Supporting Information: Concurrent atom transfer radical polymerization and nitroxide radical coupling relay polymerization

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Experimental

Materials

Methyl acrylate (MA, 99%, SigmaAldrich) and styrene (St, 99+%, SigmaAldrich) were passed through a column filled with basic alumina prior to use. Copper wire (Cu(0), diameter = 0.25 mm, 99.99%, Alfa Aesar) was washed by diluted HCl/ethanol solution and then fresh ethanol prior to use. Methyl 2-bromopropionate (MBrP, 99%, Acros Organics), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 99+%, Acros Organics), copper(II) bromide ($CuBr_2$ 99+%, Acros Organics), 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (HTEMPO, 98%, Oakwood Chemical), pyridine (99+%, Alfa Aesar), α-bromoisobutyryl bromide (98%, SigmaAldrich), 2-bromopropionyl bromide (97%, SigmaAldrich), ascorbic

acid (99.9%, SigmaAldrich), tetrahydrofuran (THF, 99.9%, Fiscer Scientific), acetonitrile (MeCN, HPLC, Oakwood Chemical) anisole (99%, Alfa Aesar) were used as received.

Characterization

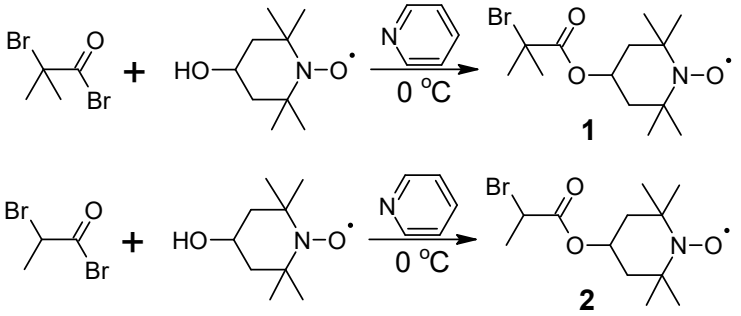
Nuclear magnetic resonance (NMR) was performed using a Bruker Avance AVIII-400 MHz NMR spectrometer or a Nanalysis 60-MHz Benchtop NMR spectrometer. The monomer conversion was determined by ^{1}H NMR using the Nanalysis 60-MHz Benchtop NMR spectrometer by comparing the signal of the vinyl group and the methyl group. All other NMR analysis was conducted using the Bruker Avance AVIII-400 MHz NMR spectrometer.

Fourier-transform infrared spectroscopy (FTIR) was performed using an Agilent Cary 630 attenuated total reflection (ATR) FTIR Spectrometer.

Mass spectroscopy (MS) analysis was conducted using a high performance liquid chromatography (HPLC) coupled to accurate mass electrospray ionization (ESI) mass spectrometry, specifically, the system consisted an Agilent 1260 Infinity II Quaternary liquid chromatography coupled to an Agilent 6230 Electrospray Time-of-Flight mass spectrometer. The samples were run in positive mode ionization with a capillary voltage of 4000 V. Drying gas (nitrogen) temperature was 325 °C delivered at 10 l/min and the fragmentor voltage was set to 150 V. No LC column was used for sample delivery, only flow through injection was utilized (direct injection from LC to mass spectrometer). Mobile phases used were A: 30% LCMS grade water with 0.1% formic acid and B: 70% LCMS grade acetonitrile with 0.1% formic acid with a flow rate of 0.4 ml/min.

Gel permeation chromatography (GPC) was employed to determine the molecular weights and the molecular weight distributions of the obtained polymers using poly(methyl methacrylate) (PMMA) standards for calibration, conducted with a Malvern Viscotek TDA

305-022 system equipped with two T6000M columns and a refractive index detector with THF as an eluent at 30 °C and at a flow rate of 1 mL/min.



