Supporting information belonging to:

Catalytic Ring Opening (Co)polymerization of Aromatic and Aliphatic (Macro)lactones

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cBT analysis

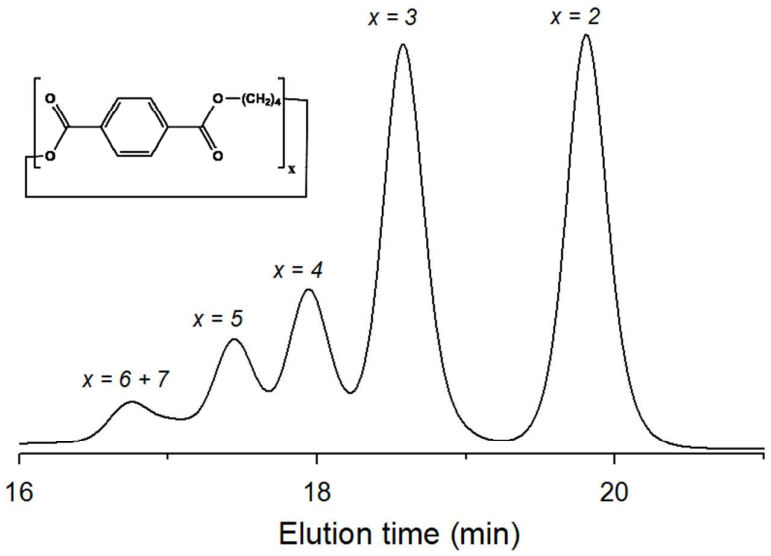


Figure SI 1. chromatogram of cBT obtained from SEC equipped with low molecular weight columns using THF as the eluent.

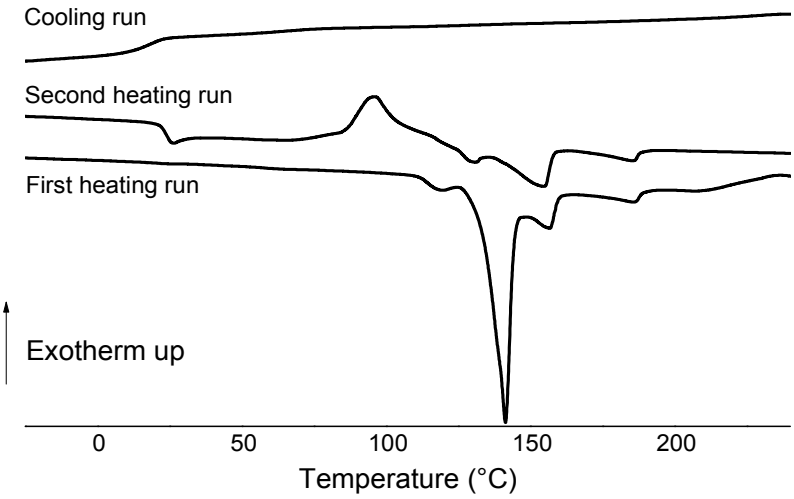


Figure SI 2. DSC thermograms of the as-received cBT at 5 °C/min heating and cooling.

