Electronic Supporting Information for

Detailed molecular movements during poly(L-lactic acid) cold-crystallization investigated by FTIR spectroscopy combined with two-dimensional correlation analysis

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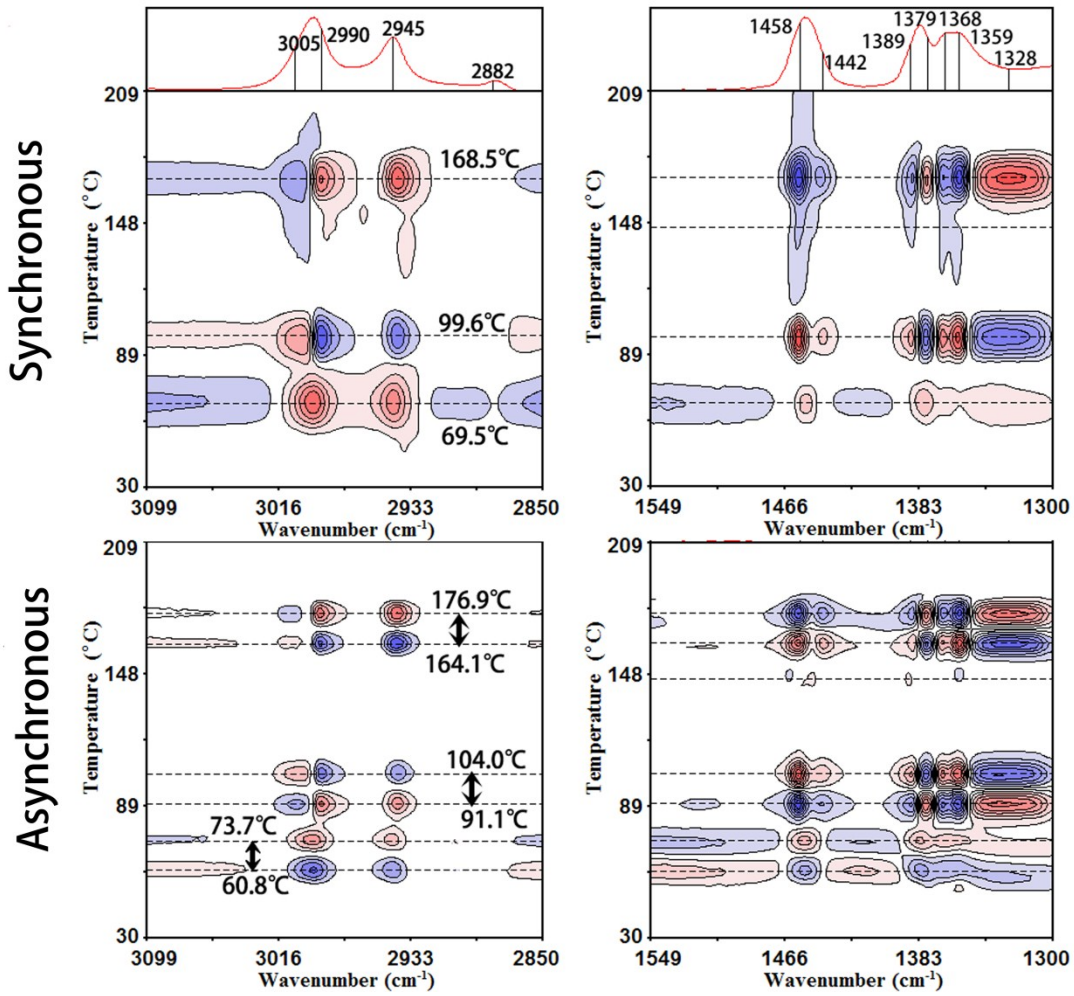

Figure S1: PCMW2D correlation FTIR spectra of PLLA in the regions of 3099-2850 cm^{-1} and 1549-1300 cm^{-1} calculated from the temperature-dependent spectroscopy.

