

Supporting information

Regioselective, Stereoselective, and Living Polymerization of Divinyl Pyridine Monomer by Rare Earth Catalysts

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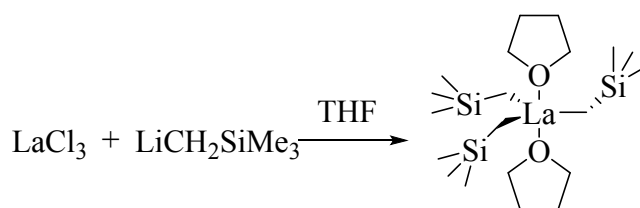
1 Experimental Section

1.1 Materials, Reagents, and Methods

All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, on a high-vacuum line, or in an argon-filled glovebox. Toluene and tetrahydrofuran (THF) were distilled from sodium/benzophenone under nitrogen, degassed and stored over fresh Na chips. 2,5-divinylpyridine (DVP), vinylpyridine (VP), pyridine (Py), n-hexane, and CH_2Cl_2 were dried over CaH_2 while stirring for 48 h and distilled before use, and then degassed and stored over 4 Å sieves. C_6D_6 was dried over sodium. CDCl_3 was dried over CaH_2 , and then degassed and stored over 4 Å sieves. NMR spectra were recorded on a Varian Inova 300 (FT 300 MHz, ^1H ; 75 MHz, ^{13}C), or a Varian Inova 400 MHz spectrometer, or a Varian Inova 500 MHz spectrometer. ^1H and ^{13}C NMR chemical shifts were referred to SiMe_4 (TMS). The molecular weight and molecular weight distribution of the polymers were measured by Agilent Technologies 1260 Infinity GPC (Column: PL gel 5 μm MIXED-C) at 30 °C using DMF as an eluent (the flowing rate is 1.0 mL/min) against poly(2- vinylpyridine) standards. Elemental analyses were performed on an Elementar Vario EL III.

Literature procedures were employed or modified for the preparation of the following complexes: $(\text{Me}_3\text{SiCH}_2)_3\text{Sc}(\text{THF})_2^1$, $(\text{Me}_3\text{SiCH}_2)_3\text{Y}(\text{THF})_2^1$, $(\text{Me}_3\text{SiCH}_2)_3\text{Lu}(\text{THF})_2^2$, $(\text{Me}_3\text{SiCH}_2)_3\text{Dy}(\text{THF})_2^3$, $(\text{Me}_3\text{SiCH}_2)_3\text{Lu}(\text{Py})_2^4$, DVP⁵.

1.2 Synthesis and characterization of catalyst 1



Scheme S1. Synthesis of catalyst 1

LaCl_3 (3.00 g, 12.23 mmol) and THF (50 mL) were added into a 250 mL single necked flask at room temperature in glove box. After stirring overnight, $\text{LiCH}_2\text{SiMe}_3$ (3.34 g, 35.47 mmol) was added slowly into the flask during 0.5 h under strong agitation. The mixture was stirred for 1 h and the solvent was removed in vacuo. The residue was washed with 10 mL n-hexane each time

for 10 times. The collected n-hexane solution was concentrated five times. After each concentration, the remaining solution was frozen for 12 h at -30 °C. Until no oil precipitated after freezing, n-hexane was removed in vacuum. The removing of n-hexane under vacuum yielded $(\text{Me}_3\text{SiCH}_2)_3\text{La}(\text{THF})_2$ as a light yellow solid (2.90 g, 5.32 mmol, 45 %). ^1H NMR (C_6D_6 , 25 °C) δ 3.92 (bs, 8H, α -THF), 1.31 (bs, 8H, β -THF), 0.29 (d, $J = 9.6$ Hz, 27H, CH_2SiMe_3), -0.70 (d, $J = 8$ Hz, 6H, CH_2SiMe_3) ppm.

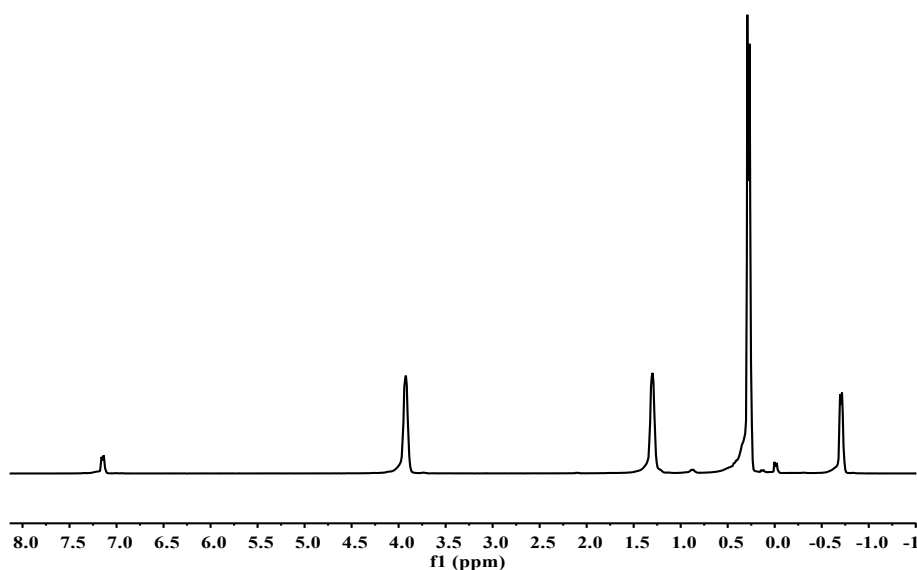
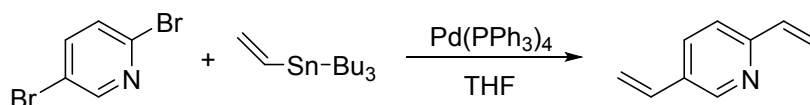


Figure S1. ^1H NMR spectrum of catalyst **1** (C_6D_6 , 25 °C).



