Supplementary information for

Can spherulitic growth rate accelerate before impingement for a semicrystalline polymer during the isothermal crystallization process?†

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Supplementary information. Figs. S1-S31 show the isothermal crystallization behaviors for PLLA film samples with confinement conditions prepared by pressing PLLA melts between cover glasses. Figs. S32-S60 show the isothermal crystallization behaviors for PLLA film samples with no confinement conditions prepared by solution cast. Figs. S61-S71 show the isothermal crystallization behaviors for PLLA film samples with no confinement conditions prepared by pressing PLLA melts between two cover glasses and then removing the top cover glass. Fig. S72 shows the Hoffman-Weeks plot to obtain the equilibrium melting point for PLLA from DSC measurements. Fig. S73 presents the AFM height image of PLLA film sample, which was prepared by pressing PLLA melts between cover glasses and after crystallization at 110 ^{o}C for 30 min the top cover glass was removed for the AFM observation. Figs. S74 and S75 show the changes of nucleus number with crystallization temperature for PLLA film samples covered with cover glass and uncovered solution cast PLLA film samples, respectively, and Table S1 lists the corresponding nucleus numbers. Fig. S76 shows the DSC heat flow curves during the first and second heating scans with a heating rate of 10 ^{o}C/min for PLLA samples crystallized between cover glasses for certain times at 135 ^{o}C. Fig. S77 shows the heat flow curves during the first and second heating scans with a heating rate of 10 ^{o}C/min for PLLA samples with free top surface (obtained from solution cast), which crystallized for certain times at different temperatures, and Table S2 lists the corresponding T_g's.

1. Isothermal crystallization processes of PLLA film samples with surface confinement. The PLLA film samples were prepared by pressing PLLA melts between two cover glasses.

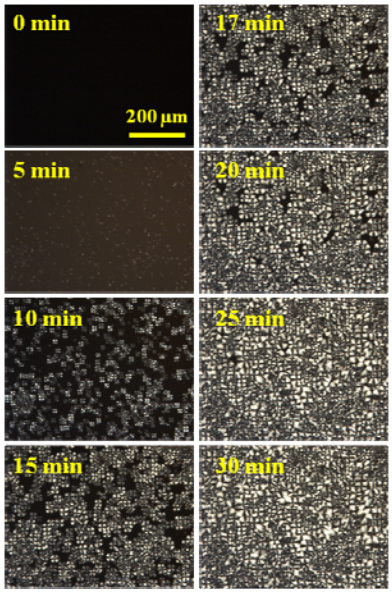


Fig. S1 Selected POM micrographs for PLLA during isothermal crystallization at 110 ^{o}C. The scale bar represents 200 μm and is applied to all the micrographs.

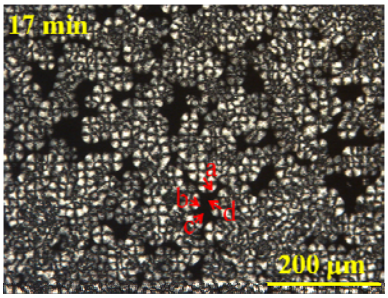
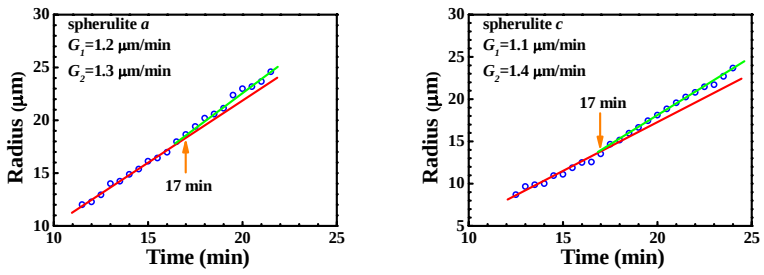


Fig. S2 Selected POM micrograph for PLLA during isothermal crystallization at 110 ^{o}C and 17 min. The four red arrows indicate the measured directions of the selected four spherulites, respectively.



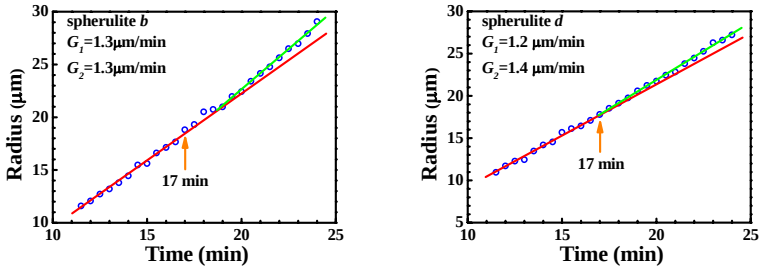


Fig. S3 Changes of radius of the selected four spherulites shown in Fig. S2 for PLLA during isothermal crystallization at 110 ^{o}C.

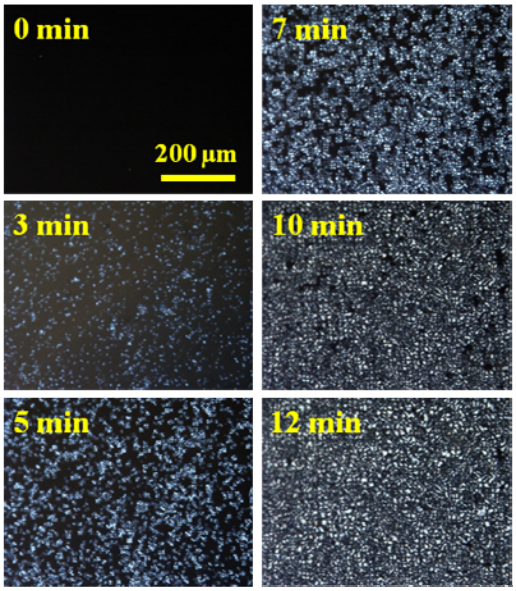


Fig. S4 Selected POM micrographs for PLLA during isothermal crystallization at 113 ^{o}C. The scale bar represents 200 μm and is applied to all the micrographs.

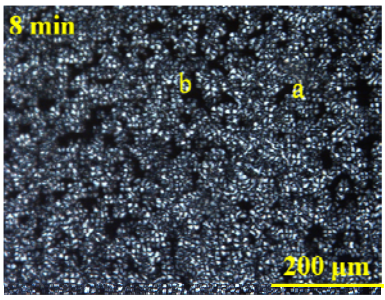


Fig. S5 Selected POM micrograph for PLLA during isothermal crystallization at 113 ^{o}C and 8 min. a and b indicate the measured two spherulites.

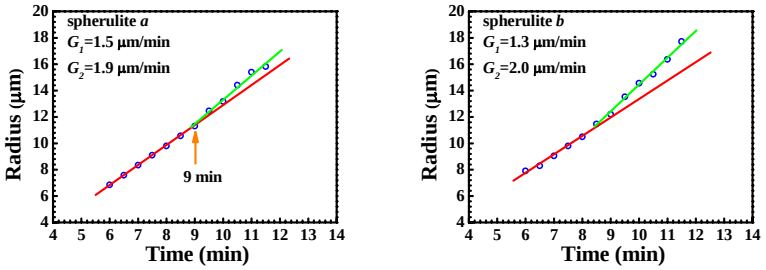


Fig. S6 Changes of radius of the selected two spherulites shown in Fig. S5 for PLLA during isothermal crystallization at 113 ^{o}C.

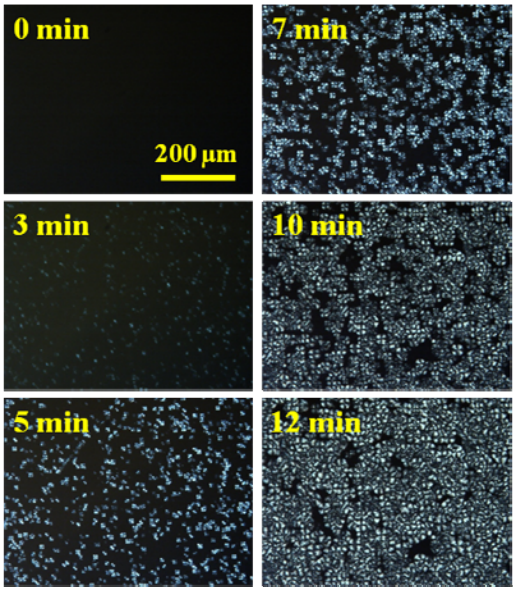


Fig. S7 Selected POM micrographs for PLLA during isothermal crystallization at 115 ^{o}C. The scale bar represents 200 μm and is applied to all the micrographs.

