

## **Supporting Information**

# **Unimolecular Ligand-Initiator dual functional Systems (ULIS) for low Copper ATRP of vinyl monomers including acrylic / methacrylic acids**

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### **Materials and characterizations**

All chemicals were purchased from Aldrich. The monomers were purified by passing through neutral alumina column and stored in a freezer before polymerizations.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a 400 MHz Bruker UltraShield AVANCE 400SB spectrometer. Residual solvent peaks were used as internal standard. High resolution mass spectra (HRMS) were recorded on Agilent 6210 TOF/LCMS. A Digilab Excalibur Series FTS3000 infra-red spectrometer was used to collect Fourier Transform Infra-red (FTIR) spectra. The THF run SEC system was equipped with Waters 515 HPLC pump, 717plus autosampler, 2414 refractive-index detector. The following Styragel GPC columns were arranged in series: guard, HR5E (×2, 4.6mm ID × 300 mm), HR1 and HR0.5. The eluent flow rate was 0.3 mL/min and the columns were maintained at 40 °C. Polystyrene standards were used for determining molecular weights and molecular weight distributions.

### **Experimental**

**Synthesis of SBLI:** This was synthesized in a two step process as mentioned below.

*Step I:* Paraformaldehyde (1.3966g, 46.50 mmol) and diethylenetriamine (4.775g, 46.28 mmol) were heated with stirring at 80°C for 1h under N<sub>2</sub> atmosphere. 2,4-Dimethylphenol (5.65g, 46.25 mmol) was added and heated for a further 2h and 30 minutes followed by the addition of pyridine-2-carboxaldehyde (9.9147g, 92.57 mmol). The reaction mixture was heated as a neat liquid at 80°C for 24h. The reaction mixture was dissolved in diethyl ether and washed repeatedly with saturated brine solution (3 × 100mL). The diethyl ether solution was subsequently dried over anhydrous MgSO<sub>4</sub> and removed in a rotary evaporator. The residue was treated with 9:1 hexane:diethyl ether mixture and cooled. The supernatant liquid was decanted off and the residue dried in a rotavapor. Yield: 15.33g (58 %). HRMS (*m/z*): calcd. for C<sub>25</sub>H<sub>29</sub>N<sub>5</sub>O 415.2372, found 416.2442 (M+H)<sup>+</sup> and 438.2263 (M+Na)<sup>+</sup>. IR (neat) cm<sup>-1</sup>: 3416, 2915, 2837, 1649, 1590, 1481, 1436, 1244, 1153, 992, 860, 775, 617.

*Step II:* The above product (10.8493g, 26.11 mmol) was dissolved in dry dichloromethane (DCM) (80 mL). The solution was cooled in an ice bath. 4-*N,N*-dimethylaminopyridine (3.239g, 26.51 mmol) was added and the solution was stirred. 2-Bromoisobutyryl bromide (6.138g, 26.70 mmol) diluted in dry DCM (20 mL) was added slowly to the solution and the reaction mixture was allowed to warm up to room temperature overnight. The reaction mixture was filtered and washed repeatedly (3 × 100mL) with saturated brine. After drying the DCM solution over anhydrous MgSO<sub>4</sub>, the organic solvent was removed in a rotary evaporator. Yield: 8.615g (59 %). HRMS (*m/z*): calcd. for C<sub>29</sub>H<sub>34</sub>BrN<sub>5</sub>O<sub>2</sub> 563.1896, found 564.1964 (M+H)<sup>+</sup> and 588.1768 (M+Na)<sup>+</sup>. IR (neat) cm<sup>-1</sup>: 3419, 2925, 1751, 1638, 1590, 1466, 1435, 1371, 1265, 1147, 1103, 866, 773, 748, 617.

**Synthesis of TALI:** This was synthesized in a two step process as mentioned below.

*Step I:* 2,4-Dimethyl-6-bis(2-(diethylamino)-ethyl)aminomethyl phenol was synthesised according to literature.<sup>1</sup> Yield: 3.25 g (76.6 %).

*Step II:* The above product (1.00 g, 2.86 mmol) was dissolved in dry dichloromethane (20 mL). Triethylamine (0.726 g, 7.00 mmol) was added to the dichloromethane solution. This reaction solution was cooled in an ice bath. 2-Bromoisobutyl bromide (0.74 g, 3.20 mmol) was then added and the bath was allowed to warm upto room temperature. The reaction mixture was stirred for a total period of 24h. The dichloromethane solution after diluting with additional dichloromethane (10 mL) was transferred to a separating funnel and washed repeatedly with deionized water (3×50 mL). It was then dried over anhydrous MgSO<sub>4</sub> and removed in a rotavapor. Honey coloured viscous oily liquid was obtained. Yield: 1.00 g (70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> (ppm)= 0.903-0.939 (12H, t, 4×CH<sub>3</sub>), 2.02 (6H, s, 2×CH<sub>3</sub>), 2.06 (s, CH<sub>3</sub>), 2.22 (s, CH<sub>3</sub>), 2.41-2.46 (q, 4×CH<sub>2</sub>), 2.49-2.6 (m, 4×CH<sub>2</sub>), 3.445 (s, CH<sub>2</sub>), 6.84 (s, 1H), 7.12 (s, 1H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> (ppm)= 11.38, 15.9, 20.88, 30.99, 47.32, 51.69, 52.35, 53.72, 55.22, 128.34, 129.71, 130.26, 131.21, 135.6, 145.26, 169.51.

HRMS (*m/z*): calcd. for C<sub>25</sub>H<sub>44</sub>BrN<sub>3</sub>O<sub>2</sub> 497.2617, found 498.26897 (M+H)<sup>+</sup>.

