Supporting Information

Facile preparation of long-chain aliphatic polycarbonates containing block copolycarbonates *via* one-pot sequential organic catalyzed polymerization of macrocyclic carbonate and trimethylene carbonate

Bingkun Yan, [a] Jiaqian Hou, [a] Chao Wei, [*a] Yan Xiao, [a] Meidong Lang[*a] and Farong Huang [a]

[a] Key Laboratory of Specially Functional Polymeric Materials and Related Technology of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai, 200237, China.

* E-mail: mdlang@ecust.edu.cn, weichao107@163.com

Contents:

Materials

1,4-Butanediol, 1,5-Pentanediol, 1,6-Hexanediol, 1,7-Heptanediol, Diphenyl carbonate (DPC), Trimethylene carbonate (TMC), 1,5,7-triazabicyclo[4.4.0] dec-5-ene (TBD), were purchased from Sigma-Aldrich and used as received unless noted otherwise. The lipase CA Novozym 435 (N-435) is an immobilized lipase extracted from Candida Antarctica and dried under vacuum for 48 hours on phosphorus pentoxide before use. Polyethylene glycol monomethyl ether (mPEG-OH, M_n = 2.0 KDa) was dried via azeotropic distillation in anhydrous toluene (TOL). Anhydrous dichloromethane (CH_2Cl_2), benzyl alcohol (BnOH) and other organic reagents are purchased from Aladdin Chemical Reagents Company and used without further purification.

Analytical Techniques

Relative number-average molecular weight (M_n) and dispersity index ($Đ_M$) of all polymers were measured by Gel Permeation Chromatography (GPC) with a Waters 1515 equipped with *N,N*-dimethylformamide (DMF) as the eluent at a flow rate of 1.0 mL min^{-1} at 50 °C and polymethyl methacrylate (PMMA) as the standard. ^{1}H NMR , ^{13}C NMR and DOSY NMR were performed on a Bruker Avance 400 or 600 MHz spectrometer at room temperature using deuterated reagents ($CDCl_3$) as the solvent, and the data were analyzed with MestReNova software. The glass transition temperature (T_g) and the the melting point of polymers were obtained using TA Instruments DSC Q2000 Differential Scanning Calorimeter at a heating and cooling rate of 10 °C min^{-1} under nitrogen atmosphere.

The synthesis of macrocyclic carbonates

The representative process for the synthesis of macrocyclic carbonate: HMC: 1.00g (8.47 mmol) 1,6-Hexanediol and 2.72g (4.85 mmol) diphenyl carbonate were dissolved in 500 mL anhydrous toluene under argon atmosphere. Then, immobilized lipase CA (2.72 g, 100 wt.% relative to diphenyl carbonate) was added and the reaction was placed in an oil bath at 70 °C. After 12 h, lipase CA was filtered off and the reaction mixture was evaporated under reduced pressure. The residue was washed with cold diethyl ether (50

mL × 2) to obliterate the by-product and the unreacted starting materials to result in white powder. The powder was subsequently recrystallized with ethyl acetate to obtain pure carbonate dimer as white crystals (~40 % yield). Alternatively, this monomer could also be purified through flash column chromatography on silica using dichloromethane as eluent. The other macrocyclic carbonates were carried out according to the same procedure.

HMC (Macrocyclic Hexatamethylene Carbonate)

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.17, 1.70, 1.50

^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 155.40, 66.86, 28.43, 21.51

ESI: (m/z) M^+ Calculated for $C_{14}H_{24}O_6Na$, 311.1; Found, 311.1

TeMC (Macrocyclic Tetramethylene Carbonate)

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.22 1.88

^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 154.92, 67.39, 24.98

ESI: (m/z) M^+ Calculated for $C_{10}H_{16}O_6Na$, 255.1; Found, 255.1

PMC (Macrocyclic Pentamethylene Carbonate)

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.25 .1.68 1.48

^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 155.32, 67.87, 28.15, 25.94

ESI: (m/z) M^+ Calculated for $C_{12}H_{20}O_6Na$, 283.1; Found, 283.1

HeMC (Macrocyclic Heptamethylene Carbonate)

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.19 1.66 1.36

^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 155.38, 67.43, 28.63, 28.35, 25.43

ESI: (m/z): M^+ Calculated for $C_{16}H_{28}O_6Na$, 339.2; Found, 339.2

The ROP of macrocyclic carbonates using TBD/ alcohol/toluene system

All polymerizations were carried out under argon atmosphere in a Schlenk Line. A general polymerization procedure of HMC monomer was given as following: BnOH (40.0 μL, 0.02 mmol), HMC (117.0 mg, 0.4 mmol), TBD (2.8 mg, 0.02 mmol) and toluene (0.625 mL) were added into a 3 mL flask containing a stir bar at 70^{o}C. After a desired time depending on the experiment settings, the reaction was quenched by drops of small

amounts of acetic acid (~20 μL). 30 μL of solution was taken and dried for ^{1}H NMR characterization to determine the conversion and for GPC to determine the molecular weight and polydispersity ($Đ_M$), respectively.

Monomer conversion was determined by comparing the area integral of the triplet at 4.17 ppm corresponding to -COOC$\underline{H_2}$- (8*H*) of monomer with that of the triplet at 4.12 ppm corresponding to -COOC$\underline{H_2}$- (8*H*) of polymer. The molecular weight (M_n) and DP were obtained by comparing the peak integral ratio at 4.12 ppm of the repeat units of polymers and 5.16 ppm of the initiator BnOH (3.65 ppm of the initiator mPEG-OH). In addition, the reaction solution was then precipitated in cold diethyl ether and dried in vacuum. Transparent viscous products, named as PHMC (BnOH-PHMC), were obtained with a yield about 80 %. The PHMC with different degree of polymerization (DP) and macroinitiator were carried out according to the same procedure.

The polymerizations of other three monomers (TeMC, PMC, HeMC) were also carried out according to the same route.

Copolymerization of macrocyclic carbonate with TMC using TBD/BnOH system

General procedures for one-pot, two-step synthesis of PHMC-*b*-PTMC block copolycarbonate

A general polymerization procedure is given as following: BnOH (40.0 μL, 0.02 mmol), HMC (117.0 mg, 0.4 mmol), TBD (2.8 mg, 0.02 mmol) and toluene (0.625 mL) were added into a 3 mL flask containing a stir bar at 70^{o}C. After 12 h of the reaction, the reaction flask was cooled to room temperature and TMC (40.8 mg, 0.4 mmol) was added into flask under argon atmosphere for continue to stir for 2 h at the room temperature. The reaction was quenched by drops of small amounts of acetic acid (~20 μL), and 30 μL of solution was taken for ^{1}H NMR characterization to determine the conversion and for GPC to determine the molecular weight and polydispersity ($Đ_M$), respectively. Afterwards, the solution was precipitated into cold diethyl ether and dried in vacuum.

PPMC-*b*-PTMC and PHeMC-*b*-PTMC block copolycarbonates were prepared through the same synthetic routs.

One-pot one-step synthesis of PHMC-*co*-PTMC random copolycarbonate

A general polymerization procedure is given as following: BnOH (40.0 μL, 0.02 mmol), HMC (117.0 mg, 0.4 mmol), TMC (40.8 mg, 0.4 mmol), TBD (2.8 mg, 0.02 mmol) and toluene (0.625 mL) were added into a 3 mL flask containing a stir bar at 70°C. After 12 hours of reaction, the reaction was quenched by drops of small amounts of acetic acid (~20 μL), and 50 μL of solution was taken for ^{1}H NMR characterization to determine the conversion and for GPC to determine the molecular weight and polydispersity (ĐM), respectively. Afterwards, the solution was precipitated into cold diethyl ether and dried in vacuum.

The ^{1}H NMR and ^{13}C NMR spectra of four macrocyclic carbonates

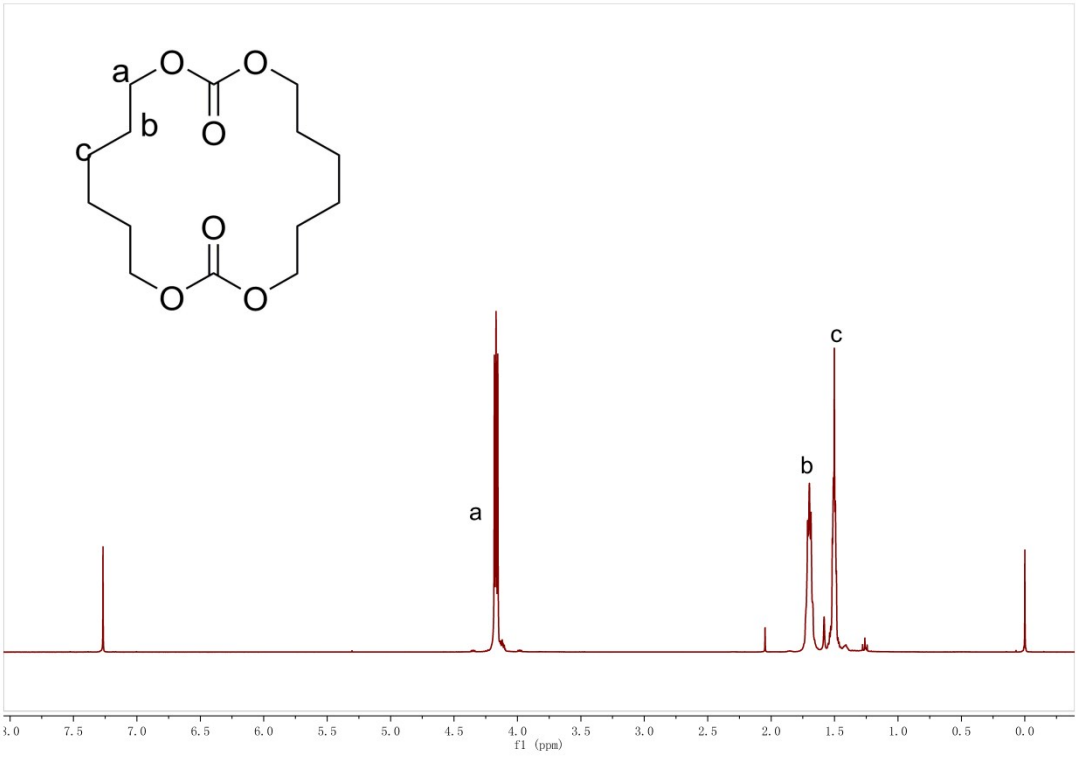

Fig. S1. The ^{1}H NMR spectrum of HMC monomer.

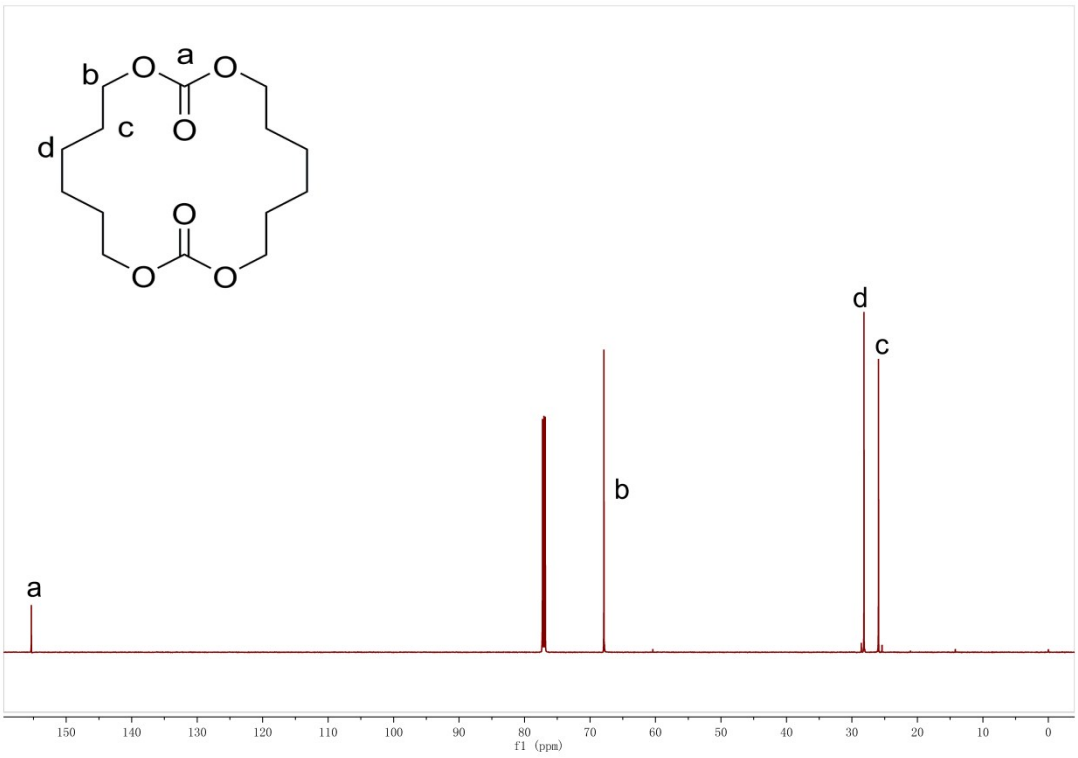

Fig. S2. The ^{13}C NMR spectrum of HMC monomer.

