Supporting Information (SI)

Synthesis and Thermo-responsive Behavior of Helical Polyacetylenes Derived from Proline

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1. Experimental Section

Materials. HPLC solvents (dichloromethane, tetrahydrofuran, methanol, toluene and chloroform), dry benzene and common organic solvents were purchased from Xilong Scientific, Concord Technolggy, and Tongguang Chem. N-(*tert*-butoxycarbonyl)-(*S*)-prolinal was purchased from OuheChem. Acetic acid, propanoic acid, butyric acid, hexanoic acid, octanoic acid, and K_2CO_3 were purchased from InnoChem. $[Rh(nbd)Cl]_2$ was purchased from Alfa Aesar. 4M HCl-dioxane was purchased from Energy Chemical. Dimethyl (1-Diazo-2-oxopropyl) phosphonate was purchased from Accela. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl) and *N*,*N*-dimethyl-4-aminopyridine (DMAP) were purchased from J&K.

Instrumentation and Analysis.

NMR spectra were recorded on a Bruker ARX 400 or 600 instrument at ambient temperature using either $CDCl_3$, DMSO or D_2O as the solvent and tetramethylsilane as the internal standard. High-resolution mass spectra were obtained on a Bruker BIFLEX III mass spectrometer. The number-averaged molecular weight (M_n), weight-averaged molecular weight (M_w), and polydistribution index (M_w/M_n) of polymer were estimated on a gel permeation chromatography (GPC) apparatus equipped with a Waters 2410 refractive index detector and a Waters 515 pump. THF was employed as the eluent at a flow rate of 1.0 mL/min at 35 °C. All GPC curves were calibrated against a series of monodispersed polystyrene standards. Thermogravimetric analyses (TGA) were carried out on a TA Instrument Q600 analyzer at a heating rate of 20 ^oC/min under a N_2 flow rate of 100 mL/min. Dynamic light scatter (DLS) measurement was conducted on a commercialized spectrometer from Brookhaven Instrument Corporation (BI-200SM Goniometer, Holtsville, NY) with a vertically polarized, 100 mW solid-state laser (GXC-III, CNI, Changchun, China) operated at 633 nm and a BITurboCo digital correlator (Brookhaven Instruments Corp.). The sample was filtered through a 0.2 μm filter. Laser Raman spectra were measured on a Thermo Scientific Nicolet NXR FT-Raman Spectrometer. UV−vis absorption measurements were conducted on a Varian Cary 1E UV−vis spectrometer. Circular dichroism (CD) spectra were performed on a JASCO J-810 spectrometer. The light path length of the quartz cell used was 10

mm. The samples were dissolved in THF, CH_2Cl_2, toluene, chloroform, or deionized water at a concentration of around 1.2×10^{-4} mol/L. pPr aggregates were measured on field emission scanning electron microscopy (Hitachi S-4800, 2.0 kV) and atomic force microscope (Nanoscope IIIa, Veeco Inc.) in scanasyst mode. The samples of SEM and AFM were prepared by dropping the sample solution on clean silicon wafer remained at 25 and 45°C for 5 min and absorbing solvent by filter paper.

Synthesis procedures.

2-*(S)*-Acetenyl-*N*-(*tert*-butoxycarbonyl)-pyrrolidine. Under N_2 atmosphere, the mixture of K_2CO_3 (40 mmol, 5.6 g) and N-(*tert*-butoxycarbonyl)-(*S*)-prolinal (20 mmol, 4.0 g) was added anhydrous methanol (40 mL) at 0°C. After the mixture was stirred for 4 h, a solution of N-(*tert*-butoxycarbonyl)-(*S*)-prolinal (40 mmol, 8.0 g) in CH_2Cl_2 (20 mL) was added. The 10mL dimethyl (1-diazo-2-oxopropyl)phosphonate (24 mmol, 4.8 g) in methanol solution was added dropwise by syringe. After stirring for 4 h, the mixture was diluted with ethyl acetate mixture (40 mL) and filtered. The filter residue was washed with ethyl acetate. The combined eluted solution was concentrated under vacuum and purified by flash chromatography with ethyl acetate-petroleum ether mixtures as the eluent to yield 3.0 g of colorless liquid. Yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.60 - 4.30 (d, 1H, NCH), 3.58 – 3.18 (d, 2H, NCH_2), 2.29-2.17 (m, 1H, C≡CH), 2.14 – 1.98 (m, 2H, CH_2), 1.96 – 1.84 (d, 2H, CH_2), 1.52 - 1.42 (m, 9H, CH_3). HRMS (m/z): $[M+H]^+$ calcd for $C_{11}H_{17}NO_2$, 196.1259; found, 196.1327.

2-*(S)*-Acetenyl-*N*-acetyl-pyrrolidine (mAc). This compound was prepared according to the procedures used by Barrett, Mariano, and coworkers (A. G. M. Barrett, B. T. Hopkins, A. C. Love, L. Tedeschi, *Org. Lett.*, 2004, *6*, 835; J. W. Zou, D. W. Cho, P. S. Mariano, *Tetrahedron*, 2010, *66*, 5955). At 0°C, 3.0 g 2-*(S)*-Acetenyl-*N*-(*tert*-butoxycarbonyl)- pyrrolidine was added 30 mL 4M HCl-dioxane in 100 mL round-bottom flask. After stirring for 2 h, the mixture was concentrated under vacuum. Then, the residue was added 50 mL dichloromethane, 1.1 g acetic acid, 5.0 g 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl) and 0.4 g *N*,*N*-dimethyl-4-aminopyridine (DMAP). After stirring for 12h at room temperature, the crude product was obtained by the removal of solvent under reduced pressure and purified by column chromatography with ethyl acetate-petroleum ether mixtures as the eluent to yield 1.7 g of faint

yellow liquid. Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.79 – 4.31 (dd, 1H, NCH), 3.67 – 3.32 (dt, 2H, NCH_2), 2.41 – 2.24 (m, 1H, C≡CH), 2.14 – 2.14 (t, 2H, CH_2), 2.11 – 2.01 (m, 3H, CH_3), 2.01 – 1.75 (dt, 2H, CH_2). HRMS (m/z): $[M+H]^+$ calcd for $C_8H_{11}NO$, 138.0841; found, 138.0912.

2-*(S)*-Acetenyl-*N*-propionyl-pyrrolidine (mPr). Yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.82 – 4.31 (dd, 1H, NCH), 3.66 – 3.34 (dt, 2H, NCH_2), 2.66 – 2.50 (q, 2H, O=CCH_2), 2.40 – 2.28 (m, 1H, C≡CH), 2.27 – 2.02 (t, 2H, CH_2), 2.00 – 1.75 (t, 2H, CH_2), 1.28 – 1.05 (t, 3H, CH_3). ^{13}C NMR (101 MHz, *d*-$CDCl_3$, δ, ppm): 172.8, 172.1, 83.7, 83.0, 82.7, 71.6, 69.7, 48.2, 47.1, 45.1, 45.6, 34.2, 32.3, 27.8, 27.6, 24.9, 22.9, 9.0, 8.6. HRMS (m/z): $[M+H]^+$ calcd for $C_9H_{13}NO$, 152.0997; found, 152.1071.

2-*(S)*-Acetenyl-*N*-butyryl-pyrrolidine (mBu). Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.83 – 4.33 (dd, 1H, NCH), 3.68 – 3.33 (dt, 2H, NCH_2), 2.57 – 2.45 (t, 2H, O=CCH_2), 2.36 – 2.26 (m, 1H, C≡CH), 2.24 – 2.11 (t, 2H, CH_2), 2.10 – 1.86 (t, 2H, CH_2), 1.78 – 1.60 (q, 2H, CH_2), 1.02 – 0.90 (t, 3H, CH_3). HRMS (m/z): $[M+H]^+$ calcd for $C_{10}H_{15}NO$, 166.1154; found, 166.1225.

2-*(S)*-Acetenyl-*N*-hexanoyl-pyrrolidine (mHex). Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.85 - 4.33 (dd, 1H, NCH), 3.67 – 3.34 (dt, 2H, NCH_2), 2.40 – 2.26 (t, 2H, O=CCH_2), 2.25 – 2.18 (m, 1H, C≡CH), 2.17 – 2.00 (t, 2H, CH_2), 2.00 – 1.79 (t, 2H, CH_2), 1.74 – 1.56 (td, 2H, CH_2) , 1.41 – 1.19 (td, 4H, CH_2), 0.98 – 0.80 (t, 3H, CH_3). HRMS (m/z): $[M+H]^+$ calcd for $C_{12}H_{19}NO$, 194.1467; found, 194.1539.

2-*(S)*-Acetenyl-*N*-octanoyl-pyrrolidine (mOct). Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.85 - 4.30 (dd, 1H, NCH), 3.68 – 3.33 (dt, 2H, NCH_2), 2.43 – 2.24 (t, 2H, O=CCH_2), 2.20 – 2.10 (m, 1H, C≡CH), 2.09 – 1.99 (td, 2H, CH_2), 1.98 – 1.78 (td, 2H, CH_2), 1.73 – 1.56 (td, 2H, CH_2), 1.40 – 1.15 (t, 8H, CH_2), 0.94 – 0.82 (t, 3H, CH_3). HRMS (m/z): $[M+H]^+$ calcd for $C_{14}H_{23}NO$, 222.1780; found, 222.1847.

2-*(S)*-Acetenyl-*N*-isobutyryl-pyrrolidine (miBu). Yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.80 - 4.38 (dd, 1H, NCH), 3.70 – 3.35 (dt, 2H, NCH_2), 2.99 – 2.55 (qd, 1H, O=CCH), 2.38 – 2.33 (m, 1H, C≡CH), 2.28 – 2.07 (t, 2H, CH_2), 2.05 – 1.84 (td, 2H, CH_2), 1.23 – 1.00 (d, 6H, CH_3). HRMS (m/z): $[M+H]^+$ calcd for $C_{10}H_{15}NO$, 166.1154; found, 166.1225.

$Rh[C(C_6H_5)=C(C_6H_5)_2](nbd)(4\text{-}FC_6H_4)_3P$ ([Rh] catalyst): the detailed synthesis procedures can refer to Masuda previous work.[1]

Polymerization.

Living polymerization condition can refer to Masuda previous work.[1]

Non-living polymerization: Monomer mPr (1.30 mmol, 200 mg) and THF (4 mL) were added to a dry ampule. After three freeze-pump-thaw cycles, to the ampule was added a solution of $[Rh(nbd)Cl]_2$ (6 mg, 0.013 mmol) and TEA (50 uL) in THF (1.0 mL). The concentrations of monomer and the rhodium catalyst were 0.26 and 0.0026 M, respectively. The color of the reaction mixture turned dark red within 1 h. After stirring for 12 h at 30°C, the resulting polymer was precipitated into a large amount of *n*-hexane and collected by filtration and washed by *n*-hexane. After drying under vacuum at room temperature for 24 h, 100 mg of yellow solids pPr-5 were obtained. Yield: 50%.

As for pEt and piBu, the polymers precipitated from THF solution during polymerization. We add moderate THF to the turbid liquid and poured the mixture into a large amount of *n*-hexane, followed by by filtration and drying under vacuum. pPr and pBu were precipitated in *n*-Hexane, but for pHex and pOct were precipitated in acetonitrile followed by filtration. pEt and pPr were soluble in water, and some less polar solvent such as chloroform. piBu was soluble in chloroform. pBu, pHex and pOct were soluble in THF, chloroform, and toluene. Because of the insolubility of pEt and piBu in THF and DMF, the molecular weight and polymer dispersity index are not accessible for these two polymers.

Table S1 Polymerization results and properties of pPr[a]

Polymer	conv.[b] (%)	M_n[c]× 10^{-4}	PDI[c]	*Cis*[d] (%)	T_d[e] (°C)	$[\alpha]_D^{20}$[f]	T_{cp}[g] (°C)
pPr-1	63	0.50	1.34	94	296	+1004	31.8
pPr-2	50	0.84	1.36	93	295	+1010	31.6
pPr-3	43	1.22	1.38	96	297	+1013	30.1
pPr-4	45	2.78	1.37	95	297	+1009	29.7

[a]Carried out at 30 °C in THF under nitrogen for 12 h; [M] = 0.26 M. [b]Hexane-insoluble part. [c]Estimated by GPC in THF on the basis of a polystyrene calibration. Determined by ^{1}H NMR analysis. [e]5% weight loss temperature under nitrogen atmosphere at a heating rate of 20 °C/min. [f] Specific optical rotation of polymers measured in $CHCl_3$. [g]The T_{cp} of polymers was determined as the temperature at 50%

of the initial transmittance at λ = 700 nm at a concentration of 1 mg/mL.

2. $^{1}H/^{13}C$ NMR and FTMS Spectra of Important Compounds and Polymers

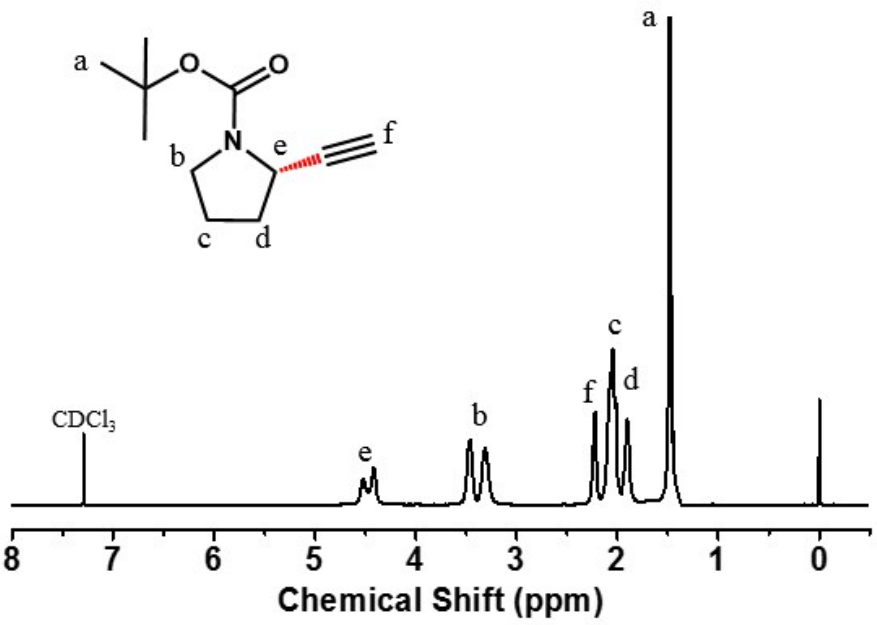

Figure S1. ^{1}H NMR spectrum of 2-*(S)*-Acetenyl-*N*-(*tert*-butoxycarbonyl)-pyrrolidine measured in $CDCl_3$ at room temperature.

