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

Supporting Information

The Structure and Volume Phase Transition Behavior of Poly(*N*-vinylcaprolactam)-Based Hybrid Microgels Containing Carbon Nanodots

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Experimental

Materials

N-Vinylcaprolactam (VCL) and 1-vinylimidazole (VIM) (Alfa Aesar) were purified by passing through an alumina column. Acrylic acid, 1,2-ethylenediamine (EDA), glycidyl methacrylate (GMA), n-hexane(Aladdin), cross-linker *N,N'*-methylenebis (acrylamide) (BIS) (TCI), cationic surfactant *N*-cetyl-*N,N,N*-trimethylammonium bromide (CTAB) and the initiator 2,2′ -azobis(2-methylpropionamidine) dihydrochloride (AIBA) (Sigma-Aldrich) were used without further purification. All the other reagents were received from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Synthesis of PCNDs

PCNDs were synthesized according to the previous reported procedure in literature.[1] Typically, 80 mmol acrylic acid and equimolar quantities of 1,2-ethanediamine were dissolved in 40 ml water. The transparent solution was transferred into a microwave oven for 7 minutes. After cooling down to room temperature, 20mL of water for dissolving the obtained CDs was added. Subsequently, 10 mL of GMA was mixed into the CD solution under vigorous stirring for 24 h at 30 °C. Then the oil phase of the solution was removed, and the remaining water phase was washed using n-hexane for removal of the residual GMA molecules. Prior to the radical polymerization reactions, the CD aqueous solution was freeze-dried, and a certain crystallinity with average lattices of 0.32 nm and a mean diameter of 3-5 nm of carbon dots were characterized using TEM (Figure S1).

Synthesis of Microgels

A series of P(VCL-*co*-VIM)/PCND hybrid microgels with different amounts of PCNDs and one without PCNDs were synthesized by aqueous free radical emulsion polymerization. During the reaction, 0.35 g of PVCL, 0.03 g of VIM, 0.0036 g of CTAB, 0.01g of BIS, and different amounts of PCNDs (0, 0.00175, 0.0035, 0.0175, 0.035, 0.175, 0.245g) were placed into a three-necked, round-bottomed flask equipped with mechanical stirrer and then dissolved in 35mL of deionized water. After 1 h of incubation at 70 °C and nitrogen purging, a solution of 0.0125g of AIBA dissolved in 1 mL of water was added under continuous stirring for initiating the polymerization. The reactions were carried out for 4 h in the atmosphere of nitrogen. After that, they were purified *via* dialysis (MWCO 14000) for a week against water to remove unreacted monomers and other small molecules. The resultant microgels were named as PVCL-0 (0g PCNDs), PVCL-10% (0.035g PCNDs) and PVCL-50% (0.175g PCNDs), according to the feed mass ratio of PCNDs to VCL, *i.e.* 0, 10wt%, 50wt%, respectively.

Characterization

The hydrodynamic diameters (D_h) of the hybrid microgels were measured using a Malvern ZetaSizer Nano ZS90 after being allowed to be equilibrated at the setting temperature for 2 min. The high-resolution transmission electron microscope (HRTEM) images were taken on a Tecnai G2 F20 S-Twin with an accelerating voltage of 200 kV. Diluted microgel dispersions were placed onto the carbon film coated copper grid and dried at room temperature. FTIR spectra were recorded using a Nicolet 6700 spectrometer. ^{1}H NMR spectrum of the PCNDs was carried out by Varian Mercury plus 400 spectrometer with D_2O as solvent (Figure S2). Fluorescence (PL) spectra were recorded using a Shimadzu RF-5301PC Spectrophotometer. Aliquots were sampled at predetermined time intervals for PVCL-10% polymerization kinetics study. The conversion of monomers and crosslinker are determined by ^{1}H NMR.

The FTIR spectra of 10 wt% P(VCL-co-VIM)/PCNDs in D_2O collected during heating with an interval of 1°C 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 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.

Introduction to PCMW

PCMW as a recently developed technique has basic principles which were first proposed by Thomas.[2] Then in 2006 Morita[3] 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.[3] 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.[4] 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.[5] 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-of 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.[6] 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.

