

Supporting Information

Vinyl Boronate Polymers with Dynamic Exchange Property

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I. General Reagent Information

Trimethyl borate (99%, Adamas), vinylmagnesium bromide (1.0 M solution in THF, Adamas), *N*-methyliminodiacetic acid (98%, Bidepharm), diethanolamine (99%, Adamas), KHF₂ (99%, Adamas), pinacol vinylboronate (97%, Adamas), 2,2-azobis(2-methylpropionitrile) (98%, TCI), triethylborane (1.0 M solution in THF, Energy Chemical), *n*-butyllithium (2.5 M solution in hexanes, Adamas), SnCl₄ (99%, Energy Chemical), Ru(bpy)₃Cl₂ (98%, Adamas), ethyl α -bromoisobutyrate (98%, Adamas), copper bromide (99%, Adamas), tris(2-pyridylmethyl)amine (98%, Energy Chemical), 1-methylimidazole (99%, Energy Chemical), iodomethane (99.5%, Energy Chemical), NaBH₄ (98%, Sinoreagent), MgSO₄ (98%, Greagent), NaHCO₃ (99.5%, Greagent), CaCl₂ (96%, Greagent), toluene (99.5%, Sinoreagent), *N,N*-dimethylformamide (DMF) (99.8% anhydrous, Adamas), dimethyl sulfoxide (99.5%, Sinoreagent), acetonitrile (MeCN) (99.9% anhydrous, Adamas), tetrahydrofuran (THF) (99.5% anhydrous, Adamas), dichloromethane (DCM) (99.9% anhydrous, Adamas), diethyl ether (Et₂O) (99.7%, Sinoreagent), acetone (99.5%, Sinoreagent), methyl methacrylate (MMA, 99%, Adamas), styrene (St, 99%, Adamas), tert-butyl acrylate (*t*-BA, 99%, Adamas), vinyl acetate (VAc, 98%, Energy Chemical), acrylonitrile (AN, 98%, TCI), isobutyl vinyl ether (IBVE, 98%, Energy Chemical) were used as received. *N*-isopropyl acrylamide (NIPAM, 98%, Energy Chemical) was recrystallized to remove inhibitors prior to use. All other reagents were obtained from TCI, Sigma Aldrich, Alfa Aesar, Energy Chemical and Adamas and used as received.

The RAFT agents were synthesized previously, including 2-cyanopropan-2-yl

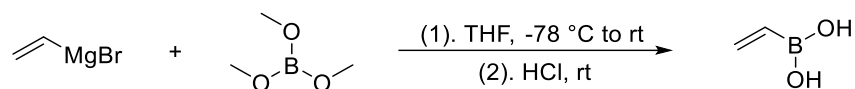
dodecyl carbonotrithioate (CPDT),¹ 2-[[[(dodecylthio) thioxomethyl] thio]-2-methylpropanoic acid (DTMPA),² 4-cyano-4-[[[(dodecylthio) thioxomethyl] thio]-pentanoic acid (CDTPA),² cumyl dithiobenzoate (CDB),³ benzyl diethylcarbamdithioate (BDCD),⁴ S-benzyl O-ethyl carbonodithioate (BzXan).⁵ PET-RAFT polymerizations were carried out under irradiation with blue light LED strips (2 meters, 20 W, 220 V).

II. General Analytical Information

^1H NMR spectra were recorded on Bruker Avance 400 (400 MHz) at room temperature using CDCl_3 or DMSO as a solvent. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak. Two GPC characterizations were adopted. One was performed in tetrahydrofuran (THF) solution at 35 °C with an elution rate of 1.0 mL min $^{-1}$ on an Agilent 1260 HPLC system equipped with a G7110B pump and a G7162A refractive index detector. The molecular weights were determined using PLgel MIXED-A column and PLgel MIXED-C column based on linear poly(methyl methacrylate) (PMMA) as standards. The second GPC characterization was performed in DMF solution at 50 °C with an elution rate of 1.0 mL min $^{-1}$ on an Agilent 1260 HPLC system equipped with a G7111A pump and a G7162A refractive index detector. The molecular weights were determined using PLgel MIXED-C column based on linear poly(methyl methacrylate) (PMMA) as standards. The UV-vis spectra were performed by the Agilent Cary 60 UV-vis spectrophotometer. Thermogravimetric analysis (TGA) experiments were carried out on samples (5.00~10.0 mg) from 30 °C to 500 °C at a heating rate of 10 °C/min in a N_2 atmosphere using a TA Instruments TGA Mettler Toledo.

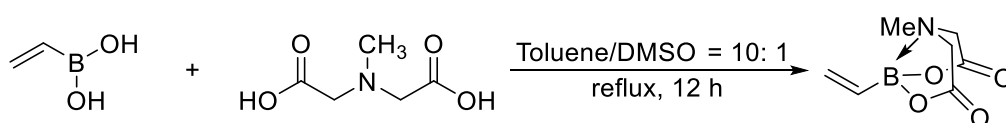
III. Synthesis of Reagents

Synthesis of Vinyl Boronic Acid



The vinyl boronic acid was synthesized with some modification according to the previously reported procedure.⁶ Trimethyl borate (12.5 g, 120 mmol) was dissolved in 50.0 mL dry THF and cooled to -78.0 °C, and a 1.0 M solution of vinylmagnesium bromide in THF (100 mL, 100 mmol) was added to it dropwise. The resulting white slurry was allowed to stir and warmed to room temperature overnight. The reaction was then quenched with the addition of 100 mL of 2.0 M HCl aqueous solution and stirred for 2 h. It was then extracted with diethyl ether for 2 times and the organic layer was dried with MgSO₄ to remove traces of water and concentrated to give the vinyl boronic acid (6.35 g, 88.2 % yield) as yellow oil.

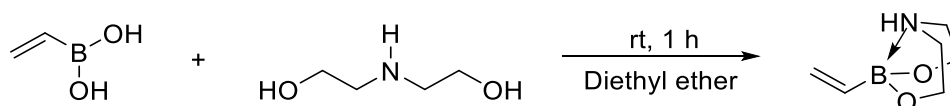
Synthesis of Vinyl MIDA Boronic Ester



Vinyl boronic acid (1.80 g 25.0 mmol), *N*-methyliminodiacetic acid (3.70 g, 25.0 mmol) and 55.0 mL mixed solvent (Tol:DMSO = 10:1) were added into a bottle equipped with a Dean-Stark. After stirring for 12 h at refluxing temperature. Remove the toluene in vacuo and then add water into the bottle. Transfer the mixed solution to the liquid separation funnel and extract with ethyl acetate for 3 times. The organic layer was collected and dried with MgSO₄ to remove traces of water and concentrated to give

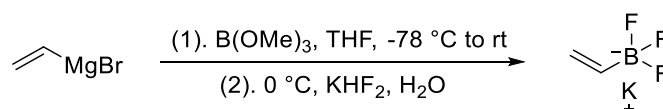
the vinyl MIDA boronic ester (1.42 g, 31.0 % yield) as white powder.

Synthesis of Vinyl DEA Boronic Ester



The vinyl DEA boronic ester was synthesized with some modification according to the previously reported procedure.⁶ At room temperature, vinyl boronic acid (5.76 g, 80.0 mmol) was dissolved in 100 mL diethyl ether and diethanolamine (8.40 g, 80.0 mmol) was added portionwise to the vigorously stirred solution. The reaction was allowed to stir for another 1 h. Then the mixture of NaHCO₃ (1.00 g) and CaCl₂ (1.50 g) was added to the reaction solution and stirred for 0.5 h to adsorb the residual diethanolamine. The solid was removed by filtration and the filtrate was then transferred to another flask and concentrated under reduced pressure. Recrystallization from tetrahydrofuran gave the desired product (3.26 g, 28.9 % yield) as a white solid.

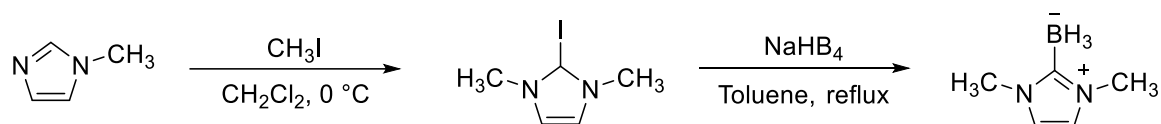
Synthesis of Potassium Vinyltrifluoroborate



The potassium vinyltrifluoroborate was synthesized with some modification according to the previously reported procedure.⁷ Trimethyl borate (2.32 g, 22.3 mmol) was dissolved in 15.0 mL dry THF and cooled to -78.0 °C and a 1.0 M solution of vinylmagnesium bromide in THF (18.0 mL, 18.0 mmol) was added to it dropwise. The resulting white slurry was allowed to stir at -78.0 °C for 20 min and warmed to room temperature for another 1 h. The mixture was then cooled to 0 °C and KHF₂ (6.97 g,

89.2 mmol) was added followed by H₂O (12.0 mL) over a period of 30 min. After stirring at room temperature for 20 min, the solution was concentrated and the crude material was dissolved in acetone, filtered, and concentrated. The resulting white solid was purified by dissolving in acetone and precipitating with Et₂O, obtaining a white solid (1.75 g, 73.0 % yield).

Synthesis of DiMe-Imd-BH₃



The diMe-Imd-BH₃ was synthesized with some modification according to the previously reported procedure.⁸

(1) Synthesis of 1,3-dimethyl-imidazol iodide.

1-Methylimidazole (3.70 g, 45.0 mmol) was added to a 50 mL Schlenk flask equipped with a magnetic stir bar. Then the flask was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Dichloromethane (10.0 mL) was placed in the Schlenk flask by syringe. After the addition of iodomethane (7.65 g, 54.0 mmol) which was slowly added by droplets in an ice bath, this reaction was maintained for 1 h at room temperature. After removing the solvent through evaporation, white solid was obtained (9.57 g, 95.0 % yield).

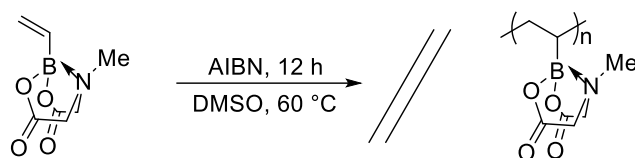
(2) Synthesis of DiMe-Imd-BH₃.

1,3-dimethyl-imidazol iodide (8.96 g, 40.0 mmol) and NaBH₄ (2.26 g, 60.0 mmol)

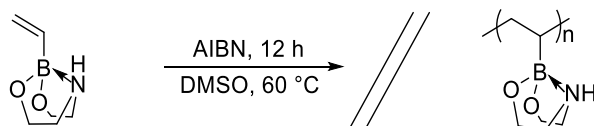
and toluene (90.0 mL) were added to a 250 mL Schlenk flask equipped with a magnetic stir bar. Then the mixture was stirred at 126 °C for 21 h. After evaporating the solvent, the crude product was purified by chromatography (ethyl acetate/petroleum ether = 2/3), obtaining white solid product (2.01 g, 45.0 % yield).

IV. General Procedure of Polymerization

Free Radical Polymerization of Vinyl Boronate Monomers

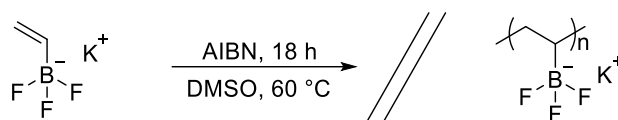


Vinyl MIDA Boronic Ester. Vinyl MIDA boronic ester (183 mg, 1.00 mmol) and AIBN (16.4 mg, 100 μ mol) were added into a 10 mL Schlenk flask equipped with a magnetic stir bar. The Schlenk flask was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DMSO (1.00 mL) was placed in the Schlenk flask by syringe. The reaction mixture was stirred at 60 °C in an oil bath for 12 h. The polymerization was quenched by removing the reaction mixture from heat and exposing to air.



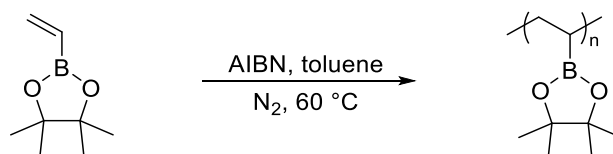
Vinyl DEA Boronic Ester. Vinyl DEA boronic ester (282 mg, 2.00 mmol) and AIBN (32.8 mg, 200 μ mol) were added into a 10 mL Schlenk flask equipped with a magnetic stir bar. The Schlenk flask was sealed and degassed via vacuum evacuation

and subsequent backfill with nitrogen for three times. Then anhydrous DMSO (3.00 mL) was placed in the Schlenk flask by syringe. The reaction mixture was stirred at 60 °C in an oil bath for 12 h. The polymerization was quenched by removing the reaction mixture from heat and exposing to air.



Potassium Vinyltrifluoroborate. Potassium vinyltrifluoroborate (134 mg, 1.00 mmol) and AIBN (16.4 mg, 100 μ mol) were added into a 10 mL Schlenk flask equipped with a magnetic stir bar. The Schlenk flask was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then anhydrous DMSO (1.00 mL) was placed in the Schlenk flask by syringe. The reaction mixture was stirred at 60 °C in an oil bath for 18 h. The polymerization was quenched by removing the reaction mixture from heat and exposing to air.

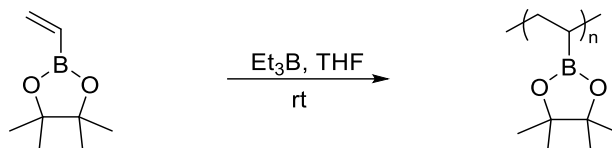
Typical Free Radical Polymerization of VB_{pin} by Thermal Initiation



A 10 mL Schlenk flask equipped with a magnetic stir bar was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then AIBN (50.0 mg/mL in toluene, 65.6 μ L, 20.0 μ mol), toluene (134 μ L), and VB_{pin} (308 mg, 2.00 mmol) were placed in the Schlenk flask by syringe. The reaction mixture was stirred at 60 °C in an oil bath. The polymerization was monitored by ¹H NMR and GPC.

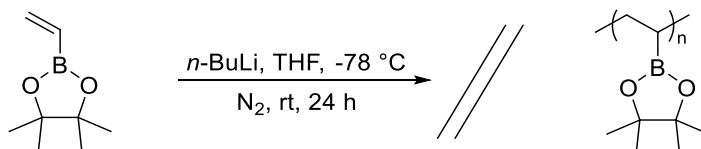
After 54 h, the polymerization was stopped by removing the reaction mixture from heat and exposing to air.

Typical Free Radical Polymerization of VB_{pin} by Oxygen Initiation



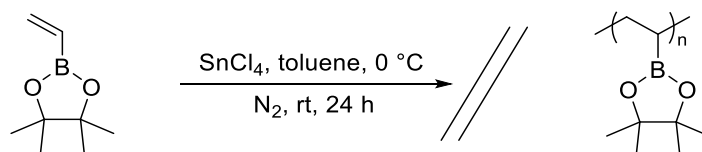
A 10 mL Schlenk flask equipped with a magnetic stir bar was sealed. Then VB_{pin} (154 mg, 1.00 mmol) and dry THF (1.00 mL) were placed in the Schlenk flask by syringe. The triethylborane (20.0 μ L of 1.0 M solution in THF, 20.0 μ mol) was added by syringe. The system was kept stirring for 2 h at room temperature. The polymerization was monitored by ¹H NMR and GPC.

