

Supporting Information

## Continuous Poly(2-oxazoline) Triblock Copolymer Synthesis in a Microfluidic Reactor Cascade

Evelien Baeten<sup>†</sup>, Bart Verbraeken<sup>§</sup>, Richard Hoogenboom<sup>\*,§</sup>, Tanja Junkers<sup>\*,†,‡</sup>

<sup>†</sup> Polymer Reaction Design Group, Institute for Materials Research (IMO), Universiteit Hasselt, Martelarenlaan 42, 3500 Hasselt, Belgium

<sup>§</sup> Supramolecular Chemistry Group, Department of Organic and Macromolecular Chemistry, Ghent University, Krijgslaan 291-S4, 9000 Gent, Belgium

<sup>‡</sup> IMO associated lab IMOMEC, Wetenschappspark 1, 3590 Diepenbeek

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## 1. Materials and instrumentation

Methyl tosylate (MeOTs) was purchased from Sigma-Aldrich and was distilled over BaO under reduced pressure. Acetonitrile (ACN) was purchased from VWR and was distilled over barium oxide under inert atmosphere. 2-Ethyl-2-oxazoline (EtOx) was kindly provided by Polymer Chemistry Innovations Inc, and has been distilled over barium oxide under inert atmosphere. The synthesis of 2-*n*-propyl-2-oxazoline (*n*PropOx) was described previously.<sup>1,2</sup> Prior to use, *n*PropOx was distilled over barium oxide under reduced pressure. Potassium hydroxide (KOH) and methanol (MeOH) for the quench solution were purchased from VWR and Acros respectively.

Monomer conversions and monomer to monomer ratios were determined via the use of Nuclear Magnetic Resonance spectra, which were recorded in  $\text{CDCl}_3$  at room temperature on a 400 Megahertz (MHz; 9.4 Tesla) Varian Inova spectrometer at 400 MHz for  $^1\text{H}$  NMR using a 5 mm OneNMR PFG probe (Agilent Technologies Inc, Santa Clara, CA, USA). The chemical shift scale ( $\delta$ ) in ppm was calibrated relative to TMS (0 ppm). Free induction decays were collected with a  $90^\circ$  pulse of  $6.9\ \mu\text{s}$ , a spectral width of 6400 Hz, an acquisition time of 3 s, a preparation delay of 12 s and 64 accumulations. A line-broadening factor of 0.2 Hz was applied before Fourier transformation to the frequency domain.

Size-exclusion chromatography (SEC) was performed on an Agilent 1260-series HPLC system equipped with a 1260 online degasser, a 1260 ISO-pump, a 1260 automatic liquid sampler (ALS), a thermostated column compartment (TCC) at  $50^\circ\text{C}$  equipped with a PLgel 5  $\mu\text{m}$  mixed-D guard column and two PLgel 5  $\mu\text{m}$  mixed-D columns in series, a 1260 diode array detector (DAD) and a 1260 refractive index detector (RID). The used eluent was DMA, containing 50mM of lithium chloride, at an optimized flow rate of 0.593 ml/min. The spectra were analyzed using the Agilent Chemstation software with the GPC add on. Molar mass and dispersities values were calculated against PMMA standards from PSS.

## 2. Microreactor set-ups

### *Microreactor set-up for homo and diblock (co)polymerizations*

Polymerizations are performed in a Labtrix® Start R2.2 system (Chemtrix BV, NL). This commercially available microreactor system can be fitted with different glass chip reactors, of which in this project a  $19.5 \mu\text{L}$  microreactor chip (Chemtrix 3227 reactor, 3 inlets) and a  $15 \mu\text{L}$  microreactor chip (Chemtrix 3224 reactor, 4 inlets,  $5 + 10 \mu\text{L}$ ) were employed. Both reactor chips employ staggered oriented ridge (SOR-2) static micromixers to assure fast mixing. Reaction temperatures are controlled via a MTTC1410 temperature controller (Melcor Thermal Solutions, temperature range  $-20$  to  $195^\circ\text{C}$ ), while the reactor pressure was maintained at 20 bar backpressure via a preset back pressure regulator (Upchurch Scientific). Reactant solutions are injected into the reactor via 1 mL gastight syringes (SGE). Flowrates vary between 0.1 and  $40 \mu\text{L min}^{-1}$ , and are controlled via syringe pumps (Chemyx).

### *Microreactor cascade set-up for triblock copolymerizations*

Triblock copolymerizations were carried out in a microreactor cascade, consisting of two coupled Labtrix® Start R2.2 systems (Chemtrix BV, NL)(described above). The first system was fitted with a  $15 \mu\text{L}$  microreactor (Chemtrix 3224 reactor, 4 inlets,  $5 + 10 \mu\text{L}$ ). The outlet of the first reactor chip was connected directly to the inlet of a second microreactor system, via a short piece of unheated PEEK 1/32" tubing and an in-line manometer to monitor and detect possible blockages at a premature stage. No additional check valves were placed in order to avoid temperature decreases between both reactors. The second microreactor system was fitted with a  $19.5 \mu\text{L}$  microreactor (Chemtrix 3227 reactor, 3 inlets). At the end of the reactor cascade, a pre-set back pressure regulator (Upchurch Scientific) was placed to maintain the system at 20 bar of backpressure.