Additional kinetic data

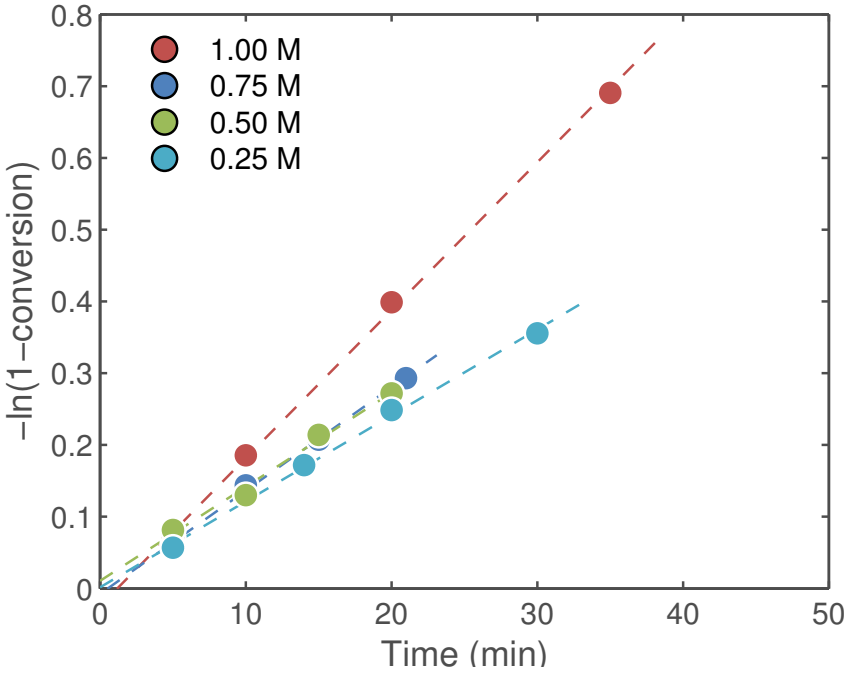


Figure SI 3. Logarithmically transformed conversion *vs.* time plot of the ROP of cBT using **1** and different [cBT]. Circles indicate experimental values, dotted lines are the corresponding fits using eq. 2. T=100°C. [**1**] = 10 mM ([cBT] = 1 M) / 8.1 mM ([cBT] = 0.75 M) / 9.6 mMol ([cBT] = 0.5 M) / 9.7 mmol ([cBT] = 0.25 mM) in TCE.

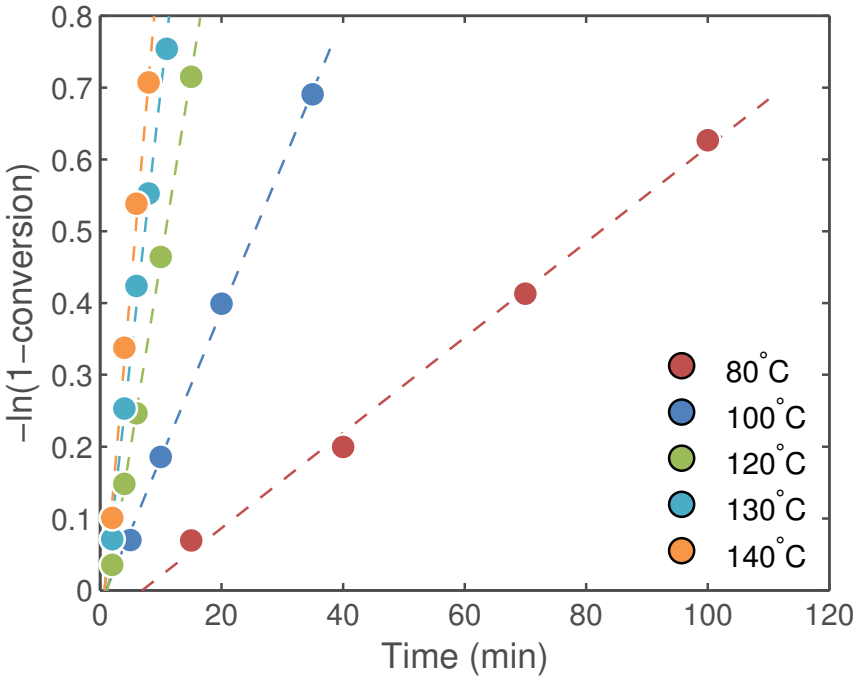


Figure SI 4. Logarithmically transformed conversion *vs.* time plot of the ROP of cBT using **1** at different temperatures. Circles indicate experimental values, dotted lines are the corresponding fits using eq. 2. [cBT] = 1.0 M, [**1**] = 10 mM in TCE.