**Synthesis of TDLI:** This was synthesized in a two step process as mentioned below.

*Step I:* Pyridine-2-carboxaldehyde (2.486g, 23.21 mol) and *N,N,N',N'*-tetraethyldiethylenetriamine (5g, 23.21 mmol) were heated with stirring at 80°C for 1h. A pale yellow liquid was obtained. 2,4-Dimethylphenol (2.836g, 23.21 mmol) followed by methanol (20 mL) was added to the yellow liquid and the reaction mixture was refluxed for 24h. Methanol was removed under vacuum in a rotary evaporator and the residue was diluted with ethyl acetate. It

was then washed repeatedly with deionized water (3×50 mL). The ethyl acetate solution was subsequently dried over anhydrous MgSO<sub>4</sub> and removed in a rotary evaporator. Yield: 7.00g (71 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> (ppm)= 0.827-0.863 (12H, t, 4×CH<sub>3</sub>), 2.118-2.153 (6H, s, 2×CH<sub>3</sub>), 2.3-2.4 (q, 4×CH<sub>2</sub>), 2.4-2.6 (m, 2×CH<sub>2</sub>), 2.6-2.7 (m, CH<sub>2</sub>), 2.7-2.8 (m, CH<sub>2</sub>), 5.012 (s, CH), 6.38 (s, 1H), 6.73 (s, 1H), 7.099-7.115 (m, 1H), 7.428-7.45 (d, 1H), 7.533-7.557 (m, 1H), 8.499-8.504 (d, 1H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> (ppm)= 11.32, 16.23, 20.42, 47.32, 49.07, 50.18, 72.46, 114.82, 122.58, 122.75, 125.34, 127.26, 130.69, 131.11, 136.78, 152.51, 152.6, 159.74.

HRMS (*m/z*): calcd. for C<sub>26</sub>H<sub>42</sub>N<sub>4</sub>O 426.33586, found 427.34431 (M+H)<sup>+</sup>.

*Step II:* The above product (2.37g, 5.56 mmol) was dissolved in dry dichloromethane (DCM) (20 mL). The solution was cooled in an ice bath. 4-*N,N*-dimethylaminopyridine (0.678g, 5.56 mmol) was added and the solution was stirred. 2-Bromoisobutyryl bromide (1.28g, 5.57 mmol) diluted in dry DCM (10 mL) was added slowly and the reaction mixture was allowed to warm up to room temperature overnight. The reaction mixture was filtered and washed repeatedly with deionized water. After drying the DCM solution over anhydrous MgSO<sub>4</sub>, the organic solvent was removed in a rotary evaporator. Yield: 1.80 g (56 %). IR (neat) cm<sup>-1</sup>: 2969, 2809, 1751, 1589, 1466, 1435, 1381, 1263, 1193, 1143, 1103, 871, 804, 752, 642. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> (ppm)= 0.801-0.837 (12H, t, 4×CH<sub>3</sub>), 1.97 (3H, s, CH<sub>3</sub>), 2.003 (3H, s, CH<sub>3</sub>), 2.026 (3H, s, CH<sub>3</sub>), 2.118 (3H, s, CH<sub>3</sub>), 2.221-2.235 (4H, d, 2×CH<sub>2</sub>), 2.273-2.327 (8H, q, 4×CH<sub>2</sub>), 2.425- 2.464 (4H, m, 2×CH<sub>2</sub>), 2.571-2.609 (4H, m, 2×CH<sub>2</sub>), 5.102 (1H, s, CH), 6.808-6.821 (1H, d, ArH), 6.944-6.994 (1H, d, ArH), 7.257-7.277 (1H, d, ArH), 7.447-7.476 (2H, m, ArH), 8.392 (1H, s, ArH). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> (ppm)= 10.46, 15.34, 20.02, 29.81, 46.21, 48.51, 49.19, 65.22, 119.9, 121.02, 122.44, 126.45, 130.09, 130.86, 132.66, 135.68, 144.04, 148.02, 160.24, 169.12.

HRMS ( $m/z$ ): calcd. for  $C_{30}H_{47}BrN_4O_2$  574.28824, found 575.29783 ( $M+H$ )<sup>+</sup>.

### **Polymerization of St (P2):**

St (2.0 mL, 17.455 mmol) and SBLI (39.4 mg,  $6.98 \times 10^{-5}$  mol) solution in toluene (1 mL) was charged into a cold glass Schlenk tube filled with CuBr (0.2 mg,  $1.39 \times 10^{-6}$  mol) under  $N_2$ . The mixture was degassed with three freeze-pump-thaw cycles using  $N_2$  gas and then placed onto a hot oil bath thermostated at 110 °C for polymerization. From time to time samples were collected for  $^1H$  NMR and GPC analysis. Polymer samples were analyzed in GPC without any purification or precipitation. Finally a brownish coloured solution was obtained which when precipitated from methanol produced light-yellow coloured powder.

**Note:** For other polymerizations with varying amounts of CuBr, the monomer quantity was suitably adjusted so that the minimum quantity of CuBr remained at 0.2mg.

### **Synthesis of diblock copolymers (P10):**

At first MMA (2.0 mL, 18.89 mmol) was polymerized in a glass Schlenk tube in toluene (2 ml) in the presence of SBLI (52.8 mg,  $9.35 \times 10^{-5}$  mol) and CuBr (0.2 mg,  $1.39 \times 10^{-6}$  mol) at 100 °C for 6 h. Polymerization was stopped by cooling down the product in liquid  $N_2$ . The excess MMA was removed under high vacuum for 2 hrs. The polymer produced was then dissolved in St (4 ml, 34.9 mmol) and CuBr (0.2 mg,  $1.39 \times 10^{-6}$  mol) was added. The mixture was degassed with three freeze-pump-thaw cycles using  $N_2$  gas and then placed onto a hot oil bath (110 °C) for polymerization. Polymer samples were analyzed in GPC without any purification or precipitation.

### **Polymerization of MAA (P17) and chain extension reaction:**

MAA (2.0 g, 23.2 mmol) and TDLI (53.5 mg,  $9.29 \times 10^{-5}$  mol) mixture in  $D_2O$  (2 mL) was charged into a cold glass Schlenk tube filled with CuBr (0.3 mg,  $2.09 \times 10^{-6}$  mol) under  $N_2$ . The

mixture was degassed with three freeze-pump-thaw cycles using N<sub>2</sub> gas and then placed onto a hot oil bath thermostated at 95 °C for polymerization. The initial dispersion mixture turned homogeneous just after a few seconds of heating. From time to time samples were collected for <sup>1</sup>H NMR and GPC analysis. For molecular weight determination polymer samples were precipitated from acetone and subsequently methylated by reacting with (trimethylsilyl) diazomethane (TMSDM)<sup>[10]</sup> and then analyzed in THF GPC. Finally a greenish viscous solution was obtained which when precipitated from acetone produced green coloured polymer (**P17**).