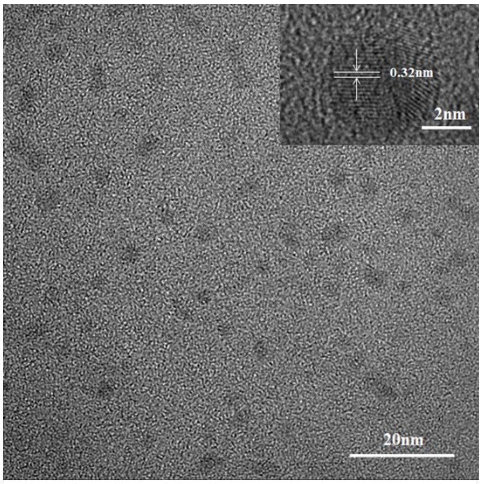

Figure S1. TEM image of PCNDs. The inset shows a magnified view of PCNDs.

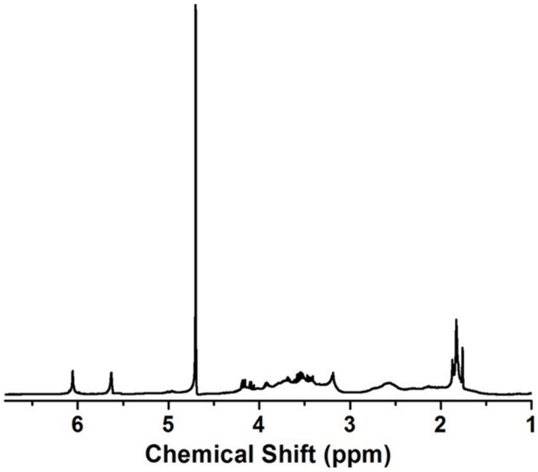

Figure S2. ^1H NMR spectrum of PCNDs in D_2O.

^1H NMR peaks appearing at δ 6.00 and δ 5.57 ($-C=CH_2$) suggest the successful linkage of the GMA molecule onto the surface of PCNDs.

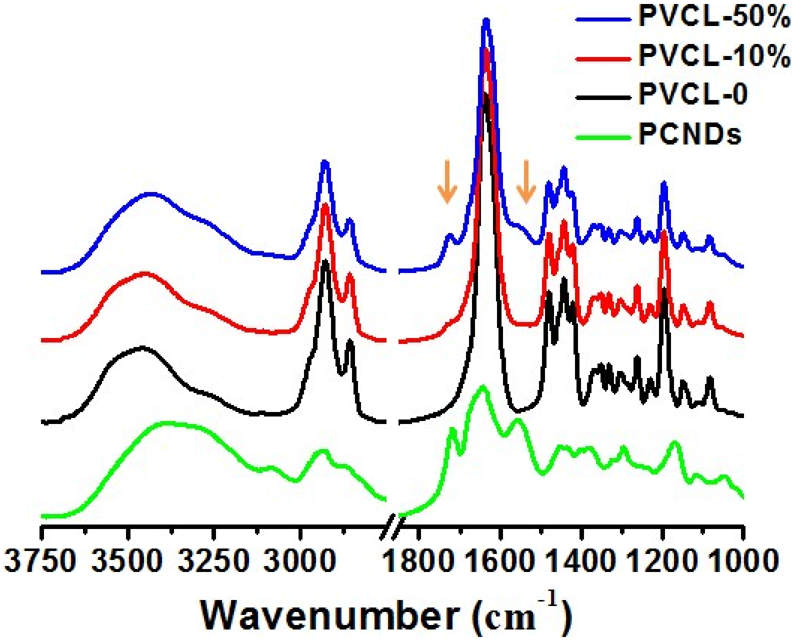

Figure S3. FTIR spectra of PCNDs and dried PVCL/PCND hybrid microgels, the two arrows point to the IR peaks at 1715 cm^{-1} (–COOR) and the band at 1558cm^{-1} (amide II) of PCNDs, respectively.

