Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information to

RAFT Polymerization of N-vinylpyrrolidone Mediated by Cyanoprop-2-yl-1-Dithionaphthalate in the Presence of Fluoroalcohol: the Possibility of Altering Monomer Property by Hydrogen Bonding?

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Materials.

N-vinylpyrrolidone (NVP, 98%, J&K Scientific LTD.) was distilled under reduced pressure. Styrene (St) (>99%) which was purchased from Shanghai Chemical Reagents Co. (Shanghai, China) was passed through a neutral aluminum oxide to remove the inhibitor. 2,2-Azobisisobutyronitrile(AIBN, Shanghai reagent four factory) was recrystallized three times from ethanol. 2-Cyanoprop-2-yl-1-dithionaphthalate (CPDN) was synthesized according to literature.[36] 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP, 99.5%) was obtained from Ji'Nan WeiDu Chemical Co. (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%) were purchased from Shanghai Chemical Reagents and they 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.

Characterization

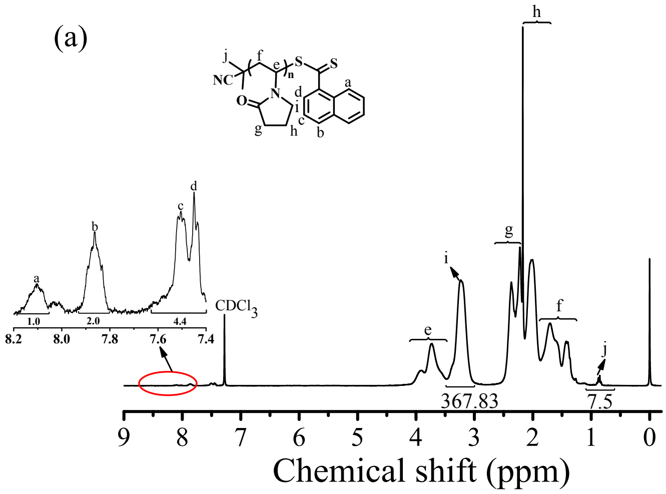
The number-average molecular weight (M_n) and polydispersity ($Đ = M_w/M_n$) of the polymers were determined by a TOSOH HLC-8320 size exclusion chromatography (SEC) equipped with refractive-index and UV detectors using two TSKgel Super Mutipore HZ-N (4.6×150 mm, 3 μm beads size) columns arranged in series, and it can separate polymers in the molecular weight range from 500 ~ 1.9×10^5 g/mol. DMF was used as the eluent at a flow rate of 0.35 mL/min at 40 °C. All the ^{1}H NMR spectra were collected on a Bruker nuclear magnetic resonance instrument (300-MHz) using deuterated chloroform ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as the internal standard. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were acquired on a Bruker Ultraflex-III TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd : YAG laser (355 nm). All spectra were measured in positive reflection mode.

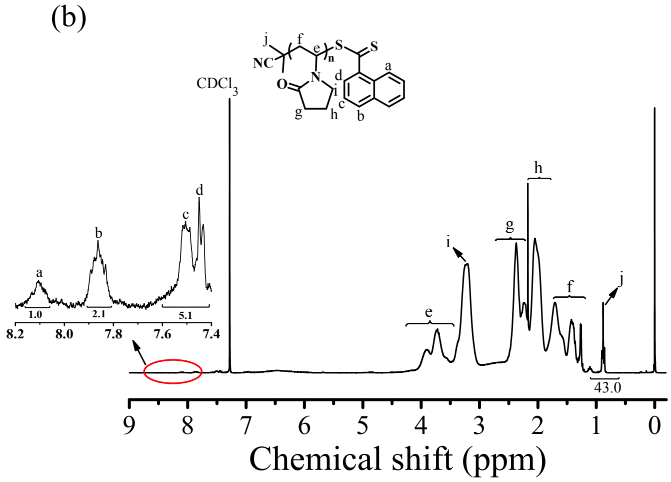
Typical procedures for CPDN-mediated CRP of NVP.

