Electronic Supporting Information.

NMP of chloromethylsytrene with minimized PDI: the role of the initiator/nitroxide system and the meta-isomer.

Elijah Bultz[†] *and Timothy P. Bender*[†,‡,§,*]

† Department of Chemical Engineering and Applied Chemistry University of Toronto, 200 College St., Toronto, Ontario, M5S 3E5

‡ Department of Chemistry, University of Toronto, 80 St. George St., Toronto, Ontario, Canada, M5S 3H6

§ Department of Materials Science and Engineering, The University of Toronto, 180 College St., Toronto, Ontario, Canada, M5S 3H6

* - to whom correspondences should be addressed. Email: tim.bender@utoronto.ca

Experimental.

Equipment.

NMR spectra were acquired on a Varian Mercury 400 with a quadnuclear - ^{1}H, ^{19}F, ^{13}C, ^{29}Si – 5 mm Nalorac probe. Data was analyzed on Spinworks 3.0 software (University of Manitoba). GPC analysis was run on a system comprising a Waters 2696 Separations Module, two Stryagel® 5μm, HR4E 7.8 x 300 mm columns in series, a Waters 410 refractometer for refractive index analysis and a Waters 2998 photodiode array detector for UV-Vis analysis. The system had a mobile phase of HPLC grade THF (not inhibited) and ran at a flow rate of 1.2 mL/min corresponding to a pressure of 800 psi. HPLCs were run using a Waters 2696 Separations Module with a SunFire™ C18 3.5 μm 3.0 x 150mm column with HPLC grade acetonitrile run at 0.60 mL/min with a Waters 410 refractometer for refractive index analysis and a Waters 2998 photodiode array detector for UV-Vis analysis. Gas chromatography was run on a Perkin Elmer Autosystem with a Rtx®-35 (Fused Silica) column of dimension 15m x 0.32mm x 1.00 μm. Helium was used as the mobile phase and a flame ionization detector was used for detection.

Materials.

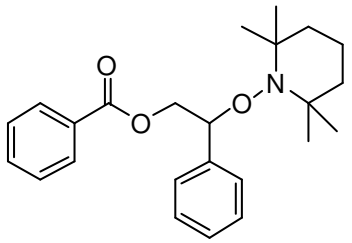
Where appropriate, anhydrous solvents are obtained from an Innovative Technology Pure Solv MD system. 4-chlromethylstyrene (4CMS) and chloromethylstyrene technical grade (tgCMS, mixture of isomers) were purchased from Sigma-Aldrich and was vacuum distilled immediately before use. 1,2,4-trichlorobenzene, TEMPO and benzoyl peroxide (Luperox® A98) were purchased from Sigma-Aldrich and used as received. 2-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl benzoate (BST) was prepared from the method described below. Styrene was purchased from Sigma-Aldrich (Reagent Plus grade) and was washed through an inhibitor remover column and then a 0.25 μm PTFE filter immediately before use.

Sampling Methods.

For GC analysis a sample of the polymerization mixture was taken and two drops placed into approximate 15 mL of methanol. If a precipitate was formed the sample was sonicated in a standard bench-top bath for a period of between 5 and 15 minutes until such time that the precipitate was sufficiently broken up. The sample was then filtered through a 0.25 μm PTFE syringe filter prior to injection into the GC. Conversion was calculated by considering the change in the ratio between the monomer(s) and the internal standard as compared to a time = 0 sample.

For GPC analysis a sample of the polymerization mixture was taken and two drops were placed into approximately 15 mL of THF (not inhibited). If a precipitate formed, the sample was sonicated in a standard bench-top bath for a period of between 5 and 15 minutes until such time that the precipitate had dissolved. The sample was then filtered through a 0.25 μm PTFE syringe filter prior to injection into the GPC. All molecular weights (M_n, M_w) and molecular weight distributions (PDI) are stated relative to a calibration performed with a series of styrene standards.

BST (2-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl benzoate) (**BST**) preparation.[1]



