Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information for

Rapid Copolymerization of Canola Oil Derived Epoxide Monomer with Anhydrides and Carbon Dioxide (CO_2)

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Summaries of Characteristic Signals from Spectroscopic Characterization:

FT-IR:

Entry	Anhydride	-COO-(cm^{-1})	-C=C-(cm^{-1})	C-O-C(cm^{-1}) [ester]	C-O-C(cm^{-1}) [ether]
1	MA	1727	1644	1207, 1157	-
2	SA	1734	-	1154	-
3	IA	1768, 1728	1653	1163	1123
4	THPA	1730	1656(weak)	1181	1112
5	PA	1723	1599, 1580, 1492,1459 (phenyl)	1121,1066	-

Table S1. Characteristic IR absorption of epoxide/anhydride copolymers.

^{1}H NMR:

Entry	Anhydride	-OCH-(ppm)	-OCH_2-(ppm)	-$OCHCH_2O$-(ppm)
1	MA	5.13	4.61-4.06	3.98-3.21
2	SA	5.07	4.36-4.01	3.88-3.17
3	IA	5.09	4.20	3.42
4	THPA	5.04	4.08	3.62
5	PA	5.32	4.45	3.90-3.20

Table S2. ^{1}H NMR Ester/ether peaks of epoxide/anhydride copolymer.

Characterizations of DMC Catalyst:

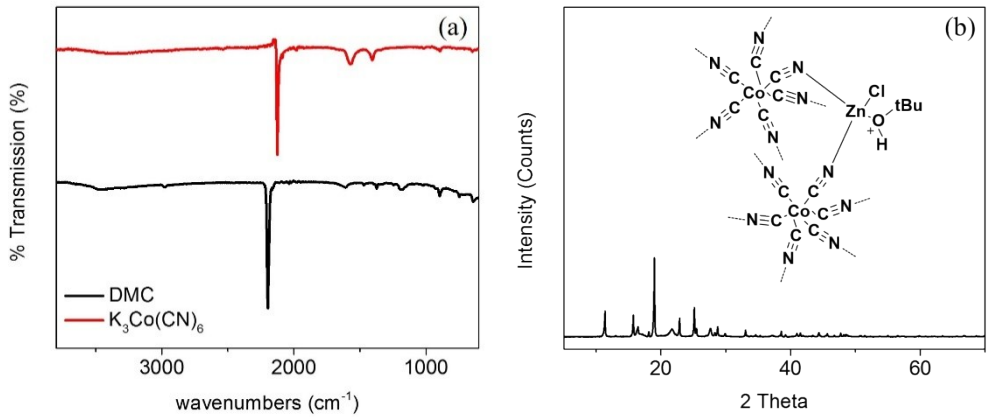
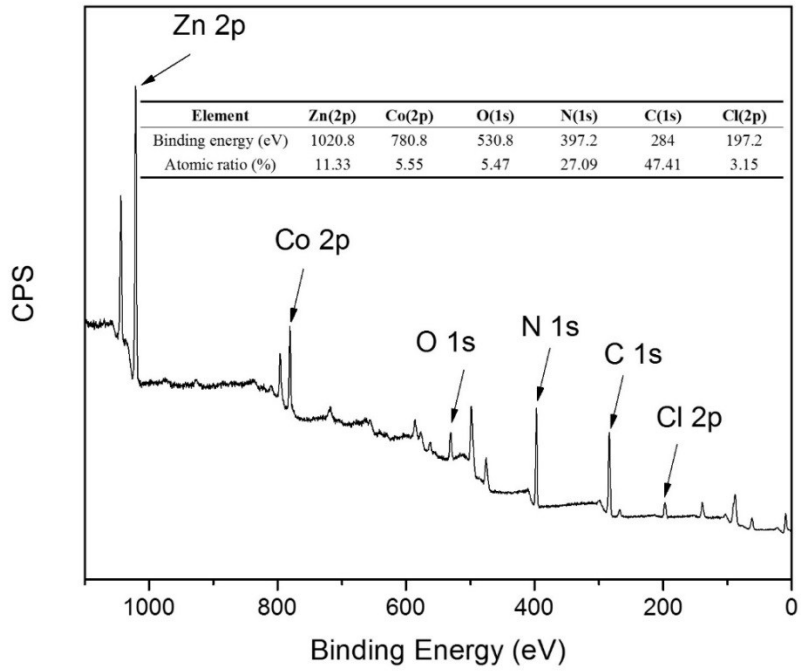


Figure S1. (a) ATR-FTIR spectra of DMC catalyst and $K_3Co(CN)_6$. (b) XRD patterns and proposed structure of DMC catalyst



Element	Zn(2p)	Co(2p)	O(1s)	N(1s)	C(1s)	Cl(2p)
Binding energy (eV)	1020.8	780.8	530.8	397.2	284	197.2
Atomic ratio (%)	11.33	5.55	5.47	27.09	47.41	3.15

Figure S2. XPS results of DMC catalyst.