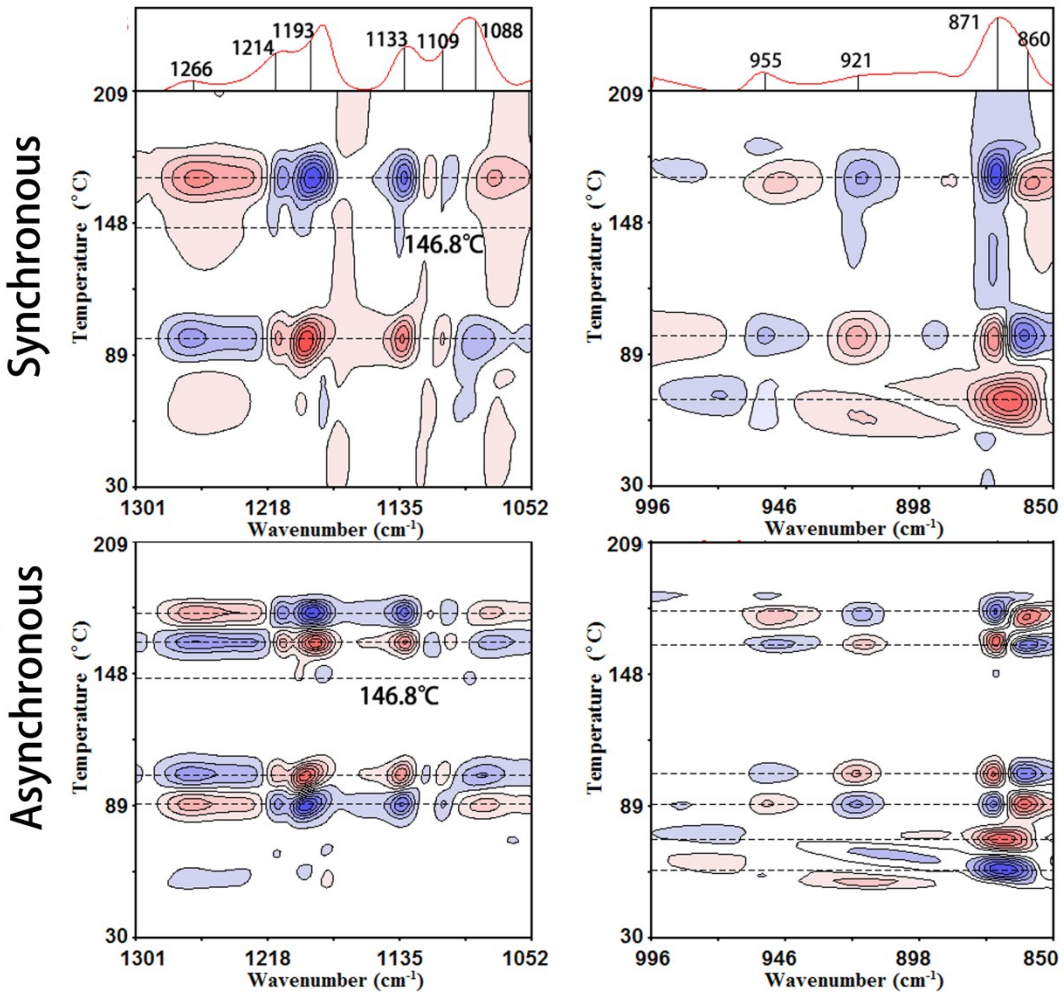

Figure S2: PCMW2D correlation FTIR spectra of PLLA in the regions of 1301-1052 cm^{-1} and 996-850 cm^{-1} calculated from the temperature-dependent spectroscopy.

To investigate the crystalline degree depending on the increasing temperature, the crystalline degree could be calculated from the following equation using the DSC data.

$$X_c = \frac{\Delta H_m}{\Delta H_m^*} \qquad \text{(S1)}$$

where X_c is the crystalline degree of PLLA, ΔH_m is the enthalpy for melting of PLLA and ΔH_m^* denotes the theoretical melting enthalpy for 100% crystalline PLLA (93.7 J/g)[S1, S2]. To determine the original crystalline degree of the PLLA sample, the extra heat absorbed by cold-crystallization process has to be subtracted from the total melting enthalpy. Therefore, the

modified equation is exhibited as follows:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^*} \quad \text{(S2)}$$

where ΔH_{cc} stands for the enthalpy of PLLA cold-crystallization. And the original crystalline degree of PLLA sample (X_c) with the value of 26.8% is calculated.

As shown in DSC curve (Fig. 4), the cold-crystallization of PLLA is observed in the temperature region of 83.5-111.3 ^oC. Before the cold-crystallization process, the crystalline degree of the sample almost remains the same, although the relaxation process takes place in this temperature range [S1, S3, S4]. Thus, the crystalline degree of the sample maintains 26.8% at the temperature lower than 83.5 ^oC.

The heating rate of DSC is 5 ^oC/min, so the equation can be written as follows:

$$T = 20^oC + \frac{5}{60}t \quad \text{(S3)}$$

When the temperature higher than 83.5 ^oC[S1, S5-S7],

$$X_c(T) = 26.8\% + \frac{-\int_{83.5}^{T} \frac{dH(T)}{dT} dT}{\Delta H_m^*} \quad \text{(S4)}$$

where $X_c(T)$ is the crystalline degree of PLLA at the temperature T.

