

Supplementary Information

Heterotellurium-containing macrocycle towards degradable tellurium-functionalized polymer

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Experimental Details

1 Materials

Polyethylene glycol monomethyl ether (mPEG, $M_n=2000$) was purified by azeotropic distillation with toluene and removing solvent under reduced pressure. 1,8-diazabicyclo(5.4.0) undec-7-ene (DBU) was purified by distillation from CaH_2 under high vacuum and stored with freshly activated 4A molecular sieves. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) was dried using a Schlenk line prior to use. Lipase CA Novozym-435 (from *Candida antarctica*) was vacuum dried over phosphorous pentoxide (P_2O_5) for 48 h before use. Diphenyl carbonate (DPC) was purchased from Shanghai Dibai Biotechnology Company. All other chemicals were used as received without further purification.

2 Methods

Synthesis of dialkyl telluride

Sodium borohydride (11.8 g, 0.40 mol) was dissolved in deionized water. Then, Te powder (5.0 g, 0.04 mol) was added to react for one hour, followed adding trimethylene bromohydrin (10.9 g, 0.08 mol) in THF under Ar flow. The system was stirred at 50 °C for 6 h and then was extracted with dichloromethane (3×200 mL). The organic layers were combined, dried, and concentrated for column chromatography with a mixture of CH_2Cl_2 and ethyl acetate as eluent. The product was obtained as light yellow liquid with a yield of about 80%. The di(1-hydroxybutylene) telluride and di(1-hydroxyamylene) telluride were carried out according to the same procedure.

di(1-hydroxyethylene) telluride

^1H NMR (400 MHz, CDCl_3 , δ , ppm): 3.88 (t, $J=6.0$ Hz, 4H), 2.87 (t, $J=6.0$ Hz, 4H).

^{13}C NMR (600 MHz, CDCl_3 , δ , ppm): 63.46, 7.74.

^{125}Te NMR (600 MHz, CDCl_3 , δ , ppm): 96.91.

di(1-hydroxypropylene) telluride

^1H NMR (400 MHz, CDCl_3 , δ , ppm): 3.71 (t, $J=6.0$ Hz, 4H), 2.73 (t, $J=6.0$ Hz, 4H),
2.02 (t, $J=6.0$ Hz, 4H).

^{13}C NMR (600 MHz, CDCl_3 , δ , ppm): 65.76, 36.56, 0.51.

^{125}Te NMR (600 MHz, CDCl_3 , δ , ppm): 232.70.

di(1-hydroxybutylene) telluride

^1H NMR (400 MHz, CDCl_3 , δ , ppm): 3.68 (t, $J=6.0$ Hz, 4H), 2.67 (t, $J=6.0$ Hz, 4H),
1.85 (t, $J=6.0$ Hz, 4H), 1.67 (t, $J=6.0$ Hz, 4H).

^{13}C NMR (600 MHz, CDCl_3 , δ , ppm): 62.04, 34.91, 28.49, 2.31.

^{125}Te NMR (600 MHz, CDCl_3 , δ , ppm): 241.38.

di(1-hydroxyamylene) telluride

^1H NMR (400 MHz, CDCl_3 , δ , ppm): 3.65 (t, $J=6.0$ Hz, 4H), 2.64 (t, $J=6.0$ Hz, 4H),
1.78 (t, $J=6.0$ Hz, 4H), 1.60 (t, $J=6.0$ Hz, 4H), 1.45 (t, $J=6.0$ Hz, 4H).

^{13}C NMR (600 MHz, CDCl_3 , δ , ppm): 62.71, 32.02, 31.98, 28.14, 2.63.

^{125}Te NMR (600 MHz, CDCl_3 , δ , ppm): 235.30.

