

Electronic Supplementary Information (ESI)

Novel Semirigid Water-Soluble Thermoresponsive Polymers Based on Mesogen-Jacketed Liquid Crystal Polymers

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Materials. The compound of 2-vinylterephthalic acid was synthesized using the method previously reported¹. *N*-Hydroxyethyl pyrrolidone (95%) was purchased from Jianhua Co. Ltd. and was distilled under reduced pressure. Azobisisbutyronitrile (AIBN) was purified by recrystallization from ethanol. Chlorobenzene (Acros, 99%) was purified by washing with concentrated sulfuric acid to remove residual thiophenes, followed by washing twice with water, once with 5% sodium carbonate solution, and again with water before being dried with anhydrous MgSO₄ and then distilled. THF and triethylamine were distilled over calcium hydride prior to use. Water utilized is the highly pure deionized water with resistivity over 18 MΩ cm⁻¹. All other reagents were used as received from commercial sources.

Instrumentation.

^1H and ^{13}C NMR spectra were recorded on a Bruker ARX400 spectrometer at room temperature using deuterated chloroform (CDCl_3) or deuterioxide (D_2O) as the solvent and tetramethylsilane (TMS) as the internal standard.

GPC measurements were performed on a PL-GPC120 setup equipped with a column set consisting of two PL gel 5 μm MIXED-D columns (7.5×300 mm, effective molecular weight range of $0.2\sim 400.0$ kg mol^{-1}) using DMF that contained 0.01 M LiBr as the eluent at 80 $^\circ\text{C}$ at a flow rate of 1.0 mL min^{-1} . Narrowly distributed polystyrene standards in the molecular weight range of $0.5\sim 7500.0$ kg mol^{-1} (PSS, Mainz, Germany) were utilized for calibration.

The temperature dependence of light scattering intensity of polymer aqueous solution was studied on a Brookhaven instrument using a BI-TCD temperature controller to precisely adjust the solution temperature. The solution was heated or cooled in steps and stabilized at each predetermined temperature for 2 min. The light scattering intensities at an angle of 90° were recorded.

TGA was performed on a TA-SDT 2960 instrument at a heating rate of 20 $^\circ\text{C}$ min^{-1} in nitrogen atmosphere. The thermal transitions of polymers were detected using DSC (TA-Q10). The temperature and heat flow were calibrated using standard materials (indium and zinc) at cooling 10 $^\circ\text{C}$ min^{-1} and heating rates 20 $^\circ\text{C}$ min^{-1} . Samples with a typical mass of 3~10 mg were encapsulated in sealed aluminum pans.

LC texture of the polymers was observed under POM (Leica DM-LM-P) coupled with a Mettler-Toledo hot stage (FP82HT). The films with thickness of ~ 10 μm were

casted from CH_2Cl_2 solution and slowly dried at room temperature.

One-dimensional wide-angle X-ray diffraction (1D WAXD) experiments were performed on a Philips X' Pert Pro diffractometer with a 3 kW ceramic tube as the X-ray source (Cu KR) and an X' celerator detector. The reflection peak positions were calibrated with silicon powder ($2\theta > 15^\circ$) and silver behenate ($2\theta < 10^\circ$). The sample stage is set horizontally, and a temperature control unit (Paar Physica TCU 100) in conjunction with the diffractometer was utilized to study the structure evolutions as a function of temperature. The heating and cooling rates in the WAXD experiments were 5°C min^{-1} .

Two-dimensional wide-angle X-ray diffraction (2D WAXD) fiber patterns were recorded on a Bruker D8 Discover diffractometer equipped with a general area detector diffraction system (GADDS) as a 2D detector, in a transmission mode at room temperature. Again, calibrations were made against silicon powder and silver behenate. Samples were mounted on the sample stage, and the point-focused X-ray beam was aligned either perpendicular or parallel to the mechanical shearing direction. Fibers were drawn at a stretching rate of about 1 m s^{-1} at 200°C and quenched to room temperature for measurements.

