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

Supporting Information

Exploration of the unusual two-step volume phase transition of the poly(*N*-vinylcaprolactam-*co*-hydroxyethyl methacrylate) hydrogel

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1. Theory of the scaling-MW2D spectroscopy based on auto-correlation

$W(v, T)$ is a $M \times N$ spectral intensity matrix. The v and T are spectral variable (e.g., wavenumber) and perturbation variable (e.g., temperature), respectively.

$$W(v,T) = \begin{pmatrix} y(v,T_1) \\ \vdots \\ y(v,T_j) \\ \vdots \\ y(v,T_M) \end{pmatrix} \tag{1}$$

The reference spectrum and dynamic spectrum in the jth submatrix of $W(v, T)$:

$$\bar{y}(v) = \frac{1}{2m+1} \sum_{J=j-m}^{j+m} y(v,T_J) \tag{2}$$

$$\tilde{y}(v,T_J) = y(v,T_J) - \bar{y}(v) \tag{3}$$

where J corresponds to the index of rows. A mean-centered jth submatrix of $W(v, T)$ is obtained.

$$w_j(v,T) = \begin{pmatrix} \tilde{y}(v,T_{j-m}) \\ \vdots \\ \tilde{y}(v,T_j) \\ \vdots \\ \tilde{y}(v,T_{j+m}) \end{pmatrix} \tag{4}$$

The $w_j(v, T)$ has $2m+1$ rows which is called the window size. The index range of the perturbation variable I of $w_j(v, T)$ is from j-m to j+m.

The generalized synchronous 2D correlation spectra is calculated from $w_j(v, T)$:

$$\Phi_j(v_1,v_2) = \frac{1}{2m} \sum_{J=j-m}^{j+m} \tilde{y}(v_1,T_J) \cdot \tilde{y}(v_2,T_J) \tag{5}$$

For each window, the standard deviations of spectral intensities at v_1 and v_2 are defined as follows.

$$\sigma(v_1) = \sqrt{\Phi_j(v_1,v_1)} \tag{6}$$

$$\sigma(v_2) = \sqrt{\Phi_j(v_2, v_2)} \tag{7}$$

The correlation coefficient $\rho(v_1,v_2)$ is defined:

$$\rho(v_1, v_2) = \Phi_j(v_1, v_2) / [\sigma(v_1) \cdot \sigma(v_2)] \tag{8}$$

The scaled forms of the synchronous correlation spectrum in each window are defined:

$$\Phi_j(v_1, v_2)^{(Scaled)} = \Phi_j(v_1, v_2) \cdot [\sigma(v_1) \cdot \sigma(v_2)]^{-\alpha} \cdot \left|\rho(v_1, v_2)\right|^{\beta} \tag{9}$$

The constant α is the scaling factor, and β is correlation enhance factor. The value of α is limited to 0−1.0.

For scaling-MW2D based on auto-correlation, the each row of the correlation matrix of scaling-MW2D is directly extracted from a diagonal line of $\Phi_j^{(Scaled)}$ matrix, namely $v_1=v_2$. Thus, the auto-correlation scaling-MW2D can be described below.

$$\Phi_j(v_1, v_1)^{(Scaled)} = \Phi_j(v_1, v_1) \cdot [\sigma(v_1) \cdot \sigma(v_1)]^{-\alpha} \cdot \left|\rho(v_1, v_1)\right|^{\beta} \tag{10}$$

$$\rho(v_1, v_1) = \Phi_j(v_1, v_1) / [\sigma(v_1) \cdot \sigma(v_1)] = 1 \tag{11}$$

$$\Phi_j(v_1, v_1)^{(Scaled)} = [\Phi_j(v_1, v_1)]^{1-\alpha} \tag{12}$$

The auto-correlation scaling-MW2D correlation spectrum is gained *via* sliding window position from $j=1+m$ to $M-m$ and repeating calculations of equation (2)-(12) at each window.