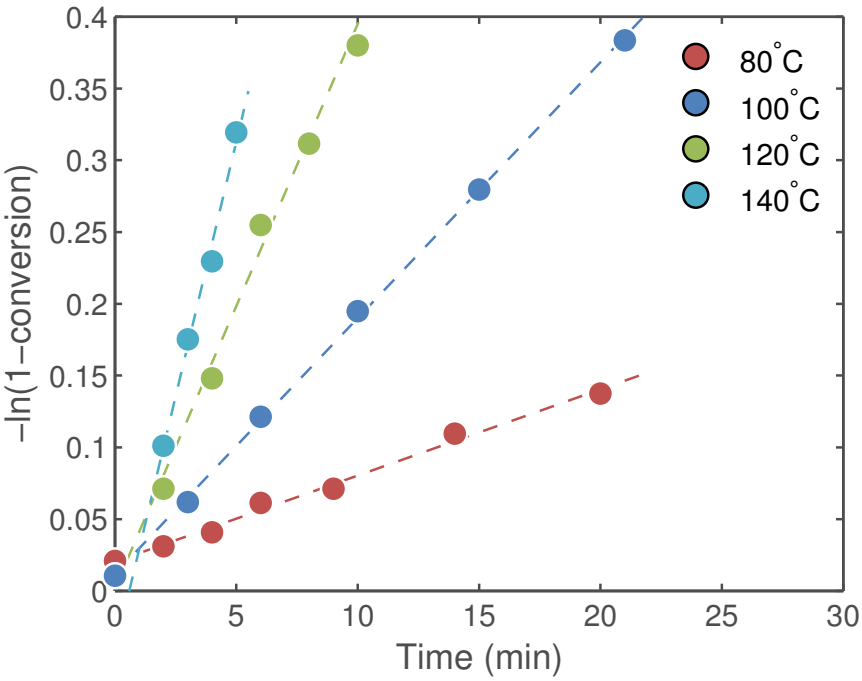


Figure SI 5. Logarithmically transformed conversion *vs.* time plot of the ROP of CL using **1** at different temperatures. Circles indicate experimental values, dotted lines are the corresponding fits using eq. 2. [CL] = 1.0 M, [**1**] = 10 mM in TCE.

SEC analysis using UV detector

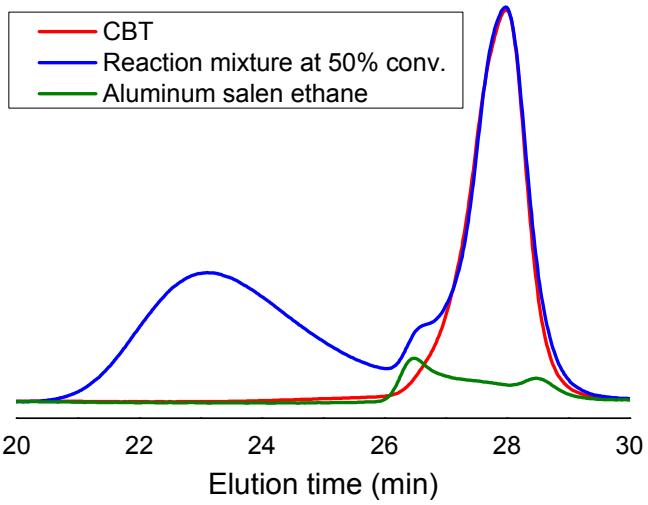


Figure SI 6. UV signal in SEC of CBT, a reaction mixture at 50% conversion, and the [Salen]AlEt catalyst.

Example calculation of block lengths in PCL / PBT copolymers

Eq. 4 and Eq. 5 have been used in this work to calculate the block lengths of PCL / PBT blocks in the copolymers. For this calculation (i) end groups are neclected and (ii) for PBT minimum sequence lengts of one B-T are considered as block (i.e. CL-B-CL and CL-T-CL are not considered as ½ sequences).

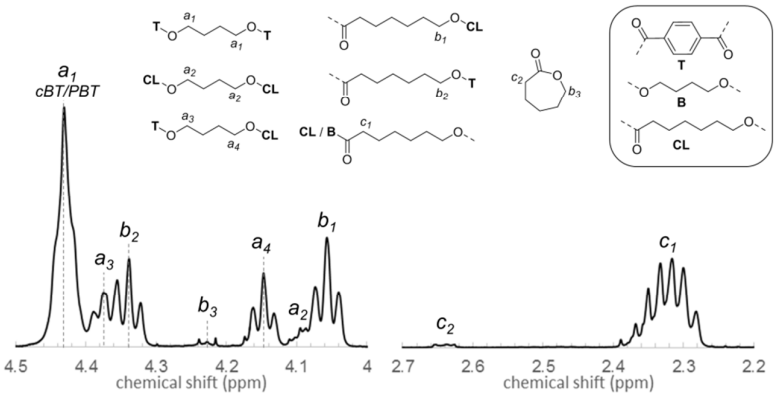


Figure SI 7. ^{1}H NMR spectrum of the product of the copolmyerization of CL and cBT.

