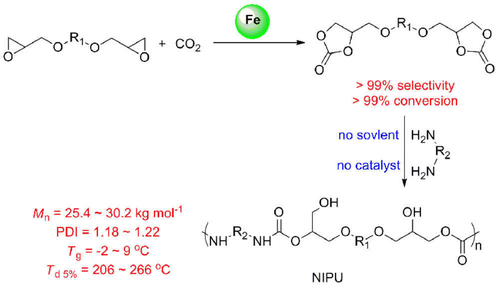
Green Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem



Polyurethanes were prepared from the polyaddition of diamines and bis(cyclic carbonate)s which were obtained via complete carbonation of diepoxides.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Quantitative Synthesis of Bis(cyclic carbonate)s by Iron Catalyst for Non-isocyanate Polyurethane Synthesis

Xingfeng Sheng,[a,b] Guanjie Ren,[a,b] Yusheng Qin,*[a] Xuesi Chen,[a] Xianhong Wang,[a] Fosong Wang[a]**

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Bis(cyclic carbonate)s were prepared quantitatively in high efficiency via the coupling reaction of carbon dioxide (CO_2) with diglycidyl ethers by [Fe(BPMCDAC)]/TBAB (Fig. 1) catalytic system, where glycol diglycidyl ether (1a) could be completely converted to the corresponding bis(cyclic carbonate) (2a) with turn over number of 1000 at 100 ^{o}C and 3 MPa in 4 h. The obtained bis(cyclic carbonate) (2a) could be used to prepare hydroxyl-functional polyurethanes via reaction with diamines, which may be one alternative for conventional polyurethanes without toxic phosgene or isocyanates. The number-average molecular weights of obtained non-isocyanate polyurethanes (NIPUs) were up to 25.4~30.2 kg mol^{-1} and the polydispersity indexes (PDIs) were relatively narrow between 1.18 and 1.22. A typical NIPU showed glass transition temperature of 9 ^{o}C and initial degradation temperature ($T_{d\ 5\%}$) of 206 ^{o}C.

Introduction

Carbon dioxide (CO_2) is regarded as the main reason for global warming,[1] but it is abundant, cheap and non-toxic, and its specific molecular structure makes it important C1 feedstock in industry. Employing CO_2 as a raw material to prepare large scale chemicals may create a new way to high value-added utilization of CO_2. Among all the reported CO_2 fixation routes, synthesis of cyclic carbonates via the coupling reaction of CO_2 with epoxides is one of the most attractive processes.[2]

Because cyclic carbonates are widely used as green solvents, electrolytes, fuel additives and intermediates for the production of biodegradable polymers,[3] numerous catalyst systems have been developed to promote this transformation.[4] Prominent among these are salen complexes of cobalt,[5] chromium,[6] zinc[7] and aluminium,[8] which show high activities under mild conditions. However, most studies have focused on the coupling reaction of CO_2 with mono-epoxides, while epoxides with two or more epoxy groups were rarely used in the literature. Lee and co-workers[9] synthesized bis(cyclic carbonate)s via the addition reaction of carbon dioxide with diglycidyl ether derivatives in N-methyl-pyrrolidone (NMP) in the presence of phase transfer catalyst, and the conversion of diepoxides was below 60% at 100 ^{o}C within 6 h. Endo *et al.*[10] prepared bis(cyclic carbonate)s via the coupling reaction of CO_2 with diepoxides in NMP at 100 ^{o}C under CO_2 atmosphere. Furthermore, Wilkes[11] found that epoxidized soybean oil could be effectively converted to carbonated soybean oil containing five-membered cyclic carbonates via reaction with CO_2 employing tetrabutylammonium bromide (TBAB) as catalyst at 110 ^{o}C. Mülhaupt and co-workers[12] reported that TBAB could catalyze the coupling reaction of limonene dioxide, epoxidized linseed and soybean oil with CO_2 at 120-140 ^{o}C, and the limonene dioxide could be completely converted to the corresponding bis(cyclic carbonate) at 140 ^{o}C and 3 MPa within 43 h. Recently, Zhang[13] reported that bis(cyclic carbonate)s could be prepared via the coupling reaction of diepoxides with CO_2 catalyzed by zinc-cobalt double metal cyanide complex, conversion of 81% could be obtained at 120 ^{o}C and 5 MPa CO_2 pressure within 9 h. Furthermore, Guillaume[14] prepared carbonate-end functionalized PTMCs through a complex series of reactions with suitable solvents. However, according to the above literatures, the complete conversion of diepoxide in the coupling reaction needed suitable solvent, relatively long time and harsh reaction conditions. Hence, though some investigations about the diepoxide/CO_2 coupling reaction have been carried out, the convenient synthesis of bis(cyclic carbonate) via the diepoxide/CO_2 coupling reaction with the complete conversion of diepoxide still remained a challenge before this work.