Scheme S1: Synthesis of functional reagents **1** and **2**

Synthesis of functional reagent 1 and 2 To a 50 mL round bottomed flask with a magnetic stirrer, HTEMPO (2 g, 11.6 mmol, 1equivalent), pyridine (1.01 g, 12.8 mmol, 1.1 equivalent) and 5 mL THF were added. For functional reagent **1**, α-bromoisobutyryl bromide (2.94 g, 12.8 mmol, 1.1 equivalent) and 10 mL THF were placed in a 25 mL pressure equalizing addition funnel. The reaction mixture was stirred at 0 °C while the α-bromoisobutyryl bromide solution was added drop-wise in about half an hour, Scheme S1. The reaction mixture was stirred at 0 °C for about 3 h and warmed up to room temperature as the ice melted gradually. Then the reaction continued overnight. The solid precipitates were removed by filtering. The liquid phase was concentrated by evaporation of the solvent. Red colored solid was obtained as the crude product. The product was further purified by flash chromatography with hexane and ethyl acetate (6/1 volume ratio) as the mobile phase. After evaporation of the solvent and drying under vacuum, red colored crystals were obtained as the final product (yield: 3.08 g, 82.7%). FTIR (ATR, cm^{-1}): 2976, 2939, 1728, 1463, 1368, 1277, 1166, 1109, 963, 685. ^{1}H NMR (400 MHz, $CDCl_3$, chemically reduced with ascorbic acid), δ (ppm): 5.25 – 5.13 (m, 1H), 2.26 – 2.16 (m, 2H), 2.10 – 1.98 (m, 2H), 1.92 (s, 6H), 1.46 (s, 6H), 1.44 (s, 6H). HR-MS (ESI-TOF): calcd. for $C_{13}H_{23}BrNO_3$ $[M]^+$: 320.0856; found: 320.0858. For functional reagent **2**, 2-bromopropionyl bromide (2.76 g, 12.8 mmol, 1.1

equivalent) was used instead of α-bromoisobutyryl bromide. The product after purification by flash chromatography was red colored crystals (yield: 2.90 g, 81.3%). FTIR (ATR, cm^{-1}): 2972, 2931, 1729, 1462, 1442, 1334, 1220, 1161, 1070, 958, 688. ^{1}H NMR (400 MHz, $CDCl_3$, chemically reduced with ascorbic acid), δ (ppm): 5.25 – 5.13 (m, 1H), 4.34 (q, J = 6.9 Hz, 1H), 2.27 – 2.13 (m, 2H), 2.08 – 1.95 (m, 2H), 1.82 (d, J = 6.9 Hz, 3H), 1.45 (s, 6H), 1.42 (s, 6H). MS (ESI-TOF): calcd. for $C_{12}H_{21}BrNO_3$ $[M]^+$: 306.0699; found: 306.0744.

General procedure for relay polymerization A piece of Cu(0) wire (diameter = 0.25 mm, length = 24 cm) was placed in a 25 mL Schlenk flask with a magnetic stirrer. The flask was sealed and then degassed by letting N_2 passing through for 1 h. A solution of 2 mL MA (1.90 g, 200 equivalent), 12.3 μL MBrP (18.4 mg, 1 equivalent), 2.46 mg $CuBr_2$ (0.1 equivalent), 6.9 μL PMDETA (5.7 mg, 0.3 equivalent) and 1 mL MeCN was placed in a 10 mL round bottomed flask, sealed with a rubber septum, and bubbled with N_2 for 1 h. Another solution of 8 mL MA (7.60 g, 800 equivalent), 0.177 g reagent **1** (5 equivalent), 0.138 mL PMEDTA (0.115 g, 6 equivalent) and 4 mL MeCN was placed in a 25 mL round bottomed flask, sealed with a rubber septum, and bubbled with N_2 for 1 h. The first solution was added to the Schlenk flask and stirred at 70 °C and the polymerization started. The second solution was taken into a 25 mL Hamilton gastight syringe and was added to the Schlenk flask in 4 h at a constant addition rate, i.e., 3.0 mL/h. Note, the second solution was scaled up by a factor of 1.1 during preparation to compensate the retention in the syringe. The amount listed above was the quantity that was finally added to the Schlenk flask. The reaction was protected by a mild N_2 air flow. Samples were taken every 1 h. The product was washed with water and ethyl ether to get a light blue colored viscous polymer. The polymer was dissolved in acetone and filtered with Al_2O_3. After evaporating of the solvent, the polymer was dried under vacuum to get a colorless product.

