

Electronic Supplementary Information (ESI)

Hydrogen Bonding Promoting Controlled Radical Polymerization of 2-Vinyl Pyridine: Supramonomer for a Better Control

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Experimental section

Materials.

2-Vinylpyridine (2VP, 98%, J & K Scientific LTD.) and 4-vinylpyridine (4VP, 95%, J & K Scientific LTD.) were distilled under reduced pressure. 3-Vinylpyridine (3VP) and 2-vinylpyrazine (2VPZ) were purchased from Longrepharm Laboratories (China), Ltd. and used as received. Ethyl-2-chloro-2-phenylacetate (ECPA)^[S1] and tris[2-(dimethylamino)ethyl] amine (Me₆TREN) were synthesized according to literature.^[S2] Copper (75 mm powder, 99%) was purchased from Sigma-Aldrich Co..

1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP, 99.5%) was obtained from Ji'Nan WeiDu Chemical Co. (China). Perfluoro tert-butanol (PFTB, 98%) and 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol (HFPP, 99%) were purchased from J & K Scientific Ltd. (China). 2,2,3,3,4,4,5,5-Octafluoro-1-pentanol (OFNP, 98%) was purchased from Alfa Aesar (ShangHai, China). 2,2,3,3-Tetrafluoro-1-propanol (TFP, 98%) was purchased from Energy Chemical Co. (ShangHai, China). 2,2,2-Trifluoroethanol (TFE, 98%) was purchased from Aladdin Chemical Co. (ShangHai, China). Dimethyl sulfoxide (DMSO, 99.9%), N,N-dimethylformamide (DMF, 99.9%) and N-methyl-2-pyrrolidone (NMP, 99.9%) were purchased from Shanghai Chemical Reagents and were purified by vacuum distillation before use. 2-Propanol (99%) was purchased from Shanghai Chemical Reagents and was dried using 4Å molecular sieve before use. All other chemicals were obtained from Shanghai Chemical Reagents and used as received unless mentioned.

Typical procedures for Cu(0)-mediated CRP of 2VP.

The monomer (2VP, 1.0 mL, 9.3 mmol), initiator (ECPA, 7.8µL, 0.046 mmol), catalyst (Cu(0), 3.0 mg, 0.047 mmol), and solvent (HFIP, 1.0 mL) were added to a 5 mL-ampoule in the following order: Cu(0), 2VP, HFIP and ECPA. The solution was deoxygenated with six standard freeze-pump-thaw cycles. The ampoule was then flame sealed and placed in a stirred water bath equipped with a thermostat at 25±1°C. After a predetermined time, the ampoule was cooled by immersion in iced water.

Afterwards, the ampoule was opened and the contents were dissolved in 5 mL of THF, then the solution was washed with saturated base solution (NaOH). The solution was passed through a small basic Al₂O₃ chromatographic column to remove any residual Cu(0) powder and Cu-ion compounds. The resulting solution was precipitated into 200 mL of cool n-hexane with stirring. The polymer was isolated by filtration and dried under vacuum until a constant weight at room temperature. The monomer conversion was determined by gravimetric calculation. The M_n and M_w/M_n values were determined by SEC with dimethyl formamide as elution and polystyrene as standards.

Characterization

The number-average molecular weight ($M_{n,SEC}$) and molecular weight distribution (M_w/M_n) values of the resultant polymers were determined using a Waters 1515 size exclusion chromatograph (SEC) equipped with a refractive-index detector (Waters 2414), using HR 1 (pore size: 100 Å, 100–5000 Da), HR 2 (pore size: 500 Å, 500–20 000 Da), and HR 4 (pore size 10 000 Å, 50–100 000 Da) columns (7.8×300 mm, 5µm beads size) with molecular weights ranging from 10² to 5 ×10⁵g/mol. DMF was used as the eluent at a flow rate of 1.0 mL/min at 30°C. SEC samples were injected using a Waters 717 plus autosampler and calibrated with poly(styrene) standards purchased from Waters. All the ¹H NMR spectra were collected on an Agilent Direct-Drive II 600MHz spectrometer equipped with four broad-band rf channels and a 5 mm ¹H-¹⁹F/¹⁵N-³¹P pulse field gradient (PFG) probe. In general, during the acquisition periods, ¹H was decoupled with Waltz-16 ($\gamma_H B_H/2\pi = 4.73$ kHz) and WURST-40

($\gamma_{\text{C}}\text{B}_\text{C}/2\pi = 8.77$ kHz) decoupler modulation, respectively. 10 μL of samples were dissolved in about 0.6 mL of CDCl_3 with TMS as a chemical shift reference in the ^1H (0 ppm) NMR spectra.

