

Study on the crystallization behavior and conformation adjustment scale of poly (lactic acid) in the terahertz frequency range

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EXPERIMENTAL SECTION

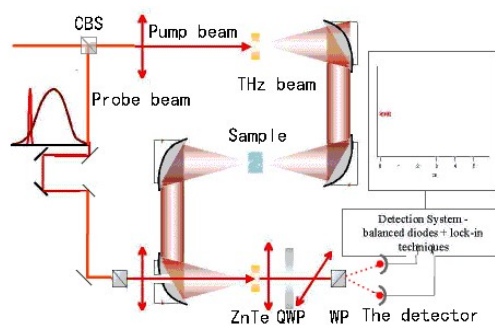


Fig. S1 Terahertz time-domain spectroscopy system: the center wavelength of laser was 800 nm, repetition frequency was 84 MHz, and pulse width was 100 fs. The spectral resolution was less than 5 GHz.

Table S1

Diffraction peak angle of the PLA films crystallized at different temperatures.

Crystallization temperature, T_c	(103)	(010)	(110/200)	(203)	(210)
40	-	-	16.61	18.95	-
50	-	-	16.61	18.95	-
55	-	-	16.61	18.95	-
60	-	-	16.61	18.95	-
65	-	-	16.61	18.95	-
70	-	14.85	16.62	18.96	22.39
75	-	14.85	16.63	18.97	22.39
80	-	14.85	16.66	18.99	22.39
90	-	14.85	16.73	19.08	22.39
100	12.46	14.89	16.76	19.12	22.4
105	12.46	14.89	16.76	19.12	22.4
110	12.46	14.89	16.76	19.12	22.4
120	12.46	14.89	16.77	19.13	22.41
130	12.46	14.89	16.77	19.13	22.41
140	12.46	14.89	16.77	19.13	22.41

