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Linear polyurethanes with excellent comprehensive properties from poly(ethylene carbonate) diol

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A B S T R A C T

The synthesis of polyurethanes (PUs) from the reaction of low molecular weight poly(ethylene carbonate) diol (PECD) is rarely investigated. This work reports a novel PU with excellent mechanical properties from the solution polymerization of 4,4′-diphenylmethane diisocyanate (MDI) with PECD that was derived from the copolymerization of carbon dioxide (CO_2) and ethylene oxide (EO). The tensile strength, the elongation at break and 300% constant tensile strength of the PECD-PU were up to 66 ± 2 MPa, 880% ± 50% and 13 MPa, respectively, higher than the control PUs from the reaction of MDI with commercial polyethers or polyesters. The PECD-PU with high CO_2 carbonate content exhibited good solvent resistance and chemical stability. Of importance, the mechanical properties and chemical resistance of PECD-PU were significantly enhanced with the increasing content of CO_2, *i.e.*, the carbonate unit in PECD. This work provides comprehensive properties of PECD-derived PUs, indicating that PECD is a competitive precursor for the preparation of PU and has broad application prospects.

The rapid growth of global carbon dioxide (CO_2) emissions poses a continuing challenge to curb the growth of carbon emissions. It is a very promising way to use CO_2 as a monomer to synthesize high-valued polymers. In the past 50 years, the synthesis of CO_2-based polymers from CO_2 and epoxides has been extensively researched, resulting in the synthesis of high molecular weight poly(propylene carbonate) (PPC) and poly(ethylene carbonate) (PEC) for the application of biodegradable plastics [1-3]. However, compared to traditional industrial synthetic materials (polyethylene, polypropylene, and polyvinyl chloride), both PPC and PEC with high molecular weights have the disadvantages of relatively insufficient mechanical properties and high production cost, which limit their applications [4].

CO_2-based diols that with two reactive hydroxyl groups are attractive precursors for the preparation of polyurethanes (PUs). In 1989, J. Kuyper developed CO_2-based diols with low molecular weight by introducing chain transfer agents in PPC synthesis [5]. These low molecular weight CO_2-based diols were successfully used as raw materials for the synthesis of polyurethanes [6-13]. Then, many researchers' groups developed a variety of catalysts for the synthesis of CO_2/epoxide-derived diols [14-31], however, it is rarely reported that the synthesis and application of poly(ethylene carbonate) diols (PECD) that was derived from the copolymerization of CO_2 and ethylene oxide (EO), probably because EO is very toxic and highly risk in use [32-34]. In recent years, our research team has devoted to the synthesis of a variety of CO_2-derived diols, including poly(propylene carbonate) diols (PPCD) and PECD and their applications such as foams, elastomers, leathers, adhesives and coatings [35-43].

PECD-based PUs are highly desired because: (1) EO is cheaper than propylene oxide, (2) more amounts of CO_2 can be incorporated, and (3) PECD with primary hydroxyl groups has higher reactivity to diisocyanate than PPCD. These advantages endow PECD with greater application potential than PPCD. However, the overall properties of linear PECD-based PUs are lacked. In this work, we report the synthesis of low molecular weight PECD using zinc-cobalt(III) double metal cyanide complex (DMC) as the catalyst, PUs from the addition reaction of PECD with 4,4′-diphenylmethane diisocyanate (MDI) and their overall properties (Scheme 1).

Firstly, PECD was synthesized from the copolymerization of EO and CO_2 using Zn-Co DMC as catalyst according to the previous work [34]. The DMC catalyst was added into a 10 L autoclave. After vacuuming and flushing nitrogen for three times, EO and diethylene glycol (DEG) were pumped, and CO_2 was added until the pressure reached to 2 MPa. The reaction was carried out at 50–60 °C, 5 MPa, for 36 h. The PECDs were vacuumed to remove by product EC at 135–140 °C for synthesizing PUs. PECDs with different molar fraction of carbonate unit and number-average molecular weight were obtained (Table S1 in Supporting information). The ^{1}H NMR

