

Electronic Supplementary Information (ESI) for

One-pot Controllable Synthesis of Oligo(carbonate-ether) Triol by Zn-Co-DMC

Catalyst: Special Role of Trimesic acid as Initiate-Transfer Agent

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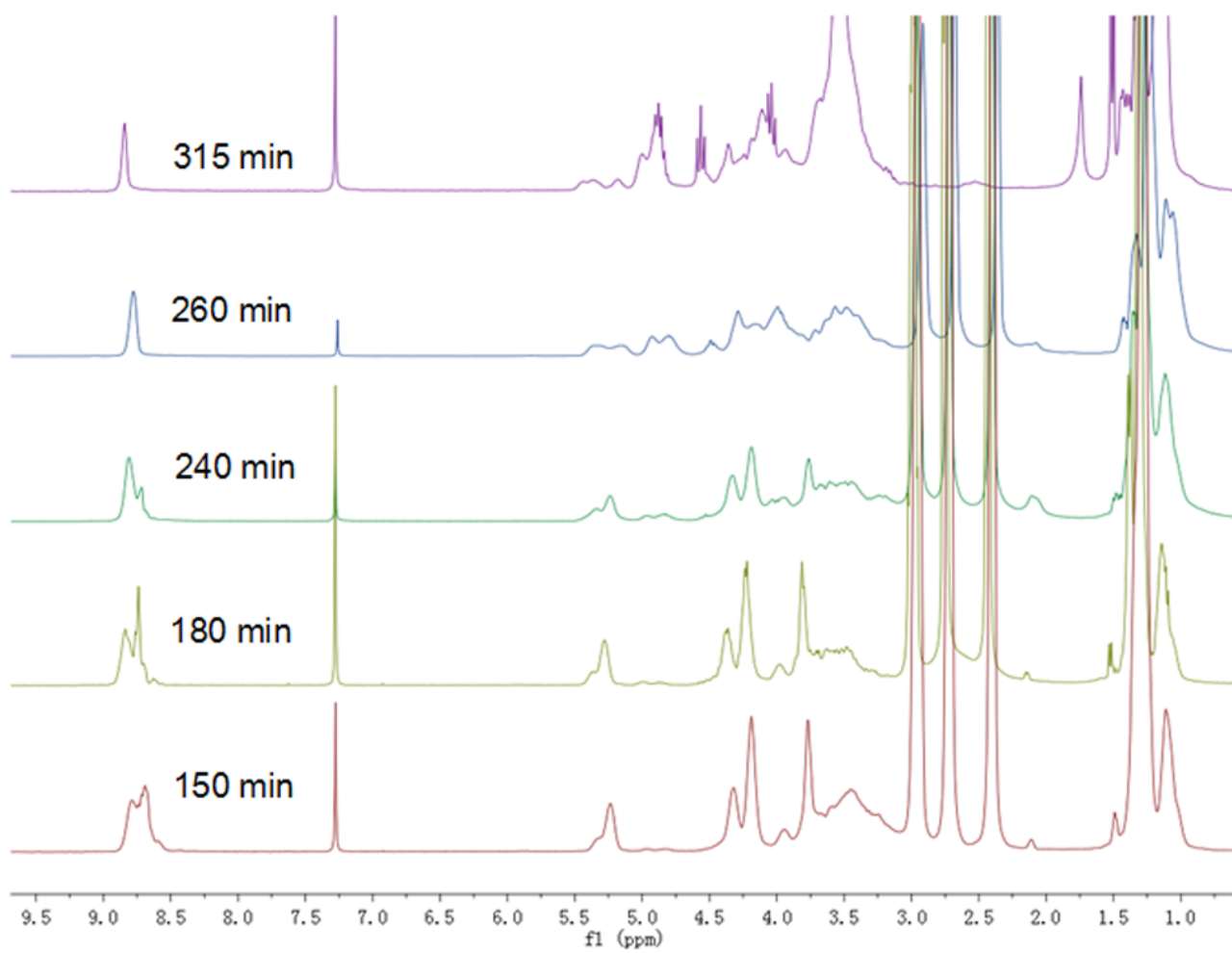


Fig. S1 ^1H NMR spectra of products from Table 2 at different reaction times.

