

## Diverse Chemically Recyclable Polymers by Cationic Vinyl and Ring-Opening Polymerizations of Cyclic Ketene Acetal Ester “Dehydroaspirin”

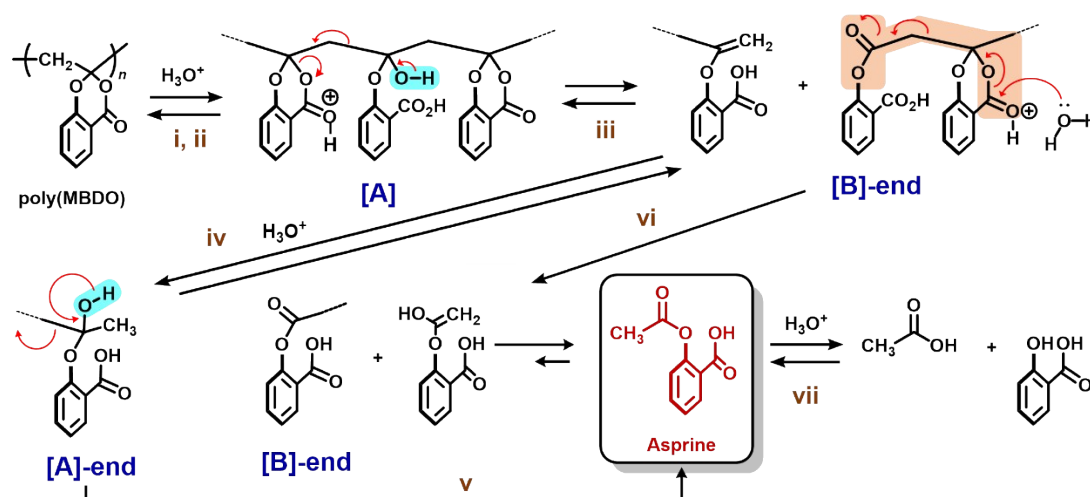
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### Electronic Supplementary Information

#### Proposed mechanism



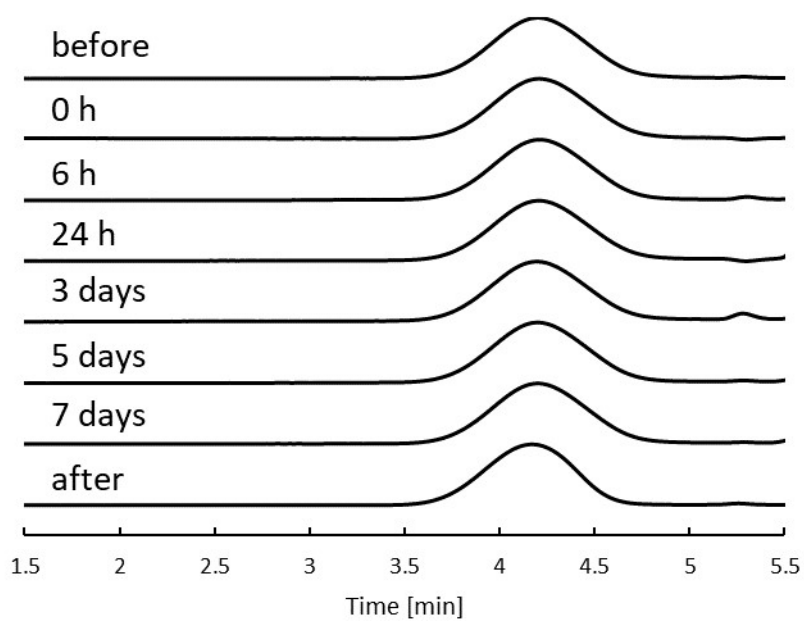
- i. A formation of hemiacetal [A] via hydrolysis of hemiacetal ester .
- ii. Protonation of the carbonyl group in neighboring unit.
- iii. Decomposition of hemiacetal [A] accompanying with main chain scission.
- iv. The formed exo-methylene accepts water addition to form hemiacetal [A]-end
- v. Elimination of aspirin from [A]-end
- vi. Hydrolysis of ester [B]-end to a similar [B]-end and aspirin in enol-form.
- vii. Hydrolysis of aspirin to acetic acid and salicylic acid

