Supporting Information for

Synthesis of Polythiourethane-Based Macro Chain Transfer Agents and Block Copolymers *via* Controlled Multimode Polymerization.

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Experimental Section

Materials. α-(Methylaminomethyl)benzyl alcohol (Aldrich Chemical, 99%), Thiophosgene (Tokyo Kasei Kogyo, >95%), diethylammonium *N*,*N*-diethyldithiocarbamate (Wako Pure Chemical Industries, Ltd., 99%), carbon disulfide (Wako Pure Chemical Industries, Ltd., 98%), 2,2'-azobis(isobutyronitrile) (Wako Pure Chemical Industries, Ltd., 98%) and Pyrrole (Aldrich Chemical, 98%) were used as received. Tetrahydrofuran (Wako Pure Chemical Industries, Ltd., >99%) was distilled from sodium wire, and trifluoromethanesulfonic acid (Aldrich Chemical, >99%) was distilled before use. Methyl trifluoromethanesulfonate (Aldrich Chemical, >99%) and Chlororbenzene (Wako Pure Chemical Industries, Ltd., 99%) was distilled over calcium hydride. A DMSO solution of sodium 1-

pyrrolecarbodithioate (1.03 M) was synthesized according to the previously reported method.[1] Styrene (St) (Wako Pure Chemical Industries, Ltd., >99%), methyl methacrylate (MMA) (Wako Pure Chemical Industries, Ltd., 99%), methyl acrylate (MA) (Wako Pure Chemical Industries, Ltd., 98%), and *N*,*N*-dimethyl acrylamide (DMAm) (Wako Pure Chemical Industries, Ltd., 98%) were purified by distillation under reduced pressure. Other reagents were used as received.

Instrumentation. ^{1}H (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded on a Varian NMR spectrometer model Unity INOVA, using tetramethylsilane (TMS) as an internal standard in $CDCl_3$. IR spectra were obtained with a JASCO FT/IR-460 spectrometer. Number-average molecular weight (M_n) and polydispersity (M_w/M_n) were estimated by size-exclusion chromatography (SEC) on a Tosoh HLC-8220 system equipped with three consecutive polystyrene gel columns [TSK-gels (bead size, exclusion limited molecular weight); super-AW4000 (6 μm, > 4 $\times 10^5$), super-AW3000 (4 μm, > 6 $\times 10^4$), and super-AW2500 (4 μm, > 2 $\times 10^3$)] and refractive index and ultraviolet detectors at 40 °C. The system was operated at a flow rate of 0.5 mL/min, using *N*,*N*-dimethylformamide (DMF) solution (50 mM lithium bromide) as an eluent. Polystyrene standards were employed for calibration.

Synthesis of 3-methyl-5-phenyl-oxazolidine-2-thione (MPOT). A solution of thiophosgene (7.6 mL, 100 mmol) in THF (1000 mL) was added dropwise to a solution of α-(methylaminomethyl)benzyl alcohol (15.1 g, 100 mmol) and triethylamine (28 mL, 200 mmol) at 60 °C and the mixture was stirred for 12 h at the same temperature. Precipitate salts were removed form the resulting mixture and the residual solution was concentrated under reduced pressure. The residual solid was purified by recrystallization from ethyl acetate. Yield = 69%, Mp = 137.3-137.8 °C. ^{1}H NMR ($CDCl_3$): δ = 3.26 (s, 3H, >N-C*H*$_3$), 3.70-3.75 (dd, *J* = 4.8 and 8.4 Hz, 1H, -(CH_3)-N-C*H*$_2$-CH<), 4.17 (t, *J* = 10.0 Hz, 1H, -(CH_3)-N-C*H*$_2$-CH<), 5.68 (t, *J* = 8.0 Hz, 1H, >C*H*-), 7.32-7.49 (m, 5H, -C_6H_5) ppm. ^{13}C NMR ($CDCl_3$): δ = 34.80 (>N-*C*H_3), 57.03 (>CH-*C*H_2-), 78.56 (>*C*H-), 125.58, 128.62, 128.84, 137.09 (-*C*$_6H_5$), 187.03 (-O-*C*(=S)-N(CH_3)-) ppm. IR (KBr): 1539 (-O*C*(=S)N(CH_3)-), 1327, 1308, 1183, 911, 770, 707 cm^{-1}. Anal. Calcd for $C_{10}H_{11}NOS$: C, 62.15; H, 5.74; N, 7.25. Found C, 62.14; H, 5.76; N, 7.32.