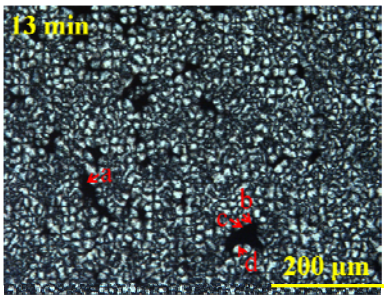


Fig. S8 Selected POM micrograph for PLLA during isothermal crystallization at 115 ^{o}C and 13 min. The four red arrows indicate the measured directions of the selected four spherulites, respectively.

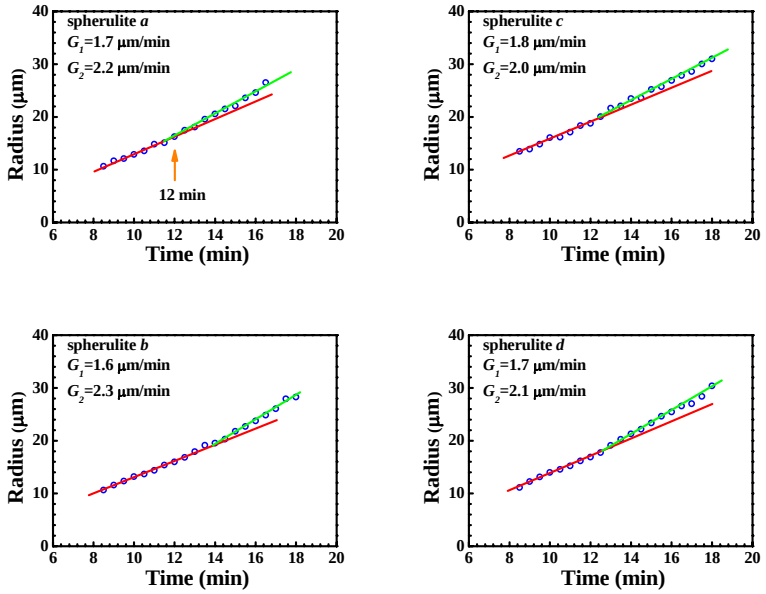


Fig. S9 Changes of radius of the selected four spherulites shown in Fig. S8 for PLLA during isothermal crystallization at 115 ^{o}C.

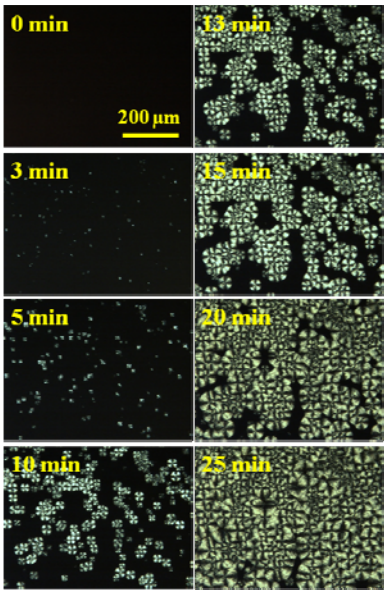


Fig. S10 Selected POM micrographs for PLLA during isothermal crystallization at 118 ^{o}C. The scale bar represents 200 μm and is applied to all the micrographs.

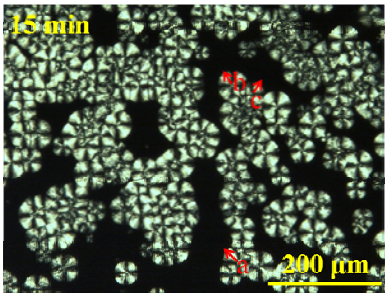


Fig. S11 Selected POM micrograph for PLLA during isothermal crystallization at 118 ^{o}C and 15 min. The three red arrows indicate the measured directions of the selected three spherulites, respectively.

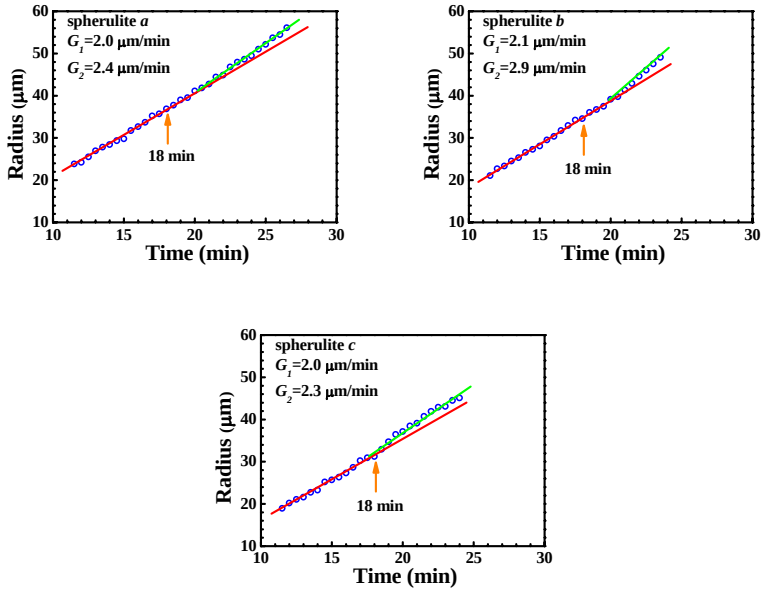


Fig. S12 Changes of radius of the selected three spherulites shown in Fig. S11 for PLLA during isothermal crystallization at 118 ^{o}C.

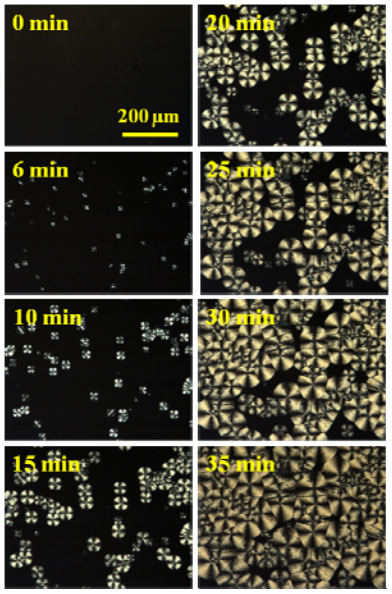


Fig. S13 Selected POM micrographs for PLLA during isothermal crystallization at 120 ^{o}C. The scale bar represents 200 μm and is applied to all the micrographs.

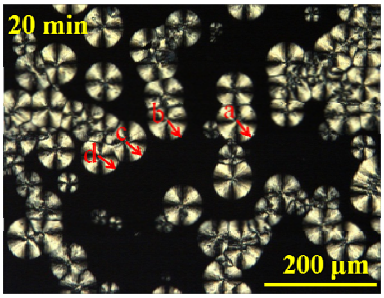
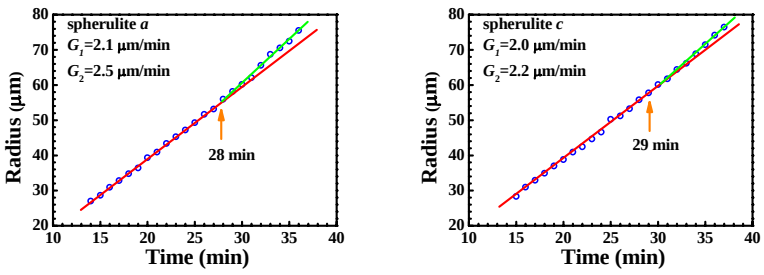


Fig. S14 Selected POM micrograph for PLLA during isothermal crystallization at 120 ^{o}C and 20 min. The four red arrows indicate the measured directions of the selected four spherulites, respectively.



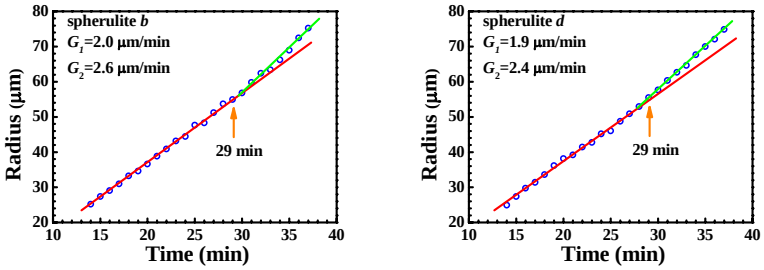


Fig. S15 Changes of radius of the selected four spherulites shown in Fig. S14 for PLLA during isothermal crystallization at 120 ^{o}C.