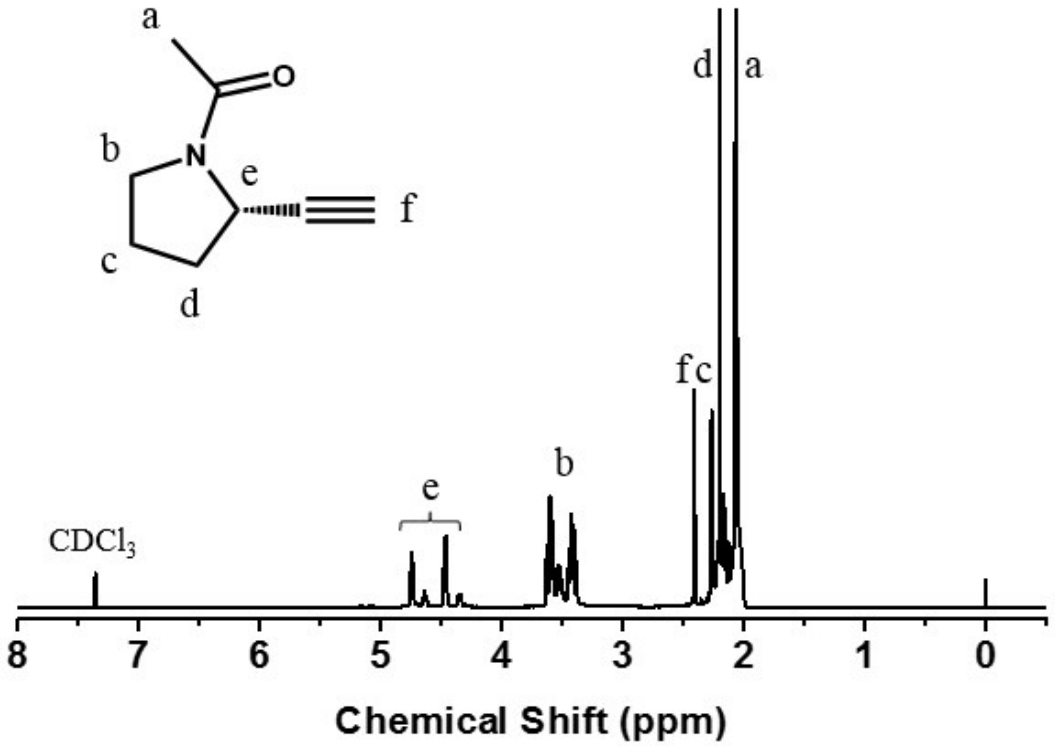

Figure S2. ^{1}H NMR spectrum of mAc measured in $CDCl_3$ at room temperature.

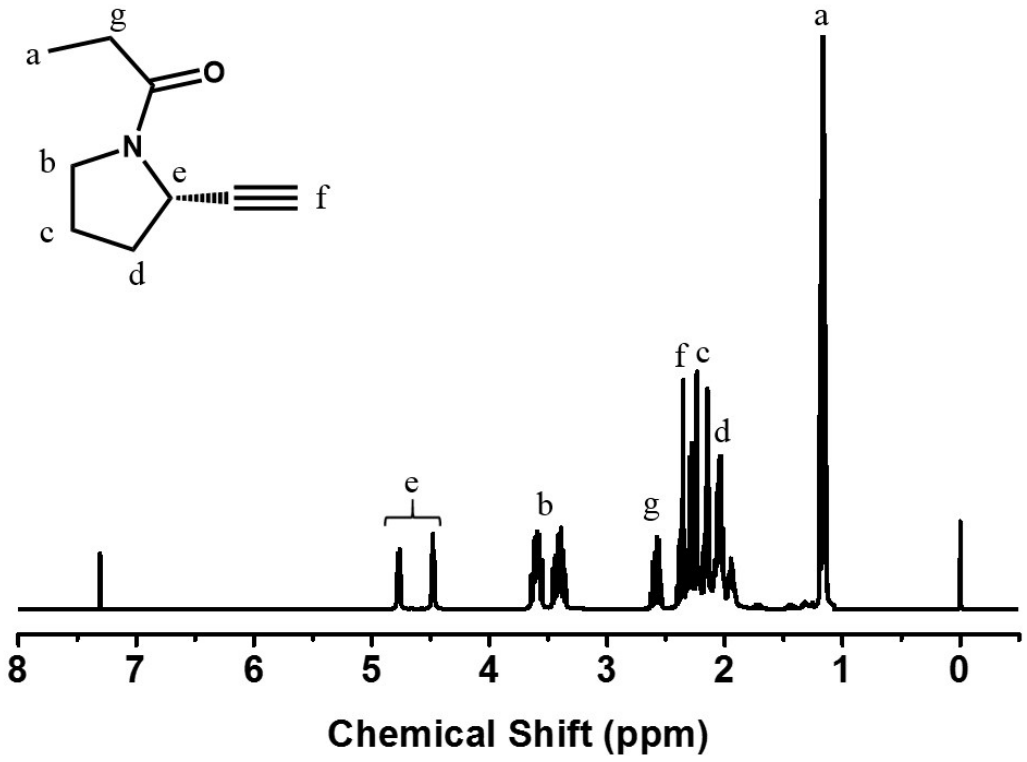

Figure S3. ^{1}H NMR spectrum of mPr measured in $CDCl_3$ at room temperature.

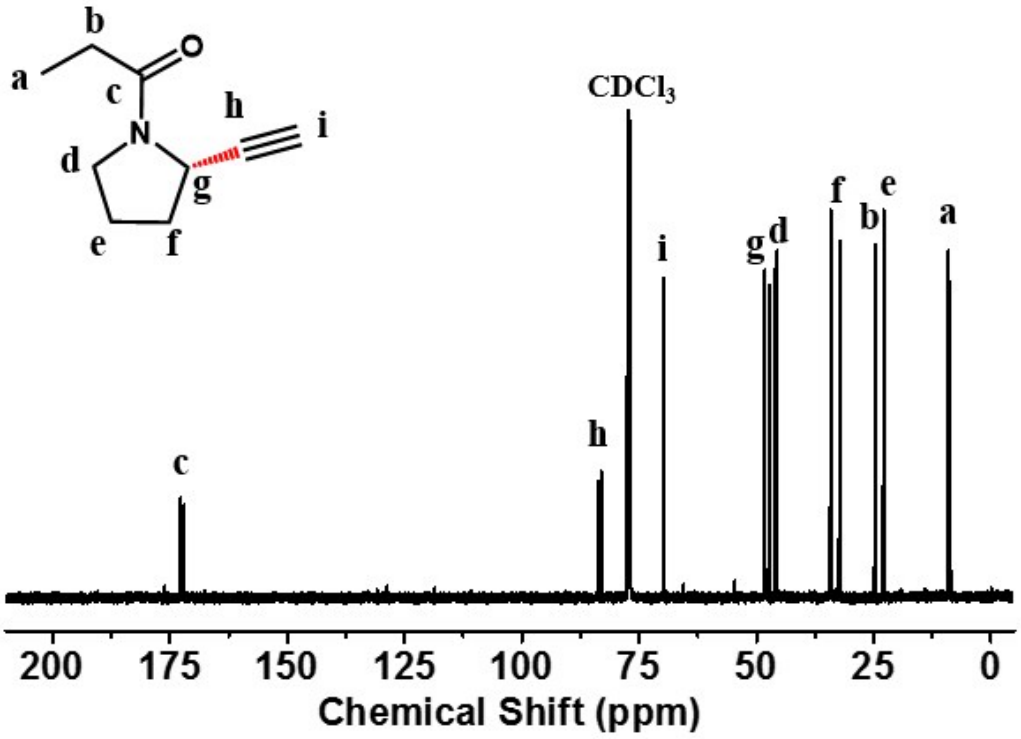

Figure S4. ^{13}C NMR spectrum of mPr measured in $CDCl_3$ at room temperature.

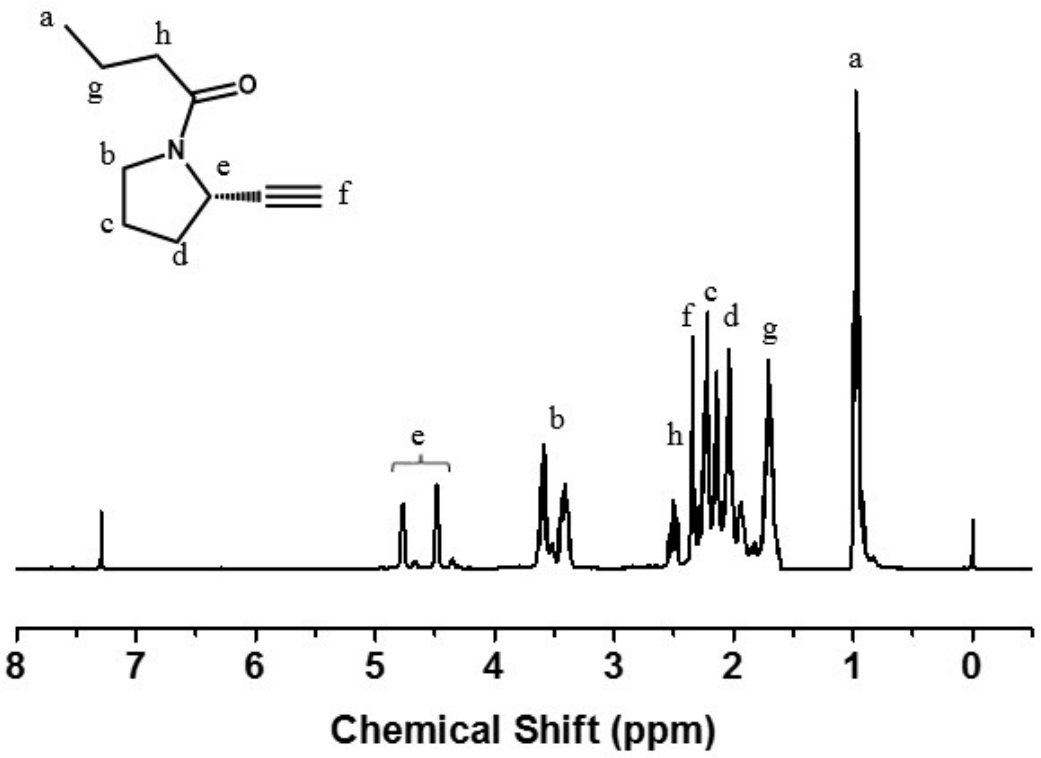

Figure S5. ^{1}H NMR spectrum of mBu measured in $CDCl_3$ at room temperature.

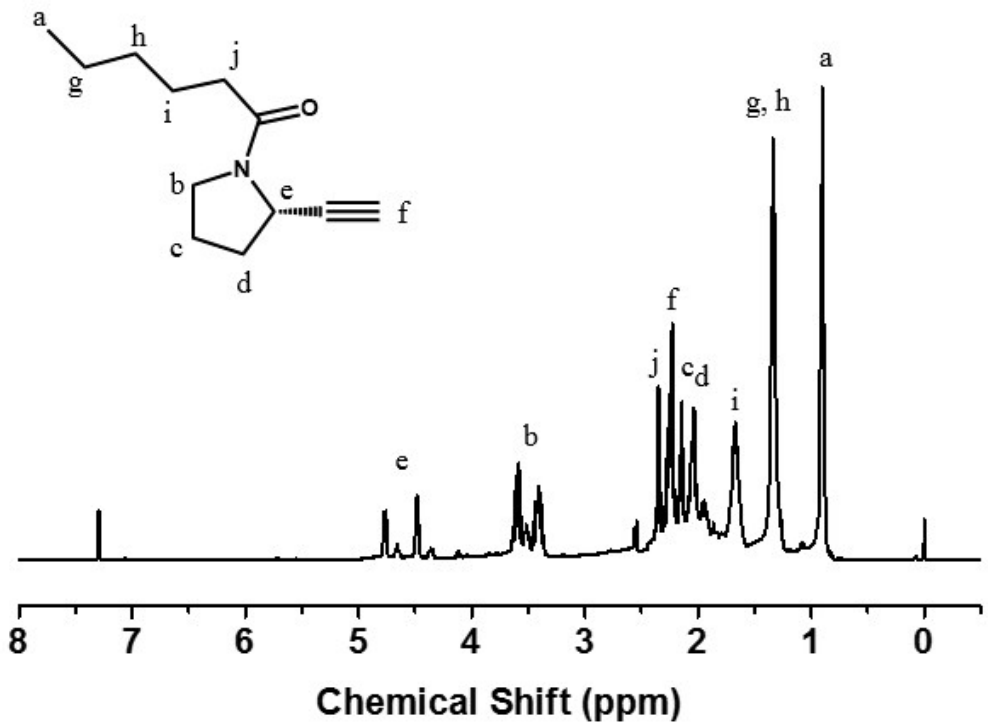

Figure S6. ^{1}H NMR spectrum of mHex measured in $CDCl_3$ at room temperature.

