Unexpected radical polymerization behavior of oligo(2-ethyl-2-oxazoline) macromonomers

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Supporting information

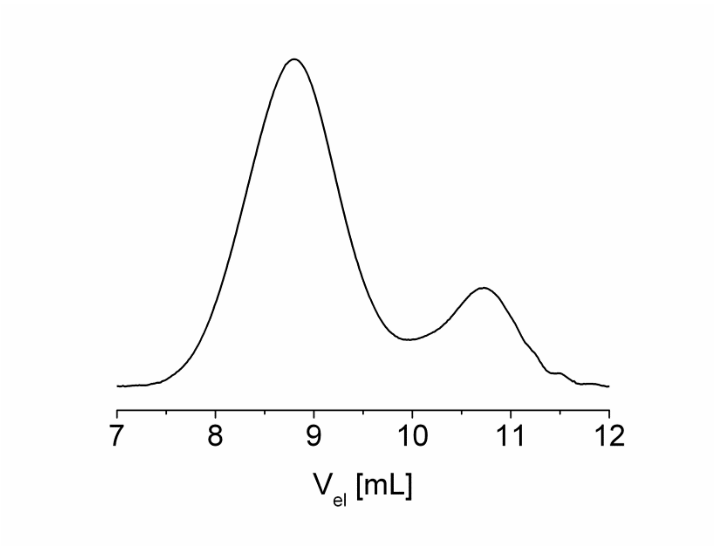

Figure SI-1: SEC trace ($CHCl_3$, RI detection) from the reaction solution of the FRP of OEtOxA. M_n = 6,080 g mol^{-1}; PDI = 1.18, conv. = 81%, M/AIBN = 240 (similar to M/CTA = 60 from RAFT), [M] = 0.5 M in EtOH, T = 70 °C, t = 17.5 h.

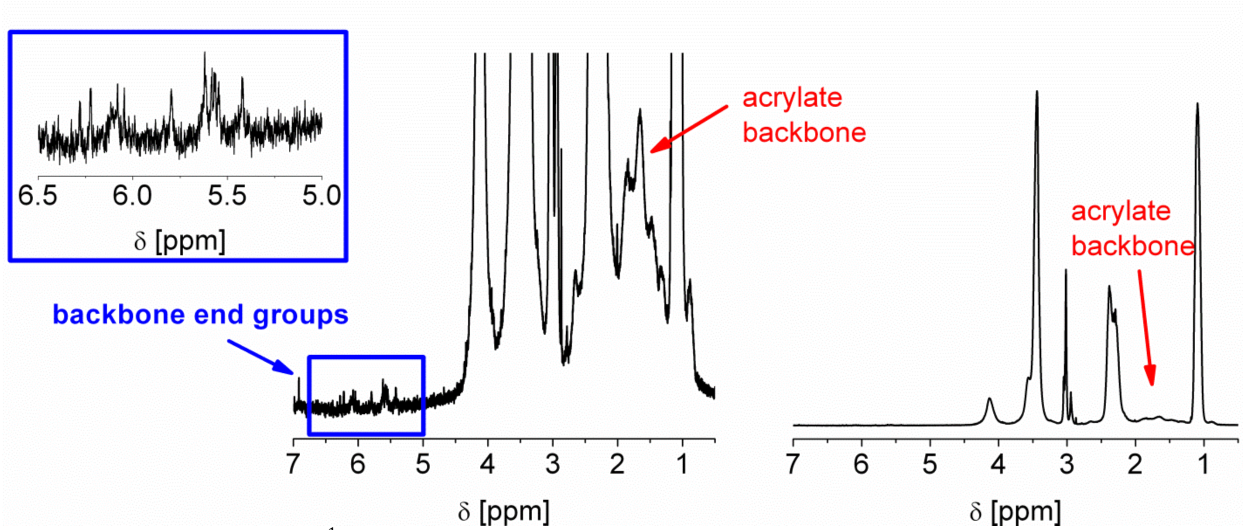

Figure SI-2: zoom into the [1]H NMR spectrum ($CDCl_3$, 300 MHz) of **P3** indicating the presence of vinylic backbone end-groups.

