Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Stereospecific Reductive Coupling Polymerization of Bis(benzylic *gem*-dibromide) via Formation of *trans* C-C Double Bond

Hua Cao, Zhe Liu and Qi Wang*

MOE Key Laboratory of Macromolecular Synthesis and Functionalization,
Department of Polymer Science & Engineering, Zhejiang University, Hangzhou,
310027, P. R. China.

1. Experimental section

1.1 Materials

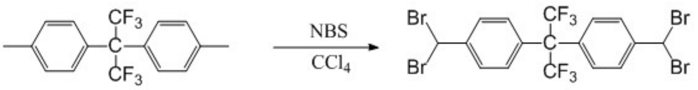
Tetrahydrofuran (THF) was distilled from sodium. Copper powder (0.50-1.5 μm, Alfa, 99.9%) was treated with hydrochloric acid and washed successively with water and acetone. N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, Alfa, 98%), tris(2-dimethylaminoethyl)amine (Me$_6$TREN, Alfa, 98%), *p*-xylene (Sinopharm Chemical Reagent, SCR), N-bromosuccinimide (NBS, SCR, 98%), benzoyl peroxide (BPO, SCR, 97%), 2,2-di(p-tolyl)-hexafluoropropane (J&K Chemistry, 95%), 5-(tert-butyl)-m-xylene (J&K Chemistry, 97%), hydroquinone (J&K Chemistry, 97%), 2,3-dimethyl-2-butene (Alfa, 98%), 1-bromooctane (Alfa, 98%), *meso*-1,2-dibromo-1,2-diphenylethane (Alfa, 99%) and 33% HBr/AcOH(w/w) solution (Alfa) were used as received. Tris[(2-pyridyl)methyl]amine (TPMA) was synthesized according to previously reported procedures.[1]

1.2 Characterization

Number- and weight- average molecular weights and molecular weight distributions were determined by gel permeation chromatograph (GPC) on a Waters 1515 equipped with two PLgel 5 μm MIXED-C columns using polystyrene standards and THF as the eluent at a flow rate of 1.0 mL/min at 40°C. NMR spectra were collected with a Bruker 400 MHz NMR using CDCl$_3$ or CD$_2$Cl$_2$ as a solvent. Elemental analyses were performed on a Flash EA1112 (Thermo Finnigan). MALDI-TOF-MS spectra were performed on a Bruker Ultraflextreme MALDI-TOF instrument operating in linear mode and dithranol (DIT) was used as the matrix. Infrared spectra were recorded on a Bruker VECTOR 220 spectrometer using KBr pressed disks. UV-visible specta were recorded on Cary100 spectrometer in THF. GC-MS (m/z) spectra were performed on a GCT Premier GC-TOFMA.

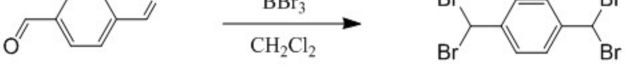
1.3 Synthesis of monomers

1.3.1 2,2-Bis(4-dibromomethyl phenyl)hexafluoropropane (**1a**)



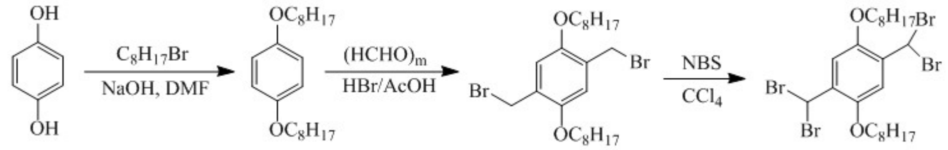
1.661 g 2,2-di(p-tolyl)-hexafluoropropane (10 mmol), 7.832 g N-bromosuccinimide (NBS, 44 mmol), 0.532 g benzoyl peroxide (BPO, 2.2 mmol) and 50 mL CCl$_4$ were placed in 100 mL three-neck round-bottom flask equipped with a reflux condenser. The solution was bubbled with N$_2$ for 10 minutes then refluxed for 4 hours. The suspension was filtered and obtained solution was concentrated resulting crude product. The crude product was purified by flash chromatography on silica-gel (300 - 400 mesh) (eluted with petroleum ether) to give compound **1a** (11% yield) as white powder. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 7.64 (m, 4H, Ar***H***), 7.39 (d, 4H, Ar***H***), 6.65 (s, 2H, ArC***H***Br$_2$). ^{13}C NMR (101 MHz, CDCl$_3$, ppm): δ = 142.69, 134.46, 130.51, 126.54, 39.42. GC-MS (EI, m/z): 567 [M-Br]$^+$, 488 [M-2Br]$^+$, 419 [M-2Br-CF$_3$]$^+$.

1.3.2 1,4-bis(dibromomethyl)benzene (**1b**)



To a stirring solution of 1,4-phthalaldehyde (1.7 mL, 15 mmol) in 30 mL of dichloromethane (CH_2Cl_2), boron tribromide (30 mL of 1.2M CH_2Cl_2 solution, 36 mmol) was added dropwise over 30 min at cold water bath conditions. After that, the reaction was stirred at room temperature for 1h and then concentrated under vacuum. The crude product was purified by flash chromatography on silica-gel (300 - 400 mesh) (eluted with petroleum ether) to give compound **1b** (80% yield) as white crystal. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.58 (s, 4H, Ar***H***), 6.63 (s, 2H, ArC***H***Br_2).