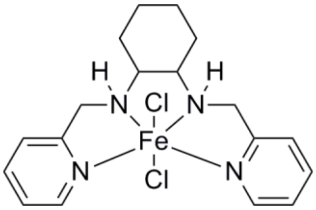
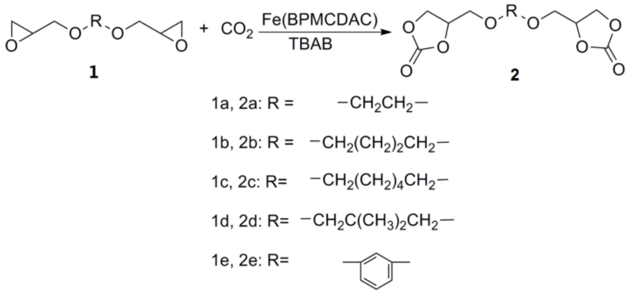


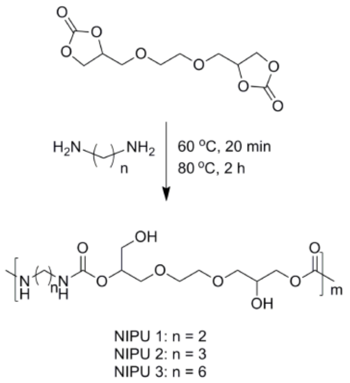
Fig. 1 Structure of Fe(BPMCDAC).

Bis(cyclic carbonate)s can react with di- or polyfunctional primary alkyl amines, leading to non-isocyanate polyurethanes (NIPUs), which is an alternative route for polyurethanes without toxic phosgene or isocyanates.[10-15] In this process, the ratio of carbonate to amine group is a major factor influencing the property of NIPUs, whose accuracy is significantly affected by the conversion of diepoxides, and the ideal ratio is 1:1. That is to say, if the epoxy groups were not completely carbonated, the product was the mixture containing mono-cyclic carbonate, bis-cyclic carbonate and diepoxide, which are difficult to separate each other, resulting in the error of the carbonate/amine group ratio. Thus, highly efficient and quantitative synthesis of bis(cyclic carbonate)s is extremely significant.



Scheme 1 Coupling reaction of CO_2 and diepoxides.

In this work, we report that an iron complex (Fig. 1), [N,N′-bis-2-pyridinylmethyl-cyclohexane-1,2-diamine]iron(II) chloride [Fe(BPMCDAC)] shows high catalytic activity in combination with TBAB towards the coupling reaction of CO_2 and diglycidyl ethers (Scheme 1), whose iron active site is environmentally friendly alternative to toxic central metal like cobalt and chromium. Under solvent-free condition, glycol diglycidyl ether (1a) could be completely converted to the corresponding bis(cyclic carbonate) (2a) with turn over number of 1000 under relatively mild conditions (100 ^{o}C and 3 MPa) in 4 h, which could be conveniently purified by flash column chromatography using CH_2Cl_2 as the eluent. Furthermore, the obtained bis(cyclic carbonate) (2a) could react with 1,2-ethane diamine (EDA), 1,3-propane diamine (PDA) or 1,6-hexane diamine (HDA) to produce NIPUs (Scheme 2) in accurate ratio of carbonate to amine group.



Scheme 2 Synthesis of NIPUs from 2a and diamines.

Experimental

Materials

Glycol diglycidyl ether (GDE) (1a) and other diglycidyl ether derivatives (1b-1e) were purchased from Ruipu Material Co. (China) and distilled over CaH_2 under reduced pressure before use. [Fe(BPMCDAC)] was prepared following a literature procedure developed in this lab.[16] Other reagents with analytical purity were used as received.

Characterization

Nuclear magnetic resonance spectra. All ^{1}H-NMR and ^{13}C-NMR measurements were recorded on a Bruker ARX-300 spectrometer at room temperature in deuterated chloroform ($CDCl_3$) or dimethyl sulfoxide (DMSO) with tetramethylsilane (TMS) as internal reference.

Differential scanning calorimetry analysis. DSC analysis was performed on a Perkin-Elmer DSC-7 instrument under a N_2 atmosphere. The samples were first heated from -50 ℃ to 50 ℃ at 10 ℃/min and then rapidly quenched to -50 ℃, followed by the second heating process in the same way as the first. The glass transition temperature (T_g) was defined as the value of midpoint of transition in the second heating process.

Fourier tansform infrared spectroscopy. Fourier transform infrared (FTIR) spectra were recorded on a Bruker Optics Tensor 27 spectrometer. The spectral resolution is 2 cm^{-1}. The characteristic IR absorptions mentioned in the text are strong bands in wavenumber (cm^{-1}).

Thermogravimetry analysis. TGA test was performed on a Perkin-Elmer Pyris 1 TGA thermal analyzer under a N_2 atmosphere at a heating rate of 10 ℃/min from ambient temperature to 500 ℃.

Gel permeation chromatography. GPC measurements were performed on Waters 410 GPC instrument. The GPC columns were eluted with DMF solution containing 0.03 M LiBr at 1.0 mL min^{-1} at 50 ^{o}C. Calibration was performed using mono-dispersed polystyrene.

Synthesis of bis(cyclic carbonate)s

Diglycidyl ethers (1a-1e in Scheme 1), Fe(BPMCDAC) and TBAB were added to a stainless-steel autoclave with a magnetic stirrer in a glove box. CO_2 was pressurized to this mixture and the reaction was operated under determined conditions. After reaction, the autoclave was cooled to room temperature, and the CO_2 pressure was released by opening the outlet valve. Then the crude reaction mixture was obtained to calculate the conversion by ^{1}H NMR spectroscopy in $CDCl_3$. The catalysts were removed by flash column chromatography using CH_2Cl_2 as the eluent and the obtained pure bis(cyclic carbonate) could be used for NIPU preparation.