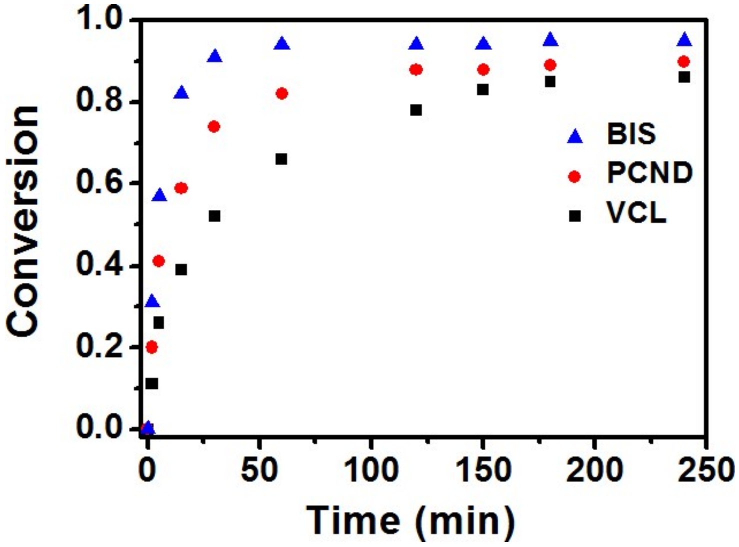

Figure S4. Evolution of the conversions of BIS, PCND and VCL for the reaction PVCL-10%

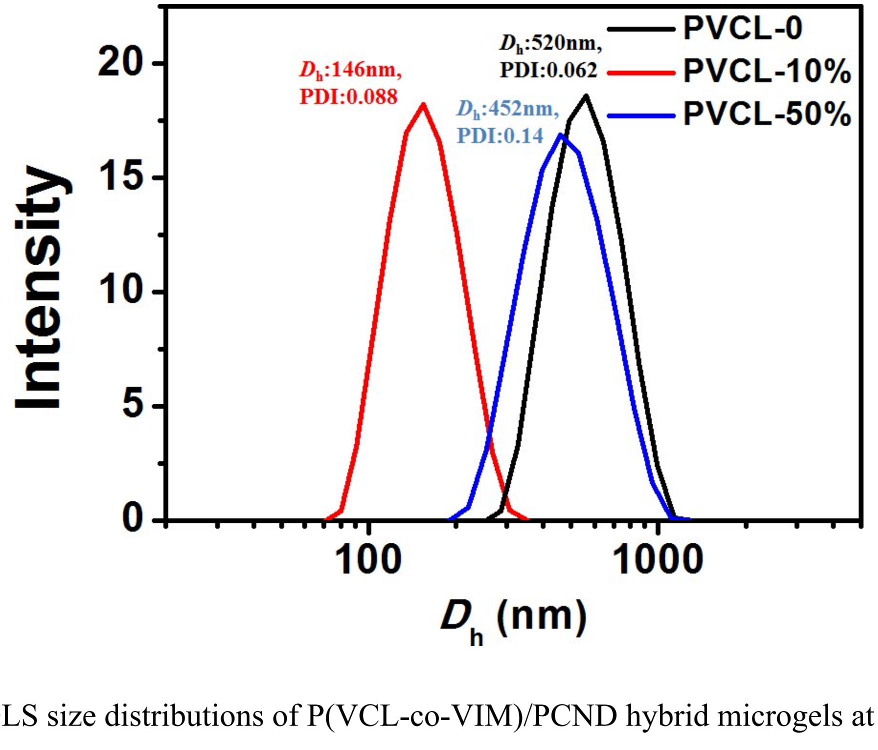

Figure S5. DLS size distributions of P(VCL-co-VIM)/PCND hybrid microgels at 25°C.

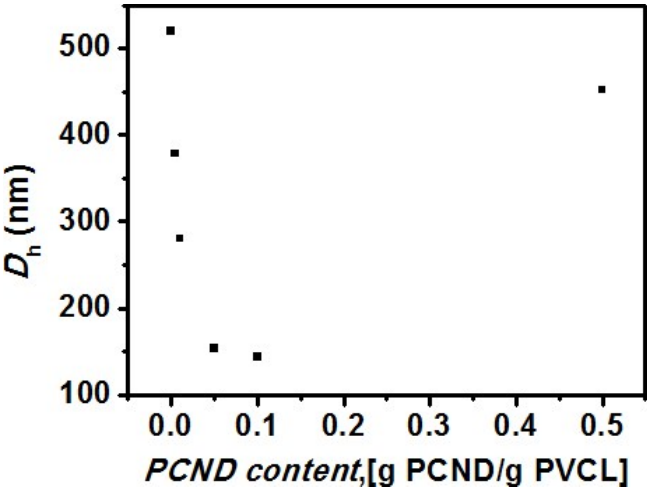

Figure S6. The hydrodynamic diameter (D_h) measured at 25 °C of P(VCL-VIM)-PCND hybrid microgels as a function of PCND content.

