

Supporting Information

Pseudoperiodic “Living” and/or Controlled Cationic Ring-Opening Copolymerization of Oxetane with Tetrahydropyran: Microstructure of Polymers vs Kinetics of Chains Growth

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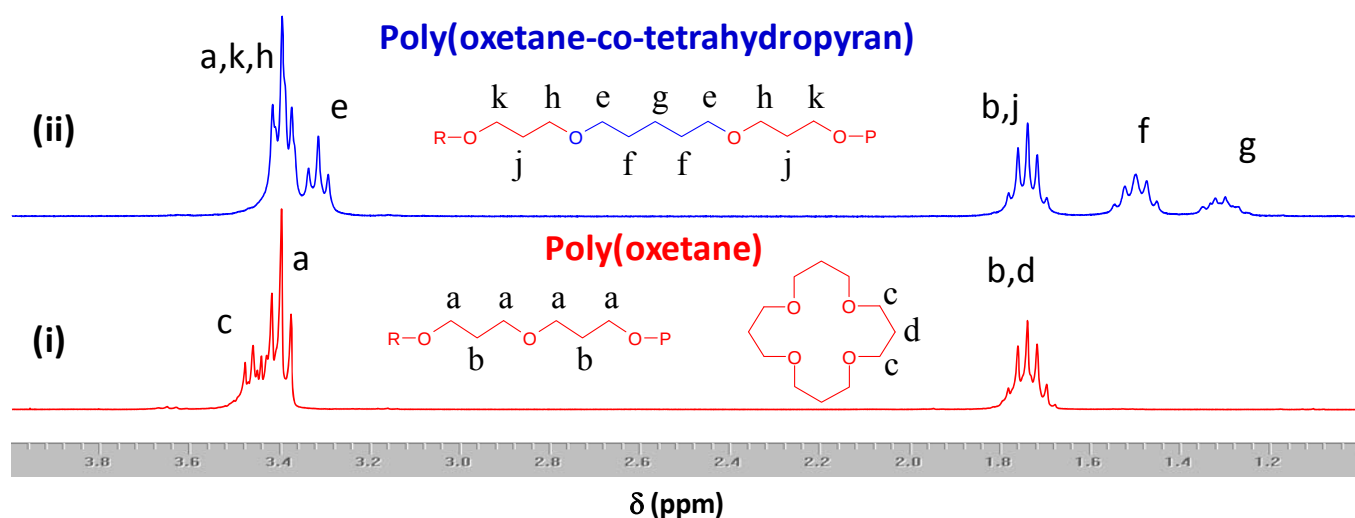


Figure S1 300 MHz ¹H NMR spectra of (i) poly(oxetane) synthesized in dichloromethane at 35°C using BF₃CH₃OH as initiating system and (ii) poly(oxetane-co-tetrahydropyran) synthesized in tetrahydropyran at 35°C with ethoxymethyl 1-oxoniacyclohexane hexafluoroantimonate (EMOA) as initiating system and 2,6-di-tert-butylpyridine (DtBP) as a non-nucleophilic proton trap. Experimental conditions: (i) Conversion = 80 % (t = 19 min), [Ox]₀ = 1 M and [BF₃:CH₃OH]₀ = 7.7 mM ;³⁹ (ii) (conversion) $x_{19h}^{Ox} = 80.3\%$, (copolymer composition in THP fragment in mole) $F_{THP} = 24.5\%$, (number-average molecular weight) $M_{n(GPC)} = 73\,000\text{ g mol}^{-1}$ and (molecular weight distribution) $M_w/M_n = 1.35$ for [Ox]₀ = 1.452 M, [THP]₀ = 9.2 M, [EMOA]₀ = 1.115 mM and [DtBP]₀ = 1.125 mM (Sample S2.8, Table S1 in Supporting Information). 75 MHz ¹³C chemical shift δ (ppm) of -CH₂- group in poly(oxetane) and poly(oxetane-co-tetrahydropyran) are listed in the Table S4. Reference 39: Bouchékif, H.; Philbin, M. I.; Colclough, E.; Amass, A. J. *Macromolecules* **2008**, *41*, 1989-95.

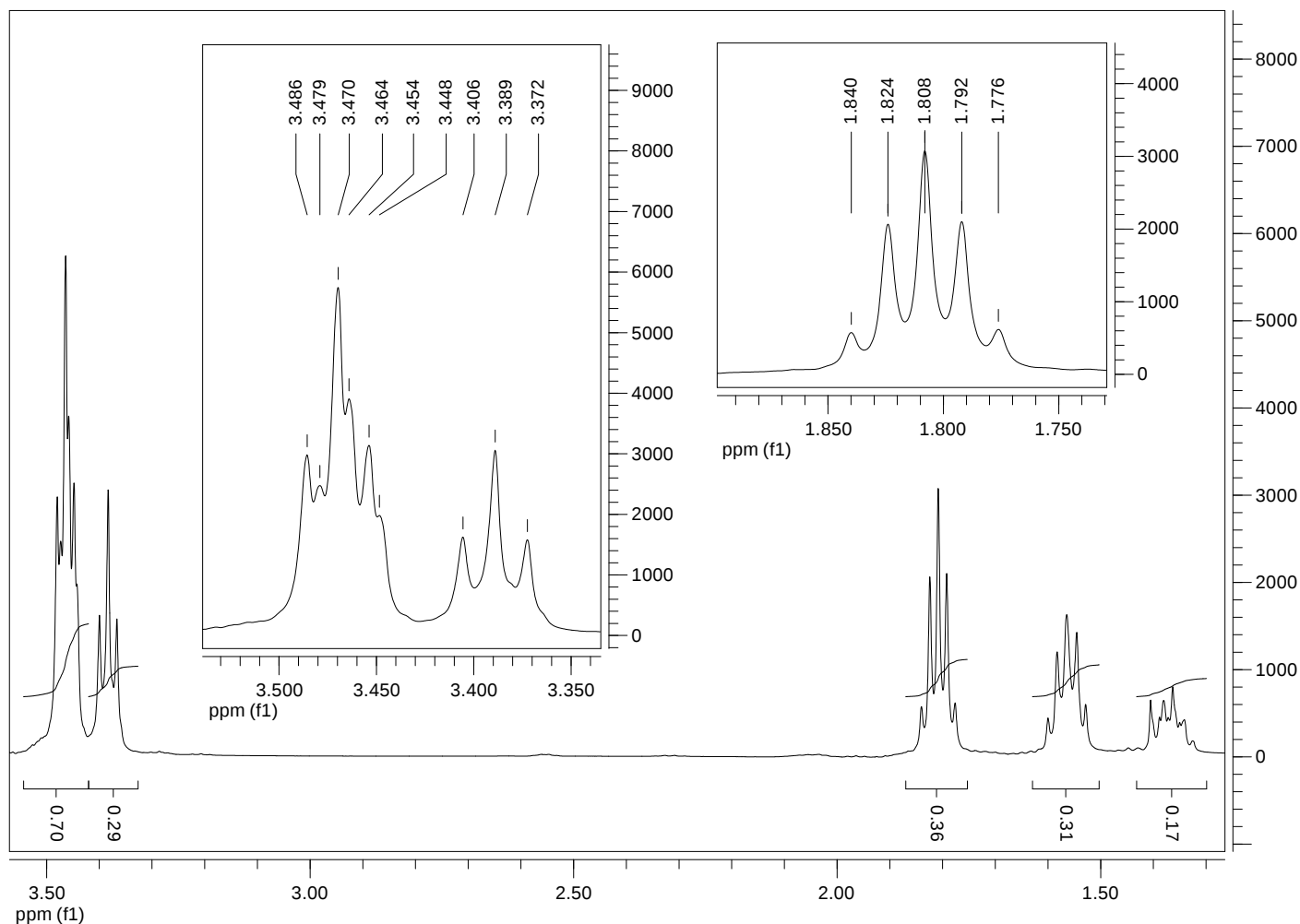


Figure S2. 300 MHz ^1H NMR spectra of poly(oxetane-co-tetrahydropyran) synthesized in tetrahydropyran at 35°C with ethoxymethyl 1-oxoniacyclohexane hexafluoroantimonate (EMOA) as initiating system and 2,6-di-tert-butylpyridine (DtBP) as a non-nucleophilic proton trap. Experimental conditions: (conversion) $x^{\text{Ox}} = 4\%$, (copolymer composition in THP fragment in mole) $F_{\text{THP}} = 29,2 \%$, (number-average molecular weight) $M_{\text{n(GPC)}} = 7300 \text{ g mol}^{-1}$ and (molecular weight distribution) $M_{\text{w}}/M_{\text{n}} = 1.6$ for $[\text{Ox}]_0 = 0.25 \text{ M}$, $[\text{THP}]_0 = 20 \text{ M}$, $[\text{EMOA}]_0 = 1.115 \text{ mM}$ and $[\text{DtBP}]_0 = 1.17 \text{ mM}$ (Sample S7.1, Table S2 in Supporting Information). 300 MHz ^1H chemical shift δ (ppm) of $-\text{CH}_2-$ group in poly(oxetane) and poly(oxetane-co-tetrahydropyran) are listed in the Table S4.