To illustrate that eq. 4 and eq. 5 are correct, we consider the chain segment below, which also includes the corresponding signals from ^{1}H NMR.

a1 a1 a1 a1 b2 b1 b1 a2 a2 b1 b2 b2 a4 a3 a3 a4 b1 b2

T−B−T−B−T−CL−CL−CL−B−CL−CL−T−CL−B−T−B−CL−CL−T

By the definition above, this means that there are 4 caprolactone blocks consisting out of a total of 8 CL units with an average length of 8/4=2 sequences. This also follows from eq. 4:

$$L_{PCL} = \frac{b_1 + b_2}{(b_2 + a_4 + a_2)/2} = \frac{4+4}{(4+2+2)/2} = 4$$

a1 a1 a1 a1 b2 b1 b1 a2 a2 b1 b2 b2 a4 a3 a3 a4 b1 b2

T−B−T−B−T−CL−CL−CL−B−CL−CL−T−CL−B−T−B−CL−CL−T

Similarly, this means that there are 2 BT blocks with and average length of (2.5+1.5)/2=2. Again this also follows from eq. 5

$$L_{PBT} = \frac{\frac{a_1}{2} + a_4}{a_4} = \frac{\frac{4}{2} + 2}{2} = 2$$

a1 a1 a1 a1 b2 b1 b1 a2 a2 b1 b2 b2 a4 a3 a3 a4 b1 b2

T−B−T−B−T−CL−CL−CL−B−CL−CL−T−CL−B−T−B−CL−CL−T

Calculation of block lengths of fully statistical copolymers

The repeat unit in PBT, *i.e.* butane diol and terephthalic acid, is an AABB type repeat unit, while caprolactone can be classified as an AB type of unit. In order to evaluate what the amount is of each of diad/triad in the system, for every composition the fully random (statistical) sequence distribution needs to be evaluated.

Therefore, we consider a polymer containing a mol fraction X_{BT} of BT units and X_{CL} of CL units. Since one BT-unit contains two alcohol/acid groups, while CL contains only one, the fraction of alcohol/acid groups is calculated using:

$$F_{BT} = \frac{2 \cdot X_{BT}}{2 \cdot X_{BT} + X_{CL}} \quad \text{(SI.1)}$$

$$F_{CL} = \frac{X_{CL}}{2 \cdot X_{BT} + X_{CL}} \quad \text{(SI.2)}$$

Where F_{BT} is the fraction of alcohol and acid groups originating from butane diol/therephthalic acid and F_{CL} is the faction of alcohol and acid groups originating for caprolactone.

In a fully statistical copolymer, the amount of linkages is the result of the chance that a certain acid unit is connected to a certain alcohol unit, which is the product of the relative amount of each of the units present:

$$a_1 = {F_{BT}}^3 \quad \text{(SI.3)}$$

$$a_2 = F_{BT} \cdot {F_{CL}}^2 \quad \text{(SI.4)}$$

$$a_3 = {F_{BT}}^2 \cdot F_{CL} \quad \text{(SI.5)}$$

$$a_4 = {F_{BT}}^2 \cdot F_{CL} \quad \text{(SI.6)}$$

$$b_1 = {F_{CL}}^2 \quad \text{(SI.7)}$$

$$b_2 = F_{BT} \cdot F_{CL} \quad \text{(SI.8)}$$

Using the fact that $F_{CL} + F_{BT} = 1$, for the random copolymer described above, the respective length of the PCL and PBT block will be:

$$L_{PCL,random} = \frac{{F_{CL}}^2 + F_{BT} \cdot F_{CL}}{(F_{BT} \cdot F_{CL} + {F_{BT}}^2 \cdot F_{CL} \quad + F_{BT} \cdot {F_{CL}}^2)/2} = \frac{1}{F_{BT}}$$

Similarly, for PBT blocks this yields

$$L_{PBT} = \frac{\frac{{F_{BT}}^3}{2} + {F_{BT}}^2 \cdot F_{CL}}{{F_{BT}}^2 \cdot F_{CL}} = \frac{F_{\mathrm{BT}}/2}{F_{\mathrm{CL}}} + 1$$

This leads to the following result for various ratios of PDL and PBT

Table SI 1. Theoretical values of fraction of links present and the corresponding fraction of ^{1}H NMR signal for a fully statistical copolymer.