Solid-state NMR experiments were performed on a Varian Infinityplus NMR spectrometer at a proton frequency of 400 MHz. The samples were placed in a zirconia rotor and a 4 mm CP/MAS probe was used. The magic angle spinning (MAS) speed was 5 kHz for ^1H MAS, ^{13}C CP/MAS and ^{13}C - ^1H 2D WISE (Two-Dimensional proton wideline separation) experiments. The ^1H and ^{13}C chemical

shifts were referenced to external TMS and HMB (hexamethylbenzene), respectively.

The experiments were carried out at room temperature (25 °C).

Synthesis of N-hydroxypropyl pyrrolidone.

3-Aminopropanol (100 mL) was added dropwise to γ -butyrolactone (100 mL) in a 500 mL round-bottom flask and stirred at room temperature for 1 h, and then transferred to autoclave and stirred at 250 °C for 8 h. The crude product was extracted using distilled water and CH_2Cl_2 . The aqueous phase was concentrated and dried over anhydrous MgSO_4 . The product was further purified by a silicon column chromatography using acetone as the eluent. ^1H NMR (CDCl_3), δ (ppm): 3.52-3.55 (m, 2H, $-\text{CH}_2-$), 3.39-3.45 (m, 4H, $-\text{CH}_2-$), 2.71 (m, 1H, $-\text{OH}$), 2.41-2.45 (m, 2H, $-\text{CH}_2-$), 2.02-2.10 (m, 2H, $-\text{CH}_2-$), 1.67-1.73 (m, 2H, $-\text{CH}_2-$).

Synthesis of bis(N-hydroxyethyl pyrrolidone) 2-vinylterephthalate (M1) Monomer.

2-Vinylterephthalic acid (2.00 g, 10.42 mmol) and thionyl chloride (40 ml) were added into a 100 mL dried round-bottom flask and stirred at 50 °C for 4 h until the solid disappeared. The excess thionyl chloride was removed by rotary evaporation. The residue was washed twice by petroleum ether, and then dissolved in THF (50 mL). N-hydroxyethyl pyrrolidone (2.96 g, 22.92 mol), DMAP (3.82 g, 31.26 mmol), triethylamine (5 mL), and THF (100 mL) were added into a 250 mL dried round-bottom flask. This flask was immersed in a thermostatic ice bath at 0 °C. The solution of 2-vinylterephthaloyl chloride was added dropwise to this flask over 2 h. The mixture was stirred at room temperature for 24 h. The solution was concentrated by

rotary evaporation, and subsequently extracted using CH_2Cl_2 , distilled water and dilute HCl until the solution was neutralized. The organic phase was dried over anhydrous MgSO_4 . The crude product was purified by a silicon column chromatography using acetone as the eluent and then was further purified by recrystallization from glacial petroleum ether. ^1H NMR (D_2O), δ (ppm): 7.82 (s, 1H, Ar-H); 7.59-7.66 (m, 2H, Ar-H), 7.00-7.07 (m, 1H, =CH-); 5.58-5.62 (d, 1H, =CH₂), 5.33-5.36 (d, 1H, =CH₂); 4.41-4.42 (m, 4H, -CH₂-); 3.64-3.65 (m, 4H, -CH₂-); 3.52-3.57 (m, 4H, -CH₂-); 2.37-2.42 (m, 4H, -CH₂-), 1.98-2.06 (m, 4H, -CH₂-). ^{13}C NMR (CDCl_3), δ (ppm): 175.38-175.39 (C=O), 165.42-166.37 (C=O), 139.67 (Ar-C), 134.63 (-CH₂=), 132.91 (Ar-C), 132.14 (Ar-C), 130.47 (Ar-C), 128.17 (Ar-C), 128.40 (Ar-C), 117.96(=CH₂), 62.57-62.77 (-CH₂-), 47.84-47.94 (-CH₂-), 41.67-41.70 (-CH₂-), 30.71-30.73 (-CH₂-), 18.09-18.14 (-CH₂-).

Synthesis of bis(N-hydroxypropyl pyrrolidone) 2-vinylterephthalate (M2)

Monomer.