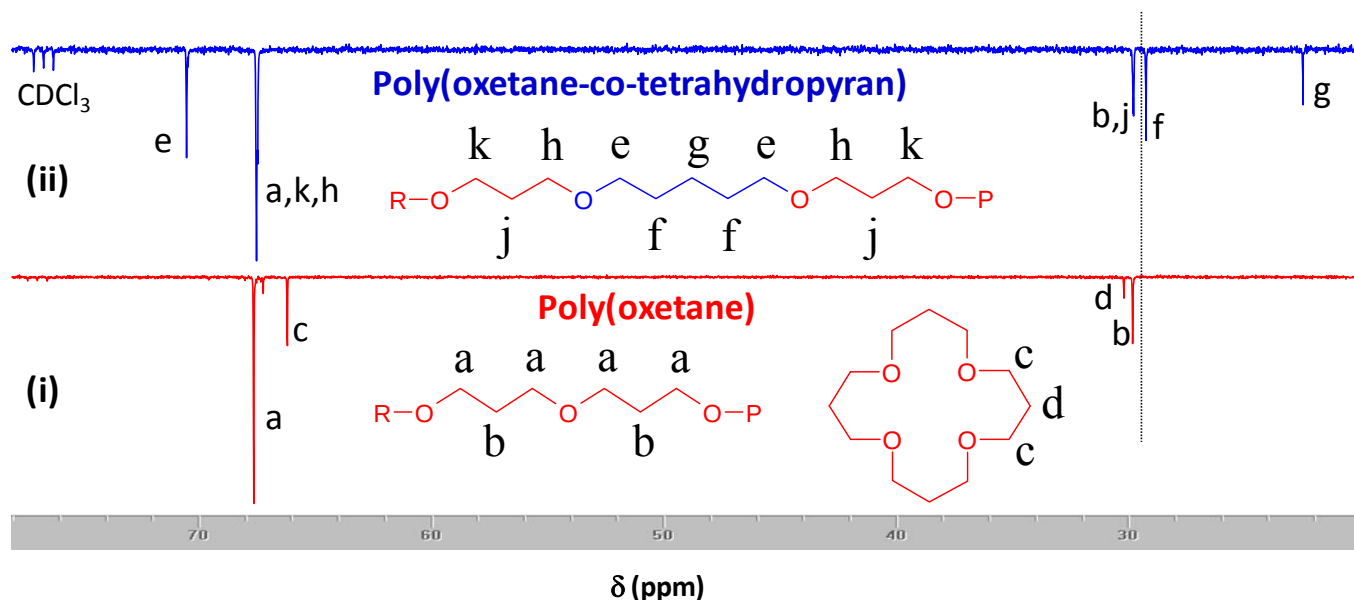


Figure S3. 75 MHz ¹³C NMR spectra of (i) poly(oxetane) synthesized in dichloromethane at 35°C using BF₃CH₃OH as initiating system and (ii) poly(oxetane-co-tetrahydropyran) synthesized in tetrahydropyran at 35°C with ethoxymethyl 1-oxoniacyclohexane hexafluoroantimonate (EMOA) as initiating system and 2,6-di-tert-butylpyridine (DtBP) as a non-nucleophilic proton trap. Experimental conditions: (i) Conversion = 80 % (t = 19 min), [Ox]₀ = 1 M and [BF₃:CH₃OH]₀ = 7.7 mM;³⁹ (ii) (conversion) x_{19h}^{Ox} = 83%, (copolymer composition in THP fragment in mole) F_{THP} = 24.5 %, (number-average molecular weight) M_{n(GPC)} = 73 000 g mol⁻¹ and (molecular weight distribution) M_w/M_n = 1.35 for [Ox]₀ = 1.452 M, [THP]₀ = 9.2 M, [EMOA]₀ = 1.115 mM and [DtBP]₀ = 1.125 mM (Sample S2.8, Table S1 in Supporting Information). 75 MHz ¹³C chemical shift δ (ppm) of -CH₂- group in poly(oxetane) and poly(oxetane-co-tetrahydropyran) are listed in the Table S4. Reference 39: Bouchékif, H.; Philbin, M. I.; Colclough, E.; Amass, A. J. *Macromolecules* **2008**, *41*, 1989-95.

