Supplementary Information (SI) for Polymer Chemistry.

Electronic Supplementary Information

Tandem Kumada–Tamao Catalyst-Transfer Condensation Polymerization and Suzuki–Miyaura Coupling for End-Functionalization and Block Copolymerization of Poly(*p*-phenylene)

Reo Nitto, Lisa Takimoto, Yu Tokita, Yoshihiro Ohta and Tsutomu Yokozawa*
Department of Materials and Life Chemistry, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan. E-mail: yokozt01@kanagawa-u.ac.jp

Table of contents

1. Materials

All starting materials were purchased from commercial suppliers (TCI, Aldrich, Wako, Kanto, and BLD Pharmatech Ltd.) and used without further purification. Commercially available dehydrated tetrahydrofuran (THF, stabilizer-free, Kanto) was used as dry solvents. *i*-PrMgCl (2.0 M solution in THF) and PEPPSI-IPr were purchased from Aldrich Inc. and used as received. 4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (**2a**), (4-methoxyphenyl)boronic acid (**2b**), methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**2c**), (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol (**2d**), and (4-vinylphenyl)boronic acid (**2f**) were purchased from TCI and used as received. *tert*-Butyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)carbamate (**2e**) was purchased from BLD Pharmatech Ltd. and used as received. 1,4-Dibromo-2,5-bis(hexyloxy)benzene,[1] 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl 2-bromo-2-methylpropanoate (**2g**),[2] 2-(5-bromo-4-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3a**),[3] and 2-(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3b**)[4] were synthesized according to literatures.

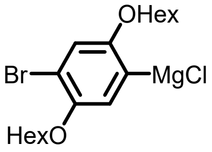
2. General

^{1}H and ^{13}C NMR spectra were obtained on JEOL ECA-600 spectrometers. The internal standard for ^{1}H NMR spectra in $CDCl_3$ was tetramethylsilane (0.00 ppm) and the internal standard for ^{13}C NMR spectra in $CDCl_3$ was the midpoint of $CDCl_3$ (77.0 ppm). IR spectra were recorded on a JASCO FT/IR-4600AC. All melting points were measured with a Yanagimoto hot stage melting point apparatus without correction. Column chromatography was performed on silica gel (Kieselgel 60, 230–400 mesh, Merck) with a specified solvent. The M_n and M_w/M_n values of polymer were measured with a Tosoh HLC-8320 gel permeation chromatography unit (GPC; eluent, chloroform; calibration, polystyrene standards) with two TSK-gel columns (2 × Multipore HZ-M). MALDI-TOF mass spectra were recorded on a Shimazu/Biotech AXIMA-Confidence in the reflectron ion mode by use of a laser (λ = 337 nm). DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) was used as the matrix for the MALDI-TOF mass measurements. The conversion of **1** was determined by analytical GC performed on a Shimadzu GC-2010 plus gas chromatograph equipped with a Restek dimethypolylsiloxane fluid Rtx-1 column (15 m) and a flame ionization detector.

3. Polymerization

3-1 Synthesis of Grignard monomer **1**

Addition of reagents into a reaction flask was carried out via a syringe from a three-way stopcock under a stream of nitrogen. A round-bottomed flask was flame-dried, and the atmosphere was replaced with argon. 1,4-Dibromo-2,5-bis(hexyloxy)benzene (508.7 mg, 1.166 mmol) and 2-ethoxynaphthalene (58.96 mg, 0.3423 mmol) as an internal standard were placed in the flask, and the atomosphere was replaced with argon. A small amount of the solution was taken from the reaction flask and analyzed by GC. Dry THF (1.2 mL) was added, and the solution was cooled to 0 °C. *i*-PrMgCl (2.0 M in THF) (0.50 mL, 1.0 mmol) was added dropwise, and the mixture was stirred at room temprature for 24 h, yielding a solution of (4-bromo-2,5-bis(hexyloxy)phenyl)magnesium chloride (**1**).



1

3-2 General procedure for polymerization

End-capping of **poly1** ([**1**]$_0$/[PEPPSI-IPr]$_0$ = 20)

Addition of reagents into a reaction flask was carried out via a syringe from a three-way stopcock under a stream of nitrogen. A round-bottomed flask was flame-dried, and the atmosphere was replaced with argon. PEPPSI-IPr (0.00592 mmol) was placed in a round-bottom flask, and the atomosphere was replaced with argon. Dry THF (0.4 mL) was added, and the solution was degassed with argon. Grignard monomer **1** (0.6 M solution in THF, 0.12 mmol) was added via a syringe and stirred at room temperature for 30 min. Ar-BPin **2** (0.0709 mmol) and K_3PO_4 (0.2833 mmol) were placed in another flask, and the atmosphere in the flask was replaced with argon. Dry THF (2.0 mL) and distilled water (0.2 mL) were added to the flask via a syringe, and the mixture was degassed with argon. The mixture of Ar-BPin and K_3PO_4 in dry THF and distilled water was added to the above reaction mixture via a cannula, and the reaction mixture was stirred at room temperature for 24 h. The reaction was quenched with 6 M hydrochloric acid, and the mixture was extracted with $CHCl_3$ and washed with brine. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was dissolved in a small amount of chloroform, followed by precipitation into a large amount of methanol to give **poly1** as a white solid.

Synthesis of block copolymer ([**1**]$_0$/[PEPPSI-IPr]$_0$ = 10, [**3**]$_0$/[PEPPSI-IPr]$_0$ = 10)

Addition of reagents into a reaction flask was carried out via a syringe from a three-way stopcock under a stream of nitrogen. A round-bottomed flask was flame-dried, and the atmosphere was replaced with argon. PEPPSI-IPr (0.01083 mmol) was placed in a round-bottom flask, and the atomosphere was replaced with argon. Dry THF (0.34 mL) was added, and the solution was degassed with argon. Grignard monomer **1** (0.6 M solution in THF, 0.12 mmol) was added via a syringe and stirred at room temperature for 30 min. Br-Ar-BPin **3** (0.01083 mmol) and K_3PO_4 (0.4329 mmol) were placed in another flask, and the atmosphere in the flask was replaced with argon. Dry THF (2.0 mL) and distilled water (0.2 mL) were added to the flask via a syringe, and the mixture was degassed with argon. The mixture of Ar-BPin and K_3PO_4 in dry THF and distilled water was added to the above reaction mixture via a cannula, and the reaction mixture was stirred at room temperature for 24 h. The reaction was quenched with 6 M hydrochloric acid, and the mixture was extracted with $CHCl_3$ and washed with brine. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give polymer.