Profiles:

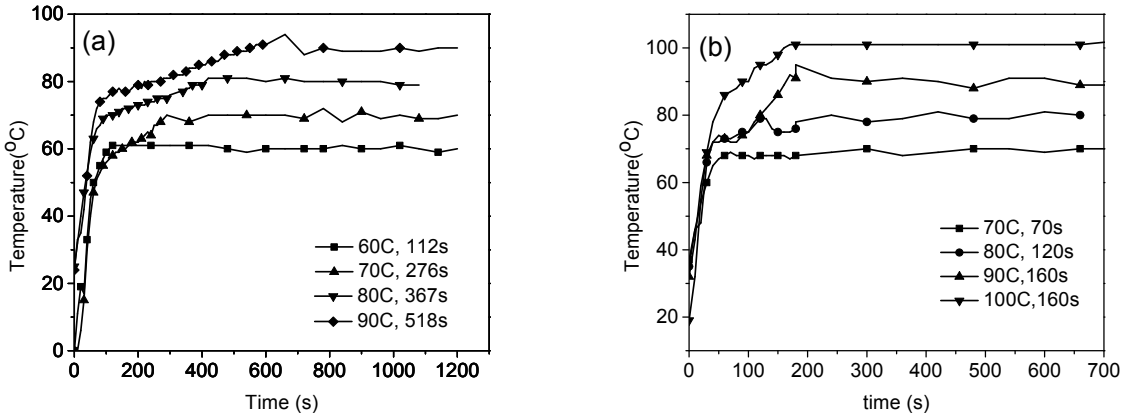


Figure S3 (a) Heat effect of microwave energy on epoxide/CO_2 reaction. 112s, 276s, 367s and 518s was necessary to achieve 60 °C, 70 °C, 80 °C, 90°C, respectively. (b) The temperature variation during microwave irradiated bulk polymerization of epoxide/MA.

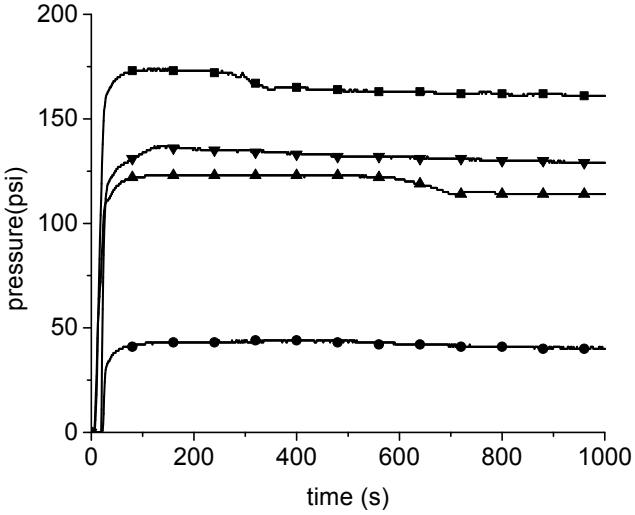


Figure S4. The pressure variation during microwave irradiated copolymerization of epoxide/CO_2.

Investigation of Copolymerization of CO_2 and Epoxide under Various Conditions:

Pressure:

Entry	Pressure(psi)	Conv (%)	Carbonate (%)	Mw[a] (kda)	PDI[a]	TON[b]	TOF[c]
1	76	91	18.3	10.381	1.38	640	3200
2	78	93	18.8	11.902	1.43	655	3275
3	82	88	34.7	11.249	1.87	620	3100
4	130	92	47.9	11.185	1.47	648	3240

Table S3. Microwave assisted copolymerization of 1,2-epoxydecane/CO_2 at 70°C for 12 min. a: Molecular weight was identified by GPC. b: Turn over number (TON) was defined as (moles of converted epoxide monomer/ moles of Zinc). c: Turn over frequency (TOF) = TON per hour. Similarly, the calculation of TONs and TOFs were also applied for the experiments recorded in the following tables.