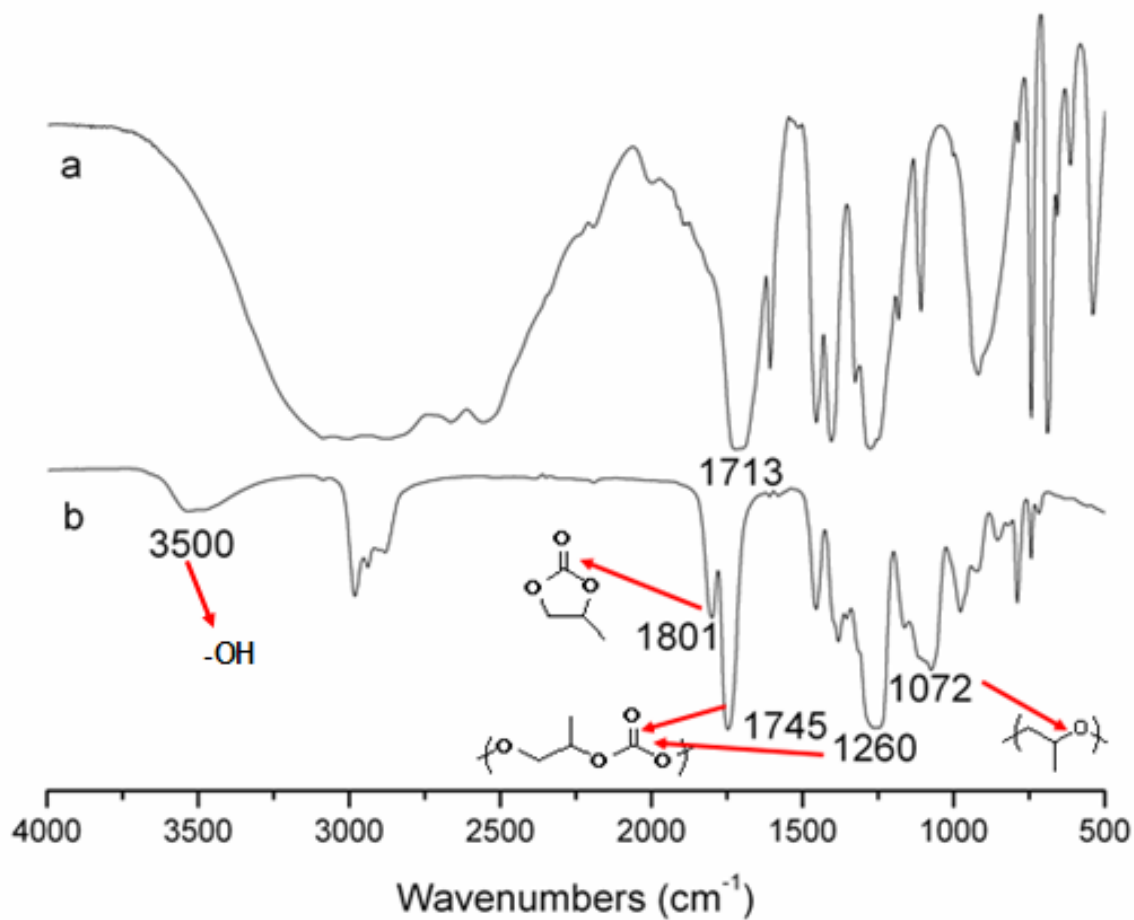


Fig. S2 IR spectra of (a)TMA and (b)oligo(carbonate-ether) triol (Entry 7, Table 1).

