Electronic Supplementary Material (ESI) for Polymer Chemistry.

Synthesis of Copolymers with Exact Alternating Sequence Using Cationic Polymerization of Pre-Sequenced Monomers

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Materials

All the materials used in this study were used as supplied, unless otherwise stated. Methyl formate (99%), benzyl formate (98%), triphenylphosphine (99%) and succinbromimide (99%) were purchased from J&K Scientific. Trifluoromethanesulfonic acid (TfOH, 98%), α-Methylstyrene (99%), dibutyl phosphate (99%), Isobutyl vinyl ether (IBVE, 95%) were purchased from TCI. Carbon disulfide and diethylamine were purchased from Sinopharm Chemical Reagents. Palladium-carbon catalyst (10% Pd) was purchased from Damas-beta. *n*-Butyllithium (2.5 M in hexane) was purchased from Energy Chemical. Solvents were dried before used in this study. Diethyl ether and dichloromethane (DCM) were distilled over CaH_2 under reduced pressure. Toluene was dried over CaH_2 and distilled over *n*-BuLi on the vacuum line. THF were purified using a solvent purification system equipped with an activated alumina column.

Measurements

NMR spectra were recorded on a Bruker AVANCE III HD 400 MHz instrument. Mass spectrometry (MS) data were collected on a JEOL LMS-T100LC instrument operated in the positive mode (electron impact ionization source，EI). Polymer molar mass (M_n) and polydispersity (M_w/M_n, $Đ$) were measured using size exclusion chromatography (SEC). The SEC system equipped with a Waters 2414 refractive index and Waters 2487 ultraviolet detectors (THF, 1 mL/min, 40 °C, three TSK-Gels columns). Polystyrene standards were employed for calibration. The conversation of the monomer were determined by HPLC. The HPLC system equipped with a Waters 1525 pump and Waters 2487 ultraviolet detectors (λ: 240 nm and 302 nm, 40 °C, acetonitrile/H_2O). Thermogravimetric analysis (TGA, PE Pyris 1) was performed in N_2 at a heating rate of 10 °C/min. Differential scanning calorimetry measurement (DSC, TA Q2000) was performed in N_2 at a heating rate of 20.0 °C/min. Fluorescence spectra were obtained using a PTI QM40 luminescence spectrophotometer.

Computational Details

First principle density functional theory (DFT) calculations were performed with the M06-2X method.[1] M06-2X is one of the most accurate hybrid DFT functionals in

predicting structures, energy barriers, and thermodynamic properties of molecules.[2] The 6-31+G(d,p) basis sets was used for all the atoms.[3] To account for solvation effect, the calculations were performed with the IEFPCM solvation model[4] in the toluene solution with radii and non-electrostatic terms for Truhlar and coworkers' SMD solvation model.[5] All the geometry optimizations and vibrational frequency analyses were performed with solvation effect considered. Default geometry convergence criterion of Gaussian 09[6] were used. All these calculations were performed by using the Gaussian 09 quantum software package.[6]

Experiments

Synthesis of 1,3-disubstituted butadiene monomers

In this work, disubstituted butadiene monomers were prepared through Wittig reaction between phosphonium salt and commercially available formates. It was reported that 1-methoxy-3-phenyl-1,3-butadiene (MeOPhB) was also obtainable through Grignard reagent routes.[7,8]

Preparation of α-(bromomethyl)styrene

α-Methylstyrene (50 mL, 385 mmol), succinbromimide (78 g, 440 mL) and $CHCl_3$ (250 mL) were mixed at room temperature. Then, the mixture was heated to reflux and stirred for 24 h under argon. The reaction was quenched by cooling the mixture to 0 ºC. The solid particles precipitated from the solution were filtered out and washed with petroleum ether. The combined organic phase was concentrated under reduced pressure. The crude product was purified by column chromatography using 95:5 (v/v) petroleum ether/ethyl acetate. The *α*-(bromomethyl)styrene was obtained as a yellow oil (65 g, 86%). The target compound is irritant substance for eyes.

Preparation of quaternary phosphonium salt (S1)

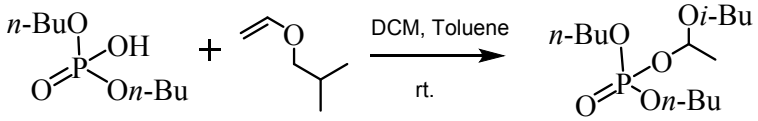
To a solution of □*α*-(bromomethyl)styrene (19.7 g, 100 mmoL) in toluene (300 mL), Ph_3P (26.2 g, 100 mmoL) was added. The obtained mixture was stirred vigorously at 60 ºC for 48 h. The reaction was monitored by TLC. When the reaction proceed completely, the white solid was filtered out and washed with toluene several times. After vacuum drying, the product was used in the next step without further purification.

Preparation of 1,3-disubstituted-1,3-butadiene monomers

n-Butyllithium solution (8 mL 2.5 M in hexane, 20 mmol) was added dropwise to a suspension of S1 (9.16 g, 20 mmol) in 100 mL anhydrous THF at -20 °C under argon. After addition, the resulted mixture was stirred for 0.5 h at -20 °C. Then, methyl formate (1.8 g, 30 mmol) was added dropwise. The mixture was stirred for another 2 h at -20 °C. Then the reaction was quenched by addition of H_2O (30 mL). The obtained mixture was extracted with EA (50 mL*3). The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on Al_2O_3 using 99/1 (v/v) petroleum ether/ethyl acetate. (*E*)-1-methoxy-3-phenyl-1,3-butadiene (MeOPhB) was obtained as yellow oil (2.3 g, 72%). ^{1}H NMR (400 MHz, d_6-Acetone): δ(TMS, ppm), 3.63(s, 3H, -OCH_3), 4.89(s, 1H, =CH_2), 5.11(s, 1H, =CH_2), 5.82(d, 1H, -CH=CH-O-), 6.51(d, 1H, -CH=CH-O-), 7.35-7.37(m, 5H, -ArH). MS: *m/z* calcd for $C_{11}H_{12}O$ M^+ = 160; found, 160.

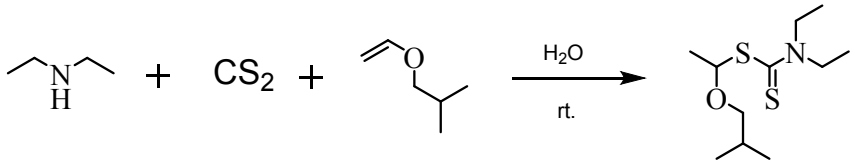
(*E*)-1-benzyloxy-3-phenyl-1,3-butadiene was synthesized using similar procedures. After purified by column chromatography on Al_2O_3, the product was obtained as yellow oil (2.9 g, 61%). ^{1}H NMR (400 MHz, d_6-Acetone) : δ(TMS， ppm), 4.83(s, 2H, -CH_2-Ph), 4.88(s, 1H, =CH_2), 5.09(s, 1H, =CH_2), 5.93(d, 1H, -CH=CH-O-), 6.88(d, 1H, -CH=CH-O-), 7.31-7.36(m, 10H, -ArH). MS: *m/z* calcd for $C_{17}H_{16}O$ M^+ = 236; found, 236.

Synthesis of dibutyl 1-isobutoxyethyl phosphate (CTA1)



According to the literature[9], dibutyl phosphate solution (1.0 mL of 1.0 M in DCM) was added into a solution of IBVE (9 mL of 0.5 M in Toluene) at 0 °C. After stirring for 24 h at room temperature, the reaction solution was concentrated under reduced pressure, and the volatiles was removed. The CTA1 was obtained as a yellow liquid.

Synthesis of dibutyl S-1-isobutoxyethyl N,N-diethyl dithiocarbamate (CTA2)



According to the literature[10], dibutyl S-1-isobutoxyethyl *N,N*-diethyl dithiocarbamate (CTA2) was synthesized through the addition reaction of CS_2, IBVE and diethylamine directly. IBVE (23 g, 0.23 mol) was added into a mixture of diethylamine (18 g，25 mL，0.24 mol), H_2O(200 mL) and carbon disulfide (20.9 g, 16.6 mL, 0.23 mol) dropwise. The reaction solution was stirred vigorously for 24 h. After removal of the water, the organic phase was washed with brine and dried over Na_2SO_4. The obtained yellow solution was concentrated under reduced pressure, and dithiocarbamate (CTA2) was obtained as yellow oil directly (37.4 g, 65%).