Procedure for insertion polymerization PMA synthesized using the method described in the previous section (1.00 g) was dissolved in St (2.00 g), and then the solution was added

to a 10 mL Schlenk flask with a magnetic stirrer. The Schlenk flask was sealed and degassed by bubbling with N_2 for 1 h. The reaction mixture was stirred at 130 °C for 3 h. The product was precipitated in ethyl ether and dried under vacuum resulting in white solid powders.

NMR and FTIR spectra

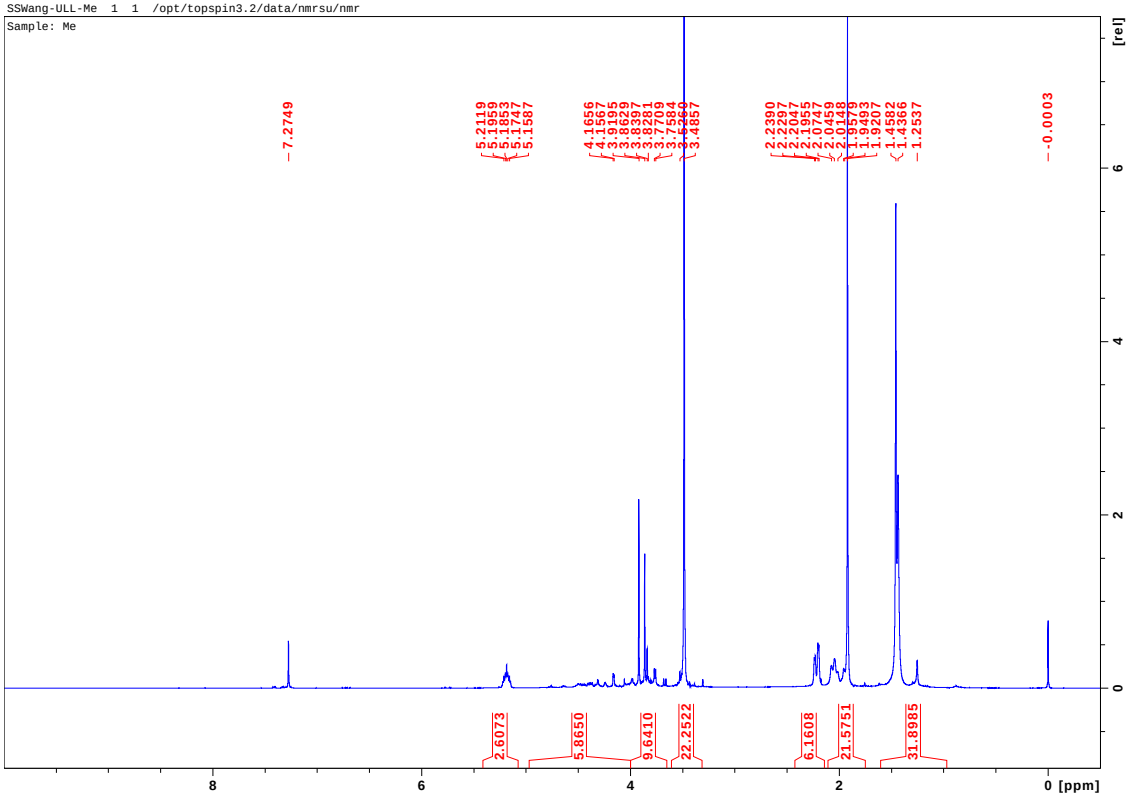


Figure S1: ^{1}H NMR spectra of functional reagents **1**.

