 3 hrs with stirring vigorously, 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 ^{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 Adamantane standard (δ=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 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. Matrix 2, 5-dihydroxybenzoic acid (DHB), was obtained from Aldrich, were used in this study. Matrix solutions were freshly prepared in water at a concentration of approximately 20 mg/mL. Thermal gravimetric analysis (TGA) experiments were performed using a PerkinElmer Thermal Analysis at a temperature rate of 10 ^{o}C min^{-1}

from room temperature up to 800 °C in an 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 -50 °C up to 180 °C in an N_2 flow. The first heating run was used to remove all effects due to thermal history of the sample and only second heating runs were used.

3. Results and discussion

In order to prepare a water soluble polyurea, as starting substrate several kinds of water soluble diamines were selected and tested firstly, it was found that 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 prerequisite for the following research such as examination of the molecular weight, evaluation of the synthesis parameter. Thus, the 4, 7, 10-trioxa-1, 13-tridecanediamine was selected as the starting material for this study.

Firstly, the FT-IR spectroscopic analyses were 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 urea functional group was confirmed to form 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 ether bond. Besides, Urea groups exist in the oligourea was also supported by the results of 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 presented at 160.0 ppm, which clearly indicates the formation of 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 methylene of the substrates.

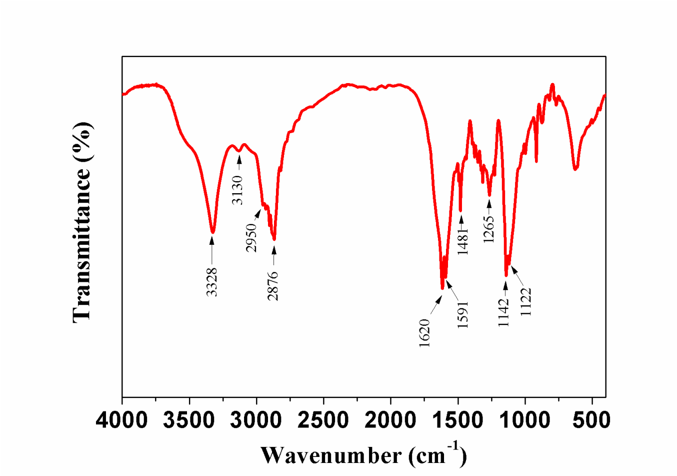


Fig.1 FTIR-spectrum of the oligourea synthesized from E2 with CO_2 at 180 °C, 11 MPa, 12 hrs.

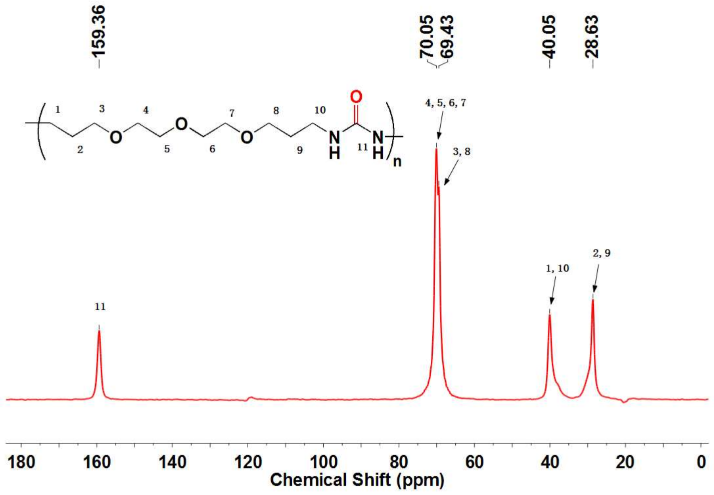


Fig. 2 ^{13}C-NMR of oligourea synthesized from E2 with CO_2 at 180 °C, 11 MPa, 12 hrs.

Table 1 Comparison of the dissolving capacity of several solvents to the prepared oligourea

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

"+" soluble at room temperature; " -" insoluble

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 solvent like hexamethylphosphoramide (HMPA), N,N'-Dimethylpropyleneurea (DMPU) and 1-methyl-2-pyrrolidinone (NMP), and the polar protic solvents such as trifluoroacetic acid (TFA) and 1,1,1,3,3,3-hexafluoro -2-propanol(HFIP). But it is not soluble in conventional solvents such as 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 is near 220 °C, the maximum decomposition temperature is 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, DSC curves showed that its highest melting temperature is about 110 °C. Compared to the aliphatic oligourea, the prepared oligourea has a lower melting point as the ether functional groups give the chain much more spin conformation and make the structure of polyurea oligomer more flexible. In addition, imperfection or different scales for crystallization of the prepared oligourea may lead to multiple melting phenomenon. Both of the ether carbon group chain and the urea functional group will affect the crystallization. Based on the thermal stability, melting behavior and water solubility, the prepared oligomer is an environmental benign material as it could be processed under a wide range of processing temperature without organic solvents.