2. Determination of the gel content

Gel content of the resultant PVCL-*co*-HEMA hydrogel was measured according to the following procedure:

The newly synthesized hydrogel was dried in a vacuum oven to the constant weight, and then the hydrogel was extracted with ethanol in a Soxhlet extractor for 48 h (90 °C). After that, the extraction product was dried again to constant weight, and the gel content was calculated as

$$W_{gel} = \frac{w_d}{w_i} \times 100\%$$

where w_d is the weight of dried gel after extraction, and w_i is the initial weight of the newly synthesized gel after drying.

The gel content of the resultant PVCL-*co*-HEMA hydrogel in our study was measured as 82.4 wt%.

3. Determination of the VCL weight fraction in the gel

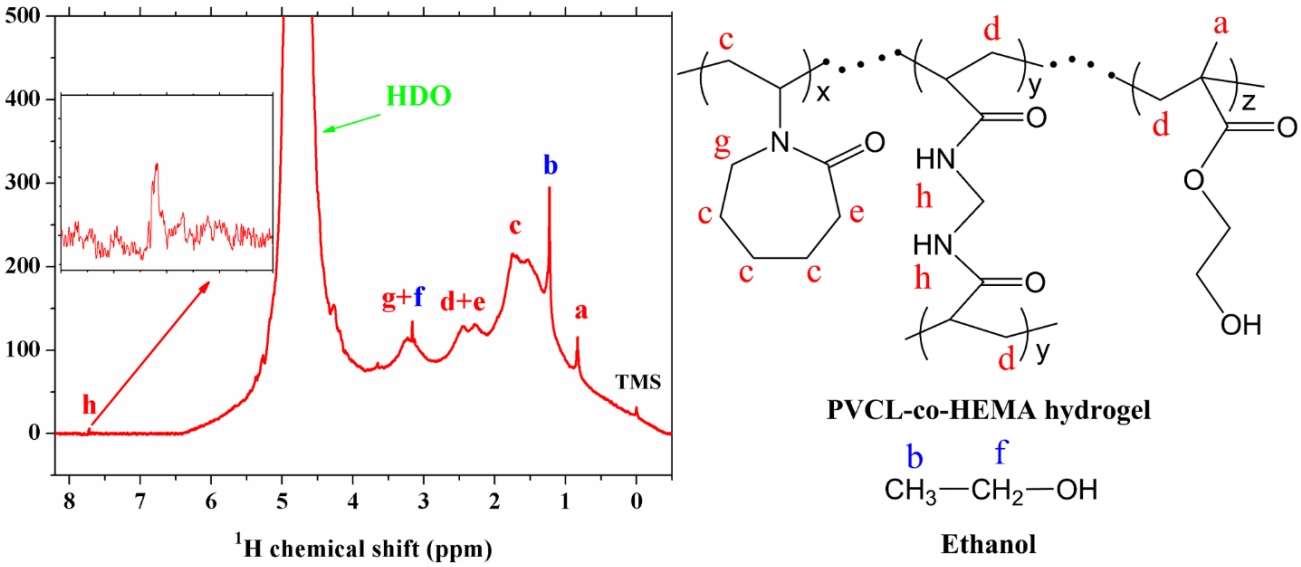

Fig. S1 ^{1}H HRMAS NMR spectrum of PVCL-*co*-HEMA hydrogel collected at 600.10 MHz.

Fig. S1 shows the ^{1}H HRMAS NMR spectrum of the swollen PVCL-*co*-HEMA hydrogel. The detailed assignments of the resonances in **Fig. S1** are summarized in **Table S1**. Based on the obtained ^{1}H HRMAS NMR spectrum, the molar fraction of VCL and HEMA in the resultant PVCL-*co*-HEMA hydrogel can be calculated:

$$x_{HEMA} = \left(\frac{A_a}{3}\right) \Big/ \left[\frac{A_c + A_{d+e} + A_{f+g} - \left(\frac{A_b}{3} \times 2\right) - A_b - \left(\frac{A_a}{3} \times 2\right) - \left(\frac{A_h}{2} \times 4\right)}{12} + \frac{A_a}{3}\right]$$

$$x_{VCL} = 1 - x_{HEMA}$$

where A represents the integral area.