General procedure for the cationic RAFT polymerization

The polymerization was carried out by the syringe technique under dry argon. The solution of monomer in toluene was added into the glass tube firstly. The polymerization was initiated by sequential addition of chain transfer agent (CTA1 or CAT 2, in DCM) and TfOH (in diethyl ether) at -30 ºC. The polymerization was terminated with small amount of methanol containing triethylamine. The quenched reaction mixture was washed with H_2O three times, then the solvent was evaporated. The polymer was obtained as pale yellow solid.

General procedure for the hydrogenation reaction

A general procedure for the hydrogenation reaction is described for PMeOPhB. Firstly, PMeOPhB (0.3 g) and palladium carbon catalyst (0.2 g) was added into the reactor, then 40 mL dioxane/alcohol (v:v=1:1) was added as the solvent. The reaction vessel was purged with H_2 two times. Under 2.5 MPa, the reaction solution was stirred vigorously at 45 ºC overnight. The mixture was filtered and the filtrate was concentrated under reduced pressure to give a white solid.

Characterization data

Cationic polymerization of MeOPhB and BnOPhB

Table S1 Cationic polymerization of MeOPhB and BnOPhB[a]

Entry	Sample Name	Solvent[b]	Temp. (ºC)	Initiator[c]	M_n,Sec (kDa)[d]	$Đ$ [d]
1	P7 3rd	Toluene/ EA	15	0.1mL ($EtAlCl_2$)	22.0	1.84
2	P7 5th	Toluene/ EA	-78	0.1mL ($EtAlCl_2$)	187.0	2.80
3	P8 2nd	Toluene/ EA	15	0.1mL ($EtAlCl_2$)	9.9	1.70

a) The concentration of the monomer was 0.1 g/mL in toluene. b) Toluene/Ethyl acetate = 8:1 (v:v). c) 1.0M solution in DCM. d) GPC analysis was performed through three TSK gel columns (THF, 1mL/min, calibrated by polystyrene standards).

NMR spectra of PMeOPhB

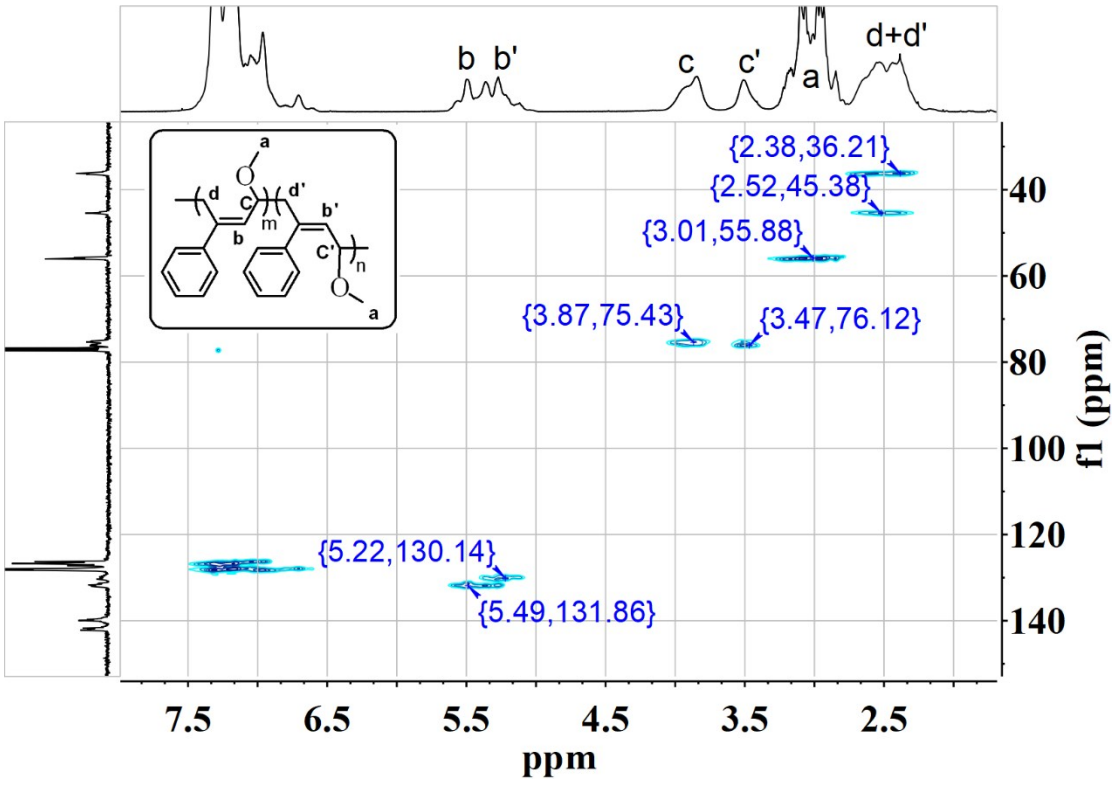


Figure S1 HSQC of PMeOPhB in $CDCl_3$.

Analysis of the CTA2-derived chain end-group using ^{1}H NMR and UV

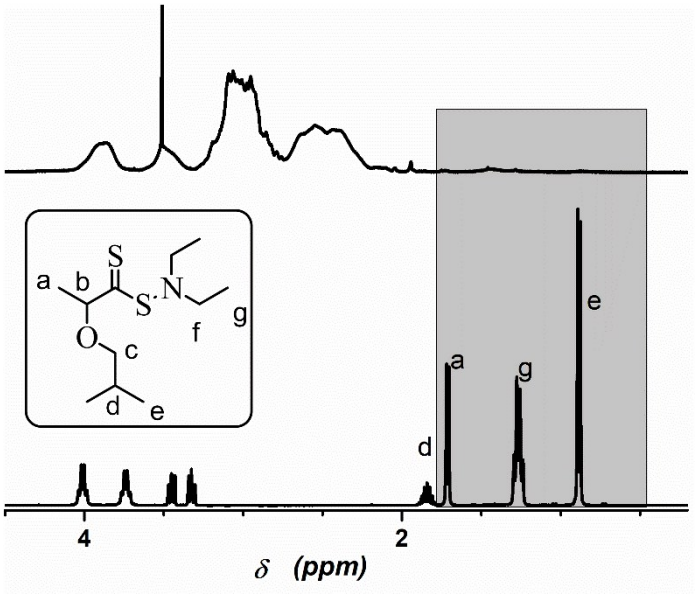


Figure S2 ^{1}H NMR spectra of PMeOPhB and CTA2 in $CDCl_3$.

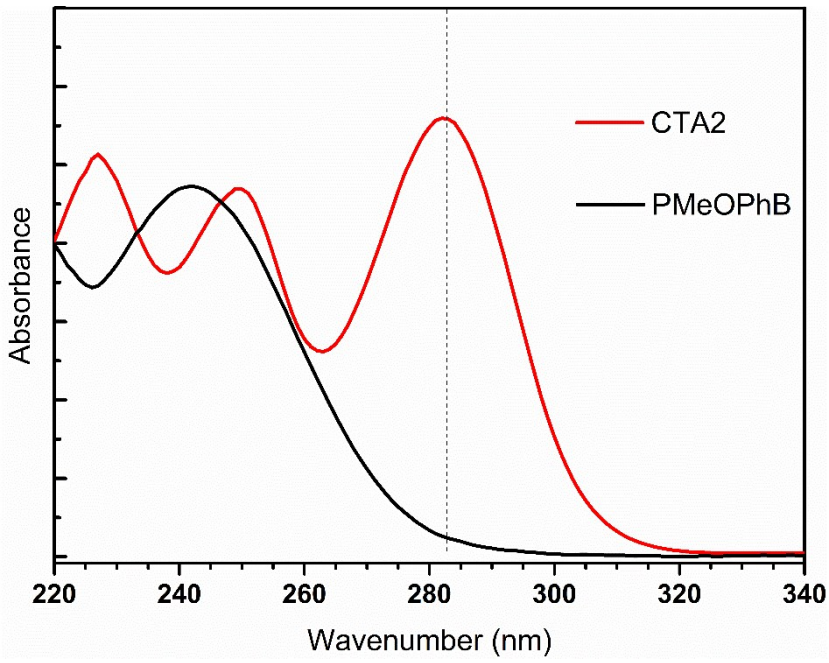


Figure S3 UV spectra (normalized) of PMeOPhB and CTA2 in THF.