To a solution of TEMPO (1.71 g, 1.1 x 10^{-2} mol) in styrene (7.5 mL) under a blanket of argon was added BPO (4.0 g, 1.7 x 10^{-2} mol) at room temperature. Initially, a significant amount of the BPO does not dissolve but slowly goes into solution as the reaction proceeds. ***CAUTION: exothermic.*** The reaction temperature was monitored and after approximately 7 minutes the temperature began to rise. As the temperature approached 35 °C, the reaction vessel was cooled with an ice bath until the reaction temperature fell to 30 °C. The ice bath was removed and the reaction temperature was allowed to rise back to 35 °C at which point it was cooled again to 30 °C. This cycle was repeated as long as there was

an observed exotherm. When an exotherm was no longer observed the reaction mixture was allowed to cool to room temperature, causing benzoic acid to crystallize out, and then left at that temperature overnight. The total reaction time was approximately 24 hours, although for the most part the reaction was complete after about 2 hours. The reaction mixture was taken up into methylene chloride (50 mL). The solution was washed with dilute (approximately 0.05 M) cold NaOH, followed by a wash with dilute (approximately 0.05 M) cold HCI and finally washed with brine. The methylene chloride solution was dried over sodium sulfate and evaporated to dryness. The reaction mixture was passed through a silica gel column with CH_2Cl_2 as the eluant. Finally the material was recrystallized from isopropyl alcohol to yield BST (1.93g, 41% yield). Purity was confirmed by HPLC analysis and ^{1}H NMR in $CDCl_3$.

Polymerization method

All polymerizations were carried out in European style pear shaped 3-necked flasks fitted with a magnetic stir bar, water jacketed condenser, an argon inlet and a septum. Nitrogen sparge was introduced via a stainless steel needle through the septum. During sparge, the vessel was stirred and the tip of the needle was below the liquid level and vigourous bubbling could be seen.

*Polymerization of 4-chloromethylstyrene (4CMS) – Entry **1***: 10.00 g of vacuum distilled 4-chloromethylstyrene (4CMS, 6.55 x 10^{-2} mol), 0.104 g of benzoyl peroxide (BPO, 4.29 x 10^{-4} mol), 0.135 g of 2,2,6,6-tetramethyl-1-piperidynyl-*N*-oxy (TEMPO, 8.64 x 10^{-4} mol) and approximately 0.5 mL of anhydrous 1,2,4-trichlorobenzene were added in that order to a round bottom flask and sparged with nitrogen for 10 minutes. An initial time = 0 sample was taken for GC analysis. The reaction was then heated to a constant internal temperature of 125 ºC under a constant pressure blanket of argon. Samples were taken at regular intervals for both GC and GPC analysis. Sampling was stopped after the reaction mixture became too viscous to stir. Polymerization mixtures were precipitated into a large amount of vigorously stirred methanol for isolation of the final polymers. After filtration each polymer powder was subjected to at least 24 hours of soxhlet extraction with methanol.

Polymerization of 4-chloromethylstyrene (4CMS) – *Entry **2***: As in the procedure of entry **1** except 0.198 g (5.20 x 10^{-4} mol) of BST was used to initiate the polymerization.

Polymerization of 4-chloromethylstyrene (4CMS) – *Entry **3***: As in the procedure of entry **1** except 0.198 g (5.20 x 10^{-4} mol) of BST and 0.016 g (1.03 x 10^{-4} mol) of TEMPO was used to initiate the polymerization and the polymerization was run at 115 ºC.

Polymerization of 4-chloromethylstyrene (4CMS) – *Entry **4***: As in the procedure of entry **1** except 0.198 g (5.20 x 10^{-4} mol) of BST and 0.016 g (1.03 x 10^{-4} mol) of TEMPO was used to initiate the polymerization.

Polymerization of 4-chloromethylstyrene (4CMS) – *Entry **5***: As in the procedure of entry **1** except 0.062 g (2.60 x 10^{-4} mol) of BPO and 0.097 g (6.21 x 10^{-4} mol) of TEMPO was used to initiate the polymerization.

Polymerization of 4-chloromethylstyrene (4CMS) – *Entry **6***: As in the procedure of entry **1** except 0.065 g (2.60 x 10^{-4} mol) of 2,2'-azobis(2,4-dimethyl valeronitrile) and 0.048 g (3.10 x 10^{-4} mol) of TEMPO was used to initiate the polymerization.

*Polymerization of chloromethylstyrene (tgCMS) – Entry **7***: As in the procedure of entry **4** except tgCMS was used in place of 4CMS.

Copolymerization of 4-chloromethylstyrene (4CMS) and *chloromethylstyrene (tgCMS) – Entry **8***: As in the procedure of entry **4** except a 1:1 mass ratio of tgCMS and 4CMS was used.

Copolymerization of 4-chloromethylstyrene (4CMS) and *chloromethylstyrene (tgCMS) – Entry **9***: As in the procedure of entry **4** except a 1:3 mass ratio of tgCMS and 4CMS was used.

Chain extension polymerization method.

pCMS obtained from run **7** (250 mg) was added to 5mL of styrene and solution was sparged for at least 10 minutes, placed under a constant pressure of argon and then placed in an oil bath which was preheated to 125 °C.