**Scheme S1.** Proposed mechanism of degradation of MBDO vinyl polymer.

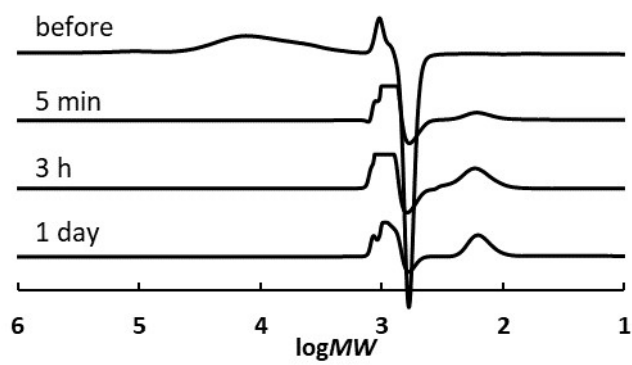
**Table S1.** Radical copolymerization of MBDO and MMA initiated by AIBN in toluene at 60 °C

Entry <sup>a</sup>	Feed <sup>b</sup>		<i>F</i>	Time [min]	Conv. [%] <sup>b</sup>			Yield [%] <sup>c</sup>		<i>f</i>	$\overline{F^2}$	$\overline{f}$	$\alpha$	$\eta$	$\xi$
	MBDO	MMA			MBDO	MMA	AV								
	[M <sub>1</sub> ] <sub>0</sub>	[M <sub>2</sub> ] <sub>0</sub>			[M <sub>1</sub> ]	[M <sub>2</sub> ]		[M <sub>1</sub> ]	[M <sub>2</sub> ]						
S1	90.8	9.16	9.92	60	5.81	38.5	22.1	2.10	50.8	49.2	1.03	95.3		0.0029	0.941
S2	70.9	29.1	2.43	120	4.56	36.9	20.7	5.06	29.2	70.8	0.412	14.3		-0.171	0.707
S3	51.4	48.6	1.06	180	1.00	30.5	15.7	11.8	16.8	83.2	0.202	5.55	5.95	-0.340	0.320
S4	31.6	68.4	0.462	180	1.27	28.8	15.0	18.6	10.4	89.6	0.116	1.85		-0.454	0.237
S5	10.4	89.6	0.116	180	7.72	33.4	20.5	20.5	3.47	96.5	0.0360	0.371		-0.490	0.059

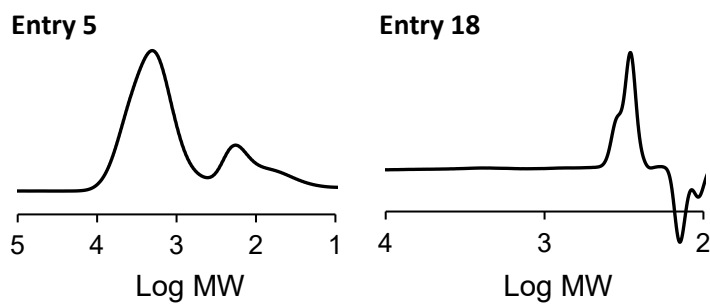
<sup>a</sup> [Monomer]<sub>0</sub>/[AIBN]<sub>0</sub> = 1/0.02., [M]= 1M. <sup>b</sup> Determined by <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C). <sup>c</sup> [Yield] = [Polymer Weight] / [Monomer Weight] × 100



