Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Molecular Level Study of the Phase Transition Process of Hydrogen-bonding UCST Polymers

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Experimental

Materials. Diacetone acrylamide (DAAM, 99%) and 2,2′-Azobis(2-methylpropionamidine) dihydrochloride (V-50, 97%) were purchased from Sigma-Aldrich. *N*-Acryloyl Glycinamide (NAGA) and the chain transfer agent (CTA) 2-ethylsulfanylthiocarbonylsulfanyl-propionic acid methyl ester were synthesized according to a previous report, respectively.[1-2]

Characterizations. Turbidimetry measurements (1 wt%) were carried out at 500 nm on a Lamda 35 UV−vis spectrometer with deionized water or water/methanol mixture as reference at a heating/cooling rate of 1 ^{o}C min^{-1}. Hydrodynamic diameters (D_h) of nanogels (1 wt%) were measured on a Malvern ZS90 after being allowed to equilibrate at the setting temperatures for 2 min. ^{1}H NMR spectra were collected on a Bruker AV 500 MHz spectrometer with D_2O as solvent. Molecular weight and dispersity were determined using Waters size exclusion chromatography (SEC) equipped with Styragel HR4 and HR5 columns and a Waters 2410 refractive index detector. The measurements were made using DMSO with LiBr (2 mg mL^{-1}) as eluent at 70 °C column temperature. Prior to the measurements, the samples were allowed to dissolve at 70 °C for 2h. The copolymer in D_2O or in D_2O/CD_3OD mixture (χ_m = 6.9 mol%) for FTIR measurement was prepared by sealing the dispersions between two ZnS tablets. All the time-resolved FTIR spectra at variable temperatures were recorded by using a Nicolet Nexus 6700 FTIR spectrometer equipped with a DTGS detector. 32 scans at a resolution of 4 cm^{-1} were accumulated to obtain an acceptable signal-to-noise ratio. Temperatures were under programmed control with an electronic cell holder at a rate of ca. 1 ^oC/3 min with an increment of 1 ^oC. The FTIR spectra of 10 wt% polymers in D_2O or in D_2O/CD_3OD mixture (χ_m = 6.9 mol%) collected during heating with an interval of 1 ^oC were selected to perform PCMW and 2D correlation analyses. Primary data processing was performed using the software 2D Shige ver. 1.3 (Shigeaki Morita, KwanseiGakuin University, Japan). The contour maps were plotted using Origin Program 2 ver. 8.0 with red and yellow as the positive intensities and blue as the negative intensities. An appropriate window size (2m + 1 =11) was chosen to generate good-quality PCMW spectra. The neat NAGA95 polymer film for FTIR measurements was prepared by drop-casting on a ZnS tablet from its aqueous solution.

Synthesis of P(NAGA-*co*-DAAM) Copolymers

CTA 2-ethylsulfanylthiocarbonylsulfanyl-propionic acid methyl ester (3.6 mg, 0.016 mmol), NAGA (390 mg, 3.04 mmol) and DAAM (27 mg, 0.16 mmol) were dissolved in 4.2 mL of water. The solution was degassed with nitrogen at 0 ^oC for 40 min before immersion into a preheated oil bath at 70 ^oC. When the temperature was stabilized, a degassed solution of V-50 (0.35 mg, 0.0013 mmol) in water was injected *via* a microsyringe. After designated time the reaction was stopped by exposing the solution to air and cooling. The polymers were purified by extensive dialysis against distilled water and isolated *via* lyophilization. The resulting copolymers was named as NAGA95. The conversion of monomers was ~90% as determined by ^{1}H NMR. $M_{\mathrm{n,theory}}$= 24200, M_n = 28000 (GPC), $M_\mathrm{w}/M_\mathrm{n}$ = 1.22 (GPC).

Perturbation correlation moving window (PCMW)

PCMW as a recently developed technique has basic principles which were first proposed by Thomas.[3] Then in 2006 Morita[4] improved this method to a wider range of applicability by introducing a perturbation variable into the correlation equation. Together with its ability to determine transition points, PCMW spectra can also be used to monitor spectral variations along the temperature perturbations, combining the signs of synchronous and asynchronous spectra by the following rules: a positive synchronous correlation indicates spectral intensity increasing, while a negative one indicates spectral intensity decreasing; a positive asynchronous correlation shows a convex spectral intensity variation while a negative one shows a concave variation.[4] The transition temperatures can be easily deduced from the synchronous map and transition temperature regions can be clearly determined by peaks in asynchronous map.