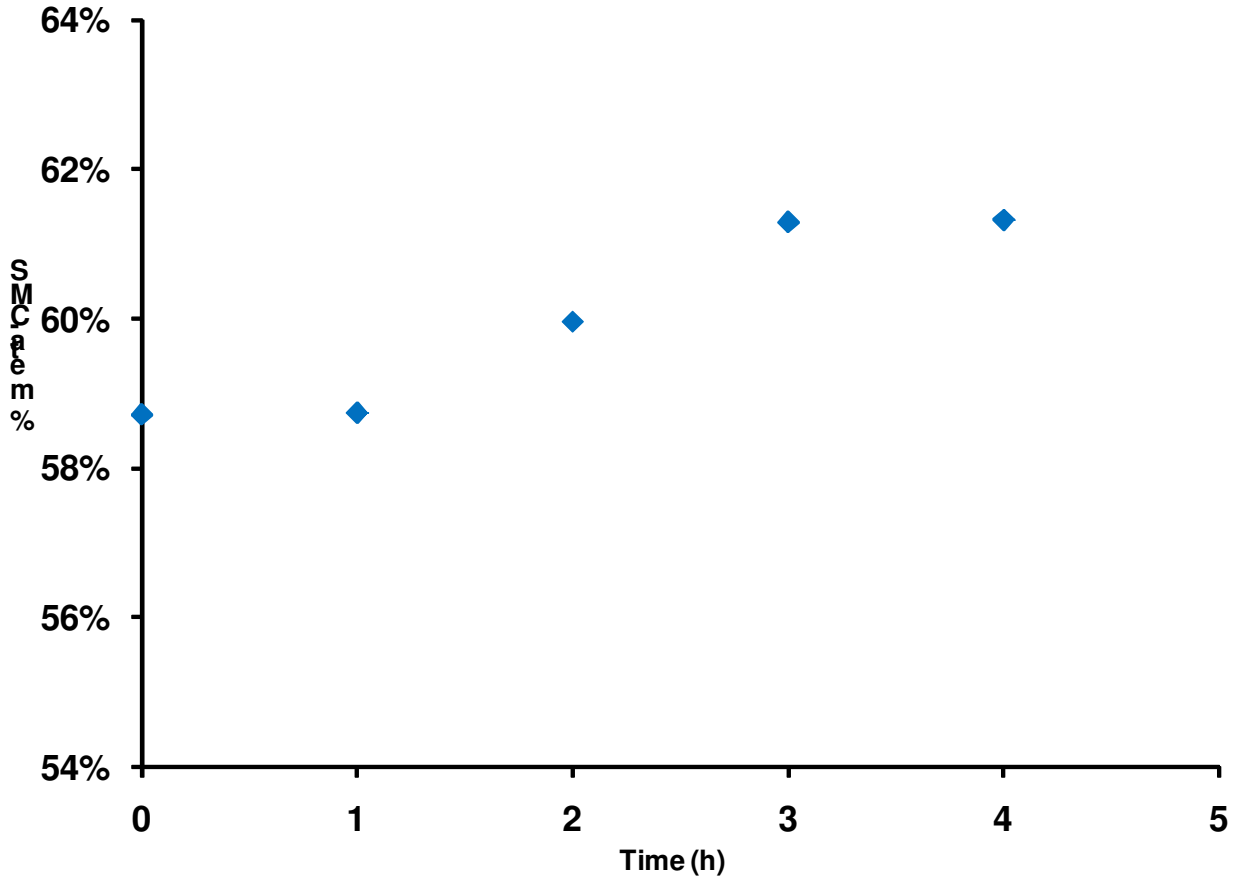


Figure S1. Percentage of meta-CMS monomer present in polymerization process during run **7**.

