Supplementary Information

Comparison of the hydrophilicity of water-soluble poly(2-alkyl-2-oxazoline)s, poly(2-alkyl-2-oxazine)s and poly(2,4-dialkyl-2-oxazoline)s

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Table of contents

Monomer synthesis

iPrOx: iPrOx synthesis was carried out as described in literature.[1] 35 mL (1 mol. equiv.) of isobutyronitrile and 1.8 g (0.02 mol. equiv.) of zinc acetate dihydrate was heated under reflux conditions to 130 °C, before dropwise addition of 27 mL (1.06 mol. equiv.) 2-aminoethanol. Reflux was continued at 130 °C for 24 hours before being cooled to room temperature. iPrOx was purified via aqueous separation with 3x washes in MilliQ water and 2x wash in brine, followed by distillation. iPrOx was then dried over BaO under N_2 flow overnight and distilled to dryness.

MeOz: MeOz synthesis was carried out as described in literature.[2] 50 mL (1 mol. equiv.) of acetonitrile and 4.2 g (0.02 mol. equiv.) of zinc acetate dihydrate was heated under reflux conditions to 84 °C, before dropwise addition of 80 mL (1.1 mol. equiv.) 3-amino-1-propanol. Reflux was continued at 130 °C for 24 hours before being cooled to room temperature. MeOz was purified via distillation and dried over BaO under N_2 overnight before being distilled to dryness.

EtOz: EtOz synthesis was carried out as described in literature.[2] 50 mL (1 mol. equiv.) of propionitrile and 3.1 g (0.02 mol. equiv.) of zinc acetate dihydrate was heated under reflux conditions to 100 °C, before dropwise addition of 59 mL (1.1 mol. equiv.) 3-amino-1-propanol. Reflux was continued at 115 °C for 24 hours before being cooled to room temperature. EtOz was purified via distillation and dried over BaO under N_2 overnight before being distilled to dryness.

iPrOz: iPrOz synthesis was carried out as described in literature.[3] 100 mL (1 mol. equiv.) of isobutyronitrile and 4.9 g (0.02 mol. equiv.) of zinc acetate dihydrate was heated under reflux conditions to 110 °C, before dropwise addition of 93 mL (1.1 mol. equiv.) 3-amino-1-propanol. Reflux was continued at 150 °C for 24 hours before being cooled to room temperature. iPrOz was purified via aqueous separation with 3x washes in MilliQ water and 1x wash in brine, followed by distillation. iPrOz was then dried over BaO under N_2 flow overnight and distilled to dryness.

R,RS-dMeOx: The synthesis of *R* and *RS*-dMeOx was carried out as described in literature.[4] 32 mL (1 mol. equiv.) of acetonitrile was added to a 100 mL two-necked round bottom flask with 4.1 g (0.026 mol equiv.) cadmium acetate dihydrate and heated to 93 °C under reflux. 50 mL (1.06 mol. equiv.) of

the appropriate 2-amino-1-propanol (*RS*-(+/-)-2-amino-1-propanol for *RS*-dMeOx; (*R*-(-)-2-amino-1-propanol for *R*-dMeOx) was added dropwise using a dropping funnel. The reaction proceeded for 24 hours for *RS*-dMeOx or 48 hours for *R*-dMeOx. Monomer was purified via distillation. Purified monomer was dried over calcium hydride under N_2 flow overnight, then distilled to dryness.

R,RS-EtMeOx: The synthesis of *R* and *RS*-EtMeOx was carried out as described in literature.[4] 42 mL (1 mol. equiv.) of propionitrile was added to a 100 mL two-necked round bottom flask with 4.1 g (0.026 mol. equiv.) cadmium acetate dihydrate and heated to either 120 °C (*R*-EtMeOx) or 150 °C (*RS*-EtMeOx) under reflux. 50 mL (1.06 mol. equiv.) of the appropriate 2-amino-1-propanol (*RS*-(+/-)-2-amino-1-propanol for *RS*-EtMeOx; (*R*-(-)-2-amino-1-propanol for *R*-EtMeOx) was added dropwise. The reaction proceeded for 24 hours and allowed to cool to room temperature. Monomer was purified via aqueous separation using 3x washes in saturated $NaCO_3$ and 1x brine, followed by distillation. Purified monomer was dried over BaO under N_2 flow overnight, then distilled to dryness.

Polymer synthesis

Purchased monomers (MeOx, EtOx, iPrOx) and MeOTs were dried over BaO and distilled to dryness before use. MeOz, EtOz, iPrOz, *R/RS*-PdMeOx and *R/RS*-PEtMeOx were synthesised as above and similarly distilled to dryness before use.

<u>KOH terminated polymers:</u>

PMeOx$_{20,50}$: Dry MeOx (2 mL, DP50: 50 mol. equiv., DP20: 20. mol equiv.), was added to dry MeOTs (DP50: 71.8 µl, DP20: 178 µL, 1.5 mol. equiv.) and ACN (DP50: 3.83 mL; DP20: 3.72 mL) in a pre-dried biotage tube under nitrogen. Solutions were sealed and stirred in an oil bath at 80 °C for 4 hours (DP50) or 1 hour 36 min (DP20), before being terminated via addition of 1M methanolic KOH (DP50: 0.7 mL DP20: 1.8 mL, 1.5 mol. equiv.) and stirring at room temperature for 10 minutes. Polymer solutions were filtered through a 0.45 µm PTFE filter and precipitated 3x in cold diethyl ether. DP50

polymers were then dialysed against MQ water (3.5 kDa membrane, Spectra/Por 3 dialysis tubing) for 1 day. Polymers were lyophilised to produce a white powder.

PEtOx$_{20,50}$: Dry EtOx (2.07 mL, DP50: 50 mol. equiv., DP20: 20 mol. equiv.) was added to dry MeOTs (DP50: 61.8 µL; DP20: 155 µL, 1 mol. equiv.) and ACN (DP50: 2.97 mL, DP20: 2.88 mL) in a pre-dried biotage tube under nitrogen. Solutions were sealed and stirred in an oil bath at 80 °C for 5 hours (DP50) or 2 hours (DP20), before being terminated via addition of 1M methanolic KOH (DP50: 0.63 mL, DP20: 1.6 mL, 1.5 mol. equiv.) and stirring at room temperature for 10 minutes. Polymer solutions were filtered through a 0.45 µm PTFE filter and precipitated 3x in cold diethyl ether. DP50 polymers were then dialysed against MQ water (3.5 kDa membrane, Spectra/Por 3 dialysis tubing) for 1 day. Polymers were lyophilised to produce a white powder.

PiPrOx$_{20,50}$: Dry iPrOx (2 mL, DP50: 52 mol. equiv., DP20: 20 mol. equiv.) was added to dry MeOTs (DP50: 50 µL, DP20: 134 µL, 1 mol. equiv.) and ACN (DP50: 2.38 mL, DP20: 2.29 mL) in a pre-dried microwave vial under nitrogen. Solutions were reacted in a CEM discover SP microwave synthesizer at 140 °C for 14 minutes (DP50) or 5 minutes (DP20). The resulting polymer was cooled to room temperature and terminated with 1M methanolic KOH (DP50: 0.50 mL, DP20: 1.3 mL, 1.5 mol. equiv.) and stirred for 10 minutes at room temperature. Solutions were filtered through a 0.45 µm PTFE filter to remove KOTs precipitate and precipitated 3x in petroleum benzine (60-80 °C b.p.). Polymers were lyophilised to produce a white powder.