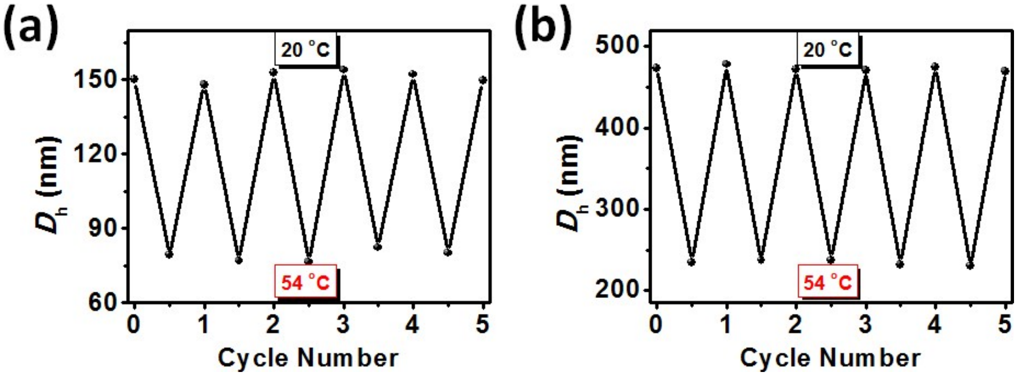

Figure S7. Hydrodynamic diameter (D_h) of (a) PVCL-10% and (b) PVCL-50% as a function of heating−cooling cycles between 20 and 54 °C

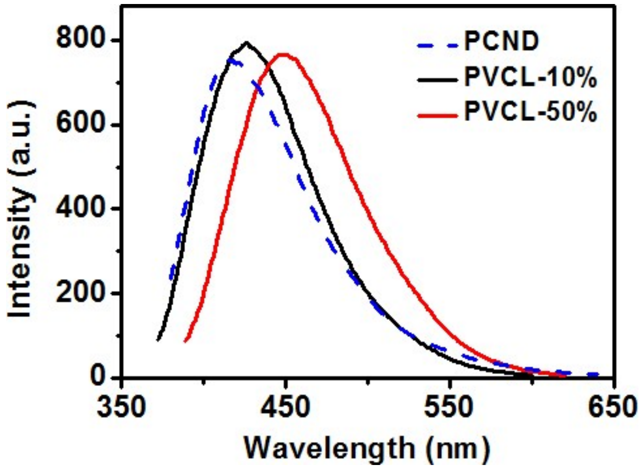

Figure S8. PL emission spectra of the PCND aqueous solution (blue dash line), the PVCL-10% (black solid line) and the PVCL-50% (red solid line) microgels (EX: 1.5 nm, EM: 3.0 nm).