1.3.3 1,4-bis(octyloxy)-2,5-bis(dibromomethyl)benzene (**1d**)

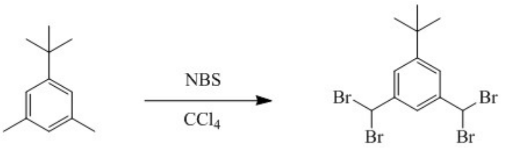


To a stirring solution of 3.480 g hydroquinone (31.6 mmol) in 180 mL N,N-dimethylformamide (DMF), 10.205 g NaOH (252.8 mmol) was added. The mixture was stirred for 2 h at 15 °C and 16 mL 1-bromooctane (91.6 mmol) was added dropwise. The mixture was stirred for 24 h at 60 °C and then poured into deionized water. The precipitate was extracted with ether, and subsequently the combined organic layer was washed with brine and dried over anhydrous magnesium sulfate. The filtrate was then evaporated at reduced pressure. The crude product was purified by flash chromatography on silica-gel (300 - 400 mesh) (eluted with the solution of 5% ethyl acetate in petroleum ether) to give 1,4-bis(octyloxy)benzene (BOB, 77% yield) as white powder. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 6.82 (s, 4H, Ar***H***), 3.89 (t, 4H, OC***H***$_2$), 1.73 (m, 4H, OCH_2C***H***$_2$), 1.28-1.56 (m, 20H, $OC_2H_4C_5$***H***$_{10}CH_3$), 0.90 (s, 6H, $OC_7H_{14}C$***H***$_3$).

To a solution of 1.201 g paraformaldehyde (40 mmol), 1.670 g BOB (5 mmol) in a 50 mL Schlenk vessel, 20 mL 33% HBr/AcOH(w/w) solution was added. The mixture was stirred for 3 h in 65 °C and cooled down to room temperature. The reaction was poured into 60 mL deionized water and filtrated, the filtrate was then dissolved in 60 mL hot chloroform. The solution was poured into 50 mL methanol, and the resulted precipitate was separated by filtration and dried to give 1,4-bis(octyloxy)-2,5-bis(bromomethyl)benzene (BOBMB, 58% yield) as white powder. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 6.85 (s, 2H, Ar***H***), 4.53 (s, 4H, ArC***H***$_2$Br), 3.98 (t, 4H, OC***H***$_2$), 1.81 (m, 4H, OCH_2C***H***$_2$), 1.38 (d, 20H, $OC_2H_4C_5$***H***$_{10}CH_3$), 0.89 (s, 6H, $OC_7H_{14}C$***H***$_3$).

1c was prepared from BOBMB by the procedure for **1a**, correspondingly the ratio of BOBMB to NBS was changed to 1:2.2. The crude product was purified by recrystallization from n-hexane to give compound **1c** (55% yield) as white powder. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.29 (s, 2H, Ar***H***), 7.09 (s, 2H, ArC***H***Br_2), 4.07 (t, 4H, OC***H***$_2$), 1.84 (m, 4H, OCH_2C***H***$_2$), 1.54 (m, 4H, OCH_2CH_2C***H***$_2$), 1.31 (m, 16H, $OC_3H_6C_4$***H***$_8CH_3$), 0.90 (m, 6H, $OC_7H_{14}C$***H***$_3$). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 147.14, 132.23, 113.60, 69.36, 34.87, 31.82, 29.32, 29.25, 29.16, 26.08, 22.69, 14.14. GC-MS (EI, m/z): 182.95 $[M\text{-}3Br\text{-}2OC_8H_{17}]^+$, 104.05 $[M\text{-}4Br\text{-}2OC_8H_{17}]^+$. Elemental analysis: Calcd. For $C_{24}H_{38}Br_4O_2$ C%: 42.51, H%: 5.65. Found C%: 42.41, H%:5.65.

1.3.4 5-(tert-butyl)-1,3-bis(dibromomethyl)benzene (**1e**)



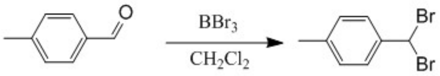
1d was prepared from 5-(tert-butyl)-*m*-xylene by the procedure for **1a**. The crude product was purified by flash chromatography on silica-gel (300 - 400 mesh) (eluted with petroleum ether) to give compound **1d** (22% yield) as white crystal. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 7.60 (t, 1H, Ar***H***), 7.52 (d, 2H, Ar***H***), 6.64 (s, 2H, ArC***H***Br$_2$), 1.36 (s, 9H, ArC(C***H***$_3$)$_3$). ^{13}C NMR (101 MHz, CDCl$_3$, ppm): δ = 152.64, 142.02, 125.05, 122.07, 40.35, 35.14, 31.13. GC-MS (EI, m/z): 397 [M-Br]$^+$, 318 [M-2Br]$^+$. Elemental analysis: Calcd. For $C_{12}H_{14}Br_4$ C%: 30.16, H%: 2.95. Found C%: 29.99, H%: 2.91.

1.4 Procedure for the Polymerization

In a typical procedure, for example, 64.8 mg **1a** (0.10 mmol), 58.0 mg TPMA (0.20 mmol) and 14.1 mg Cu (0.22 mol) were added to ampule equipped with a stir bar. The ampule was degassed, backfilled four times with N$_2$, and then left under N$_2$. Deoxygenated 4 mL of THF was then added. The ampule was heated at 40 °C for 1.5 h. The ampule was immersed in liquid nitrogen and the mixture was diluted with CH$_2$Cl$_2$, after filtration the resulted solution was precipitated in methanol. The precipitate was isolated and washed by methanol for 4 times, then dried under vacuum at 40 °C to yield polymer. The yield of polymerization was calculated.

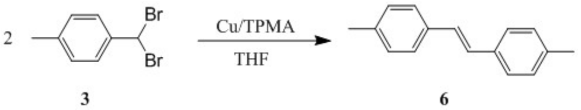
1.5 Reactions of the model compound

1.5.1 Preparation of 4-methyl benzal bromide (MBB, 3)



3 was prepared from *p*-tolualdehyde by the procedure for **1b**, correspondingly the ratio of *p*-tolualdehyde to boron tribromide was changed to 1 1.2. The crude product was purified by flash chromatography to give compound **3** **(**74% yield) **as** white crystal. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 7.49 (m, 2H, Ar***H***), 7.17(d, 2H, Ar***H***), 6.63(s, 1H, ArC***H***Br$_2$), 2.37(s, 3H, ArC***H***$_3$). ^{13}C NMR(101MHz, CDCl$_3$, ppm): δ = 140.10, 139.26, 129.27, 126.40, 41.13, 21.29. GC-MS (EI, m/z): 183 [M-Br]$^+$, 104 [M-2Br]$^+$. Elemental analysis: Calcd. For $C_8H_8Br_2$ C%: 36.40, H%: 3.06. Found C%: 36.42, H%: 3.14.