Firstly, the monomer (NVP, 1.0 mL, 9.3 mmol) and solvent (HFIP, 1.0 mL) were added to a 5 mL-ampoule due to the exothermic effect of the mixture of them, initiator (AIBN, 1.5mg, 0.009 mmol) and chain transfer agent (CPDN, 5.2 mg, 0.019 mmol) were then added. 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 60±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 acetone, then the 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 60 ^{o}C. The monomer conversion was determined by gravimetrical calculation. The M_n and M_w/M_n values were determined by SEC with dimethyl formamide as elution and polystyrene as standards.

Chain extension of PNVP using PNVP as macroinitiator

A predetermined quantity of obtained PVP was dissolved in solution with predetermined quantity of MA, St and HFIP. The polymerization temperature was then stabilized at 60 °C. The rest of the procedure was identical to that described earlier except that CPDN replaced by obtained PVP.





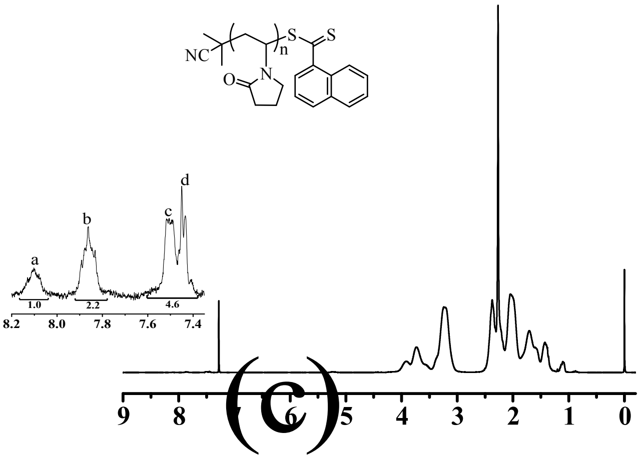
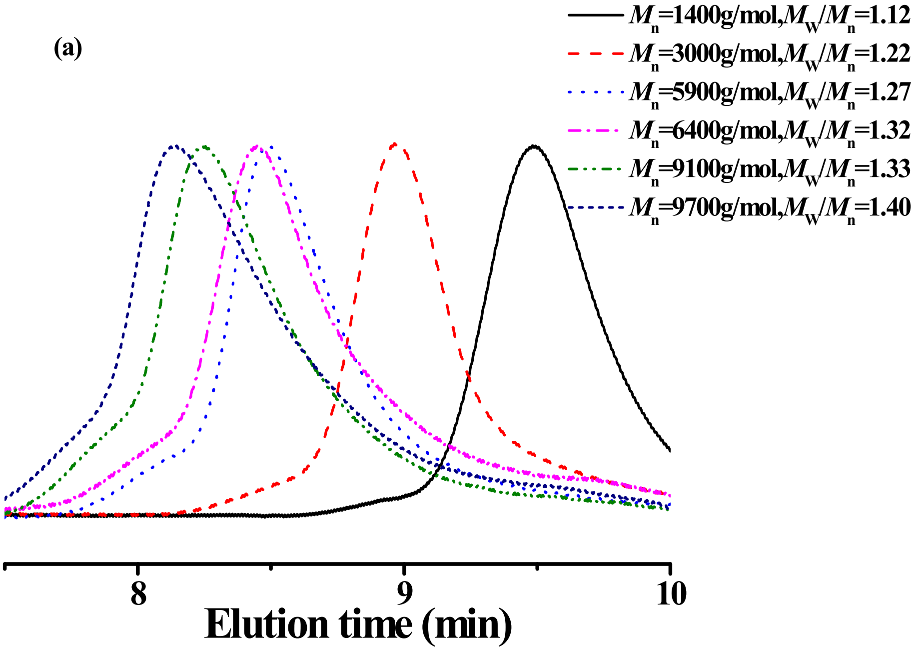
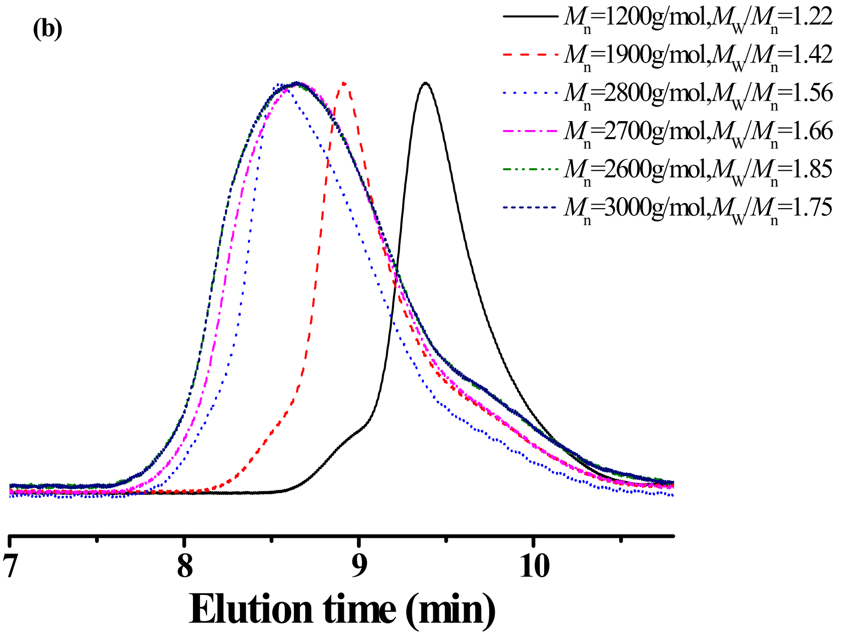