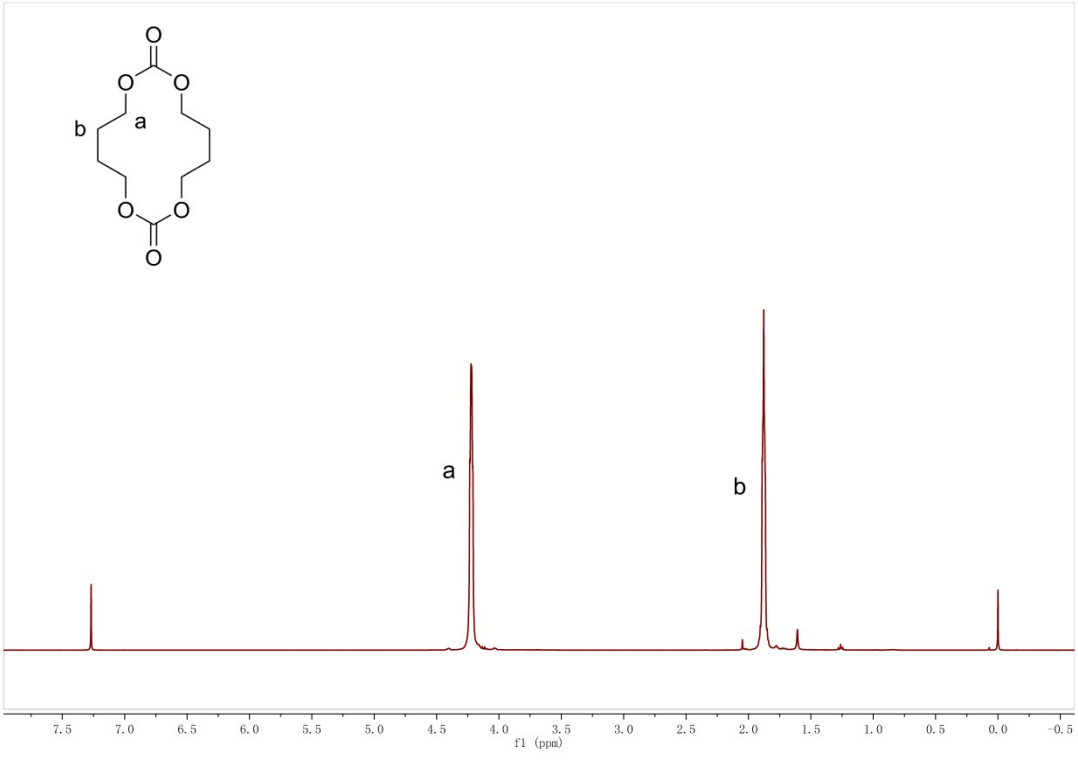

Fig. S3. The ^{1}H NMR spectrum of TeMC monomer.

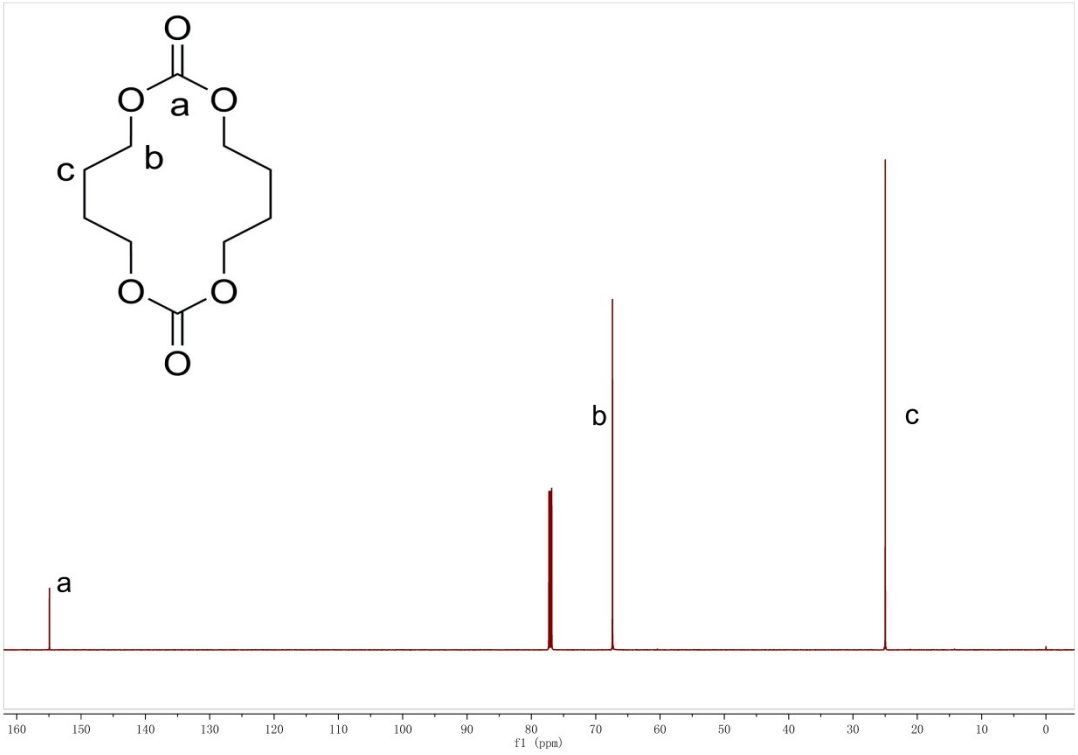

Fig. S4. The ^{13}C NMR spectrum of TeMC monomer.

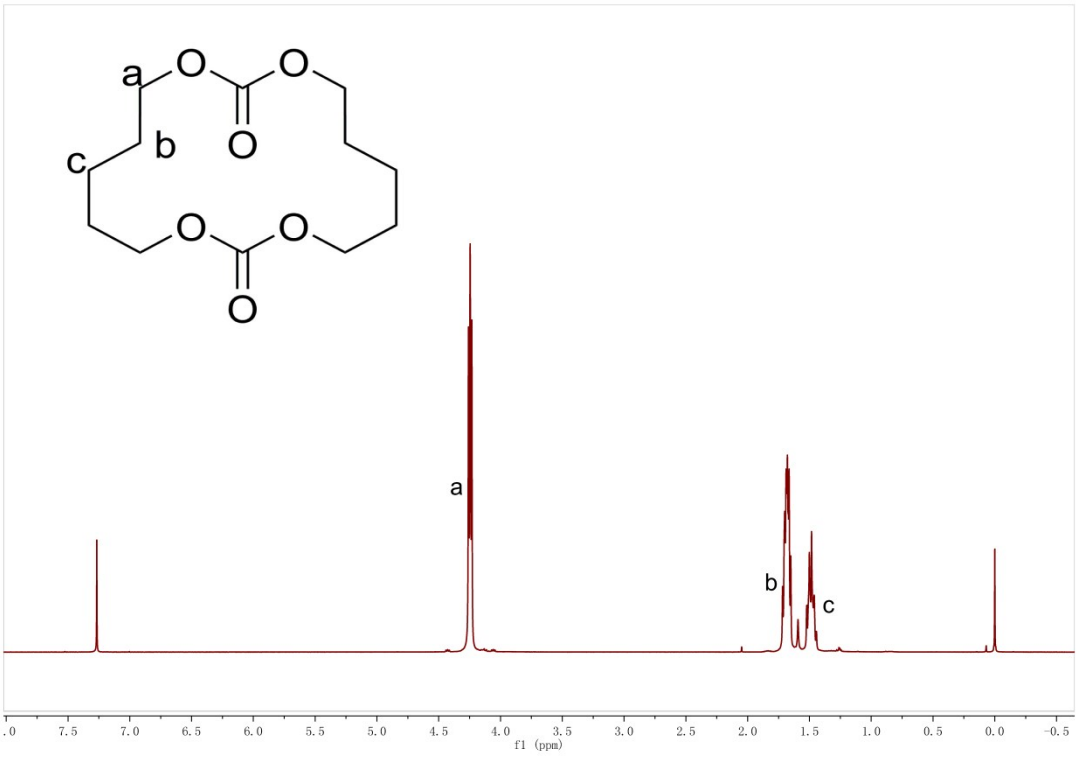

Fig. S5. The ^{1}H NMR spectrum of PMC monomer.

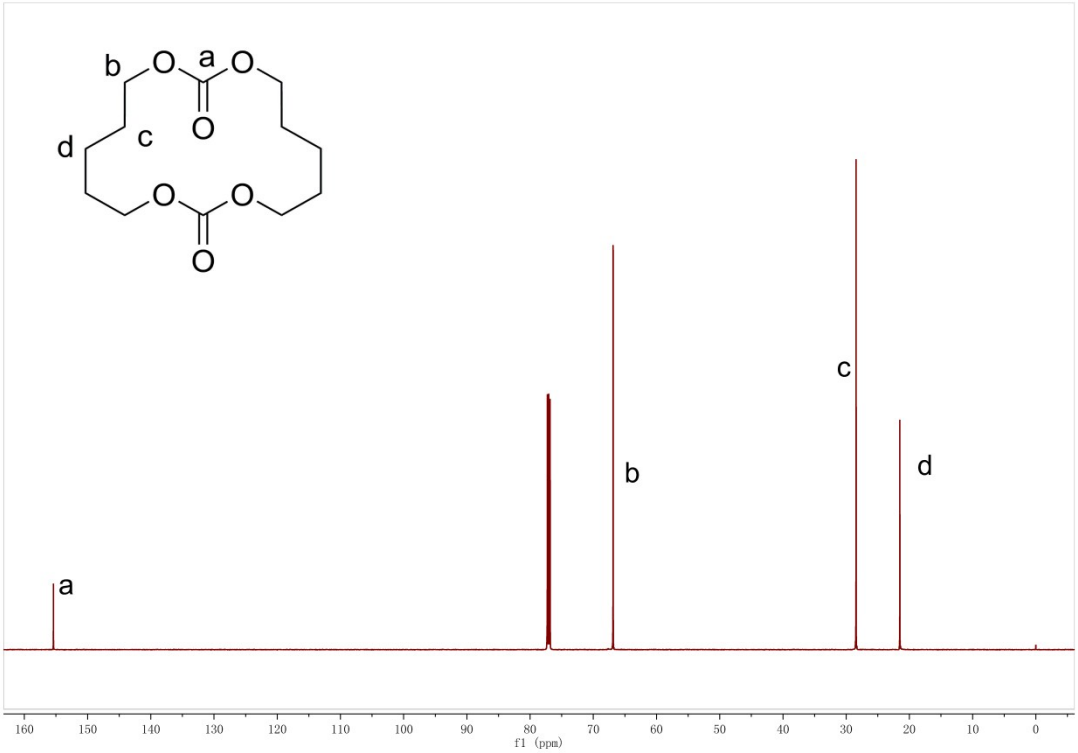

Fig. S6. The ^{13}C NMR spectrum of PMC monomer.