1.5.2 Control coupling reactions



In a general procedure, for example, 26.4 mg of **3** (0.10 mmol), 29.0 mg of TPMA (0.10 mmol) and 7.1 mg of copper powder (0.11 mmol) were added to an ampule equipped with a stir bar. The ampule was degassed, backfilled four times with N$_2$, and then left under N$_2$. Deoxygenated 2 mL of THF was then added. The ampule was heated at 40°C for 10 min. The ampule was immersed in liquid nitrogen and the mixture was diluted with THF and purified by passing through a neutral alumina column. The crude product containing trace of solvent was obtained after removal of solvent under vacuum, which was measured by ^{1}H-NMR using DMSO as internal standard, giving yield of the corresponding compounds. ^{1}H NMR of **6** (400 MHz, CDCl$_3$): δ= 7.39 (m, 4H, Ar***H***), 7.17 (d, 4H, Ar***H***), 7.04 (s, 1H, ArC***H***), 2.35 (s, 6H, ArC***H***$_3$).

The crude product in the coupling reaction condition [Cu]/[**3**] = 0.5:1(Run 2 in Table 3) was further measured by GC-MS and ^{1}H NMR, demonstrated the complex mixture to be four components: (a) for 4-methyl benzal bromide, m/z(EI): 183 $[M\text{-}Br]^+$, 104 $[M\text{-}2Br]^+$, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (m, 2H, Ar***H***), 7.17(d, 2H, Ar***H***), 6.63(s, 1H, ArC***H***Br_2), 2.37(s, 3H, ArC$\boldsymbol{H}_3$).; (b) for p-methyl benzaldehyde: m/z(EI): 120 $[M]^+$, 91 $[M\text{-}CHO]^+$, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (m, 2H, Ar***H***), 7.32 (d, 2H, Ar***H***), 9.97 (s, 1H, ArC***H***O), 2.44 (s, 3H, ArC$\boldsymbol{H}_3$); (c) for *E*-4,4'-dimethylstilbene: m/z(EI): 208 $[M]^+$, 178 $[M\text{-}2CH_3]^+$, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (m, 4H, Ar***H***), 7.17 (d, 4H, Ar***H***), 7.04 (s, 1H, ArC***H***), 2.35 (s, 6H, ArC$\boldsymbol{H}_3$); (d) and (e) for *d,l*-1,2-dibromo-1,2-di(*p*-tolyl)ethane: m/z(EI): 287 $[M\text{-}Br]^+$, 208 $[M\text{-}2Br]^+$, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07 (m, 4H, Ar***H***), 6.99 (d, 4H, Ar***H***), 5.48 (s, 1H, ArC***H***Br), 2.25 (s, 6H, ArC$\boldsymbol{H}_3$).

1.5.3 Reactions of 4-methyl benzal bromide with alkenes

In a general procedure, for example, 26.4 mg of **3** (0.10 mmol), 29.0 mg of TPMA (0.10 mmol) and 7.1 mg of copper powder (0.11 mmol) were added to an ampule equipped with a stir bar. The ampule was degassed, backfilled four times with N_2, and then left under N_2. 2 mL of THF solution containing 118 µL 2,3-dimethyl-2-butene (1.00 mmol) was deoxygenated and then added. The ampule was heated at 40°C for 3 hours. The ampule was immersed in liquid nitrogen and the mixture was diluted with THF and purified by passing through a neutral alumina column. The crude product containing trace of solvent was obtained after removal of solvent under vacuum. The yields of the corresponding compounds were determined by ^{1}H NMR spectroscopy using DMSO as internal standard.

Table S1 The reactions of **3** with different alkenes[a]

Entry	Alkene(A)	Temperature (^{o}C)	Yield(%)[b] coupling product	cycloadduct
1	2,3-dimethyl-2-butene	40	91	0
2	2,3-dimethyl-2-butene	0	89	0
3	cyclohexene	0	94	0
4	styrene	0	95	0
5	benzaldehyde	0	98	0

a. Reaction conditions: [**3**]:[A]:[Cu]:[TPMA]=1:10:1.1:1，[**3**]=0.05M, in THF, 3 hrs. b. The yield of the product was determined by ^{1}H-NMR using DMSO as internal standard.