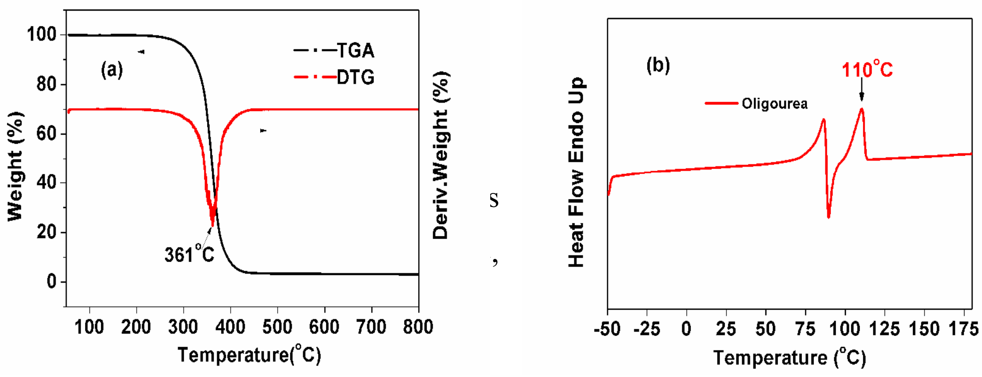


Fig. 3 TGA (a) and DSC (b) analysis for the oligourea synthesized at 180 °C, 11 MPa, 12 hrs.

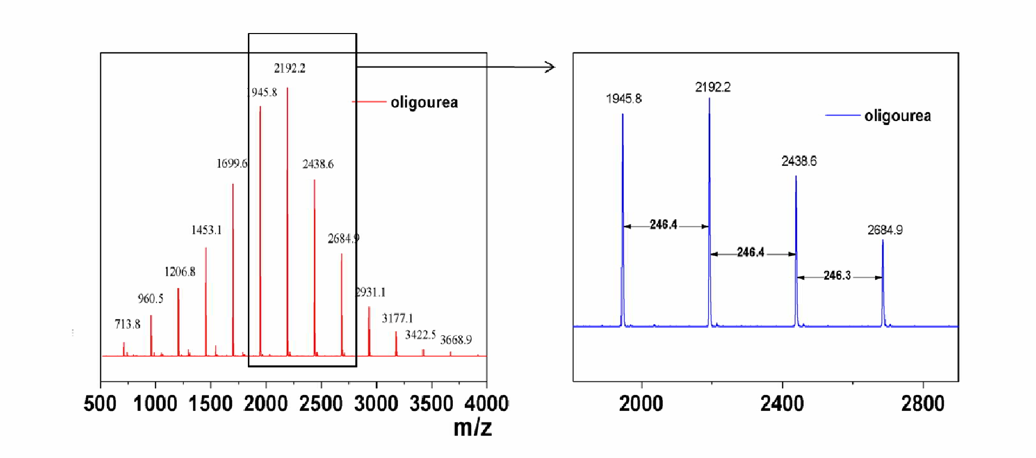


Fig. 4 MALDI-TOF of the oligourea synthesized at 180 ^{o}C, 11 MPa, 12 hrs.

The average molecular weight of the obtained water soluble oligomer was detected by MALDI-TOF mass spectrometer. The MALDI-TOF MS spectrum of the oligourea synthesized at 180 ^{o}C, 11 MPa, 12 hrs showed a symmetric distribution of molecular weight (Fig. 4). The weight average molecular weight is 2210, for which the degree of the polymerization is near 8-9. Besides, the repetitive unit is 246.4 Da, which is equal to formula weight of the chemical repetitive 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 the amino groups which maybe contain one hydrogen proton. These amino groups as the end group are chemical active, and so as a building block, the oligourea can be widely utilized in the synthesis of various polymeric materials.