R-PdMeOx$_{20,50}$: Dry R-dMeOx (2 mL, DP50: 60 mol. equiv., DP20: 24 mol. equiv.) was added to dry MeOTs (DP50: 51 µL, DP20: 127 µL, 1 mol. equiv.) and ACN (DP50: 8.05 mL, DP20: 7.97 mL) in a pre-dried microwave vial under nitrogen. Solutions were reacted in a CEM discover SP microwave synthesizer at 140 °C for 75 minutes (DP50) or 32 minutes (DP20). The resulting polymer was cooled to 0 °C and terminated with 1M methanolic KOH (DP50: 0.50 mL, DP20: 1.26 mL, 1.5 mol. equiv.) and stirred overnight at room temperature. Solutions were filtered through a 0.45 µm PTFE filter to remove KOTs precipitate and precipitated 1x into cold diethyl ether, before being dialysed against MQ water (1 kDa membrane, Spectra/Por 6 dialysis tubing) for 1 day. Polymers were lyophilised to produce a white powder.

RS-PdMeOx$_{20,50}$: Dry RS-dMeOx (2 mL, DP50: 60 mol. equiv., DP20: 24 mol. equiv.) was added to dry MeOTs (DP50: 51 µL, DP20: 127 µL, 1 mol. equiv.) and ACN (DP50: 8.05 mL, DP20: 7.97 mL) in a pre-dried microwave vial under nitrogen. Solutions were reacted in a CEM discover SP microwave synthesizer at 140 °C for 75 minutes (DP50) or 32 minutes (DP20). The resulting polymer was cooled to 0 °C and terminated with 1M methanolic KOH (DP50: 0.50 mL, DP20: 1.26 mL, 1.5 mol. equiv.) and stirred overnight at room temperature. Solutions were filtered through a 0.45 µm PTFE filter to remove KOTs precipitate and precipitated 1x into cold diethyl ether, before being dialysed against MQ water (1 kDa membrane, Spectra/Por 6 dialysis tubing) for 1 day. Polymers were lyophilised to produce a white powder.

R-PEtMeOx$_{20,50}$: Dry R-EtMeOx (2 mL, DP50: 60 mol. equiv., DP20: 24 mol. equiv.) was added to dry MeOTs (DP50: 45 µL, DP20: 112 µL, 1 mol. equiv.) and ACN (DP50: 6.79 mL, DP20: 6.73 mL) in a pre-dried microwave vial under nitrogen. Solutions were reacted in a CEM discover SP microwave synthesizer at 140 °C for 110 minutes (DP50) or 44 minutes (DP20). The resulting polymer was cooled to 0 °C and terminated with 1M methanolic KOH (DP50: 0.44 mL, DP20: 1.10 mL, 1.5 mol. equiv.) and stirred overnight at room temperature. Solutions were filtered through a 0.45 µm PTFE filter to remove KOTs precipitate and precipitated 1x into cold diethyl ether, before being dialysed against MQ water (1 kDa membrane, Spectra/Por 6 dialysis tubing) for 1 day. Polymers were lyophilised to produce a white powder.

RS-PEtMeOx$_{20,50}$: Dry RS-EtMeOx (2 mL, DP50: 60 mol. equiv., DP20: 24 mol. equiv.) was added to dry MeOTs (DP50: 45 µL, DP20: 112 µL, 1 mol. equiv.) and ACN (DP50: 6.79 mL, DP20: 6.73 mL) in a pre-dried microwave vial under nitrogen. Solutions were reacted in a CEM discover SP microwave synthesizer at 140 °C for 110 minutes (DP50) or 44 minutes (DP20). The resulting polymer was cooled to 0 °C and terminated with 1M methanolic KOH (DP50: 0.44 mL, DP20: 1.10 mL, 1.5 mol. equiv.) and stirred overnight at room temperature. Solutions were filtered through a 0.45 µm PTFE filter to remove KOTs precipitate and precipitated 1x into cold diethyl ether, before being dialysed against MQ water (1 kDa membrane, Spectra/Por 6 dialysis tubing) for 1 day. Polymers were lyophilised to produce a white powder.

$PMeOz_{20,50}$: Dry MeOz (2 mL, DP50: 52 mol. equiv., DP20: 22 mol. equiv.) was added to dry MeOTs (DP50: 59 µL, DP20: 139 µL, 1 mol. equiv.) and ACN (DP50: 2.99 mL, DP20: 2.91 mL) in a pre-dried microwave vial under nitrogen. Solutions were reacted in a CEM discover SP microwave synthesizer at 140 °C for 18.5 minutes (DP50) or 7.8 minutes (DP20). The resulting polymer was cooled to room temperature and terminated with 1M methanolic KOH (DP50: 0.033 mL, DP20: 0.077 mL, 1.5 mol. equiv.) and stirred for 10 minutes at room temperature. Solutions were filtered through a 0.45 µm PTFE filter to remove KOTs precipitate and precipitated 3x in petroleum benzine (60-80 °C b.p.), followed by dialysis against MQ water with a (1 kDa membrane, Spectra/Por 6 dialysis tubing) day for the DP50 polymer. Polymers were lyophilised to produce a white powder.

$PEtOz_{20,50}$: Dry EtOz (2 mL, DP50: 52 mol. equiv., DP20: 22 mol. equiv.) was added to dry MeOTs (DP50: 51 µL, DP20: 122 µL, 1 mol. equiv.) and ACN (DP50: 2.37 mL, DP20: 2.30 mL) in a pre-dried microwave vial under nitrogen. Solutions were reacted in a CEM discover SP microwave synthesizer at 140 °C for 28.2 minutes (DP50) or 11.9 minutes (DP20). The resulting polymer was cooled to room temperature and terminated with 1M methanolic KOH (DP50: 0.029 mL, DP20: 0.068 mL, 1.5 mol. equiv.) and stirred for 10 minutes at room temperature. Solutions were filtered through a 0.45 µm PTFE filter to remove KOTs precipitate and precipitated 3x in petroleum benzine (60-80 °C b.p.). Polymers were lyophilised to produce a white powder.

$PiPrOz_{20,50}$: Dry iPrOz (2 mL, DP50: 52 mol. equiv., DP20: 22 mol. equiv.) was added to dry MeOTs (DP50: 46 µL, DP20: 108 µL, 1 mol. equiv.) and ACN (DP50: 1.89 mL, DP20: 2.82 mL) in a pre-dried microwave vial under nitrogen. Solutions were reacted in a CEM discover SP microwave synthesizer at 140 °C for 43.3 minutes (DP50) or 18.3 minutes (DP20). The resulting polymer was cooled to room temperature and terminated with 1M methanolic KOH (DP50: 0.5 mL, DP20: 1.1 mL, 1.5 mol. equiv.) and stirred for 10 minutes at room temperature. Solutions were filtered through a 0.45 µm PTFE filter to remove KOTs precipitate and precipitated 3x in petroleum benzine (60-80 °C b.p). The DP50 polymer was dialysed against MQ water (3.5 kDa, Spectra/Por 3 dialysis tubing) for 3 days. Polymers were lyophilised to produce a white powder.

TMAH terminated polymers:

$PEtOx_{20}$: TMAH-terminated $PEtOx_{20}$ was synthesised using a modified procedure based on that outlined in literature.[5] Dry EtOx (1 mL, 22 mol. equiv.) was added to dry MeOTs (69.4 µL, 1 mol. equiv.) and ACN (1.45 mL) in a pre-dried microwave vial under nitrogen to create a 4M solution. The solution was sealed with a septum and polymerised in an oil bath at 80 °C for 2 hours. The solution was cooled to 0 °C and terminated with methanolic TMAH (25 wt%) (0.145 mL, 3 mol. equiv.) and stirred at room temperature overnight (18 hours). The resulting solution was filtered through a 0.45 µm PTFE filter to remove salts, ACN evaporated, and the crude polymer resuspended in DCM, before being washed 3x with saturated $NaCO_3$ and 1x with brine. The resulting organic fraction was dried, DCM evaporated, and the polymer precipitated 3x in cold diethyl ether. The polymer was subsequently lyophilised to form a white powder.