Scheme S2. Synthesis of DVP

Under nitrogen protection, 2, 5-dibromopyridine (15.00 g, 63.32 mmol) and tributyl(vinyl)tin (52.00 g, 163.99 mmol) were added into a three-necked flask, then THF (50 mL) was added to dissolve the raw materials. After 4 h of reflux, $\text{Pd}(\text{PPh}_3)_4$ (0.20 g) was added into the flask, and then reflux for 5 days. The solvent was removed under vacuum, the crude product was purified by column chromatography. 2, 5-DVP was obtained as a light yellow liquid (7.60 g, 57.93 mmol, 91.5 %). The product was then stirred with CaH_2 under nitrogen protection over night, and a

colorless transparent liquid was obtained by distillation under reduced pressure. ^1H NMR (CDCl_3 , 25°C): δ 8.55 (d, $J = 2.2$ Hz, 1H), 7.67 (dd, $J = 8.2, 2.3$ Hz, 1H), 7.28 (d, $J = 8.2$ Hz, 1H), 6.79 (dd, $J = 17.5, 10.8$ Hz, 1H), 6.67 (dd, $J = 17.7, 11.0$ Hz, 1H), 6.17 (dd, $J = 17.5, 1.2$ Hz, 1H), 5.79 (d, $J = 17.6$ Hz, 1H), 5.45 (dd, $J = 10.8, 1.2$ Hz, 1H), 5.33 (d, $J = 11.0$ Hz, 1H) ppm.

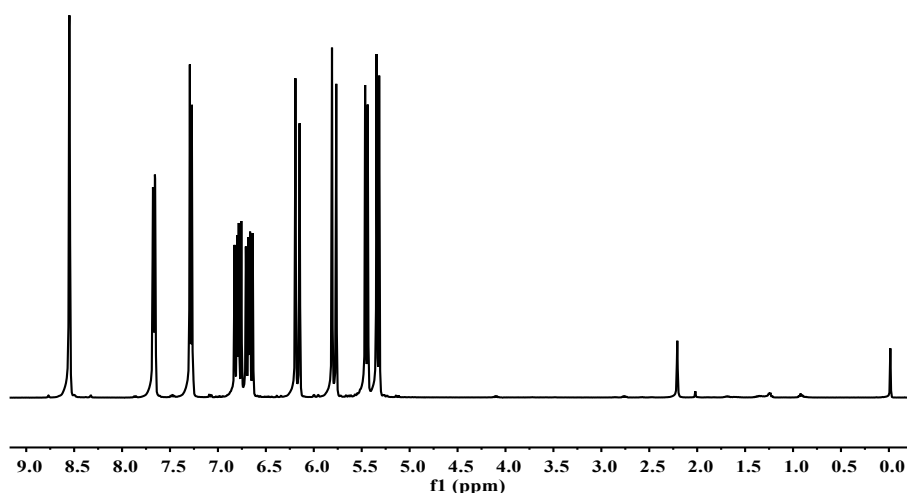


Figure S2. ^1H NMR spectrum of DVP (CDCl_3 , 25°C).

1.3 Typical polymerization procedure

Polymerizations were performed in 20 mL oven-dried glass reactors inside the glovebox under 25°C . Complex (10 μmol) was first dissolved in 3.9 mL of toluene, and the polymerization was started by rapid addition of DVP (0.13 g, 1 mmol). After the measured time interval, a 0.1 mL aliquot was taken from the reaction mixture via syringe and quickly quenched into a 2- mL vial containing 0.5 mL of undried “wet” CDCl_3 stabilized by 250 ppm of BHT; the quenched aliquots were analyzed by ^1H NMR to obtain the percent monomer conversion data. The polymerization was immediately quenched, after the removal of the aliquot, by addition of 5 mL wet n-hexane. The quenched mixture was precipitated into 100 mL of n-hexane, stirred for 1 h, filtered, washed with n-hexane, and dried in a vacuum oven at 25°C overnight to a constant weight. The each entry in Table 1 was performed two times.

1.4 Polymer characterizations

Polymer number (M_n) and weight (M_w) average molecular weights and polydispersity index ($= M_w/M_n$) were measured by gel permeation chromatography (GPC) analyses carried out at 30 °C and a flow rate of 1.0 mL/min with DMF as the eluent, on an Agilent 1260 GPC instrument equipped with four PLgel 5 μ m mixed-C columns (Polymer Laboratories; linear range of molecular weight = 200 – 2,000,000). The instrument was calibrated with 10 P(2-VP) standards.

1.5 Typical click reaction procedure

Click reaction of triblock polymers were performed in 25 mL Schlenk bottles under nitrogen protection. Triblock polymer (0.28 g, containing 0.445 mmol vinyl groups), azodiisobutyronitrile (AIBN, 0.008 g, 0.05 mmol) and corresponding thiol (1 mmol) were first dissolved in 5 mL of THF. Then the reactor was sealed, and the reaction was started by stirring the mixture at 65 °C. After 4 h, the reaction was cooled to room temperature, and the mixture solution was concentrated to 2 mL. Then the solution was precipitated into 100 mL of n-hexane, stirred for 1 h, filtered, washed with n-hexane, and dried in a vacuum oven at 50 °C overnight to a constant weight .