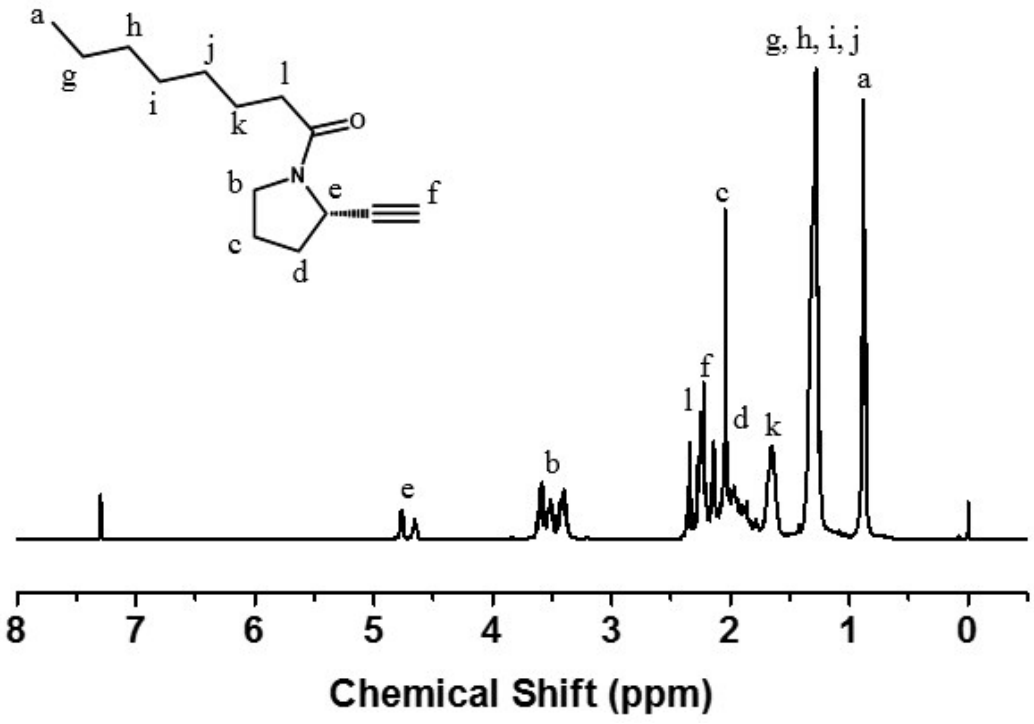

Figure S7. ^{1}H NMR spectrum of mOct measured in $CDCl_3$ at room temperature.

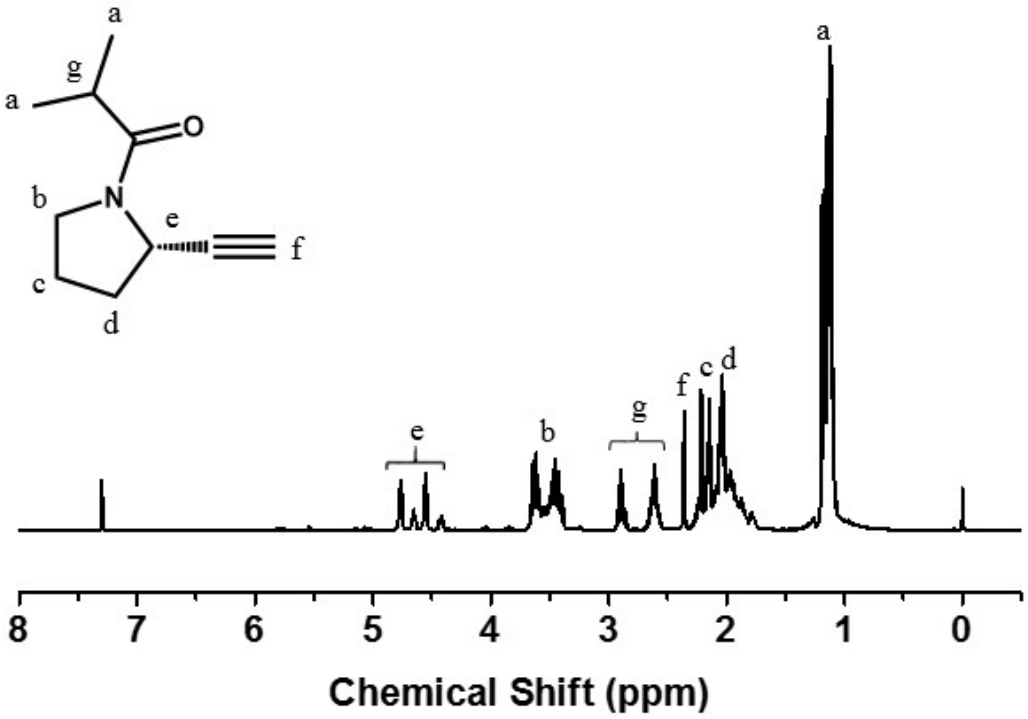

Figure S8. ^{1}H NMR spectrum of miBu measured in $CDCl_3$ at room temperature.

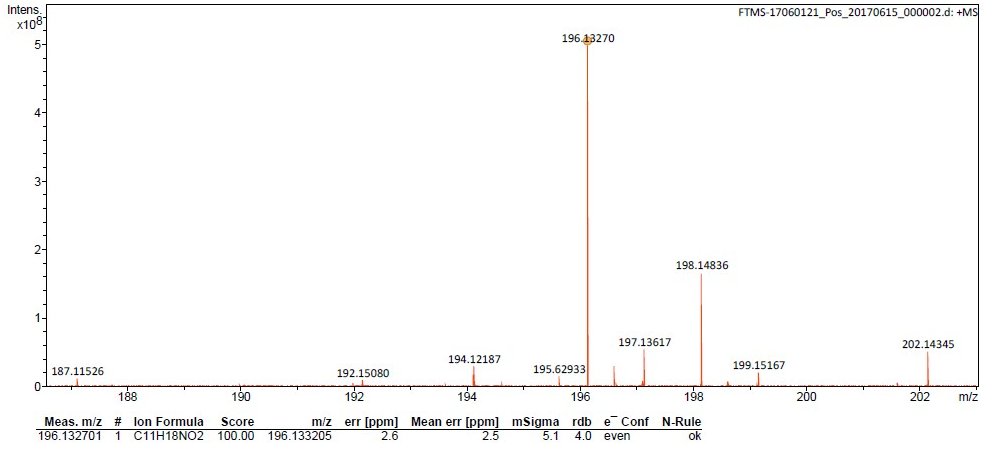

Figure S9. FTMS spectrum of 2-*(S)*-Acetenyl-*N*-(*tert*-butoxycarbonyl)-pyrrolidine.

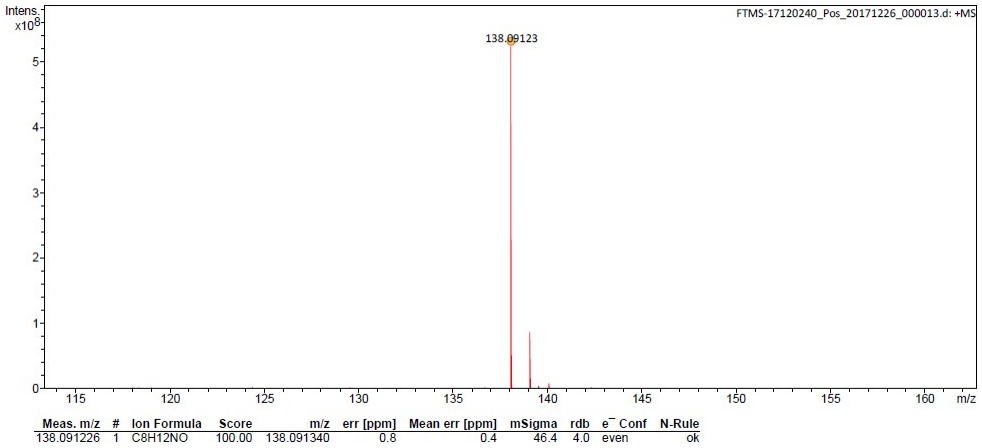

Figure S10. FTMS spectrum of mAc.

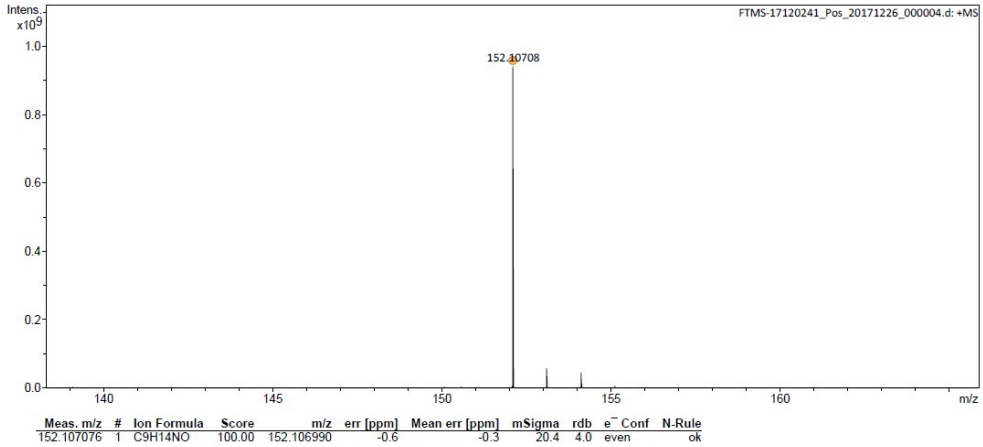

Figure S11. FTMS spectrum of mPr.

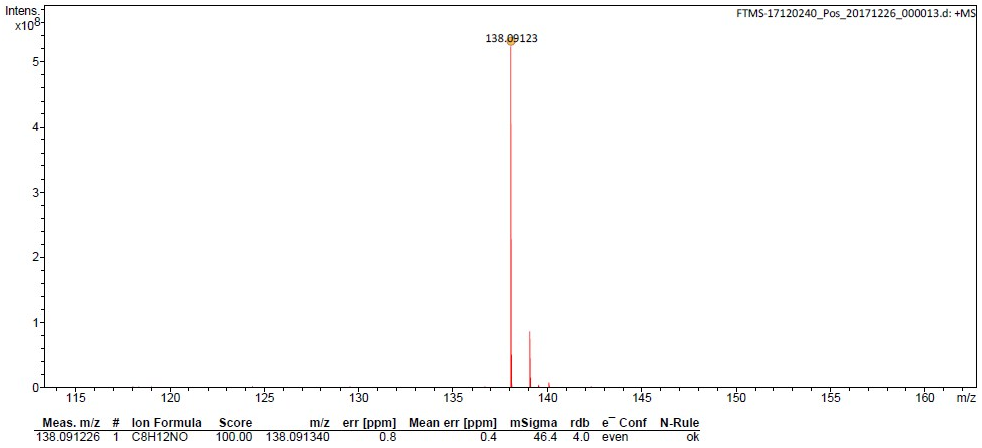

Figure S12. FTMS spectrum of **mBu**.

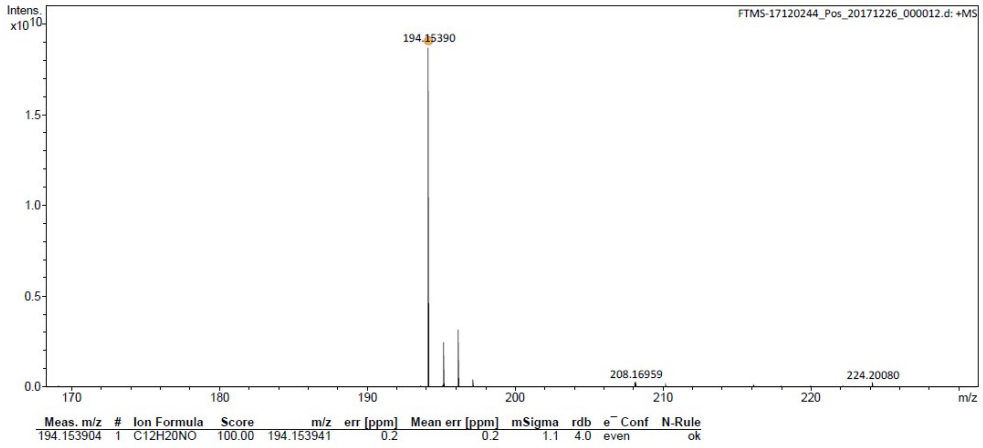

Figure S13. FTMS spectrum of **mHex**.

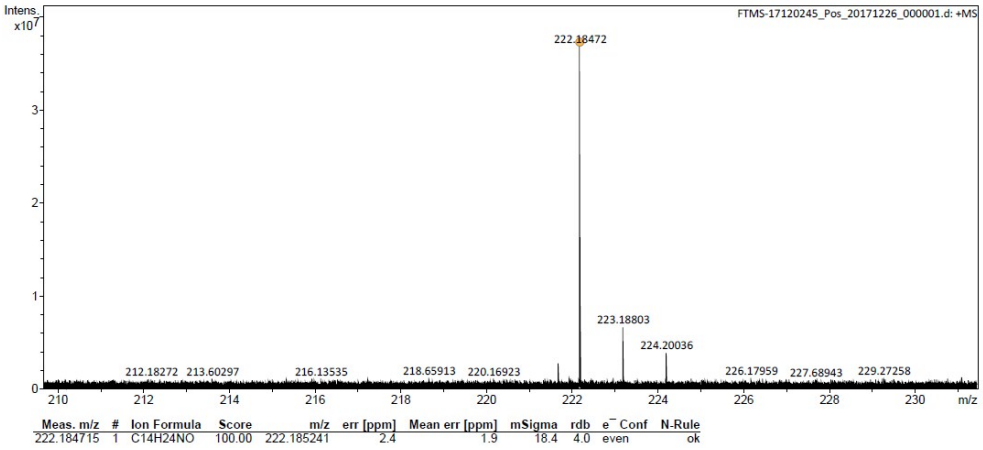

Figure S14. FTMS spectrum of **mOct**.