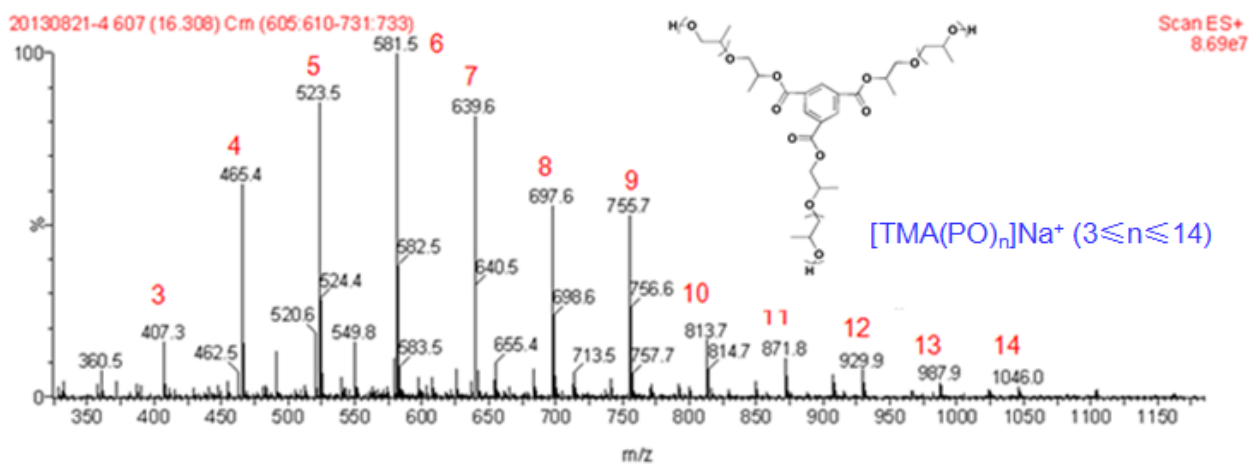
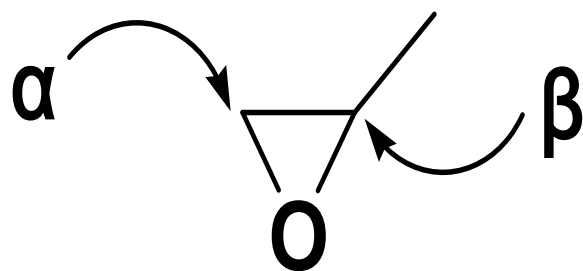


Fig. S3 ESI-MS spectra of the oligo-ether triol (Entry 1, Table 2).



