Supporting Information

Catalyst-free synthesis of high-molecular weight poly(alkylene oxalate)s

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CONTENT

Supplementary Figures and Tables

Figure S1 shows the ^{1}H NMR spectrum of OEO in DMSO at 80 °C. There were four proton signals: 4.55ppm (a, 4H), methylene hydrogen of ethylene oxalate (EO); 4.27 ppm (b, 2H) and 3.67 ppm (d, 2H), ethyl hydrogen of 2-hydroxyethyl oxalate (TE); 3.84 ppm (c, 3H), methyl hydrogen of methyl oxalate. The weak proton signals located at δ = 4.67 ppm and δ = 3.84 ppm were ascribed to methylene hydrogens of 1,4-dioxane-2,3-dion and ethylene glycol (EG), respectively. The number-averaged degree of polymerization (DP_n) of OEO was estimated to be 6.9, according to equation (1). The concentration of ethyl glycol oxalate repeating units (C_{EO}, mol/kg) in OEO was estimated to be 8.1 mol/kg., according to equation (3). The concentration of ethyl glycol repeating units (C_{EG}, mol/kg) in OEO was estimated to be 8.7 mol/kg., according to equation (3).

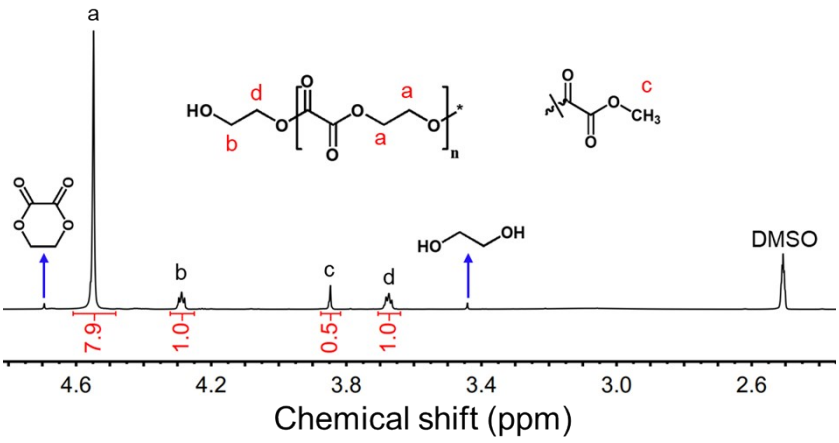


Figure S1. Chemical structure and ^{1}H NMR spectrum of OEO.

The M_n, C_{EO} and C_{EG} of OEO1 were also calculated by using equation 1-3:

$$DP_n = (I_a + I_b + I_d + 4I_c/3)/(I_d + I_c/1.5) - 1 \quad (1)$$

$$C_{EO} = DP_n/(116DP_n + 47) \quad (2)$$

$$C_{EG} = (DP_n + 0.5)/(116DP_n + 47) \quad (3)$$

Where I_a, I_b, I_c, and I_d are the integrated areas of H_a, H_b, H_c, and H_d, respectively.

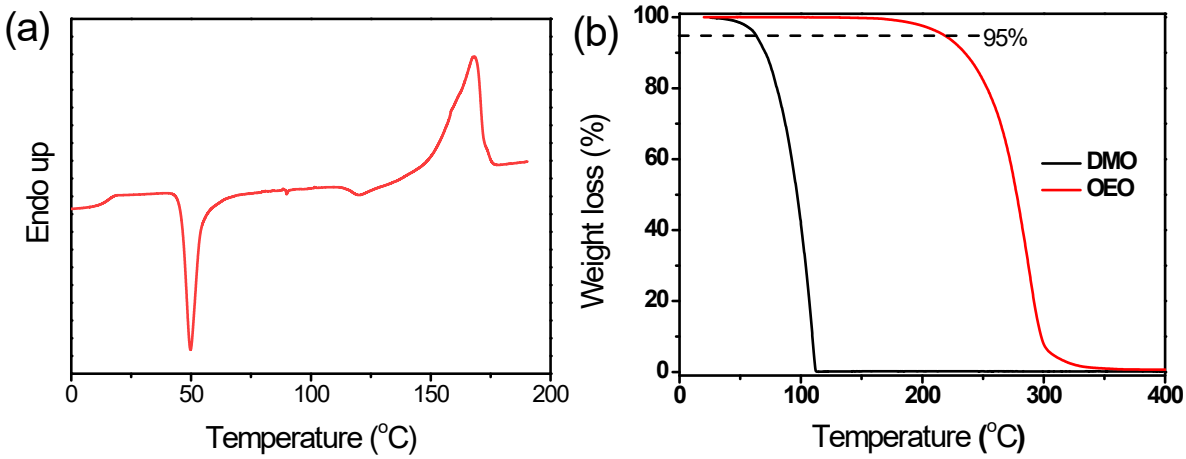


Figure S2. 2nd DSC heating curve (a) and TGA curves of DMO and OEO (b).

Figure S3. Sublimation of DMO at 120 °C.

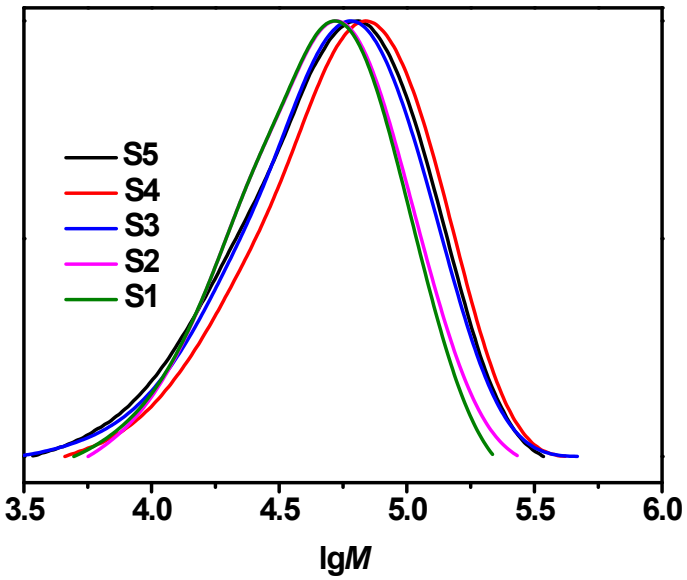


Figure S4. GPC curves of the synthesized samples S1-S5.