Synthesis of CTA1. A solution of MPOT (0.96 g, 5.00 mmol) in CH_2Cl_2 (10 mL) was placed in test tube under nitrogen atmosphere. The tube was sealed after the addition TfOMe (0.90 mL, 7.50 mmol), and the mixture was stirred for 2 h at 30 °C. After that, a solution (1.03 M) of sodium 1-pyrrolecarbodithioate (1.00 mL, 15.0 mmol) in DMSO (10 mL) was added to the mixture, and the mixture was stirred for 24 h at 0 °C. The solution was washed with water and an aqueous sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent of filtrate was evaporated under reduced pressure, and the residue was purified by slica gel chromatography eluted with a mixed solvent of ethyl acetate and *n*-hexane (1/12 = v/v), followed by recrystallization from a mixed solvent of ethyl acetate and *n*-hexane to obtain model CTA1 as a yellow solid. Yield = 62 %. Mp = 111.8-112.2 °C. ^{1}H NMR ($CDCl_3$): δ = 2.29 (s, 3H, -S-C*H*$_3$), 3.00 (s, 3H, >N-C*H*$_3$), 3.97-4.16 (m, 2H, -(CH_3)N-C*H*$_2$-CH<), 5.49 (t, *J* = 8.4 Hz, 1H, >C*H*-), 6.32 (t, J = 2.4 Hz, 2H, >N-C*H*=C*H*-), 7.63-7.43 (m, 5H, -C_6H_5), 7.68-7.69 (m, 2H, >N-C*H*=C*H*-) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.69 (*C*H_3-SC(=O)-N(CH_3)-), 37.20 (CH_3-S(=O)-N(*C*H_3)-) 54.50 (-CH_2-*C*H<), 56.09 (-*C*H_2-CH<), 116.90 (>N-CH=*C*H-), 123.33 (>N-*C*H=CH-), 131.11, 131.31, 130.90, 139.45 (-C_6H_5), 172.18 (CH_3-S*C*(=O)-N(CH_3)-), 200.24 (-S*C*(=S)-N<) ppm. IR (KBr): 1652, 1461, 1307, 1255, 1107, 1095, 1048, 1030, 812 cm^{-1}. Anal. Calcd for $C_{16}H_{18}NOS_3$: C, 54.82; H, 5.18; N, 7.99. Found C, 54.82; H, 5.16; N, 8.05.

Synthesis of CTA2. The synthesis of model CTA2 was similar to that of model CTA1, except that a acetonitrile solution of diethylammonium *N*,*N*-diethyldithiocarbamate was added instead of a DMF solution of sodium 1-pyrrolecarbodithioate. Yield = 73 %. Yellow oil. ^{1}H NMR ($CDCl_3$): δ = 1.26 (t, *J* = 6.8 Hz, 6H, -N(CH_2C*H*$_3$)$_2$), 2.23 (s, 3H, -S-CH_3), 3.05 (s, 3H, >N-CH_3), 3.53-4.46 (m, 6H, -N(CH_3)-C*H*$_2$-CH< and -N(C*H*$_2$$CH_3$)$_2$), 5.50 (m, 1H, >C*H*-), 7.10-7.69 (m, 5H, -C_6*H*$_5$) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.84 (-N(CH_2*C*H_3)$_2$), 11.85 (-S-*C*H_3), 33.57 (>N-*C*H_3), 46.04 (>*C*H-), 48.91 (-N(*C*$H_2$$CH_3$)$_2$), 52.70 (-*C*$H_2$-CH<), 127.14, 127.81, 127.93, 131.11 (-*C*$_6H_5$), 168.34 (-S-*C*(=O)-N(CH_3)-), 192.54 (-S-*C*(=S)-N(CH_3)-) ppm. HRMS calcd for $C_{16}H_{24}N_2OS_3$: 356.11; found (M^+): 356.11.