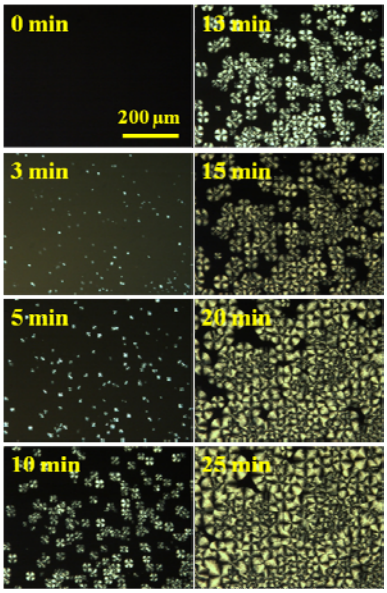


Fig. S16 Selected POM micrographs for PLLA during isothermal crystallization at 122 ^{o}C. The scale bar represents 200 μm and is applied to all the micrographs.

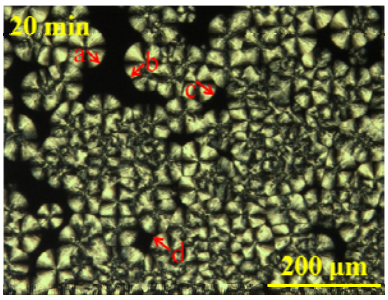


Fig. S17 Selected POM micrograph for PLLA during isothermal crystallization at 122 ^{o}C and 20 min. The four red arrows indicate the measured directions of the selected four spherulites, respectively.

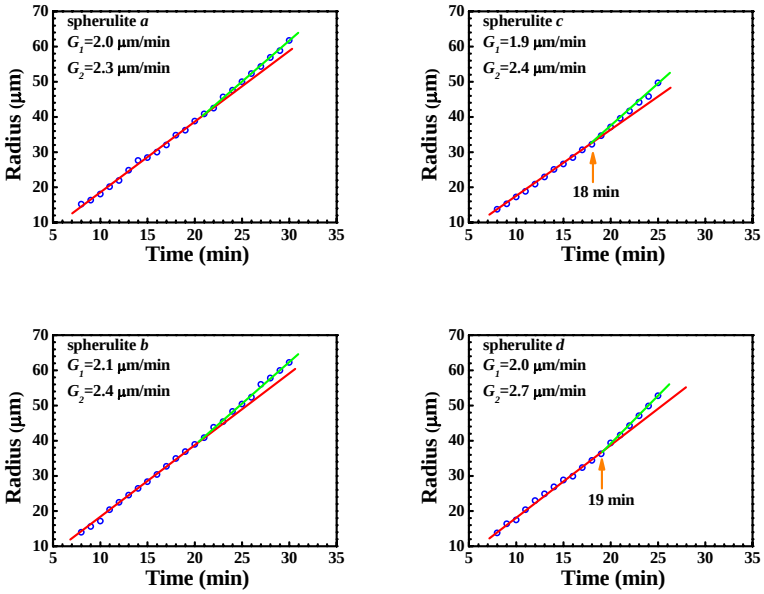


Fig. S18 Changes of radius of the selected four spherulites shown in Fig. S17 for PLLA during isothermal crystallization at 122 ^{o}C.

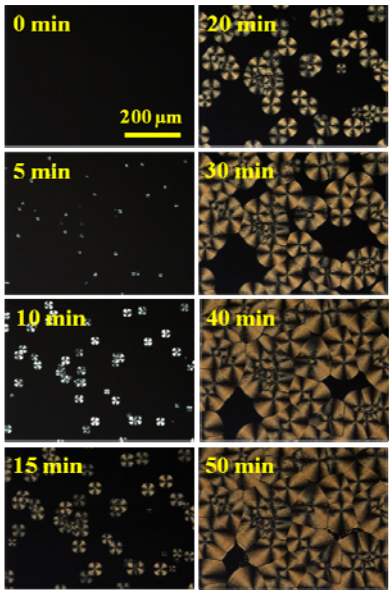


Fig. S19 Selected POM micrographs for PLLA during isothermal crystallization at 125 ^{o}C. The scale bar represents 200 μm and is applied to all the micrographs.

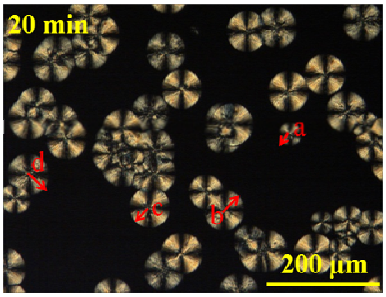


Fig. S20 Selected POM micrograph for PLLA during isothermal crystallization at 125 ^{o}C and 20 min. The four red arrows indicate the measured directions of the selected four spherulites, respectively.

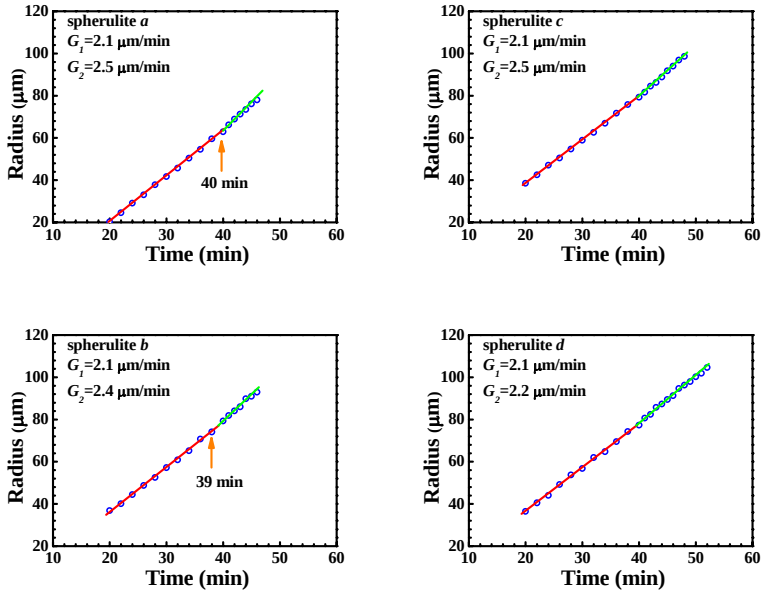


Fig. S21 Changes of radius of the selected four spherulites shown in Fig. S20 for PLLA during isothermal crystallization at 125 ^{o}C.

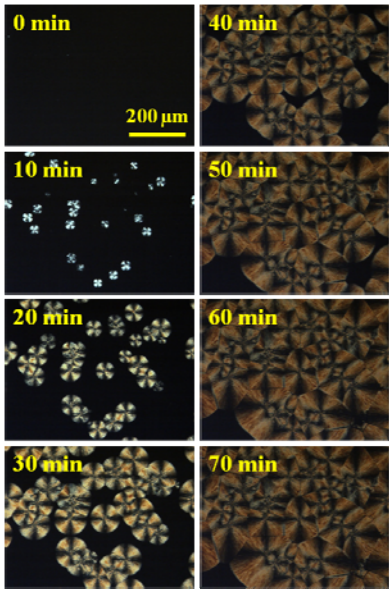


Fig. S22 Selected POM micrographs for PLLA during isothermal crystallization at 128 ^{o}C. The scale bar represents 200 μm and is applied to all the micrographs.

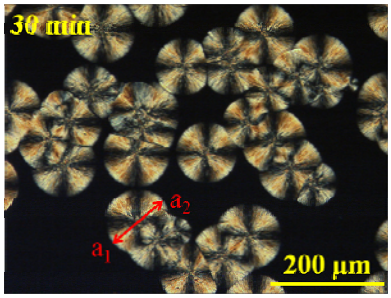


Fig. S23 Selected POM micrograph for PLLA during isothermal crystallization at 128 ^{o}C and 30 min. The two red arrows indicate the two measured directions of the selected spherulite, respectively.

