

## ELECTRONIC SUPPORTING INFORMATION

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### $\epsilon$ -Caprolactone Derived 2-Oxazoline Inimer for the Synthesis of Graft Copolymers

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### Supplementary Material

**Materials** All solvents and chemicals were purchased from Sigma Aldrich and used as received unless otherwise stated. Tris[2-(dimethylamino)ethyl]-amine (Me<sub>6</sub>TREN) was synthesized according to literature procedure<sup>8</sup> and stored at 4 °C. Inhibitor/stabiliser containing monomers were filtered over a short column of basic alumina prior to use.

**<sup>1</sup>H NMR spectroscopy** NMR spectra were recorded either on Bruker Avance III HD 300 or 400 MHz spectrometer at room temperature using deuterated chloroform. The resonance signal of residual CHCl<sub>3</sub> at 7.2 ppm served as a reference for the chemical shift,  $\delta$ .

**Size Exclusion Chromatography (SEC)** SEC measurements were carried out at 40 °C with an Agilent 1260 infinity system with a THF + 2% TEA eluent, equipped with a refractive index detector and variable wavelength detector, 1  $\times$  PLgel 5 mm mixed-C column (300  $\times$  7.5 mm) and autosampler. Narrow linear poly(methyl methacrylate) standards were used to calibrate the system. All samples were filtered through 0.2  $\mu$ m PTFE filters before analysis.

**Synthesis of caprolactone derived hydroxyl oxazoline**  $\epsilon$ -caprolactone (30.01 g, 262.84 mmol) was added to a flask and heated to 80 °C under inert conditions. Ethanolamine (17.45 mL, 262.84 mmol) was then added to the flask and subsequently heated at 120 °C for 2 hr.

Titanium (IV) butoxide (0.5 mL) was then added to the reaction mixture and heated at 230 °C for 2 hr. The reaction mixture was then distilled *in vacuo* to obtain  $\epsilon$ -hydroxy-pentyl oxazoline as a clear yellow oil (7.53 g, 18.2 %)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.18 (t,  $J$  = 9.3 Hz, 2H), 3.76 (t,  $J$  = 9.4 Hz, 2H), 3.56 (t,  $J$  = 5.8 Hz, 2H), 2.23 (t,  $J$  = 7.2 Hz, 2H), 1.61 (d,  $J$  = 14.6 Hz, 2H), 1.52 (d,  $J$  = 6.4 Hz, 2H), 1.39 (d,  $J$  = 6.6 Hz, 2H).

**Synthesis of inimer**  $\epsilon$ -hydroxy-pentyl oxazoline (5.50 g, 35.00 mmol) was placed in a round bottom flask with DCM. To this mixture, 4-(dimethylamino) pyridine (DMAP, 0.44 g, 3.50 mmol) and  $\alpha$ -bromoisobutyric acid (5.89 g, 35.00 mmol). The solution was then cooled to in an ice bath and *N,N'*-diisopropylcarbodiimide (5.5 mL, 35.00 mmol) was slowly added dropwise and left to stir overnight. The urea byproduct was then filtered off and the crude was washed with saturated NaHCO<sub>3</sub> and brine. The solvent was then removed *in vacuo* and the product was purified by flash chromatography (silica gel, EA, TEA 2%) to obtain the inimer as a colourless oil (6.74 g, 62.9 %) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  4.14 (t,  $J$  = 9.5 Hz, 2H), 4.10 (t,  $J$  = 6.6 Hz, 2H), 3.73 (t,  $J$  = 9.5 Hz, 2H), 2.21 (t,  $J$  = 7.4 Hz, 2H), 1.85 (s, 6H), 1.61 (m,  $J$  = 7.7 Hz, 4H), 1.39 (m,  $J$  = 7.6 Hz, 2H).