Therefore, the weight fraction of VCL and HEMA in the gel can be obtained:

$$\omega_{VCL} = \frac{x_{VCL} \times M_{VCL}}{x_{VCL} \times M_{VCL} + x_{HEMA} \times M_{HEMA}} \times 100\%$$

$$\omega_{HEMA} = 1 - \omega_{VCL}$$

where M_{VCL} and M_{HEMA} represent the relative molecular mass of VCL and HEMA, respectively.

Based on these two equations, the molar fraction of VCL and HEMA in the resultant

PVCL-*co*-HEMA hydrogel was calculated as 88.6 % and 11.4 %, respectively. Besides, the weight fraction of VCL and HEMA in the gel was 89.3 % and 10.7 %, respectively.

Table S1. ^{1}H resonances of PVCL-*co*-HEMA hydrogel observed in **Fig. S1**

	^{1}H chemical shifts (ppm)	**Assignment**	**References**
a	0.83	–CH_3, PHEMA	1
b	1.23	–CH_3, ethanol	2, 3
c	1.63	–CH_2, PVCL	4, 5
d	2.29	–CH_2, PHEMA+BIS	1, 6
e	2.45	–CH_2, PVCL	4, 5
f	3.16	–CH_2, ethanol	2, 3
g	3.23	–CH_2, PVCL	4, 5
h	7.72	–NH, BIS	6
	4.75	HDO	7

4. Digital photographs of the Gel-2 hydrogel and the Gel-12 hydrogel

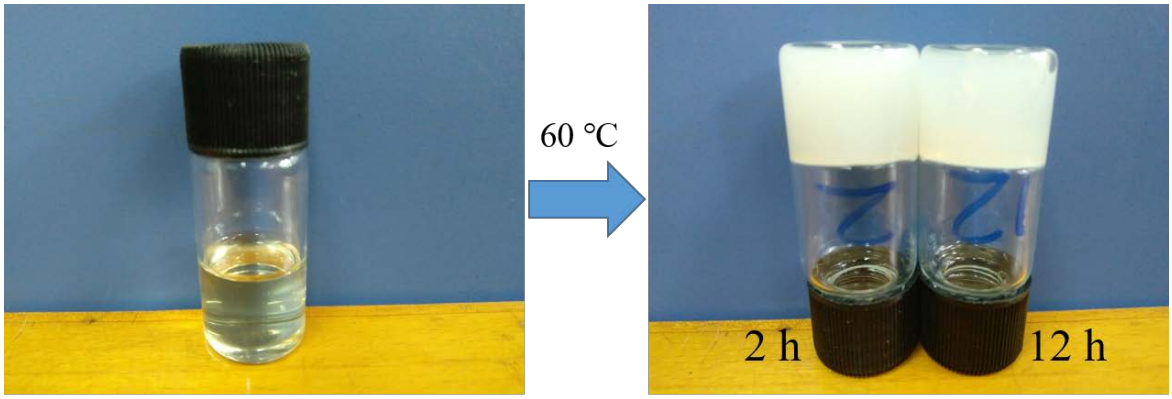

Fig. S2 Photographs of the monomer solution (left) and the resultant PVCL-*co*-HEMA hydrogels (right).