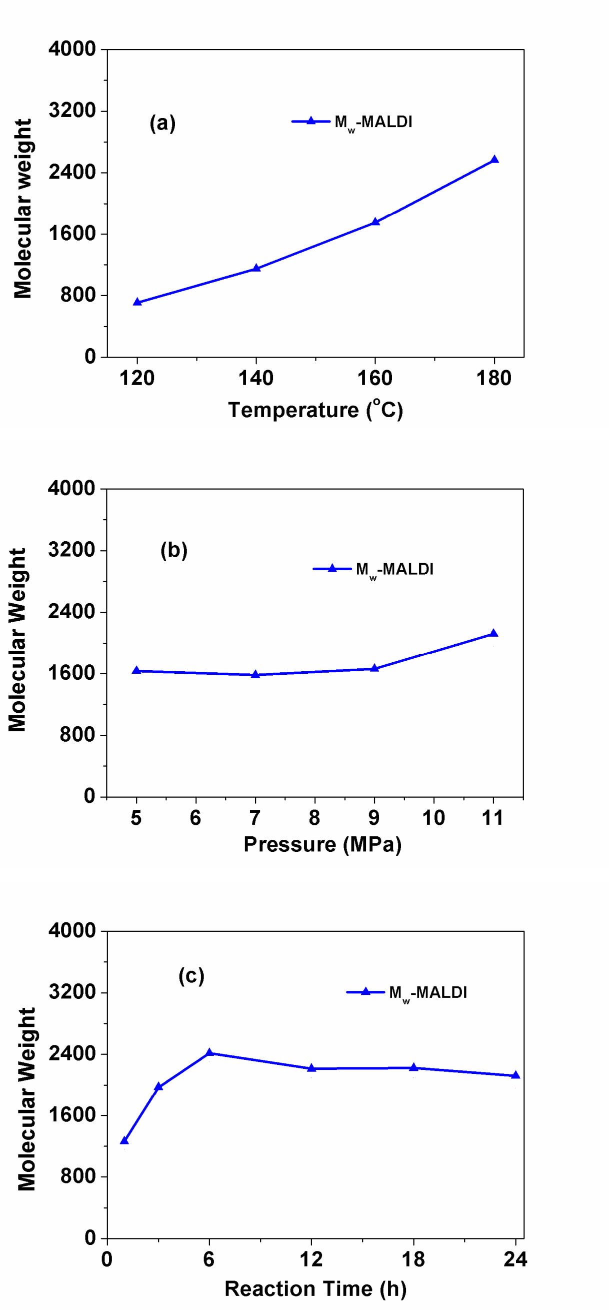


Fig. 5 The relationship of the parameters with the average molecular weight

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

Besides, the phase-behavior of the reaction that 4, 7, 10-Trioxa-1, 13 -tridecanediamine (E2) react with CO_2 was observed using a high pressure view-cell (Fig. 6). Transferred 15 mL of E2 into an 80 mL view-cell at room temperature, then heated the view-cell to 180 ^{o}C and introduced CO_2 to view-cell with continuously stirring. It was found that the volume of liquid phase was increased with introduction of 11 MPa CO_2 because that CO_2 could dissolve into the liquid phase of reactant, thus the volume was expanded. It is clear that the color of the reaction mixture turn from transparent to light blue with increasing of temperature, and then turn to light

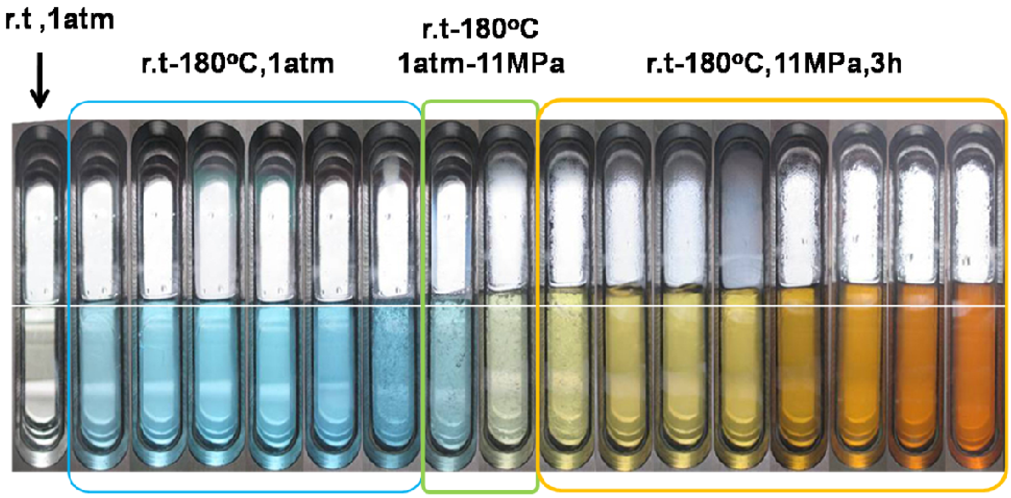
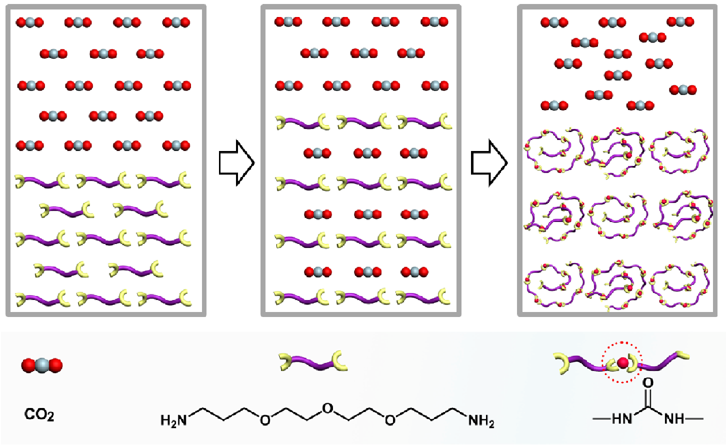


Fig. 6 Phase behavior of the reaction of E2 with CO_2 at 180 ^{o}C,11 MPa, 3 hrs



Scheme 2 Illustration of phase behavior for the reaction of E2 with CO_2

yellow after introducing 11 MPa CO_2, finally it turn to yellow after maintaining at180 ^{o}C, 11 MPa for 3 h. These color changes may be caused by the following reactions: the reactant polyether diamine reacted with carbon dioxide to form a carbamate, and the polycondensation of carbamate with diamine to form polyurea as shown in Scheme 2.

Over all, we successfully prepared a water soluble polyurea oligomer with using CO_2 as 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 diisocyanate, diester or diacid, the prepared oligourea would be used to make the foaming plastic, greases, spun fiber and high strength polymer materials.