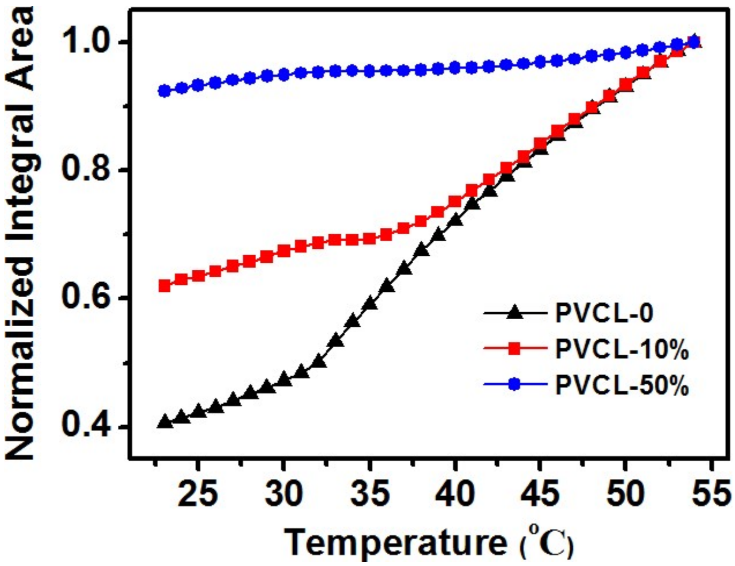

Figure S9. Temperature-dependent normalized integral area changes of the C=O band of the three microgels in D_2O (10 wt%) during the heating process.

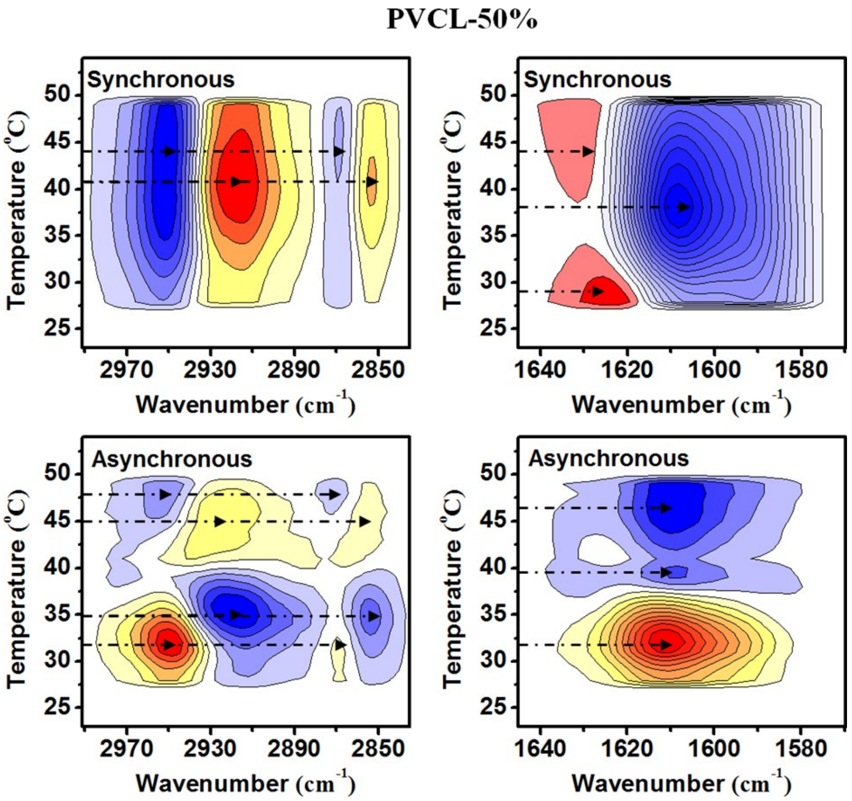

Figure S10. PCMW synchronous and asynchronous spectra of PVCL-50% during heating from 23 to 54 °C, respectively. Herein, warm colors (red and yellow) are defined as positive intensities, while cool colors (blue) are defined as negative ones.

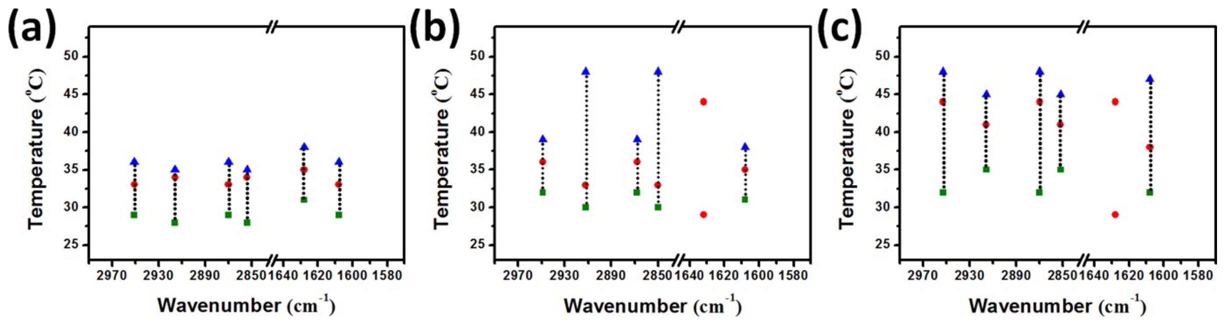

Figure S11. Corresponding transition temperatures and transition temperature regions of (a) PVCL-0, (b) PVCL-10% and (c) PVCL-50% in D_2O (10 wt%) during heating read from PCMW synchronous and asynchronous spectra