Anionic Polymerization of VB_{pin}



A 10 mL Schlenk flask equipped with a magnetic stir bar was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then dry THF (500 μ L) and VB_{pin} (308 mg, 2.00 mmol) were placed in Schlenk flask by syringe. It was cooled to -78.0 °C. After the addition of *n*-BuLi (2.5 mol/L in *n*-hexane, 40.0 μ L, 0.10 mmol), the reaction mixture was raised to room temperature and reacted for 24 h. The reaction process was monitored by ¹H NMR and GPC. After 24 h, the conversion of VB_{pin} was less than 1%.

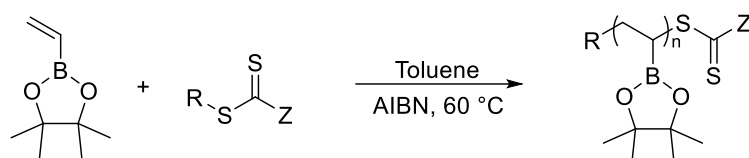
Cationic Polymerization of VB_{pin}



A 10 mL Schlenk flask equipped with a magnetic stir bar was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then dry toluene (2.00 mL) and VB_{pin} (308 mg, 2.00 mmol) were placed in Schlenk flask by syringe. It was cooled to 0 °C. After the addition of SnCl₄ (2.5 mol/L in n-hexane, 40.0 μL, 0.10 mmol), the reaction mixture was raised to room temperature and reacted for 24 h. The reaction process was monitored by ¹H NMR and SEC. After 24 h, conversion of VB_{pin} was less than 1%.

V. General Procedure of RAFT Polymerization

Typical RAFT Polymerization of VB_{pin}

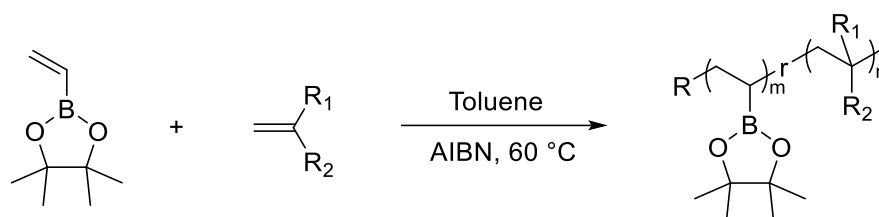


A 10 mL Schlenk flask equipped with a magnetic stir bar was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then AIBN (50.0 mg/mL in toluene, 52.4 μL, 16.0 μmol), chain transfer agent CPDT (50.0 mg/mL in toluene, 138 μL, 20.0 μmol), toluene (10.0 μL) and VB_{pin} (308 mg, 2.00 mmol) were placed in the Schlenk flask by syringe. The reaction mixture was stirred at 60 °C in an oil bath. The polymerization was monitored by ¹H NMR and GPC. After 36 h, the polymerization was stopped by removing the reaction mixture from heat and

exposing to air.

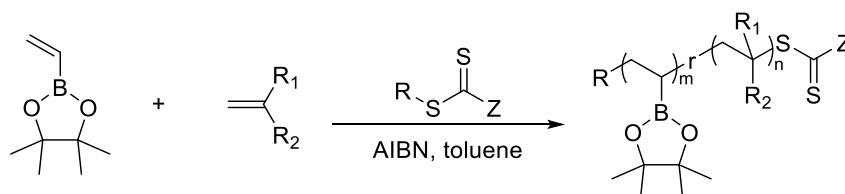
VI. General Procedure of Copolymerization

Typical Free Radical Copolymerization of VB_{pin} by Thermal Initiation



A 10 mL Schlenk flask equipped with a magnetic stir bar was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then AIBN (50.0 mg/mL in toluene, 65.6 μ L, 20.0 μ mol), toluene (134 μ L), styrene (208 mg, 2.00 mmol) and VB_{pin} (308 mg, 2.00 mmol) were placed in the Schlenk flask by syringe. The reaction mixture was stirred at 60 °C in an oil bath. The polymerization was monitored by ¹H NMR and GPC. After 24 h, the polymerization was stopped by removing the reaction mixture from heat and exposing to air. The free radical polymerizations of other copolymers were similar to this general procedure.

Typical RAFT Copolymerization of VB_{pin} by Thermal Initiation



A 10 mL Schlenk flask equipped with a magnetic stir bar was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then AIBN (50.0 mg/mL in toluene, 65.6 μ L, 20.0 μ mol), chain transfer agent CPDT (50.0

mg/mL in toluene, 138 μ L, 20.0 μ mol), styrene (208 mg, 2.00 mmol) and VB_{pin} (308 mg, 2.00 mmol) were placed in the Schlenk flask by syringe. The reaction mixture was stirred at 60 °C in an oil bath. The polymerization was monitored by ¹H NMR and GPC. After 48h, the polymerization was stopped by removing the reaction mixture from heat and exposing to air. The RAFT polymerizations of other copolymers were similar to this general procedure.

Synthesis of Block Copolymers

(1) Synthesis of Macro-CTAs by RAFT Polymerization

A 10 mL Schlenk flask equipped with a magnetic stir bar was sealed. Then AIBN (50.0 mg/mL in DMSO, 65.6 μ L, 20.0 μ mol), chain transfer agent CPDT (50.0 mg/mL in DMSO, 690 μ L, 100 μ mol), styrene (590 mg, 5.00 mmol) and DMSO (1.74 mL) were placed in the Schlenk flask by syringe. After the system was degassed by three freeze-pump-thaw cycles, the flask was purged with nitrogen and placed in an oil bath set at 60 °C to start polymerization. The polymerization was monitored by ¹H NMR and GPC. After 24 h, the polymerization was stopped by removing the reaction mixture from heat and exposing to air. PS-CTAs were precipitated in methanol and filtered to obtain yellow powders. The RAFT polymerizations of other macro-CTAs were similar to this general procedure.

(2) Synthesis of VB_{pin} Block Copolymers by RAFT Polymerization

A 10 mL Schlenk flask equipped with a magnetic stir bar was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then

AIBN (50.0 mg/mL in toluene, 65.6 μL , 20.0 μmol), PS-CTAs (40.0 mg in 234 μL toluene, 20.0 μmol) and VB_{pin} (154 mg, 1.00 mmol) were placed in the Schlenk flask by syringe. The reaction mixture was stirred at 60 $^{\circ}\text{C}$ in an oil bath. The polymerization was monitored by ^1H NMR and GPC. After 24 h, the polymerization was stopped by removing the reaction mixture from heat and exposing to air. The polymerization of other copolymers was similar to this general procedure.

VII. General Procedure of Reduction of Chain-End



$\text{P}(\text{St-}r\text{-VB}_{\text{pin}})\text{-CTA}$ (38.4 mg, 5.00 μmol), diMe-Imd-BH_3 (5.50 mg, 50.0 μmol), AIBN (10.0 mg/mL in acetonitrile, 82.0 μL , 5.00 μmol), MeCN (1.12 mL) and THF (1.00 mL) were added to a 10 mL Schlenk flask equipped with a magnetic stir bar. The resulting mixture was degassed by three freeze-pump-thaw cycles and purged with nitrogen, then placed in an oil bath set at 70 $^{\circ}\text{C}$ for 8 h. The flask was opened to air, and the resulting mixture was precipitated into methanol for obtaining white solid. The removal processes of other polymers from RAFT were similar to this general procedure.

VIII. Solubility Test of Vinyl Boronic Acid Polymer

The vinyl boronic acid polymer networks cannot be dissolved in any solvents, including petroleum ether (PE), ethyl acetate (EA), tetrahydrofuran (THF), and dimethyl sulfoxide (DMSO), etc.

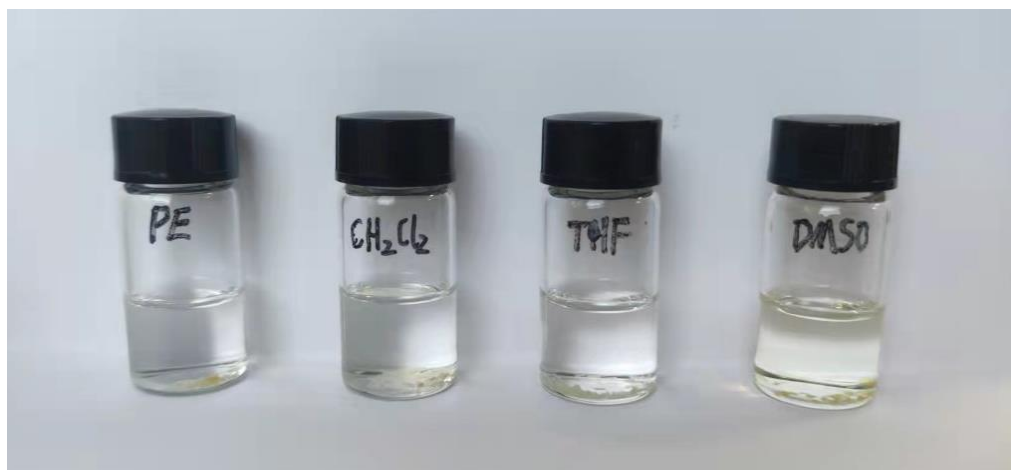


Figure S1. Vinyl Boronic Acid Polymer in Different Solvents.

Solubility in Solutions of Different pH

First of all, a small amount of gelatinous substance was soaked in 2.00 mol/L NaOH aqueous solution. Part of the insoluble matter was slowly dissolved after being immersed for several days and the aqueous solution also gradually changed from colorless to light yellow whose color is similar to the vinyl boronic acid monomer. However, a large amount of flocs remain in the solution, even after more than two weeks. By comparison, the insoluble matter did not show any dissolution in the same concentration of H₂SO₄ aqueous solution, which indicates its stability under acidic conditions. We further use the organic and alkali mixed solutions to soak the insoluble matter. In the mixed solution of tetrahydrofuran and sodium hydroxide, we can observe the disappearance of insoluble matter and finally form two transparent layers. In the upper layer, there is a colorless tetrahydrofuran solution that dissolves the polymer, while in the lower layer, it is an alkaline aqueous solution that dissolves some small molecular monomers.



Figure S2. Vinyl Boronic Acid Polymer in Mixed Alkaline Solvents (pH>7).



Figure S3. Vinyl boronic Acid Polymer in Mixed Acid Solvents (pH<7).

IX. Sol-Gel Transition of VB_{pin} Polymer

Gel Observation

A solution of VB_{pin} polymer (100 mg) at 65 wt% in toluene was prepared with 2 % mass equivalent of benzyl alcohol (2.00 mg, 2.00 μ L). Place the closed system in an oil bath at 110 °C for 12 h, the polymer formed a gel. After the addition of toluene (the final concentration was 25 wt % PVB_{pin}), the gel started to dissociate to afford a clear solution. The process is repeatable over several cycles.

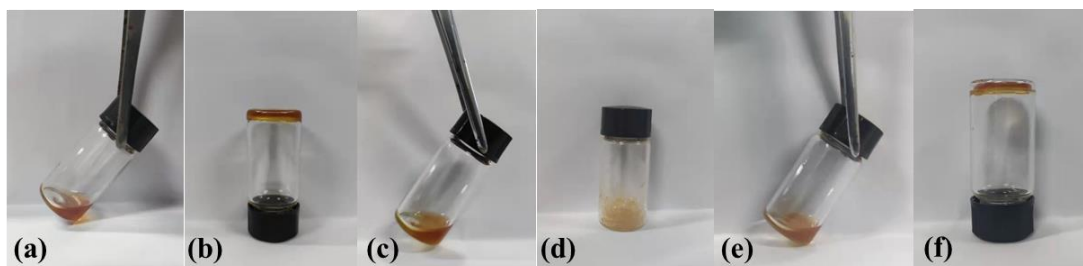


Figure S4. Macroscopic of the VB_{pin} polymer in solution was observed during different steps, (a) Initial solution of PVB_{pin} at 65 wt% in toluene, (b) After 12 h at 110 °C, (c) After the addition of toluene, (d) Recovery of the polymer powder, (e) Solubilization in toluene (65 wt%), (f) After 12 h at 110 °C.

Stability and Recoverability of the VB_{pin} Polymer

We measured the molecular weight of the VB_{pin} polymer before and after one cycle. The GPC traces (Figure S5) obtained prove the recovery of the polymer chain structure. The shouldering at low molecular weight range is likely due to the small amount of polymer decomposition at high temperature.

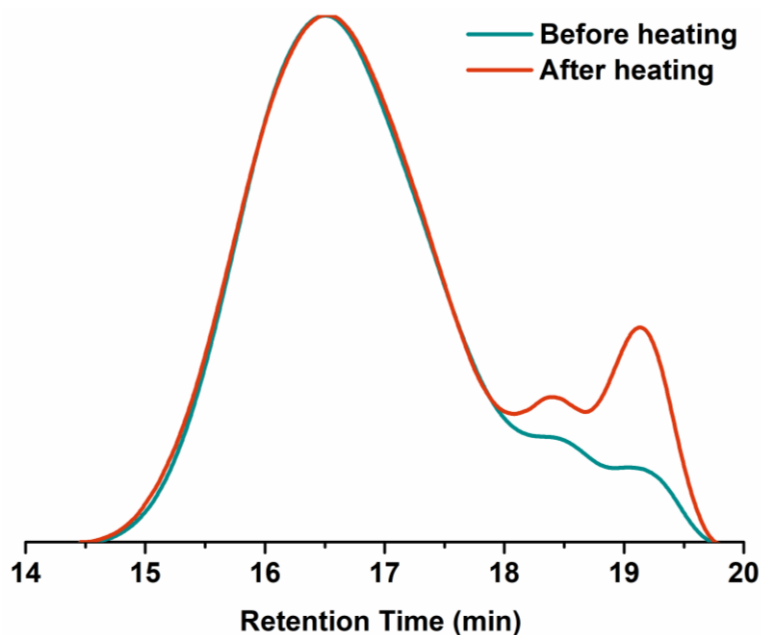


Figure S5. GPC Traces of VB_{pin} Polymer before and after One Cycle.

X. Analytical Data of the Polymers

Table S1. Synthesis of VB_{pin} Polymers by Radical Polymerization^a

Entry	[M] ₀ /[I] ₀	Time (h)	Conv ^b (%)	M _n , GPC ^c	M _w /M _n ^c
1	20:1	24	85	2490	2.30
2	50:1	48	95	2720	2.34
3	100:1	54	86	3410	2.45
4	200:1	96	93	7280	1.91

^aReaction conditions: [M]₀ = 10.0 M in toluene. Reaction temperature is 60 °C under a N₂ atmosphere. ^bDetermined by ¹H NMR spectroscopy. ^cDetermined by GPC in THF, based on linear PMMA as a calibration standard.