**General procedure for Cationic Ring Opening Polymerisation (CROP)** Monomer, *p*-toluenesulfonic acid (in appropriate molar ratios) were sealed into microwave vial and purged with N<sub>2</sub> for several minutes. Dry acetonitrile was then added to the reaction mixture to form a 4 M solution and the vial was resealed. The reaction mixture was then left to stir at 60 °C until full or near full conversion, which was confirmed by GPC and <sup>1</sup>H NMR.

**General procedure for Cu(0)-mediated RDRP** The acrylate monomer, brush initiator, deactivator (Cu<sub>2</sub>Br), ligand (Me<sub>6</sub>TREN), in ratio of [Monomer : 1 : 0.05 : 0.18] and solvent (isopropanol, 50 wt %) were charged to a *Schlenk* tube in the following order: deactivator,

ligand, initiator, monomer, solvent. After sealing with a rubber septum and purging the mixture under inert atmosphere for at least 30 min, 5 cm of pre-activated Cu wire (0.25 mm) wrapped in a magnetic stirrer was added. The reaction mixture was then placed in an oil bath set to 25 °C and left to stir until full conversion. Conversion was measured by  $^1\text{H}$  NMR spectroscopy and SEC analysis was carried out with samples diluted in THF which were filtered over basic alumina prior to analysis to remove residual copper species.

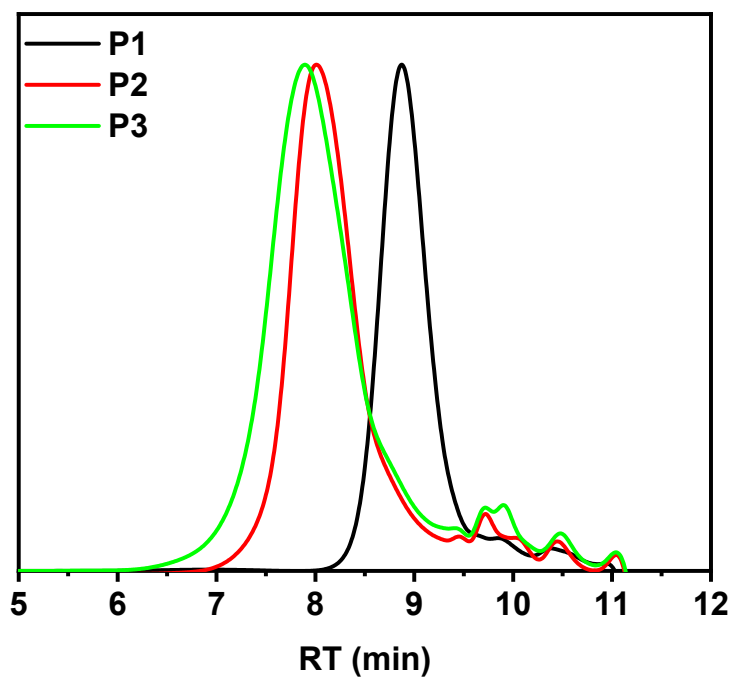
**General procedure for the synthesis of brush polymers *via* Cu(0)-RDRP with chain extension** The acrylate monomer, brush initiator, deactivator ( $\text{Cu}_2\text{Br}$ ), ligand ( $\text{Me}_6\text{TREN}$ ), in ratio of [Monomer : 1 : 0.05 : 0.18] and solvent (isopropanol, 50 wt %) were charged to a *Schlenk* tube in the following order: deactivator, ligand, initiator, monomer, solvent. After sealing with a rubber septum and purging the mixture under inert atmosphere for at least 30 min, 5 cm of pre-activated Cu wire (0.25 mm) wrapped in a magnetic stirrer was added. The reaction mixture was then placed in an oil bath set to 25 °C and left to stir until full conversion. Conversion was measured by  $^1\text{H}$  NMR spectroscopy and SEC analysis was carried out with samples diluted in THF which were filtered over basic alumina prior to analysis to remove residual copper species.