Cartesian coordinates of optimized geometries

Structure 2VP

C	0.66815100	-2.11987700	0.00000000
C	-0.64697700	-1.66224100	0.00000000
C	0.00000000	0.53969900	0.00000000
C	1.34929800	0.16816000	0.00000000
C	1.68580100	-1.17691200	0.00000000
H	0.87942000	-3.18155100	0.00000000
H	-1.47134600	-2.36978500	0.00000000
H	2.11802900	0.93151500	0.00000000
H	2.72517000	-1.48335600	0.00000000
C	-0.36904300	1.96276100	0.00000000
C	-1.61597700	2.42843000	0.00000000
H	0.46405600	2.65974000	0.00000000
H	-1.81550400	3.49231500	0.00000000
H	-2.46179500	1.75262600	0.00000000
N	-0.98079300	-0.37737600	0.00000000

Structure 2VP-HFIP

C	-3.63910200	-1.90825200	-0.10763600
C	-2.38403200	-1.38707300	-0.39219000
C	-3.04591900	0.77297300	0.09115600
C	-4.33106800	0.31852700	0.40608300
C	-4.63104500	-1.03022100	0.30458900
H	-3.82265900	-2.97011000	-0.20301300
H	-1.57407100	-2.03620600	-0.70651600
H	-5.08404800	1.02979800	0.72127200
H	-5.62472700	-1.38986500	0.54314100
C	-2.75133800	2.20868900	0.17914400
C	-1.64655200	2.82158200	-0.24147600
H	-3.54628600	2.80303100	0.61941800
H	-1.54055600	3.89347000	-0.13308200
H	-0.82309000	2.29521900	-0.70499800
N	-2.08756000	-0.09118600	-0.29472800

O	0.55251200	0.18028100	-0.99138500
C	1.36893700	-0.01022300	0.11101500
H	0.83958000	0.10670700	1.06419600
C	1.93152100	-1.44683500	0.11317700
C	2.46628100	1.06969300	0.09883800
F	2.67967300	-1.71653800	-0.95946700
F	0.89997900	-2.31827600	0.11860200
F	2.66641900	-1.70049200	1.20853100
F	3.31466600	0.93344000	1.13283700
F	1.89330600	2.28206900	0.20916000
F	3.18471300	1.06084300	-1.02720000
H	-0.40624000	0.14143700	-0.72461300

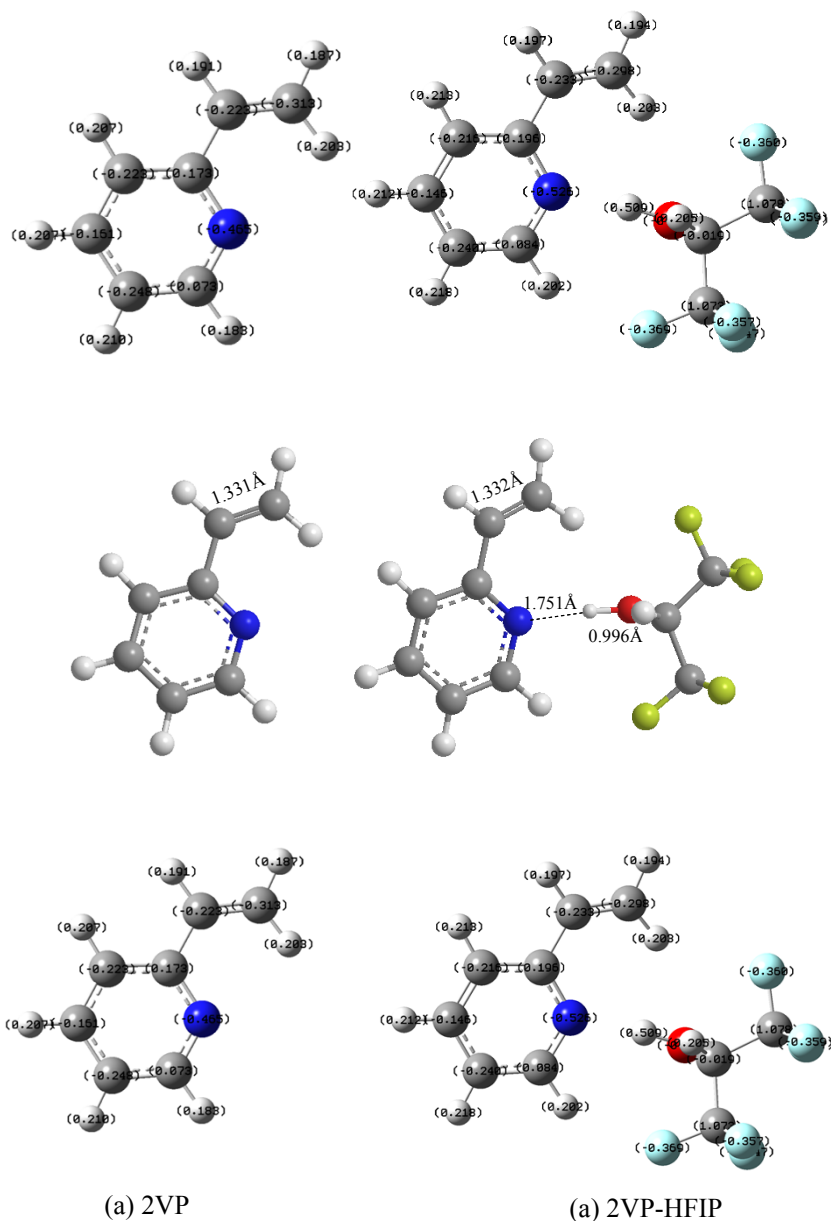


Figure S1. The NBO charges of the 2VP (a) and 2VP-HFIP (b) at the level of B3LYP/6-311++G(2df,p).