Mol fraction based on monomer		Mol fraction based on ester groups		Fraction of linkages					Fraction of signals in ^{1}H NMR							Sequence length	
X_{BT}	X_{CL}	F_{BT}	F_{CL}	CL-T	B-CL	CL-CL	B-T	Total	a1	a2	a3	a4	b1	b2	Total	$L_{PCL,random}$	$L_{PBT,random}$
1	0	1.000	0.000	0.000	0.000	0.000	1.000	1	1.000	0.000	0.000	0.000	0.000	0.000	1	1.00	-
0.9	0.1	0.947	0.053	0.050	0.050	0.003	0.898	1	0.850	0.003	0.047	0.047	0.003	0.050	1	1.06	10.00
0.8	0.2	0.889	0.111	0.099	0.099	0.012	0.790	1	0.702	0.011	0.088	0.088	0.012	0.099	1	1.13	5.00
0.7	0.3	0.824	0.176	0.145	0.145	0.031	0.678	1	0.559	0.026	0.120	0.120	0.031	0.145	1	1.21	3.33
0.6	0.4	0.750	0.250	0.188	0.188	0.063	0.563	1	0.422	0.047	0.141	0.141	0.063	0.188	1	1.33	2.50
0.5	0.5	0.667	0.333	0.222	0.222	0.111	0.444	1	0.296	0.074	0.148	0.148	0.111	0.222	1	1.50	2.00
0.4	0.6	0.571	0.429	0.245	0.245	0.184	0.327	1	0.187	0.105	0.140	0.140	0.184	0.245	1	1.75	1.67
0.3	0.7	0.462	0.538	0.249	0.249	0.290	0.213	1	0.098	0.134	0.115	0.115	0.290	0.249	1	2.17	1.43
0.2	0.8	0.333	0.667	0.222	0.222	0.444	0.111	1	0.037	0.148	0.074	0.074	0.444	0.222	1	3.00	1.25
0.1	0.9	0.182	0.818	0.149	0.149	0.669	0.033	1	0.006	0.122	0.027	0.027	0.669	0.149	1	5.50	1.11
0	1	0.000	1.000	0.000	0.000	1.000	0.000	1	0.000	0.000	0.000	0.000	1.000	0.000	1	-	1.00

The calculated values corresponding to the sequential feed copolymerization described in the paper (figure 6) are given as an example in Table SI 2

Table SI 2. Theoretical values of diads and triads for a fully statistical copolymer corresponding to the experimental sequential feed copolymerization in Figure 6 .

Time (min)	X_{BT}	X_{CL}	F_{BT}	F_{CL}	a_1	a_2	a_3	a_4	b_1	b_2	$L_{PBT,random}$	$L_{PCL,random}$	R
0	1.00	0.00	1.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00			0.00
10	0.75	0.25	0.86	0.14	0.63	0.02	0.10	0.10	0.02	0.12	4.01	1.17	0.34
25	0.57	0.43	0.73	0.27	0.38	0.05	0.14	0.14	0.08	0.20	2.32	1.38	0.43
40	0.51	0.49	0.68	0.32	0.31	0.07	0.15	0.15	0.10	0.22	2.05	1.48	0.51
60	0.49	0.51	0.66	0.34	0.29	0.08	0.15	0.15	0.12	0.22	1.97	1.52	0.60
90	0.48	0.52	0.65	0.35	0.28	0.08	0.15	0.15	0.12	0.23	1.94	1.53	0.67
145	0.48	0.52	0.65	0.35	0.28	0.08	0.15	0.15	0.12	0.23	1.93	1.54	0.75
300	0.48	0.52	0.65	0.35	0.27	0.08	0.15	0.15	0.12	0.23	1.93	1.54	0.85