**Table S1:** Table of polymers using inimer

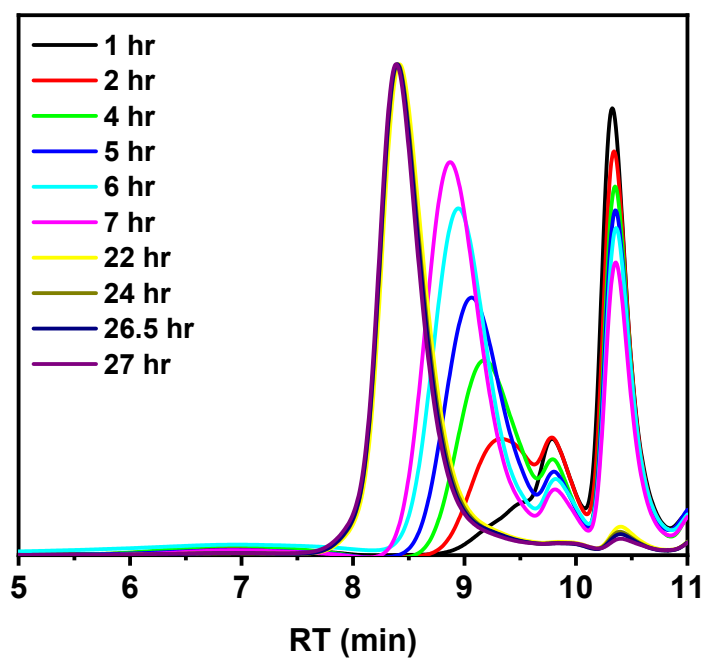
<b>Polymer</b>	<b>Type</b>	<b>M<sub>1</sub> / M<sub>2</sub></b>	<b>DP (M<sub>1</sub> / M<sub>2</sub>)</b>	<b>Time (h)</b>	<b>M<sub>n,theo</sub> (Da)</b>	<b>M<sub>n,SEC</sub> (Da)</b>	<b>Conversion (%)</b>	<b>Đ</b>
<b>P1</b>	Homo	In	10 / 0	20	2,800	2,200	90	1.32
<b>P2</b>	Homo	In	50 / 0	60	15,100	7,300	99	1.58
<b>P3</b>	Homo	In	100 / 0	72	31,000	7,700	96	2.20
<b>P4</b>	Homo	In/ EtOx	0 / 10	3	810	990	88	1.20
<b>P5</b>	Random	In/ EtOx	25/25	48	10,000	6,300	95	1.46
<b>P6</b>	Random	In/ EtOx	10 / 40	27	7,000	5,500	98	1.36

**Table S2:** Table of brush polymers

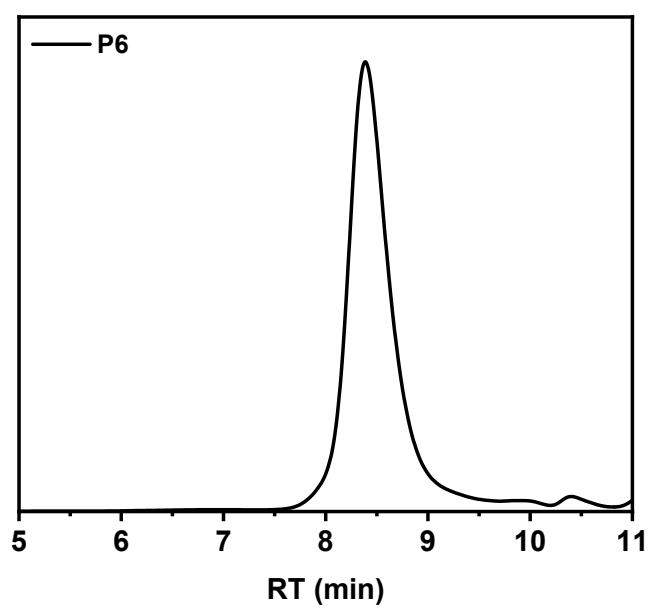
<b>Polyme r</b>	<b>Backbone</b>	<b>M<sub>n,SEC</sub> (Da)</b>	<b>Brush monomer</b>	<b>Brush DP</b>	<b>M<sub>n,theo</sub> (Da)</b>	<b>M<sub>n,SEC</sub> (Da)</b>	<b>Conversion (%)</b>	<b>Đ</b>
<b>B1</b>	<b>P1</b>	2,200	EHA	10	21,000	14,100	97	1.24
<b>B2</b>	<b>P1</b>	2,200	EHA / OEGA	10 / 5	45,800	27,000	<99	1.25
<b>B3</b>	<b>P6</b>	5,500	EHA	20	32,500	43,000	77	1.46