The microreactor cascade thus consists of two coupled microreactors. The first reactor chip is made up of two separate reactor parts ( $5 + 10 \mu\text{L}$ ), where the first two blocks can be polymerized in a continuous mode. The coupling of the second reactor ( $19.5 \mu\text{L}$ ) leads to the possibility of triblock copolymer synthesis.



Figure S1: Microreactor cascade set-up as used for the triblock copolymerizations.

### 3. Homopolymerization of 2-ethyl-2-oxazoline (EtOx)

Stock solutions composed of 4M EtOx in acetonitrile and a ratio of [EtOx]/[MeOTs] = 60 were used in the homopolymerization reactions. Accordingly, typical stock solutions were prepared of 2 mL EtOx, 0.05 mL MeOTs and 3 mL acetonitrile and were injected into a 19.5  $\mu$ L microreactor by employing two syringes filled under nitrogen atmosphere. A third injecting syringe was used for acetonitrile at the last inlet of the reactor, to avoid blockages at the outlet. In addition, salt precipitation was avoided in the reactor by quenching the reaction mixture with KOH/MeOH (1M) in the collection vial. Reaction temperatures were screened between 120°C and 180°C, while the pressure was kept constant at 20 bar. Full conversions were obtained after 12 min 30 at 140°C, 5 min at 160°C and 2 min at 180°C. Other obtained results are described below.

140°C			
Residence Time	Conversion / %	$M_n^{\text{app}}$ / g mol <sup>-1</sup>	PDI
2 min	36.8	4470	1.12
2 min 30	48.3	5490	1.14
3 min	52.8	6050	1.10
3 min 30	61.6	6670	1.09
4 min	65.5	6680	1.12
5 min	75.7	7610	1.19
7 min 30	89.6	8440	1.17
10 min	94.9	9750	1.14
12 min 30	100.0	9760	1.15

160°C			
Residence Time	Conversion / %	$M_n^{\text{app}}$ / g mol <sup>-1</sup>	PDI
50 s	42.7	5140	1.08
75 s	58.6	6550	1.08
80 s	60.5	6670	1.10
100 s	66.8	8960	1.10
2 min	77.0	8380	1.10
2 min 30	86.8	9440	1.10
3 min	91.3	9960	1.10
4 min	97.7	10460	1.10
5 min	100.0	10240	1.11

180°C			
Residence Time	Conversion / %	$M_n^{\text{app}}$ / g mol <sup>-1</sup>	PDI
20 s	36.6	6010	1.09
40 s	67.2	6960	1.12
50 s	78.1	7690	1.12
1 min	84.3	8760	1.11
75 s	88.2	9490	1.11
80 s	84.5	9520	1.11
100 s	97.1	10590	1.11
2 min	100.0	10280	1.12

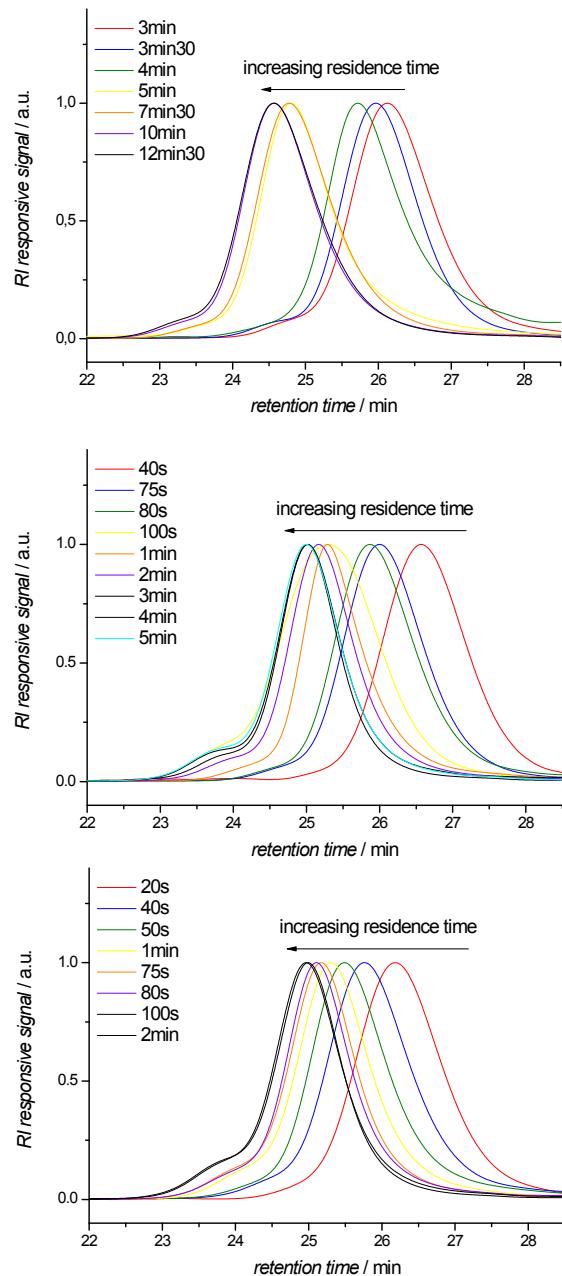


Figure S2: Results of the EtOx homopolymerizations at 140°C, 160°C and 180°C. Tables include conversions, molecular weights and polydispersities for different residence times at each temperature. Overlay of SEC elugrams are shown as well for the same conditions.

