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Synthesis and characterization of amino-functionalized poly(propylene carbonate)

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The first synthesis of amino-functionalized poly(propylene carbonate) (PPC) by terpolymerization of carbon dioxide (CO_2), propylene oxide (PO), and N,N-Dibenzyl Amino Glycidol (DBAG) following the removal of benzyl protecting groups. The copolymerization conditions were investigated in detail. PPC with varying monomer DBAG contents (0-3.3 mol %) were obtained in high yield. The benzyl groups of terpolymers could be completely removed to provide amino-functionalized PPC without backbone degradation. Thermal properties and contact angles of the functionalized PPCs were measured, showing the dependence of glass transition temperature (T_g) on molecular weight and the expected increase in hydrophilicity with increasing content of amino entities.

Carbon dioxide (CO_2) is the main gas leading to the greenhouse effect, and it is also a non-toxic, cheap, renewable and abundant C_1 resources. Nowadays use CO_2 as the raw material of synthetic chemicals and materials gradually becoming the focus of attention in the promotion of the rational use of resources.[1-4] The alternating copolymerization of CO_2 and epoxides, which was first reported by Inoue and co-workers in 1960s,[5] has been considered as one of the most promising processes to produce a variety of aliphatic polycarbonates.[6] Among these, poly(propylene carbonate) (PPC) derived from CO_2 and propylene oxide (PO) is known as a cheap and biodegradable polymer material due to its good properties such as compatibility, translucence, innocuousness etc.[7] PPC has great potential application in the development of plastic, elastomer, fiber, adhesive, and so on.[8] However, the practical application of PPC in the biomedical field has been limited by the lack of functional groups in the backbone.

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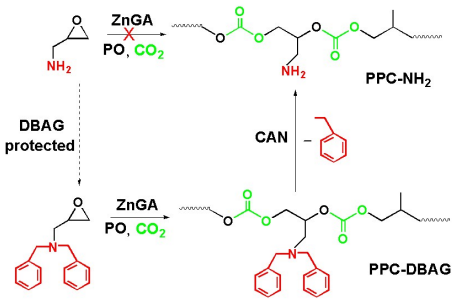
It has been reported that linear aliphatic functional polycarbonate exhibit great potential for medical devices, drug delivery systems and in tissue engineering.[9,10] Therefore, many approaches have been developed to the synthesis of functional PPC, such as copolymerization of CO_2 and functional epoxides,[11] terpolymerization of CO_2, PO and functional epoxides.[12,13] In fact, copolymerization of CO_2 and functional epoxides major depends on the activities of epoxides and catalyst, leading to the increase of cost. For example, Frey reported that the copolymerization of carbon dioxide and glycidyl ether to prepare the functional aliphatic polycarbonates, but molecular weight of the resulting copolymers was low.[14] In contrast, terpolymerization of CO_2, PO and functional epoxides is an efficient method to prepare functional PPC. The preparation of functional aliphatic polycarbonates from CO_2 PO and epoxides with functional groups randomly distributed along the PPC backbone requires a suitable functional comonomer to tolerate the polymerization conditions. Therefore, this strategy often requires two steps including the incorporation of the third monomer into PPC chains and the post-treatment of terpolymer. It is reported that "click chemistry" or the deprotection of functional groups have been used for post-polymerization reactions. Frey et al.[15] reported the terpolymerization of CO_2, PO and 1, 2-epoxy-5-hexene following with thiol-ene reaction

using mercaptoethanol and thioglycolic acid to obtain hydroxyl and carboxyl functional PPC. Theato et al.[16] reported the terpolymerization of CO_2, PO and 2-[[(2-nitrophenyl) methoxy]-Methyl] oxirane, and then by ultraviolet (UV) light irradiation for removing the protection group to obtain hydroxyl functional PPC. Frey et al.[17] reported the synthesis of hydroxy functional polycarbonates by direct random copolymerization of CO_2 with 1, 2-isopropylidene glyceryl glycidyl ether as a protected bishydroxy-functional glycidyl ether. Furthermore, glycidyl methyl ether has also been employed in a terpolymerization to tailor both functionality and solubility. Subsequent acidic hydrolysis resulted in stable aliphatic polycarbonates with 1, 2-diol side chains without degradation of the polymer backbone.