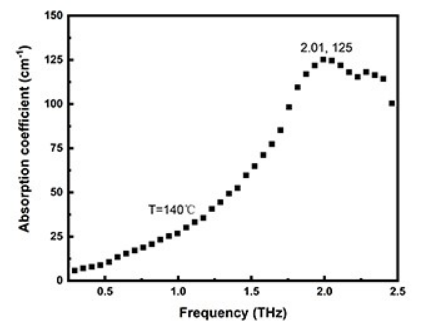
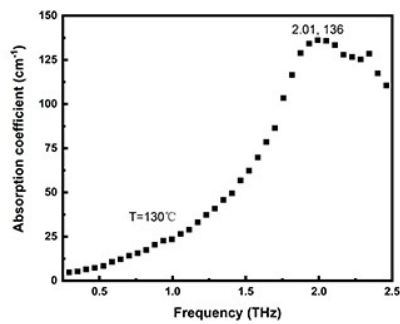
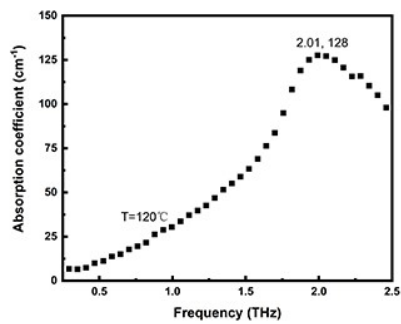
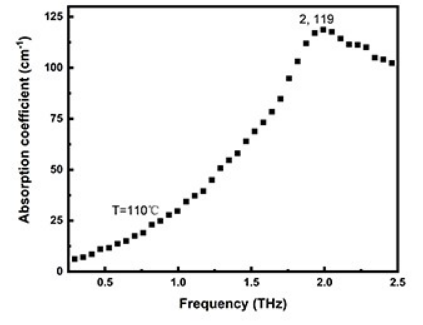
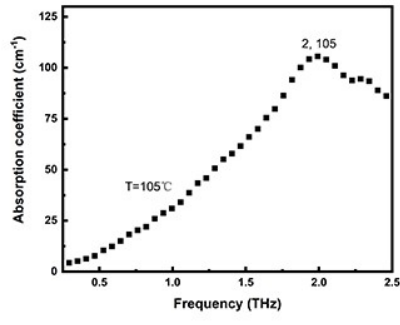
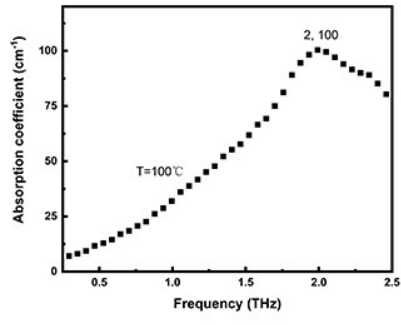
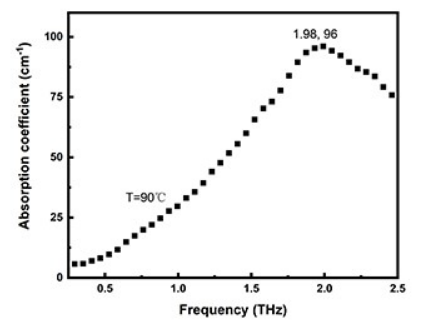
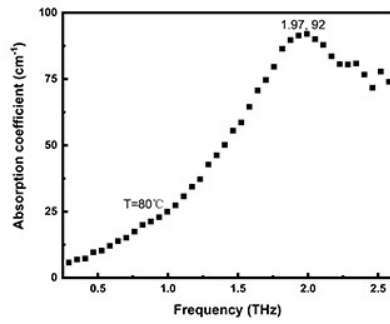
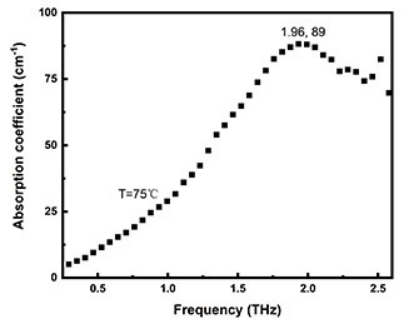
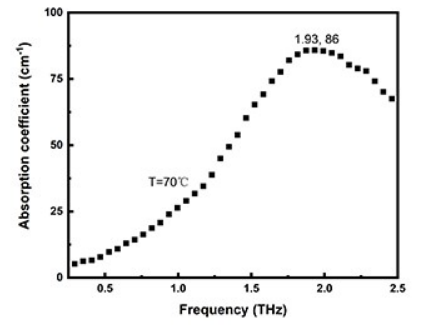
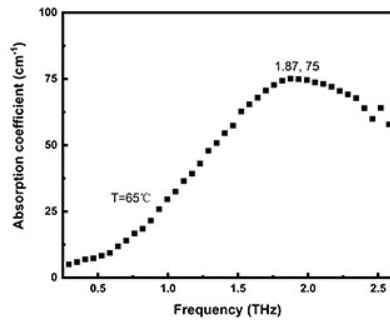
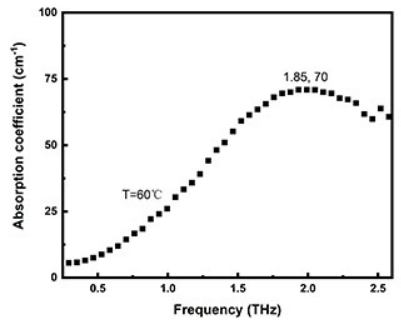
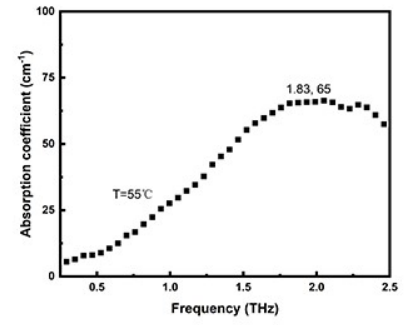
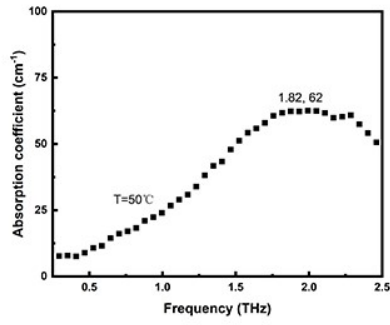
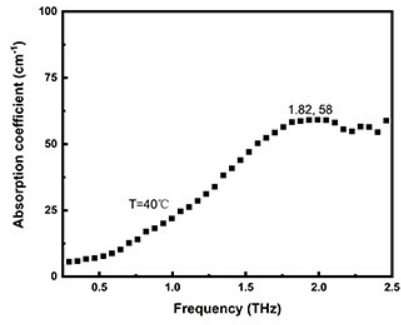


Fig. S2 THz absorption spectra of the PLA films crystallized at 40-140°C in the 0.25-2.5 THz.