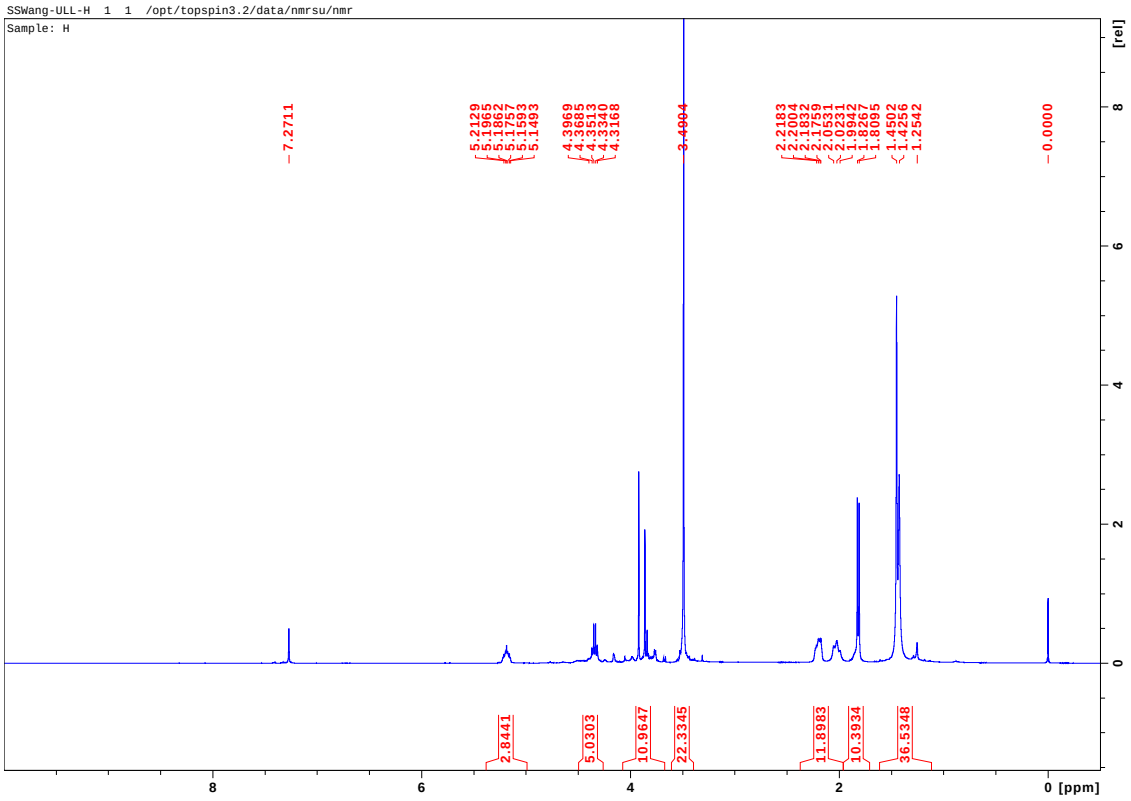


Figure S2: ^{1}H NMR spectra of functional reagents **2**.

