Supporting Information

Biomimetic Tough Self-Healing Polymers Enhanced by Crystallization Nanostructures

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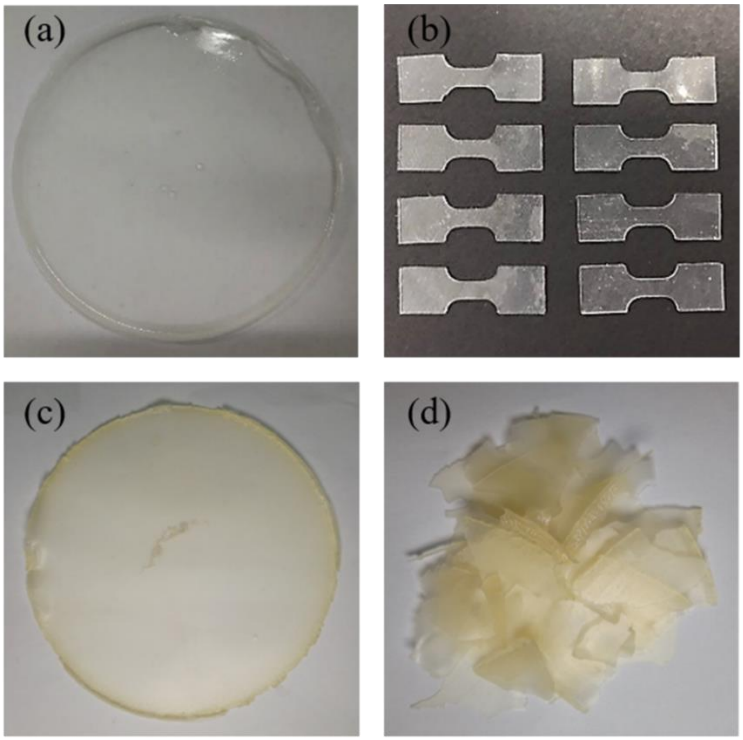

Figure S1. Representative images of solution-cast specimens. (a, b) SP-PLLA5; (c, d) SP-PLLA50. The SP-PLLA5 film was flexible and could be cut into dumbbell-shaped specimens (b), while the SP-PLLA50 was too brittle to form a film (d).

Table S1. Band assignments for the FT-IR spectroscopy of PLLA.

Assignment	Wavenumber (cm^{-1})
νC=O	1747
$\delta_{as}CH_3$	1456
$\delta_{s}CH_3$	1385 ~ 1360
ν_{as}C-O-C+ $r_{as}CH_3$	1211 ~ 1180
$r_{as}CH_3$	1128
νC-CH_3	1043

Subscript as=asymmetric, subscript s=symmetric.

The PLLA polymer was characterized by FT-IR spectroscopy and the adsorption peaks were summarized in Table S1. The peak at 1747 cm-1 is assigned to C=O stretching vibrations. The peaks at 1456, 1385 ~ 1360 cm-1 is attributed to the CH3 asymmetric and symmetric stretching vibrations.[1]

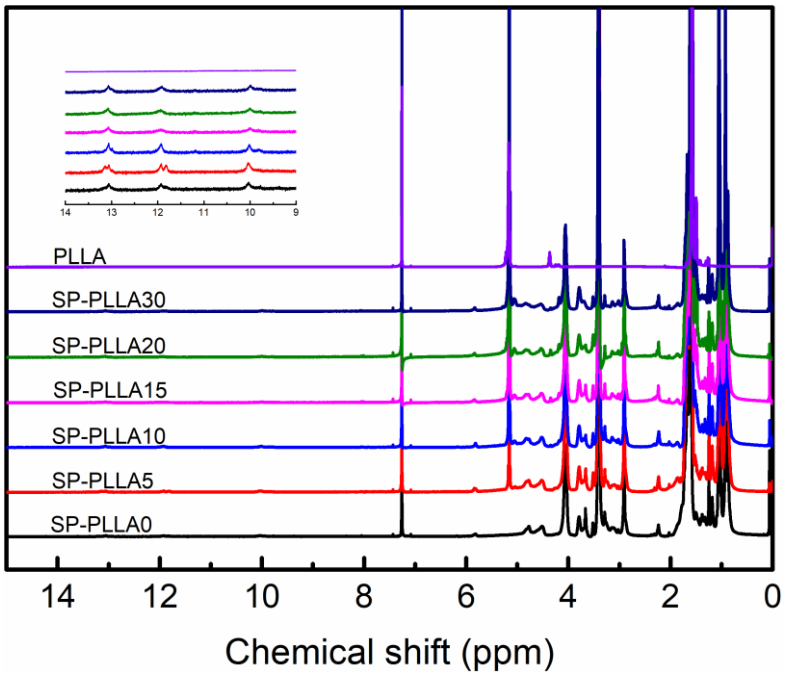

Figure S2. ^{1}H NMR spectra for the PLLA and SP-PLLA.