NMR spectra of PBnOPhB

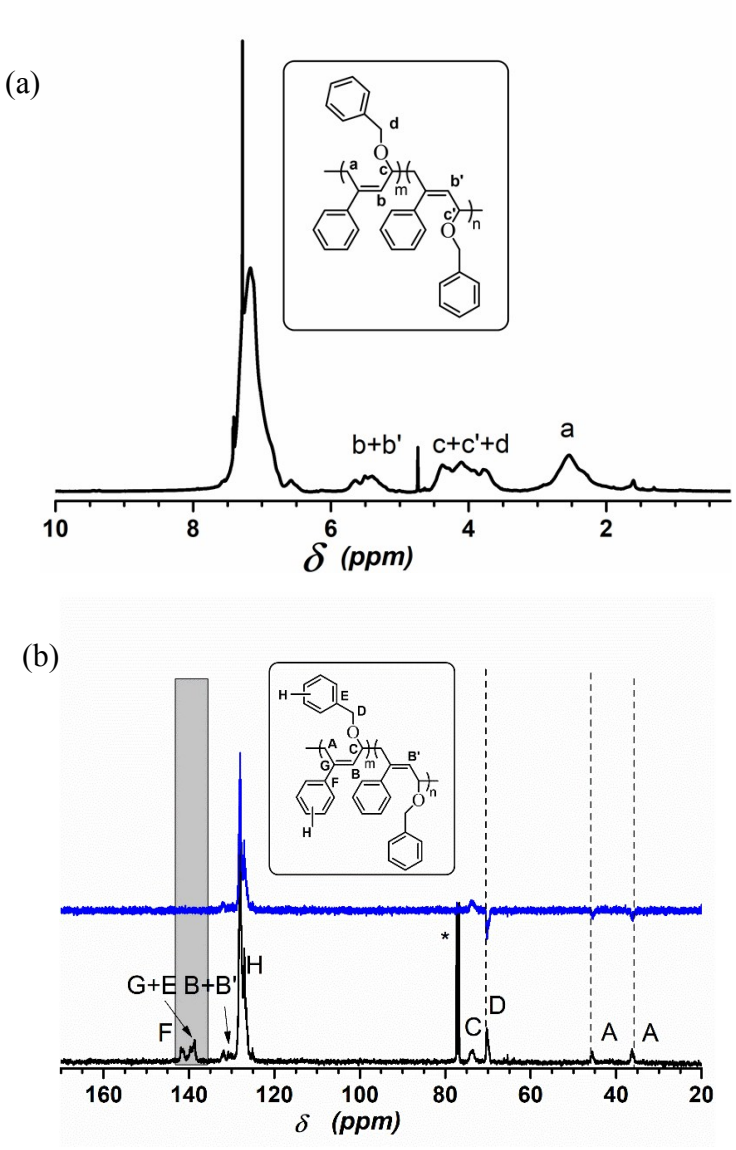


Figure S4 ^{1}H NMR, ^{13}C NMR and DEPT 135º spectra of PBnOPhB in $CDCl_3$.

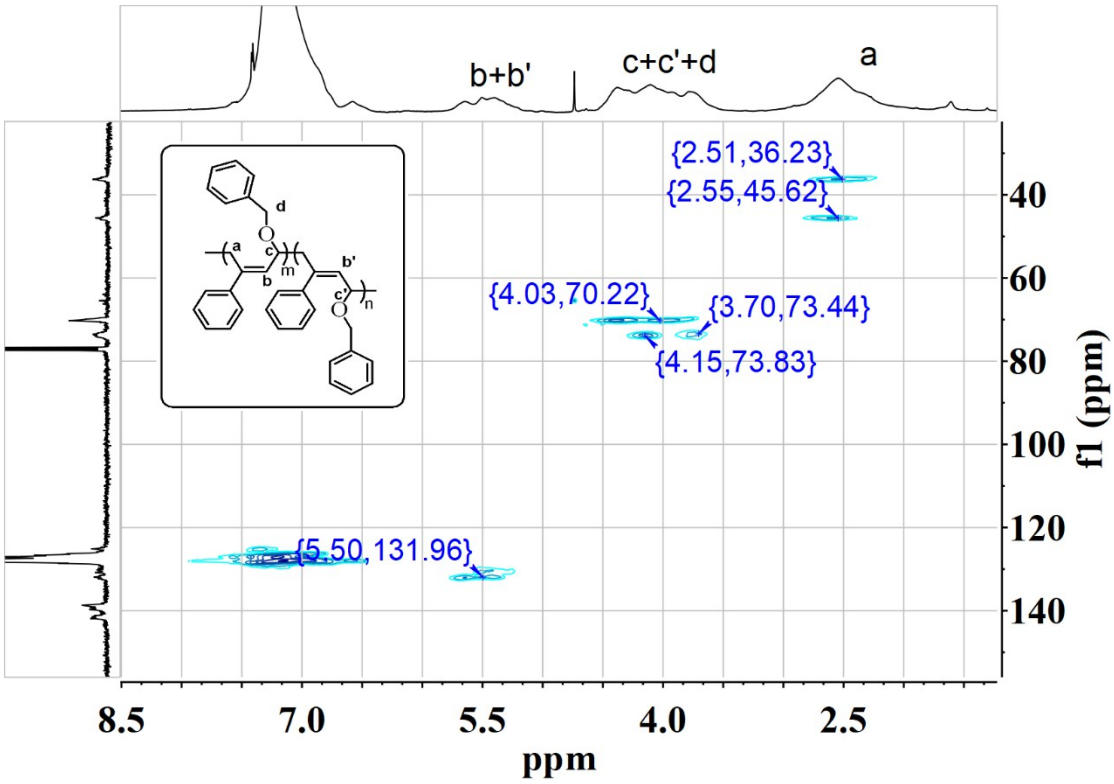


Figure S5 HSQC of PBnOPhB in $CDCl_3$.

GPC traces of PMeOPhB and PS-VOMe

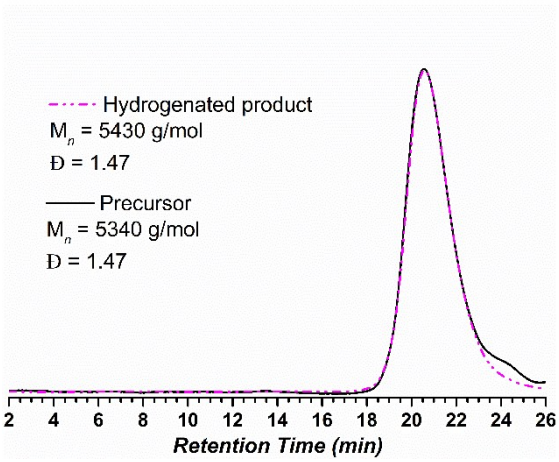


Figure S6 GPC traces of PMeOPhB and PS-VOMe.

NMR spectra of PMeOPhB and PS-VOMe

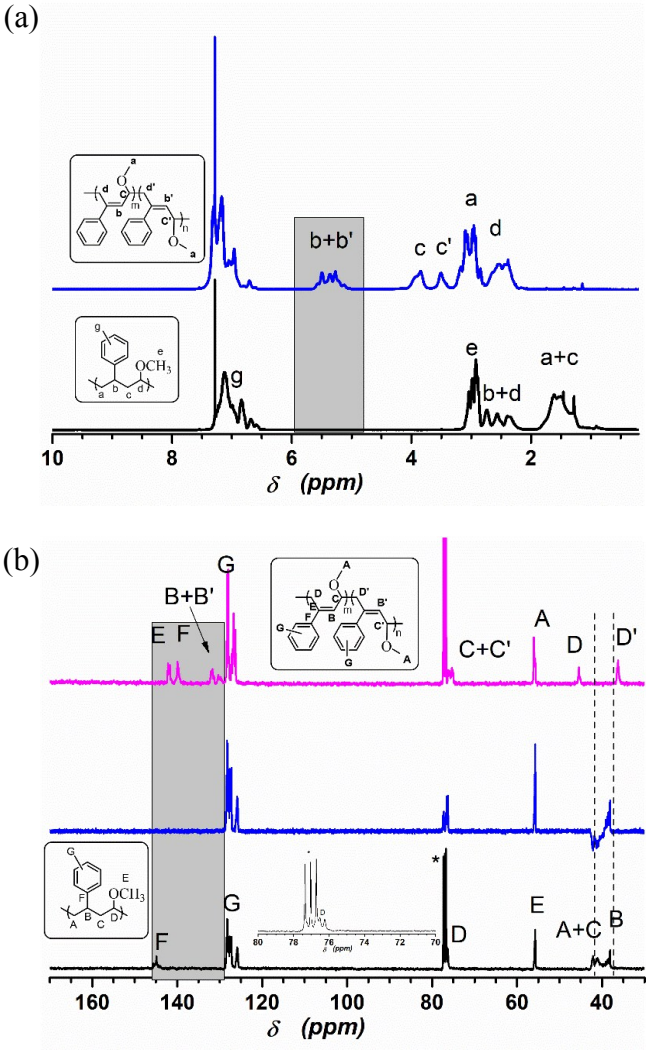


Figure S7 ^{1}H NMR, ^{13}C NMR of PMeOPhB and PS-VOMe in $CDCl_3$.