5. Second-derivative spectra in the region of C–H stretching vibration

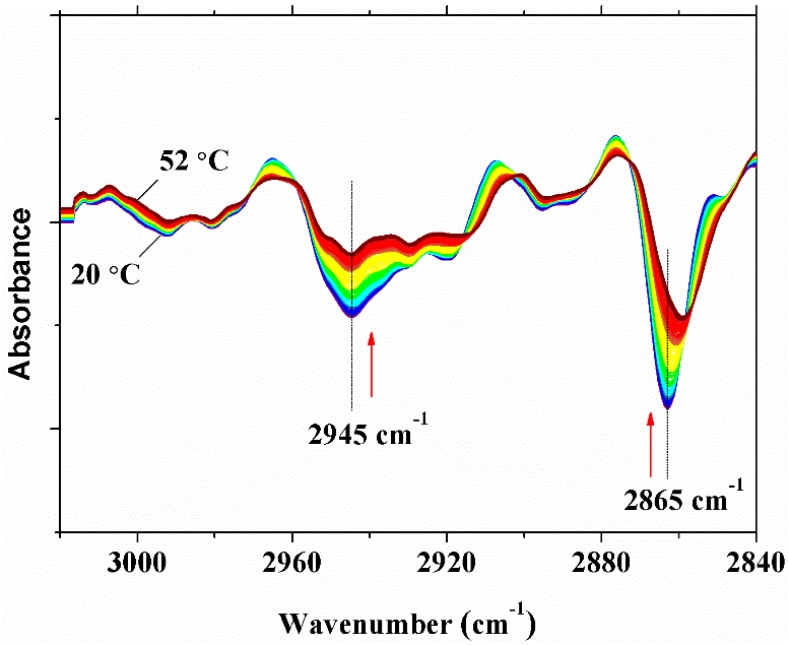

Fig. S3 Second-derivative FTIR spectra of the temperature-dependent FTIR spectra in the region of C−H stretching (3020−2840 cm^{-1}).