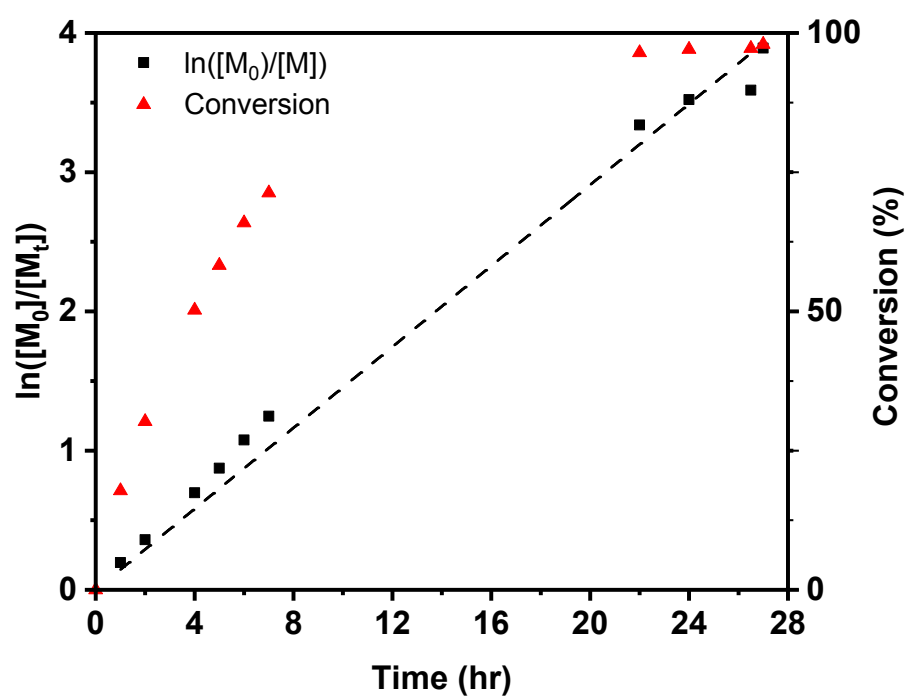
**Figure S1:** SEC traces of P1, P2 and P3



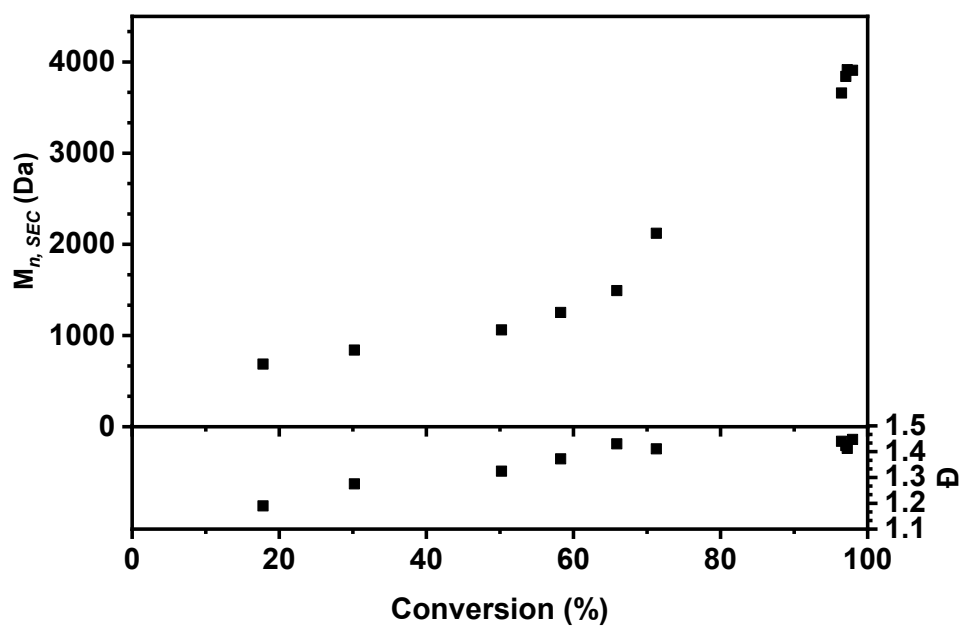
**Figure S2:** Evolving SEC traces of P6.