2 Spectra of monomers and polymers

2.1 ^{1}H NMR spectra of monomers

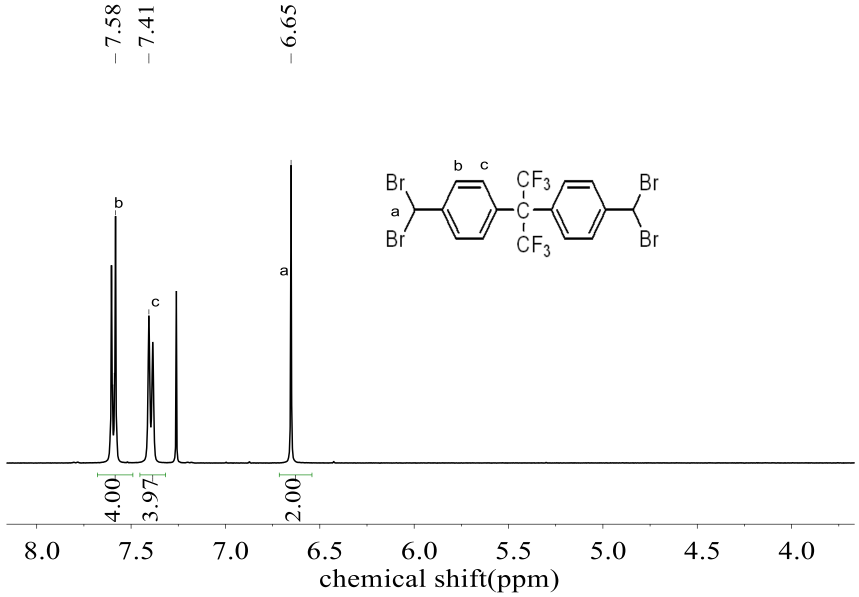


Figure S1 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1a**

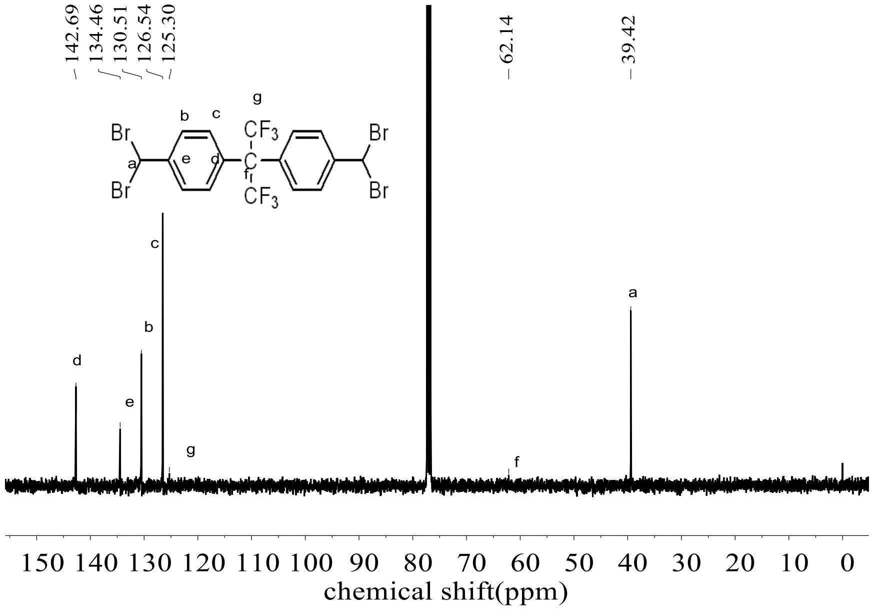


Figure S2 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **1a**

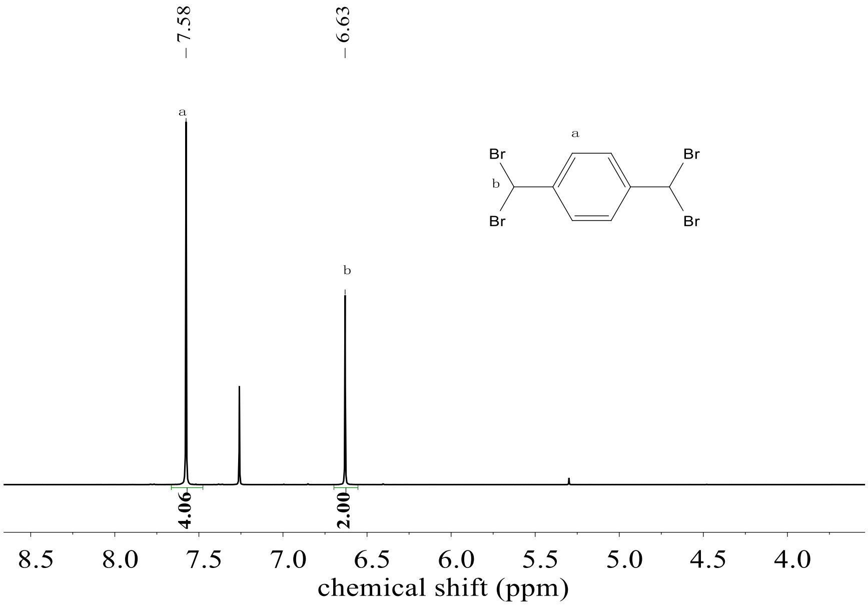


Figure S3 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1b**

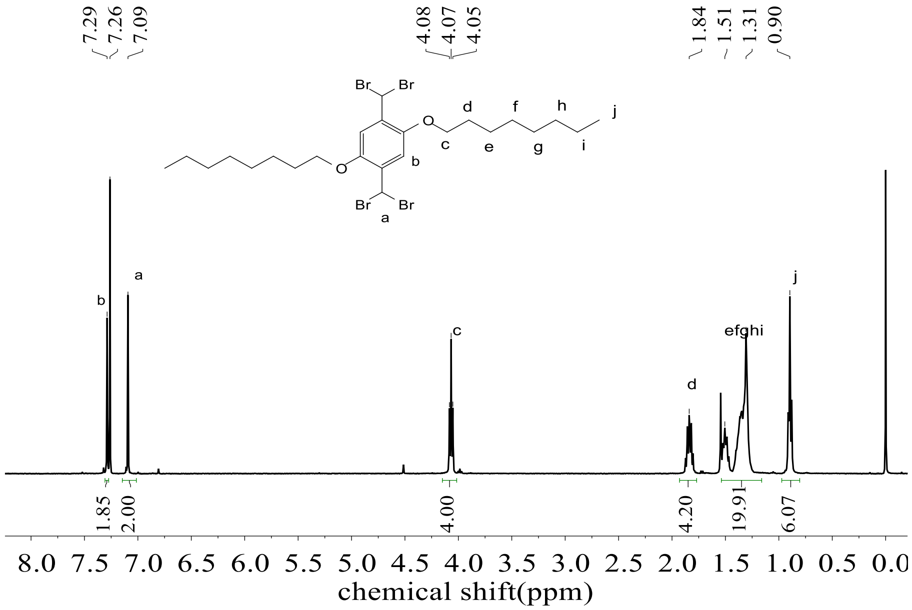


Figure S4 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1d**