6. Generalized 2D correlation FTIR spectra

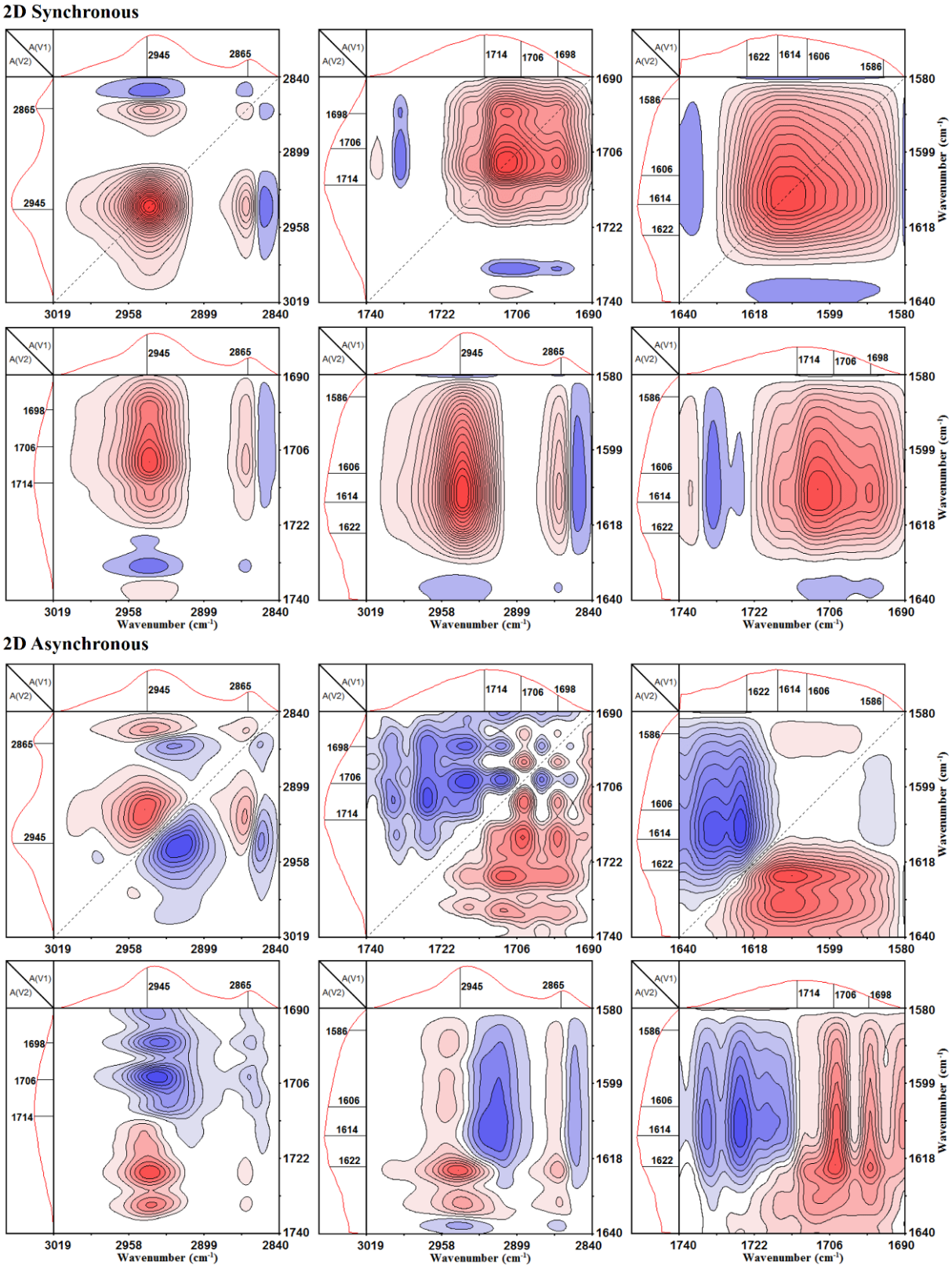

Fig. S4 Synchronous (top) and asynchronous (bottom) generalized 2D correlation FTIR spectra of PVCL-*co*-HEMA hydrogel calculated from the temperature-dependent FTIR spectra within the step I (25.0-32.3 °C). Herein, the red color is defined as positive correlation intensity, while blue color represents the negative correlation.