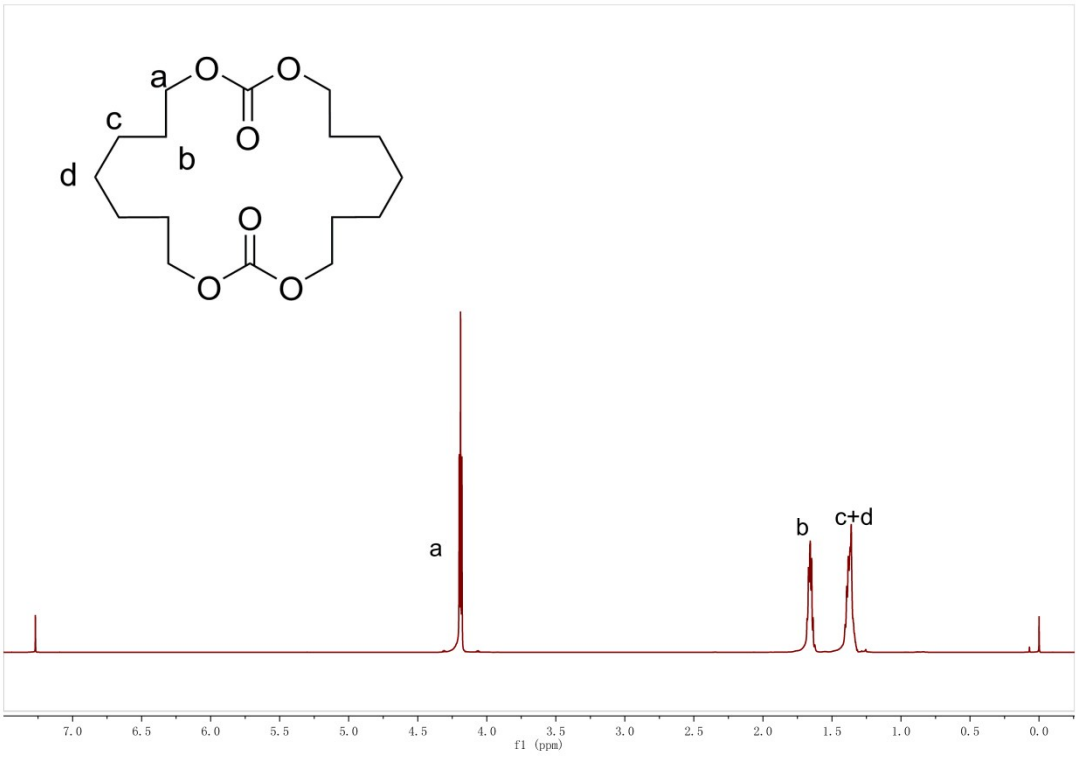

Fig. S7. The ^{1}H NMR spectrum of HeMC monomer.

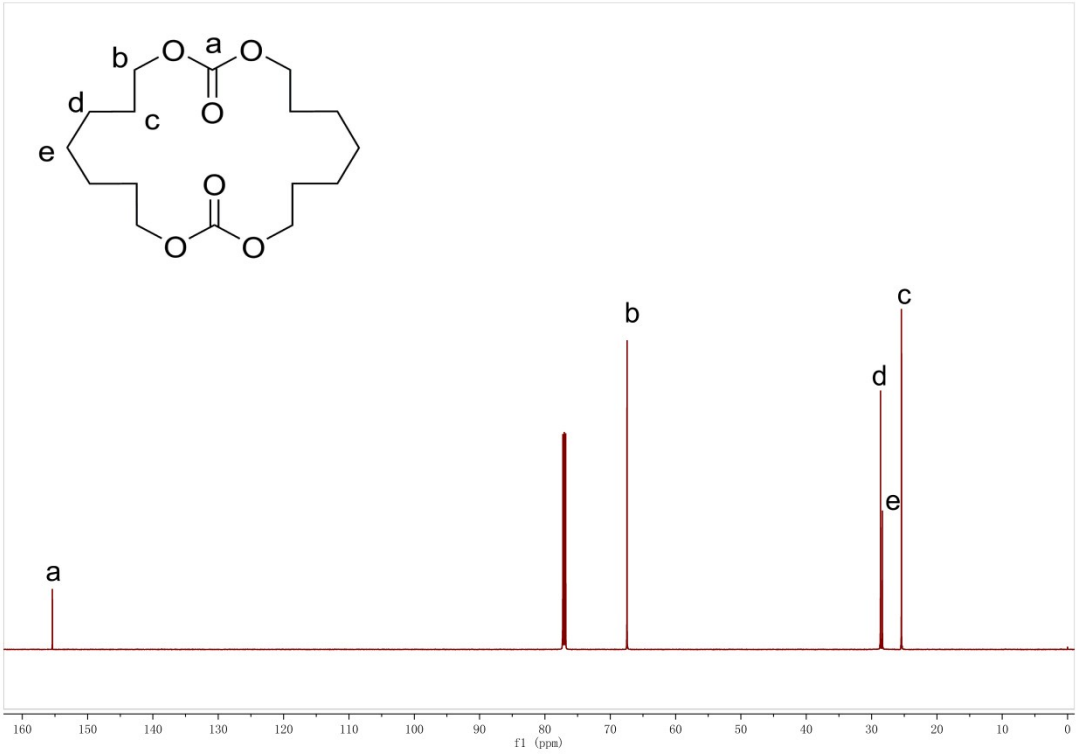

Fig. S8. The ^{13}C NMR spectrum of HeMC monomer.

Typical characterization of long chain polycarbonates (PHMC, PTeMC, PPMC and PHeMC).

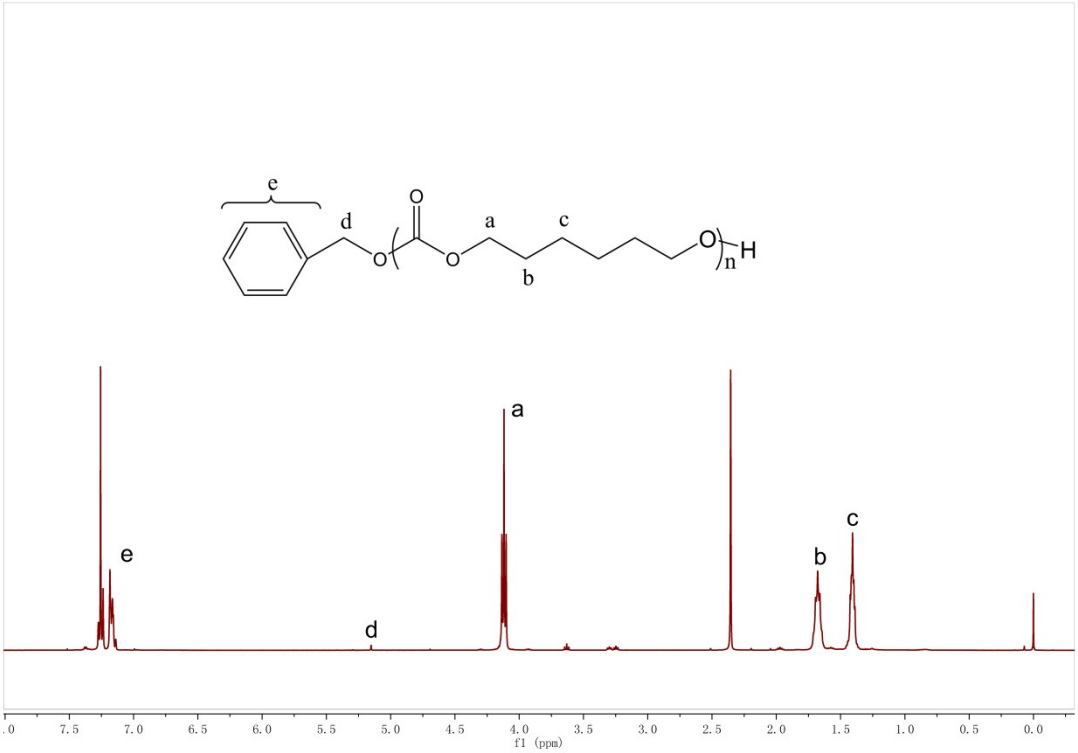

Fig. S9. The ^{1}H NMR spectrum of PHMC homopolymer.

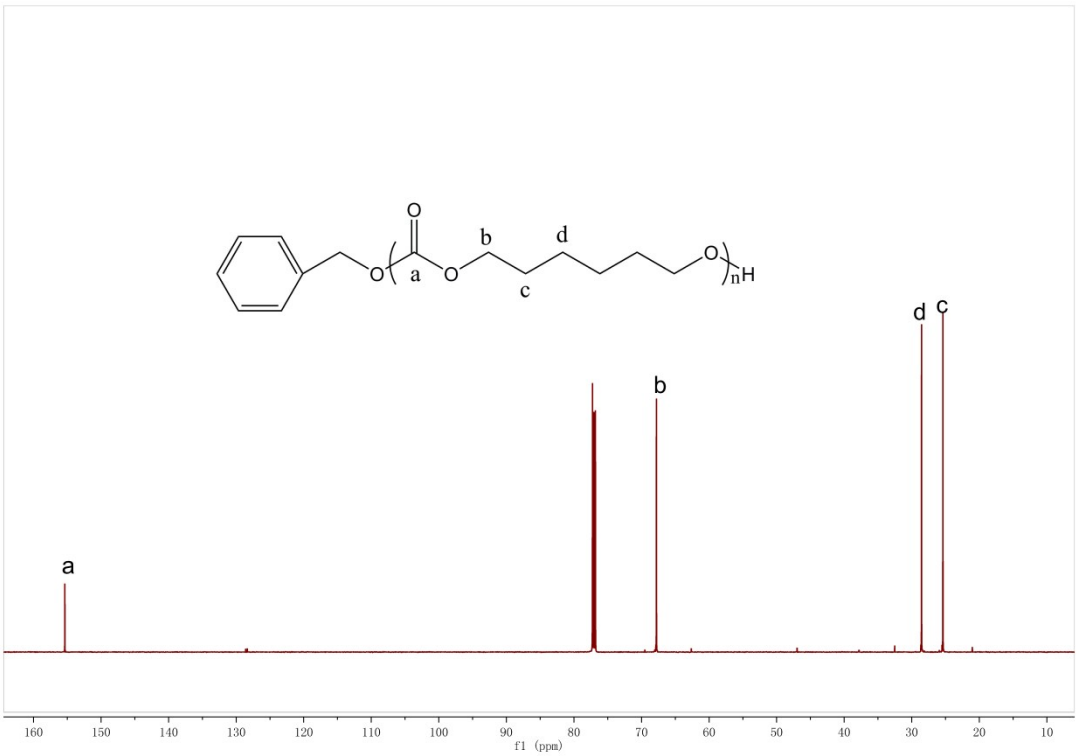

Fig. S10. The ^{13}C NMR spectrum of PHMC homopolymer.