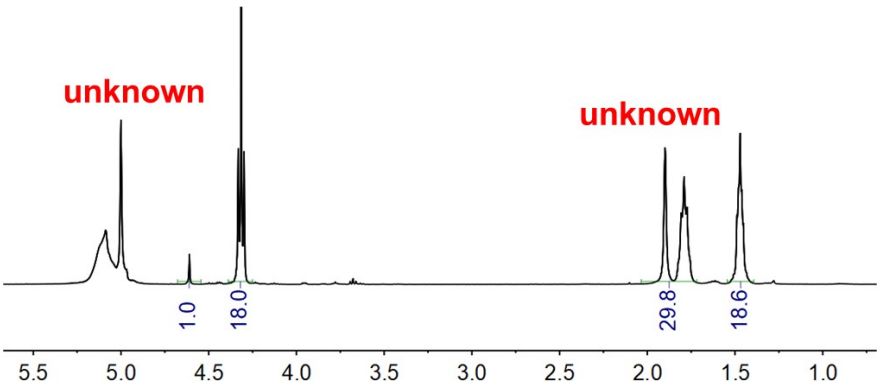


Figure S5. ^{1}H NMR spectrum of the polyoxalate by using OEO1 as oxalate feedstock.

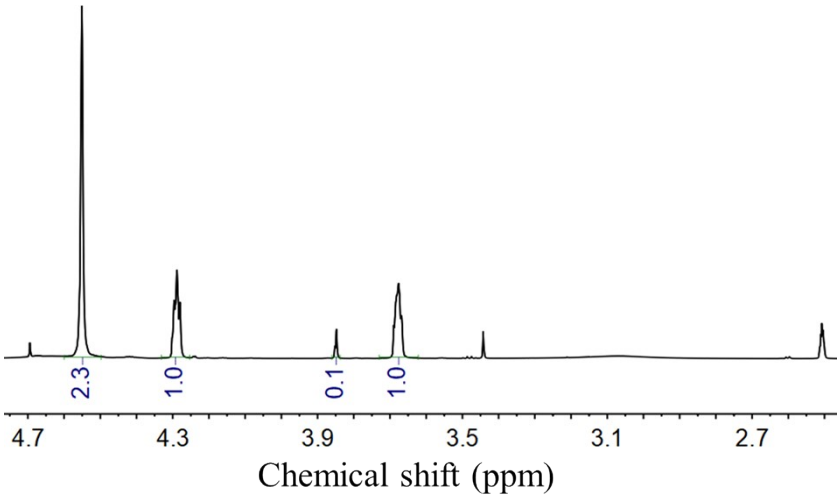


Figure S6. ^{1}H NMR spectrum of OEO2.

The M_n, C_{EO} and C_{EG} of OEO2 were also calculated by using equation 1-3.

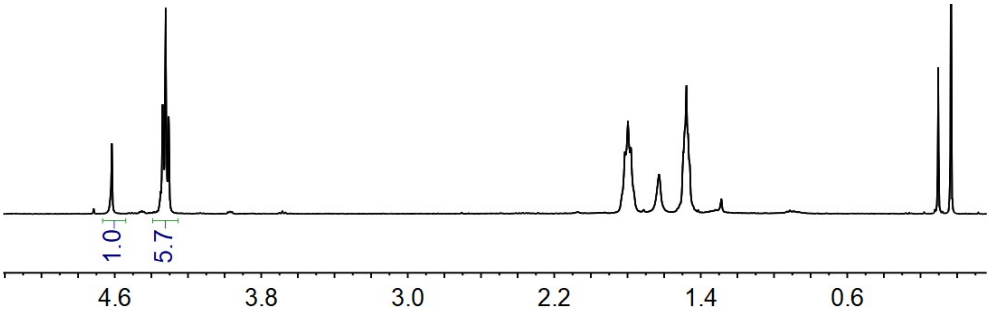


Figure S7. ^{1}H NMR spectrum of polyoxalate by using OEO2 as oxalate feedstock.

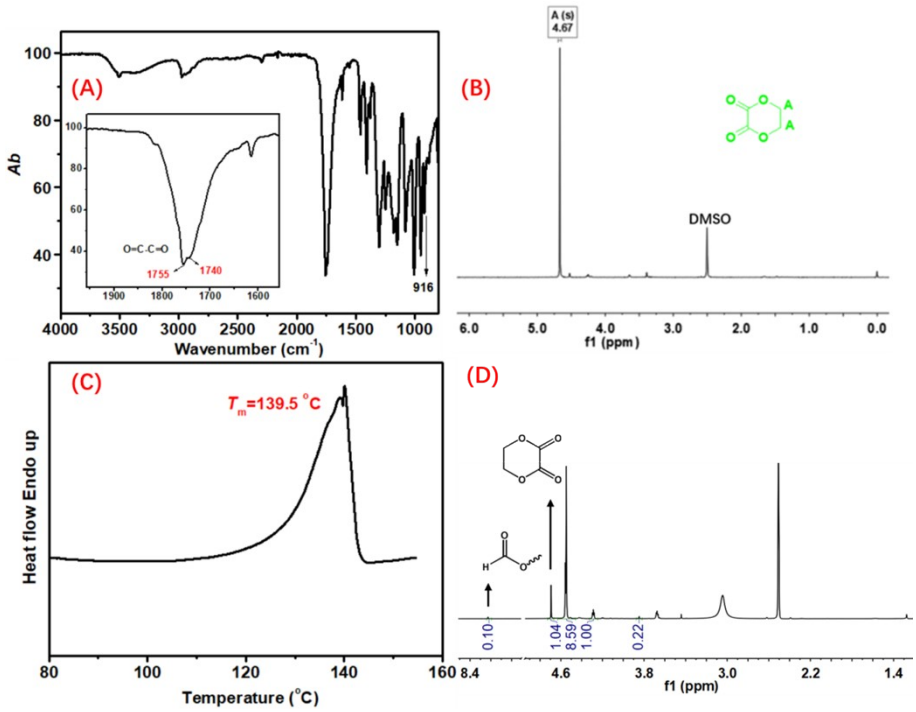


Figure S8. (A) FTIR spectrum, (B) ^{1}H NMR spectrum, (C) DSC curve of the produced 1,4-dioxane-2,3-dion and (D) ^{1}H NMR spectrum of residual solid.