GPC traces of PBnOPhB and PS-VOH

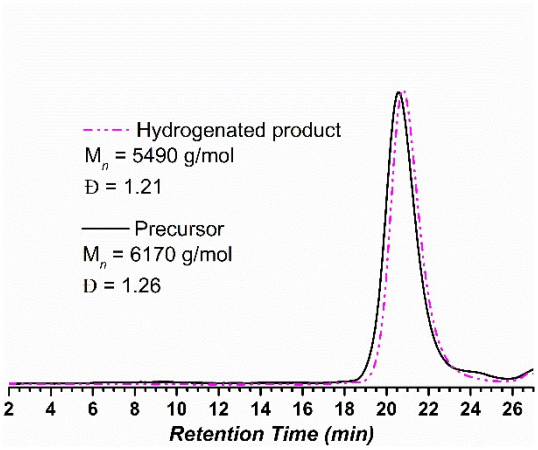


Figure S8 GPC traces of PBnOPhB and PS-VOH.

NMR spectra of PBnOPhB and PS-VOH

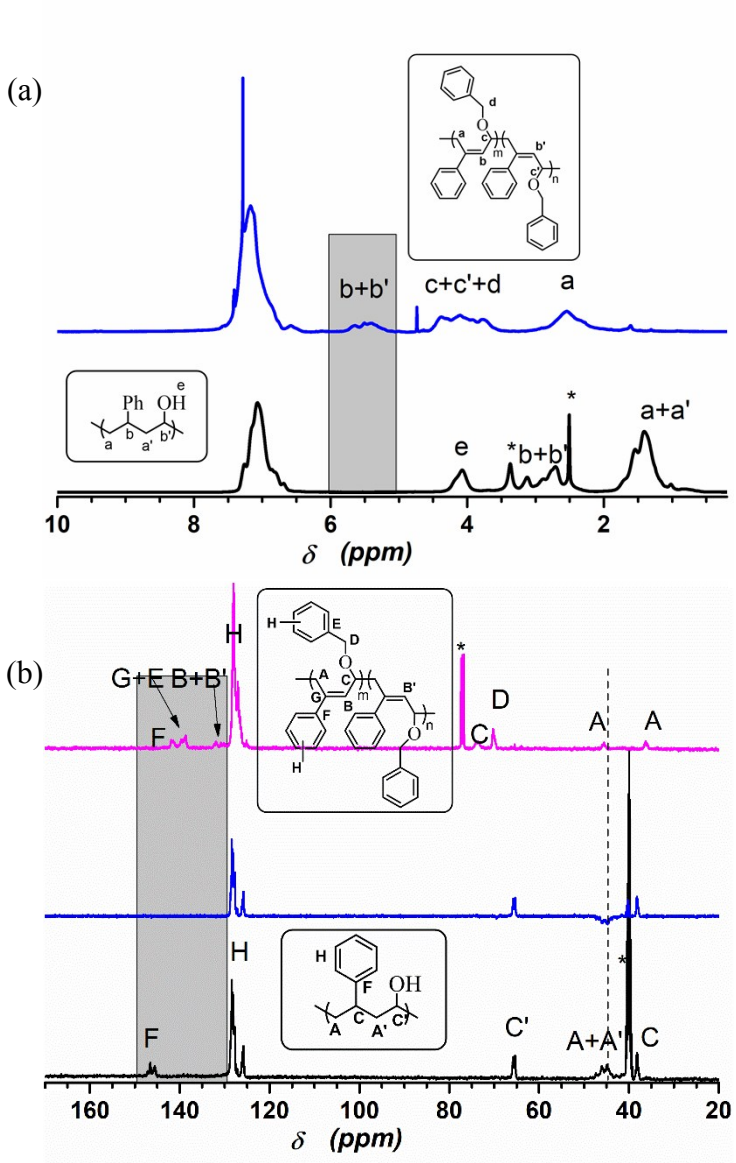


Figure S9 ^{1}H NMR, ^{13}C NMR of PBnOPhB and PS-VOH in d_6-DMSO.

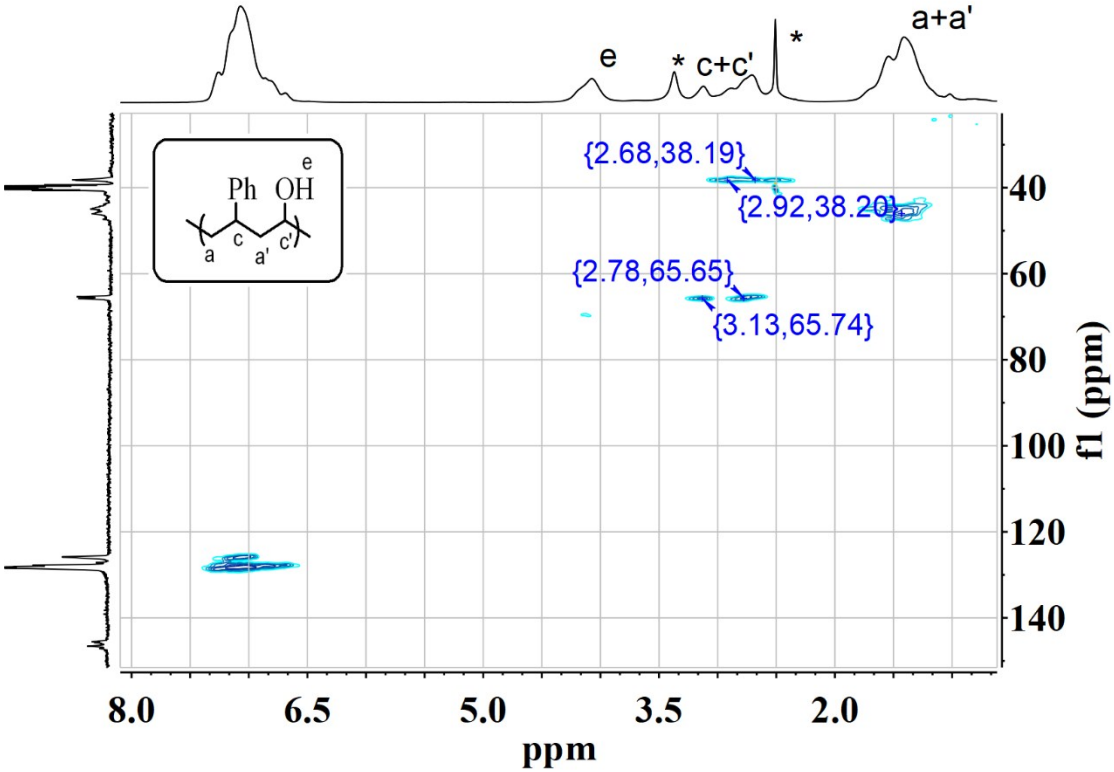


Figure S10 HSQC of PS-VOH in d_6-DMSO.

UV and Raman spectra

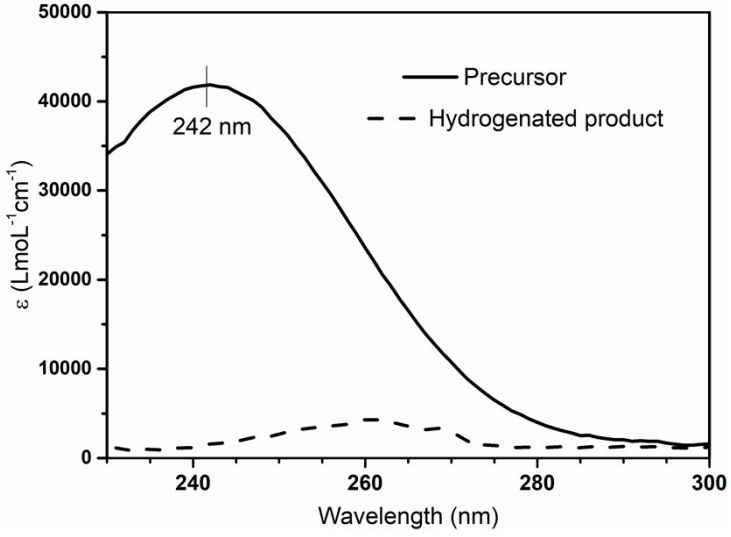


Figure S11 UV spectra of PMeOPhB and PS-VOMe in THF (concentration: 10 μg/mL).