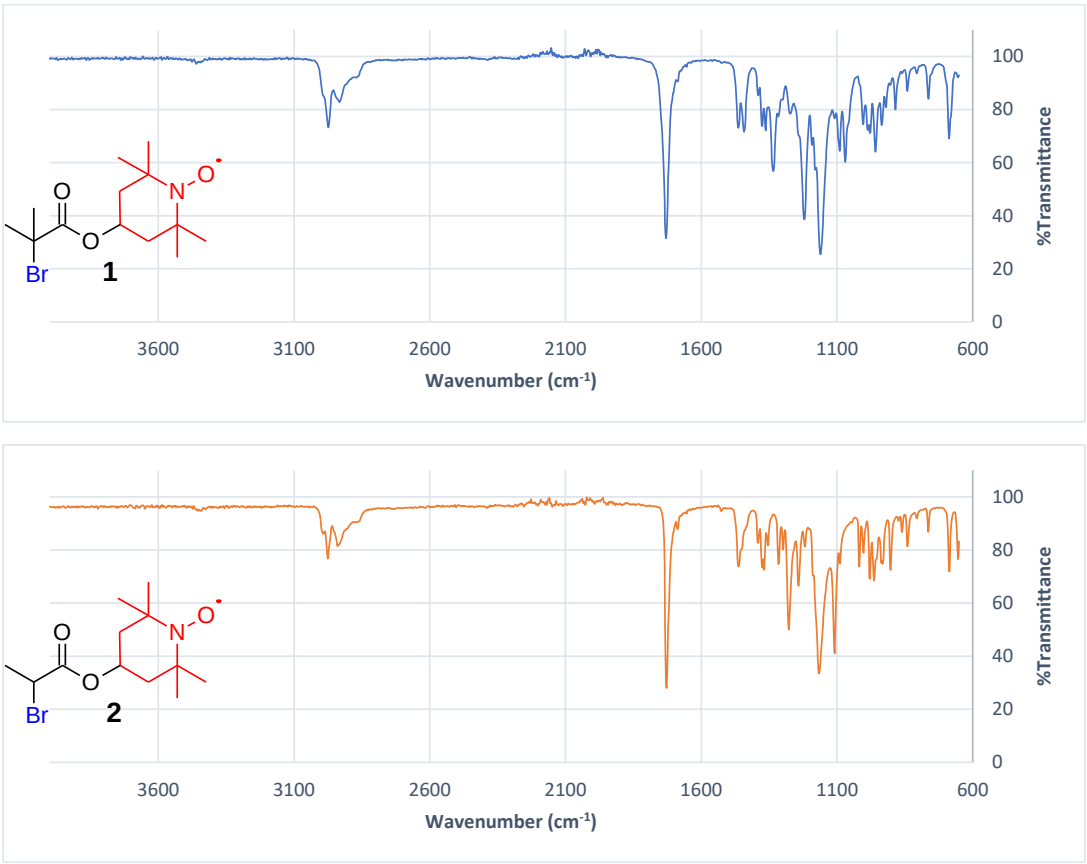


Figure S3: FTIR spectra of functional reagents **1** and **2**.