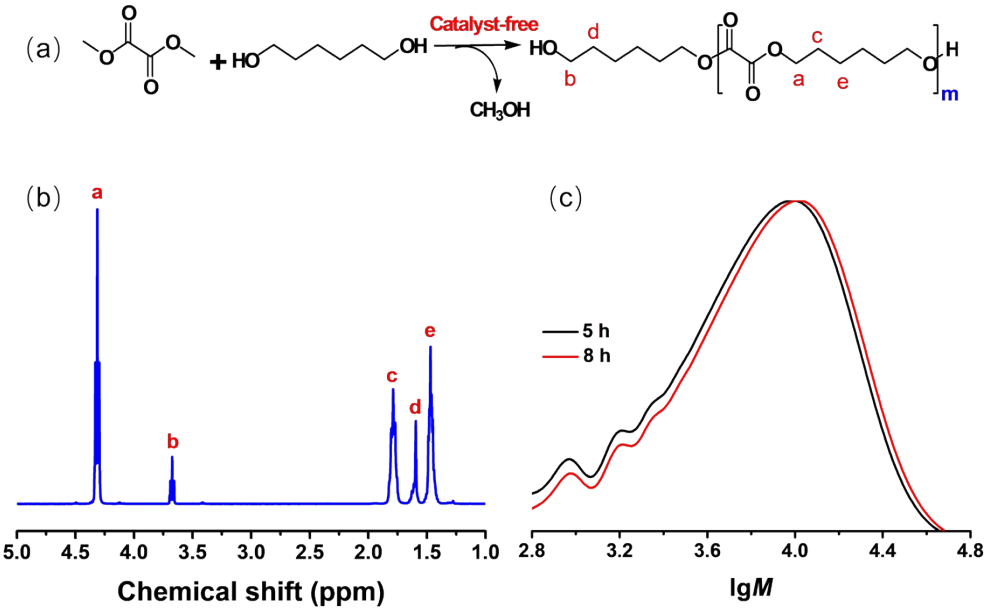


Figure S9. (a) The route of catalyst-free polycondensation of dimethyl oxalate and HDO. (b) ^{1}H NMR spectrum and (c) GPC curves of CS.

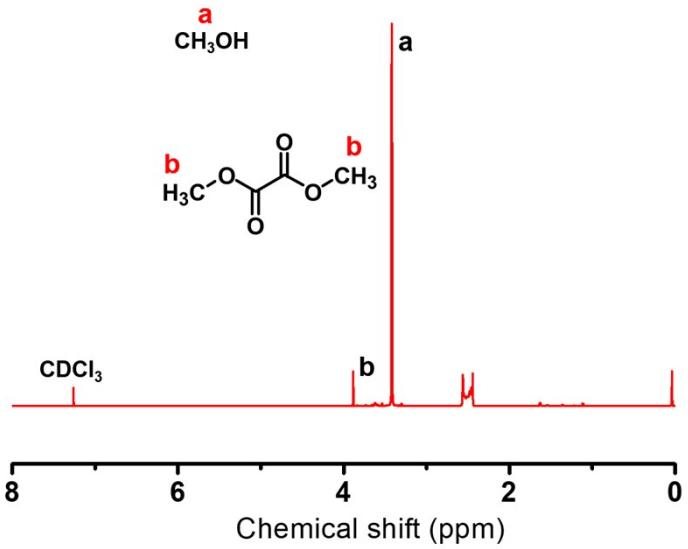


Figure S10. [1]H NMR spectrum of byproducts for CS.

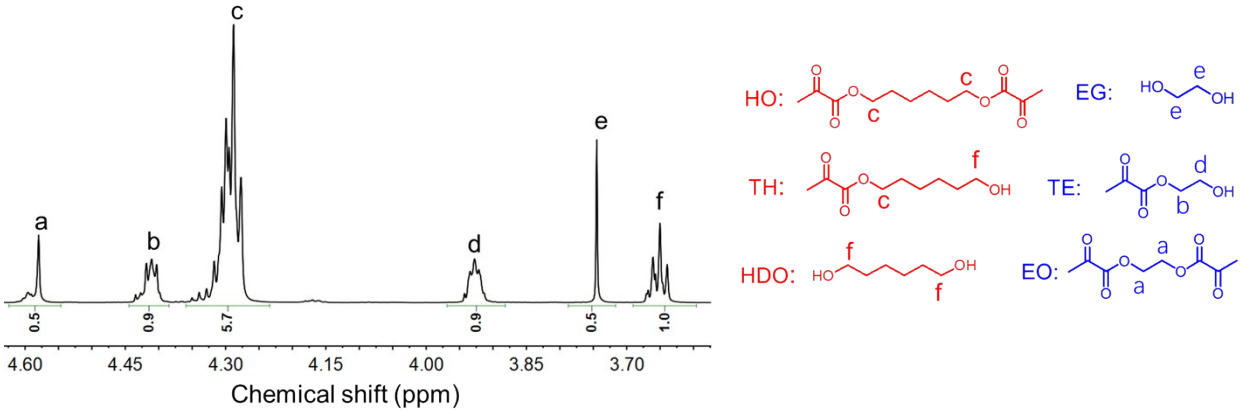


Figure S11. [1]H NMR spectrum of the sample (Table 1, entry S5) after transesterification at 170 °C under atm for 3 h.

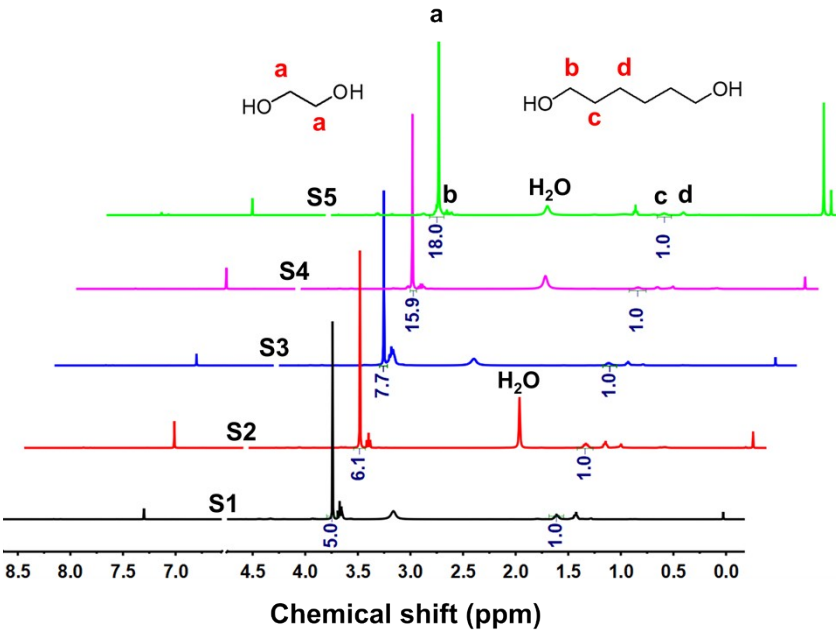


Figure S12. ^{1}H NMR spectra of the distillate for S1-S5.