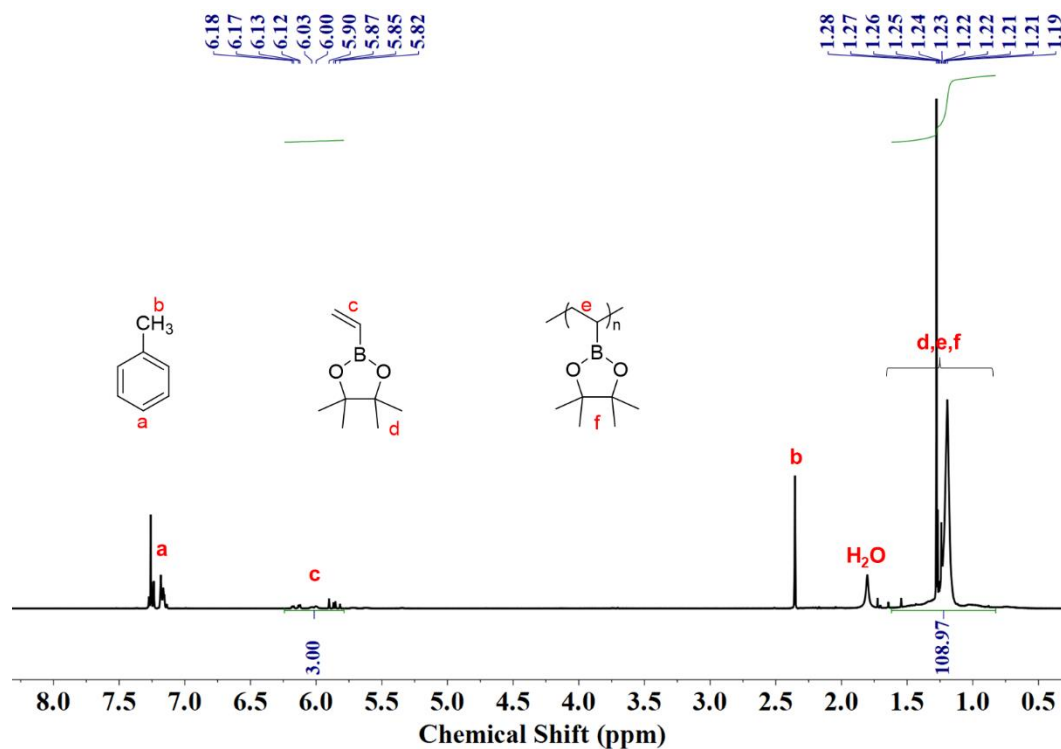


Figure S6. ¹H NMR Spectrum of Reaction Stock Solution in CDCl₃.

The conversion rate can be calculated as following equation:

$$\text{Conv (\%)} = \frac{S_{d,e,f} - 4 \cdot S_c}{S_{d,e,f} + S_c}$$

GPC Characterization of VB_{pin} Polymers

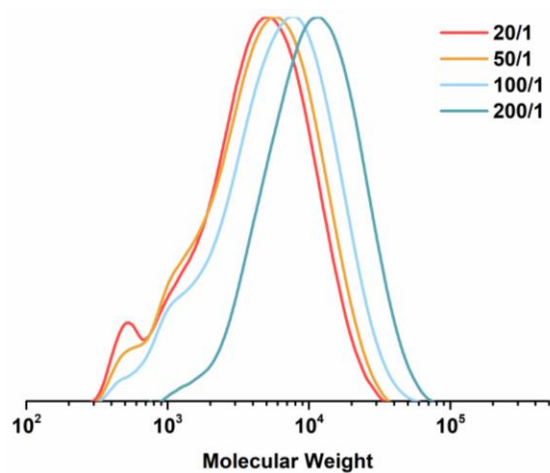


Figure S7. GPC Traces of Homopolymers in Table S1.

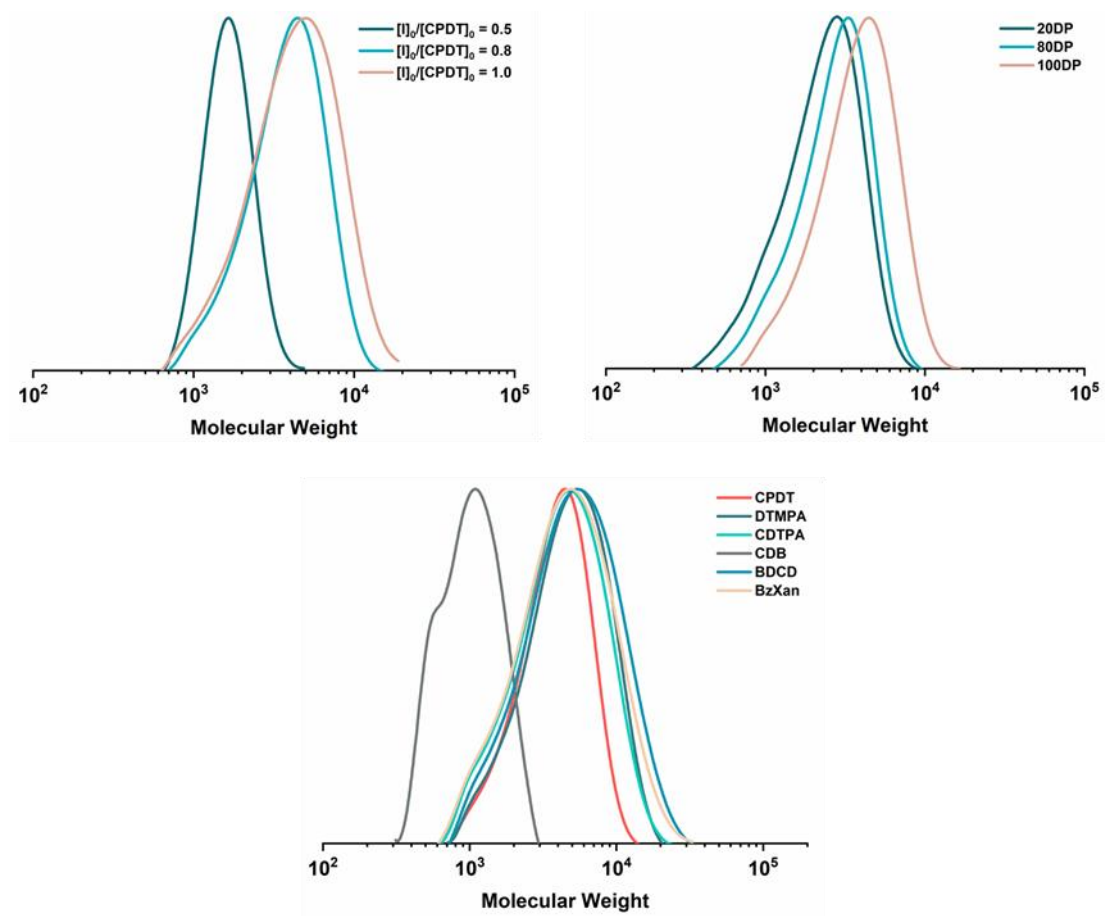
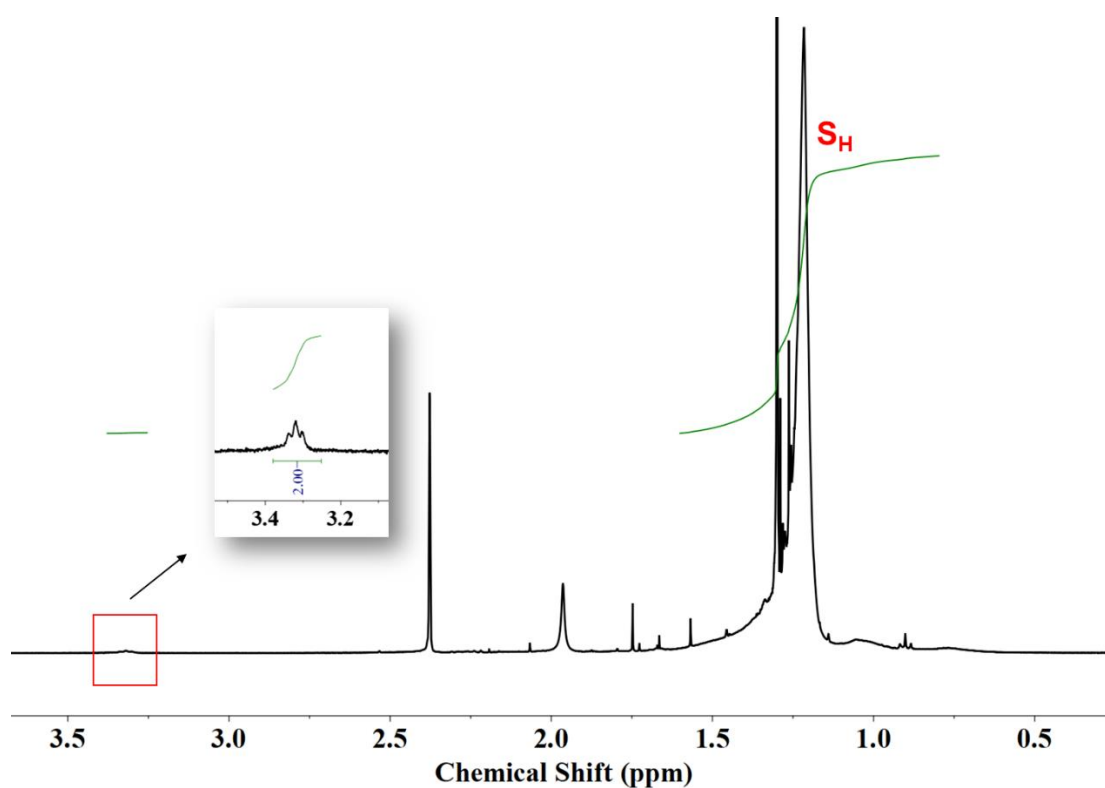


Figure S8. GPC Traces of Homopolymers in Table 1.

Table S2. Synthesis of VB_{pin} Polymers by Oxygen-Initiated Radical Polymerization^a

Entry	[M] ₀ /[Et ₃ N] ₀	Time (h)	M _{n, GPC} ^b	M _w /M _n ^b
1	20:1	2	567	1.05
2	50:1	2	706	1.15
3	100:1	2	838	1.19

^aReaction conditions: [M]₀ = 1.00 M in toluene. Reaction at room temperature under a N₂ atmosphere. ^bDetermined by GPC in THF, based on linear PMMA as a calibration standard.

**Figure S9.** ¹H NMR Spectrum of PVB_{pin}-CTA polymer in CDCl₃.

The peak around 3.3 ppm is originated from methylene protons neighboring to trithiocarbonyl group (Figure S9). The peaks between 0.8 to 1.6 ppm are originated from monomer units and terminus. Therefore, the number-averaged molecular weight can be approximately calculated as follows:

$$M_{n,NMR} = M_{CTA} + 154 * \frac{S_H}{15}$$

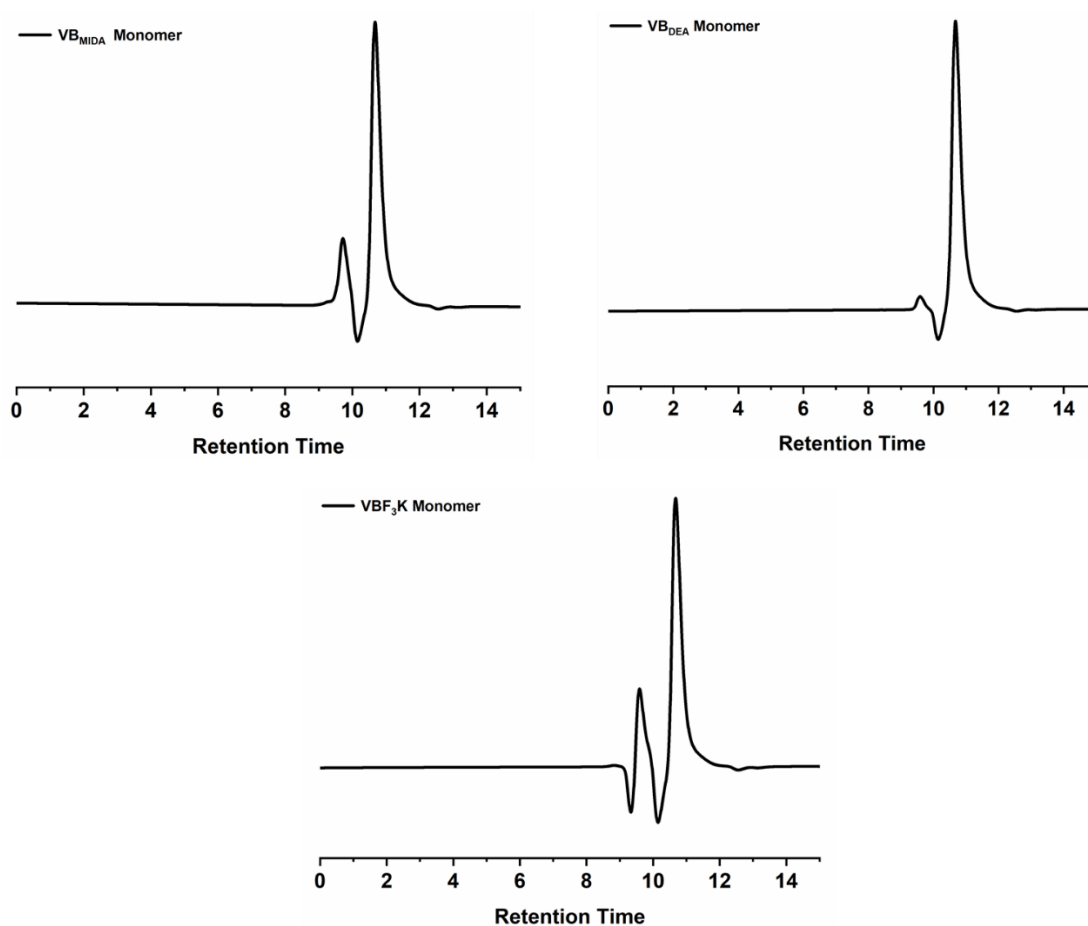


Figure S10. GPC Traces of Radical Polymerization of Different Vinyl Boronate.