R-$PdMeOx_{20}$: Dry *R*-dMeOx (0.5 mL, 24 mol. equiv.) was added to dry MeOTs (31.9 µL, 1 mol. equiv.) and ACN (2.00 mL) in a pre-dried Biotage microwave vial under nitrogen to create a 2M solution. The vial was sealed and reacted in a Biotage microwave reactor for 32 minutes. The solution was cooled to 0 °C and terminated with methanolic TMAH (25 wt%) (0.067 mL, 3 mol. equiv.) and stirred at room temperature overnight (18 hours). The resulting solution was filtered through a 0.45 µm PTFE filter to remove salts, ACN evaporated, and the crude polymer precipitated 3x in cold diethyl ether. The polymer was subsequently dialysed against MQ water for 24 hours (1 kDa membrane, Spectra/Por 6 dialysis tubing) and lyophilised to form a white powder.

RS-$PdMeOx_{20}$: Dry *RS*-dMeOx (0.5 mL, 24 mol. equiv.) was added to dry MeOTs (31.9 µL, 1 mol. equiv.) and ACN (2.00 mL) in a pre-dried Biotage microwave vial under nitrogen to create a 2M solution. The vial was sealed and reacted in a Biotage microwave reactor for 32 minutes. The solution was cooled to 0 °C and terminated with methanolic TMAH (25 wt%) (0.067 mL, 3 mol. equiv.) and stirred at room temperature overnight (18 hours). The resulting solution was filtered through a 0.45 µm PTFE filter to remove salts, ACN evaporated, and the crude polymer precipitated 3x in cold diethyl ether. The polymer was subsequently dialysed against MQ water for 24 hours (1 kDa membrane, Spectra/Por 6 dialysis tubing) and lyophilised to form a white powder.

PEtOz$_{20}$: Dry EtOz (1 mL, 22 mol. equiv.) was added to dry MeOTs (60.9 µL, 1 mol. equiv.) and ACN (1.16 mL) in a pre-dried Biotage microwave vial under nitrogen to create a 2M solution. The vial was sealed and reacted in a Biotage microwave reactor for 32 minutes. The solution was cooled to 0 °C and terminated with methanolic TMAH (25 wt%) (0.128 mL, 3 mol. equiv.) and stirred at room temperature overnight (18 hours). The resulting solution was filtered through a 0.45 µm PTFE filter to remove salts, ACN evaporated, and the crude polymer precipitated 3x in cold diethyl ether. The polymer was subsequently dialysed against MQ water for 24 hours (1 kDa membrane, Spectra/Por 6 dialysis tubing) and lyophilised to form a white powder.

Polymer characterisation

Table S1. Additional number of carbons assignment of PCIEs compared to unsubstituted POx.

Polymer	Additional side chain carbons	Additional backbone carbons	Total additional carbons
Unsubstituted POx	0	0	0
PMeOx	1	0	1
PMeOz	1	1	2
R/RS-PdMeOx	1	1	2
PEtOx	2	0	2
PEtOz	2	1	3
R/RS-PEtMeOx	2	1	3
PiPrOx	3	0	3

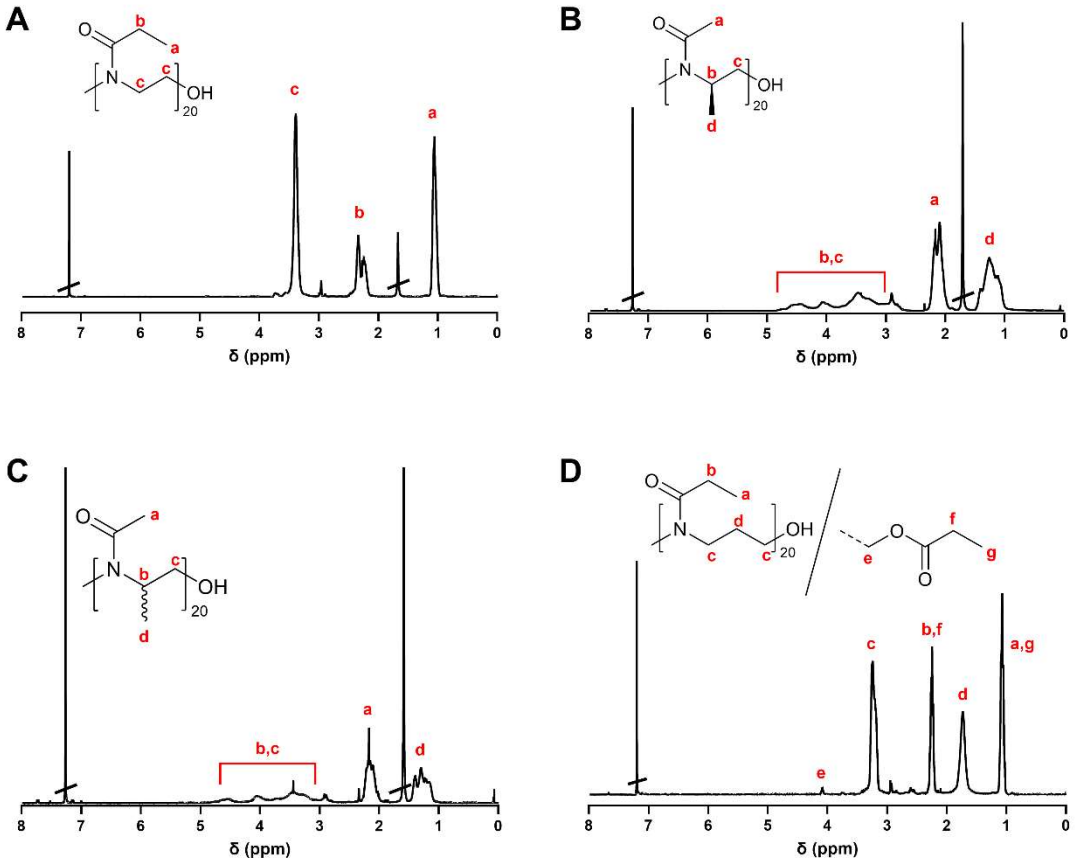

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) assignment for TMAH terminated PCIEs. **(A)** $PEtOx_{20}$, **(B)** *R*-$PdMeOx_{20}$, **(C)** *RS*-$PdMeOx_{20}$, **(D)** $PEtOz_{20}$; note the alternative amine ester end group identified in the ^{1}H NMR trace via the presence of a peak at 4.1 ppm (peak e).

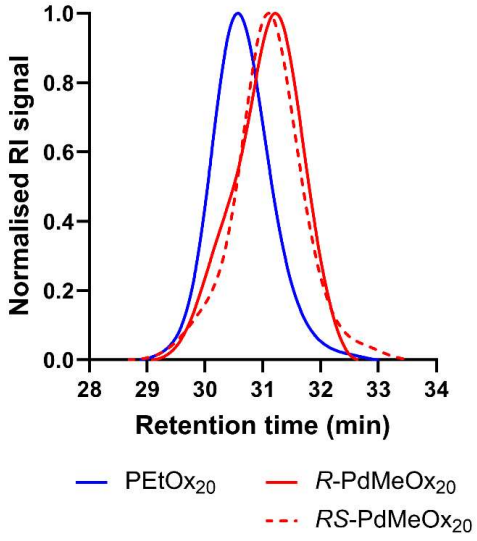

Figure S2. SEC traces (DMAc + 0.03% LiBr, polystyrene standard) for TMAH terminated $PEtOx_{20}$ (blue), *R*-$PdMeOx_{20}$ (red solid) and *RS*-$PdMeOx_{20}$ (red dashed).