M2 was synthesized from N-hydroxypropyl pyrrolidone and vinylterephthal chloride by a procedure similar to that for the synthesis of M1. ^1H NMR (CDCl_3), δ (ppm): 8.24 (s, 1H, Ar-H), 7.93-7.98 (m, 2H, Ar-H), 7.38-7.45 (m, 1H, =CH-), 5.76-5.80 (d, 1H, =CH₂), 5.43-5.46 (d, 1H, =CH₂), 4.34-4.40 (m, 4H, -CH₂-), 3.40-3.49 (m, 8H, -CH₂-), 2.36-2.41 (m, 4H, -CH₂-), 2.01-2.06 (m, 8H, -CH₂-). ^{13}C NMR (CDCl_3), δ (ppm): 175.11-175.13 (C=O), 165.60-166.65 (C=O), 139.49 (Ar-C), 134.78 (-CH₂=), 133.14 (Ar-C), 132.50 (Ar-C), 130.34 (Ar-C), 128.28 (Ar-C), 128.09 (Ar-C), 117.77(=CH₂), 63.11-62.97 (-CH₂-), 47.31-47.30 (-CH₂-), 39.63-39.60

(-CH₂-), 30.88-30.87 (-CH₂-), 26.64-26.58 (-CH₂-), 17.93-19.98 (-CH₂-).

Synthesis of Polymers

The polymerizations of the monomers were carried out in chlorobenzene at 65 °C using AIBN as initiator. Take P1 for example, M1 (0.30 g), 0.01 M AIBN solution in chlorobenzene (60 μL), and chlorobenzene (1.20 g) were charged in a dry glass tube, and the mixture was degassed by three freeze-pump-thaw cycles and sealed under vacuum. Polymerization was carried out at 65 °C for 24 h with constant stirring. The polymer was isolated by precipitating the contents of the flask in diethyl ether and then dried in a vacuum oven overnight at room temperature.

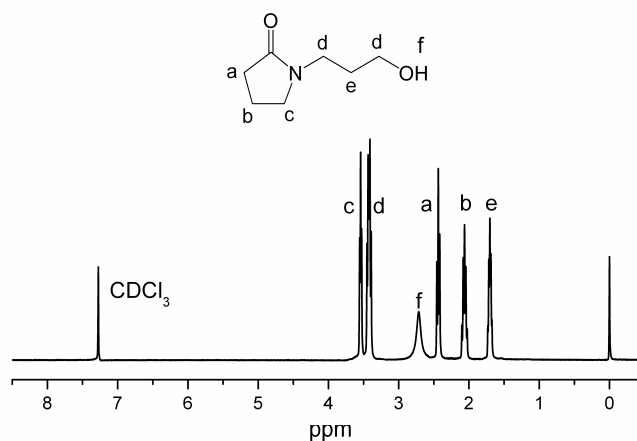
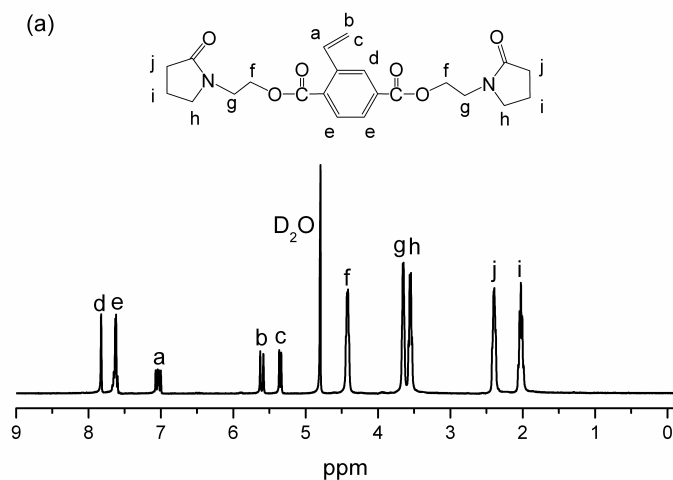


Figure S1. ¹H NMR spectrum of N-hydroxypropyl pyrrolidone in CDCl₃ solution.