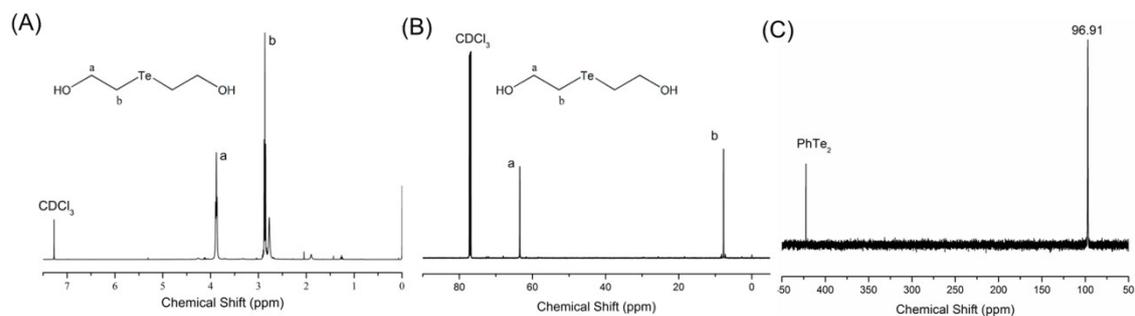


Fig S1 ^1H NMR, ^{13}C NMR and ^{125}Te NMR of di(1-hydroxyethylene) telluride

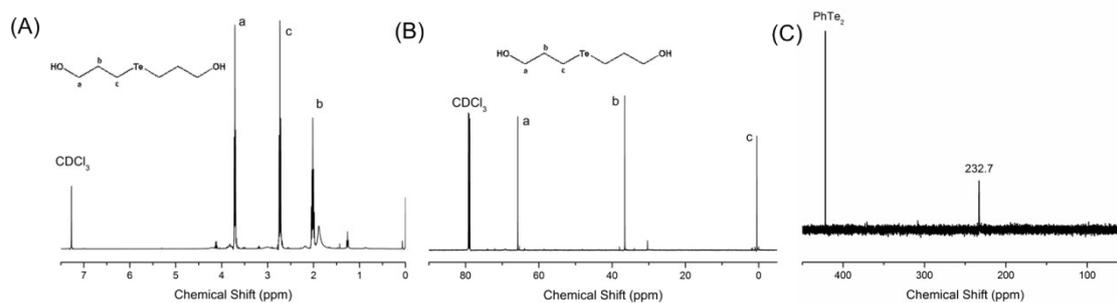


Fig S2 ^1H NMR, ^{13}C NMR and ^{125}Te NMR of di(1-hydroxypropylene) telluride

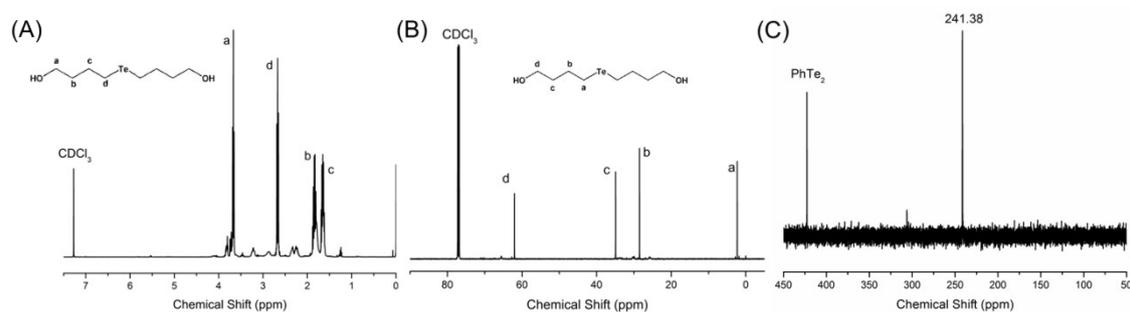


Fig S3 ^1H NMR, ^{13}C NMR and ^{125}Te NMR of di(1-hydroxybutylene) telluride

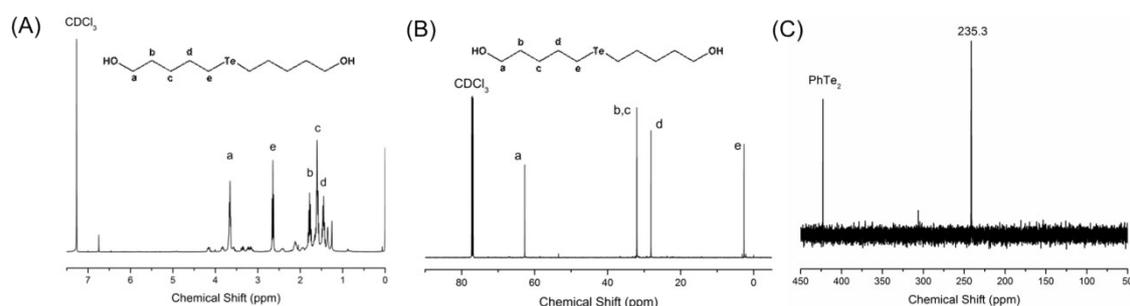
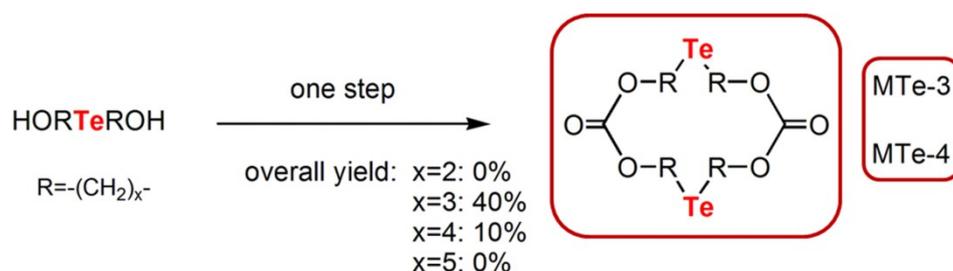


Fig S4 ^1H NMR, ^{13}C NMR and ^{125}Te NMR of di(1-hydroxyamylene) telluride

Synthesis of monomers

Di(1-hydroxypropylene) telluride (1.2 g, 4.89 mmol) and diphenyl carbonate (1.6 g, 7.48 mmol) were dissolved in dried toluene under Ar flow. Afterwards, dried lipase CA (1.6 g) was added rapidly and the system was stirred at 70 °C for about 8 h. After the reaction, lipase CA was removed by filtration and the solvent was evaporated under reduced pressure. The crude reaction mixture was firstly washed with cold diethyl ether

to clear away by-products and a few of oligomers. Finally, the monomer MTe-3 was purified by flash column chromatography using a mixture of CH₂Cl₂ and petroleum ether (PE) as eluent (~40% yield). The monomer MTe-4 was carried out according to the same procedure and the yield of MTe-4 was only 10%. The catalytic mechanism of Novozym 435 is that the ester group of DPC is ruptured by the hydroxyl group of enzyme, which results in the formation of an enzyme-activated inter-mediate (EAI). This EAI is then attacked by telluride diols through a nucleophilic addition followed by a half of cyclic carbonates in a dilute solution, then the synthesis of product tend to form a ring oligomer which is the complete macrocyclic carbonate monomer.



Scheme S1 The synthesis of macrocyclic carbonates with different ring sizes.

Tellurium-Containing Cyclic Carbonate Dimer

MTe-3

¹H NMR (400 MHz, CDCl₃, δ, ppm): 4.21 (t, J=6.3 Hz, 8H), 2.73 (t, J=6.3 Hz, 8H), 2.10 (t, J=6.3 Hz, 8H).

¹³C NMR (600 MHz, CDCl₃, δ, ppm): 156.87, 70.52, 32.99, 1.57.

¹²⁵Te NMR(600 MHz, CDCl₃, δ, ppm): 246.2.

FT-IR (ν, cm⁻¹): 1740.32 (C=O), 1261.77 (C-Te).

LRMS (EI, m/z): M+ Calculated for C₁₄H₂₄O₆Te₂, 543.5; Found, 544.0.

T_m=39.30 °C (DSC). ΔH=37.92J/g.

$T_d=282.7\text{ }^\circ\text{C}$ (TG).