The molar percentage of HDO in byproduct of S1-S5 can be calculated by equation 1:

$$\emptyset_{HDO} = \frac{H_a}{H_a + H_b} * 100\% \qquad (7)$$

where H_a and H_b stand for the integral area of corresponding hydrogen signals, and the data was summarized in Table S1.

Table S1. The ϕ_{HDO} in byproduct of S1-S5.

Sample	ϕ_{HDO} (mol%)
S1	16.7
S2	14.1
S3	11.5
S4	5.9
S5	5.3

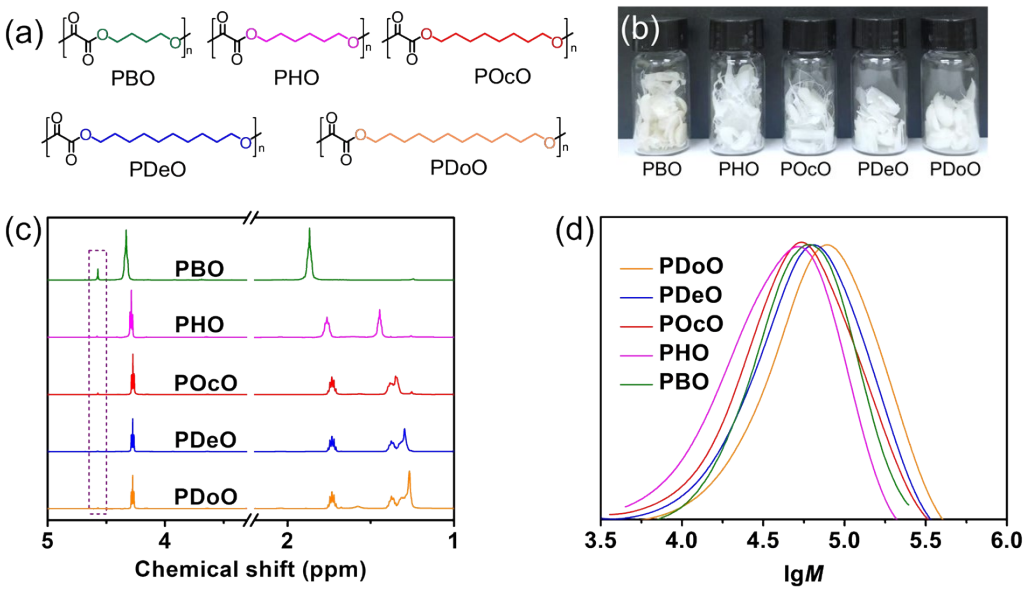


Figure S13. Chemical structures (a), photographs (b), ^{1}H NMR spectra (c) and GPC curves (d) of the synthesized PAOs.

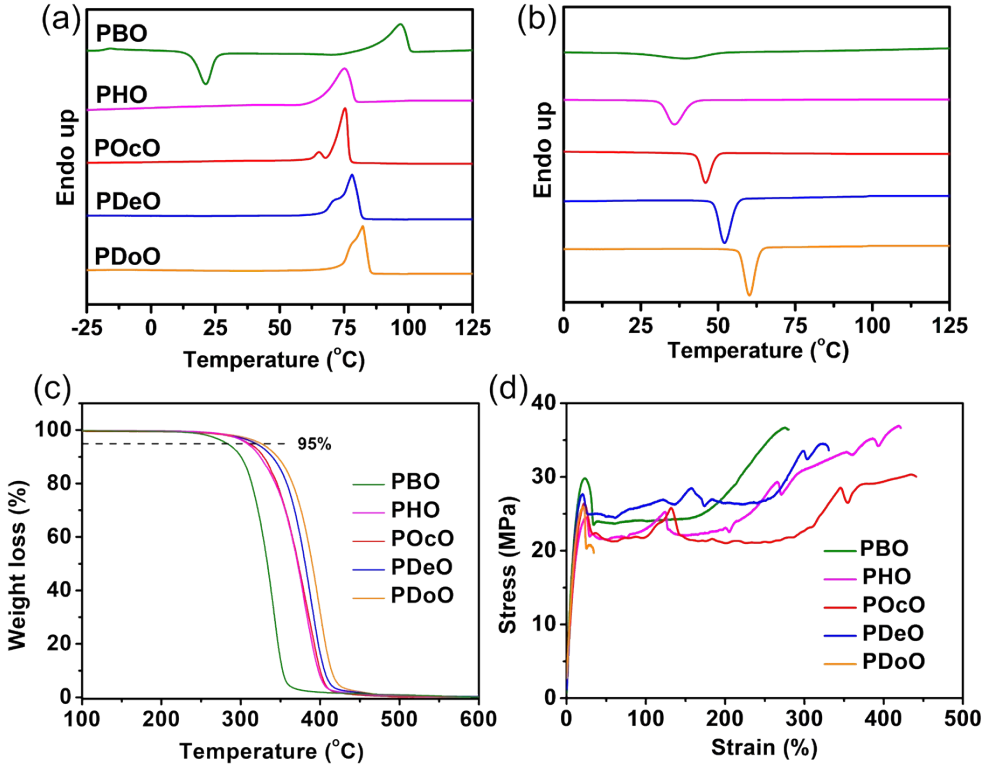


Figure S14. DSC heating curves (a) and cooling curves (b), TGA curves (c) and stress−strain curves of the synthesized PAOs.