The crystalline degree of PLLA as a function of temperature calculated from DSC data is shown in Figure S3.

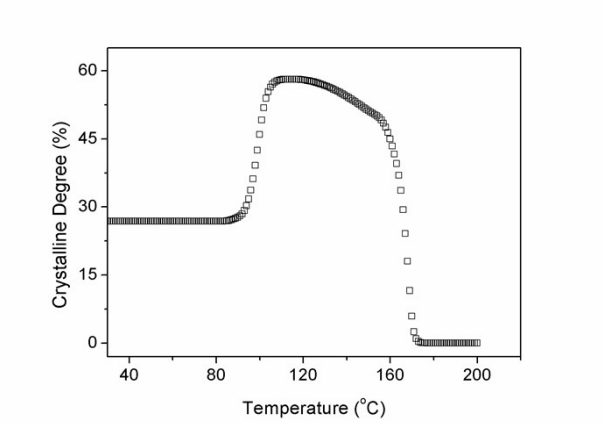

Figure S3: The crystalline degree of PLLA as a function of temperature calculated from DSC curve.

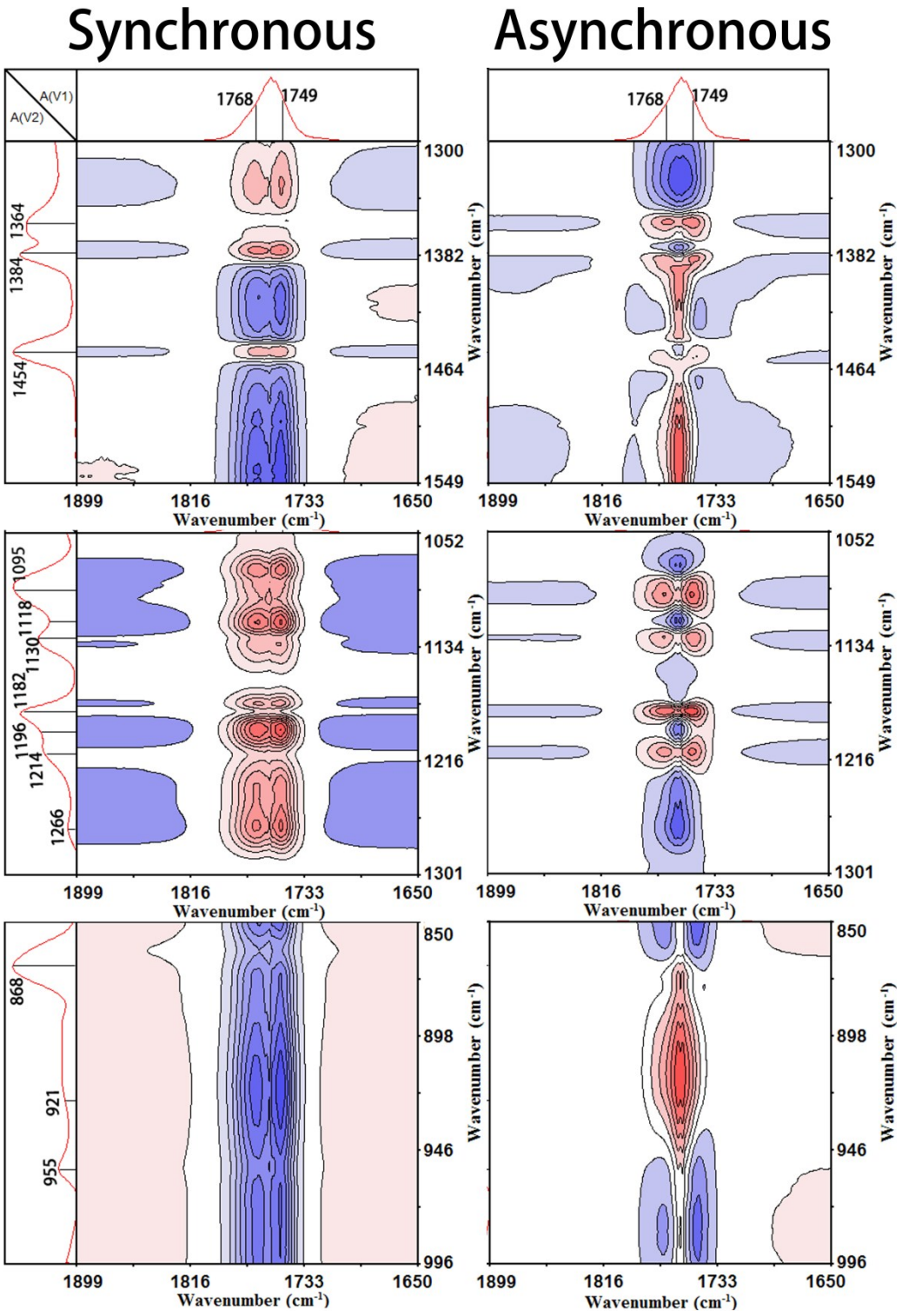

Figure S4: Synchronous (left) and asynchronous (right) 2D correlation FTIR spectra calculated from the temperature-dependent spectra of Process I (60.8-73.7 ^{o}C) in the regions 