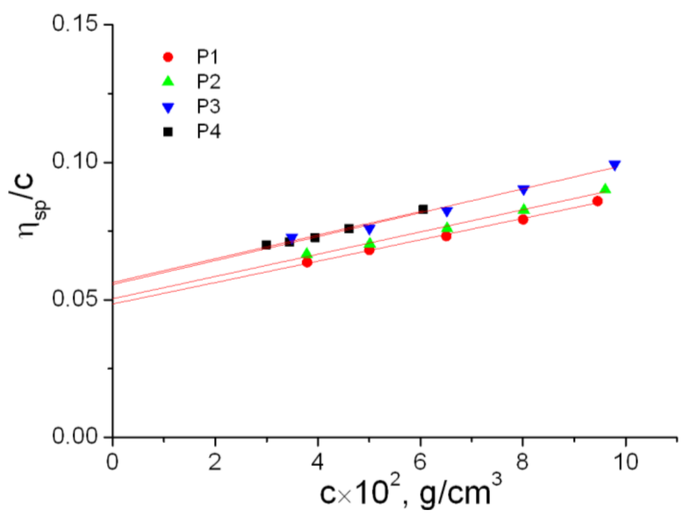

Figure SI-3. Dependence of η_{sp}/c on the solute concentration for the determination of the intrinsic viscosity.

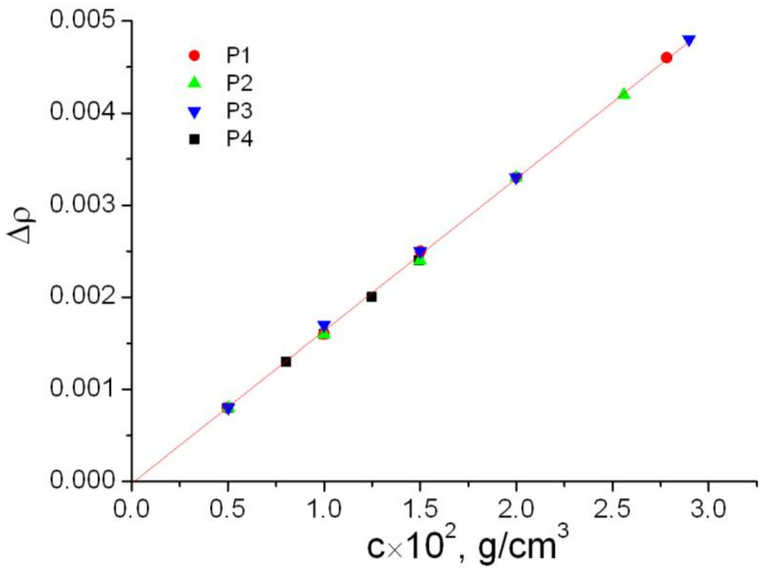

Figure SI-4. Dependence of $\Delta\rho = (\rho\text{-}\rho_0)$ on the solute concentration, where ρ and ρ_0 are the density of the solution and solvent respectively. The slope $\Delta\rho/\Delta c$ corresponds to the buoyancy factor $(1\text{-}\upsilon\rho_0) = 0.166 \pm 0.01$, which yields $\upsilon = 0.835 \pm 0.004$ $cm^3 \cdot g^{-1}$ for the partial specific volume.