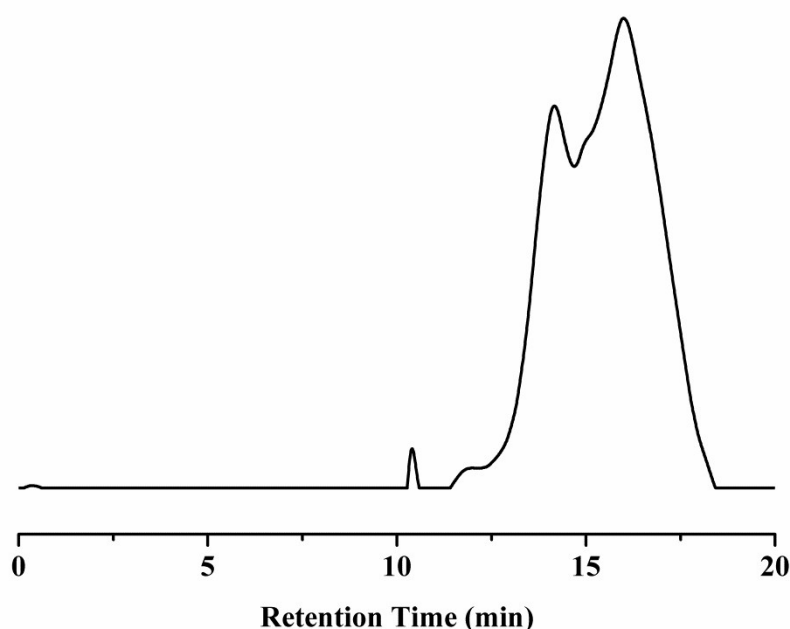


Figure S3. The GPC trace of the PDVP produced by catalyst **2**: $M_n = 9.98$ kg/mol, $PDI = 3.04$ (run 2, Table 1).

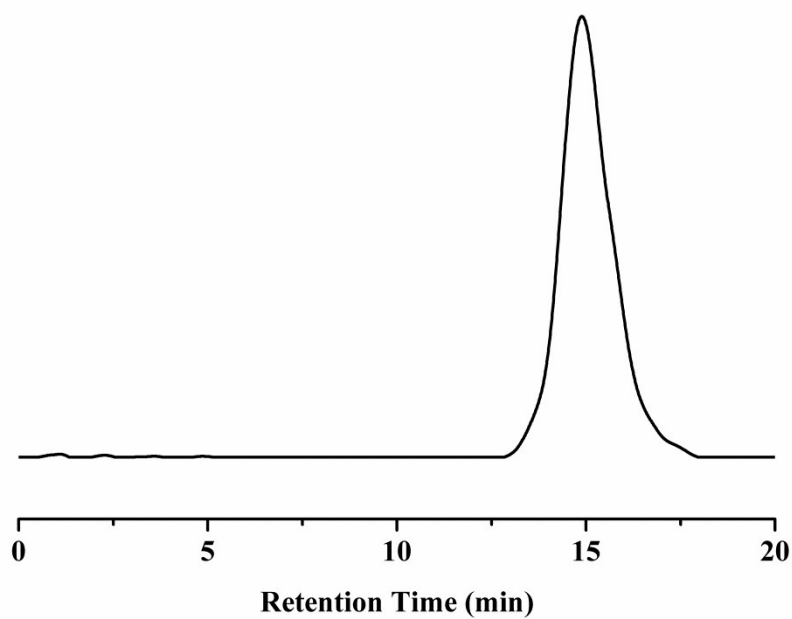


Figure S4. The GPC trace of the PDVP produced by catalyst **3**: $M_n = 20.3$ kg/mol, $PDI = 1.36$ (run 3, Table 1).

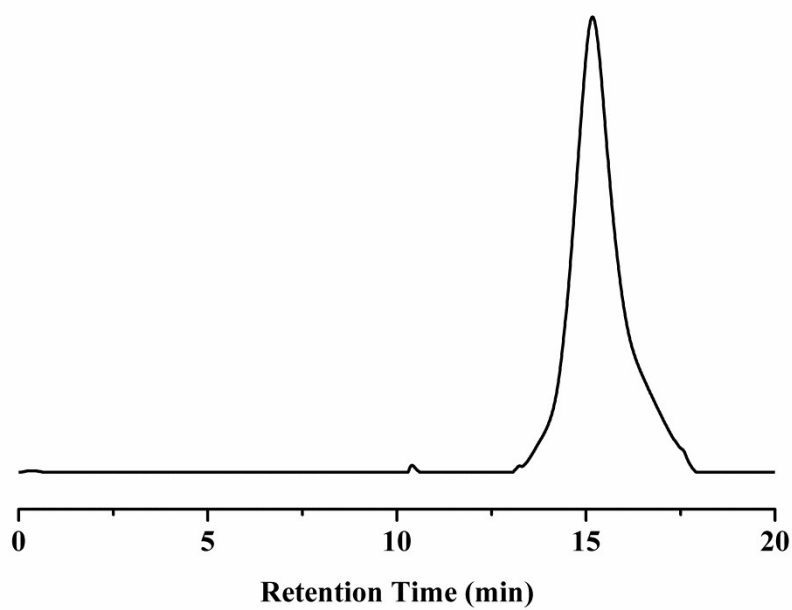


Figure S5. The GPC trace of the PDVP produced by catalyst **4**: $M_n = 14.5$ kg/mol, $PDI = 1.40$ (run 3, Table 1).