The investigation of kinetics of the homopolymerization of EtOx – by employing the information described above – led to a first order kinetic plot, which is represented in the main paper, (Figure 1a). By calculating the slope at each temperature, an Arrhenius plot was made. Calculated activation energy was  $73.5 \pm 3.8 \text{ kJ} \cdot \text{mol}^{-1}$ , and frequency factor A  $1.39 \pm 0.37 \cdot 10^8 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ .

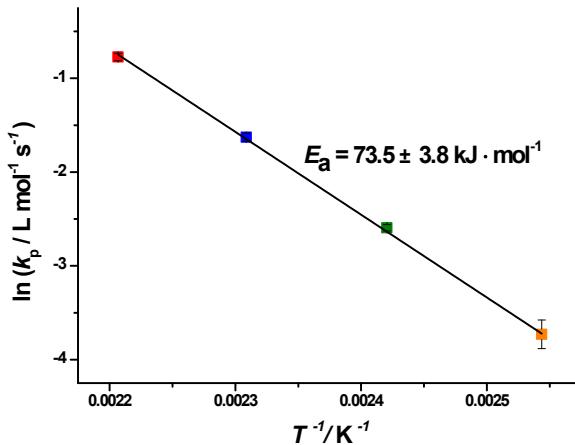


Figure S3: Arrhenius pot of the EtOx homopolymerization.

To assure full conversions for the first block, same conditions were also tested in the first reactor part ( $5 \mu\text{L}$ ) of a  $15 \mu\text{L}$  microreactor by employing the third inlet as an outlet. Same conversions were observed for all chosen residence times at  $140^\circ\text{C}$ ,  $160^\circ\text{C}$  and  $180^\circ\text{C}$ .

The molecular weight of the poly(2-ethyl-2-oxazoline) homopolymers can easily be varied by changing the monomer/initiator ratio. Hereby, the monomer concentration was kept constant while initiator concentrations were varied. By applying the optimized conditions for the homopolymerization (5 min at  $160^\circ\text{C}$ ), full conversions at higher initiator concentrations could be obtained, leading to lower molecular weights (DP 15 and DP 30). At lower initiator concentrations and thus higher molecular weights (DP 120), no full monomer consumption was observed.

Table S1: Results of the homopolymerization of EtOx with an increasing degree of polymerization.

	Conversion / %	$M_n^{\text{app}}$ / g mol <sup>-1</sup>	PDI	$M_p^{\text{app}}$ / g mol <sup>-1</sup>
DP 15	100	3510	1.10	3740
DP 30	100	6830	1.08	7150
DP 60	100	10240	1.11	11040
DP 120	89.3	16200	1.16	18300

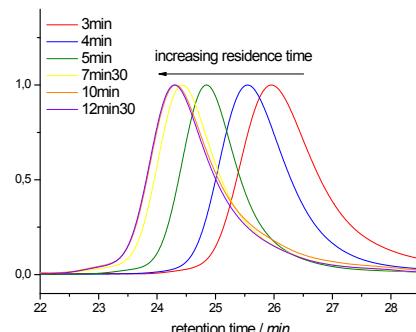
#### 4. Homopolymerization of *n*-propyl-2-oxazoline (*n*PropOx)

A similar straightforward optimization strategy was carried out for *n*PropOx. Stock solutions of 2.35 mL *n*PropOx (4M), 0.05 mL MeOTs and 3 mL acetonitrile were injected into a 19.5  $\mu$ L microreactor, employing two syringes filled under nitrogen atmosphere. A third injecting syringe was used for acetonitrile at the last inlet of the reactor, to avoid blockages at the outlet. In addition, salt precipitation was avoided in the reactor by quenching the reaction mixture with KOH/MeOH (1M) in the collection vial. Reaction temperatures were screened between 140°C and 180°C, while the pressure was kept constant at 20 bar.

Due to its comparable propagation kinetics to EtOx, full conversions were also obtained for the homopolymerization of *n*PropOx after 12 min 30 at 140°C, 5 min at 160°C and 2 min at 180°C.

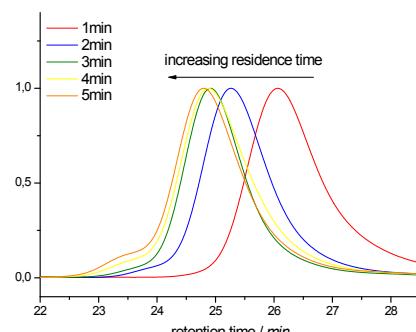
**140°C**

Residence Time	Conversion / %	$M_n^{\text{app}}$ / g mol <sup>-1</sup>	PDI
3 min	52.0	4290	1.22
4 min	65.7	5590	1.18
5 min	76.1	7680	1.15
7 min 30	91.0	8720	1.20
10 min	96.2	8560	1.26
12 min 30	99.3	8950	1.24



**160°C**

Residence Time	Conversion / %	$M_n^{\text{app}}$ / g mol <sup>-1</sup>	PDI
1 min	41.6	4210	1.19
2 min	76.6	6610	1.18
3 min	91.0	7880	1.18
4 min	97.1	7770	1.22
5 min	100	8170	1.23



**180°C**

Residence Time	Conversion / %	$M_n^{\text{app}}$ / g mol <sup>-1</sup>	PDI
30 s	54.6	5360	1.13
40 s	68.1	6800	1.12
50 s	75.0	7010	1.14
1 min	85.1	7010	1.19
75 s	92.8	7580	1.19
80 s	93.8	7790	1.19
100 s	98.4	8530	1.18
2 min	99.5	9240	1.16

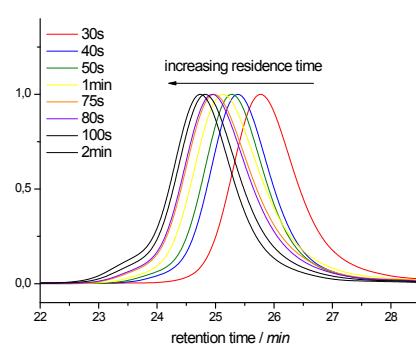


Figure S4: Results of the *n*PropOx homopolymerizations at 140°C, 160°C and 180°C. Tables include conversions, molecular weights and polydispersities for different residence times at each temperature. Overlay of SEC elugrams are shown as well for the same conditions.