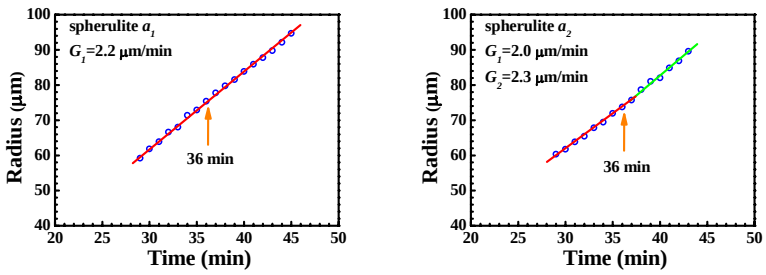


Fig. S24 Changes of radius of the selected spherulite shown in Fig. S23 for PLLA during isothermal crystallization at 128 ^{o}C.

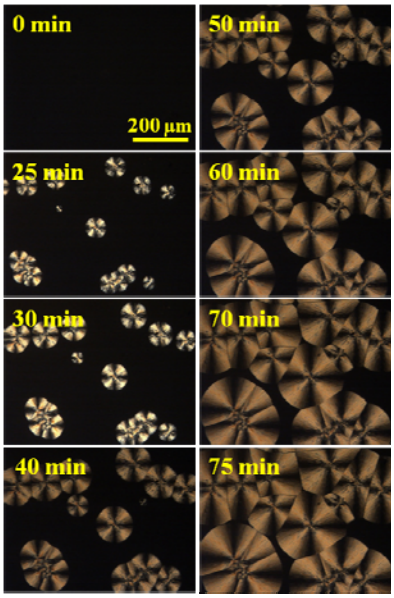


Fig. S25 Selected POM micrographs for PLLA during isothermal crystallization at 130 ^{o}C. The scale bar represents 200 μm and is applied to all the micrographs.

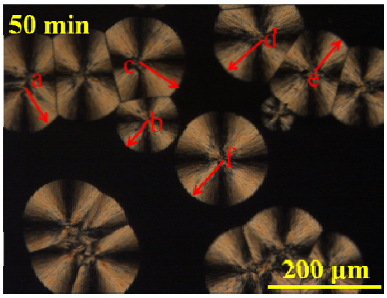
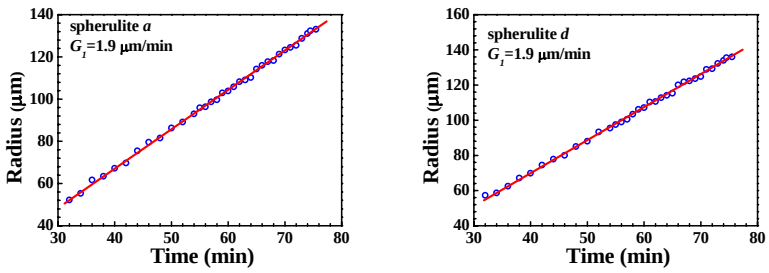


Fig. S26 Selected POM micrograph for PLLA during isothermal crystallization at 130 ^{o}C and 50 min. The six red arrows indicate the measured directions of the selected six spherulites, respectively.



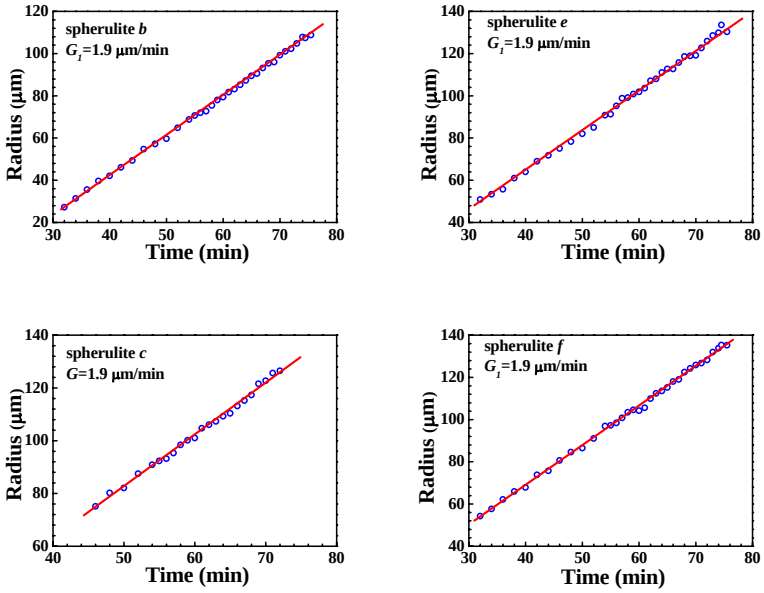


Fig. S27 Changes of radius of the selected six spherulites shown in Fig. S26 for PLLA during isothermal crystallization at 130 ^{o}C.

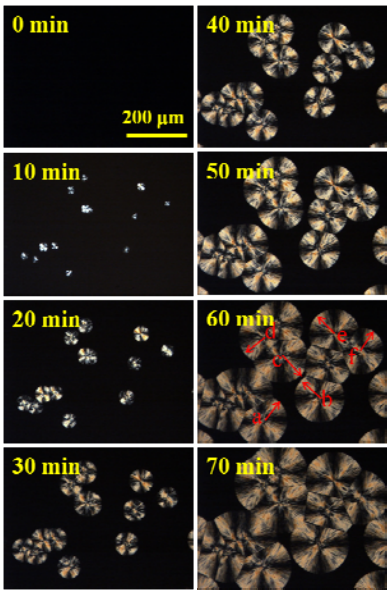


Fig. S28 Selected POM micrographs for PLLA during isothermal crystallization at 135 ^{o}C. The scale bar represents 200 μm and is applied to all the micrographs. The six red arrows in the micrograph at 60 min indicate the measured directions of the selected six spherulites, respectively.

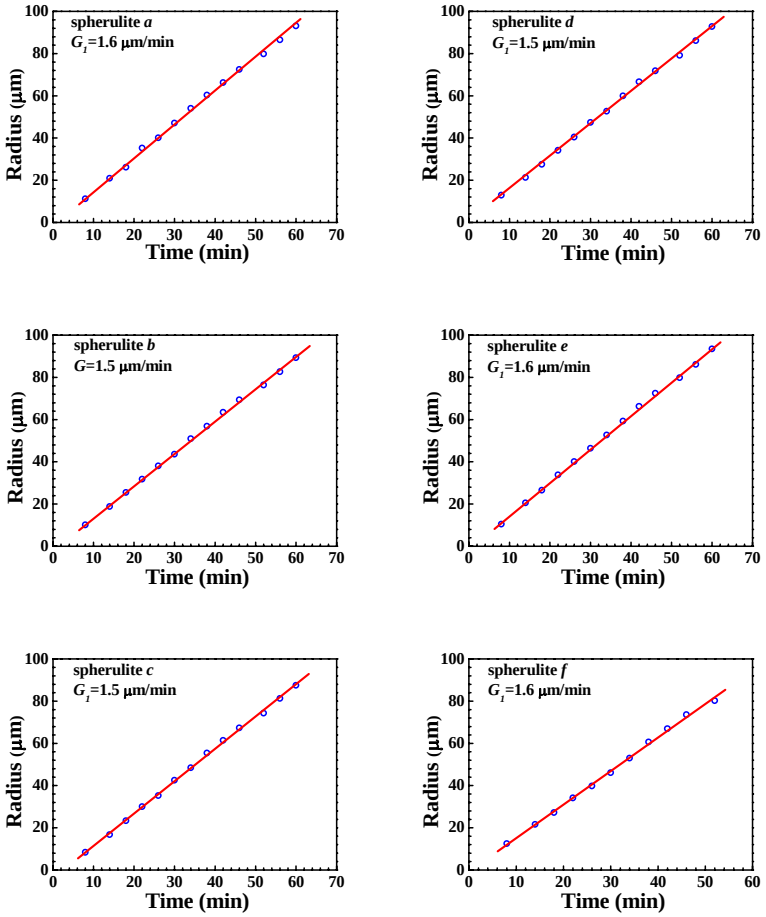


Fig. S29 Changes of radius of the selected six spherulites shown in Fig. S28 for PLLA during isothermal crystallization at 135 ^{o}C.