1899-1650 cm^{-1} vs. 1549-1300 cm^{-1}, 1899-1650 cm^{-1} vs. 1301-1052 cm^{-1}, and 1899-1650 cm^{-1} vs. 996-850 cm^{-1}.

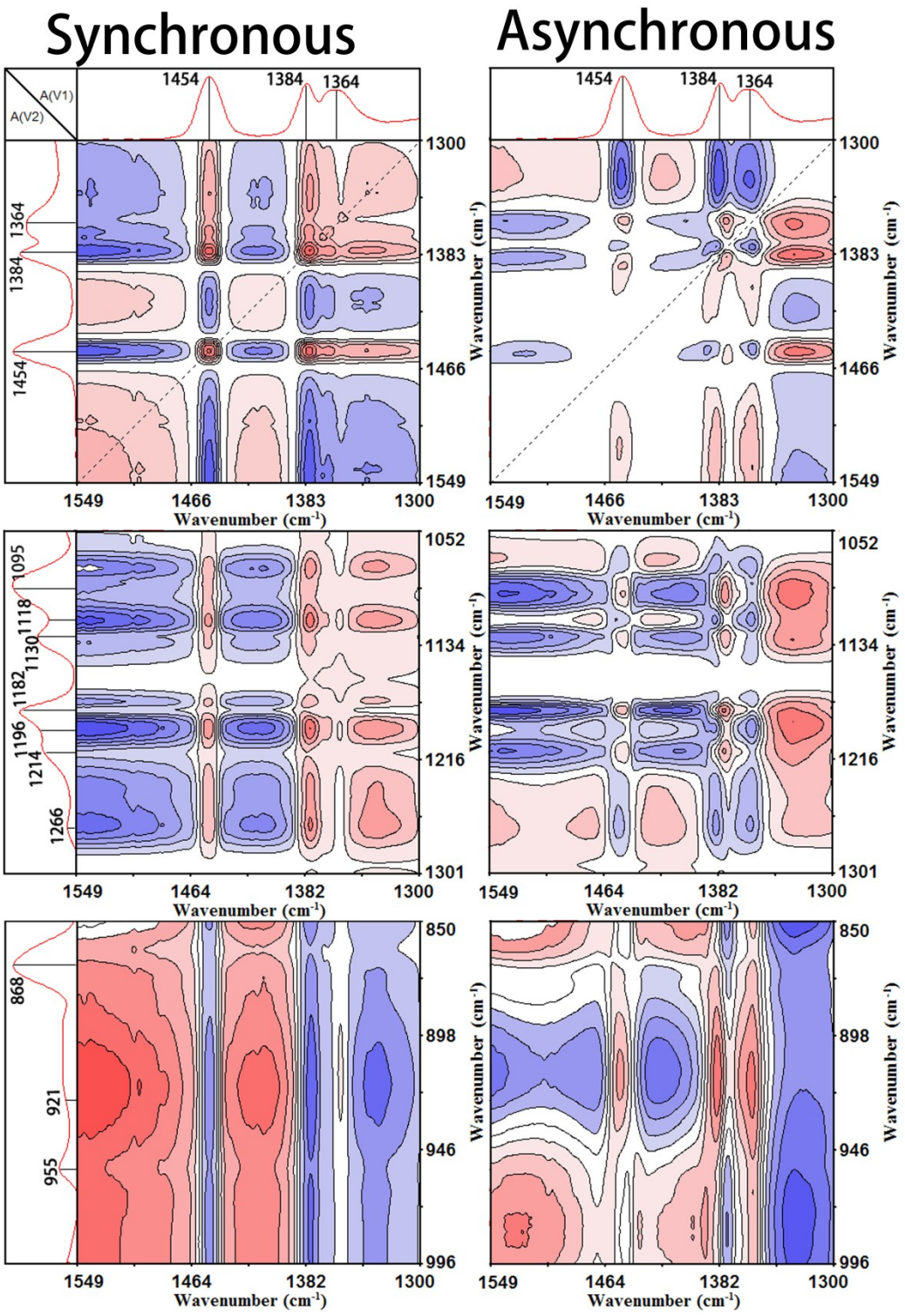

Figure S5: Synchronous (left) and asynchronous (right) 2D correlation FTIR spectra calculated from the temperature-dependent spectra of Process I (60.8-73.7 ^{o}C) in the regions 1549-1300 cm^{-1} vs. 1549-1300 cm^{-1}, 1549-1300 cm^{-1} vs. 1301-1052 cm^{-1}, and 1549-1300 cm^{-1} vs. 996-850 cm^{-1}.

