

Electronic Supporting Information

Oxazoline-Methacrylate Graft-Copolymers with Upper Critical Solution Temperature Behaviour in Yubase Oil

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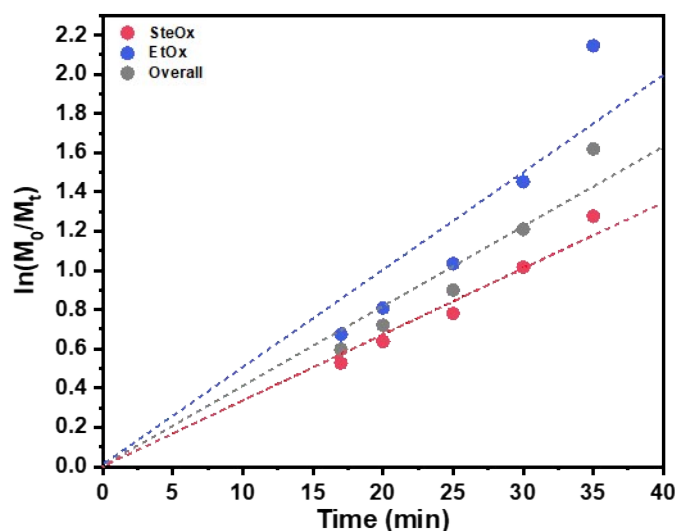


Figure S1. First order kinetic plot for the copolymerisation of EtOx and SteOx (DCM as solvent, 100°C, [M]= 1.4, MeTos as initiator, [M]/[I]= 28).

Table S1. Apparent propagation rate constants ($k_{p,app}$), propagation rate constants (k_p), and apparent reactivity ratios (r_1 and r_2) obtained for the copolymerisation of EtOx with SteOx.

Monomer 1	Monomer 2	$k_{pEtOx,app}$ ($10^{-3} s^{-1}$)	$k_{pSteOx,app}$ ($10^{-3} s^{-1}$)	k_{pEtOx} ($L mol^{-1} s^{-1}$)	k_{pSteOx} ($L mol^{-1} s^{-1}$)	r_1 (k_{pEtOx}/k_{pSteOx})	r_2 (k_{pSteOx}/k_{pEtOx})
EtOx	SteOx	50±4	34±1	1±0.08	0.68±0.02	1.47	0.68

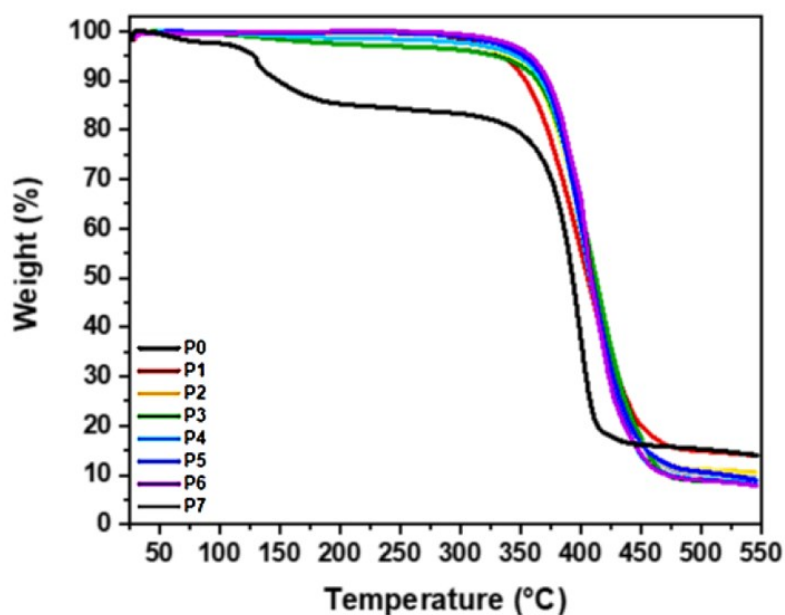


Figure S2. Thermogravimetric analyses of SteOx-EtOx homo and copolymers.

Calibration method used for the calculation of the brush yield. A series of poly(SteOx-*r*-EtOx) (SteOx:EtOx= 12.5:12.5, DP=25) solutions in THF were prepared at decreasing concentrations. The GPC curve of each solution was measured and the peak area was plotted as a function of the concentration (**Table S1**). A linear fitting was found (**Figure S2**). In order to calculate the brush yield of the synthesized graft-copolymers, graft-copolymer samples at a known concentration were prepared and their GPC traces were measured. For each sample, the peak area of the unreacted poly(oxazoline) side chains was fit in the equation of the calibration curve. From the obtained result and from the conversion of the poly(oxazoline) side chains obtained from the ¹H NMR spectrum, it is possible to obtain the concentration of unreacted monomer in the measured sample. By removing the concentration of unreacted monomer and of unreacted poly(oxazoline) from the initial sample concentration, it is possible to obtain the brush yield. An example is shown below.