MTe-4

^1H NMR (400 MHz, CDCl_3 , δ , ppm): 4.38 (t, $J=6.3$ Hz, 8H), 2.70 (t, $J=6.3$ Hz, 8H), 1.88 (t, $J=6.3$ Hz, 8H), 1.86 (t, $J=6.3$ Hz, 8H).

^{13}C NMR (600 MHz, CDCl_3 , δ , ppm): 156.92, 68.50, 31.10, 29.45, 2.95.

^{125}Te NMR(600 MHz, CDCl_3 , δ , ppm): 228.07.

FT-IR (ν , cm^{-1}): 1744.03 (C=O), 1246.17 (C-Te).

LRMS (EI, m/z): M^+ Calculated for $\text{C}_{18}\text{H}_{32}\text{O}_6\text{Te}_2$, 599.2; Found, 600.0.

$T_m=14.86\text{ }^\circ\text{C}$ (DSC). $\Delta H=1.87\text{ J/g}$.

$T_d=251.0\text{ }^\circ\text{C}$ (TG).

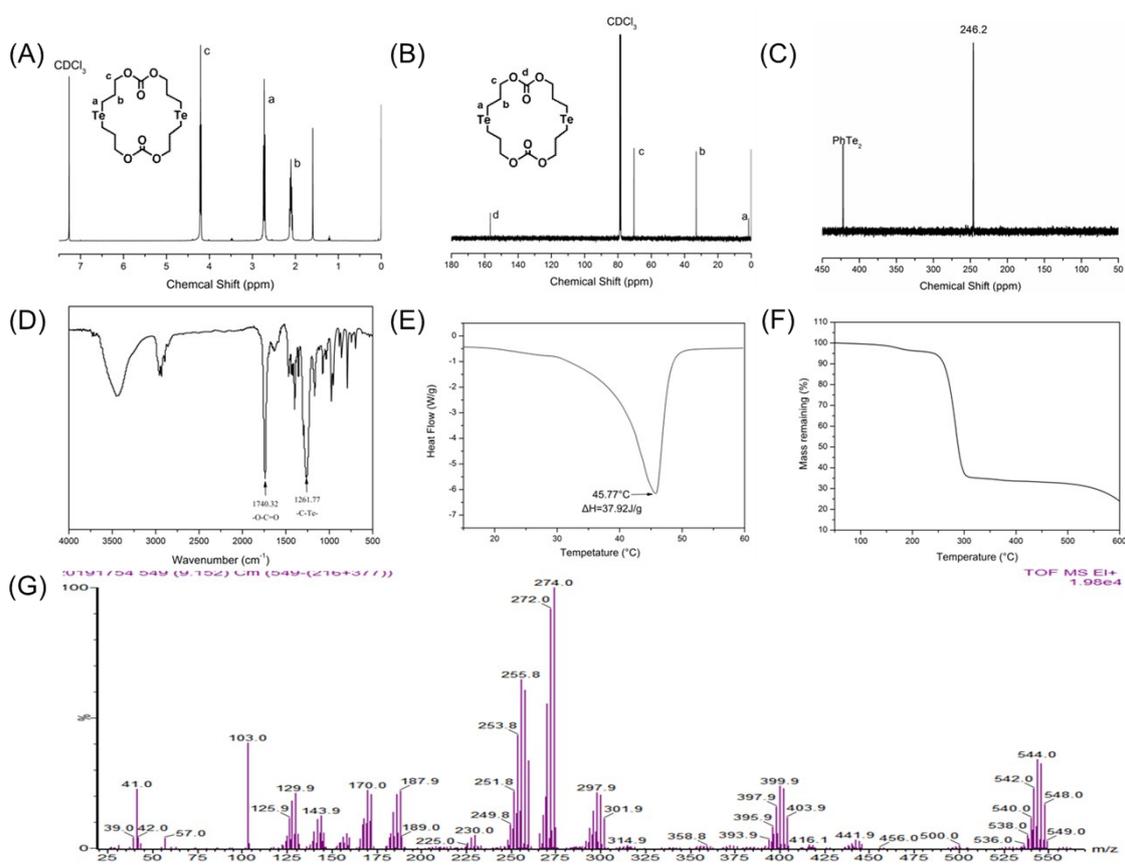


Fig S5 Characterization of MTe-3: (A) ^1H NMR; (B) ^{13}C NMR; (C) ^{125}Te NMR; (D) FT-IR; (E)

DSC; (F) TGA; (G) EI-MS.