1a: ^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 3.72 (m, 2H), 3.62 (m, 4H), 3.36 (m, 2H), 3.10 (m, 2H), 2.72 (m, 2H), 2.54 (m, 2H).

1b: ^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 3.60 (m, 2H), 3.40 (m, 4H), 3.26 (m, 2H), 3.03 (m, 2H), 2.68 (m, 2H), 2.50 (m, 2H), 1.55 (m, 4H).

1c: ^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 3.61 (m, 2H), 3.41 (m, 4H), 3.26 (m, 2H), 3.03 (m, 2H), 2.68 (m, 2H), 2.48 (m, 2H), 1.48 (m, 4H), 1.26 (m, 4H).

1d: ^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 3.66 (m, 2H), 3.35 (m, 2H), 3.21 (m, 4H), 3.09 (m, 2H), 2.73 (m, 2H), 2.56 (m, 2H), 0.86 (m, 6H).

1e: ^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 7.17 (m, 1H), 6.51 (m, 3H), 4.21 (m, 2H), 3.91 (m, 2H), 3.34 (m, 2H), 2.88 (m, 2H), 2.74 (m, 2H).

2a: ^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 4.80 (m, 2H), 4.49 (m, 2H), 4.40 (m, 2H), 3.62-3.79 (m, 8H).

2b: ^{1}H-NMR (CDCl$_3$, TMS, 300 MHz): δ (ppm) = 4.76 (m, 2H), 4.43 (m, 2H), 4.30 (m, 2H), 3.44-3.63 (m, 8H), 1.55 (m, 4H).

2c: ^{1}H-NMR (CDCl$_3$, TMS, 300 MHz): δ (ppm) = 4.74 (m, 2H), 4.41 (m, 2H), 4.28 (m, 2H), 3.56 (m, 2H), 3.50 (m, 2H), 3.40 (m, 4H), 1.47 (m, 4H), 1.26 (m, 4H).

2d: ^{1}H-NMR (CDCl$_3$, TMS, 300 MHz): δ (ppm) = 4.78 (m, 2H), 4.42 (m, 4H), 3.62 (m, 2H), 3.52 (m, 2H), 3.18 (m, 4H), 0.86 (m, 6H).

2e: ^{1}H-NMR (CDCl$_3$, TMS, 300 MHz): δ (ppm) = 7.20 (m, 1H), 6.52 (m, 3H), 5.02 (m, 2H), 4.59 (m, 2H), 4.49 (m, 2H), 4.20 (m, 2H), 4.10 (m, 2H).

Synthesis of NIPUs

NIPUs could be synthesized through the polyaddition of the bis(cyclic carbonate) (2a) and diamines (Scheme 2). 2a (60 mmol) and diamine (60 mmol) were added in a flask under N_2 atmosphere. The mixture was stirred at 60 °C for 20 min, then the temperature was raised to 80 °C and maintained for 2 h. All of the procedures were performed under N_2 atmosphere.

NIPU 1: ^{1}H-NMR (d$_6$-DMSO, TMS, 300 MHz): δ (ppm) = 7.12-6.75 (-NH), 4.65 (-OCH(CH$_2$OH)CH$_2$-), 3.36-3.91 (-OCH(CH$_2$OH)CH$_2$-, -CH$_2$O-, -OCH$_2$CH(OH)CH$_2$-), 3.00 (-NHCH$_2$). ^{13}C-NMR (d$_6$-DMSO, TMS, 75 MHz): δ (ppm) = 156.42, 156.06, 73.43, 72.33, 70.22, 69.79, 67.80, 65.69, 60.15, 40.22.

NIPU 2: ^{1}H-NMR (d$_6$-DMSO, TMS, 300 MHz): δ (ppm) = 7.09-6.72 (-NH), 4.66 (-OCH(CH$_2$OH)CH$_2$-), 3.36-4.05 (-OCH(CH$_2$OH)CH$_2$-, -CH$_2$O-, -OCH$_2$CH(OH)CH$_2$-), 2.97 (-NHCH$_2$), 1.50 (-CH$_2$-). ^{13}C-NMR (d$_6$-DMSO, TMS, 75 MHz): δ (ppm) = 156.46, 156.12, 73.37, 72.39, 70.28, 69.85, 67.89, 65.67, 60.25, 38.03, 29.90.

NIPU 3: ^{1}H-NMR (d$_6$-DMSO, TMS, 300 MHz): δ (ppm) = 7.09-6.75 (-NH), 4.66 (-OCH(CH$_2$OH)CH$_2$-), 3.36-3.88 (-OCH(CH$_2$OH)CH$_2$-, -CH$_2$O-, -OCH$_2$CH(OH)CH$_2$-), 2.93 (-NHCH$_2$), 1.50-1.22 (-CH$_2$-). ^{13}C-NMR (d$_6$-DMSO, TMS, 75 MHz): δ (ppm) = 156.33, 155.97, 73.14, 72.37, 70.20, 69.77, 67.84, 65.48, 60.19, 40.23, 29.43, 26.03.