Introduction to 2Dcos

2Dcos is a mathematical method, whose basic principles were proposed first by Noda.[5] It has been widely applied to study spectral variations of different chemical groups that respond to external perturbations, *i.e.*, temperature, pH, concentration, electromagnetic and so on.[6] Through spreading the original spectra along a second dimension, it can extract additional important information about conformational changes or molecular motions, which are not easily obtained from the conventional IR spectra.

The 2Dcos spectra are characterized by two independent wavenumber axes (v_1, v_2) and a correlation intensity axis. Two types of spectra, 2D synchronous and asynchronous spectrum are obtained generally. The correlation intensity in the 2D synchronous and asynchronous maps represents the relative degree of in-phase and out-phase response, respectively. The 2D synchronous spectra are symmetric in relation to the diagonal in the correlation map. Some peaks appearing along the diagonal are called auto-peaks, and the symbols of them are always positive, as auto-peaks reflect the degree of autocorrelation of perturbation-induced molecular vibrations. Where the auto-peak appears, the peak at this wavenumber would change greatly under environmental perturbation. 2D asynchronous spectra can not only enhance spectral resolution but also identify the specific order occurring in the effect of external perturbation as well. The judging rule can be extracted from Noda's rule.[7] In brief, when the cross-peaks (v_1,v_2, and assume $v_1 > v_2$) in synchronous and asynchronous spectra possess the same symbol, it indicates the variation at v_1 prior to that of v_2, and vice versa.

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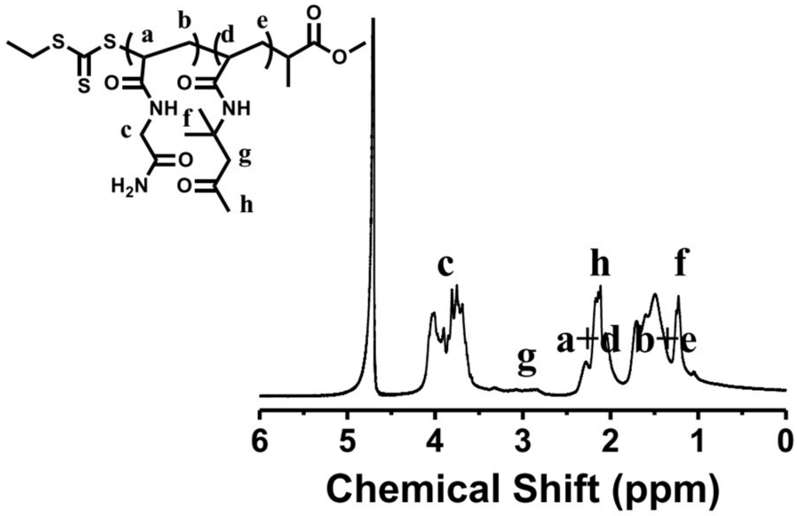

Figure S1. ^1H NMR spectrum of the NAGA95 polymer in D_2O.