Synthesis of macroCTA1 and maroCTA2. Dry CH_2Cl_2 (3 mL) and TfOMe (23 μL, 2.00×10^{-4}mmol) were introduced to a polymerization tube containing MPOT (0.39 g, 2.00 mmol) subsequently. The resulting mixture was stirred at 30 °C for 17 h under nitrogen atmosphere. After being quenched with 2.5 mL of a acetonitrile solution (10 mL) of diethylammonium *N*,*N*-diethyldithiocarbamate (2.30 g, 10.3 mmol) or 1.0 mL of a DMSO solution (1.03 M) of sodium 1-pyrrolecarbodithioate at 0 °C, the resulting mixture was stirred for 24 h, and was poured into methanol (200 mL) to precipitate a polymer. The polymer was collected by filtration with suction and dried under vacuum.

MacroCTA1: M_n = 2200, M_w/M_n = 1.10. Yield = 98%. ^{1}H NMR ($CDCl_3$): δ = 2.07-2.39 (initiating end, S-C*H*$_3$), 2.56-3.04 (3H, >N-C*H*$_3$), 3.12-4.24 (2H, -(CH_3)-N-C*H*$_2$-CH<), 4.50-4.97 (1H, -C*H*<), 5.21-5.54 (terminal end, >C*H*-), 6.25-6.45 (terminal end, pyrrole), 6.78-7.49 (5H, -C_6H_5), 7.49-7.77 (terminal end, pyrrole) ppm. ^{13}C NMR ($CDCl^3$): δ = 35.54 (>N-*C*H_3), 47.82 (>*C*H-), 54.24 (-*C*H_2-), 128.75, 129.34, 129.60, 139.33 (-*C*$_6H_5$), 167.93 (-S-*C*(=O)-N(CH_3)-) ppm. IR (KBr): 1654 (-S*C*(=O)N(CH_3)-), 1379, 1075, 697 cm^{-1}.

MacroCTA2: M_n = 2100, M_w/M_n = 1.11. Yield = 97%.^{1}H NMR ($CDCl_3$): δ = 1.02-1.38 (terminal end, -N(CH_2C*H*$_3$)$_2$), 2.13-2.37 (initiating end, S-C*H*$_3$), 2.46-3.10 (3H, >N-C*H*$_3$), 3.13-4.18 (2H, -(CH_3)-N-C*H*$_2$-CH< and terminal end; -N(C*H*$_2$$CH_3$)$_2$), 4.47-4.98 (1H, -C*H*<), 5.28-5.60 (terminal end, >C*H*-), 7.01-8.00 (5H, -C_6H_5), ppm. ^{13}C NMR ($CDCl^3$): δ = 35.69 (>N-*C*H_3), 47.72 (>*C*H-), 54.15 (-*C*H_2-), 128.79, 129.36, 129.59, 139.45 (-*C*$_6H_5$), 167.84 (-S-*C*(=O)-N(CH_3)-) ppm. IR (KBr): 1654 (-S*C*(=O)N(CH_3)-), 1378, 1075, 697, 668 cm^{-1}.

RAFT polymerization of vinyl monomers using model CTAs. For a typical polymerization, vinyl monomer (2.0 mmol), modelCTA1 (14.0 mg, 4.0×10^{-5} mmol), AIBN (3.3 mg, 4.0×10^{-5} mmol), and chlorobenzene (1.0 mL) were placed in a glass ampule equipped with a magnetic stirring bar, and then solution was degassed by three freeze-evacuate-thaw cycles. The ampule was flame-sealed off under vacuum, and it was stirred at 60 °C for desired time. The characteristic yellow color remained during the polymerization. The reaction was stopped by rapid cooling with liquid nitrogen. For the

determination of the monomer conversion, the ^{1}H NMR spectrum of the polymerization mixture was measured in $CDCl_3$.

Synthesis of block copolymer using macroCTA1 and St or DMAm. For a typical polymerization, vinyl monomer (5.00 mmol), modelCTA1 (M_n = 1500 g/mol, 75.0 mg, 5.0×10^{-5} mmol), AIBN (4.10 mg, 2.5×10^{-5} mmol), and chlorobenzene (2.5 mL) were placed in a glass ampule equipped with a magnetic stirring bar, and then solution was degassed by three freeze-evacuate-thaw cycles. The ampule was flame-sealed off under vacuum, and it was stirred at 60 °C for desired time. The characteristic yellow color remained during the polymerization. The reaction was stopped by rapid cooling with liquid nitrogen. For the determination of the monomer conversion, the ^{1}H NMR spectrum of the polymerization mixture was measured in $CDCl_3$.

Reference

Nagai, D.; Sato, M.; Ochiai, B.; Endo, T. *J. Polym. Sci., Part A: Polym Chem.* **2006**, *44*, 4795-4803.