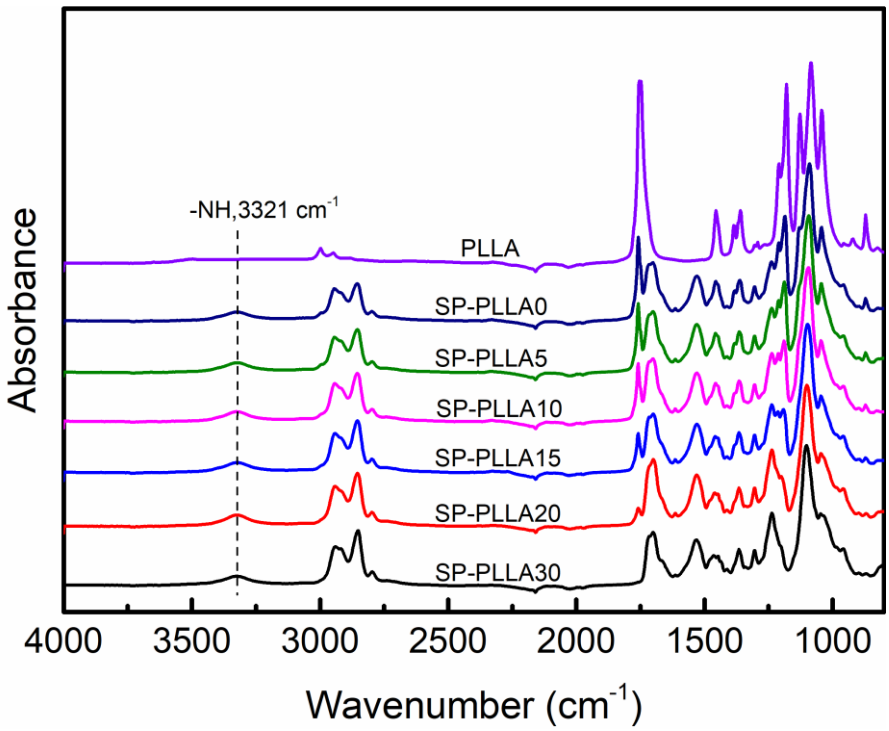

Figure S3. FT-IR spectra for PLLA and SP-PLLA.

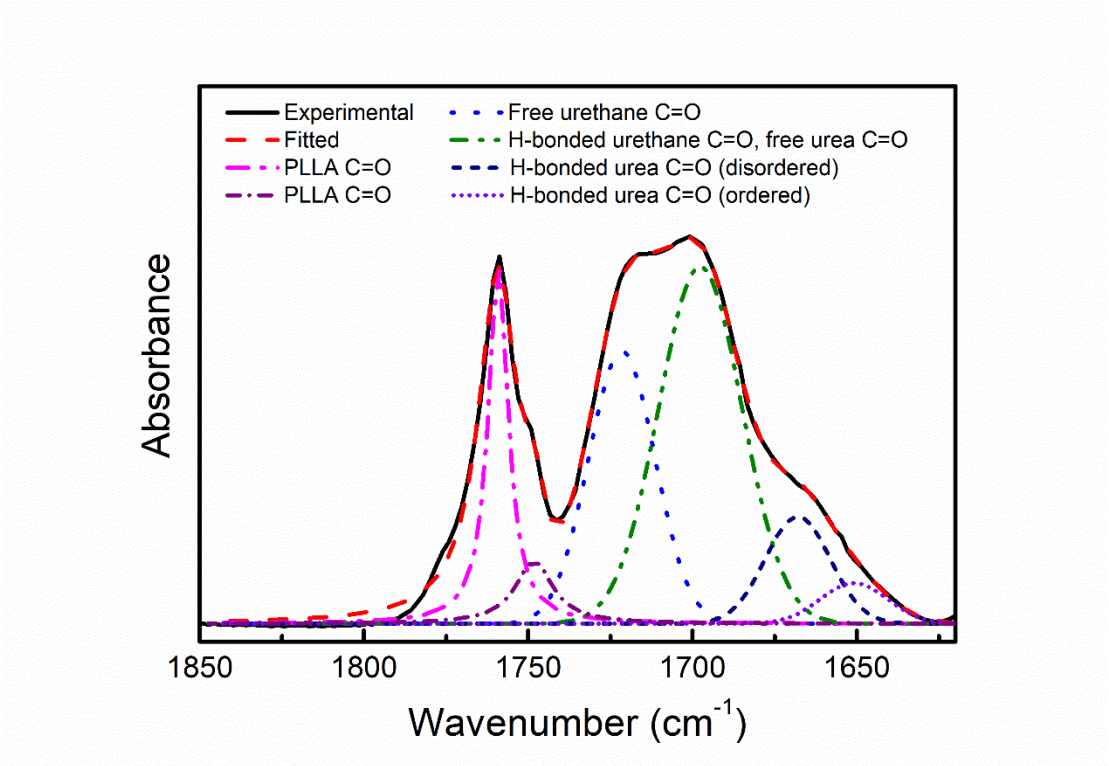

Figure S4. Attribution of the FT-IR spectra for C=O groups in the polyurethane chain by peak fitting[2-3].