Results and discussion

Reactions of carbon dioxide with glycol diglycidyl ether

Bis(cyclic carbonate)s were prepared by the cycloaddition reaction of diepoxides and CO$_2$ catalyzed by Fe(BPMCDAC). Moreover, the selection of suitable co-catalysts was extensively investigated, and TBAB was found to be an effective co-catalyst in activating the iron catalytic system for cycloaddition of epoxides and CO$_2$ (in Supplementary Table S1), which was consistent with our recent work.[16] With TBAB as the co-catalyst, Fe(BPMCDAC) could effectively catalyze the coupling reaction of glycol diglycidyl ether (1a) and CO$_2$ to generate the corresponding carbonate (2a). The data were listed in Table 1.

The formation of the cyclic carbonate groups was monitored quantitatively via IR spectroscopy and ^{1}H-NMR spectroscopy. Fig.2 displayed the IR spectra of diepoxide (1a) before and after carbonation (2a). The strongest peak at 1795 cm^{-1} was ascribed to the carbonyl group of 2a. The ^{1}H-NMR analysis was used to track the conversion of 1a to 2a at various time. Fig.3 showed the ^{1}H-NMR spectra of coupling products at 100 °C and 3 MPa (Entries 1-4) using Fe(BPMCDAC)/TBAB as catalyst. The signals between 2.54 and 3.10 ppm were ascribed to the methylene and methine protons of epoxy group. Due to the decreased signal intensity at δ = 2.54-3.10 ppm, the conversion of 1a could be monitored. New signals at δ = 4.40-4.80 ppm were attributed to the methylene and methine protons of cyclic carbonate group.

Table 1 Coupling reaction of 1a/CO$_2$ in Fe(BPMCDAC)/TBAB catalytic system[a]

Entry	Temperature (°C)	Pressure (MPa)	Time (h)	Conversion (%)[b]	TON[c]	TOF (h^{-1})[d]
1	100	3	1	73	730	730
2	100	3	2	91	910	455
3	100	3	3	96	960	320
4	100	3	4	100	1000	250
5	80	3	2	52	520	260
6	120	3	2	100	1000	500
7	100	1	2	91	910	455
8	100	2	2	90	900	450

[a] Reaction conditions: 0.1 mol-% Fe(BPMCDAC), 0.1 mol-% TBAB (relative to epoxy group). [b] Conversion was determined by 1H NMR spectroscopy. [c] Moles of epoxy group per mole of catalyst. [d] Moles of epoxy group produced per mole of catalyst per hour.

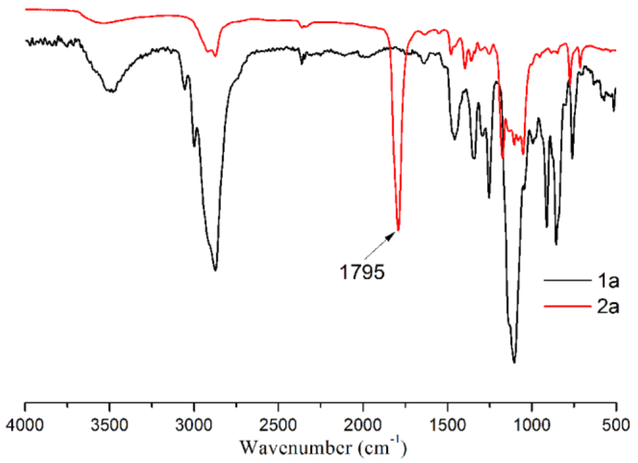


Fig. 2 IR spectra of bis(cyclic carbonate) (2a) and diepoixde (1a).