Table S2. The thermal parameters of the synthesized PAOs.

entry	Sample	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	$T_{d5\%}$ (°C)
P1	PBO	-17.8	97.8	55.3	41.1	55.6	283.4
S1	PHO	-37.8	75.3	50.1	35.3	55.6	309.0
P2	POcO	-40.1	75.8	53.9	46.1	63.6	311.2
P3	PDeO	-34.2	78.0	58.2	52.2	65.3	318.5
P4	PDoO	-22.6	82.6	73.7	60.2	71.8	325.4

Table S3. The mechanical properties of the synthesized PAOs.

entry	Sample	E (MPa)	σ_y (MPa)	ε (%)
P1	PBO	280±5	36.7±0.5	279±5
S1	PHO	180±5	36.7±1.2	440±15
P2	POcO	240±6	30.3±0.4	440±15
P3	PDeO	280±5	34.0±1.5	350±20
P4	PDoO	260±3	26.5±0.6	30±3

E stands for Young's modulus; σ_y stands for tensile strength; ε stands for elongation at break.

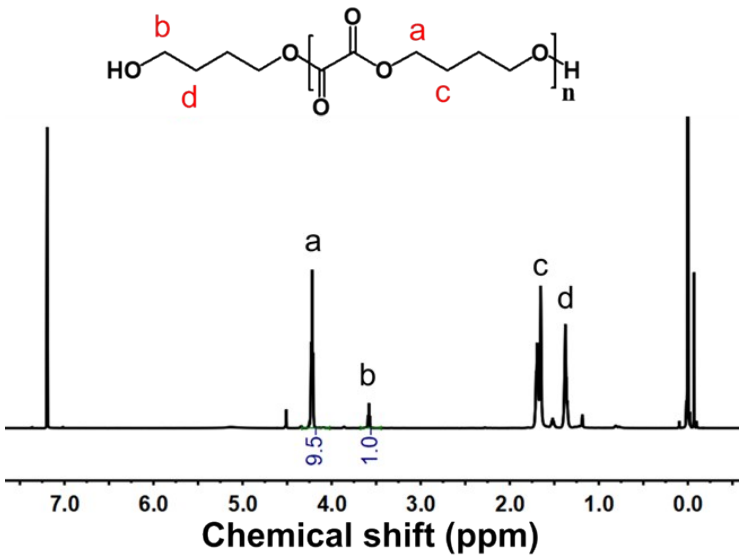


Figure S15. The ^{1}H NMR of PBO after degradation in seawater for 60 days.

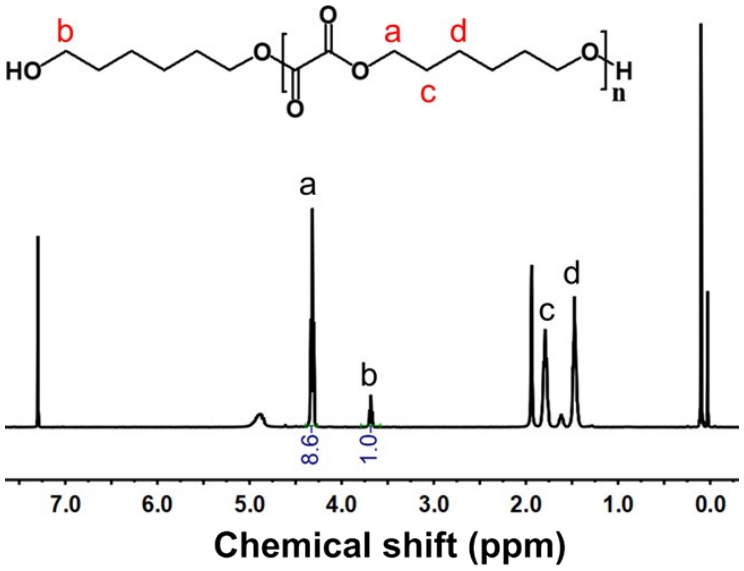


Figure S16. The ^{1}H NMR of PHO after degradation in seawater for 60 days.

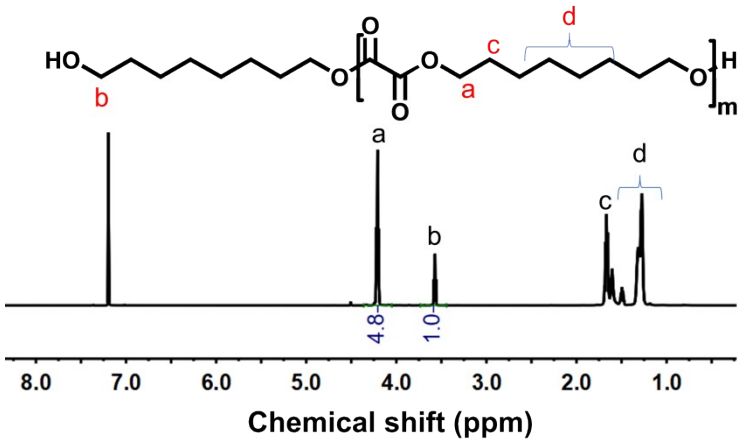


Figure S17. The ^{1}H NMR of POcO after degradation in seawater for 60 days.

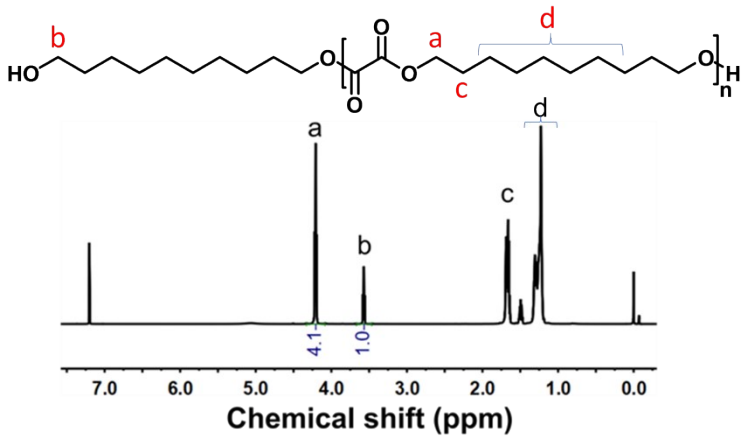


Figure S18. The ^{1}H NMR of PDeO after degradation in seawater for 60 days.