Single feed copolymerization results

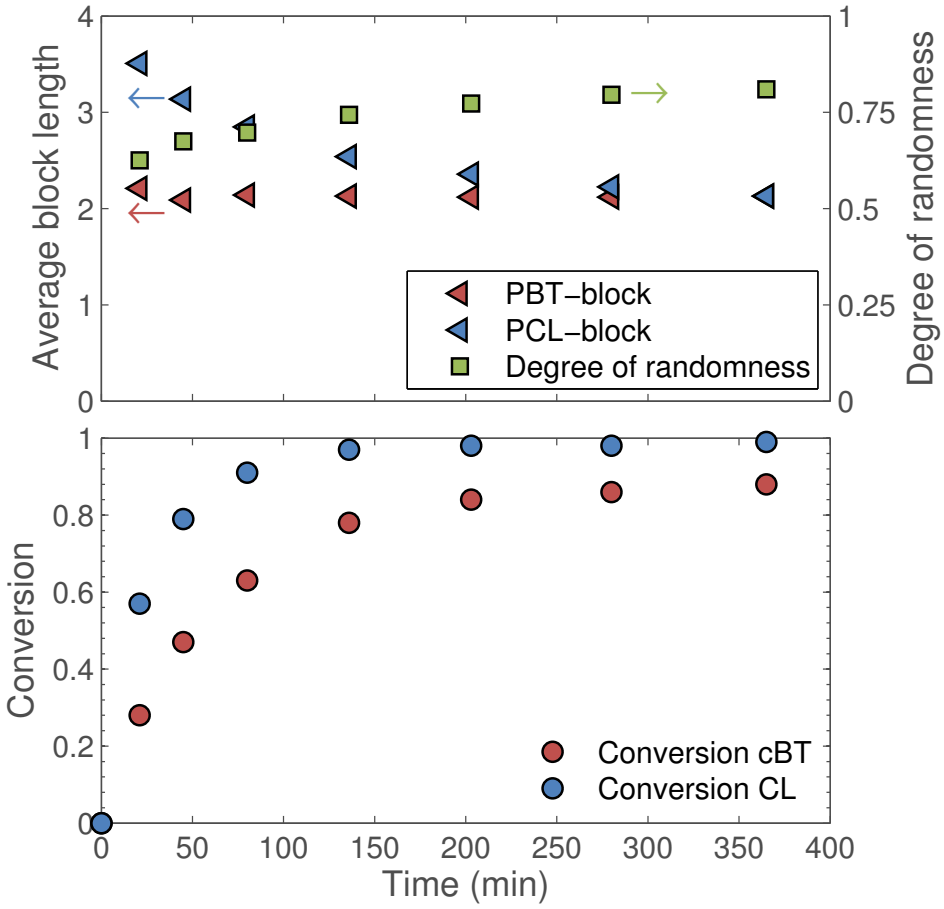


Figure SI 8. Conversion vs. time plot of the single feed copolymerization of cBT and CL (bottom) and the corresponding calculated PBT-, PCL-block length and degree of randomness (top). T = 100 °C, [cBT] = 0.5 M, [CL] = 0.5 M, [1] = 10 mM, solvent = TCE.