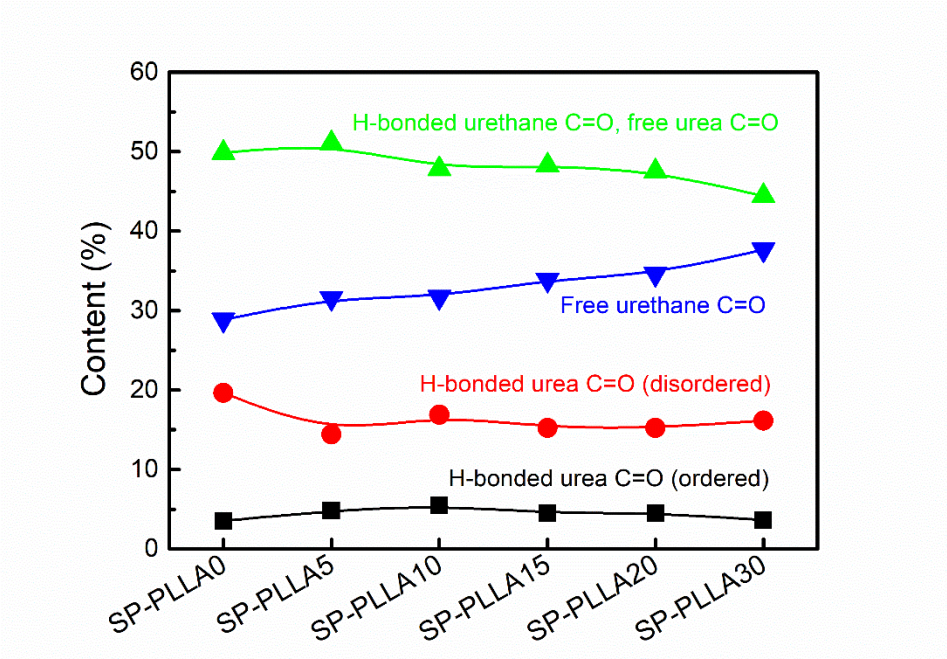

Figure S5. Contents of H-bonded and free C=O in urethane and urea structure of different SP-PLLA samples.

Table S2. Thermal properties of SP-PLLA obtained from the DSC heating scan.

Sample	T_{cc} (ºC)
SP-PLLA0	--
SP-PLLA5	--
SP-PLLA10	105.1
SP-PLLA15	102.0
SP-PLLA20	101.8
SP-PLLA30	101.0

T_{cc} = cold crystallization temperature.

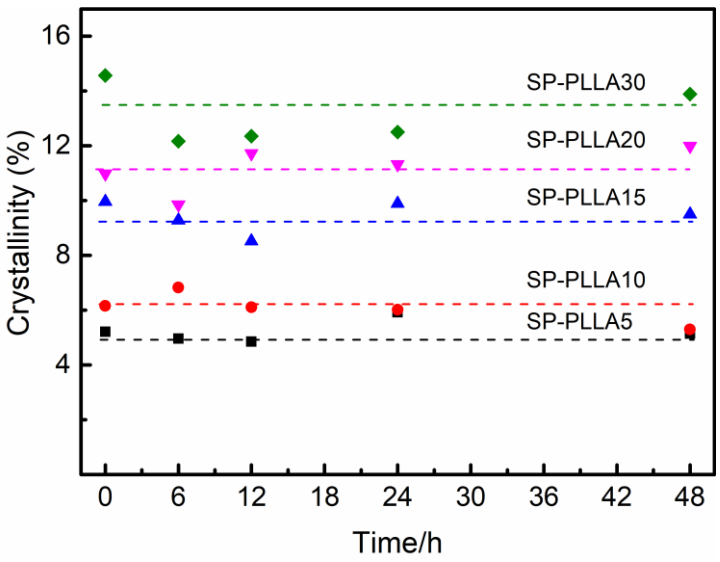

Figure S6. The calculated crystallinity obtained from XRD curves of SP-PLLA treated at 80 ºC for different time.