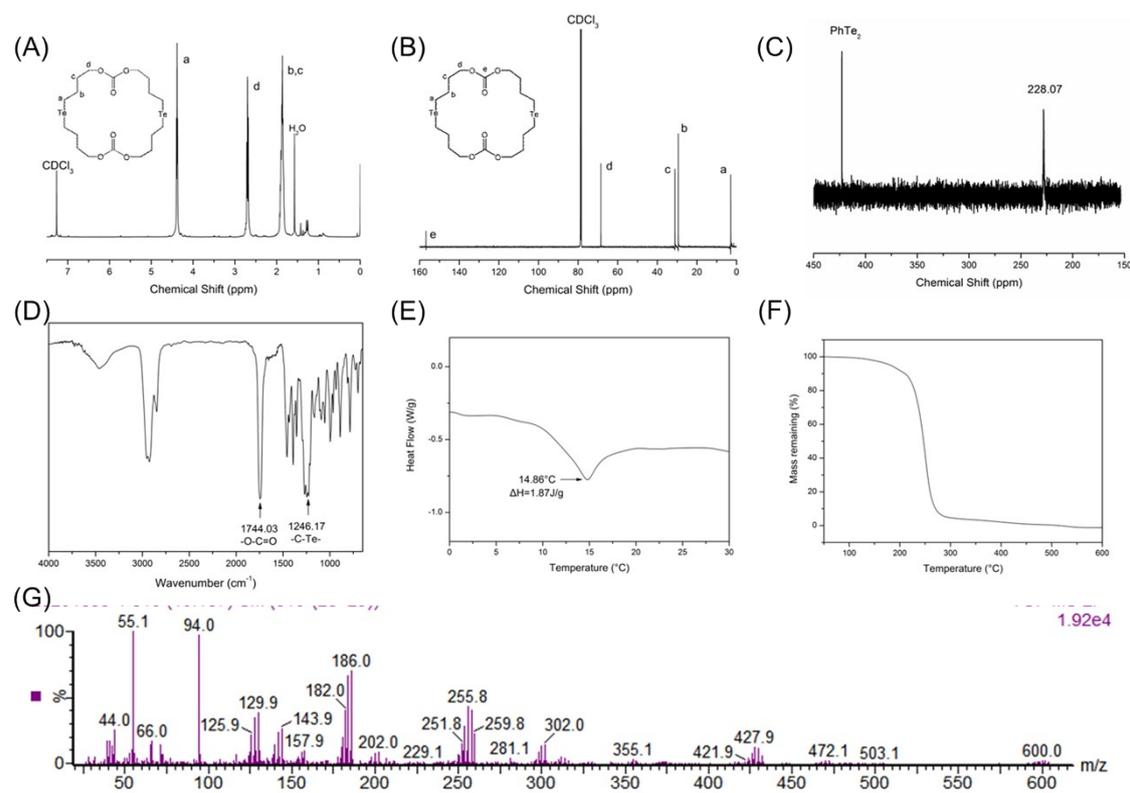


Fig S6 Characterization of MTe-4: (A) ^1H NMR; (B) ^{13}C NMR; (C) ^{125}Te NMR; (D) FT-IR; (E) DSC; (F) TGA; (G) EI-MS.

Table S1 Thermodynamic characterization of monomers

entry	monomer	$T_m(^{\circ}\text{C})$	$\Delta H(\text{J/g})$	$T_d(^{\circ}\text{C})$
1	MTe-3	45.77	37.92	282.7
2	MTe-4	14.86	1.87	251.0

Cyclic Carbonate Dimer

1,7-Heptandiol (0.8 g, 6.06 mmol) and diphenyl carbonate (1.95 g, 9.09 mmol) were dissolved in dried toluene (500 mL) under Ar flow. Afterwards, dried lipase CA (1.8 g) was added rapidly and the system was stirred at 70 °C for about 8 h. After the reaction, lipase CA was removed by filtration and the solvent was evaporated under reduced pressure. The crude reaction mixture was firstly washed with cold diethyl ether to clear away by-products and a few of oligomers. Finally, the monomer MC-20 was

obtained.

MC-20

^1H NMR (400 MHz, CDCl_3 , δ , ppm): 4.19 (t, $J=6.3$ Hz, 8H), 1.66 (t, $J=6.3$ Hz, 8H), 1.64 (t, $J=6.3$ Hz, 8H), 1.36 (t, $J=6.3$ Hz, 8H).

^{13}C NMR (600 MHz, CDCl_3 , δ , ppm): 155.36, 67.44, 28.63, 28.35, 25.43.

LRMS (EI, m/z): M^+ Calculated for $\text{C}_{16}\text{H}_{32}\text{O}_6$, 316; Found, 316.2.

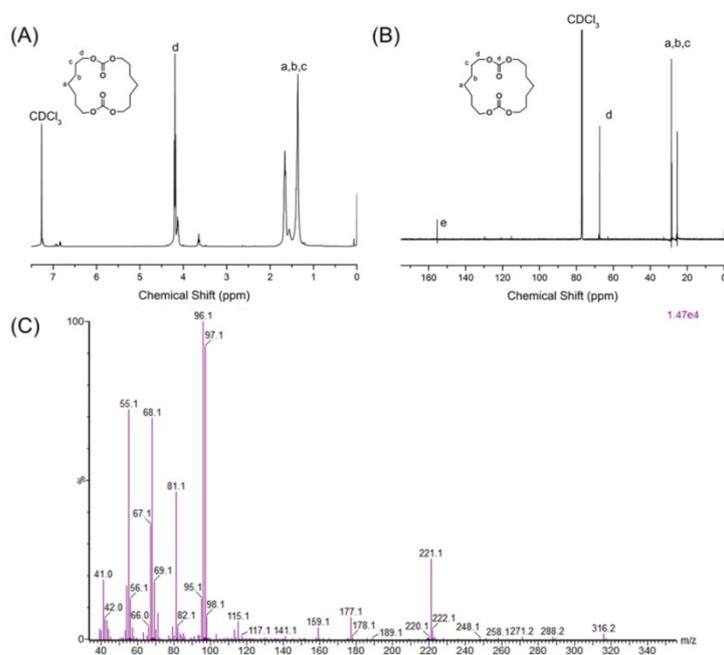


Fig S7 Characterization of MC-20: (A) ^1H NMR; (B) ^{13}C NMR; (C) EI-MS.

General procedure for organocatalytic ring-opening polymerization

Typically, MTe-3 (200 mg, 3.68 mmol) and benzyl alcohol (20 μL , 0.018 mmol) were added to a 10 mL flame-dried Schlenk flask under argon flow (Table 1, entries 3). The flask was then degassed under vacuum to remove the moisture completely, afterwards 1, 5, 7-triazabicyclo[4.4.0]dec-5-ene (TBD) (2.6 mg) (or 20 mg Lipase CA Novozym-435) was added. The polymerization reaction was carried out at 70 $^\circ\text{C}$ for 24 h. The solution was precipitated into cold anhydrous diethyl ether and then dried in

vacuo to get yellow viscous PTe in a yield about 80 %. The molecular weight (M_n) was obtained by comparing the peak integral ratio at 4.18 ppm or 2.68 ppm of the repeat units of polymers and 5.17 ppm of the initiator. The PTe with different degree of polymerization (DP) and macroinitiator mediated ROP were carried out according to the same procedure. And the ring-opening polymerization of MTe-4 and MC-20 were also carried out according to the same procedure.

