Electronic Supplementary Information

Novel comb polymers from alternating N-acylated poly(aminoester)s obtained by spontaneous zwitterionic copolymerization

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Experimental Details

Materials

Acrylic acid (AA, 99%, anhydrous, Sigma-Aldrich), acetonitrile (ACN, 99.8%, Sigma-Aldrich), 4-methoxyphenol (MEHQ, 99%, Sigma-Aldrich), diethyl ether (DEE, >98%, Sigma-Aldrich), ethanol (> 99.8%, Sigma-Aldrich), 1,4-dioxane (>99%, Sigma-Aldrich), Luperox® TBH70X tert-butyl hydroperoxide solution (tBuOOH, 70% wt.% in H2O, Sigma-Aldrich) and L-ascorbic acid (AsAc, Sigma Aldrich) were used as received. Dimethyl 2,2’-azobis(2-methyl propionate) (V-601) was obtained from Wako Pure Chemical Industries, Ltd. 2-Ethyl-2-oxazoline (EtOx, >99%, Sigma-Aldrich) and 2-methyl-2-oxazoline (MeOx, 98%, Sigma-Aldrich) were distilled to dryness over barium oxide (BaO) and stored in a nitrogen atmosphere. The chain transfer agent (CTA), 2-(((butylthio)-carbonothioyl)thio)propanoic acid was prepared according to a literature procedure.[1]

Instrument and analysis

^{1}H spectra were recorded on a Bruker DPX-400 spectrometer using deuterated solvents obtained from Sigma-Aldrich. IR spectra were collected on a Bruker VECTOR-22 FT-IR spectrometer using a Golden Gate diamond attenuated reflection cell. MALDI-ToF MS spectra were recorded in reflection mode on a Bruker Daltonics Autoflex II MALDI-ToF mass spectrometer, equipped with a nitrogen LASER delivering 2 ns laser pulses at 337 nm with positive ion ToF detection performed using an accelerating voltage of 25 kV. The matrix solution was prepared by dissolving 2,5-dihydroxybenzoic acid (DHB) in MeOH (200 mg/mL). Sodium iodide was dissolved in MeOH (2 mg/ mL). Polymer samples were dissolved in MeOH (1 to 5 mg/mL). Samples were prepared by mixing 5 μL of polymer solution, 5 μL of salt solution and 20 μL of matrix solution. Calibration was performed with a poly(ethylene glycol) methyl ether acrylate M_w 1100 g mol^{-1} standard. Size exclusion chromatography (SEC) measurements were performed on an Agilent PL50 equipped with 2 Agilent Polargel Medium Columns eluting with dimethylformamide containing 0.1 M LiBr as an additive at 50°C. The flow rate was 1 ml/min and detection was achieved using simultaneous refractive index (RI) and UV (λ = 280 nm) detectors. Molecular weights were calculated relative to narrow PMMA standards. All samples were passed through 0.45 µm PTFE filter before analysis. Cloud point temperatures were recorded on an Agilent Technologies Cary 60 UV-Vis at a wavelength of 500 nm using a cuvette with 1cm path length. The solutions (5 mg mL^{-1}) were heated and cooled (temperature range: 15 – 90 °C) at a rate of 1 °C min^{-1} while stirring at 12000 rpm. The cloud point was determined as the temperature where the transmittance decreased to 50% in the third heating run. DSC and TGA spectra were recorded on a Mettler Toledo DSC1 and Mettler Toledo TGA1, respectively.

General procedure for the spontaneous zwitterionic copolymerization of EtOx and AA

To a dried Schlenk flask equipped with a magnetic stirring bar, EtOx (2.46 g, 0.025 mol), AA (1.78 g, 0.025 mol), ACN (2.5 mL) and MEHQ (0.001 g, 8.06×10^{-6} mol) were added under nitrogen. The mixture was placed in a thermostated oil bath set at 70 °C for 24 h. After cooling, the polymer solution was poured into ice-cold DEE and the polymer was isolated by centrifugation. This purification procedure was repeated in total three times. After removal of residual DEE under vacuum the product oligo(EtOx-*stat*-AA)A was obtained as a yellowish oil. The repeating units and molar mass of the oligomer were calculated by ^{1}H NMR, by the ratio of the integrals of the vinyl end group and the ring-opened EtOx and AA repeating unit signals: M_n = 590 g mol^{-1}, corresponding to oligo(EtOx-*stat*-AA)$_3$A (M1). SEC (DMF, LiBr) = 600 g mol-1, Đ = 1.4).