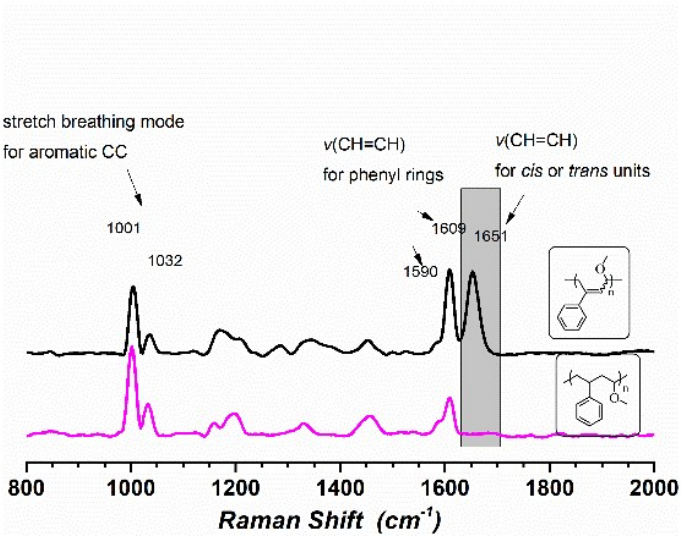


Figure S12 Raman spectra of PMeOPhB and PS-VOMe.

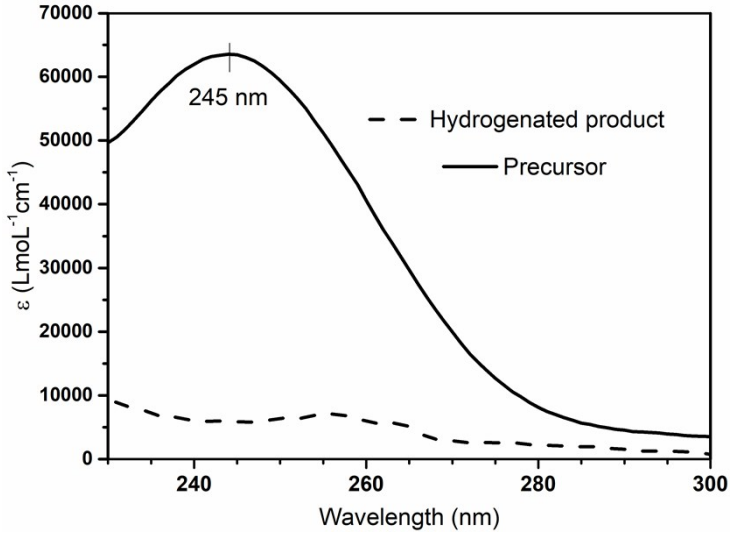


Figure S13 UV spectra of PBnOPhB and PS-VOH in THF (concentration: 10 μg/mL).

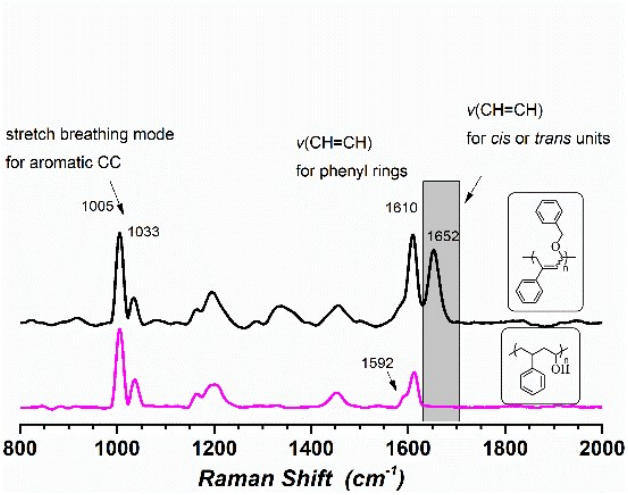


Figure S14 Raman spectra of PBnOPhB and PS-VOH in THF.

TGA and DSC thermograms

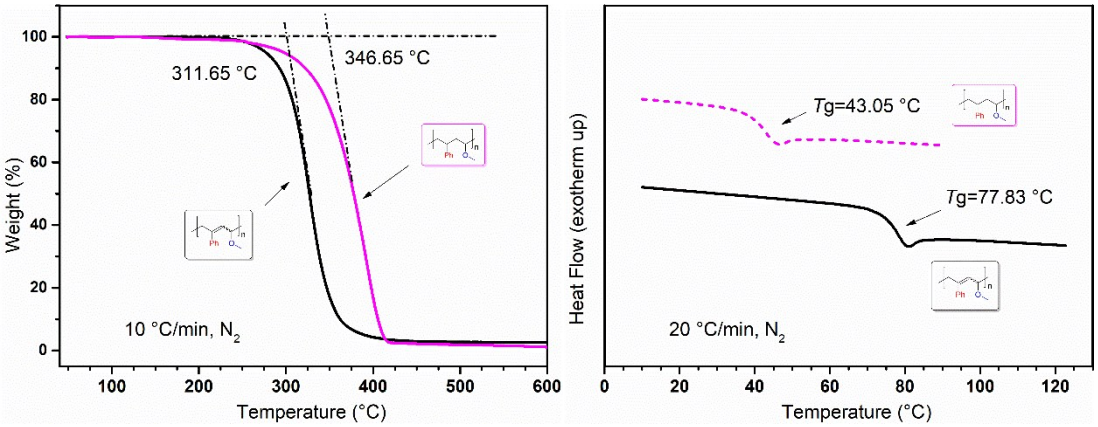


Figure S15 TGA and DSC results of PMeOPhB and its hydrogenated product.

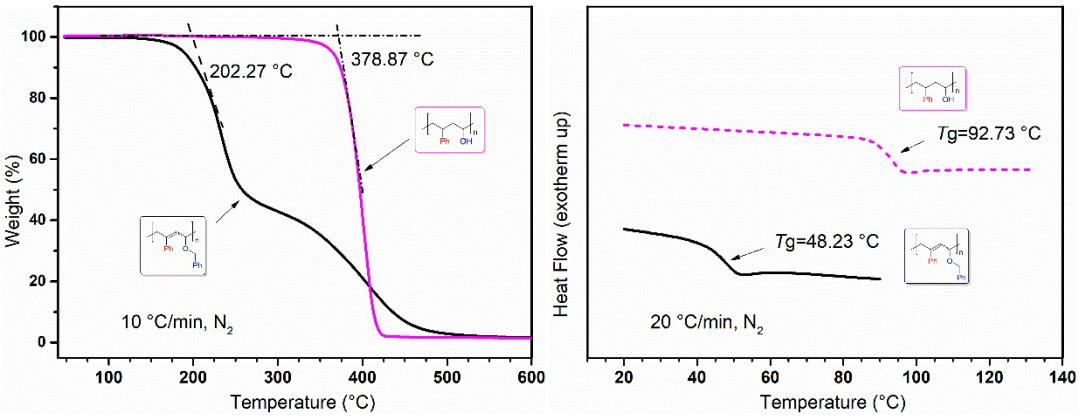


Figure S16 TGA and DSC results of PBnOPhB and its hydrogenated product.

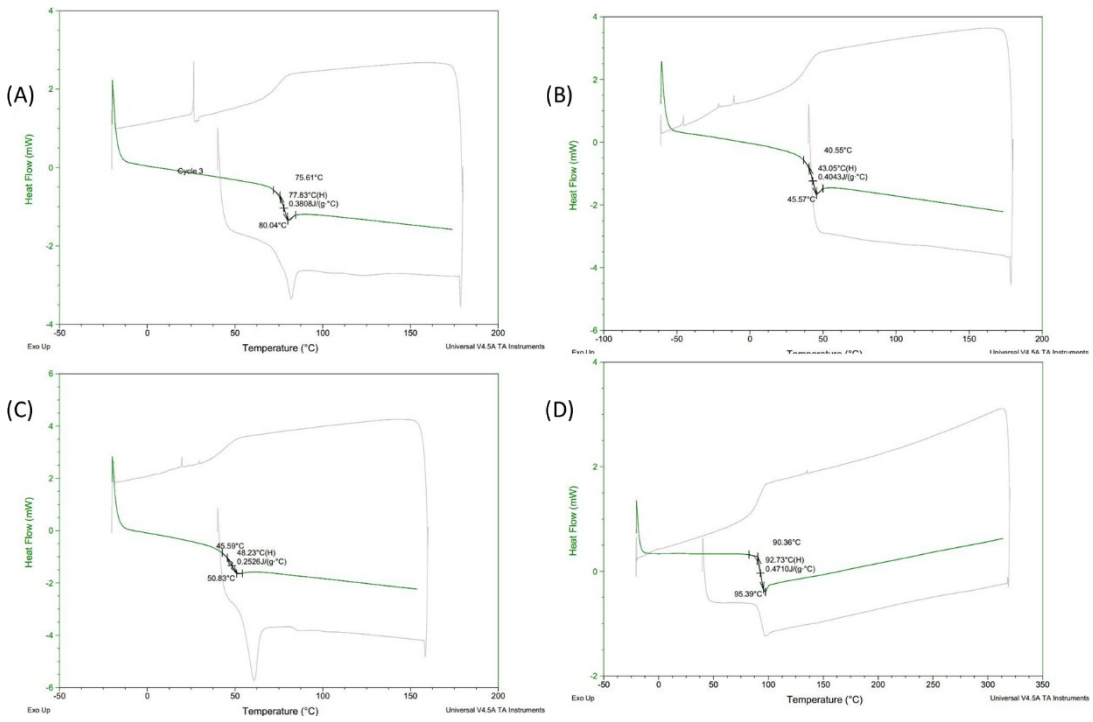


Figure S17 Full DSC thermograms of PMeOPhB(A), PS-VOMe(B), PBnOPhB(C) and PS-VOH(D).