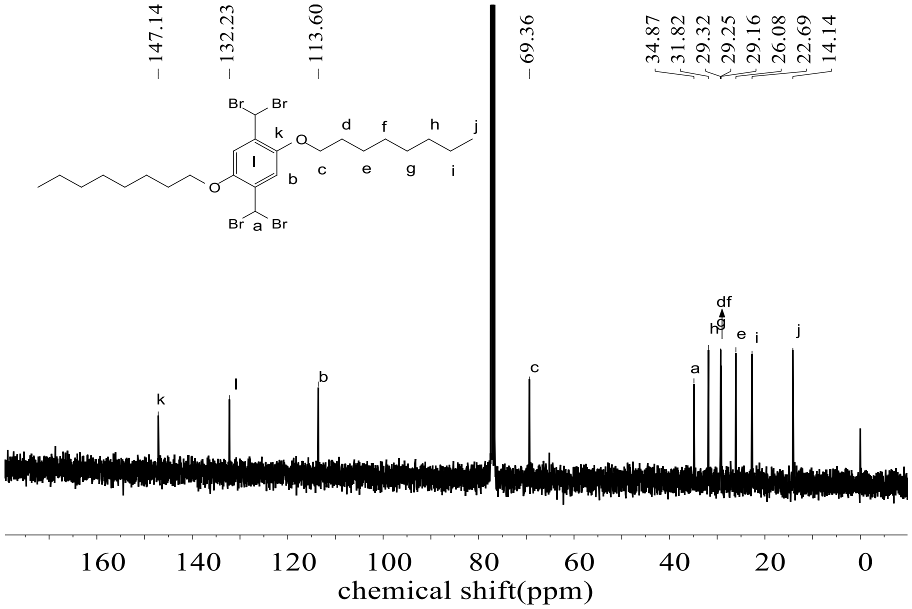


Figure S5 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **1d**

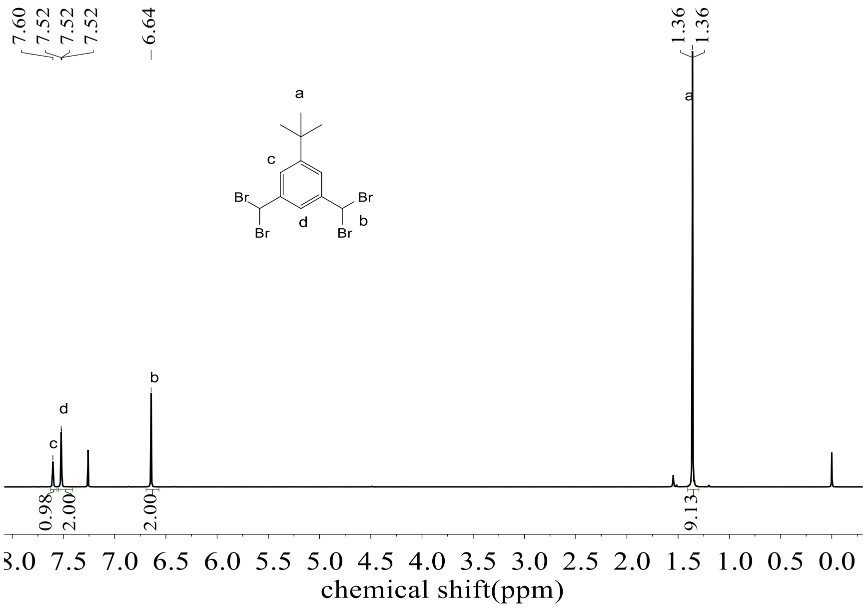


Figure S6 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1e**

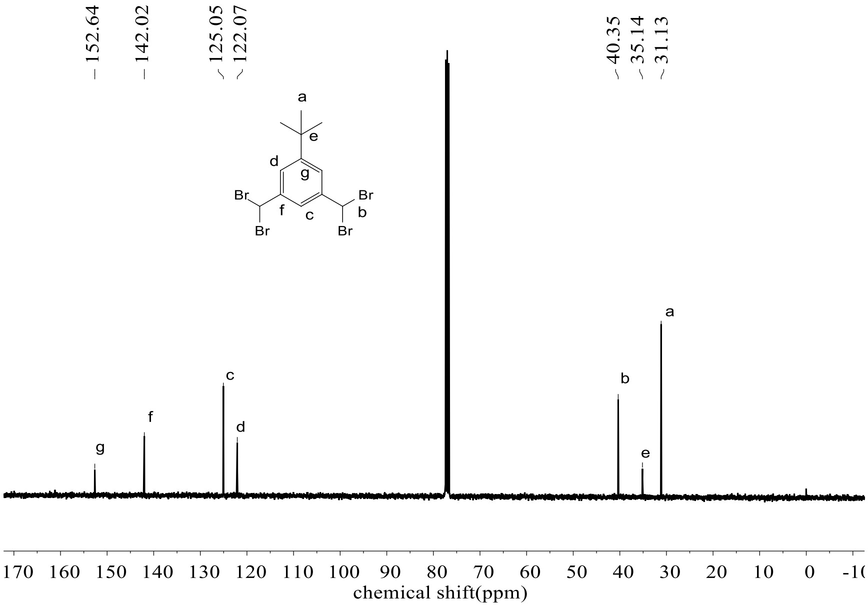


Figure S7 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **1e**

2.2 Spectra of polymers

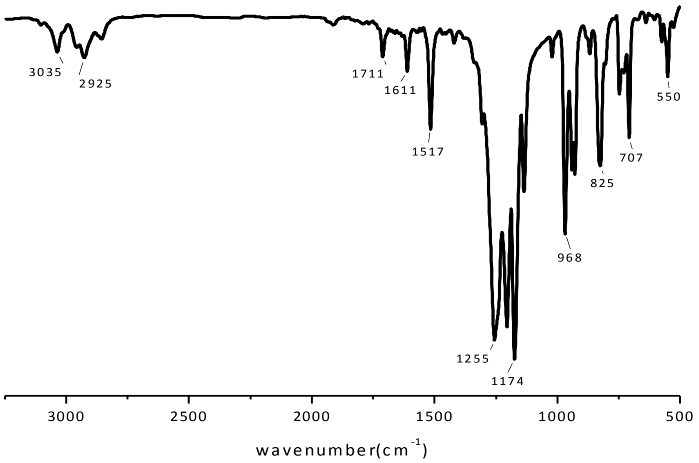


Figure S8 IR spectrum of polymer of **2b**.

