Supporting Information

Poly(L-Lactic Acid) Crystallization in Pressurized CO₂: An In-situ Microscopic Study and A New Model For The Secondary Nucleation From Supercritical CO₂

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1 Supporting data

1.1 Isothermal isobaric crystallization results



Figure S1 Polarized light microscopic images of PLLA1 sample after isothermal isobaric crystallization at different temperatures and different CO₂ pressures. The scale labels of these images are same and given in the bottom right corner.



Figure S2 Statistical results of the average grain size and grain density of PLLA1 spherulite formed by isothermal isobaric crystallization at different temperatures and

different CO2 pressures.



Figure S3 The average growth rates of PLLA1 spherulite formed by isothermal isobaric crystallization at different temperatures and different CO₂ pressures.

In order to integrally understand the influence of temperature and CO₂ pressures on the PLLA crystallization, the images and statistical data of PLLA1 crystal formed at 50 and 90 °C was shown again in this Supporting Information, although they've been shown in the main body of this paper. Moreover, it should be noted that no spherulite structure was found at 0.1 MPa / 50 °C and 27.59 MPa / 90 °C, and the spherulite boundary cannot be distinguished at 0.1 MPa / 60 °C, as shown as Figure S1. Hence, the corresponding growth rate data of the PLLA spherulite formed at these two conditions are not given in Figure 2.

From the Figure S1-S2, at the same pressure condition, with the increase of temperature, the density of PLLA spherulite decreases, and the finally size of PLLA spherulite increases. This is because the crystallization degree of supercooling is reduced by the high temperature. Thus, the primary nucleation rate of the polymer crystallization decreases, correspondingly.

1.2 Experimental data statistics

To confirm data reproducibility, the estimating methods of error bars in Figure 1, 2 and 3 in the main body of this paper is given as follows:

1) In Figure 1(a), 10 crystals were randomly selected in the view field of each POM image, and then the diameter of the final crystal was measured by using Nanomeasure software. All the crystals in images with fewer crystals (e.g. 90 °C, 13.79/17.24/20.69 MPa) were measured. The error bars were determined based on the standard deviations of the 10 measured data.

2) The data in Figure 1(c) were based on the in-situ POM images recorded during the growth of PLLA crystals. Nanomeasure software was used to measure the crystal radius at different shooting time points, and then the change in radius was divided by the change in time to calculate the growth rate of crystals. Five crystals were selected from each sample for tracking, and all the crystals in images with fewer crystals (e.g., 90 °C, 13.79/17.24/20.69) were measured. The error bars were determined based on the standard deviations of the growth rate data of five crystals.

3) The calculation method of error bars in Figure 2(j) and Figure 3(j) was consistent with that in Figure 1(a). The difference was that Figure 2(j) and Figure 3(j) showed the statistical results of dendritic crystals width, and the selection method of samples was shown in Figure S4(b) in the Supporting Information.

4) The data in Figure 2(k) and Figure 3(k) were obtained according to the in-situ microscopic image of snowflake crystal growth process. The linear density of dendritic crystal was obtained according to the statistics method shown in Figure S4(a)

in Supporting Information. Under each pressure condition, 5 crystal edges were randomly selected, and the error bars were determined according to the standard deviation of the crystal linear density data at these 5 edges.

5) The calculation method of error bars in Figure 2(l) and Figure 3(l) was consistent with that in Figure 1(b). The difference was that Figure 2(l) and Figure 3(l) gave the circumcircle radii of the snowflake crystal.



Figure S4 Statistical methods of branch density and size. In Figure (a), there are 8 distinguishable branch tips distributed at the edge of crystal with a length of 241.69 μ m, and the linear density of branch is calculated as 0.033 / μ m; in Figure (b), the mature body behind the branch tip is selected as the measuring position of branch

width.