3-3 GPC elution curves

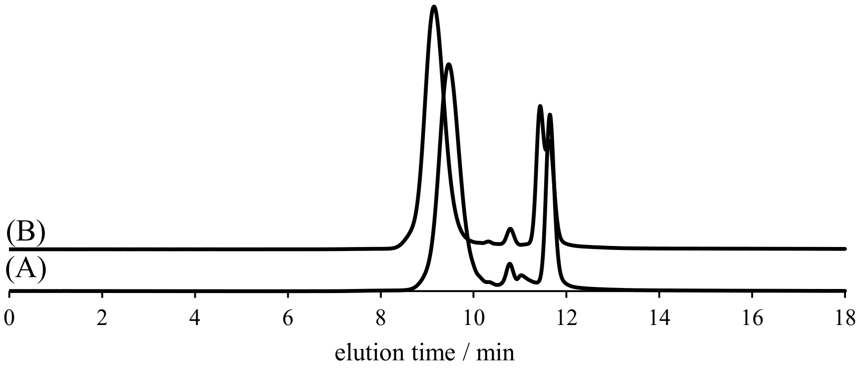


Fig. S1 GPC profiles of （A） **poly1** (M_n = 2790, M_w/M_n = 1.23), obtained by Kumada-Tamao CTCP of **1** with 10 mol% of Pd-PEPPSI-IPr at rt for 3.5 h, and (B) block copolymer (M_n = 4750, M_w/M_n = 1.19), obtained by successive Kumada-Tamao CTCP of equimolar **4** at rt for 2 h.

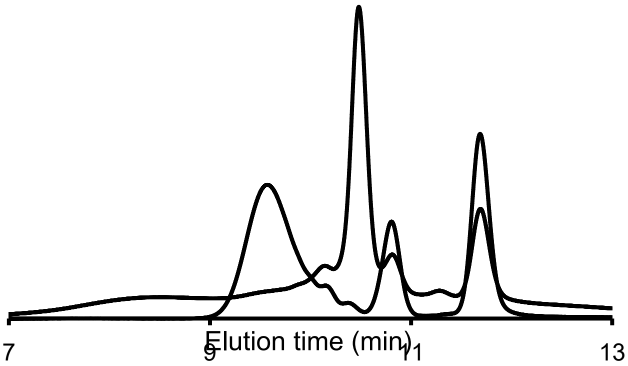


Fig. S2. GPC profiles of **poly1** (dashed line, M_n = 2180, M_w/M_n = 1.25), obtained by Kumada-Tamao CTCP of **1** with 10 mol% of PEPPSI-IPr at rt for 30 min, and products (solid line, M_n = 17270, M_w/M_n = 2.39), obtained by successive Suzuki-Miyaura polymerization of equimolar **3b** in the presence of K_3PO_4 in H_2O/THF (= 0.1 (v/v)) at rt for 1 day.

3-4 MALDI-TOF mass spectra

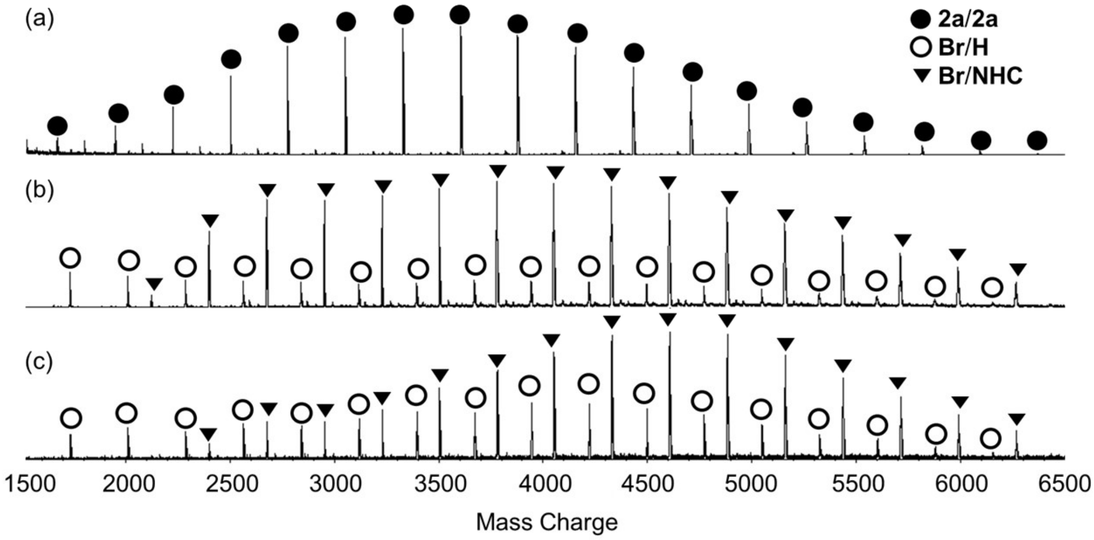


Fig. S3. MALDI-TOF mass spectra of (a) **poly1** with **2a**/**2a** ends (M_n = 5270, M_w/M_n = 1.17), (b) **poly1** with Br/NHC ends (M_n = 5500, M_w/M_n = 1.33), and (c) a mixture of the same amount of **poly1** with Br/NHC ends and **poly1** with **2a**/**2a** ends.

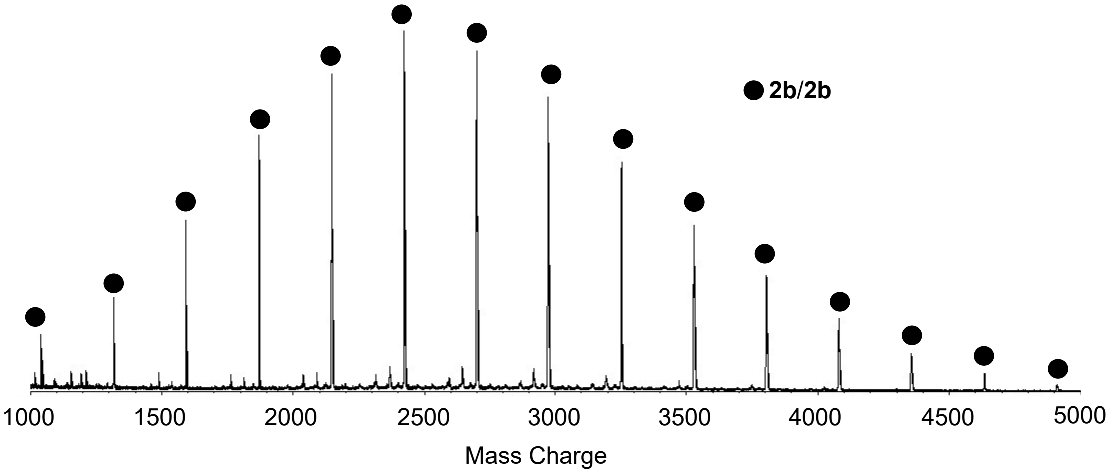


Fig. S4. MALDI-TOF mass spectrum of the products, obtained by Kumada-Tamao CTCP of **1** with 5 mol% of PEPPSI-IPr in THF at rt for 30 min, followed by Suzuki-Miyaura coupling with 60 mol% of **2b** and K_3PO_4 in water/THF at rt for 24 h.