NMR spectra of monomers

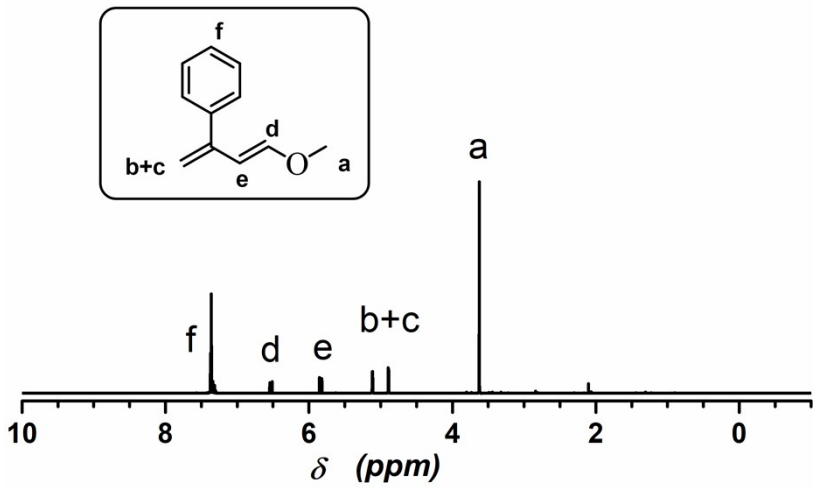


Figure S18 ^{1}H NMR spectrum of monomer MeOPhB.

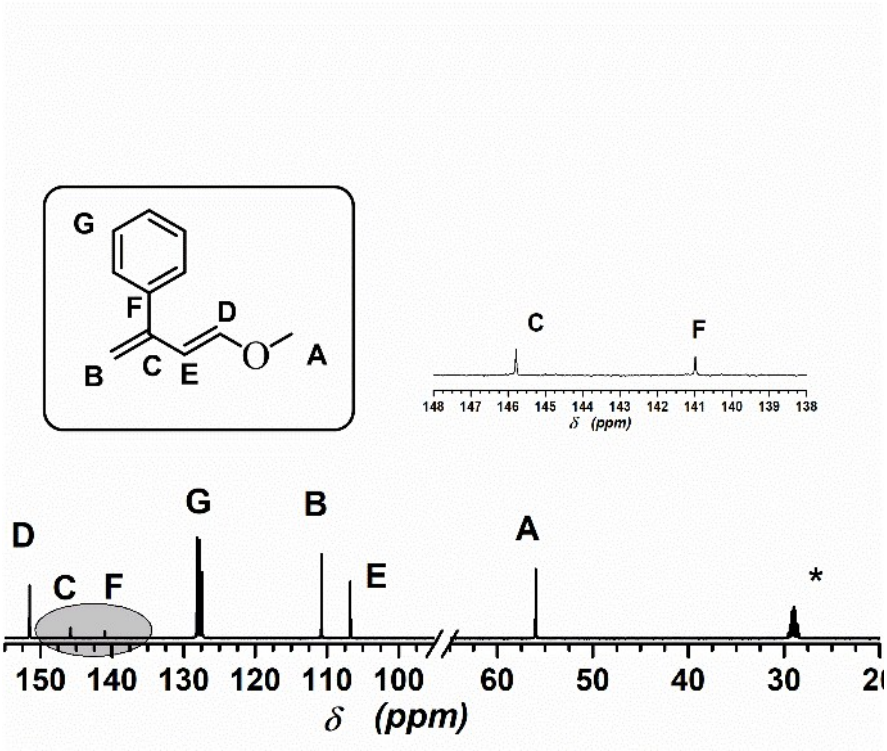


Figure S19 ^{13}C NMR spectrum of monomer MeOPhB.

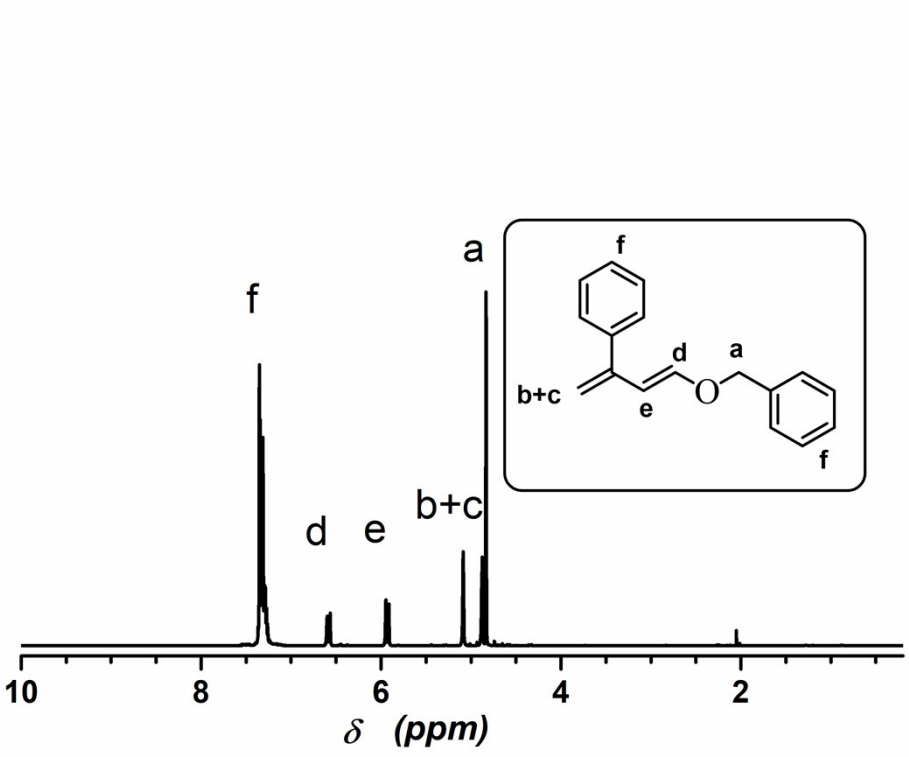


Figure S20 ^{1}H NMR spectrum of monomer BnOPhB.

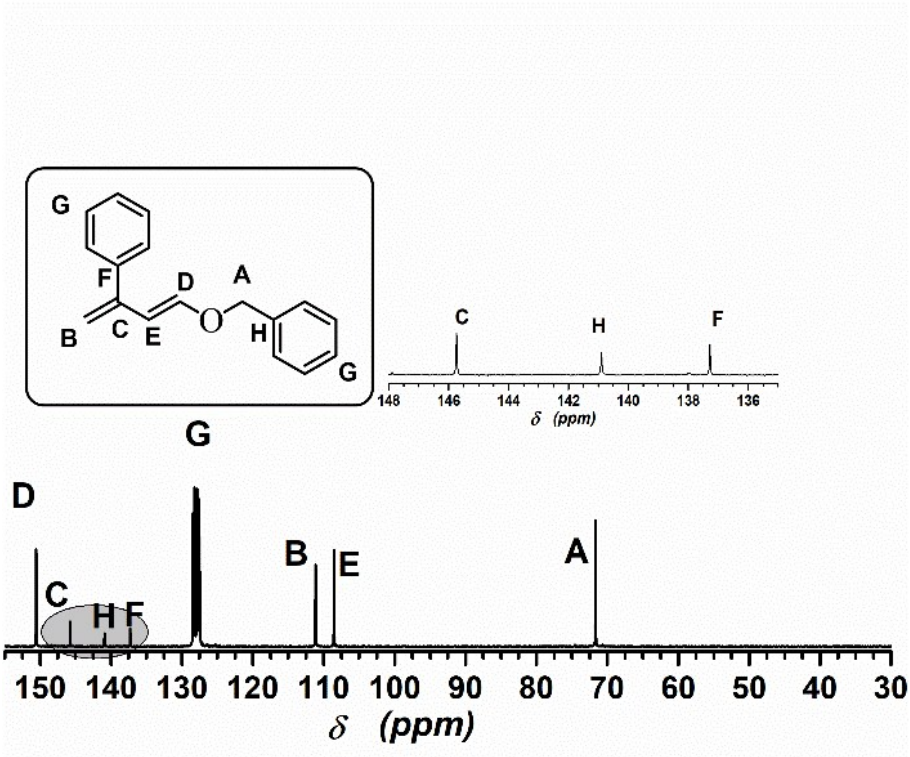


Figure S21 ^{13}C NMR spectrum of monomer BnOPhB.