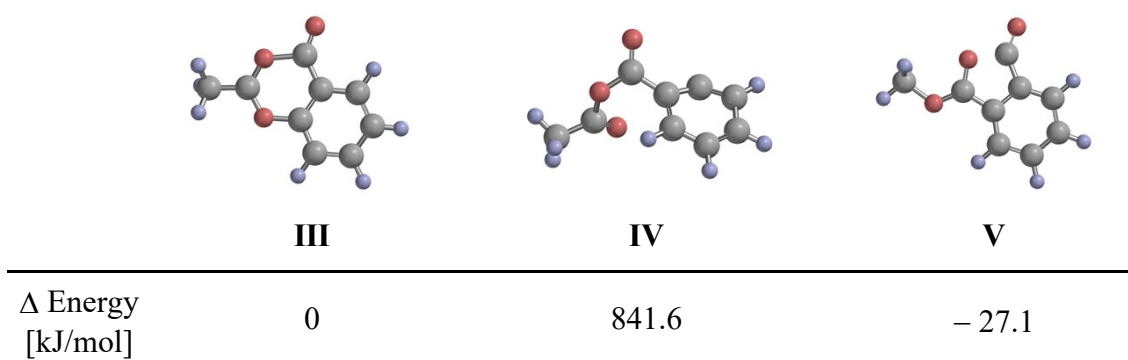
**Figure S1.** SEC spectra of acid hydrolysis of poly(MBDO-co-MMA). (40 °C, THF)



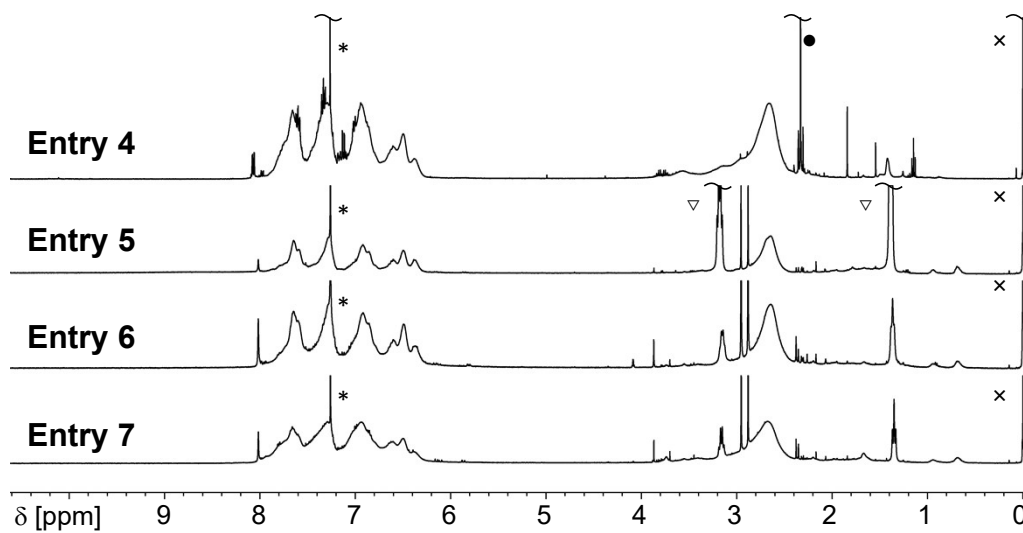
**Figure S2.** SEC spectra at each reaction time of base hydrolysis of vinyl poly(MBDO). (40 °C, DMF)