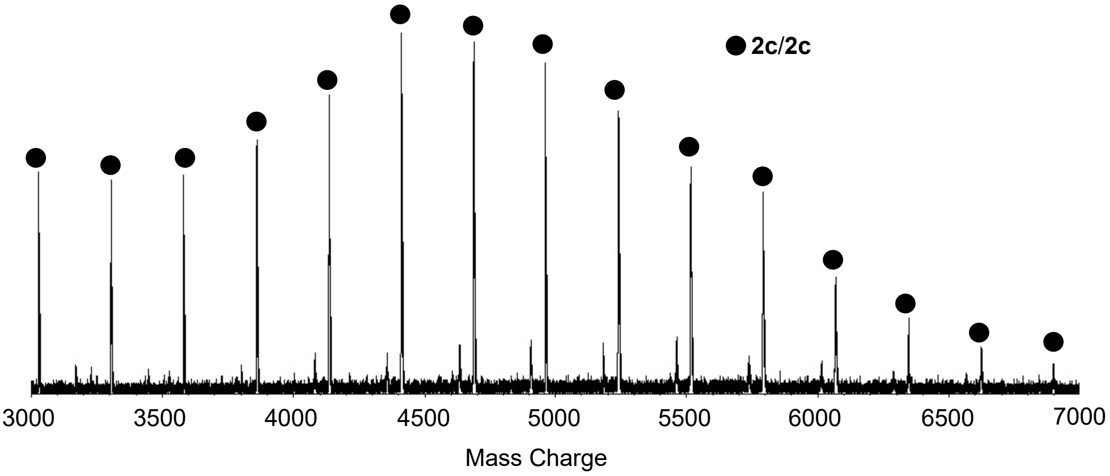


Fig. S5. MALDI-TOF mass spectrum of the products, obtained by Kumada-Tamao CTCP of **1** with 5 mol% of PEPPSI-IPr in THF at rt for 30 min, followed by Suzuki-Miyaura coupling with 60 mol% of **2c** and K_3PO_4 in water/THF at rt for 24 h.

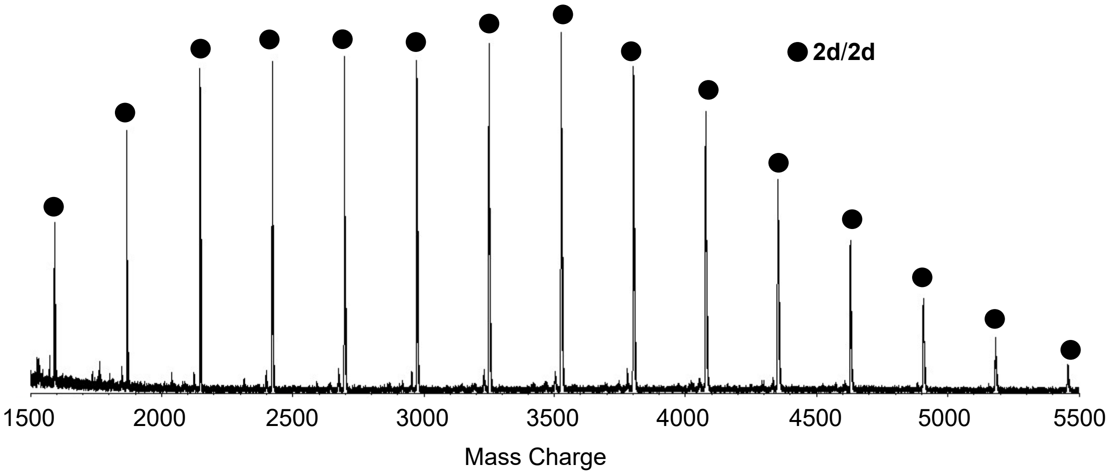


Fig. S6. MALDI-TOF mass spectrum of products, obtained by Kumada-Tamao CTCP of **1** with 5 mol% of PEPPSI-IPr in THF at rt for 30 min, followed by Suzuki-Miyaura coupling with 60 mol% of **2d** and K_3PO_4 in water/THF at rt for 24 h.

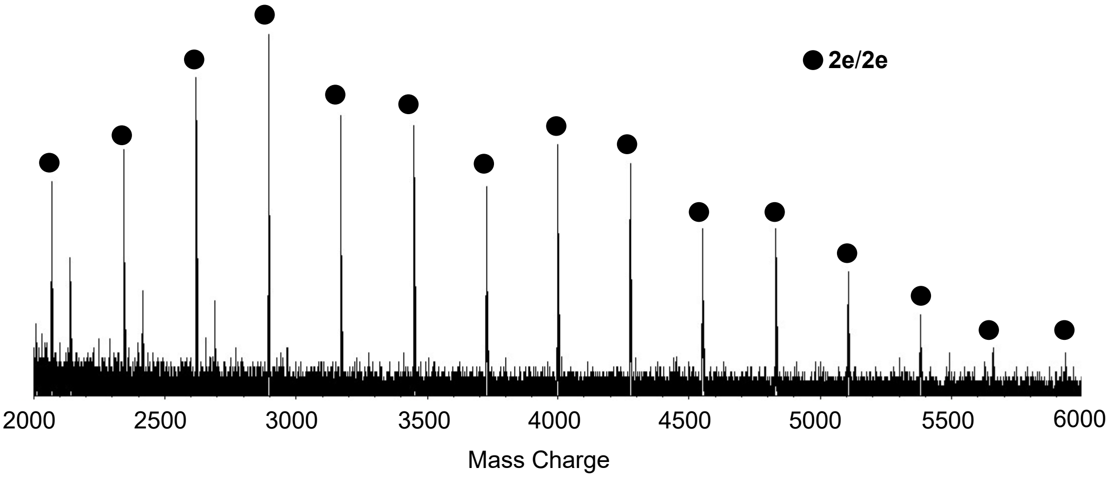


Fig. S7. MALDI-TOF mass spectrum of the products, obtained by Kumada-Tamao CTCP of **1** with 5 mol% of PEPPSI-IPr in THF at rt for 30 min, followed by Suzuki-Miyaura coupling with 60 mol% of **2e** and K_3PO_4 in water/THF at rt for 24 h.

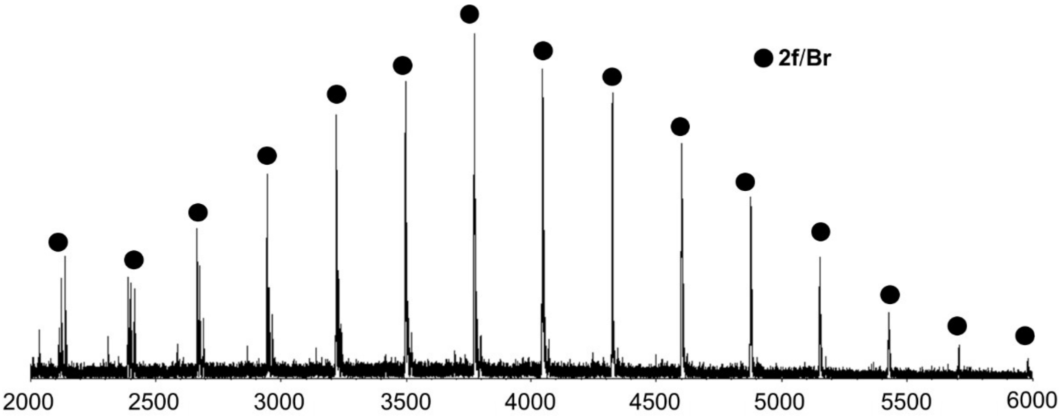


Fig. S8. MALDI-TOF mass spectrum of the products, obtained by Kumada-Tamao CTCP of **1** with 5 mol% of PEPPSI-IPr in THF at rt for 30 min, followed by Suzuki-Miyaura coupling with 60 mol% of **2f** and K_3PO_4 in water/THF at rt for 24 h.

