Synthesis of Aliphatic Carbonate Macrodiols and Their Application as Sustainable Feedstock for Polyurethane

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**ABSTRACT:** High-molecular-weight poly(propylene carbonate) (PPC) [number-average molecular mass ($M_n$): 80 000–100 000] is readily alcoholized into PPC macrodiols in the presence of 1,2-propanediol (PDO), 1,4-butanediol (BDO), or 1,6-hexanediol (HDO). The high-molecular-weight PPC and small amount of diols, such as PDO, BDO, or HDO, were stirred at elevated temperatures to convert the extremely viscous high-molecular-weight polymer to low-molecular-weight macrodiols with gel permeation chromatography-measured $M_n$ of about 3000 Da. The chopping reaction of the high-molecular-weight PPC was studied in detail, such as the influences of the catalyst residue, the kinds of alcoholysis agents, reaction temperature, and time. The reaction mechanism of alcoholysis is proposed according to the experimental results. The results indicate that the presence of a trace residue of zinc catalyst (Zn-G-III) in PPC, excess diol feeding, and higher temperature can accelerate the alcoholysis. Moreover, different diols can produce different PPC macrodiols with varying end-capping. Finally, polycarbonate ether urethane can be successfully synthesized using as-synthesized PPC macrodiols and poly(propylene glycol) ($M_n$ ≈ 3000) as the soft segment and 4,4′-diphenylmethane diisocyanate or BDO as the hard segment. The full evaluation for the synthesized PPC macrodiols demonstrates their potential applications in the polyurethane industry.

**INTRODUCTION**

Owing to their good mechanical properties, polyurethanes are widely used as therapeutic materials. Oligoethers and oligoesters are typically used as the soft segments in the preparation of polyurethanes to acquire the desired elasticity and good biological affinities. Typical polyurethanes based on oligoethers undergo autoxidation, metal ion oxidation, and environmental stress cracking and have poor strength. However, the polyurethanes prepared from aliphatic polycarbonate diols (PCDLs) have superior strength and hardness, together with a better in vitro, in vivo, and chemical stability when compared with poly(ether urethane). In this connection, poly(carbonate urethane)s (PCUs) are often used in long-term and high mechanical strength applications.

For the polyurethanes containing a carbonate moiety, there are many innovative studies for preparing new polyurethanes with superior properties. With new functional properties, the polyurethanes containing a carbonate moiety can be found in many advanced applications. Moreover, because of environmental concerns, the synthesis of sustainable and environmentally friendly polyurethanes has attracted increasing attention. In this connection, an alternative approach to synthesize environmentally friendly polyurethanes is to switch from petro-based ones to bio-based polyhydroxyurethanes, most of which are synthesized from bio-based polyols like vegetable oil. However, the synthesized polyols are still ester-type ones rather than carbonate-type ones.

The most typical preparation method of PCDLs is the polycondensation of phosgene and aliphatic diol, which has been eliminated because of the toxicity of the phosgene. So far, many investigations on the preparation of PCDLs using immortal copolymerization have been reported. For example, Gao and his co-workers have synthesized the PCDLs with tunable carbonate by immortal copolymerization of CO$_2$/propylene oxide (PO) in the presence of sebacic acid (SA) as the chain transfer agent and zinc−cobalt double metal cyanide complex (Zn−Co−DMCC) as the catalyst. The synthesis of PCDLs is also disclosed via polycondensation of diethyl carbonate with an aliphatic diol. Meanwhile, ring-opening polymerization has been used to synthesize PCDLs as well. Nevertheless, many of these methods will suffer the problem of high polyether (PE) segment content.