4, Table 1).

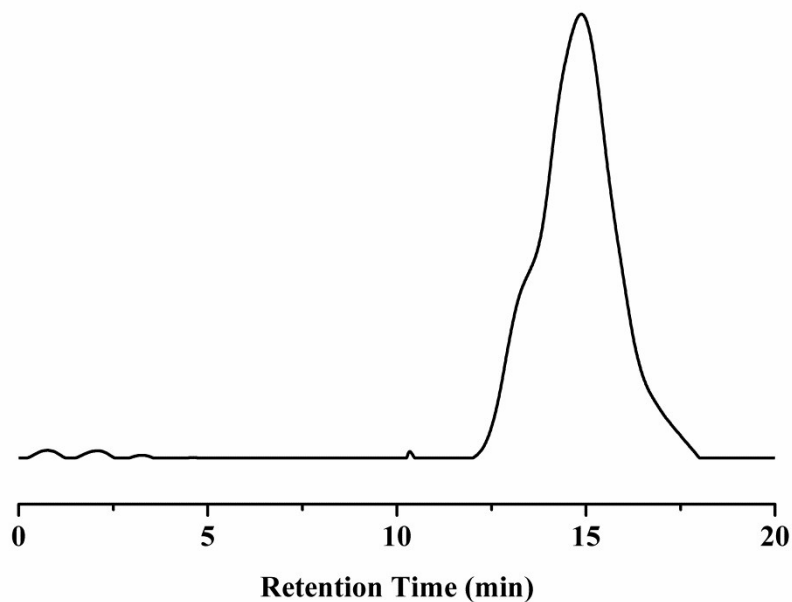


Figure S6. The GPC trace of the PDVP produced by catalyst **5**: $M_n = 24.7$ kg/mol, $\text{PDI} = 2.03$ (run 5, Table 1).

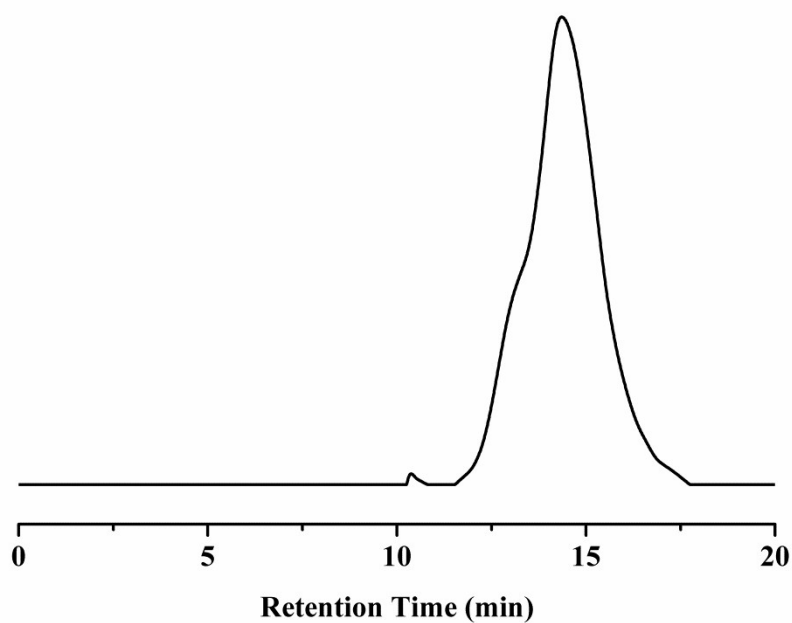


Figure S7. The GPC trace of the PDVP produced by catalyst **6**: $M_n = 32.2$ kg/mol, $\text{PDI} = 2.32$ (run

7, Table 1).

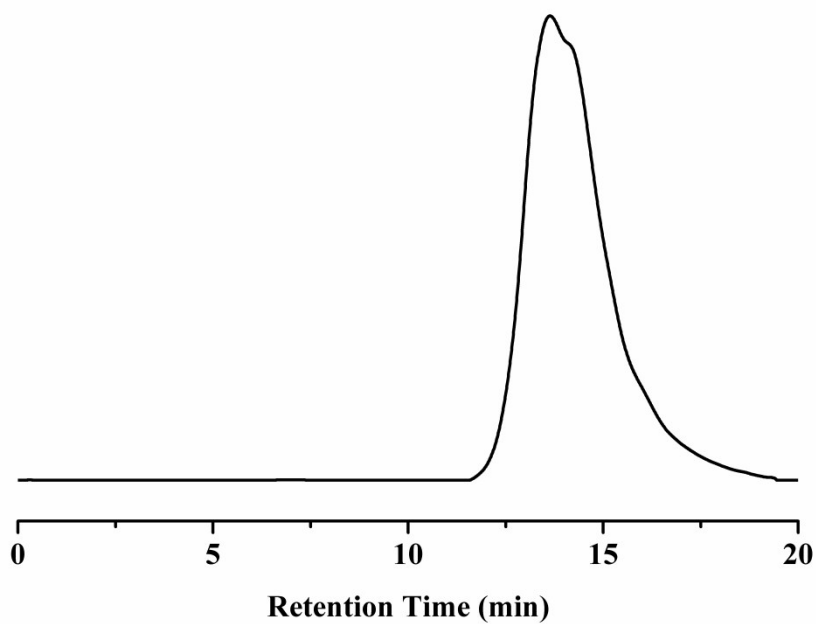


Figure S8. The GPC trace of the PDVP produced by catalyst **6** and $\text{B}(\text{C}_6\text{F}_5)_3$: $M_n = 28.4 \text{ kg/mol}$, $\text{PDI} = 3.21$ (run 8, Table 1).