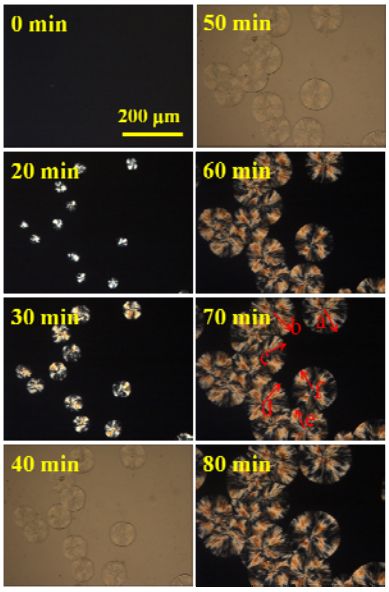
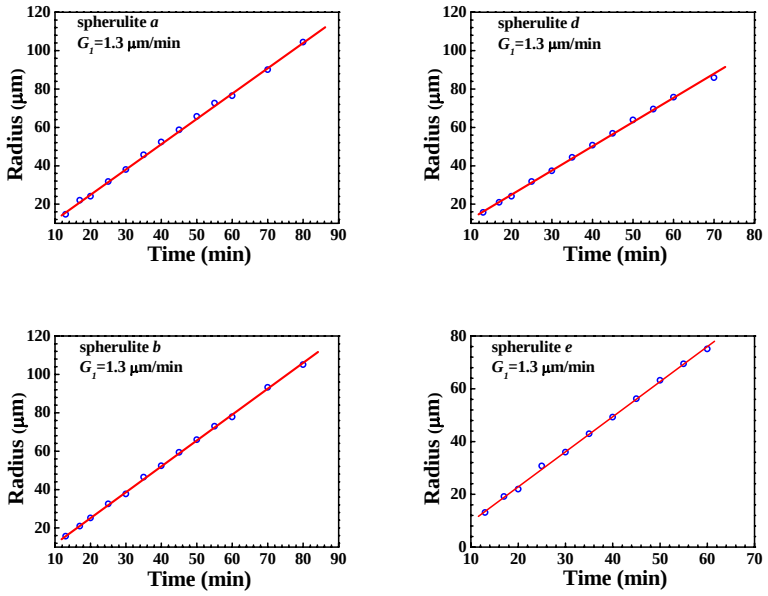


Fig. S30 Selected POM micrographs for PLLA during isothermal crystallization at 140 ^{o}C. The scale bar represents 200 μm and is applied to all the micrographs. The micrographs at 40 and 50 min were collected under bright field. The six red arrows in the micrograph at 70 min indicate the measured directions of the selected six spherulites, respectively.



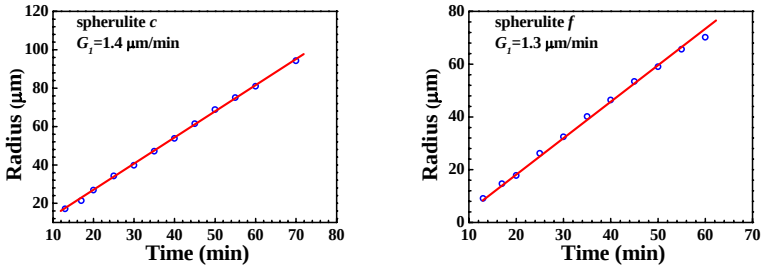


Fig. S31 Changes of radius of the selected six spherulites shown in Fig. S30 for PLLA during isothermal crystallization at 140 ^{o}C.

2. Isothermal crystallization processes of PLLA film samples with no surface confinement. The PLLA film samples with free top surface were prepared by solution cast.

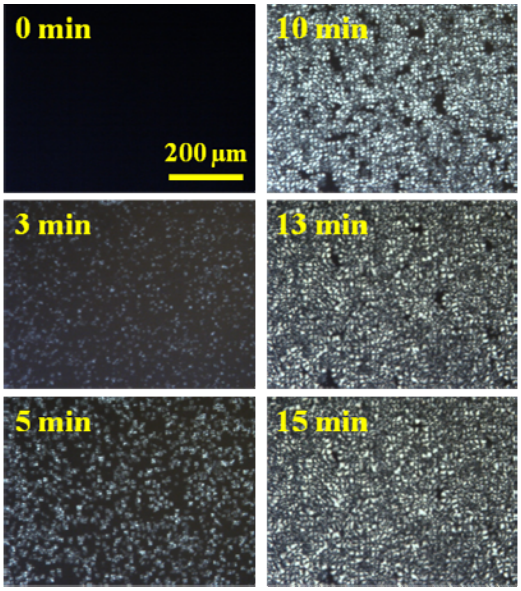


Fig. S32 Selected POM micrographs for PLLA during isothermal crystallization at 110 ^{o}C. The PLLA film was prepared by solution cast with free top surface. The scale bar represents 200 μm and is applied to all the micrographs.

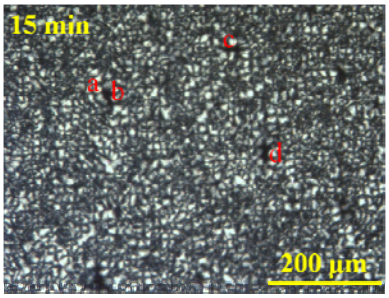


Fig. S33 Selected POM micrograph for PLLA during isothermal crystallization at 110 ^{o}C and 15 min. The four red letters indicate the measured four spherulites, respectively.

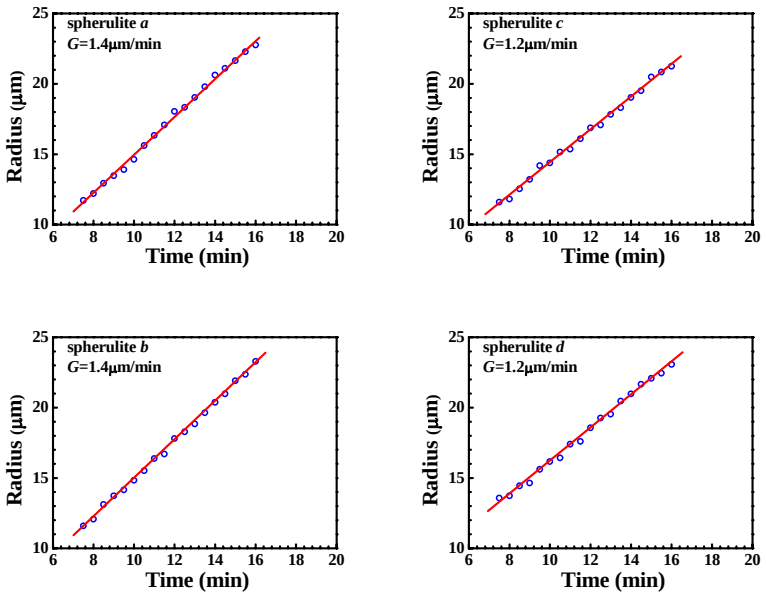


Fig. S34 Changes of radius of the selected four spherulites shown in Fig. S33 for PLLA during isothermal crystallization at 110 ^{o}C.

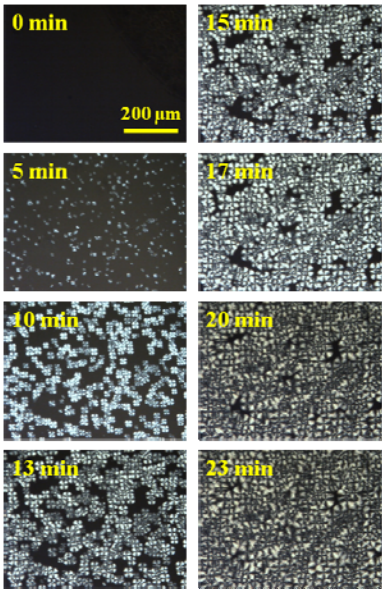


Fig. S35 Selected POM micrographs for PLLA during isothermal crystallization at 115 ^{o}C. The PLLA film was prepared by solution cast with free top surface. The scale bar represents 200 μm and is applied to all the micrographs.

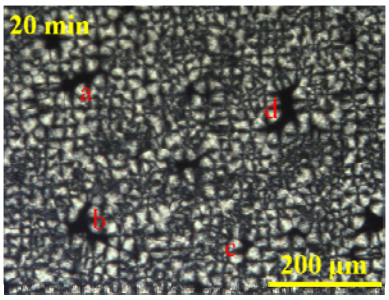
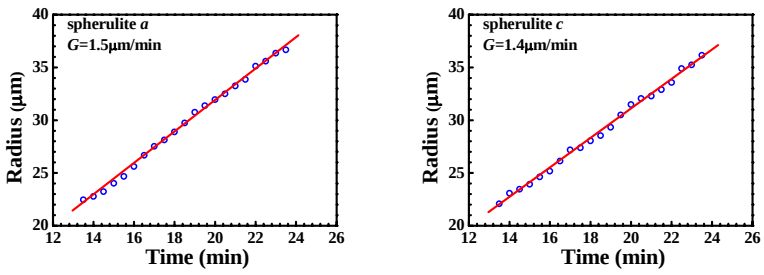


Fig. S36 Selected POM micrograph for PLLA during isothermal crystallization at 115 ^{o}C and 20 min. The four red letters indicate the measured four spherulites, respectively.