4. Conclusion

In conclusion, we prepared a new kind of water soluble oligourea by a direct reaction between CO_2 and polyether diamine without any solvents or additives. The produced oligomer has an initial decomposition temperature of 220 ^oC and melting temperature around 110 ^oC. Under 180 ^oC, 11 MPa reacting for 12 hrs, the number average molecular weight of the oligourea is near 2100 Da detected by MALDI-TOF mass spectrum. The relationship between reaction parameters and average molecular weight shows that the effect of temperature is more significant than reaction pressure. The higher temperature can benefit for a higher polymerization degree after reaching equilibrium. While, as the prepared oligourea has an initial decomposition temperature around 220 ^oC and a melting temperature about 110 ^oC, the suitable reaction temperature in this work was selected at range of 120-180 ^oC. The reaction will attain a chemical equilibrium finally after reaction for 6 hrs at 180 ^{o}C, 11 MPa. In addition, due to the end group is the chemical active amino group, the oligourea 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 transform CO_2 into useful and value-added polymeric materials.

Acknowledgements

This work was financially supported by the NSFC and NSFC-JSPS International cooperation project (21273222).

Notes and References

1. V. Sendijarevic, A. Sendijarevic, I. Sendijarevic, R. E. Bailey, D. Pemberton and K. A. Reimann, *Environ. Sci. Technol.*, 2004, **38**, 1066–1072.

2. N. Samson, F. Mechin and J. P. Pascault, *J. Appl. Polym. Sci.*, 1996, **65**, 2265–2280.

3. K. Holzworth, Z. Jia, A. V. Amirkhizi, J. Qiao and S. Nemat-Nasser, *Polym.*, 2013, **54**, 3079–3085.

4. X. P. Liu, T. L. Zheng and J. P. Xiong, *Int. J. Electrochem. Sci.*, 2013, **8**, 11588–11595.

---

5. L. Feng and J. O. Iroh, *Prog. Org. Coat.*, 2014, **77**, 590–599.

6. M. A. Shenoy and D. J. D'Melo, *Surf. Coat. Int. Part B-Coat.Trans.*, 2006, **89**, 221–230.

7. L. I. Borisenko and Y. L. Ishchuk, *Chem. Technol. Fuels Oils*, 2004, **40**, 415–417.

8. Z. M. Nikishina, V. V. Butovets, I. V. Lendel and M. Y. Strashenko, *Chem. Technol. Fuels Oils*, 1987, **23**, 172–174.

9. L. Liu and H. W. Sun, *Lubr. Sci.*, 2010, **22**, 405–413.

10. P. D. Tatiya, R. K. Hedaoo, P. P. Mahulikar and V. V. Gite, *Ind. Eng. Chem. Res.*, 2013, **52**, 1562–1570.

11. K. J. Hong and S. M. Park, *Mater. Res. Bull.*, 1999, **34**, 963–969.

12. D. J. Primeaux, *J. Elastomers Plast.*, 1992, **24**, 323-336.

13. D. J. Primeaux, R. A. Grigsby and D. M. Rice, *CA*2034169-C, 1991.

14. S. W. Yang, D. J. Primeaux and D. H. Champion, *US*5082917-A, 1992.

15. Toyo Koatsu Ind Inc, *GB*981813A, 1965.

16. Toyo Koatsu Ind Inc, *GB*900787A, 1962.

17. Toyo Koatsu Ind Inc, *GB*900788A, 1962.

---

18. W. C. Pan, C. H. Lin and S. A. Dai, *J. Polym. Sci., Part A: Polym. Chem.*, 2014, **52**, 2781–2790.

19. A. K. Qaroush, A. S. Al-Hamayda, Y. K. Khashman, S. I. Vagin, C. Troll and B. Rieger, *Catal. Sci. Technol.*, 2013, **3**, 2221–2226.

20. Q. W. Song, L. N. He, J. Q. Wang, H. Yasuda and T. Sakakura, *Green Chem.*, 2013, **15**, 110–115.

21. J. Sun, J. Q. Wang, W. G. Cheng, J. X. Zhang, X. H. Li, S. J. Zhang and Y. B. She, *Green Chem.*, 2012, **14**, 654–660.

22. A. L. Zhu, T. Jiang, B. X. Han, J. C. Zhang, Y. Xie and X. M. Ma., *Green Chem.*, 2007, **9**, 169–172.

23. M. S. Liu, B. Liu, L. Shi, F. X. Wang, L. Liang and J. M. Sun., *RSC Adv.*, 2015, **5**, 960–966.

24. D. B. Gerard and H. R. Neil, *US*2550767, 1947.

25. N. Yamazaki, F. Higashi and T. Iguchi, *J. Polym. Sci., Part C: Polym. Lett.*, 1974, **12**, 517–521.

26. N. Yamazaki, T. Iguchi and F. Higashi, *J. Polym. Sci., Part A: Polym. Chem.*, 1975, **13**, 785–795.

27. N. Yamazaki, T. Tomioka and F. Higashi, *J. Polym. Sci., Part C: Polym. Lett.*,

1976, **14**, 55–57.

28. C. Wu, H. Cheng, R. Liu, Q. Wang, Y. Hao, Y. Yu and F. Zhao, *Green Chem.*, 2010, **12**, 1811–1816.

29. C. Wu, J. Wang, P. Chang, H. Cheng, Y. Yu, Z. Wu, D. Dong and F. Zhao, *Phys. Chem. Chem. Phys.*, 2012, **14**, 464–468.