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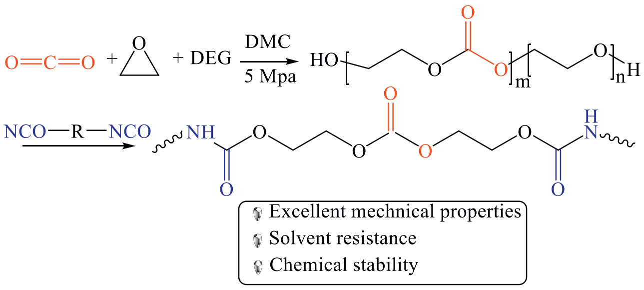

Scheme 1. The preparation of PECD and PECD-derived PUs.

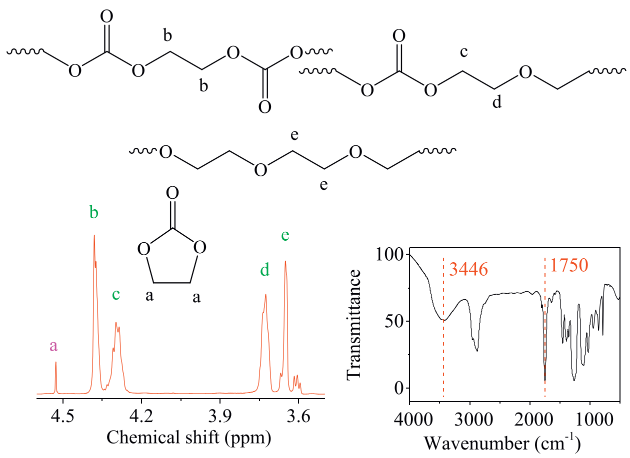

Fig. 1. ^{1}H NMR (400 MHz, $CDCl_3$) and FT-IR spectra of $PECD_3$.

spectrum of PECD (Fig. 1) showed that the chemical shifts at 4.25–4.41 ppm were attributed to the CH_2 unit adjacent to the carbonate segments, and the chemical shifts at 3.59–3.76 ppm were assigned to the CH_2 unit in the ether segments. Therefore, F_{CO_2} was calculated from the peak integral area was 30.0% (Eq. S1 in Supporting information). The FT-IR spectrum (Fig. 1) showed that the peaks at 1750 cm^{-1} and 1265 cm^{-1} were attributed to the stretching vibrations of C=O group and C–O group in the carbonate group. The peak at 3346 cm^{-1} was attributed to the stretching vibration of the hydroxyl group.

We then synthesized a variety of PUs using PECD and commercial diols such as PPCD, PBA, PPG, PTMG, PCL and PCDL as the soft segments under the same reaction conditions. The feeding ratio of diols with MDI was set as 1.0 according to the OH value of diols (Table S1). PECD, 1,4-butanediol, dimethyl formamide, tin octoate and MDI were added to a 500 mL flask with a mechanical agitator. The reaction was carried out for 3 h at 350 rpm at 70 °C. Then, the remaining MDI and dimethylformamide were gradually added until the PU solution with a solid content of 30.0%, high viscosity and good fluidity was obtained. Then methanol was added and reacted at 70 °C for about 0.5 h. The PU solution was diluted with dimethylformamide to a solid content of 10%−15% and poured into the polyethylene plate mold, and dried at 80 °C for 12 h, and thoroughly dried at 120 °C for 2 h.

Taking the PU obtained by the reaction of PECD and MDI as the example, FT-IR (Fig. S1 in Supporting information) and GPC results listed in Table 1 showed that the successful preparation of hydroxyl–terminated polyurethane, and the molecular weights and PDI of PUs prepared from different diols were 111.4–137.5 kg/mol and nearly the same values with the products from the reaction of commercial diols with MDI.