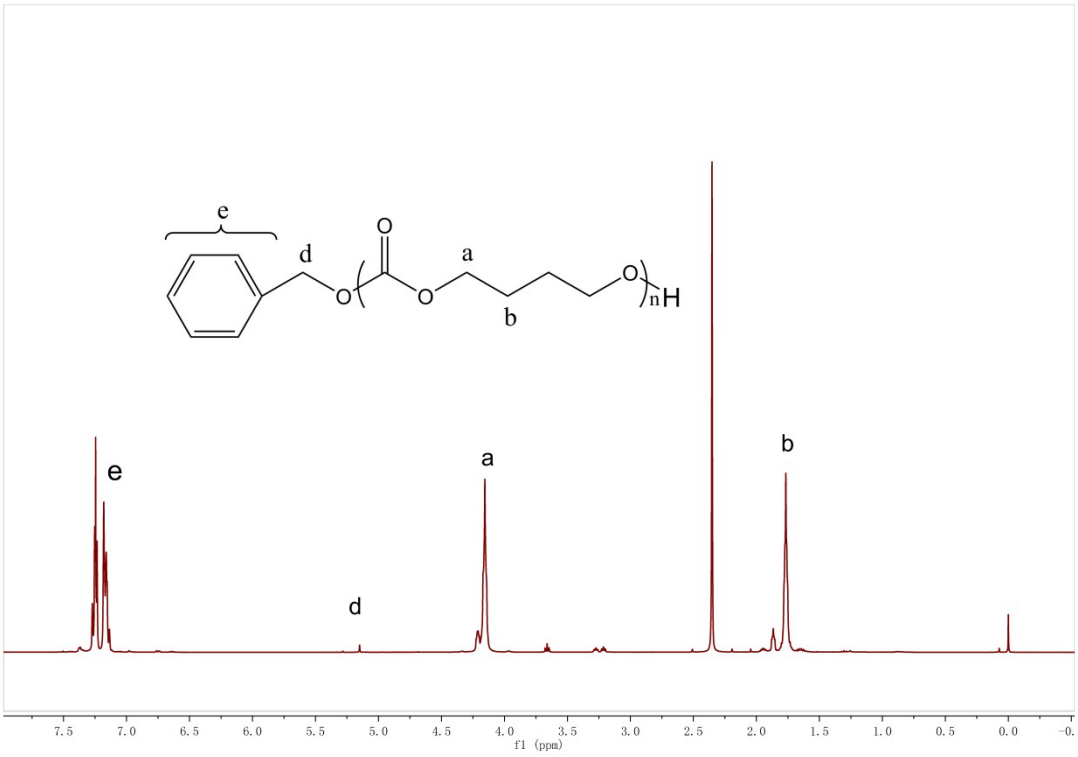

Fig. S11. The ^{1}H NMR spectrum of PTeMC homopolymer.

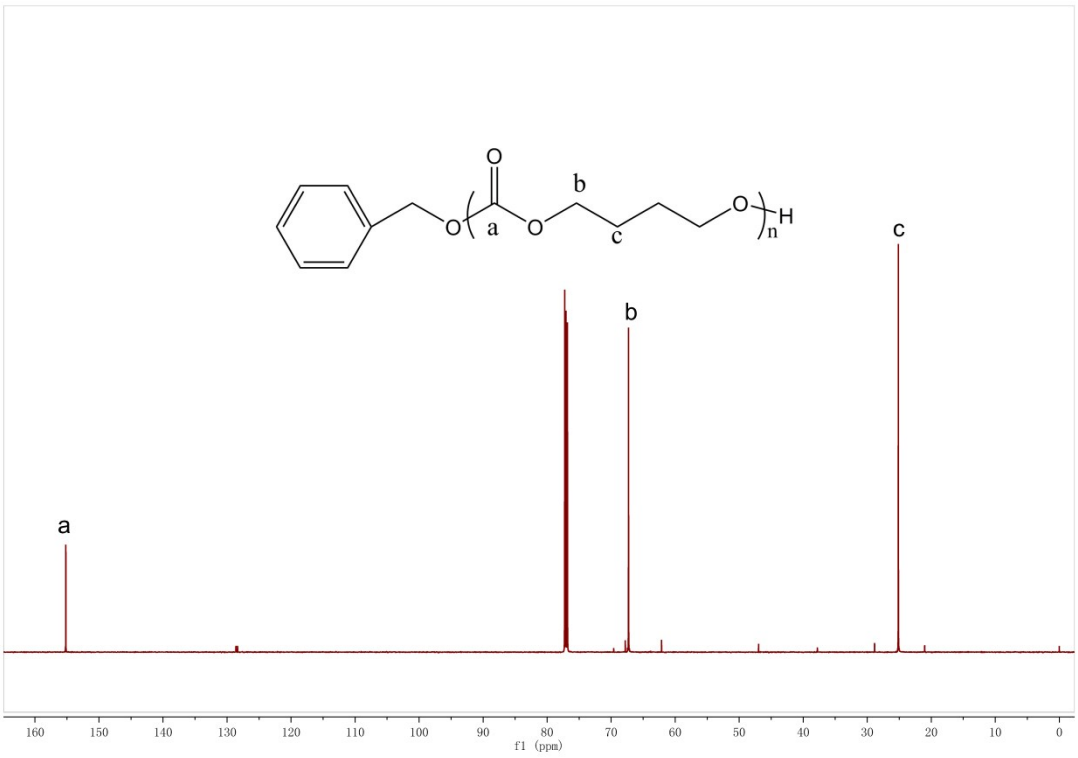

Fig. S12. The ^{13}C NMR spectrum of PTeMC homopolymer.

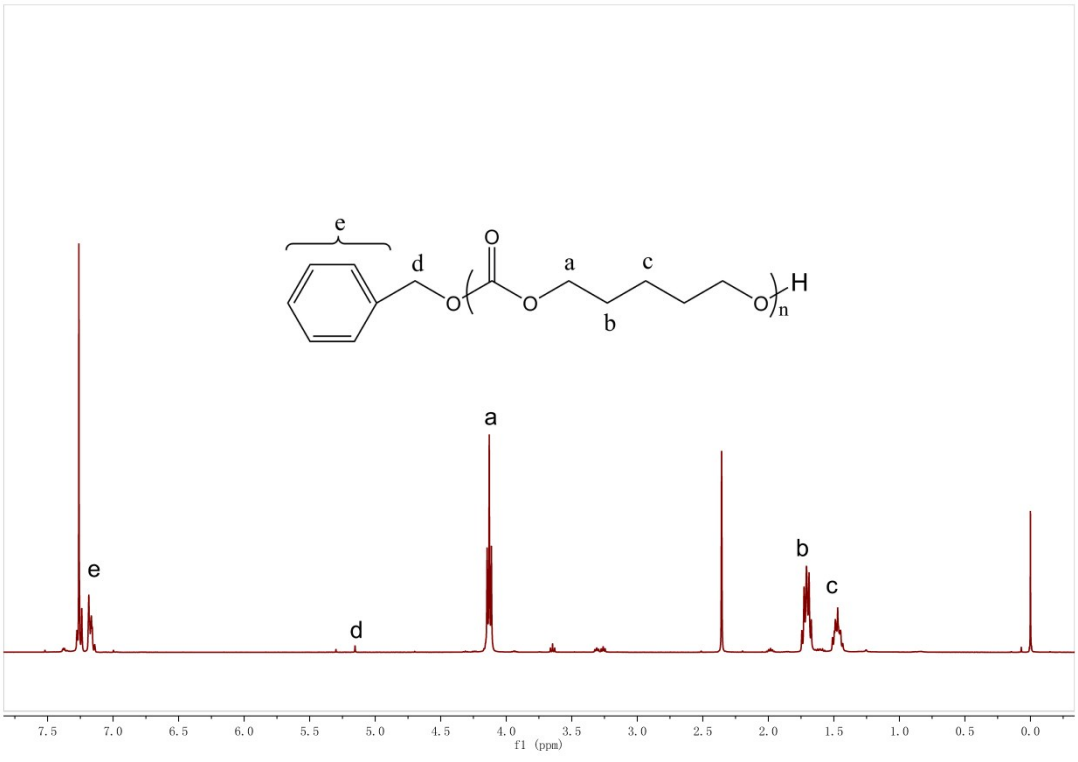

Fig. S13. The ^{1}H NMR spectrum of PPMC homopolymer.

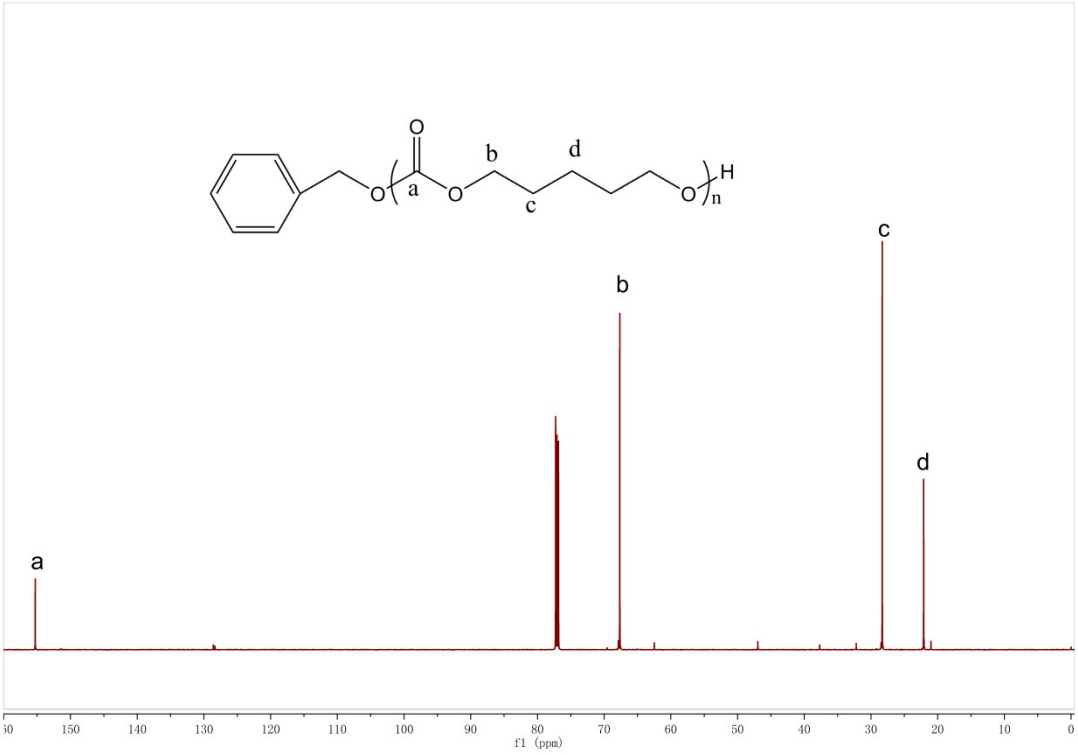

Fig. S14. The ^{13}C NMR spectrum of PPMC homopolymer.

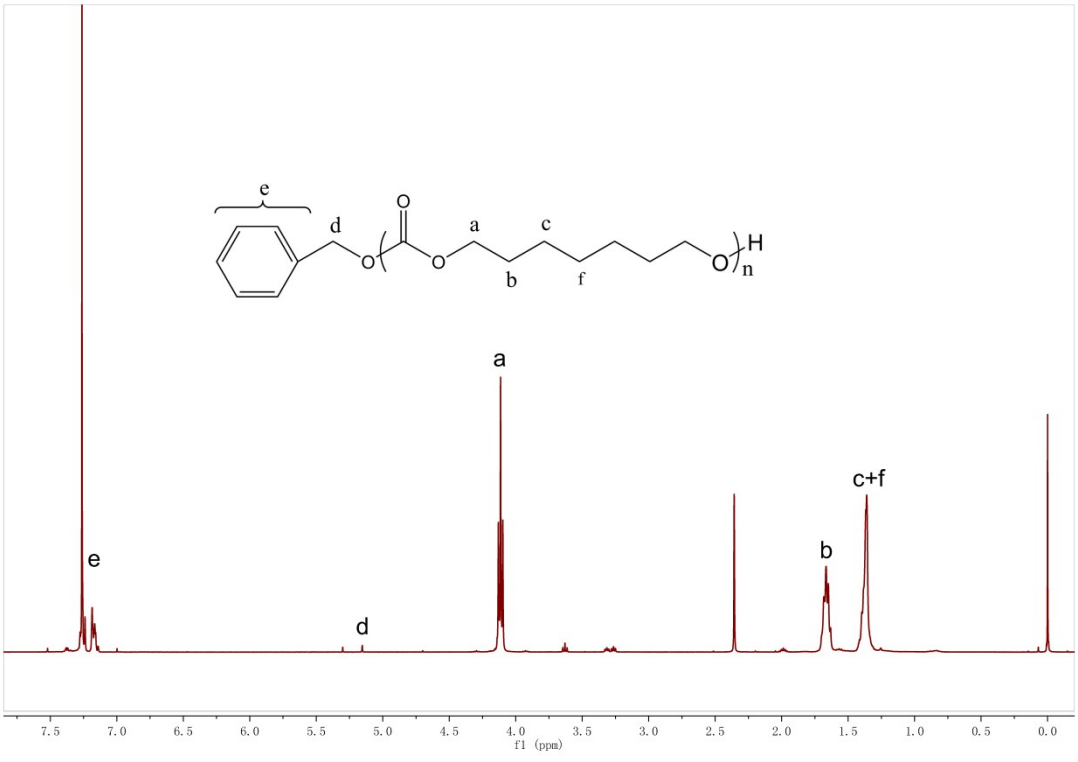

Fig. S15. The ^{1}H NMR spectrum of PHeMC homopolymer.