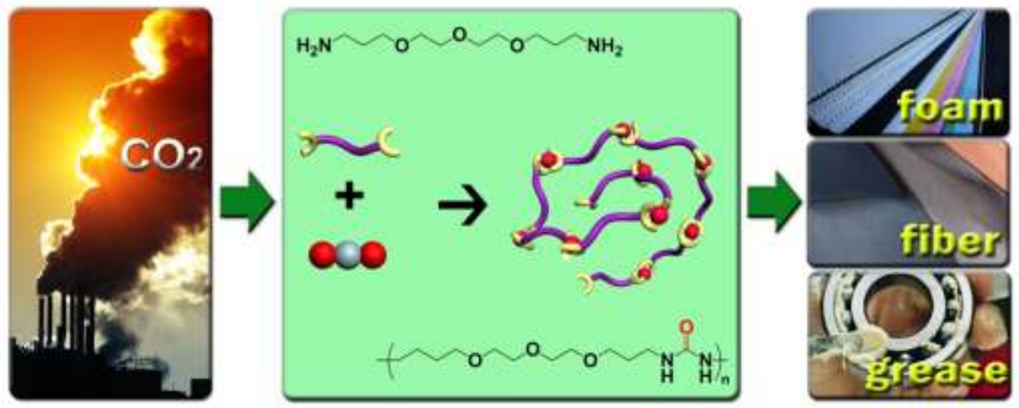
30. J. Mattia and P. Painter, *Macromol.*, 2007, **40**, 1546–1554.

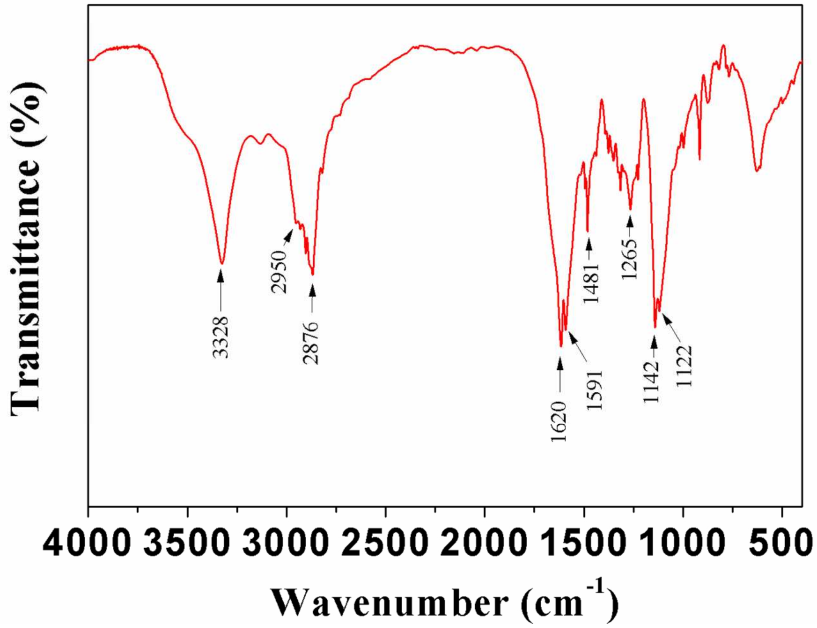
31. E. Yilgor, E. Burgaz, E. Yurtsever and I. Yilgor, *Polym.*, 2000, **41**, 849–857.

32. G. Odian, *Principle of Polymerizaiton*, John Wiley & Sons, Ltd, 2004, pp. 65–67.

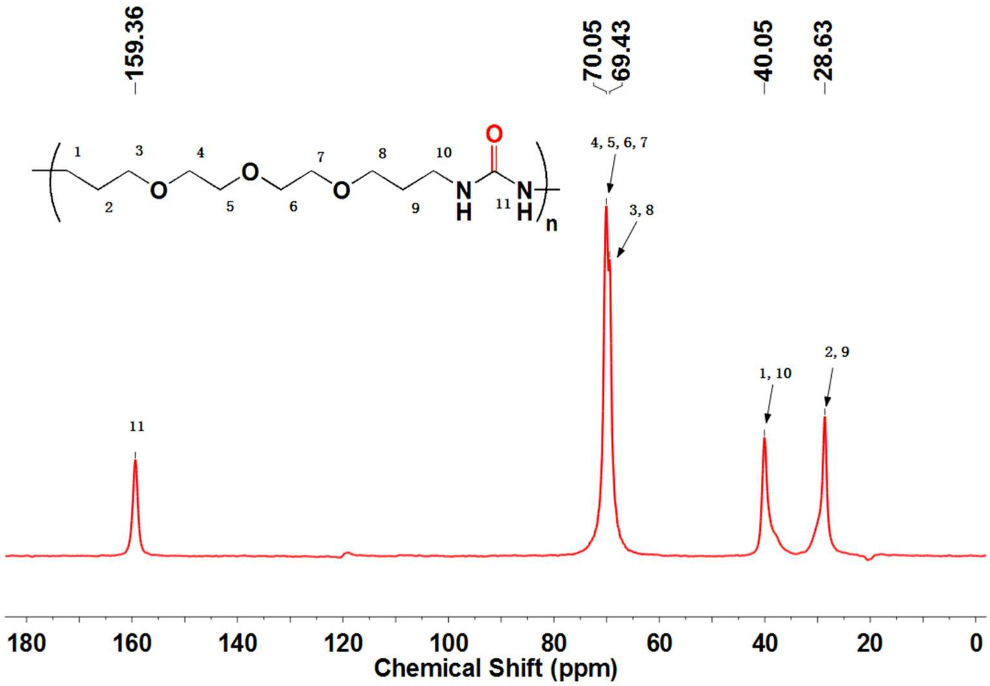
Utilization of carbon dioxide to build a basic block for polymeric materials: An isocyanate-free route to synthesize soluble oligourea

A water soluble oligourea was synthesized by an isocyanate-free route from carbon dioxide and diamine through a green process, which may have wide applications in the macromolecule field as a building block.