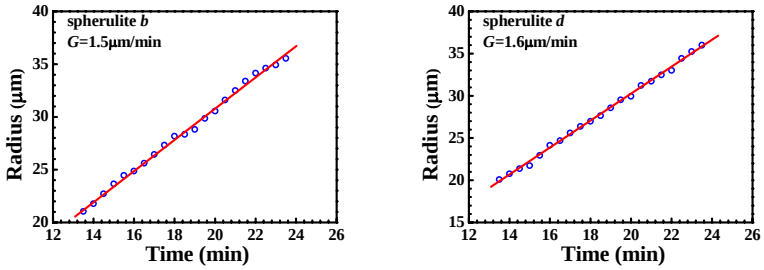


Fig. S37 Changes of radius of the selected four spherulites shown in Fig. S36 for PLLA during isothermal crystallization at 115 ^{o}C.

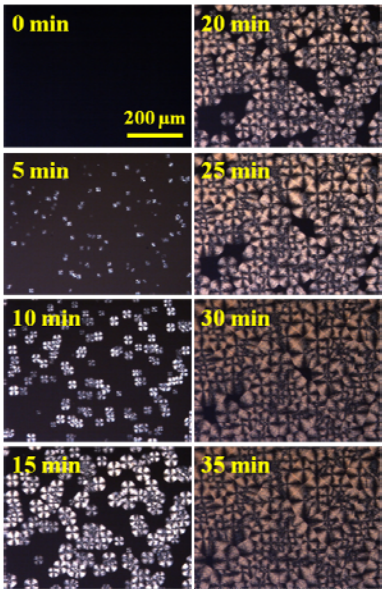


Fig. S38 Selected POM micrographs for PLLA during isothermal crystallization at 118 ^{o}C. The PLLA film was prepared by solution cast with free top surface. The scale bar represents 200 μm and is applied to all the micrographs.

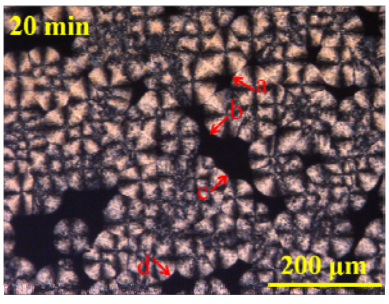


Fig. S39 Selected POM micrograph for PLLA during isothermal crystallization at 118 ^{o}C and 20 min. The four red arrows indicate the measured directions of the selected four spherulites,

respectively.

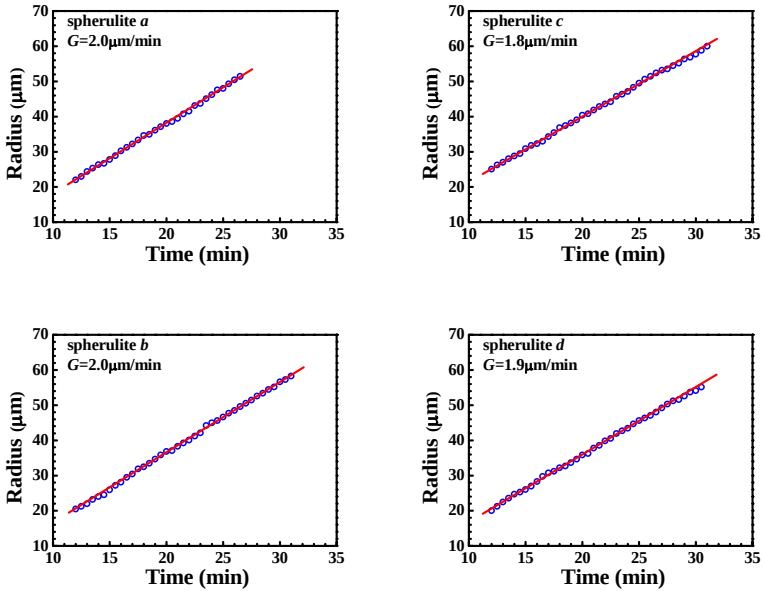


Fig. S40 Changes of radius of the selected four spherulites shown in Fig. S39 for PLLA during isothermal crystallization at 118 ^{o}C.

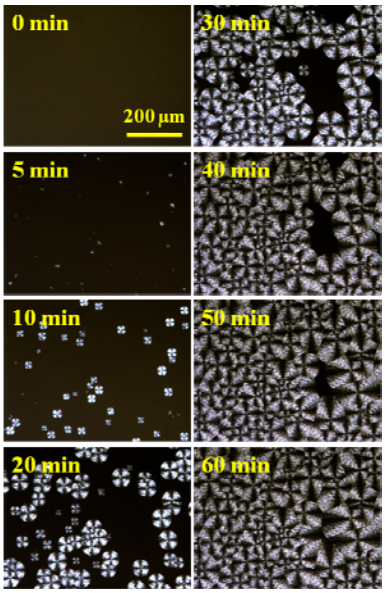


Fig. S41 Selected POM micrographs for PLLA during isothermal crystallization at 120 ^{o}C. The PLLA film was prepared by solution cast with free top surface. The scale bar represents 200 μm and is applied to all the micrographs.

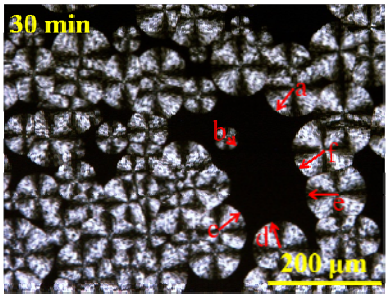


Fig. S42 Selected POM micrograph for PLLA during isothermal crystallization at 120 ^{o}C and 30 min. The six red arrows indicate the measured directions of the selected six spherulites, respectively.

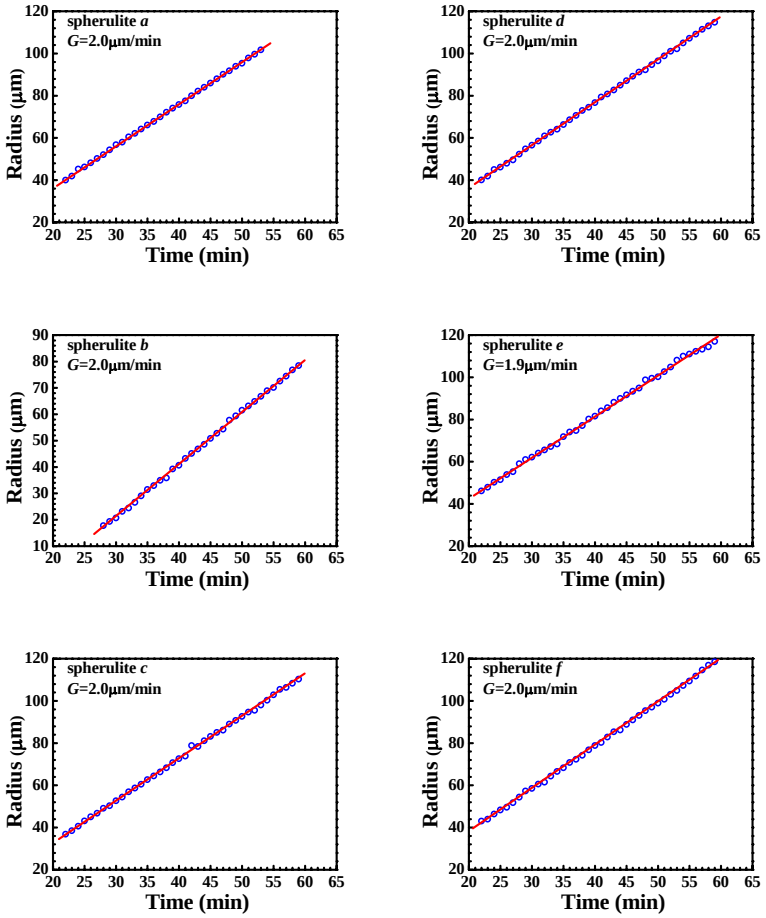


Fig. S43 Changes of radius of the selected six spherulites shown in Fig. S42 for PLLA during isothermal crystallization at 120 ^{o}C.