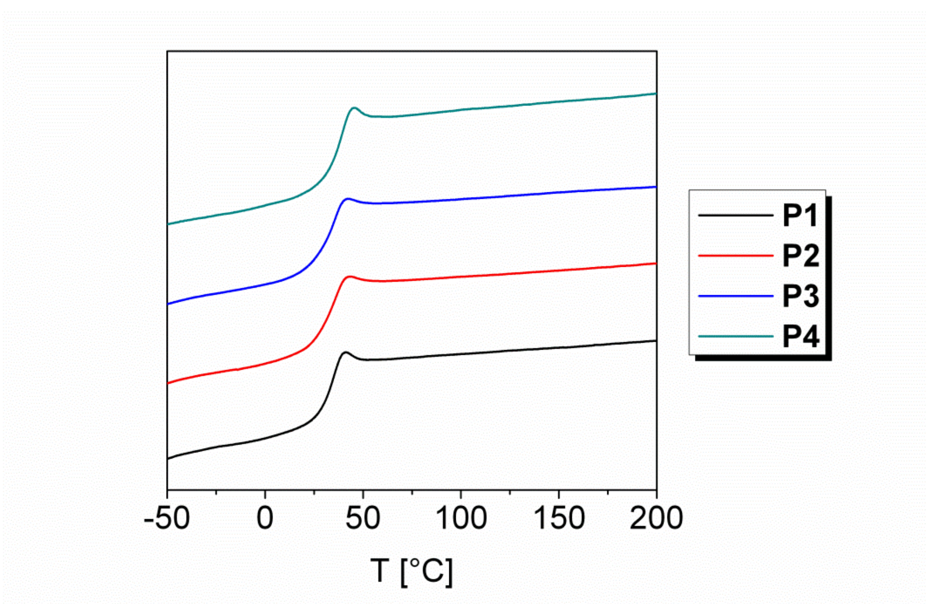

Figure SI-5: DSC thermograms of **P1-P4** (second heating run, heating rate 20 K min^{-1}).

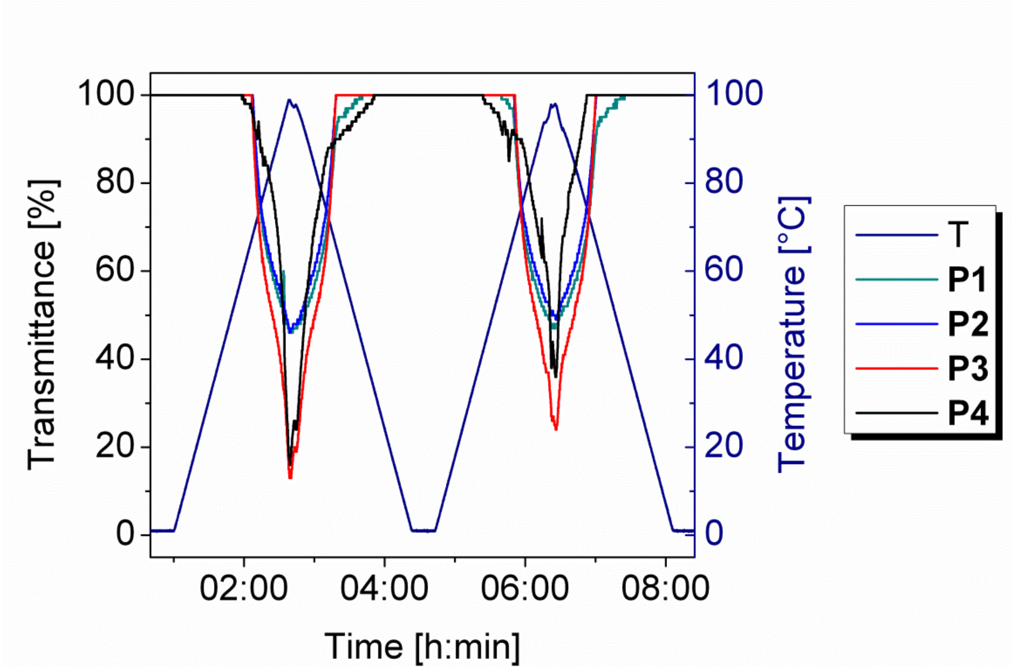

Figure SI-6: Turbidity curves of aqueous solutions of POEtOxA **P1-P4** (c = 5 mg mL^{-1}, heating rate 1 K min^{-1}).

Table SI-1: Parameters obtained by FISH model fitting of the SANS data for **P1-P4** in D_2O.