As mentioned above, PCDLs can be synthesized through various routes. However, most of the concerns focus on...
developing new highly active and selective catalysts with well-defined structure for preparing PCDLs “from bottom to top”, whereas much less attention has been paid for the synthesis of PCDLs “from top to bottom”, even though lots of preparation methods of the high-molecular-weight aliphatic polycarbonates have been reported and even commercialized.14−15

Poly(propylene carbonate) (PPC) is a carbon dioxide-based polymer, which is the copolymerization of CO2 and PO in the presence of Zn-G-III as the catalyst. Being well-known, CO2 is a low-cost, renewable, and sustainable feedstock. PPC derived from CO2 is an innocuous and biodegradable material. Using PPC as the feedstock to synthesize polyols has the advantages of being innocuous and sustainable. For the past 15 years, our research group has already developed the entire industrial technology to produce high-molecular-weight PPC in a capacity of 25 000 t/a in Tianguan Enterprise Group Company (Nanyang City of Henan Province, China). Zn-G-III is kind of support zinc glutarates catalyst for the industrial copolymerization of carbon dioxide and PO. High-molecular-weight PPC has already been commercialized in Tianguan Enterprise Group Co. Ltd. Its well-defined structure has been reported in the previous literature.16 Because of the very high catalytic activity and structural selectivity, this industrial synthetic method can produce high-molecular-weight PPC with superior comprehensive properties.14−16 However, there is an increasing need for aliphatic carbonate macrodiols for various applications. This drives researchers to develop simple and low-cost methodology to produce the said macrodiols.

Herewith, in this article, we report a method to prepare PPC macrodiols by the alcoholysis of high-molecular-weight PPC in the presence of small molecular diols. The side reaction mechanism and influence factors of alcoholysis are summarized, proposed, and discussed accordingly. Moreover, the possible catalytic mechanisms and the end-capping mechanisms are also suggested. Consequently, the PPC macrodiols were used to synthesize a series of PPC-based polyurethane, followed by the investigation of its mechanical properties. This article provides a new methodology to synthesize the PPC oligomer. Compared with the traditional ways of producing PPC oligomer, this method does not need a high pressure reaction process. This is the first report that successfully synthesizes the PPC oligomer in bulk with a high carbonate content.

■ RESULTS AND DISCUSSION

Alcohololytic Chopping of High-Molecular-Weight PPC.

PCU, possessing good biocompatibility and mechanical properties, is known as a new kind of biomaterial used in the long-term implantation devices.18 In this connection, the synthesis of carbonate macrodiols from a polycarbonate falls into an interesting topic. Being well-known, many kinds of polyesters, such as polycaprolactone and poly(lactide), can undergo transesterification reaction with or without the presence of a catalyst, resulting in low-molecular-weight oligomers. However, the alcoholysis of high-molecular-weight polycarbonate has rarely been reported.

Commercially available PPC with a very high molecular weight of 82 kDa (Figure 1a) was chopped using 1,2-propylene glycol as an alcoholysis reagent at 180 °C. Liquid 1,2-propanediol (PDO) can also serve as a rheological additive to accelerate the reaction rate of alcoholysis of PPC and to decrease the reaction temperature. The viscosity of the reaction system decreased gradually owing to the decrease in molecular weight of the resulting macrodiols. Finally, viscous, turbid liquid was obtained. After removing the trace amount of byproduct, a colorless and a transparent waxy solid (Figure 1b) was afforded upon being washed with 5% HCl and deionized water.

The proton nuclear magnetic resonance (1H NMR) and the Fourier transform infrared (FTIR) technologies were adopted to investigate the composition of the alcoholysate and predict the reactions occurred. The 1H NMR spectrum of alcoholysate is shown in Figure 2. It can be seen that the peaks at δ 1.3, 4.2,
According to the above $^1$H NMR assignment, the alcoholysate contains not only PPC macrodiols and unreacted PDO but also PE segments and PC byproducts. The formation of PC byproducts and PE segments results from the occurrence of unzipping and decarboxylation reaction, respectively, during the alcoholysis process. There is no evidence for the occurrence of a random chain-scission reaction because no signal of C==CH$_2$ group is observed in $^1$H NMR spectrum.

As shown in Figure S1, there are almost no unsaturated segments of C==C signal at 1640 cm$^{-1}$ were observed, demonstrating no occurrence of random chain-scission, which leads to the formation of vinyl end-ground. Consequently, the random chain-scission contributes little to the decrease in the molecular weight of PPC.