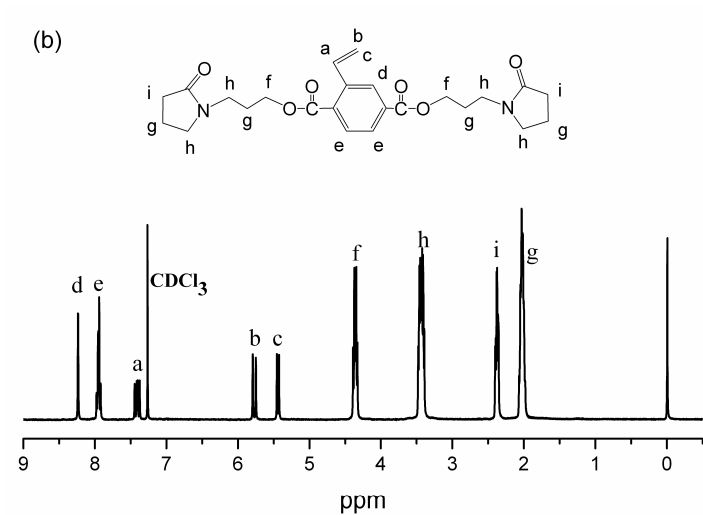


Figure S2. ^1H NMR spectra of M1 in D_2O solution (a) and M2 in CDCl_3 solution (b).

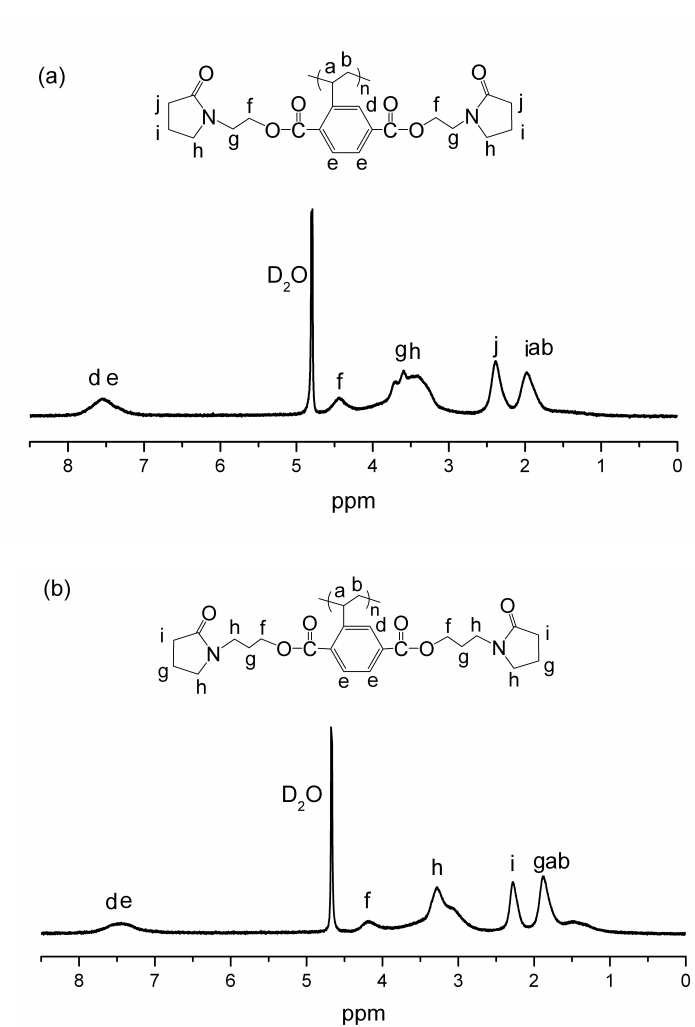


Figure S3. ^1H NMR spectra of P1 (a) and P2 (b) in D_2O solution.

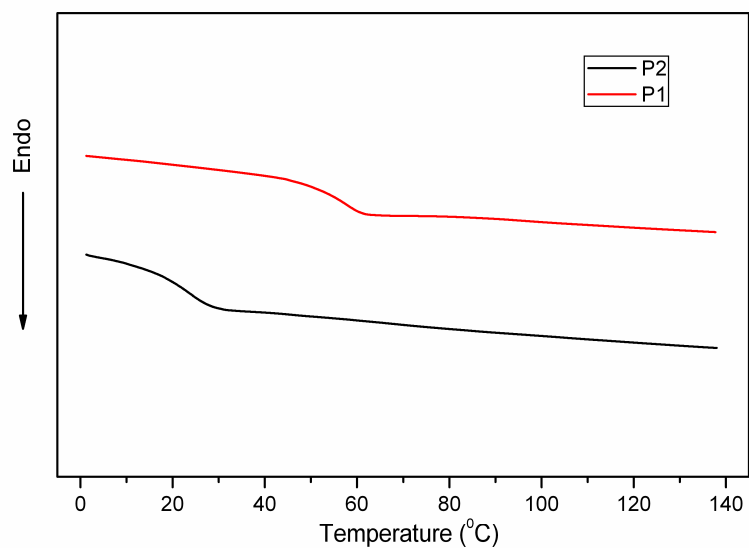


Figure S4. The glass transition temperatures were measured by DSC at a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$ under N_2 during the second heating process.