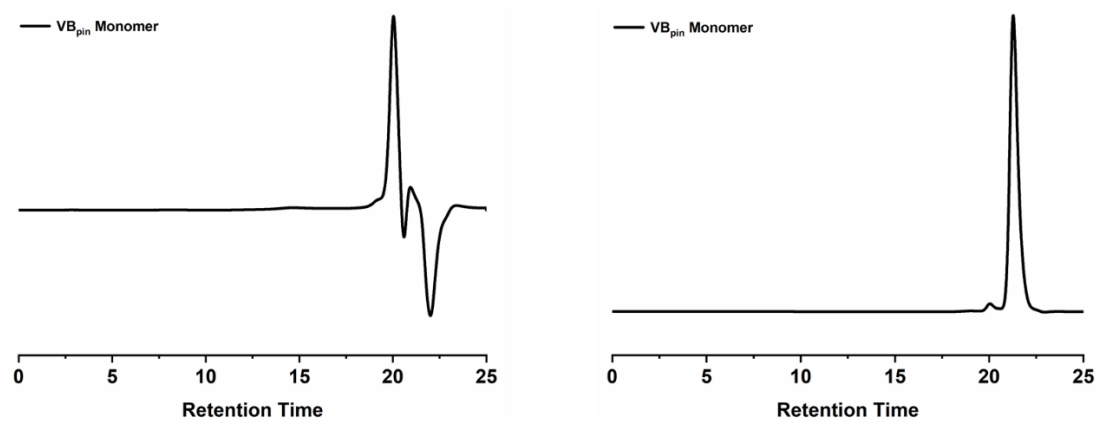
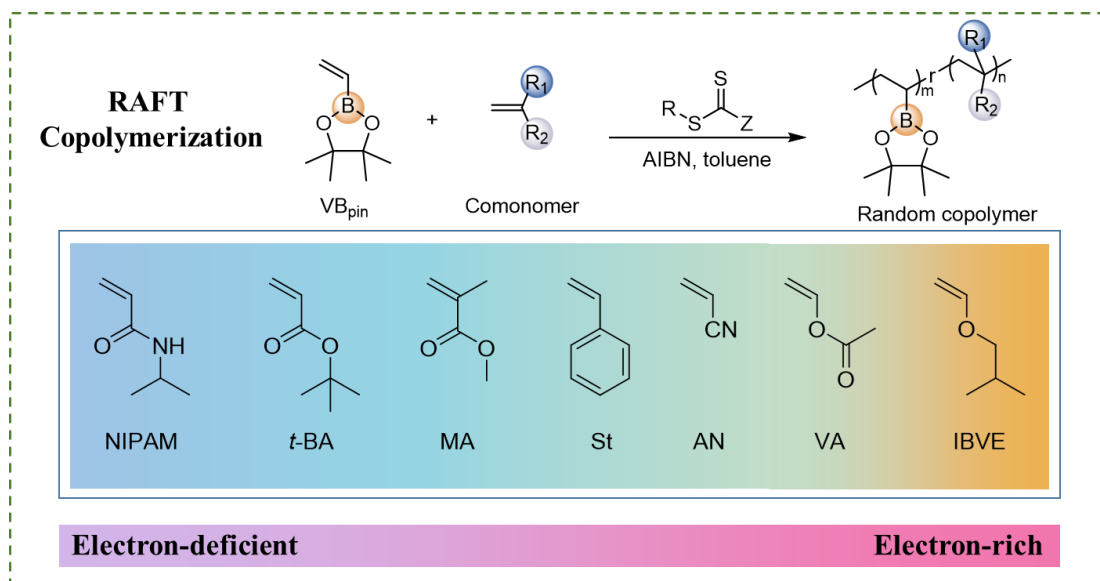


Figure S11. GPC Traces of Anionic Polymerization(Left) and Cationic Polymerization(Right) of VB_{pin} Monomer.



Scheme S1. Monomers to be copolymerized with VB_{pin}.

Table S3. Free Radical Copolymerization of VB_{pin} with Various Types of Monomers^a

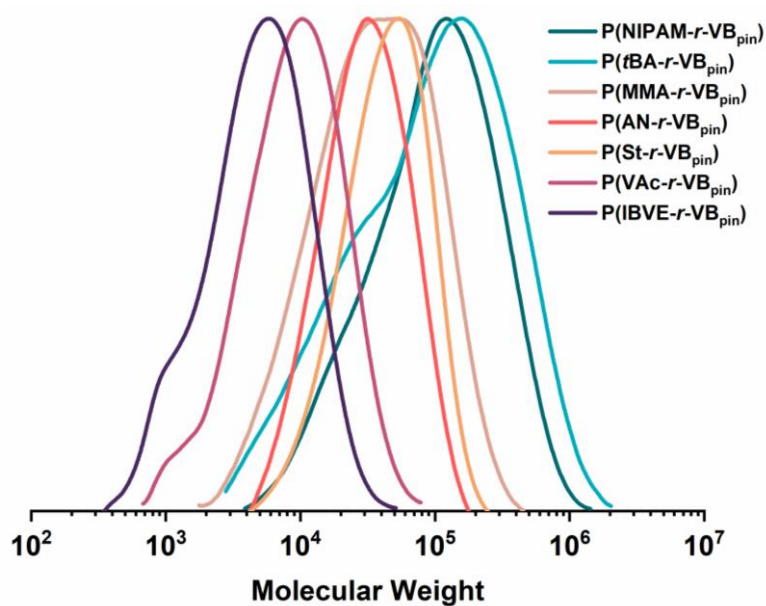
Entry	M ₂	[M ₁] ₀ : [M ₂] ₀ : [I] ₀	Time (h)	Conv1 ^b (%)	Conv2 ^b (%)	M _{n,GPC} ^c	M _w /M _n ^c
1	NIPAM	100:100:1	24	55	99	44150	3.33
2	<i>t</i> -BA	100:100:1	24	86	97	35270	5.45
3	MMA	100:100:1	24	76	85	19970	2.80
4	AN	100:100:1	24	49	76	23000	1.68
5	S	100:100:1	24	14	63	31280	1.71
6	VAc	50:50:1	24	98	47	5690	2.15
7	IBVE	50:50:1	24	94	-	3020	2.21

^aReaction conditions: M₁ = VB_{pin}, [M₁]₀ = [M₂]₀ = 10.0 M. Reaction temperature is 60 °C in toluene under N₂ atmosphere. ^bDetermined by ¹H NMR spectroscopy. ^cEntry 1 is determined by GPC in DMF; Entries 2-7 is determined by GPC in THF, all based on linear PMMA as a calibration standard.

Table S4. RAFT Copolymerization of VB_{pin} with Various Types of Monomers^a

Entry	M ₂	[M ₁] ₀ :[M ₂] ₀ :[CTA] ₀ :[I] ₀	Time (h)	Conv1 ^b (%)	Conv2 ^b (%)	M _{n, GPC} ^c	M _w /M _n ^c
1	MMA	10:100:1:0.5	24	76	97	9900	1.45
2	MMA	20:100:1:0.5	24	71	95	10600	1.42
3	MMA	100:100:1:1	24	57	82	12600	1.40
4	<i>t</i> -BA	10:100:1:0.5	24	96	98	17300	1.46
5	<i>t</i> -BA	20:100:1:0.5	24	93	99	19200	1.32
6	<i>t</i> -BA	100:100:1:1	36	82	88	19100	1.42
7	St	10:100:1:0.5	48	76	81	7700	1.41
8	St	20:100:1:0.5	48	68	83	7300	1.53
9	St	100:100:1:1	48	54	82	7100	1.46
10	AN	10:100:1:0.5	24	56	78	19600	1.51
11	AN	20:100:1:0.5	24	75	86	15800	1.45
12	AN	100:100:1:1	24	55	78	10300	1.37

^aReaction conditions: M₁ = VB_{pin}, [M₂]₀ = 10.0 M. Reaction temperature is 60 °C in toluene under N₂ atmosphere. ^bDetermined by ¹H NMR spectroscopy. ^cDetermined by GPC in THF, based on linear PMMA as a calibration standard.

**Figure S12.** GPC Traces of Copolymers in Table S3.

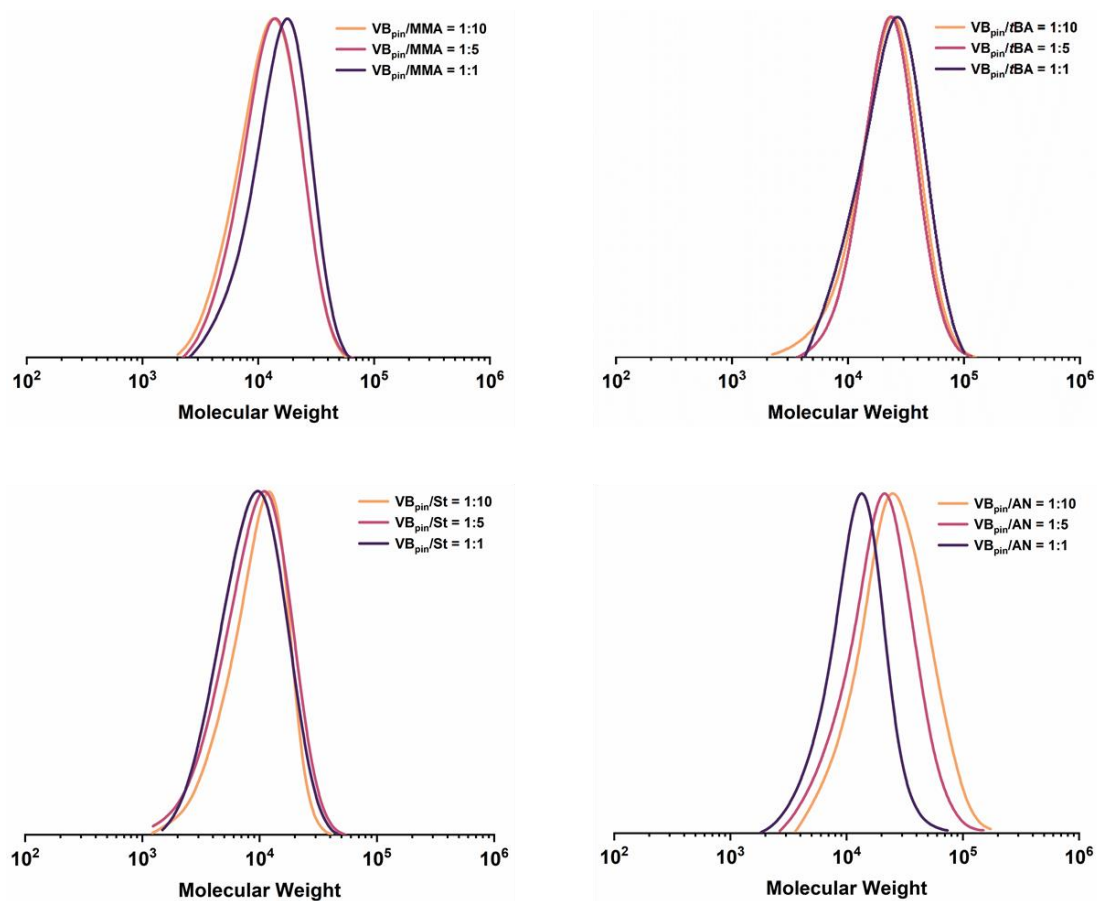


Figure S13. GPC Traces of Copolymers in Table S4.

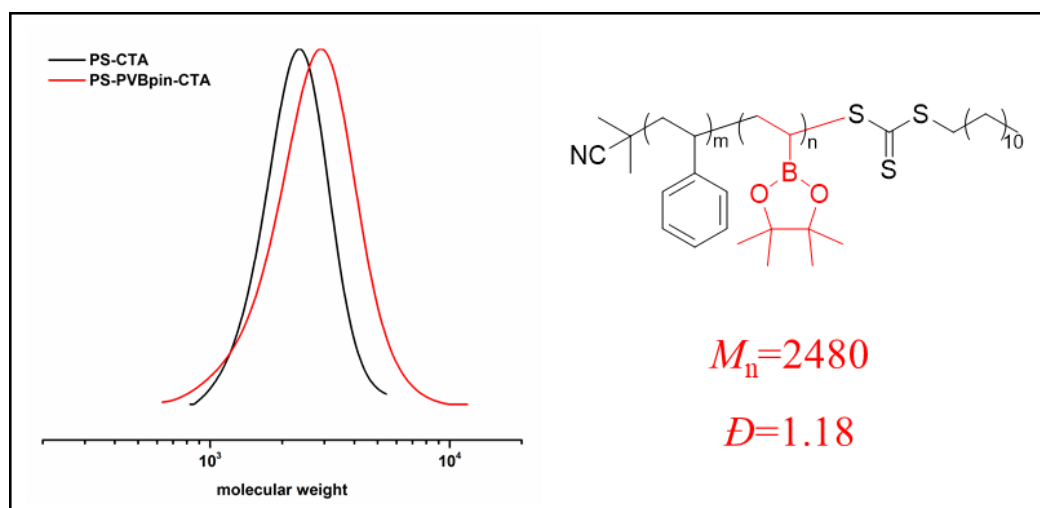


Figure S14. Evolution of GPC Traces for Chain Extension with VB_{pin} from PS-CTA.

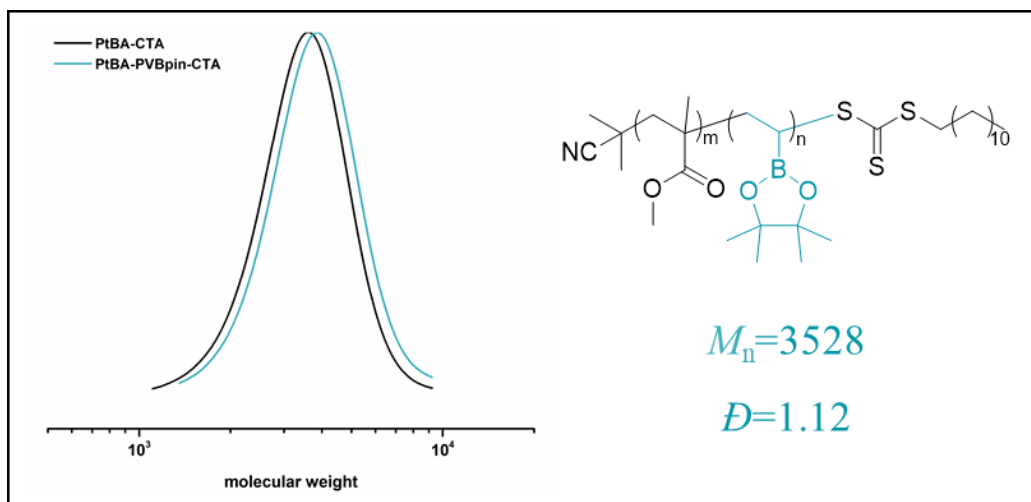


Figure S15. Evolution of GPC Traces for Chain Extension with VB_{pin} from Pt-BA-CTA.

XI. Copies of Spectroscopic Data

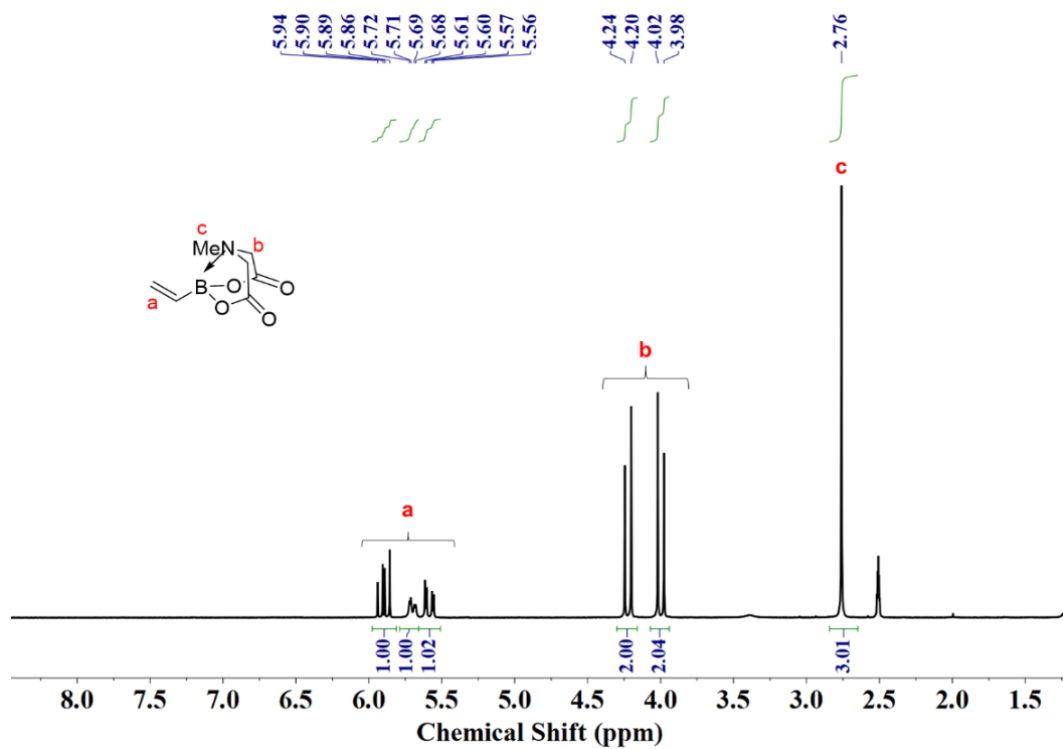


Figure S16. ¹H NMR Spectrum of Vinyl MIDA Boronic Ester in DMSO-*d*₆.