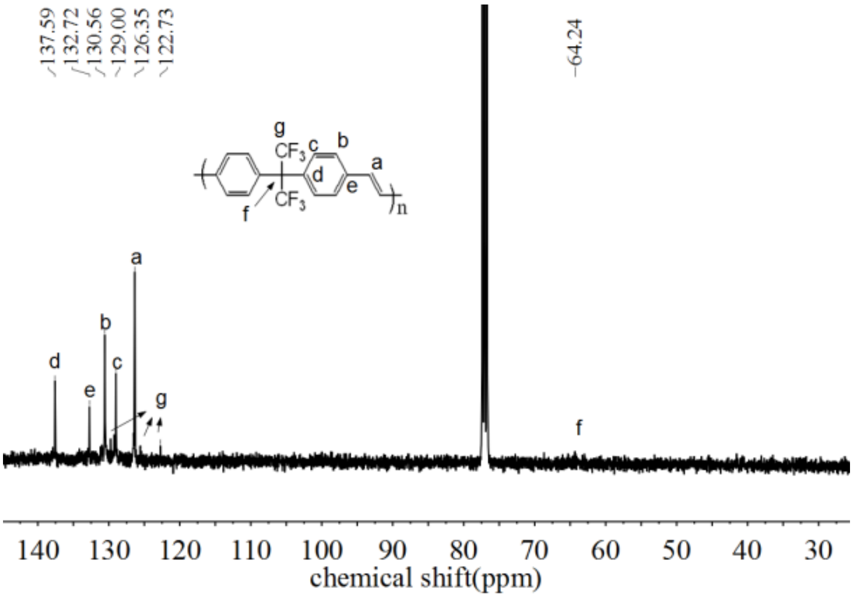


Figure S9 ^{13}C NMR (101 MHz) spectrum of **2a**.

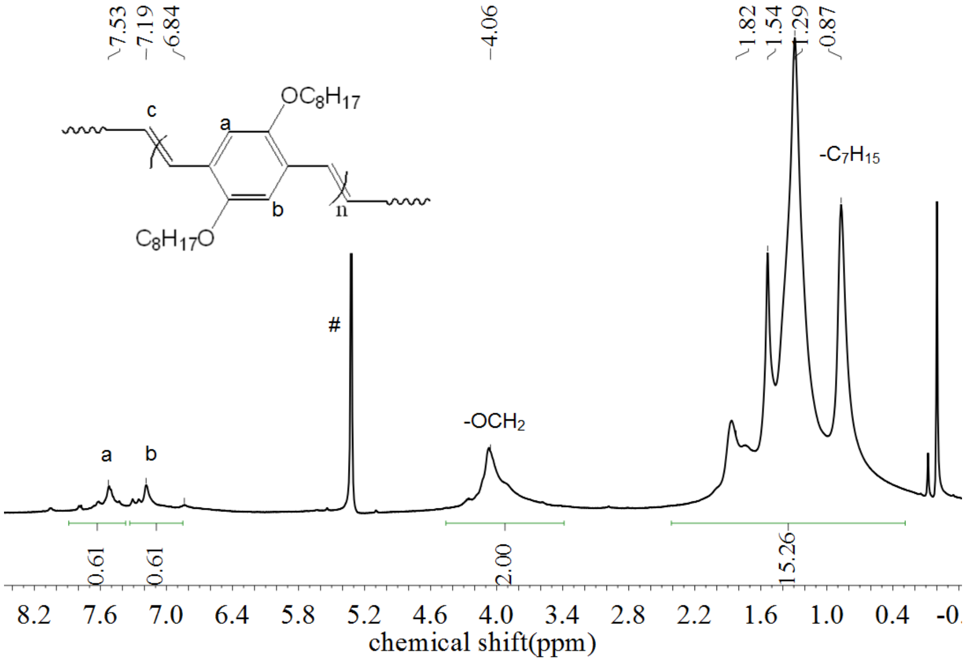


Figure S10 ^{1}H-NMR(400 MHz) spectrum of polymer **2c** in CD_2Cl_2 (solvent #)

