Supporting Information for

Uncovering a Radical-Mediated Mechanism in the Kumada Catalyst Transfer Polymerization of Glycolated Polythiophenes

Abdulrahman Bakry,[a,c] Preeti Yadav,[a] Wissem Khelifi,[a] Julia Khusnutdinova,[b] and Christine Luscombe *[a]

a. Pi-Conjugated polymers unit, Okinawa Institute of Science and Technology Graduate University, Kunigami-gun, Okinawa 904-0495, Japan. E-mail: christine.luscombe@oist.jp
b. Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University, Kunigami-gun, Okinawa 904-0495, Japan.
c. Faculty of Science, Chemistry Department, Kafrelsheikh University, El Giesh Street, Kafrelsheikh 33516, Egypt.

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1. Experimental section

1.1. Materials and methods

All chemicals were purchased from either Sigma-Aldrich or Tokyo Chemical Industries and used as received unless otherwise noted. Deuterated chloroform and dichloromethane solvents were obtained from EURISOTOP. Trimethoxybenzene was obtained from Fujifilm Wako Pure Chemical Corporation and used as an internal standard for ^{1}H NMR studies. Anhydrous tetrahydrofuran (THF) was purchased from Sigma-Aldrich and used inside the glovebox. ^{1}H NMR spectra were recorded on a Bruker 400 or 500 MHz spectrometer using $CDCl_3$ or CD_2Cl_2. The polymers were characterized using size exclusion chromatography with a Malvern Viscotek TDA 305 GPC equipped with a UV detector. The eluent was THF at a temperature of 35 °C, and the flow rate was 1 mL min^{-1}. Molecular weights were determined relative to polystyrene standards. LC-MS analyses were performed using a Q Exactive Plus hybrid quadrupole-Orbitrap mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA), which offers sub-ppm mass accuracy and combines high resolution (up to 140,000 FWHM at m/z 200). EPR analyses were performed using a JES-X330 spectrometer (JEOL Ltd., Tokyo, Japan), which provides high sensitivity and resolution for detecting unpaired electron species. For EPR measurements, 50 µL quartz capillary tubes were used at room temperature. Simulation of the experimental spectrum were done using the Easyspin package[1] in Matlab R2016b[2] using "garlic" function; esfit function was used for fitting simulation parameters. All polymerization reactions were performed in screw-cap septum vials that were dried overnight in an oven at 120 °C before use. The monomer (Br-3MEEMT-Br) was first dried in the vacuum oven for 1 h at 60 °C. Both monomers (Br-3MEEMT-Br and Br-3HT-Br) were dried using the standard Schlenk techniques under a dry nitrogen atmosphere. Anhydrous THF and trimethoxybenzene (used as an internal standard for ^{1}H NMR studies) were added inside the glovebox.

1.2. KCTP of Br-3MEEMT-Br under different conditions

After developing the appropriate conditions for the Grignard metathesis step, we focused on screening the polymerization conditions. All the polymerization studies were carried out at room temperature using Ni(dppe)Cl_2 catalyst at 1 mol% with respect to the Br-3MEEMT-Br or Br-3HT-Br monomer. We previously found that the polymerization of 3MEEMT via KCTP was affected by monomer concentration, and a minimum monomer concentration of 0.15 M was needed to obtain the polymer. Based on this observation, polymerization was carried out with 0.3 M monomer concentration.

Polymerization of 3MEEMT was carried out by following the procedure reported in the literature.[3] 2,5-Dibromo-3-methoxyethoxyethoxymethylthiophene (374.09 mg, 1.0 mmol) and the reference standard, 1,3,5-trimethoxybenzene (8.0 mg, 0.08 mmol) were degassed for 30 min with N_2. 3.3 mL of THF was added, the screw-cap septum vial was cooled to −78 °C, *i*-PrMgCl.LiCl (145.0 mg, 0.77 mL, 1.0 mmol, 1.3 M) was added dropwise over 10 min, and the reaction was allowed to proceed for 2 h at room temperature. Ni(dppe)Cl_2 (5.3 mg, 0.01 mmol, 1 mol%) was added in one portion, and the polymerization was allowed to continue for 10 minutes at room temperature. For reaction involving TEMPO, TEMPO (1 eq) was added to the Grignard mixture and stirred for 20 minutes before catalyst addition. In polymerizations in the presence of DIPEA, 1 eq was added with respect to the monomer and stirred for 20 minutes before catalyst addition. In the polymerization in the presence of TMEDA, 1 eq was added with respect to the monomer and stirred for 20 minutes before the catalyst addition. Polymerization aliquots were taken from the reaction by withdrawing a 0.2 mL aliquot from the reaction mixture using a syringe needle, quenched with 2 mL of DCM acidified with drops of dil HCl (aq), dried over Na_2SO_4, filtered, and analyzed using ^1H NMR. In the $MgCl_2$ experiment, $MgCl_2$ (1 eq) was added and stirred for 60 minutes before catalyst addition. Polymerization aliquots in this case were taken at times intervals of 1, 2, 4, 8, 12, 16, 20, 30, 40, and 60 minutes. The GPC analyses were done by drying the aliquots of ^1H NMR under vacuum for 24 h, then dissolving in THF, and filtering.

1.3. Synthesis of 2-bromo-5-iodo-3-((2-(2-methoxyethoxy)ethoxy)methyl)thiophene

Synthesis of (2-bromothiophen-3-yl)methanol

THF (20.0 mL) and 3-thiophenemethanol (1.14 g, 10 mmol) were added to a bottom-rounded flask, followed by degassing nitrogen bubbles through the solution for 15 min. After degassing, recrystallized NBS (1.96 g, 11.0 mmol) was quickly added to the reaction in one portion. The reaction was allowed to stir for 2 hr at room temperature while covered in aluminum foil. The reaction mixture was quenched with cooled water, filtered to remove the precipitated succinimide, and the solvent was removed using rotary evaporation. The residue was purified using column chromatography using a 9:1 hexane:ethyl acetate eluent, providing a pale-white oil in 77 % yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.29 (d, *J* = 5.6 Hz, 1H), 7.03 (d, *J* = 5.6 Hz, 1H), 4.59 (s, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 141.04, 128.02, 126.35, 110.18, 59.43.

Synthesis of 2-bromo-3-(bromomethyl)thiophene

(2-bromothiophen-3-yl)methanol (1.93 g, 10.00 mmol) was added to a round-bottom flask containing 20 ml of DCM and then cooled for 20 min in ice. After cooling, PBr_3 (2.70 g, 10.00 mmol) was added dropwise over 15 min, and the reaction was allowed to stir overnight at room temperature. 150 mL of 10% $NaHCO_3$ aqueous solution was added to quench the reaction. The product was extracted using DCM, then washed with brine, dried with Na_2SO_4, filtered, and the solvent removed. The product was obtained as a colorless oil in 91% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.30 (d, *J* = 5.8 Hz, 1H), 7.02 (d, *J* = 5.6 Hz, 1H), 4.48 (s, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 137.28, 128.38, 126.63, 113.08, 25.88.

Synthesis of 2-bromo-3-((2-(2-methoxyethoxy)ethoxy)methyl)thiophene

Diethylene glycol monomethyl ether (1.20 g, 10.00 mmol) and THF (100 mL) were added to a 3-neck flask equipped with a dropping funnel. NaH (0.48 g, 40.00 mmol) was added in one portion, the flask was quickly recapped, and NaH was allowed to react for 20 min until H_2 gas evolution had stopped. 2-bromo-3-(bromomethyl)thiophene (2.56 g, 10.0 mmol) was dissolved in the dropping funnel containing 100 mL of THF. It was then added dropwise over 15 min, after which the reaction was allowed to stir for 5 hr. The product was then filtered over Celite to remove precipitated salts and rinsed with THF to ensure complete product elution. The solvent was removed using a rotary evaporator, and the product was purified using column chromatography with 85:15 hexane:ethyl acetate, resulting in a pale white oil in 92% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.18 (d, *J* = 5.6 Hz, 1H), 6.92 (d, *J* = 5.6 Hz, 1H), 4.39 (s, 2H), 3.51 (s, 4H), 3.49 (d, *J* = 6.0

Hz, 2H), 3.41 (d, *J* = 4.7 Hz, 2H), 3.24 (s, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 138.92, 128.76, 126.40, 111.27, 72.33, 70.84, 70.09, 67.35, 60.62, 59.03.

Synthesis of 2-bromo-5-iodo-3-((2-(2-methoxyethoxy)ethoxy)methyl)thiophene

THF (100 mL) and 2-bromo-3-((2-(2-methoxyethoxy)ethoxy)methyl)thiophene (2.95 g, 10.00 mmol) were added to a round-bottom flask, followed by degassing nitrogen gas through the solution for 15 min. After degassing, NIS (2.25 g, 10.0 mmol) was quickly added to the reaction in one portion. The reaction was allowed to stir at room temperature for 24 hr, after which the reaction was quenched with cooled water, filtered to remove the precipitated succinimide, and then the solvent was removed using rotary evaporation. The residue was purified using column chromatography using a 9:1 hexane:ethyl acetate eluent, resulting in a pale-white oil in 75 % yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.29 (d, *J* = 5.6 Hz, 1H), 7.03 (d, *J* = 5.6 Hz, 1H), 4.59 (s, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 141.04, 128.02, 126.35, 110.18, 59.43.

2. NMR spectrum

2.1. ^{1}H NMR analyses of polymerization aliquots (normal conditions).

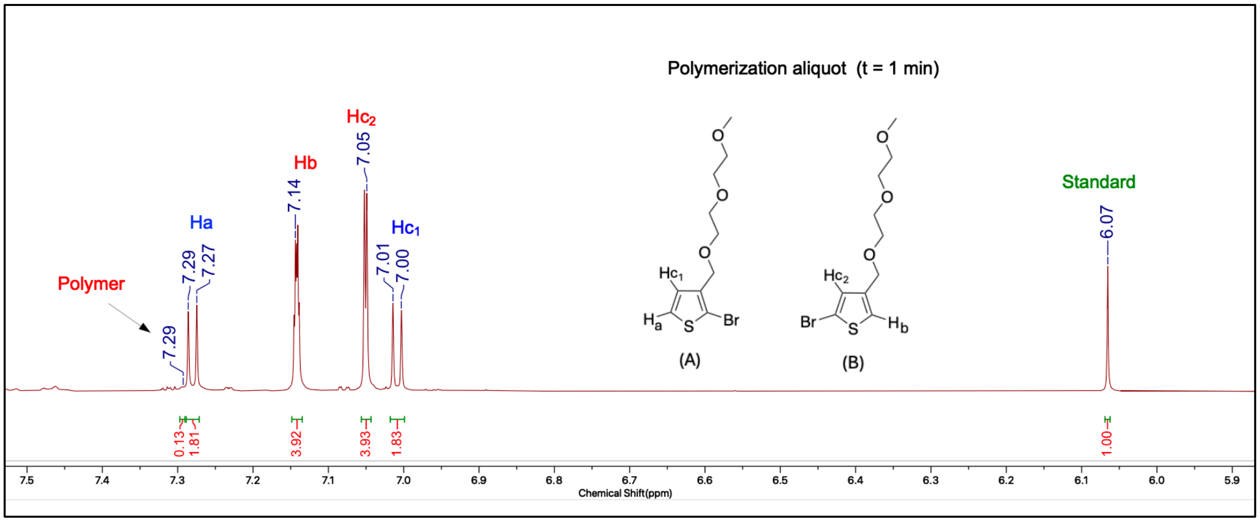

Fig. S1 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br (t = 1 min) with *i*-PrMgCl.LiCl used for Grignard metathesis (normal conditions).

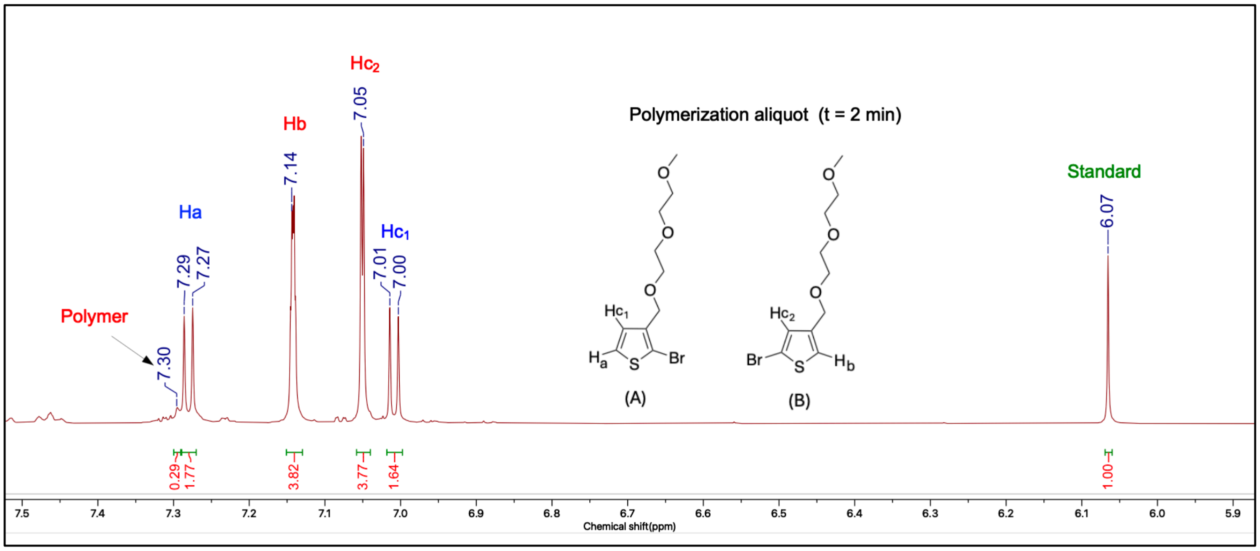

Fig. S2 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br (t = 2 min) with *i*-PrMgCl.LiCl used for Grignard metathesis (normal conditions).

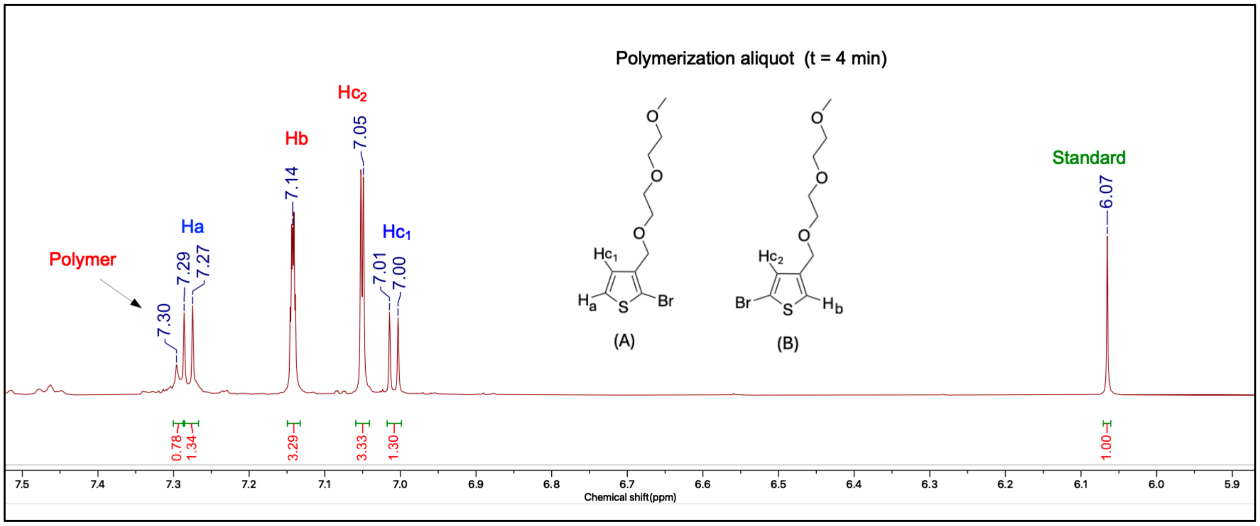

Fig. S3 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br (t = 4 min) with *i*-PrMgCl.LiCl used for Grignard metathesis (normal conditions).