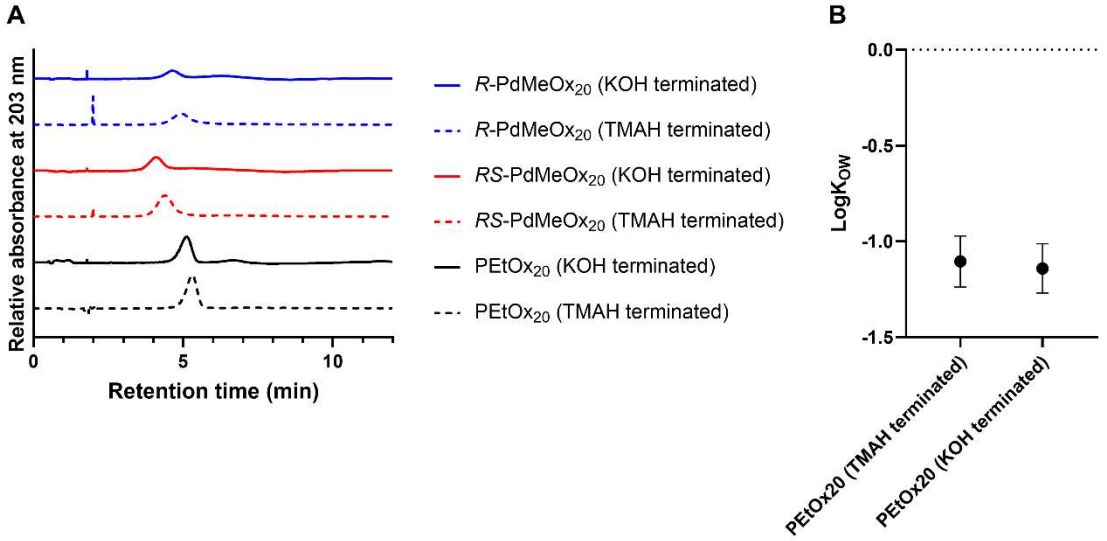

Figure S3. (A) HPLC spectra and **(B)** $LogK_{OW}$ values for $PEtOx_{20}$ terminated with KOH or TMAH. *R*-$PdMeOx_{20}$ and *RS*-$PdMeOx_{20}$ terminated with KOH or TMAH all partitioned completely into the aqueous phase and thus no $LogK_{OW}$ could be calculated. HPLC spectra were obtained from a 20 – 80% MQ+0.1%FA-ACN gradient elution in a C8 column over a total of 12 minutes. Absorbance was measured at 203 nm.

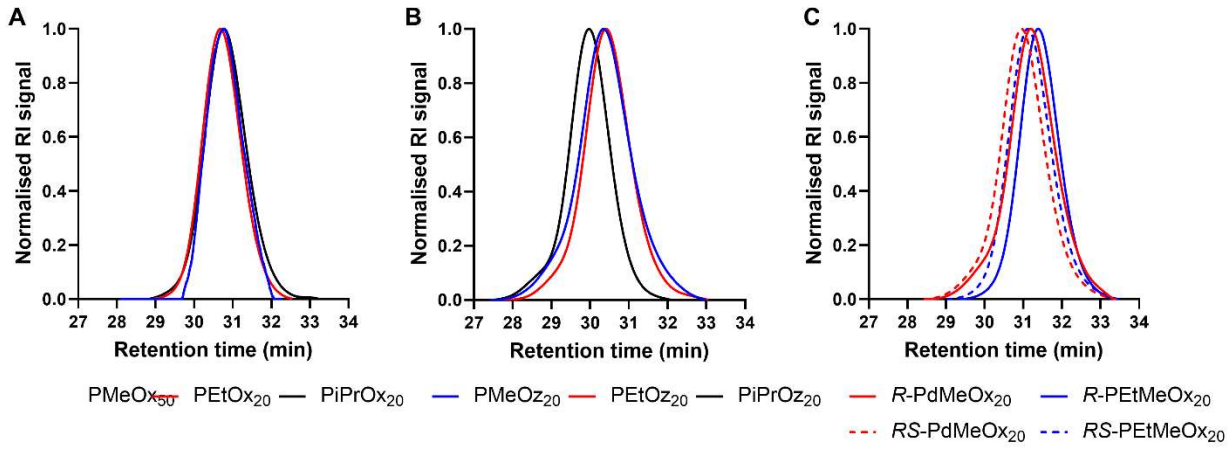

Figure S4. SEC traces (DMAc + 0.03% LiBr, polystyrene standard) for synthesised DP20 KOH terminated **(A)** Poly(2-alkyl-2-oxazoline)s, **(B)** poly(2-alkyl-2-oxazine)s, and **(C)** poly(2,4-dialkyl-2-oxazoline)s.