Scheme 1 Synthesis of amino-functionalized poly(propylene carbonate)

Although several attempts have been achieved to incorporated functional groups into the backbone of PPC, there has been no report for the synthesis of amino-functionalized PPC. In fact, the amino group is a very interesting functionality, which is utilized in many organic reactions as a consequence of its versatile reactivity, especially in drug delivery and tissue engineering.[18-20] Therefore, in the current work, we created the amino functional PPC by the terpolymerization of CO_2, PO and N, N-Dibenzyl Amino Glycidol (DBAG) following the reaction to remove the benzyl group of terpolymers. The results showed that the third monomer DBAG can not impede the compolymerization conditions, the benzyl group of terpolymers can be completely removed without damaging the backbone structure. The copolymerization conditions and properties of the amino functional aliphatic polycarbonates were studied in this work.

The synthetic strategy developed to obtain the amino-functionalized PPC is shown in Scheme 1. Comonomer DBAG can be prepared from dibenzylamine and epichlorohydrin in mild conditions (Scheme S1 in ESI†).[21] Moreover, it has been reported that the benzyl group of DBAG can be completely removed to produce amino group.[22] Thus, amino-functionalized PPC prepared from the terpolymerization of CO_2, PO and DBAG catalyzed by zinc glutarate (ZnGA) following the removal of benzyl group from polymer backbone.

The copolymerization conditions of CO_2, PO and DBAG was detailed investigated. As shown in Table S1,† the optimum copolymerization conditions were 80 □, 20 h and 5.0 MPa CO_2 pressure. Under these conditions, the terpolymerization of CO_2, PO and DBAG was achieved in high yield. As shown in Table 1, the yield of the copolymerization was between 5365 to 7091 g/mol Zn. The content of DBAG in terpolymers increased from 1.3 to 3.3 mol %. However, M_n of the terpolymers (PPC-DBAGs) derived from CO_2, PO and DBAG decreased from 41000 to 19000 g/mol corresponding to DBAG/PO molar feed ratios varying from 0 to 15. It is concluded that the activity of DBAG copolymerized with CO_2 was lower than that of PO. So there has no polymer obtained when the DBAG/PO molar feed ratio increasing to 20.

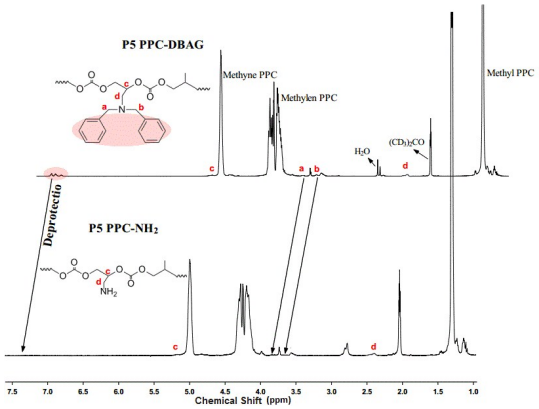


Figure. 1 ^{1}H NMR spectra of P5 PPC-DBAG and P5 PPC-NH_2

Table 1 Characterization data of copolymer samples[a]

sample	DBAG/PO feed (mol %)	Yield (g/mol of Zn)	DBAG[b] in polymer (mol %)	Carbonate linkages[c] (%)	M_n[d] PPC-DBAG (g mol^{-1})	M_w/M_n[d] PPC-DBAG	M_n PPC-NH_2 (g mol^{-1})	M_w/M_n PPC-NH_2
P1	0	6195	0	94%	41000	3.2	39500	3.1
P2	2.5	7091	1.3	98%	35600	3.1	31300	3.1
P3	5	6235	1.9	95%	29100	2.8	26100	2.6
P4	10	5998	2.5	93%	25000	2.5	21600	2.3
P5	15	5365	3.3	92%	19000	2.0	14900	2.1
P6[e]	20							

[a] Copolymerization conditions: CO_2 pressure 5.0 MPa, temperature 80 °C, reaction time 20 h. [b]Comonomer DBAG content, calculated from ^{1}H NMR spectra of the PPC-DBAG polymer samples. [c]By ^{1}H NMR spectroscopy. [d]By gel permeation chromatography (GPC) calibrated to polystyrene standards in THF at room temperature. [e]No polymer obtained.