Computational Details: With Gaussian03 programs,[S3] we employed density functional theory with the three-parameter hybrid functional (B3LYP) with no symmetry constraints to investigate the optimized geometries of 2VP and 2VP-HFIP with a 6-311++G(2df,p) basis set. The charges calculated by the natural population analysis (NPA) are obtained by using the NBO program[S4] as implemented in Gaussian 03.

Structure 2VP•

C	-1.91265500	0.93479800	0.00006700
C	-2.23351200	-0.42618400	0.00008200
C	-1.18234700	-1.35026900	0.00002300
C	0.42843800	0.30536000	-0.00009600
C	-0.58202100	1.30705100	-0.00001000
H	-2.69432800	1.68648200	0.00011800
H	-3.26196700	-0.76595600	0.00013600
H	-1.39954000	-2.41608600	0.00001000
H	-0.29575300	2.35282400	-0.00000200
N	0.10254200	-1.02134500	-0.00006800
C	1.79969500	0.65372200	-0.00010300
H	2.04682300	1.71018500	0.00003900
C	2.90338800	-0.34745700	0.00000200
H	2.83897500	-1.00999800	-0.87130400
H	3.88097200	0.13728000	-0.00177000
H	2.84110800	-1.00743800	0.87345800

Structure 2VP•-HFIP

C	-4.58504000	-1.17583400	0.39067200
C	-3.51917000	-2.02466000	0.07610800
C	-2.28845600	-1.44602000	-0.23597400
C	-3.10237700	0.71706300	0.03439900
C	-4.38054500	0.18891900	0.37157800
H	-5.55808400	-1.58154000	0.64346200
H	-3.63029200	-3.10131100	0.07278200
H	-1.43662200	-2.07339200	-0.48058200
H	-5.18612400	0.87496100	0.60522400
N	-2.06572900	-0.13286600	-0.25641600
C	-2.90640500	2.11512100	-0.00936100
H	-3.76173900	2.72351700	0.26686500
C	1.37631100	-0.05009400	0.10791500
H	0.82926900	-0.06077400	1.05896200
O	0.55740500	0.18026000	-0.98668100

H	-0.40032200	0.14781400	-0.71314600
C	2.03429600	-1.44246200	-0.01256300
C	2.39543500	1.10192500	0.22054500
F	1.05984600	-2.38066400	-0.09163500
F	2.80489900	-1.56920100	-1.10014300
F	2.78346200	-1.74601500	1.06654500
F	3.12682600	1.26063900	-0.88992300
F	3.24414300	0.92715000	1.25481700
F	1.73213600	2.25815200	0.44294700
C	-1.64306600	2.81372000	-0.36915500
H	-1.85116100	3.81999700	-0.73962700
H	-0.98757800	2.92794200	0.50579600
H	-1.06418400	2.27416000	-1.11982700

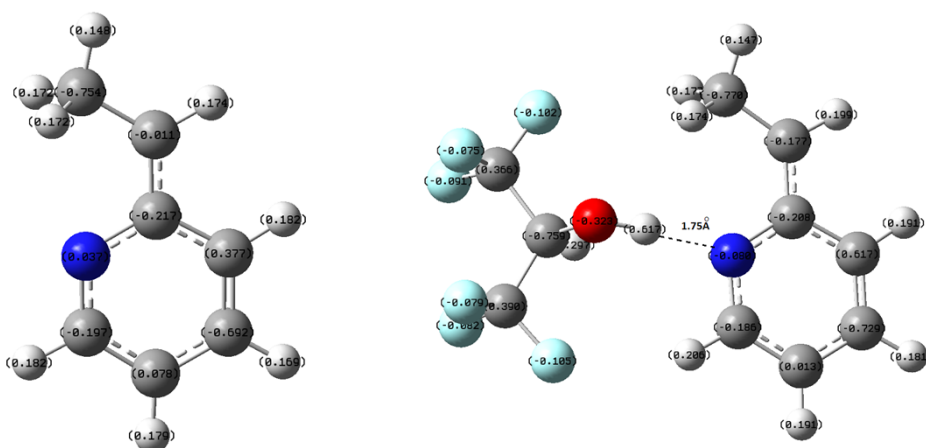


Figure S2. The NBO charges of the 2VP• (a) and 2VP•-HFIP (b) at the level of B3LYP/6-311++G(d,p) implemented in the GAUSSIAN 09 package.