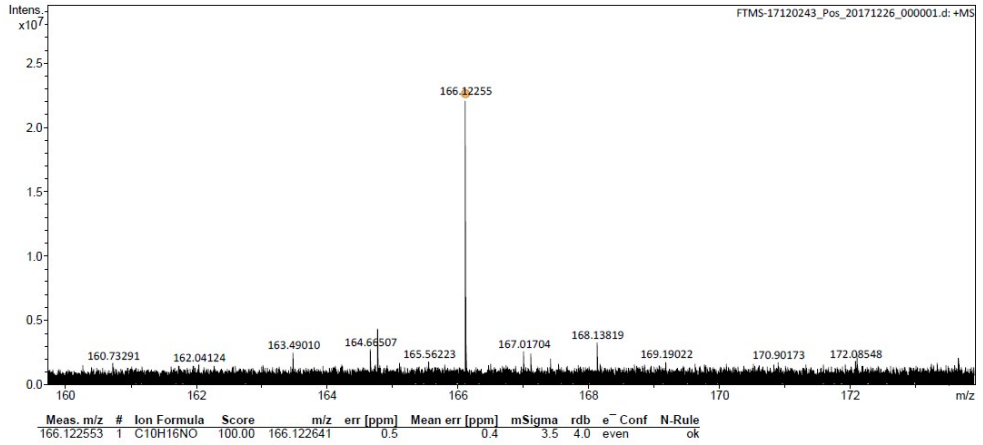

Figure S15. FTMS spectrum of **miBu**.

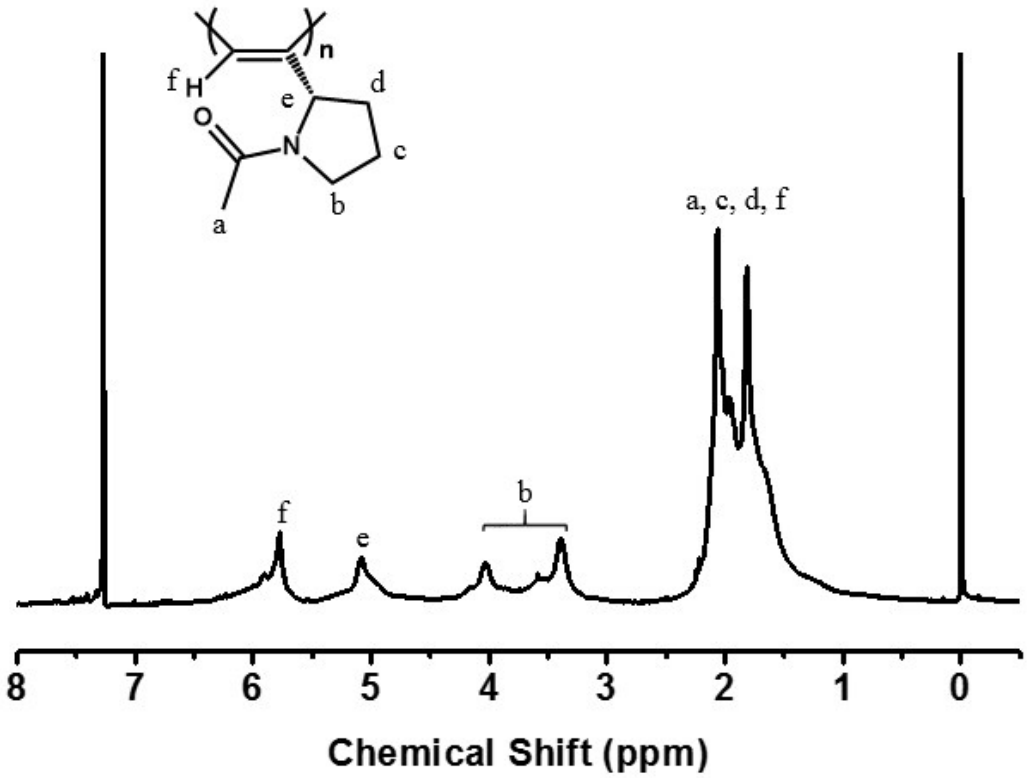

Figure S16. ^{1}H NMR spectrum of pAc measured in $CDCl_3$ at room temperature.

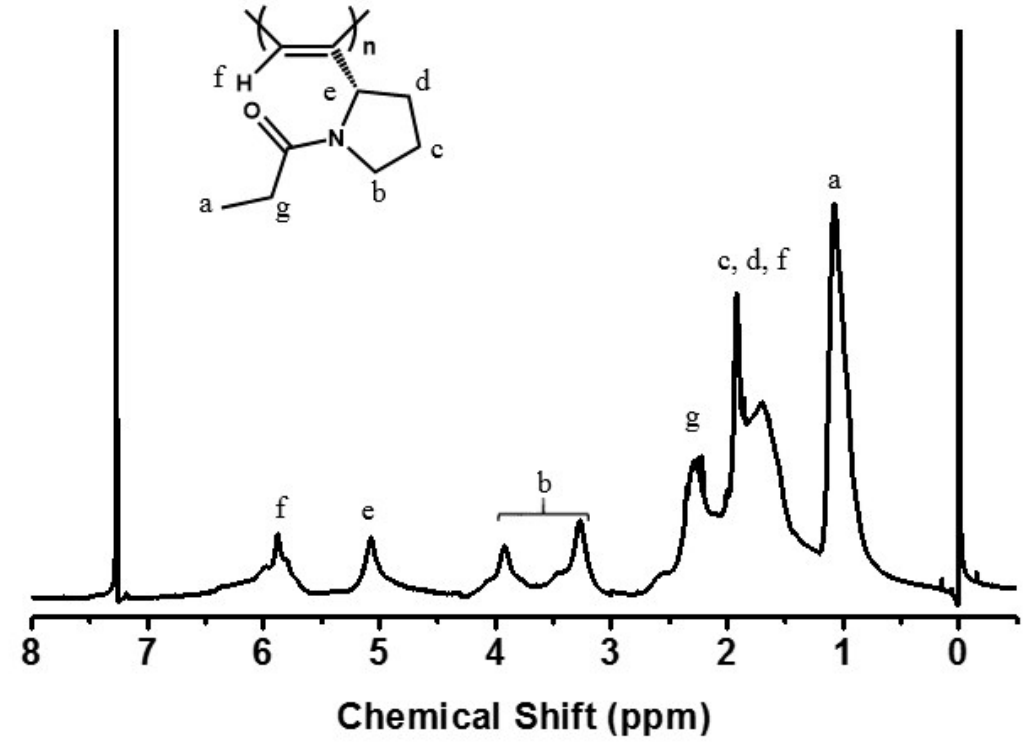

Figure S17. ^{1}H NMR spectrum of pPr measured in $CDCl_3$ at room temperature.

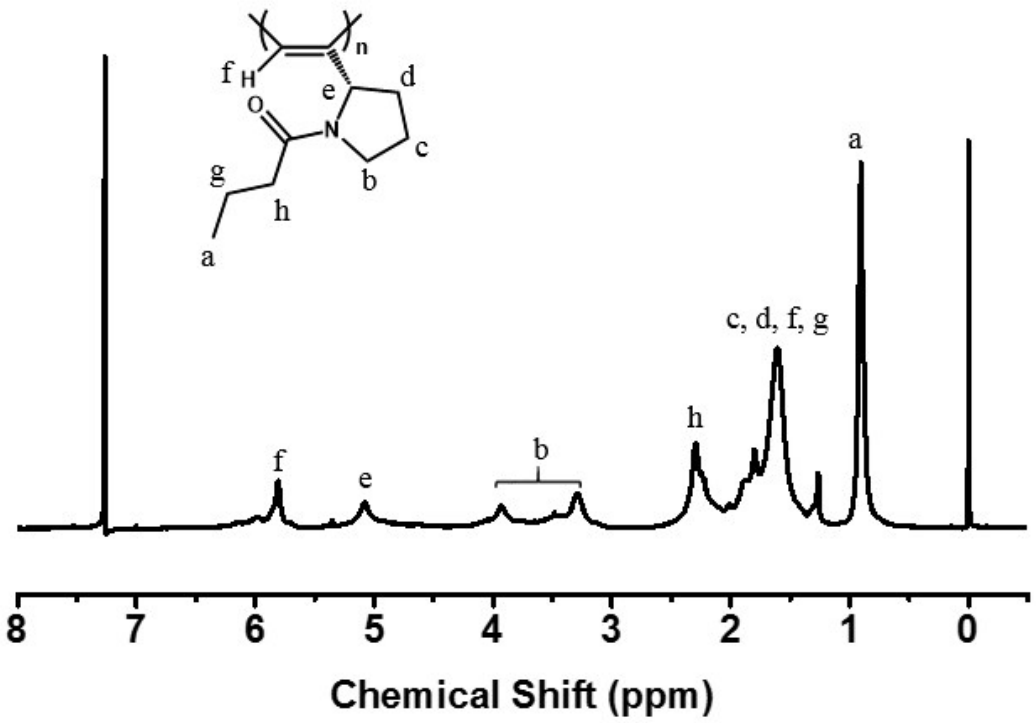

Figure S18. ^{1}H NMR spectrum of pBu measured in $CDCl_3$ at room temperature.

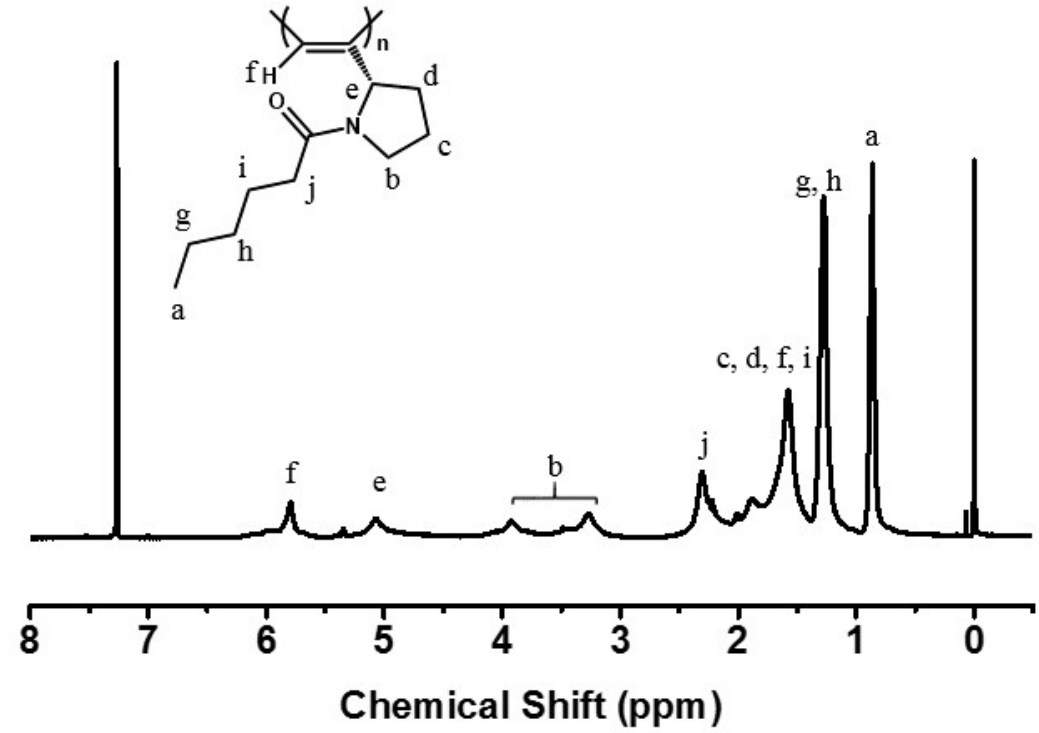

Figure S19. ^{1}H NMR spectrum of pHex measured in $CDCl_3$ at room temperature.

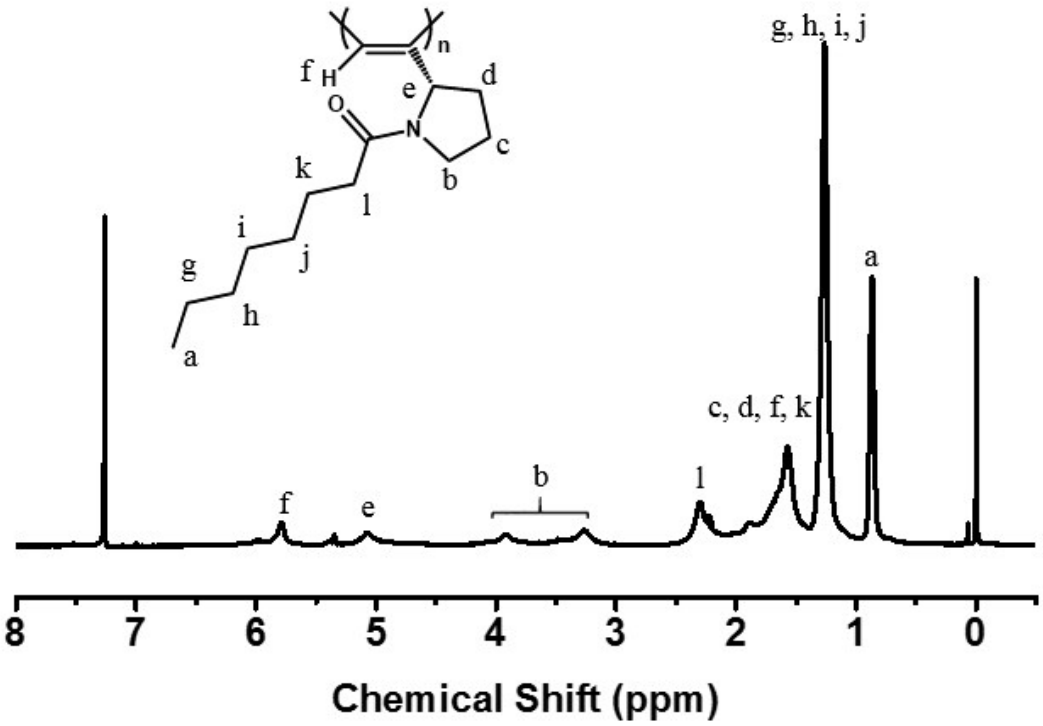

Figure S20. ^{1}H NMR spectrum of pOct measured in $CDCl_3$ at room temperature.