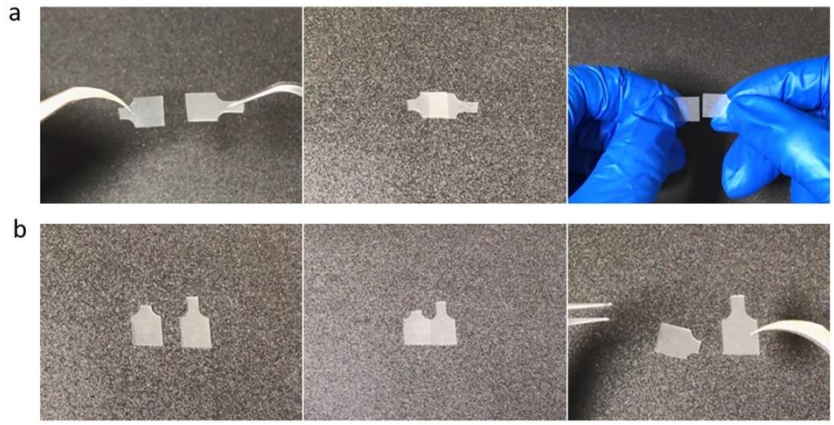

Figure S7. (a) The two fresh samples were overlapped partially, put together at 80 ºC for 5 min, stretched and then broke out easily. (b) The two fresh samples were contacted by the side surfaces, stayed at 80 ºC for 5 min, stretched and disconnected immediately.

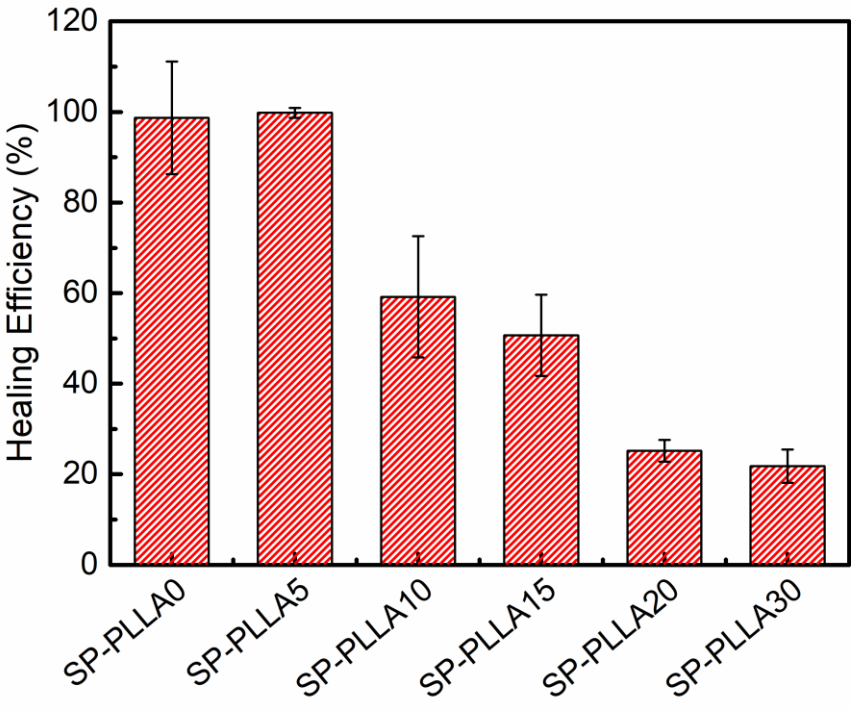

Figure S8. Self-healing efficiency of SP-PLLA after healing at 80 ºC for 24 h.