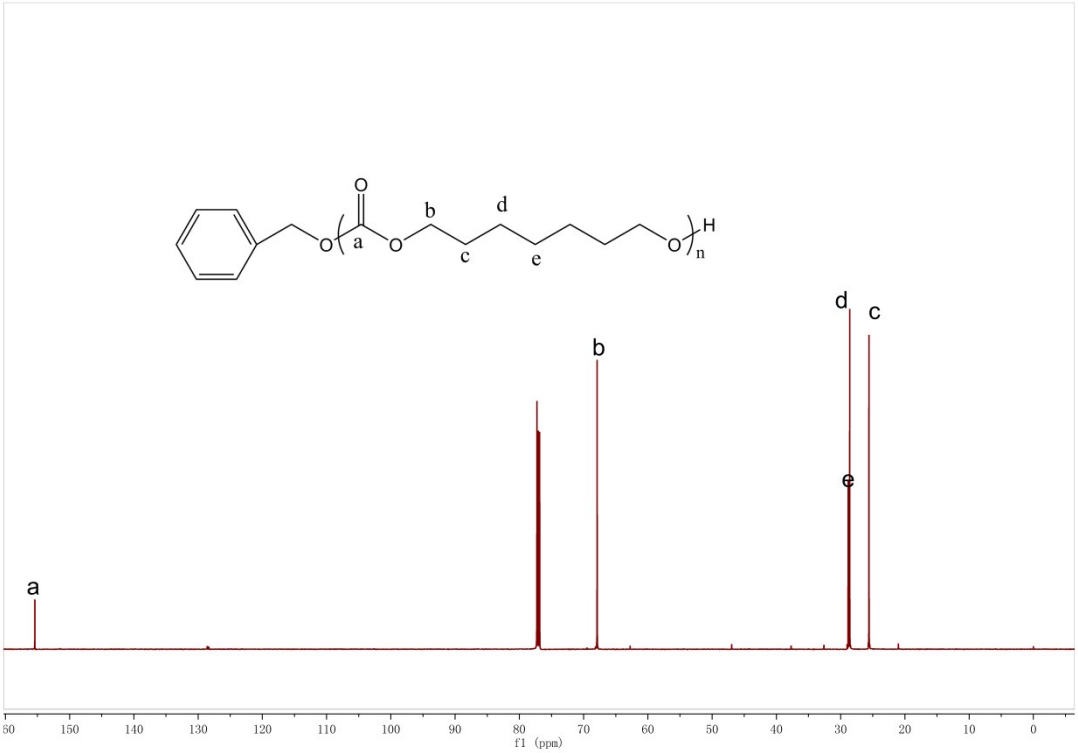

Fig. S16. The ^{13}C NMR spectrum of PHeMC homopolymer.

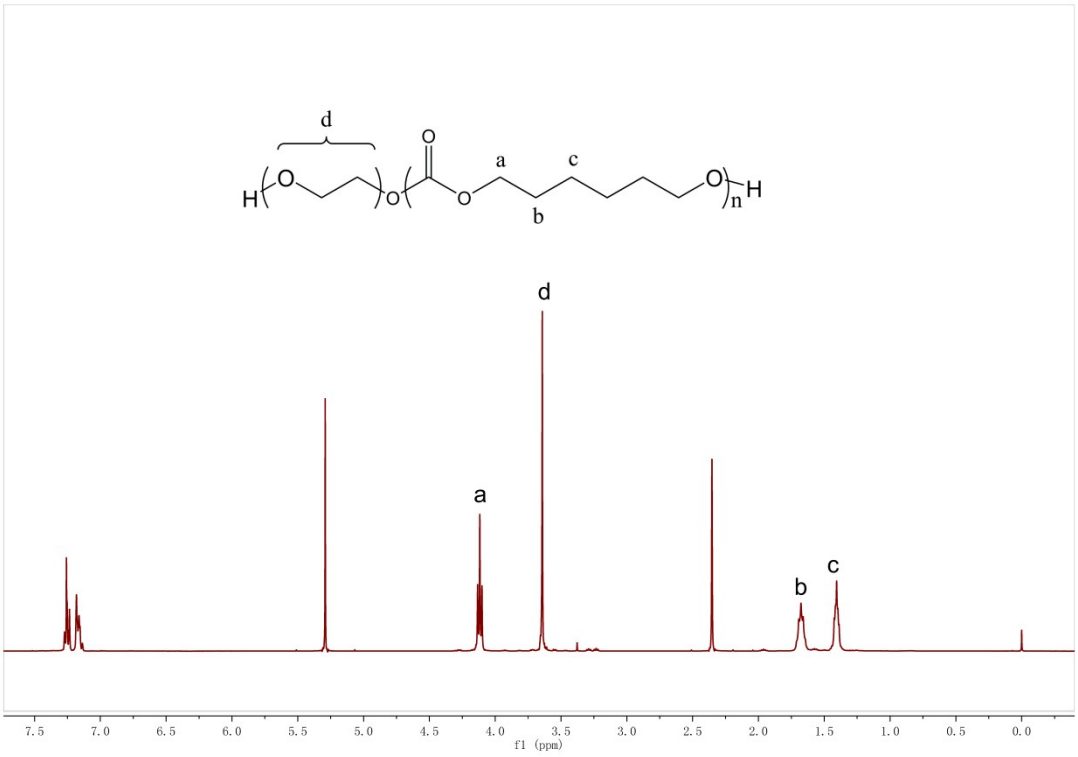

Fig. S17. The ^{1}H NMR spectrum of mPEG-*b*-PHMC.

Typical characterization of copolycarbonates

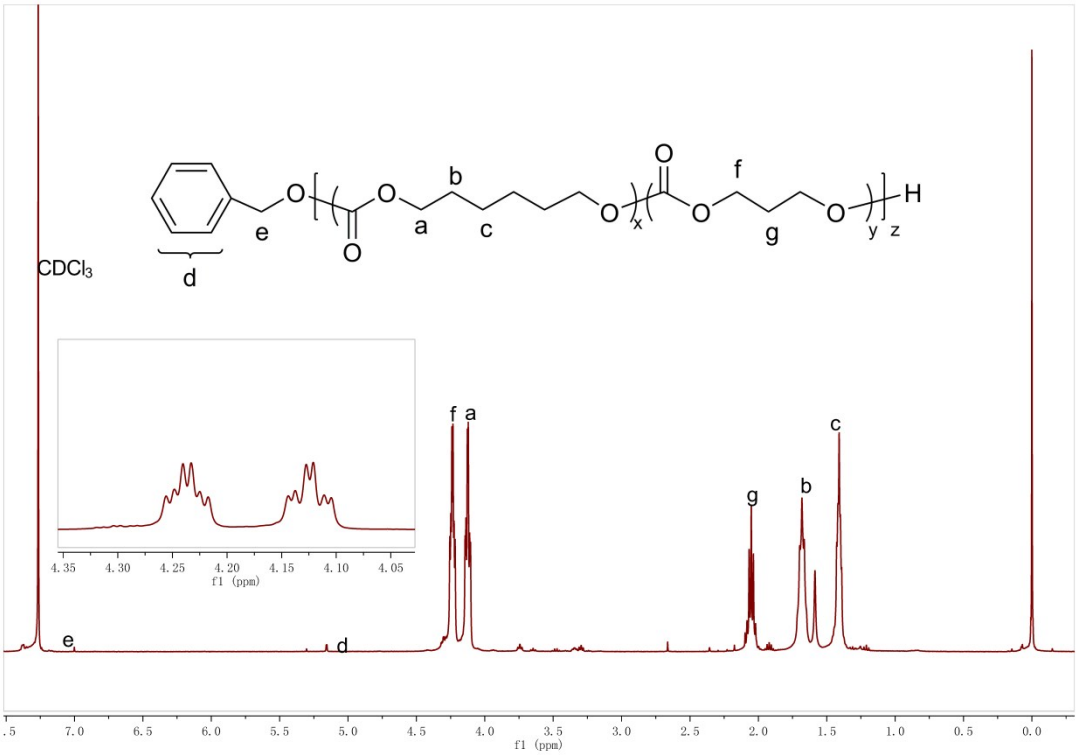

Fig S18. The ^{1}H NMR spectrum of $PHMC_{20}$-*co*-$PTMC_{40}$ random copolycarbonate.

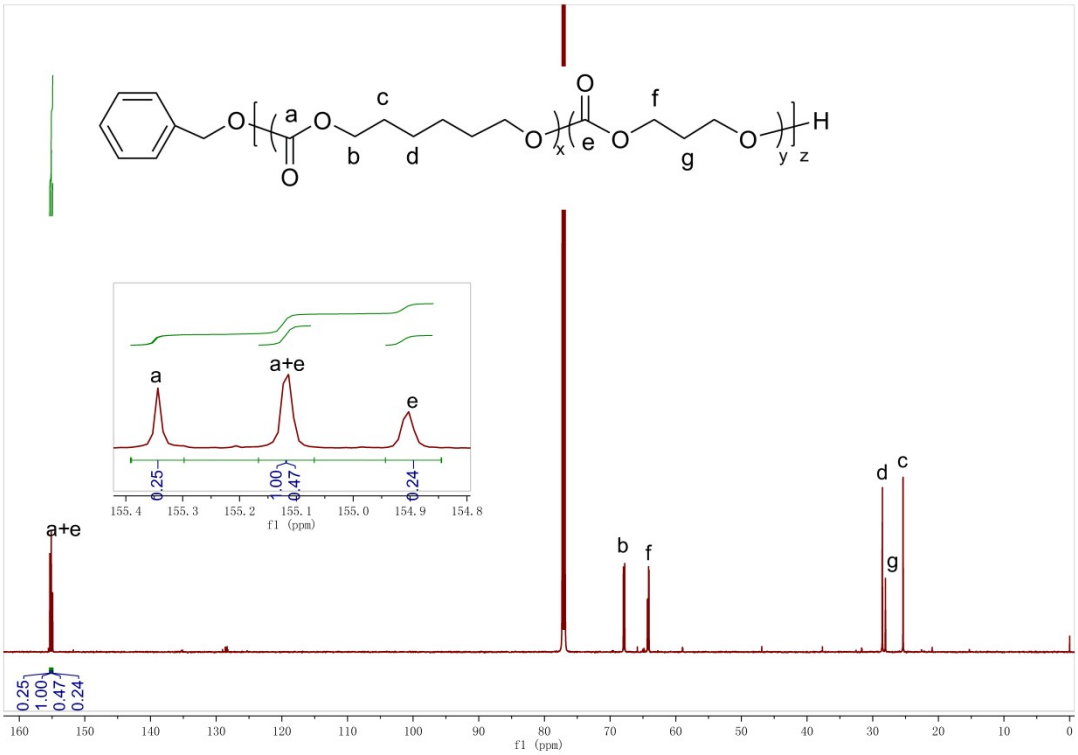

Fig S19. The quantitative ^{13}C NMR spectrum of $PHMC_{20}$-*co*-$PTMC_{40}$ (Table 2, entry 4).