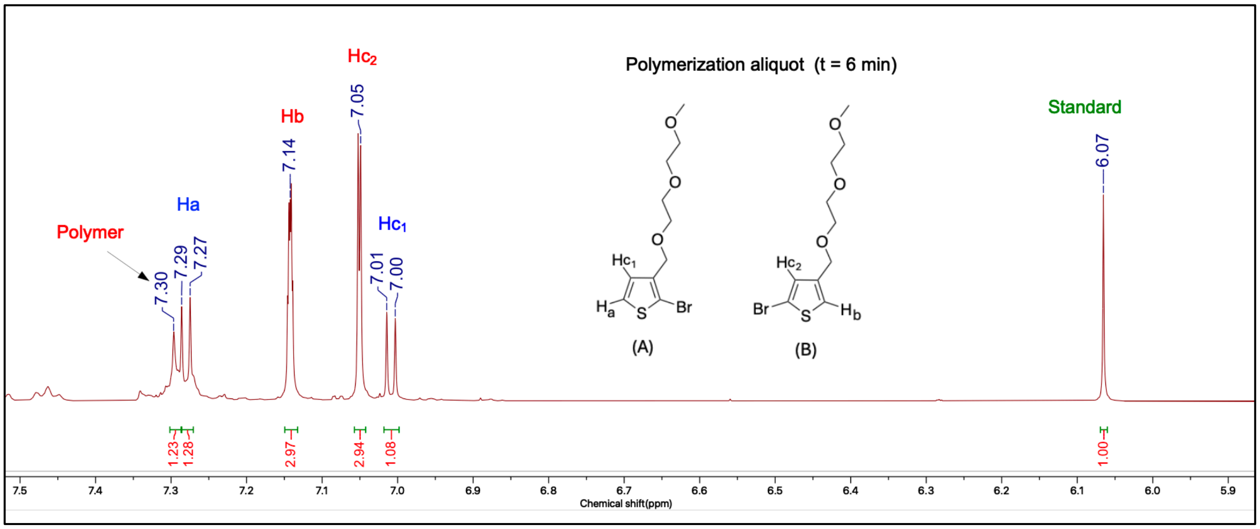

Fig. S4 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br (t = 6 min) with *i*-PrMgCl.LiCl used for Grignard metathesis (normal conditions).

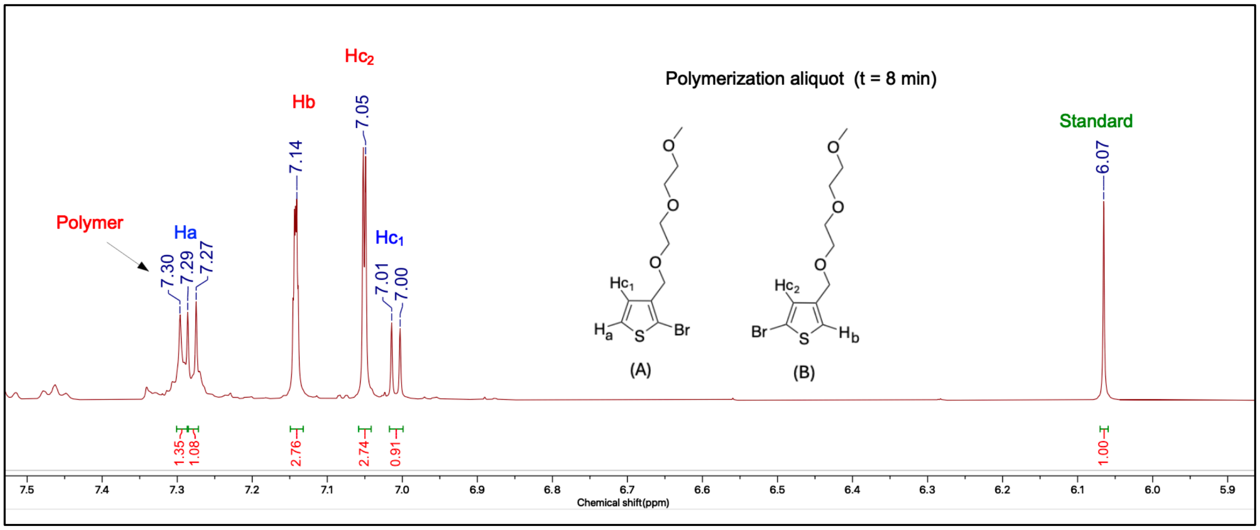

Fig. S5 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br (t = 8 min) with *i*-PrMgCl.LiCl used for Grignard metathesis (normal conditions).

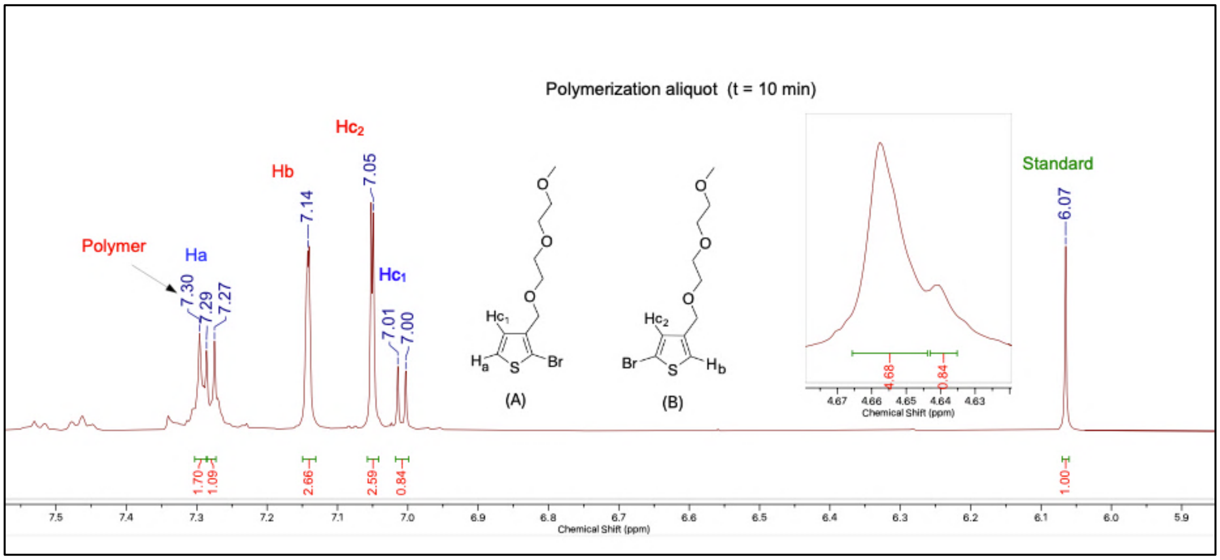

Fig. S6 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br (t = 10 min) with *i*-PrMgCl.LiCl used for Grignard metathesis (normal conditions).

2.2. ^{1}H NMR and ^{13}C NMR analyses of synthesis of 2-bromo-5-iodo-3-((2-(2-methoxyethoxy)ethoxy)methyl)thiophene.

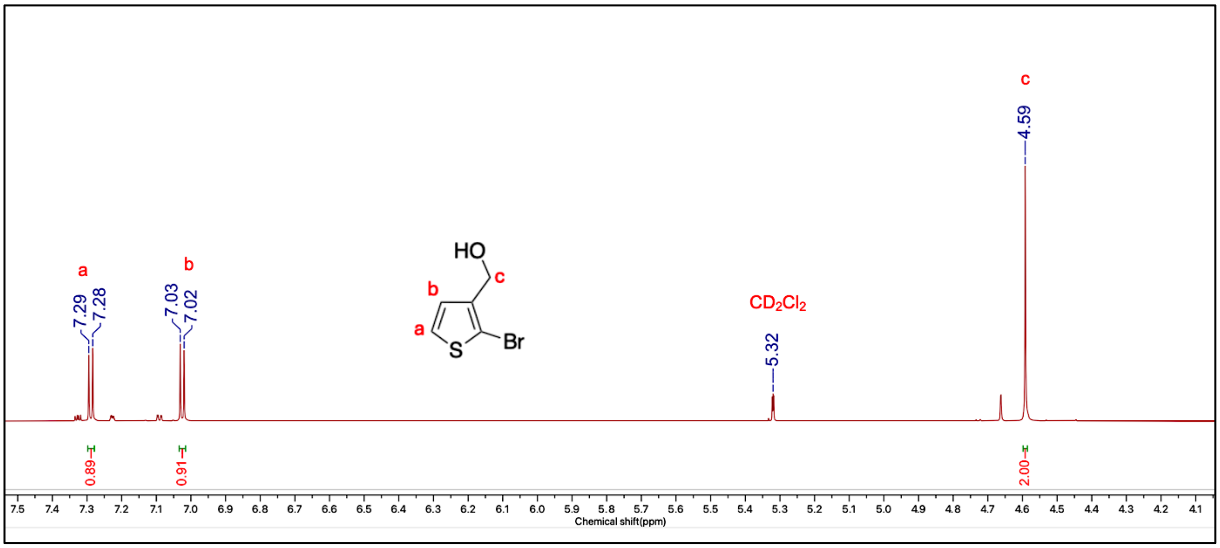

Fig. S7 ^{1}H NMR spectrum of (2-bromothiophen-3-yl)methanol.

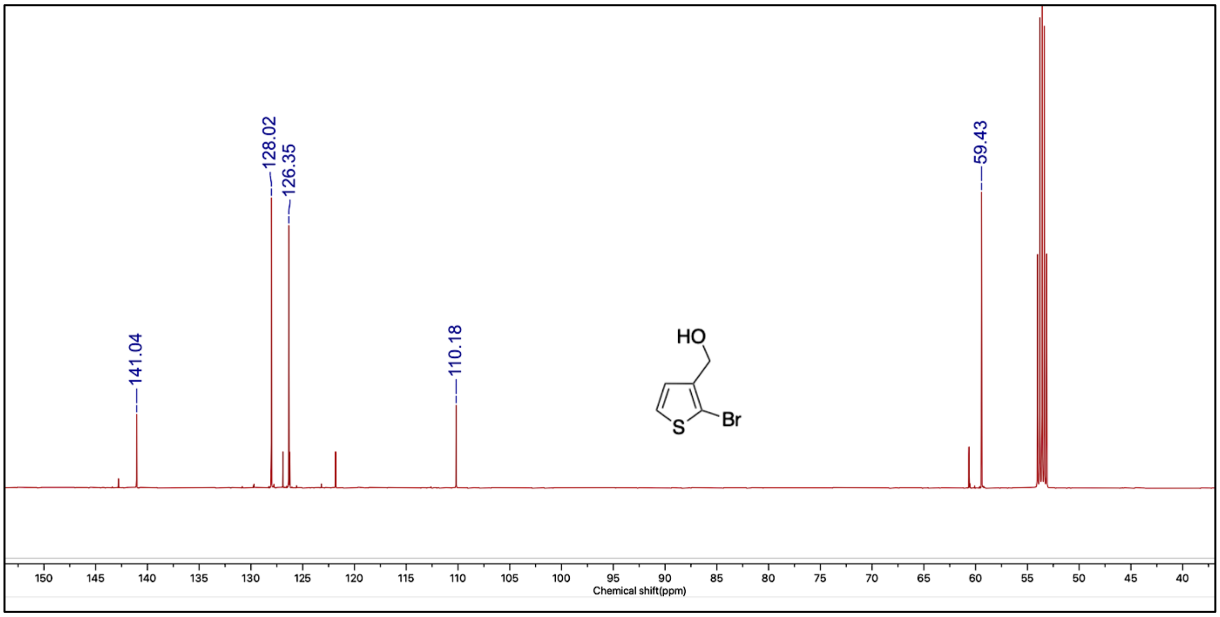

Fig. S8 ^{13}C NMR spectrum of (2-bromothiophen-3-yl)methanol.

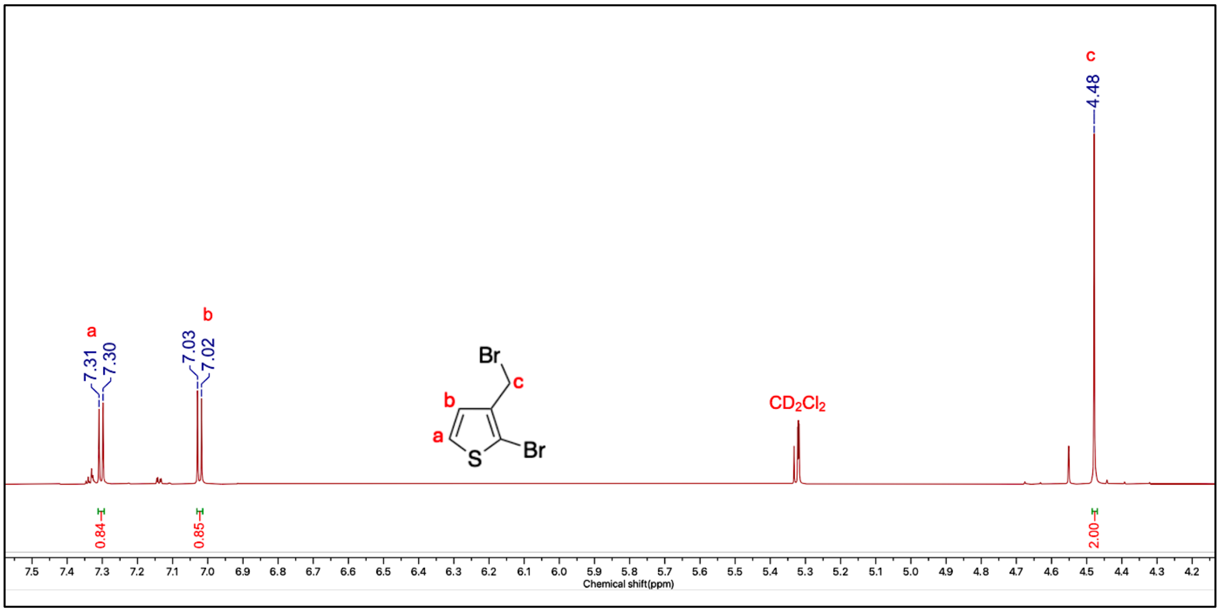

Fig. S9 ^{1}H NMR spectrum of 2-bromo-3-(bromomethyl)thiophene.

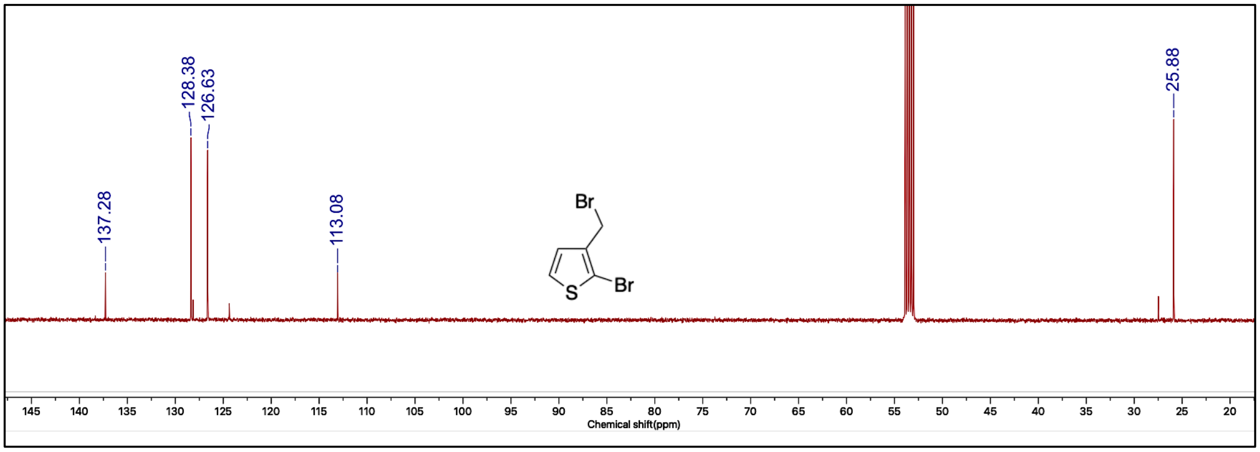

Fig. S10 ^{13}C NMR spectrum of 2-bromo-3-(bromomethyl)thiophene.