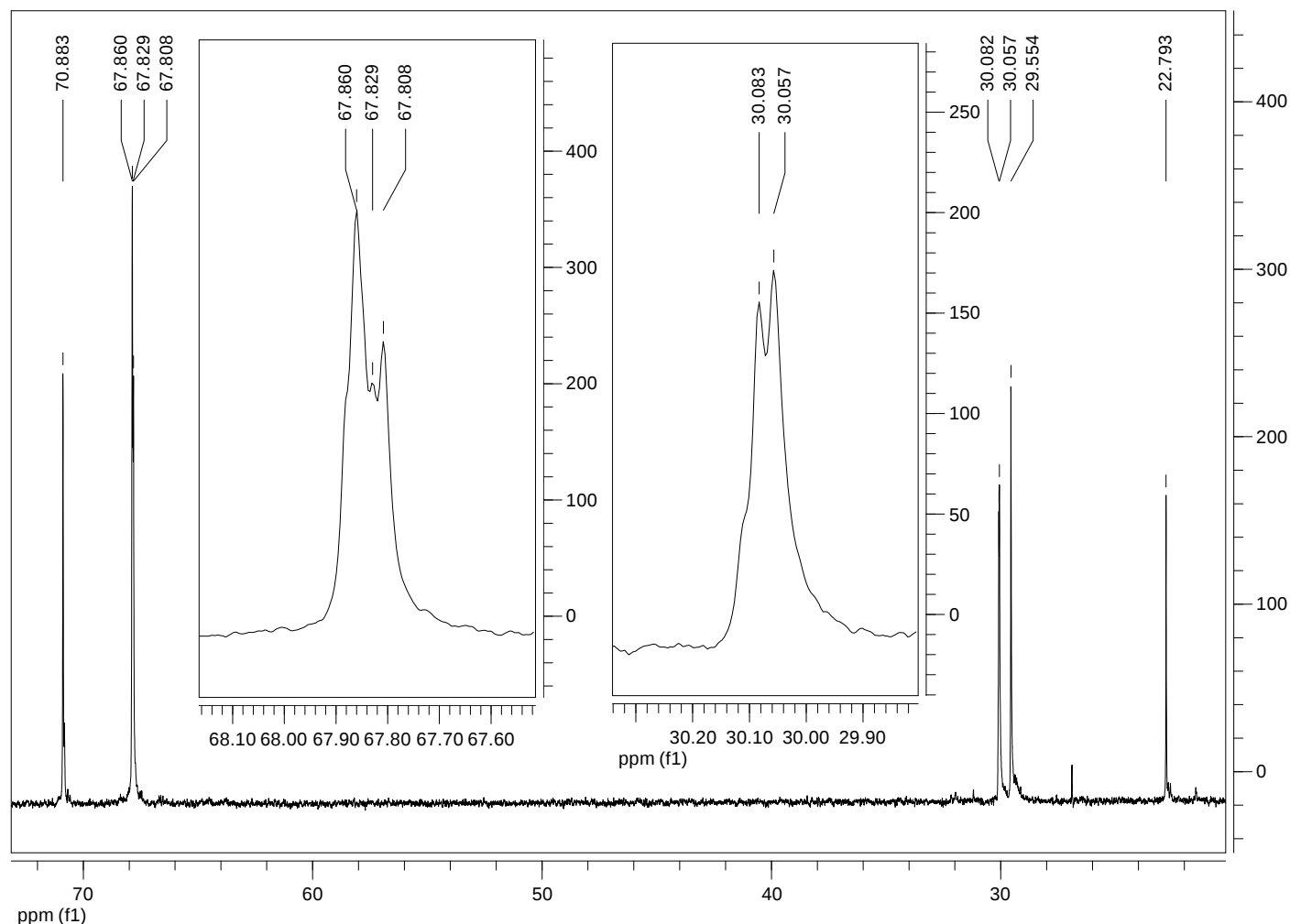


Figure S4. 75 MHz ^{13}C NMR spectra of poly(oxetane-co-tetrahydropyran) synthesized in tetrahydropyran at 35°C with ethoxymethyl 1-oxoniacyclohexane hexafluoroantimonate (EMOA) as initiating system and 2,6-di-tert-butylpyridine (DtBP) as a non-nucleophilic proton trap. Experimental conditions: (conversion) $x^{\text{Ox}} = 4\%$, (copolymer composition in THP fragment in mole) $F_{\text{THP}} = 29,2\%$, (number-average molecular weight) $M_{\text{n(GPC)}} = 7300 \text{ g mol}^{-1}$ and (molecular weight distribution) $M_{\text{w}}/M_{\text{n}} = 1.6$ for $[\text{Ox}]_0 = 0.25 \text{ M}$, $[\text{THP}]_0 = 20 \text{ M}$, $[\text{EMOA}]_0 = 1.115 \text{ mM}$ and $[\text{DtBP}]_0 = 1.17 \text{ mM}$ (Sample S7.1, Table S2 in Supporting Information). ^{13}C chemical shift δ (ppm) of $-\text{CH}_2-$ group in poly(oxetane) and poly(oxetane-co-tetrahydropyran) are listed in the Table S4.

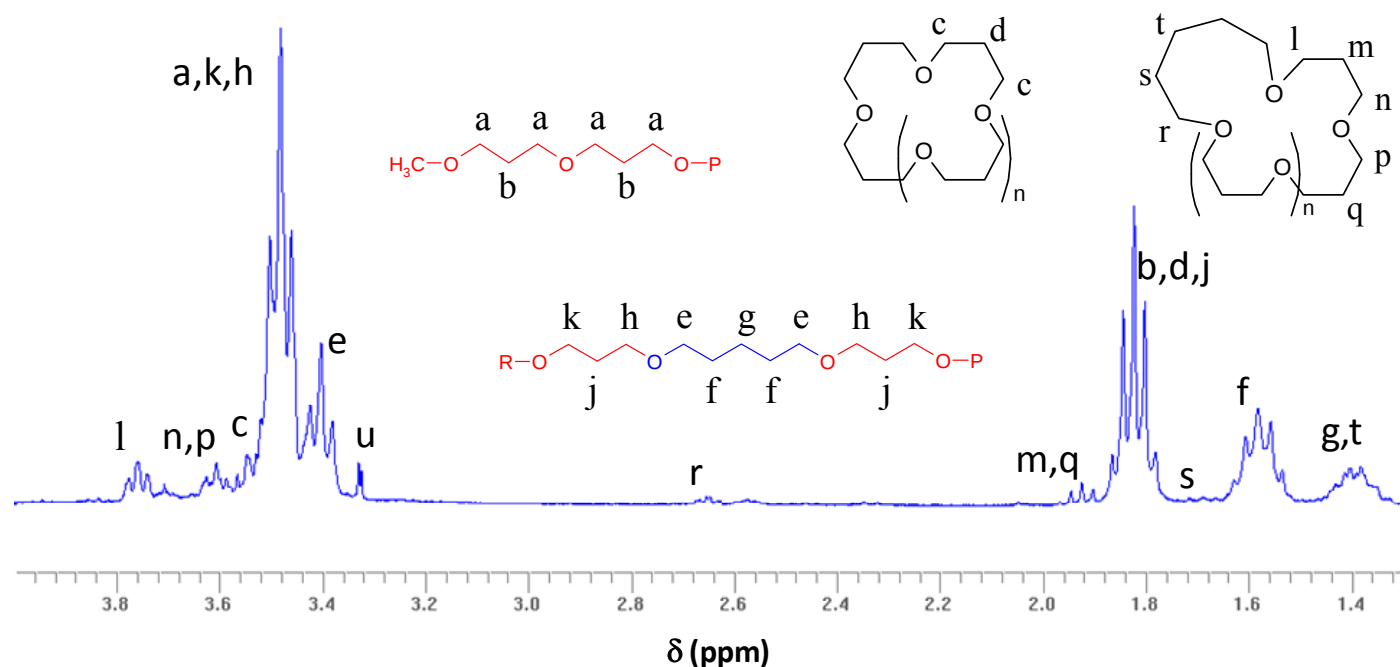


Figure S5 300 MHz ^1H NMR spectra of poly(oxetane-co-tetrahydropyran) synthesized in tetrahydropyran at 35°C with $(\text{BF}_3\text{CH}_3\text{OH})_{\text{THP}}$ as initiating system. Experimental conditions: (conversion) $x^{\text{Ox}} = 77\%$, (copolymer composition in THP fragment in mole) $F_{\text{THP}} = 24\%$, (number-average molecular weight) $M_{\text{n(GPC)}} = 7900 \text{ g mol}^{-1}$ and (molecular weight distribution) $M_{\text{w}}/M_{\text{n}} = 1.85$ for $[\text{Ox}]_0 = 1 \text{ M}$, $[\text{THP}]_0 = 9.6 \text{ M}$, $[\text{BF}_3\text{CH}_3\text{OH}]_0 = 0.7 \text{ mM}$ (Sample S5.8, Table S3 in Supporting Information). 300 MHz ^1H chemical shift δ (ppm) of $-\text{CH}_2-$ group in poly(oxetane) and poly(oxetane-co-tetrahydropyran) are listed in the Table S4.