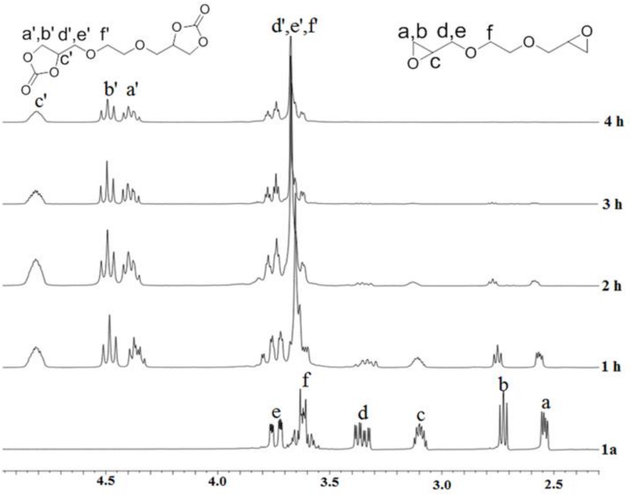


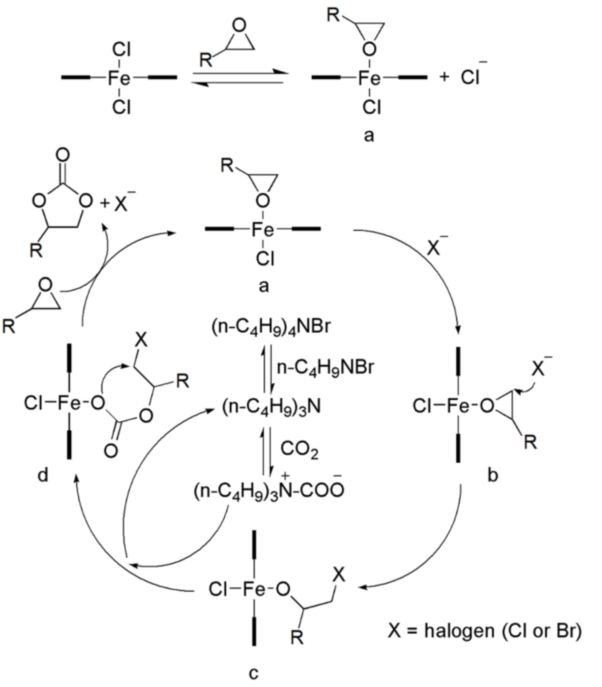
Fig.3 ^{1}H-NMR spectra of the coupling products at different time at 100 °C and 3MPa using Fe(BPMCDAC)/TBAB as catalyst.

The signals between 2.54 and 3.10 ppm disappeared completely at 100 ^{o}C and 3 MPa after 4 h, indicating that 1a could be converted to 2a completely under the reaction conditions, i.e., quantitative synthesis of bis(cyclic carbonate) (2a) could be realized. This is extremely important for preparation of NIPUs with high molecular weight.

The reaction temperature was an important factor to the catalytic activity. As shown in Table 1, the catalytic activity increased significantly when the temperature increased from 80 to 120 ^{o}C. 1a was completely converted into the corresponding carbonate in 2 h at 120 ^{o}C (Entry 6), while it took 4 h at 100 ^{o}C (entry 4). Higher temperature was beneficial for the conversion of quaternary ammonium salt into amine,[17] the amine subsequently formed a carbamate salt with carbon dioxide, therefore, the activation of carbon dioxide was accelerated, leading to faster coupling reaction.

The reactions with the iron catalyst were also conducted under different pressures. Using Fe(BPMCDAC) as catalyst, the catalytic activities varied insignificantly when CO_2 pressure increased from 1 MPa to 3 MPa, indicating that the rate of the coupling reaction was independent of CO_2 pressure in this range.

Therefore, considering the catalytic performance, the easiness of operation as well as economical efficiency, the optimal conditions for the coupling reaction of diepoxides/CO_2 catalyzed by Fe(BPMCDAC) should be carried out at 100 ^{o}C and 3 MPa for 4 h, in molar ratio [epoxy group/Fe(BPMCDAC)/TBAB] of 1000:1:1.



Scheme 3 Proposed reaction mechanism for diepoxide/CO_2 coupling.

Furthermore, a reaction mechanism was proposed (Scheme 3). As reported in the literatures,[8c, 17-18] coupling reaction of carbon dioxide with epoxides to generate corresponding cyclic carbonates requires activation, *i.e.*, the Lewis acid activates the epoxide while the Lewis base acts as a nucleophile to open the epoxide ring. Besides, the cocatalyst also plays a key role in the catalytic cycle. Based on the molecular structure of the complexes and the coupling reaction results, we propose a possible reaction pathway for the coupling reaction of diepoxides and carbon dioxide. It is possible that a chloride ligand which is able to ring-open epoxy group dissociate from the iron centre forming a cationic iron species, which can coordinate and activate epoxide.[19] Furthermore, the cocatalyst (TBAB) has two key roles in the catalytic cycle,[17a] one is to provide bromide for the ring-opening of the epoxide, and the other to form tributylamine which reacts with CO_2 to form a carbamate salt for better CO_2 activation. The activated CO_2 can insert into the metal alkoxide bond to give a metal carbonate which experiences ring-closing to form the cyclic carbonate.

Reactions of carbon dioxide with a series of diglycidyl ether derivatives

To evaluate the versatility of Fe(BPMCDAC) catalyst for other diepoxides, cycloaddition of CO_2 with a variety of diepoxides (1b-1e) were investigated, the results were summarized in Table 2. In some cases it was necessary to use dichloromethane as the solvent during the conversion to avoid high viscosity and/or solid nature of the reaction mixture.

Table 2 Coupling reaction of CO_2/ diglycidyl ether derivatives [a]

Entry	Epoxide	Product	Time （h）	Conversion （%）	TON	TOF (h^{-1})
1[b]	1a	2a	2	91	910	455
2[b]	1a	2a	4	100	1000	250
3	1b	2b	2	81	810	405
4	1b	2b	4	97	970	243
5	1c	2c	2	46	460	230
6	1c	2c	4	68	680	170
7	1d	2d	2	75	750	188
8	1d	2d	4	85	850	213
9	1e	2e	2	93	930	465
10	1e	2e	4	100	1000	250
11[c]	1e	2e	2	39	390	195
12[c]	1e	2e	4	55	550	138
13[d]	1b	2b	72	74	132	1.8
14[e]	1b	2b	9	82	--[f]	--[f]

[a] Reaction conditions: 0.1 mol-% Fe(BPMCDAC), 0.1 mol-% TBAB (relative to epoxy group), 3 MPa, 100 ^{o}C. [b] Entry 2 and Entry 4 from Table 1 were reproduced here for reference. [c] Dichloromethane as solvent, and the ratio of epoxide to solvent was 1:1 (v/v). [d] Data from ref 10c. [e] Data from ref 13. [f] TON and TOF cannot be calculated due to heterogeneous catalysts.