Table S2

THz spectral parameters of the PLA films crystallized at different temperatures.

Crystallization temperature, T_c	Peak frequency (THz)	Absorption coefficient (cm^{-1}) ¹⁾
40	1.82	58
50	1.82	62
55	1.83	65
60	1.85	70
65	1.87	75
70	1.93	86
75	1.96	89
80	1.97	92
90	1.98	96
100	2	100
105	2	105
110	2	119
120	2.01	128
130	2.01	136
140	2.01	125

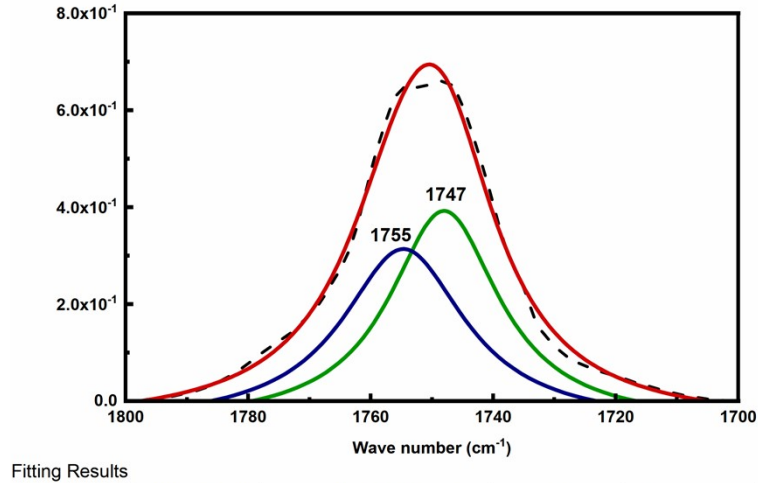


Fig. S3 Example of calculating relative conformational content of PLA film samples by FTIR spectra (1800-1700 cm^{-1}). Black dashed line represents experimental data. The solid red line represents the fitted curve. The blue solid line represents the fitted peak at 1755cm^{-1} . The green solid line represents the fitted peak at 1747cm^{-1} . All fitting results $R^2 > 0.99$.

$$X_{\text{conformation}} = \frac{A_i}{\sum A_i} \times 100$$

where $i = 1747$ or 1755 . A_{1747} and A_{1755} is the integrated intensity of the bands at 1747, 1755, respectively. Brant et al. established a rotational isomeric state (RIS) model of PLA and the corresponding conformational energy map. The four lowest-energy states of PLA predicted by the RIS model correspond to four typical conformations: tt (trans, [t]), gt (gauche, [g]), gg , and tg . gt conformation has the lowest energy, corresponding to 3_1 or 10_3 helix. gg conformation with the second lowest energy state, showing a highly compressed 4_1 helix, and the other two relatively higher energy tt and tg conformations correspond to 2_1 and 5_1 helix, respectively.

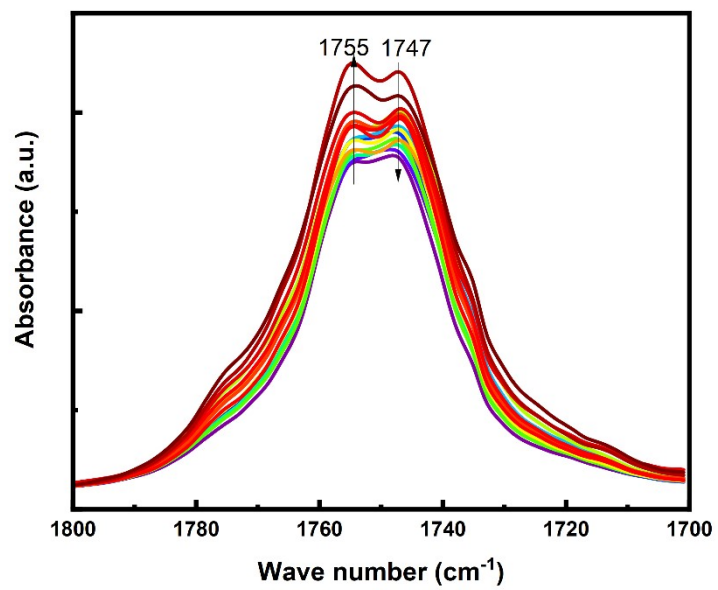


Fig. S4 FTIR of the PLA films crystallized at different temperatures in the 1800-1700 cm^{-1} .