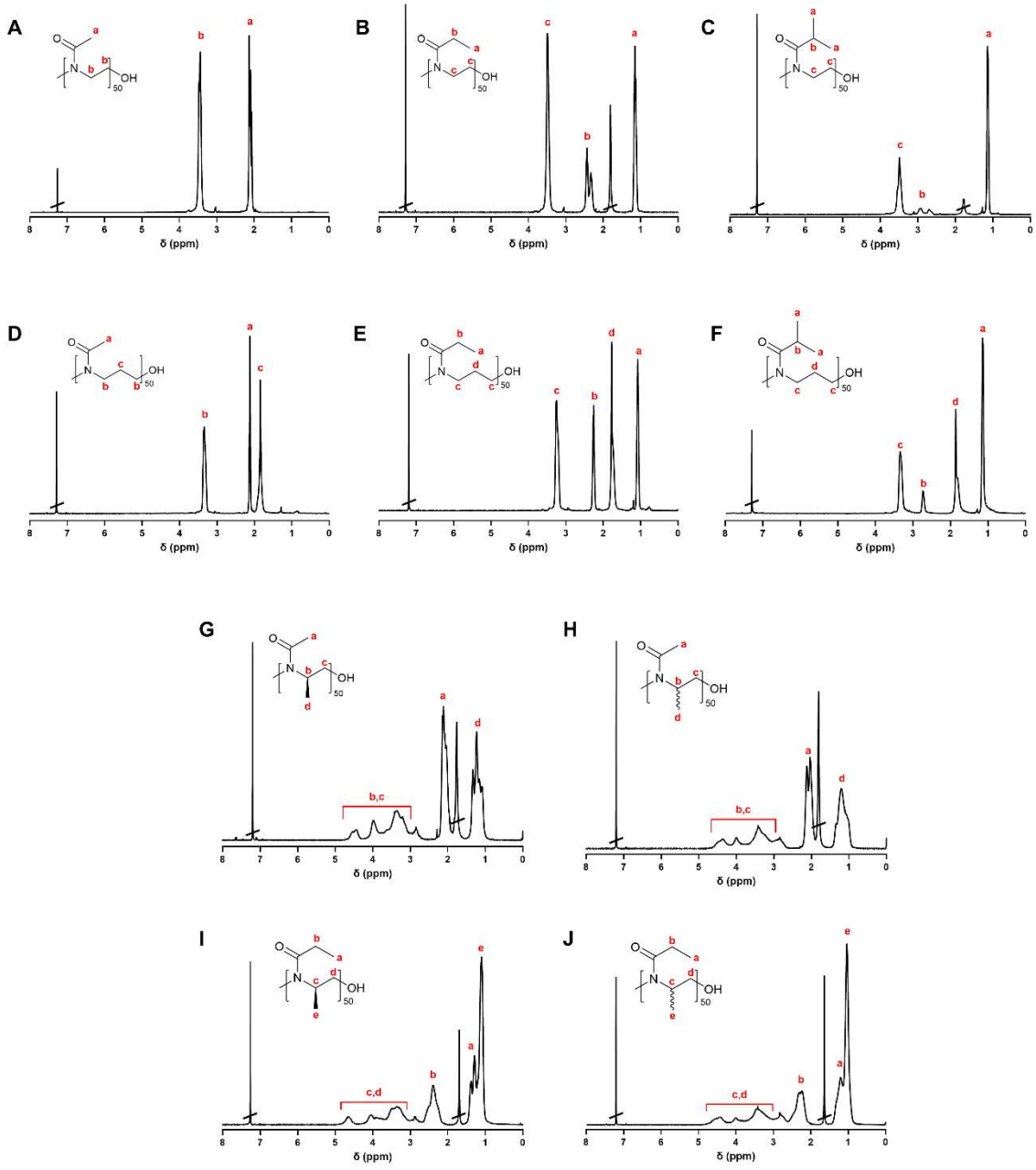

Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) assignment for DP50 PCIEs. **(A)** $PMeOx_{50}$, **(B)** $PEtOx_{50}$, **(C)** $PiPrOx_{50}$, **(D)** $PMeOz_{50}$, **(E)** $PEtOz_{50}$, **(F)** $PiPrOz_{50}$, **(G)** *R*-$PdMeOx_{50}$, **(H)** *RS*-$PdMeOx_{50}$, **(I)** *R*-$PEtMeOx_{50}$, **(J)** *RS*-$PEtMeOx_{50}$.

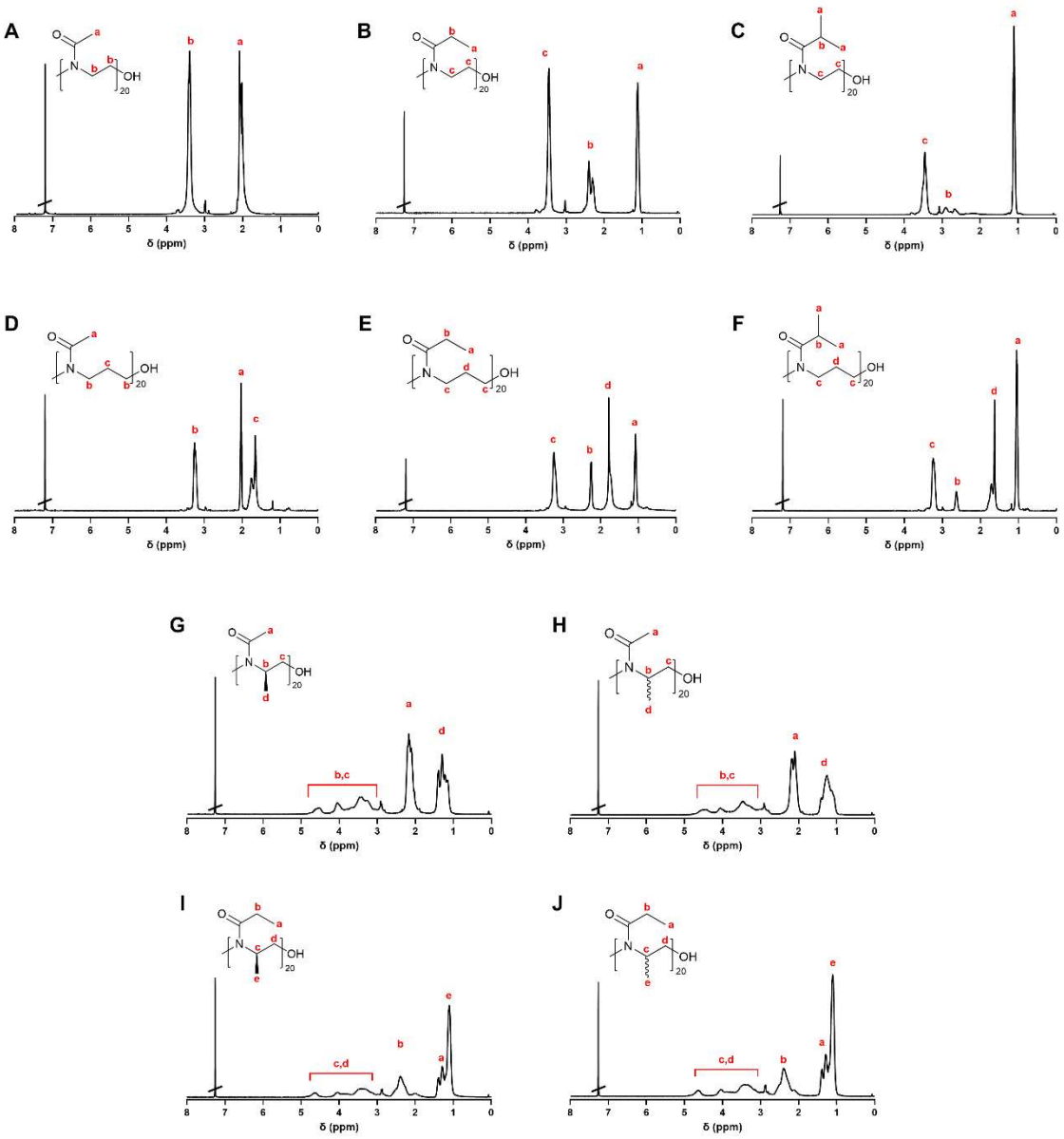

Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) assignment for DP20 PCIEs. **(A)** $PMeOx_{20}$, **(B)** $PEtOx_{20}$, **(C)** $PiPrOx_{20}$, **(D)** $PMeOz_{20}$, **(E)** $PEtOz_{20}$, **(F)** $PiPrOz_{20}$, **(G)** *R*-$PdMeOx_{20}$, **(H)** *RS*-$PdMeOx_{20}$, **(I)** *R*-$PEtMeOx_{20}$, **(J)** *RS*-$PEtMeOx_{20}$.

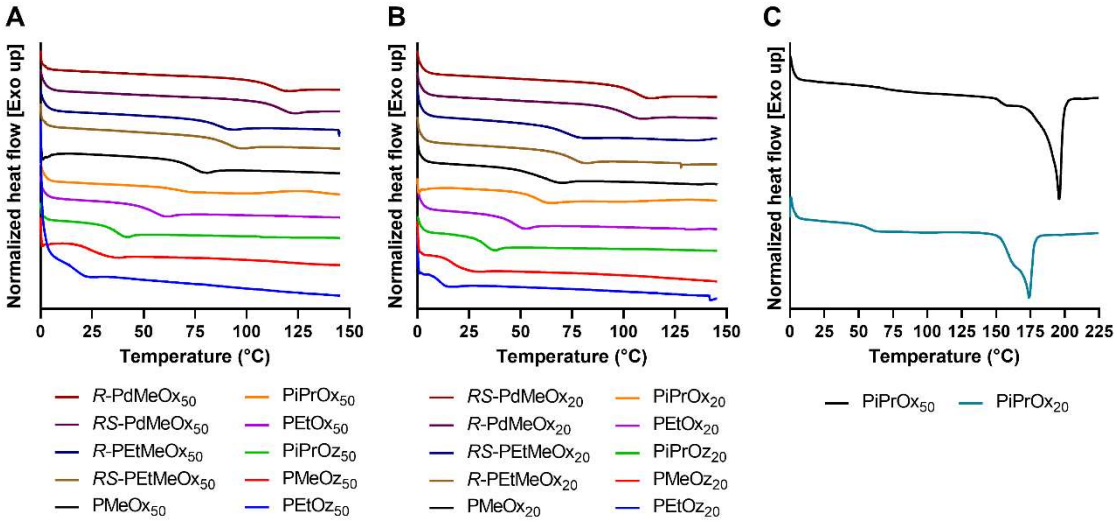

Figure S7. (A) DSC traces for T_g determination for DP50 polymers, **(B)** DSC traces for T_g determination for DP20 polymers, **(C)** DSC traces for T_m determination for semicrystalline $PiPrOx_{50}$ and $PiPrOx_{20}$.