The structure of PPC-DBAGs was confirmed by ^{1}H NMR spectroscopy (Fig. 1 and Fig. S3 in ESI†). Compared with PPC, the absorption peaks at 1.3, 4.2 and 5.0 ppm were assigned to CH_3, CH_2 and CH in the carbonate unit, respectively. Agreement of the DBAG fraction in the copolymers with the composition of the epoxide monomer feed is confirmed by ^{1}H NMR spectroscopy from the comparison of the polycarbonate backbone signals a, b, c and d (3.9, 3.7, 5.2, and 2.4 ppm), the absorption peaks at 7.2-7.5 ppm were assigned to the phenyl group of DBAG, indicating that DBAG were incorporated into the PPC backbone successfully.

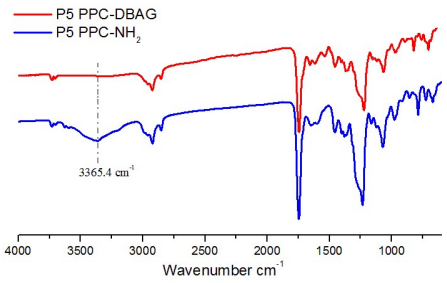


Figure. 2 FT-IR spectra of P5 PPC-DBAG and P5 PPC-NH_2

It has been reported that the benzyl group of DBAG could be transformed into amino group by using ceric ammonium nitrate (CAN) at room temperature.[22] Therefore, amino-functionalized PPC (PPC-NH_2) were easily prepared by removing the benzyl protecting group of PPC-DBAG. The resulting PPC-NH_2 polymers were characterized by ^{1}H NMR spectroscopy with respect to its composition (Fig.1 and Fig. S4 in ESI†). From ^{1}H NMR spectroscopy of PPC-NH_2, the absorption peaks at 3.7, 3.9 and 7.2-7.5 ppm assigned to the benzyl group of DBAG have disappeared. Meanwhile, the FT-IR spectra (Fig.2) directly proved that PPC-NH_2 was successfully obtained. Compared with PPC-DBAG the new characteristic absorption at 3365 cm^{-1} was assigned to the amino stretching vibration. The molecular weights determined by GPC of the PPC-NH_2 samples are very comparable to corresponding PPC-DBAG samples (Table 1). It may thus be anticipated that main chain degradation is not remarkably taking place during the removal of benzyl groups from the backbone of PPC-DBAG. Note that the molecular weight decreased after the deprotection due to the loss of the benzyl protecting groups.

Table 2 Glass transition temperature and contact angle of polymer samples

sample	T_g[a] (°C)	T_g(°C)	CA[b] (deg)	CA (deg)
based on	PPC-DBAG	PPC-NH_2	PPC-DBAG	PPC-NH_2
P1	37.0	37.1	70.7	70.1
P2	37.6	36.6	71.1	66.7
P3	37.4	36.3	72.4	64.1
P4	37.0	35.8	73.8	62.1
P5	35.3	34.6	76.1	60.2

[a]Glass transition temperature (T_g) determined by DSC. [b]Contact angle.

The glass transition temperature (T_g) of PPC-DBAG and PPC-NH_2 samples are listed in Table 2. It can be seen that P2 PPC-DBAG exhibits the highest T_g of 37.6□ owing to the incorporation of DBAG into the backbone of PPC. However, T_g of PPC-DBAG decreased with increasing DBAG content, which ascribes to the decrease of the molecular weight of PPC-DBAG. T_g of PPC-NH_2 polymers are slightly lower than those of PPC-DBAG due to the removal of benzyl protecting group.