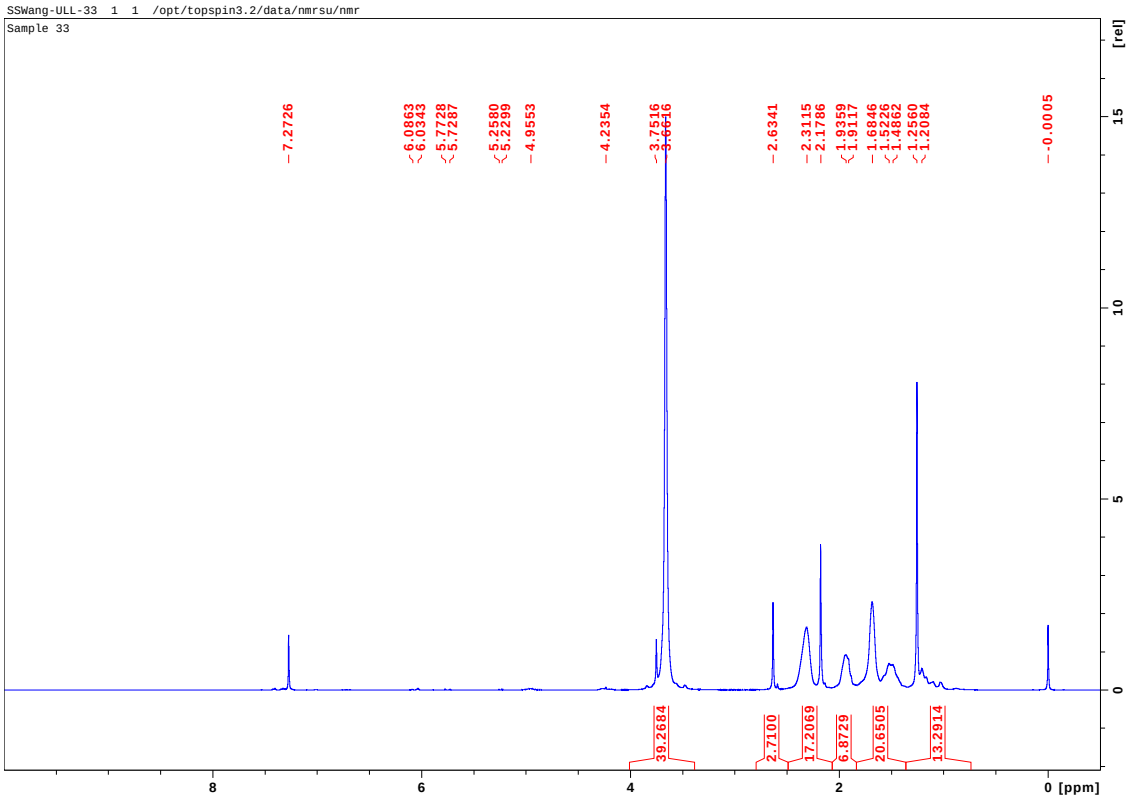


Figure S4: ^{1}H NMR spectra of poly(methyl acrylate) synthesized by relay polymerization.

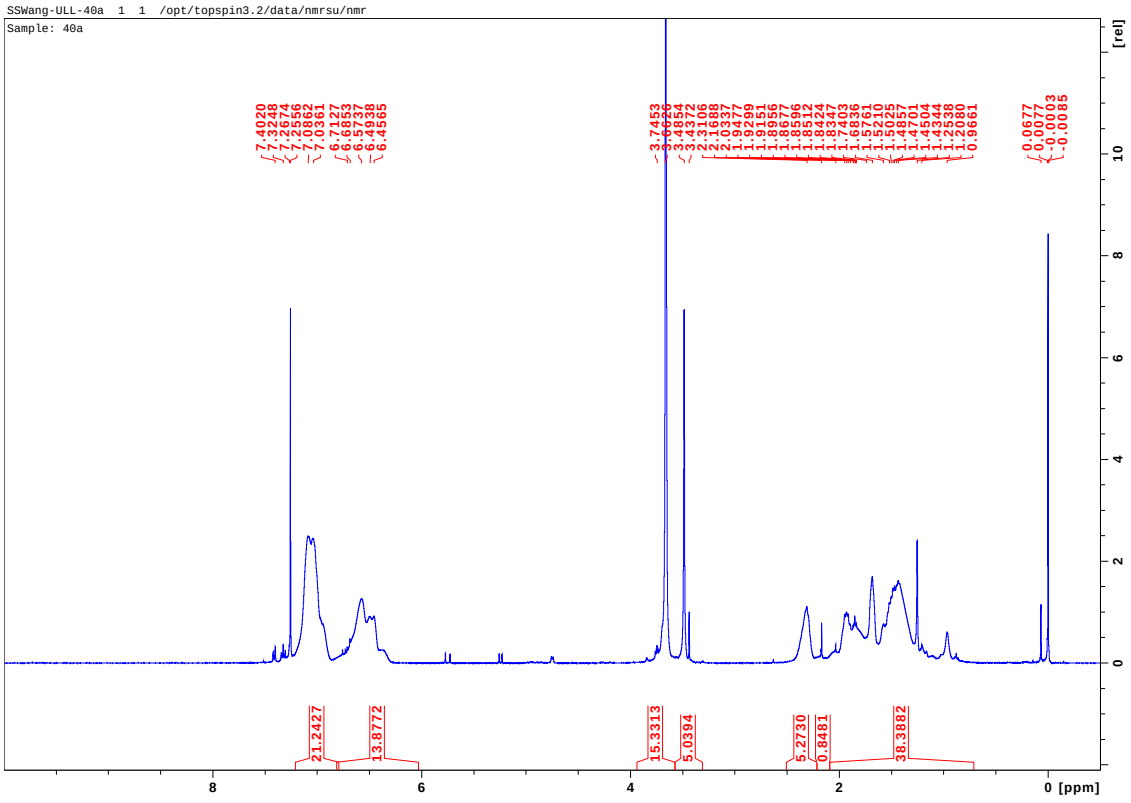


Figure S5: ^{1}H NMR spectra of alternating block copolymer of methyl acrylate and styrene synthesized by relay polymerization and nitroxide mediated polymerization.