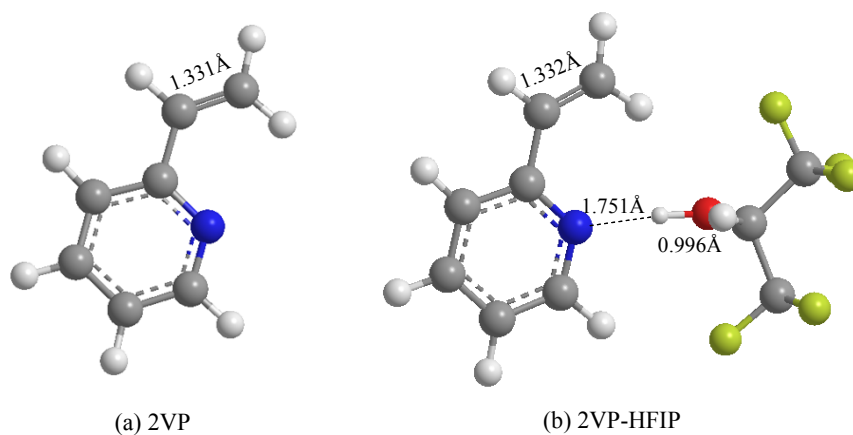
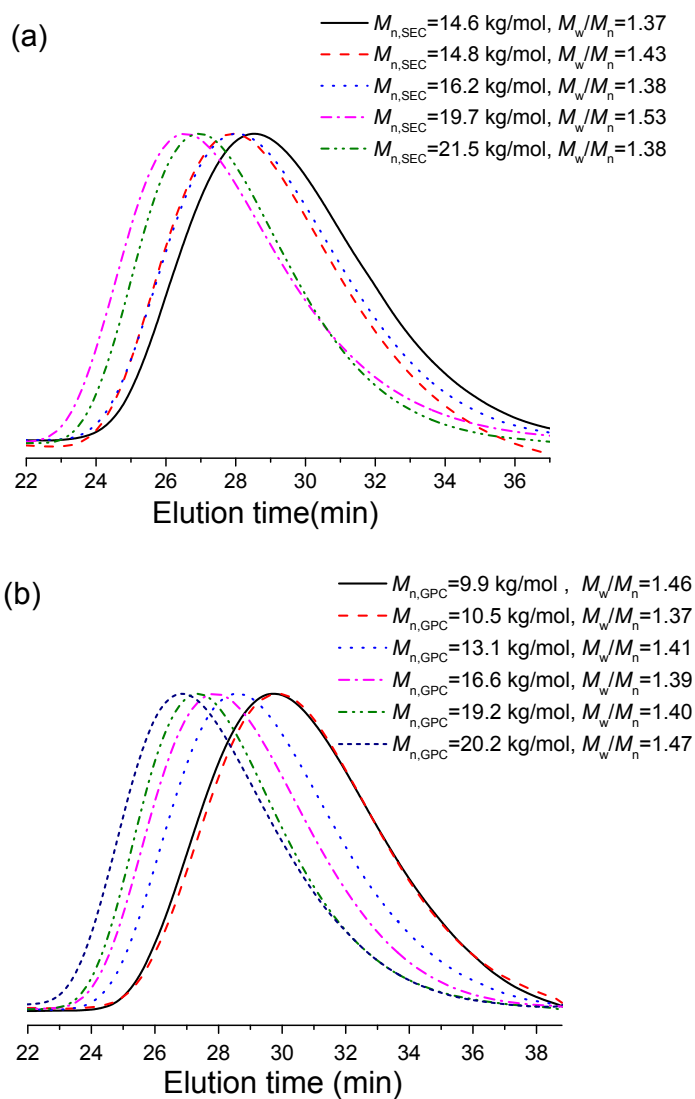


Figure S3. The optimized geometries of 2VP (a) and 2VP-HFIP (b) at the level of B3LYP/6-311++G(2df,p).



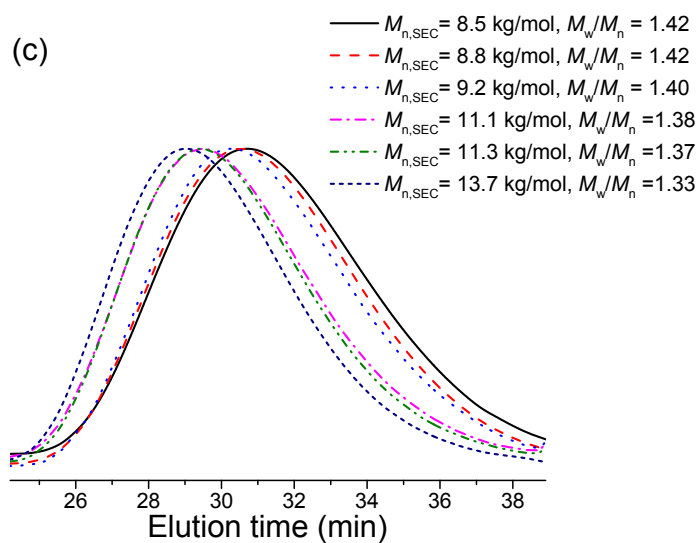


Figure S4. Evolution of SEC traces of the prepared P2VP in HFIP with $[\text{HFIP}]_0/[\text{2VP}]_0 = 1/1$, $[\text{2VP}]_0/[\text{ECPA}]_0/[\text{Cu(0)}]_0 = 200/1/1.25$. $T = 25 \text{ }^\circ\text{C}$ (a), $40 \text{ }^\circ\text{C}$ (b) and $60 \text{ }^\circ\text{C}$ (c).