We next examined the overall properties of the resultant PECD-PUs. It was found that PECD-PUs had excellent thermal resistance,

Table 1
GPC results of PUs from the reaction of diols with MDI.[a]

Sample	Diol M_n (kg/mol)	PU M_n (kg/mol)	PDI
PECD1-PU	2.0	131.0	2.4
PECD2-PU	2.2	111.4	2.1
PECD3-PU	2.1	137.5	2.2
PPCD-PU	2.0	160.0	2.5
PBA-PU	2.0	138.9	2.5
PPG-PU	2.0	112.8	2.5
PTMG-PU	2.0	107.0	2.2
PCL-PU	2.0	123.6	2.2
PCDL-PU	2.0	117.0	1.7

PECD1: CO_2 content 23.0%; PECD2: CO_2 content 26.7%; PECD3: CO_2 content 30%; PBA: poly(butylene adipate)diol; PPG: polypropylene glycol; PTMG: polytetramethylene glycol; PCL: polycaprolactone diol; PCDL: polycarbonate diol.

[a] GPC was carried out using poly(methyl methacrylate) as standard and *N,N*-dimethylformamide as eluent.

Table 2
Chemical resistance rate of PU with different diol.[a]

Sample	Acid (%)	Alkali (%)	Salt (%)
PECD1-PU	36	Broken	98
PECD2-PU	88	54	97
PECD3-PU	91	56	96
PPCD-PU	73	70	98
PBA-PU	18	52	96
PPG-PU	76	66	98
PTMG-PU	89	72	98
PCL-PU	96	90	98
PCDL-PU	96	84	98

[a] Samples were soaked in 10% sulfuric acid, sodium hydroxide, or sodium chloride solution at 25 °C for 24 h, then removed, rinsed with deionized water, dried at 80 °C for 3 h, and cooled at room temperature for 24 h. The tensile tests were carried out according to ISO1184–1983. The chemical retention rate was calculated by the tensile strength before and after soaked.

Table 3
Solvent absorption rate of PUs with different diols.[a]

Sample	Water (%)	Methanol (%)	Ethyl acetate (%)	Toluene (%)	Butanone (%)
PECD1-PU	6.2	6.8	17.9	12.6	21.2
PECD2-PU	2.8	5.4	16.6	10.9	21.5
PECD3-PU	2.3	5.7	15.2	10.7	17.0
PPCD-PU	1.1	12.5	57.7	25.3	63.2
PBA-PU	1.5	6.4	18.2	16.8	39.3
PPG-PU	3.0	19.5	52.2	38.0	67.3
PTMG-PU	0.8	9.9	19.0	25.8	59.2
PCL-PU	0.8	4.3	16.1	18.7	16.2
PCDL-PU	0.8	4.6	17.5	19.5	58.7

[a] The PUs were cut into 20 mm × 20 mm square samples, and soaked in solvents at room temperature for 24 h, and then the solvent on the surface of the film was removed with filter paper. The mass before and after immersion was measured and recorded as m_1 and m_2 respectively. Solvent absorption rate was calculated as $(m_2-m_1)/m_1 \times 100\%$.

the 5% thermal decomposition temperature of PECD-PUs was about 255 °C as shown in Fig. S2 (Supporting information), which is suitable to many applications of PUs. Previous studies shown that PECD could change from hydrophilic to hydrophobic with the increase of carbonate content [44]. Herein, we found that, with the increase of carbonate content in PECD, the resistance properties of PECD-PUs to water, acid and alkali increased significantly. The water absorption decreased from 6.2% to 2.3%, the acid resistance from 36% to 91%, and the alkali resistance up to 56%, while the carbonate content in PECD increased from 23.0% to 30.0% (Table 2). Compared with other diols derived PUs, PECD3-PU exhibited excellent acid, salt resistance, but moderate alkali resistance. Even so, the alkali resistance of PECD3-PU is better than most other products in Table 2.