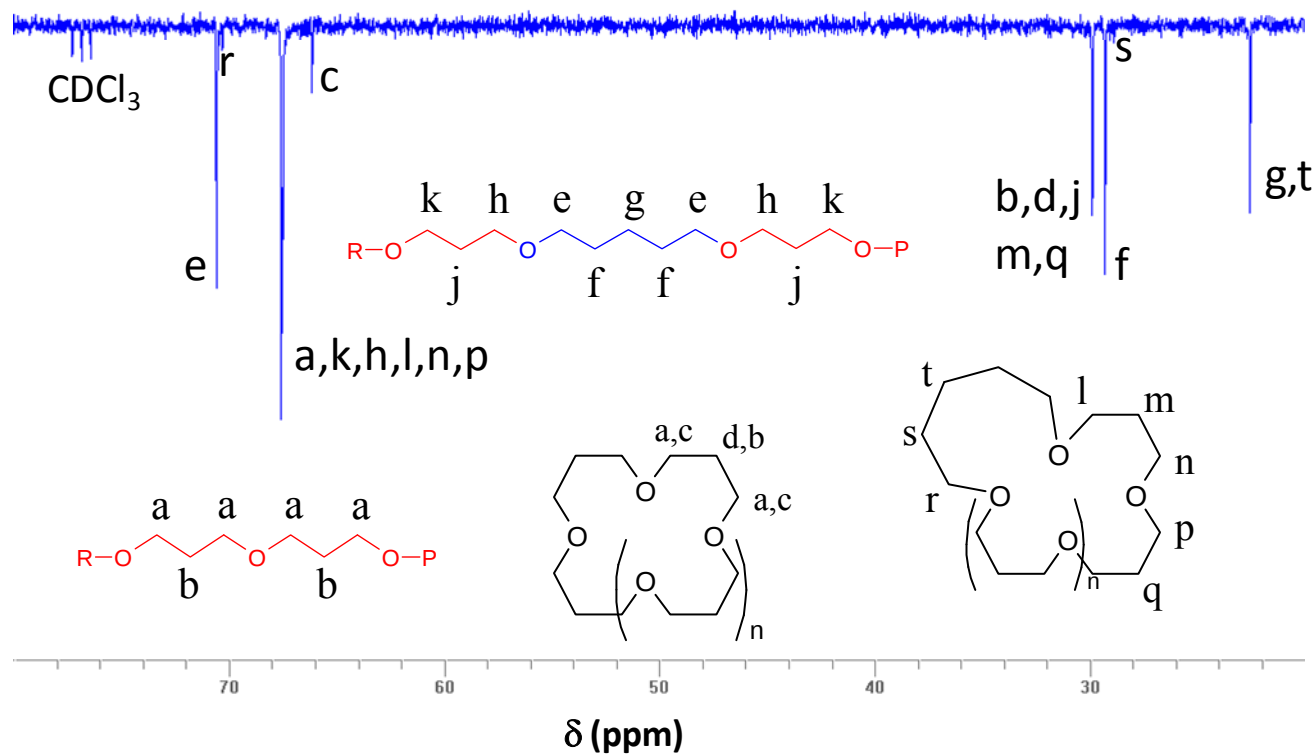


Figure S6 75 MHz ^{13}C NMR spectra of poly(oxetane-co-tetrahydropyran) synthesized in tetrahydropyran at 35°C with $(\text{BF}_3\text{CH}_3\text{OH})_{\text{THP}}$ as initiating system. Experimental conditions: (conversion) $x^{\text{Ox}} = 77\%$, (copolymer composition in THP fragment in mole) $F_{\text{THP}} = 24\%$, (number-average molecular weight) $M_{\text{n(GPC)}} = 7900 \text{ g mol}^{-1}$ and (molecular weight distribution) $M_{\text{w}}/M_{\text{n}} = 1.85$ for $[\text{Ox}]_0 = 1 \text{ M}$, $[\text{THP}]_0 = 9.6 \text{ M}$, $[\text{BF}_3\text{CH}_3\text{OH}]_0 = 0.7 \text{ mM}$ (Sample S5.8, Table S3 in Supporting Information). 75 MHz ^{13}C chemical shift δ (ppm) of $-\text{CH}_2-$ group in poly(oxetane) and poly(oxetane-co-tetrahydropyran) are listed in the Table S4.

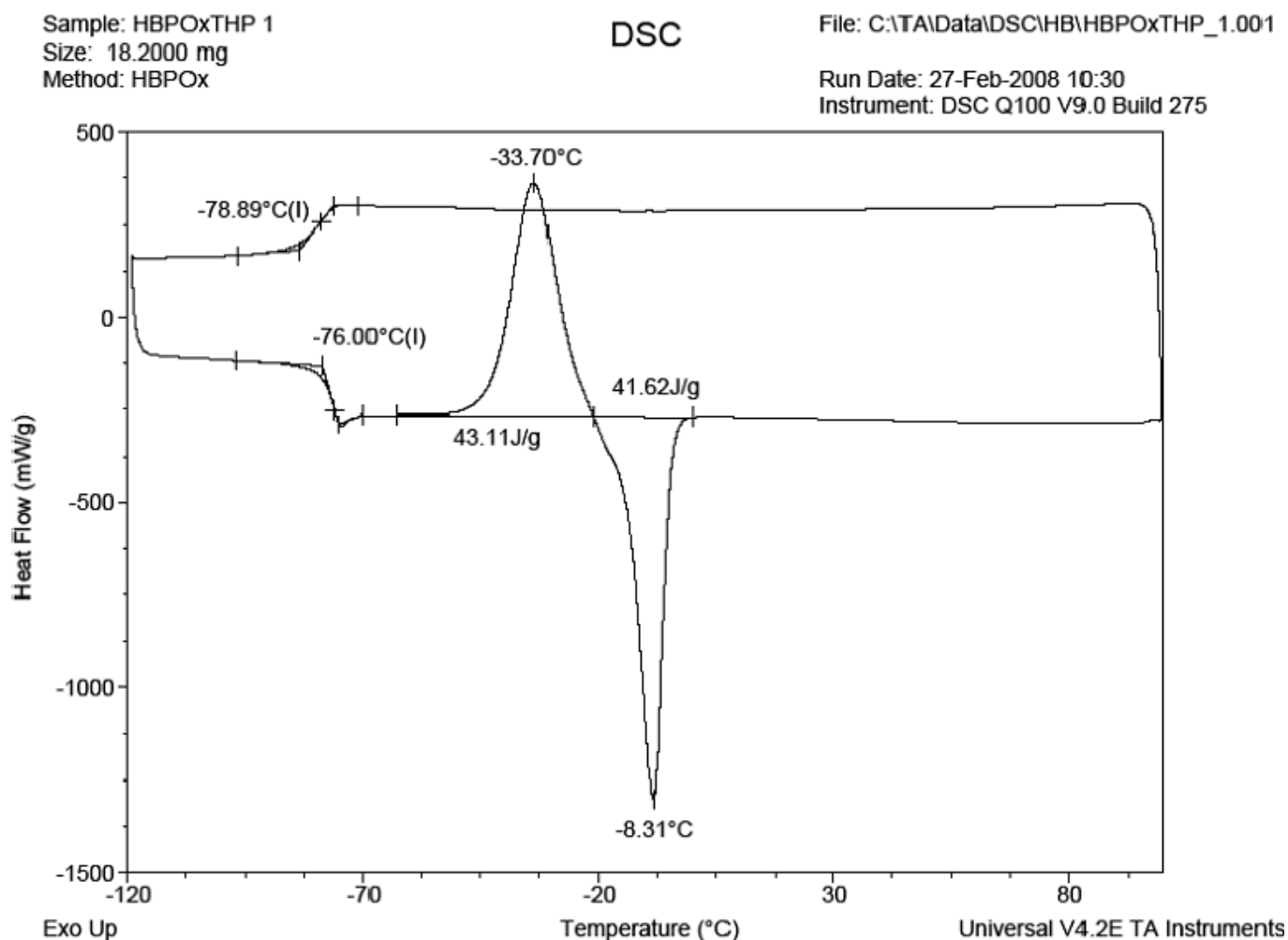


Figure S7.1 DSC thermogram of poly(oxetane-co-tetrahydropyran). Experimental conditions: (conversion) $x^{\text{Ox}} = 35.5\%$, (copolymer composition in THP fragment in mole) $F_{\text{THP}} = 15.7\%$, (number-average molecular weight) $M_{\text{n(GPC)}} = 41\,400\text{ g mol}^{-1}$ and (molecular weight distribution) $M_{\text{w}}/M_{\text{n}} = 1.28$ for $[\text{Ox}]_0 = 1.81\text{ M}$, $[\text{THP}]_0 = 9\text{ M}$, $[\text{EMOA}]_0 = 1.115\text{ mM}$ and $[\text{DtBP}]_0 = 1.17\text{ mM}$ (Sample S1.3, Table S1 in Supporting Information). Temperature range from -120 to 100°C at the heating and cooling temperature of $10^\circ\text{C min}^{-1}$. Data analysis was performed using Rheology Advantage Data analysis version 5.1.4.2.