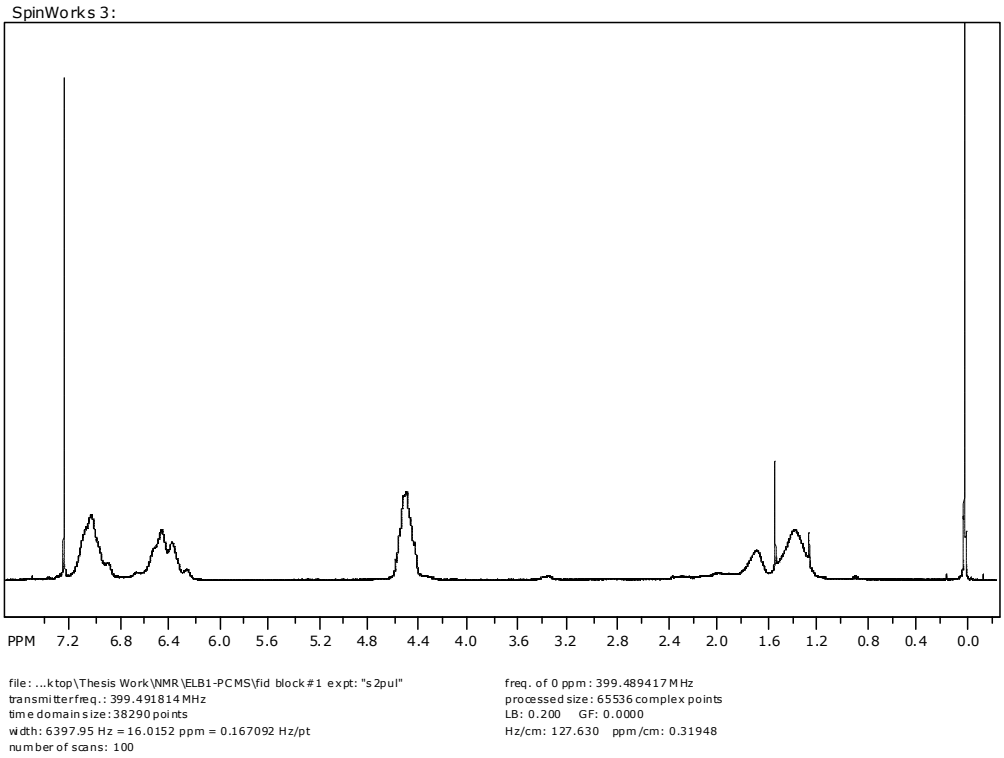


Figure S2. ^{1}H NMR spectrum of pCMS from 4CMS (run **4**).

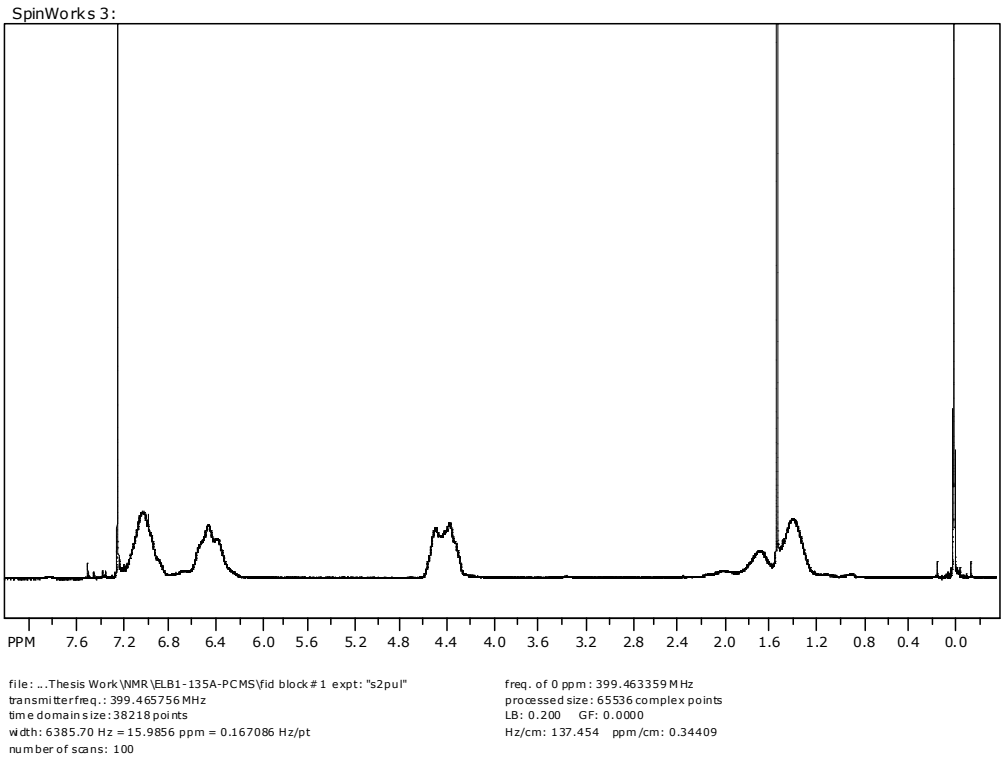


Figure S3. ^{1}H NMR spectrum of pCMS from tgCMS (run **7**).

References.

[1] The procedure for the synthesis of BST was kindly provided to our group by Prof Michael Georges (The University of Toronto at Mississauga) in a private communication.