General procedure for the spontaneous zwitterionic copolymerization of MeOx and AA

To a dried Schlenk flask equipped with a magnetic stirring bar, MeOx (4.26 g, 0.05 mol), AA (3.56 g, 0.05 mol), ACN (5 mL) and MEHQ (0.002 g, 1.61×10^{-5} mol) were added under nitrogen. The mixture was placed in a thermostated oil bath set at 70 °C for 24 h. After cooling, the polymer solution was poured into ice-cold DEE and the polymer was isolated by centrifugation. This purification procedure was repeated in total three times. After removal of residual DEE under vacuum the product oligo(MeOx-*stat*-AA)A was obtained as a yellowish oil. The repeating units and molar mass of the oligomer were calculated by ^{1}H NMR, by the ratio of the integrals of the vinyl end group and the ring-opened MeOx and AA repeating unit signals: M_n = 540 g mol^{-1}, corresponding to oligo(MeOx-*stat*-AA)$_3$A (M2). SEC (DMF, LiBr) = 400 g mol-1, Đ = 1.52).

Free radical polymerization of oligo(EtOx-*stat*-AA)$_3$A (M1)

(A) M1 (0.4 g, 0.69 mmol) and V-601 (0.65 mg, 0.003 mmol) were added to a sample vial equipped with a magnetic stir bar and ethanol (0.85 mL) was added. The solution was deoxygenated for 20 min and the vial was placed in a thermostated water bath set at 70 °C for 16 h.

(B) M1 (0.12 g, 0.21 mmol) was introduced into a sample vial equipped with a magnetic stir bar and dissolved in H_2O (0.065 mL) and 1,4-dioxane (0.048 mL). AsAc (0.054 mg, 3×10^{-4} mmol) in H_2O (0.05 mL) was added and the solution was deoxygenated for 10 min. Subsequently, a deoxygenated solution of tbuOOH (0.054 mg, 6×10^{-4} mmol) in H_2O (0.015 mL) was transferred into the sample vial via a syringe. The sample vial was placed in a thermostated water bath set at 25 °C for 1 h.

Typical procedure for the synthesis of comb polymers by Redox-RAFT (RRAFT)

CTA, macromonomer and AsAc were added to a sample vial equipped with a magnetic stir bar and dissolved in deionized H_2O and 1,4-dioxane. The mixture was deoxygenated by bubbling with nitrogen for 15 min. In parallel, an aqueous stock solution of tBuOOH was deoxygenated. An aliquot of the latter was added to the sample vial via a nitrogen-purged syringe. The sample vial was placed in a thermostated water bath set at 25 °C for 24 h. Subsequently, ^{1}H NMR and SEC samples were taken to determine the conversion of the polymerization. The comb polymers were purified by dialysis (MWCO = 3500 g mol^{-1}) against deionized water for two days. Amounts and concentrations of the individual RRAFT polymerizations are provided in Table S1.

Table S1 RRAFT conditions used to prepare comb polymers of different degree of polymerization (DP) in H_2O/1,4-dioxane (v/v, 75%/25%) at 25 °C using tBuOOH/AsAc as redox initiator. P1 and P2 are based on oligo(EtOx-*stat*-AA)$_3$A (M1) and oligo(MeOx-*stat*-AA)$_3$A (M2), respectively. All polymerizations are performed in 250 mg and 500 mg scale of M1 and M2, respectively.

code	DP	$[M]_0$ [mol L^{-1}]	[CTA] [mmol L^{-1}]	[AsAc] [mmol L^{-1}]	[tBuOOH] [mmol L^{-1}]
P1a	100	0.8	8.1	1.01	2.02
P1b	50	1.6	32.4	4.05	8.1
P1c	25	1.6	64.8	5.4	10.8
P2a	100	0.87	8.7	1.09	2.18
P2b	50	1.75	34.8	4.35	8.7
P2c	25	1.75	69.6	5.8	11.6