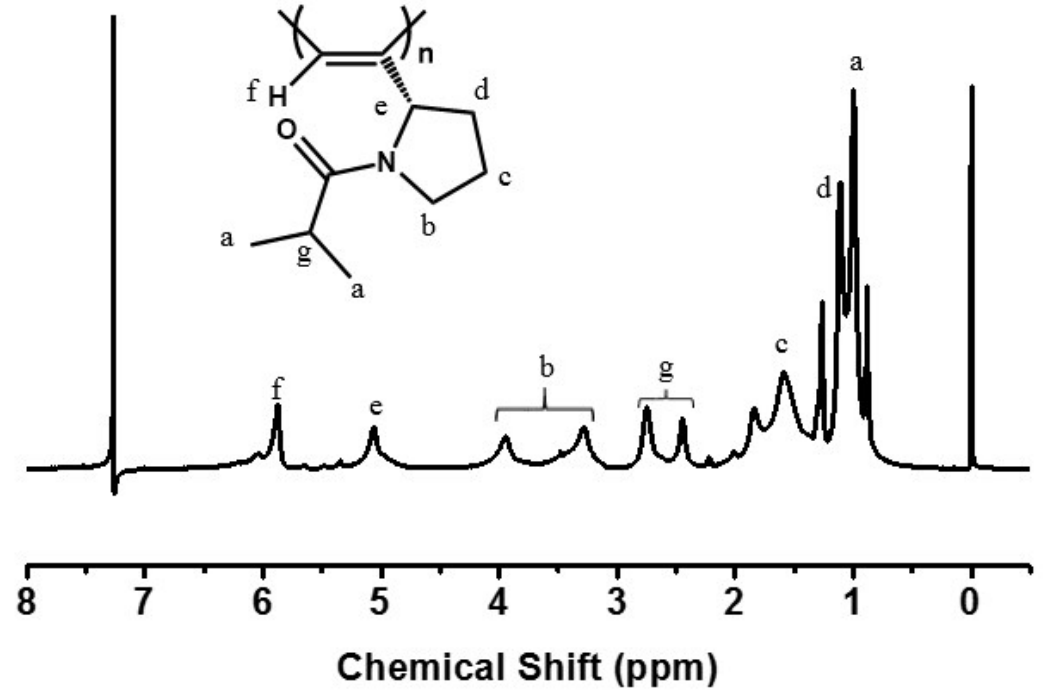

Figure S21. ^{1}H NMR spectrum of piBu measured in $CDCl_3$ at room temperature.

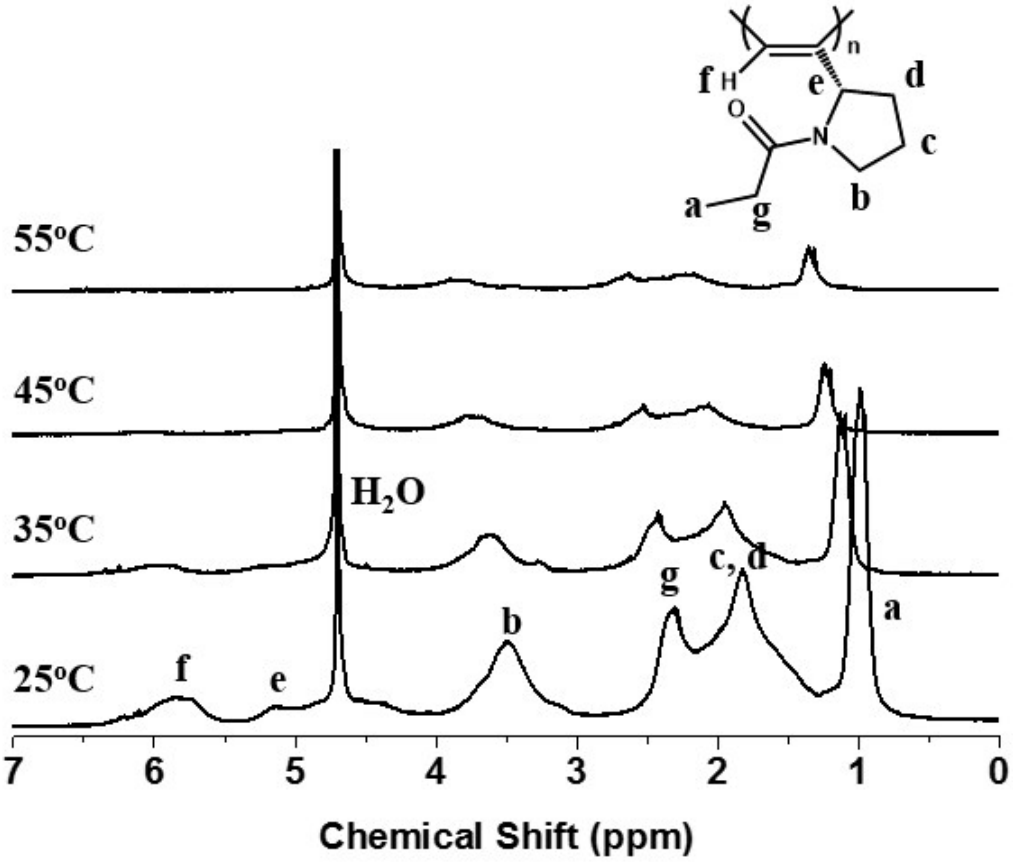

Figure S22. Temperature-varied ^{1}H NMR spectrum of pPr (1.5 wt %) in D_2O.

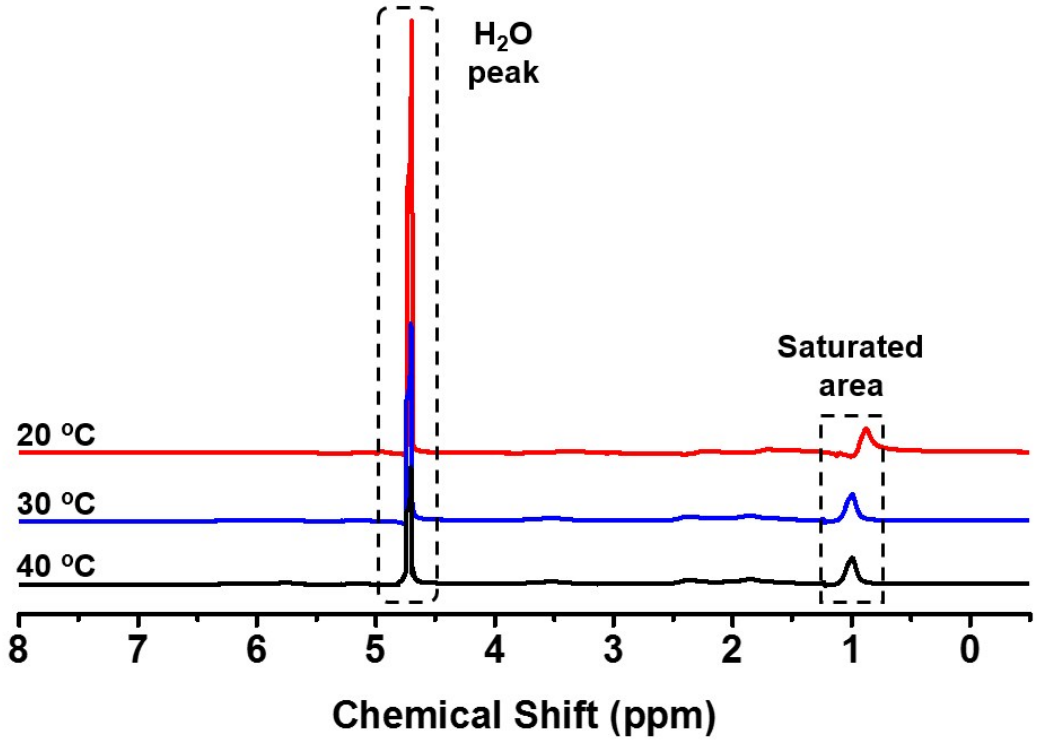

Figure S23. STD NMR experiments (600 MHz) of pPr in D_2O with the addition of 10 vol% H_2O.

3. Raman Spectra

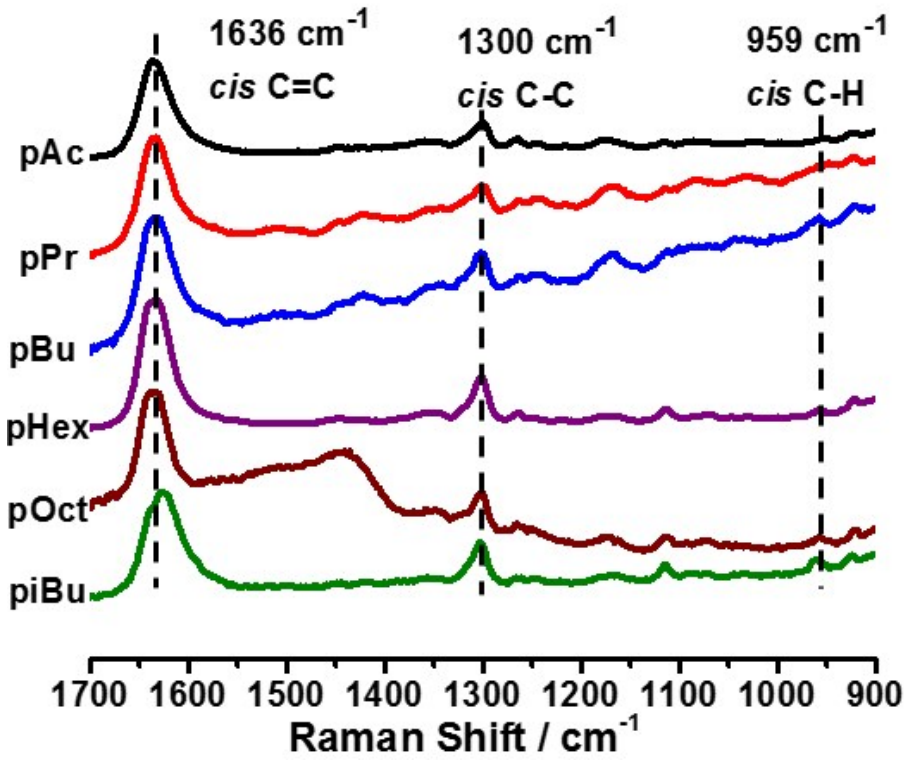

Figure S24. Raman spectrum of polymers pAc ~ piBu.

4. Thermogravimetric and DSC Curves of Polymers

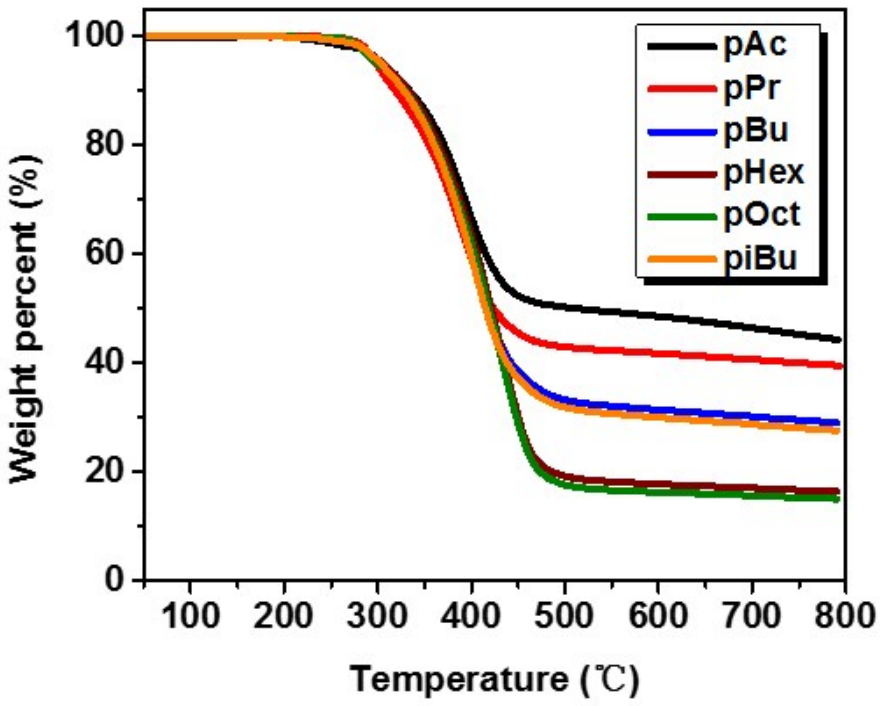

Figure S25. TGA curves of polymers pEt ~ piBu recorded under nitrogen at a heating rate of 20 °C/min.