**Figure S3.** SEC curves of Entry 5 and 18 in Table 2. Entry 5 is THF-soluble fraction.

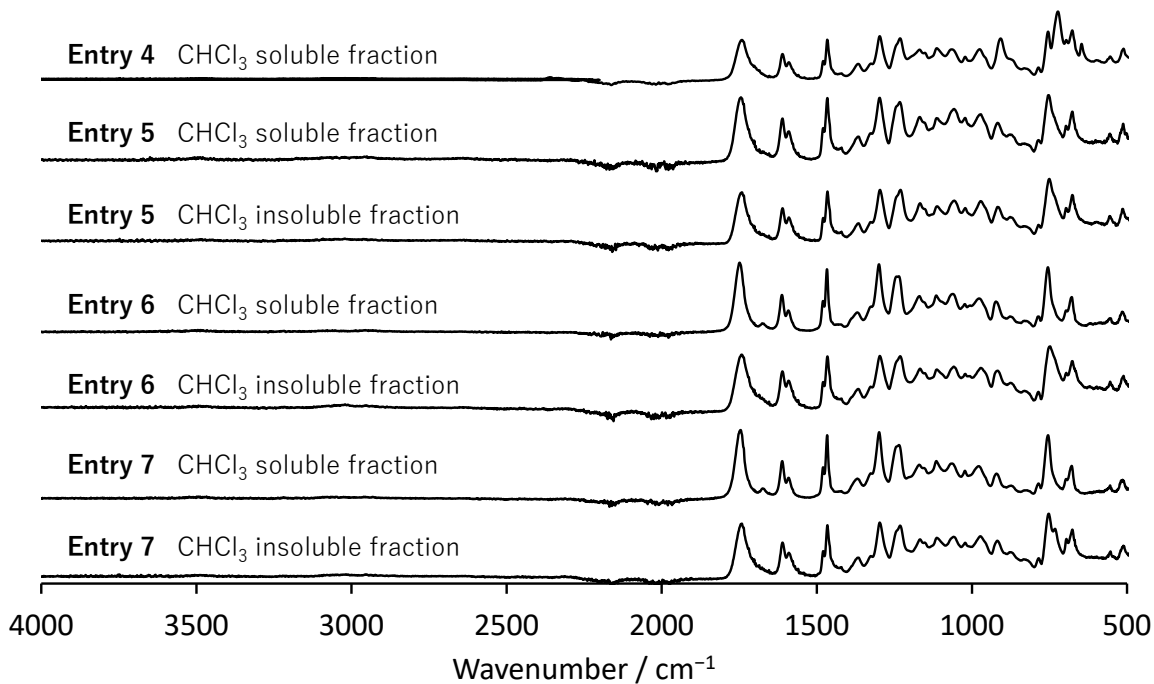


**Figure S4.** Structure of hemiacetal ester cation predicted by DFT calculation (B3LYP 6-31+G\*).

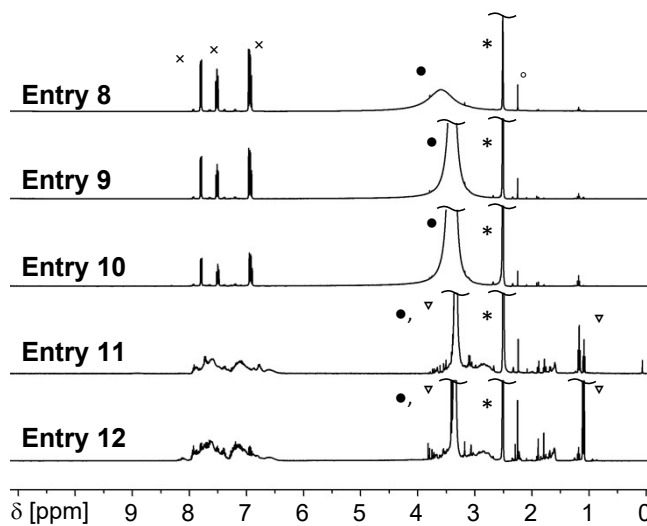


**Figure S5.**  $^1\text{H}$  NMR spectra of cationic polymerization of MBDO initiated by  $\text{BF}_3\text{Et}_2\text{O}$  and IBVE-OAc. (400 MHz, 26 °C,  $\text{CDCl}_3$ ).