Fig S20. The quantitative ^{13}C NMR spectrum of $PHMC_{20}$-*b*-$PTMC_{40}$ (Table 2, entry 1).

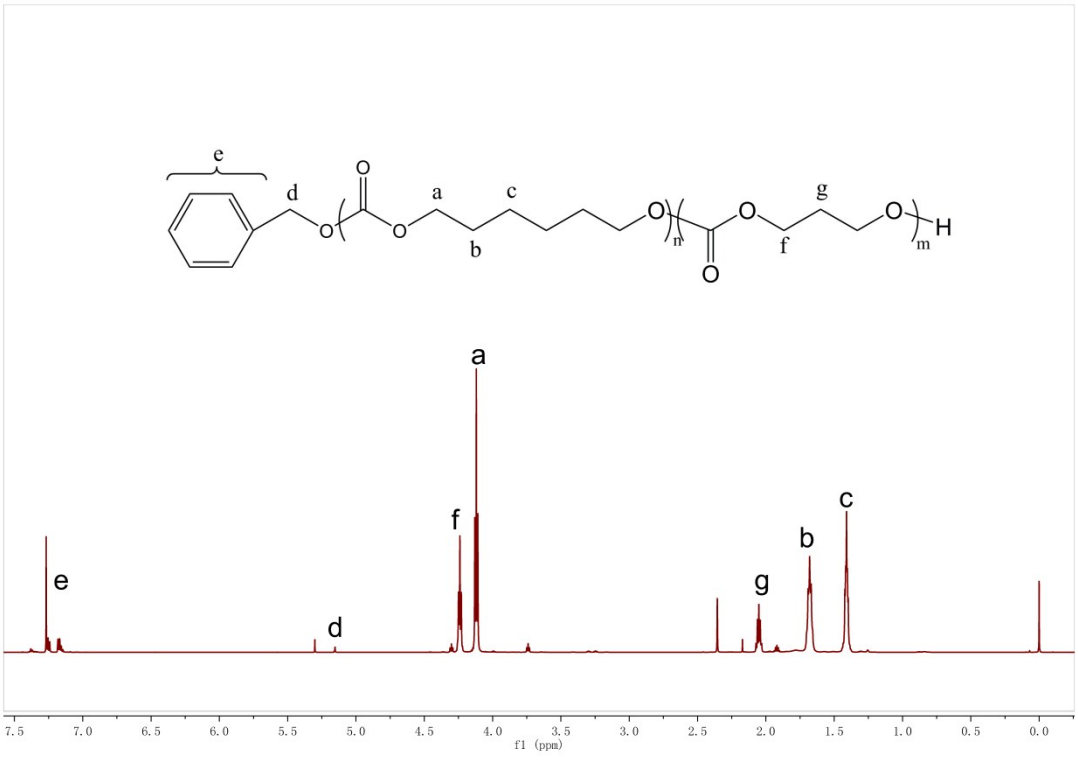

Fig. S21. The ^{1}H NMR spectrum of $PHMC_{20}$-*b*-$PTMC_{20}$ block copolycarbonate.

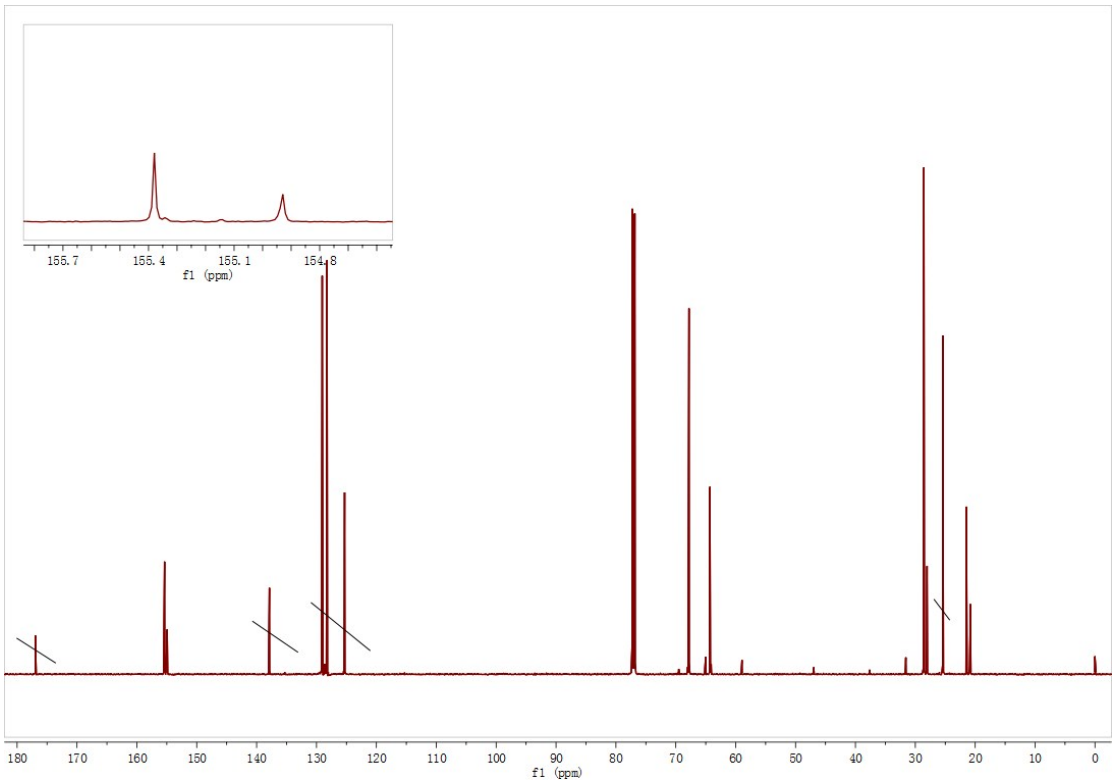

Fig. S22. The ^{13}C NMR spectrum of $PHMC_{20}$-*b*-$PTMC_{20}$ block copolycarbonate.

The inset picture is the enlargement of the characteristic peak of the carbonyl. 177 ppm is the peak of acetic acid peak; 140-120 ppm & 25 ppm are the peaks of toluene solvent.

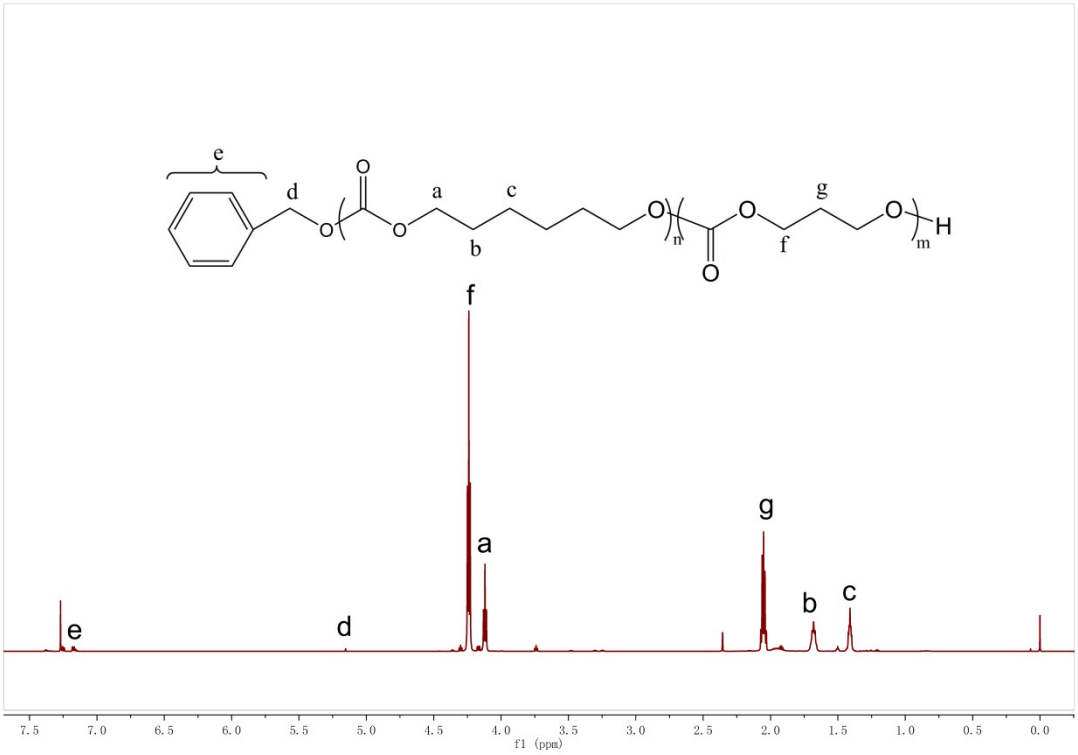

Fig. S23. The ^{1}H NMR spectrum of $PHMC_{20}$-*b*-$PTMC_{100}$ block copolycarbonate.

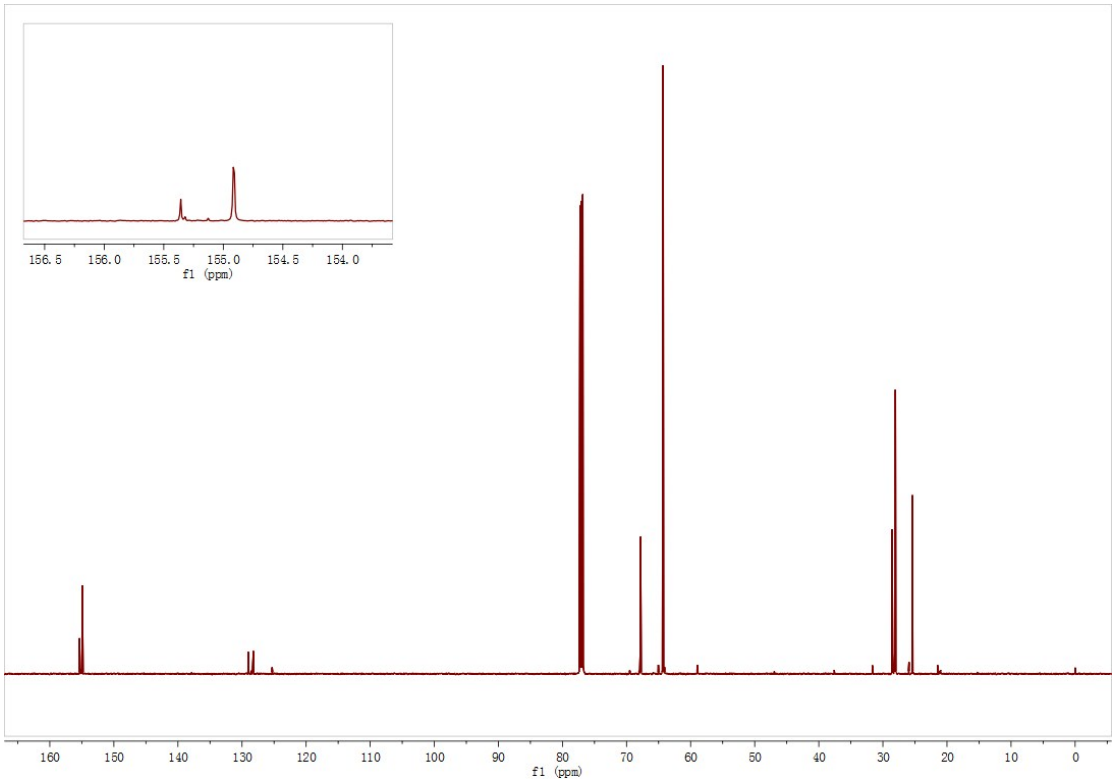

Fig. S24. The ^{13}C NMR spectrum of $PHMC_{20}$-*b*-$PTMC_{100}$ block copolycarbonate.