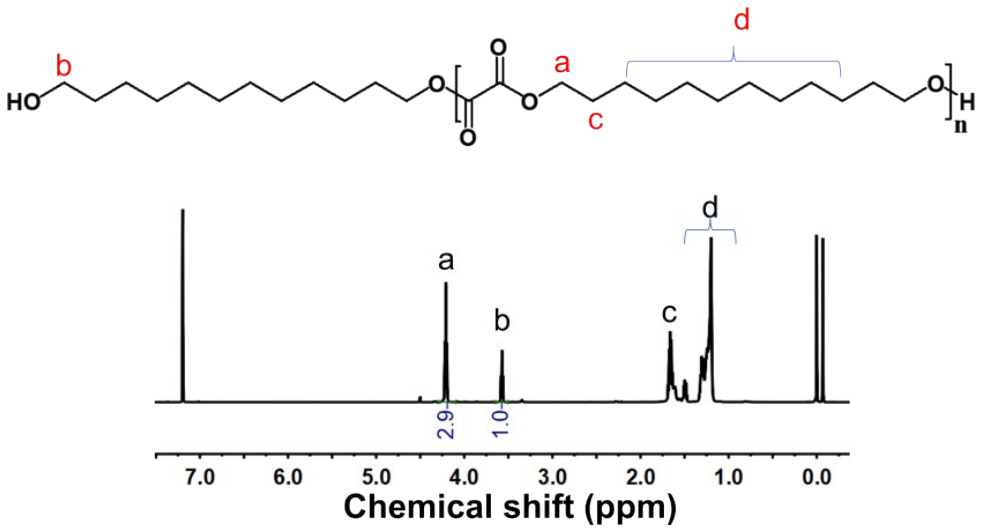


Figure S19. The ^{1}H NMR of PDoO after degradation in seawater for 60 days.

Table S4. The number-averaged molecular weight decreases of the synthesized PAOs after degradation in seawater for 60 days.

Sample	M_n (kDa)		M_n decrease[a] (%)
	Before degradation	After degradation	
P1	9.5	1.5	84.2
S1	15.5	1.6	89.7
P2	18.4	1.1	94.0
P3	20.5	1.1	94.6
P4	22.0	0.9	95.9

Theoretical calculation

All quantum chemistry computations were performed based on Gaussian 16, and the molecular construction was performed in the GaussView 5.0. The optimization was computed at the B3LYP/6-31G $^{+}$ (d, p) level of theory. The relevant wavefunction analysis (Fukui function and frontier molecular orbital) were performed by Multiwfn 3.8[1]. The isosurface maps of the dual descriptor were visualized by GaussView 5.0. Fukui function is defined as [2–4]:

$$f(r) = [\frac{\partial \rho(r)}{\partial N}]_v \quad (1)$$

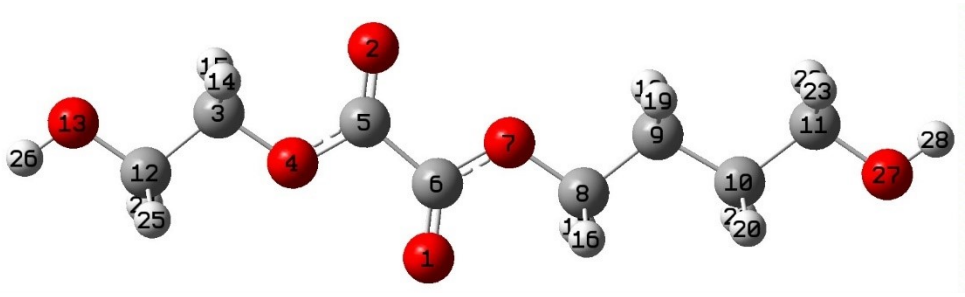
where ρ(r) is the electron density at a point r in space, N is total electron number in present system, and the constant term v in the partial derivative is external potential. For a given molecular system, Fukui function was calculated using electron density of three states:

$$f^+(r) = \rho_{N+1}(r) - \rho_N(r) \approx \rho^{LUMO}(r) \quad (2)$$

$$f^-(r) = \rho_N(r) - \rho_{N-1}(r) \approx \rho^{HOMO}(r) \quad (3)$$

$$f^0(r) = \frac{f^+(r) + f^-(r)}{2} = \frac{\rho_{N+1}(r) + \rho_{N-1}(r)}{2} \approx \frac{\rho^{HOMO}(r) - \rho^{HOMO}(r)}{2} \quad (4)$$

where N is the number of electrons in the molecular system. The $N-1$ and $N+1$ states share the same molecular geometry as the N state. For nucleophiles, f^- is the reactivity descriptor, while for electrophiles, f^+ is the descriptor. f^0 is reactivity descriptor for radical attack. Atoms with larger Fukui function tend to have higher reactivities.



E(N): -764.598743 Hartree
E(N+1): -764.571146 Hartree
E(N-1): -764.270874 Hartree
E_HOMO(N): -0.264993 Hartree, -7.2108 eV
E_HOMO(N+1): 0.111602 Hartree, 3.0368 eV

E_HOMO(N-1): -0.398296 Hartree, -10.8382 eV

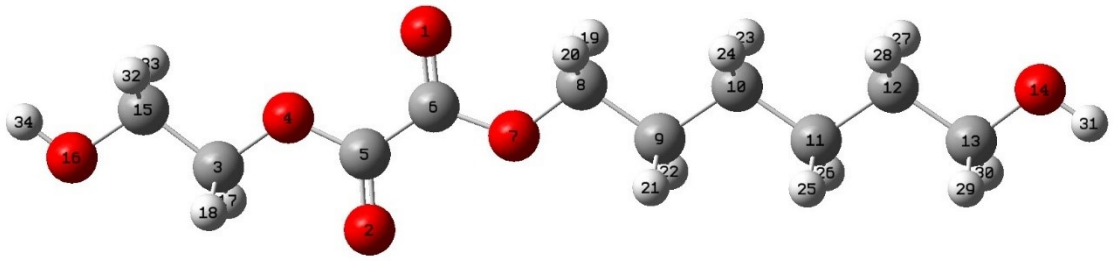
Hardness (=fundamental gap): 0.355466 Hartree, 9.6727 eV