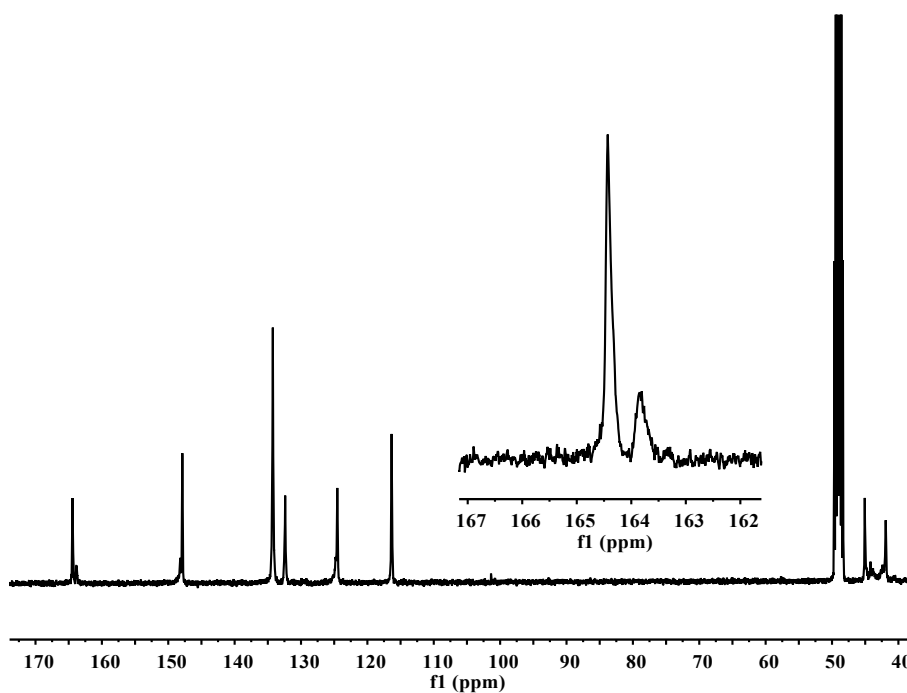


Figure S9. The ^{13}C NMR spectrum of PDVP obtained from DVP by using catalyst **2** in toluene at 25°C in CD_3OD (run 2, Table 1).

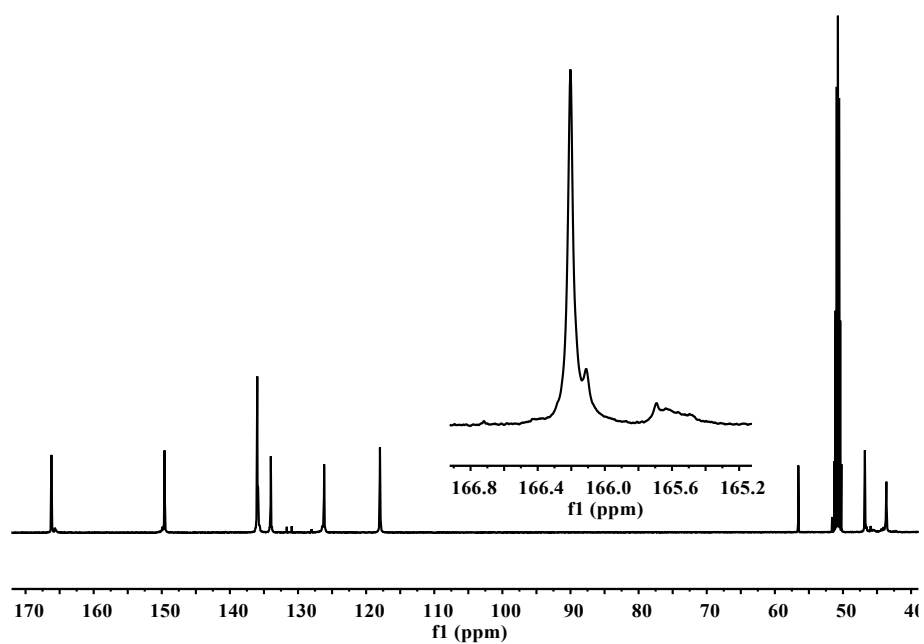


Figure S10. The ^{13}C NMR spectrum of PDVP obtained from DVP by using catalyst **3** in toluene at 25 °C in CD_3OD (run 3, Table 1) .