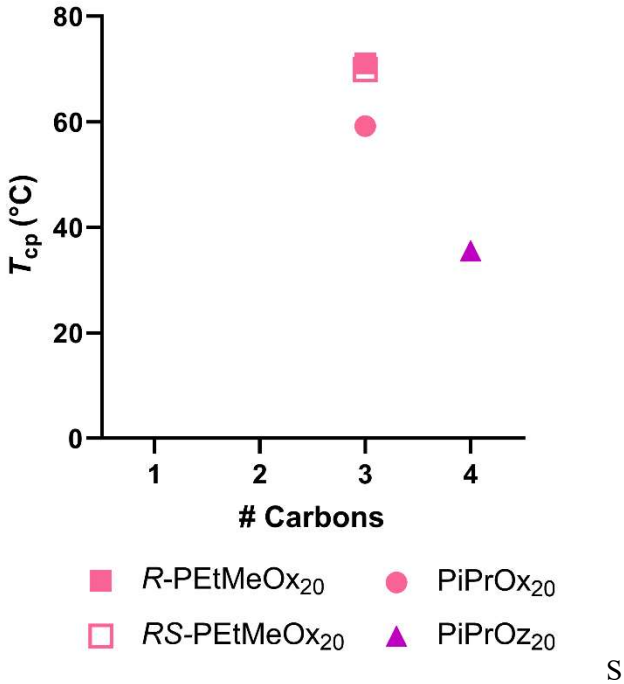

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Figure S8. T_{cp} values for DP20 thermoresponsive polymers according to number of additional carbons as illustrated in Scheme 1B.

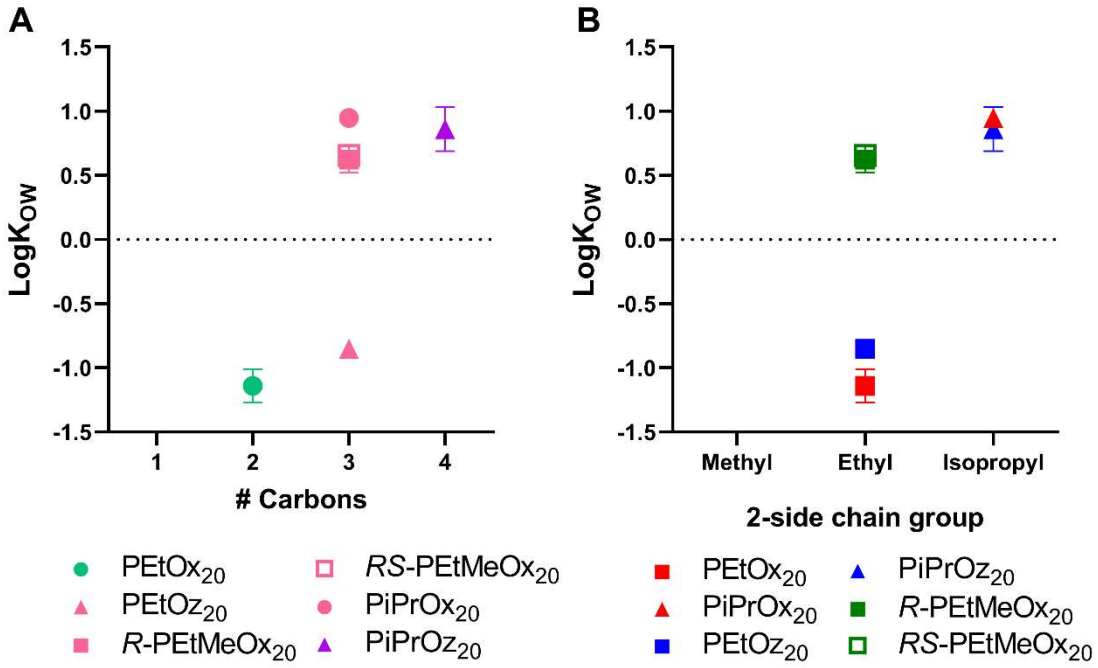

Figure S9. (A) $LogK_{OW}$ values for DP20 polymers, plotted in terms of additional carbons as established in Scheme 1B. **(B)** $LogK_{OW}$ values for DP20 polymers plotted in terms of 2-side chain group and polymer family as established in Scheme 1A.

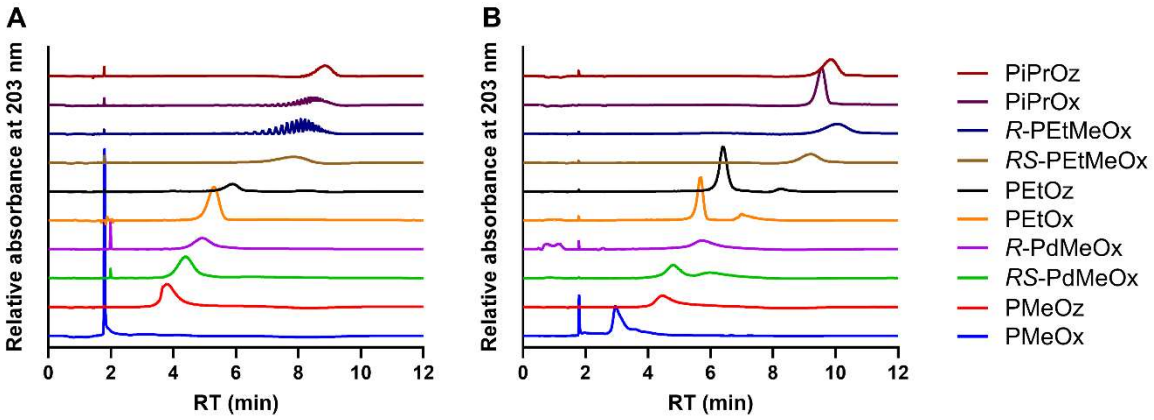

Figure S10. HPLC spectra for **(A)** DP20 polymers and **(B)** DP50 polymers. $PEtOx_{20}$, *R*-$PdMeOx_{20}$, and *RS*-$PdMeOx_{20}$ were terminated with TMAH, the remaining polymers were terminated with KOH. Spectra were obtained from a 20 – 80% MQ+0.1%FA-ACN gradient elution in a C8 column over a total of 12 minutes. Absorbance was measured at 203 nm. Where relevant, only major peaks were used for determination of retention time.