**Factors Influencing the Alcoholysis.** First, commercial PPC contains about 2 wt % residual catalyst, which has an obvious effect on the alcoholysis of PPC. However, the catalyst concentration can be readily controlled by washing with 5% HCl. The alcoholysis results of PPCs with different residual catalyst concentrations are listed at entry 2, 5, and 6 in Table 1. It is interesting to note that the alcoholysis rate decreases with the decrease in the content of the catalyst in PPC, suggesting that the zinc catalyst also acts as a catalyst for the alcoholysis reaction. Consequently, the catalyst residue favors the alcoholysis of PPC in the presence of small molecular diols.

Second, the molecular weight of PPC macrodiols is a critical factor in the synthesis of PCU. In this connection, the feeding amount of alcoholysis agent, reaction temperature, and time was changed to investigate their effect on the molecular weight of PPC macrodiols. The experimental results are summarized in Table 1; from the results of entry 2, 5, and 6, it can be seen that the alcoholysis rate increases obviously with the increase in the feeding amount of PDO. It took only 30 min to obtain PPC macrodiols with an $M_n$ of about 3 kDa in the case when 30 mmol diol was charged. Compared with entry 5, 7, and 8, it is apparent that higher reaction temperature can decrease the reaction time to obtain PPC macrodiols with low $M_n$ indicating that the alcoholysis reaction follows the time—temperature equivalence principle. This means that we can design and afford any molecular weight PPC by simply adjusting the reaction temperature and time.

Besides the molecular weight, the composition of the resulted PPC macrodiols can greatly affect the practical application in the synthesis of polyurethane. Therefore, the PPC, PE unit, and PC contents of the alcoholysate can be calculated from the $^1$H NMR results and are listed in Table 2.

### Table 1. Influence of Alcoholysis Conditions on the Molecular Weight of PPC Macrodiols

| entry |
|-------|
|     |
| PPC$^a$/mmol | diol$^b$/mmol | catalyst$^c$/wt % | temp$^d$/°C | time/min | $M_n$$^e$/kDa | PDI$^f$ |
|-------|
| 1 | 50 | 0 | 2.20 | 180 | 120 | 59.3 | 2.07 |
| 2 | 50 | 7.5 | 2.20 | 180 | 120 | 3.00 | 1.18 |
| 3 | 50 | 7.5 | 1.00 | 180 | 120 | 9.80 | 1.38 |
| 4 | 50 | 7.5 | 0.35 | 180 | 120 | 14.5 | 1.53 |
| 5 | 50 | 15 | 2.20 | 180 | 60 | 3.40 | 1.33 |
| 6 | 50 | 30 | 2.20 | 180 | 30 | 3.20 | 1.30 |
| 7 | 50 | 15 | 2.20 | 190 | 50 | 3.80 | 1.41 |
| 8 | 50 | 15 | 2.20 | 200 | 40 | 3.90 | 1.50 |

$^a$Number-average molecular mass ($M_n$) = 82 kDa. $^b$Diol = HOCH$_2$CH(CH$_3$)OH. $^c$Calculated by thermogravimetric analyzer (TG). $^d$From gel permeation chromatography (GPC).

### Table 2. Influence of Alcoholysis Agents on the Selectivity of Alcoholysis

| entry |
|-------|
|     |
| PPC$^a$/mmol | diol$^b$/mmol | temp$^d$/°C | time/min | $M_n$$^e$/kDa | PDI$^f$ |
|-------|
| 2$^g$ | 50 | 15 | 180 | 60 | 3440 | 1.33 |
| 9$^g$ | 50 | 15 | 180 | 60 | 3360 | 1.38 |
| 10$^g$ | 50 | 15 | 180 | 60 | 3620 | 1.43 |

$^a$Diol = HO(CH$_2$)$_n$OH. $^b$Diol = HOCH$_2$CH(CH$_3$)OH. $^c$Diol = HO(CH$_2$)$_n$OH.

**According to the above $^1$H NMR assignment, the alcoholysate contains not only PPC macrodiols and unreacted PDO but also PE segments and PC byproducts.** The formation of PC byproducts and PE segments results from the occurrence of unzipping and decarboxylation reaction, respectively, during the alcoholysis process. There is no evidence for the occurrence of a random chain-scission reaction because no signal of C==CH$_2$ group is observed in $^1$H NMR spectrum.