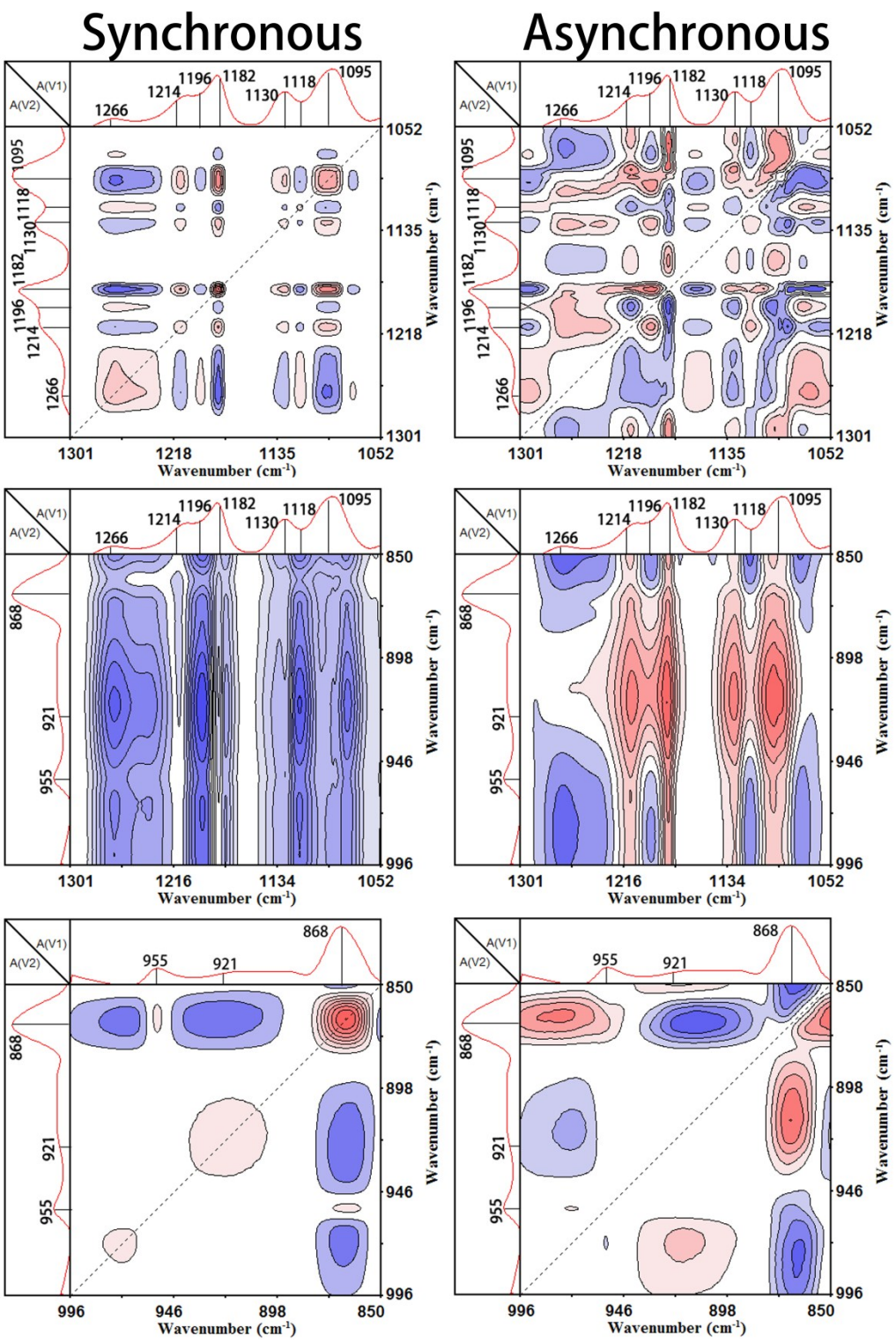

Figure S6: Synchronous (left) and asynchronous (right) 2D correlation FTIR spectra calculated from the temperature-dependent spectra of Process I (60.8-73.7 ^{o}C) in the regions 1301-1052 cm^{-1} vs. 1301-1052 cm^{-1}, 1301-1052 cm^{-1} vs. 996-850 cm^{-1}, and 996-850 cm^{-1} vs. 996-850 cm^{-1}.