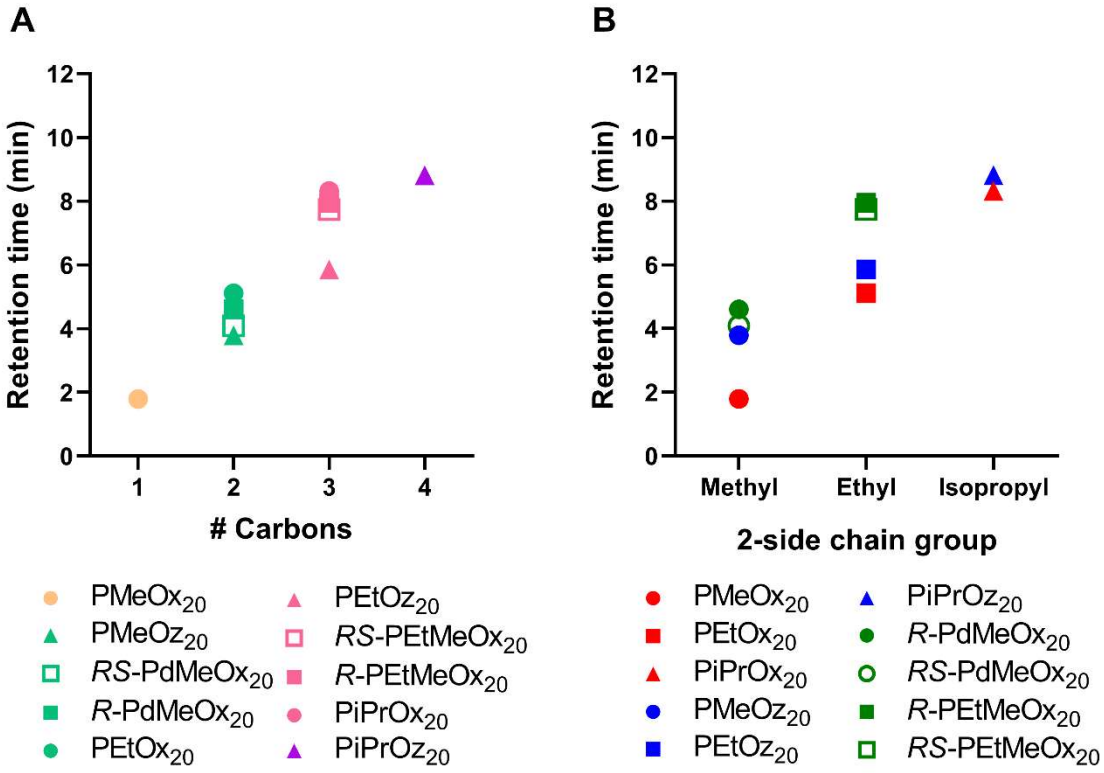

Figure S11. (A) Retention times for DP20 polymers, plotted in terms of additional carbons as established in Scheme 1B. **(B)** Retention times for DP20 polymers, plotted in terms of 2-side chain group and polymer family as established in Scheme 1A.

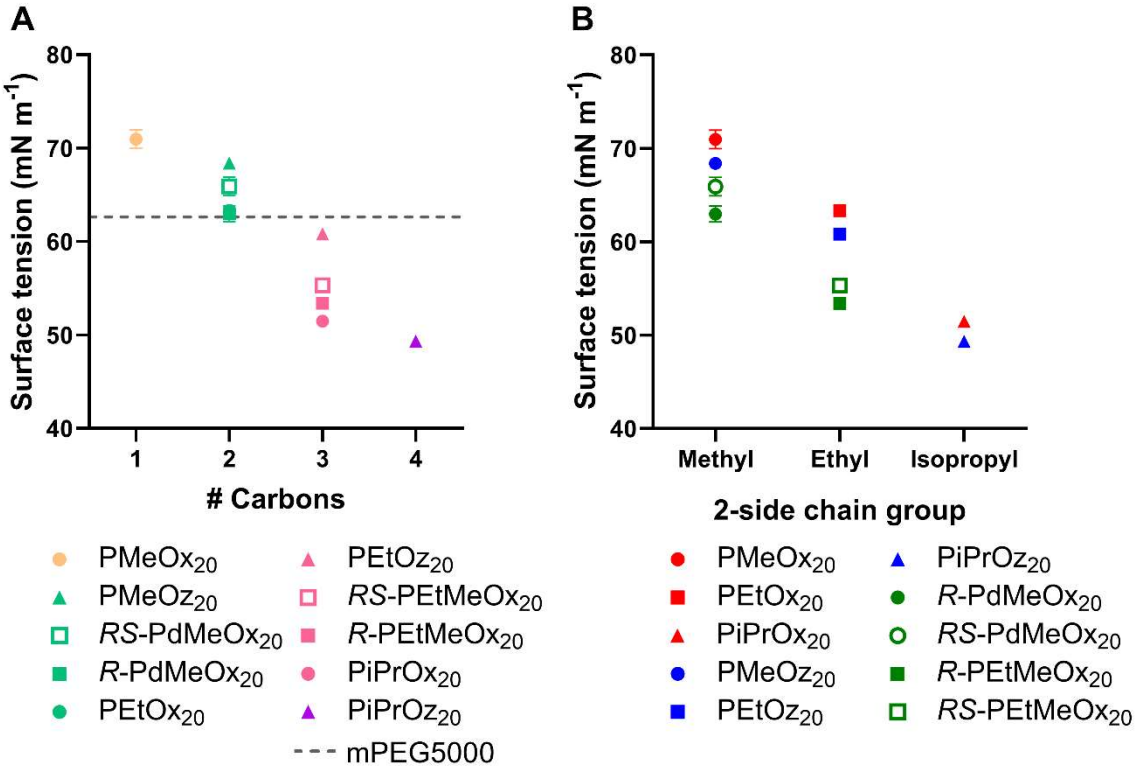

Figure S12. (A) Surface tension for DP20 polymers, plotted in terms of additional carbons as established in Scheme 1B. Grey dotted line = mPEG5000. **(B)** Surface tension for DP20 polymers, plotted in terms of 2-side chain and polymer family as established in Scheme 1A.

Table S2. t set up for T_1 measurement.

t (s)											
0.01	0.05	0.1	0.25	0.5	1	2	4	8	12	16	20

Table S3. CPMG loop cycles for T_2 measurement.