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Besides the molecular weight, the composition of the resulted PPC macrodiols can greatly affect the practical application in the synthesis of polyurethane. Therefore, the PPC, PE unit, and PC contents of the alcoholysate can be calculated from the $^1$H NMR results and are listed in Table 2. Three component contents can be calculated from the following equations:

$$F_{PPC} = \frac{(A_{5.0} + A_{4.2} - 2 \times A_{4.55})}{(A_{5.0} + A_{4.2} - 2 \times A_{4.55}) + (A_{3.5} - A_{1.68}) + 3 \times A_{4.55}}$$

(1)

$$F_{PE} = \frac{A_{3.5} - A_{1.68}}{(A_{5.0} + A_{4.2} - 2 \times A_{4.55}) + (A_{3.5} - A_{1.68}) + 3 \times A_{4.55}}$$

(2)

$$F_{PC} = \frac{3 \times A_{4.55}}{(A_{5.0} + A_{4.2} - 2 \times A_{4.55}) + (A_{3.5} - A_{1.68}) + 3 \times A_{4.55}}$$

(3)

where the letter “A” refers to the integral area of the signal, the subscript nearby showing the corresponding signal location.

For entry 2 with 1,2-propylene glycol as the alcoholysis agent, the alcoholysate contains 58.1% PPC segment, 9.1% PE segment, and 32.8% PC byproduct subjected to the alcoholysis at 180 °C for 60 min. The existence of relatively large amount of PC indicates that the unzipping reaction dominates the side reaction during alcoholysis.
To increase the yield of PPC macrodiols, 1,4-butanediol (BDO) and 1,6-hexanediol (HDO) were further used as the alcoholysis reagent. Table 2 presents the comparison among PDO, BDO, and HDO as alcoholysis reagents. From this table, it can be seen that both BDO and HDO can obviously increase the selectivity of the formation of PPC macrodiols. The content of the PC byproduct decreases from 32.8 to 19.4% (entry 9) and 17.2% (entry 10). Nevertheless, it should be mentioned that the formation of PC byproduct cannot be completely avoided (see Scheme 1).

Proposed Mechanism of the Alcoholysis. In previous works, it has been well-documented that PPC exhibits a relatively poor thermal stability. The thermal decomposition may occur at temperatures higher than 180 °C. This phenomenon can be observed as the molecular weight decreases in the absence of the alcoholysis agent (entry 1 in Table 1). For the thermal decomposition mechanism of PPC, several proposals have been reported elsewhere in the literature. It has been reported that, at a relatively high temperature, unzipping reaction and random chain-scission occur in PPC polymer chain. In the unzipping reaction, the hydroxyl end group backbites and reacts with the nearest carbonyl carbon atom in the PPC backbone, leading to the formation of a 5-member ring compound, that is, PC. Compared with the unzipping reaction, random chain-scission reaction needs higher energy to induce the cleavage C–O bond leading to the formation of CO₂ and two PPC chains with lower molecular weight. The occurrence of unzipping PPC can explain the existence of PC in alcoholysate (entry 2 in Table 2). It should be noted that other poly(aliphatic carbonate) also suffer the same thermal degradation. In this work, Li et al. reported that during the decomposition of poly(butylene carbonate) (PBC), the decarboxylation reaction occurs and yields the PE segment that was found in the alcoholysate (entry 2 in Table 2). These proposals are summarized into three mechanisms as shown in Scheme 2, that is, unzipping, random chain scission, and decarboxylation.

In conclusion, the PC byproducts and the PE segments of the alcoholysate result mainly from its unzipping and decarboxylation, which do not contribute to the decrease in the molecular weight of PPC. The main contribution to the decrease in the molecular weight of PPC lies on the alcoholysis or random chain scission. From the results of 1H NMR (Figure 2) and FTIR (Figure S1) techniques, the absence of C=O signal demonstrates that the alcoholysis is the predominant reaction to yield PPC macrodiols.