Figure S1. ^{1}H NMR spectrum of PNVP (a: $M_{n,SEC}$ = 5.9 × 10^3 g/mol, $Đ$ = 1.27; b: $M_{n,SEC}$ = 2.7 × 10^3 g/mol, $Đ$ = 1.66; $M_{n,SEC}$ = 2.3 × 10^3 g/mol, M_w/M_n = 1.71). $CDCl_3$ was used as the solvent and tetramethylsilane (TMS) as an internal standard. Polymerization conditions: $[NVP]_0/[AIBN]_0/[CPDN]_0$ = 200/0.2/0.4. (a): $[NVP]_0/[HFIP]_0$ = 1.0/1.0, NVP = 1.0 mL; time = 24 h, conversion = 39.6%, temperature = 60 °C. (b): NVP = 1.0 mL, Dioxane = 1.0 mL; time = 72 h, conversion = 35.2%, temperature = 60 °C. **(c)**: $[NVP]_0/[AIBN]_0/[CPDN]_0$ = 200/0.2/0.4. NVP = 1.0 mL; isopropanol = 1mL, time = 72 h, conversion = 37.5%, temperature = 60 °C. f = Functionality(%) =100× $I_{8.10}$ / ($I_{0.88}$/6)=10.8.

Table S1. Molecular weights detected by SEC and NMR

Entry	**Conv. (%)**	$M_{n,SEC}$ **(g/mol)**	$M_{n,\,NMR}$ **(g/mol)**
1	8.82	1400	3300
2	21.52	2900	4900
3	39.57	5900	6400
4	51.47	6300	7600
5	60.71	8200	8000
6	66.27	9000	8600
7	68.06	9600	9800


(a)
M_n=1400g/mol,M_w/M_n=1.12
M_n=3000g/mol,M_w/M_n=1.22
M_n=5900g/mol,M_w/M_n=1.27
M_n=6400g/mol,M_w/M_n=1.32
M_n=9100g/mol,M_w/M_n=1.33
M_n=9700g/mol,M_w/M_n=1.40
8
9
10
Elution time (min)


(b)
M_n=1200g/mol,M_w/M_n=1.22
M_n=1900g/mol,M_w/M_n=1.42
M_n=2800g/mol,M_w/M_n=1.56
M_n=2700g/mol,M_w/M_n=1.66
M_n=2600g/mol,M_w/M_n=1.85
M_n=3000g/mol,M_w/M_n=1.75
7
8
9
10
Elution time (min)