The molecular weight ($M_{n,NMR}$) of P2VP can be calculated from the integrals in

^1H NMR, according to eq. S1:

$$M_{n,NMR} \text{ (g/mol)} = (I_{7.90-9.00}) \times 105.14 / (I_{3.6}) + 198.65 \quad (\text{S1})$$

where 105.14 and 198.65 are the molecular weights of 2VP and ECPA, respectively.

$I_{7.90-9.00}$ and $I_{3.6}$ are the integration values of the protons from pyridyl groups of 2VP repeat units (a, 1H) and methylene from ECPA (f, 1H), respectively.

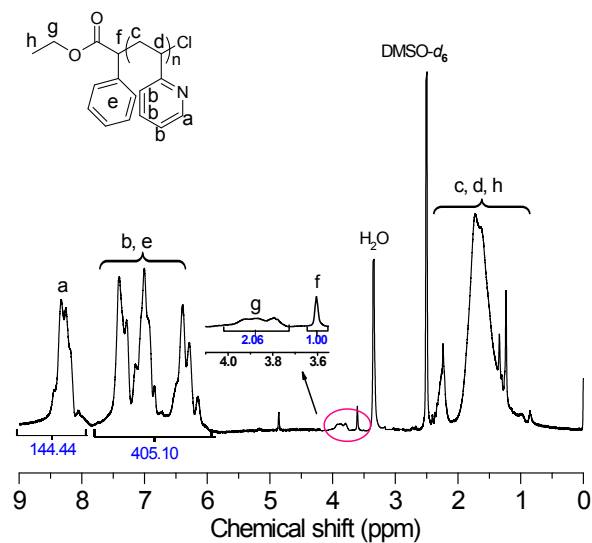


Figure S5. ^1H NMR spectrum of P2VP ($M_{n,SEC} = 1.48 \times 10^4$ g/mol, $M_w/M_n = 1.43$). DMSO- d_6 was used as the solvent and tetramethylsilane (TMS) as an internal standard. Polymerization conditions: $[2VP]_0/[ECPA]_0/[Cu(0)]_0 = 200/1/1$, $[2VP]_0/[HFIP]_0 = 1.0/1.0$, 2VP = 1.0 mL; time = 40 h, conversion = 53.0%; temperature = 25 $^\circ\text{C}$.

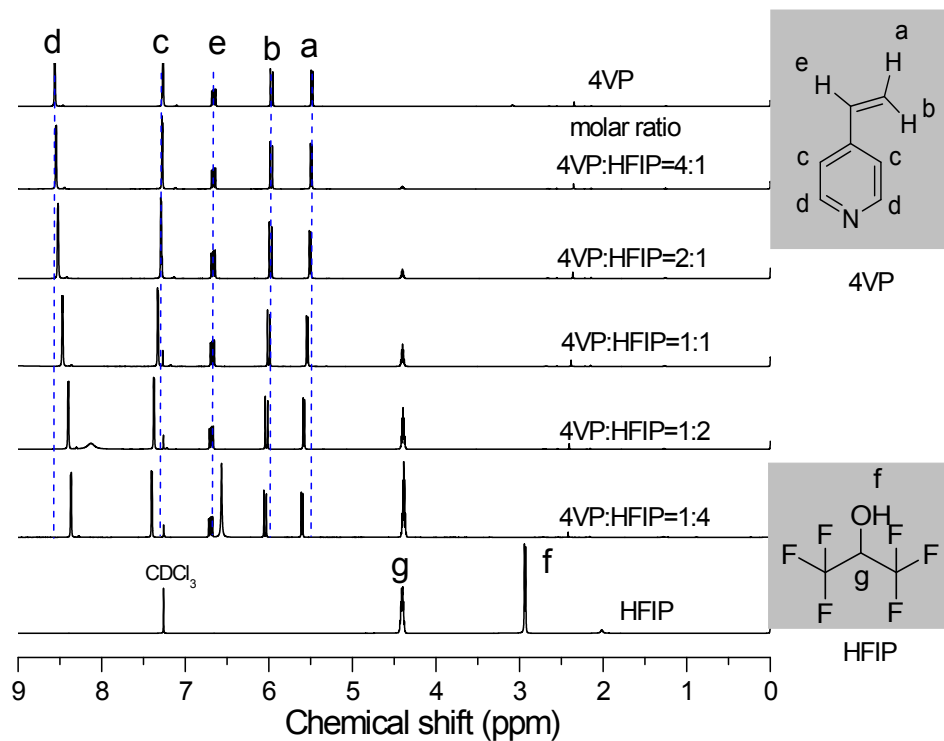


Figure S6. ^1H NMR spectra of 4VP and HFIP at different molar ratios.