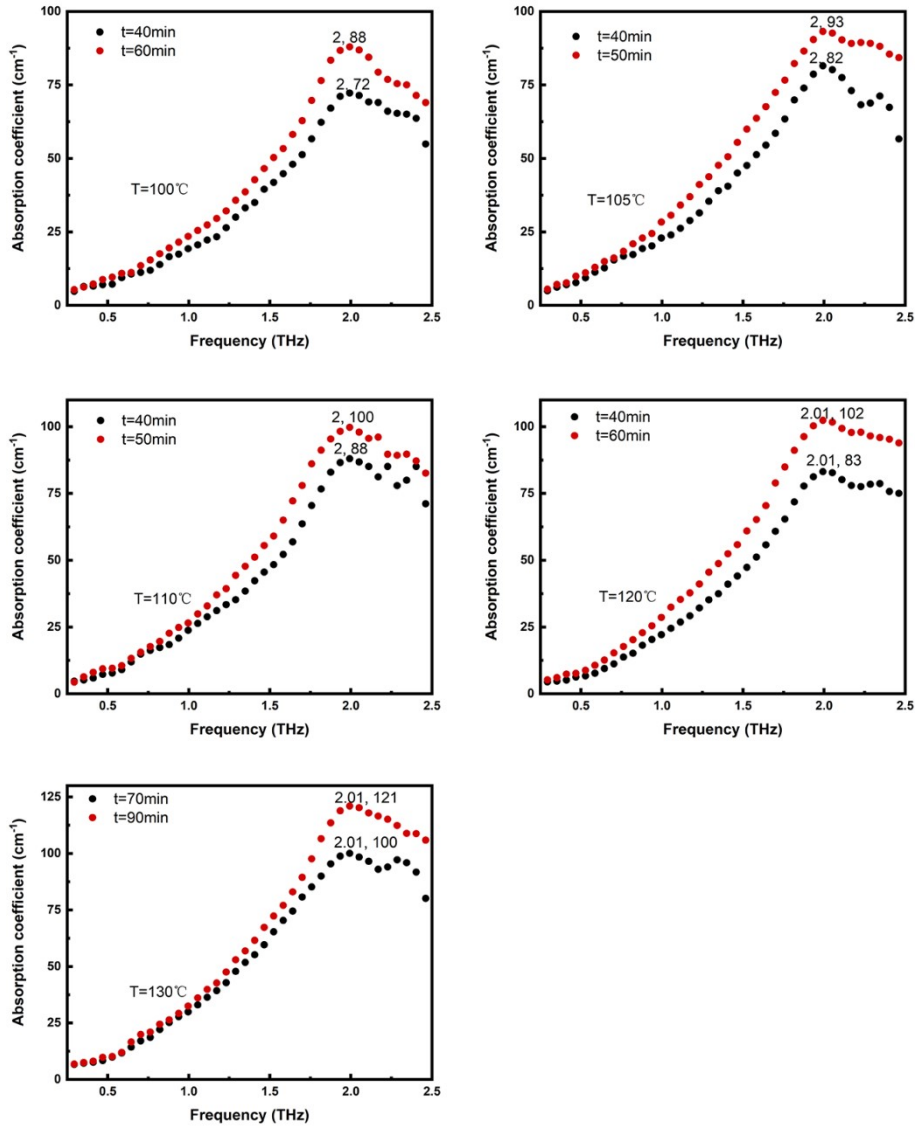


Fig. S5 Variation of absorption coefficient with time during crystallization at different heating temperatures.

Table S3

Crystallization dynamic parameters and half crystallization time of the PLA films.

Crystallization temperature, T_c	100	105	110	120	130
n	3	3.04	2.54	2.59	2.78
k/min^{-1}	5.57×10^{-6}	9.04×10^{-6}	5.48×10^{-5}	1.85×10^{-4}	6.1×10^{-7}
$t_{1/2}/\text{min}$	48.01	40.5	41.3	51.08	66.1