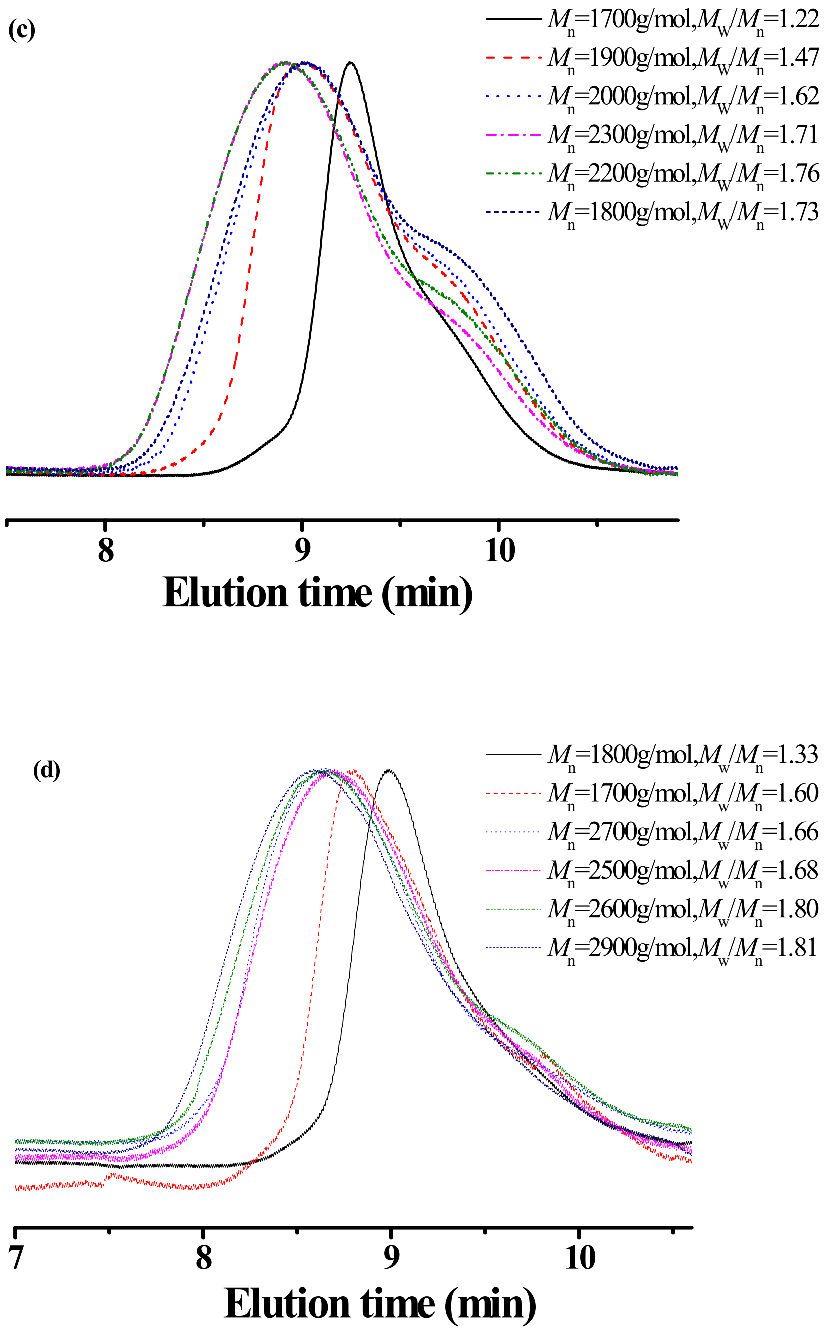


Figure S2. Evolution of SEC traces of the prepared PNVP with $[NVP]_0/[AIBN]_0/ [CPDN]_0$ = 200/0.2/0.4, NVP = 1mL, T = 60 °C. (a) HFIP = 1mL, (b) Dioxane = 1.0 mL, (c) isopropanol = 1mL, (d) TFE = 1.0 mL.