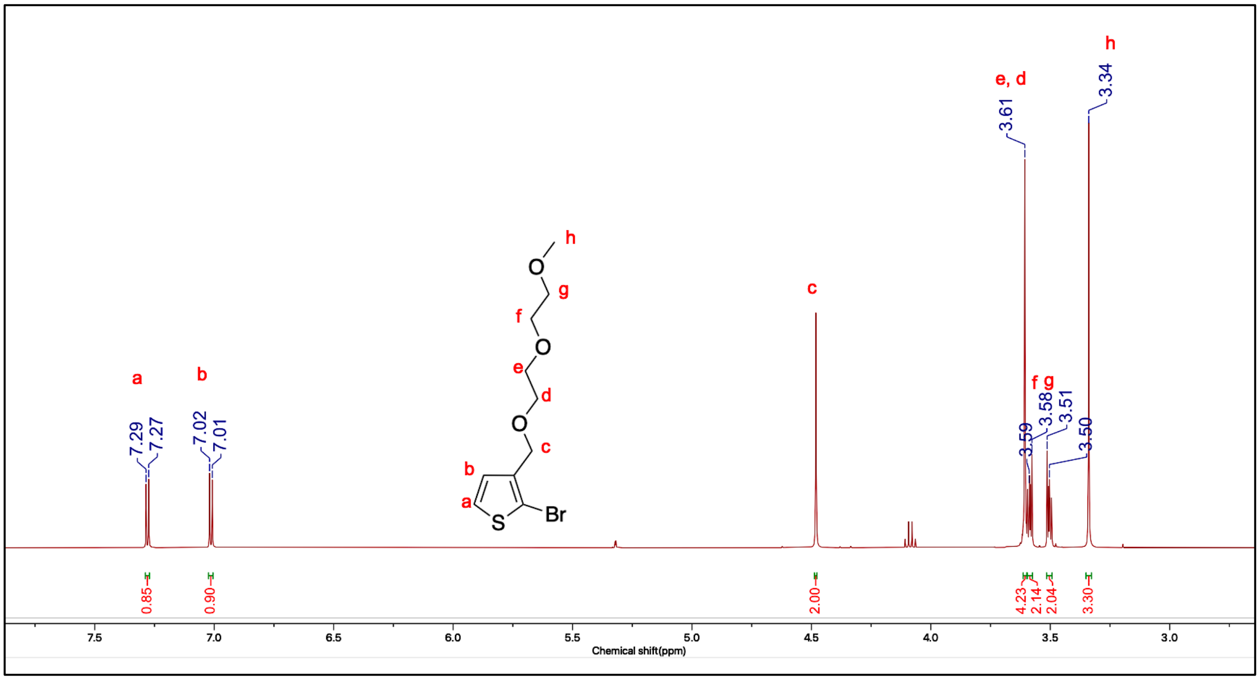

Fig. S11 ^{1}H NMR spectrum of 2-bromo-3-((2-(2-methoxyethoxy)ethoxy)methyl)thiophene.

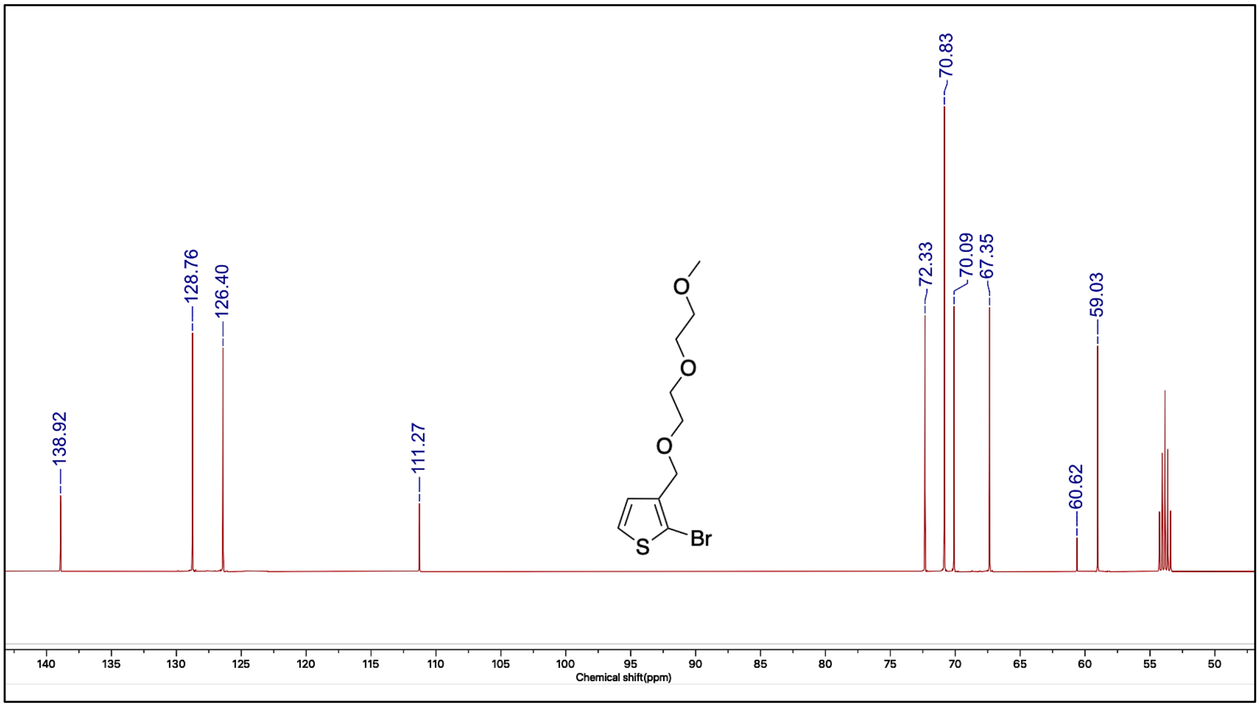

Fig. S12 ^{13}C NMR spectrum of 2-bromo-3-((2-(2-methoxyethoxy)ethoxy)methyl)thiophene.

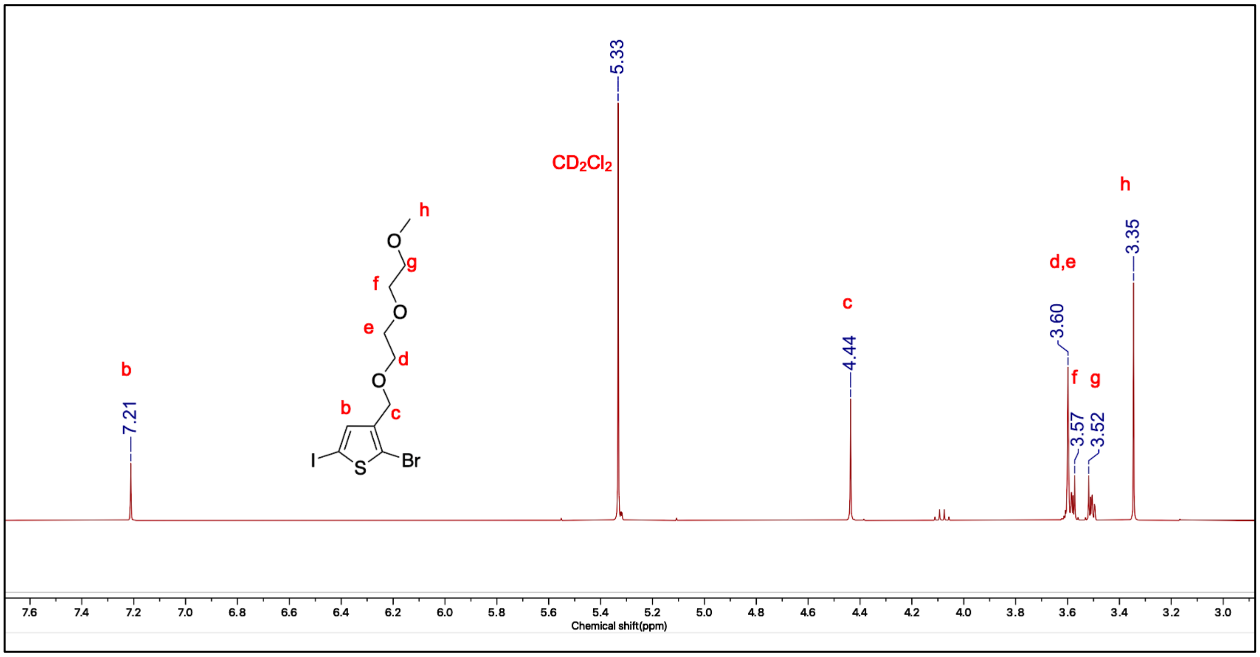

Fig. S13 ^{1}H NMR spectrum of 2-bromo-5-iodo-3-((2-(2-methoxyethoxy)ethoxy)methyl)thiophene.

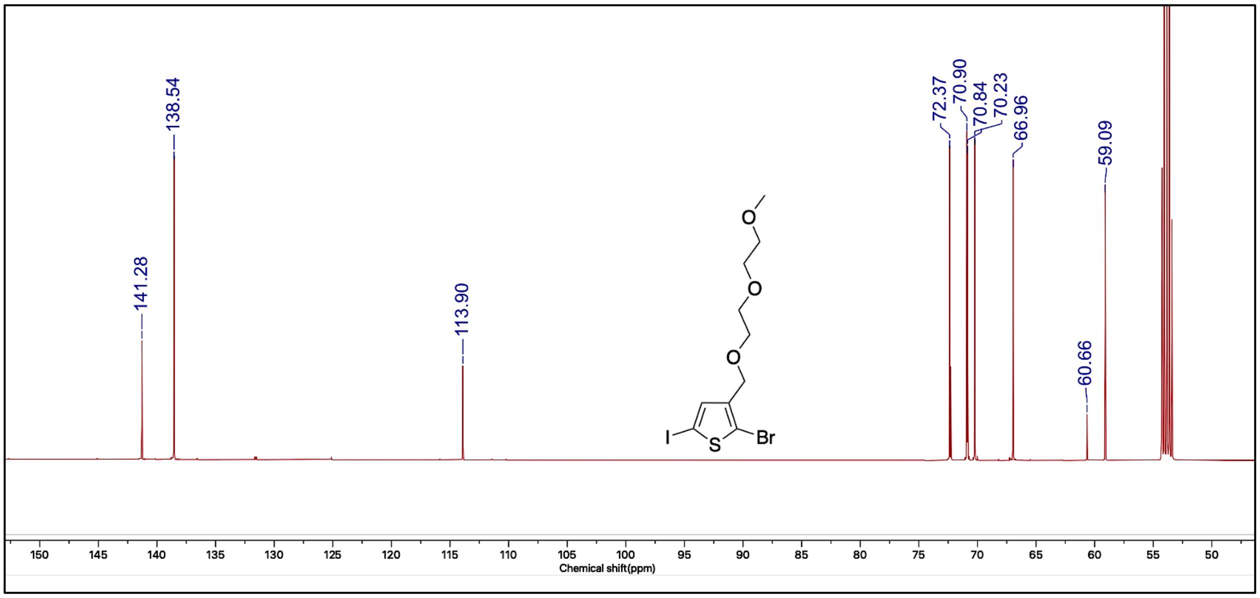

Fig. S14 ^{13}C NMR spectrum of 2-bromo-5-iodo-3-((2-(2-methoxyethoxy)ethoxy)methyl)thiophene.

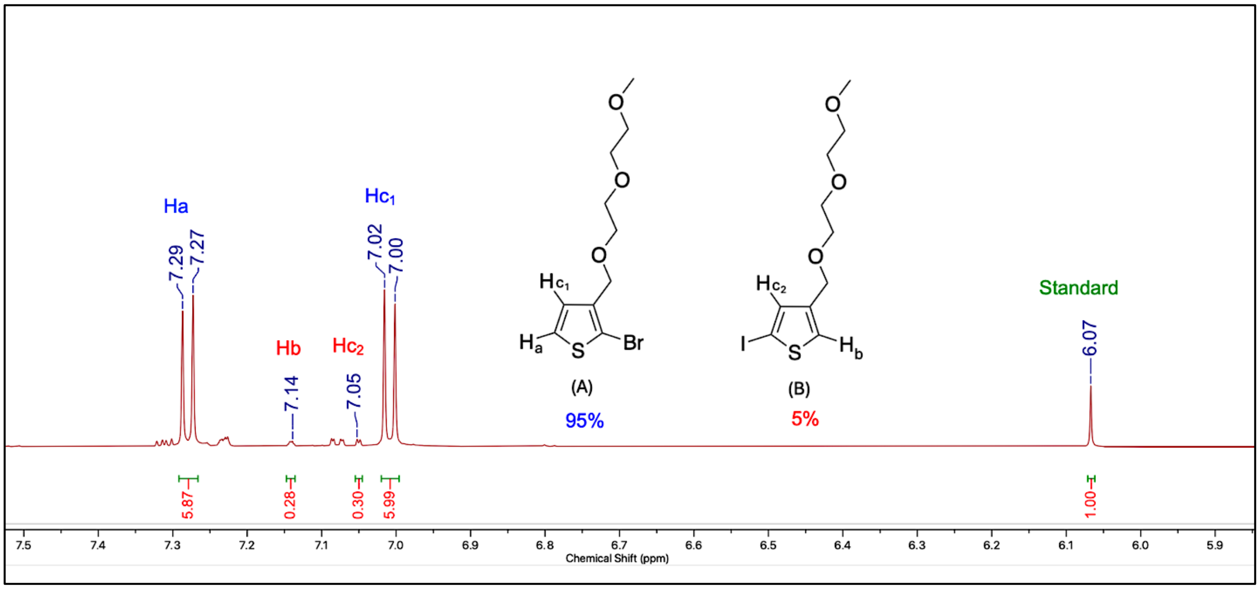

Fig. S15 ^{1}H NMR spectrum of Grignard metathesis of 2-bromo-5-iodo-3-((2-(2-methoxyethoxy)ethoxy)methyl)thiophene using *i*-PrMgCl.LiCl.

KCTP of 2-bromo-5-iodo-3-methoxyethoxyethoxymethylthiopene, (I-3MEEMT-Br).

2-bromo-5-iodo-3-methoxyethoxyethoxymethylthiopene (421.00 mg, 1.00 mmol) and 1,3,5-trimethoxybenzene (8.00 mg, 0.01 mmol) used as an internal standard were added to a screw-cap septum vial, degassed under a high vacuum, and then purged with N_2 for 30 min. THF (3.3 mL) was added, the flask was cooled to -78 °C, *i*-PrMgCl.LiCl (145.0 mg, 0.77 mL, 1.0 mmol, 1.3 M) was added dropwise over 10 min, and the reaction was allowed to proceed for 2 hours at room temperature. Ni(dppe)Cl_2 (5.30 mg, 0.01 mmol, 1%mol) was added in one portion, and the mixture was allowed to stir for 24 h at room temperature. To quench the polymerization, the polymer was precipitated into 150 mL of MeOH acidified with HCl (0.5 mL, 5.0 M), but no polymer was obtained in this case.