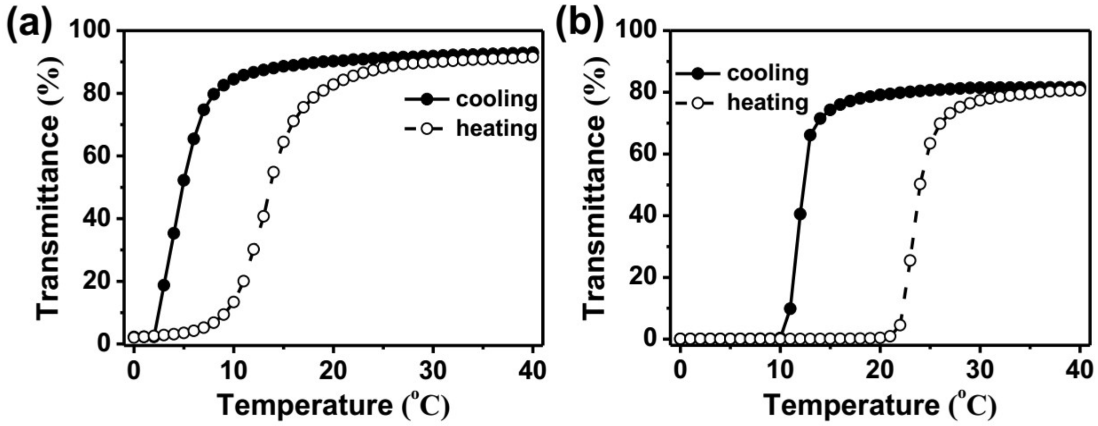

Figure S2. Thermal transitions of UCST-type copolymers NAGA95 measured in (a) water and (b) water/methanol mixture (χ_m = 6.9 mol%) (1 wt%) by turbidimetry during cooling and heating cycle.

Table S1. Tentative band assignments of NAGA95 in D_2O according to the 2Dcos analysis.[8-11]

Wavenumber (cm^{-1})	**Tentative Assignments**
2954	v_{as}(hydrated CH_2)
2937	v_{as}(dehydrating CH_2)
2920	v_{as}(dehydrated CH_2)
2895	v(CH)
2850	v_s(CH_2)
1680	v(free C=O, NAGA)
1649	v(C=O···D-O-D···O=C, NAGA)
1622	v(C=O···D-N, NAGA)
1601	v(--(-C=O···D-N--)$_n$-, NAGA)

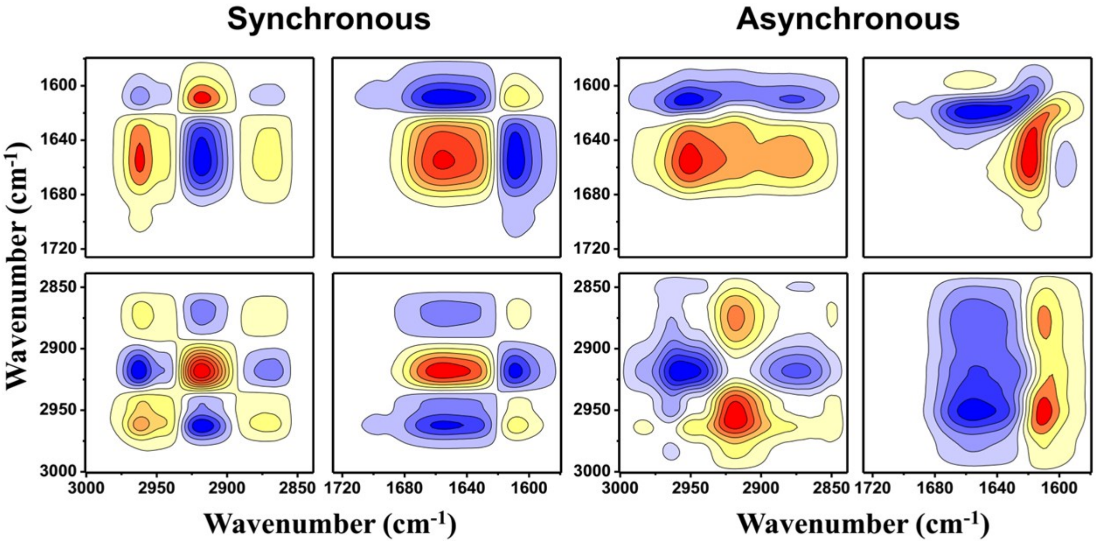

Figure S3. 2D synchronous and asynchronous spectra of NAGA95 in D_2O/CD_3OD mixture (10 wt%) during heating between 25 and 55 ^{o}C. Warm colors (red and yellow) represent positive intensities, and cool colors (blue) represent negative ones.

Table S2 Tentative band assignments of NAGA95 in D_2O/CD_3OD mixture according to the 2Dcos analysis.[8-11]

Wavenumber (cm^{-1})	Tentative Assignments
2956	ν_{as}(hydrated CH_2)
2918	ν_{as}(dehydrated CH_2)
2875	ν_s(CH_3)
2850	ν_s(CH_2)
1655	ν(C=O⋯D-O-D⋯O=C, NAGA)
1620	ν(C=O⋯D-N, NAGA)
1597	ν(--(-C=O⋯D-N--)$_n$-, NAGA)