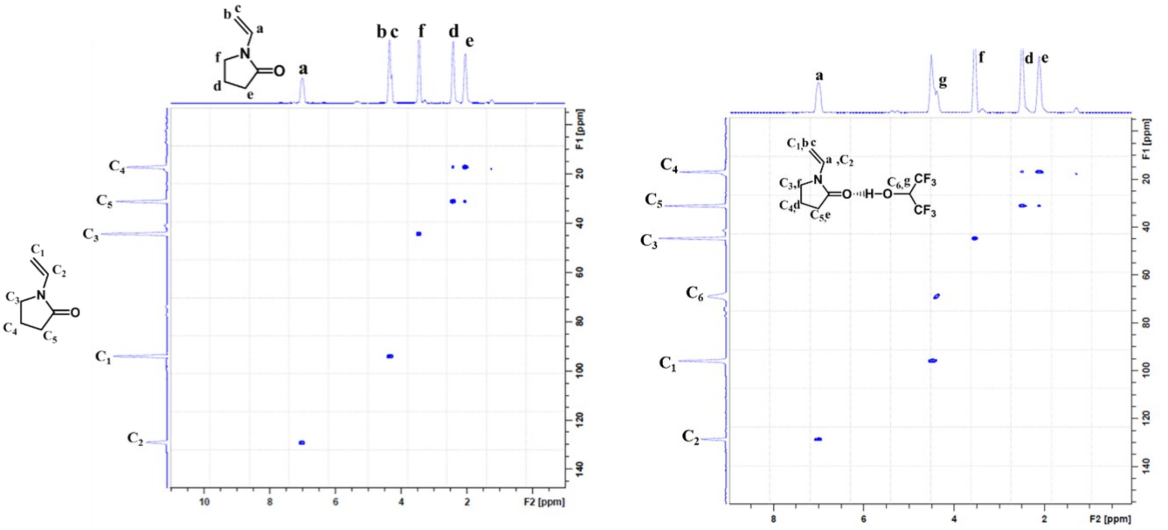


Figure S3. The HSQC spectra of NVP and NVP-HFIP (NVP/HFIP = 1/1, molar ratio) at 25 ^{o}C.

Structure **NVP**

C	-0.01783200	-1.39072300	0.09450700
C	-1.53219400	-1.36179000	-0.18837500
C	-1.95472900	0.07393200	0.14817300
C	-0.68044900	0.89265700	0.00696700
N	0.38473400	0.00565200	-0.02845700
C	1.70447400	0.43521100	-0.04676800
C	2.77922600	-0.35149600	0.02670600
O	-0.58494800	2.10012400	-0.04306000
H	0.52839400	-2.00776000	-0.62153500
H	0.21130500	-1.76198500	1.10000500
H	-2.06524800	-2.11619300	0.38914000
H	-1.71058600	-1.56651500	-1.24547000
H	-2.30008200	0.17407000	1.18179800
H	-2.73564400	0.47645700	-0.49550100
H	1.78312100	1.51239100	-0.12673400
H	3.76483100	0.09042600	-0.00130000
H	2.71938100	-1.42818700	0.11601300

Structure **NVP-HFIP**

C	-4.67173000	-0.48311800	0.67392200
C	-3.78888300	-1.05677200	1.79856000
C	-2.42925900	-1.30342700	1.12907000
C	-2.43001000	-0.37859500	-0.07100900
N	-3.70713000	0.06351500	-0.28070900
C	-4.05377800	0.86708100	-1.36564600
C	-5.29205000	1.24660300	-1.67599000
O	-1.46941700	-0.07857700	-0.77239800
H	-5.33903100	0.30517300	1.02536000
H	-5.28151000	-1.25084200	0.18637200

H	-4.22169600	-1.95678600	2.23246800
H	-3.68470800	-0.32018700	2.59653000
H	-2.32547300	-2.32814600	0.75793200
H	-1.56825700	-1.10399000	1.76656600
H	-3.19393600	1.16211500	-1.95280400
H	-5.45395100	1.87704400	-2.53837600
H	-6.16277700	0.95409400	-1.10443200
C	1.93094300	0.05944700	-0.34262400
H	1.63443900	0.57222500	-1.26384800
O	0.95320300	-0.80197700	0.13733000
H	0.07527600	-0.54284200	-0.22972200
C	2.21798900	1.16878900	0.68771400
C	3.16968400	-0.77682600	-0.70005800
F	1.06712300	1.81411300	0.96516400
F	2.70516300	0.69798900	1.84370600
F	3.08423800	2.08466300	0.21488300
F	3.62435500	-1.49289600	0.33604300
F	4.18061700	-0.00437100	-1.14285400
F	2.85892600	-1.63584400	-1.68740600