2 Model Parameters and Calculation Method

2.1 Calculation of Characteristic Parameters of S-L equation of state

To calculate the S-L equation of state of polymer/CO₂ mixture system, the characteristic parameters, including P^* , T^* and ρ^* of this system, are given by the following mixing rules. In the following equations, P_i^* , T_i^* , ρ_i^* and r_i^0 are the

characteristic pressure, temperature, density and size parameter of neat polymer and CO₂. The subscript i = 1 stands for CO₂ and i = 2 for polymer.

$$\phi_i^0 = \frac{\phi_i(\frac{P_i^*}{T_i^*})}{\phi_1(\frac{P_1^*}{T_1^*}) + \phi_2(\frac{P_2^*}{T_2^*})}$$
(S1)

$$\phi_{i} = \frac{\frac{w_{i}}{\rho_{i}^{*}}}{\frac{w_{1}}{\rho_{1}^{*}} + \frac{w_{2}}{\rho_{2}^{*}}}$$
(S2)

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - RT \phi_1 \phi_2 \chi_{12}$$
(S3)

$$\chi_{12} = \frac{P_1^* + P_2^* - 2(P_1^* P_2^*)^{0.5} (1 - k_{12})}{RT}$$
(S4)

$$T^* = P^* \left(\frac{\phi_1^0 T_1^*}{P_1^*} + \frac{\phi_2^0 T_2^*}{P_2^*} \right)$$
(S5)

$$\frac{1}{\rho^*} = \frac{w_1}{\rho_1^*} + \frac{w_2}{\rho_2^*} \tag{S6}$$

$$\frac{1}{r} = \frac{\phi_1^0}{r_1^0} + \frac{\phi_2^0}{r_2^0} \tag{S7}$$

where k_{12} is the binary interaction parameter. ϕ_1 and ϕ_2 are the volume fractions of CO₂ and polymer, respectively. w_1 and w_2 are the mass fractions of CO₂ and polymer, respectively.

When the polymer/CO₂ mixture system reaches the solution equilibrium, the chemical potentials of CO₂ in gas phase, μ_1^G , and that in polymer phase, μ_1^P , achieve a balance expressed as:

$$\mu_1^G = \mu_1^P \tag{S8}$$

where

$$\mu_{1}^{G} = RTr_{1}^{0} \left[-\frac{\rho_{1}T_{1}^{*}}{\rho_{1}^{*}T} + \frac{P\rho_{1}^{*}T_{1}^{*}}{P_{1}^{*}\rho_{1}T} + \left(\frac{\rho_{1}^{*}}{\rho_{1}} - 1\right) \ln\left(1 - \frac{\rho_{1}}{\rho_{1}^{*}}\right) + \frac{1}{r_{1}^{0}} \ln\left(\frac{\rho_{1}}{\rho_{1}^{*}}\right) \right]$$
$$= RTr_{1}^{0} \left[-\frac{\widetilde{\rho_{1}}}{\widetilde{T_{1}}} + \frac{\widetilde{P_{1}}}{\widetilde{\rho_{1}}\widetilde{T_{1}}} + \left(\frac{1}{\widetilde{\rho_{1}}} - 1\right) \ln(1 - \widetilde{\rho_{1}}) + \frac{1}{r_{1}^{0}} \ln(\widetilde{\rho_{1}}) \right]$$
(S9)

$$\begin{split} \mu_{1}^{p} &= RT \ln \phi_{1} + RT \phi_{2} \left(1 - \frac{r_{1}^{0} T_{1}^{*} P_{2}^{*}}{r_{2}^{0} T_{2}^{*} P_{1}^{*}} \right) \\ &+ \frac{Rr_{1}^{0} \rho T_{1}^{*} \phi_{2}^{2}}{P_{1}^{*} \rho^{*}} \left[P_{1}^{*} + P_{2}^{*} - 2(1 - k_{12})(P_{1}^{*} P_{2}^{*})^{0.5} \right] \\ &+ RTr_{1}^{0} \left[-\frac{\rho T_{1}^{*}}{\rho^{*} T} + \frac{P\rho^{*} T_{1}^{*}}{P_{1}^{*} \rho T} + \left(\frac{\rho^{*}}{\rho} - 1 \right) \ln \left(1 - \frac{\rho}{\rho^{*}} \right) + \frac{1}{r_{1}^{0}} \ln \left(\frac{\rho}{\rho^{*}} \right) \right] \\ &= RT\{ \ln \phi_{1} + \phi_{2} \left(1 - \frac{r_{1}^{0} T_{1}^{*} P_{2}^{*}}{r_{2}^{0} T_{2}^{*} P_{1}^{*}} \right) + V_{1}^{*} \tilde{\rho} \phi_{2}^{2} \chi_{12} \\ &+ r_{1}^{0} \left[-\frac{\tilde{\rho}}{\tilde{r_{1}}} + \frac{\tilde{P_{1}}}{\tilde{\rho}\tilde{r_{1}}} + \left(\frac{1}{\tilde{\rho}} - 1 \right) \ln (1 - \tilde{\rho}) + \frac{1}{r_{1}^{0}} \ln(\tilde{\rho}) \right] \} \end{aligned}$$
(S10)