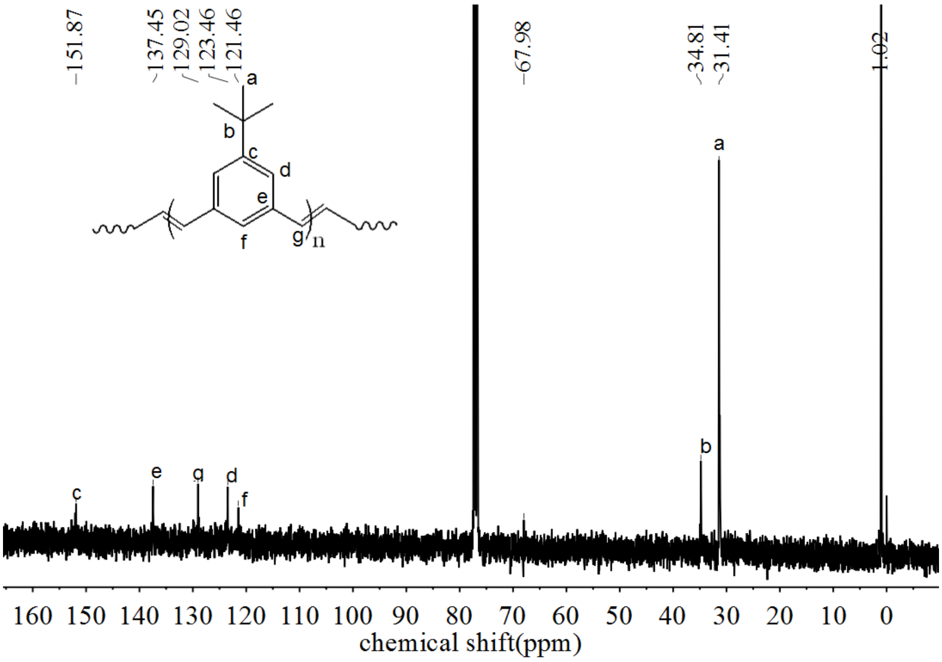


Figure S11 ^{13}C-NMR(101 MHz) spectrum of polymer **2d**

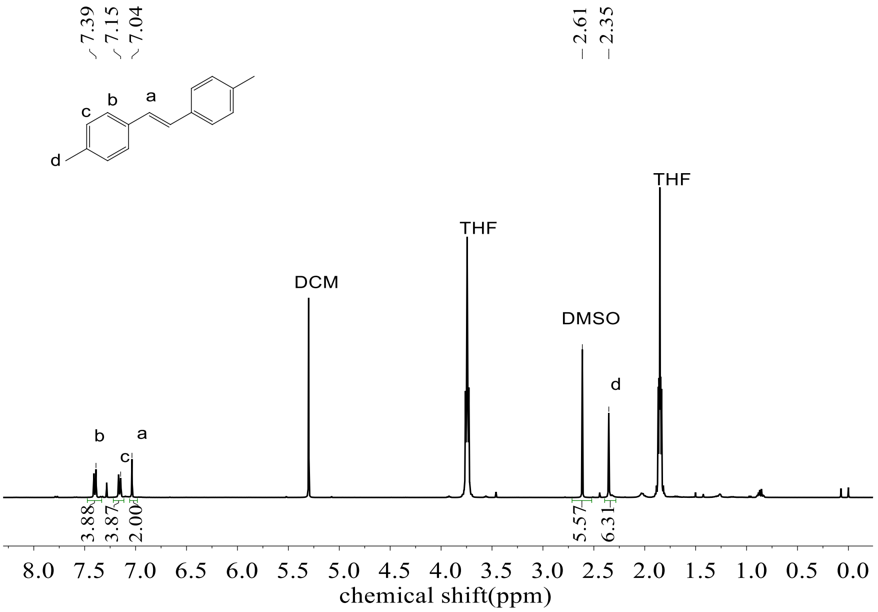


Figure S12 ^{1}H-NMR spectrum of crude product of run 1 in Table 3. (reaction conditions: [**3**]:[Cu]:[TPMA]=1:1.1:1, [**3**]=0.05M, THF, 40^{o}C, 10min. Addition of 3.6 mg DMSO as internal standard.**)**

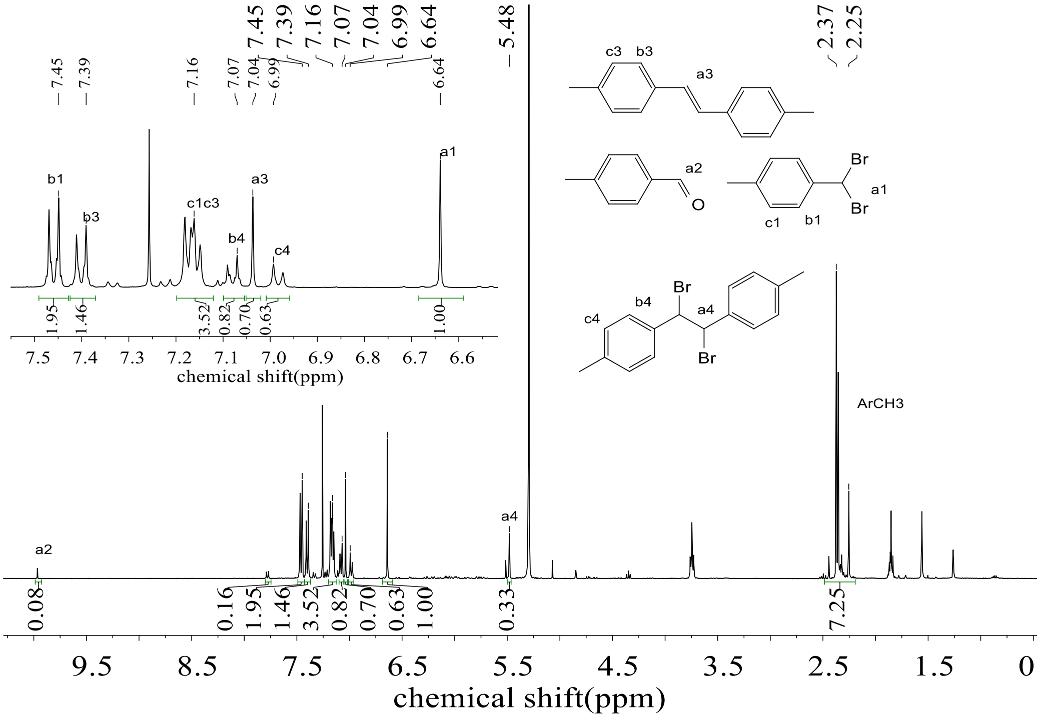


Figure S13 ^{1}H-NMR(400 MHz) spectrum of crude product of run 2 in Table 3.
([**3**]:[Cu]:[TPMA]=1:0.5:0.5, [**3**]=0.05M, THF, 40^{o}C, 10min.**)**