Time:

Entry	Time(min)	Conv (%)	CC[a] (%)	Mw (kDa)	PDI	TON	TOF
1	6	92	2	10.1	1.69	648	6480
2	9	94	2	9.0	1.61	662	4413
3	12	93	2	11.9	1.43	655	3275
4	15	91	3	10.5	1.91	640	2560
5	27	98	3	8.8	1.54	690	1533
6	30	>99	11	7.3	1.75	697	1394
7[b]	2 h	-	-	-	-	-	-

Table S4. Microwave assisted copolymerization of 1,2-epoxydecane/CO_2 at 70°C for different time. a: percentage of cyclic carbonate estimated by ^{1}H NMR. b: no copolymer was observed after 2 h microwave-assisted reaction of epoxide/CO2 without DMC catalyst.

Temperature:

Entry	T(°C)	Conv (%)	Carbonate (%)	CC[a] (%)	Mw (kDa)	PDI	TON	TOF
1	60	55	80.6	<1	14.2	1.44	387	774
2	70	99	35.3	11	7.3	1.75	697	1394
3	80	97	32.3	6	7.8	1.84	683	1366
4	90	95	18.6	3	8.5	1.74	669	1338
5	100	94	22.3	1	9.2	1.68	662	1324

Table S5. Microwave assisted copolymerization of 1,2-epoxydecane/CO_2 for 30 min. a: percentages of cyclic carbonate (CC%) were estimated by ^{1}H NMR of crude products.

Solvents:

Entry	Solv	Conv (%)	Carbonate (%)	Mw (kDa)	PDI	TON	TOF
1	Hexane	52	87.7	15.2	1.30	366	732
2	THF	97	19.4	9.3	1.53	683	1366

Table S6. Microwave assisted copolymerization of 1,2-epoxydecane/CO_2 at 70°C for 30 min in different solvent.

Investigation of Copolymerization of Anhydrides and Epoxide under Various Conditions:

Temperature:

Entry	T(°C)	Time (min)	Conv[b] (%)	Ester (%)	Mw (kDa)	PDI	TON	TOF
1	90	10	-	-	-	-	-	-
2	80	20	100	82.3	8.151	1.23	704	2112
3	90	20	100	92.3	8.692	1.27	704	2112
4	100	10	100	91.1	8.212	1.28	704	4224
5	110	10	100	85.9	10.659	1.57	704	4224
6[a]	110	20	-	-	-	-	-	-
7[c]	90	5h	100	75.0	6.013	1.52	704	141
8[d]	80	1h	-	-	-	-	-	-

Table S7. Copolymerization of 1,2-epoxydecane/MA. a: insoluble polymer was obtained. b: the conversion was determined by the epoxide residue measured by ^{1}H NMR. c: the experiment was performed under conventional heating condition. d: the experiment was performed without DMC catalyst and no copolymer was observed after 1 h microwave-assisted reaction.

Catalyst Loading:

Entry	DMC loading	Time (min)	Conv (%)	Ester (%)	Mw (kDa)	PDI	TON	TOF
1	0.3mg	20	100	87.7	6.311	1.32	1408	4224
2	0.6mg	10	100	91.1	8.212	1.28	704	4224
3	0.9mg	10	100	90.5	8.421	1.25	469	2814

Table S8. Copolymerization of 1,2-epoxydecane/MA at 100°C.

Solvents:

Entry	Solv	Ester (%)	Mw (kDa)	PDI
1	Hexane	91.2	8.171	1.43
2	THF	69.3	7.336	1.17

Table S9. Copolymerization of 1,2-epoxydecane/MA for 20 min at 100°C in different solvents.

Epoxy to Anhydride Ratio:

Entry	Epoxy: MA	Ester (%)	Mw (kDa)	PDI
1	1.0:1.4	70.8	6.922	1.31
2	1.0:1.8	67.5	6.731	1.28

Table S10. Copolymerization of 1,2-epoxydecane/MA for 10 min at 100°C.