2.3. ^{1}H NMR analyses of polymerization using TEMPO (radical scavenger)

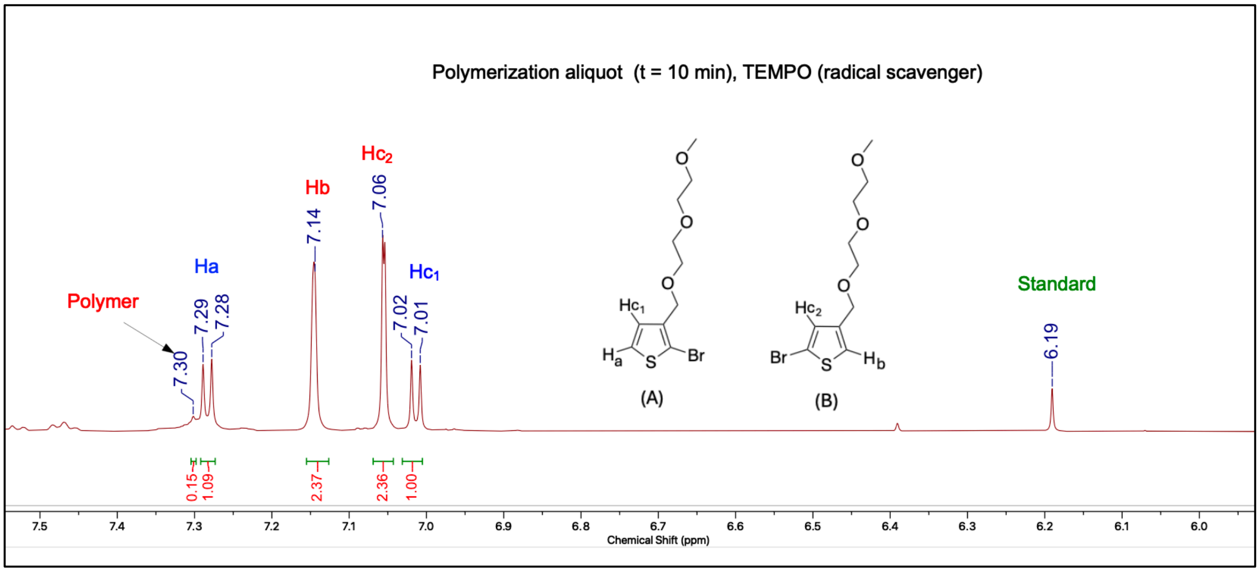
Polymerization aliquot (t = 10 min), TEMPO (radical scavenger)

Fig. S16 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br (t = 10 min), *i*-PrMgCl.LiCl used for Grignard metathesis with TEMPO added.

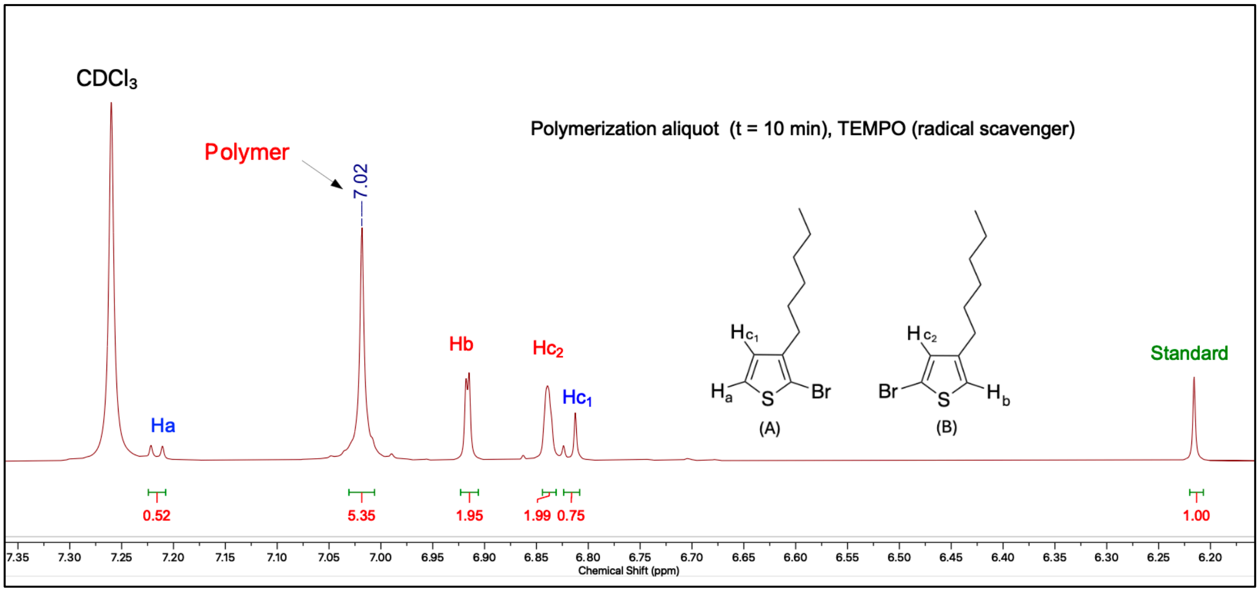

Fig. S17 ^{1}H NMR analysis of polymerization aliquot of Br-3HT-Br (t = 10 min), *i*-PrMgCl.LiCl used for Grignard metathesis and TEMPO added.

2.4. ^{1}H NMR analyses of polymerization aliquots (dark conditions)

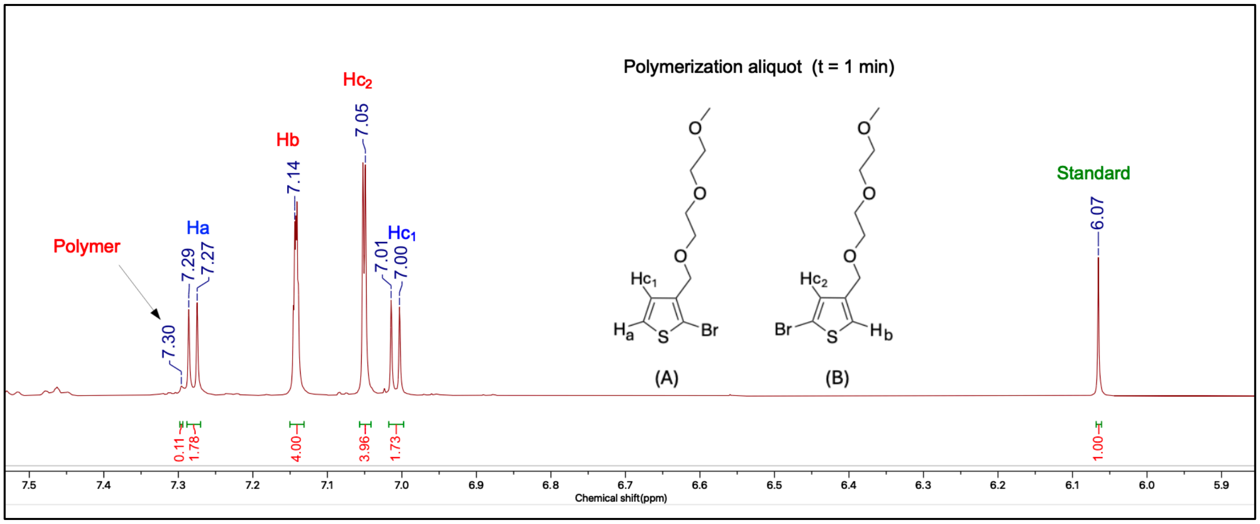

Fig. S18 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br (t = 1 min) with *i*-PrMgCl.LiCl used for Grignard metathesis (dark conditions).

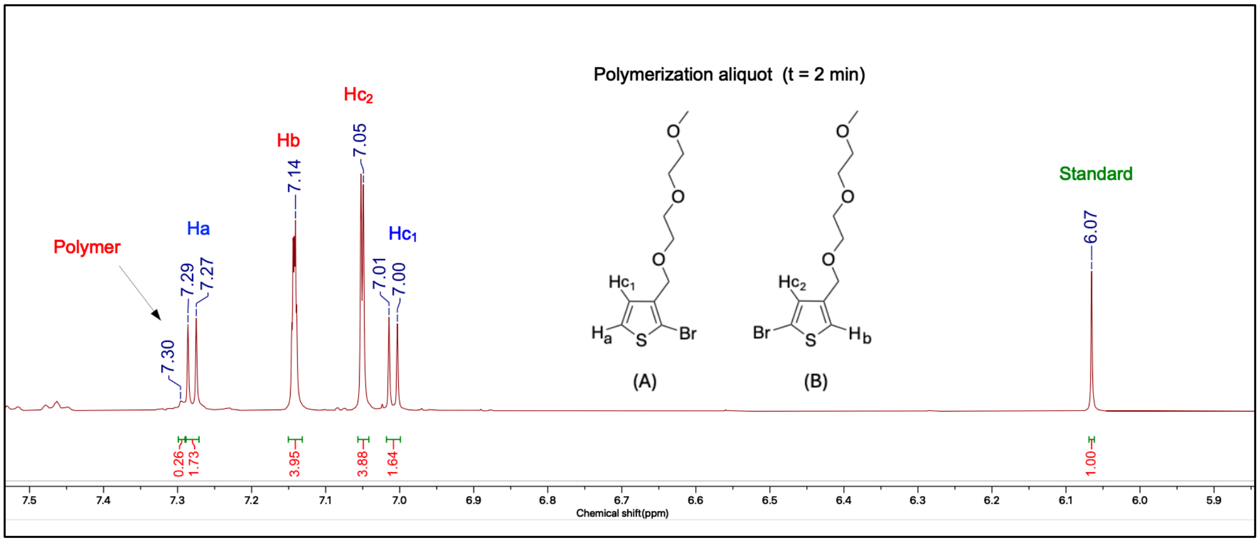

Fig. S19 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br (t = 2 min) with *i*-PrMgCl.LiCl used for Grignard metathesis (dark conditions).

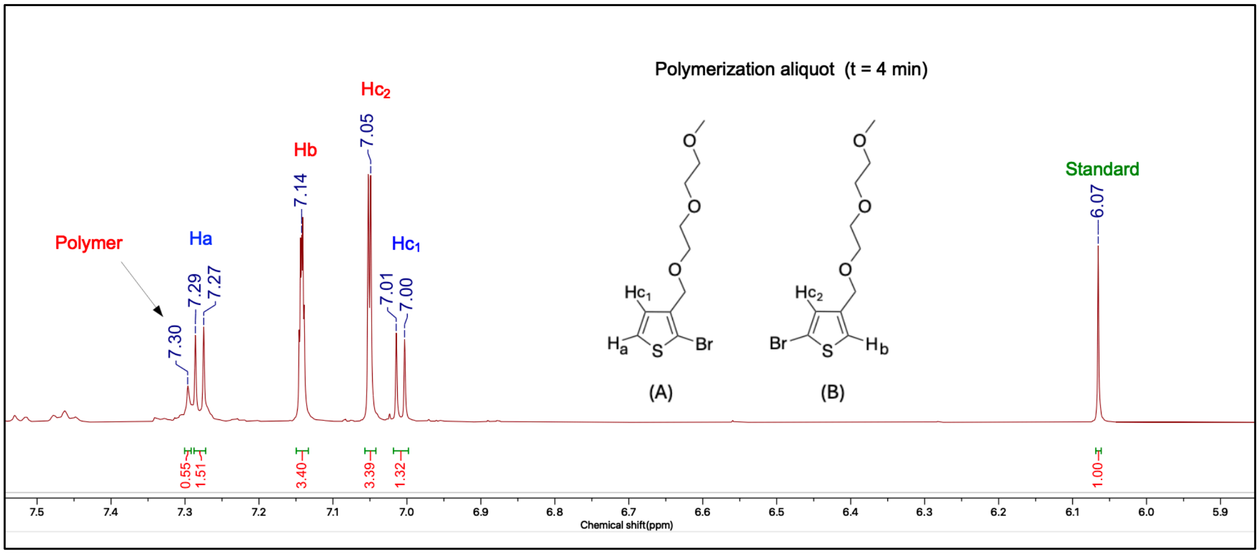

Fig. S20 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br (t = 4 min) with *i*-PrMgCl.LiCl used for Grignard metathesis (dark conditions).

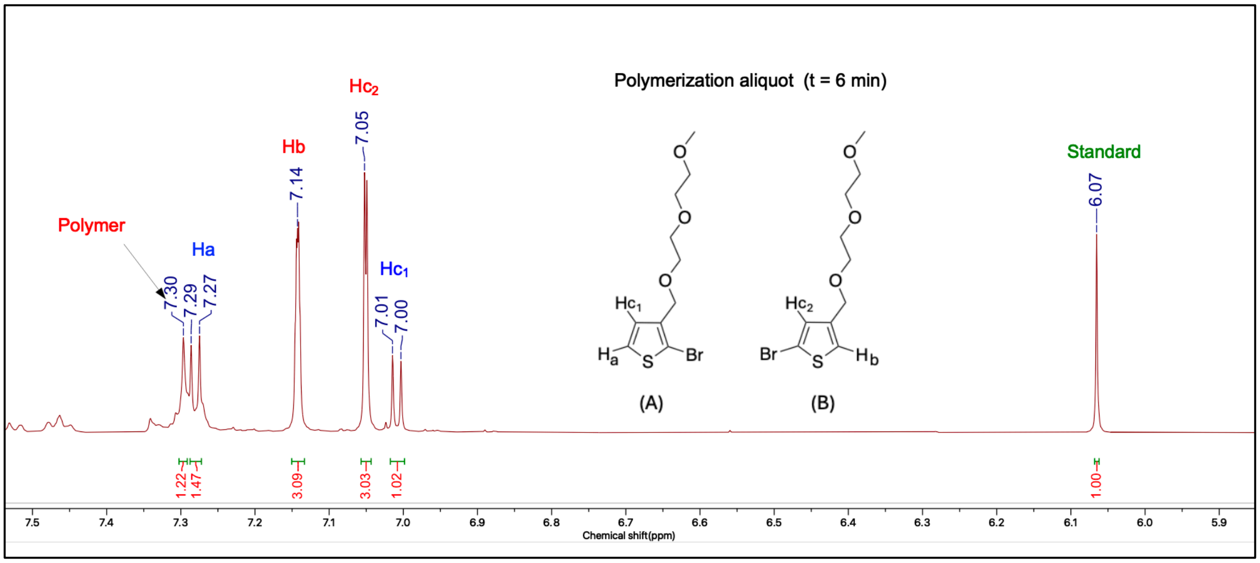

Fig. S21 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br (t = 6 min) with *i*-PrMgCl.LiCl used for Grignard metathesis (dark conditions).

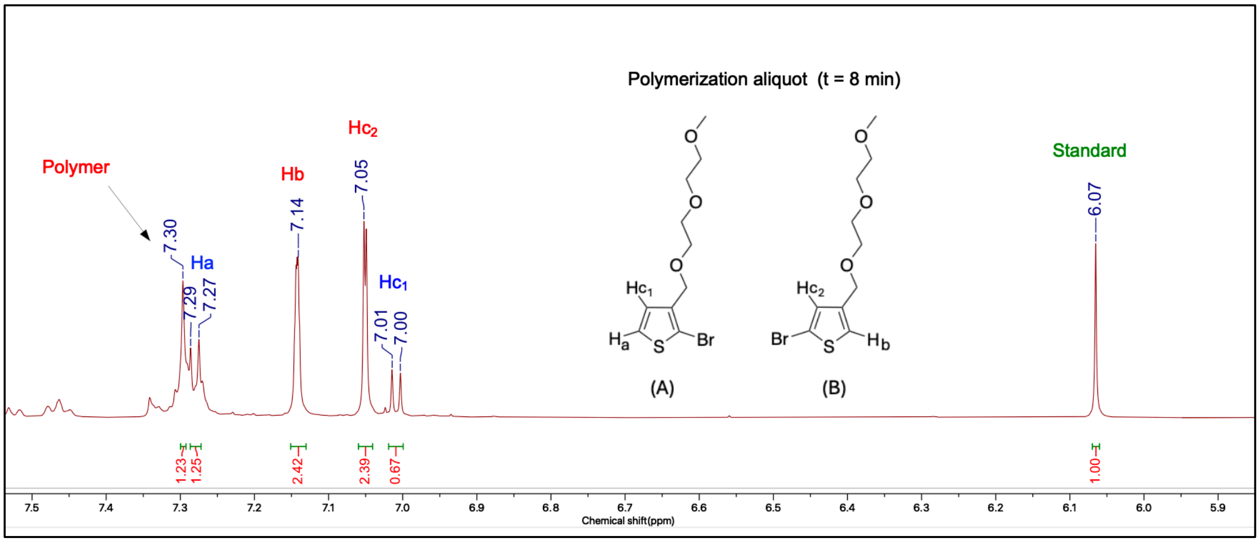

Fig. S22 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br (t = 8 min) with *i*-PrMgCl.LiCl used for Grignard metathesis (dark conditions).