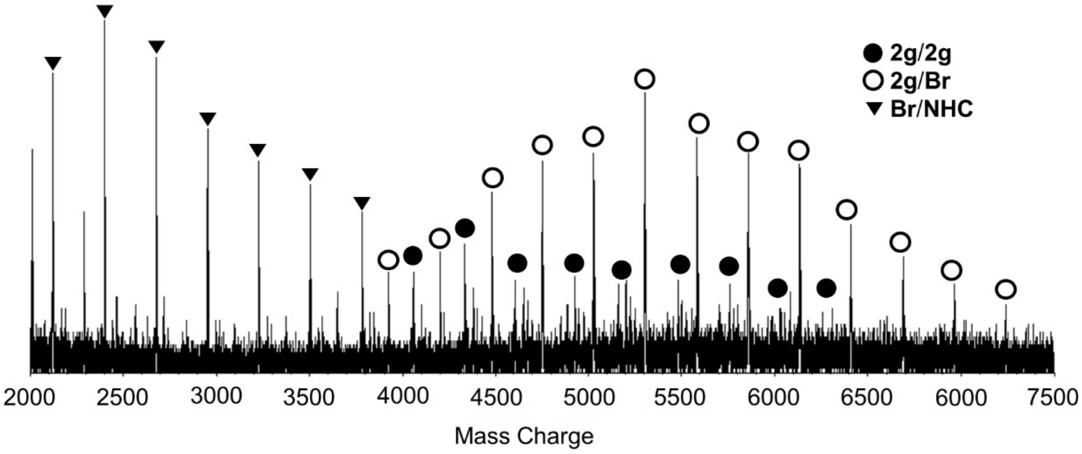


Fig. S9. MALDI-TOF mass spectrum of the products, obtained by Kumada-Tamao CTCP of **1** with 5 mol% of PEPPSI-IPr in THF at rt for 30 min, followed by Suzuki-Miyaura coupling with 60 mol% of **2g** and K_3PO_4 in water/THF at rt for 24 h.

3-5 ^{1}H NMR spectra

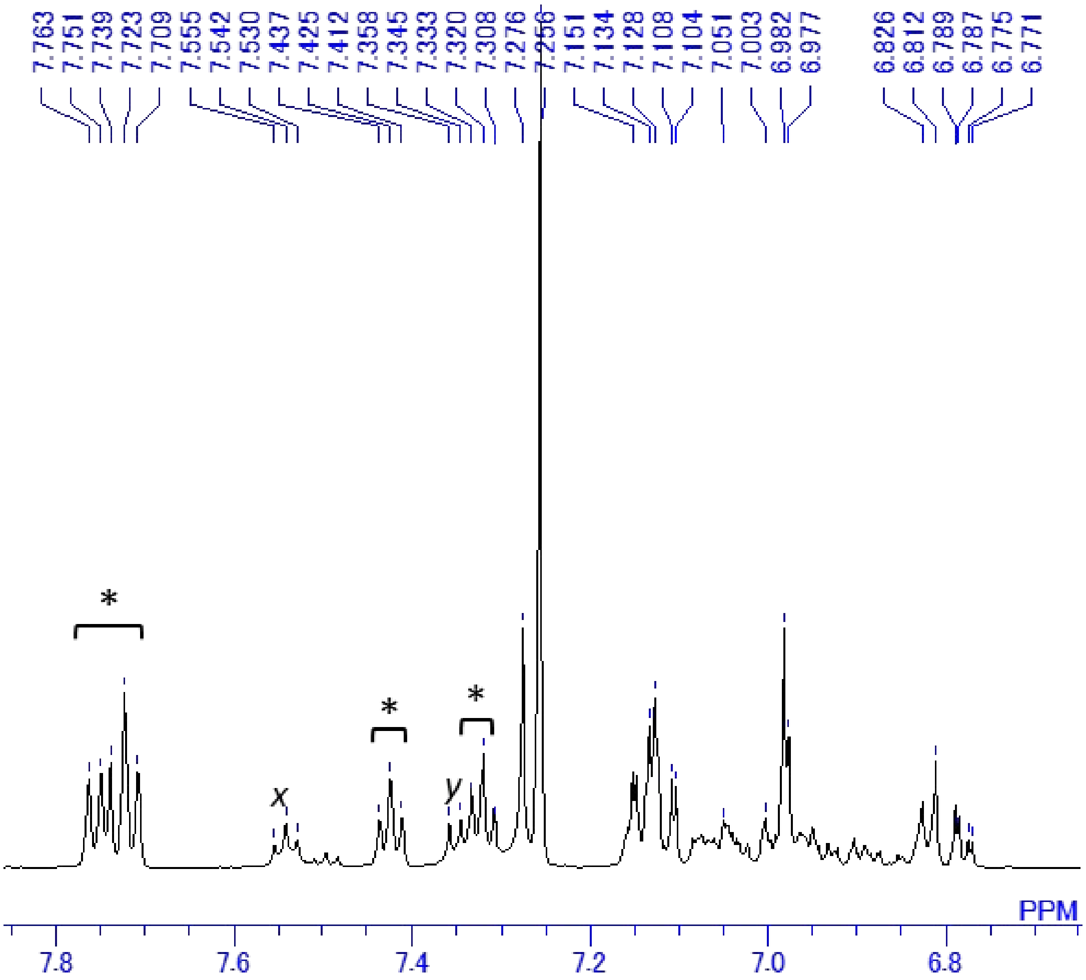


Fig. S10. ^{1}H NMR spectrum of the products, obtained by Kumada-Tamao CTCP of **1** with 20 mol% of PEPPSI-IPr in THF at rt for 1 h. * 3-ethoxynaphthalene as an internal standard for estimation of the conversion of monomers.