Softness: 2.813206 Hartree^-1, 0.1034 eV^-1

Electrophilicity index: 0.031706 Hartree, 0.8628 eV

Nucleophilicity index: 0.070205 Hartree, 1.9104 eV

Atom	q(N)	q(N+1)	q(N-1)	f^-	f^+	f^0	CDD
1(O)	-0.2569	-0.4182	-0.1454	0.1115	0.1613	0.1364	0.0498
2(O)	-0.2528	-0.4148	-0.1434	0.1093	0.1621	0.1357	0.0527
3(C)	0.0404	0.0204	0.0515	0.0111	0.0200	0.0156	0.0089
4(O)	-0.1102	-0.1689	-0.0789	0.0313	0.0587	0.0450	0.0274
5(C)	0.2048	0.0598	0.2417	0.0369	0.1450	0.0910	0.1081
6(C)	0.2034	0.0592	0.2402	0.0368	0.1442	0.0905	0.1074
7(O)	-0.1105	-0.1690	-0.0770	0.0335	0.0585	0.0460	0.0250
8(C)	0.0427	0.0243	0.0530	0.0103	0.0185	0.0144	0.0082
9(C)	-0.0473	-0.0526	-0.0407	0.0065	0.0053	0.0059	-0.0012
10(C)	-0.0473	-0.0529	-0.0395	0.0078	0.0056	0.0067	-0.0022
11(C)	0.0270	0.0214	0.0588	0.0318	0.0056	0.0187	-0.0263
12(C)	0.0262	0.0167	0.0501	0.0238	0.0096	0.0167	-0.0143
13(O)	-0.2411	-0.2585	-0.1428	0.0983	0.0174	0.0579	-0.0809
14(H)	0.0467	0.0242	0.0618	0.0151	0.0225	0.0188	0.0074
15(H)	0.0466	0.0242	0.0613	0.0146	0.0224	0.0185	0.0078
16(H)	0.0419	0.0210	0.0540	0.0121	0.0208	0.0165	0.0087
17(H)	0.0418	0.0210	0.0541	0.0123	0.0207	0.0165	0.0085
18(H)	0.0356	0.0274	0.0443	0.0087	0.0082	0.0084	-0.0005
19(H)	0.0357	0.0275	0.0442	0.0085	0.0082	0.0083	-0.0003
20(H)	0.0347	0.0281	0.0469	0.0122	0.0067	0.0094	-0.0055
21(H)	0.0347	0.0281	0.0474	0.0127	0.0067	0.0097	-0.0060
22(H)	0.0241	0.0188	0.0638	0.0396	0.0053	0.0225	-0.0343
23(H)	0.0242	0.0188	0.0632	0.0390	0.0053	0.0222	-0.0337
24(H)	0.0320	0.0212	0.0594	0.0274	0.0107	0.0191	-0.0167
25(H)	0.0321	0.0213	0.0605	0.0285	0.0107	0.0196	-0.0178
26(H)	0.1721	0.1527	0.2055	0.0333	0.0194	0.0264	-0.0139
27(O)	-0.2470	-0.2566	-0.1029	0.1442	0.0096	0.0769	-0.1346
28(H)	0.1663	0.1553	0.2091	0.0428	0.0110	0.0269	-0.0318



E(N): -843.226344 Hartree

E(N+1): -843.198375 Hartree

E(N-1): 842.904055 Hartree

E_HOMO(N): -0.264239 Hartree, -7.1903 eV

E_HOMO(N+1): 0.111667 Hartree, 3.0386 eV

E_HOMO(N-1): -0.386860 Hartree, -10.5270 eV

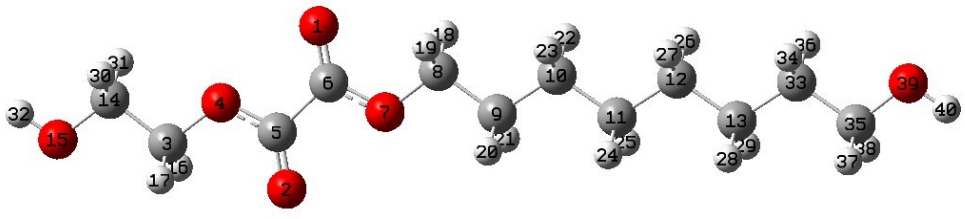
Hardness (=fundamental gap): 0.350257 Hartree, 9.5310 eV

Softness: 2.855044 Hartree^-1, 0.1049 eV^-1

Electrophilicity index: 0.030915 Hartree, 0.8412 eV

Nucleophilicity index: 0.070959 Hartree, 1.9309 eV

Atom	q(N)	q(N+1)	q(N-1)	f^-	f^+	f^0	CDD
1(O)	-0.2577	-0.4186	-0.1489	0.1089	0.1609	0.1349	0.0520
2(O)	-0.2527	-0.4147	-0.1474	0.1053	0.1620	0.1337	0.0567
3(C)	0.0403	0.0203	0.0507	0.0104	0.0200	0.0152	0.0097
4(O)	-0.1104	-0.1690	-0.0803	0.0301	0.0586	0.0444	0.0285
5(C)	0.2048	0.0597	0.2405	0.0356	0.1451	0.0904	0.1094
6(C)	0.2032	0.0592	0.2387	0.0355	0.1441	0.0898	0.1086
7(O)	-0.1104	-0.1690	-0.0770	0.0334	0.0585	0.0460	0.0251
8(C)	0.0416	0.0232	0.0503	0.0087	0.0184	0.0136	0.0097
9(C)	-0.0488	-0.0537	-0.0436	0.0052	0.0049	0.0050	-0.0003
10(C)	-0.0438	-0.0486	-0.0377	0.0061	0.0048	0.0055	-0.0014
11(C)	-0.0451	-0.0486	-0.0400	0.0052	0.0035	0.0043	-0.0017
12(C)	-0.0505	-0.0533	-0.0441	0.0064	0.0028	0.0046	-0.0037
13(C)	0.0249	0.0220	0.0580	0.0330	0.0029	0.0180	-0.0302
14(O)	-0.2489	-0.2546	-0.0969	0.1521	0.0057	0.0789	-0.1464
15(C)	0.0262	0.0167	0.0472	0.0210	0.0095	0.0153	-0.0115
16(O)	-0.2411	-0.2585	-0.1549	0.0863	0.0174	0.0518	-0.0689
17(H)	0.0466	0.0242	0.0601	0.0135	0.0224	0.0180	0.0089
18(H)	0.0466	0.0242	0.0605	0.0139	0.0224	0.0181	0.0085
19(H)	0.0408	0.0201	0.0513	0.0105	0.0206	0.0156	0.0102
20(H)	0.0408	0.0202	0.0513	0.0104	0.0206	0.0155	0.0102
21(H)	0.0353	0.0273	0.0417	0.0065	0.0079	0.0072	0.0014
22(H)	0.0352	0.0273	0.0416	0.0064	0.0079	0.0071	0.0016
23(H)	0.0293	0.0235	0.0360	0.0067	0.0059	0.0063	-0.0008
24(H)	0.0293	0.0235	0.0358	0.0065	0.0059	0.0062	-0.0006
25(H)	0.0276	0.0237	0.0341	0.0065	0.0039	0.0052	-0.0027
26(H)	0.0276	0.0237	0.0340	0.0065	0.0039	0.0052	-0.0026
27(H)	0.0323	0.0290	0.0440	0.0117	0.0033	0.0075	-0.0085
28(H)	0.0323	0.0290	0.0440	0.0117	0.0033	0.0075	-0.0084
29(H)	0.0222	0.0194	0.0644	0.0422	0.0028	0.0225	-0.0394
30(H)	0.0222	0.0193	0.0633	0.0411	0.0028	0.0220	-0.0383
31(H)	0.1647	0.1580	0.2081	0.0435	0.0066	0.0250	-0.0368
32(H)	0.0320	0.0213	0.0571	0.0252	0.0107	0.0179	-0.0145
33(H)	0.0319	0.0212	0.0561	0.0242	0.0107	0.0175	-0.0135
34(H)	0.1721	0.1527	0.2019	0.0298	0.0194	0.0246	-0.0105