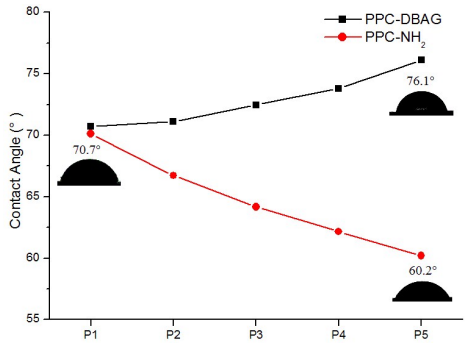


Figure. 3 Contact angle analysis of PPC-DBAG and PPC-NH_2 samples

Consistently, the hydrophilicity of the respective polymers P1-P5 PPC-DBAG and PPC-NH_2 are different. The change in polarity is for instance expressed in the contact angle of polymer thin films to water (Table 2). Contact angles of PPC-DBAG polymers are in the range of 70.7°-76.1°, corresponding to DBAG/PO molar feed ratios varying from 0 to 15. The contact angle of P1-P5 PPC-DBAG is showing an upward tendency may be attributed to the increasing DBAG content, indicating that the hydrophilic gradually reduced. Meanwhile, the PPC-NH_2 polymers have a significantly decreased contact angle from 70.1° to 60.2°. The higher the content of comonomer units in the PPC-NH_2, the lower the contact angle is (Fig.3).

In conclusion, a new type of amino-functionalized, aliphatic polycarbonate random copolymers from CO_2, PO, and a protected glycidyl ether derivative (DBAG) has been synthesized. The protecting groups of DBAG can be completely removed by CAN with no impact on the backbone of PPC. The amino group content of PPC-NH_2 polymers could be adjusted by varying the molar ratio feed of DBAG comonomer. The composition, glass transition temperature and hydrophilicity of terpolymers have been investigated. The resulting PPC-NH_2 polymers with high hydrophilic are expected to be used in wide application fields and as a general precursor for the post-functionalized PPCs.

Acknowledgements

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References

1 M. Cokoja, C. Bruckmeier, and B. Rieger, *Chem. Int. Ed.*, 2011, **50**, 8510-8517.
2 T. Sakakura, J. C. Choi, and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365-2387.
3 E. J. Beckman, *Science.*, 1999, **283**, 946-947.
4 T. Sakakura, K. Kohno, *Chem. Commun.*, 2009, **11**, 1312-1330.
5 S. Inoue, H. Konuma, and T. Tsuruta, *Polym. Lett.*, 1969, **7**, 287 −292.
6 D. J. Darensbourg, *Chem. Rev*., 2007, **107**, 2388-2410.
7 G. A. Luinstra , E. Borchardt, *Adv. Polym. Sci.*, 2012, **245**, 29-48.
8 G. A. Luinstra, *Polym. Rev.*, 2008, **48**, 192-219.
9 J. Feng, R. X. Zhuo, and X. Z. Zhang, *Prog. Polym. Sci.*, 2012, **37**, 211-236.
10 H. Tian, Z. Tang, and X. Zhuang, *Prog. Polym. Sci.*, 2012, **37**, 237-280.
11 J. Hilf, H. Frey, *Macromol. Rapid Commun.*, 2013, **34**, 1395-1400.
12 J. Geschwind, F. Wurm, and H. Frey, *Macromol. Chem. Phys.*, 2013, **214**, 892-901.
13 J. Hilf, A. Phillips, and H Frey, *Polym. Chem.*, 2014, **5**, 814-818.
14 J. Geschwind, H. Frey, *Macromolecules.*, 2013, **46**, 3280 −3287.
15 J. Geschwind, F. Wurm, and H. Frey, *Macromol. Chem. Phys.*, 2013, **214**, 892-901.
16 X. Wu, H. Zhao, and B. Nörnberg, *Macromolecules.*, 2014, **47**, 492-497.
17 J. Geschwind, H. Frey, *Macromol. Rapid Commun.*, 2013, **34**, 150-155.
18 D. M. Ryan, B. L. Nilsson, *Polym. Chem.*, 2012, **3**, 18-33.
19 W. Tang, S. C. Ng, *Nat. Protoc.*, 2008, **3**, 691-697.
20 J. Ding, F. Shi, and C. Xiao, *Polym. Chem.*, 2011, **2**, 2857-2864.
21 B. Obermeier, F. Wurm, and H. Frey, *Macromolecules.*, 2010, **43**, 2244-2251.
22 S. D. Bull, S. G. Davies, and P M. Kelly, *J. Chem. Soc. Perkin. Trans.*, 2001, **23**, 3106-3111.