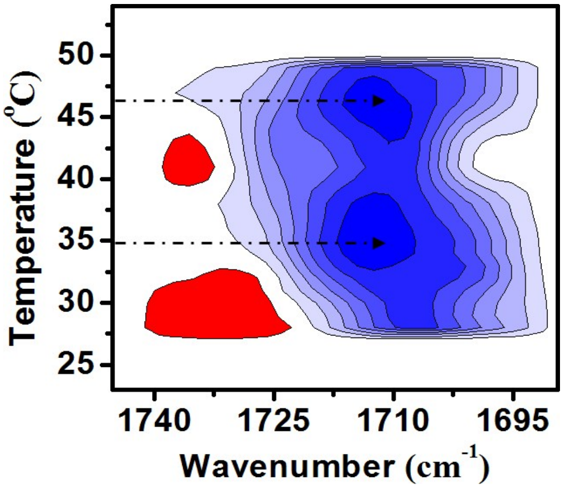

Figure S12. PCMW synchronous spectra of the PCNDs during heating from 23 to 54 ^{o}C. Herein, warm colors (red) are defined as positive intensities, while cool colors (blue) are defined as negative ones.

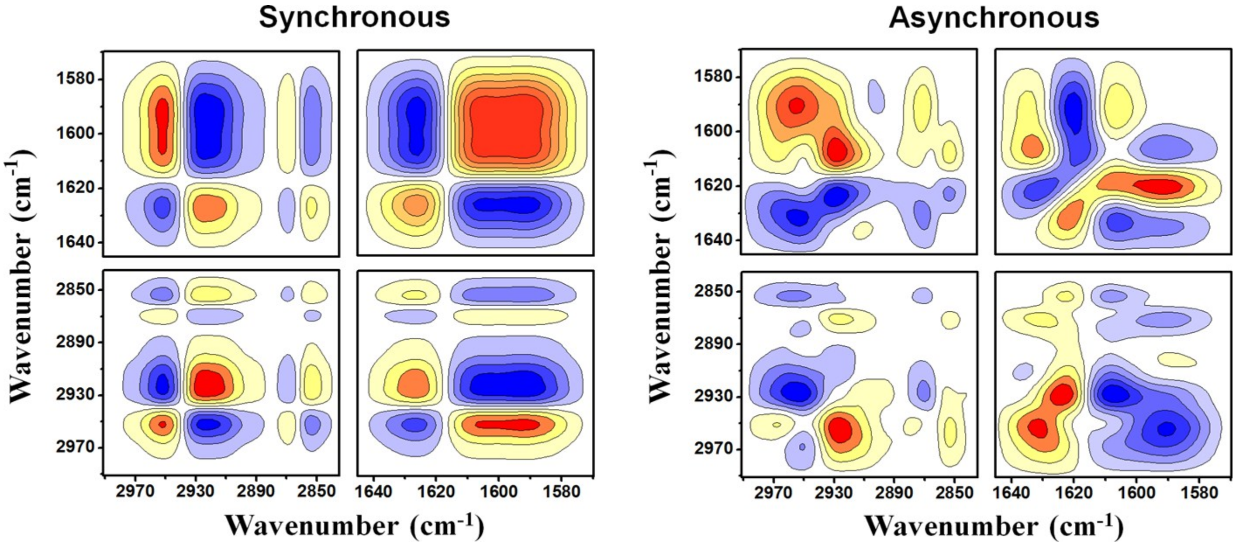

Figure S13. 2Dcos synchronous and asynchronous spectra of PVCL-0 during heating from 23 to 54 ^{o}C, respectively. Herein, warm colors (red and yellow) are defined as positive intensities, while cool colors (blue) are defined as negative ones.