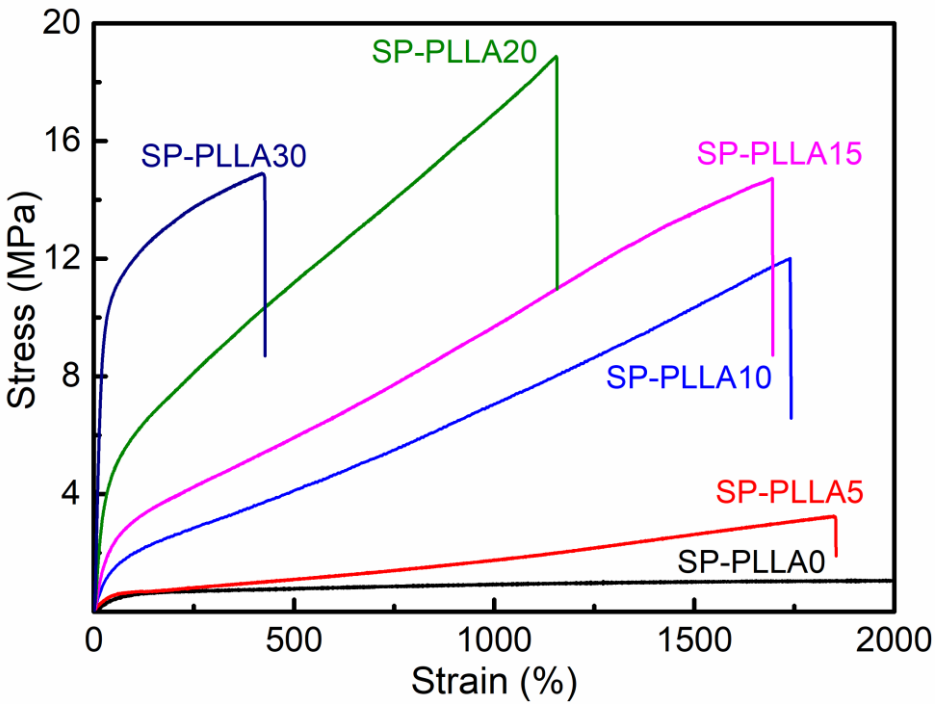

Figure S9. The tress-strain curves for the samples with a strain rate of 100 mm min^{-1} at room temperature.

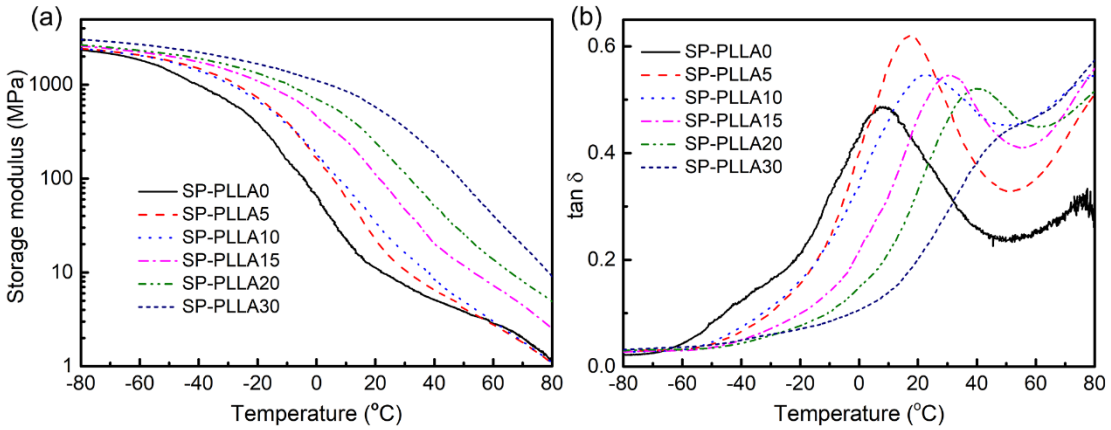

Figure S10. Temperature dependence of the storage modulus (a) and tan δ (b) for SP-PLLA.

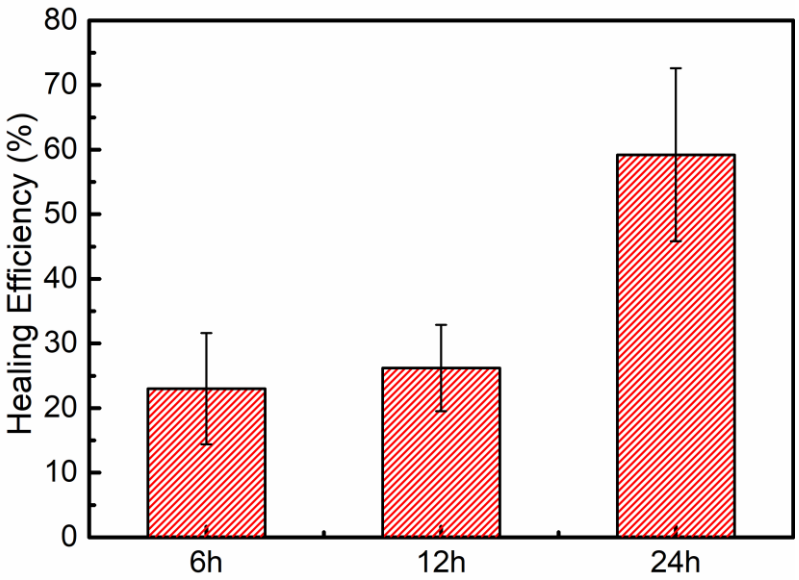

Figure S11. Self-healing efficiency of SP-PLLA10 after healing at 80 ºC for 6 h, 12 h and 24 h, respectively.