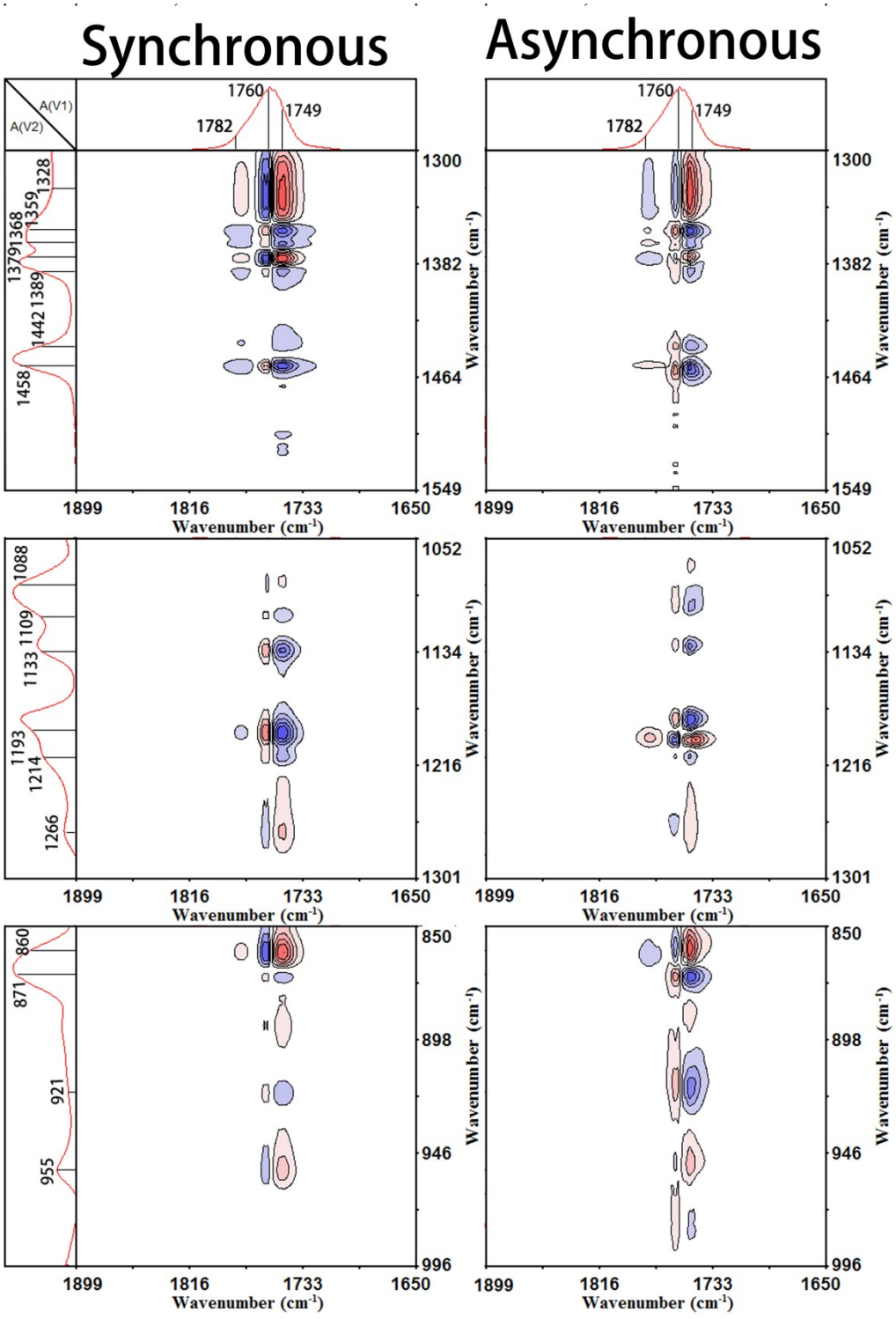

Figure S7: Synchronous (left) and asynchronous (right) 2D correlation FTIR spectra calculated from the temperature-dependent spectra of Process I (91.1-104.0 ^{o}C) in the regions 1899-1650 cm^{-1} vs. 1549-1300 cm^{-1}, 1899-1650 cm^{-1} vs. 1301-1052 cm^{-1}, and 1899-1650 cm^{-1} vs. 996-850 cm^{-1}.