Table S2 Molecular characteristic of the tellurium-containing polycarbonates

Entry	Initiator	[M]:[I]:[C] ^a	Solvent	T (°C)	Time (h)	Conv ^b (%)	Expected M_n^c (kDa)	M_n^b (kDa)	M_n^d (kDa)	\bar{D}^d M_w/M_n
1	BnOH	5:1:0.25	Toluen e	70	12	96.2	2.62	5.51	4.30	1.15
2	BnOH	10:1:0.5	Toluen e	70	12	90.1	4.90	8.10	6.81	1.17
3	BnOH	20:1:1	Toluen e	70	12	94.3	10.26	11.97	10.30	1.20
4	BnOH	50:1:2.5	Toluen e	70	12	89.5	24.34	31.55	27.51	1.15
5	BnOH	100:1:5	Toluen e	70	12	91.7	49.88	59.02	56.82	1.13
6	BnOH	10:1:0.5	Toluen e	90	1	84.0	4.57	6.76	7.14	1.27
7	BnOH	10:1:0.5	Toluen e	50	24	80.1	4.36	5.17	9.05	1.22
8	BnOH	10:1:0.5	Toluen e	25	72	16.3	0.89	0.88	- ^e	- ^e
9	BnOH	10:1:0.5	CH ₂ Cl ₂	25	72	24.6	1.34	1.33	- ^e	- ^e
10	BnOH	20:1:1	DMF	70	12	94.1	10.24	11.34	8.79	1.25

11	mPEG _{2k}	20:1:1	Toluen	70	12	92.6	11.93	16.04	11.78	1.32
			e							
12	mPEG _{2k}	100:1:5	Toluen	70	24	92.9	52.40	69.32	55.99	1.30
			e							

^a [Monomer] : [ROH] : [Catalyst]. ^b Determined by ¹H NMR (Fig S9) in CDCl₃ using integrals of the characteristic signals. ^c Molecular weight (kDa) calculated by the feed ratios and conversion of monomer. ^d Determined in DMF by PS calibrated GPC. ^e Cannot be detected by GPC. The ring-opening polymerization was catalyzed by TBD.

Table S3 Molecular characteristic of the tellurium-containing polycarbonates

Entry	Initiator	[M]:[I]:[C] ^a	Solvent	T (°C)	Time (h)	Conv ^b (%)	Expected Mn ^c (kDa)	Mn ^b (kDa)	Mn ^d (kDa)	Đ ^d M _w /M _n
1	BnOH	20:1:1	Toluene	70	48	0	13.60	-	-	-
2	BnOH	20:1:5	Toluene	70	48	0	13.60	-	-	-
3	mPEG _{2k}	20:1:1	Toluene	70	48	0	15.60	-	-	-
4	BnOH	20:1:1	DMF	70	48	0	13.60	-	-	-
5	BnOH	20:1:1	DMF	120	48	0	13.60	-	-	-

^a [Monomer] : [ROH] : [catalyst]. ^b Determined by ¹H NMR in CDCl₃ using integrals of the characteristic signals. ^c Molecular weight (kDa) calculated by the feed ratios. ^d Determined in DMF by PS calibrated GPC. ^e Cannot be detected by GPC. The ring-opening polymerization was catalyzed by DBU.

Tellurium-Containing Polycarbonate

P₁Te

¹H NMR (400 MHz, CDCl₃, δ, ppm): 4.18 (t, J=6.3 Hz, 4nH), 2.68 (t, J=6.3 Hz, 4nH), 2.11 (t, J=6.3 Hz, 4nH), 5.17 (t, J=6.3 Hz, 2H).

¹³C NMR (600 MHz, CDCl₃, δ, ppm): 157.34, 71.19, 33.35, 2.14.

¹²⁵Te NMR (600 MHz, CDCl₃, δ, ppm): 255.09.

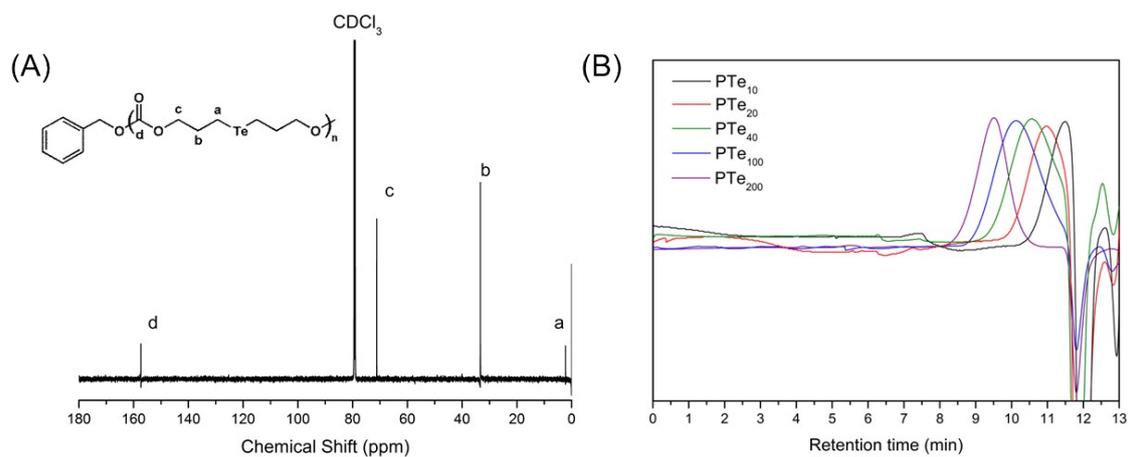


Fig S8 ¹³C NMR and GPC spectra of poly(tellurium-containing carbonate) (PTe)