Low loadings of catalyst (0.1 mol %) and co-catalyst (0.1 mol %) were generally effective at 100 ^{o}C and 3 MPa. All diepoxides can be effectively converted into the corresponding organic carbonates, and conversion of over 50% was achieved, indicating the good versatility of this catalytic system. It should be noted that all diepoxides could be completely converted into the corresponding organic carbonates in enough reaction time. As anticipated, the conversions were time-dependent, it increased with longer reaction periods while the turnover frequencies (TOFs) decreased. Furthermore, the catalyst system could not only catalyze the cycloaddition of the linear diepoxides and carbon dioxide, but also tolerate the diepoxides which contain side chains or aromatic rings. Under the applied conditions, on prolonging the carbon chains, the conversions gradually decreased (Entries 1, 3 and 5). A 91% conversion was obtained in 2 h for 1a, while it decreased to 81% for 1b, and only 46% was converted for 1c. Besides, a 75% conversion of 1d with side chain was obtained in 2 h (Entry 7), though it was much lower than that of 1a. Therefore we assumed that the catalytic activity was affected by aliphatic chain length in the monomer.[9] As aliphatic chain length increased, addition of carbon dioxide was hindered because of chain folding or the fluidity of chains and the hindrance of methyl groups. The diepoxide 1e containing aromatic ring had a relatively higher conversion, it reached 93% in 2 h, which was even higher than that for 1a (91%). The existence of aromatic ring could increase the rigidity of chains and decrease the chain folding. Furthermore, phenoxy group could increase the Lewis acidity of epoxy group to activate diepoxide. Dichloromethane was used as solvent due to the solid nature of the product (2e) at room temperature (Entries 11 and 12). Unfortunately, the conversion of 1e decreased significantly compared to that without solvent, since the solvent may reduce the diepoxide density leading to slow reaction rate. Furthermore, for diepoxides like 1b, Fe(BPMCDAC) exhibited great catalytic activity, a 97% conversion of 1b could be obtained in 4 h, which was much higher than the data in the literature (Entries 4, 13 and 14).[10c, 13]

Preparation of NIPUs

The obtained bis(cyclic carbonate)s could be applied to synthesize poly(hydroxyurethane)s via polyaddition reaction with diamines. The polyaddition reactions of 2a with 1,2-ethane diamine (EDA), 1,3-propane diamine (PDA) and 1,6-hexane diamine (HDA) to produce NIPUs were carried out by a solvent-free and catalyst-free method, resulting in three polyurethanes with different backbones. The results were summarized in Table 3.

Table 3 Polyaddition reaction of 2a with EDA, PDA and HAD[a]

Entry	Diamine	NIPU	M_n[b] (kg mol^{-1})	PDI[b] (M_w/M_n)	T_g[c] (°C)	$T_{d\,5\%}$[d] (°C)	$T_{d\,max}$[d] (°C)
1	EDA	NIPU 1	25.4	1.18	9	206	241
2	PDA	NIPU 2	27.9	1.19	4	234	276
3	HAD	NIPU 3	30.2	1.22	-2	266	319

[a] Reaction conditions: 2a:diamine (mol/mol) = 1:1, 60 °C for 20min, then 80 °C for 2 h. [b] Determined by GPC using dimethyl formamide (DMF) as eluent. [c] Measured by DSC. [d] Measured by TGA.

The polyadditon reactions of 2a and diamines were monitored by FT-IR spectroscopy. The FT-IR spectra in Fig.4 showed the vibration peak at 1795 cm^{-1} which was assigned to the carbonyl group of the cyclic carbonate. After polyaddition, the vibration peak at 1795 cm^{-1} disappeared , and new peaks at 1700, 1540 and 3340 cm^{-1} appeared, which were typical for the carbonyl IR absorption of the urethane groups, N-H deformation of the urethane groups, and hydroxyl groups, respectively.

As shown in Table 3, GPC analysis showed that the number-average molecular weights of the obtained NIPUs were between 25.4 and 30.2 kg mol^{-1}, which were remarkable under solvent-free and catalyst-free condition. Moreover, compared with the data in the literature[10, 12a, 13, 15b], the polydispersity indexes (PDIs) were relatively narrow between 1.18 and 1.22. Though the number-average molecular weights showed a slight decrease in comparison with the literature,[14] the procedure to synthesis of NIPUs was simple without any solvent. Interestingly, the degrees of polymerization (DPs) of the resultant NIPUs were similar [m(NIPU 1) = 78.8, m(NIPU 2) = 82.9, m(NIPU 3) = 79.8] (Scheme 2), which were independent of the chain length of diamines.