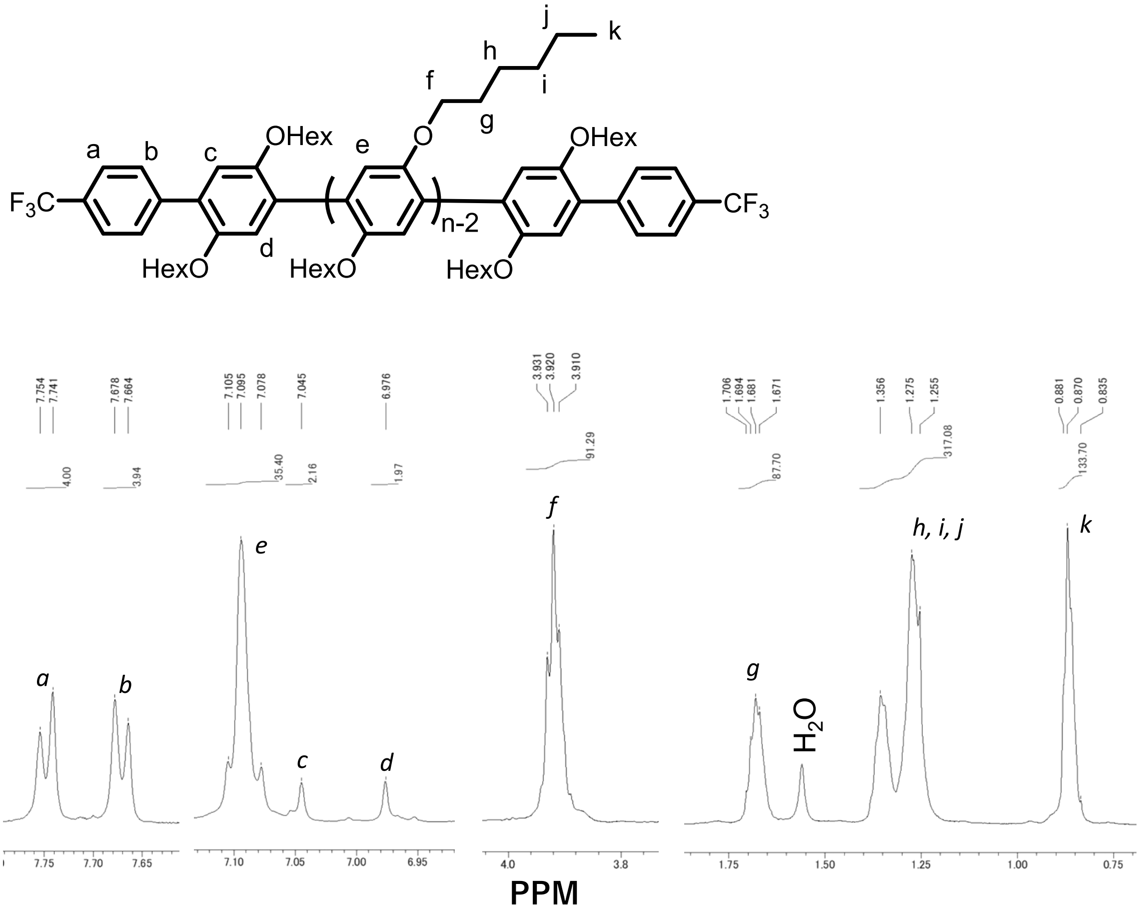


Fig. S11. ^{1}H NMR spectrum of the products, obtained by Kumada-Tamao CTCP of **1** with 5 mol% of PEPPSI-IPr in THF at rt for 30 min, followed by Suzuki-Miyaura coupling with 60 mol% of **2a** and K_3PO_4 in water/THF at rt for 24 h.

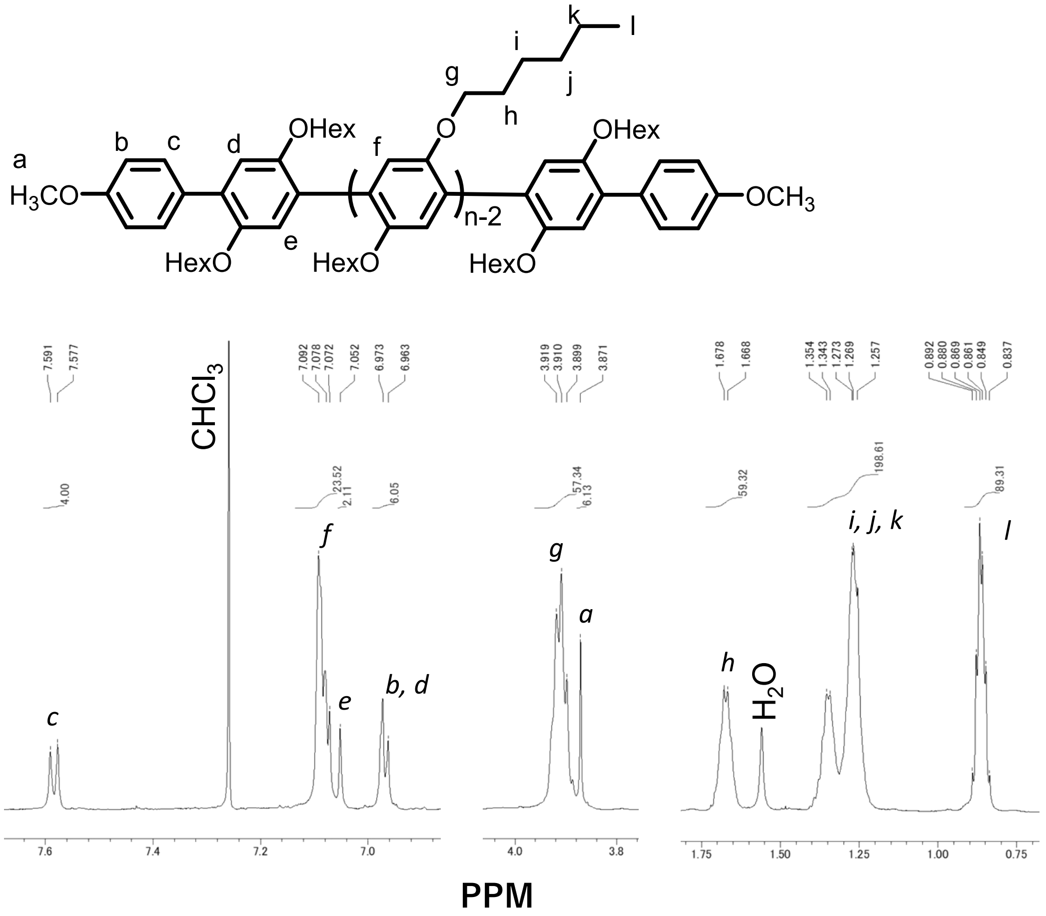


Fig. S12. ^{1}H NMR spectrum of the products, obtained by Kumada-Tamao CTCP of **1** with 5 mol% of PEPPSI-IPr in THF at rt for 30 min, followed by Suzuki-Miyaura coupling with 60 mol% of **2b** and K_3PO_4 in water/THF at rt for 24 h.

