

Synthesis of poly(vinylacetylene) block copolymers by atom transfer radical polymerization

Supporting Information

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1. Synthesis

1-1. Synthesis of PVATMS by ATRP at various temperatures

Deoxygenated toluene (1 mL), VATMS (1 mL, 0.7767 g, 6.25×10^{-3} mol) and EBiB (9.24 μL , 6.25×10^{-5} mol) were mixed together in a 50 mL Schlenk flask, and the mixture was degassed by three freeze-pump-thaw cycles. CuBr (8.97 mg, 6.25×10^{-5} mol) and dNbpy (51.1 mg, 1.25×10^{-4} mol) were then added, and the flask was placed in an oil bath thermostated at 90, 60, 40 or 20 °C. The reaction was monitored by ^1H -NMR and GPC and was stopped by cooling the reaction down to room temperature and opening the flask to air. PVATMS was obtained as a white powder by precipitation of the polymer by adding the solution to methanol and drying the solid under vacuum.

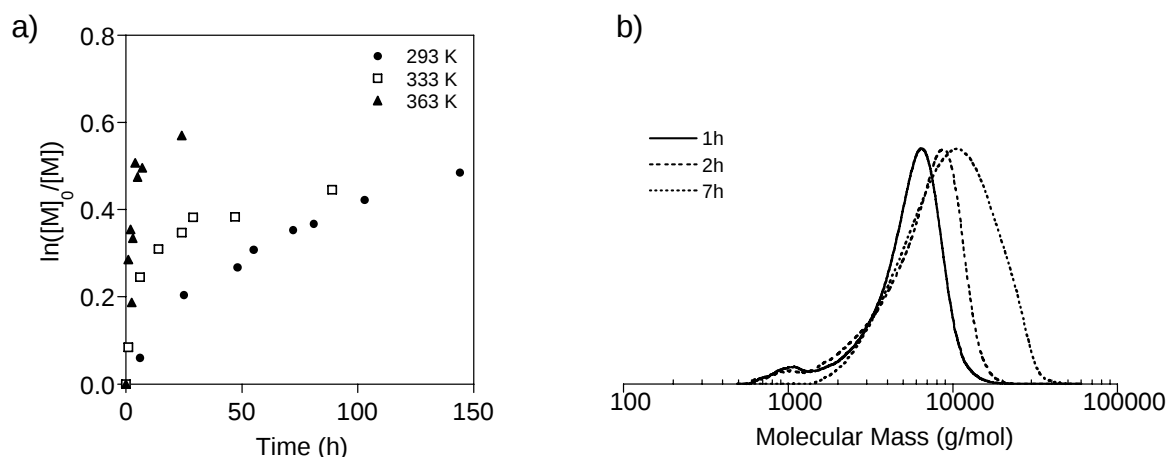


Figure S1. Kinetic plots for ATRP of VATMS at different temperatures (a) and evolution of GPC traces for ATRP of VATMS at 90 °C.

1-2. Synthesis of VATMS by ARGET ATRP

VATMS (0.456 g, 0.0367 mol) and anisole (0.3 mL) were added to a dry Schlenk flask followed by addition of the initiator, EBiB (5.4 μL , 0.0367 mmol). A solution of $\text{Cu}^{\text{II}}\text{Br}_2$ complex (0.082 mg, 0.367 μmol)/TPMA (0.32 mg, 1.10 μmol) in anisole (0.2 mL) was then added to the flask. The resulting mixture was degassed by four freeze-pump-thaw cycles. After melting the mixture, a solution of the $\text{Sn}(\text{EH})_2$ (1.18 μL , 3.67 μmol) in anisole (0.1 mL) was slowly added to the reaction medium. An initial sample was taken and the sealed flask was placed in an oil bath thermostated at 40 °C. Samples were taken at timed intervals and analyzed by ^1H NMR and gel permeation chromatography (GPC) to follow the progress of the reaction. The rate of polymerization was slow and conversion reached 57% after 300 h, providing PVATMS with $M_{n(\text{GPC})} = 11,000$ and $M_w/M_n = 1.5$.