Temperatures of Polymer Degradation:

Entry	Anhydride	$T_{5\%}$(°C)	$T_{10\%}$(°C)	$T_{20\%}$(°C)	$T_{50\%}$(°C)
(a)	MA	308	330	348	372
(b)	SA	289	318	342	365
(c)	IA	282	308	334	367
(d)	PA	276	304	321	342
(e)	Isomerization of (a)	204	301	337	369
(f)	THPA	205	257	305	353

Table S11. Decomposition temperature (5%, 10%, 20%, 50% weight loss) for polyesters.

DSC Characterization of copolymers:

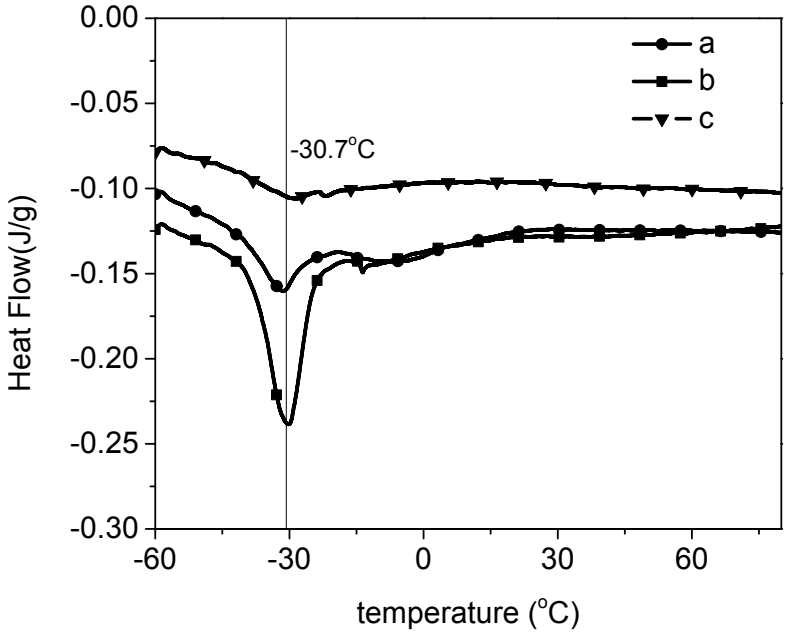


Figure S5. DSC curves(Exo up) of polymer contains different percentage of carbonate linkage. (a) Carbonate% = 35.3% (Entry 2, Table S5). (b) Carbonate% = 19.4% (Entry 2, Table S6). (c) Carbonate% = 87.7% (Entry 1, Table S6).

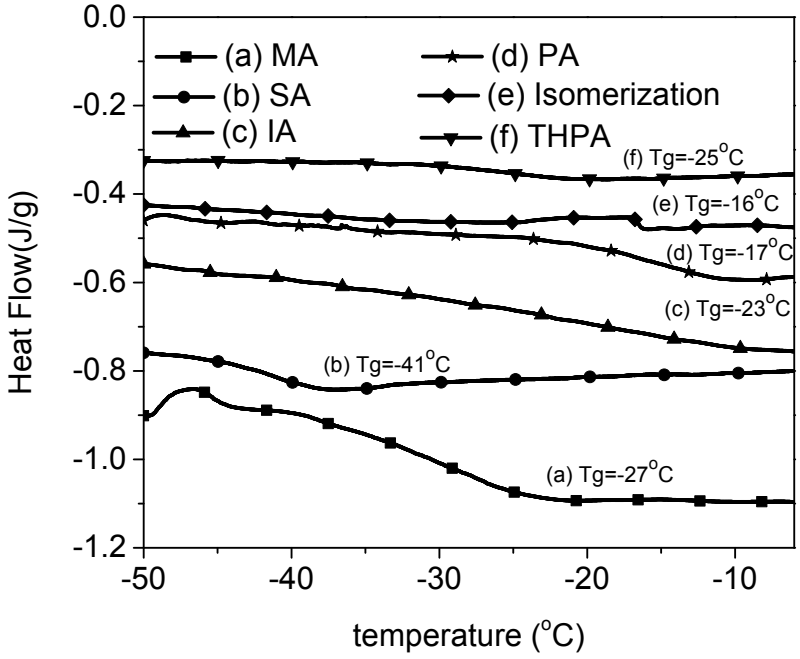


Figure S6. DSC curves (Exo up) of polyester using different anhydrides. The T_{gs} were determined by Universal Analysis 2000 Software automatically.