Supplementary Information

Synthesis of poly(vinyl acetate) block copolymers by successive RAFT and ATRP with a bromoxanthate iniferter

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Experimental Section

Materials. Methyl acrylate (MA, 99%), methyl methacrylate (MMA, 99%), styrene (St, 99%) and vinyl acetate (VAc, 99%) were purchased from Aldrich and purified by passing through a column filled with basic alumina to remove the inhibitors or antioxidants. Vinyl acetate was further purified by distillation over sodium sulphate. 2,2'-Azobis(isobutyronitrile) (AIBN, 98%) purchased from Aldrich was recrystallized from methanol and stored in a refrigerator prior to use. Tris(2-(dimethylamino)ethyl)amine (Me6TREN) was synthesized following the previously reported procedures.¹All other reagents - anhydrous ethylene glycol, 2-bromoisobutyryl bromide, 2-bromopropionyl bromide, 4,4'-dinonyl-2,2'-bipyridyne (dNbpy), 2,2'-bipyridyne (bpy), *N*,*N*,*N'*,*N''*,*N''*-pentamethyldiethylenetriamine (PMDETA), potassium ethyl xanthogenate, pyridine, CuBr, CuBr₂, CuCl, CuCl₂-and solvents were purchased from Aldrich with the highest purity available and used as received without further purification.

Analyses. NMR spectra were recorded on a Bruker instrument operating at 300 MHz. Monomer conversions were determined by ¹H NMR. Molecular weight and polydispersity were determined by size exclusion chromatography (SEC). The SEC analysis was conducted with a Waters 515 pump and Waters 410 differential refractometer using Polymer Standards Services (PSS) columns (Styrogel 10^5 , 10^3 , and 10^2 Å) in THF as eluent at 35°C and at a flow rate of 1 mL/min. The apparent molecular weights ($M_{n,RI}$ and $M_{w,RI}$) and polydispersities (M_w/M_n) were determined with a calibration based on linear poly(methyl methacrylate) (PMMA) or polystyrene (PSt) standards.

Synthesis of 2-Hydroxyethyl 2-Bromopropionate, 3. Anhydrous ethylene glycol (301 g, 4.84 mol) and pyridine (8.1 mL, 100 mmol) were diluted with dry tetrahydrofuran (100 mL). The reaction mixture was cooled in an ice-water bath, and a solution of 2-bromopropionyl bromide (10 mL, 95.5 mmol) in dry tetrahydrofuran (50 mL) was slowly added while stirring. The mixture was stirred in the cooling bath for 1 h and then at room temperature for 16 h. The reaction mixture was then poured into acidic water (pH = 2, 800 mL) and extracted with dichloromethane (6 x 100 mL). The organic fractions were combined, extracted with water, dried on MgSO₄ and evaporated to dryness to afford 14.4 g (yield = 76.7 %) of a colourless liquid.¹H NMR (CDCl₃, δ , ppm): 4.35 (q, 1H, *J* = 6.89 Hz), 4.19 (t, 2H, *J* = 4.75 Hz), 3.75 (t, 2H, *J* = 4.75 Hz), 3.00 (s, 1H, OH), 1.75 (d, 3H, *J* = 6.96 Hz).¹³C NMR (CDCl₃, δ): 170.53, 67.18, 60.35, 39.93, 21.50.

Synthesis of S-(1-Methyl-4-Hydroxyethyl Acetate)O-Ethyl Dithiocarbonate, 4. A 50 mL, round-bottomed flask equipped with a dropping funnel was charged with a magnetic stirring bar, potassium ethyl xanthogenate (3.65 g, 22.7 mmol), and acetone (15 mL). A solution of 2-

hydroxyethyl 2-bromopropionate, **3**, (4 g, 20.3 mmol) in acetone (15 mL) was added dropwise at room temperature over a period of 30 min. Stirring was continued for 12 hr at RT. Solids were removed by filtration to afford a clear pale yellow solution. The solids on the funnel were washed with acetone (total of 50 mL). The combined washing and filtrate solutions were concentrated under vacuum to dryness to furnish a yellow viscous liquid that was dissolved in dichloromethane (100 mL). This solution was washed with water (75 mL), dried over MgSO₄ and evaporated to dryness to afford 4.56 g (94.3%) of a yellow viscous liquid.¹H NMR (CDCl₃, δ , ppm): 4.57 (q, 2H, *J* = 7.13 Hz), 4.34 (q, 1H, *J* = 7.38 Hz), 4.20 (t, 2H, *J* = 4.79 Hz), 3.82-3.70 (m, 2H), 2.61-2.50 (broad peak, 1H, OH), 1.52 (d, 3H, *J* = 7.50 Hz), 1.35 (t, 3H, *J* = 7.14 Hz). ¹³C NMR (CDCl₃, δ): 212.03, 171.63, 70.35, 67.09, 60.63, 47.04, 16.72, 13.59.