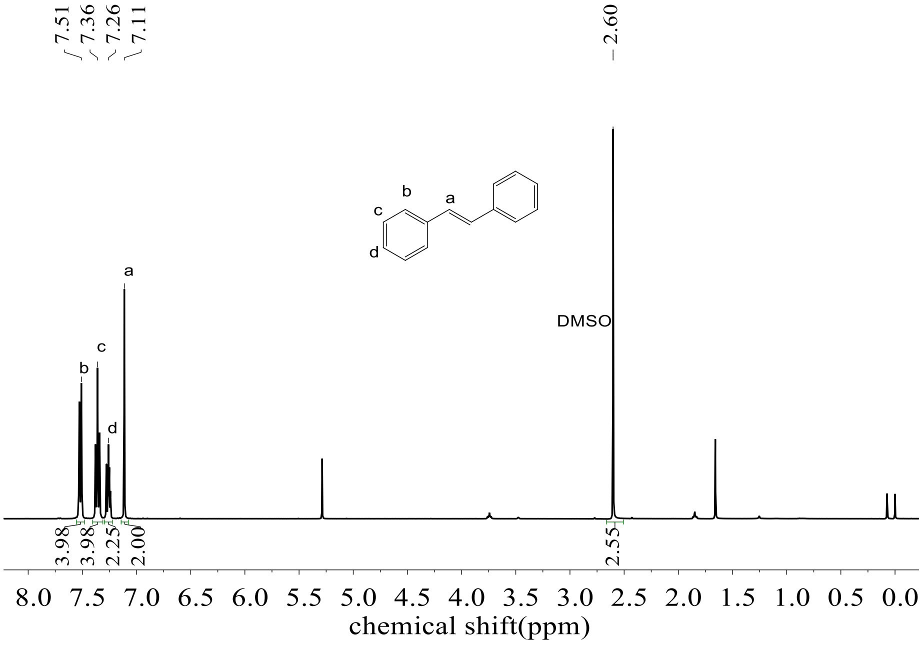


Figure S14 ^{1}H-NMR(400 MHz) spectrum of crude product of run 3 in Table 3. ([**7**]:[Cu]:[TPMA]=1:1.1:1, [**7**]=0.05M, THF, 40^{o}C, 10min. Addition of 2.4 mg DMSO as internal standard)

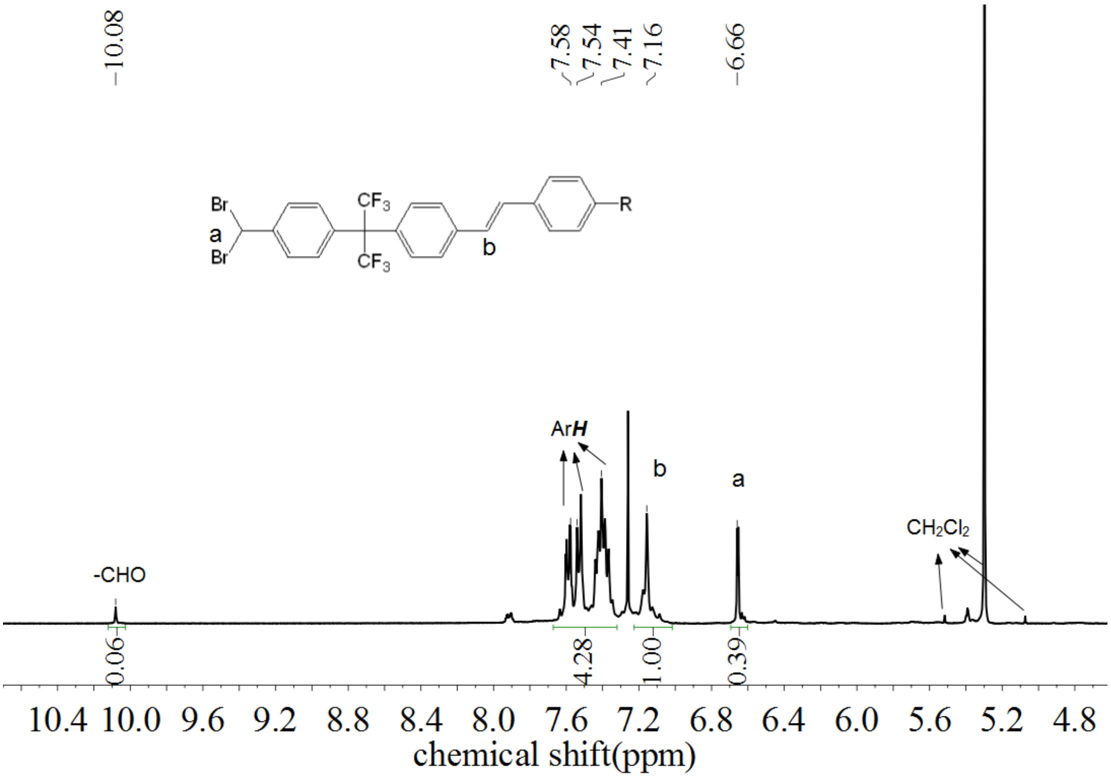


Figure S15 ^1H NMR(400 MHz) spectrum of product prepared by [Cu]:[**1a**] = 1:1

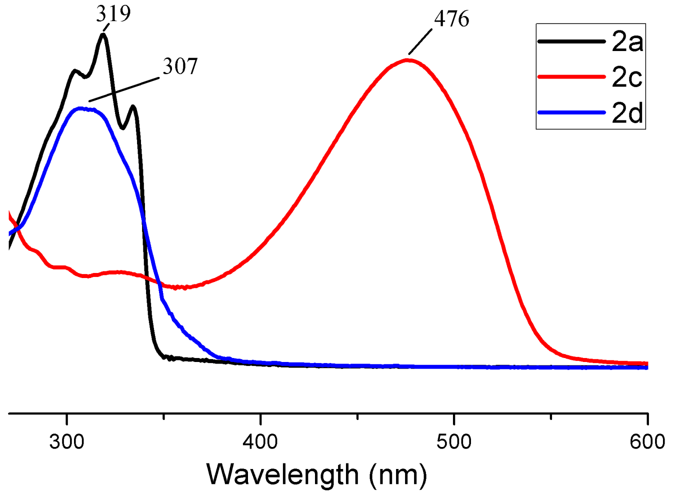


Figure S16 UV-visible spectra of polymer 2a, 2c and 2d in THF

References

(1) Tyeklar, Z.; Jacobson, R. R.; Wei, N.; Murthy, N. N.; Zubieta, J.; Karlin, K. D. *Journal of the American Chemical Society* **1993**, *115*, 2677.