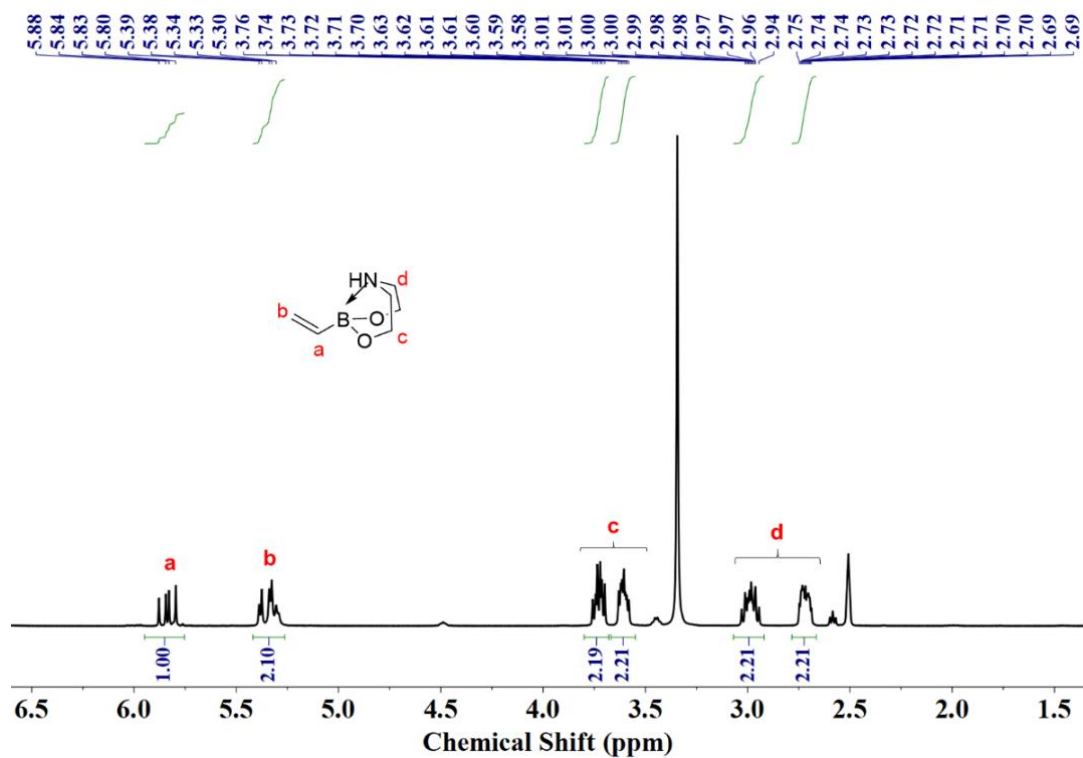


Figure S17. ¹H NMR Spectrum of Vinyl DEA Boronic Ester in DMSO-*d*₆.

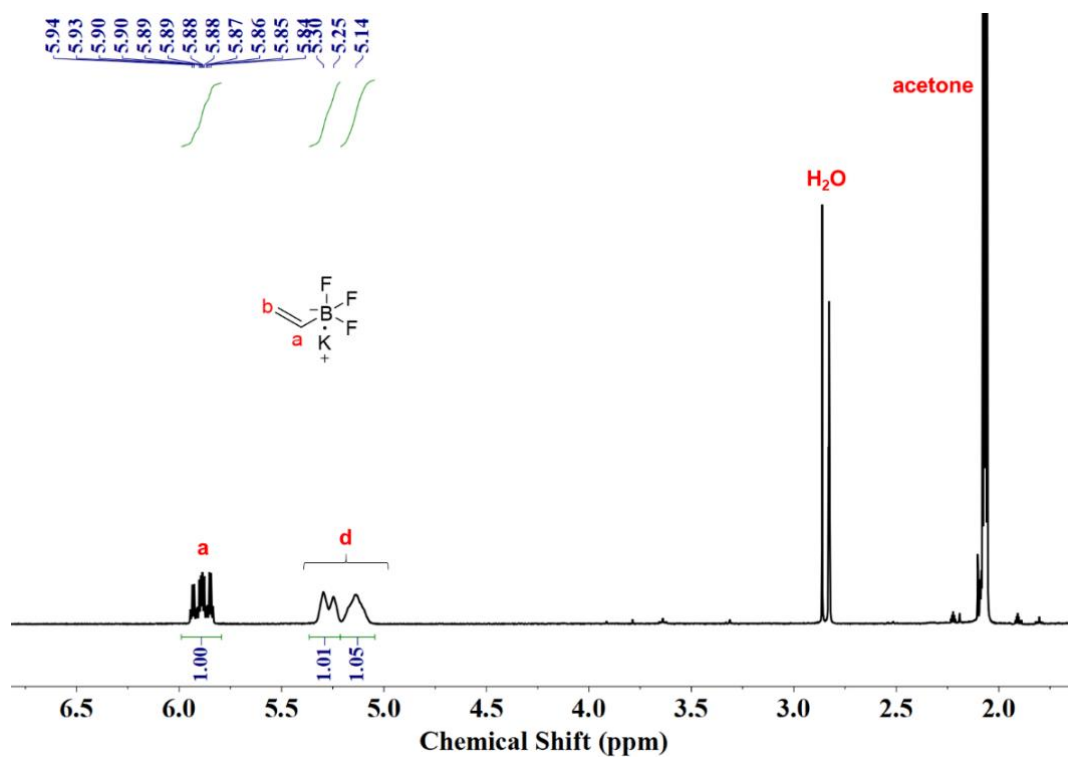


Figure S18. ¹H NMR Spectrum of Potassium Vinyltrifluoroborate in Acetone-*d*₆.

The 2-cyanopropan-2-yl dodecyl carbonotrithioate (CPDT)

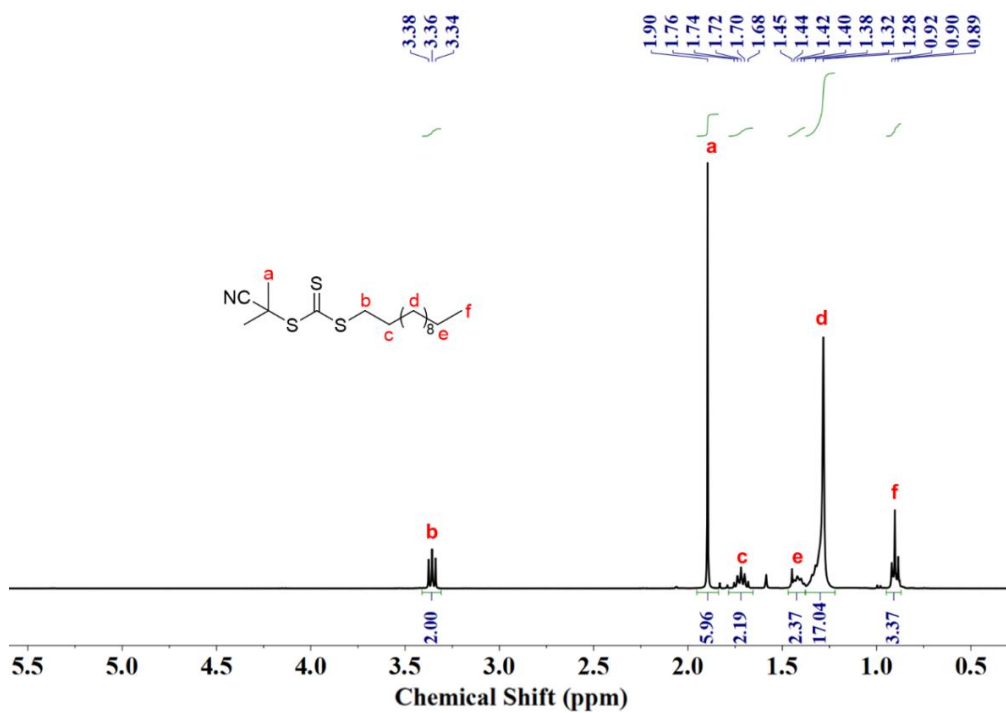


Figure S19. ^1H NMR Spectrum of CPDT in CDCl_3 .

The 2-[[[(dodecylthio) thioxomethyl]thio]-2-methylpropanoic acid (DTMPA)

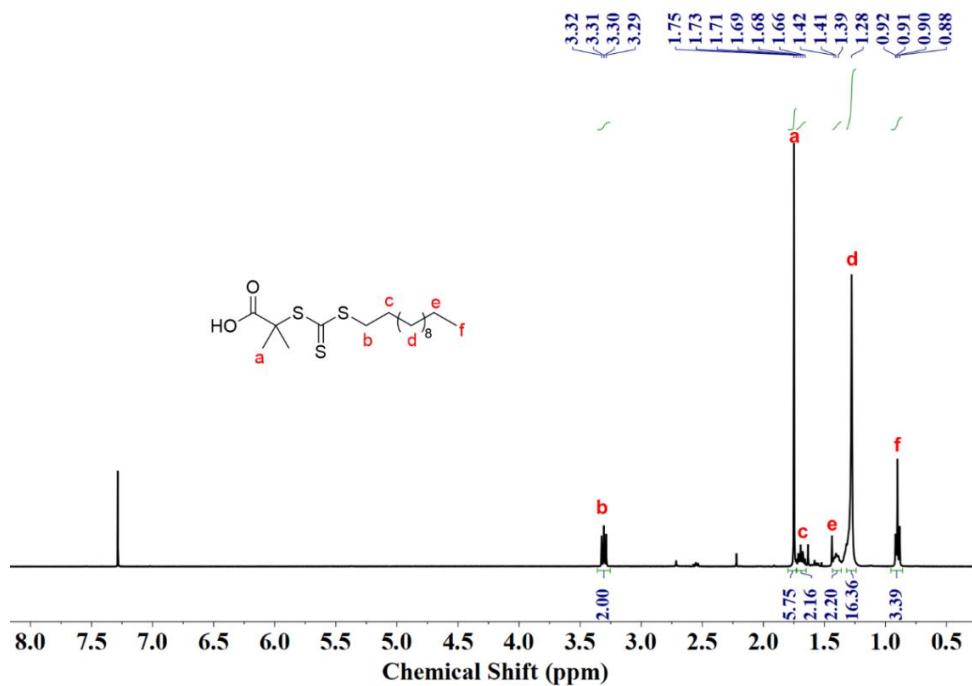


Figure S20. ^1H NMR Spectrum of DTMPA in CDCl_3 .

The 4-cyano-4-[[[(dodecylthio) thioxomethyl] thio]-pentanoic acid (CDTPA)

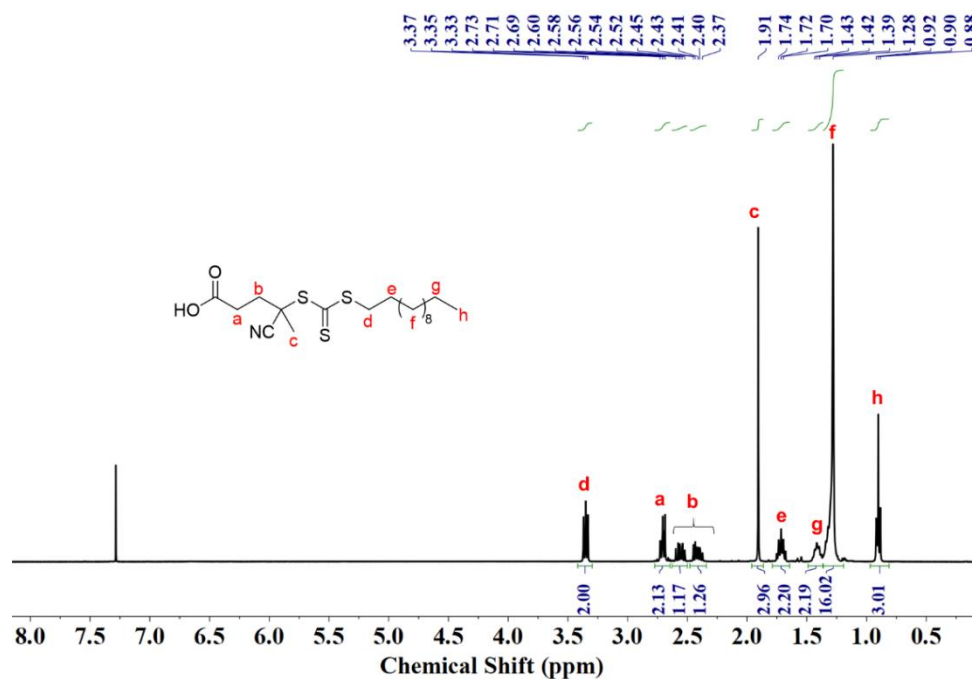


Figure S21. ¹H NMR Spectrum of CDTPA in CDCl₃.

The cumyl dithiobenzoate (CDB)

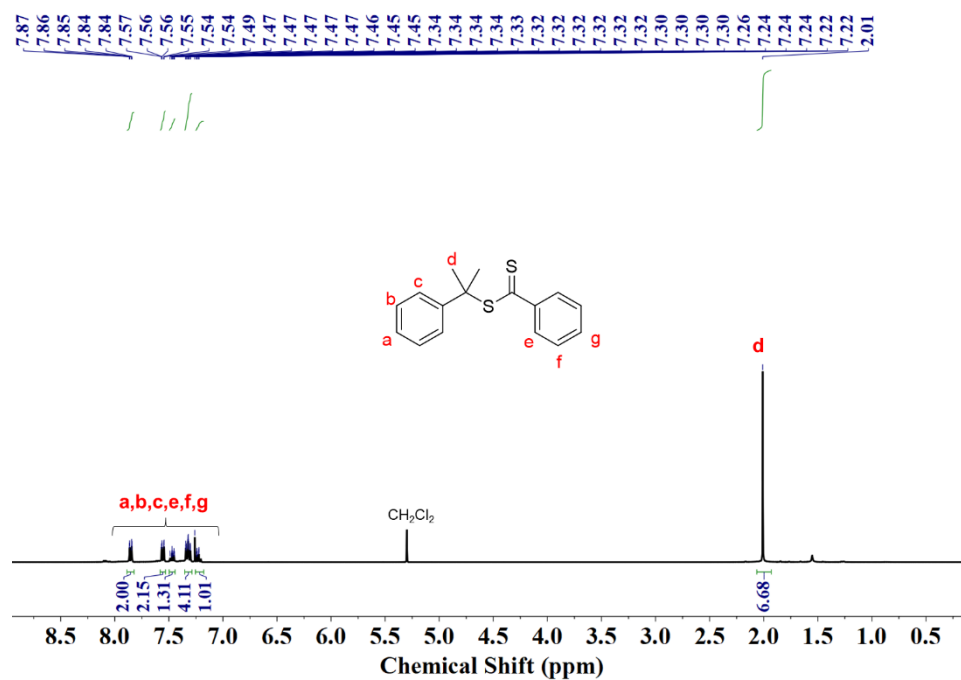


Figure S22. ¹H NMR Spectrum of CDB in CDCl₃.