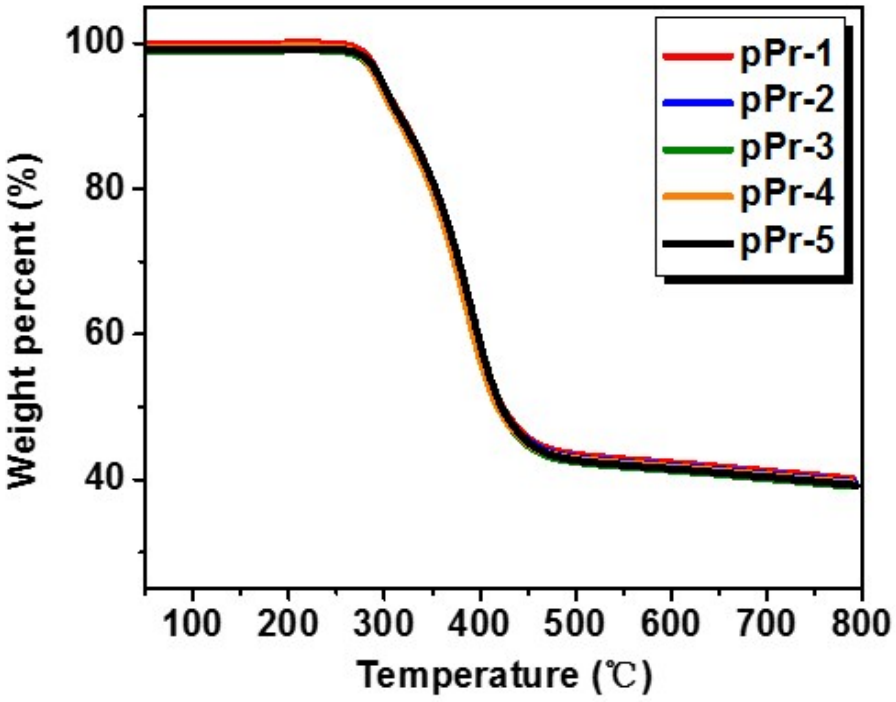

Figure S26. TGA curves of polymers pPr-1 ~ pPr-5 recorded under nitrogen at a heating rate of 20 °C/min.

5. Optical rotation

Table S2. Chiroptical properties of monomers and polymers

Monomer	$[\alpha]_D^{20}(^o)^a$				Polymer	$[\alpha]_D^{20}(^o)^b$			
	$CHCl_3$	THF	Toluene	H_2O		$CHCl_3$	THF	Toluene	H_2O
mAc	-109	-107	-102	-104	**pAc**	+1390	×	×	+632
					pPr-1	+1004	+1010	+967	+651
					pPr-2	+1010	+992	+982	+673
mPr	-109	-101	-104	-108	**pPr-3**	+1013	+1028	+989	+663
					pPr-4	+1009	+1017	+984	+682
					pPr	+1003	+1022	+977	+689
mBu	-116	-110	-111	×	**pBu**	+1256	+1371	+1288	×
mHex	-119	-115	-113	×	**pHex**	+1252	+1324	+1162	×
mOct	-98	-98	-100	×	**pOct**	+1107	+1056	+1066	×
miBu	-118	-112	-111	×	**piBu**	+1410	×	×	×

[a]c = 0.2 g/dL. [b]c = 0.02 g/dL. ×: insoluble.

6. UV-Vis Absorption and CD Spectra

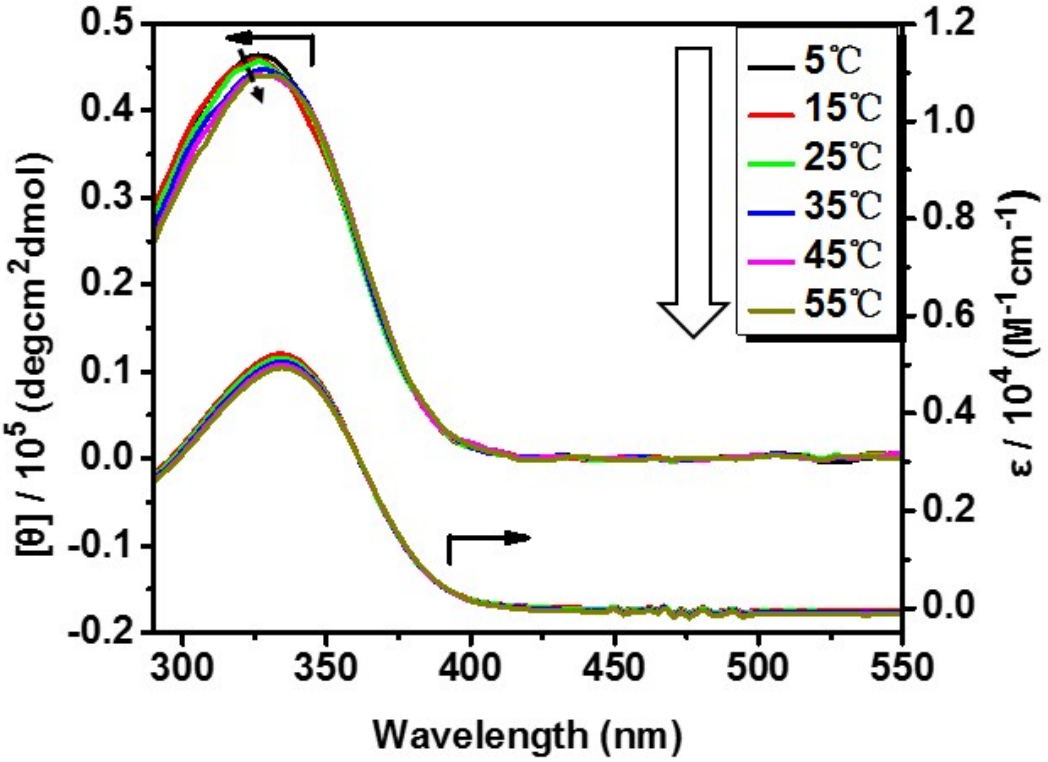

Figure S27. UV-Vis absorption and CD spectra of pAc in $CHCl_3$ at various temperatures.

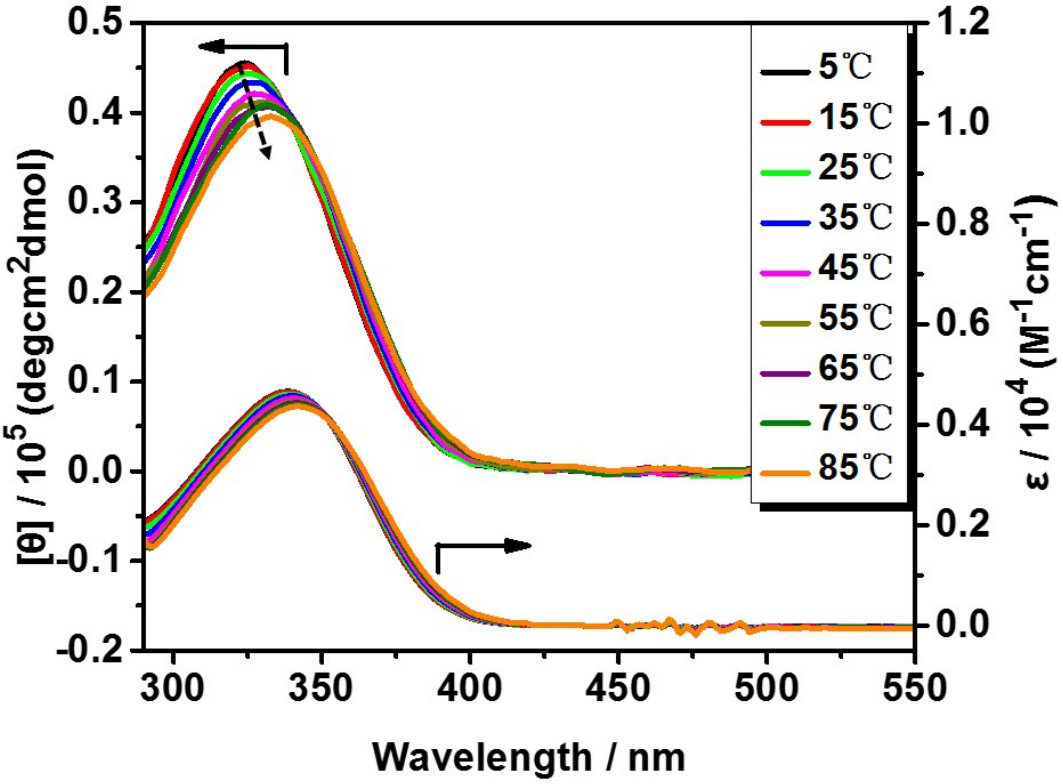

Figure S28. UV-Vis absorption and CD spectra of pBu in toluene at various temperatures.

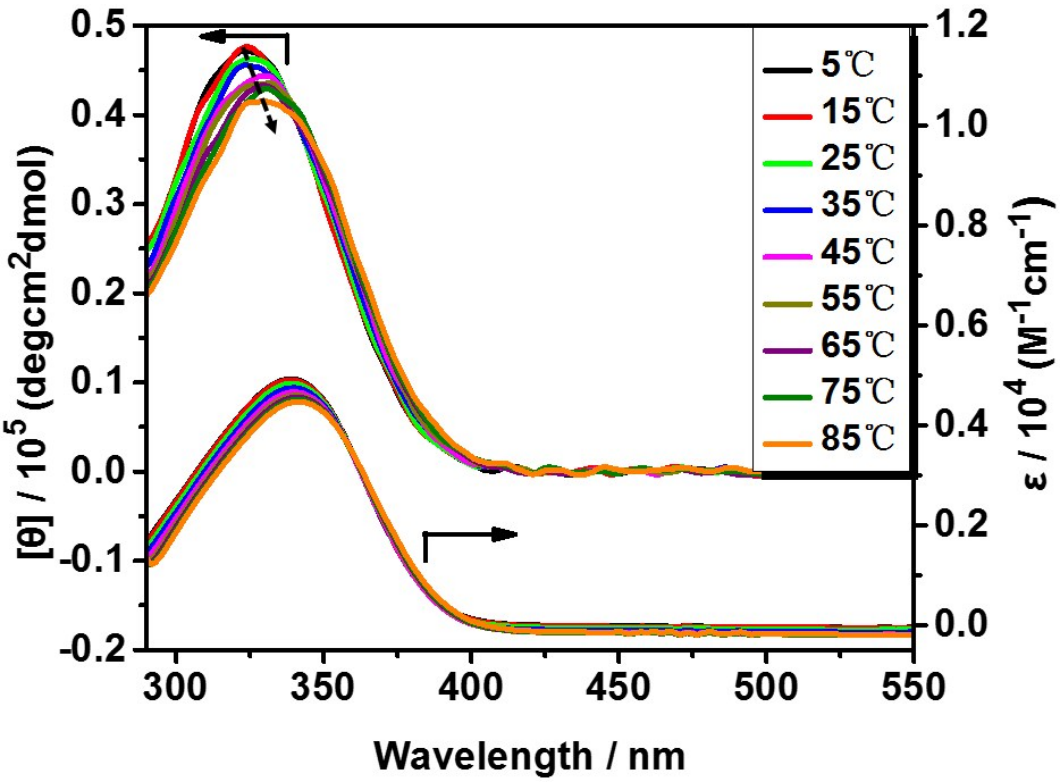

Figure S29. UV-Vis absorption and CD spectra of pHex in toluene at various temperatures.

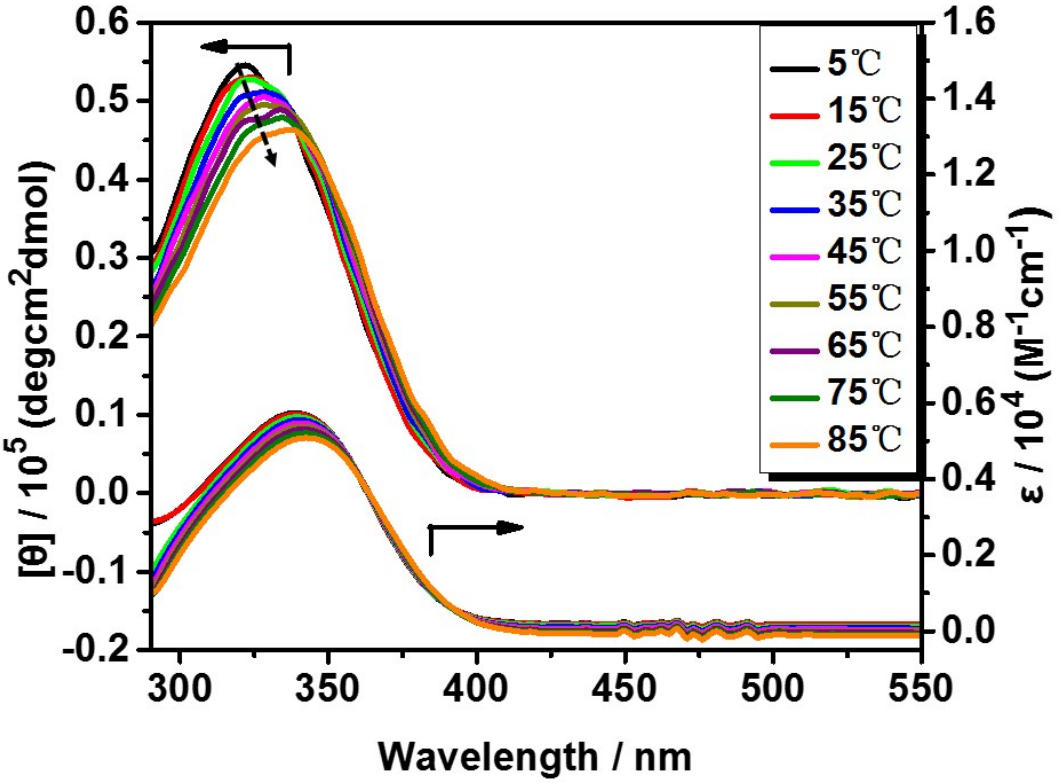

Figure S30. UV-Vis absorption and CD spectra of pOct in toluene at various temperatures.