As discussed above, the catalyst residue favors the alcoholysis of PPC in the presence of diols. It is apparent that the catalyst residue acts as the catalyst of alcoholysis as well. Presumably, carbonyl oxygen coordinates with the zinc catalyst and withdraws the electron on the carbonyl carbon. The hydroxyl
oxygen of PDO then attacks the carbonyl carbon and forms a tetrahedron transient state, resulting in the chopping of PPC chains. In this mechanism, BDO inserts into the PPC polymer chain and terminated it with hydroxyl, resulting in the formation of PPC segments as verified by the existence of PBC segment in PPC macrodiols in both 1H NMR (chemical shift δ 4.2 and δ 1.77) and matrix-assisted laser desorption/ ionization-time of flight (MALDI-TOF) spectrum (Figure 3). Moreover, this proposed mechanism is analogous to the alcoholysis of PBC catalyzed by alkoxide reported by Lee’s group.23

Unlike PDO that yields two extra PPC ends for each polymer chain chopping, the alcoholysis using BDO (or HDO) produces one PBC or [polyhexylene carbonate (PHC)] chain end. As the corresponding backbite product, butylene carbonate (or hexylene carbonate) is thermodynamically unstable and PBC or PHC chain end is rather difficult to form the cyclic compound, then the repeating PC release can be stopped. When using PDO as an alcoholysis reagent to attack the carbonyl carbon and chop the long polymer chain, two more terminal hydroxyl groups with adjoining PC segments will be formed leading to an autocacceleration of the unzipping process.

When using BDO as the alcoholysis reagent, BDO units can then eliminate, even though longer chain diols are used as an alcoholysis reagent. Most macrodiols contain one or two BDO units, suggesting that BDO was inserted into the PPC macrodiols backbone and did take part in the alcoholysis. Most macrodiols were synthesized. The appearance of the products is shown in Figure 1c. Figure 4 shows the 1H NMR spectrum of the synthesized PPC macrodiols obtained using BDO as the alcoholysis reagent (entry 9). Similar to common polymers, the molecular weight distribution of the synthesized PPC macrodiols also exhibits a Gaussian model. However, the PPC macrodiols possess diversity because of the varying structural segments of the alcoholysate. As shown in Figure 3, there are more than seven kinds of structures in the PPC macrodiols, implying its very complicated structure. From these macrodiols, it can be observed that there are pretty little ether units because of their low content in original PPC. When BDO was used as the alcoholysis reagent, BDO units can then be found in the resulted PPC macrodiols backbone (Figure 3). This shows the evidence that BDO was inserted into the PPC macrodiols backbone and did take part in the alcoholysis. Most macrodiols contain one or two BDO units, suggesting that BDO functions as an end-capping agent and can effectively inhibit the thermally unzipping degradation. Conclusively, the as-prepared PPC macrodiols show a relatively wide molecular dispersity and complicated composition.

**Synthesis of PCEU.** For ease of comparison, both PCEU and PE urethane were synthesized. The appearance of the products is shown in Figure 1c. Figure 4 shows the 1H NMR spectrum of the synthesized PCEU (40% PPC/PPG).

**Chemical Structure of PPC Macrodiols.** Figure 3 shows the MALDI-TOF mass spectrum of PPC macrodiols obtained using BDO as the alcoholysis reagent (entry 9). Similar to common polymers, the molecular weight distribution of the synthesized PPC macrodiols also exhibits a Gaussian model. However, the PPC macrodiols possess diversity because of the varying structural segments of the alcoholysate. As shown in Figure 3, there are more than seven kinds of structures in the PPC macrodiols, implying its very complicated structure. From these macrodiols, it can be observed that there are pretty little ether units because of their low content in original PPC. When BDO was used as the alcoholysis reagent, BDO units can then be found in the resulted PPC macrodiols backbone (Figure 3). This shows the evidence that BDO was inserted into the PPC macrodiols backbone and did take part in the alcoholysis. Most macrodiols contain one or two BDO units, suggesting that BDO functions as an end-capping agent and can effectively inhibit the thermally unzipping degradation. Conclusively, the as-prepared PPC macrodiols show a relatively wide molecular dispersity and complicated composition.