Sample: HBPOxTHP 2
Size: 20.5000 mg
Method: HB

DSC

File: C:\TA\Data\DSC\HB\HBPOxTHP_2.001

Run Date: 27-Feb-2008 13:26

Instrument: DSC Q100 V9.0 Build 275

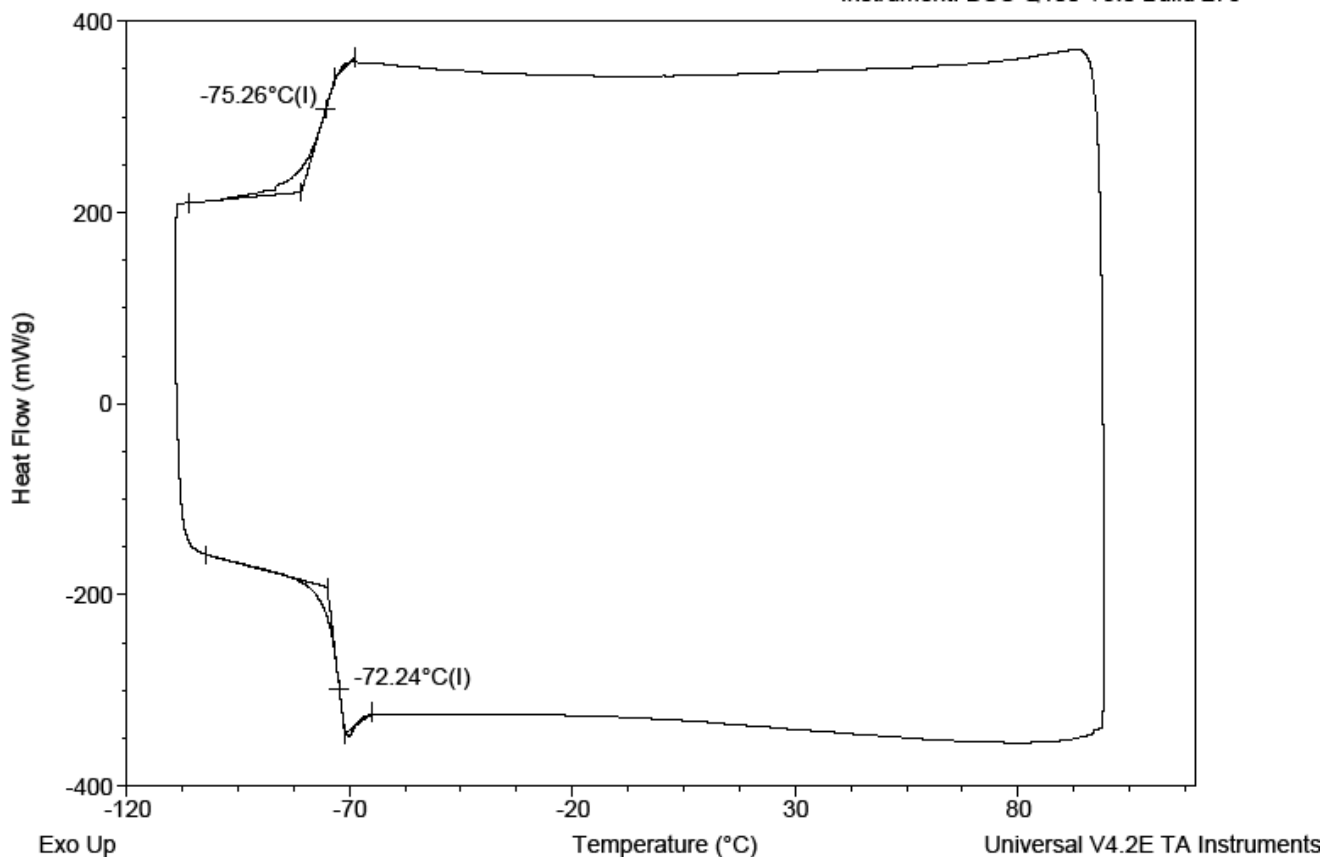


Figure S7.2 DSC thermogram of poly(oxetane-co-tetrahydropyran). Experimental conditions: (conversion) $x^{\text{Ox}} = 84\%$, (copolymer composition in THP fragment in mole) $F_{\text{THP}} = 23.4\%$, (number-average molecular weight) $M_{n(\text{GPC})} = 33\,430\text{ g mol}^{-1}$ and (molecular weight distribution) $M_w/M_n = 1.41$ for $[\text{Ox}]_0 = 1.452\text{ M}$, $[\text{THP}]_0 = 9.1\text{ M}$, $[\text{EMOA}]_0 = 1.115\text{ mM}$ and $[\text{DtBP}]_0 = 1.17\text{ mM}$ (Sample S3.8, Table S2 in Supporting Information). Temperature range from -120 to 100°C at the heating and cooling temperature of $10^\circ\text{C min}^{-1}$. Data analysis was performed using Rheology Advantage Data analysis version 5.1.4.2.

Sample: HBPOX
Size: 15.3000 mg
Method: HB

DSC

File: C:\TA\Data\DSC\HB\HBPOX

Run Date: 27-Sep-2007 11:16

Instrument: DSC Q100 V9.0 Build 275

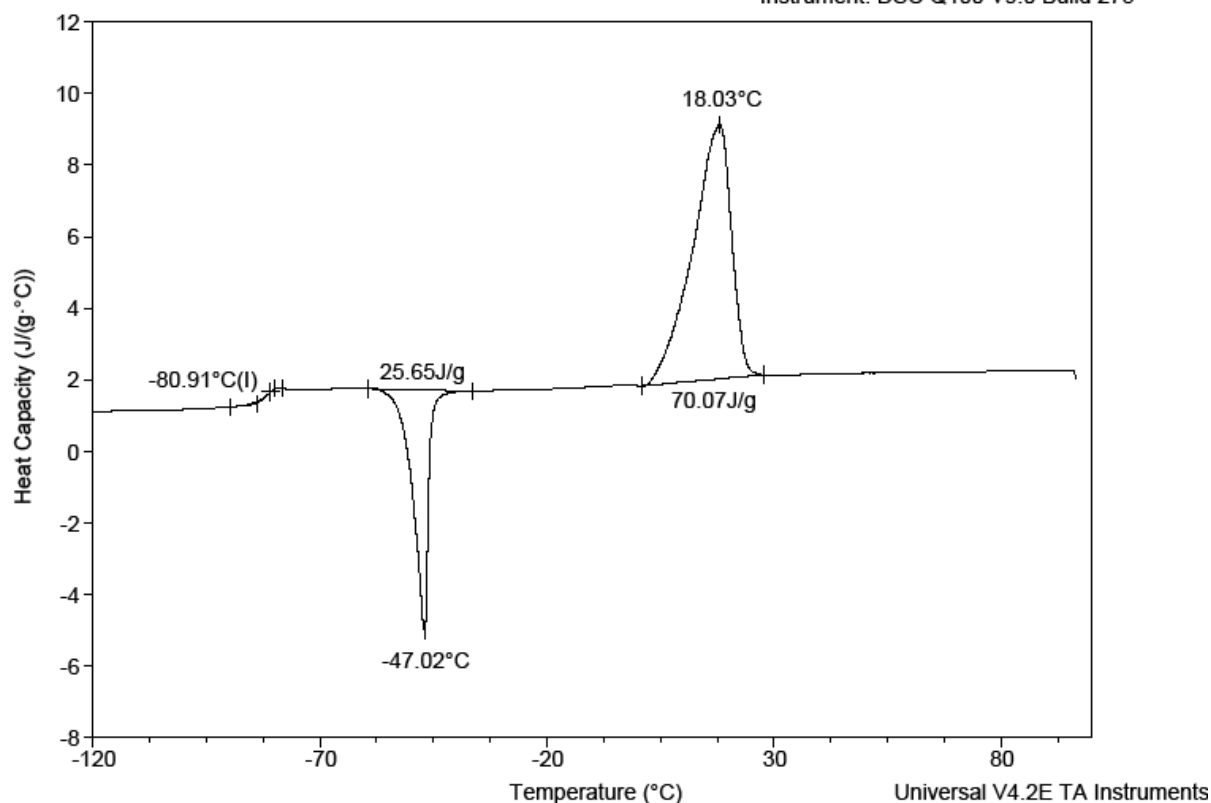


Figure S7.3 DSC thermogram of poly(oxetane-co-1,4-dioxane).³⁹ Experimental conditions: (conversion) x^{Ox} = 84%, (copolymer composition in THP fragment in mole) $F_{1,4\text{-D}} < 1\%$, (number-average molecular weight) $M_{n(\text{GPC})} = 51\,700\text{ g mol}^{-1}$ and (molecular weight distribution) $M_w/M_n = 1.22$ for $[\text{Ox}]_0 = 1.254\text{ M}$, $[1,4\text{-D}]_0 = 9.1\text{ M}$, $[3\text{-PPOA}]_0 = 1.115\text{ mM}$ and $[\text{DtBP}]_0 = 1.254\text{ mM}$. Reference 39: Bouchékif, H.; Philbin, M. I.; Colclough, E.; Amass, A. J. *Macromolecules* **2008**, *41*, 1989-95. Temperature range from - 150 to 100°C at the heating temperature of 10°C min⁻¹. Data analysis was performed using Rheology Advantage Data analysis version 5.1.4.2.