Scheme S1 Ring opening modes of PO

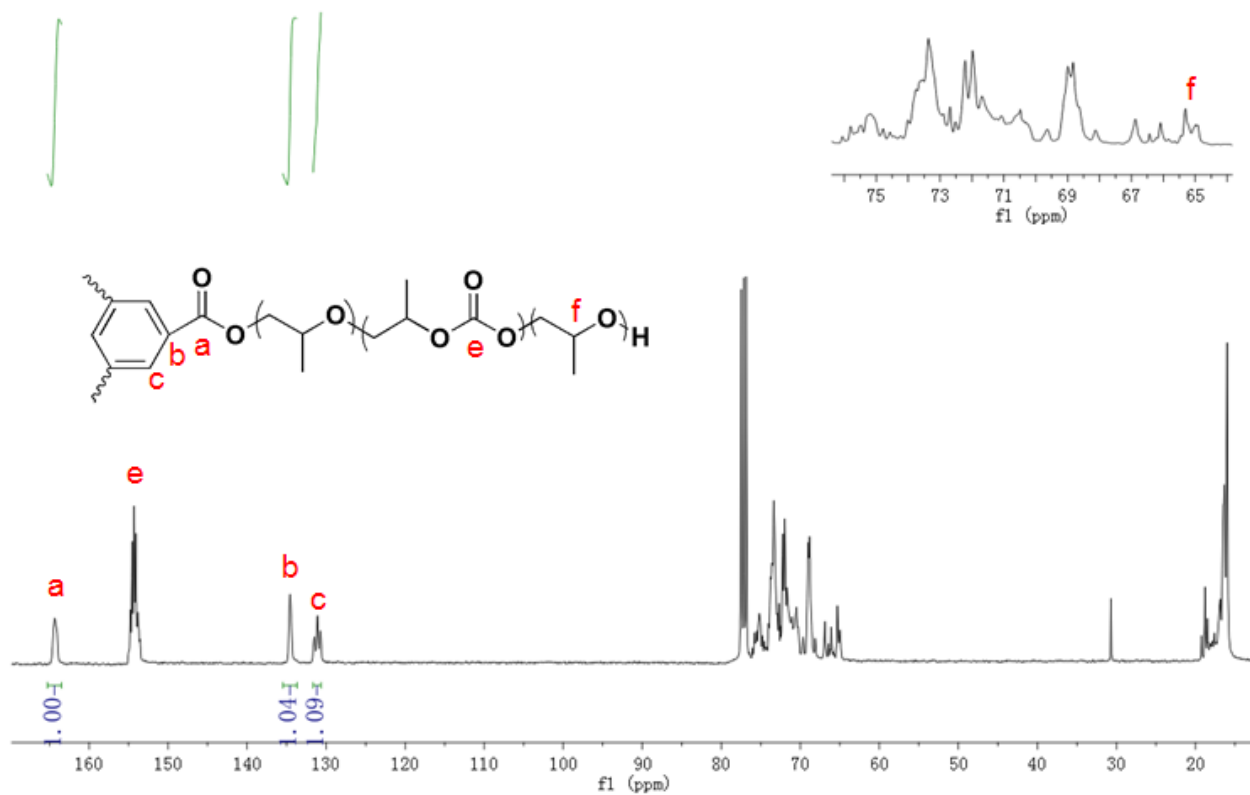


Fig. S4 ^{13}C NMR spectra of the oligo(carbonate-ether) triol (Entry 7, Table 1).

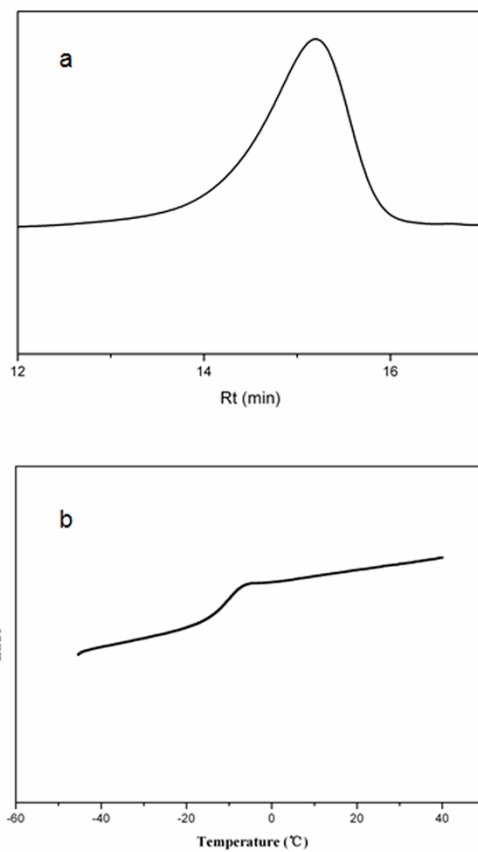


Fig. S5 The GPC (a) and DSC (b) curve of the oligo(carbonate-ether) triol (Entry 7, Table 1).