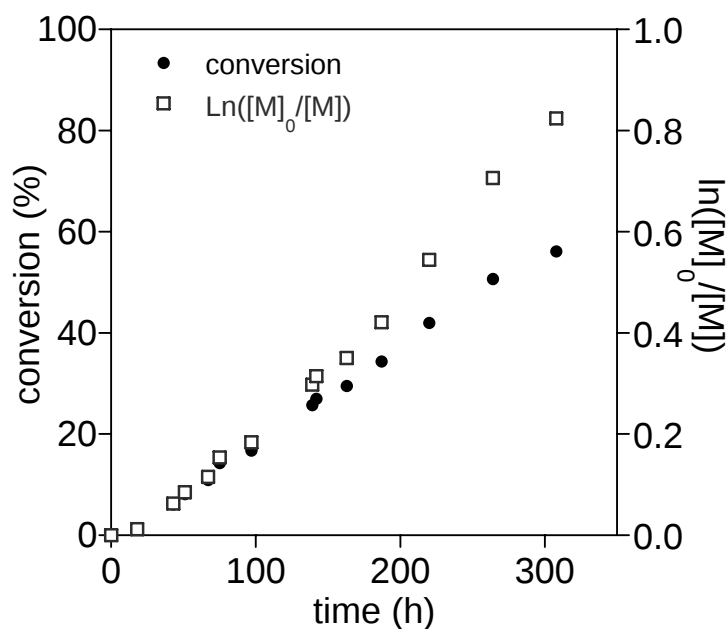


Figure S2. Kinetic plots for ARGET ATRP of VATMS at 40 °C.

1-3. Chain extension of PVATMS with MMA

PVATMS macroinitiator ($M_n = 5500$, PDI = 1.15) (50 mg, 9.00×10^{-6} mol) and anisole (0.6 mL) were added to a dry Schlenk flask followed by methyl methacrylate (0.58 mL, 5.40 mmol). A 0.1 mL of solution of CuBr (4.5 mg, $3.15 \mu\text{mol}$)/CuBr₂ (3.0 mg, $1.35 \mu\text{mol}$)/PMDETA (0.96 μL , $4.50 \mu\text{mol}$) complex in anisole (1.0 mL) was added to the flask. The resulting mixture was degassed by four freeze-pump-thaw cycles. An initial sample was taken and the sealed flask was placed in an oil bath thermostated at 40 °C. Samples were taken at timed intervals and analyzed by ¹H NMR and gel permeation chromatography (GPC) to follow the progress of the reaction. The polymerization was stopped by opening the flask after 10h and exposing the catalyst complex in the solution to air.

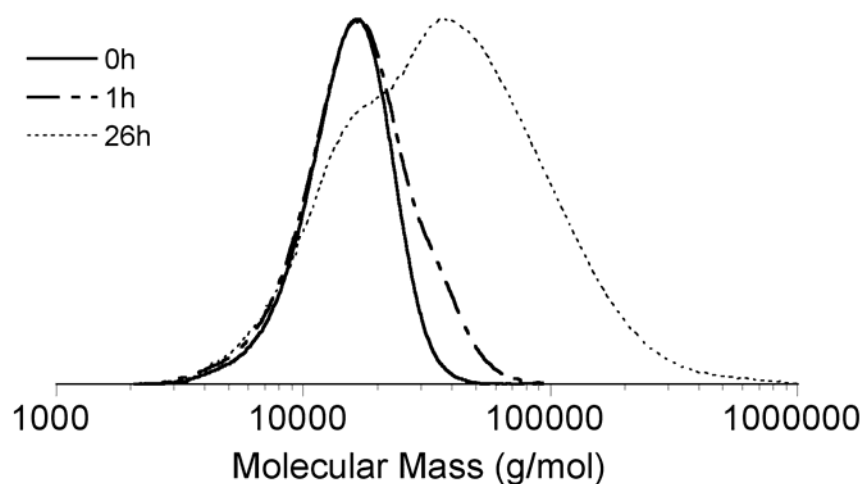
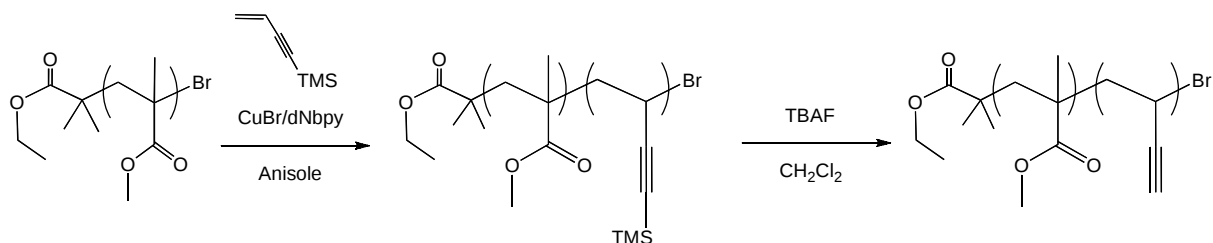


Figure S3. Evolution of GPC traces during block extension of PVA-TMS with MMA.