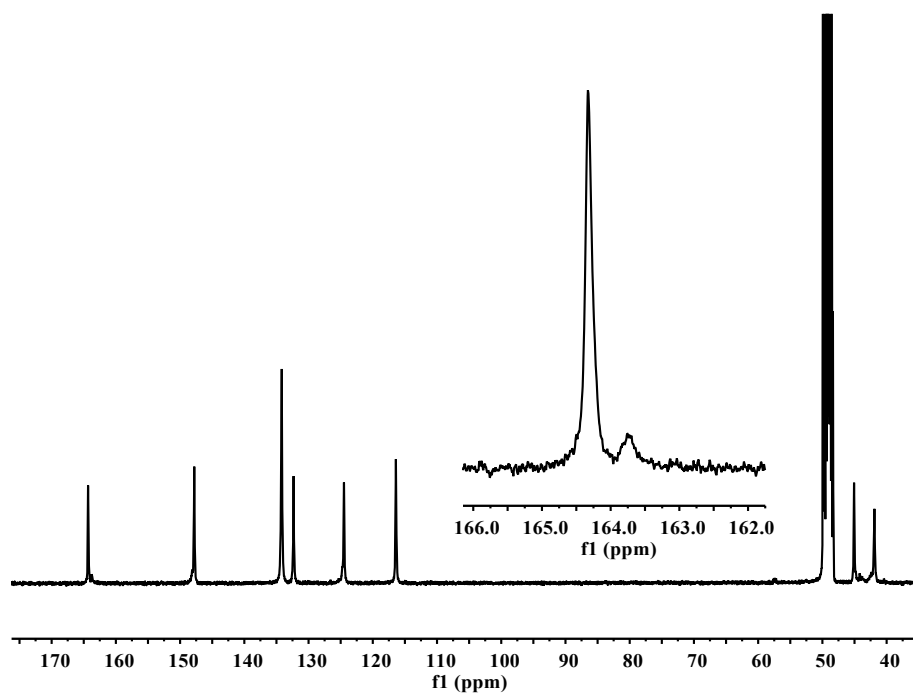


Figure S11. The ^{13}C NMR spectrum of PDVP obtained from DVP by using catalyst **4** in toluene at 25 °C in CD_3OD (run 4, Table 1) .

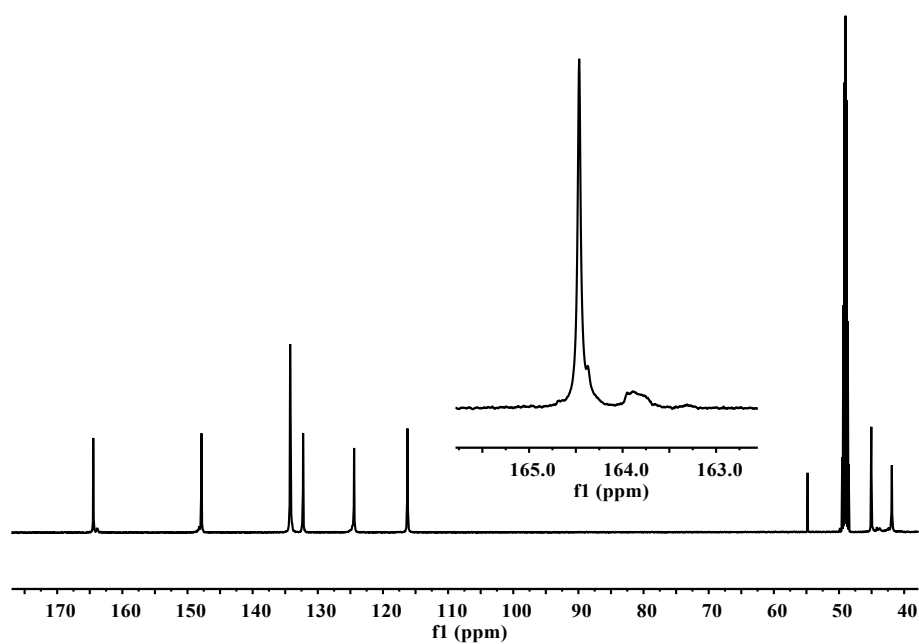


Figure S12. The ^{13}C NMR spectrum of PDVP obtained from DVP by using catalyst **5** in toluene at 25 °C in CD_3OD (run 5, Table 1) .

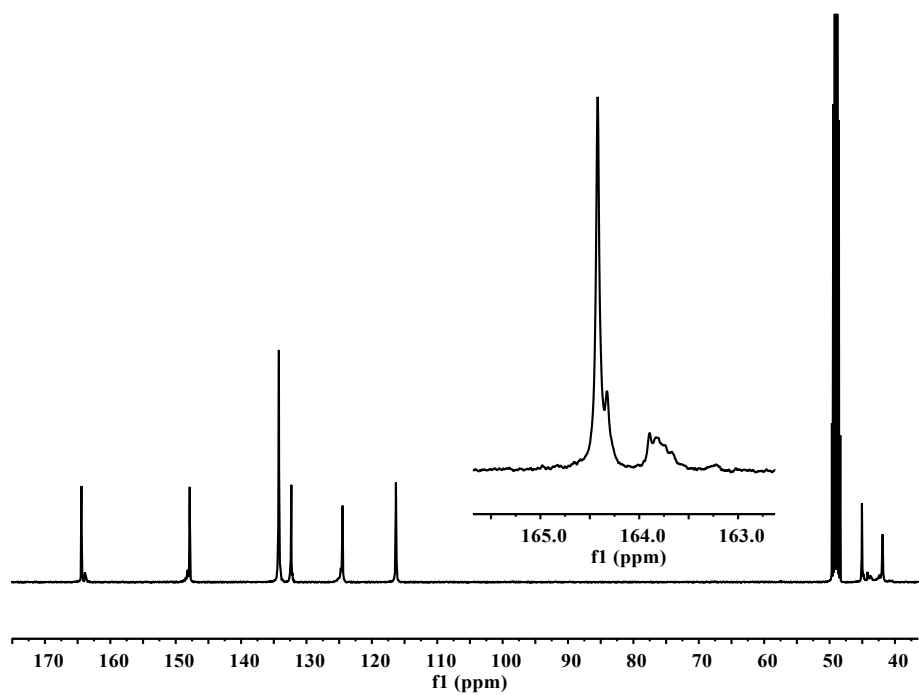


Figure S13. The ^{13}C NMR spectrum of PDVP obtained from DVP by using catalyst **6** in toluene at 25 °C in CD_3OD (run 7, Table 1) .