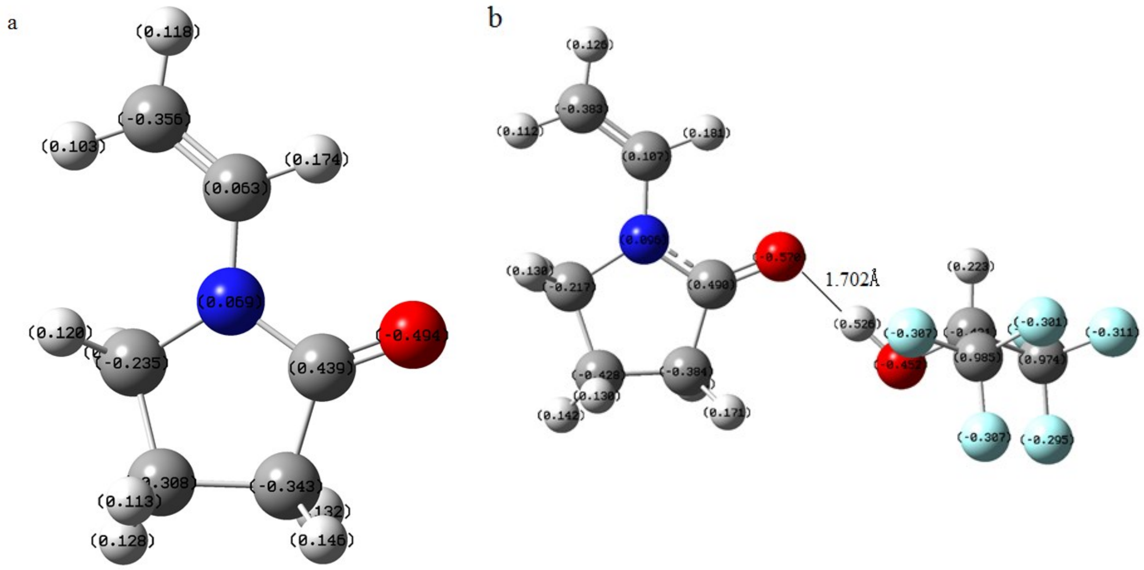


Figure S4. The NBO charges and the optimized geometries of the NVP (a) and NVP-HFIP (b) at the level of B3LYP/6-311++G(2df,p).