	Ellipsoid[a]			Rod[b]		Rod Theo.		Ellipse or Rod?
	R_1 / Å	X	R_2 / Å	R / Å	L / Å	R / Å	L / Å	
P1	7.9	3.9	30.8	10.2	44.5	22	20	Rod
P2	8.6	4.0	34.4	13.0	47.6	22	37	Rod
P3	12.8	3.2	41.0	12.2	60.8	22	110	Rod
P4	15.7	2.6	40.8	14.2	62.1	22	276	Rod

[a] R_1 and R_2 are the radii of the ellipse, and $X = R_2/R_1$.

[b] R corresponds to the radius and L to the length of the rod.

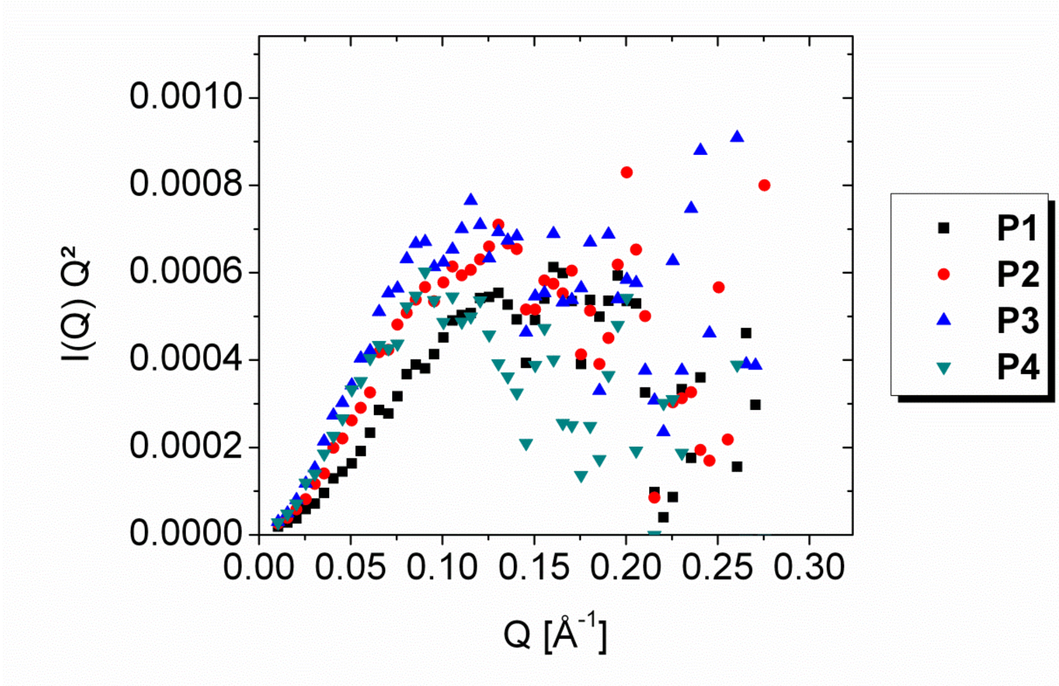

Figure SI-7: Kratky plots for SANS data of solutions of **P1-P4** in D_2O (c = 5 mg mL^{-1}).