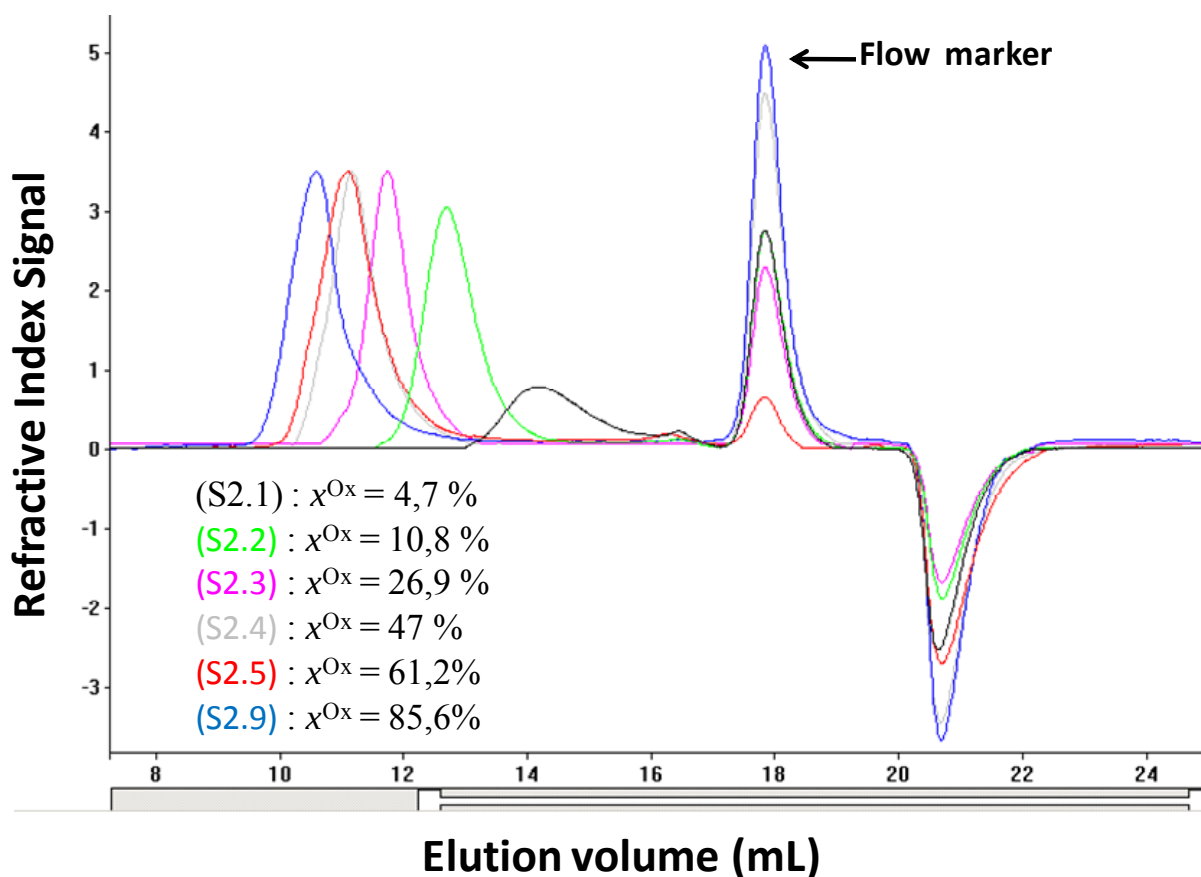


Figure S8 Gel permeation Chromatography traces of poly(oxetane-co-tetrahydropyran) obtained at different monomer conversion (*i.e.* x^{Ox}) for the bulk copolymerization of oxetane (Ox) with tetrahydropyran (THP) at 35 °C with ethoxymethyl 1-oxoniacyclohexane hexafluoroantimonate (EMOA) as initiating systems and 2,6-di-tert-butylpyridine (DtBP) as a non-nucleophilic proton trap. Experimental conditions: $[\text{Ox}]_0 = 1.452$ M, $[\text{EMOA}]_0 = 1.156$ mM, $[\text{DtBP}]_0 = 1.17$ mM. For additional experimental details see Table S1 series S2.

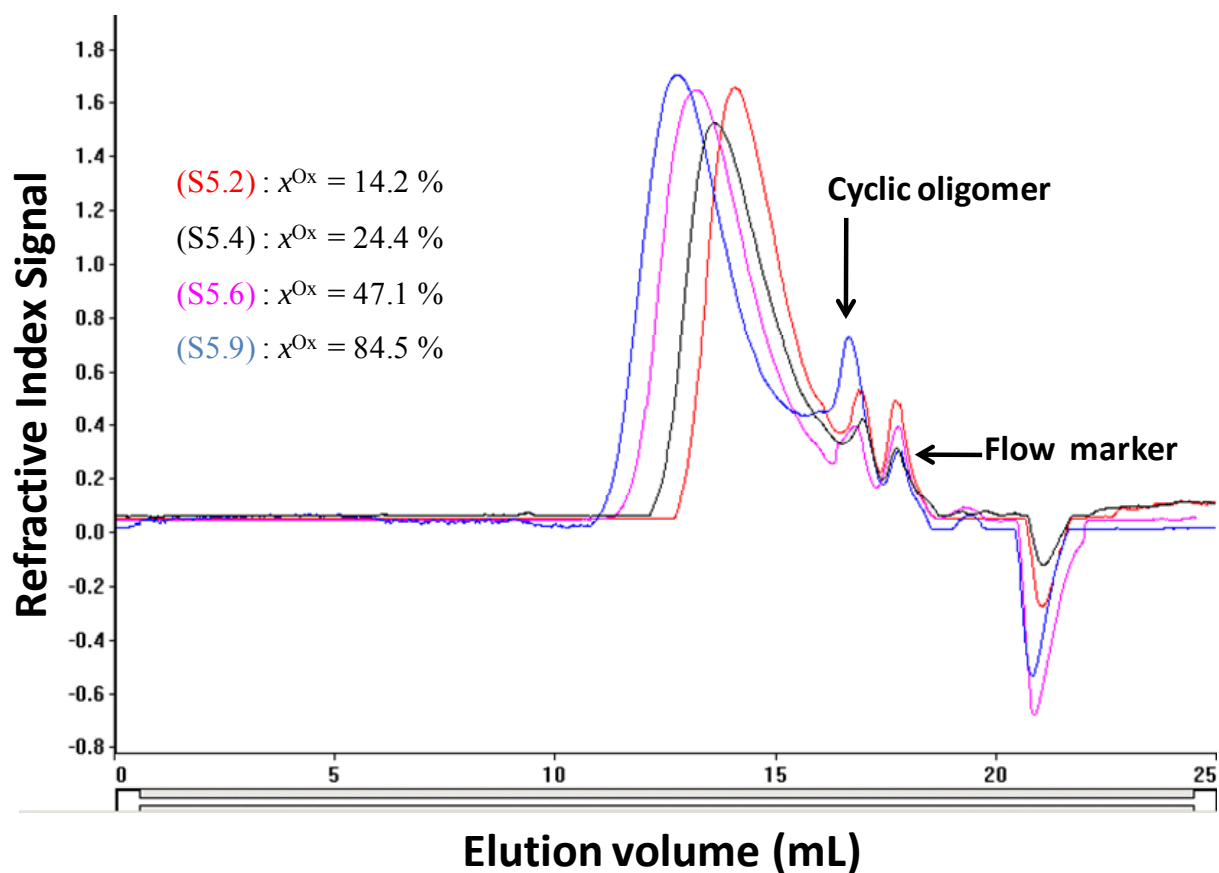


Figure S9 Gel permeation Chromatography traces of poly(oxetane-co-tetrahydropyran) obtained at different monomer conversion (*i.e.* x^{Ox}) for the bulk copolymerization of oxetane (Ox) with tetrahydropyran (THP) at 35 °C with $(\text{BF}_3 \cdot \text{CH}_3\text{OH})_{\text{THP}}$ as initiating systems. Experimental conditions: $[\text{Ox}]_0 = 1 \text{ M}$, $[\text{THP}]_0 = 9.6 \text{ M}$, $[\text{BF}_3 \cdot \text{CH}_3\text{OH}]_0 = 1.156 \text{ mM}$. For additional experimental details see Table S1 series S2.