Under the phase equilibrium condition, the volume fraction of CO₂, ϕ_1 , in the polymer/CO₂ mixture phase can be obtained by solving equation (S-9). The related parameters used in S-L equation of state of PLLA/CO₂ mixture system are given in Table S1.

Value Ref. Quantity $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ R, gas constant k_{12} , binary interaction parameter -0.115 [1] Parameters about CO₂ [1] P_1^* , characteristic pressure 720.3 MPa [1] (208.9+0.459T-0.000756T²) K T_1^* , characteristic temperature [1] ρ_1^* , characteristic density 1.58 g/cm^3 [1] r_1^0 , characteristic size 8.4 [2] Parameters about polymer (PLLA) [1] P_2^* , characteristic pressure 560.2 MPa [1] T_2^* , characteristic temperature 592.2 K [1] ρ_2^* , characteristic density 1.35 g/cm^3 [1] r_2^0 , characteristic size ∞ [2]

Table S1 The Related Parameters used in S-L Equation of State of PLLA/CO₂ Mixture System

Pressurized CO ₂		
Quantity	Value	Ref.
Crystallographic		
a ₀ , width of stem	$5.97 \times 10^{-10} \text{ m}$	[3]
b_0 , layer thickness	$5.17 \times 10^{-10} \text{ m}$	[3]
l_u , projected length per 'virtual' bond in	0.27×10^{-11} m	(a)
crystallographic chain	9.27×10 ⁻¹ III	(a)
Parameters about CO ₂		
<i>M</i> , molecular mass	$0.044 \text{ kg} \cdot \text{mol}^{-1}$	
C_0 , parameter in adsorption affinity equation	$8.402 \times 10^{-11} \text{ N}^{-1} \cdot \text{m}^{-2}$	(b)
Q', parameter in adsorption affinity equation	3.25814×10 ³ K	(b)
P_c , critical pressure	$7.38 \times 10^6 N \cdot m^2$	[6]
T_c , critical temperature	304.15 K	[6]
A _m , cross-sectional area	$1.87 \times 10^{-19} \text{ m}^2$	[7]
Parameters about polymer (PLLA)		
C_{∞} , characteristic ratio	2.34	[3]
m_0 , relative molecular mass per backbone bond	0.02402 kg·mol ⁻¹	(c)
l_0 , length of 'virtual' bond	$1.432 \times 10^{-10} \text{ m}$	[4]
α , dilution exponent	4/3	[9]
M_e^0 , entanglement molecular weight of pure polymer	3.959 kg⋅mol ⁻¹	[4]
T_m^0 , equilibrium melting temperature	470.35 K or 454.75 K	(d)
Δh_f , enthalpy of fusion per unit volume	$1.2074 \times 10^{6} \text{J/m}^{3}$	[10]
σ_e , end surface energy	0.06089 J/m ²	[11]
Parameters about polymer/ CO ₂ mixture system		
b_1 , parameter in interaction parameter equation	3.69	
b_2 , parameter in interaction parameter equation	-5.99	
d_0 , parameter in interaction parameter equation	24.77	[12]
d_1 , parameter in interaction parameter equation	1.54	
d_2 , parameter in interaction parameter equation	-4.23	
$E_{\rm CO_2-carbonyl}$, bonding energy of CO ₂ /carbonyl	$1.222 \times 10^4 \text{ J} \cdot \text{mol}^{-1}$	[13]
$E_{\text{interaction}}$	1 0 2 5 1 0 4 1 1-1	[10]
$E_{\rm CO_2-ether}$, bonding energy of CO ₂ /ether interaction	$1.235 \times 10^{4} \text{ J} \cdot \text{mol}^{-1}$	[13]
V_{poly} , hard-core specific volume of PLLA	$0.71/4 \text{ cm}^3/\text{g}$	[14]
$V_{co_2}^{\circ}$, hard-core specific volume of CO ₂	$0.589 \text{ cm}^3/\text{g}$	[15]
\mathcal{L}_1 , Parameters of Willian-Landel-Ferry equation	1.04×10 ⁻²⁰ J	
C_2 , Parameters of Willian-Landel-Ferry equation	30 K	[17]
Physical constants		
<i>R</i> , gas constant	8.314 $J \cdot mol^{-1} \cdot K^{-1}$	
<i>k</i> , Boltzmann constant	$1.381 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$	
N_a , Avogadro constant	$6.022 \times 10^{23} \text{ mol}^{-1}$	
h, Planck constant	6.626×10 ⁻³⁴ J·s	