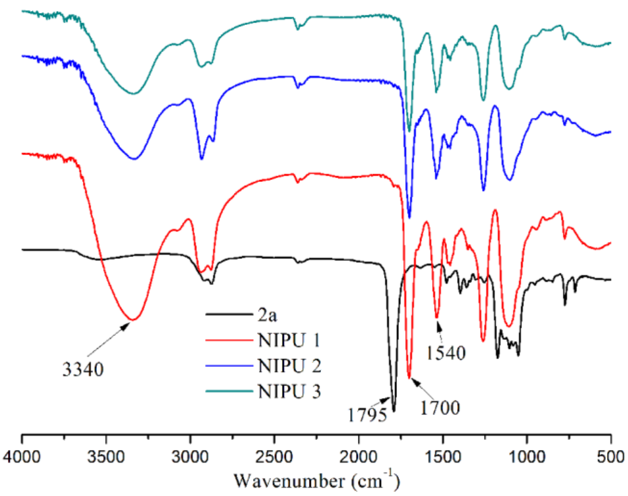


Fig.4 IR spectra of various NIPUs from diamine and 2a.

The thermal properties of the NIPUs were characterized by DSC and TGA. The DSC thermograms are shown in Fig. S1 and the evaluated data are presented in Table 3. The T_g values depend on the chemical structure of NIPUs. As expected, NIPU 1 had the highest T_g (9 °C) among the synthesized materials because of its smaller spacer length that limited the mobility of polymer chain segments for higher T_g.[20] The thermal decomposition analysis under nitrogen of various NIPUs was investigated by TGA from ambient temperature to 500 °C. As shown in Fig. S2, these NIPUs demonstrated initial degradation (T_d = 5%) temperature between 206 and 266 °C, and maximum decomposition rate between 241 and 319 °C. NIPU 3 having longest carbon chain possessed the highest initial degradation temperature at 266 °C, its maximum rate of degradation occurred at relatively high temperature (319 °C), which was very interesting for this kind of NIPUs, where NIPU containing longest spacer length showed highest thermal stability.

Acknowledgements

The authors thank financial support from the National Natural Science Foundation of China (Grant No. 51321062, 51273197 and 21134002).

Notes and references

[a] *Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China. Fax: +86 431 85262252; Tel: +86 431 85262252; E-mail: ysqin@ciac.jl.cn. Fax: +86 431 85689095; Tel: +86 431 85262250; E-mail: xhwang@ciac.jl.cn*
[b] *University of Chinese Academy of Sciences, Beijing 100039, People's Republic of China*

† Electronic Supplementary Information (ESI) available: Detailed

experimental results, DSC and TGA thermograms of various NIPUs are included. See DOI: 10.1039/b000000x/

1 (a) M. Aresta and A. Dibenedetto, *Dalton Trans.*, 2007, 2975; (b) M. Mikkelsen, M. Jorgensen and F. C. Krebs, *Energy Environ. Sci.*, 2010**, 3**, 43.

2 (a) D. J. Darensbourg and M. W. Holtcamp, *Coordin. Chem. Rev.*, 1996**, 153**, 155; (b) T. Sakakura and K. Kohno, *Chem. Commun.*, 2009, 1312; (c) W.-L. Dai, S.-L. Luo, S.-F. Yin and C.-T. Au, *Appl. Catal. A-gen.*, 2009**, 366**, 2; (d) C. Maeda, Y. Miyazaki and T. Ema, *Catal Sci Technol*, 2014**, 4,** 1482; (e) P. P. Pescarmona and M. Taherimehr, *Catal Sci Technol*, 2012**, 2**, 2169; (f) I. Omae, *Coordin. Chem. Rev.*, 2012**, 256**, 1384.

3. (a) G. Rokicki, *Prog. Polym. Sci.*, 2000**, 25**, 259; (b) J. H. Clements, *Ind. Eng. Chem. Res.*, 2003**, 42**, 663; (c) G. Rokicki and P. G. Parzuchowski, *Polymer Science: A Comprehensive Reference*, 2012, 247.

4. (a) M. North, R. Pasquale and C. Young, *Green Chem.*, 2010**, 12**, 1514; (b) A. Decortes, A. M. Castilla and A. W. Kleij, *Angew. Chem. Int. Edit.*, 2010**, 49**, 9822; (c) J. M. Sun, S. I. Fujita, F. Y. Zhao, M. Hasegawa and M. Arai, *J. Catal.*, 2005**, 230**, 398; (d) H. S. Kim, J. J. Kim, H. Kim and H. G. Jang, *J. Catal.*, 2003**, 220**, 44; (e) H. Yasuda, L. N. He and T. Sakakura, *J. Catal.*, 2002**, 209**, 547; (f) Y. M. Shen, W. L. Duan and M. Shi, *J. Org. Chem.*, 2003**, 68**, 1559; (g) Y. Zhang, S. Yin, S. Luo and C. T. Au, *Ind. Eng. Chem. Res.*, 2012**, 51**, 3951; (h) Y. Xie, Z. Zhang, T. Jiang, J. He, B. Han, T. Wu and K. Ding, *Angew. Chem. Int. Edit.*, 2007**, 46**, 7255.

5. (a) R. L. Paddock and S. T. Nguyen, *Chem. Commun.*, 2004, 1622; (b) X.-B. Lu and D. J. Darensbourg, *Chem. Soc. Rev.*, 2012**, 41**, 1462; (c) A. Sibaouih, P. Ryan, M. Leskela, B. Rieger and T. Repo, *Appl. Catal. A-gen.*, 2009**, 365**, 194; (d) T. Roy, R. I. Kureshy, N.-u. H. Khan, S. H. R. Abdi and H. C. Bajaj, *Catal Sci Technol*, 2013**, 3**, 2661.