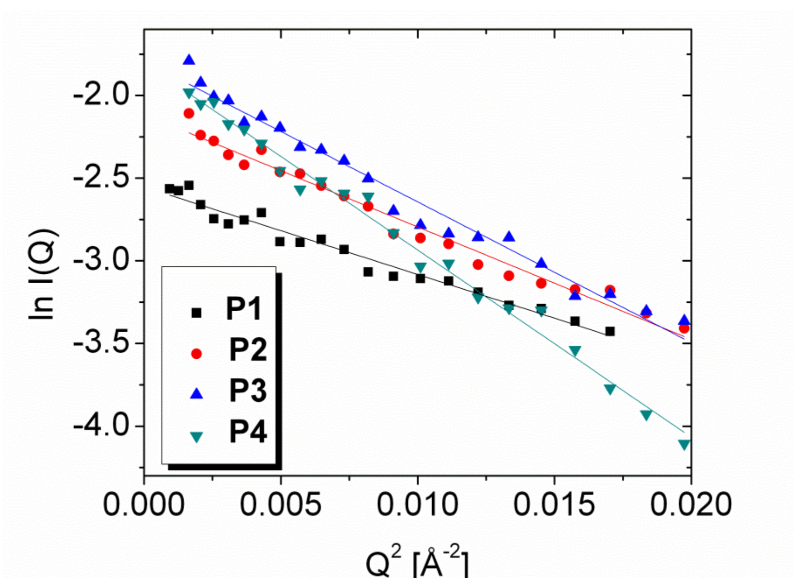

Figure SI-8: Guinier plot for SANS data of **P6** in D_2O (c = 5 mg mL^{-1}). The radius of gyration R_g is calculated from the slope of the linear fit according to $R_g = \sqrt{-3 \cdot slope}$ in the low Q range.

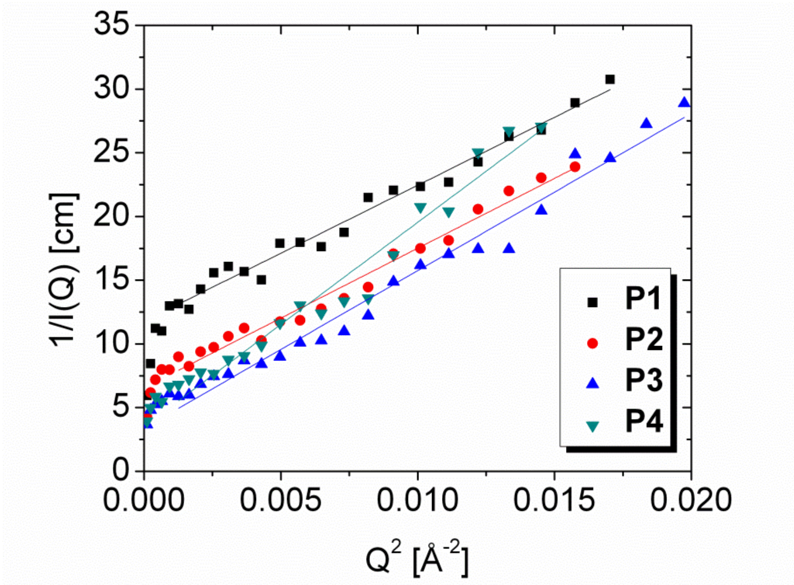

Figure SI-9: Zimm plots for SANS data of **P1-P4** in D_2O (c = 5 mg mL^{-1}). The correlation length ξ is obtained from linear fitting according to $\xi = \sqrt{slope/intercept}$ and was used to calculate R_g.

Table SI-2. Radii of gyration (R_g) calculated from linear fitting of the Zimm and Guinier plots of the SANS data of **P1-4** in D_2O.

	I_0 [cm^{-1}]	ξ [Å][a]	R_g [Å] Zimm (low Q)[b]	R_g [Å] Zimm (high Q)[c]	R_g [Å] Guinier	R_g [Å] cyl. fit[d]	R_g [Å] ell. fit[e]
P1	0.085	9.5	16	13	13	14	15
P2	0.15	13	22	18	15	15	17
P3	0.29	19	33	27	17	18	20
P4	0.28	21	37	30	19	18	21

[a] correlation length obtained from Zimm analysis.
[b] calculated according to $R_g = \xi\sqrt{3}$.
[c] calculated according to $R_g = \xi\sqrt{2}$.
[d] calculated according to $R_g = \sqrt{\frac{L^2}{12} + \frac{R^2}{2}}$ from the cylindrical fit.
[e] calculated according to $R_g = \sqrt{\frac{2R_1^2 + 2R_2^2}{5}}$ from the ellipsoid fit.