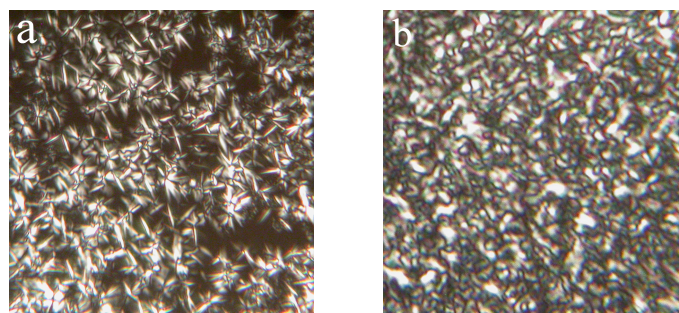
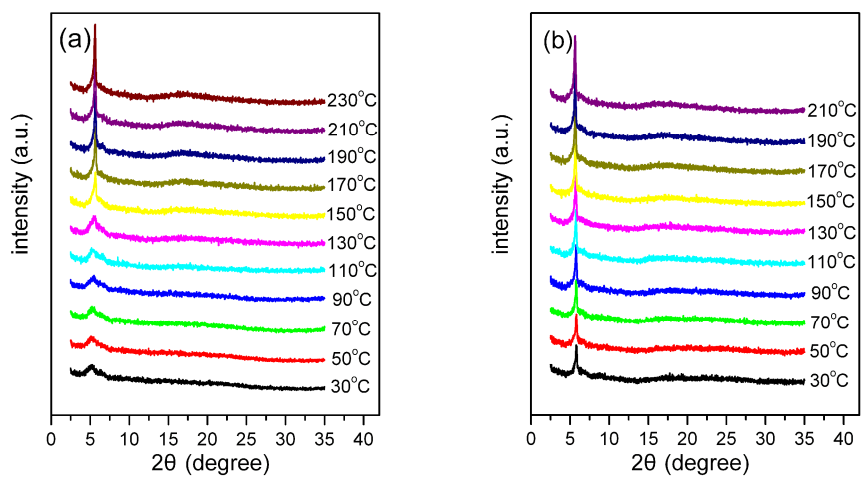


Figure S5. Representative POM images of the textures of P1 (a) and P2 (b) at $185\text{ }^{\circ}\text{C}$.



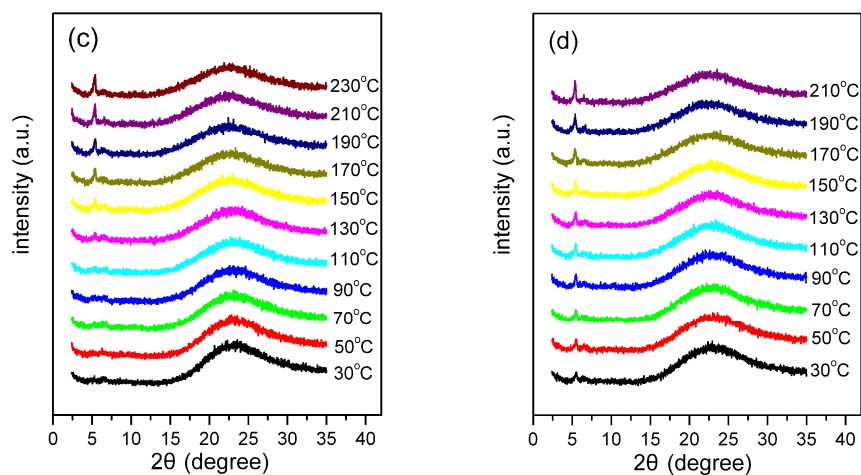


Figure S6. Sets of 1D WAXD powder patterns of P1 (a) and P2 (c) obtained during the first heating of the as-cast films. The corresponding first cooling WAXD powder patterns are shown in (b) and (d).