Synthesis of S-[1-Methyl-4-(6-Bromopropionate)Ethyl Acetate] O-Ethyl Dithiocarbonate, 5. 4 (2 g, 8.39 mmol) and pyridine (0.934 mL, 11.6 mmol) were dissolved in dry dichloromethane (10 mL). The reaction mixture was cooled in an ice-water bath and a solution of 2bromopropionyl bromide (1.1 mL, 10.5 mmol) in dry dichloromethane (5 mL) was slowly added while stirring. The mixture was stirred in the cooling bath for 1h and then at room temperature for 16 h. Excess of 2-bromo-2-methylpropionyl bromide was neutralized with 0.1 mL of water and the reaction mixture was then poured into a solution of hydrochloric acid (80 mL, 0.3 M). The organic layer was then washed with a solution of sodium hydroxide (80 mL, 0.3 M), dried over magnesium sulphate and concentrated under vacuum. The product was then purified by flash column chromatography on basic alumina using diethyl ether as solvent to afford 2.48 g (yield = 79.1 %) of yellow viscous liquid. ¹H NMR (CDCl₃, δ , ppm): 4.64 (q, 2H, *J* = 7.08 Hz), 4.47-4.32 (overlapped m, 6H), 1.83 (d, 3H, *J* = 6.96 Hz), 1.58 (d, 3H, *J* = 7.50 Hz), 1.42 (t, 3H, *J* = 7.13 Hz). ¹³C NMR (CDCl₃, δ): 212.09, 171.38, 170.14, 70.49, 63.37, 63.01, 47.20, 39.71, 21.70, 16.87, 13.84.

Synthesis of S-[1-Methyl-4-(6-Bromoisobutyrate)Ethyl Acetate] O-Ethyl Dithiocarbonate, 6. **4** (10 g, 42 mmol) and triethylamine (8 mL, 57.4 mmol) were dissolved in dry tetrahydrofuran (50 mL). The reaction mixture was cooled in an ice-water bath and a solution of 2-bromo-2-methylpropionyl bromide (6 mL, 48.5 mmol) in dry tetrahydrofuran (20 mL) was slowly added while stirring. The mixture was stirred in the cooling bath for 1h and then at room temperature for 16 h. Excess of 2-bromo-2-methylpropionyl bromide was neutralized with 0.5 mL of water and the reaction mixture was then poured into a solution of hydrochloric acid (400 mL, 0.3 M) and extracted with dichloromethane (3 x 100 mL). The combined organic layers were washed with a solution of sodium hydroxide (400 mL, 0.3 M), dried over magnesium sulphate and concentrated under vacuum to afford 16.18 g (yield = 99.5 %) of yellow viscous liquid. ¹H NMR (CDCl₃, δ , ppm): 4.63 (q, 2H, *J* = 7.13 Hz), 4.47-4.32 (overlapped m, 5H), 1.93 (s, 6H), 1.58 (d, 3H, *J* = 7.50 Hz), 1.41 (t, 3H, *J* = 7.13 Hz). ¹³C NMR (CDCl₃, δ): 212.09, 171.56, 171.34, 70.46, 63.47, 63.03, 55.46, 47.23, 30.8, 16.91, 13.83.

General Procedure for RAFT Polymerization of Vinyl Acetate. In a typical experiment, 5 (39.4 mg, 1.06×10^{-1} mmol), AIBN (8.2 mg, 5×10^{-2} mmol) and anisole (0.6 mL) were charged to a flask and purged with N₂ for 30 minutes. Deoxygenated VAc (2.4 mL, 26 mmol) was added and an initial sample was taken. The flask was placed in an oil bath thermostated at 60°C for 14 hours. At timed intervals, samples were withdrawn via a syringe for measurement of monomer conversion and polymer molecular weight by ¹H NMR and SEC, respectively. The

polymerization was stopped by quenching the reaction in an ice bath ($M_n = 8,350$ g/mol, $M_w/M_n = 1.29$, conversion = 38.8%).

General Procedure for ATRP of MMA, MA and St with 5, 6 or a PVAc macroiniferter. In a typical experiment, PVAc macroiniferter (148 mg, 50 x 10^{-3} mmol, $M_n = 2,950$ g/mol, $M_w/M_n = 1.26$) and anisole (3 mL) were charged to a flask and purged with N₂ for 30 minutes. Deoxygenated styrene (3 mL, 26.2 mmol), CuBr (6.5 m g, 45 x 10^{-3} mmol), CuBr₂ (1.1 m g, 5 x 10^{-3} mmol) and PMDETA (10.5 x 10^{-3} mL, 50 x 10^{-3} mmol) were added. An initial sample was taken and the solution was stirred at 90°C for 22 hours. At timed intervals, samples were withdrawn via a syringe for measurement of monomer conversion and polymer molecular weight by ¹H NMR and SEC, respectively. The polymerization was stopped via exposure to air and dilution in THF ($M_n = 30,700$ g/mol, $M_w/M_n = 1.20$, conversion = 44.2%).

