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

Supporting Information

Two-step volume phase transition mechanism of poly(N-vinylcaprolactam) hydrogel online tracked by two-dimensional correlation spectroscopy

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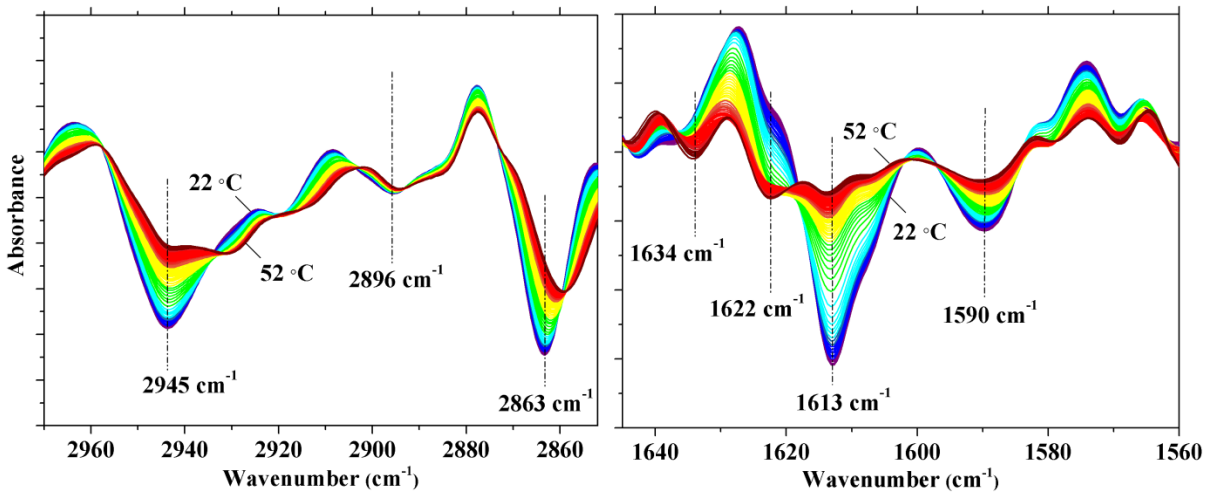

Figure S1. Second derivative FTIR spectra (2970-2840 cm^{-1} and 1645-1560 cm^{-1}) of temperature-dependent FTIR spectra of PVCL hydrogel in D_2O upon heating from 22 °C to 52 °C.

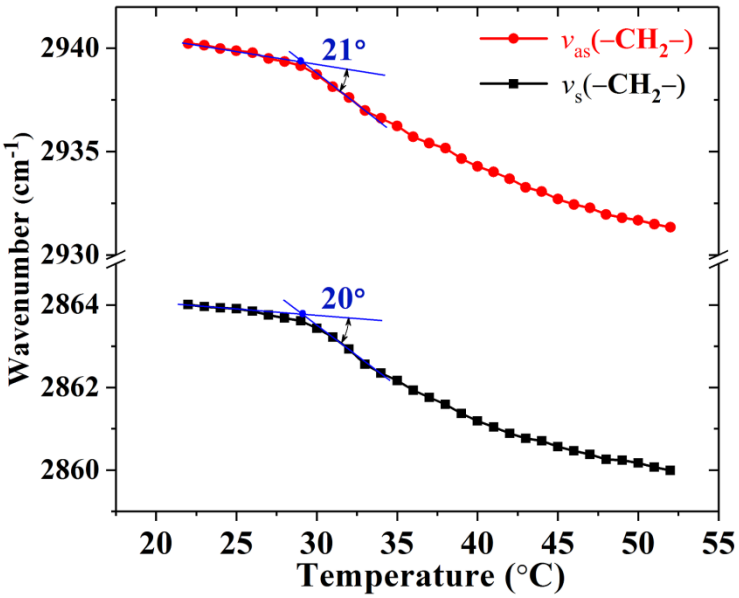

Figure S2. Intersection angle between the tangent lines of the curve on both sides of the turning point for the wavenumber shift curves of $\nu_{as}(-CH_2)$ and $\nu_s(-CH_2)$ of PVCL hydrogel.

The meaning of the continuity of curve change is that its intensity change is gradual (smooth), rather than a cliff-like abrupt change (suddenly dropping). This continuity can be quantitatively expressed by the intersection angle between the tangent lines of the curve on both sides of the turning point. In general, a smaller intersection angle means the curve change is more continuous.

For PVCL hydrogel, the results shows that these intersection angles of the wavenumber shift curves of $\nu_{as}(-CH_2)$ and $\nu_s(-CH_2)$ are determined as 21° and 20°, respectively. For

PVCL aqueous solution, we directly measured this angle from Ref. 23 by a protractor, and the intersection angle between the tangent lines of the wavenumber shift curves of $\nu_{as}(-CH_2)$ and $\nu_s(-CH_2)$ are 40° and 41°, respectively. Through this quantitative way, it is found that the wavenumber change of PVCL hydrogel is more continuous (or smooth) than that of PVCL aqueous solution.

Table S1. The sequential order of step I (29.0-35.7 °C) gained from the synchronous and asynchronous FTIR spectra in **Fig. 5**.

Cross peaks (cm^{-1}, cm^{-1})	**Synchronous**	**Asynchronous**	**Sequential order**
(2945, 2867)	+	-	2867→2945
2867 cm^{-1} → 2945 cm^{-1}			
(1620, 1610)	+	-	1610→1620
(1620, 1590)	+	-	1590→1620
(1610, 1590)	+	-	1590→1610
1590 cm^{-1} → 1610 cm^{-1} → 1620 cm^{-1}			
(2945, 1620)	+	-	1620→2945
(2945, 1610)	+	-	1610→2945
(2945, 1590)	+	-	1590→2945
(2867, 1620)	+	-	1620→2867
(2867, 1610)	+	-	1610→2867
(2867, 1590)	+	-	1590→2867
1590 cm^{-1} → 1610 cm^{-1} → 1620 cm^{-1} →2867 cm^{-1}→2945 cm^{-1}			

Table S2. The sequential order of step II (35.7-47.5 °C) gained from the synchronous and asynchronous FTIR spectra in **Fig. 6**.

Cross peaks (cm^{-1}, cm^{-1})	**Synchronous**	**Asynchronous**	**Sequential order**
(2945, 2898)	-	+	2898→2945
(2945, 2867)	+	-	2867→2945
(2898, 2867)	-	-	2898→2867
2898 cm^{-1} → 2867 cm^{-1}→ 2945 cm^{-1}			
(1620, 1610)	+	+	1620→1610
(1620, 1590)	+	+	1620→1590
(1610, 1590)	+	+	1610→1590
1620 cm^{-1} → 1610 cm^{-1} → 1590 cm^{-1}			
(2945, 1620)	+	-	1620→2945
(2945, 1610)	+	-	1610→2945
(2945, 1590)	+	+	2945→1590
(2898, 1620)	-	-	2898→1620
(2898, 1610)	-	-	2898→1610
(2898, 1590)	-	-	2898→1590
(2867, 1620)	+	+	2867→1620
(2867, 1610)	+	+	2867→1610
(2867, 1590)	+	+	2867→1590
2898 cm^{-1} → 2867 cm^{-1} → 1620 cm^{-1} → 1610 cm^{-1} → 2945 cm^{-1} → 1590 cm^{-1}			