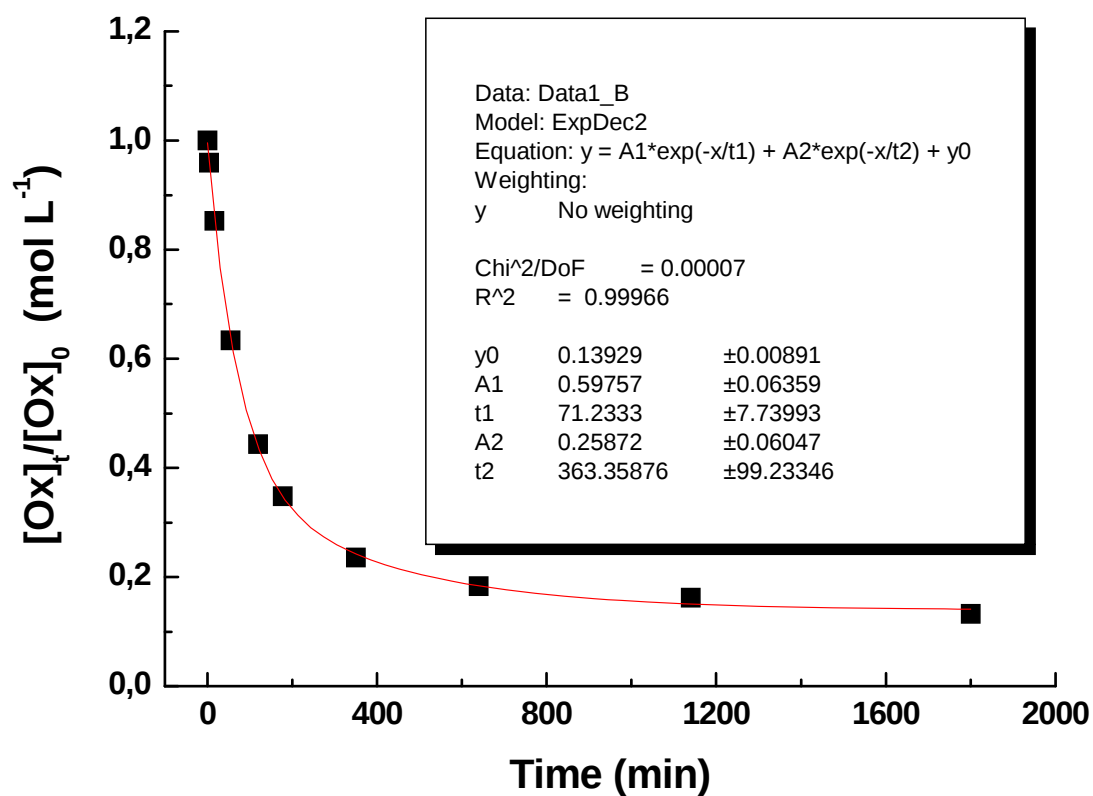


Figure S10 $[Ox]_t/[Ox]_0$ - time curve using a second-order fit exponential regression for the series S2. Experimental conditions: $[Ox]_0 = 1$ M, $[THP]_0 = 9.6$ M, $[BF_3 \cdot CH_3OH]_0 = 1.156$ mM. For additional experimental details see Table S1.

Table S1 Results for the bulk copolymerization of oxetane (Ox) with tetrahydropyran (THP) initiated by C₂H₅OCH₂Cl/AgSbF₆ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) ([EMCl]/[AgSbF₆]/[DtBP] 1/1.1/1.1 (n/n/n)) at 35°C.

Polymer No.	Time Min	[Ox] mol.L ⁻¹	P ^d %	F ₁₃ ^e THP C _{NMR} %	G ₁₃ ^e THP C _{NMR} %	X _t ^f OX %	X _t ^f THP %	M _n ^g th. g.mol ⁻¹	M _n ^h (GPC) g.mol ⁻¹	PDI ^h
S1.0^a	0	1.81	0	0	0	0	0	0	0	-
S1.1	3	1.73	4.5	14.4	20	4.3	0.2	4760	4500	1.5
S1.2	10	1.61	13.6	14.6	20.2	11.4	0.75	12000	16300	1.22
S1.3	40	1.17	45.8	15.7	21.6	35.5	1.42	40000	41400	1.28
S1.4	100	0.7	79.3	16.2	22.3	59.8	2.72	69000	68800	1.32
S1.5	154	0.52	92	17.9	24.3	70.7	3.23	81700	81300	1.38
S1.6	390	0.269	113.7	18.4	25.5	85.1	3.74	98900	95000	1.43
S1.7	600	0.212	118.1	18.6	25.3	88.2	4.1	102700	100500	1.52
S1.8	980	0.15	122.9	18.7	25.4	91.6	4.3	106800	104000	1.6
S2.0^b	0	1.452	0	0	0	0	0	0	0	-
S2.1	6	1.38	6	17	20.7	4.7	0.139	3020	6000	1.54
S2.2	17	1.29	14.2	18.5	23.9	10.8	0.381	10 900	8260	1.18
S2.3	52	1.06	36.4	20.1	26	26.9	1.06	27300	22600	1.31
S2.4	131	0.77	65.9	21.2	28.6	47	2.11	44030	38800	1.38
S2.5	225	0.567	87.5	22.5	30	61.2	2.95	52050	49200	1.41
S2.6	385	0.39	106	23	30.7	73.5	3.66	60700	62300	1.43
S2.7	700	0.33	112.1	23.3	31.2	77.1	3.93	64300	66100	1.42
S2.8	1100	0.29	117	23.3	31.5	80.1	4.14	65800	70500	1.48
S2.9	1800	0.195	128.2	23.4	32.5	85.6	4.68	70000	71000	1.52
S4.0^{ac}	0	1.452	0	0	0	0	0	0	0	-
S4.1	8	1.41	3.5	16.5	22.6	2.7	0.09	4720	4800	1.43
S4.2	28	1.32	11.1	17.2	23.4	8.4	0.3	15170	13400	1.2
S4.3	80	1.156	27.5	19.3	26.2	20.3	0.8	36600	33200	1.35
S4.4	250	0.82	61	21.3	28.4	43.6	1.96	80400	73500	1.48
S4.5	480	0.56	87.9	22.6	30.1	61.5	2.96	114900	98000	1.52
S4.6	600	0.49	95.1	23.2	30.9	65.9	3.3	123900	112000	1.6
S4.7	1200	0.3	115	23.4	31.1	79.1	4	149400	138000	1.62
S4.8	2400	0.228	124	24.3	32.2	84.3	4.46	160400	145000	1.68
S4.9	4800	0.158	131	24.5	32.7	89.1	4.81			

^a The bulk copolymerization of 1.81 M of oxetane with 9 M of tetrahydropyran was initiated by 1.115 mM of **EMOA** in the presence of 1.17 mM of DtBP at 35°C.

^b The bulk copolymerization of 1.452 M of oxetane with 9.2 M of tetrahydropyran was initiated by 1.115 mM of **EMOA** in the presence of 1.17 mM of DtBP at 35°C.

^c The bulk copolymerization of 1.452 M of oxetane with 9.2 M of tetrahydropyran was initiated by 0.5 mM of **EMOA** in the presence of 0.53 mM of DtBP at 35°C.

^d Evaluation by gravimetric measurement. $P = wgt_{(polymer)} / wgt_{(oxetane)}$

^e Copolymer composition, on the basis of ¹H NMR data, in mole (F_{THP}) and in weight (G_{THP}).