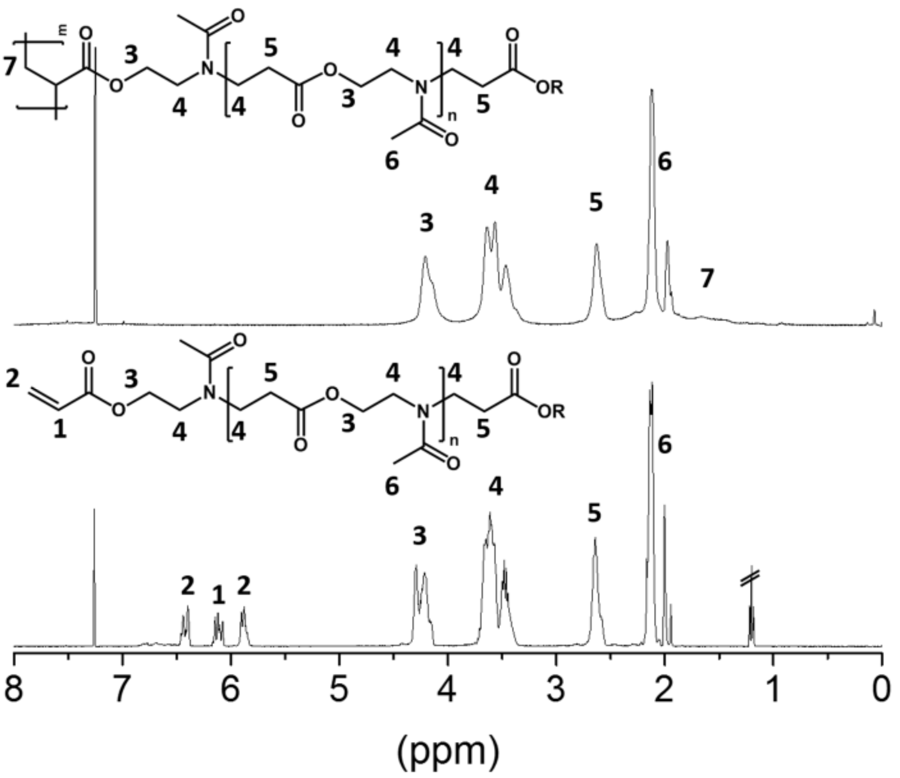

Fig. S1 ^{1}H NMR spectra (400 MHz, $CDCl_3$) of oligo(MeOx-*stat*-AA)$_3$A (bottom) and the corresponding comb polymer (poly(oligo(MeOx-*stat*-AA)$_3$A) (top).