The Benzyl diethylcarbamodithioate (BDCD)

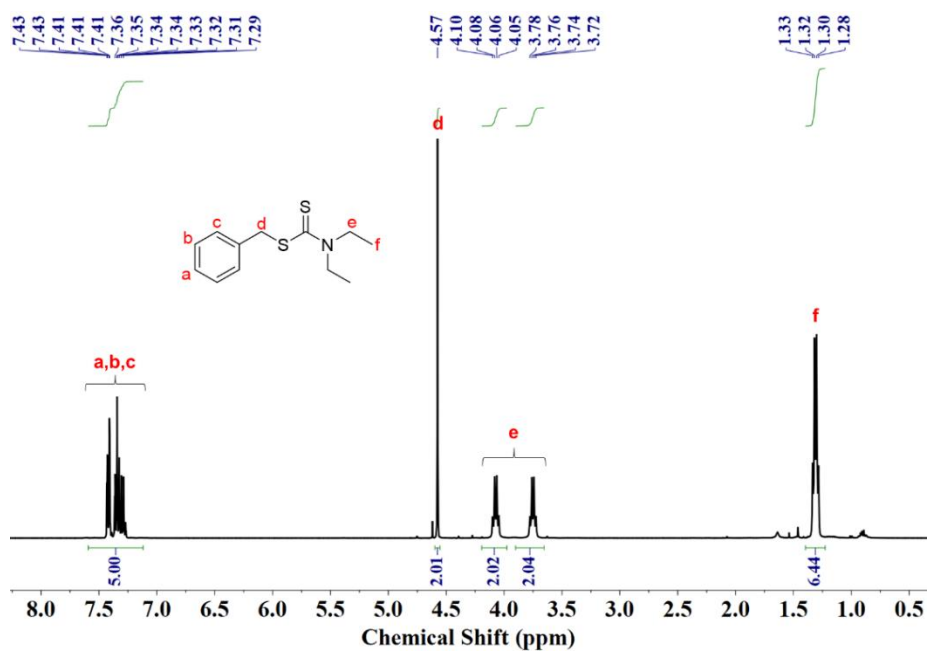


Figure S23. ^1H NMR Spectrum of BDCD in CDCl_3 .

The S-benzyl O-ethyl carbonodithioate (BzXan)

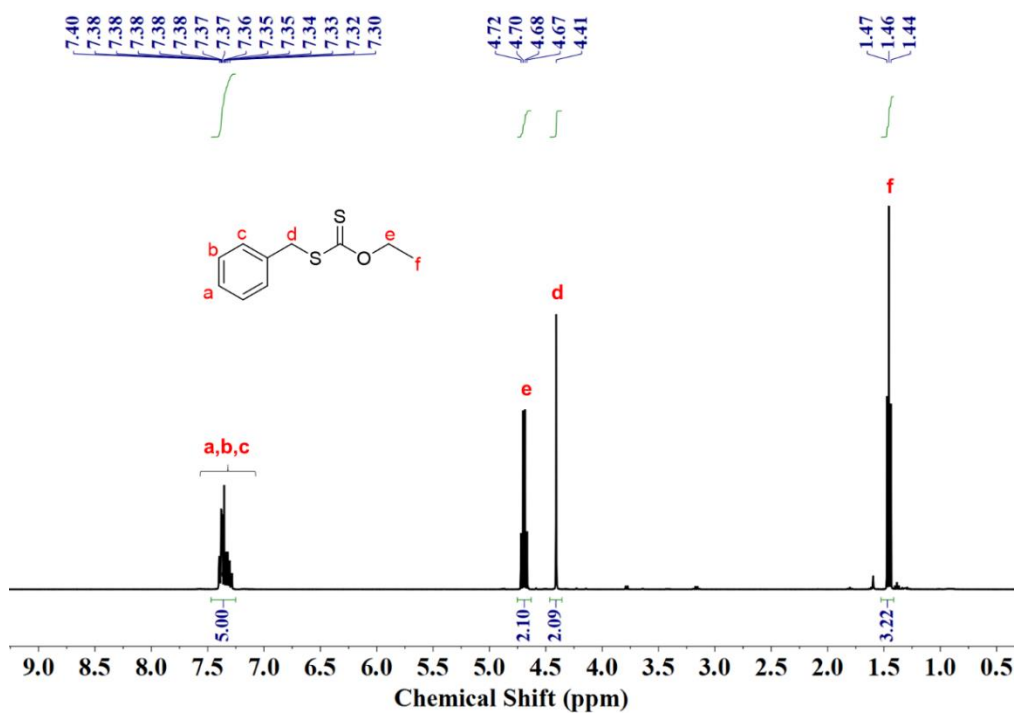


Figure S24. ^1H NMR Spectrum of BzXan in CDCl_3 .

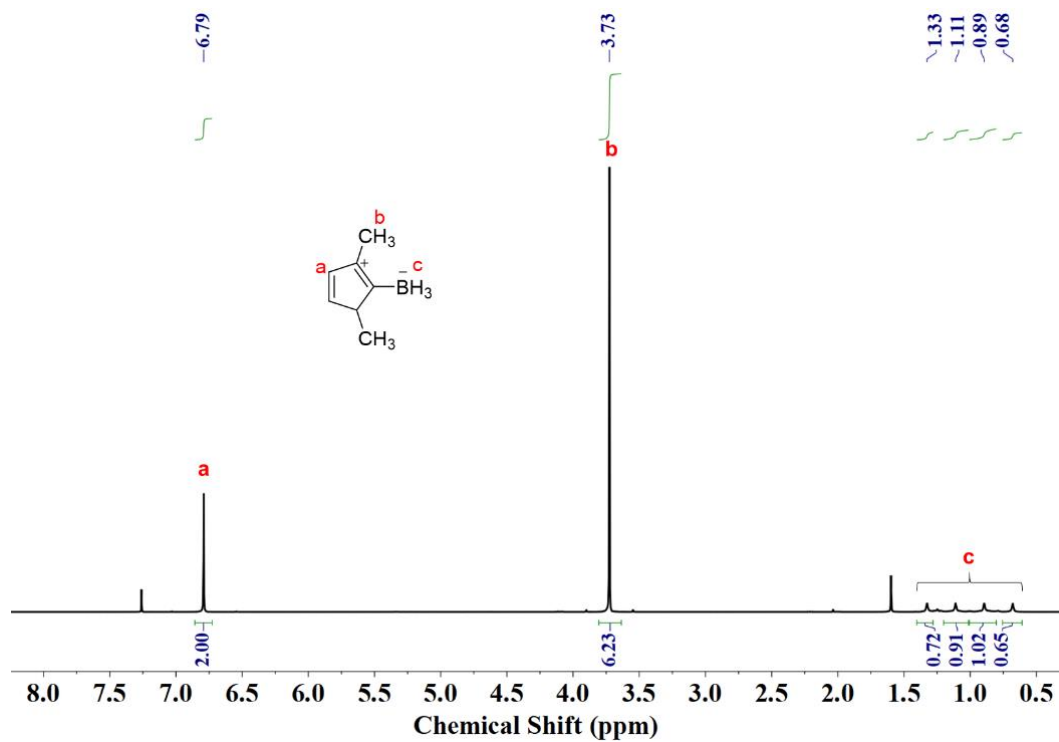


Figure S25. ¹H NMR Spectrum of DiMe-Imd-BH₃ in CDCl₃.

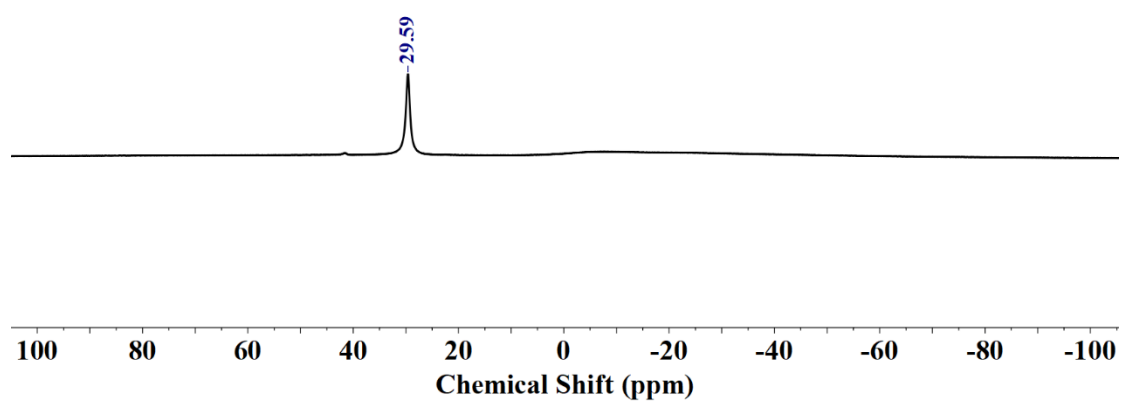


Figure S26. ¹¹B NMR Spectrum of VB_{pin} Monomer.

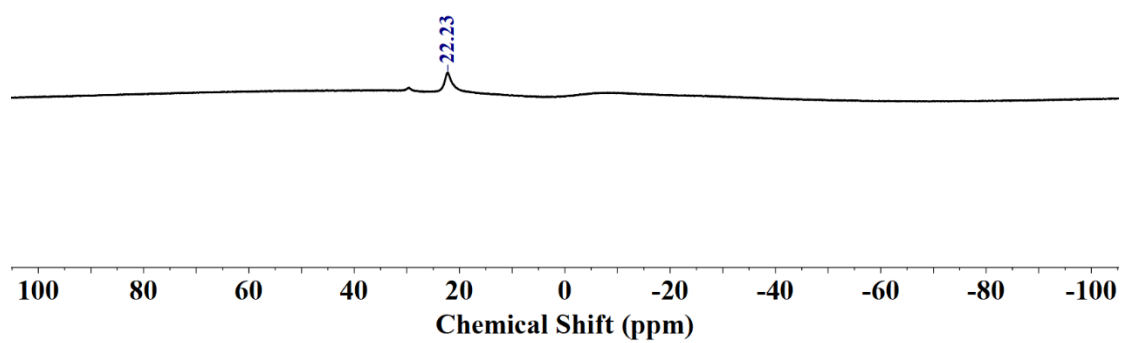


Figure S27. ^{11}B NMR Spectrum of VB_{pin} Polymer.

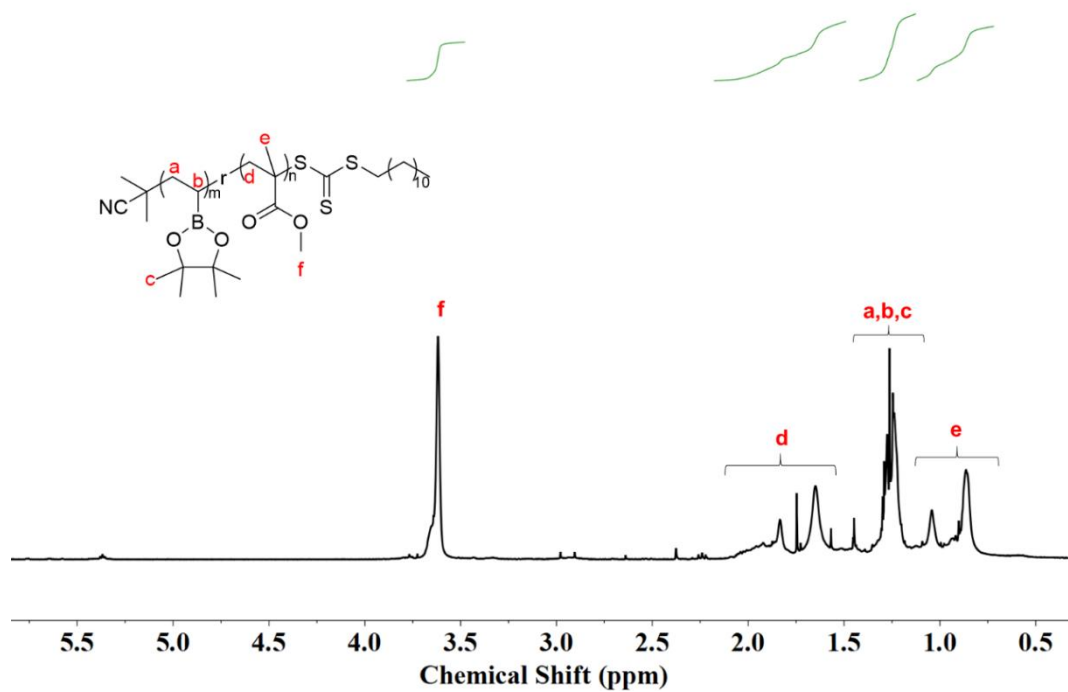


Figure S28. ^1H NMR Spectrum of $\text{P}(\text{MMA}-r\text{-VB}_{\text{pin}})$ Copolymer in CDCl_3 .

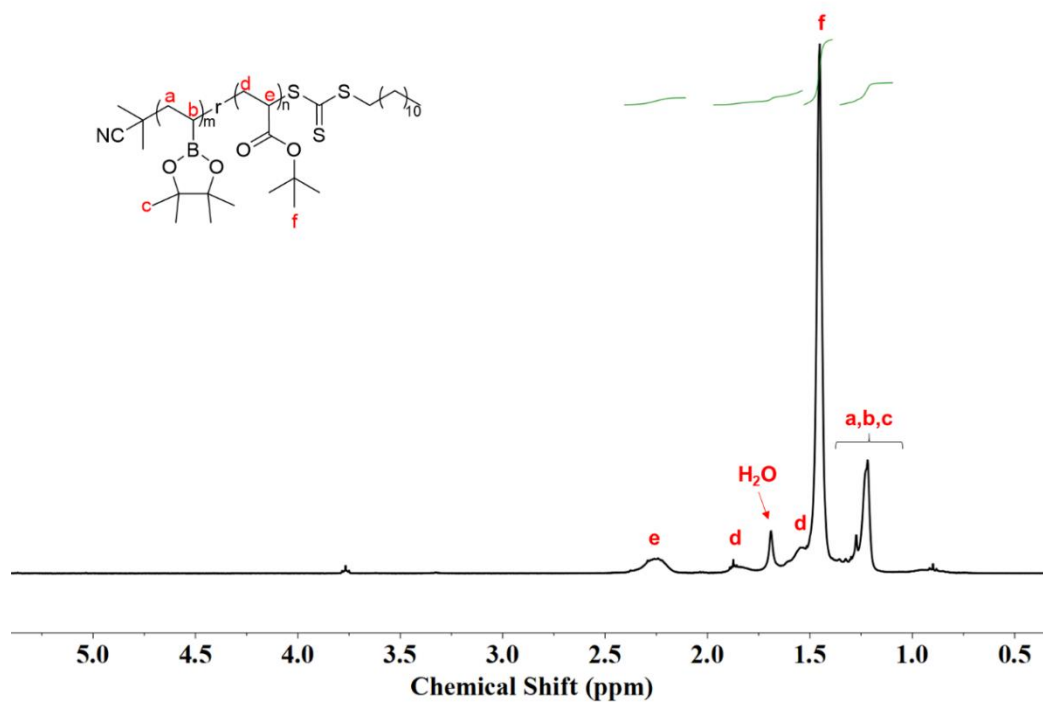


Figure S29. ^1H NMR Spectrum of $\text{P}(t\text{-BA-}r\text{-VB}_{\text{pin}})$ Copolymer in CDCl_3 .