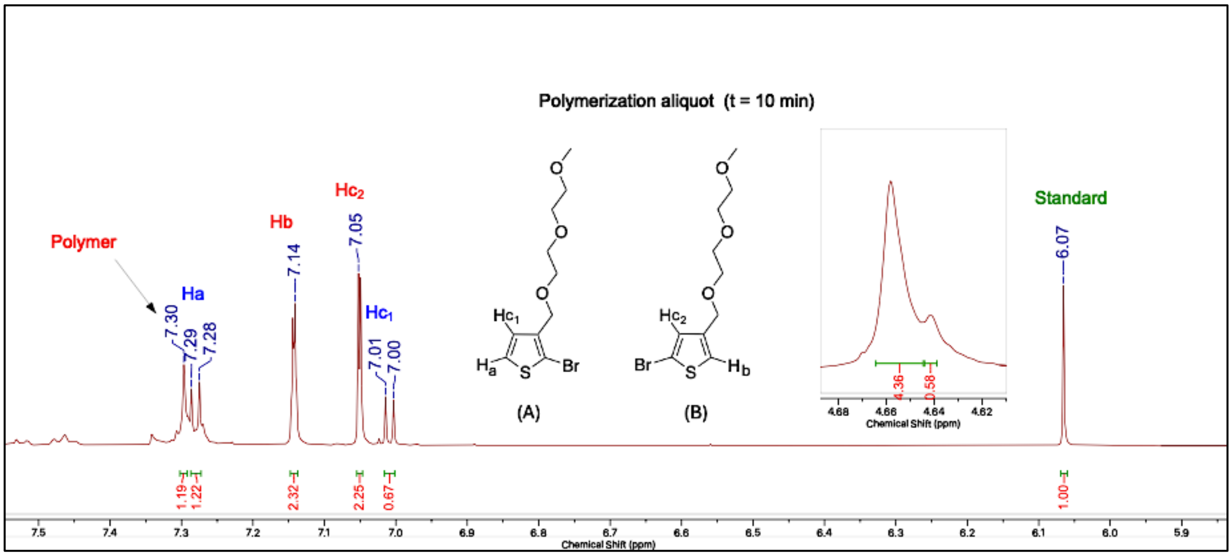

Fig. S23 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br (t = 10 min) with *i*-PrMgCl.LiCl used for Grignard metathesis (dark conditions).

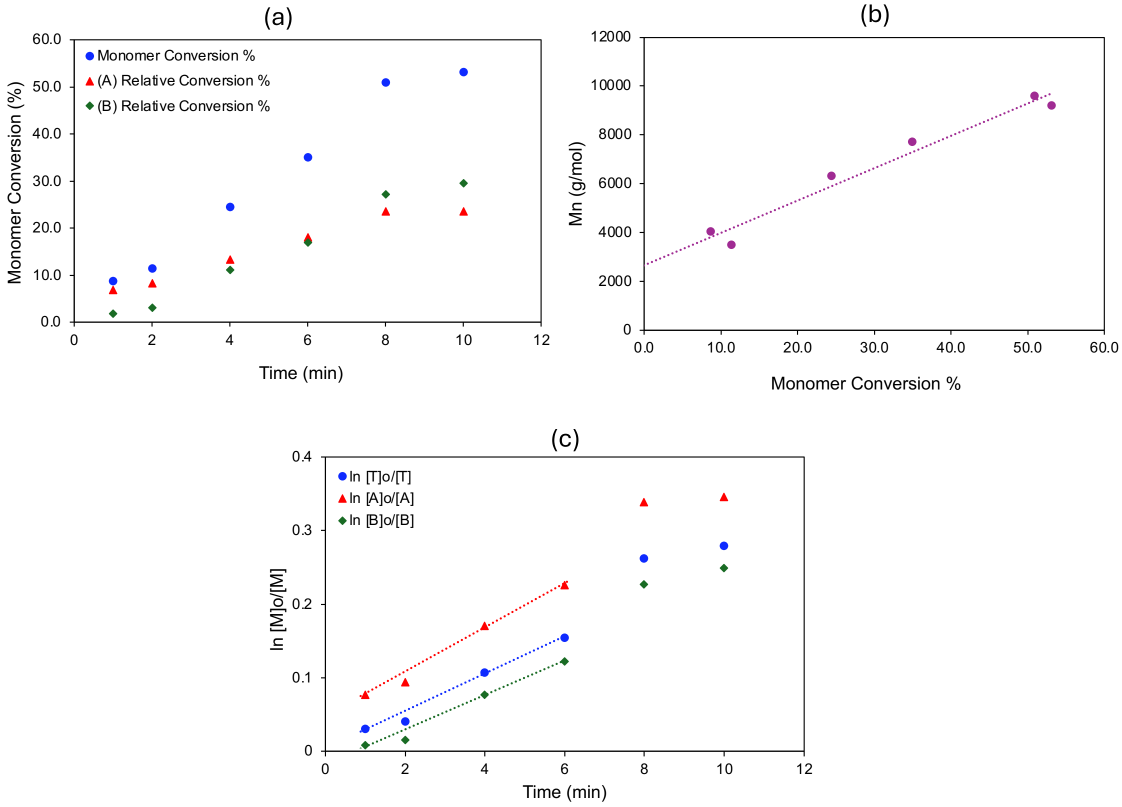

Fig. S24 a) Monomer conversion vs time, b) M_n vs monomer conversion, c) ln $[M]_0/[M]$ vs time, dark conditions.

2.5 ^{1}H NMR analyses of polymerization aliquots with added $MgCl_2$ (1 eq)

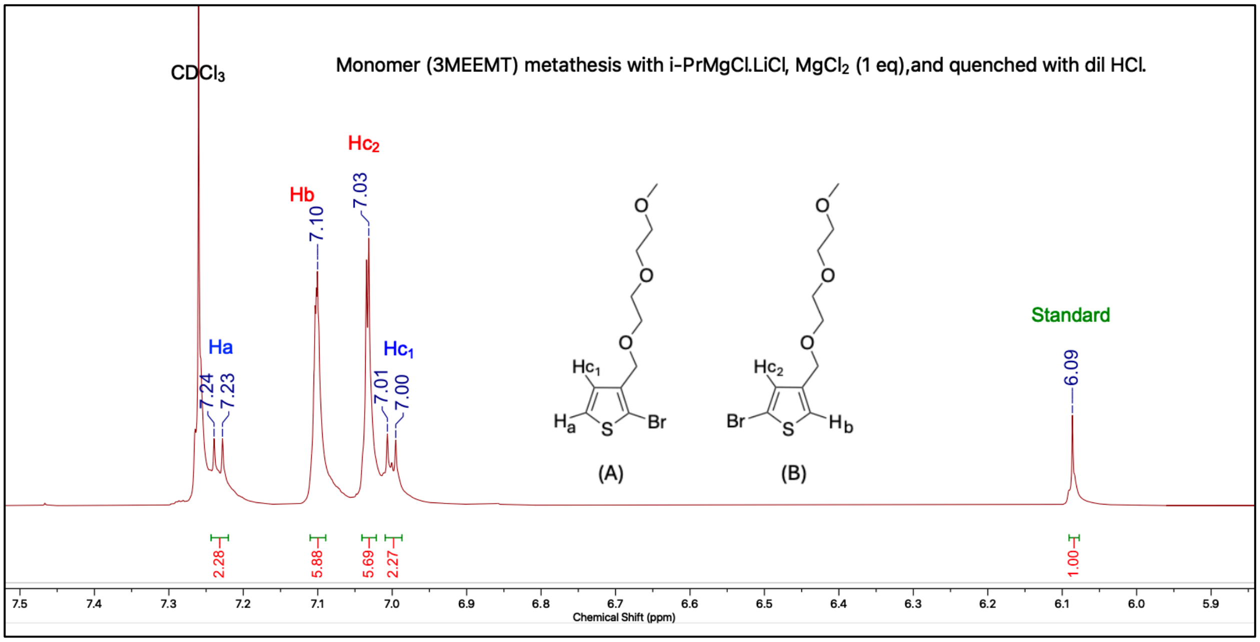

Fig. S25 ^{1}HNMR analysis of Grignard metathesis of Br-3MEEMT-Br with *i*-PrMgCl.LiCl in THF, $MgCl_2$ (1 eq), and quenched with dil HCl.

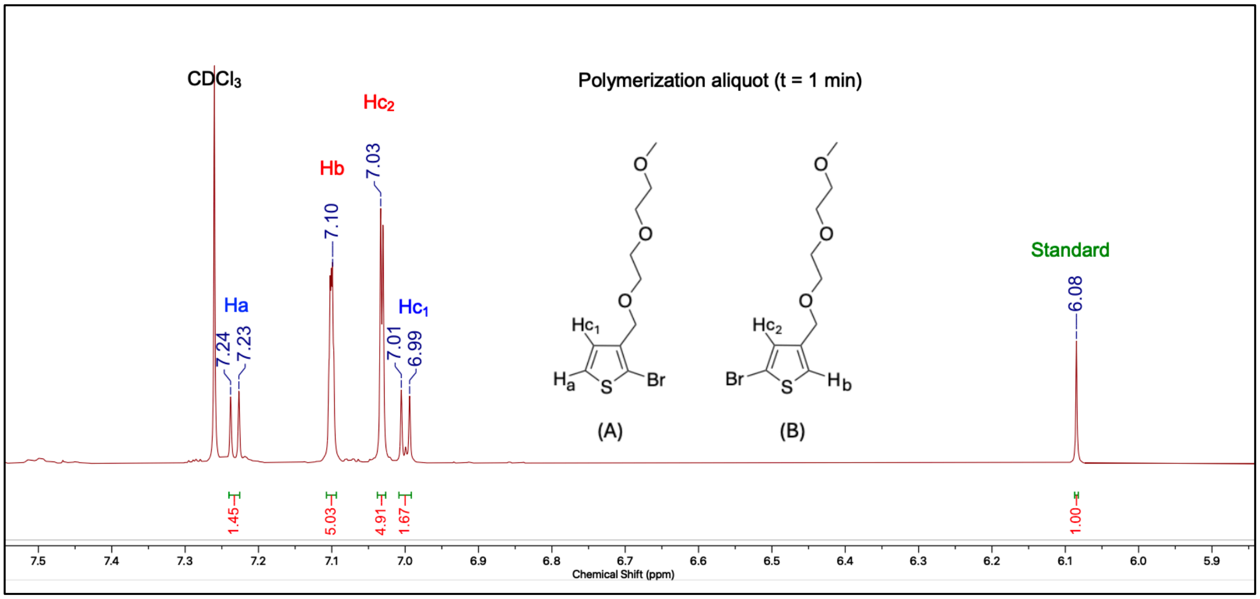

Fig. S26 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br, $MgCl_2$ (1 eq), (t = 1 min) with *i*-PrMgCl.LiCl used in the Grignard metathesis.

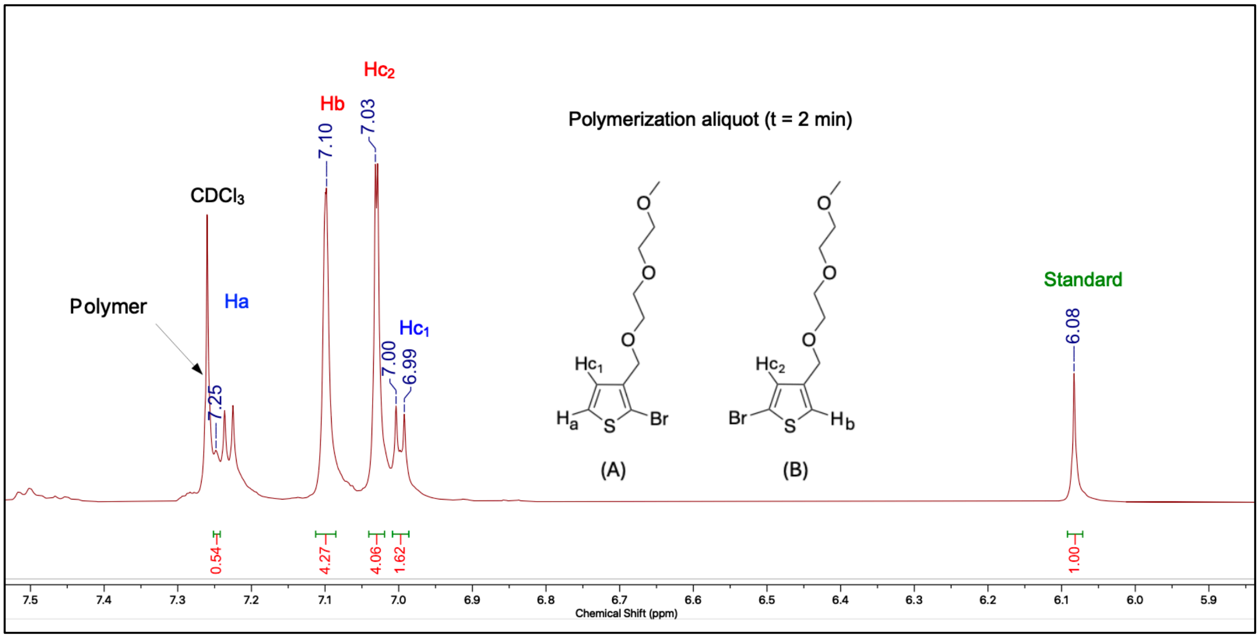

Fig. S27 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br, $MgCl_2$ (1 eq), (t = 2 min) with *i*-PrMgCl.LiCl used for Grignard metathesis.