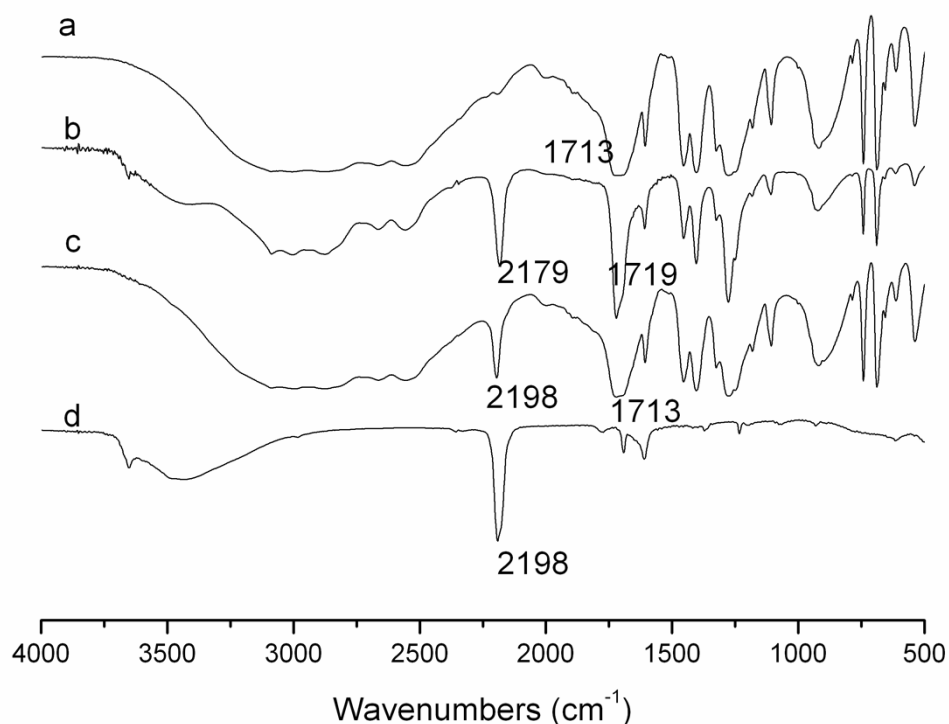


Fig. S6 IR spectra of DMC: (a) TMA ; (b) the reaction product of DMC and TMA , where the reaction was carried out at room temperature for 5h in CH_2Cl_2 , then washed with excessive deionized water until no TMA was detected, the product was centrifuged and dried at 50°C under vacuum to a constant weight; (c) the blend of TMA and DMC; (d) pure DMC treated under the same condition of (b).

In Fig. S6, the ν (CN) of b (about 2179 cm^{-1}) shifted to lower wave numbers compared to the ν (CN) of c and d (about 2198 cm^{-1}), the blue shift of the CN indicated a change of the microenvironment for the corresponding metal elements due to the coordination of TMA to DMC; the infrared spectra of c (blend of TMA and DMC) did not show a shift of the ν (CN) band compared with d (pure Zn-Co DMC), confirming that the reaction product of TMA and DMC was not a blend.