Synthesis of PVAc macroiniferter 7. 5 (187 mg, 5 x 10^{-1} mmol), AIBN (41.1 mg, 2.5 x 10^{-1} mmol) and anisole (2.07 mL) were charged to a flask and purged with N₂ for 30 minutes. Deoxygenated VAc (4.15 mL, 45 mmol) was added and an initial sample was taken. The flask was placed in an oil bath thermostated at 60°C for 8 hours. At timed intervals, samples were withdrawn via a syringe for measurement of monomer conversion and polymer molecular weight by ¹H NMR and SEC, respectively. The polymerization was stopped by quenching the reaction in an ice bath ($M_n = 2,950$ g/mol, $M_w/M_n = 1.26$, conversion = 37.1%). The monomer and the solvent were removed under vacuum and the polymer was purified by 2 successive precipitations in hexanes (m=1.41 g; yield = 98.1%).



Figure S1. SEC trace of PVAc macroiniferter 7. [VAc]/[5]/[AIBN] = 90/1/0.5 in anisole 33 % in volume; 60°C for 8 hours.

RAFT polymerization of VAc with a PMA macroiniferter prepared with 6.



Figure S2. Evolution of SEC traces during VAc polymerization with a PMA macroiniferter prepared with **6**. [VAc]/[PMA macroiniferter]/[AIBN] = 200/1/0.3, MA/anisole = 2/1 v/v, 60°C

Polymerization kinetics and SEC traces for ATRP of MA and MMA with 6.



Figure S3. Kinetic, M_n and M_w/M_n vs conversion plots for MA polymerization with **6**. [MA]/[**6**]/[Cu⁰]/[PMDETA] = 500/1/1/1, MA/acetone = 1/1 v/v, 25°C



Figure S4. Evolution of SEC traces during MA polymerization with **6**. $[MA]/[6]/[Cu^0]/[PMDETA] = 500/1/1/1$, MA/acetone = 1/1 v/v, $25^{\circ}C$



Figure S5. Kinetic, M_n and M_w/M_n vs conversion plots for MMA polymerization with **6**. [MMA]/[**6**]/[CuBr]/[CuBr₂]/[PMDETA] = 500/1/1/0.1/2.2, MMA/anisole = 1/1 v/v, 90°C



Figure S6. Evolution of SEC traces during MMA polymerization with **6**. [MMA]/[**6**]/[CuBr]/[CuBr₂]/[PMDETA] = 500/1/1/0.1/2.2, MMA/anisole = 1/1 v/v, 90°C



Figure S7. SEC traces of PS, PMA and PMMA prepared by ATRP with 6



Polymerization kinetics and SEC traces for RAFT polymerization of VAc with 6.

Figure S8. Kinetic, M_n and M_w/M_n vs conversion plots for VAc polymerization with **6**. [VAc]/[**6**]/[AIBN] = 200/1/0.2, bulk, 60°C



Figure S9. Evolution of SEC traces during VAc polymerization with **6**. [VAc]/[**6**]/[AIBN] = 200/1/0.2, bulk, 60°C

Polymerization of BA, St and MMA with macroiniferter 7 and AIBN.



Figure S10. Evolution of SEC traces during BA polymerization with macroiniferter **7** and AIBN. [BA]/[7]/[AIBN] = 151/1/0.1, BA/anisole = 1/1 v/v, 60°C .



Figure S11. Evolution of SEC traces during St polymerization with macroiniferter 7 and AIBN. [St]/[7]/[AIBN] = 145/1/0.1, St/anisole = 1/1 v/v, 60° C.



Figure S12. Evolution of SEC traces during MMA polymerization with macroiniferter **7** and AIBN. [MMA]/[7]/[AIBN] = 156/1/0.1, MMA/anisole = 1/1 v/v, 60° C.





Figure S13. Kinetic, M_n and M_w/M_n vs conversion plots for MMA polymerization with 7. [MMA]/[7]/[CuBr]/[CuBr_2]/[bpy] = 560/1/1/0.1/2.2, MMA/DMF = 1/1 v/v, 50°C



Figure S14. Evolution of SEC traces during MMA polymerization with macroiniferter 7. $[MMA]/[7]/[CuBr_2]/[bpy] = 560/1/1/0.1/2.2$, MMA/DMF = 1/1 v/v, 50°C



Figure S15. Kinetic, M_n and M_w/M_n vs conversion plots for MMA polymerization with 7. [MMA]/[7]/[CuCl]/[CuCl_2]/[bpy] = 560/1/1.8/0.2/4, MMA/DMF = 1/1 v/v, 50°C



Figure S16. Evolution of SEC traces during MMA polymerization with macroiniferter7. [MMA]/[7]/[CuCl₂]/[bpy] = 560/1/1.8/0.2/4, MMA/DMF = 1/1 v/v, 50°C

Reference:

(1) Xia, J.; Gaynor, S. G.; Matyjaszewski, K. Macromolecules 1998, 31, 5958-5959.