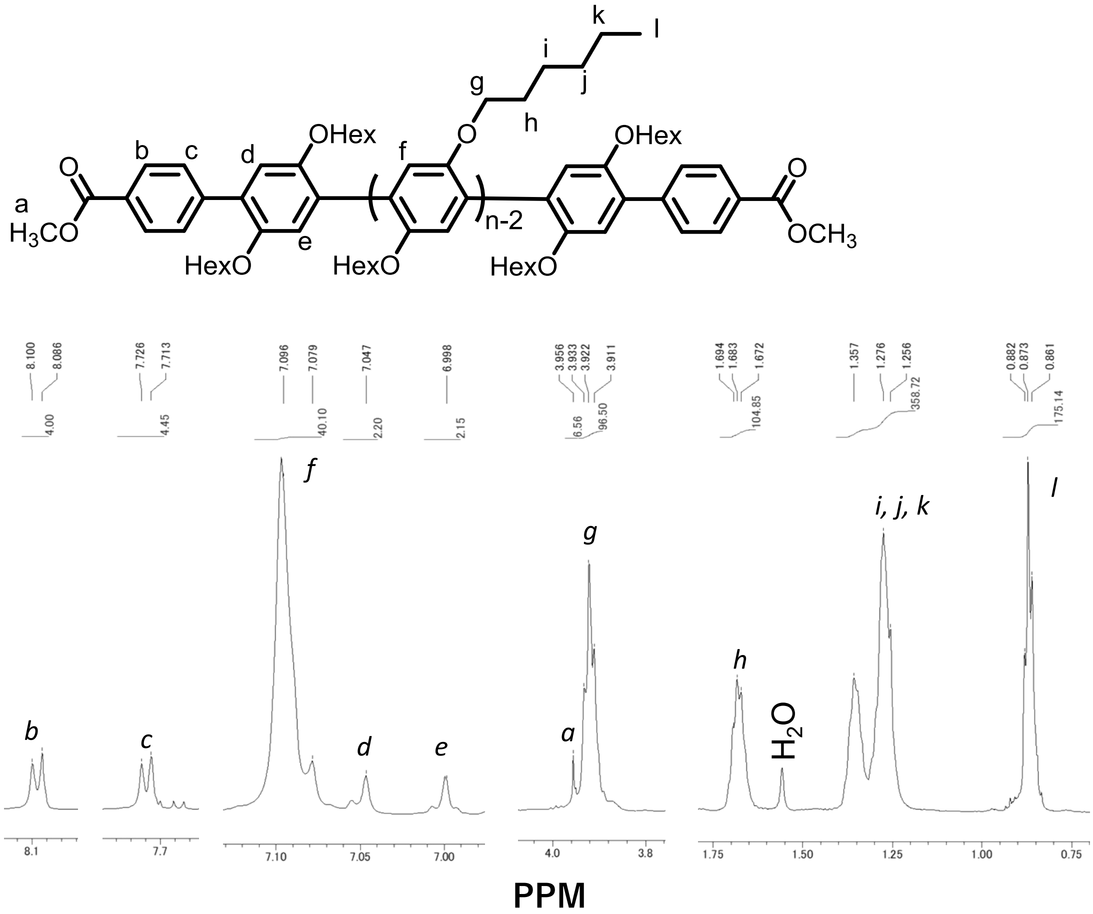


Fig. S13. ^{1}H NMR spectrum of the products, obtained by Kumada-Tamao CTCP of **1** with 5 mol% of PEPPSI-IPr in THF at rt for 30 min, followed by Suzuki-Miyaura coupling with 60 mol% of **2c** and K_3PO_4 in water/THF at rt for 24 h.

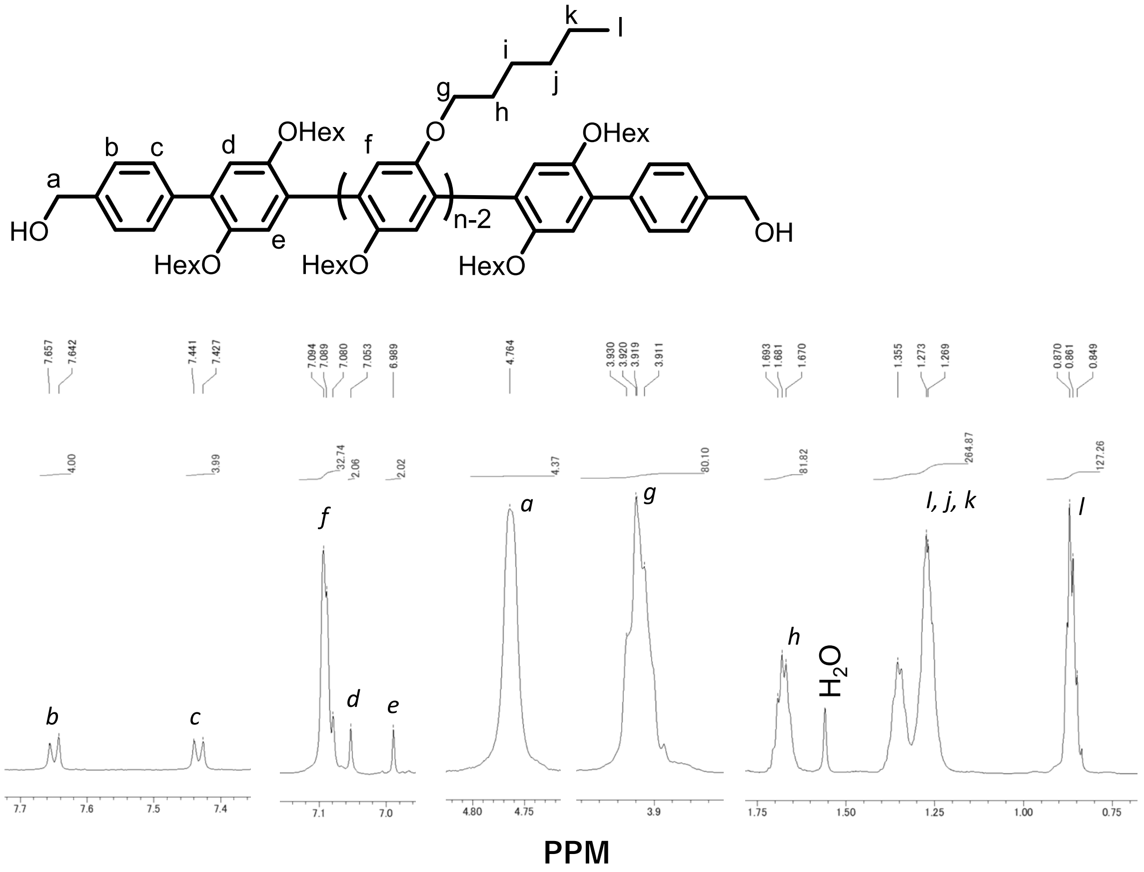


Fig. S14. ^{1}H NMR spectrum of the products, obtained by Kumada-Tamao CTCP of **1** with 5 mol% of PEPPSI-IPr in THF at rt for 30 min, followed by Suzuki-Miyaura coupling with 60 mol% of **2d** and K_3PO_4 in water/THF at rt for 24 h.