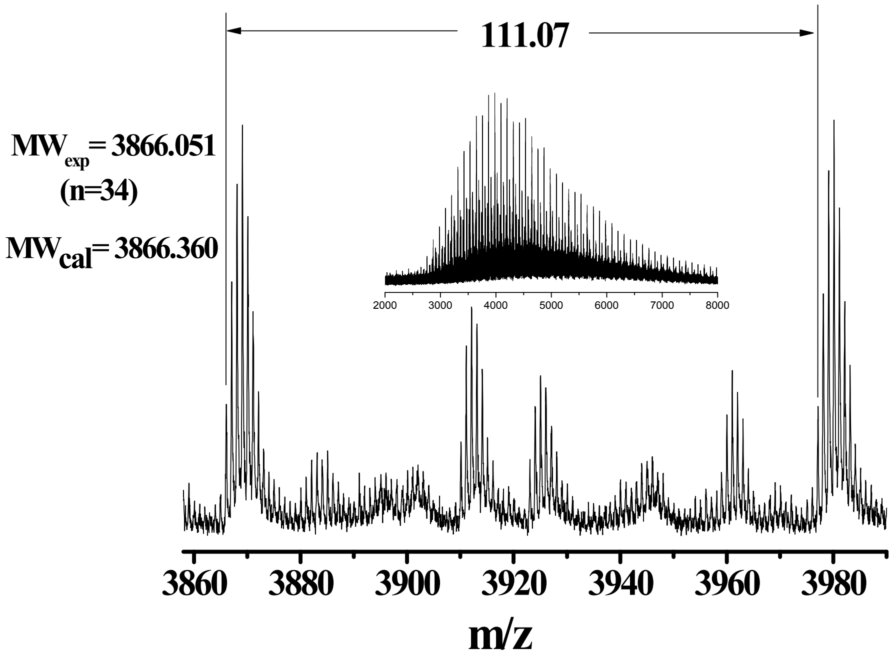


Figure S5. Matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry of poly(*N*-Vinylpyrrolidone) (PNVP, $M_{n,SEC}$ = 5900, M_w/M_n = 1.27) from $[NVP]_0/[AIBN]_0/[CPDN]_0$ = 200/0.2/0.4, $[NVP]_0/[HFIP]_0$ = 1.0/1.0, NVP = 1.0 mL; time = 24 h, conversion = 39.6%, temperature = 60 °C.

Table S2. RAFT polymerization of VAc in HFIP

Entry	Time (h)	Conversion (%)	$M_{n,SEC}$ (g/mol)	*Đ*
1[a]	48	0	---	---
2[a]	96	0	---	---
3[b]	25	0	---	---
4[b]	216	6	6300	1.97
5[c]	18	80.7	19800	2.07
6[c]	24	87.9	20200	2.06
7[d]	48	39.7	9700	1.9
8[d]	96	35.5	10600	1.96

a: $[VAc]_0/[HFIP]_0/[AIBN]_0/[CPDN]_0$ = 200/200/1/2，VAc = 1mL. T = 60 °C.
b: $[VAc]_0/[HFIP]_0/[AIBN]_0/[CPDN]_0$ = 200/200/1/0.5，VAc = 1.0 mL. T = 60 °C
c: $[VAc]_0/[HFIP]_0/[AIBN]_0/[CPDN]_0$ = 200/200/4/0.5，VAc = 1.0 mL. T = 60 °C
d: $[VAc]_0/[HFIP]_0/[AIBN]_0/[CPDN]_0$ = 200/200/2/0.5，VAc = 1.0 mL. T = 60 °C

Table S3. Polymerization of NVP with 2-cyanoprop-2-yl-1-dithiophenyl (CPDB) as chain transfer agent

Entry	Time (h)	Conversion (%)	$M_{n,SEC}$ (g/mol)	Đ
1[a]	24	13.5	2100	1.32
2[a]	48	24.1	4000	1.47
3[b]	24	4.9	1000	1.17
4[b]	48	8.6	1200	1.31

a: $[NVP]_0/[HFIP]_0/[AIBN]_0/[CPDB]_0 = 200/200/0.2/0.4$, NVP = 1.0 mL, T = 60 °C.

b: $[NVP]_0/[AIBN]_0/[CPDB]_0 = 200/200/0.2/0.4$, NVP = 1.0 mL, isopropanol = 1.0 mL, T = 60 °C.