2.2 Parameters of the secondary nucleation model

Table S2 Input Data for Analysis of PLLA Crystallization Kinetics inPressurized CO2

Notes:

(a) In correspondence with the definition of m_0 and l_0 [4], for PLLA, l_u equals to $l_{mu}/3$ where l_{mu} is defined as the length of the elementary monomer unit with a value of 0.278 nm given by Ref. [3].

(b) The parameters in adsorption affinity equation are obtained by data fitting from Ref. [5] with a fitting degree of 0.9885.

(c) For PLLA, lactic acid has a molecular weight of 72.06 g/mol and contributes 3 backbone bonds [8].

(d) According to the research results of Y. He et al [16] on the T_m^0 based on the nonlinear Hoffman-Weeks model of different molecular weights, we estimated that the T_m^0 value of PLLA1 (MW ≈ 64500 g/mol) used in this research is about 470.35 K, and the T_m^0 value of PLLA2 (MW ≈ 5500) used is about 454.75 K.

(e) based on Ref. [17], $C_1 = 1500 \text{ cal/mol} = (1500 \times 4.18/N_a) \text{ J} = 1.04 \times 10^{-20} \text{ J}.$

2.3 Calculation Method

This work used MATLAB R2018b software to perform mathematical modeling and calculations, the calculation process of the secondary nucleation rate model established in this paper is as follows:

Step 1, the data in table S1 and the SL equation of state shown as equation (1) were used to solve the equilibrium density of pure CO₂ at different pressures and temperatures, and then the equation (S8) was used to solve the chemical potential of CO₂ in the gas state, μ_1^G .

Step 2, by using the mixing rule shown as equations (S1)-(S7), the characteristic parameters of PLLA/CO₂ mixed system in the SL equation of state were solved. Then, the μ_1^G obtained from the step 1 and equation (S10) were substituted into equation (S8).

Step 3, the SL equation of state of the mixed system and the chemical equilibrium equation (S8) were assembled into an equation set. The fsolve function of MATLAB was called, and the levenberg-marquardt algorithm was used to iteratively

solve the nonlinear equation set to obtain the mass fraction of CO_2 , the density of CO_2 in the mixed system, the polymer volume fraction, the density of the mixed system and other data.

Step 4, the data in table S2 and the calculation results obtained in step 3 were called. The temperature and pressure values were set. The equations (5) was calculated to obtain the diffusion activation energy, ΔE . The equations of (7) and (8) were calculated to obtain σ and σ'_e . Then, σ and σ'_e were substituted into equations (6) to calculate the critical nucleation free energy, ΔG^* . At the same time, for size parameters of the two-dimension crystal nucleus, a^* , l^* and L, were obtained.