PMAA (**P17**, 200 mg) was soaked in dry DMF (3 mL) for 24 h to dissolve completely, mixed with St (1 mL) and the mixture was transferred to a cold glass Schlenk tube filled with CuBr (0.2 mg, 1.39×10<sup>-6</sup> mol) under N<sub>2</sub>. After degassing for three freeze-pump-thaw cycles using N<sub>2</sub> gas, the mixture was placed onto a hot oil bath thermostated at 110 °C for 50 h. St conversion as estimated by <sup>1</sup>H NMR analysis was 28.7 %. Finally the PMAA-*b*-PS was precipitated from DEE, methylated using TMSDM<sup>[10]</sup> and characterized in THF GPC.

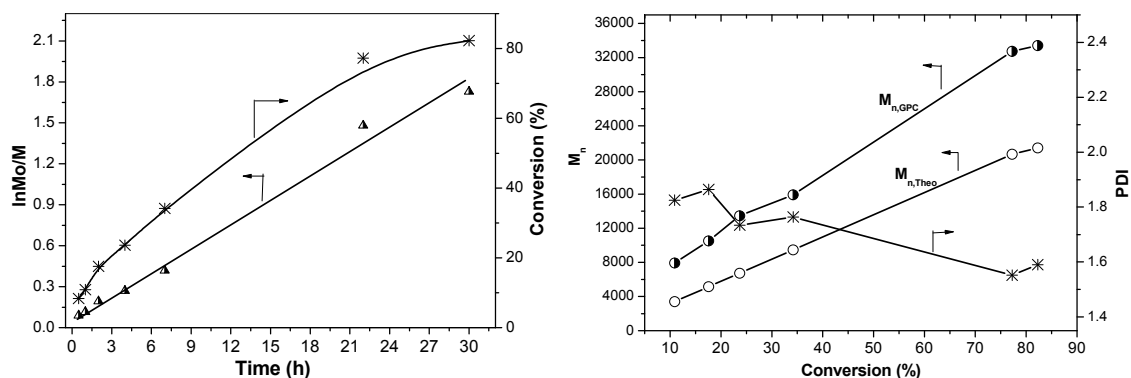


Figure S1. Kinetics of polymerization of St (P2) using SBLI with 80 ppm of CuBr

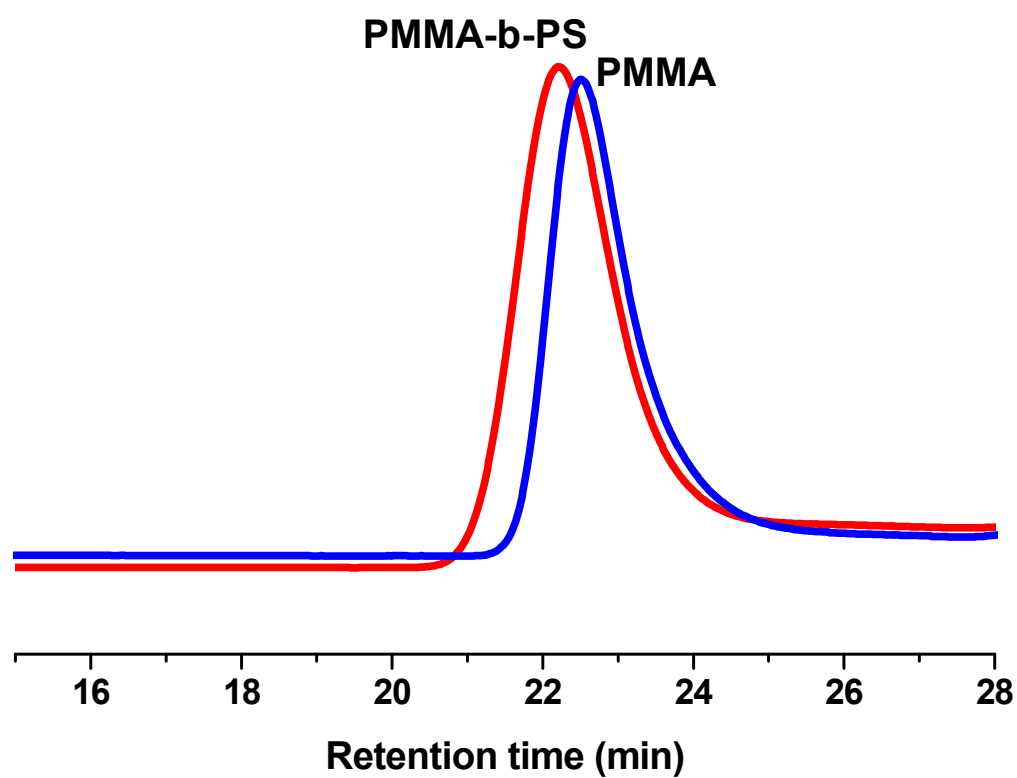
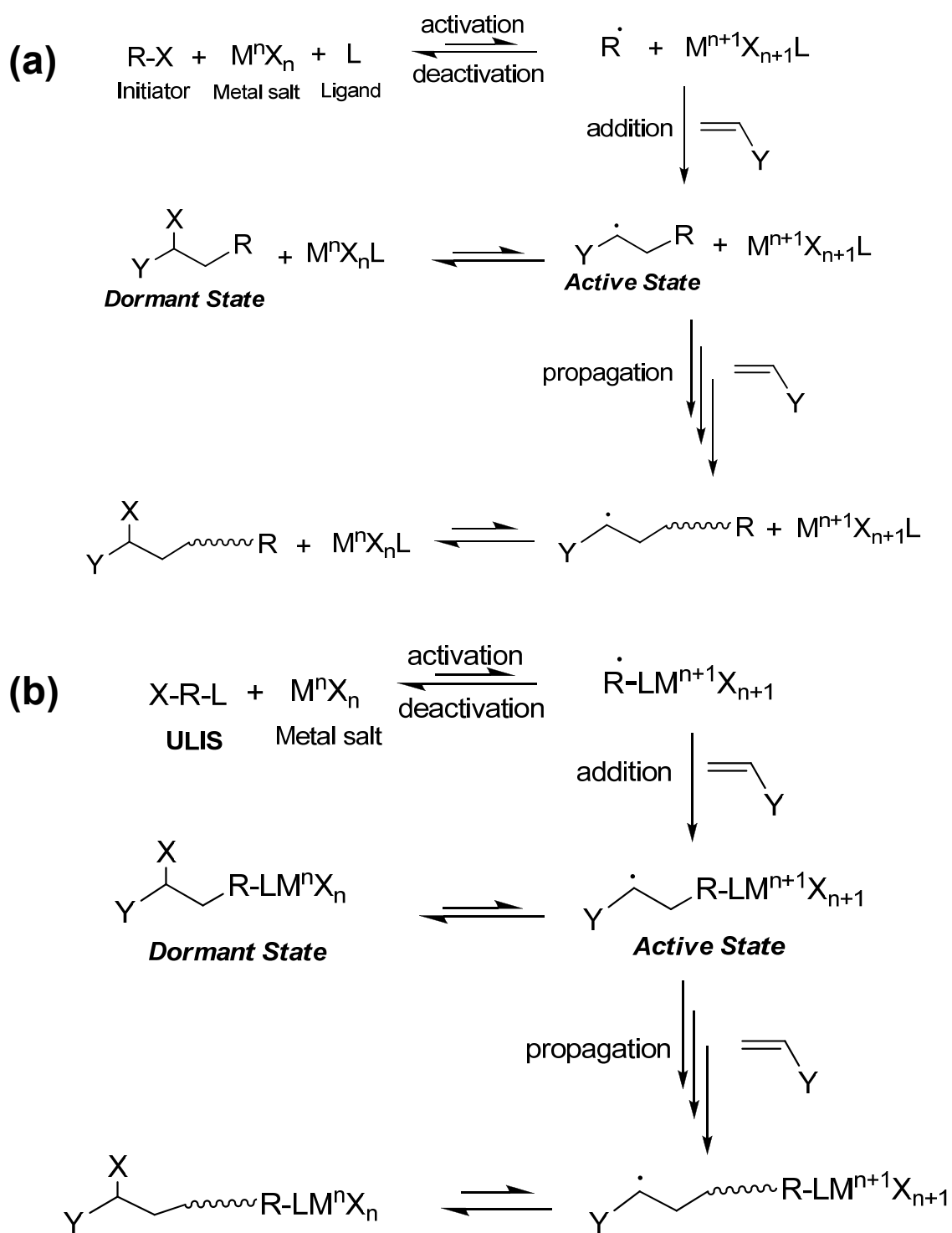