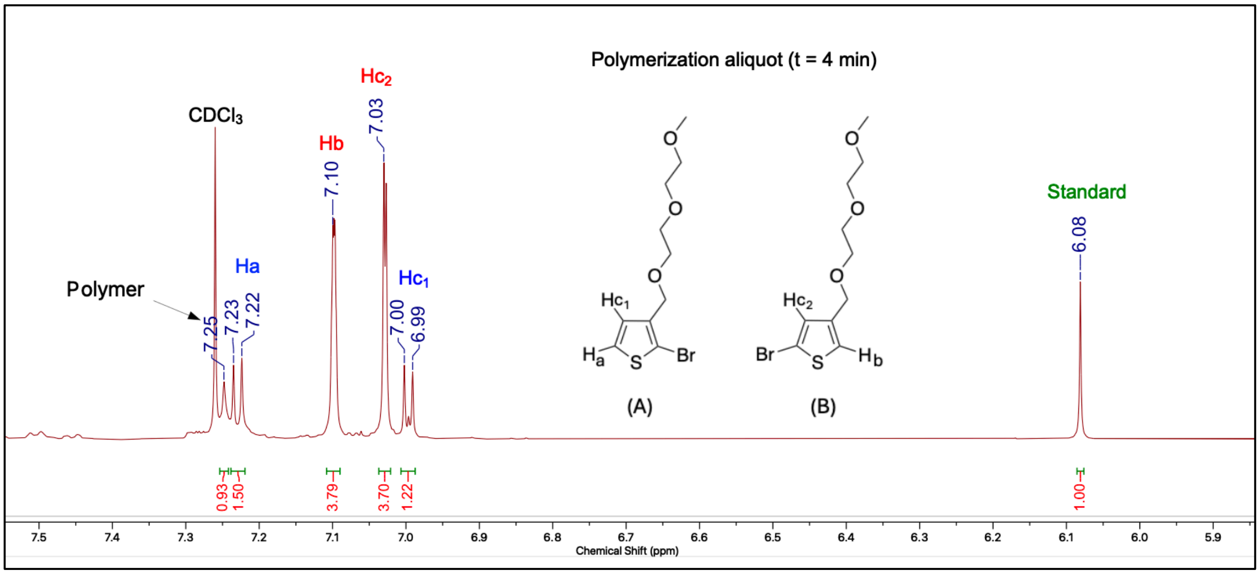

Fig. S28 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br, $MgCl_2$ (1 eq), (t = 4 min) with *i*-PrMgCl.LiCl used for Grignard metathesis.

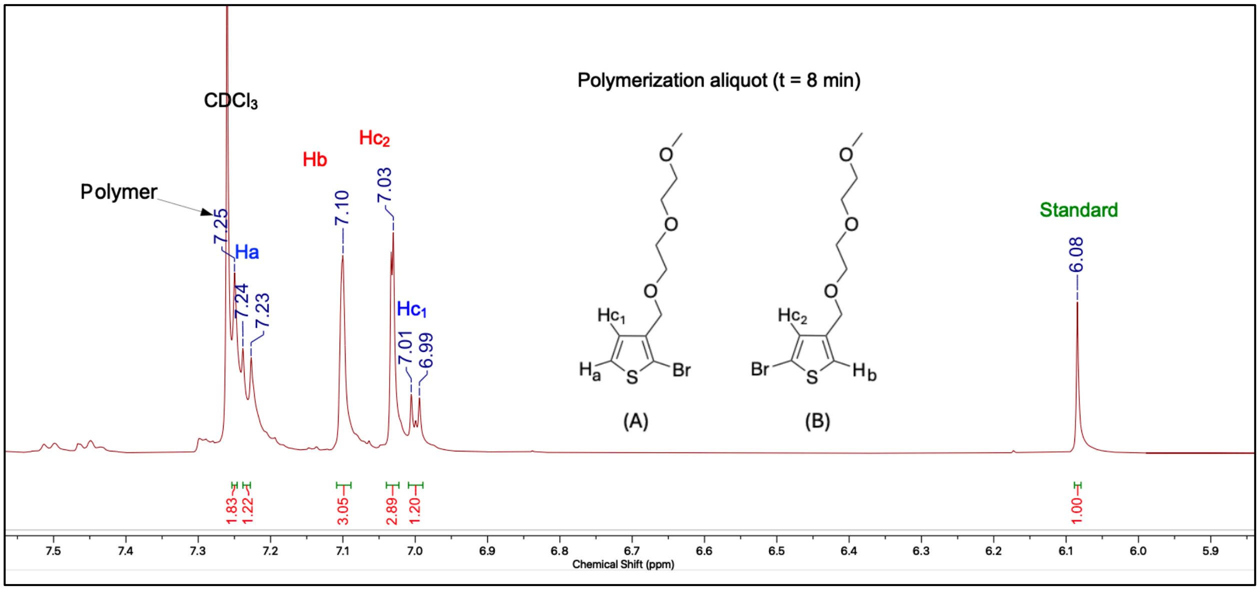

Fig. S29 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br, $MgCl_2$ (1 eq), (t = 8 min) with *i*-PrMgCl.LiCl used for Grignard metathesis.

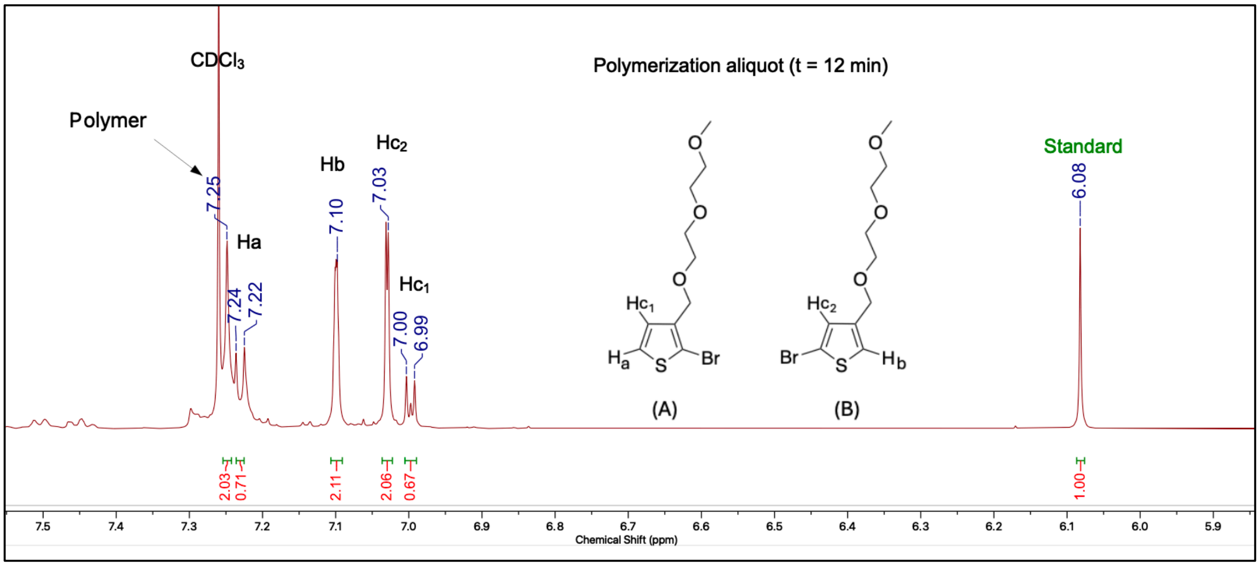

Fig. S30 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br, $MgCl_2$ (1 eq), (t = 12 min) with *i*-PrMgCl.LiCl used for Grignard metathesis.

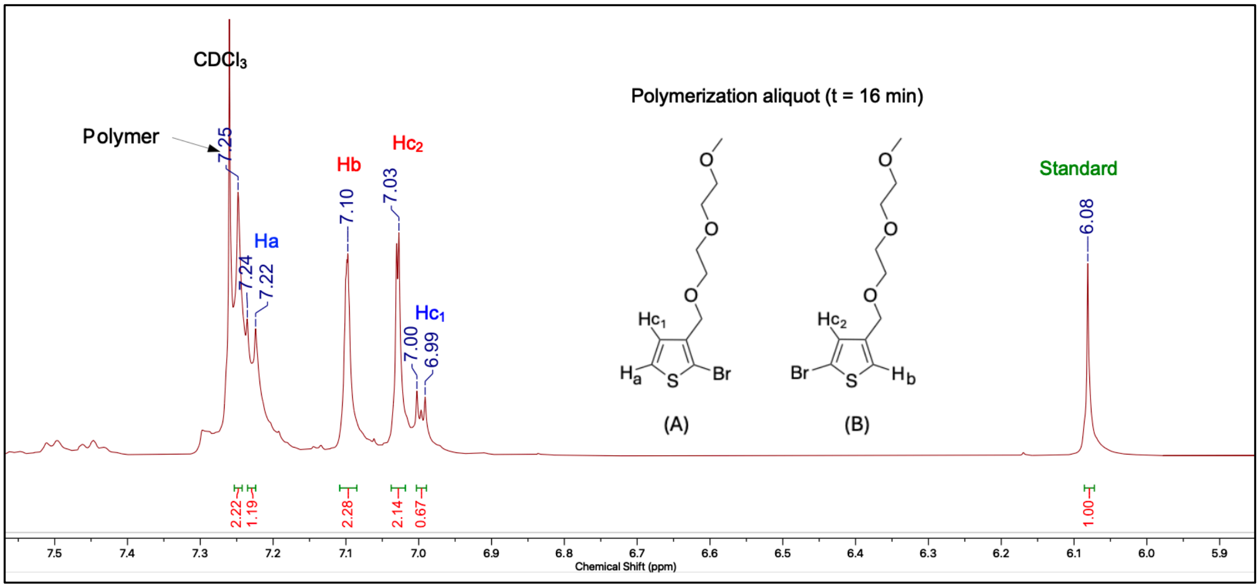

Fig. S31 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br, $MgCl_2$ (1 eq), (t = 16 min) with *i*-PrMgCl.LiCl used for Grignard metathesis.

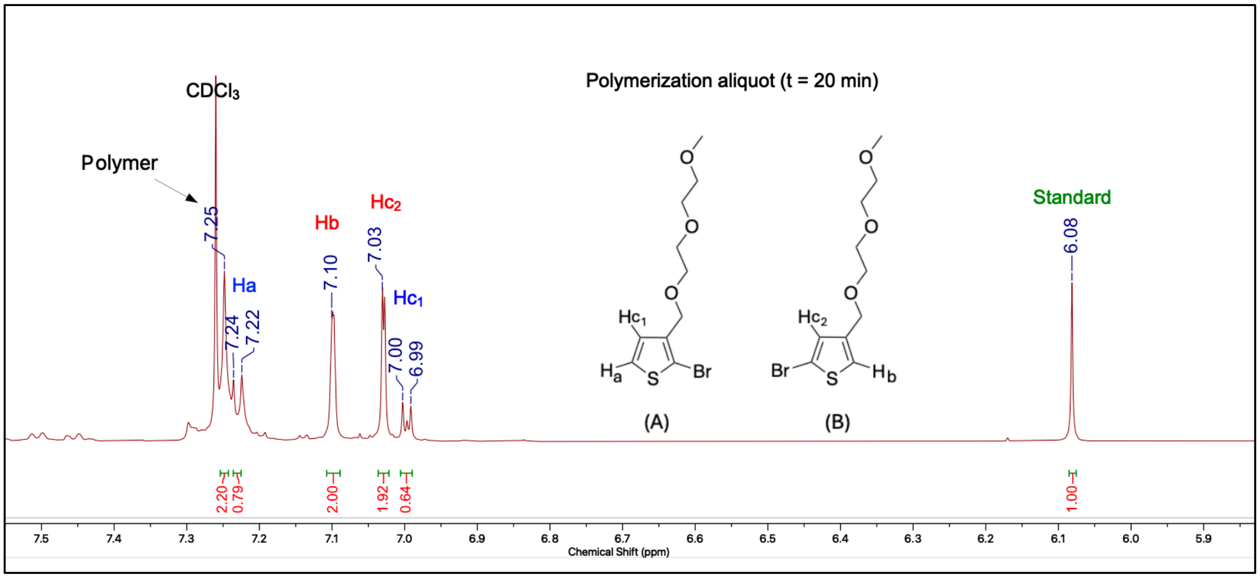

Fig. S32 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br, $MgCl_2$ (1 eq), (t = 20 min) with *i*-PrMgCl.LiCl used for Grignard metathesis.

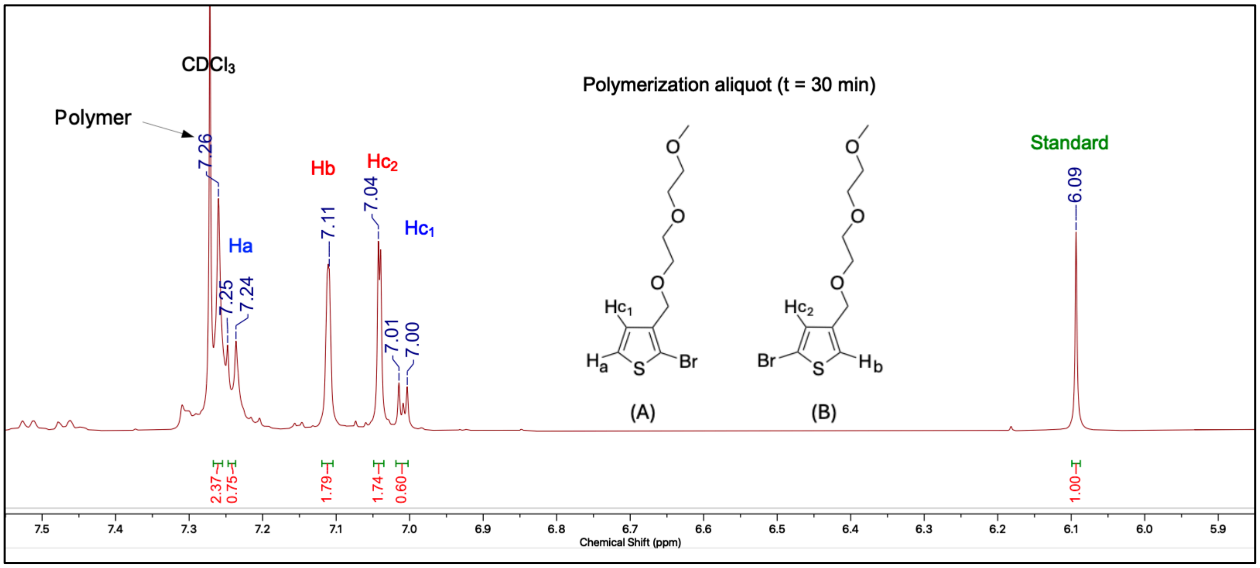

Fig. S33 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br, $MgCl_2$ (1 eq), (t = 30 min) with *i*-PrMgCl.LiCl used for Grignard metathesis.

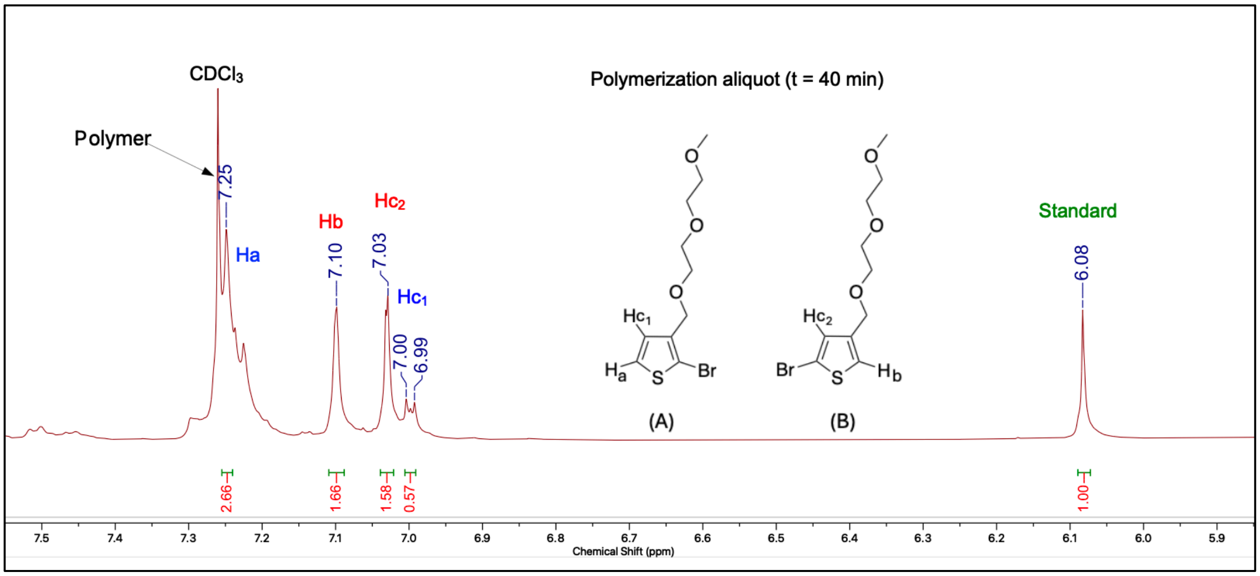

Fig. S34 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br, $MgCl_2$ (1 eq), (t = 40min) with *i*-PrMgCl.LiCl used for Grignard metathesis.

