Supporting information

Syndiotactic Poly(*N*-*n*-propylacrylamide) shows Highly Cooperative Phase Transition

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Materials

N-*n*-Propylacrylamide (NNPAM) was prepared as previously reported.[1] Toluene was purified through washing with sulfuric acid, water, and 5% aqueous NaOH; this was followed by fractional distillation. Methanol (MeOH) was fractionally distilled before use. Tri-*n*-butylborane (n-Bu_3B) as a THF solution (1.0M) (Aldrich Chemical Co.) and 3-methyl-3-pentanol (3Me3PenOH) (Tokyo Kasei Kogyo Co.) were used without further purification for polymerization reaction.

Polymerization

Typical polymerization procedure is as follows; NNPAM (0.314 g, 2.8 mmol) was dissolved in toluene to prepare a 5 mL solution (0.56 mol/L). Four milliliter of the solution was transferred to the glass ampoule and cooled at 0°C. The polymerization was initiated by adding n-Bu_3B solution (0.22 mL) into the monomer solution.[2] After 24h, the reaction was terminated with a small amount of THF solution of 2,6-di-*t*-butyl-4-methylphenol at polymerization temperature. The polymerization mixtures were poured into a large amount of diethyl ether. The precipitated polymers were collected by centrifugation, and dried *in vacuo*. The polymer yields were determined gravimetrically. The results are summarized in Table S1.

Table S1. Radical polymerization of NNPAM in toluene for 24h in the absence or presence of alcohol compounds[a]

Added alcohol	Temp. °C	Yield %	*r* diad (%)[b] ^{1}H NMR	Triad tacticity (%)[c]			n_m[d]	n_r[d]	*r* diad (%) Calcd[e]	M_n[f] x 10^{-4}	M_w[f] / M_n
				mm	*mr*	*rr*					
None	0	>99	51.8	21.1	51.2	27.7	1.82	2.08	53.3	3.44	2.8
MeOH[g]	–20	>99	56.8	18.9	50.3	30.8	1.75	2.22	56.0	2.71	2.7
3Me3PenOH	0	>99	65.6	12.4	43.6	44.0	1.57	3.02	65.8	3.86	2.5
3Me3PenOH	–20	>99	68.2	11.1	38.4	50.5	1.58	3.63	69.7	5.57	2.6
3Me3PenOH	–40	>99	70.9	8.3	37.7	54.0	1.44	3.86	72.9	5.50	3.0

[a] $[\mathrm{NNPAM}]_0 = 0.5$ mol/L, $[\mathrm{R\text{-}OH}]_0 = 2.0$ mol/L, $[n\text{-}\mathrm{Bu_3B}]_0 = 0.05$ mol/L.

[b] Determined by ^{1}H NMR signals due to methylene and methine groups in chain.

[c] Determined by ^{13}C NMR signals due to methyne groups in chain.

[d] Calculated with $n_\mathrm{r} = (rr + mr/2) / (mr/2)$ and $n_\mathrm{m} = (mm + mr/2) / (mr/2)$.

[e] Calculated with $r = rr + mr/2$.

[f] Determined by SEC (polystyrene standards).

[g] $[\mathrm{MeOH}]_0 = 0.25$ mol/L.

Characterization

The ^{1}H and ^{13}C NMR spectra were measured on an EX-400 or ECX-400 spectrometer (JEOL Ltd.) operated at 400 MHz for ^{1}H and at 100 MHz for ^{13}C. The diad tacticities of the obtained polymers were determined from ^{1}H NMR signals due to both methylene and methine groups in main chain, measured in deuterated dimethyl sulfoxide (DMSO-d_6) at 150°C. The triad tacticities were determined from ^{13}C NMR signals due to the main-chain methine carbons, measured in mixed solvent (DMSO-d_6 : D_2O : $CHF_2(CF_2)_3CH_2OH$ = 75 : 10 : 15 wt%) at 100 °C. The molecular weights and molecular weight distributions of the polymers were determined by size exclusion chromatography (SEC) (HLC 8220 instrument, Tosoh Co.) equipped with TSK gels (SuperHM-M and SuperHM-H, Tosoh Co.) using dimethylformamide (LiBr 10 mmol/l) as an eluent at 40°C ([polymer] = 1.0 mg/ml, flow rate = 0.35 ml/min). The SEC chromatogram was calibrated with standard polystyrene samples.