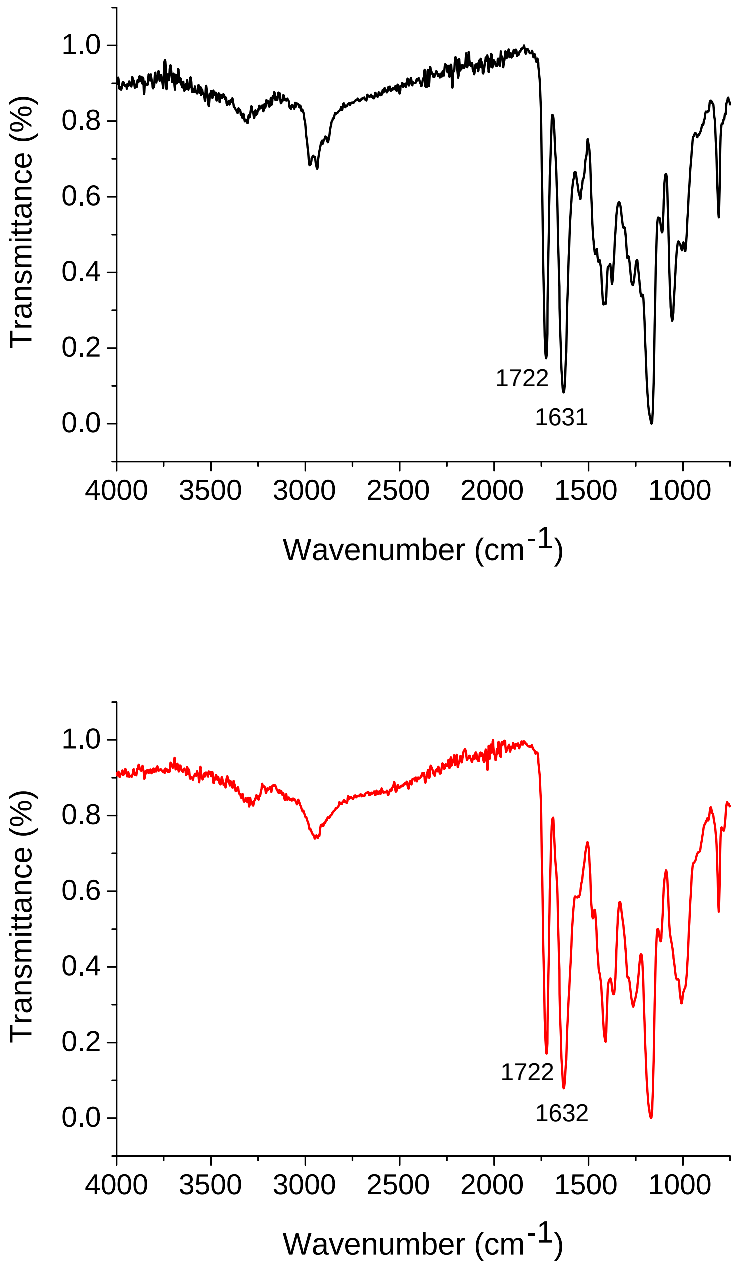

Fig. S2 IR spectra of M1 (top) and M2 (bottom).