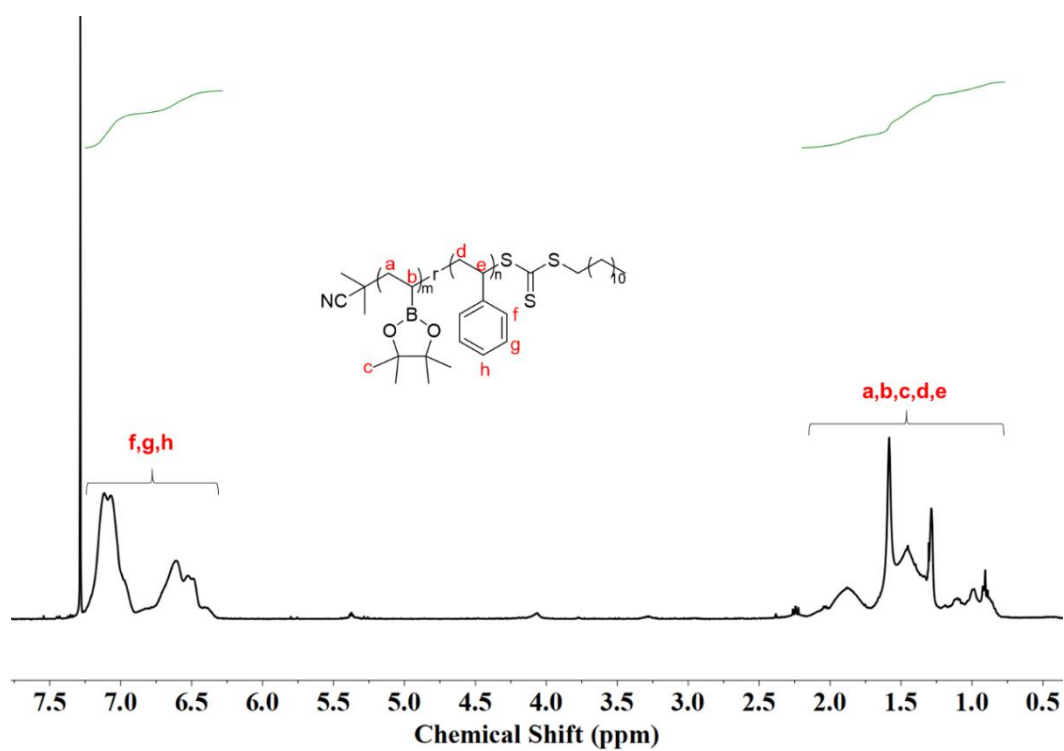


Figure S30. ^1H NMR Spectrum of $\text{P}(\text{St-}r\text{-VB}_{\text{pin}})$ Copolymer in CDCl_3 .

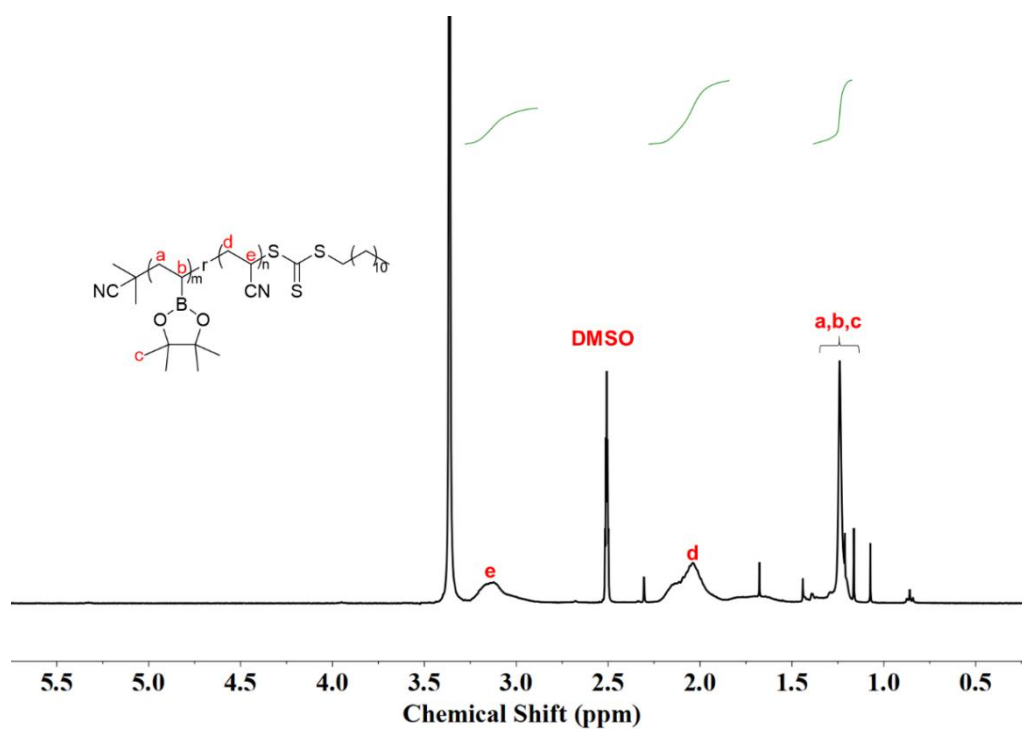


Figure S31. ¹H NMR Spectrum of P(AN-*r*-VB_{pin}) Copolymer in DMSO-*d*₆.

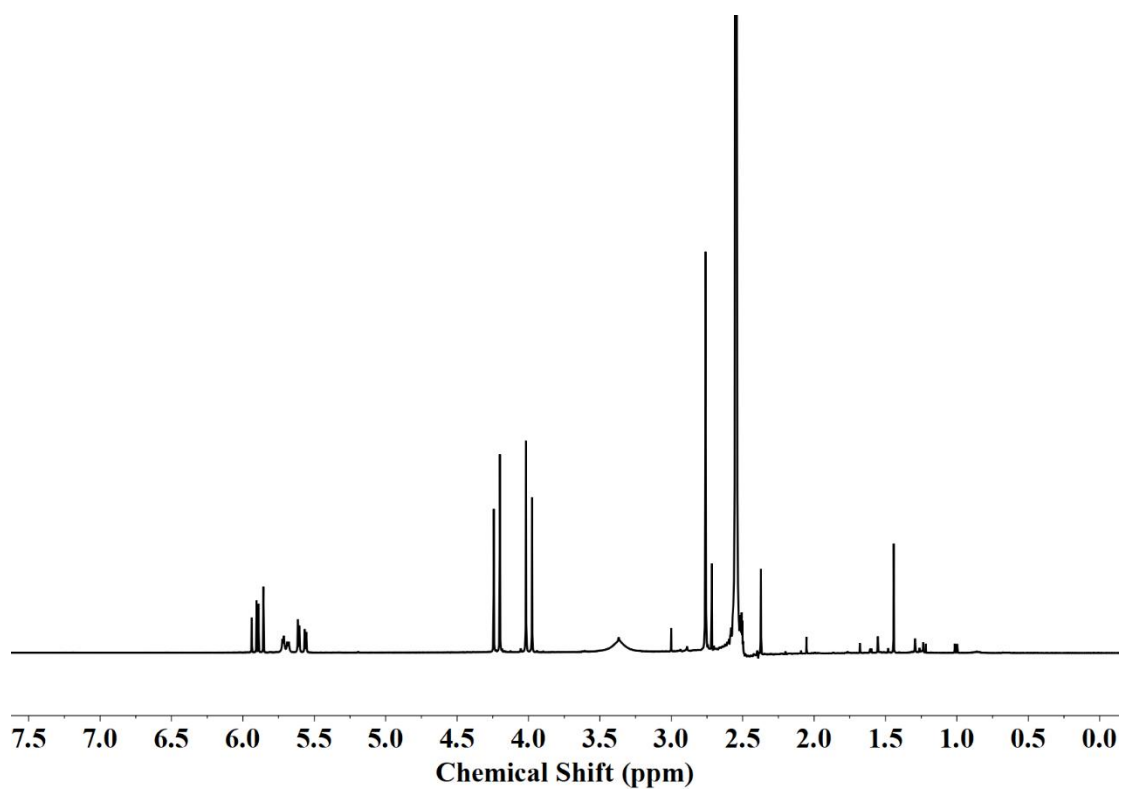


Figure S32. ¹H NMR Spectrum of Radical Polymerization of VB_{MIDA} in DMSO-*d*₆.

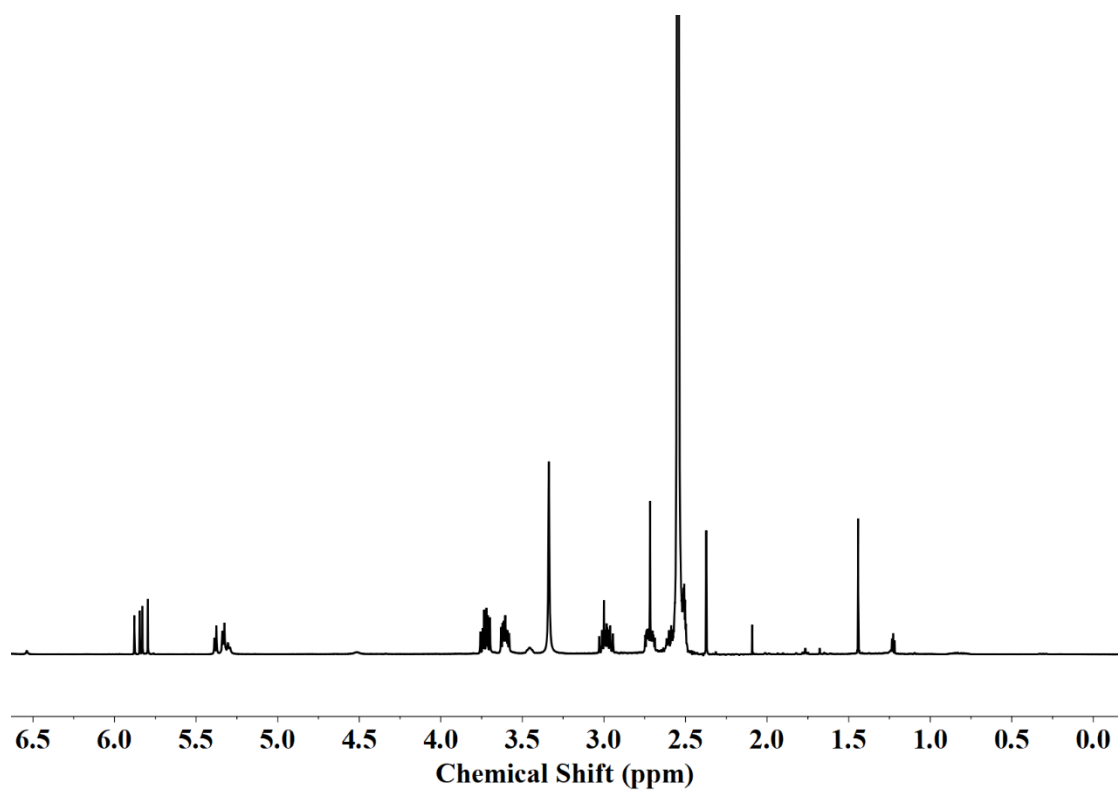


Figure S33. ^1H NMR Spectrum of Radical Polymerization of VB_{DEA} in $\text{DMSO-}d_6$.

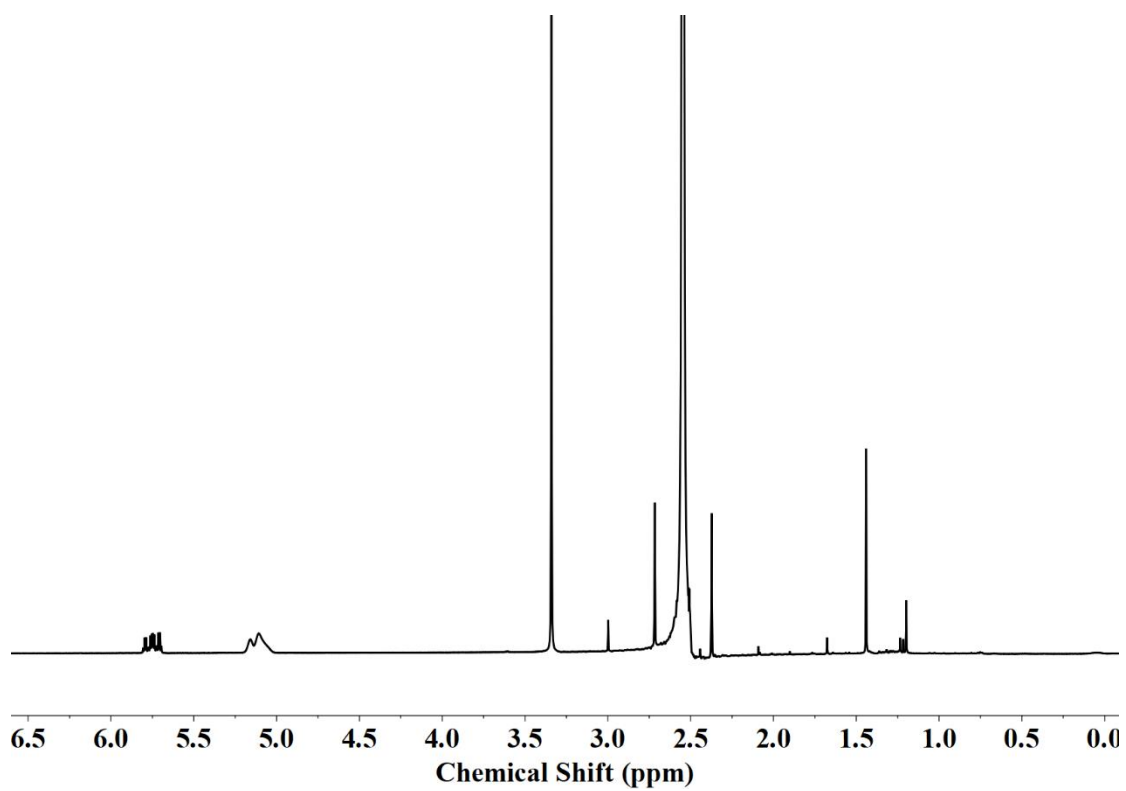


Figure S34. ^1H NMR Spectrum of Radical Polymerization of VBF_3K in $\text{DMSO-}d_6$.