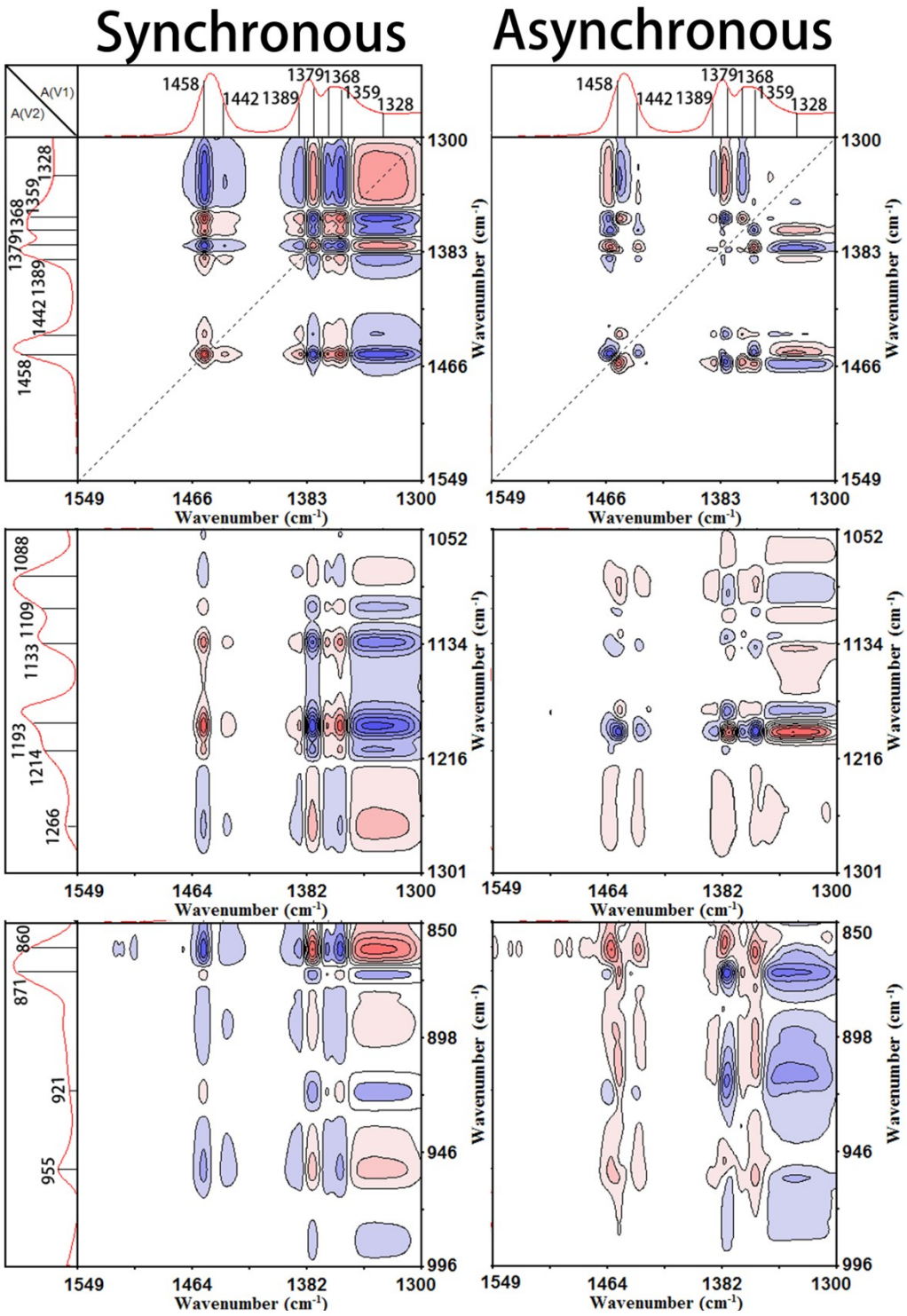

Figure S8: Synchronous (left) and asynchronous (right) 2D correlation FTIR spectra calculated from the temperature-dependent spectra of Process II (91.1-104.0 ^{o}C) in the regions 1549-1300 cm^{-1} vs. 1549-1300 cm^{-1}, 1549-1300 cm^{-1} vs. 1301-1052 cm^{-1}, and 1549-1300 cm^{-1} vs. 996-850 cm^{-1}.