The kinetics of the homopolymerization of *n*PropOx were investigated as well. The obtained conversions of the experiments described above were employed to develop a first order kinetic plot (shown below). By calculating the slope at each temperature, an Arrhenius plot was made to determine its activation energy:  $70.9 \pm 8.2 \text{ kJ}\cdot\text{mol}^{-1}$ , and its frequency factor A:  $0.68 \pm 0.12 \cdot 10^8 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ . This Arrhenius plot (solid line) is shown below in comparison with the Arrhenius plot of 2-ethyl-2-oxazoline (dotted line). The amount of overlap proves again the similarity in kinetics between both 2-oxazolines.

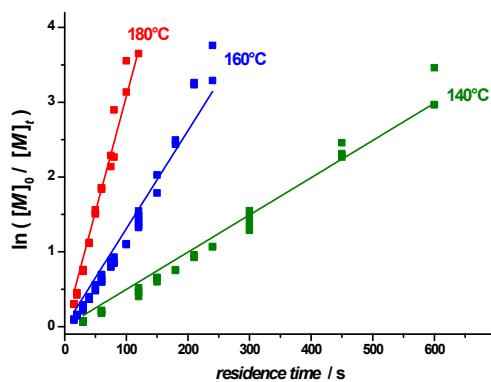


Figure S5: First order kinetic plot of the homopolymerization of *n*PropOx at 140°C, 160°C and 180°C.

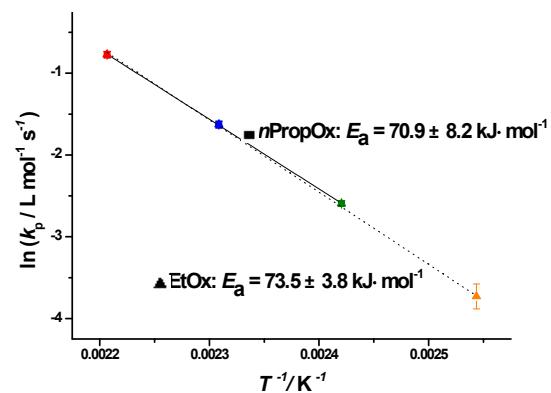


Figure S6: Arrhenius plot of the homopolymerization of *n*PropOx (solid line) in comparison to EtOx (dotted line).

## 5. Diblock Copolymerizations of EtOx and *n*PropOx

The synthesis of diblock copolymers was carried out in a 15  $\mu$ L reactor (5 + 10  $\mu$ L) at 160°C. To assure full monomer conversions for the first block, optimized conditions of the homopolymerization were applied for the first reactor part (5  $\mu$ L). Employed stock solutions were thus identical to the ones of the homopolymerization (2 mL EtOx or 2.35 mL *n*PropOx (4M), 0.05 mL MeOTs in 3 mL acetonitrile). Due to the intrinsic volume of the first reactor part, the stock solution was injected via two inlets at a total flow rate of 1  $\mu$ L/min leading to 5 min residence time.

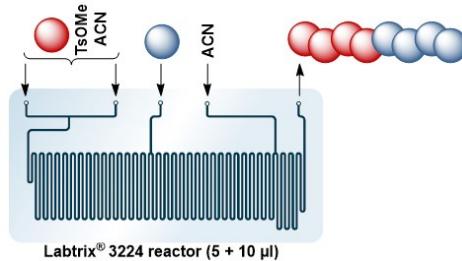


Figure S7: Representation of the 15  $\mu$ L reactor (5 + 10  $\mu$ L).

The second monomer was injected via the third inlet in bulk – no additional dilution was required since the polymer solution does not cause viscosity problems at high temperatures. Hence, the injection rate of the ‘pure’ monomer directly correlates to the density and thus to the amount of injected monomer. This way, a flexible set-up is obtained where changing the flow rate leads to a change in monomer 1/monomer 2 ratios. For EtOx-*b*-*n*PropOx diblock copolymers, a 0.47  $\mu$ L/min *n*PropOx injection leads to a 1/1 EtOx/*n*PropOx ratio. On the other hand, *n*PropOx-*b*-EtOx diblock copolymers in a 1/1 ratio require an EtOx injection at a 0.4  $\mu$ L/min flow rate. Doubling the injection rate of the second monomer leads to a 1/2 ratio, etc.

Nevertheless, due to the increase of the total flow rate, a larger reactor volume is required to have residence times comparable to the first block. The employed reactor does provide this by having an intrinsic volume of 10  $\mu$ L in the second part of the reactor. In addition, acetonitrile was injected at the last inlet of the reactor to avoid blockages at the outlet. Salt precipitation was avoided in the reactor by quenching with KOH/MeOH (1M) in the collection vial.