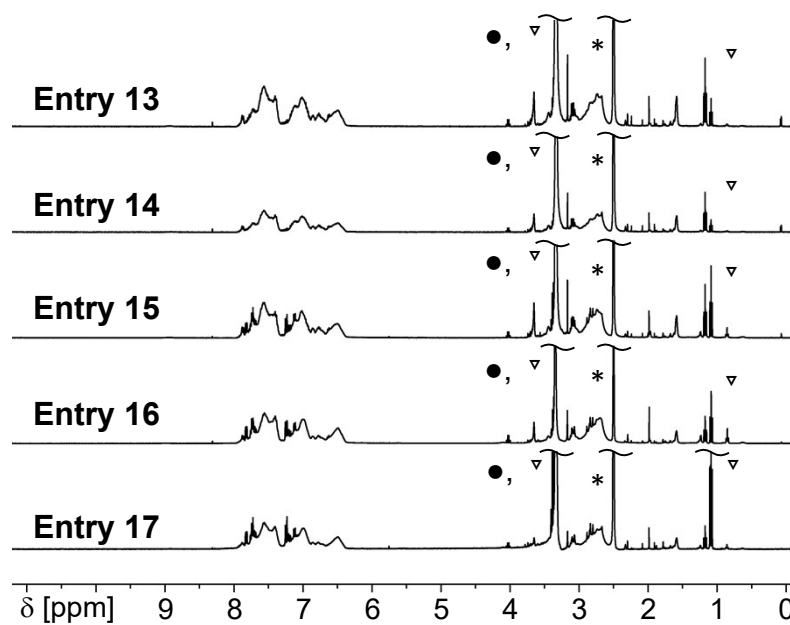
\*:  $\text{CHCl}_3$ , •: Acetone, ▽: diethyl ether, x: TMS.



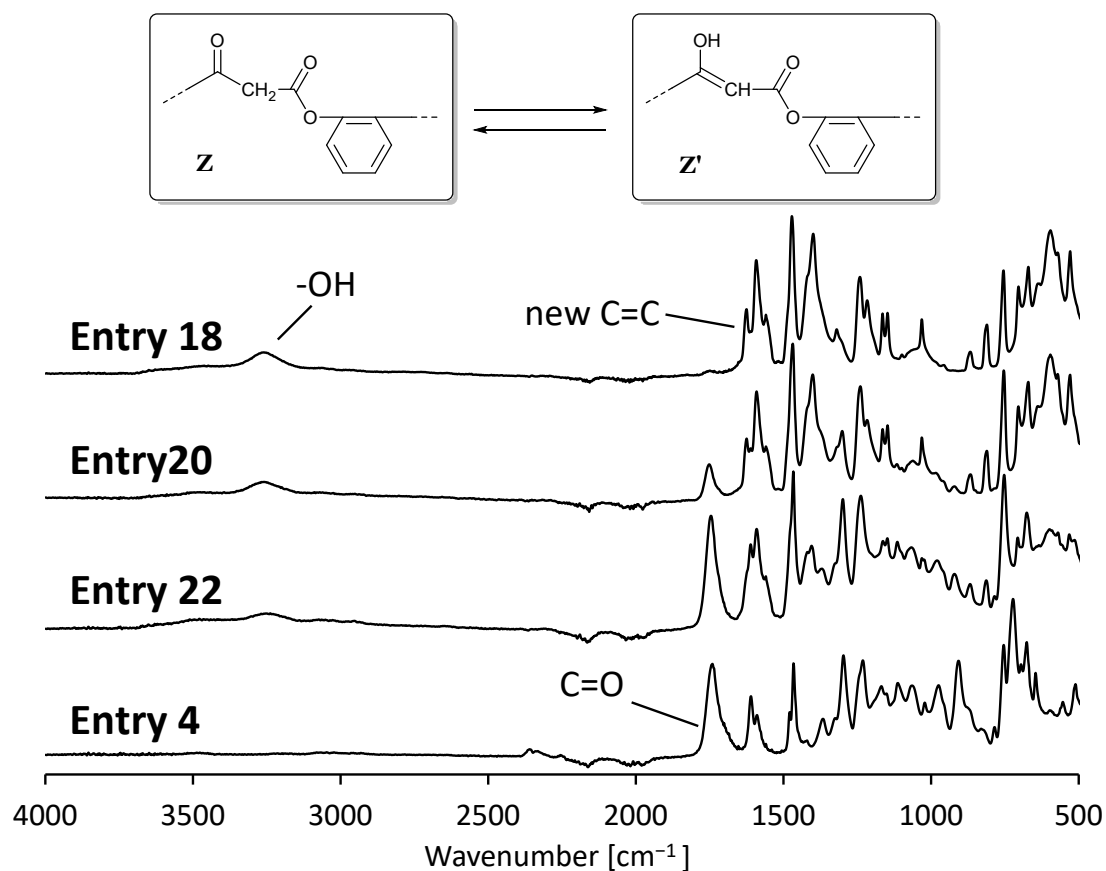
**Figure S6.** IR spectra of  $\text{CHCl}_3$  soluble and insoluble fraction of Entries 0-3.