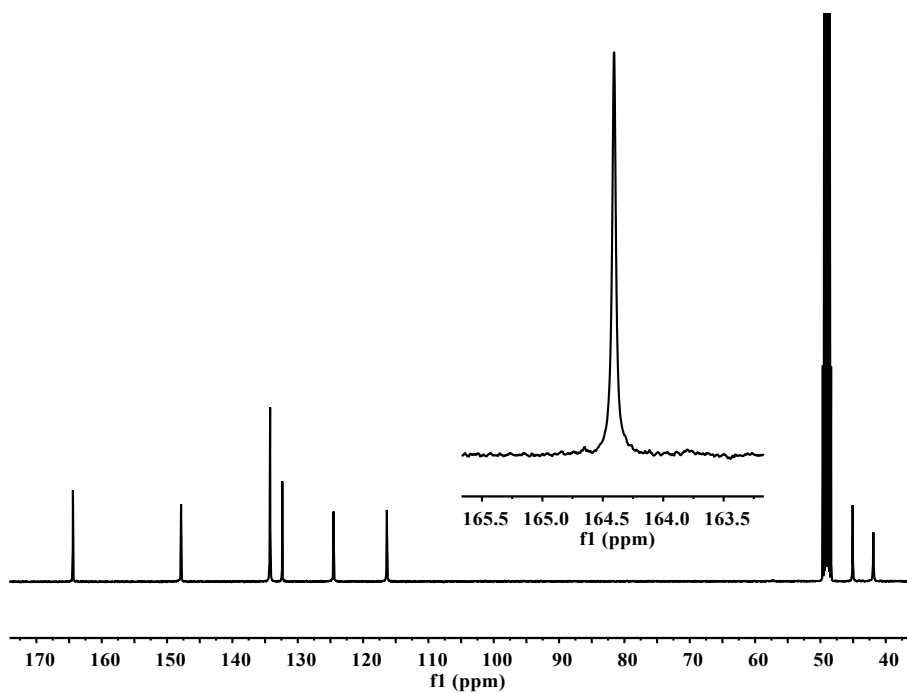


Figure S14. The ^{13}C NMR spectrum of PDVP obtained from DVP by using catalyst **6** and $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene at 25 °C (run 8, Table 1) in CD_3OD .

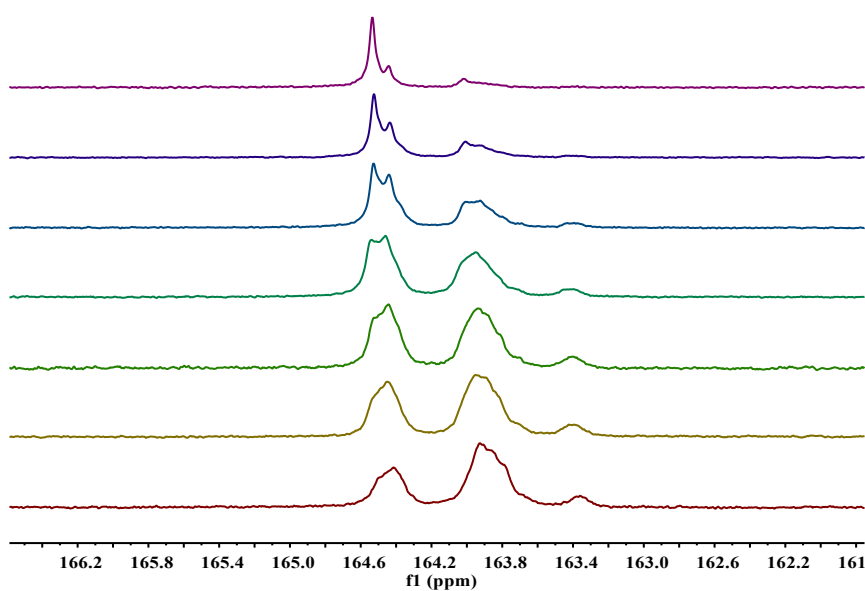


Figure S15. Overlay of ^{13}C NMR (CD_3OD , 125 MHz) spectra of PDVP produced by catalyst **5** with the addition of different amount of THF ($[\text{THF}]/[\mathbf{5}] = 20, 50, 100, 200, 400, 800$ from top to bottom, the last polymerization was conducted in THF).