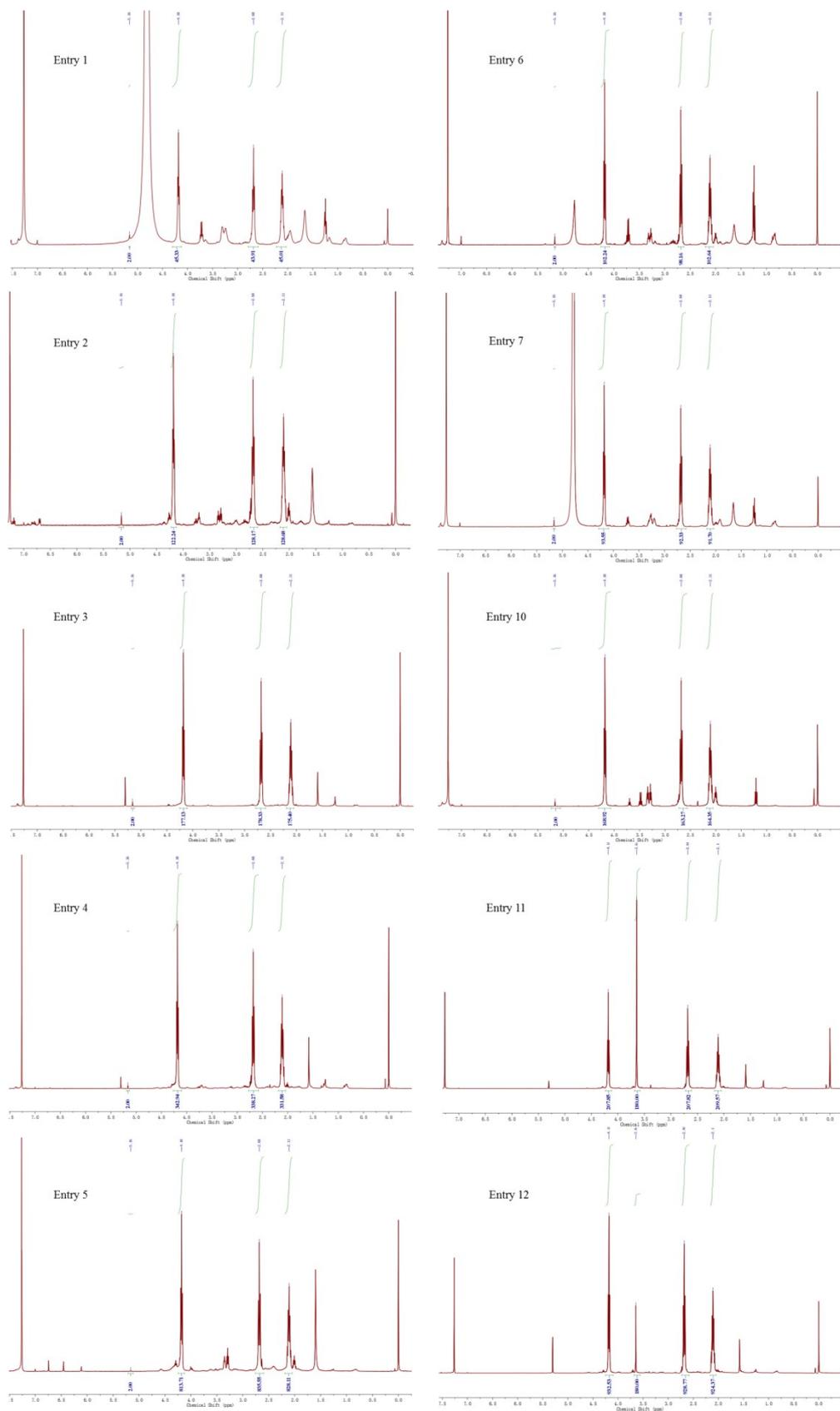


Fig S9 ^1H NMR of poly (tellurium-containing carbonate) (PTE) (Entries 1-7, Entries 10-12 in Table S2) in reaction solutions.

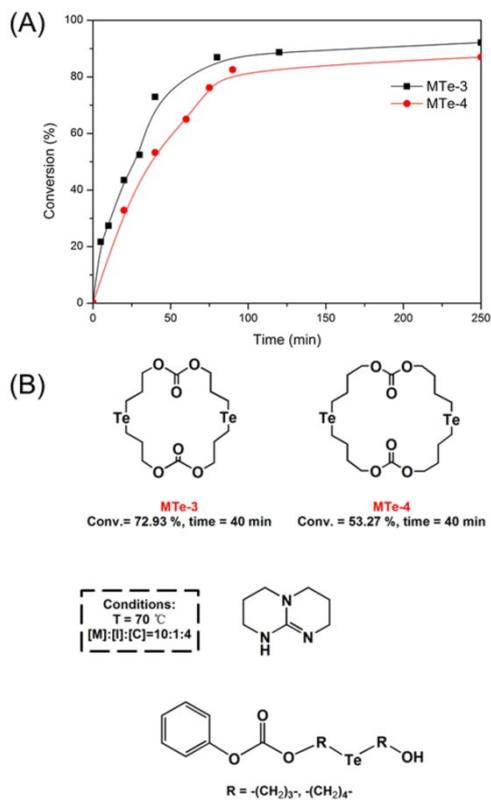


Fig S10 Ring-opening polymerizations of MTe-3 and MTe-4 catalyzed by TBD

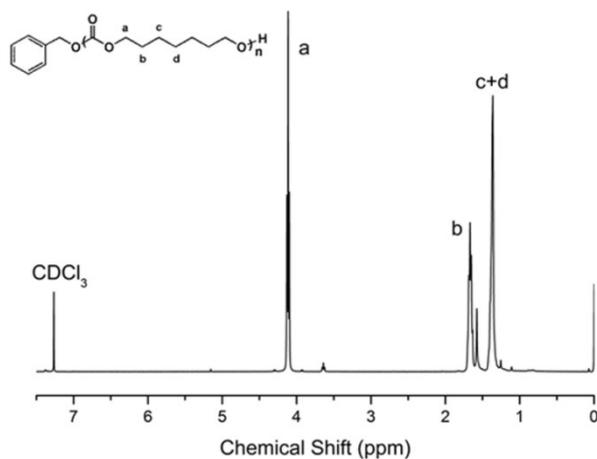


Fig S11 ¹H NMR spectra of PC₄₀

Polymerization kinetics experiment

In a 10 mL vial equipped with a stir bar, MTe (150 mg, 0.28 mmol), benzyl alcohol (30 μ L, 0.028 mmol) and TBD (15 mg) were added with the designed degree of polymerization (DP) of 20 ($[M]_0/[I]_0/[C]_0=10/1/4$). Then, \sim 0.9 mL anhydrous toluene

was added to initiate polymerization. The reaction mixture was allowed to stir at 70 °C and the solution (25 μL) was taken out from the reaction system at a determined time intervals for ^1H NMR spectroscopy analysis. Monomer conversion was calculated by comparing the area integral of the triplet at 2.73 ppm, corresponding to $-\text{CH}_2\text{TeCH}_2-$ (8H) of monomer with that of the triplet at 2.68 ppm, corresponding to $-\text{CH}_2\text{TeCH}_2-$ (8H) of polymer. The polymerization kinetics experiments with different temperatures were carried out according to the same procedure.