MS spectra of monomers

Figure S22 MS spectrum of monomer MeOPhB (*m/z* calcd: 160; found: 160).

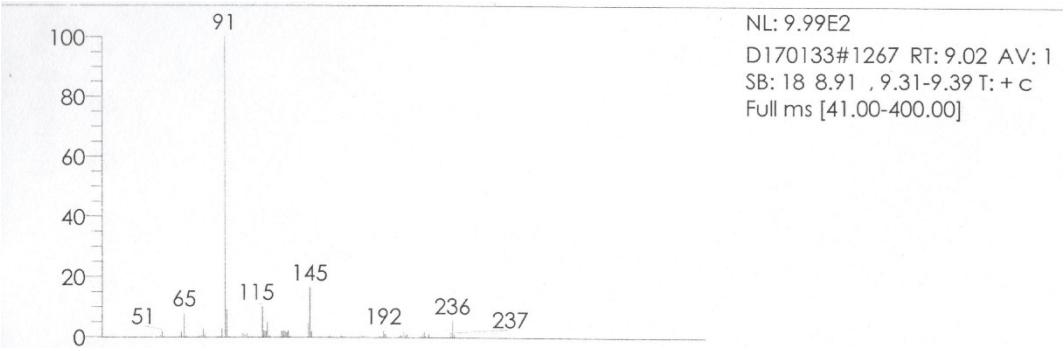


Figure S23 MS spectrum of monomer BnOPhB (*m/z* calcd: 236; found: 236).

NMR spectra of chain transfer agents

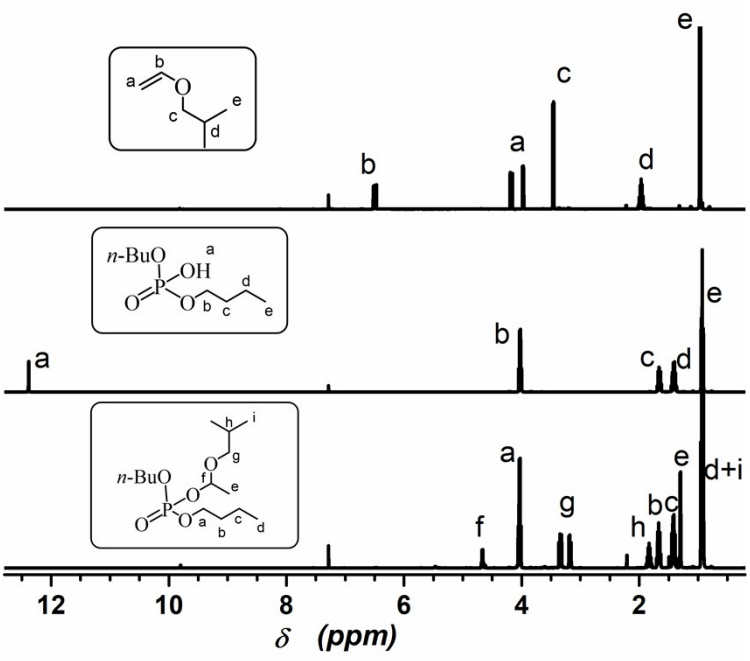


Figure S24 ^{1}H NMR spectra for the synthesis of CTA1.

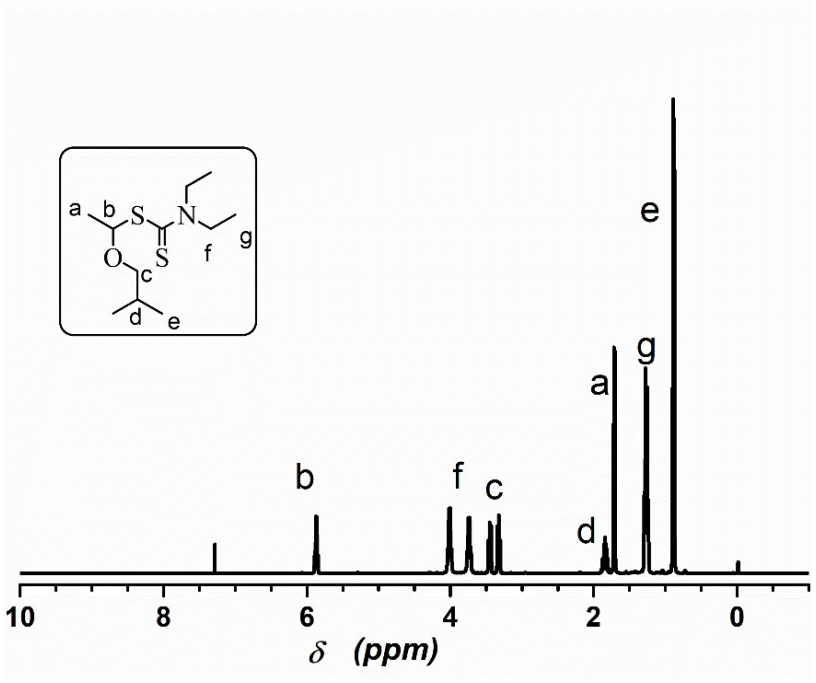
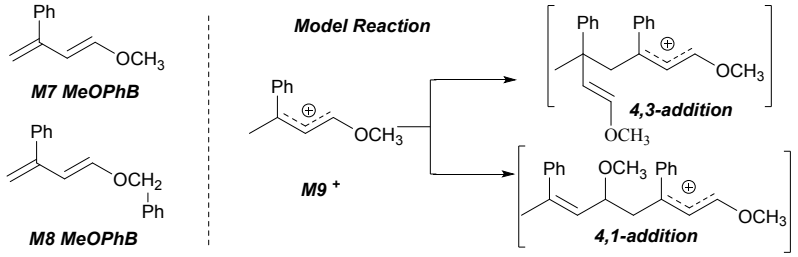


Figure S25 ^{1}H NMR spectra for the synthesis of CTA2.

Results of the DFT calculations



Equations used to compute 4,1-/4,3-addition ratio

$$lnK = \frac{-\Delta G}{RT} \quad (1)$$

$$r = \frac{K_{4,1\,-\,addition}}{K_{4,3\,-\,addition}} \quad (2)$$

M7 m06-2x/6-31+G(d,p)

Charge = 0 Multiplicity = 1

Redundant internal coordinates found in file.

C,0,-2.8533213008,-1.6321158877,-0.1162883419

C,0,-1.8302633371,-1.7526277182,0.8246627084

C,0,-0.8851443849,-0.7397116294,0.9658284702
C,0,-0.9545803399,0.414850534,0.1752074766
C,0,-1.9832782578,0.5249230236,-0.7655637819
C,0,-2.9267810882,-0.490779334,-0.9112883703
H,0,-3.5878902721,-2.4237114619,-0.2274947534
H,0,-1.7725796145,-2.6351644002,1.4548371902
H,0,-0.0953694211,-0.8287684748,1.7071909565
H,0,-2.0318884796,1.4125120013,-1.3899309096
H,0,-3.7174694184,-0.3905754132,-1.6486443719
C,0,0.0223999129,1.530104865,0.3464285373
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C,0,-0.3652749846,2.783032076,0.4693125412
H,0,0.3668472747,3.5822950051,0.537440936
H,0,-1.4143240324,3.0513026494,0.5387511723
C,0,1.438573789,1.1536656708,0.2393978785
C,0,1.903257575,-0.0543920539,-0.0949961306

H,0,2.160457125,1.9401198243,0.4464640105
H,0,1.267504399,-0.9023624024,-0.3409663097
O,0,3.2447375334,-0.3064037149,-0.0864107955
C,0,3.7198909283,-1.3064191045,-0.8994328454
C,0,4.8916273506,-1.9395465396,-0.4861388538
C,0,3.1016942943,-1.657236653,-2.0985533366
C,0,5.4399599922,-2.9428436327,-1.2767052067
H,0,5.3489593829,-1.6352335566,0.4492850554
C,0,3.6596869443,-2.6721151783,-2.8762609513
H,0,2.21206475,-1.1325004068,-2.4307787572
C,0,4.8244894965,-3.3185044473,-2.4723422011
H,0,6.3503947638,-3.4385133244,-0.9545191048
H,0,3.1795272694,-2.9481139427,-3.809848158
H,0,5.253367488,-4.1049725885,-3.0841696036