**Synthesis of PCEU.** For ease of comparison, both PCEU and PE urethane were synthesized. The appearance of the products is shown in Figure 1c. Figure 4 shows the 1H NMR spectrum of the synthesized PCEU. The peaks at δ 3.75, 7.0 (b, and 7.3b), and 9.5 are assigned to CH3 between the benzene rings, CH on the benzene ring, and the NH on the urethane bond, in their turns. While the signals at δ 4.0 and δ 1.68 are ascribed to BDO linkages as another part of the hard segment, the peaks at δ 1.2, 4.1, and 4.88 correspond to CH3, CH2, and CH of the PPC soft segment, respectively, when using DMSO-d6 as the solvent, in which the chemical shifts of each peak are slightly different when using chloroform as the solvent. For PE soft segment, the chemical shifts of CH3 and CH2 (and CH) of the PE segment are observed at δ 1.1 and δ 3.4, respectively. The disappearance of the signal ascribed to 4,4’-diphenylmethane diisocyanate (MDI) implies the successful synthesis of PCEU.

From the integral area in 1H NMR, the composition ratio of the synthesized PU can be calculated. The content of the carbonate unit in the soft segment and the total hard segment in the synthesized PCEU can be calculated by the following formula and are summarized in Table 3.

\[
\text{Carbonate unit %} = \frac{A_{4.88} + 2/3A_{4.12}}{(A_{4.88} + 2/3A_{4.12}) + A_{1.0}} \times 100
\]
It should be pointed out that both the carbonate content in the soft segment and the content of the hard segment of resulting PCEU are very close to the feeding ratio. For example, in PCEU\(_{(80\% \text{ PPC/PPG})}\), the feeding ratio of carbonate (in soft segment) and the hard segment (MDI) are 80% and 30 wt %, respectively, whereas the calculated ratio is 79.94% and 30.67 wt %, demonstrating that the synthesized PPC macrodilors exhibit similar reactivity as the ether diols during the polyurethane synthesis.

### Mechanical Properties and Hardness of PCEU

The mechanical performance and hardness (Shore A) of PCEU and PU are shown in Table 4. The PU synthesized from poly(propylene glycol) (PPG) is named PU\(_{(\text{PPG})}\), whereas the one from the mixture of PPG and PPC is called PCEU\(_{(80\% \text{ PPC/PPG})}\); the number following the “PPC” indicates the mole percent of the carbonate unit in the soft segment.

Because of the low glass transition temperature of PPG, PU\(_{(\text{PPG})}\) behaves in a very soft nature with a Shore A hardness of 31. Similarly, tensile strength (\(\sigma_t\)) of PU\(_{(\text{PPG})}\) is lower than 2 MPa with an elongation at break (\(\varepsilon_b\)) of greater than 88%. In case that 40% carbonate was inserted into the soft segment, Shore A hardness of PCEU\(_{(40\% \text{ PPC/PPG})}\) increases dramatically from 31 to 81. Meanwhile, the tensile strength and elongation at break increase to 29.81 MPa and 1198%, respectively. With a further increase in the carbonate content, Shore A hardness of PCEU\(_{(80\% \text{ PPC/PPG})}\) slightly increases to 88 as shown in Figure 5. On the other hand, the tensile strength at 100 and 300% elongation increase with an increase in the carbonate content. For example, the tensile strength of PCEU\(_{(80\% \text{ PPC/PPG})}\) at 300% elongation increases to 29.85 MPa. The strain–stress curve versus the carbonate contents is presented in Figure 6.