Figure S2. GPC traces of PMMA and PMMA-*b*-PS copolymer (**P10**) synthesized using SBLI.



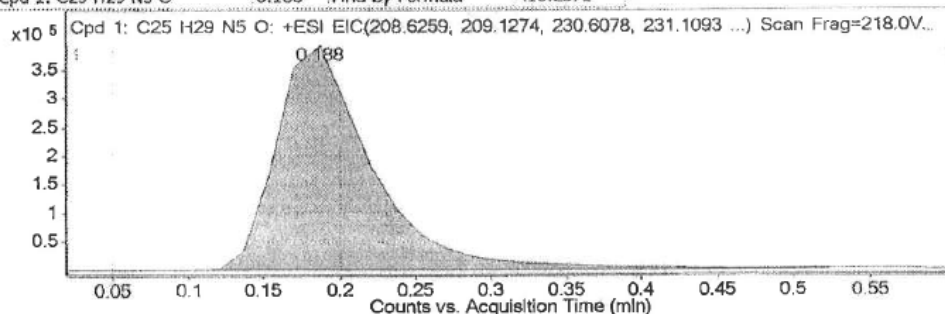
Scheme S1. Comparison of possible mechanism of (a) ATRP and (b) ATRP promoted by ULIS.



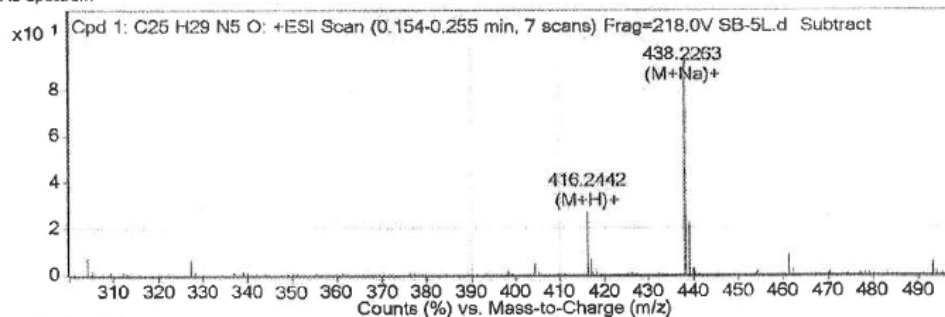
Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C <sub>25</sub> H <sub>29</sub> N <sub>5</sub> O	0.188	415.2371	55986	C <sub>25</sub> H <sub>29</sub> N <sub>5</sub> O	415.2372	-0.33

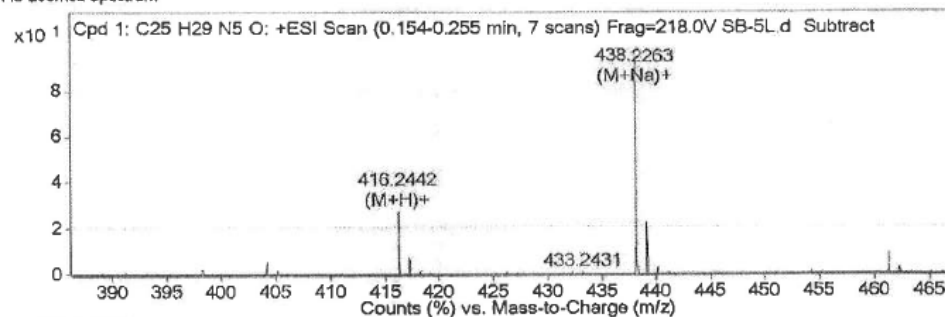
Compound Label	RT	Algorithm	Mass
Cpd 1: C <sub>25</sub> H <sub>29</sub> N <sub>5</sub> O	0.188	Find By Formula	415.2371