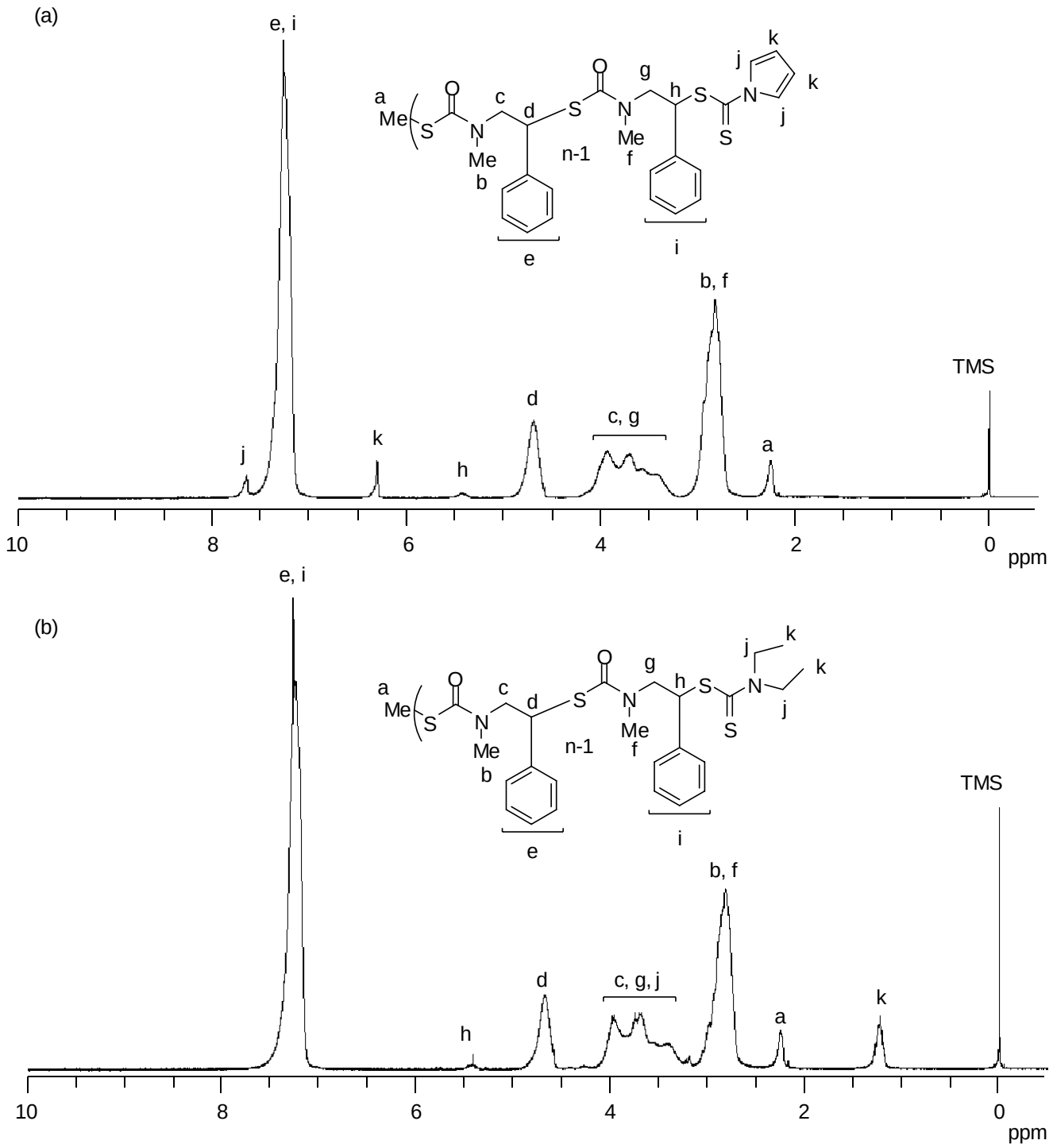

Figure 1S. ^{1}H NMR spectra ($CDCl_3$) of macroCTAs; (a) macroCTA1 and (b) macroCTA2.