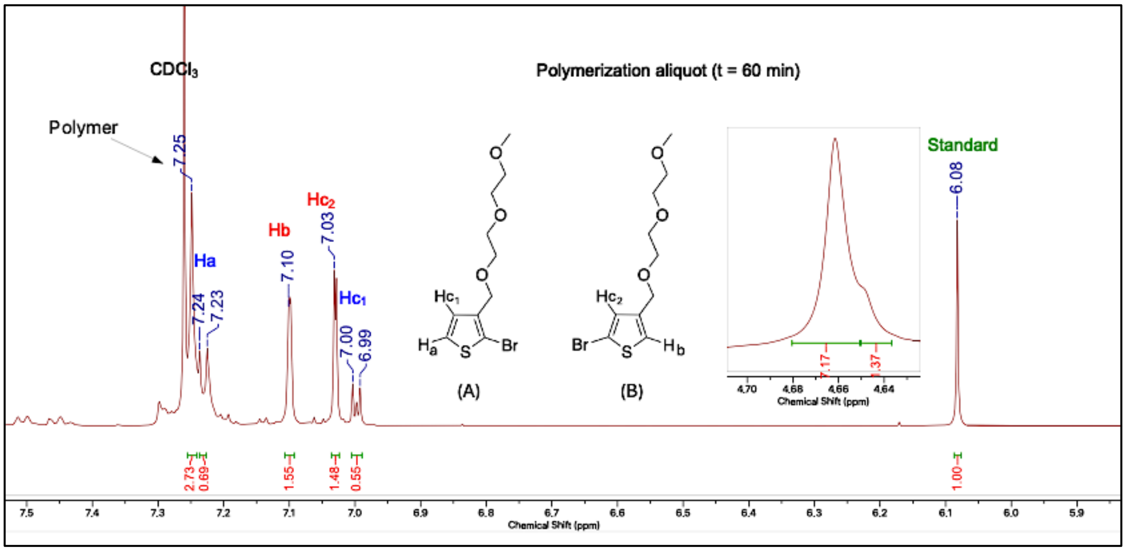

Fig. S35 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br, $MgCl_2$ (1 eq), (t = 60 min) with *i*-PrMgCl.LiCl used for Grignard metathesis.

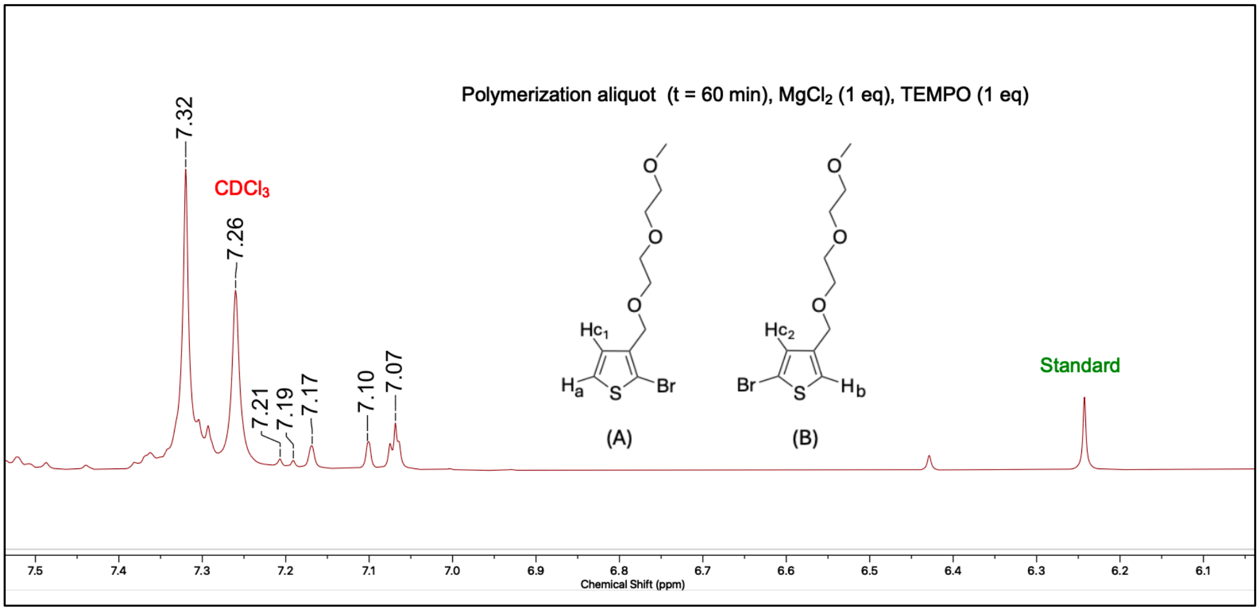

Fig. S36 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br, $MgCl_2$ (1 eq), TEMPO (1 eq) with *i*-PrMgCl.LiCl used for Grignard metathesis.

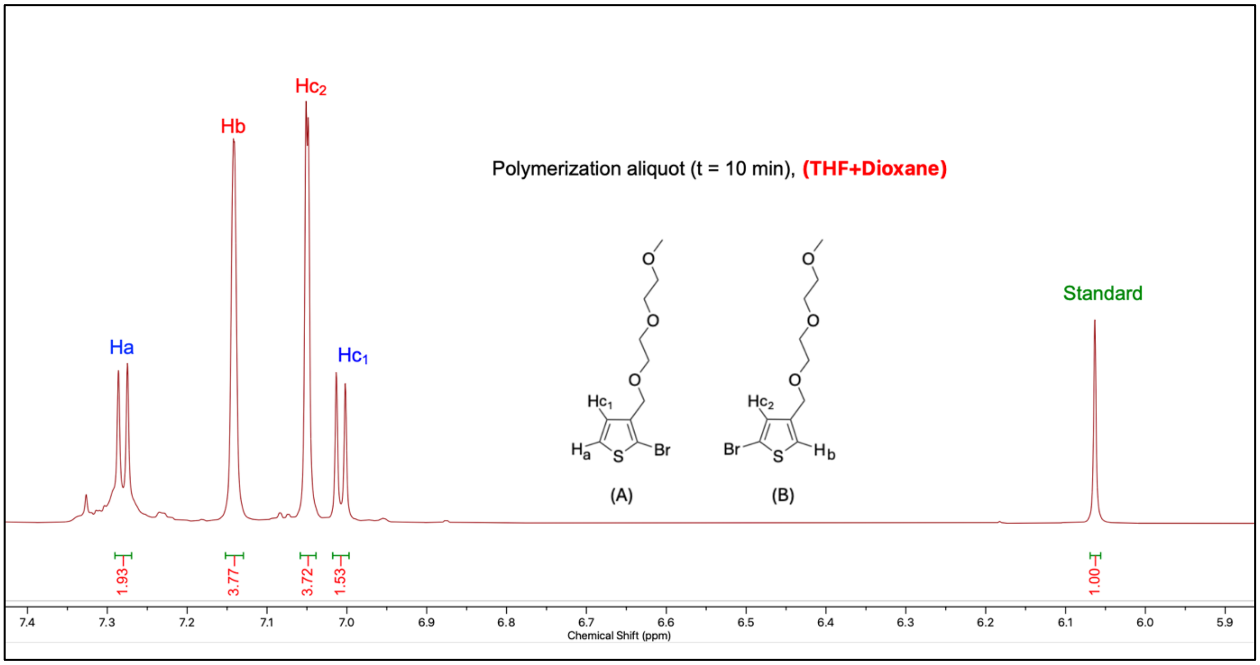

Fig. S37 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br in (THF+dioxane) (t = 10 min).

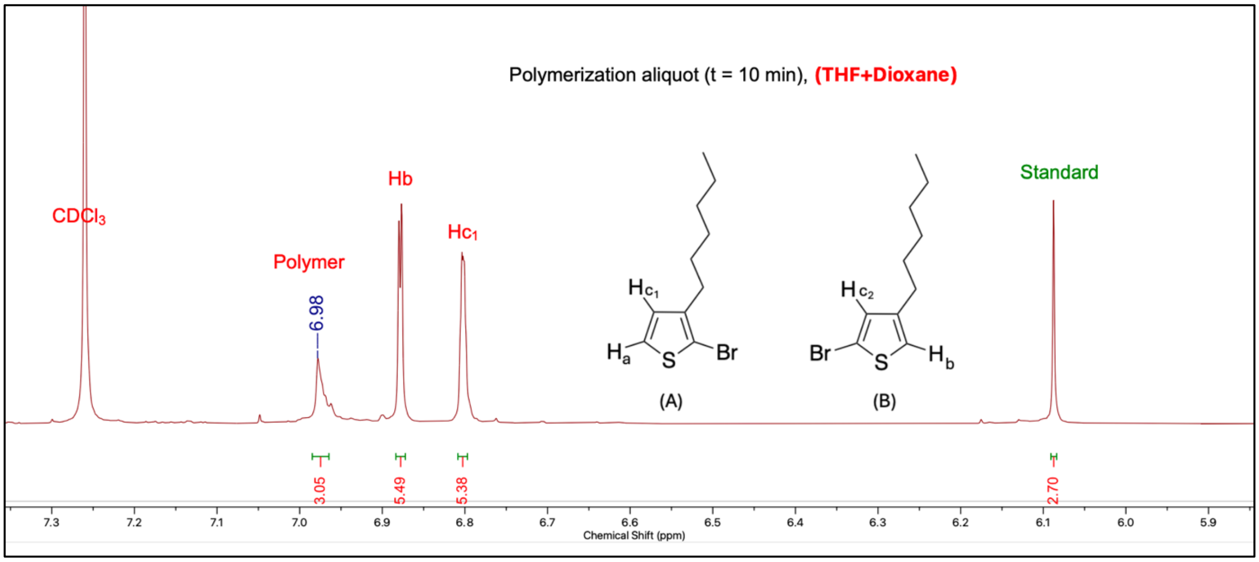

Fig. S38 ^{1}H NMR analysis of polymerization aliquot of Br-3HT-Br in (THF+dioxane) (t = 10 min).

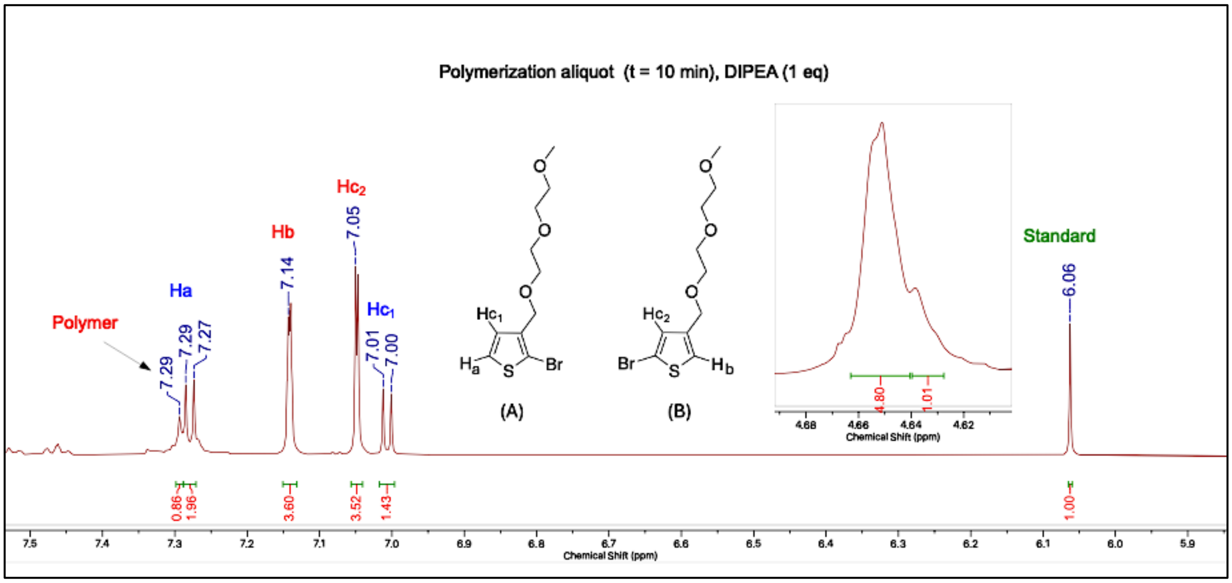

Fig. S39 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br (t = 10 min) with DIPEA (1 eq).

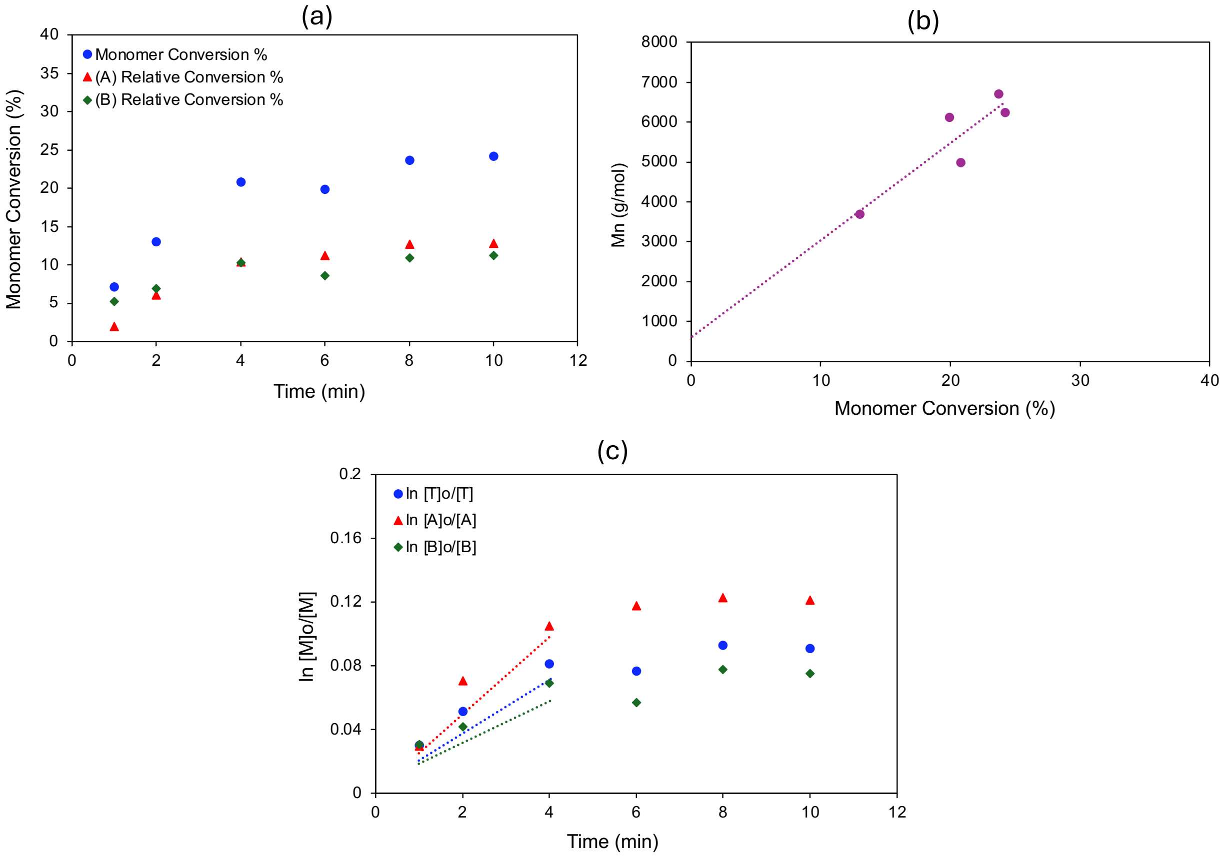

Fig. S40 a) Monomer conversion vs time, b) M_n vs monomer conversion, c) ln $[M]_0/[M]$ vs time, (*i*-PrMgCl.LiCl, DIPEA (1 eq).