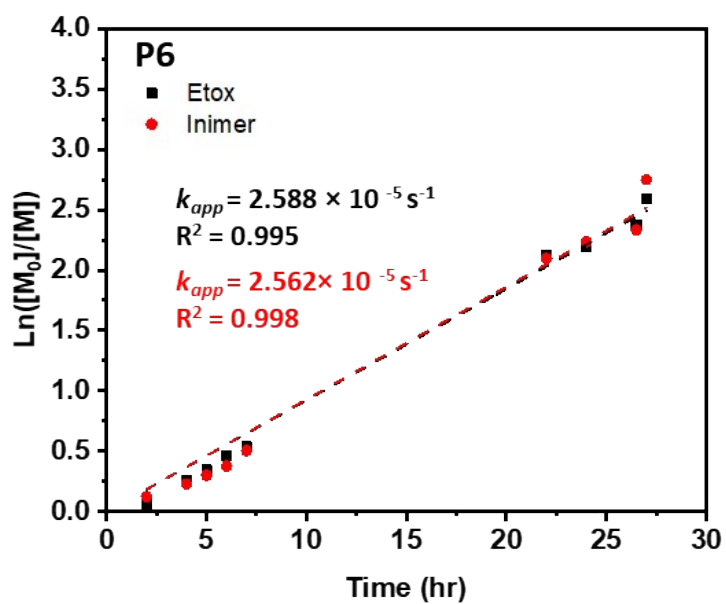
**Figure S3:** SEC trace of final P6 sample.



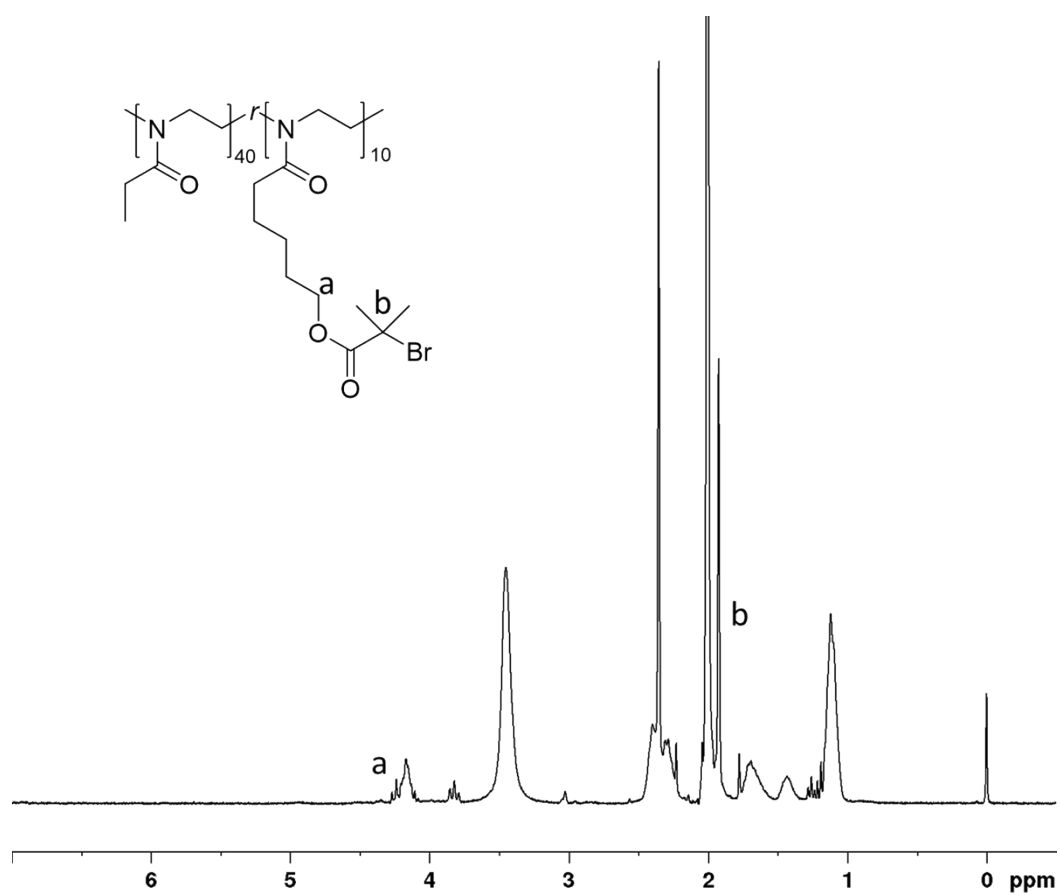
**Figure S4:** Semi-logarithmic kinetic plot of P6.