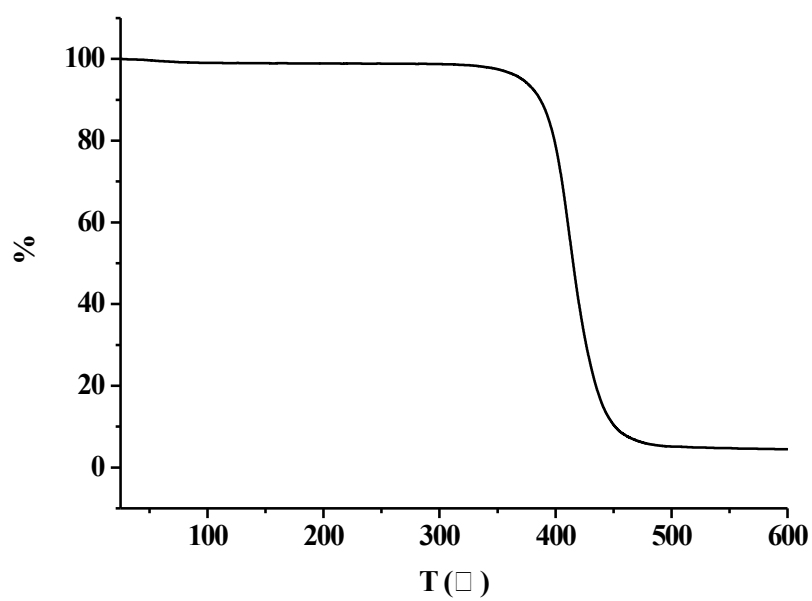


Figure S16. Overlays of TGA curves of PVP-*b*-PDVP-*b*-PVP-1.

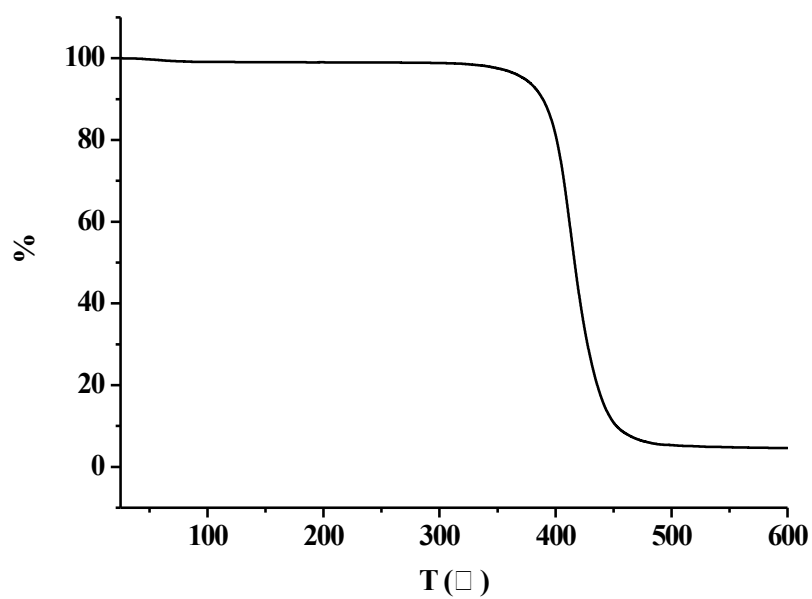


Figure S17. Overlays of TGA curves of PVP-*b*-PDVP-*b*-PVP-2.

Table S1. Results of diblock polymerization of VP and DVP using catalyst **5**^a

No.	[VP]/[DVP] ^b	Conv. ^c (%)	$M_{n, \text{exp}}^d$ (kg/mol)	PDI (M_w/M_n)	mm (%) ^e
1	100: 0	>99	13.5	1.26	93
2	100: 100	>99	28.7	1.39	93/80

^aReaction conditions: 25 °C, toluene, [VP] = [DVP] = 0.25 M, and 10 μmol of catalyst **5**. ^b100 equiv. of DVP was added in situ after the full conversion of VP. ^cThe monomer conversions were analyzed by ¹H NMR spectroscopy. ^dThe molecular weight (M_n) was obtained by gel permeation chromatography (GPC) in DMF relative to P2VP. ^eTacticity was measured by ¹³C NMR in CD₃OD.

Table S2. Results of triblock polymerization of VP and DVP using catalyst **5** and 400 equiv. of THF^a

No.	[VP]/[DVP]/[VP] ^b	Conv. ^c (%)	$M_{n, \text{exp}}^d$ (kg/mol)	PDI (M_w/M_n)
1	100: 0: 0	>99	18.3	1.16
2	100: 50: 0	>99	27.3	1.20
3	100: 50: 100	>99	44.3	1.28

^aReaction conditions: 25 °C, toluene 4 mL, and 10 μmol of catalyst **5**. ^b50 equiv of DVP was added in situ after the full conversion of VP, and another 100 equiv of VP was added in situ after the full conversion of DVP. ^cThe monomer conversions were analyzed by ¹H NMR spectroscopy. ^dThe molecular weight (M_n) was obtained by gel permeation chromatography (GPC) in DMF relative to PVP.

Table S3. Results of triblock polymerization of VP and DVP using catalyst **5** and 100 equiv. of THF^a

No.	[VP]/[DVP]/[VP] ^b	Conv. ^c (%)	$M_{n, \text{exp}}$ ^d (kg/mol)	PDI (M_w/M_n)
1	100: 0: 0	>99	15.7	1.23
2	100: 50: 0	>99	25.0	1.23
3	100: 50: 100	>99	39.2	1.35

^aReaction conditions: 25 °C, toluene 4 mL, and 10 μ mol of catalyst **5**. ^b50 equiv of DVP was added in situ after the full conversion of VP, and another 100 equiv of VP was added in situ after the full conversion of DVP. ^cThe monomer conversions were analyzed by ¹H NMR spectroscopy.

^dThe molecular weight (M_n) was obtained by gel permeation chromatography (GPC) in DMF relative to PVP.

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