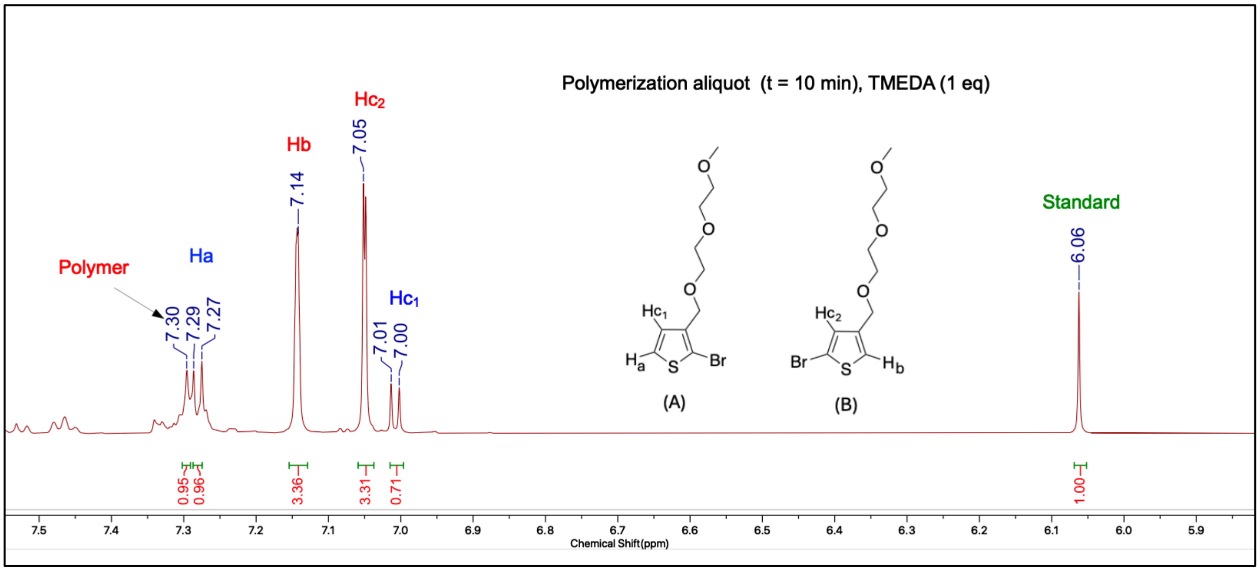

Fig. 41 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br (t = 10 min) with TMEDA (1 eq).

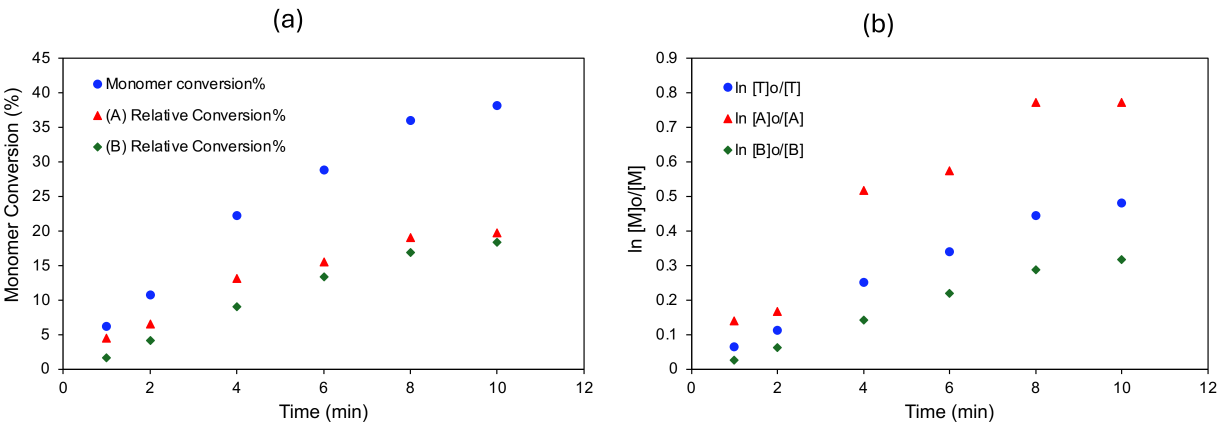

Fig. 42 a) Monomer conversion vs time, b) ln $[M]_0/[M]$ vs time, (*i*-PrMgCl.LiCl, TMEDA(1 eq).

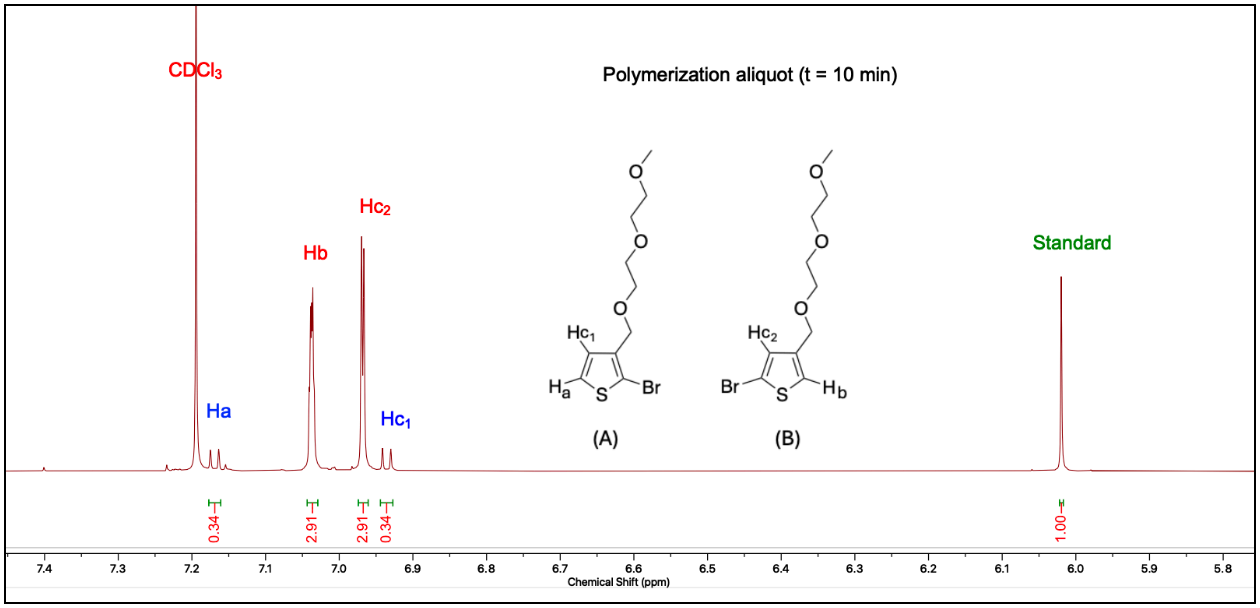

Fig. S43 ^{1}H NMR analysis of polymerization aliquot of Br-3MEEMT-Br (t = 10 min) in toluene and quenched with dil HCl.

3. GPC measurements

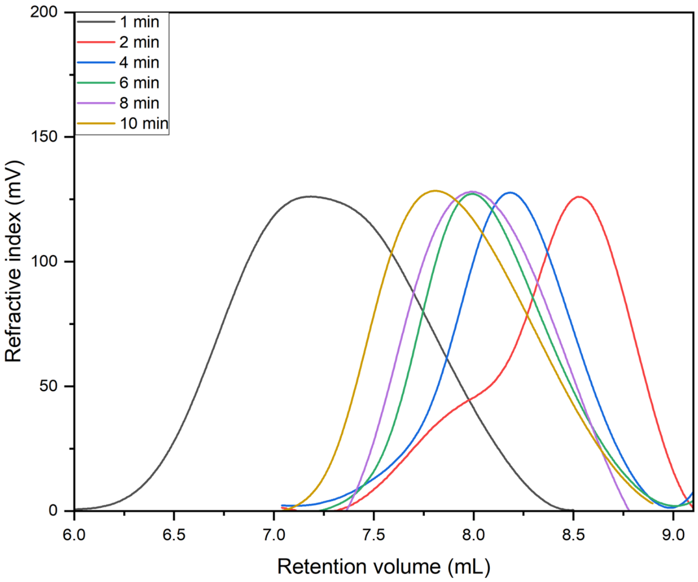

Fig. S44 GPC measurements of polymerization aliquots under standard conditions.

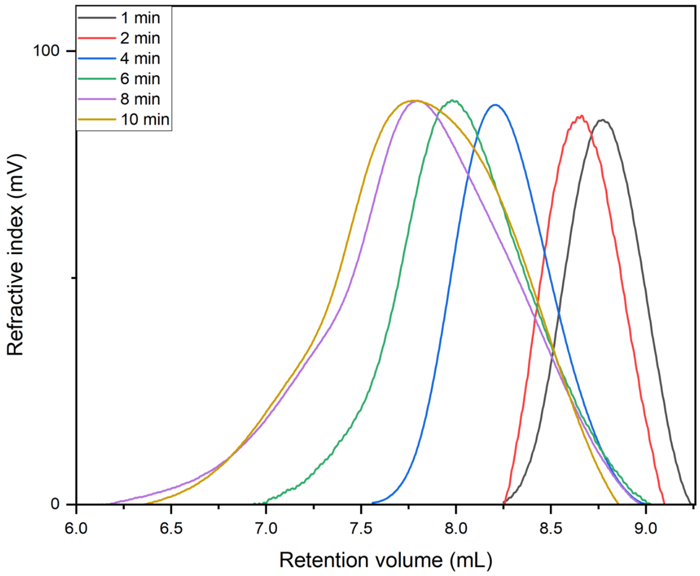

Fig. S45 GPC measurements of polymerization aliquots under dark conditions.

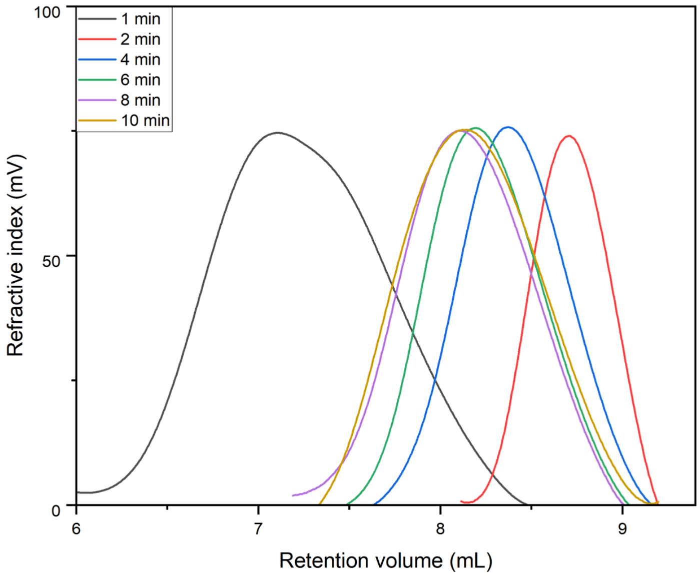

Fig. S46 GPC measurements of polymerization aliquots with DIPEA (1 eq) after the Grignard metathesis process.

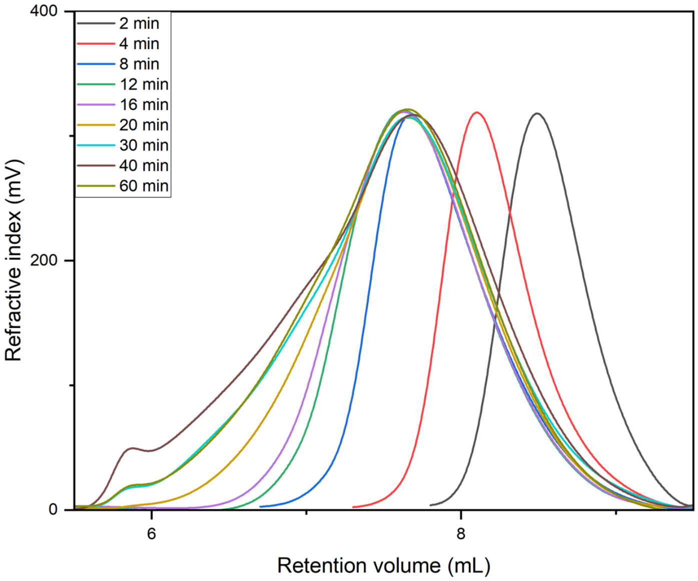

Fig. S47 GPC measurements of polymerization aliquots with $MgCl_2$ (1 eq) after the Grignard metathesis process.

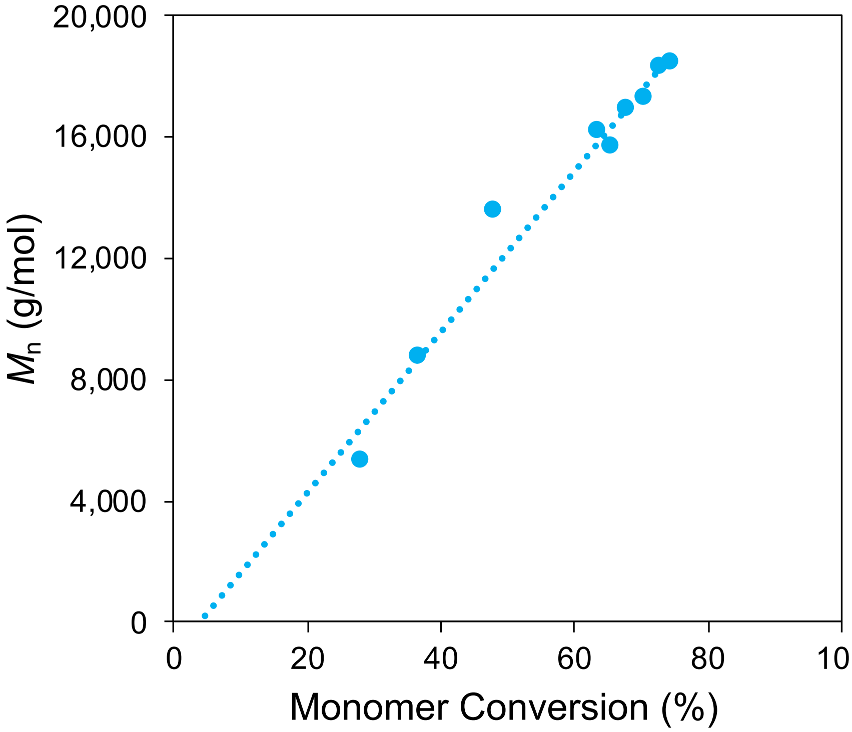

Fig. S48 M_n vs monomer conversion for polymerization conducted with $MgCl_2$ (1 eq) after the Grignard metathesis process.

Table S1 M_n and $Đ$ at different times for polymerization conducted with $MgCl_2$ (1 eq) after the Grignard metathesis process.

Time	2 min	4 min	8 min	12 min	16 min	20 min	30 min	40 min	60 min
M_n(g/mol)	5,300	8,800	13,600	15,700	16,200	16,900	17,300	18,300	18,500
$Đ$	1.19	1.24	1.41	1.51	1.59	1.94	2.54	3.04	2.42

4. References

1) S. Stoll and A. Schweiger, J. Magn. Reson., **2006**, 178, 42-55.
2) MATLAB (R2016b). Natick, Massachusetts: The MathWorks Inc.
3) A. Bakry, P. Yadav, S. Y. E. Chen, C. K. Luscombe, *Faraday Discuss.*, **2024**, 250, 74–82.