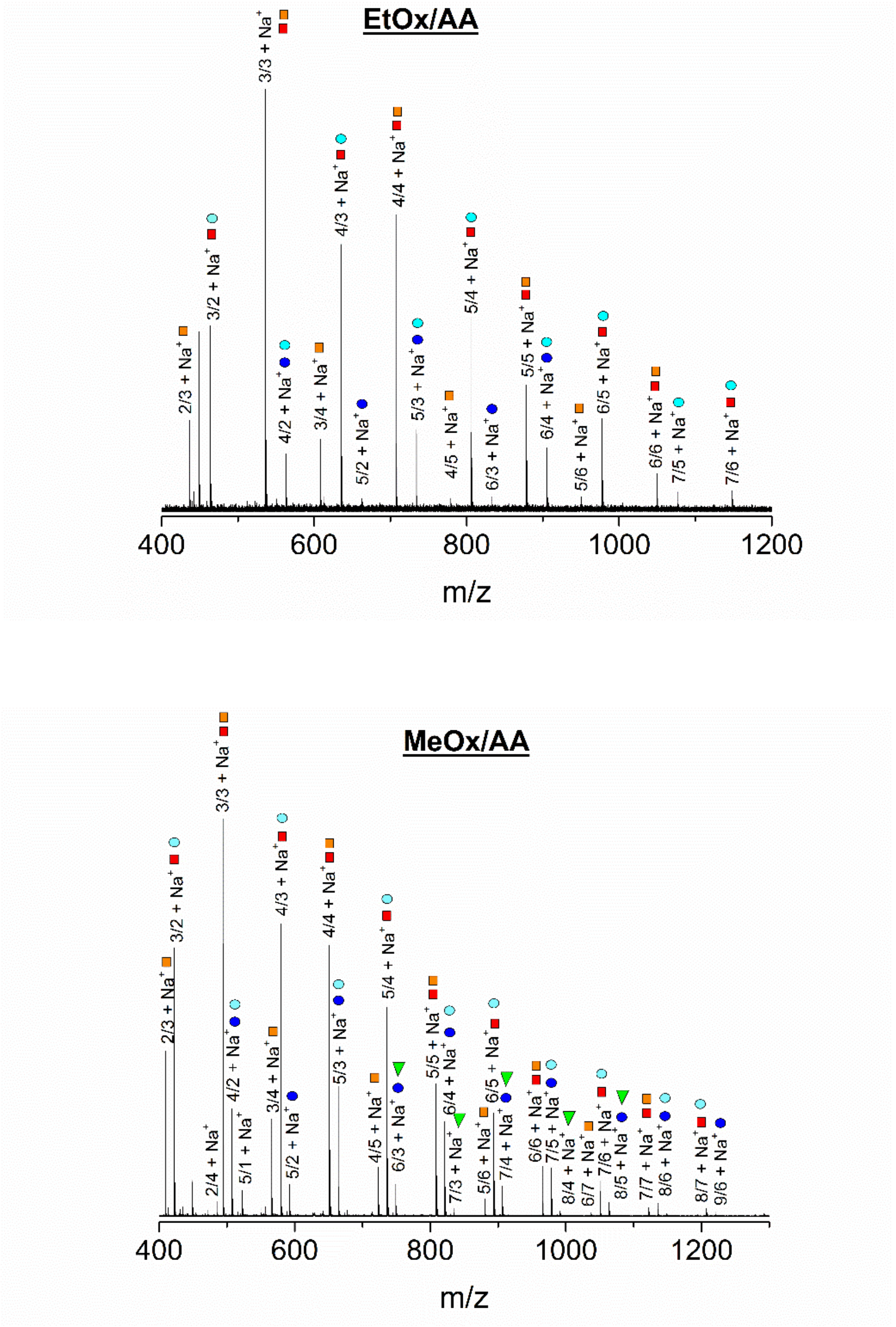

Fig. S3 MALDI-ToF spectra of macromonomer M1 (top) and M2 (bottom). Individual symbols represent different distributions. Rectangular symbols assign distributions with alternating addition of EtOx (M1; increment 99.07 g mol^{-1})) or MeOx (M2; increment 85.1 g mol^{-1}) and acrylic acid (AA; increment 72.06 g mol^{-1}). Circluar and triangular symbols demonstrate distributions which deviate from the ideal alternating composition with a higher number of EtOx or MeOx units incorporated.

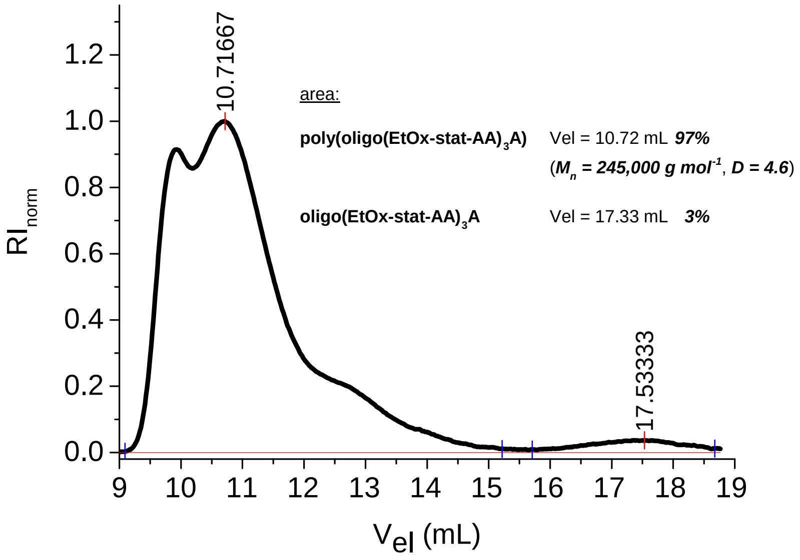

Fig. S4 SEC spectrum of the crude product of free radical polymerization of M1 initiated with the redox pair AsAc/tBuOOH.