Sequential feed copolymerization DSC results

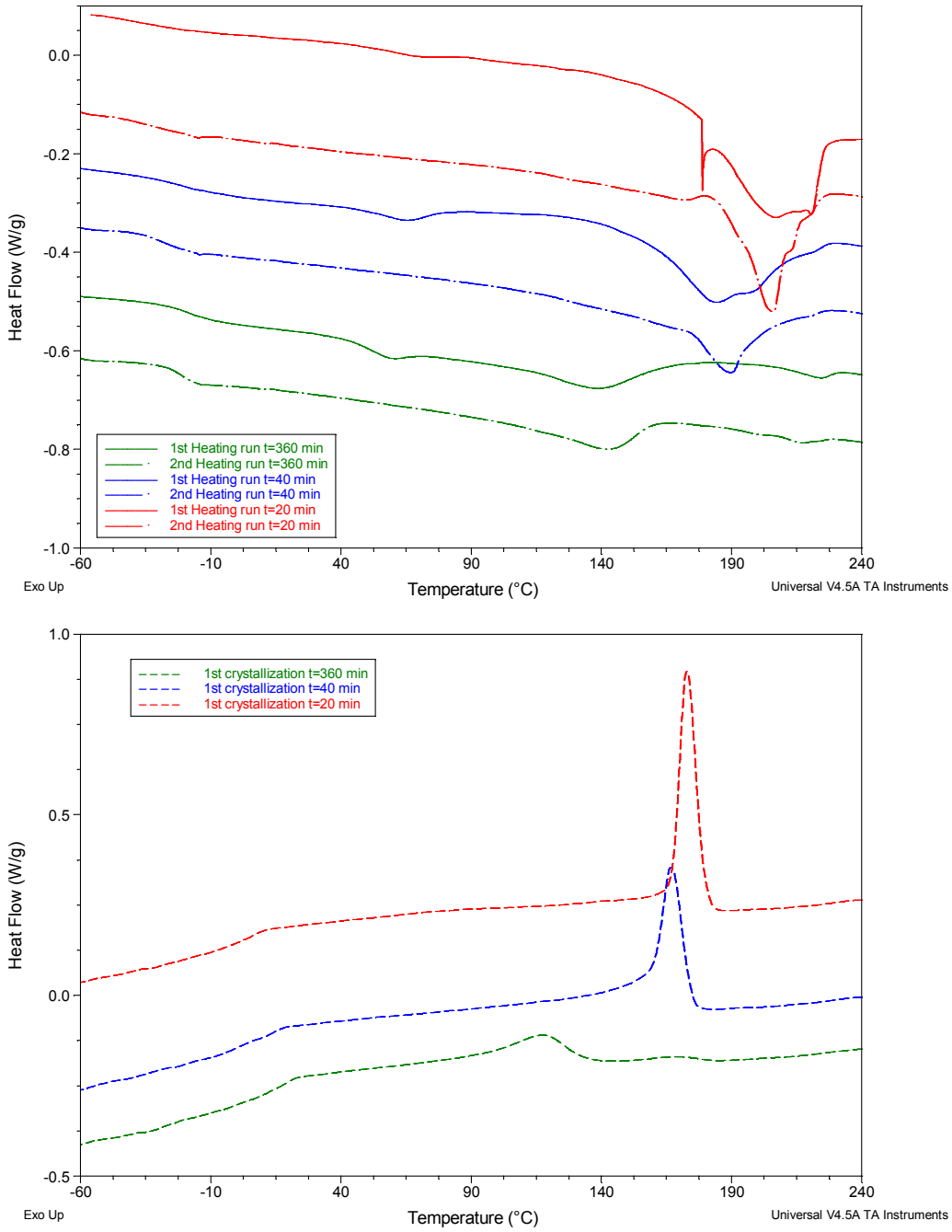
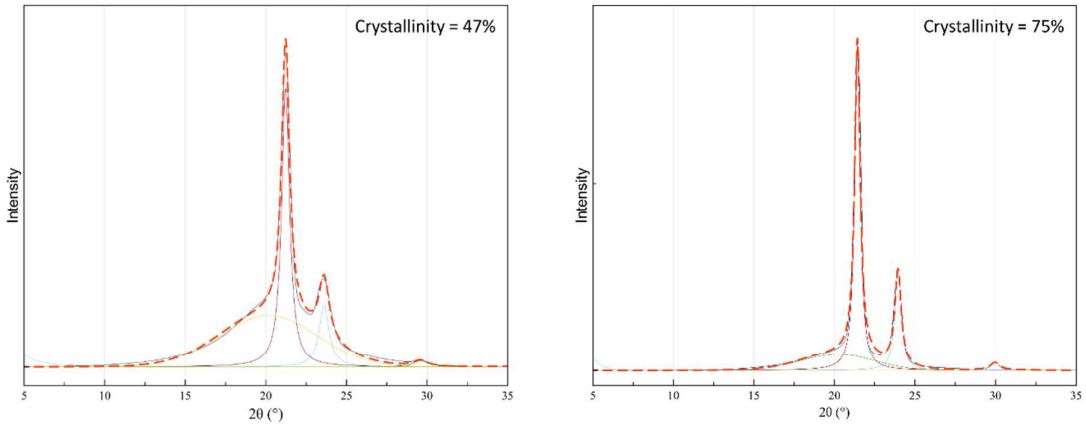


Figure SI 9. DSC 1st and 2nd melting (top) and 1st crystallization (bottom) thermograms of the sequential feed copolymerization of cBT and CL (bottom) after 20, 40, and 360 min of CL reaction time.

Crystallinity determination using WAXD



(a) (b)

Figure SI 10. Wide Angle X-ray pattern of (a) cBT-PDL copolymer (30/70 mol%) and (b) PPDL showing the corresponding fitted pattern (red dotted lines), including the individual amorphous halo and crystalline peaks.