M9 m06-2x/6-31+G(d,p)

Charge = 1 Multiplicity = 1
Redundant internal coordinates found in file.
C,0,-2.8765467825,-1.5982620445,-0.1352176434
C,0,-1.7312895247,-1.8223838203,0.6269602924
C,0,-0.7704773794,-0.8243387885,0.7441672423
C,0,-0.9516769268,0.4180423943,0.1020228282
C,0,-2.1359213359,0.6449155866,-0.6266746933
C,0,-3.0772077949,-0.3644343788,-0.7607371462
H,0,-3.6260520835,-2.3776581533,-0.2273710546
H,0,-1.5987345117,-2.7645701193,1.1479803344
H,0,0.0820458918,-0.9709988563,1.4014983204
H,0,-2.299633225,1.5987863365,-1.1175882004
H,0,-3.9734165737,-0.1913902453,-1.3467780985
C,0,0.0389765555,1.4804321817,0.2381559512
C,0,-0.4385553172,2.8904218104,0.3683561534
H,0,0.3631421391,3.562804811,0.6738911509
H,0,-0.8048378103,3.2326982017,-0.6084565581
C,0,1.403582597,1.2338298339,0.2562266094
C,0,1.9472193273,0.046444417,-0.2309729185
H,0,2.1003081108,2.0174478351,0.5384655568
H,0,1.3321255753,-0.7233482755,-0.7029288811
O,0,3.218063642,-0.1385341028,-0.1923341355
C,0,3.8108257204,-1.2993517037,-0.8196853442
H,0,4.3661999367,-0.9481484575,-1.6885197473
H,0,4.4860801292,-1.7349493629,-0.0858550017
H,0,3.0333613437,-2.0088471374,-1.1095183192
H,0,-1.2757262935,2.9587759281,1.0672125825

M9-41 m06-2x/6-31+G(d,p)

Charge = 1 Multiplicity = 1

Redundant internal coordinates found in file.

C,0,-0.6637366724,0.6096584345,-4.732696713
C,0,0.4729183791,0.7903654188,-3.9462987672
C,0,0.4286579987,0.5220887523,-2.5815529674
C,0,-0.75253646,0.0716408232,-1.9765920269
C,0,-1.881742675,-0.1273923789,-2.7817478773
C,0,-1.8403764416,0.1484961807,-4.1459432683
H,0,-0.6302403821,0.816154874,-5.7975087071
H,0,1.3997911994,1.1284009423,-4.398652524
H,0,1.3280143711,0.6358692231,-1.9828557012
H,0,-2.8077353127,-0.4859193982,-2.3424200855
H,0,-2.7286122699,-0.0012270801,-4.7513574608
C,0,-0.8009741625,-0.2091342269,-0.5140043919
C,0,-1.6382276949,-1.3929122274,-0.094562403
H,0,-1.4488625075,-1.7043041582,0.9332579962
H,0,-2.7059771119,-1.1652342878,-0.1814277646
C,0,-0.1170362983,0.5765041949,0.3353547517
C,0,0.0068114171,0.4266447143,1.8255380676
H,0,0.4421527128,1.4190999742,-0.0720614747
O,0,1.3325564313,0.0816814139,2.2107911392
C,0,1.7239375604,-1.2152574148,1.7910411803
H,0,2.7479762282,-1.3619849063,2.1335577045
H,0,1.0744153168,-1.9817801934,2.2388958274
H,0,1.6849169206,-1.3093119973,0.7005572306
H,0,-1.437165184,-2.2434501669,-0.7519139549
C,0,-0.2884244029,1.763268387,2.5040059554
C,0,-0.3952988573,1.7804677611,3.9959157873
H,0,-1.2014971936,2.2002248468,2.0825711689
H,0,0.5113395121,2.4730236646,2.2381479434
C,0,-0.9173154804,3.0015248041,4.6190633943
C,0,0.0346831664,0.7045880567,4.7570574635
C,0,-0.2377268936,3.5724383013,5.7133257245
C,0,-2.0626118113,3.6455211202,4.1146237928
C,0,-0.3388498913,0.5773875249,6.0927448489
H,0,0.6057802142,-0.0957019933,4.2981977718
C,0,-0.7007635934,4.7482594593,6.2942374809
H,0,0.6935596579,3.1298855582,6.0558993284
C,0,-2.5369021901,4.8010021935,4.7204427152
H,0,-2.6098293594,3.2181168455,3.2807209652
H,0,-1.0260401119,1.2766620189,6.5747952146

O,0,0.081785232,-0.4211993428,6.7865663058
C,0,-1.8555070507,5.3569152979,5.8058041673
H,0,-0.1524531411,5.1960142314,7.1161195713
H,0,-3.4365906219,5.2748511066,4.3428604772
C,0,-0.3953543162,-0.6261851245,8.1347280002
H,0,-2.2191721029,6.2725800237,6.2603887129
H,0,0.4858239436,-0.7531780681,8.7609308645
H,0,-0.9875979258,0.2310937305,8.4606227836
H,0,-0.9936872656,-1.5364913249,8.1296619198
H,0,-0.6908119694,-0.3363476187,2.2067891528

M9-43 m06-2x/6-31+G(d,p)

Charge = 1 Multiplicity = 1
Redundant internal coordinates found in file.
C,0,-2.565989011,-1.2863400538,1.3777713727
C,0,-1.6026972282,-1.6233092684,0.4273412127
C,0,-0.8881460122,-0.6238907696,-0.2266914013
C,0,-1.1201993543,0.73027659,0.0463321255
C,0,-2.0785738633,1.0537842458,1.0111760913
C,0,-2.7974519627,0.05512589,1.6692239099
H,0,-3.1183030822,-2.0626784706,1.897476188
H,0,-1.3960591386,-2.6657482441,0.20584976
H,0,-0.1258235038,-0.8996390933,-0.951287466
H,0,-2.2803078649,2.0889387062,1.2669811496
H,0,-3.533143968,0.3313100542,2.4182854447
C,0,-0.3458185746,1.7989161317,-0.7401765075
C,0,-0.3954111278,3.1730351829,-0.0516504857
H,0,0.2112594154,3.892413673,-0.6124999445
H,0,-1.410578264,3.5708956584,0.0381480876
C,0,1.1123950349,1.3956193162,-0.8206082416
C,0,1.8235047377,1.093767595,-1.909100035
H,0,1.6271608648,1.3485575757,0.1377947459
H,0,1.4121918244,1.07049601,-2.9203743963
O,0,3.141124093,0.803245642,-1.8205471478
C,0,3.7222155847,0.2303752683,-2.9828808227
H,0,4.7879383544,0.1358393571,-2.7813673728
H,0,3.2997665004,-0.7601433796,-3.1833642925
H,0,3.5735225738,0.8800500592,-3.8535846532
H,0,0.0299278765,3.102587466,0.9530343988
C,0,-0.9308332092,1.9189040013,-2.2006446732
C,0,-2.2938504009,2.5318979754,-2.2605399175
H,0,-0.9614554325,0.9139683324,-2.6321679709
H,0,-0.2231710684,2.4962252827,-2.7972484994

C,0,-3.4459747419,1.744471595,-1.8557415128
C,0,-2.4959594182,3.8603233427,-2.6462480288
C,0,-4.553014,2.3754933758,-1.245009459
C,0,-3.4621047736,0.3414102186,-1.9996287625
C,0,-1.472003295,4.7328468163,-2.9675107369
H,0,-3.5032794165,4.2533269417,-2.733565401
C,0,-5.6216900517,1.6272707281,-0.7785545116
H,0,-4.5440582808,3.4470425644,-1.0737921517
C,0,-4.5476484243,-0.3988770412,-1.5584053288
H,0,-2.6369387534,-0.1727621384,-2.4774644831
H,0,-0.4176974049,4.4530493768,-2.9486083537
O,0,-1.7487566671,5.9505424434,-3.3021228509
C,0,-5.6226340535,0.2396399816,-0.9385563905
H,0,-6.4507336413,2.1202827354,-0.282664635
H,0,-4.5504011263,-1.4761041621,-1.6840110722
C,0,-0.688967599,6.846855161,-3.6982548988
H,0,-6.4625539287,-0.3450271604,-0.5767891059
H,0,-0.9389125499,7.8194219181,-3.2802236812
H,0,0.2690344875,6.4946964888,-3.3102631505
H,0,-0.679332165,6.8925449406,-4.7875814136

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