The inset picture is the enlargement of the characteristic peak of the carbonyl.

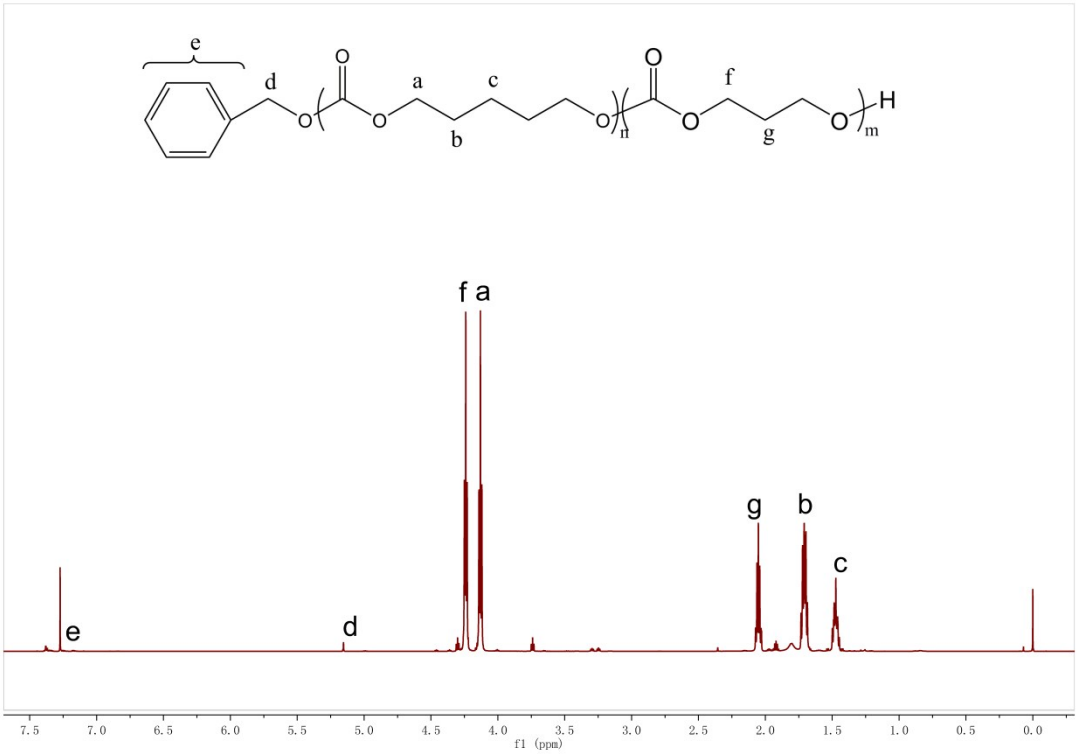

Fig. S25. The ^{1}H NMR spectrum of $PPMC_{20}$-*b*-$PTMC_{40}$ block copolycarbonate.

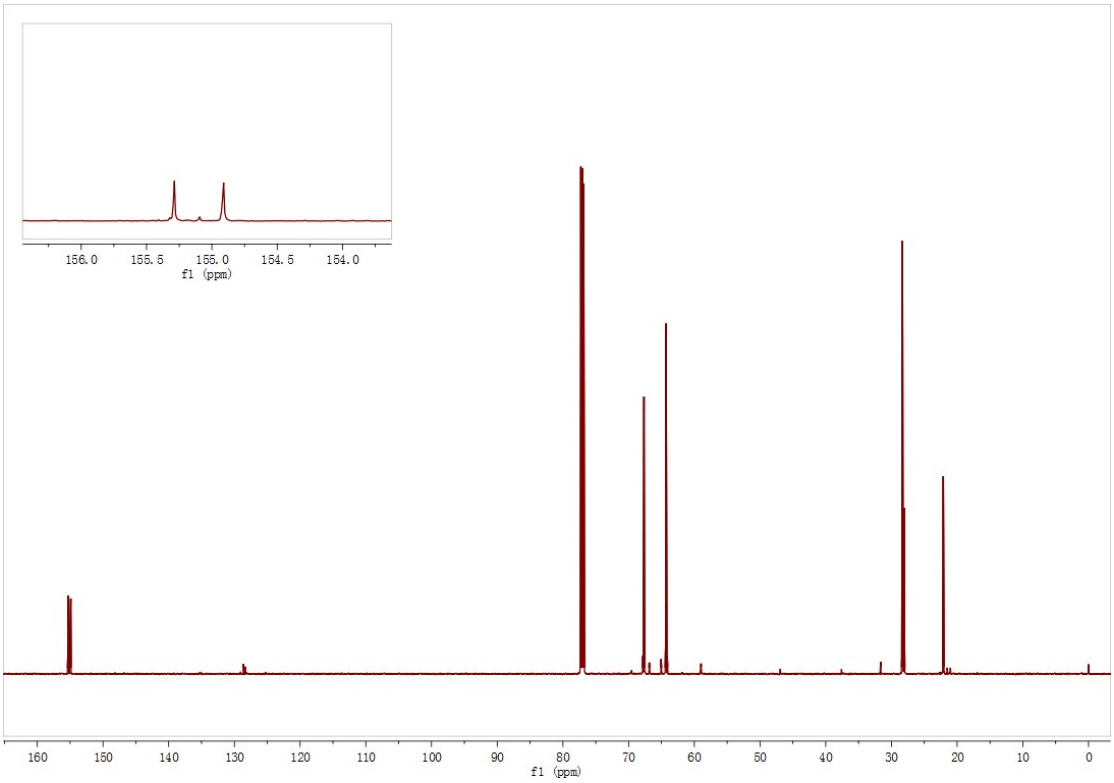

Fig. S26. The ^{13}C NMR spectrum of $PPMC_{20}$-*b*-$PTMC_{40}$ block copolycarbonate.

The inset picture is the enlargement of the characteristic peak of the carbonyl.

Fig. S27. The ^{1}H NMR spectrum of $PHeMC_{20}$-*b*-$PTMC_{40}$ block copolycarbonate.

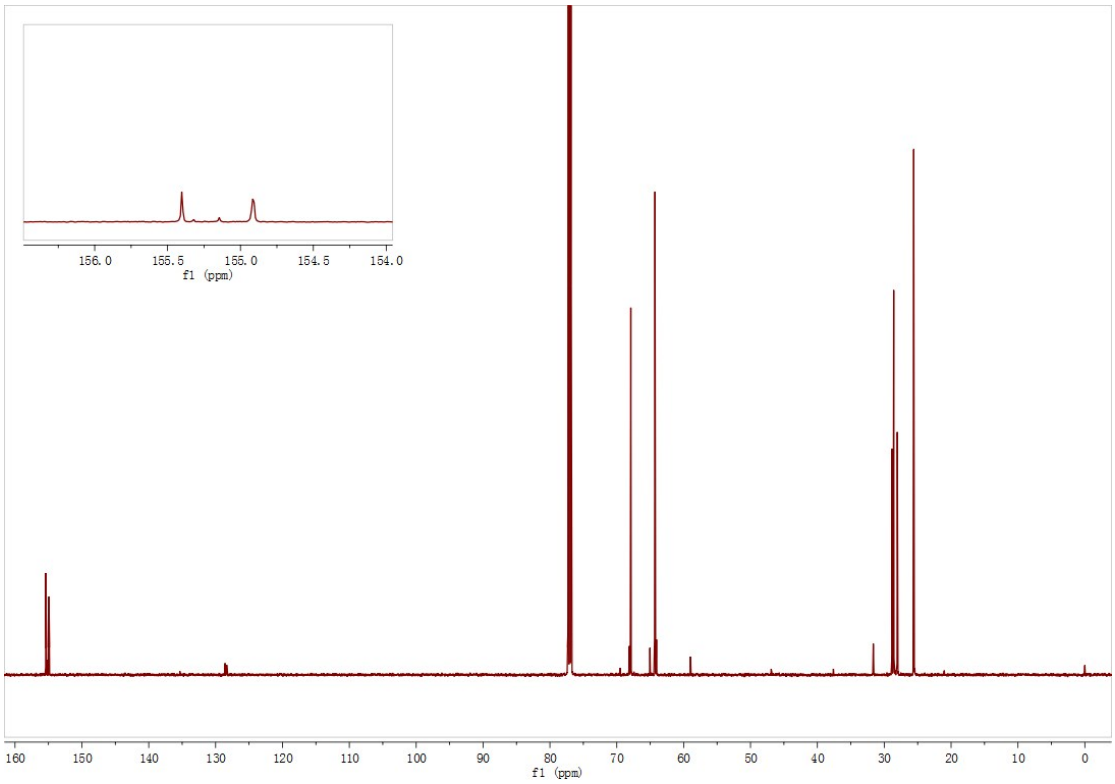

Fig. S28. The ^{13}C NMR spectrum of $PHeMC_{20}$-*b*-$PTMC_{40}$ block copolycarbonate. The inset picture is the enlargement of the characteristic peak of the carbonyl.

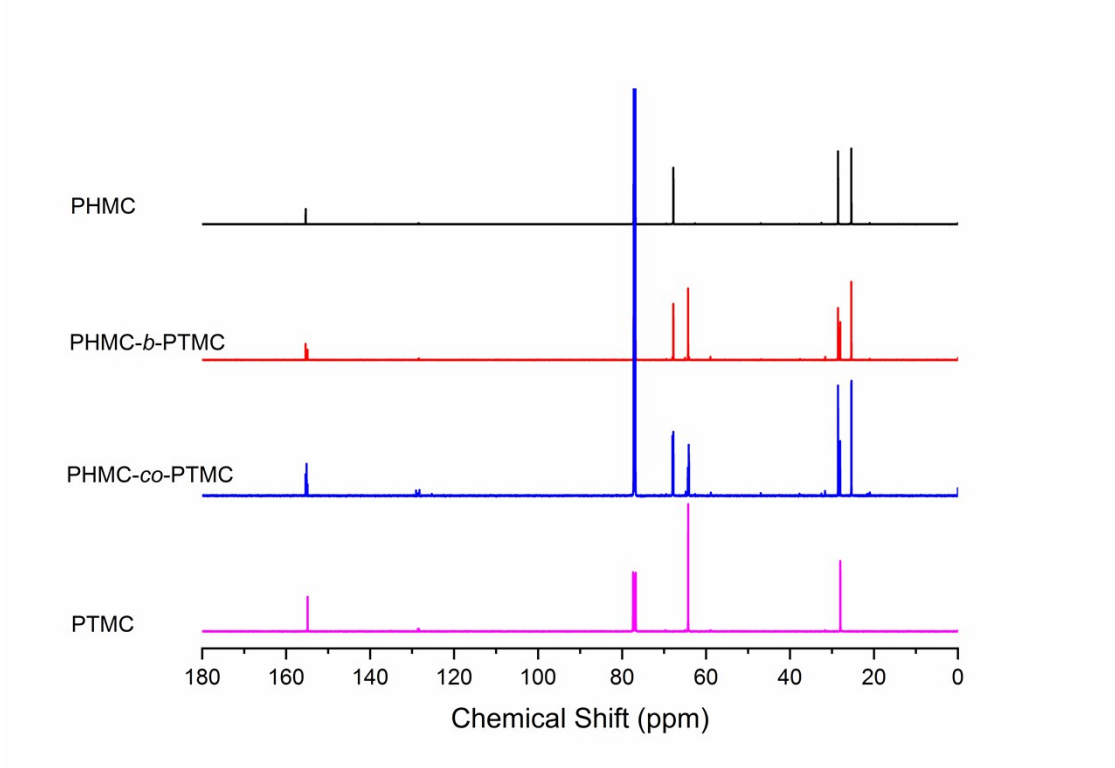

Fig. S29. The complete ^{13}C NMR of block copolycarbonate PHMC-*b*-PTMC (Table 2, entry 1) and random copolycarbonate PHMC-*co*-PTMC (Table 2, entry 4).