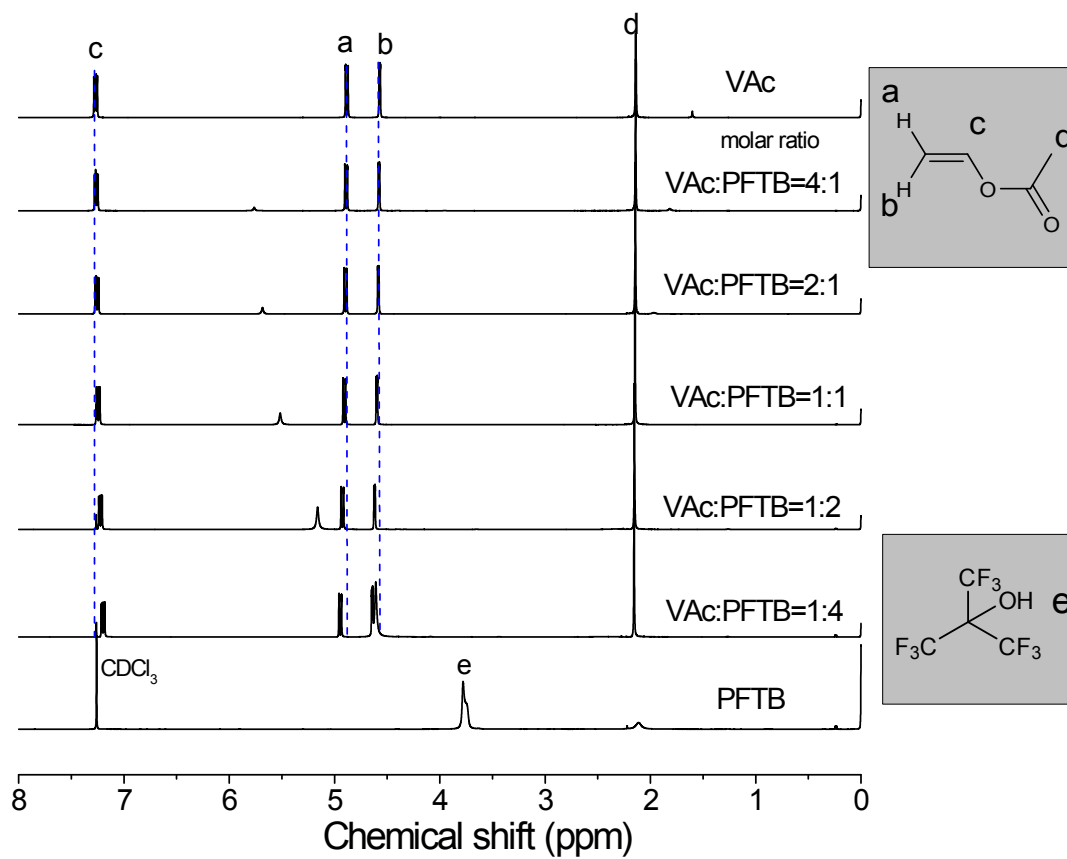


Figure S7. ^1H NMR spectra of VAc and PFTB at different molar ratios.