In this study, five types of polyurethanes with varying contents of PPC moiety were synthesized under the same reaction conditions. As shown in Table 4, although the molecular weights and polydispersity index (PDI) of the polyurethanes are different, it can be easily seen that the contributions of the polycarbonate content and molecular weights to mechanical properties. For example, comparing the

\[
\text{Hard content} \% = \left[ \frac{1}{2} (A_{7,0} + A_{7,3}) \times 268 \right. \\
+ \frac{1}{2} (A_{1,68} \times 72) / \left[ \frac{1}{2} (A_{3,0} + A_{3,3}) \times 268 \right. \\
+ \frac{1}{2} (A_{1,68} \times 72 + (A_{4,89} + A_{1,2}) \times 102 \\
+ \frac{4}{3} (A_{1,0} \times 58) \times 100 \\
\]

(5)
samples with similar molecular weight (PCEU(80% PPC/PPG), PCEU(60% PPC/PPG), and PCEU(40% PPC/PPG)), it is apparent that the mechanical strength increases with the increase in the content of the PPC moiety. The increase in the carbonate content can increase both tensile strength and hardness of the synthesized PCEU because of both rigidity of carbonate moiety and the hydrogen-bond formation between carbonate groups with urethane. In conclusion, the performance of synthesized PCEU can be readily tailored by simply adjusting the ratio of the carbonate group content to the PPG content.

### Conclusions

An effective method to prepare low-molecular-weight PPC macrodiols by alcoholysis of high-molecular-weight PPC has been successfully developed. The residual zinc catalyst in commercial PPC was confirmed to be also a catalyst for the alcoholysis reaction. The PPC macrodiols with desirable molecular weight can be readily synthesized by controlling the amount of alcoholysis agent, reaction temperature, and time. Thermal decarboxylation and unzipping reaction were observed during the alcoholysis reaction, but it can be eliminated to very limited content. When using BDO and HDO as alcoholysis agents, the formation of cyclic carbonate “byproduct” can be greatly decreased owing to the formation of PPC macrodiols with BDO or HDO end-capped groups. The as-synthesized PPC macrodiols can be used as a diol to synthesize PCU or PCEU. The performance of the synthesized PCEU can be readily tailored by simply adjusting the ratio of the carbonate group content to the PPG content. Moreover, PPC macrodiol is a special polyol with its biodegradability; this character can produce a biodegradable polyurethane. In conclusion, the PPC macrodiols synthesized by alcoholysis show a bright future in the potential applications of the polyurethane industry.

### Experimental Section

**Materials.** Commercial PPC with an $M_n$ of 82 kDa was purchased from Henan Tianguan Enterprise Group Co., Ltd., which was synthesized using Zn-G-III as the catalyst. PDO, BDO, and HDO were purchased from Aladdin Co., and a 3 Å molecular sieve was used to get rid of water. N,N′-Dimethylacetamide (DMAC), stannous octoate, and MDI were purchased from Aladdin Co. DMAC was refluxed over CaH$_2$ and distilled under dry nitrogen gas flow. Stannous octoate and MDI were used directly without further purification. PPG with average molecular weight of 3000 Da was purchased from Jining Baiyi Co. Ltd.

**Preparation of Macrodiol.** A typical process for the preparation of PPC macrodiols is as follows: PDO (0.57 g 7.5 mmol) and high-molecular-weight PPC (5.1 g 50 mmol) were added to a three-necked flask (25 mL), which was connected to a manifold equipped with vacuum and N$_2$ gas lines and equipped with a mechanical stirrer. The flask was purged and vacuumed several times using nitrogen to guarantee free of oxygen and moisture before it was immersed in a hot-oil bath (180 °C). The chopping reaction was performed for 120 min. After cooling to room temperature under the protection of an inert atmosphere, the resultant PPC macrodiols were washed using 5% hydrochloric acid and deionized water thrice to remove the trace residual catalyst.

The residual zinc catalyst content in the commercial high-molecular-weight PPC can be controlled by washing it times with 5% hydrochloric acid. High-molecular-weight PPC was dissolved in the chloroform before washing with HCl. Vigorous stirring was carried out for at least 5 min to afford a satisfactory purification, followed by precipitating into ethanol and drying under vacuum at 80 °C for 24 h.

**Preparation of PCEU.** In this study, PCEU was synthesized by the traditional two-step solution polymerization. Both MDI and BDO were used as hard segments and chain extenders, respectively, and their total contents were set to be 30 wt %. The soft segment was the mixture of PPC macrodiols ($M_n \approx 3000$ kDa, obtained from alcoholysis) and PPG ($M_n \approx 3000$ kDa).