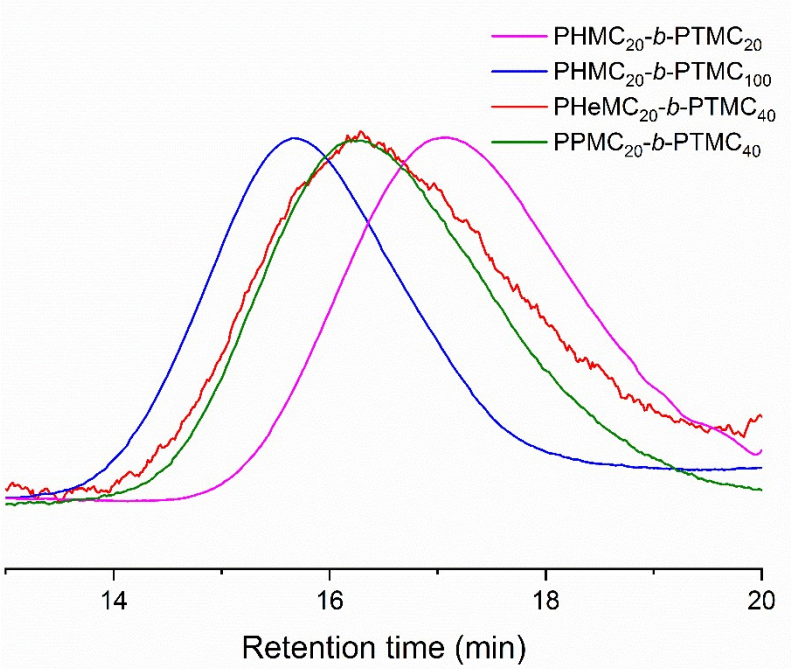

Fig. S30. The GPC traces of block aliphatic polycarbonates.

The complete ^{1}H NMR spectrum of homopolycarbonates and copolycarbonates

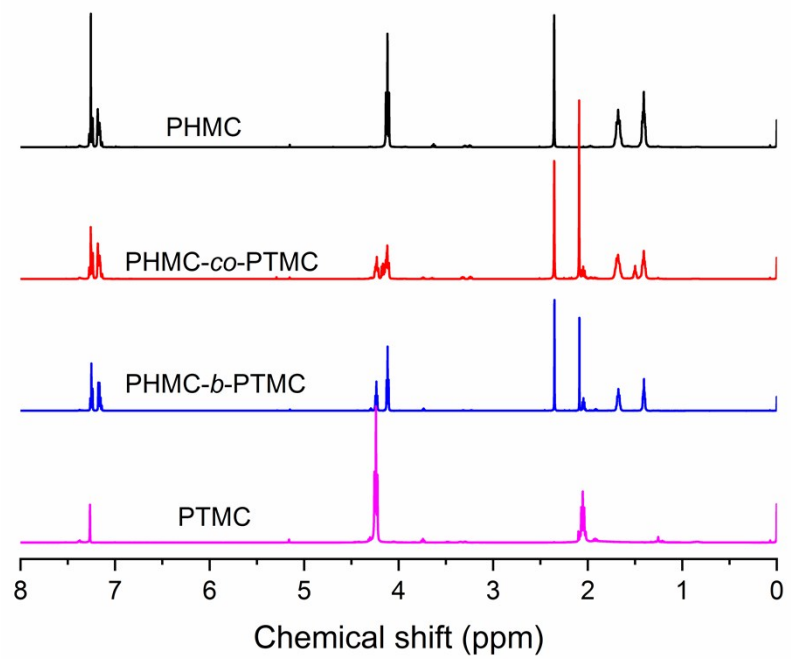

Fig. S31. The complete ^{1}H NMR spectrum of PTMC and PHMC homopolycarbonates and PHMC-*b*-PTMC and PHMC-*co*-PTMC copolycarbonates.

The transformation from block copolycarbonate into random copolycarbonate with the increase of reaction time

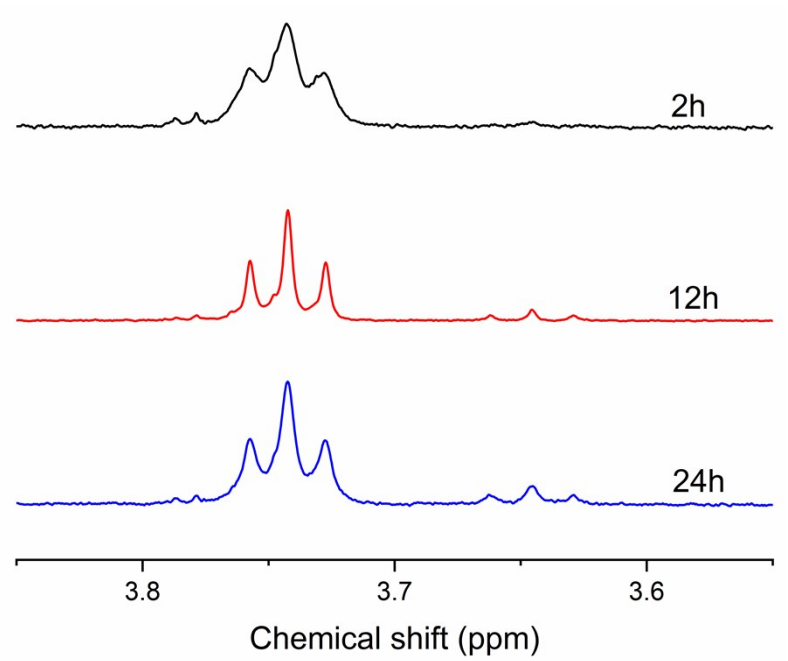

Fig. S32. Change of characteristic methylene peak belonging to the end of $PHMC_{20}$-*b*-$PTMC_{40}$ (-C*H*$_2$-OH) with the increase of reaction time in ^{1}H NMR spectra.

The DSC analysis of homopolycarbonates and block copolycarbonates

Table S1. T_m and T_g values of the polymers.

Sample	T_g (°C)	T_m (°C)
$PTMC_{20}$	-37.0	-
$PPMC_{20}$	-44.7	-
$PHMC_{20}$	-46.5	53.3
$PHeMC_{20}$	-47.1	49.6
$PPMC_{20}$-*b*-$PTMC_{20}$	-37.5	-
$PHMC_{20}$-*b*-$PTMC_{20}$	-36.2	49.7
$PHMC_{20}$-*co*-$PTMC_{20}$	-47.2	-
$PHeMC_{20}$-*b*-$PTMC_{20}$	-35.9	44.6

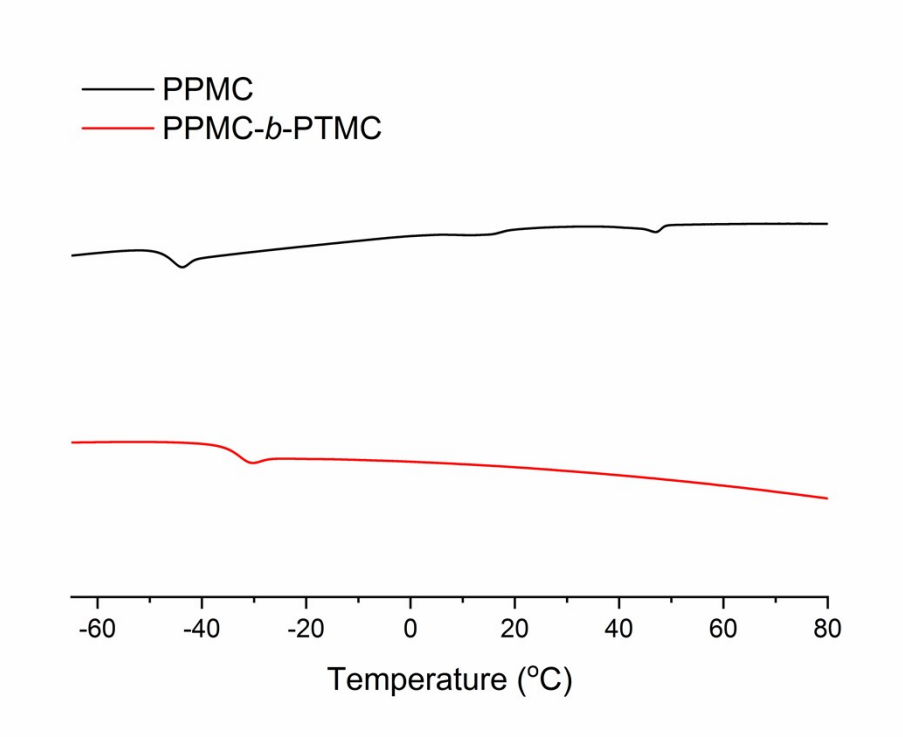

Fig. S33 DSC curves of homopolycarbonate PPMC (Table 1, entry 11) and block copolycarbonate $PPMC_{20}$-*b*-$PTMC_{40}$.

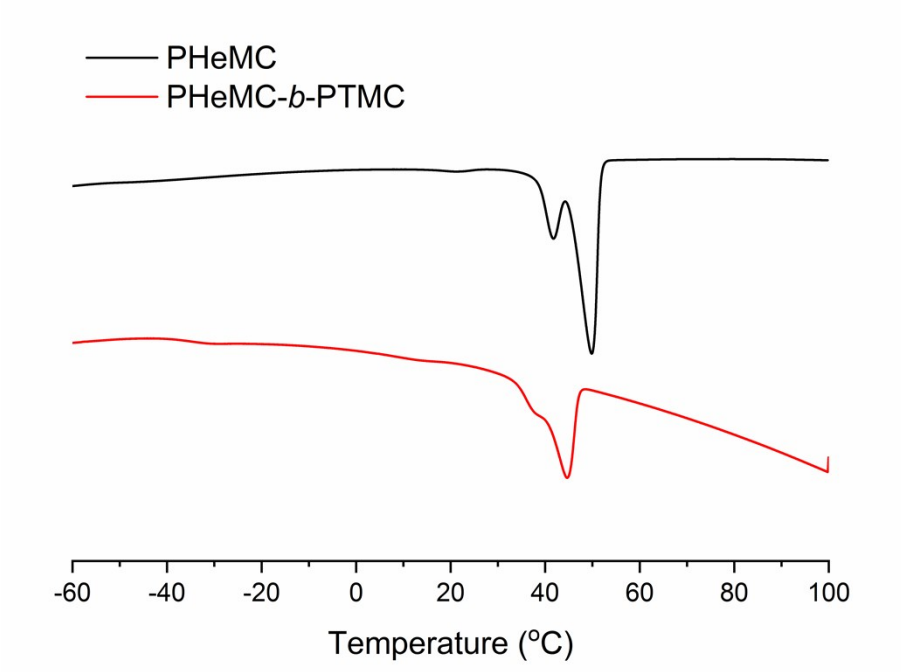

Fig. S34 DSC curves of homopolycarbonate $PHeMC_{20}$ (Table 1, entry 13) and block copolycarbonate $PHeMC_{20}$-*b*-$PTMC_{40}$.

The homopolycarbonate PPMC (Table 1, entry 11) is an amorphous polymer with no melting point and the T_g is about -44.7 °C, which is similar to the results in the literature.[1]

Because PTMC is amorphous and has no melting point, the block copolycarbonate PPMC-*b*-PTMC (Table 3, entry 4) does not have a melting point and T_g is about -37.5 ^oC. In correspondently, the T_g of homopolycarbonate PHeMC (Table 1, entry 13) is about -42.0 ^oC and the T_m is about 49.6 ^oC. The DSC curve of the block copolycarbonate PHeMC-*b*-PTMC (Table 3, entry 5) showed a T_g at -35.9 ^oC and a T_m at 44.6 ^oC, which further validating the structure of the block copolycarbonate.

Reference

1. W. Su, J. Feng, H.-F. Wang, X.-Z. Zhang and R.-X. Zhuo, *Polymer*, 2010, **51**, 1010-1015.