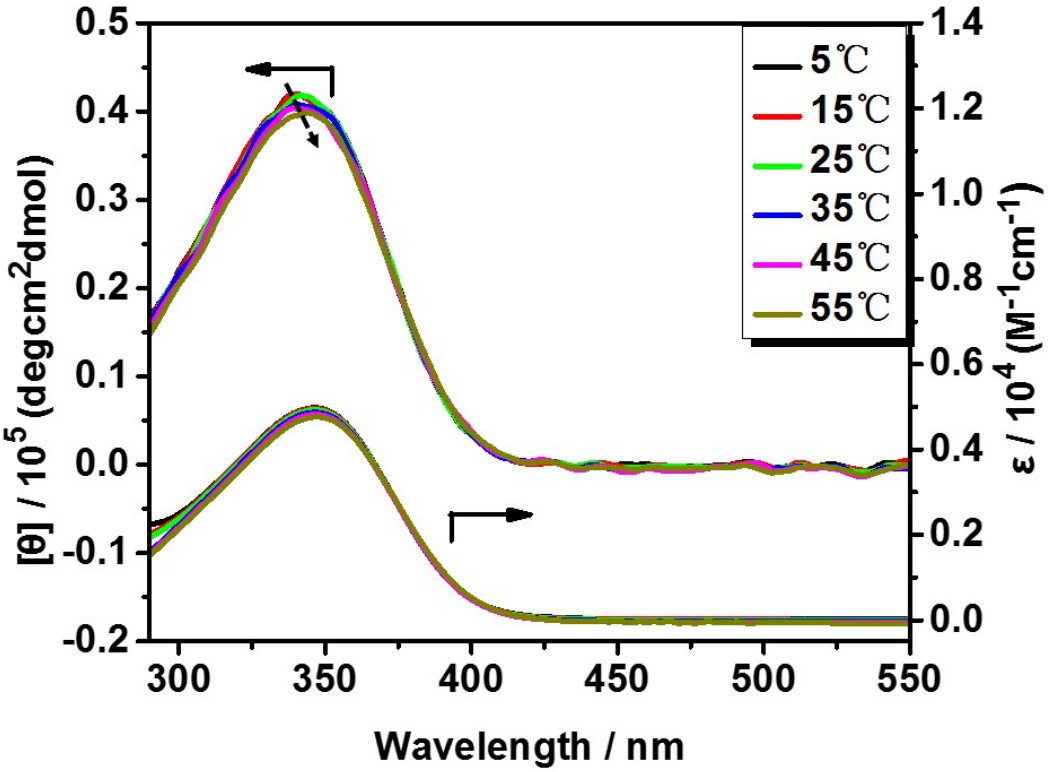

Figure S31. UV-Vis absorption and CD spectra of piBu in chloroform at various temperatures.

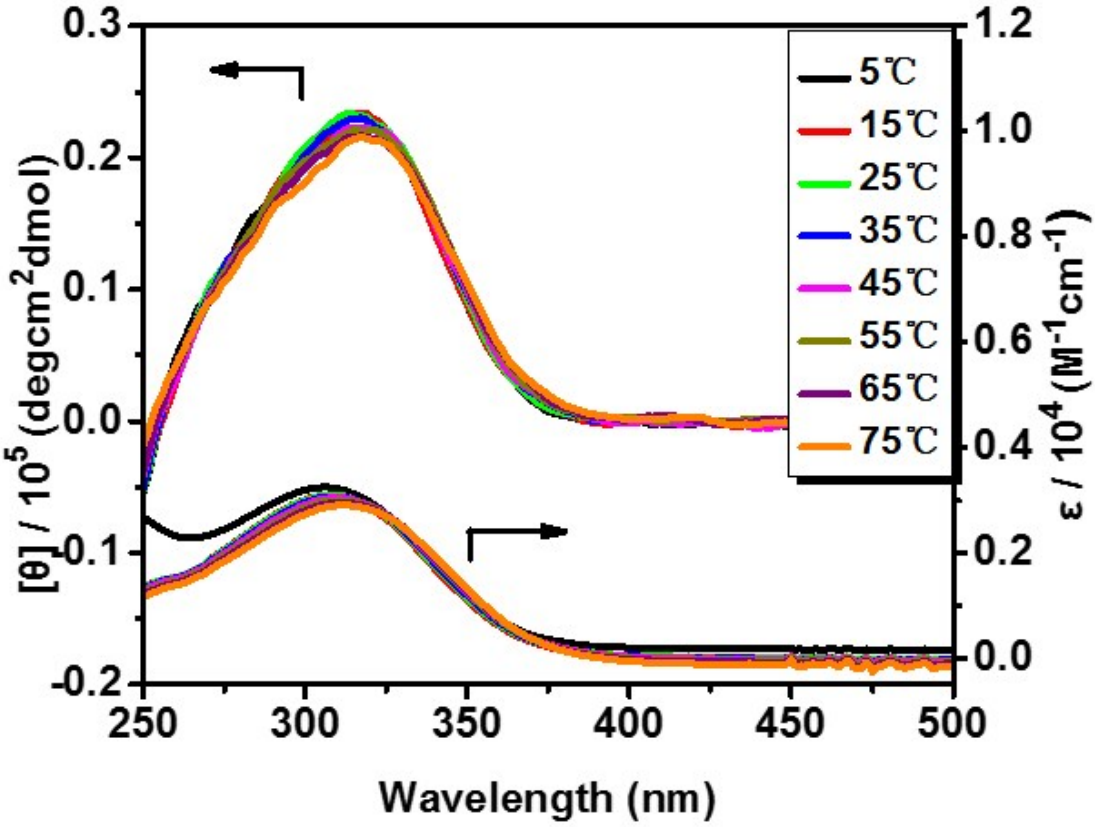

Figure S32. UV-Vis absorption and CD spectra of pAc in water at various temperatures.

7. SLS and DLS Spectra

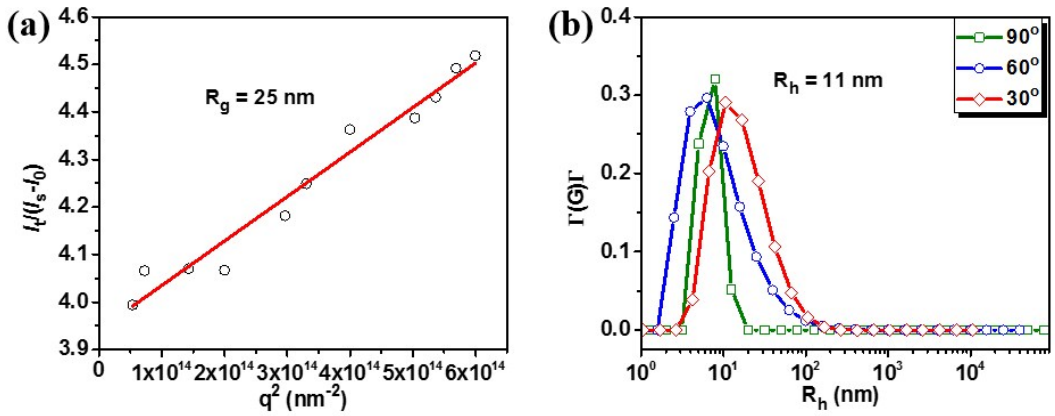

Figure S33. The (a) SLS and (b) DLS spectra of pPr in aqueous solution (0.5 mg/mL).

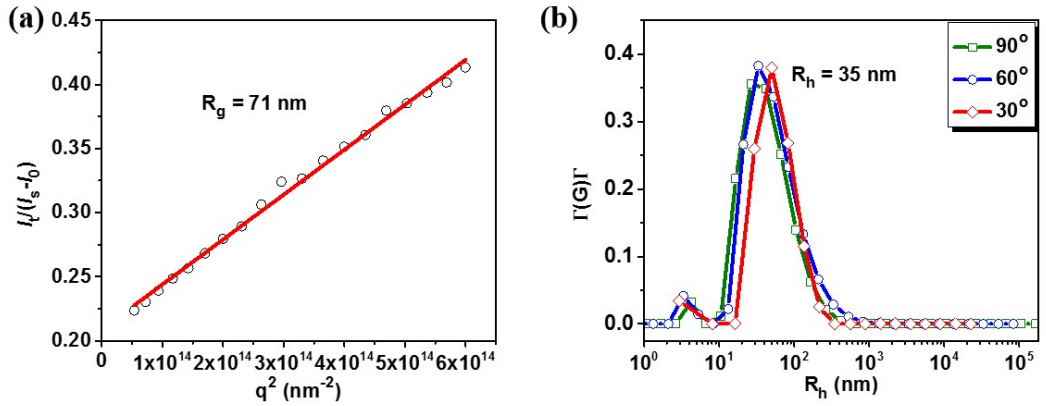

Figure S34. The (a) SLS and (b) DLS spectra of pAc in chloroform solution (0.5 mg/mL).

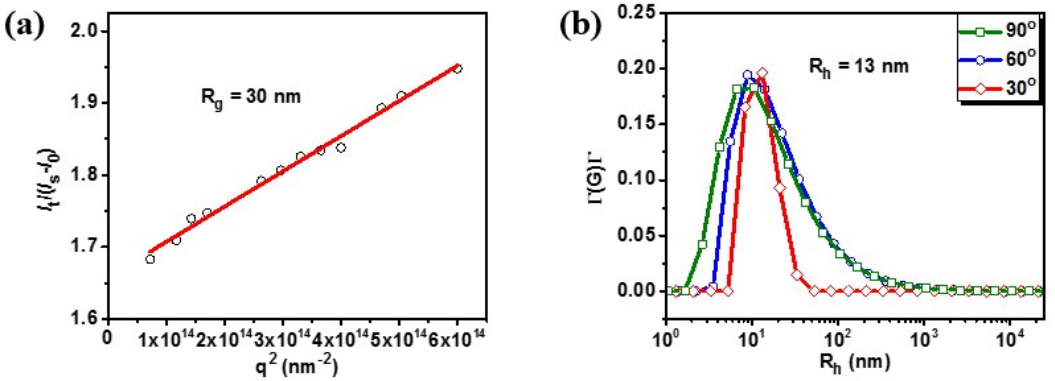

Figure S35. The (a) SLS and (b) DLS spectra of pPr in chloroform solution (0.5 mg/mL).

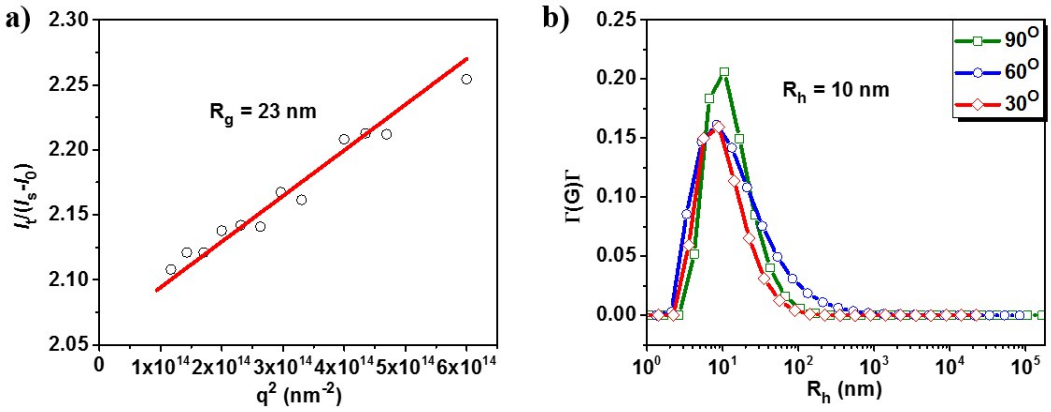

Figure S36. The (a) SLS and (b) DLS spectra of pBu in chloroform solution (0.5 mg/mL).

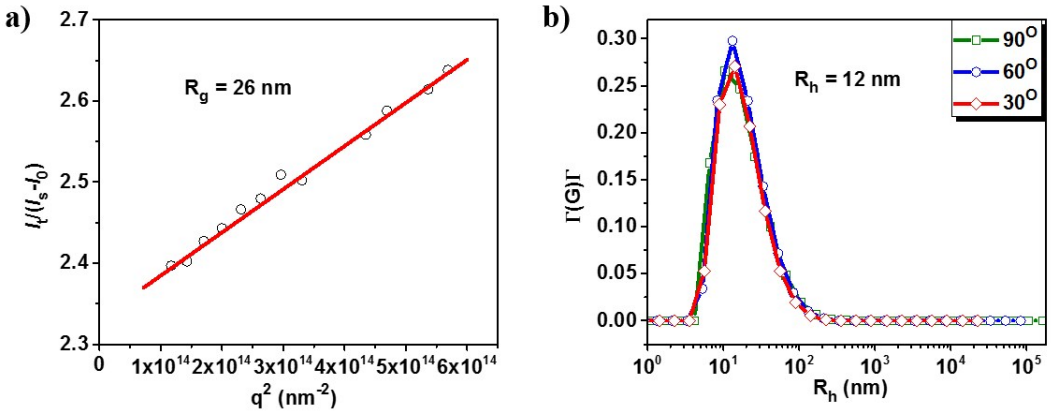

Figure S37. The (a) SLS and (b) DLS spectra of pHex in chloroform solution (0.5 mg/mL).