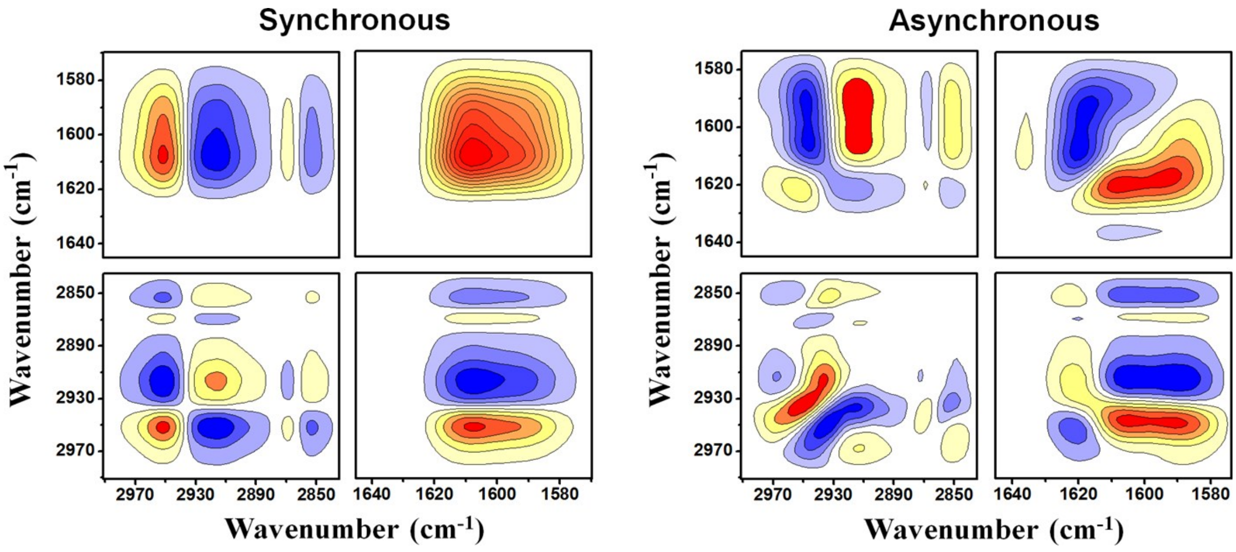

Figure S14. 2Dcos synchronous and asynchronous spectra of PVCL-50% during heating from 23 to 54 °C, respectively. Herein, warm colors (red and yellow) are defined as positive intensities, while cool colors (blue) are defined as negative ones.

Table S1. Tentative band assignments of PVCL-0 in D_2O according to the 2Dcos analysis.[7-9]

Wavenumber (cm^{-1})	Tentative Assignments
2968	$v_{as}(CH_2)$
2952	v_{as}(hydrated CH_2)
2924	v_{as}(dehydrated CH_2)
2877	$v_s(CH_2)$
2870	v_s(hydrated CH_2)
2852	v_s(dehydrated CH_2)
1632	v(free C=O)
1622	v(C=O···D-O-D···O=C)
1608	v(C=O···D-O-D)
1589	v(C=O···$(D\text{-}O\text{-}D)_2$)

Table S2. Tentative band assignments of PVCL-50% in D_2O according to the 2Dcos analysis.[7-9]

Wavenumber (cm^{-1})	Tentative Assignments
2968	$\nu_{as}(CH_2)$
2960	ν_{as}(CH_2, close to PCNDs)
2950	ν_{as}(hydrated CH_2)
2943	ν_{as}(hydrated CH_2, close to PCNDs)
2935	ν_{as}(dehydrated CH_2)
2914	ν_{as}(dehydrated CH_2, close to PCNDs)
2870	ν_s(hydrated CH_2)
2852	ν_s(dehydrated CH_2)
1635	ν(free C=O)
1618	$\nu(C{=}O\cdots D\text{-}O\text{-}D\cdots O{=}C)$
1606	$\nu(C{=}O\cdots D\text{-}O\text{-}D)$
1589	$\nu(C{=}O\cdots(D\text{-}O\text{-}D)_2)$

Notes and references

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