6. (a) R. L. Paddock and S. T. Nguyen, *J. Am. Chem. Soc.*, 2001**, 123**, 11498; (b) D. Adhikari, S. T. Nguyen and M.-H. Baik, *Chem. Commun.*, 2014**, 50**, 2676; (c) S. Iksi, A. Aghmiz, R. Rivas, M. D. González, L. Cuesta-Aluja, J. Castilla, A. Orejón, F. El Guemmout and A. M. Masdeu-Bultó, *J. Mol. Catal. A-Chem.*, 2014**, 383**, 143; (d) M.-H. Baik, D. Adhikari and S. Nguyen, *Chem. Commun.*, 2014**, 50**, 2676; (e) Y. Niu, W. Zhang, H. Li, X. Chen, J. Sun, X. Zhuang and X. Jing, *Polymer*, 2009**, 50**, 441.

7. (a) Z. Wang, Z. Bu, T. Cao, T. Ren, L. Yang and W. Li, *Polyhedron*, 2012**, 32**, 86; (b) D. Anselmo, V. Bocokic, A. Decortes, E. C. Escudero-Adan, J. Benet-Buchholz, J. N. H. Reek and A. W. Kleij, *Polyhedron*, 2012**, 32**, 49; (c) C. Martin, C. J. Whiteoak, E. Martin, M. Martinez Belmonte, E. C. Escudero-Adan and A. W. Kleij, *Catal Sci Technol*, 2014**, 4**, 1615; (d) M. Taherimehr, A. Decortes, S. M. Al-Amsyar, W. Lueangchaichaweng, C. J. Whiteoak, E. C. Escudero-Adan, A. W. Kleij and P. P. Pescarmona, *Catal Sci Technol*, 2012**, 2**, 2231.

8. (a) J. Melendez, M. North and R. Pasquale, *Eur. J. Inorg. Chem.*, 2007, DOI: Salen Al, 3323; (b) J. Melendez, M. North and P. Villuendas, *Chem. Commun.*, 2009, 2577; (c) D. Tian, B. Liu, Q. Gan, H. Li and D. J. Darensbourg, *Acs Catalysis*, 2012, 2029; (d) S. Supasitmongkol and P. Styring, *Catal Sci Technol*, 2014**, 4**, 1622; (e) R. Luo, X. Zhou, S. Chen, Y. Li, L. Zhou and H. Ji, *Green Chem.*, 2014**, 16**, 1496; (f) J. A. Castro-Osma, A. Lara-Sanchez, M. North, A. Otero and P. Villuendas, *Catal Sci Technol*, 2012**, 2**, 1021.

9. M. R. Kim, S. R. Jeon, D. W. Park and J. K. Lee, *J. Ind. Eng. Chem.*, 1998**, 4**, 122.

10. (a) A. Steblyanko, W. Choi, F. Sanda and T. Endo, *J. Polym. Sci. Pol. Chem*, 2000**, 38**, 2375; (b) B. Ochiai, S. Inoue and T. Endo, *J. Polym. Sci. Pol. Chem*, 2005**, 43**, 6613; (c) N. Kihara and T. Endo, *J. Polym. Sci. Pol. Chem*, 1993**, 31**, 2765.

11. B. Tamami, S. Sohn and G. L. Wilkes, *J. Appl. Polym. Sci.*, 2004**, 92**, 883.

12. (a) M. Baehr, A. Bitto and R. Muelhaupt, *Green Chem.*, 2012**, 14**, 1447; (b) M. Baehr and R. Muelhaupt, *Green Chem.*, 2012**, 14**, 483.

13. R.-j. Wei, X.-h. Zhang, B.-y. Du, Z.-q. Fan and G.-r. Qi, *RSC Advances*, 2013**, 3**, 17307.

14. M. Helou, J.-F. Carpentier and S. M. Guillaume, *Green Chem.*, 2011**, 13**, 266.

15. (a) I. Javni, D. P. Hong and Z. S. Petrovic, *J. Appl. Polym. Sci.*, 2013**, 128**, 566; (b) A. Boyer, E. Cloutet, T. Tassaing, B. Gadenne, C. Alfos and H. Cramail, *Green Chem.*, 2010**, 12**, 2205.

16. X. Sheng, L. Qiao, Y. Qin, X. Wang and F. Wang, *Polyhedron*, 2014**, 74**, 129.

17. (a) M. North and R. Pasquale, *Angew. Chem. Int. Edit.*, 2009**, 48**, 2946; (b) W. Clegg, R. W. Harrington, M. North and R. Pasquale, *Chem-eur. J.*, 2010**, 16**, 6828.

18. X. B. Lu, B. Liang, Y. J. Zhang, Y. Z. Tian, Y. M. Wang, C. X. Bai, H. Wang and R. Zhang, *J. Am. Chem. Soc.*, 2004**, 126**, 3732.

19. J. E. Dengler, M. W. Lehenmeier, S. Klaus, C. E. Anderson, E. Herdtweck and B. Rieger, *Eur. J. Inorg. Chem.*, 2011, 336.

20. V. Besse, G. Foyer, R. Auvergne, S. Caillol and B. Boutevin, *J. Polym. Sci. Pol. Chem*, 2013**, 51**, 3284.