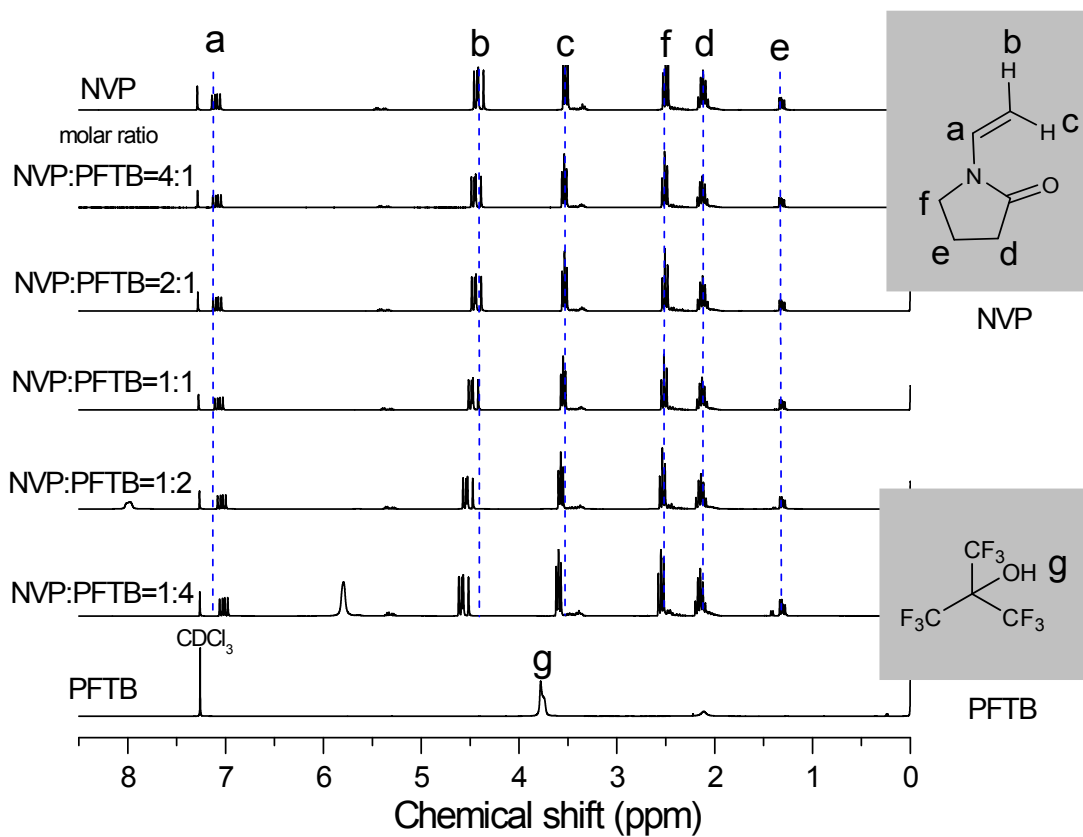


Figure S8. ^1H NMR spectra of NVP and PFTB at different molar ratios.

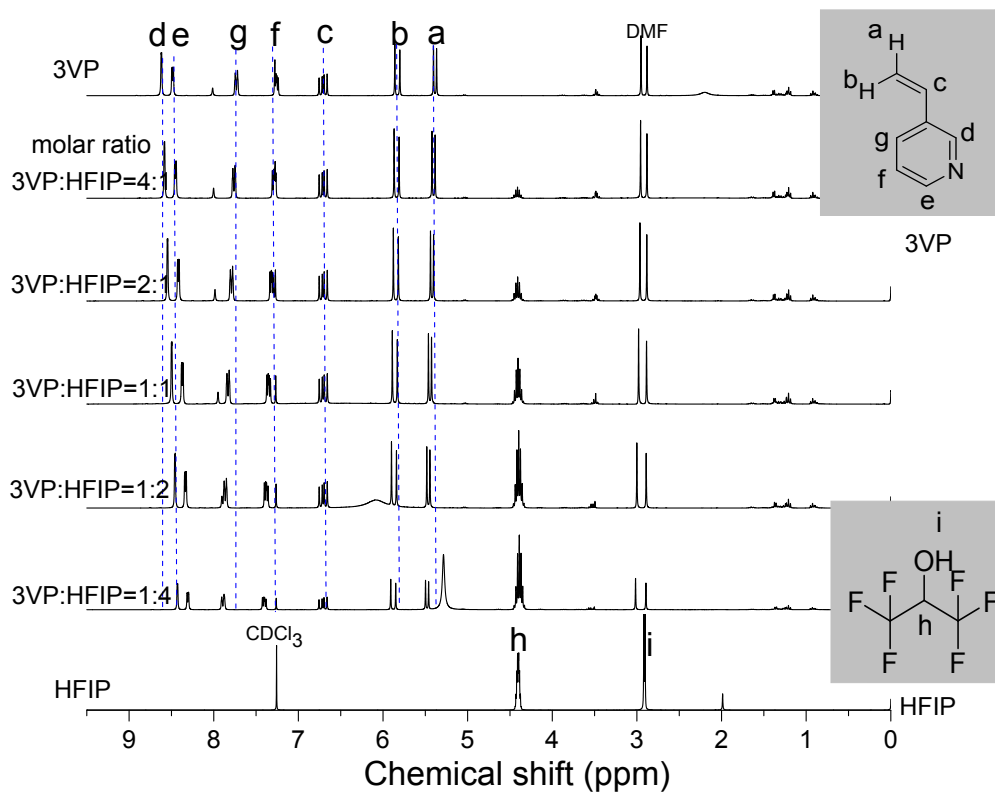


Figure S9. ^1H NMR spectra of 3VP and HFIP at different molar ratios.