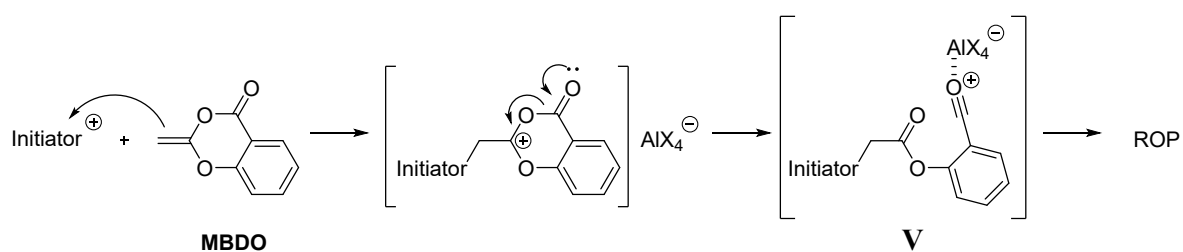
**Figure S7.**  $^1\text{H}$  NMR spectra of cationic polymerization of MBDO initiated by IBVE-OAc,  $\text{ZnCl}_2$  and ethyl acetate (400 MHz, 26 °C,  $\text{DMSO}-d_6$ ). \*:DMSO, •:water, °:acetic acid, ▽ :diethyl ether, x: salicylic acid.



**Figure S8.**  $^1\text{H}$  NMR spectra of cationic polymerization of MBDO initiated by IBVE-OAc,  $\text{SnCl}_4$  and ethyl acetate (400 MHz, 26 °C,  $\text{DMSO-}d_6$ ). \*: DMSO, ●: water, ▽: diethyl ether.



**Figure S9.** IR spectra of cationic polymerization of MBDO initiated by IBVE-OAc, EtAlCl<sub>2</sub> and ethyl acetate

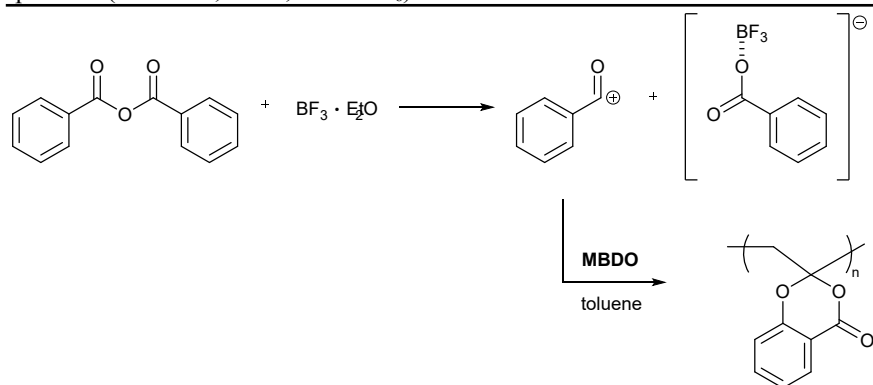


**Scheme S2.** Cationic polymerization of MBDO initiated with IBVE-OAc and EtAlCl<sub>2</sub> in the presence of ethyl acetate in toluene.

**Table S2.** Cationic polymerization of MBDO initiated with IBVE-OAc and EtAlCl<sub>2</sub> in the presence of ethyl acetate in toluene.