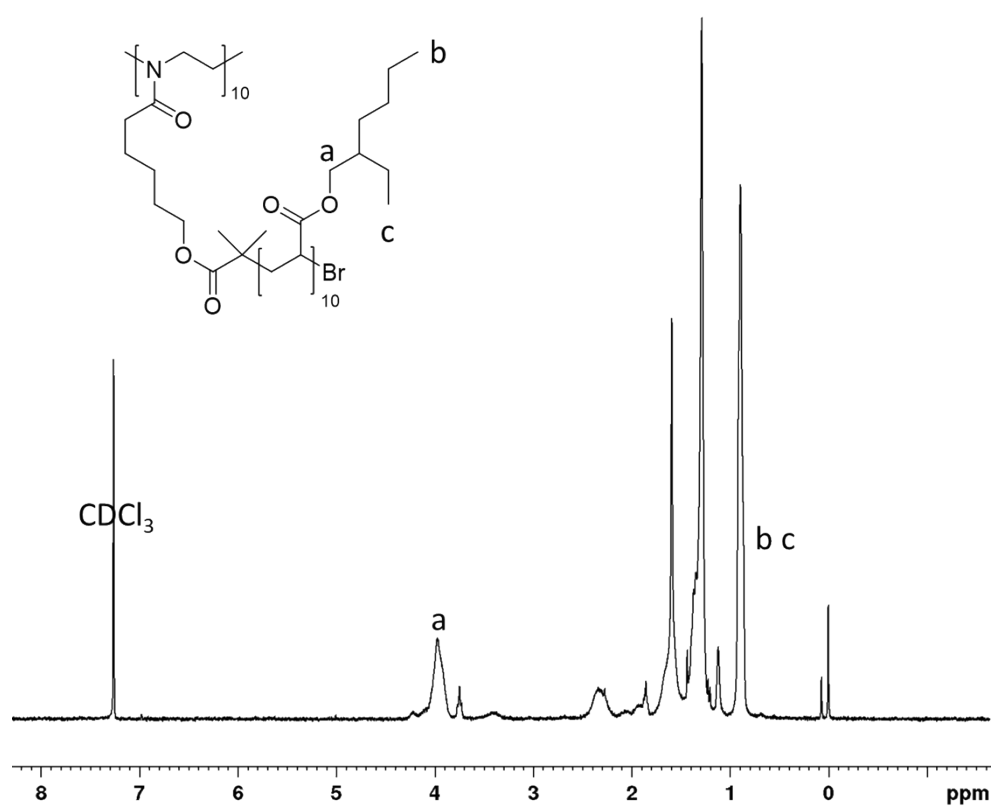
**Figure S5:** Evolution of  $M_n$  and corresponding dispersity values of **P6**.