Tabel S2: Overview of the obtained diblock copolymers of EtOx and *n*PropOx.

a) *EtOx-b-n*PropOx diblock copolymers:

Targeted DP EtOx / <i>n</i> PropOx	residence time EtOx block	residence time <i>n</i> PropOx block	conversion <i>n</i> PropOx block	$M_n^{\text{app}}$ / g mol <sup>-1</sup>	PDI	$M_p^{\text{app}}$ / g mol <sup>-1</sup>	Observed EtOx / <i>n</i> PropOx
30 / -	5 min	-	-	6830	1.08	7160	1 / -
30 / 15	5 min	8 min 08	100 %	8030	1.18	9720	1 / 0.49
30 / 30	5 min	6 min 48	100 %	9370	1.19	12890	1 / 1.10
30 / 60	5 min	5 min 08	91 %	11230	1.31	17400	1 / 2.07
15 / -	5 min	-	-	3510	1.10	3790	1 / -
15 / 15	5 min	6 min 48	100 %	6140	1.12	7130	1 / 0.96
15 / 30	5 min	5 min 08	76%	9350	1.13	11710	1 / 5.15

b) *n*PropOx-*b*-EtOx diblock copolymers:

Targeted DP <i>n</i> PropOx / EtOx	residence time <i>n</i> PropOx block	residence time EtOx block	conversion EtOx block	$M_n^{\text{app}}$ / g mol <sup>-1</sup>	PDI	$M_p^{\text{app}}$ / g mol <sup>-1</sup>	Observed <i>n</i> PropOx / EtOx
30 / -	5 min	-	-	6510	1.09	7130	1 / -
30 / 15	5 min	8 min 20	100 %	6670	1.21	9230	1 / 0.53
30 / 30	5 min	7 min 09	95 %	10670	1.16	13640	1 / 1.05
30 / 60	5 min	5 min 33	100 %	13640	1.23	16040	1 / 2.22
15 / -	5 min	-	-	3940	1.09	4220	1 / -
15 / 15	5 min	7 min 09	100 %	5540	1.17	6490	1 / 1.18
15 / 30	5 min	5 min 33	100 %	7690	1.17	9340	1 / 2.24
15 / 60	5 min	3 min 51	100 %	17360	1.13	17450	1 / 5.80