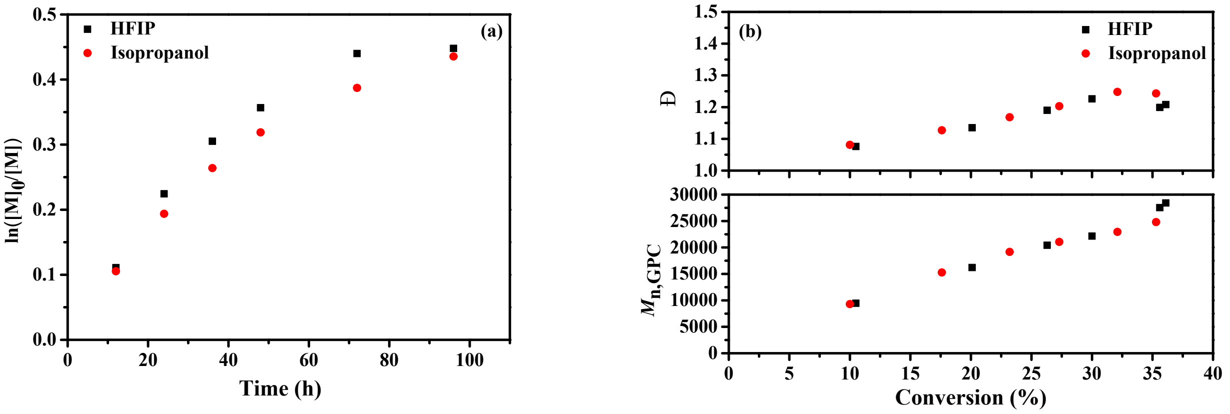
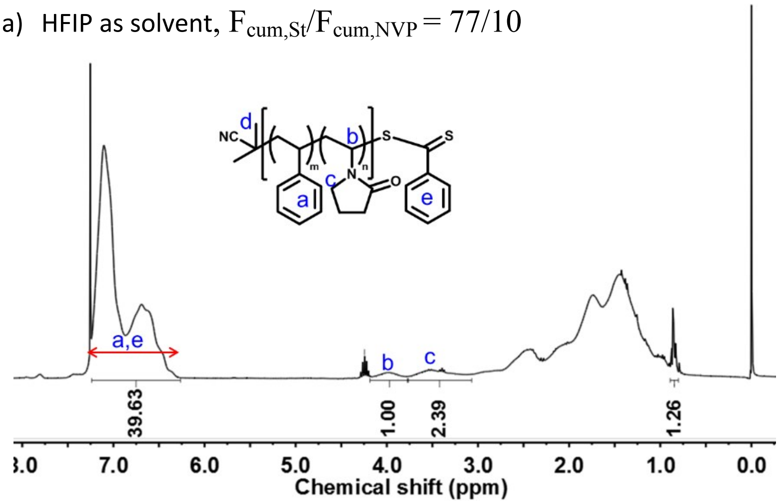


Figure S6. (a) $\ln([M]_0/[M])$ as a function of time and (b) number-average molecular weights ($M_{n,GPC}$) and molecular weight distributions (M_w/M_n) versus conversion for CPDN-mediated copolymerization of NVP and St with HFIP and isopropanol as solvent. $[NVP]_0/[St]_0/[AIBN]_0/[CPDN]_0 = 200:200:0.2:0.4$, NVP = 1mL, solvent = 1mL, temperature = 60 °C. $[M]_0$ and $[M]$ refer to the initial concentration and current concentration of monomer, respectively.



(b) Isopropanol as solvent, $F_{cum,St}/F_{cum,NVP} = 60/10$

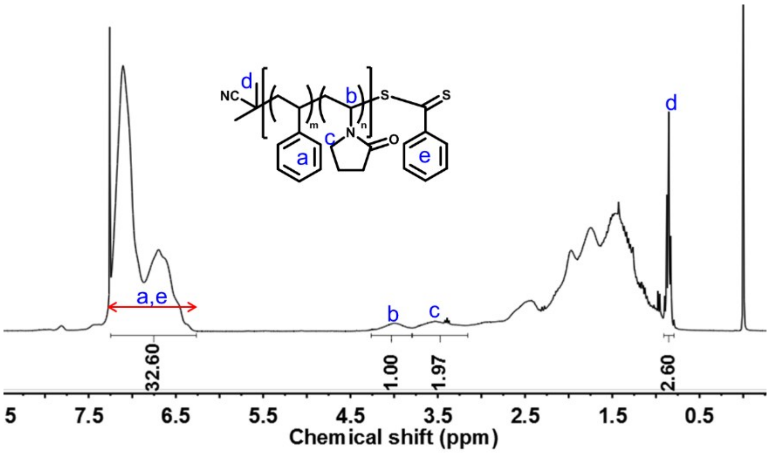


Figure S7. ^{1}H NMR of copolymers produced from CPDN-mediated copolymerization of NVP and St with HFIP and isopropanol as solvent. $[NVP]_0/[St]_0/[AIBN]_0/[CPDN]_0$ = 200:200:0.2:0.4, NVP = 1.0 mL, solvent = 1.0 mL, temperature = 60 ^{o}C.