**Figure S6:** Semi-logarithmic kinetic plot of In and **P6**.

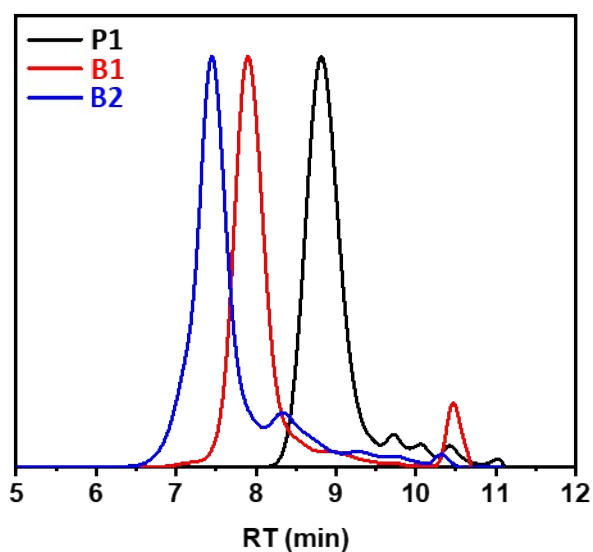


**Figure S7:**  $^1\text{H}$  NMR of P6

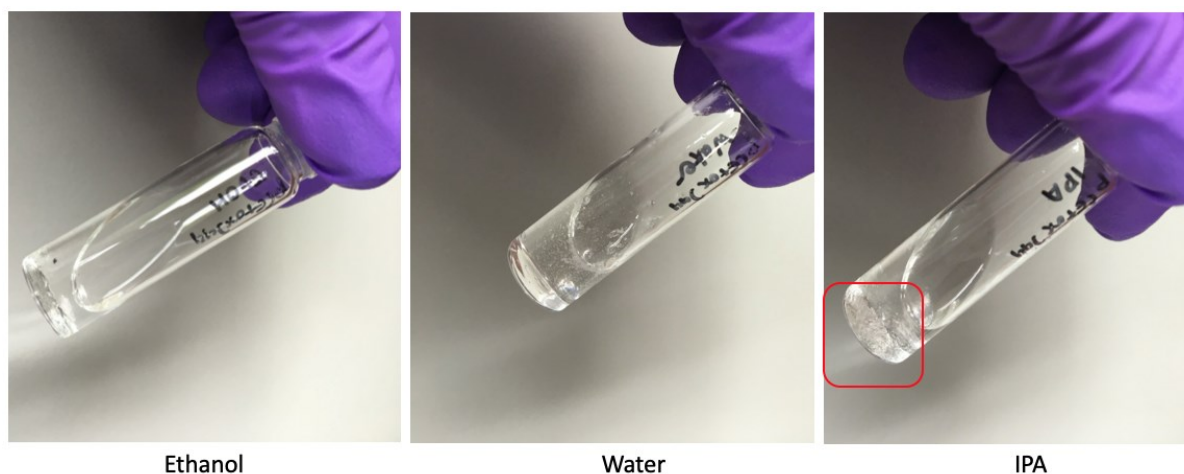


**Figure S8:**  $^1\text{H}$  NMR of B1.





**Figure S9:** Evolution of SEC traces from backbone (**P1**) to EHA brush (**B1**) to EHA-OEGA block brush polymer (**B2**).



**Figure S10:** Solubility test for poly(2-ethyl-2-oxazoline) in ethanol, water and IPA. These images are taken a minute after the solvent was added on to the polymer. Relatively lower solubility was observed in the case of IPA but it should be noted that they all became clear solutions over extended periods (>30 minutes).