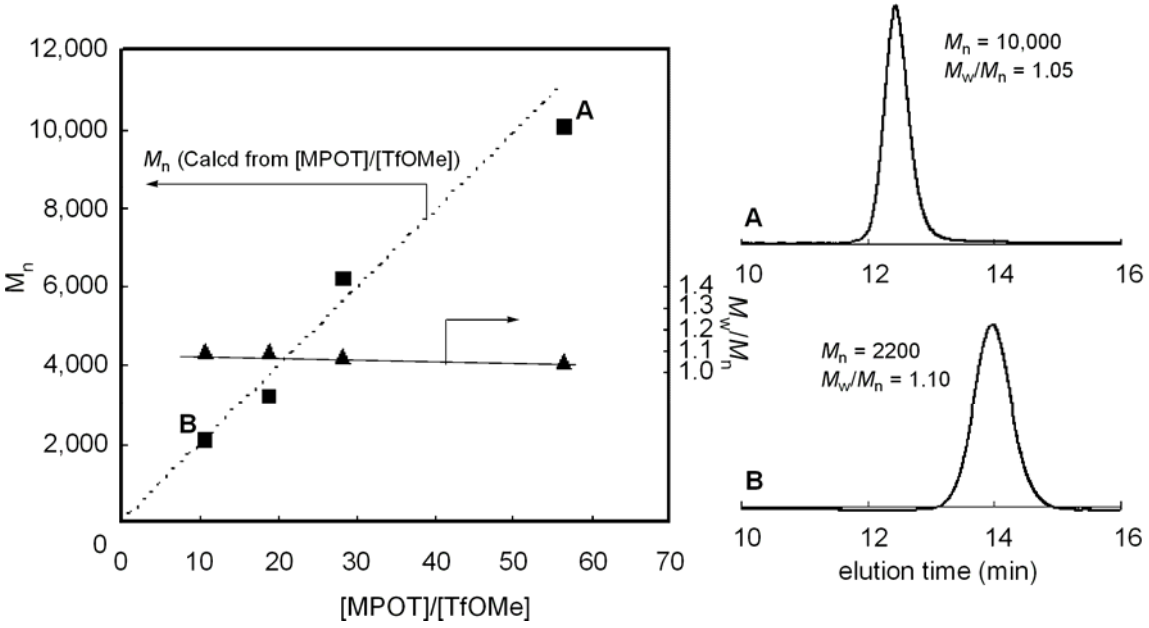

Figure 2S. Dependence of the number-average molecular weight and molecular weight distribution on the $[MPOT]_0$:$[TfOMe]_0$ ratio for the polymerization when diethylammonium *N,N*-diethyldithiocarbamate was employed.

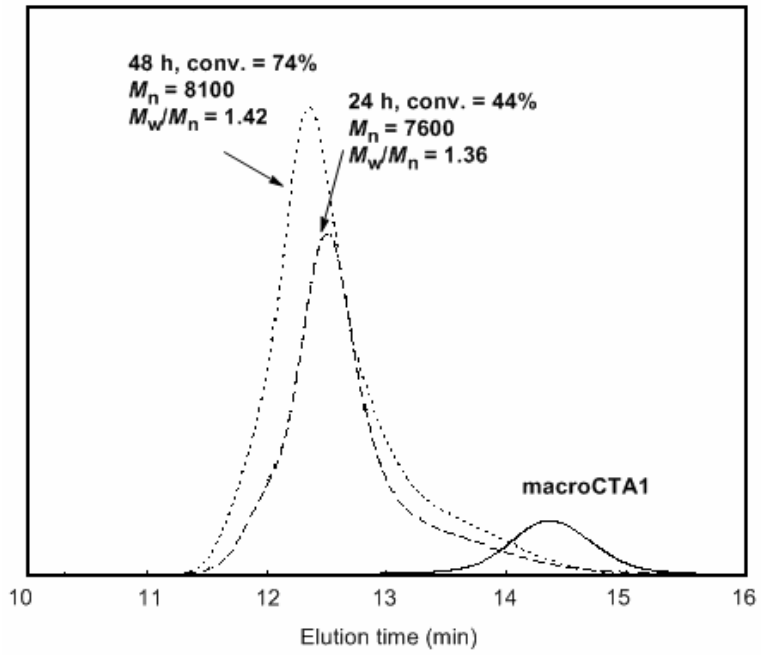

Figure 3S. Evolution of SEC traces with conversion for the polymerization of St with AIBN in the presence of macroCTA1 in PhCl at 60 °C $[macroCTA1]_0/[AIBN]_0 = 2$.