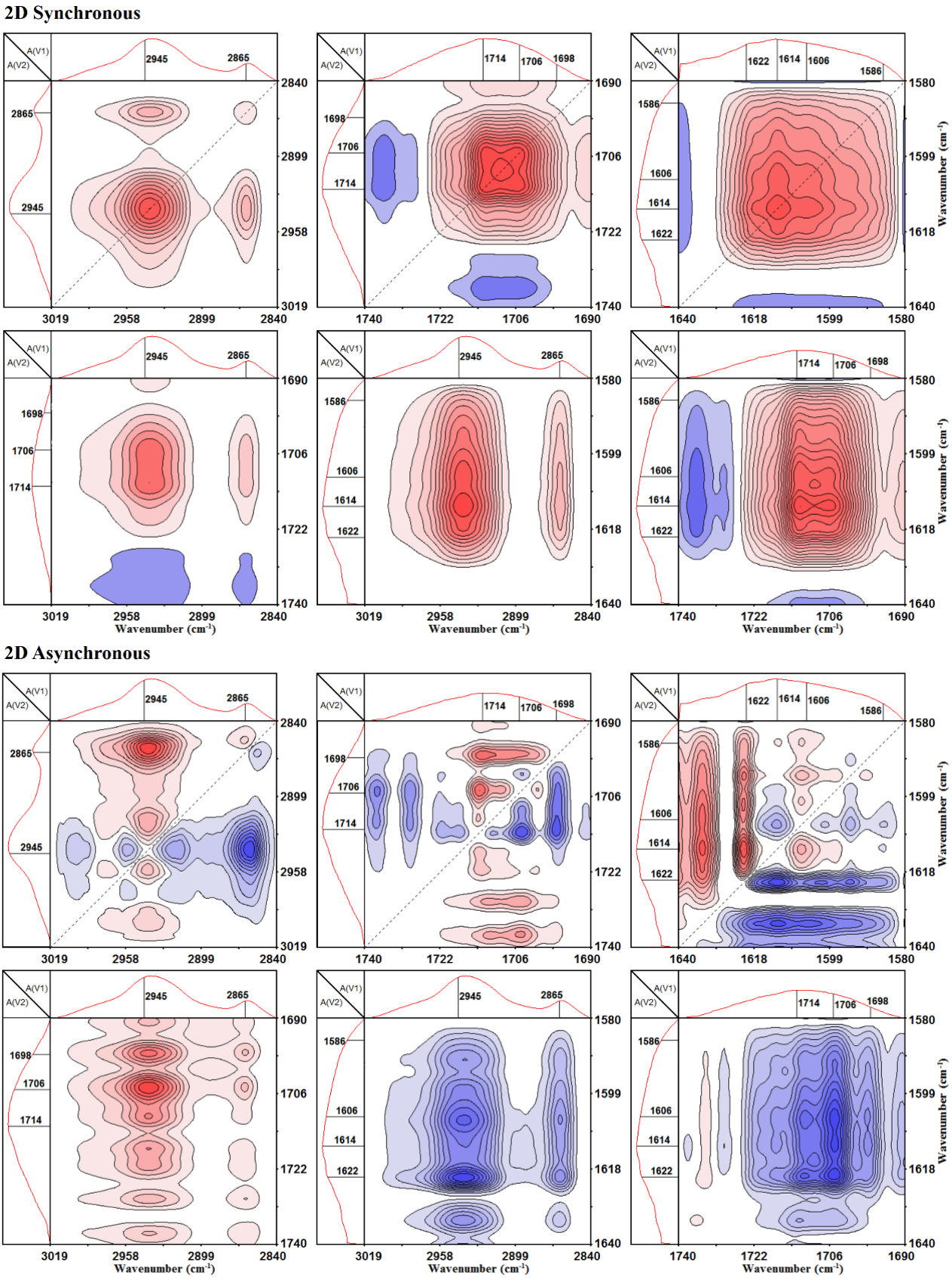

Fig. S5 Synchronous (top) and asynchronous (bottom) generalized 2D correlation FTIR spectra of PVCL-*co*-HEMA hydrogel calculated from the temperature-dependent FTIR spectra within the step II (32.3-46.8 °C).

Table S2. The sequential order of step I (25.0-32.3 °C) obtained from the synchronous and asynchronous generalized 2D correlation FTIR spectra of **Fig. S4**

Cross peaks (cm^{-1}, cm^{-1})	Synchronous	Asynchronous	Sequential order
(2945, 2865)	+	-	2865→2945
2865 cm^{-1} → 2945 cm^{-1}			
(1714, 1706)	+	-	1706→1714
(1714, 1698)	+	-	1698→1714
(1706, 1698)	+	+	1706→1698
1706 cm^{-1} → 1698 cm^{-1} → 1714 cm^{-1}			
(1622, 1614)	+	-	1614→1622
(1622, 1606)	+	-	1606→1622
(1622, 1586)	+	-	1586→1622
(1614, 1606)	+	-	1606→1614
(1614, 1586)	+	+	1614→1586
(1606, 1586)	+	+	1606→1586
1606 cm^{-1} → 1614 cm^{-1} → 1586 cm^{-1} → 1622 cm^{-1}			
(2945, 1714)	+	-	1714→2945
(2945, 1706)	+	-	1706→2945
(2945, 1698)	+	-	1698→2945
(2865, 1714)	+	-	1714→2865
(2865, 1706)	+	-	1706→2865
(2865, 1698)	+	-	1698→2865
1706 cm^{-1} → 1698 cm^{-1} → 1714 cm^{-1} → 2865 cm^{-1} → 2945 cm^{-1}			
(2945, 1622)	+	+	2945→1622
(2945, 1614)	+	+	2945→1614
(2945, 1606)	+	+	2945→1606
(2945, 1586)	+	+	2945→1586
(2865, 1622)	+	+	2865→1622
(2865, 1614)	+	+	2865→1614
(2865, 1606)	+	+	2865→1606
(2865, 1586)	+	+	2865→1586
2865 cm^{-1} → 2945 cm^{-1} →1606 cm^{-1} → 1614 cm^{-1} → 1586 cm^{-1} → 1622 cm^{-1}			
(1714, 1622)	+	+	1714→1622
(1714, 1614)	+	+	1714→1614
(1714, 1606)	+	+	1714→1606
(1714, 1586)	+	+	1714→1586
(1706, 1622)	+	+	1706→1622
(1706, 1614)	+	+	1706→1614
(1706, 1606)	+	+	1706→1606
(1706, 1586)	+	+	1706→1586
(1698, 1622)	+	+	1698→1622
(1698, 1614)	+	+	1698→1614
(1698, 1606)	+	+	1698→1606
(1698, 1586)	+	+	1698→1586

