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

Supporting Information for

On the Abnormal "Forced Hydration" Behavior of P(MEA-*co*-OEGA) Aqueous Solutions in the LCST Phase Transition from Infrared Spectroscopic Insights

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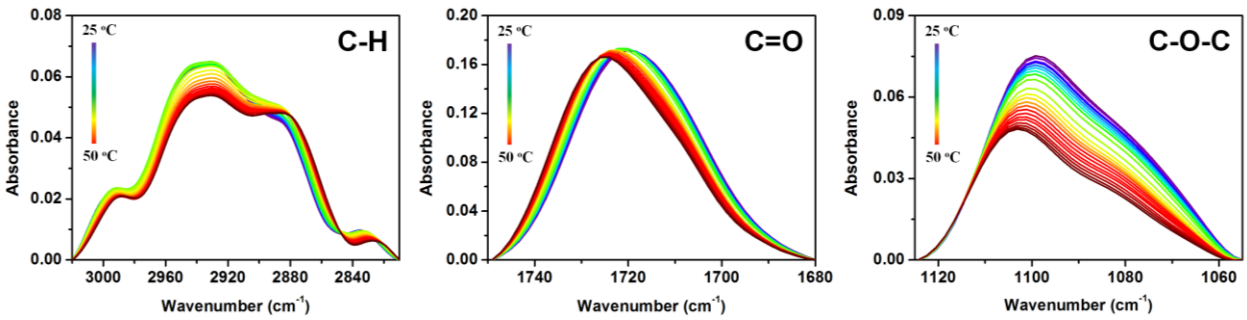

Figure S1. Temperature-dependent FTIR spectra of poly(oligo ethylene glycol methacrylate) (POEGMA) (M_n = 1.2*10^4 g/mol, M_w/M_n = 1.13, determined in DMF) in 10 wt% D_2O solution during heating from 25 to 50 °C.

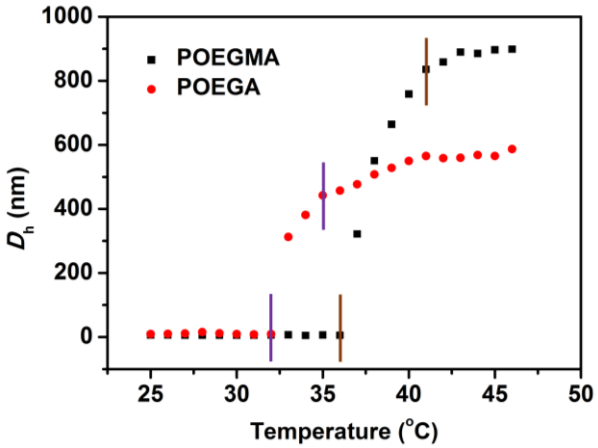

Figure S2. DLS curves of POEGMA and POEGA in water (0.1 wt%) during heating.

Introduction of PCMW

PCMW is a newly developed technique with basic principles dating back to conventional moving window provided by Thomas et al. Then, Morita has improved it in 2006. PCMW analysis method correlates the external perturbation directly with infrared peaks so that it enables us to determine exact critical conditions, like transition points and changing mode of various peaks. PCMW maps exist in pairs and consist of synchronous and asynchronous map.

The transition temperatures can easily deduced from the synchronous map and transition temperature regions can be clearly determined by peaks in asynchronous map. Take PCMW maps in this Article, for example: the x-axis is wavenumber and y-axis is temperature. The correlation peak (ν_1 cm^{-1}, a °C) in the synchronous map tells us that a °C is the transition temperature of peak ν_1, whereas a pair of correlation peaks with the same wavenumber in the asynchronous map, (ν_1 cm^{-1}, b °C) and (ν_1 cm^{-1}, c °C) tells us that peak ν_1 starts to change at b °C and ends at c °C. Moreover, PCMW can also monitor

the spectral variations along temperature perturbation combining the signs of synchronous and asynchronous spectra by the following rules: positive synchronous correlation represents spectral intensity increasing, while negative one represents decreasing; positive asynchronous correlation can be observed for a convex spectral intensity variation while negative one can be observed for a concave variation. According to symbols of correlation peaks in both PCMW maps, we can infer the changing style of peak v_1. For example, when the correlation peak is: (1) positive in both maps, we can infer peak v_1 changes in  style; (2) positive in synchronous map and negative in asynchronous map, it changes in  style; (3) negative in both maps, it changes like  ; (4) negative in synchronous map and positive in asynchronous map, it changes like  .

Introduction of 2Dcos

2Dcos was originally proposed by Noda in 1993; this method enables the investigation of spectral intensity fluctuations under an external perturbation like temperature, time, pH, concentration, and so on. By spreading peaks over the second dimension, 2Dcos can also greatly improve the spectral resolution; for example, they can separate overlapped peaks in the 1D spectra and discern the exact vibration positions of peaks, which is very important for understanding the accurate microstructures of chemicals.

The red-colored and green-colored areas in the 2Dcos contour maps represent positive and negative cross-peaks respectively throughout this paper. 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 in general. The correlation intensity in the 2D synchronous and asynchronous maps reflects the relative degree of in-phase or out-of phase response, respectively. The 2D synchronous spectra are symmetric with respect to the diagonal line in the correlation map. Some peaks appearing along the diagonal are called the auto-peaks, and the symbols of them are always positive, as auto-peaks represent 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. Off-diagonal peaks, named cross-peaks ($\Phi(v_1, v_2)$), may be positive or negative, which represent the simultaneous or coincidental changes of spectra intensity variations measured at v_1 and v_2. Positive cross-peaks (the symbol of $\Phi(v_1, v_2)$ is positive) demonstrates that the intensity variations of the two peaks at v_1 and v_2

are taking place in the same direction (both increase or both decrease) under the environmental perturbation; while the negative cross-peaks (the symbol of $\Phi(v_1, v_2)$ is negative) help to infer that the intensities of the two peaks at v_1 and v_2 change in opposite directions (one increases, while the other one decreases) under perturbation.

The 2D asynchronous spectra are asymmetric with respect to the diagonal line in the correlation map. Unlike synchronous spectra, only off-diagonal cross-peaks would appear in asynchronous spectra, and these cross-peaks can also be either positive or negative. The intensity of the asynchronous spectrum ($\Psi(v_1, v_2)$) represents sequential or successive changes of spectral intensities observed at v_1 and v_2. With the cross-peaks both in synchronous and asynchronous maps, we can get the specific order of the spectral intensity changes taking place while the sample is subjected to an environmental perturbation. According to Noda's rule, when $\Phi(v_1, v_2) > 0$, if $\Psi(v_1, v_2)$ is positive (red-colored area), band v_1 will vary prior to band v_2; if $\Psi(v_1, v_2)$ is negative (green-colored area), band v_1 will vary after v_2. However, this rule is reversed when $\Phi(v_1, v_2) < 0$. Be brief, if the symbols of the cross-peak in the synchronous and asynchronous maps are the same (both positive or both negative), band v_1 will vary prior to band v_2; While if the symbols of the cross-peak are different in the synchronous and asynchronous spectra (one positive, and the other one is negative), band v_1 will vary after v_2 under the environmental perturbation.