E(N): -921.853866 Hartree

E(N+1): -921.825714 Hartree

E(N-1): -921.534994 Hartree

E_HOMO(N): -0.262581 Hartree, -7.1452 eV

E_HOMO(N+1): 0.111734 Hartree, 3.0404 eV

E_HOMO(N-1): -0.379397 Hartree, -10.3239 eV

Hardness (=fundamental gap): 0.347024 Hartree, 9.4430 eV

Softness: 2.881648 Hartree^-1, 0.1059 eV^-1

Electrophilicity index: 0.030444 Hartree, 0.8284 eV

Nucleophilicity index: 0.072617 Hartree, 1.9760 eV

Atom	q(N)	q(N+1)	q(N-1)	f^-	f^+	f^0	CDD
1(O)	-0.2581	-0.4188	-0.1507	0.1074	0.1608	0.1341	0.0534
2(O)	-0.2527	-0.4147	-0.1497	0.1030	0.1620	0.1325	0.0590
3(C)	0.0403	0.0203	0.0502	0.0099	0.0200	0.0150	0.0101
4(O)	-0.1105	-0.1691	-0.0811	0.0294	0.0586	0.0440	0.0292
5(C)	0.2048	0.0597	0.2398	0.0350	0.1451	0.0900	0.1101
6(C)	0.2031	0.0591	0.2380	0.0348	0.1440	0.0894	0.1092
7(O)	-0.1104	-0.1689	-0.0768	0.0335	0.0586	0.0461	0.0250
8(C)	0.0415	0.0231	0.0497	0.0082	0.0184	0.0133	0.0102
9(C)	-0.0489	-0.0537	-0.0441	0.0047	0.0048	0.0048	0.0001
10(C)	-0.0450	-0.0497	-0.0398	0.0052	0.0047	0.0049	-0.0004
11(C)	-0.0466	-0.0499	-0.0422	0.0044	0.0033	0.0038	-0.0011
12(C)	-0.0470	-0.0492	-0.0419	0.0051	0.0023	0.0037	-0.0028
13(C)	-0.0469	-0.0486	-0.0422	0.0047	0.0017	0.0032	-0.0030
14(C)	0.0262	0.0166	0.0455	0.0193	0.0095	0.0144	-0.0098
15(O)	-0.2411	-0.2585	-0.1625	0.0786	0.0174	0.0480	-0.0612
16(H)	0.0466	0.0242	0.0599	0.0133	0.0224	0.0178	0.0091
17(H)	0.0466	0.0242	0.0595	0.0129	0.0224	0.0176	0.0095
18(H)	0.0406	0.0200	0.0505	0.0099	0.0206	0.0152	0.0107
19(H)	0.0406	0.0200	0.0505	0.0099	0.0206	0.0152	0.0107
20(H)	0.0352	0.0273	0.0408	0.0056	0.0079	0.0067	0.0023
21(H)	0.0352	0.0273	0.0408	0.0056	0.0079	0.0067	0.0023
22(H)	0.0282	0.0225	0.0332	0.0050	0.0058	0.0054	0.0008
23(H)	0.0283	0.0225	0.0333	0.0050	0.0058	0.0054	0.0007
24(H)	0.0272	0.0235	0.0317	0.0045	0.0037	0.0041	-0.0008
25(H)	0.0272	0.0235	0.0317	0.0045	0.0037	0.0041	-0.0008
26(H)	0.0269	0.0241	0.0323	0.0054	0.0028	0.0041	-0.0026
27(H)	0.0269	0.0241	0.0323	0.0054	0.0028	0.0041	-0.0026
28(H)	0.0258	0.0238	0.0316	0.0058	0.0019	0.0039	-0.0039
29(H)	0.0258	0.0238	0.0316	0.0059	0.0019	0.0039	-0.0040
30(H)	0.0319	0.0213	0.0542	0.0222	0.0107	0.0165	-0.0115
31(H)	0.0319	0.0212	0.0551	0.0232	0.0107	0.0169	-0.0125
32(H)	0.1720	0.1527	0.1997	0.0276	0.0194	0.0235	-0.0083
33(C)	-0.0510	-0.0525	-0.0449	0.0061	0.0015	0.0038	-0.0045
34(H)	0.0317	0.0299	0.0432	0.0115	0.0018	0.0067	-0.0098
35(C)	0.0245	0.0228	0.0579	0.0334	0.0017	0.0176	-0.0318
36(H)	0.0317	0.0299	0.0431	0.0114	0.0018	0.0066	-0.0096
37(H)	0.0216	0.0200	0.0635	0.0418	0.0017	0.0217	-0.0402
38(H)	0.0216	0.0200	0.0647	0.0431	0.0017	0.0224	-0.0415
39(O)	-0.2496	-0.2532	-0.0952	0.1544	0.0036	0.0790	-0.1508
40(H)	0.1641	0.1597	0.2074	0.0434	0.0043	0.0238	-0.0391

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