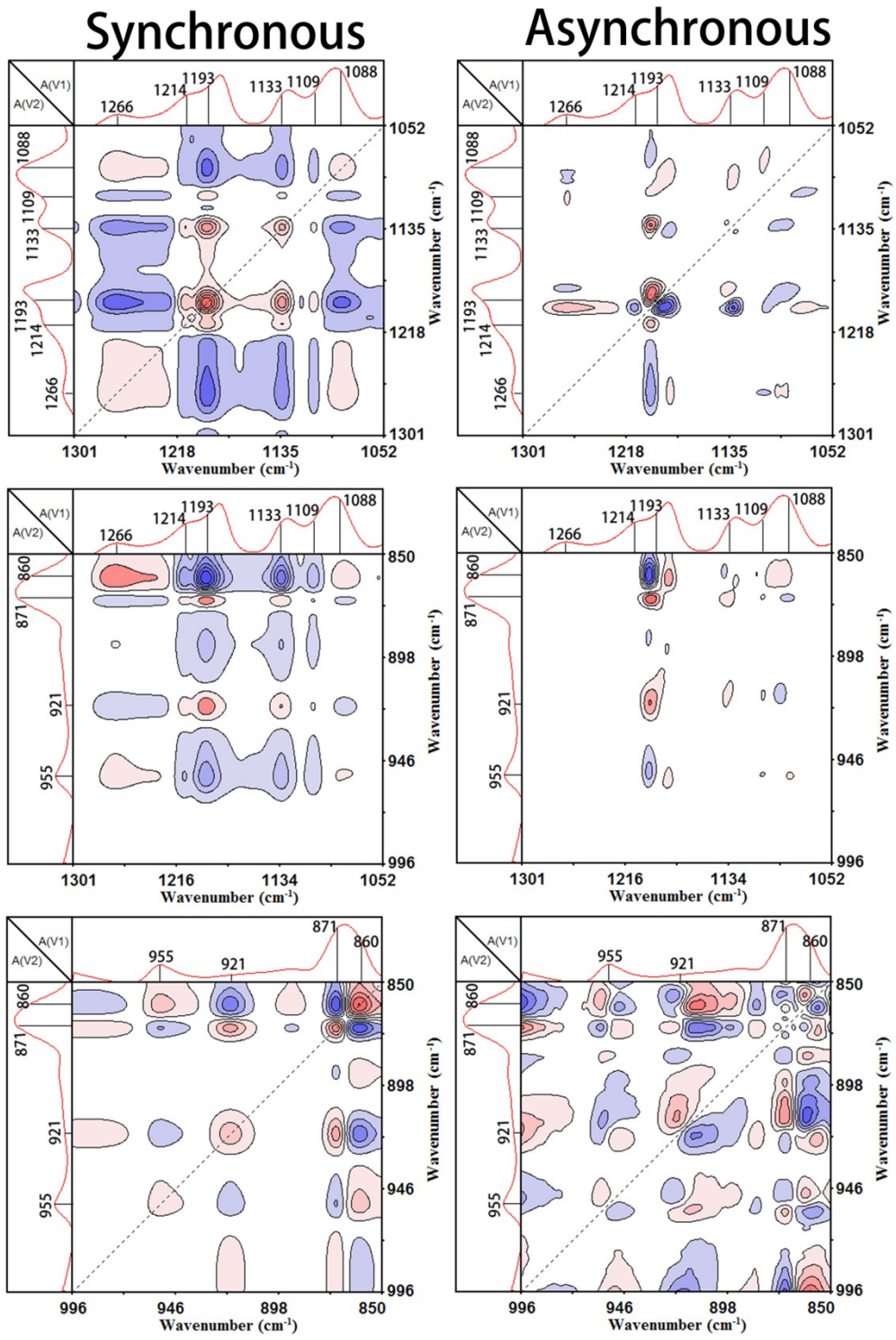

Figure S9: Synchronous (left) and asynchronous (right) 2D correlation FTIR spectra calculated from the temperature-dependent spectra of Process II (91.1-104.0 ^{o}C) in the regions 1301-1052 cm^{-1} vs. 1301-1052 cm^{-1}, 1301-1052 cm^{-1} vs. 996-850 cm^{-1}, and 996-850 cm^{-1} vs. 996-850 cm^{-1}.

References:

[S1] L. Qin, J. Qiu, M. Liu, S. Ding, L. Shao, S. Lv, G. Zhang, Y. Zhao and X. Fu, Chem. Eng. J., 2011, **166**, 772-778.

[S2] B. Xue, D. Guo and J. Bao, J. Polym. Eng., 2016, **36**, 381-390.

[S3] I. M. Hodge, Macromolecules, 1983, **16**, 898-902.

[S4] A. R. Berens and I. M. Hodge, Macromolecules, 1982, **15**, 756-761.

[S5] P. Song, G. Chen, Z. Wei, Y. Chang, W. Zhang and J. Ling, Polymer, 2012, **53**, 4300-4309.

[S6] L. Wen and Z. Xin, Chinese J. Chem. Eng., 2010, **18**, 899-904.

[S7] H. Xiao, D. Guo and J. Bao, J. Appl. Polym. Sci., 2015, **132**, 41454-41463.