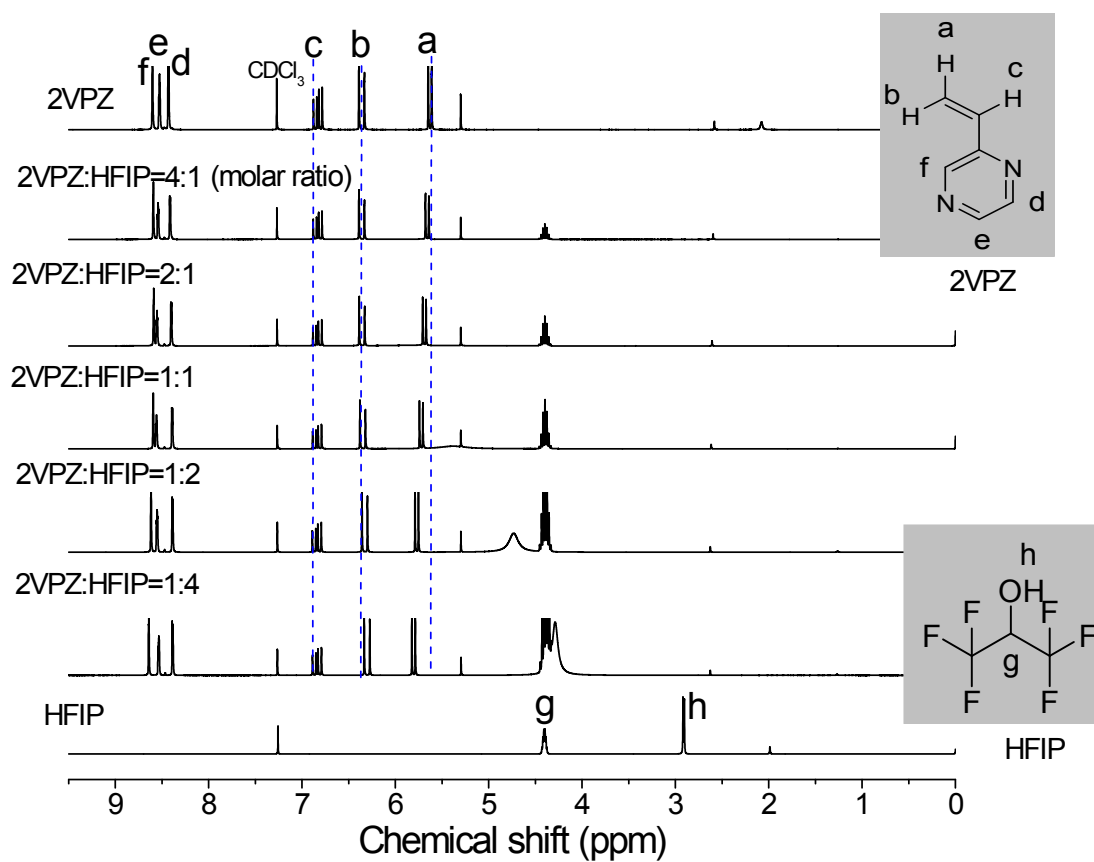


Figure S10. ^1H NMR spectra of 2VPZ and HFIP at different molar ratios.

Table S1. Polymerization of 3VP and 2VPZ in different solvents.

Entry ^a	Solvent	Time (h)	Conv. (%)	$M_{n,SEC}$ (kg/mol)	M_w/M_n	$M_{n,th}$ (kg/mol)
1	(CF ₃) ₂ CHOH = 0.50 mL	24	48.5	60.0	1.76	10.4
2	(CF ₃) ₃ COH = 0.65 mL	24	60.8	82.1	1.81	13.0
3	CHF ₂ CF ₂ CF ₂ CF ₂ CH ₂ OH = 0.65 mL	24	53.7	64.5	1.88	11.5
4	CHF ₂ CF ₂ CH ₂ OH = 0.41 mL	24	50.1	71.7	1.78	10.7
5	CF ₃ CH ₂ OH = 0.34 mL	24	45.8	26.5	1.64	9.8
6	PhC(CF ₃) ₂ OH = 0.78 mL	24	59.8	77.9	1.93	12.8
7	2-propanol = 0.50 mL	24	9	17.1	1.62	2.1
8	toluene = 0.50 mL	42	34.3	13.7	1.54	7.4
9	DMF = 0.50 mL	42	34.8	17.8	1.73	7.5
10	(CF ₃) ₂ CHOH = 0.98 mL	72	1.2	13.0	1.08	0.5
11	(CF ₃) ₃ COH = 1.30 mL	72	0.8	--	--	--
12	CHF ₂ CF ₂ CF ₂ CF ₂ CH ₂ OH = 1.29 mL	72	14.8	16.2	1.35	3.3
13	CHF ₂ CF ₂ CH ₂ OH = 0.83 mL	72	22.6	20.0	1.39	5.0
14	CF ₃ CH ₂ OH = 0.68 mL	72	26.0	22.7	1.22	5.7
15	PhC(CF ₃) ₂ OH = 1.56 mL	72	3.9	--	--	--
16	2-propanol = 1.00 mL	96	15.6	32.0	1.45	3.5
17	toluene = 1.00 mL	96	11.5	26.2	1.27	2.6
18	DMF = 1.00mL	96	16.2	23.5	1.32	3.6

^a 25 °C, entries 1-9: [3VP]₀/[ECPA]₀/[Cu(0)]₀ = 200/1/1, 3VP = 0.5 mL; entries 10-18: [2VPZ]₀/[ECPA]₀/[Cu(0)]₀ = 200/1/1, 2VPZ = 0.48 mL.

[S1] Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *Journal of Polymer Science Part A: Polymer Chemistry* **2002**, *40* (12), 1937-1944.

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[S3] Frisch, M. J., et al. GAUSSIAN 03 (Revision B.04), Gaussian, Inc., Wallingford, CT, 2003. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara,

M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.04; Gaussian, Inc.: Wallingford, CT, 2003.

[S4] Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO, Version 3.1, Gaussian, Inc., Pittsburgh PA, **2003**.