1706 cm^{-1} → 1698 cm^{-1} → 1714 cm^{-1}→1606 cm^{-1} → 1614 cm^{-1} → 1586 cm^{-1} → 1622 cm^{-1}
1706 cm^{-1} → 1698 cm^{-1} → 1714 cm^{-1}→2865 cm^{-1} → 2945 cm^{-1} →1606 cm^{-1} → 1614 cm^{-1} → 1586 cm^{-1} → 1622 cm^{-1}

Table S3. The sequential order of step II (32.3-46.8 °C) obtained from the synchronous and asynchronous generalized 2D correlation FTIR spectra of **Fig. S5**

Cross peaks (cm^{-1}, cm^{-1})	**Synchronous**	**Asynchronous**	**Sequential order**
(2945, 2865)	+	+	2945→2865
2945 cm^{-1} → 2865 cm^{-1}			
(1714, 1706)	+	+	1714→1706
(1714, 1698)	+	+	1714→1698
(1706, 1698)	+	+	1706→1698
1714 cm^{-1} → 1706 cm^{-1} → 1698 cm^{-1}			
(1622, 1614)	+	+	1622→1614
(1622, 1606)	+	+	1622→1606
(1622, 1586)	+	+	1622→1586
(1614, 1606)	+	-	1606→1614
(1614, 1586)	+	+	1614→1586
(1606, 1586)	+	+	1606→1586
1622 cm^{-1} → 1606 cm^{-1} → 1614 cm^{-1} → 1586 cm^{-1}			
(2945, 1714)	+	+	2945→1714
(2945, 1706)	+	+	2945→1706
(2945, 1698)	+	+	2945→1698
(2865, 1714)	+	+	2865→1714
(2865, 1706)	+	+	2865→1706
(2865, 1698)	+	+	2865→1698
2945 cm^{-1} → 2865 cm^{-1} →1714 cm^{-1} → 1706 cm^{-1} → 1698 cm^{-1}			
(2945, 1622)	+	-	1622→2945
(2945, 1614)	+	-	1614→2945
(2945, 1606)	+	-	1606→2945
(2945, 1586)	+	-	1586→2945
(2865, 1622)	+	-	1622→2865
(2865, 1614)	+	-	1614→2865
(2865, 1606)	+	-	1606→2865
(2865, 1586)	+	-	1586→2865
1622 cm^{-1} → 1606 cm^{-1} → 1614 cm^{-1} → 1586 cm^{-1}→ 2945 cm^{-1} → 2865 cm^{-1}			
(1714, 1622)	+	-	1622→1714
(1714, 1614)	+	-	1614→1714
(1714, 1606)	+	-	1606→1714
(1714, 1586)	+	-	1586→1714
(1706, 1622)	+	-	1622→1706
(1706, 1614)	+	-	1614→1706
(1706, 1606)	+	-	1606→1706
(1706, 1586)	+	-	1586→1706

(1698, 1622)	+	-	1622→1698
(1698, 1614)	+	-	1614→1698
(1698, 1606)	+	-	1606→1698
(1698, 1586)	+	-	1586→1698
1622 cm^{-1} → 1606 cm^{-1} → 1614 cm^{-1} → 1586 cm^{-1} →1714 cm^{-1} → 1706 cm^{-1} → 1698 cm^{-1}			
1622 cm^{-1} → 1606 cm^{-1} → 1614 cm^{-1} → 1586 cm^{-1} →2945 cm^{-1} → 2865 cm^{-1}→1714 cm^{-1} → 1706 cm^{-1} → 1698 cm^{-1}			

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