PPC macrodiols (8.38 g, OH 10.34 mmol) and PPG (5.84 g, −OH grounds 5.76 mmol) were charged into a three-necked flask (100 mL), which was connected to a manifold equipped with vacuum and N$_2$ gas lines, and equipped with a mechanical stirrer. Before MDI was added into the flask, the system was dried for 2 h at 120 °C and 300 Pa. After the completion of vacuum drying, N$_2$ gas was charged into the system. When the system temperature was cooled to 70 °C, MDI [5.00 g, −isocyanate (NCO) grounds 40 mmol] was charged into the flask. The prepolymerization was performed until the NCO groups decreased to the theoretical value that can be detected by titration using dibutylamide. The calculated amount of DMAC (51 mL), BDO (1.11 g, −OH grounds 24.67 mmol), and stannous octoate (21 μL) were added into the flask in turn, and the reaction temperature was increased to 75 °C. The reaction was performed until no existence of the NCO group by FTIR confirmation was found. Upon cooling to ambient temperature, the resulting mixture was slowly poured into methanol. The final product was filtered and dried under vacuum at 80 °C for 24 h. The schematic synthesis of the PCEU is shown in Scheme 2.

**Measurement.** $^1$H NMR spectra of the synthesized PPC macrodiols were recorded on a Bruker DRX-400 NMR spectrometer at room temperature using CDCl$_3$ as a solvent. The $M_n$ and PDI of the resultant PPC macrodiols were measured using a GPC system (Waters 515 HPLC Pump, Waters 2414 detector) with a set of three columns (Waters Styragel 500, 10 000, and 100 000 Å) and chloroform [high-performance liquid chromatography (HPLC) grade] as an eluant. When PPC was used to measure the $M_n$ and PDI of PU, tetrahydrofuran (THF) (HPLC grade) was used as an eluant. The GPC system was calibrated by a series of polystyrene standards with polydispersities of 1.02 standards. MALDI-TOF spectra were recorded on a Bruker ultraflxeXtreme MALDI-TOF spectrometer, with 2,5-dihydroxybenzoic acid as the matrix and THF as solution.

The residual catalyst in commercial PPC was measured using a PerkinElmer thermogravimetric/differential thermal analyzer (TG/DTG) instrument against alumina as a reference. For each measurement, 10 mg of the samples were used. The experiments were performed under dry air atmosphere at 100 mL/min flow rates. Heating rates were adopted at 10 °C/min, from room temperature to 600 °C. Equation 1 shows the calculation formula of the content of the catalyst (Zn-G-III) in commercial PPC

$$Zn-G-III\ wt \% = \frac{m_{350} - m_{400}}{m_{30}} \times \frac{M_{Zn-G-III}}{M_{ZnO}} \times 100$$

(6)
where $m_{\text{res}}$, $m_{\text{350}}$, and $m_{\text{10}}$ mean the residual mass at 600, 350, and 30 °C, respectively, while $M_{\text{Zn-G-III}}$ and $M_{\text{ZnO}}$ refer to the molar mass of Zn-G-III and ZnO.

The THF solution of PPC–PU and PPG–PU were casted on the Teflon culture dish to obtain a roundness film. The dumb-bell-shaped samples were cut from the film, with the same length and width of 25 mm and 4 mm, respectively. The stress–strain test was performed on a temperature-controlled universal testing machine at 25 °C with an extension rate of 50 mm/min. Shore A hardness test of PPC–PU and PPG–PU was characterized by a Shandu sclerometer; each sample should have a thickness over 6 mm.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00183.

Experimental details including characterization data and selected spectra (PDF)

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### Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

PDO, 1,2-propanediol; HDO, 1,6-hexanediol; BDO, 1,4-butanediol; PPC, poly(propylene carbonate); PPG, poly(propylene glycol); PC, poly(propylene carbonate); PE, polyether; PCDLs, polycarbonate diols; PCEU, polycarbonate ether urethane; MDA, 4,4′-diphenylmethane diisocyanate; SA, sebamic acid; DMAC, dimethylacetamide; DHB, 2,5-dihydroxybenzoic acid

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