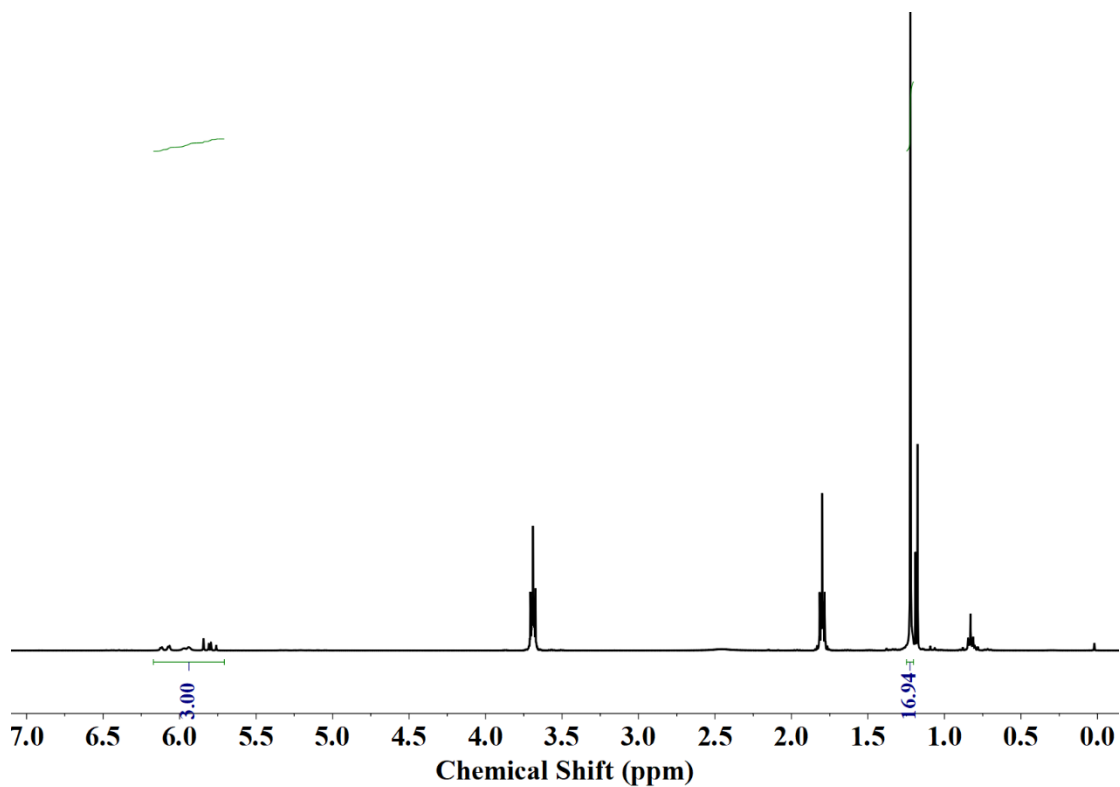


Figure S35. ¹H NMR Spectrum of Anionic Polymerization of VB_{pin} in CDCl₃.

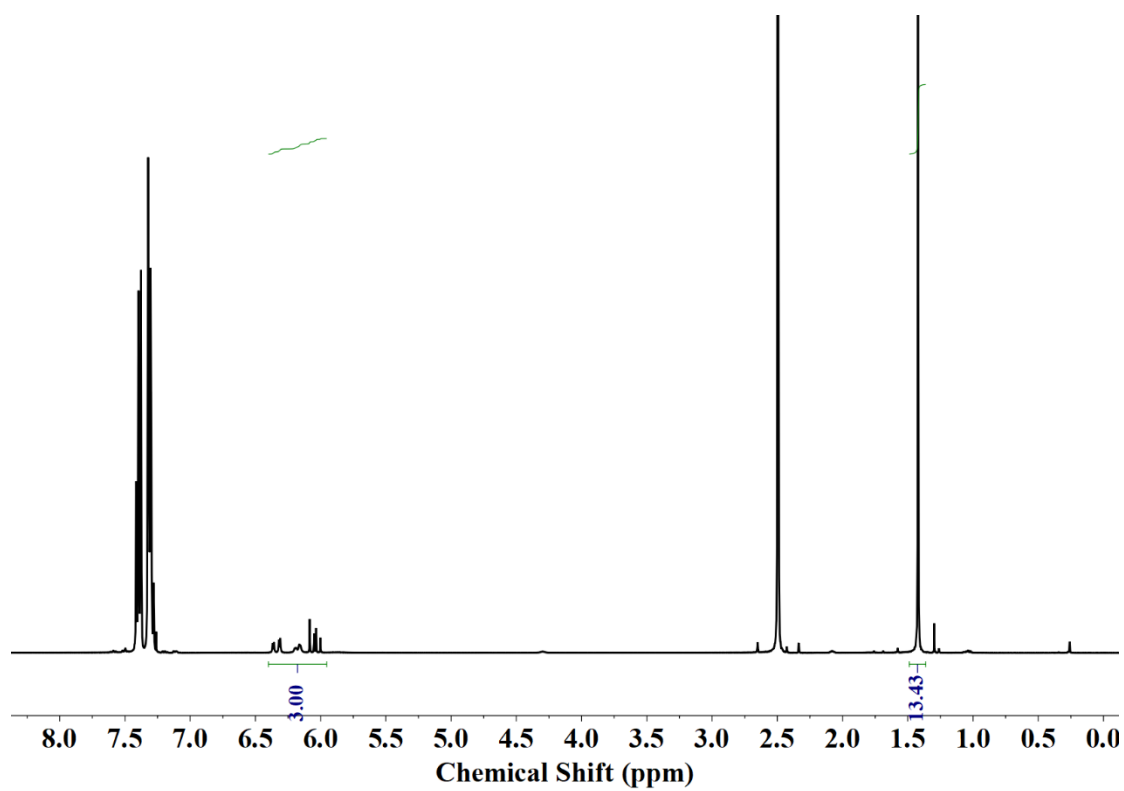


Figure S36. ¹H NMR Spectrum of Cationic Polymerization of VB_{pin} in CDCl₃.

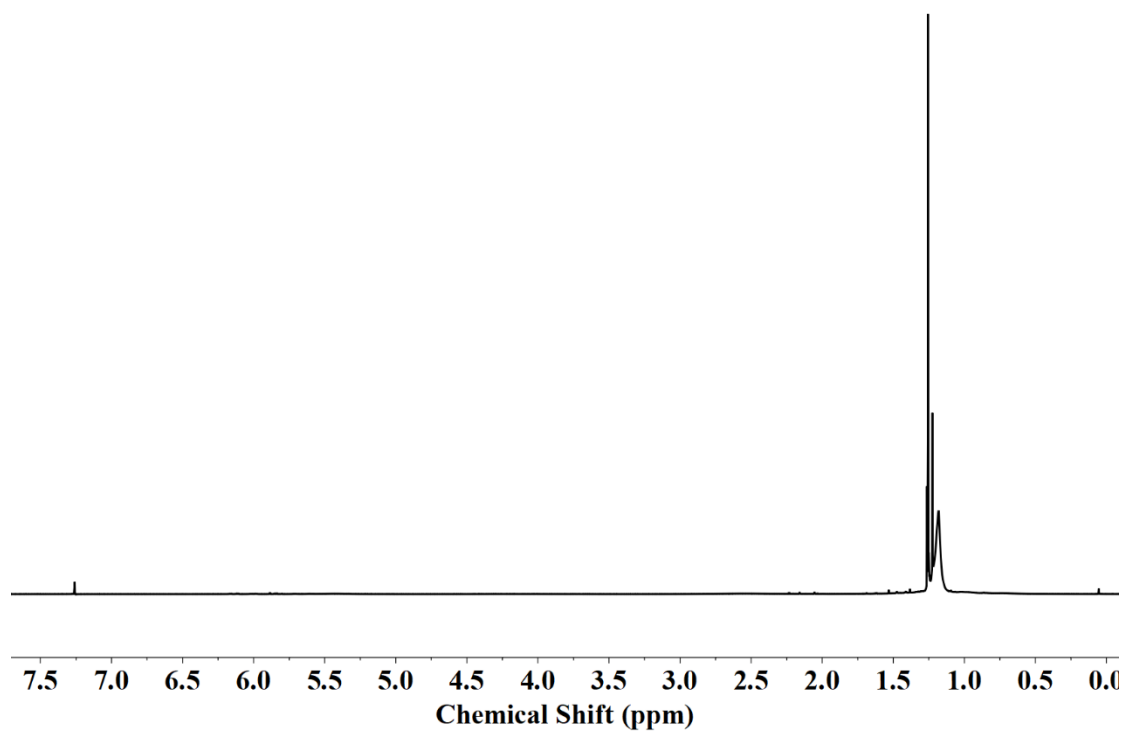


Figure S37. ¹H NMR Spectrum of VB_{pin} Polymer before cycle in CDCl₃.

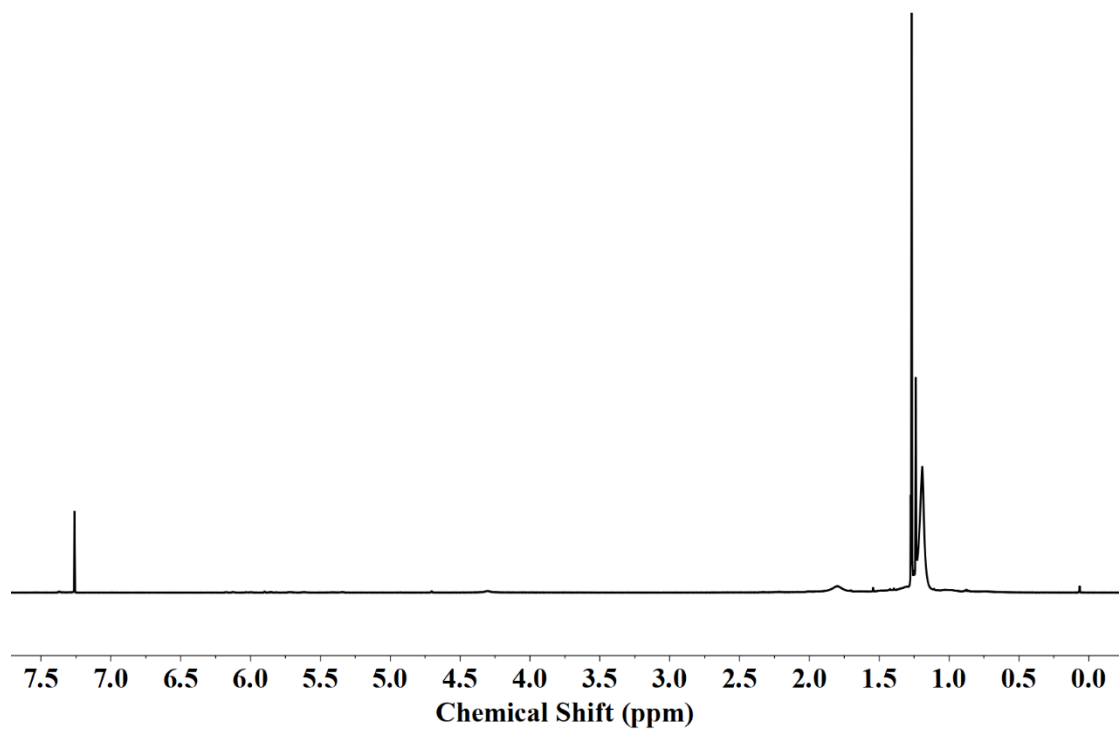


Figure S38. ¹H NMR Spectrum of VB_{pin} Polymer after one cycle in CDCl₃.

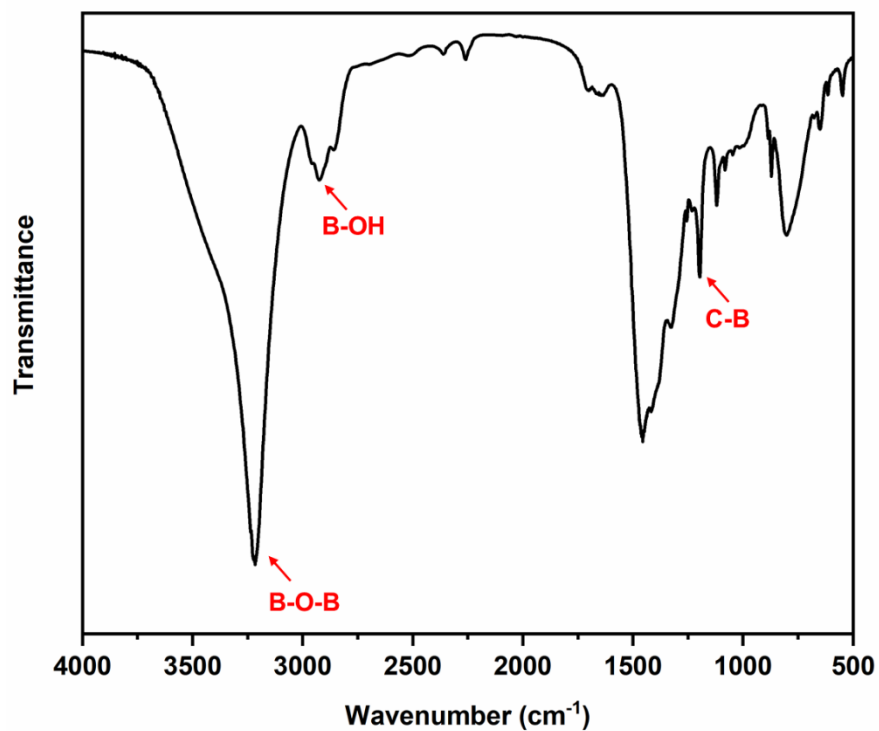


Figure S39. FT-IR Spectra of VB(OH)₂ polymers obtained by radical polymerization.

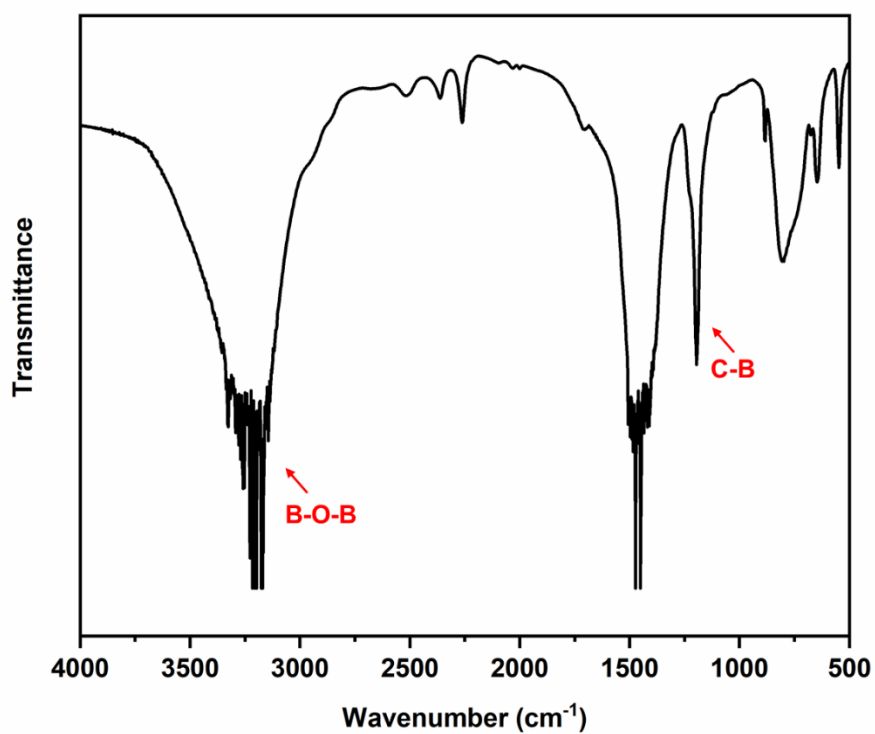


Figure S40. FT-IR Spectra of the self-polymerization product of VB(OH)₂.

XII. References

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