Equation of calibration curve: $y = 10522.77221x - 1445.30139$

Exact concentration of sample $C_0 = 3.5 \text{ mg/mL}$

Measurement of polyOx peak area from GPC curve (4182.42065)

From equation of the calibration curve: $x = 0.5348$

Conversion of polyOx from ¹H NMR: 82% (18% is monomer)

$0.5348 \cdot 82 = x \cdot 18$

$x = 0.1174$

Tot conc - monomer conc: $3.5 - 0.1174 = 3.3826$ (polyOx+graft-copolymer)

$3.3826 = x + 0.5348$

$x = 3.3826 - 0.5348 = 2.8478$ graft-copolymer

Brush yield% = $(2.8478 / 3.3826) \cdot 100 = 84\%$

Table S2. Measured concentration (mg mL^{-1}) and calculated peak areas for a series of polyOx solutions in THF.

Concentration (mg mL^{-1})	Peak Area
3	30305.47466
2.4	23319.71927
1.92	18627.37544
1.536	15054.60907
1.2288	11972.69407
0.6144	4633.56357

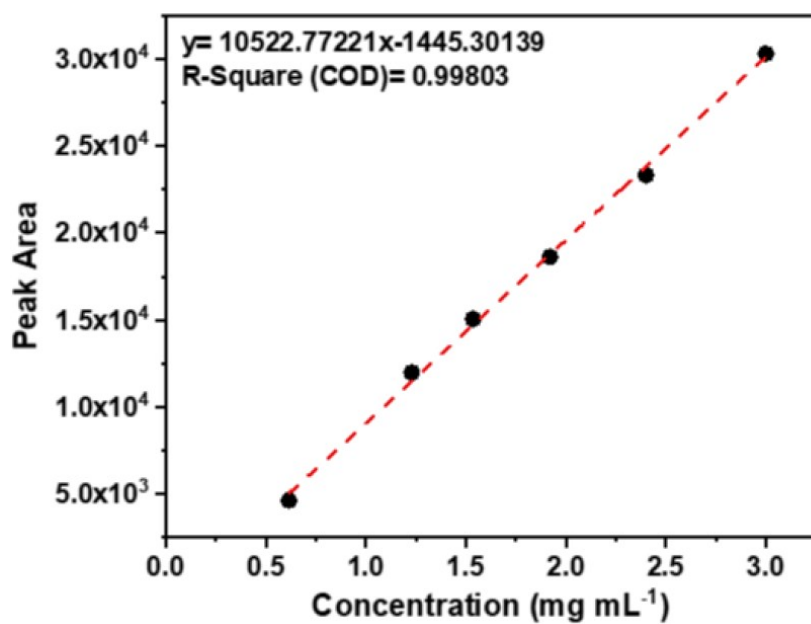


Figure S3. Calibration curve and linear fitting equation obtained by plotting the peak area of the GPC traces of polyOx solutions in THF as a function of their concentration.

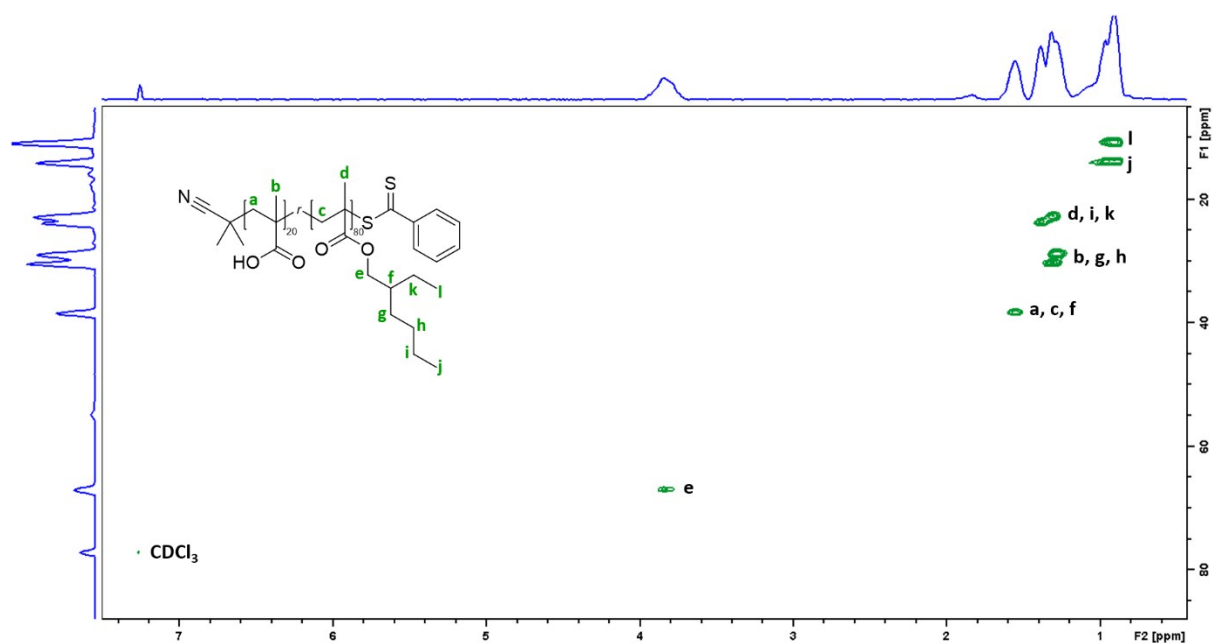


Figure S4. HSQC spectrum (500 MHz, CDCl₃) and structure of the poly(methacrylic acid)-*r*-(2-ethylhexyl) methacrylate copolymer (poly(xMA)).