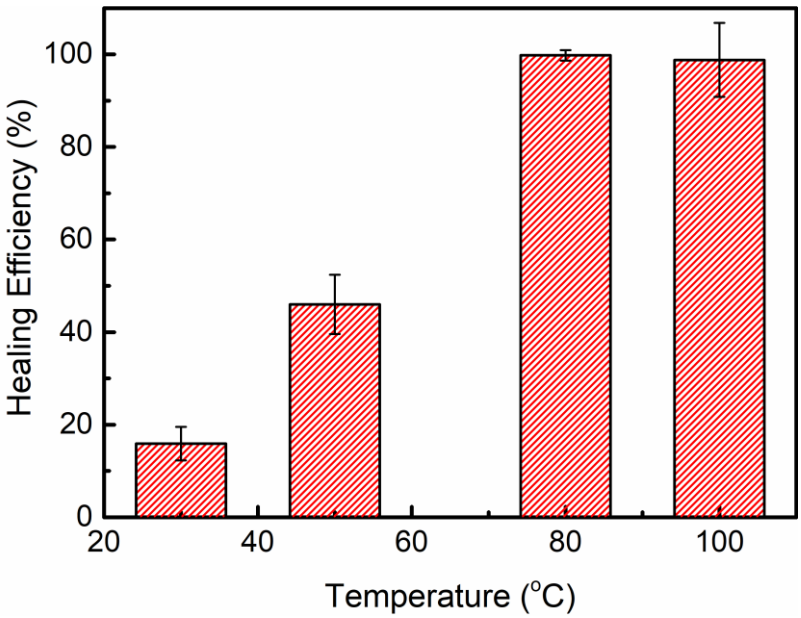

Figure S12. Self-healing efficiency of SP-PLLA5 after healing for 24 h at 30 ºC, 50 ºC, 80 ºC and 100 ºC, respectively.

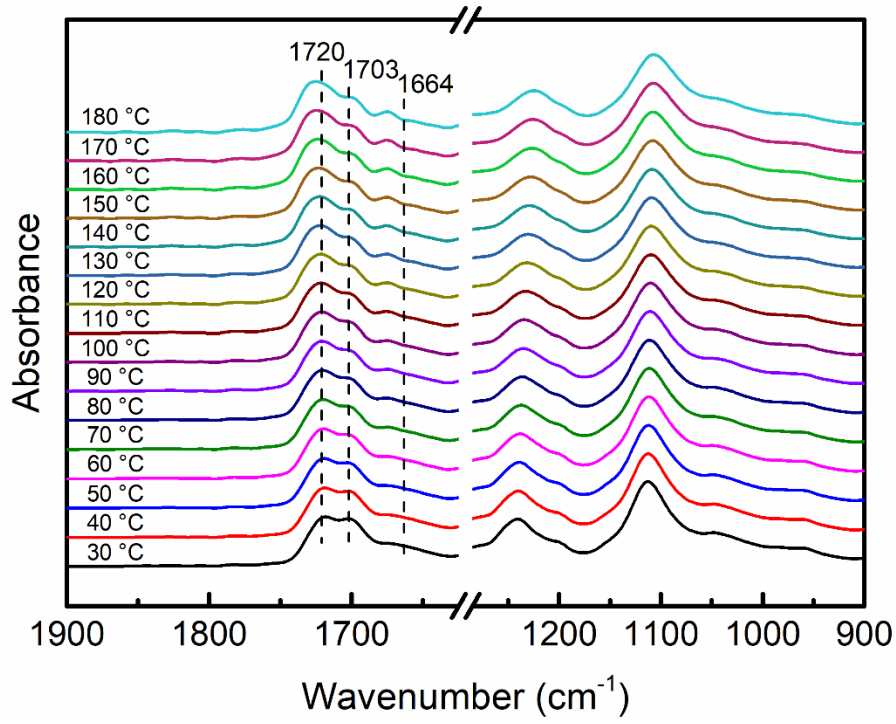

Figure S13. Temperature-dependent FT-IR spectra of the SP-PLLA0 film heated from 30 ºC to 180 ºC.

Table S3. Periodicity (L) of the as-prepared polymers calculated from SAXS results.

Samples	q_{max} (nm^{-1})	L (nm)
SP-PLLA0	0.294	21.4
SP-PLLA5	0.288	21.81
SP-PLLA10	0.271	23.2
SP-PLLA15	0.274	22.9
SP-PLLA20	0.302	20.8
SP-PLLA30	0.319	19.7