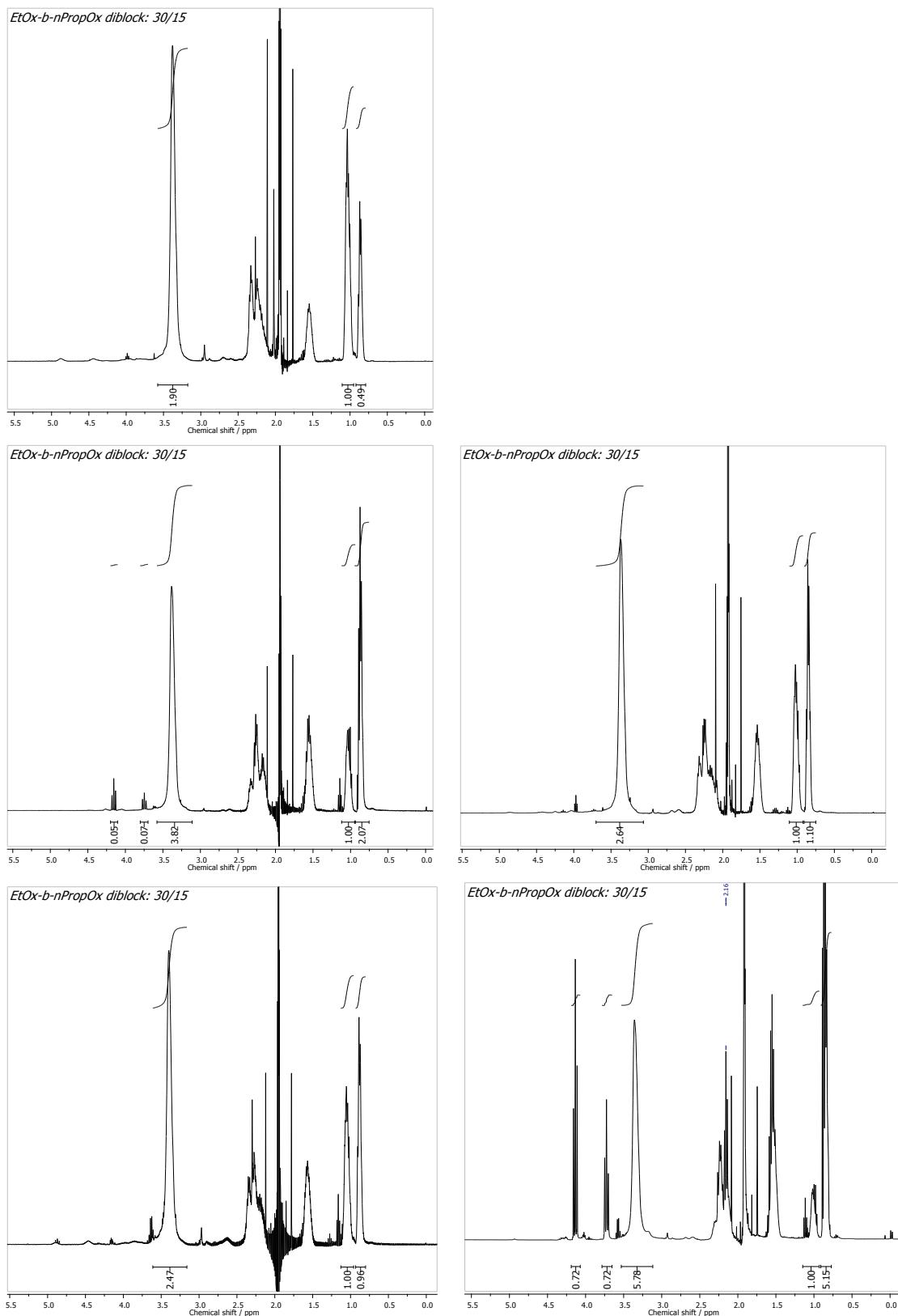


Figure S7:  $^1\text{H}$  NMR spectra of the EtOx-*b*-nPropOx diblock copolymers. Monomer compositions were determined via the integration of the  $\text{CH}_3$  peak of EtOx (1.04 ppm) and the  $\text{CH}_3$  peak of nPropOx (0.89 ppm). Deviations of the expected ratios are observed for the block copolymers with largely differing block lengths due to slight peak overlaps.

(peak assignment: 7.26 ppm ( $\text{CDCl}_3$ ), 4.20 (t,  $\text{CH}_2$  EtOx monomer), 4.14 (t,  $\text{CH}_2$  nPropOx monomer), 3.80 (t,  $\text{CH}_2$  EtOx monomer), 3.74 (t,  $\text{CH}_2$  nPropOx monomer), 2.26 (q,  $\text{CH}_2$  EtOx), 2.17 (t,  $\text{CH}_2$  nPropOx), 1.94 (ACN), 1.57 (q,  $\text{CH}_2$  nPropOx), 1.04 (t,  $\text{CH}_3$  EtOx), 0.89 (t,  $\text{CH}_3$  nPropOx) )