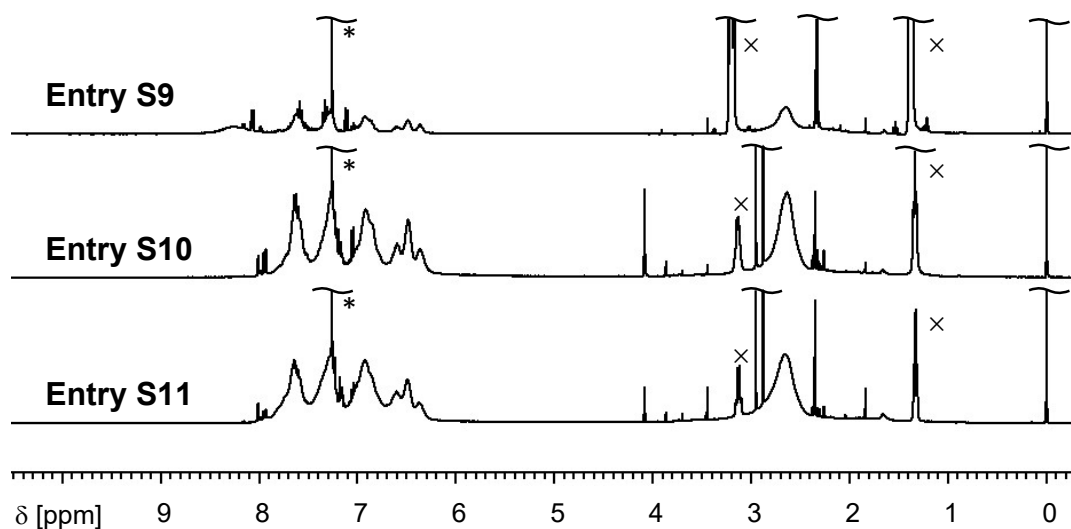
Entry	Temp [°C]	Conv. <sup>a</sup> [%]	Yield [%]	$M_n^b$	$\bar{D}^b$	ROP <sup>c</sup> [%]
18	− 78	53.8	4.3	1600	1.21	100
S6	− 63	60.9	2.4	N. D.	N. D.	100
19	− 40	35.3	3.3	1700	1.21	100
S7	− 20	31.4	2.2	600 <sup>d</sup>	1.06 <sup>d</sup>	100
20	□ □ 0	35.1	10.0	1600 <sup>d</sup>	1.24 <sup>d</sup>	73.4
21	□ □ 25	28.2	11.3	1800 <sup>d</sup>	1.36 <sup>d</sup>	49.7
22	□ □ 40	23.4	07.9	1800 <sup>d</sup>	1.43 <sup>d</sup>	42.2
S8	□ □ 60	44.1	02.2	1400 <sup>d</sup>	1.53 <sup>d</sup>	45.9

<sup>a</sup>Determined by GC. <sup>b</sup>Determined by SEC (40.0 °C, THF). <sup>c</sup>Determined by <sup>13</sup>C NMR spectrum (100 MHz, 25 °C, DMSO-*d*<sub>6</sub>). <sup>d</sup>Insoluble in THF.



**Scheme S3.** Cationic polymerization of MBDO initiated with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  and benzoic anhydride in toluene.





**Figure S10.**  $^1\text{H}$  NMR spectra of the polymers obtained via cationic polymerization of MBDO initiated with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  and benzoic anhydride in toluene. (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ). \*:  $\text{CDCl}_3$ , x: diethyl ether.

**Table S3.** Cationic polymerization of MBDO initiated with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  and benzoic anhydride in toluene.

Entry	Temp [ $^\circ\text{C}$ ]	Conv. <sup>a</sup> [%]	Yield [%]	$M_n^b$	$\bar{D}^b$
S9	− 78	19.9	14.9	2000 <sup>d</sup>	1.23 <sup>d</sup>
S10	0	38.5	32.8	1200 <sup>d</sup>	1.07 <sup>d</sup>
S11	40	70.0	14.9	1700 <sup>d</sup>	1.46 <sup>d</sup>

<sup>a</sup>Determined by GC. <sup>b</sup>Determined by SEC(40.0  $^\circ\text{C}$ , THF). <sup>c</sup>Determined by  $^{13}\text{C}$  NMR spectrum(400 MHz, 25  $^\circ\text{C}$ ,  $\text{DMSO}-d_6$ ). <sup>d</sup>Insoluble in THF.