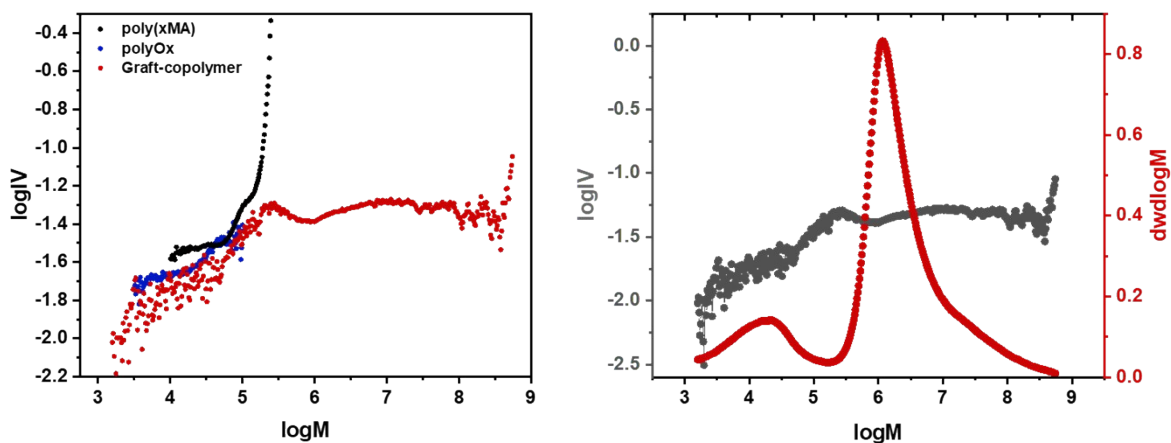


Figure S5. Mark-Houwink plot of the poly(xMA) backbone (black), a 12.5:12.5 SteOx:EtOx copolymer corresponding to the unreacted polyOx side chains (blue), and one of the graft-copolymers (red) (left), and the Mark-Houwink plot overlaid with the molecular weight distribution trace of the graft-copolymer (right).

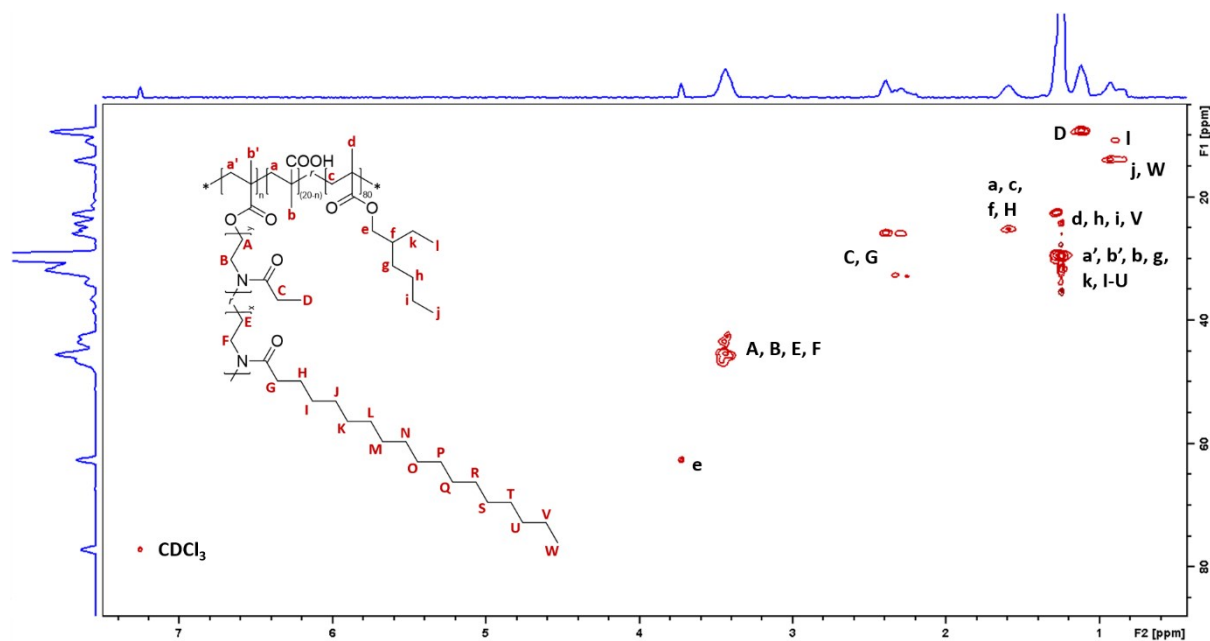


Figure S6. HSQC spectrum (500 MHz, CDCl_3) and structure of one of the graft-copolymers.