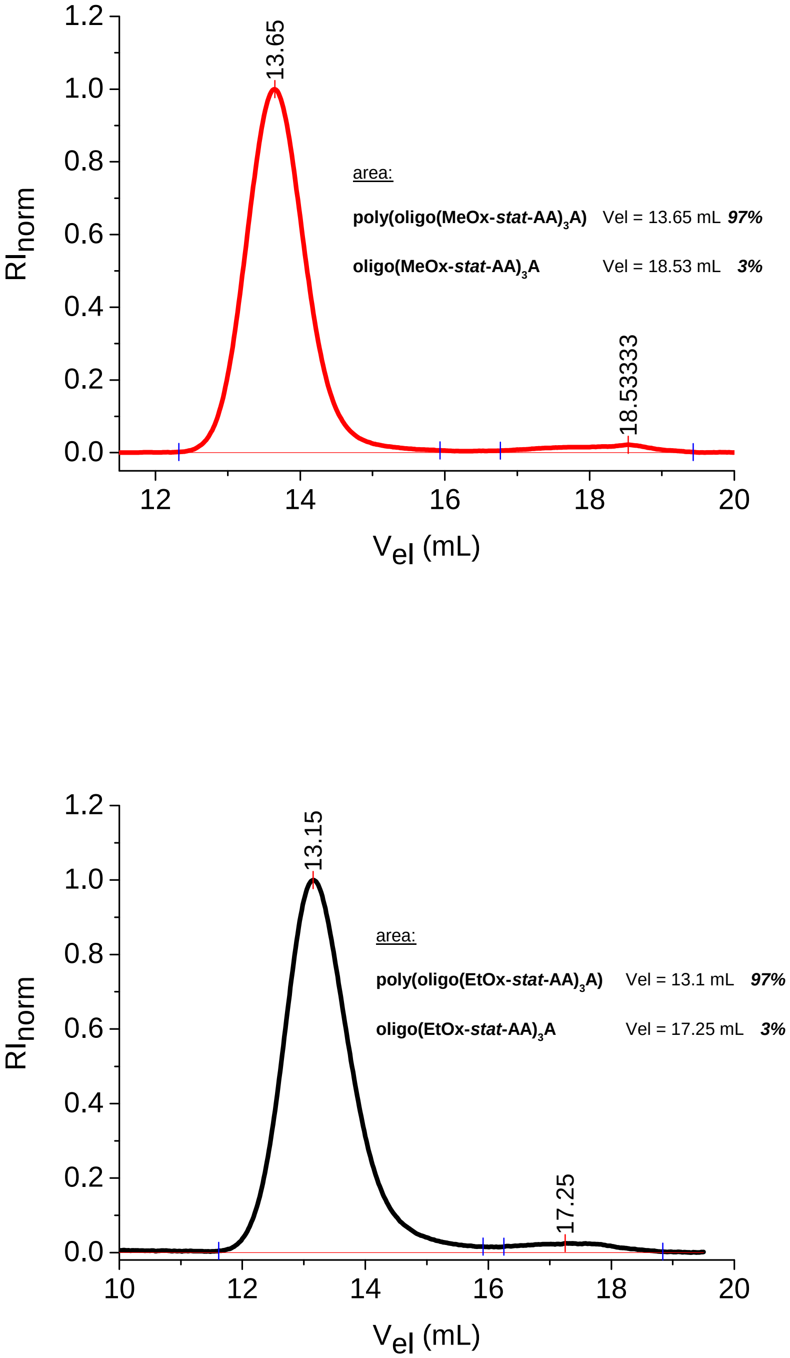

Fig. S5 SEC spectra of crude polymer solutions, taken after 24 h reaction time: poly(oligo(MeOx-*stat*-AA)$_3$A) (top) and poly(oligo(EtOx-*stat*-AA)$_3$A) (bottom).

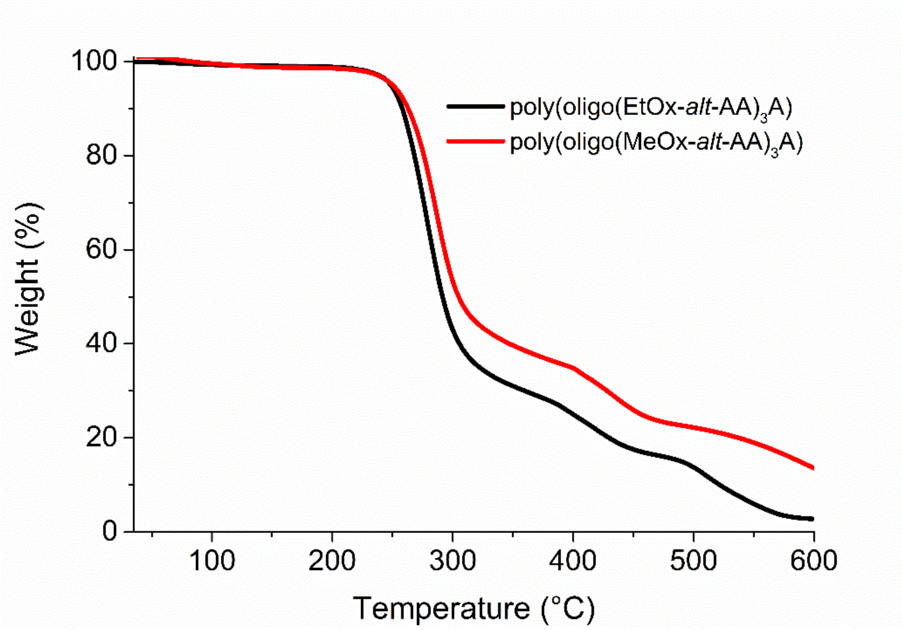

Fig. S6 TGA curves of poly(oligo(MeOx-*alt*-AA)$_3$A) (P2a) and poly(oligo(EtOx-*alt*-AA)$_3$A) (P1a).

References

1. C. J. Ferguson, R. J. Hughes, D. Nguyen, B. T. T. Pham, R. G. Gilbert, A. K. Serelis, C. H. Such and B. S. Hawkett, *Macromolecules*, 2005, **38**, 2191-2204.