Turbidimetry

The transmittance of a PNNPAM solution (1.0 mg/mL) was monitored at 500 nm as a function of temperature with a UV/VIS spectrophotometer (V-550, JASCO Co.) equipped with a peltier thermostatted single cell holder (ETC-505, JASCO Co.). The temperature was changed at 1.0 °C/min. The cloud point (T_c) was defined as the temperature at which the transmittance is 50%.

High-sensitive DSC

Measurements were performed on a VP-DSC MicroCalorimeter (MicroCal Inc.) with a cell volume of 0.5975 mL at heating rate of 0.2 or 1.0 ºC/min in the range of 2-60 ºC under elevated pressure (> 28 psi). Deionized water was used as a reference. For each experiment, three heating scans were normally performed. The prescan time at 2 ºC was 15 min to allow the entangled globule chains to dissolve completely.

FT-IR measurements

Details of the method for conducting FT-IR measurements have been described in a previous paper.[3] The copolymer was dissolved in D_2O to a concentration of 1.0×10^2 mg/mL. The copolymer solution (10 μL) was placed between two CaF_2 windows at a path length of 10 μm. The IR cell was attached to a metal cell holder, and the temperature was controlled using a circulating water bath. The background spectrum of the first measurement cycle was obtained with a sample solution equilibrated at a starting temperature. IR spectra were then collected continuously at a certain temperature while changing the IR cell at a rate of ca. 1 °C/min. D_2O was used as solvent to avoid the overlapping of amide I and O-H bending of H_2O.

Quantum chemical calculation

Quantum chemical calculation based on density functional theory was performed using Gaussian 98[4] at the B3LYP level with the STO-3G basis set.

References

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Table S2. Effect of molecular weight of PNNPAMs with almost constant *r* content on cooperativity

r [a]	M_n x10^{-4} [b]	M_w/M_n [b]	T_p [c], ºC	$\Delta T_{1/2}$ [d], ºC	ΔH [e]	ΔC_p [f]	ΔH_v [g]	N [h]
69.3 [i]	3.68	2.6	25.3	0.47	1.45	2.2	1.31	900
69.8 [j]	4.56	3.1	25.5	0.43	1.53	2.3	1.43	930
70.9 [k]	5.50	3.0	25.4	0.41	1.68	2.8	1.51	900

[a] Determined by ^{1}H- and ^{13}C-NMR. [b] Determined by SEC. [c] Temperature of endothermic peak. [d] Maximum half-width of endothermic peak. [e] Calorimetric enthalpy (kcal/mol-monomer). [f] Endothermic peak height (kcal/ºC/mol-monomer). [g] van't Hoff enthalpy (Mcal/mol-monomer) calculated form the equation, $\Delta H_v = 6.9T_p^2/\Delta T_{1/2}$. [h] Number of cooperative units, $n = \Delta H_v / \Delta H$. [i] Polymerization conditions; $[\text{Monomer}]_0 = 0.25$ mol/L; $[\text{3Me3PenOH}]_0 = 2.0$ mol/L $[n\text{-Bu}_3\text{B}]_0 = 0.05$ mol/L; temp. = -20 ºC. [j] polymerization conditions are same with (i) except for temp. (-40 ºC). [k] Taken from *r*71 of Table 1.

