

Macromolecules

Macromolecules, 1998, 31(18), 6380-6382, DOI:[10.1021/ma980216+](https://doi.org/10.1021/ma980216+)

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Detailed Experimental procedure for Supplemental Material

Chemicals for all syntheses were obtained from Aldrich and used without further purification. Polymerizations were carried out with styrene from Aldrich which was freshly distilled prior to use. GPC data was collected on a Jordi-Gel 500 Å column with THF as the mobile phase. Detection was accomplished by a Shimadzu UV detector operating at 254 nm. Analysis was performed using Sechrom-GPC software in combination with Grams 386 for chromatography. ^1H and ^{13}C NMR spectroscopy were carried out at 300 MHz and 75 MHz respectively using a Varian NMR spectrometer.

General Procedure for Preparation of Tertiary Amines. A dry 100-mL round-bottomed flask was charged with 1.0 g (7.1 mmol) 2,2,6,6-tetramethylpiperdine, 1 equivalent of desired halide, and 1 g K_2CO_3 in 50 mL of dry acetone. The mixture was heated to reflux for 12 h. The flask was cooled and the contents filtered. The solvent present in the filtrate was removed under reduced pressure. The crude product was purified by column chromatography over silica gel. The purified products were then characterized by ^1H -NMR spectroscopy: **2a**, ^1H NMR (CDCl_3) δ 5.84 (m, 1H), 5.11 (dq, 1H), 4.89 (dq, 1H), 3.10, (m, 2H), 1.53 (m, 2H), 1.41 (m, 4H), 0.99 (s, 12H); **2b**, ^1H NMR (CDCl_3): δ 5.14 (m, 1H), 3.04 (m, 2H), 1.58 (d, 6H), 1.51 (m, 2H), 1.40 (m, 4H), 1.0 (s, 12H); **2c**, ^1H NMR (acetone- d_6): δ 7.18-7.43(m, 5H), 6.55 (m, 1H), 6.25 (m, 1H), 3.30 (dd, 2H), 1.57 (m, 2H), 1.45 (m, 4H), 1.05 (s, 12H); and **2d**, ^1H NMR (acetone- d_6): δ 7.48-7.06 (m, 5H), 3.83 (s, 2H), 1.61 (m, 2H), 1.52 (m, 4H), 1.0 (s, 12H).

General Procedure for Oxidation and Subsequent Meisenheimer Rearrangement. The allyl 2,2,6,6-tetramethylpiperdine (1 g) and chloroform (30 mL) were placed in a 100-mL round-bottomed flask equipped with an addition funnel and magnetic stirring bar. The solution was cooled to 0 °C in an ice-water bath. A solution comprised of *m*-CPBA (67%, 1 eq) and chloroform (30 mL) was added over 20 min. The flask was removed from the ice bath and allowed to stir at room temperature for 12 h. The solution was then washed with 2 30 mL portions of aqueous K_2CO_3 . The chloroform layer was dried over MgSO_4 and solvent was

removed under reduced pressure. The crude product was purified by column chromatography over silica gel with hexanes/ethyl acetate 6:1 as eluent. Characterization was accomplished using ^1H - and ^{13}C -NMR spectroscopy. New compounds were also analyzed by high resolution mass spectroscopy (HRMS): **4a**; ^1H NMR (acetone- d_6) δ 5.91 (m, 1H), 5.29 (dq, 1H), 5.12 (m, 1H), 4.32, (dt, 2H), 1.60 (m, 1H), 1.48 (m, 4H), 1.37 (m, 1H), 1.16 (d, 12H); ^{13}C NMR (acetone- d_6) δ 129.9, 110.6, 73.7, 54.9, 35.0, 28.0, 15.0, 12.4; HRMS exact mass calculated for $\text{C}_{12}\text{H}_{23}\text{NO}$ 197.1781, found 197.1779. **4b**; ^1H NMR (acetone- d_6) δ 5.31 (m, 1H), 3.24 (d, 2H), 1.67 (d, 6H), 1.55 (m, 1H), 1.42 (m, 4H), 1.30 (m, 1H), 1.12 (d, 12H); ^{13}C NMR (CDCl_3) δ 131.5, 115.9, 69.8, 55.1, 35.2, 28.6, 21.4, 15.7, 13.78, 12.7; HRMS exact mass calculated for $\text{C}_{14}\text{H}_{27}\text{NO}$ 225.2094, found 225.2088. **4b'**; (acetone- d_6) δ 6.12(dd, 1H), 4.94 (ddd, 2H), 1.72-1.21 (m, 12H), 1.08 (d, 12H). **4c**; ^1H NMR (CDCl_3) δ 7.47-7.22 (m, 5H), 6.58 (d, 1H), 6.28 (m, 1H), 4.32 (d, 2H), 1.25-1.6 (m, 6H), 1.15 (d, 12H); ^{13}C NMR (acetone- d_6) δ 126.8, 124.1, 123.0, 121.9, 121.1, 73.5, 55.0, 35.1, 28.2, 15.1, 12.4; HRMS exact mass calculated for $\text{C}_{18}\text{H}_{27}\text{NO}$ 273.2093, found 273.2093; **4d**; ^1H NMR (acetone- d_6) δ 7.34 (m, 5H), 4.80 (s, 2H), 1.59 (m, 1H), 1.47 (m, 4H), 1.30 (m, 1H), 1.17 (d, 12H); ^{13}C NMR (acetone- d_6): δ 126.8, 124.1, 123.0, 121.9, 121.1, 73.5, 55.0, 35.1, 28.2, 15.1, 12.4; HRMS exact mass calculated for $\text{C}_{16}\text{H}_{25}\text{NO}$ 247.1937, found 247.1936.

Procedure for Polymerizations. The unimolecular initiator of interest (5 mg) was added to a argon-filled dry 25-mL flask equipped with a reflux condenser, stirring bar, and rubber septum. Styrene (10 mL, distilled prior to use) was added by syringe. The solution was immersed in an oil bath which had been preheated to 125 °C. The solution was stirred at 125 °C for 72 h. Aliquots were taken at various intervals and analyzed by GPC and ^1H -NMR spectroscopy. The experiment in which the M_n was compared to the percent conversion of monomer was carried out in like manner using ^1H NMR spectroscopy with *p*-xylene as an internal standard.