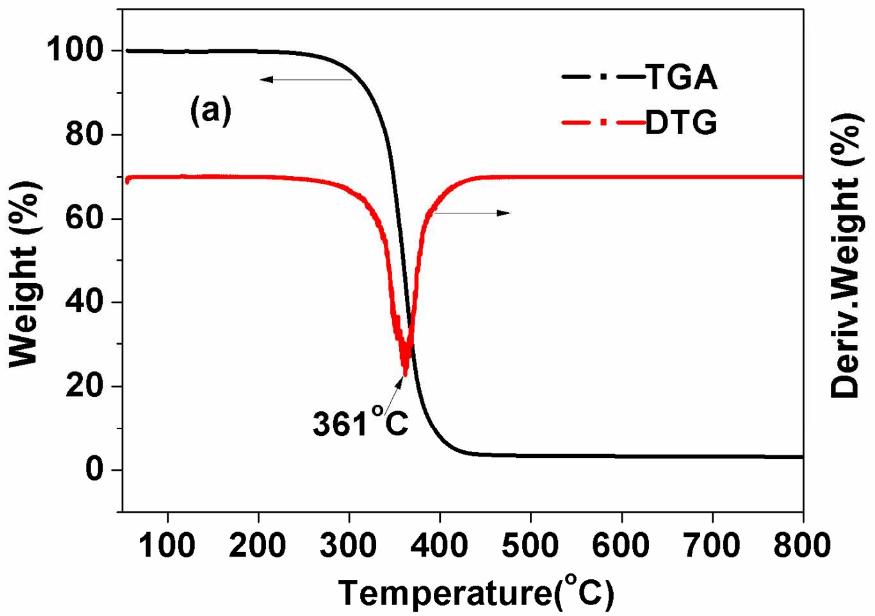




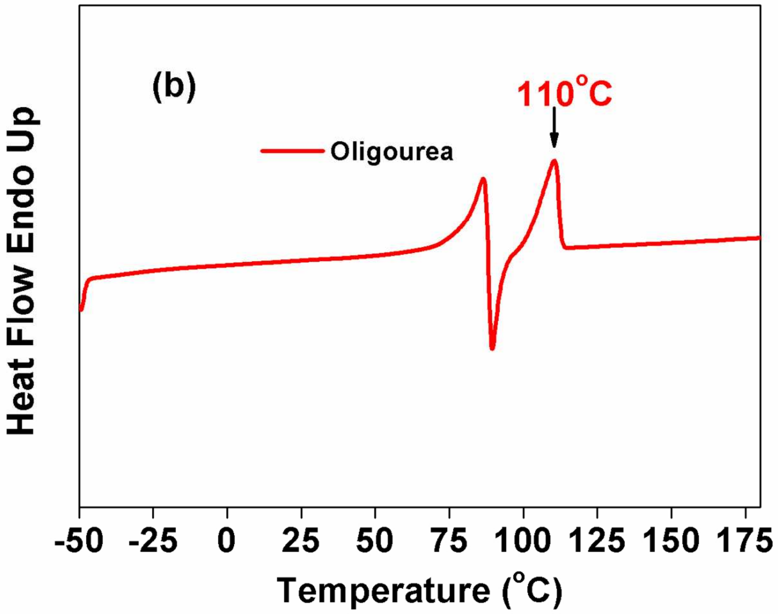
287x201mm (150 x 150 DPI)



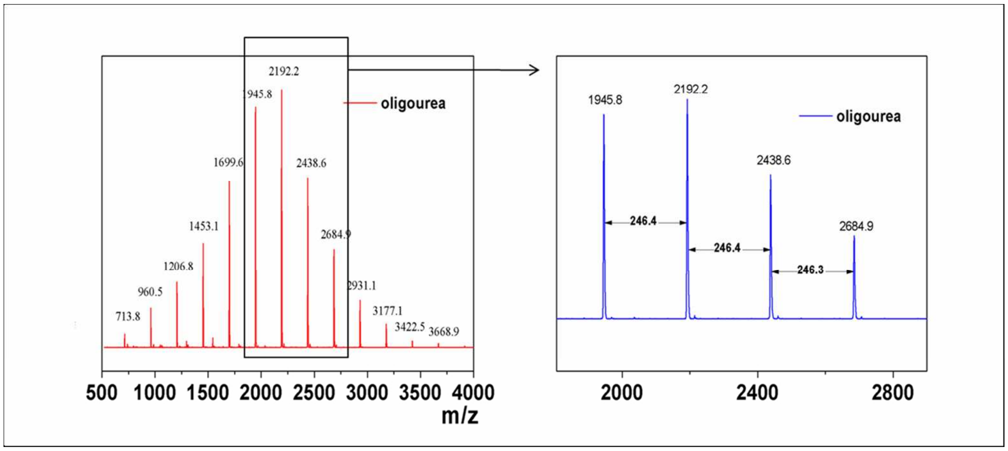
383x268mm (72 x 72 DPI)