The solvent absorption rate of PUs synthesized from different diols were evaluated, as shown in Table 3. The variation of carbon-

Table 4
Mechanical properties of PUs with different diols.[a]

Sample	Tensile strength (MPa)	Elongation at break (%)	100% Tensile strength (MPa)	300% Tensile strength (MPa)
PECD1-PU	41 ± 2	932 ± 50	4.0	7.8
PECD2-PU	51 ± 2	890 ± 50	5.5	10.8
PECD3-PU	66 ± 2	880 ± 50	6.5	13.0
PPCD-PU	48 ± 2	775 ± 50	4.8	10.6
PBA-PU	57 ± 2	505 ± 40	4.2	9.3
PPG-PU	43 ± 2	692 ± 40	3.0	6.0
PTMG-PU	46 ± 2	601 ± 40	4.0	8.0
PCL-PU	56 ± 2	864 ± 30	4.3	8.0
PCDL-PU	60 ± 2	521 ± 30	5.0	9.3

[a] Mechanical properties were carried out according to ISO1184-1983 using a universal testing machine.

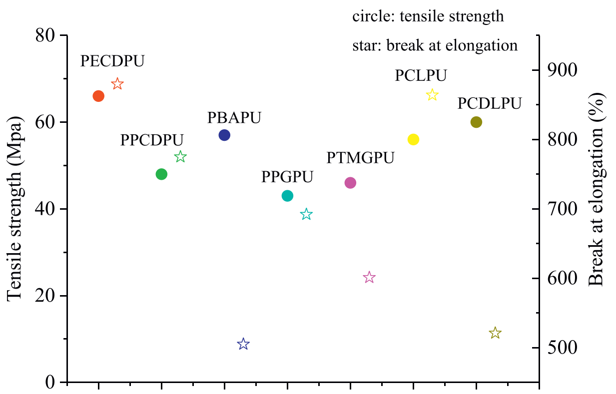

Fig. 2. Mechanical properties of PUs with different diols.

ate content in PECD had a small influence on the solvent absorption rate, and high carbonate content in PECD leads to low water and solvent absorption rate, showing good solvent resistance. As compared with other diols derived PUs, PECD3-PU showed higher water absorption rate but clearly lower solvent absorption rate because of the PEG segment in PECD3-PU. This result indicates that PECD3 is a promising candidate to replace the commercial polyols in some applications.

The mechanical properties of various PUs were carried out, and the results were shown in Table 4 and Fig. 2. The results showed that the influence of carbonate content in PECD on tensile properties was greater than that on the flexibility. With increasing the carbonate content in PECD, the tensile strength of PECD-PU increased significantly. When the carbonate content in PECD increased by 30.4%, from 23.0% to 30.0%, the tensile strength of PECD-PU dramatically increased by 61%, from 41 MPa to 66 MPa, while the elongation at break decreased just from 932% to 880%, respectively. Significantly, PECD3-PU exhibited excellent tensile properties and flexibility compared with other PUs (Fig. 2). This may be due to the random chain structure including 30% of polycarbonate and 70% of polyether units (*i.e.*, PEG segment), which possibly provide crystallinity that benefits the mechanical properties. In contrast, PECD3-PU showed stronger tensile properties and higher flexibility than PPCD-PU because PPCD diol is completely amorphous state due to side methyl groups in PPCD. The mechanical test result suggests that PECD can be used to produce PU with both high tensile strength and high flexibility.

In summary, we described the synthesis of linear polyurethanes from the reaction of low molecular weight PECD with diisocyanate and disclosed the overall properties of PECD-derived PUs. As compared with PUs derived from a variety of commercial polyethers, polyesters and PPCD, these PECD-derived PUs with excellent mechanical properties and chemical resistance are competitive. It was observed that, with the increase of CO_2 content in PECD, the mechanical properties, solvent resistance and chemical resistance of the PECD-PUs were significantly improved. This result of this study demonstrates that the diols from EO and CO_2 is a promising candidate for making high performance thermal plastics.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Xinyu Liu: Writing – original draft, Validation, Validation, Investigation, Data curation, Conceptualization. **Jialin Yang:** Software, Methodology, Data curation. **Zonglin He:** Software, Resources, Investigation. **Jiaoyan Ai:** Supervision, Conceptualization. **Lina Song:** Writing – review & editing, Supervision, Project administration, Investigation. **Baohua Liu:** Writing – review & editing, Supervision, Project administration.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2024.110236.

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