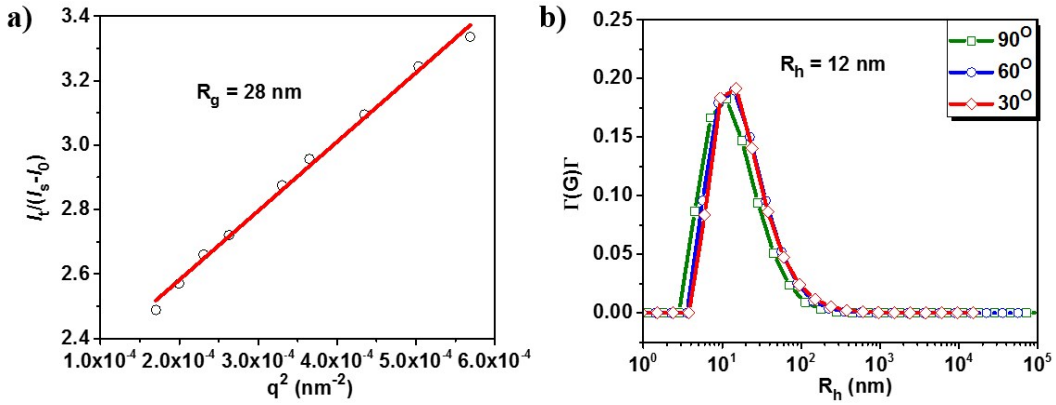

Figure S38. The (a) SLS and (b) DLS spectra of pOct in chloroform solution (0.5 mg/mL).

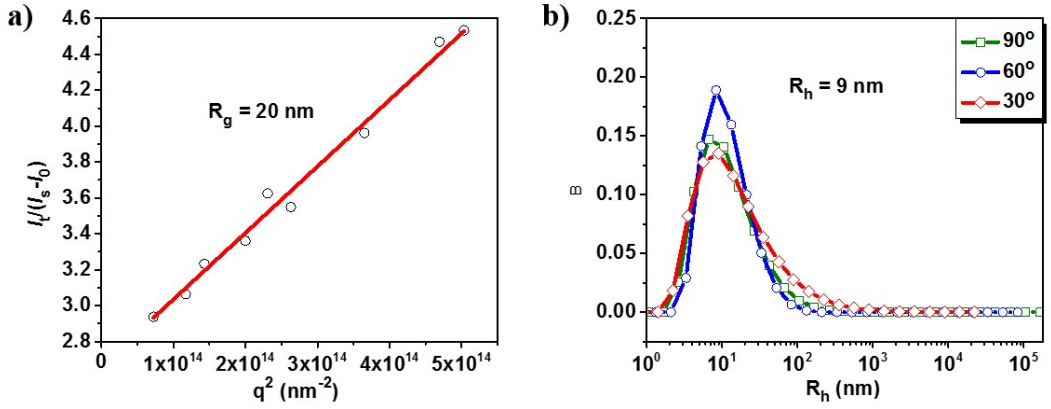

Figure S39. The (a) SLS and (b) DLS spectra of piBu in chloroform solution (0.5 mg/mL).

8. Turbidity Curves of Polymers

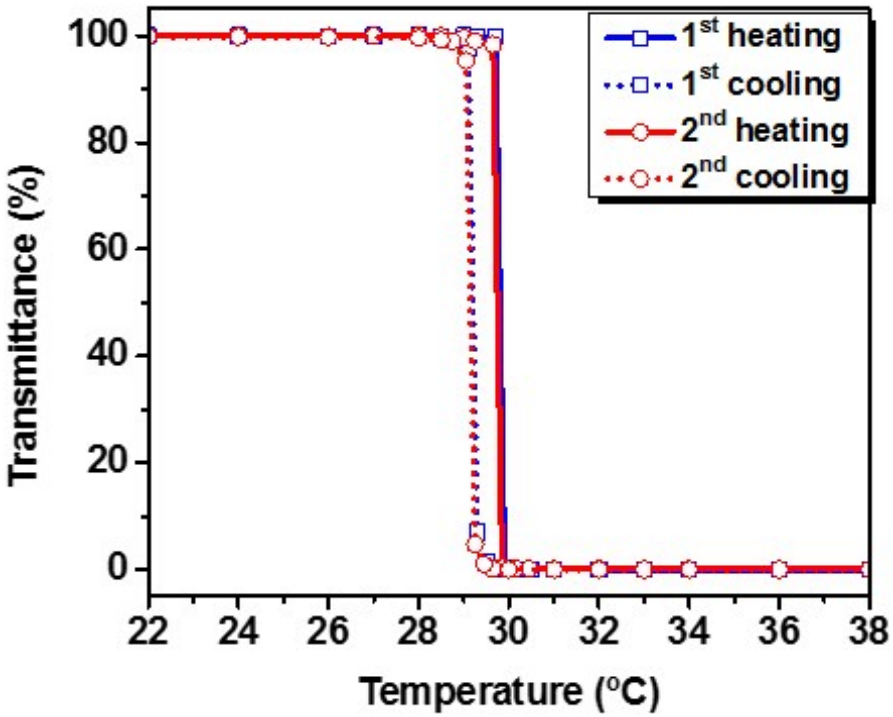

Figure S40. Turbidity curves for pPr-1 aqueous solution at various temperature. Heating and cooling rate 0.2 K min^{-1} at a concentration of 5 mg/mL.

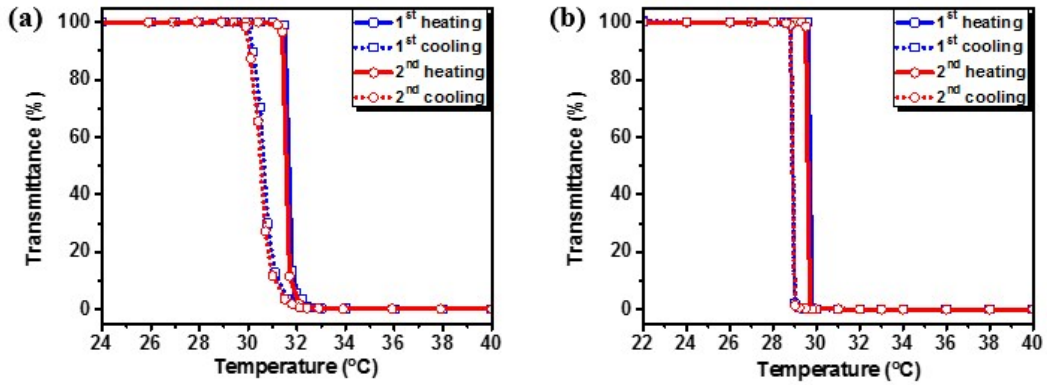

Figure S41. Turbidity curves for pPr-2 aqueous solution with (a) 1 mg/mL and (b) 5 mg/mL at various temperature. Heating and cooling rate 0.2 K min^{-1}.

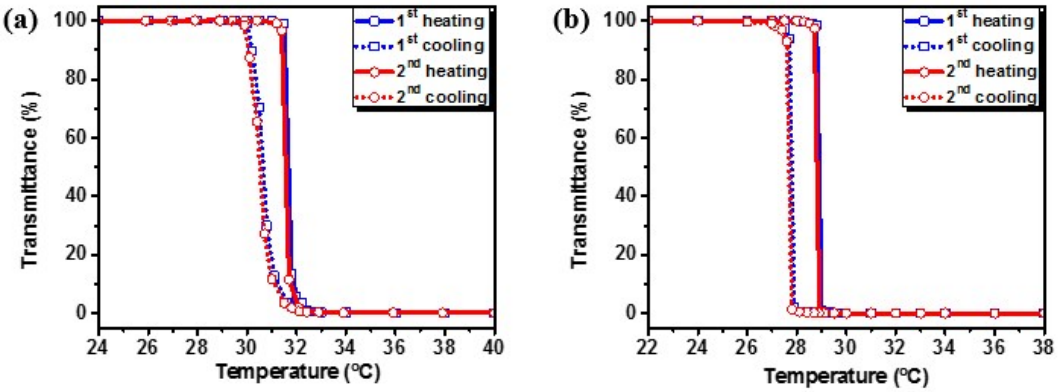

Figure S42. Turbidity curves for pPr-3 aqueous solution with (a) 1 mg/mL and (b) 5 mg/mL at various temperature. Heating and cooling rate 0.2 K min^{-1}.

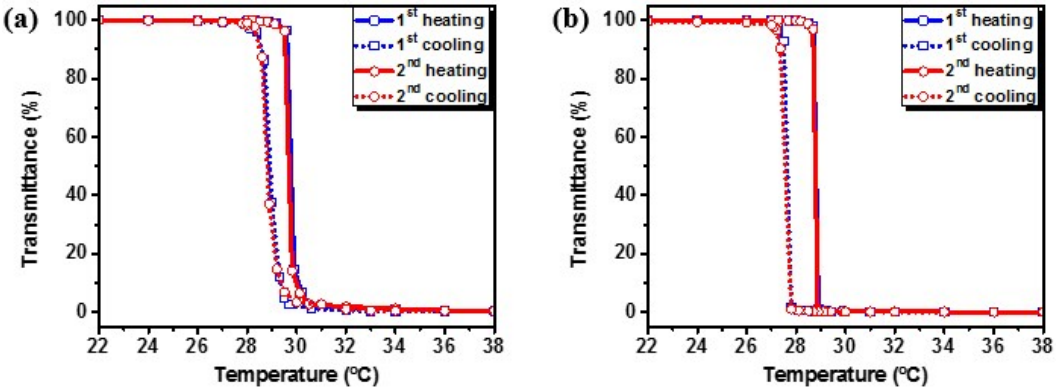

Figure S43. Turbidity curves for pPr-4 aqueous solution with (a) 1 mg/mL and (b) 5 mg/mL at various temperature. Heating and cooling rate 0.2 K min^{-1}.

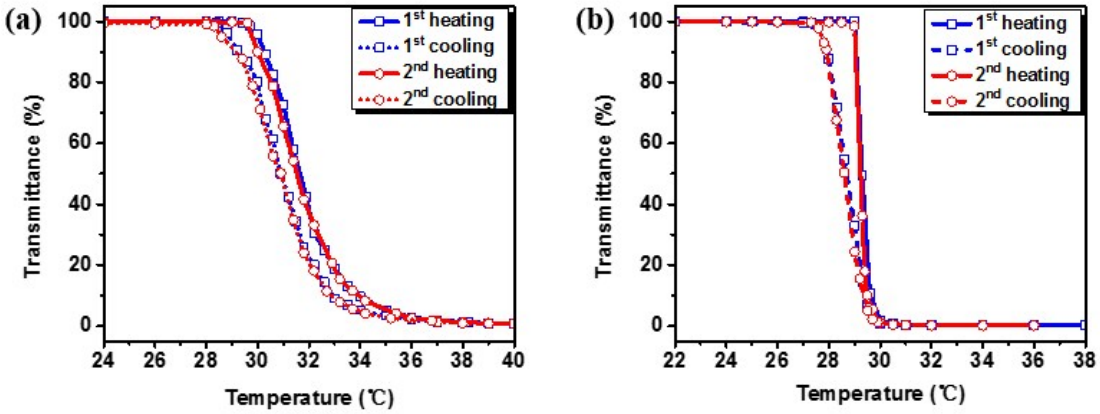

Figure S44. Turbidity curves for pPr aqueous solution with (a) 1 mg/mL and (b) 5 mg/mL at various temperature. Heating and cooling rate 0.2 K min^{-1}.

9. AFM spectra of pPr

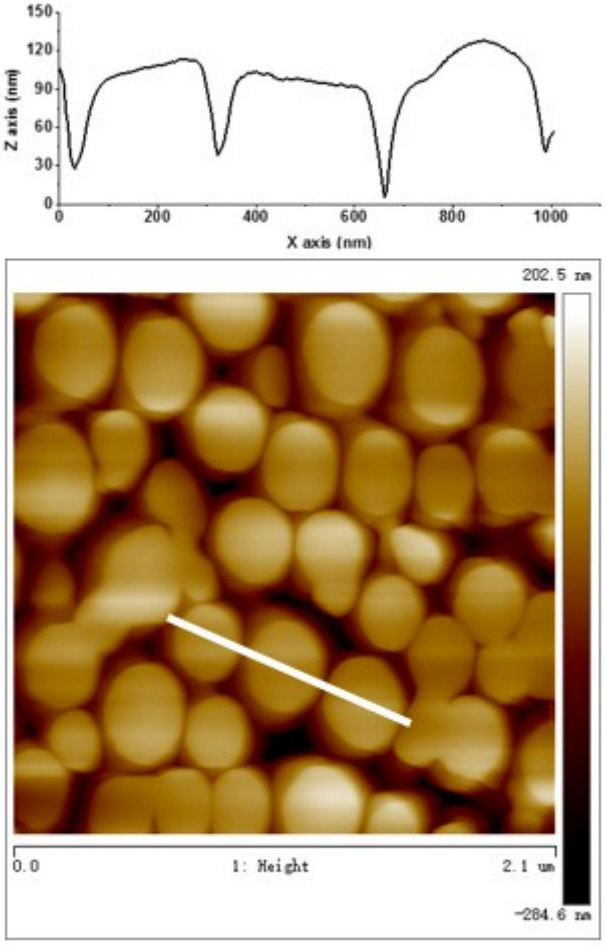

Figure S45. AFM spectrum of pPr-1 mesoglobules at 45 °C (0.5 mg/mL).

10. Reference

1. Miyake, M.; Misumi, Y.; Masuda, T. Living Polymerization of Phenylacetylene by Isolated Rhodium Complexes, Rh[C(C_6H_5)=C(C_6H_5)$_2$](nbd)(4-XC_6H_4)$_3$P (X = F, Cl). *Macomolecules* **2000**, *33*, 6636-6639.