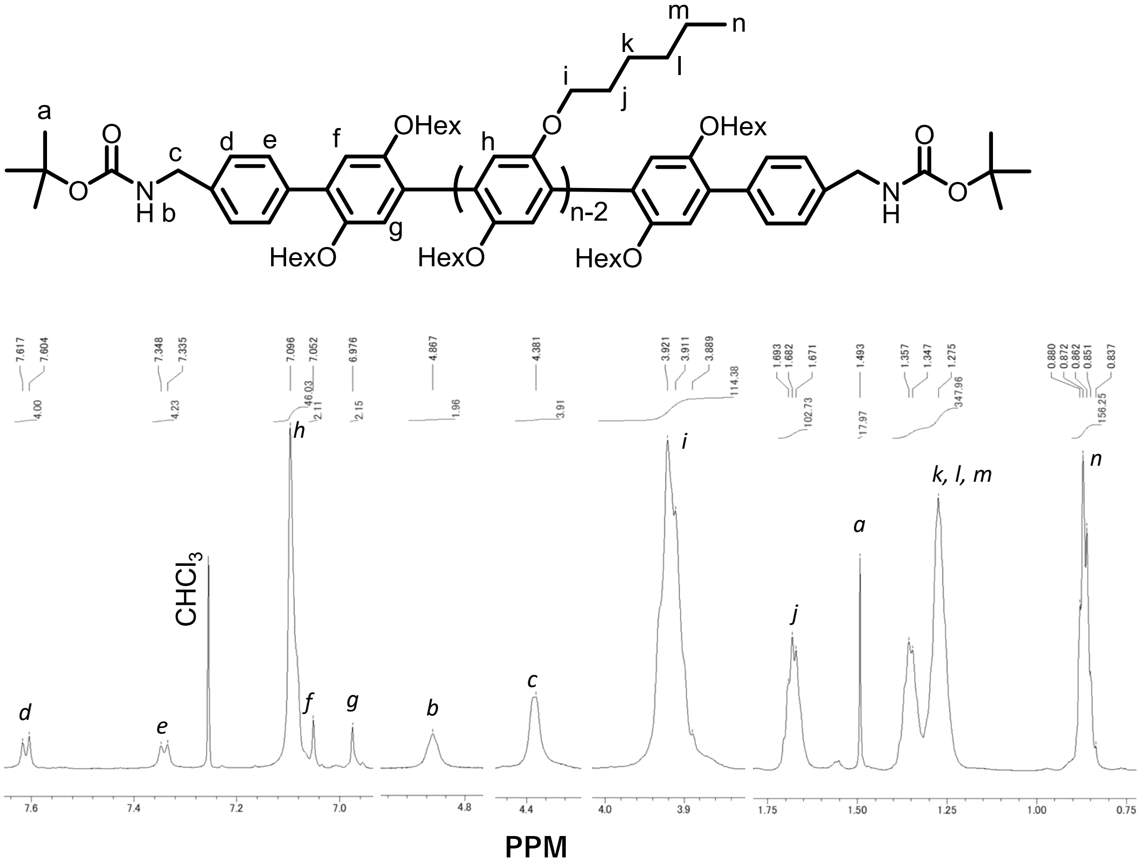


Fig. S15. ^{1}H NMR spectrum of products, obtained by Kumada-Tamao CTCP of **1** with 5 mol% of PEPPSI-IPr in THF at rt for 30 min, followed by Suzuki-Miyaura coupling with 60 mol% of **2e** and K_3PO_4 in water/THF at rt for 24 h.

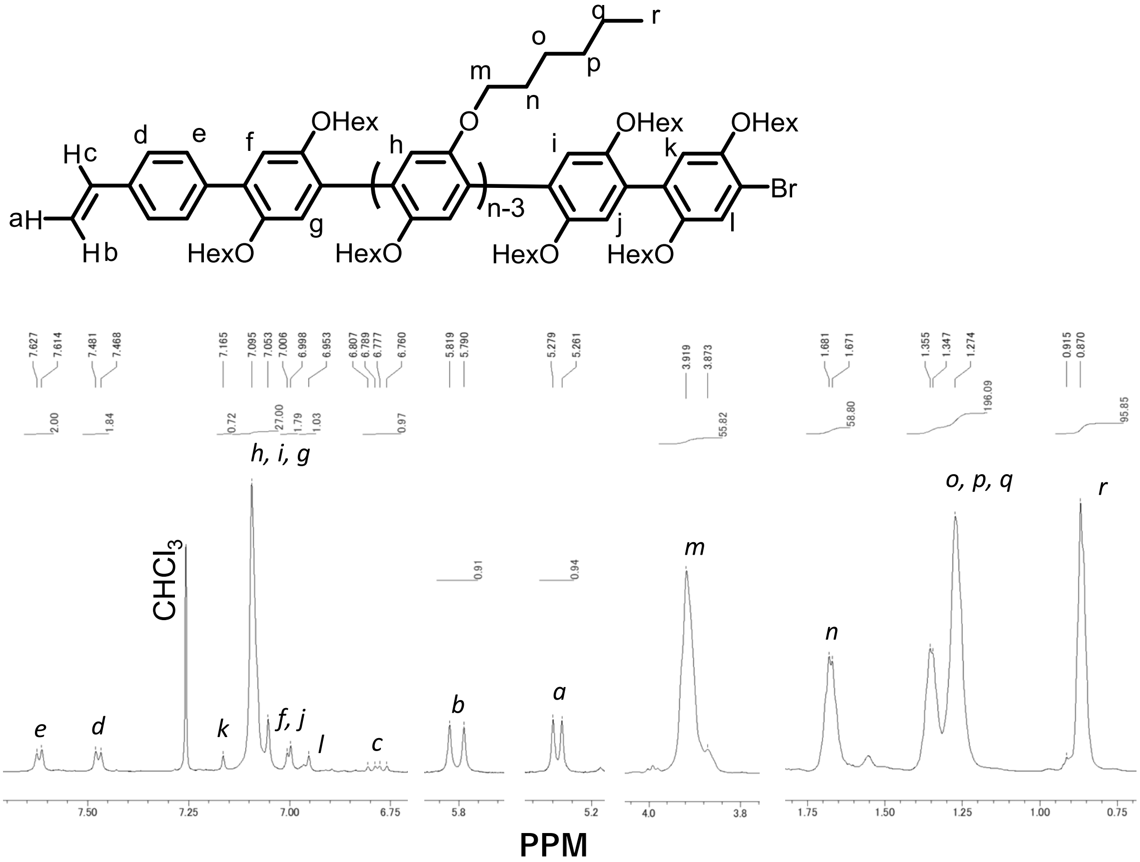


Fig. S16. ^{1}H NMR spectrum of products, obtained by Kumada-Tamao CTCP of **1** with 5 mol% of PEPPSI-IPr in THF at rt for 30 min, followed by Suzuki-Miyaura coupling with 60 mol% of **2f** and K_3PO_4 in water/THF at rt for 24 h.