1-4. Synthesis of PMMA-*b*-PVA



Poly(methyl methacrylate) macroinitiator ($M_n=15400$, $PDI=1.15$) (0.27 g, 1.86×10^{-5} mol) and anisole (1.0 mL) were added to a dry Schlenk flask followed by VTMS (0.463 g, 0.0372 mmol). A solution of CuBr complex (2.67 mg, $1.86 \mu\text{mol}$)/dNbpy (15 mg, $3.72 \mu\text{mol}$) in anisole (0.1 mL) was then added to the flask. The resulting mixture was degassed by four freeze-pump-thaw cycles. An initial sample was taken and the sealed flask was placed in an oil bath thermostated at 40°C . Samples were taken at timed intervals and analyzed by ^1H NMR and gel permeation chromatography (GPC) to follow the progress of the reaction. The polymerization was stopped by opening the flask after 48h and exposing the catalyst complex in the solution to air, giving a block copolymer with $M_n=21600$ g/mol, $PDI=1.16$ from GPC (THF). The molecular weight of the PVATMS segment in block copolymer was estimated as 29% by gpc, and 28% by NMR measurements.

PMMA-*b*-PVATMS ($M_n=21600$ by GPC; 32.3 mg) was dissolved in dichloromethane (10 mL). Tetrabutylammonium fluoride (TBAF) (1M in THF solution; 0.15 mL, 0.15 mol) was then added drop wise to the mixture and stirred at room temperature during 24 h. The reaction mixture was passed through an alumina column to remove TMS fluoride and concentrated in vacuo. The polymer was freeze dried from benzene solution to give a white powder in 70 % yield (20 mg, $M_n=19,000$, $M_w/M_n=1.27$) calculated by GPC with a degree of deprotection of 94 % as determined by ^1H NMR.