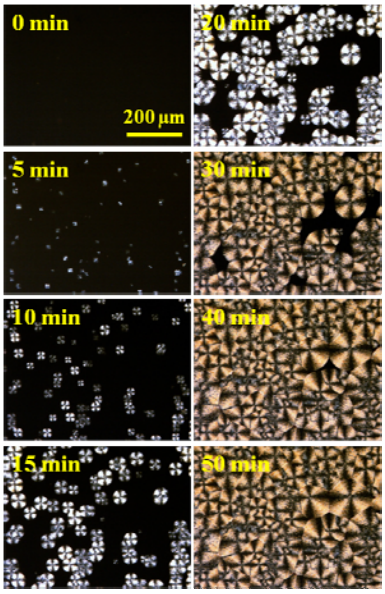


Fig. S44 Selected POM micrographs for PLLA during isothermal crystallization at 122 ^{o}C. The PLLA film was prepared by solution cast with free top surface. The scale bar represents 200 μm and is applied to all the micrographs.

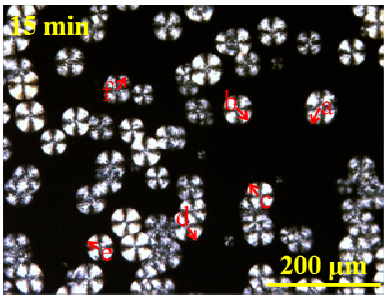
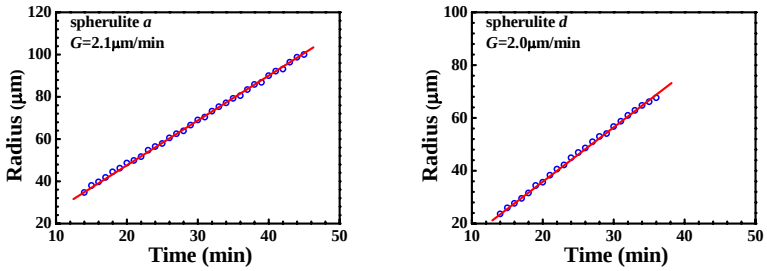


Fig. S45 Selected POM micrograph for PLLA during isothermal crystallization at 122 ^{o}C and 15 min. The six red arrows indicate the measured directions of the selected six spherulites, respectively.



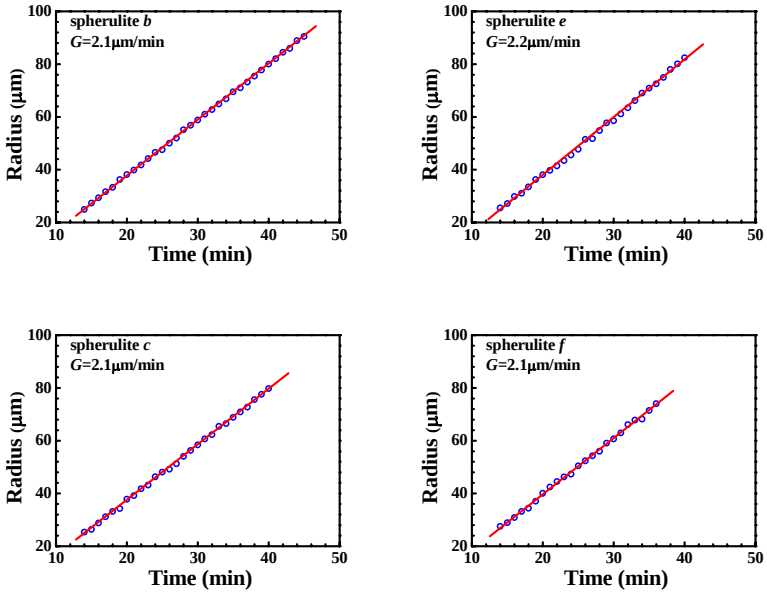


Fig. S46 Changes of radius of the selected six spherulites shown in Fig. S45 for PLLA during isothermal crystallization at 122 ^{o}C.

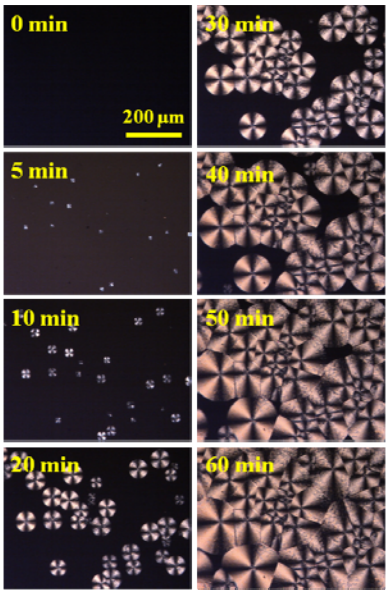


Fig. S47 Selected POM micrographs for PLLA during isothermal crystallization at 125 ^{o}C. The PLLA film was prepared by solution cast with free top surface. The scale bar represents 200 μm and is applied to all the micrographs.

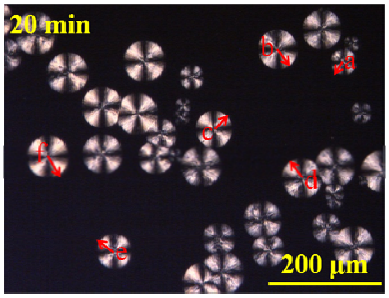


Fig. S48 Selected POM micrograph for PLLA during isothermal crystallization at 125 ^{o}C and 20 min. The six red arrows indicate the measured directions of the selected six spherulites, respectively.

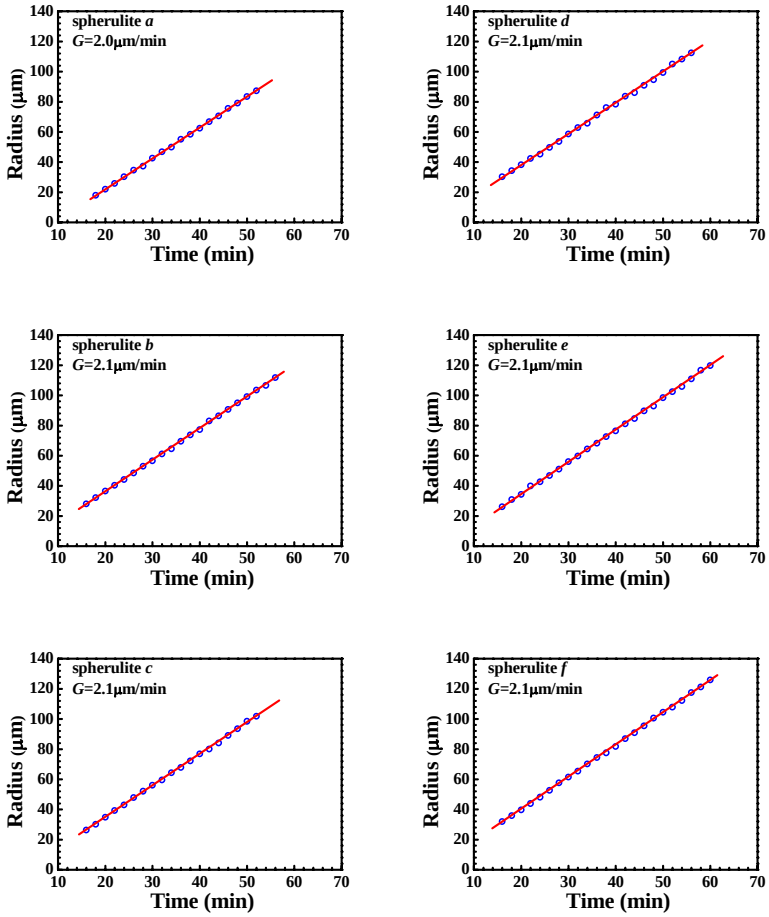


Fig. S49 Changes of radius of the selected six spherulites shown in Fig. S48 for PLLA during isothermal crystallization at 125 ^{o}C.