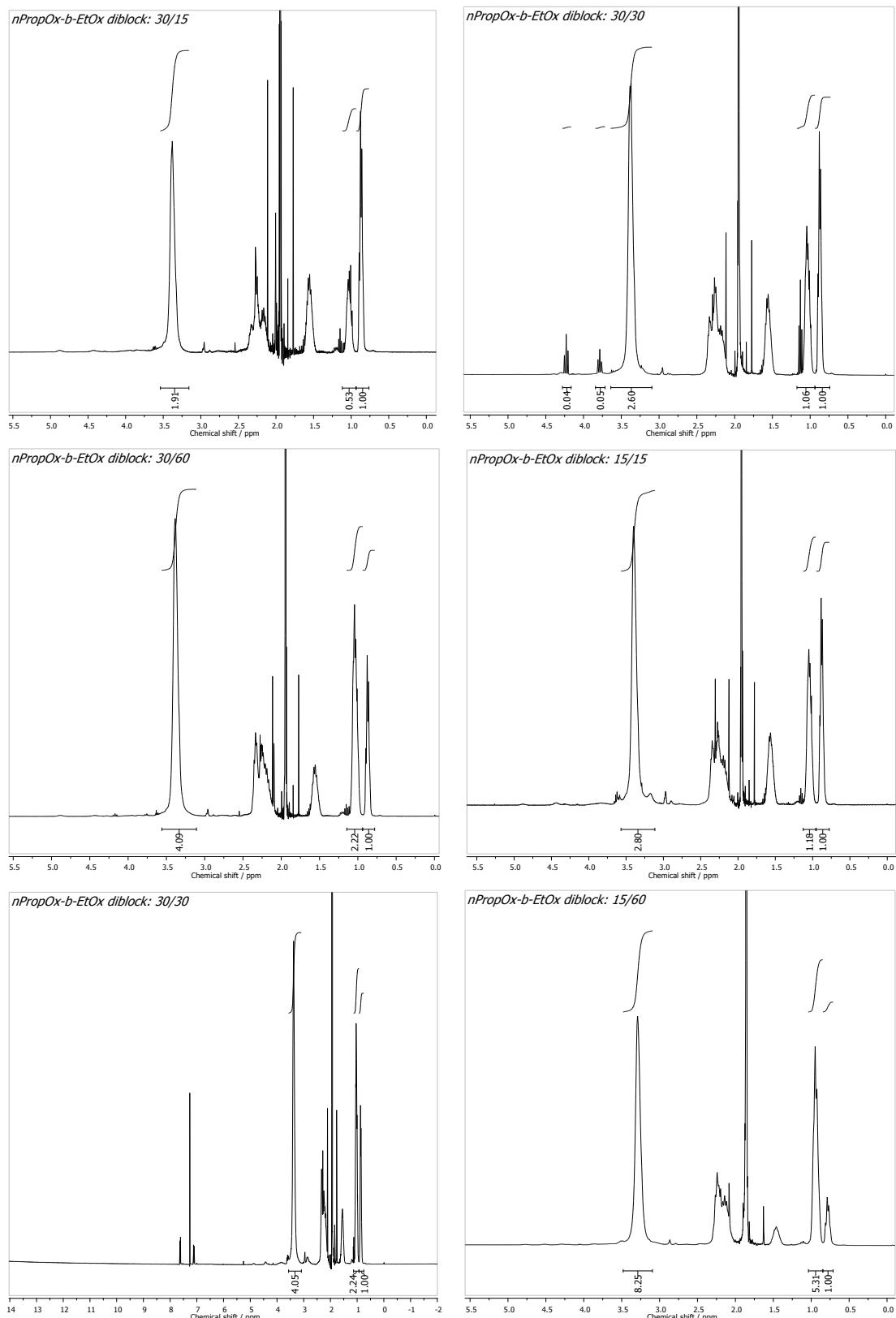


Figure S8:  $^1\text{H}$  NMR spectra of the *n*PropOx-*b*-EtOx diblock copolymers. Monomer compositions were determined via the integration of the  $\text{CH}_3$  peak of EtOx (1.04 ppm) and the  $\text{CH}_3$  peak of *n*PropOx (0.89 ppm). Deviations of the expected ratios are observed for the block copolymers with largely differing block lengths due to slight peak overlaps.

(peak assignment: 7.26 ppm ( $\text{CDCl}_3$ ), 4.20 (t,  $\text{CH}_2$  EtOx monomer), 4.14 (t,  $\text{CH}_2$  *n*PropOx monomer), 3.80 (t,  $\text{CH}_2$  EtOx monomer), 3.74 (t,  $\text{CH}_2$  *n*PropOx monomer), 2.26 (q,  $\text{CH}_2$  EtOx), 2.17 (t,  $\text{CH}_2$  *n*PropOx), 1.94 (ACN), 1.57 (q,  $\text{CH}_2$  *n*PropOx), 1.04 (t,  $\text{CH}_3$  EtOx), 0.89 (t,  $\text{CH}_3$  *n*PropOx) )

## 6. Triblock Copolymerizations of EtOx and nPropOx

The synthesis of triblock copolymers was carried out in a microreactor cascade of two coupled microreactors. A 15  $\mu$ L reactor (5 + 10  $\mu$ L), was used to make the first two blocks in a similar way as for the diblock copolymers. The first reactor part with an intrinsic volume of 5  $\mu$ L was used to make the first block. Therefore, the stock solution (identical to the homopolymerization: 2 mL EtOx or 2.35 mL nPropOx (4M), 0.05 mL MeOTs in 3 mL acetonitrile) was injected via two inlets at a total flow rate of 1  $\mu$ L/min leading to 5 min residence time. The second block was polymerized in the second reactor part (10  $\mu$ L) by injecting the second monomer via the third inlet in bulk. Employed flowrates directly correlate to the monomer density, and was calculated to give a 1:1 ratio with the first block to assure full monomer conversions for the second block as well. As second reactor, a 19.5  $\mu$ L reactor was coupled directly to the outlet of the first reactor to assure fully inert conditions. By injecting the third monomer in bulk, its injecting rate correlates to its density and determines the residence time of the last block. (Since the targeted triblock copolymers are mirror images, the residence time of the last block is thus identical.)

Temperature of the whole microreactor cascade was kept constant at 160°C, while the backpressure was maintained at 20 bar. Acetonitrile was injected at the last inlet of each reactor, to avoid blockages between both reactors or after the outlet of the second reactor. In this case, acetonitrile was thus also injected at the last inlet of the first reactor, leading to an additional dilution factor for the third block. To avoid salt precipitation in the reactor, quenching of the reaction mixture with KOH/MeOH (1M) occurred in the collection vial.

Table S3: Overview of the obtained triblock copolymers of EtOx and nPropOx, in comparison to the obtained homo- and diblocks with similar block lengths.

a) *EtOx-b-nPropOx-b-EtOx triblock copolymers:*

Targeted DP	residence time EtOx block	residence time nPropOx block	residence time 2 <sup>nd</sup> EtOx block	$M_n^{\text{app}}$ / g mol <sup>-1</sup>	PDI	$M_p^{\text{app}}$ / g mol <sup>-1</sup>	Observed EtOx / nPropOx
30 homoblock	5 min	-	-	6830	1.08	7150	1 / -
30 / 30 diblock	5 min	6 min 48	-	9370	1.19	12900	1 / 1.10
30 / 30 / 30 triblock	5 min	6 min 48	6 min 48	9850	1.33	14970	2 / 0.98
15 homoblock	5 min	-	-	3510	1.10	3740	1 / -
15 / 15 diblock	5 min	6 min 48	-	6140	1.12	7130	1 / 1.18
15 / 15 / 15 triblock	5 min	6 min 48	6 min 48	7400	1.25	10910	2 / 1.02

b) *nPropOx-b-EtOx b-nPropOx triblock copolymers:*

Targeted DP	residence time nPropOx block	residence time EtOx block	residence time 2 <sup>nd</sup> nPropOx block	$M_n^{\text{app}}$ / g mol <sup>-1</sup>	PDI	$M_p^{\text{app}}$ / g mol <sup>-1</sup>	Observed nPropOx / EtOx
30 homoblock	5 min	-	-	6510	1.09	7130	1 / -
30 / 30 diblock	5 min	7 min 09	-	10670	1.16	13640	1 / 1.05
30 / 30 / 30 triblock	5 min	7 min 09	6 min 48	11410	1.29	16650	2 / 1.11
15 homoblock	5 min	-	-	3940	1.09	4210	1 / -
15 / 15 diblock	5 min	7 min 09	-	5540	1.17	6490	1 / 1.18
15 / 15 / 15 triblock	5 min	7 min 09	6 min 48	7320	1.21	9660	2 / 1.13