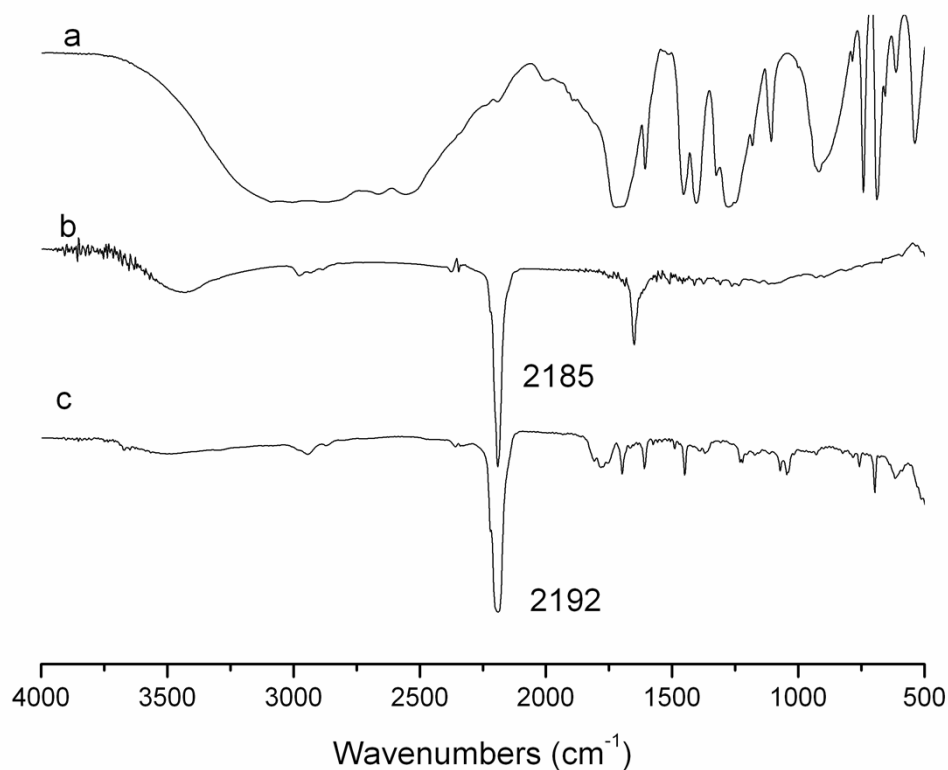


Fig. S7 IR spectra of DMC: (a) TMA ; (b) DMC obtained during induction period, where the reaction was carried out at 80°C, 4MPa, for 15 min with 10 mg DMC, 0.5 g TMA, 2 ml PO, then washed with excessive deionized water and acetone, the product was centrifuged and dried at 50°C under vacuum to a constant weight; (c) pure DMC treated under the same condition of (b).

In Fig. S7, the ν (CN) of (b) shifted to lower wavenumber compared with (c), indicating the coordination of TMA-based oligo-ether triol to DMC, and (b) did not contain the absorption peak of TMA, differed from the catalyst from Fig. S7 (b), proved the weak interaction between DMC and oligo-ether triol. Therefore, the coordinated oligo-ether triol could be easily replaced with protonic compounds, just coinciding with the characteristics of immortal polymerization, where rapid reversible chain transfer reaction existed between TMA or hydroxyl terminated intermediate and the active center.^{1, 2} Thus, all the TMA convert to oligo-ether triol by the rapid chain transfer reaction during the induction period.

Table S1. Control experiments of copolymerization of CO₂/PO catalyzed by Zn-Co DMC in the presence of TMA

Entry	reaction condition	reaction products
1	The reaction was carried out with 12mg Zn-Co DMC, 10 ml PO, 0.25 g TMA at 4 MPa, 80°C for 2 h.	the product was oligo(carbonate-ether) triol
2	(1) the reaction was carried out with 0.25 g TMA, 2 ml PO, 12 mg Zn-Co DMC at 80°C for 1h. (2) then stopped and cooled to room temperature, adding the rest of 8 ml PO.	(1) the reaction product was a transparent, viscous liquid (2) PO explosive polymerization in less than 1 min at room temperature
3	(1) the reaction was carried out with 0.25 g TMA, 2 ml PO at 80°C for 1h. (2) then stopped and cooled to room temperature, adding 12 mg Zn-Co DMC and the rest of 8 ml PO, then the reaction was carried out at 80°C, 4 MPa for 2 h.	(1) the reaction product was a milky suspension liquid (2) the product was oligo(carbonate-ether) triol

In order to confirm that it was the reaction of TMA and PO that resulted in the induction period of copolymerization, control experiments were carried out as listed in Table S1. Compared to the one-pot reaction (Entry 1, Table S1), the stepwise polymerization reaction of Entry 2 was almost explosive in less than 1 min at room temperature, suggesting that the reaction of TMA and PO indeed resulted in the induction period of the reaction.

1. S. Inoue, *Journal of Polymer Science Part a-Polymer Chemistry*, 2000, **38**, 2861-2871.
2. S. Asano, T. Aida and S. Inoue, *J. Chem. Soc., Chem. Commun.*, 1985, 1148-1149.