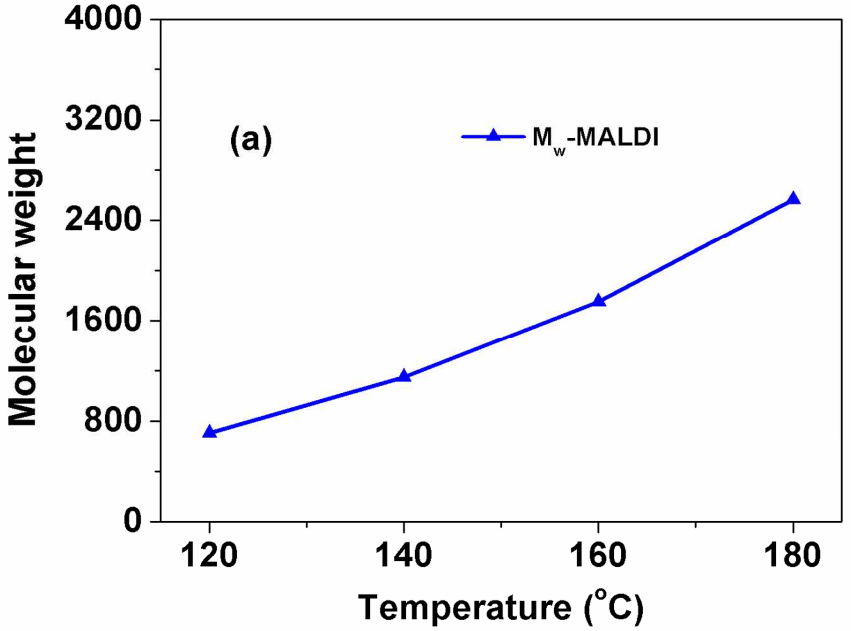
287x201mm (150 x 150 DPI)



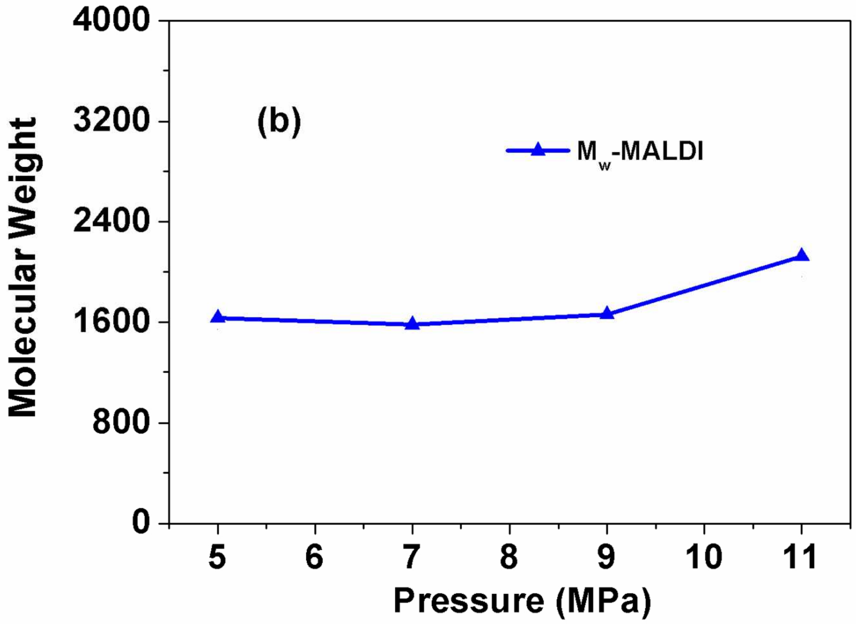
287x201mm (150 x 150 DPI)



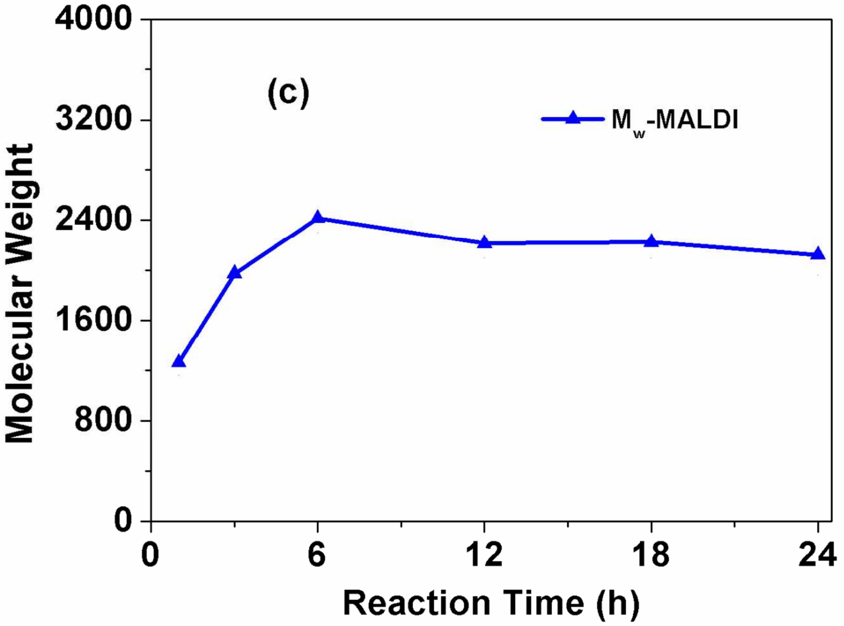
463x205mm (80 x 80 DPI)