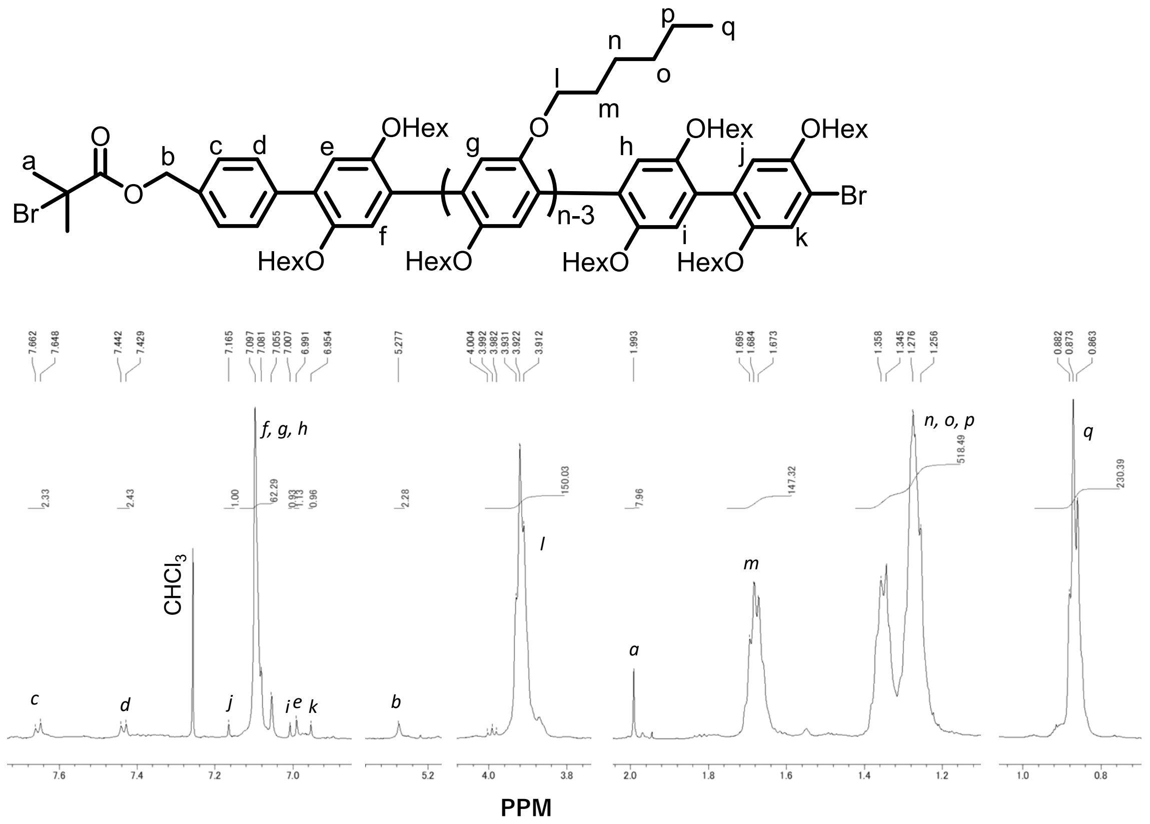


Fig. S17. ^{1}H NMR spectrum of products, obtained by Kumada-Tamao CTCP of **1** with 5 mol% of PEPPSI-IPr in THF at rt for 30 min, followed by Suzuki-Miyaura coupling with 60 mol% of **2g** and K_3PO_4 in water/THF at rt for 24 h.

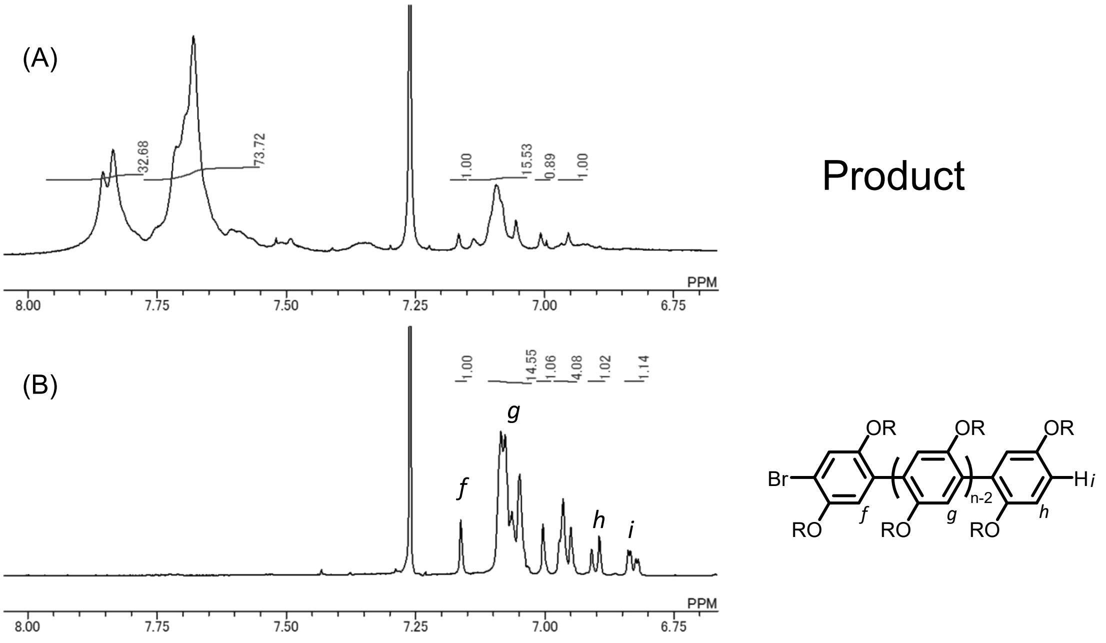


Fig. S18. ^{1}H NMR spectra of (A) copolymer (M_n = 17270, M_w/M_n = 2.39), obtained by Kumada-Tamao CTCP of **1** with 5 mol% of Pd-PEPPSI-IPr at rt for 30 min, followed by Suzuki-Miyaura polymerization of **3b** in the presence of K_3PO_4 in H_2O/THF (= 0.1 (v/v)) at rt for 1 day and (B) **poly1** with Br/H ends.

References

1. M. Nojima, K. Kosaka, M. Kato, Y. Ohta and T. Yokozawa, *Macromol. Rapid Commun.*, 2016, **37**, 79-85.
2. Y. Tokita, T. Uchida, T. Kamigawara, K. Hoka, R. Nitto, Y. Ohta and T. Yokozawa, *Chem. Commun.*, 2023, **59**, 13139-13142.
3. J. K. Lee, S. Ko and Z. Bao, *Macromol. Rapid Commun.*, 2012, **33**, 938-942.
4. A. Gutacker, C.-Y. Lin, L. Ying, T.-Q. Nguyen, U. Scherf and G. C. Bazan, *Macromolecules*, 2012, **45**, 4441-4446.