Step 5, the solution of intermediate variable. Based on the molecular weight data, the number of 'virtual' bonds unit, n, was determined. Equation (17), (16), (12) and (15) were calculated to obtain entanglement molecular weight, M_e , reptating tube length, L_t , binary interaction parameters, χ , and molecular number of CO₂ in the reptating tube, N_s , respectively.

Step 6, equation (10) was calculated to obtain the phase separating free energy of the mixed system ΔG_m . Equations (21) and (22) were calculated to obtain the adsorbed amount of CO₂ molecules on the crystal surface θ . Equations (18)-(20) were calculated to obtain the adsorption energy of strong interactions ΔG_{as} . Equations (25)-(27) were calculated to obtain the translational free energy of CO₂ molecules ΔG_t .

Step 7, based on the obtained ΔG_m , ΔG_t , ΔG_{as} and ΔG_{aw} , the total extra free energy ΔG_s caused be CO₂ was calculated. Then, ΔE , ΔG^* and ΔG_s were

substituted into equation (3) to calculate the nucleation rate I.

3 Calculation results

3.1 Calculation results of S-L equation of state



Figure S5 Calculation results of S-L equation of state of pure CO₂, (a) dependence of density on pressure, (b) dependence of chemical potentials of CO₂ on pressure



Figure S6 Calculation results of S-L equation of state of PLLA/CO₂ mixture system, (a) dependence of mass fraction of CO₂ on pressure, (b) dependence of volume fraction of polymer on pressure, (c) dependence of specific volume of mixture on pressure.

In the model established in this paper, we used SL model to solve some state parameters of PLLA/CO₂ system. Figure S6 shows the mass fraction and volume obtained by solving the SL model. It can be seen from the Figure S6 that there are abnormal fluctuations in the curves within the range of 0-7MPa. The critical pressure of CO₂ is 7.38 MPa. When the system pressure is higher than the critical pressure, CO_2 is in a supercritical fluid state; when the system pressure is lower than the critical pressure, CO_2 is in the gas phase. Therefore, when the system pressure is too low, CO_2 in the gas phase is very unstable, and the volume of CO_2 is very sensitive to pressure and temperature, which will cause concentration fluctuation or energy fluctuation in the PLLA/ CO_2 system, and lead to phase transition or phase separation. At this point, the PVT relationship of the PLLA/ CO_2 system is very complex, and it is difficult to describe PVT relationship of the system including phase transition and phase separation by the state equation based on the homogeneous system. Therefore, according to the physical nature of CO_2 at low pressure and the calculation results of SL model, our model can give relatively reasonable and accurate results at the pressure greater than 7 MPa, i.e. supercritical state.

3.2 Diffusion activation energy and critical nucleation free energy



Figure S7 Calculation results of molecular nucleation model of PLLA1/CO2 mixture

system.

3.3 Extra free energy caused by CO₂ in the nucleation process



Figure S8 Calculation results of extra free energy caused by CO₂, (a) dependence of adsorption energy of strong interaction on pressure, (b) dependence of adsorption energy of weak interaction on pressure.



Figure S9 Calculation results of extra free energy caused by CO₂, (a) dependence of mixing free energy on pressure, (b) dependence of translational free energy on

pressure.

Video 1 Screen recording of crystal morphological evolution and pressure data obtained by *in-situ* HPM system. The PLLA film is prepared by 10 μ l PLLA2/CH₂Cl₂ solution with a concentration of 15 mg/ml and the crystallization temperature is 100 °C.

Video 2 Screen recording of crystal morphological evolution and pressure data obtained by *in-situ* HPM system. The PLLA film is prepared by 10 μ l PLLA2/CH₂Cl₂ solution with a concentration of 15 mg/ml and the crystallization temperature is 60 °C.

In the videos, the main window shows the crystal morphology observed by *in-situ* high-pressure microscopic system, the data shown below the main window is the current output of pressure transducer mounted on the sample cell. The pressure measuring range of the transducer is 0-35 MPa, and the current output range is 4-20 mA. The real-time pressure value *P* can be calculated by

$$P = \left[35 \times \frac{I_{\text{current}} - 4}{20 - 4}\right] MPa$$

4 Reference

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