$F_{THP} = I_{1.81} / (I_{1.81} + (I_{1.57}/2 + I_{1.37})/2)$; $G_{THP} = F_{THP} \times M_{THP} / (F_{THP} \times M_{THP} + (1 - F_{THP}) \times M_{Ox})$. See Table S4

^f Evaluation by gravimetric measurement and copolymer composition calculated. $x_t^{Ox} = P \times (1 - G_{THP})$;

$$x_t^{THP} = P \times G_{THP}$$

^g $M_{n(th)} = (n_{Ox}/n_{Initiator}) \times (M_{Ox} + M_{THP} \times F_{THP}) \times x_t^{Ox}$.

^h Determined by GPC calibrated with M_n values obtain from PS standards.

Table S2 Results for the bulk copolymerization of oxetane (Ox) with tetrahydropyran (THP) initiated by $C_2H_5OCH_2Cl/AgSbF_6$ in the presence of 2,6-di-*tert*-butylpyridine (DtBP) ($[EMCl]/[AgSbF_6]/[DtBP]$ 1/1.1/1.1 (n/n/n)) at 35°C.

Polymer No.	Time Min	[Ox] mol.L ⁻¹	P ^d %	F ₁₃ ^m C NMR %	G ₁₃ ^m THP C NMR %	X _t ^{ox f} %	X _t ^{THP f} %	M _{n th} ^h g.mol ⁻¹	M _{n (GPC)} ^f g.mol ⁻¹	PDI ^f
S3.0	0	1.452	0	0	0	0	0	0	0	-
S3.1	2	1.39	4.9	17.2	23.5	4.6	0.12	2110	1450	1.28
S3.2	6	1.3	12.4	18	24.5	10.1	0.36	4817	5300	1.2
S3.3	20	1	7.9	19.1	25.9	29.4	1.1	13790	13200	1.24
S3.4	42	0.757	58.3	20.7	27.9	45	1.94	21500	23400	1.3
S3.5	70	0.587	77.3	22.45	30	59.5	2.61	29000	26800	1.3
S3.6	130	0.348	100.7	22.9	30.6	76	3.46	37230	33100	1.32
S3.7	220	0.254	111	23.1	30.8	82.5	3.81	40500	32400	1.35
S3.8	480	0.232	112.1	23.4	31.2	84	3.92	41360	33430	1.41
S3.9	1400	0.15	120	23.7	31.7	89.6	4.28	44370	36230	1.44
S6.0	0	0.479	0	0	0	0	0	0	0	-
S6.1	20	0.467	3.7	23	30.7	3	0.127	870	1400	1.4
S6.2	120	0.413	19.8	23.2	30.9	13.6	0.69	4700	5400	1.38
S6.3	420	0.318	49.3	24	31.9	33.6	1.77	11530	10920	1.35
S6.4	1400	0.221	80.5	24.9	33	53.8	3	18700	16500	1.45
S6.5	2800	0.173	95.8	25.1	33.2	62.9	3.6	22150	21000	1.58
S7.1	0	0.25	0	0	0	0	0	0	0	-
S7.2	420	0.236	8	29.1	37.8	5.6	0.4	1000	-	1.7
S7.3	1600	0.214	14	27.5	36	9	0.6	3600	7300	1.6

^a The bulk copolymerization of 1.452 M of oxetane with 9.2 M of tetrahydropyran was initiated by 2.3 mM of **EMOA** in the presence of 2.415 mM of DtBP at 35°C (series S3).

^b The bulk copolymerization of 0.479 M of oxetane with 9.9 M of tetrahydropyran was initiated by 1.115 mM of **EMOA** in the presence of 1.17 mM of DtBP at 35°C (series S6).

^c The bulk copolymerization of 0.25 M of oxetane with 20 M of tetrahydropyran was initiated by 1.115 mM of **EMOA** in the presence of 1.17 mM of DtBP at 35°C (series S7).

^{d,e,f,g,h} Refer to Tables S2

Table S3 Results for the bulk copolymerization of 1 M of oxetane (Ox) with 9.1 M of tetrahydropyran (THP) initiated by 0,7 mM of (BF₃:CH₃OH)_{THP} at 35°C.

Polymer No.	Time Min	[Ox] mol.L ⁻¹	P ^d %	F ₁₃ ^m THP C NMR %	G ₁₃ ^m THP C NMR %	x _t ^f OX %	x _t ^f THP %	M _n ^h th. g.mol ⁻¹	M _n ^f (GPC) g.mol ⁻¹	PDI ^f
S5.0	0	1	0	0	0	0	0	0	0	-
S5.1	4	0.94	8.2	21.4	28.7	45.8	0.17	637	2000	1.49
S5.2	11	0.86	19.96	21.2	28.5	14.2	0.4	1553	2300	1.54
S5.3	15.6	0.8	27.6	21.8	29.2	19.5	0.57	2141	2870	1.68
S5.4	19.5	0.76	34.7	22.1	29.6	24.4	0.72	2685	3260	1.7
S5.5	26.6	0.67	47.7	22.5	30.1	33.3	1	3680	4520	1.68
S5.6	37.6	0.53	68	23	30.7	47.1	1.47	5236	5820	1.78
S5.7	180	0.28	105	23.5	31.3	72.1	2.31	8060	8660	1.82
S5.8	280	0.23	113	24	31.9	77	2.53	8650	9100	1.85
S5.9	1440	0.15	126	24.7	32.7	84.5	2.9	9596	9700	1.87

d,e,f,g,h Refer to Tables S2

Table S4 ^1H and ^{13}C chemical shift δ (ppm) of $-\text{CH}_2-$ group in poly(oxetane) and poly(oxetane-co-tetrahydropyran).

Structure		Peak ^r	Chemical shift ^a			
			^{13}C NMR		^1H NMR	
			δ (ppm)	Intensity	δ (ppm)	Intensity
Chains	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}^{\text{d}}$	(a)	67.86	I_1	t :3.47	I_1
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}^{\text{d}}$	(b)	30.06	I_2	p :1.81	$\text{I}_1 = 2\times\text{I}_2^{\text{d}}$
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$	(g)	22.79	I_3	p :1.37	I_3
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$	(f)	29.55	I_4	p :1.57	$\text{I}_4 = 2\times\text{I}_3$
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$	(e)	70.88	I_5	t :3.39	$\text{I}_5 = 2\times\text{I}_3$
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$	(h)	67.83	$\text{I}_6 \sim \text{I}_5$	t :3.46	$\text{I}_6 = 2\times\text{I}_3$
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$	(j)	67.81	$\text{I}_7 \sim \text{I}_5$	t :3.47	$\text{I}_7 = 2\times\text{I}_3$
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$	(k)	30.08	$\text{I}_8 \sim \text{I}_5$	p :1.81	$\text{I}_8 = 2\times\text{I}_3$
Ring	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ (small cyclic oligomers) ^c	(c)	66.07	I_8	t :3.54 ^c	I_8
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ (large cyclic oligomers) ^c	(e)	67.08	I_9	t :3.48 ^c	I_9
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ (large cyclic oligomers) ^c	(e)	67.44	I_{10}		b
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}^{\text{c}}$	(d)	30.15	I_{11}	q :1.81 ^c	I_{11}
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$	(t)	22.74	I_{12}	q :1.37 ^c	I_{12}
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$	(s)	29.48	I_{13}	q :1.68 ^c	I_{13}
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$	(r)	70.81	I_{14}	q :2.68 ^c	I_{14}
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$	(l)	66.07	I_8	q :3.75 ^c	I_8
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$	(n)	66.07	I_8	q :3.62 ^c	I_8
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$	(m)	30.17	I_{11}	q :1.92 ^c	I_{11}
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$	(p)	66.07	I_{18}	q :3.62 ^c	I_{18}
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$	(p)	66.07	I_{18}	q :1.92 ^c	I_{18}
	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$	(q)	30.18	I_{11}	q :3.62 ^c	I_{11}

^a CDCl_3 was used as solvent.

^b Peaks overlap

^c Chemical shift obtained from NMR analysis of the isolated cyclic oligomer.

^d Chemical shift obtained from NMR analysis of linear poly(oxetane) free of cyclic oligomer.

^r Symbol associated to chemical shift in Figures S1, S3, S5, S6.