MS Spectrum



MS Zoomed Spectrum



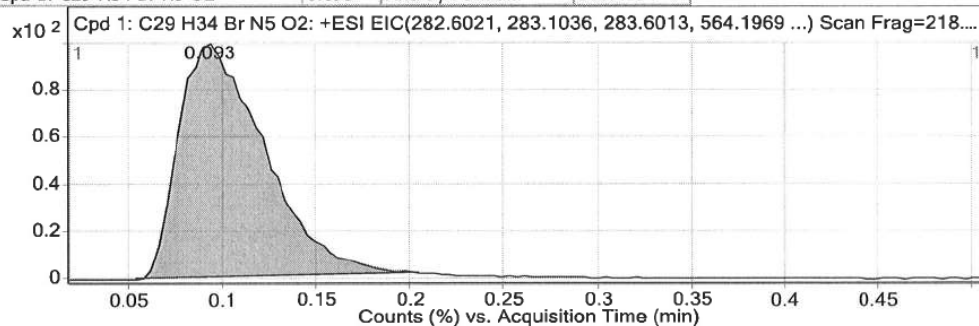
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Figure S3. HRMS of SBL (precursor of SBLI).

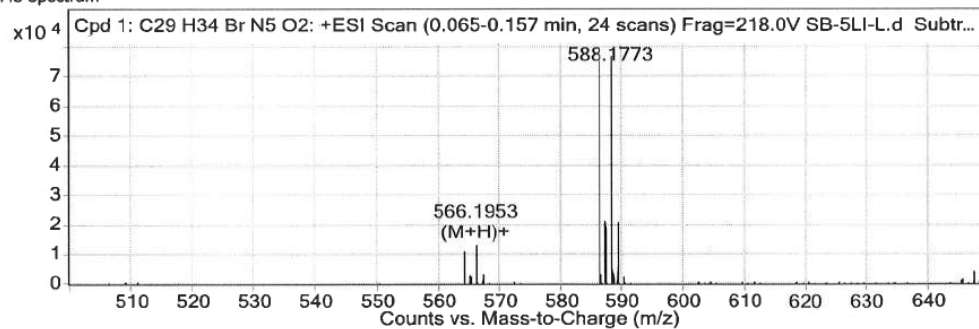
### Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C <sub>29</sub> H <sub>34</sub> BrN <sub>5</sub> O <sub>2</sub>	0.093	563.1894	13192	C <sub>29</sub> H <sub>34</sub> BrN <sub>5</sub> O <sub>2</sub>	563.1896	-0.37

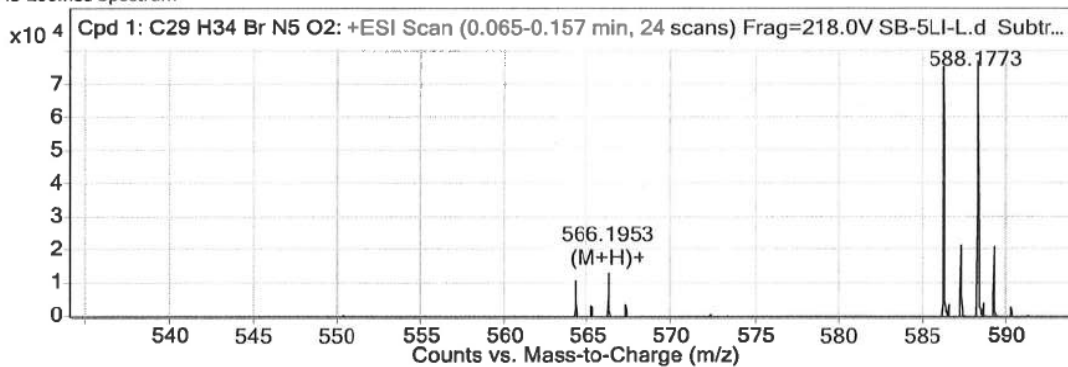
Compound Label	RT	Algorithm	Mass
Cpd 1: C <sub>29</sub> H <sub>34</sub> BrN <sub>5</sub> O <sub>2</sub>	0.093	Find By Formula	563.1894