CPMG loop cycles									
2	4	6	8	10	20	30	50	70	100

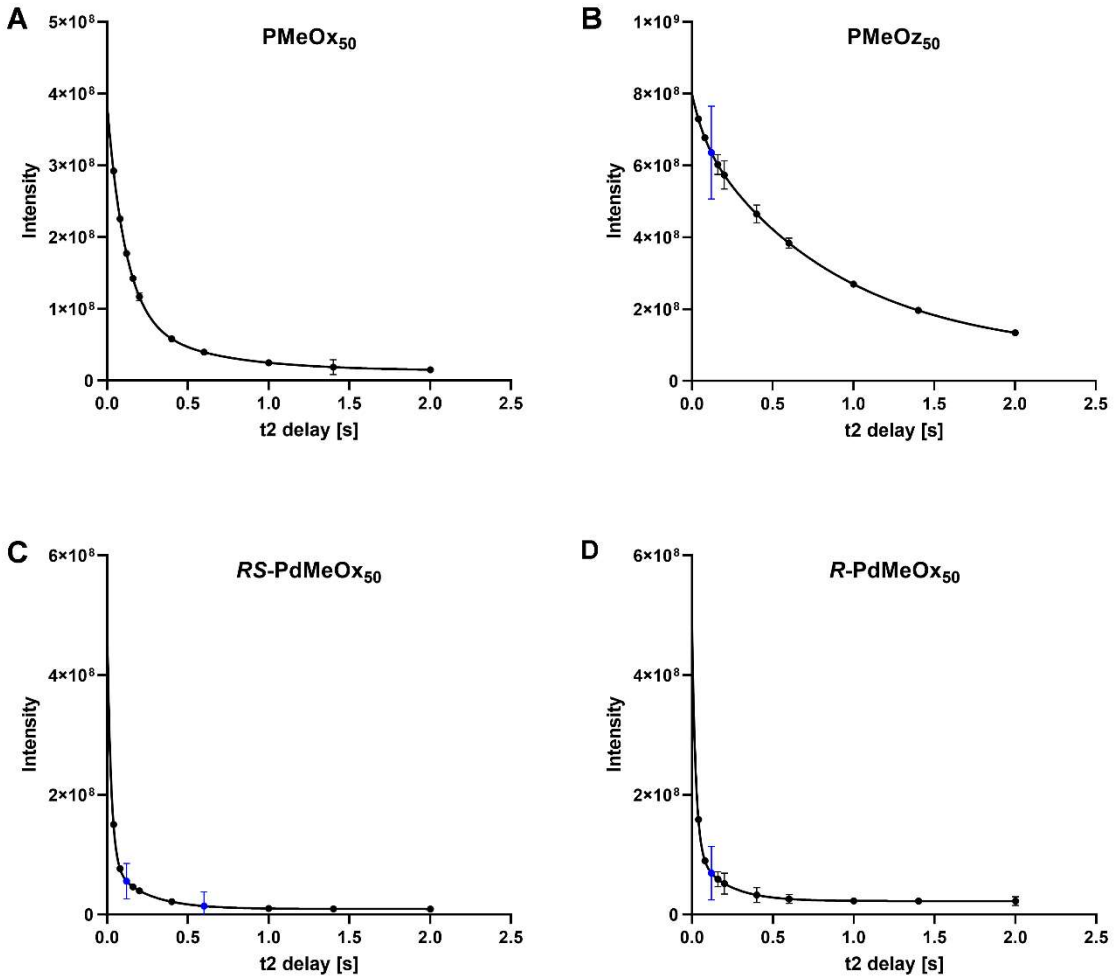

Figure S13. Double exponential decay T_2 fits for **(A)** $PMeOx_{50}$, **(B)** PMeOz50, **(C)** *RS*-$PdMeOx_{50}$, **(D)** *R*-$PdMeOx_{50}$. Error bars represent absolute difference between measured and fitted values. Points highlighted in blue were identified as outliers and not used in curve fitting.

Table S4. Summary of values for properties characterised for PCIE polymer library

Polymer	DP[a]	M_n, SEC (g/mol)	$Đ$	T_{CP} in MQ (°C)	T_{CP} in D-PBS (°C)	T_g (°C)	T_m (°C)	Surface tension (mN/m)	T_1 (s)	$T_{2(fast)}$ (s)	$T_{2(slow)}$ (s)	LogKow	HPLC retention time (mins)
$PMeOx_{50}$	47	6800	1.11	*n.d.*	*n.d.*	73.8	*n.d.*	70.7 ± 1.0	1.040	0.079	0.360	*n.d*	2.961
$PMeOx_{20}$	21	3000	1.07	*n.d.*	*n.d.*	63.1	*n.d.*	71.0 ± 0.8	*n.d.*	*n.d.*	*n.d.*	*n.d*	1.792
$PEtOx_{50}$	47	7500	1.09	*n.d.*	*n.d.*	55.1	*n.d.*	61.0 ± 0.3	*n.d.*	*n.d.*	*n.d.*	-0.89 ± 0.07	5.677
$PEtOx_{20}$	21	3100	1.09	*n.d.*	*n.d.*	47.6	*n.d.*	62.9 ± 0.7	*n.d.*	*n.d.*	*n.d.*	-1.14 ± 0.10	5.107
$PiPrOx_{50}$	46	6900	1.08	45.3	44.1	69.0	195.9	48.1 ± 1.1	*n.d.*	*n.d.*	*n.d.*	1.15 ± 0.04	9.554
$PiPrOx_{20}$	18	2900	1.11	59.2	56.8	58.8	174.0	51.4 ± 0.2	*n.d.*	*n.d.*	*n.d.*	0.95 ± 0.02	8.323
$PMeOz_{50}$	51	9500	1.09	*n.d.*	*n.d.*	23.1	*n.d.*	68.7 ± 0.1	0.693	0.055	0.611	*n.d*	4.447
$PMeOz_{20}$	21	5000	1.08	*n.d.*	*n.d.*	16.5	*n.d.*	68.4 ± 0.5	*n.d.*	*n.d.*	*n.d.*	*n.d*	3.789
$PEtOz_{50}$	48	9100	1.10	61.9	60.0	17.1	*n.d.*	58.4 ± 1.4	*n.d.*	*n.d.*	*n.d.*	-0.69 ± 0.03	6.400
$PEtOz_{20}$	20	3600	1.15	*n.d.*	*n.d.*	10.9	*n.d.*	60.8 ± 0.2	*n.d.*	*n.d.*	*n.d.*	-0.85 ± 0.02	5.856
$PiPrOz_{50}$	49	10 200	1.05	27.9	26.7	36.9	*n.d.*	46.8 ± 0.1	*n.d.*	*n.d.*	*n.d.*	0.95 ± 0.05	9.836
$PiPrOz_{20}$	19	4800	1.12	35.6	33.9	33.2	*n.d.*	49.3 ± 0.2	*n.d.*	*n.d.*	*n.d.*	0.86 ± 0.14	8.814
R-$PdMeOx_{50}$	48	6000	1.16	*n.d.*	*n.d.*	114.0	*n.d.*	62.6 ± 0.3	0.866	0.016	0.131	*n.d*	5.670
R-$PdMeOx_{20}$	22	2300	1.17	*n.d.*	*n.d.*	102.0	*n.d.*	63.3 ± 0.2	0.842	0.017	0.151	*n.d*	4.604
RS-$PdMeOx_{50}$	47	6500	1.15	*n.d.*	*n.d.*	117.1	*n.d.*	64.9 ± 0.6	*n.d.*	*n.d.*	*n.d.*	*n.d*	4.799
RS-$PdMeOx_{20}$	20	2600	1.15	*n.d.*	*n.d.*	106.6	*n.d.*	65.9 ± 0.8	*n.d.*	*n.d.*	*n.d.*	*n.d*	4.082
R-$PEtMeOx_{50}$	52	4700	1.10	52.0	49.0	86.6	*n.d.*	51.1 ± 0.7	*n.d.*	*n.d.*	*n.d.*	1.01 ± 0.10	9.991
R-$PEtMeOx_{20}$	17	2100	1.10	71.1	67.2	75.9	*n.d.*	53.4 ± 0.1	*n.d.*	*n.d.*	*n.d.*	0.62 ± 0.08	7.944
RS-$PEtMeOx_{50}$	48	5500	1.10	50.7	49.1	91.6	*n.d.*	53.3 ± 0.7	*n.d.*	*n.d.*	*n.d.*	0.97 ± 0.08	9.153
RS-$PEtMEOx_{20}$	20	2300	1.13	69.9	65.8	79.8	*n.d.*	55.3 ± 0.1	*n.d.*	*n.d.*	*n.d.*	0.65 ± 0.06	7.738
mPEG5000	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	62.6 ± 0.9	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*

[a] DP determined via ^{1}H NMR integration of CH_2 backbone immediately following polymerisation (400 MHz, $CDCl_3$); *n.d.* = not determined

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