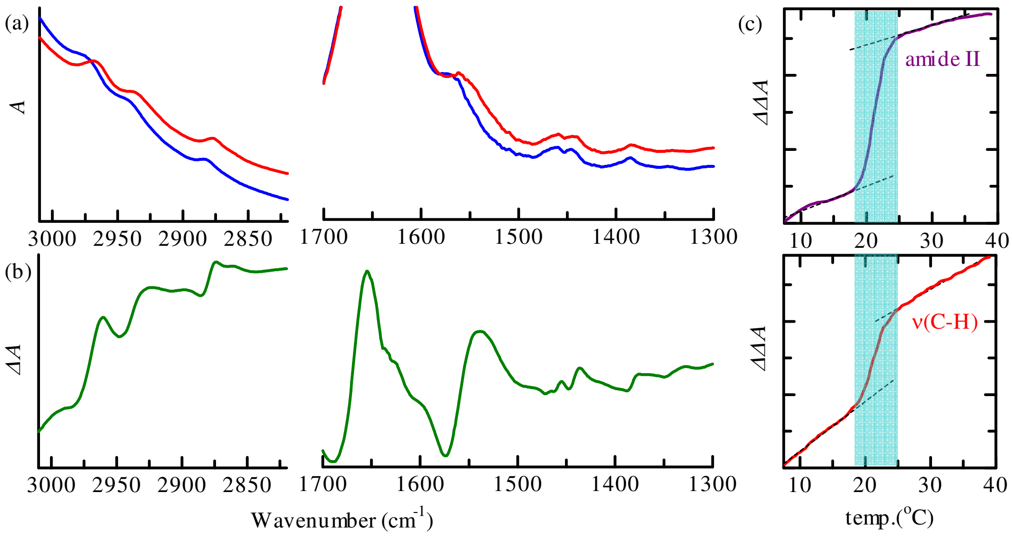

Figure S1. (a) FT-IR spectra of *r*52 measured in H_2O below (blue, 7 ºC) and above (red, 39 ºC) the phase transition temperature. (b) Differential IR spectra between the above two temperatures. (c) Temperature dependence of ΔΔ*A* for amide II and ν_{as}(C-H) bands. Shaded area shows temperature range of phase transition (18-25 ºC, Δ*T* = 7 ºC), and this range is identical with that of D_2O (Figure 2C upper panel). Polymer concentration = $1.0\text{x}10^2$ mg/mL. Heating rate = ca. 1 ºC/min.

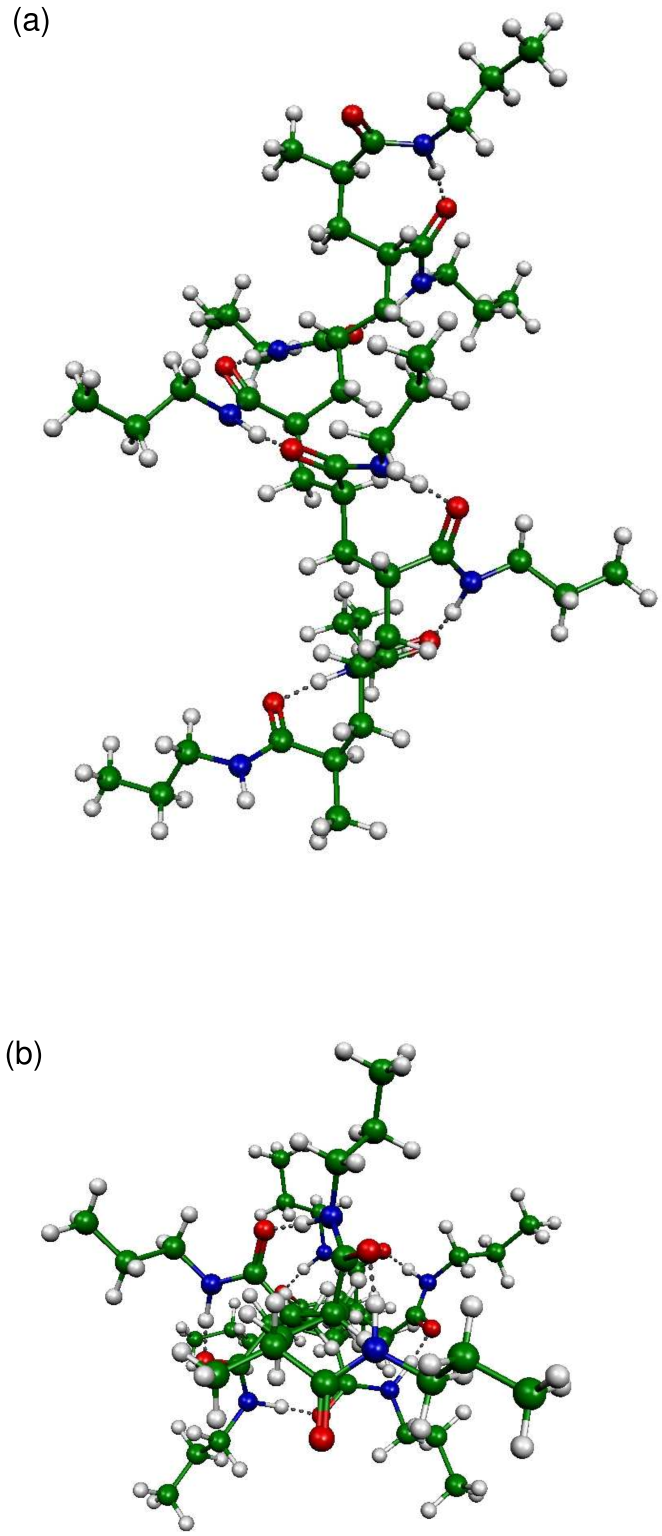

Figure S2. Quantum chemical calculation results of octamer of syndiotactic PNNPAM. (a) Side view and (b) top view. PNNPAM forms helical structure with intramolecular hydrogen-bonding among adjacent monomeric units.