### MS Spectrum

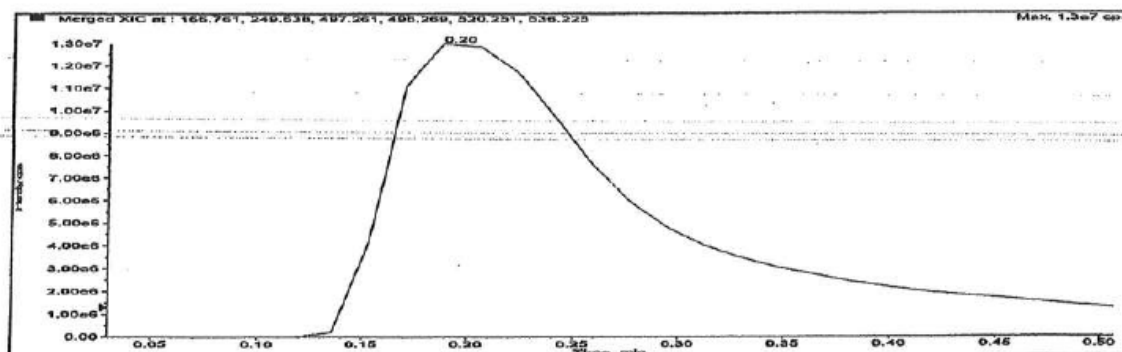


### MS Zoomed Spectrum

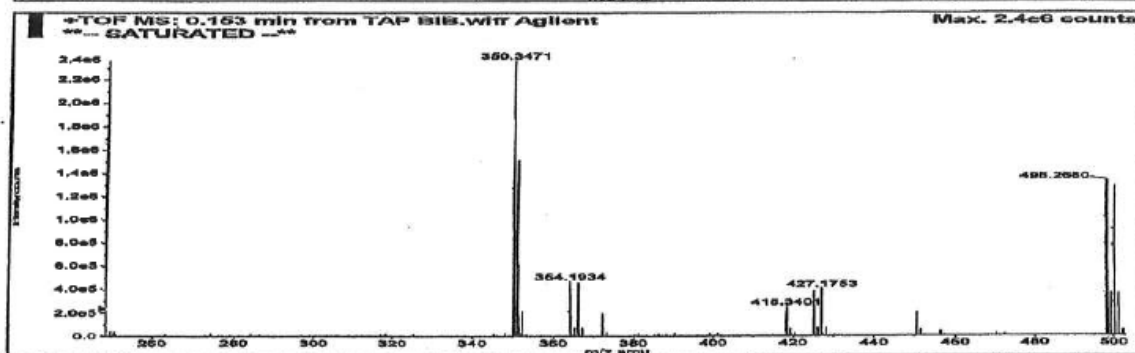
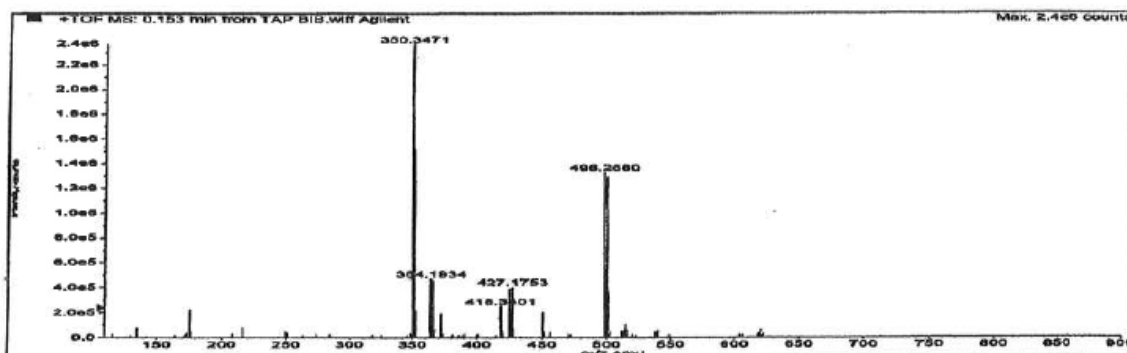


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Figure S4. HRMS of SBLI.



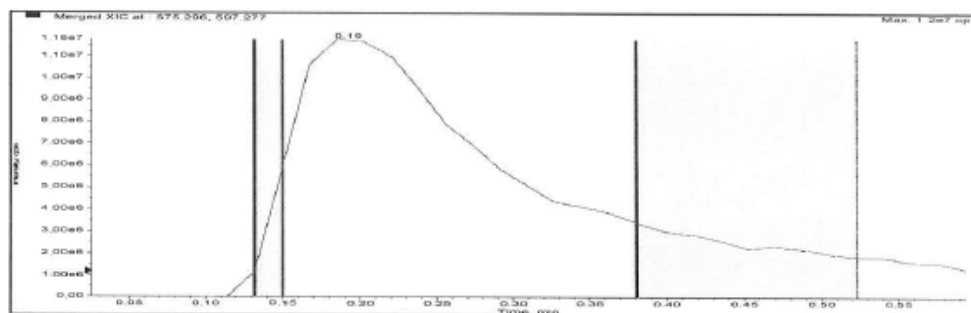
Merged XIC, Period#: 1 Experiment#: 1



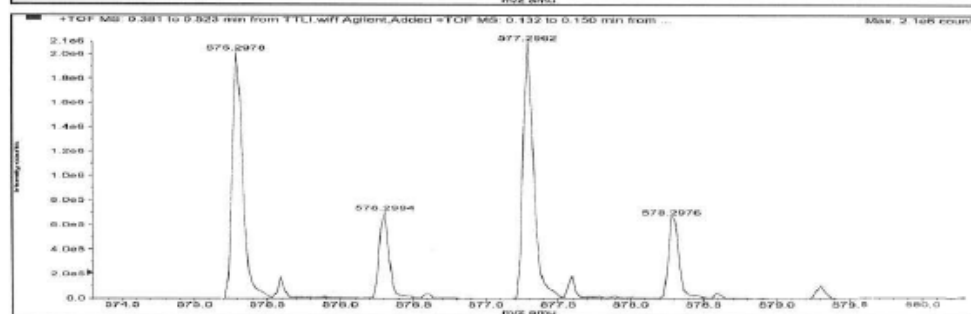
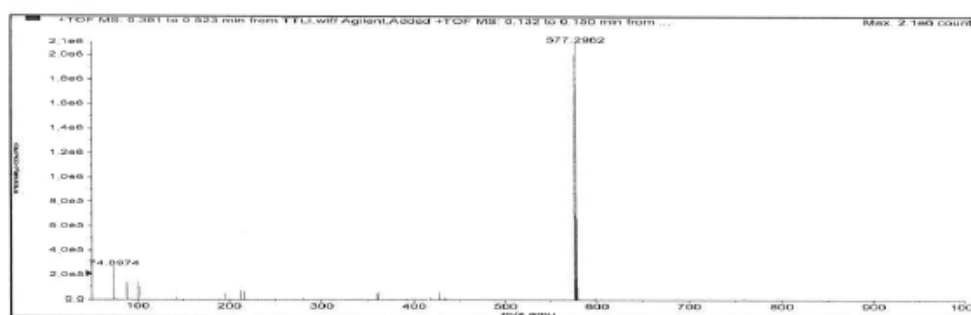
Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C <sub>25</sub> H <sub>41</sub> O <sub>2</sub> N <sub>3</sub> Br	--	497.26169	0.20	9.28859 E7	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+2H] <sup>2+</sup>	47668.65	249.63812	249.63716	-0.95944	-3.84	--
[M+H] <sup>+</sup>	1349056.03	498.26897	498.26801	-0.96016	-1.93	--

Figure S5. HRMS of TALI.



Merged XIC, Period# : 1 Experiment# : 1



Formula	Compound name	Mass	Peak RT (min)	Peak area	Description
C30H47BrN4O2	--	574.28824	0.19	1.17344 E8	--

Species	Abundance (counts)	Ion Mass	Measured Mass	Error (mDa)	Error (ppm)	Ret. Time Error (min)
[M+H] <sup>+</sup>	2041994.75	575.29552	575.29783	2.31466	4.02	--

Figure S6. HRMS of TDLI.