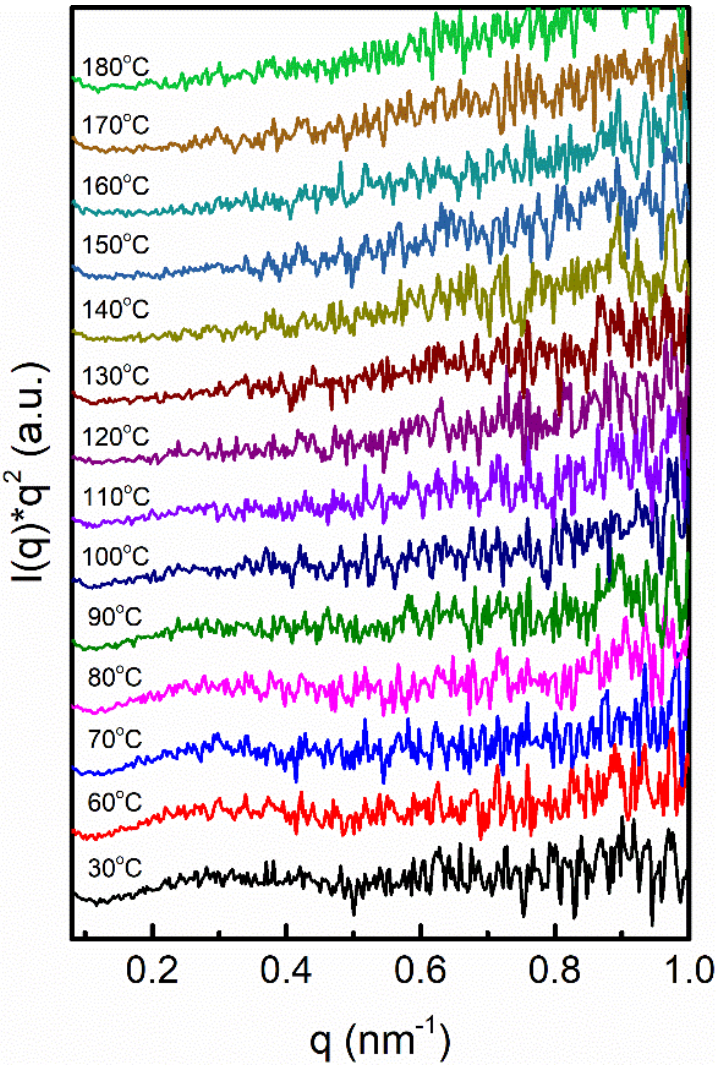

Figure S14. *In situ* SAXS profiles for the SP-PLLA0 film heated from 30 ºC to 180 ºC.

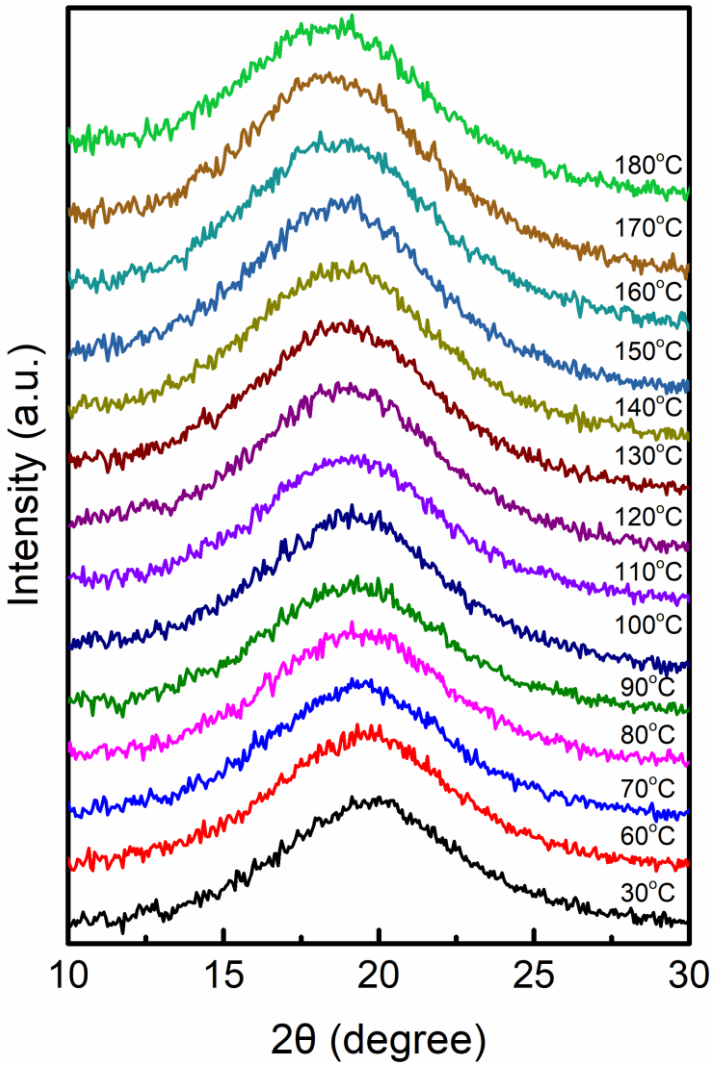

Figure S15. *In situ* WAXS profiles of the SP-PLLA0 film heated from 30 ºC to 180 ºC.