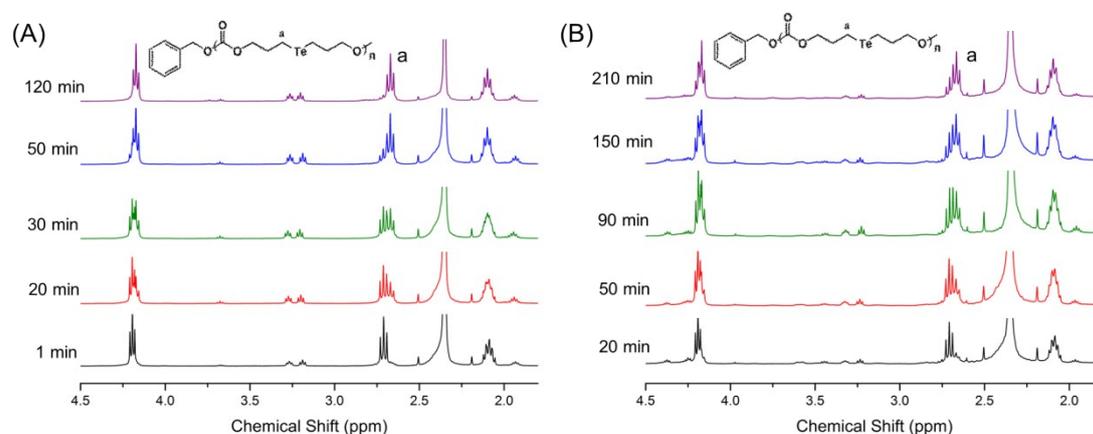


Fig S12 ^1H NMR spectra of the chemical shift of the ortho-protons of PTe at specific time in CDCl_3 at (A) 70 °C. (B) 50 °C.

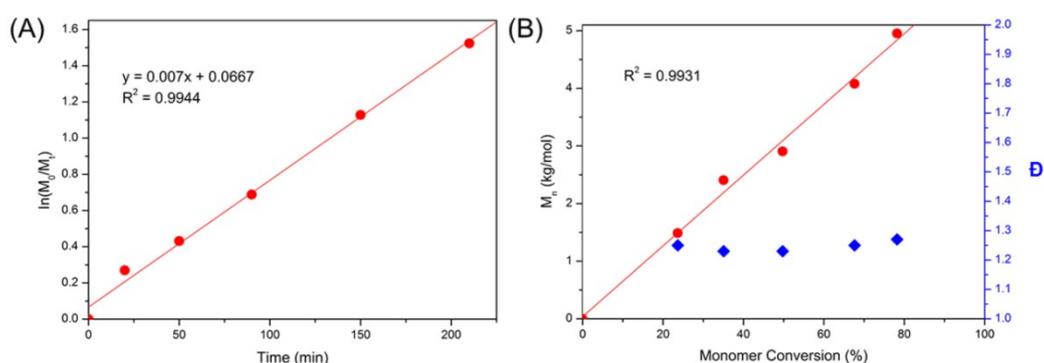


Fig S13 Kinetic studies. Reactions were run with BnOH as an initiator. (A) With $[\text{M}]/[\text{I}]/[\text{C}]$ of 10/1/4, kinetic plot of $\ln([\text{M}]_0/[\text{M}]_t)$ vs time, $k_{\text{app}} = 0.007 \text{ min}^{-1}$ (determined by the slope), 50 °C. (B) Evolution of M_n GPC and molecular weight distribution (D_M) vs conversion. Monomer conversions

were determined by ^1H NMR spectra.

Hydrolytic degradation study

10 mg of the PTe₄₀ was dissolved by DCM (1 mL) in a series of 2 ml vials. Then, the DCM was removed by a vacuum oven to prepare a skinny polymer layer in vials. 1 ml of Phosphate buffered saline (PBS) (pH = 7.4) was added to the series of vials. The vials were sealed and incubated at 37 °C. After specified time intervals, each vial was taken out, freeze-dried, and analyzed by ^1H NMR to monitor the degree of degradation. The benchmark substrate polymer PC which has approximate molecular weight with PTe₄₀ was obtained in the same way. And the degradation of copolymers PTe_{20-co}-PC₂₀ was also obtained in the same way.