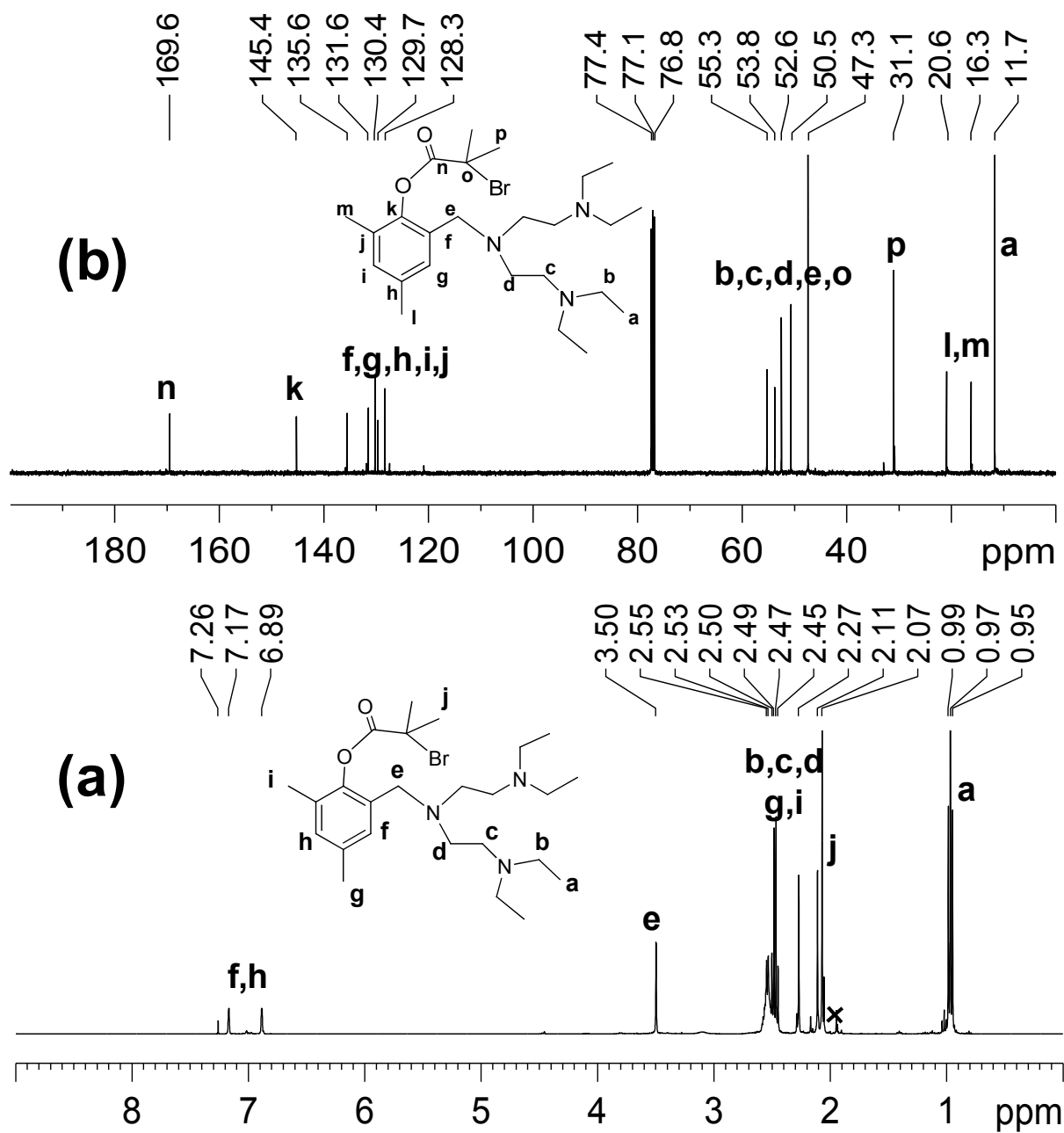


Figure S7. (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR spectra of TALI.