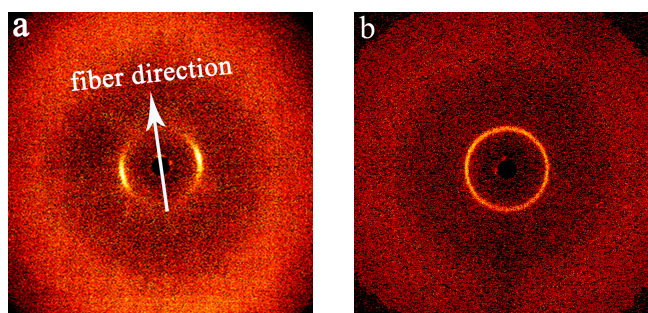


Figure S7. 2D WAXD patterns of P1 obtained with the X-ray beam perpendicular (a) and parallel (b) to the fiber direction (X direction).

Solid-state NMR experiments

The ^1H line reflects the nature of the dipolar interaction between the protons and thus can be used to monitor the dynamic behavior of polymer chains, broad if rigid and narrow if mobile. The dynamic difference between the mobile and rigid components of the sample is clearly visible in the ^1H MAS spectrum as shown in Figure S8, this indicates that P2 should be “semi-rigid”.

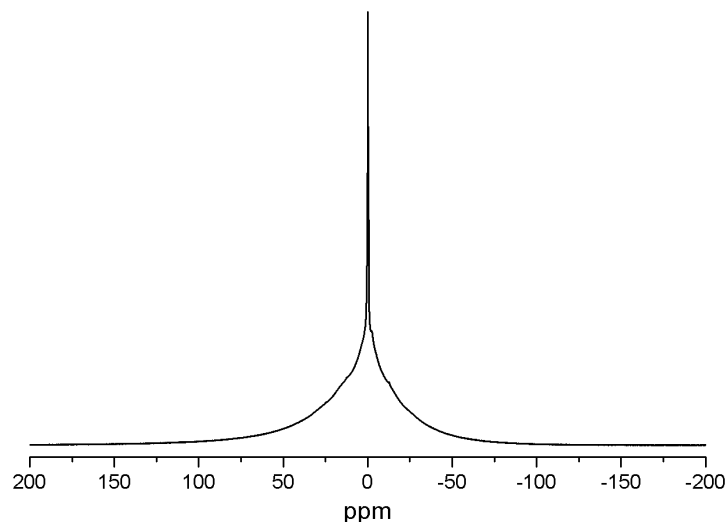


Figure S8. ^1H MAS NMR spectrum of P2 at room temperature (25 °C).

To get a better understanding of the mobility of individual groups, ^{13}C - ^1H 2D WISE NMR experiment was further used to determine the heterogeneous dynamics in P2. 2D WISE experiment correlates the high-resolution ^{13}C CP/MAS spectrum (F2 dimension) with the proton wide line spectrum (F1 dimension) due to ^1H - ^1H and ^{13}C - ^1H interactions. Different regions are distinguished by ^1H wide line spectrum, broad if rigid and narrow if mobile. At the same time, the observed ^{13}C chemical shifts indicate the segmental composition of the regions.

Figure S9 displays the ^{13}C - ^1H WISE spectrum and corresponding ^1H projection at different carbon sites of P2. The peaks from the slice projection at 19.3, 28.0, 35.7 and 47.2 ppm exhibit both narrow and broader lines corresponding to mobile and immobilized components, respectively. The narrow peak at center of the line should be attributed to alkyl and pyrrolidone groups, while the broader lines should be attributed to the backbone protons which overlap with some of the alkyl and pyrrolidone peaks. Whereas the phenyl group at 130 ppm exhibits remarkably

broadened NMR lines, this implies that these groups are rigid. It is interesting to note that $-\text{CH}_2\text{O}$ peak at 63.6ppm also exhibit broader lines, indicating this group is also immobilize. The above solid-state NMR results clearly show distinctly different mobility for the individual component and confirm our suggestion that this polymer is semi-rigid.