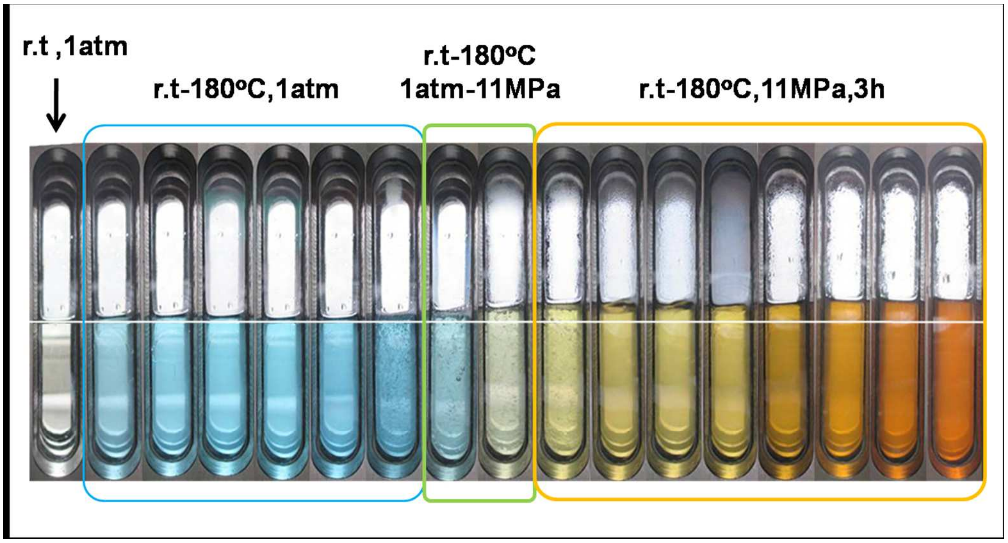
287x201mm (150 x 150 DPI)



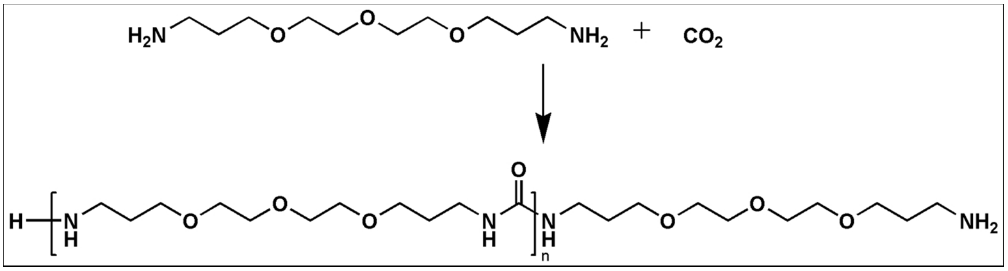
287x201mm (150 x 150 DPI)



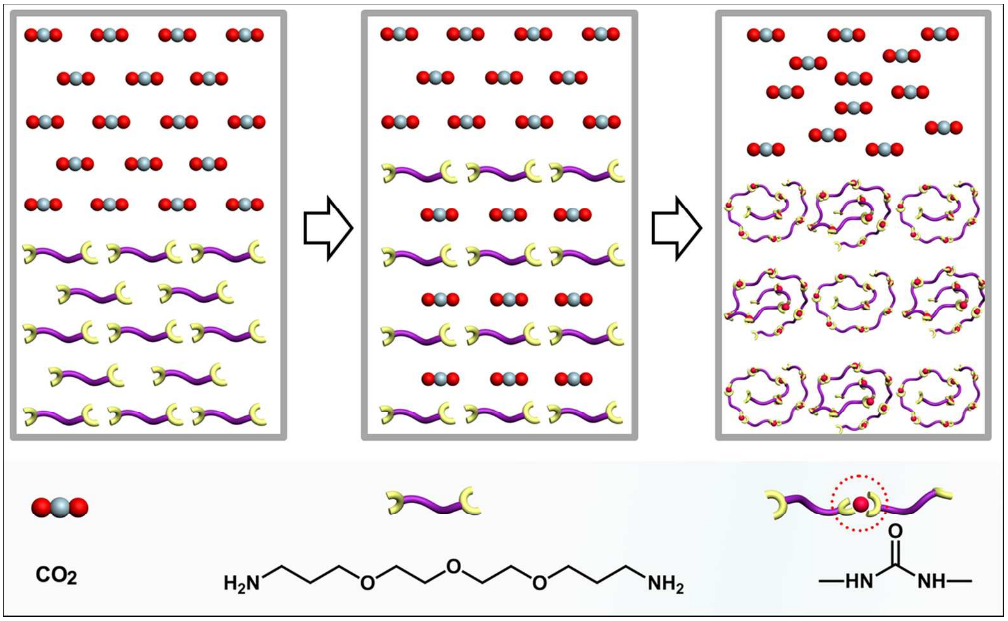
287x201mm (150 x 150 DPI)



230x123mm (150 x 150 DPI)



242x63mm (150 x 150 DPI)



224x137mm (150 x 150 DPI)