2. Characterization

2-1. ^1H NMR and ^{13}C NMR spectra of PVATMS

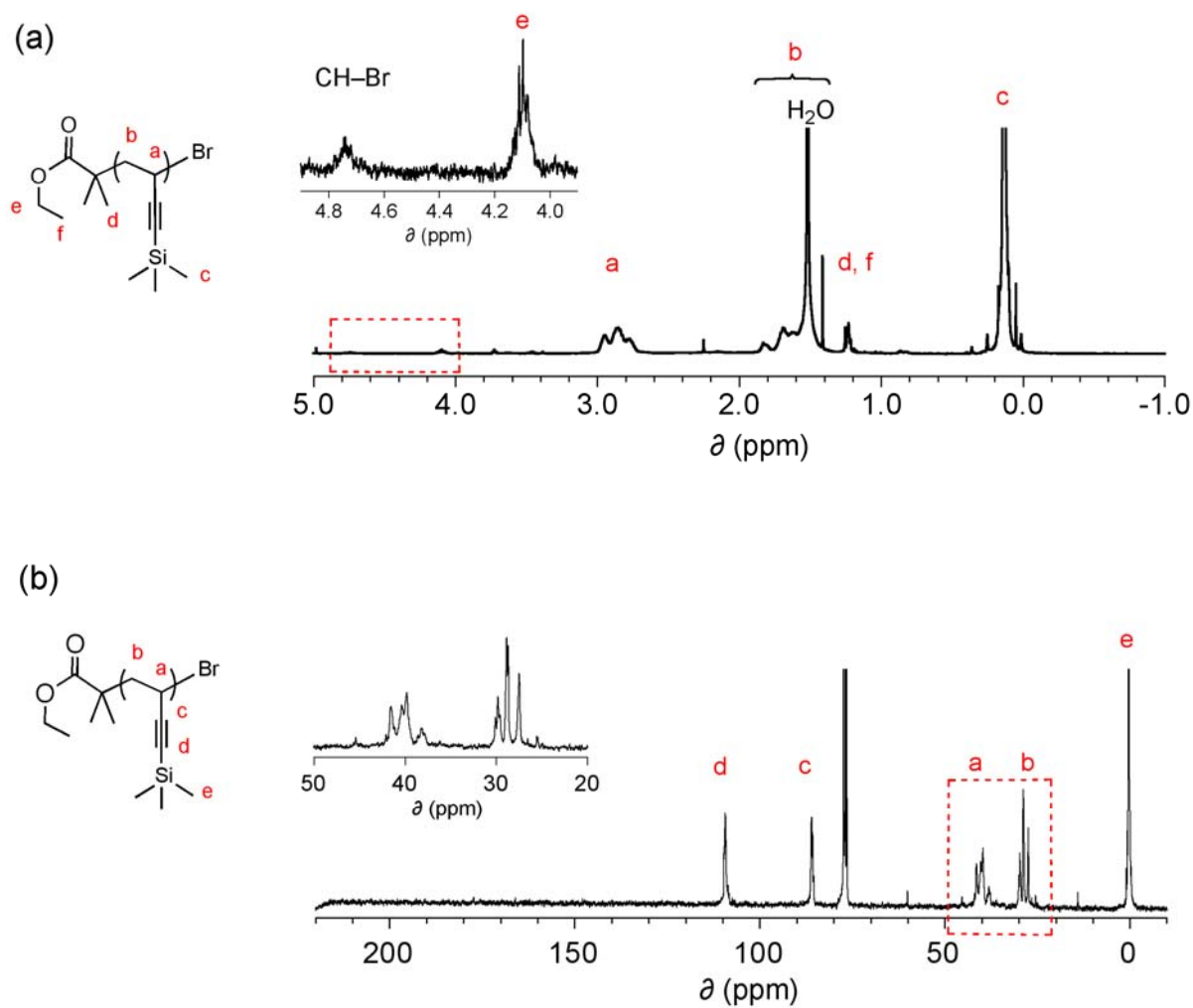


Figure S4. ^1H NMR (a) and ^{13}C NMR (b) spectra of PVATMS ($M_n=8,900$ by ARGET ATRP) in CDCl_3 at 303 K.

2-2. ^1H NMR spectra of PMMA-*b*-PVATMS and PMMA-*b*-PVAH block copolymers

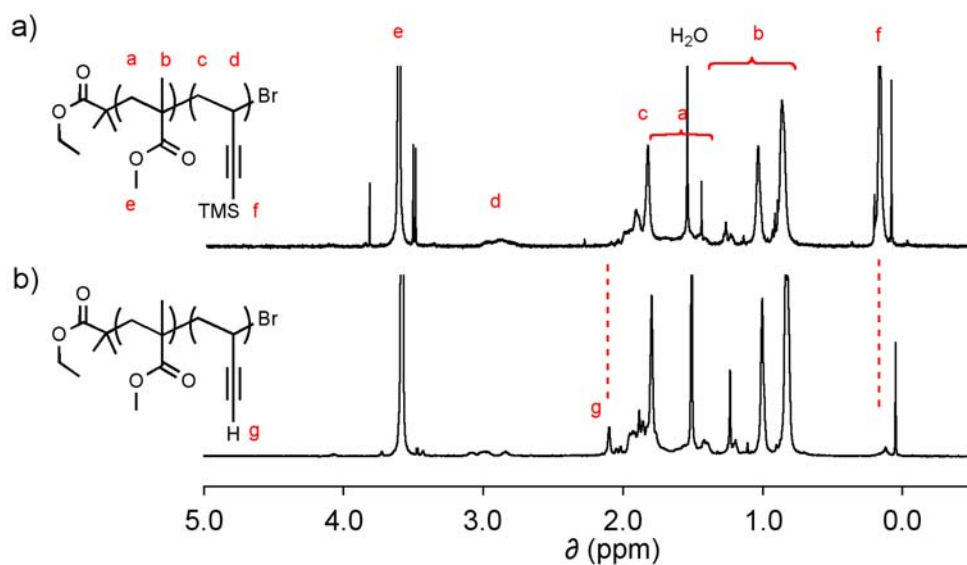


Figure S5. ^1H NMR spectra (500 MHz) of PMMA-*b*-PVATMS (a) and PMMA-*b*-PVAH (b) in CDCl_3 at 303K.

2-3. IR Spectra of PMMA-*b*-PVATMS and PMMA-*b*-PVA block copolymers

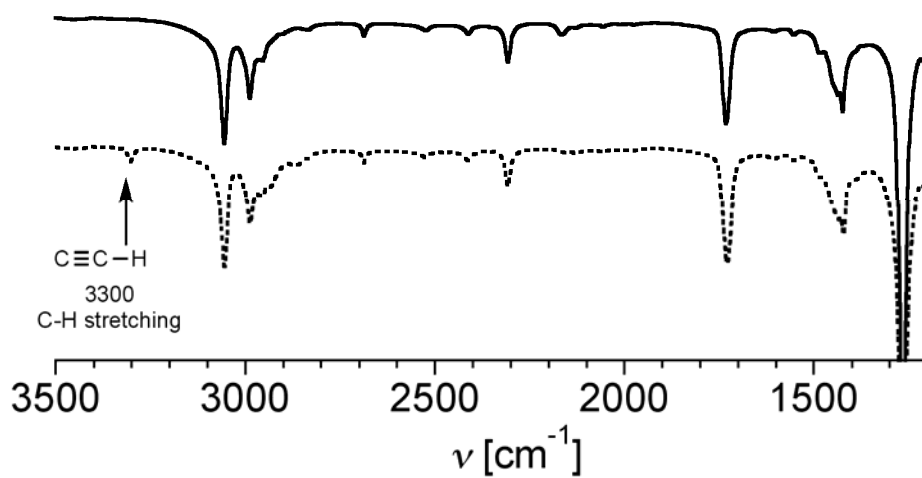


Figure S6. IR spectra of PMMA-*b*-PVATMS (solid line) and PMMA-*b*-PVAH (dashed line).