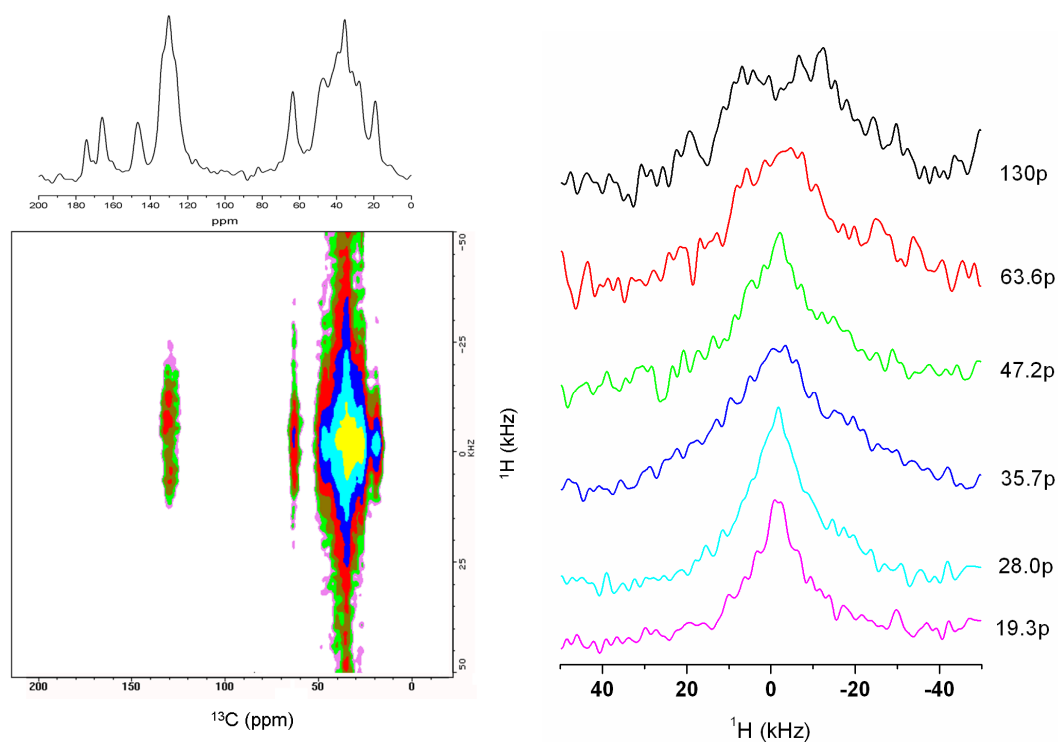


Figure S9. ^{13}C - ^1H 2D WISE spectrum of P2 (left) and corresponding ^1H projection at different carbon sites (right). ^{13}C CP/MAS spectrum was shown on the top of the 2D WISE spectrum. All experiments were performed at room temperature.

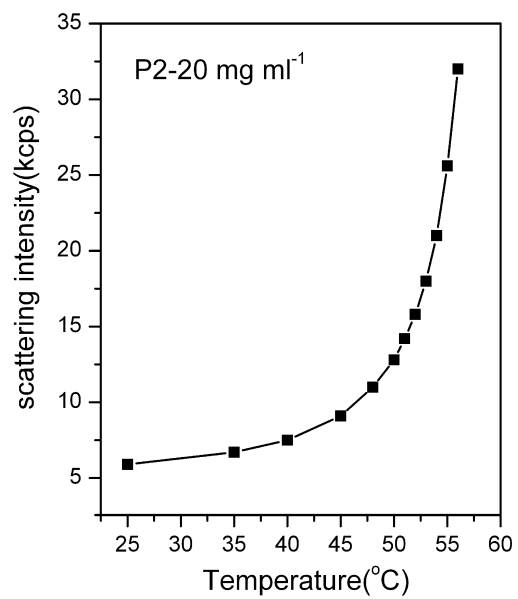


Figure S10. Light scattering intensity of 20.0 mg mL⁻¹ P2 polymer aqueous solution as a function of solution temperature on heating.

Reference

1 Y. X. Liu, D. Zhang, X. H. Wan and Q. F. Zhou, *Chin. J. Polym. Sci.*, 1998, 16, 283.