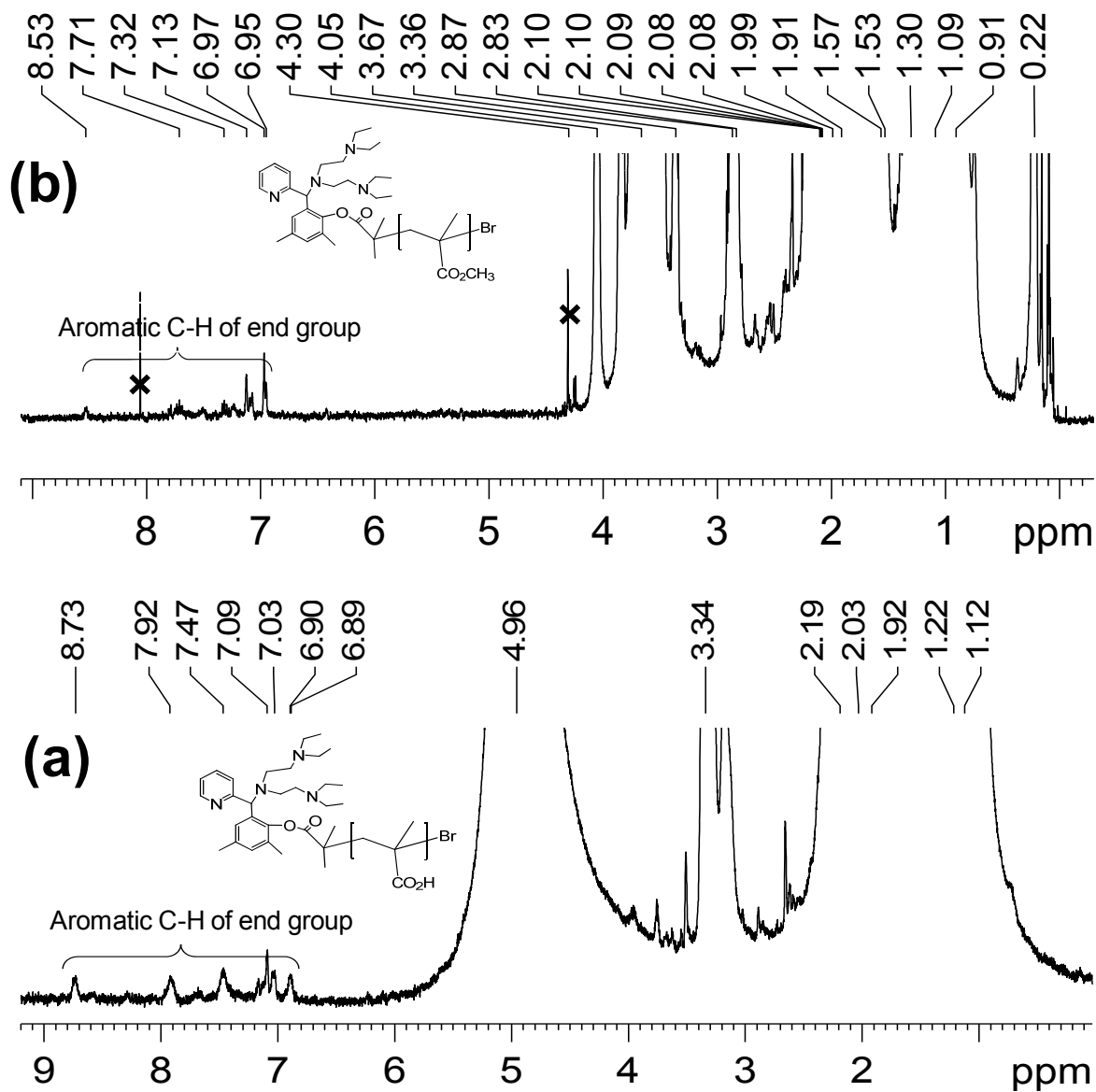


Figure S8. <sup>1</sup>H NMR spectrum of (a) PMAA (in d<sub>4</sub>-methanol) synthesized using TDLI in D<sub>2</sub>O (P17) and of (b) corresponding methylated product i.e. PMMA (P17m, in d<sub>6</sub>-acetone).



Figure S9. (a). PMAA and (b). PMAA-*b*/ran-PS (as collected from the reaction flask after the reaction).

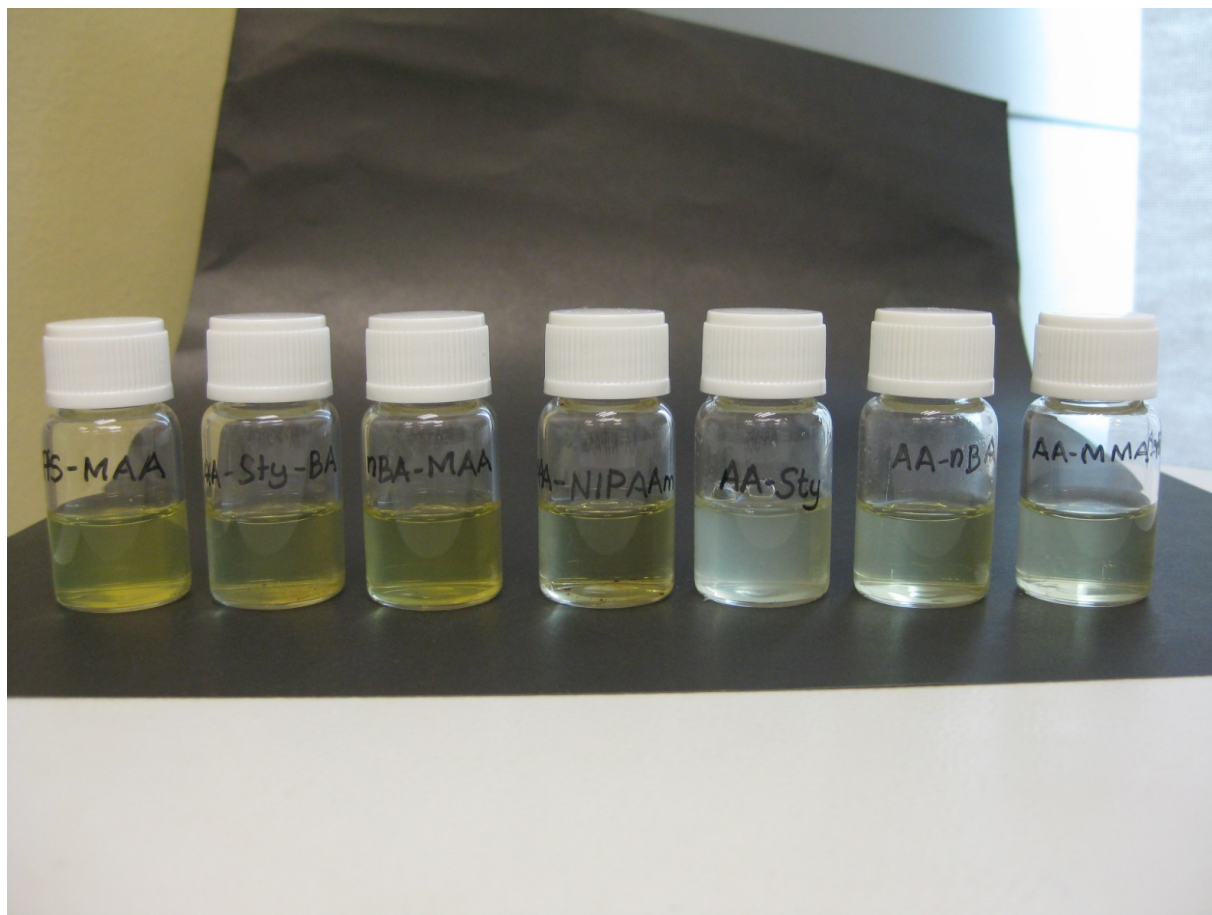


Figure S10. Aqueous alkali solutions of copolymers (L to R): PS-MAA; AA-Sty-nBA; MAA-nBA; AA-NIPAAm; AA-Sty; AA-nBA; AA-MMA-nBA.

#### REFERENCE

1. (a) M. Lubben, R. Hage, A. Meetsma, K. Byma, B. L. Feringa, *Inorg. Chem.* 1995, **34**, 2217.  
(b) Y. Inoue, K. Matyjaszewski, *Macromolecules* 2003, **36**, 7432.