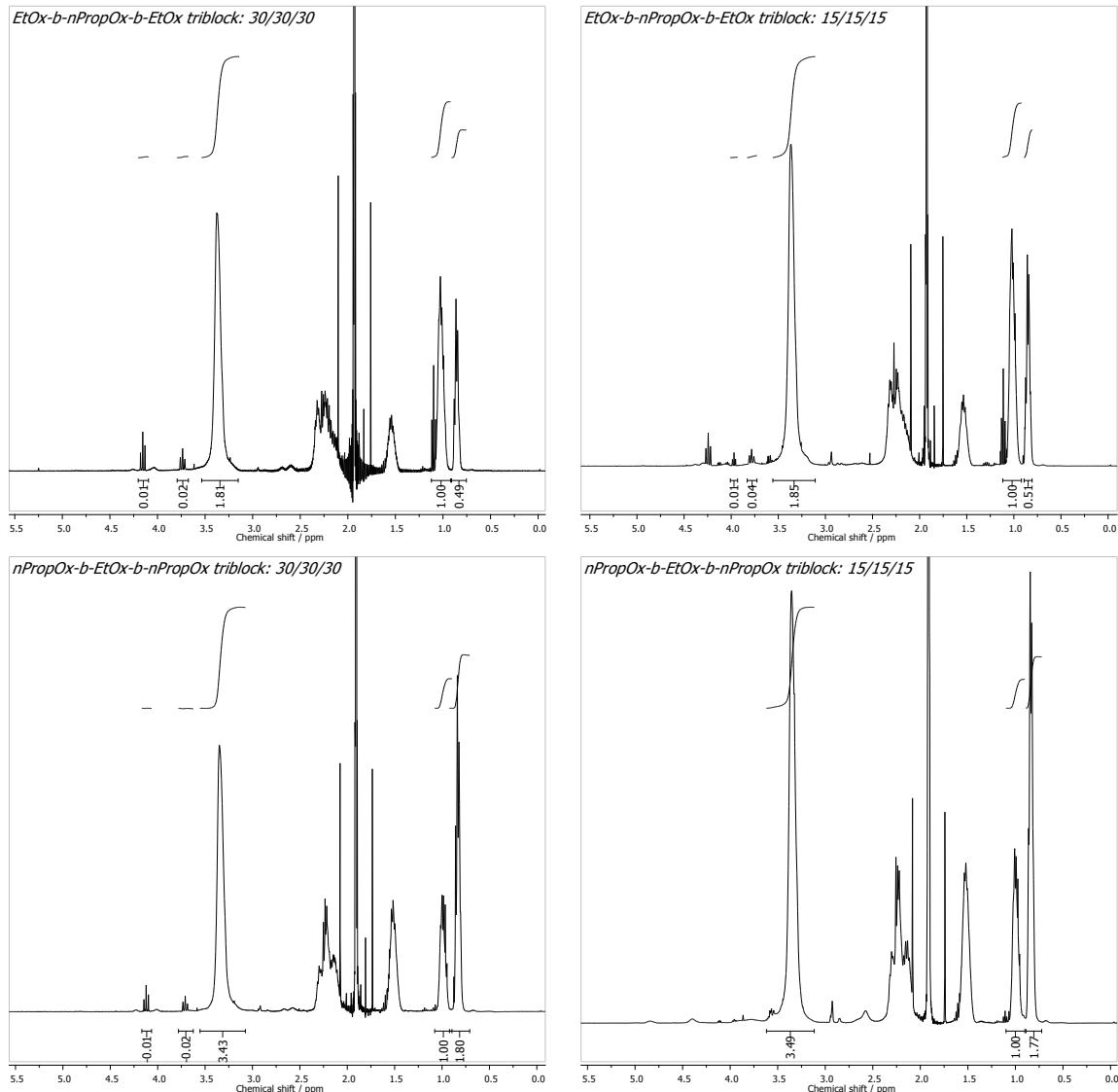


Figure S9:  $^1\text{H}$  NMR spectra of the EtOx-*b*-nPropOx-*b*-EtOx and nPropOx-*b*-EtOx-*b*-nPropOx triblock copolymers. Monomer compositions were determined via the integration of the  $\text{CH}_3$  peak of EtOx (1.04 ppm) and the  $\text{CH}_3$  peak of nPropOx (0.89 ppm), nevertheless deviations of the expected ratios can be seen to the Lorentzian peak shape of both methyl groups.

(peak assignment: 7.26 ppm ( $\text{CDCl}_3$ ), 4.20 (t,  $\text{CH}_2$  EtOx monomer), 4.14 (t,  $\text{CH}_2$  nPropOx monomer), 3.80 (t,  $\text{CH}_2$  EtOx monomer), 3.74 (t,  $\text{CH}_2$  nPropOx monomer), 2.26 (q,  $\text{CH}_2$  EtOx), 2.17 (t,  $\text{CH}_2$  nPropOx), 1.94 (ACN), 1.57 (q,  $\text{CH}_2$  nPropOx), 1.04 (t,  $\text{CH}_3$  EtOx), 0.89 (t,  $\text{CH}_3$  nPropOx) )

## 7. References

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- (2) Goossens, H.; Catak, S.; Glassner, M.; de la Rosa, V. R.; Monnery, B. D.; De Proft, F.; Van Speybroeck, V.; Hoogenboom, R. *ACS Macro Letters* **2013**, *2*, 651.