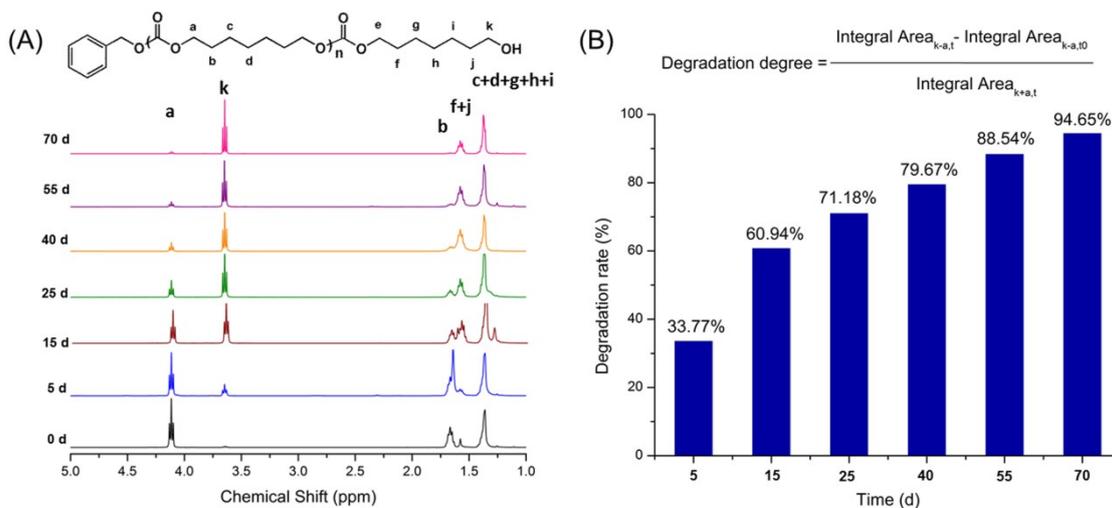


Fig S14 (A) ^1H NMR (CDCl_3 , 400 MHz, 25 °C) spectra of hydrolyzed PC₄₀ at 37 °C (PBS solution of pH 7.4) up to 70 days and (B) the degradation degree vs time histogram.

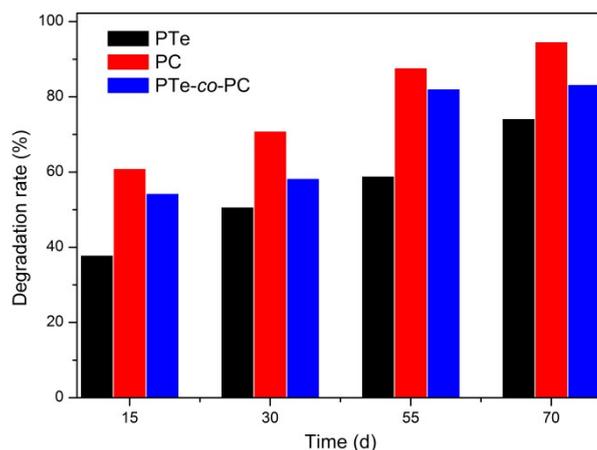


Fig S15 the contrastive degradation degree vs time histogram (hydrolyzed PC_{20-co-PC}₂₀ at 37 °C (PBS solution of pH 7.4) up to 70 days; determined by ¹H NMR (CDCl₃, 400 MHz, 25 °C)).

Photo-irradiation and oxygen stability studies

10 mg of the PTe₄₀ was dissolved by DCM (1 mL) in a series of 2 ml vials. Then, the DCM was removed by a vacuum oven to prepare a skinny polymer layer in vials. The vials were divided into four groups which exposed to natural light, air, both or none of them respectively and incubated at room temperature. After specified time intervals, each vial was analyzed by ¹H NMR to monitor the degree of degradation. The calculation method is the same as that of hydrolytic degradation in the previous paper. The water stability of PTe was studied in the same way.

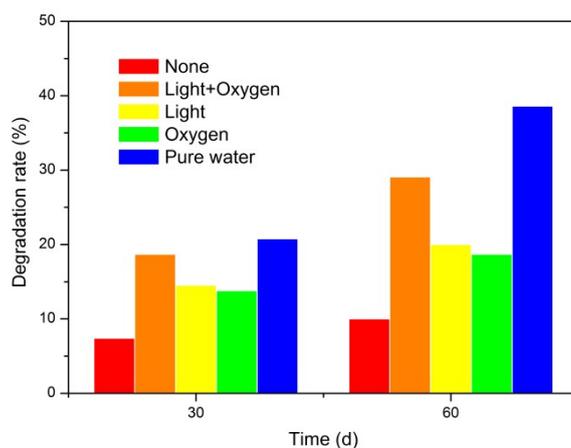


Fig S16 The degradation degree vs time histogram (determined by ¹H NMR).

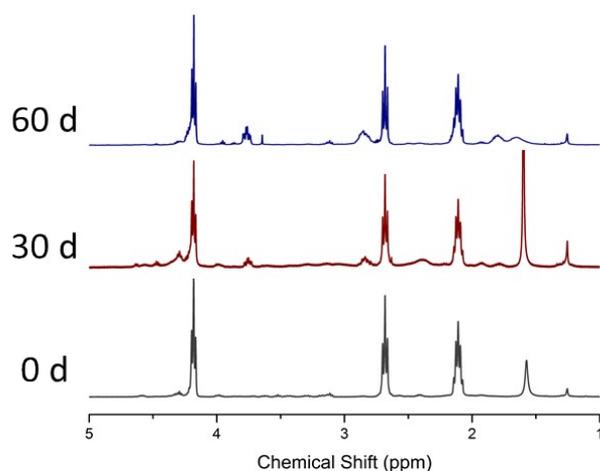


Fig S17 ^1H NMR (CDCl_3 , 400 MHz, 25 °C) spectra of hydrolyzed PTe_{40} at 37 °C (pure water) up to 60 days.

3 Characterization

Nuclear Magnetic Resonance (NMR) was used to confirm the chemical structure. The ^1H -NMR, ^{13}C -NMR and ^{125}Te -NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz) and a Bruker Avance 600 spectrometer (600 MHz), with deuterated chloroform (CDCl_3) as the solvent. Fourier Transform infrared spectroscopy (FT-IR) were recorded on a Nicolet 5700 FT-IR spectrometer ranging from 500 to 4000 cm^{-1} at room temperature, and the samples were prepared by the KBr sample holder method. The molecular weight of the monomers was determined on an Electron bombardment (EI)-High resolution time of flight mass spectrometer (GCT Premier). The molecular weight and chain structure of the polymers were determined on Matrix-Assisted Laser Desorption/ Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS).

The molecular weight and polydispersities (M_w/M_n) of the products were determined on Gel Permeation Chromatography (GPC) using DMF as the eluent at a flow rate of 1.0 mL min^{-1} against polystyrene (PS) standard. The melting point (T_m) of

monomer was determined with a US Dimond differential scanning calorimeter (DSC) under N₂ atmosphere, with a heating rate of 10 °C/min. Thermo-gravimetric analysis (TGA) was performed under N₂ atmosphere on STA409PC apparatus with a heating rate of 10 °C/min.