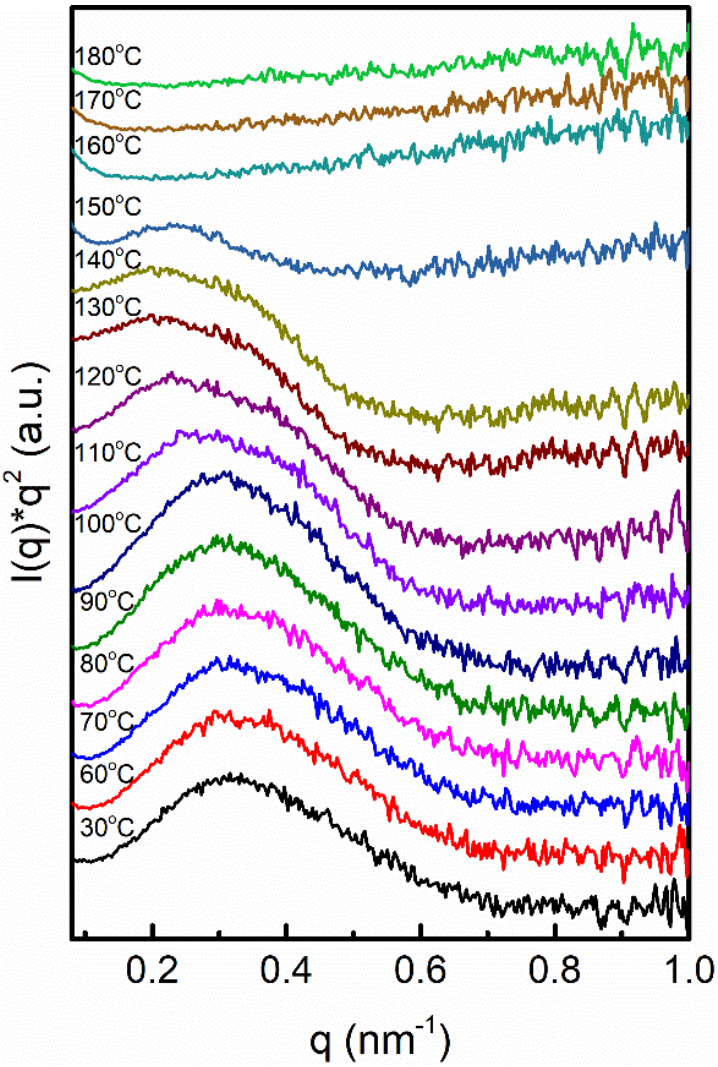

Figure S16. *In situ* SAXS profiles for the SP-PLLA30 film heated from 30 ºC to 180 ºC.

Table S4. Periodicity (L) of the as-prepared polymers obtained from SAXS curves at different temperatures.

Temperature	SP-PLLA0		SP-PLLA15		SP-PLLA30	
(°C)	q_{max} (nm^{-1})	L (nm)	q_{max} (nm^{-1})	L (nm)	q_{max} (nm^{-1})	L (nm)
30	0.295	21.3	0.270	23.3	0.305	20.6
60	0.295	21.3	0.270	23.3	0.305	20.6
70	0.295	21.3	0.270	23.3	0.305	20.6
80	0.295	21.3	0.270	23.3	0.305	20.6
90	0.295	21.3	0.270	23.3	0.305	20.6
100	0.295	21.3	0.270	23.3	0.305	20.6
110	0.295	21.3	0.247	25.4	0.305	20.6
120	---	---	0.247	25.4	0.218	28.8
					0.372	16.9
130	---	---	0.178	35.3	0.218	28.8
			0.411	15.3	0.372	16.9
140	---	---	0.178	35.3	0.218	28.8
			0.411	15.3	0.372	16.9
150	---	---	0.236	26.6	0.249	25.2
160	---	---	---	---	---	---
170	---	---	---	---	---	---
180	---	---	---	---	---	---

References

(1) Krikorian, V.; Pochan, D. J. Crystallization Behavior of Poly(L-Lactic Acid) Nanocomposites: Nucleation and Growth Probed by Infrared Spectroscopy. *Macromolecules* **2005**, *38* (15), 6520-6527.

(2) Pan, P.; Zhu, B.; Kai, W.; Dong, T.; Inoue, Y. Effect of Crystallization Temperature on Crystal Modifications and Crystallization Kinetics of Poly(L-lactide). *J. Appl. Polym. Sci.* **2008**, *107* (1), 54-62.

(3) Kuo, S. W.; Tsai, H. T. Self-Complementary Multiple Hydrogen Bonding Interactions Increase the Glass Transition Temperatures to Supramolecular Poly(methyl methacrylate) Copolymers. *J. Appl. Polym. Sci.* **2012**, *123* (6), 3275-3282.