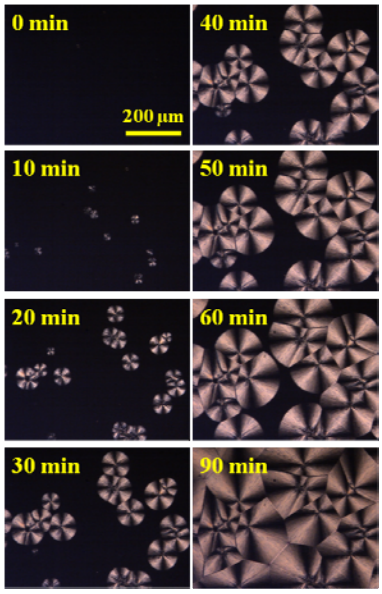


Fig. S50 Selected POM micrographs for PLLA during isothermal crystallization at 130 ^{o}C. The PLLA film was prepared by solution cast with free top surface. The scale bar represents 200 μm and is applied to all the micrographs.

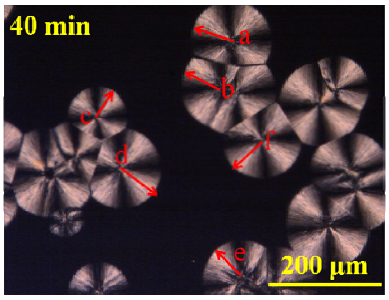
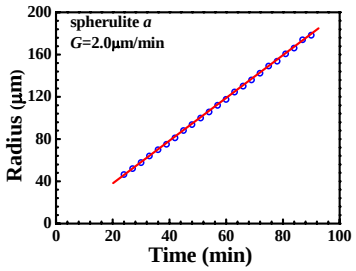
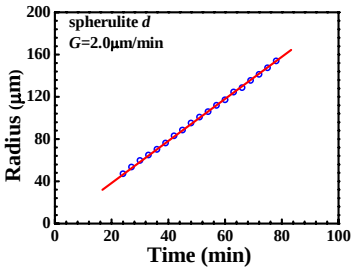


Fig. S51 Selected POM micrograph for PLLA during isothermal crystallization at 130 ^{o}C and 40 min. The six red arrows indicate the measured directions of the selected six spherulites, respectively.





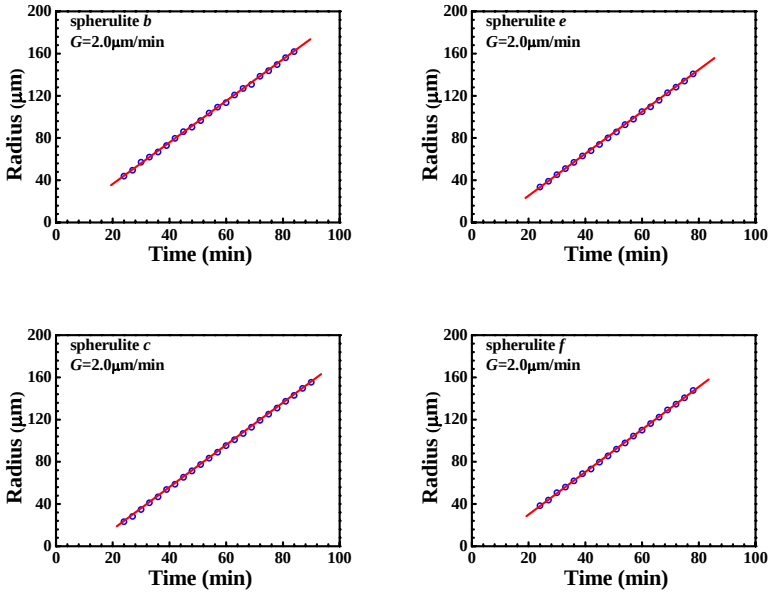


Fig. S52 Changes of radius of the selected six spherulites shown in Fig. S51 for PLLA during isothermal crystallization at 130 ^{o}C.

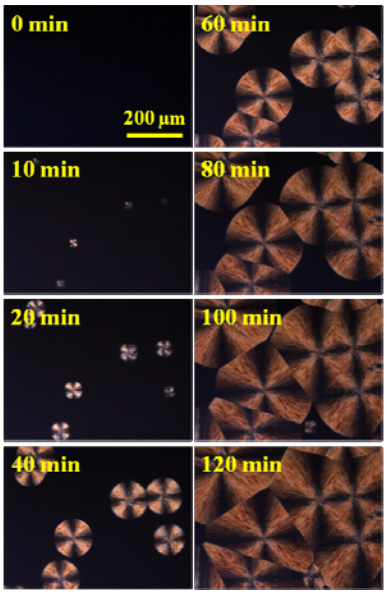


Fig. S53 Selected POM micrographs for PLLA during isothermal crystallization at 135 ^{o}C. The PLLA film was prepared by solution cast with free top surface. The scale bar represents 200 μm and is applied to all the micrographs.

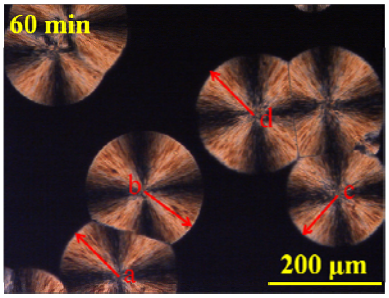


Fig. S54 Selected POM micrograph for PLLA during isothermal crystallization at 135 ^{o}C and 60 min. The four red arrows indicate the measured directions of the selected four spherulites, respectively.

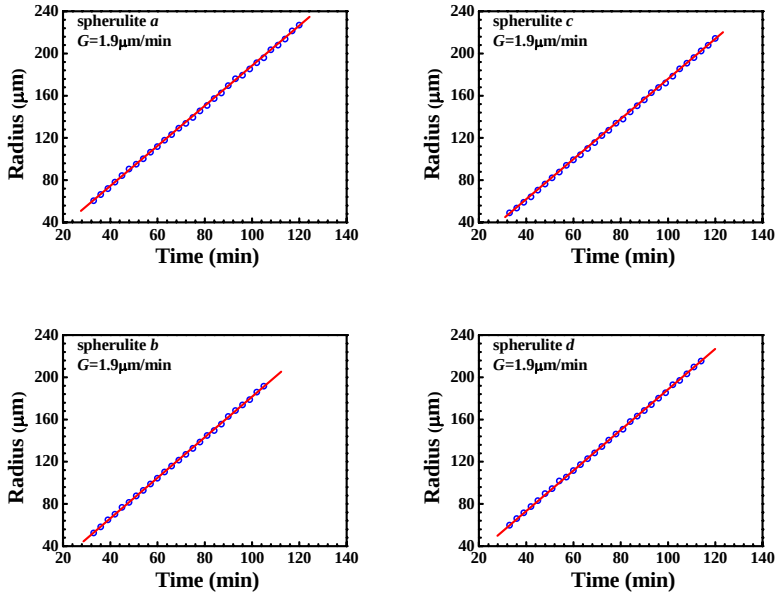


Fig. S55 Changes of radius of the selected four spherulites shown in Fig. S54 for PLLA during isothermal crystallization at 135 ^{o}C.

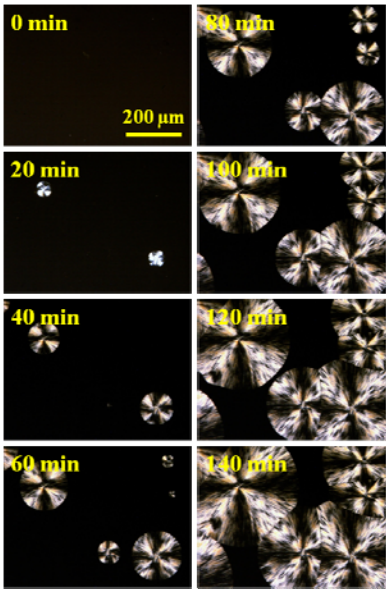


Fig. S56 Selected POM micrographs for PLLA during isothermal crystallization at 140 ^{o}C. The PLLA film was prepared by solution cast with free top surface. The scale bar represents 200 μm and is applied to all the micrographs.

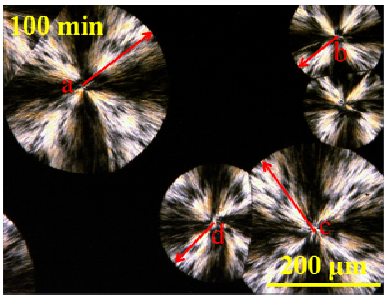
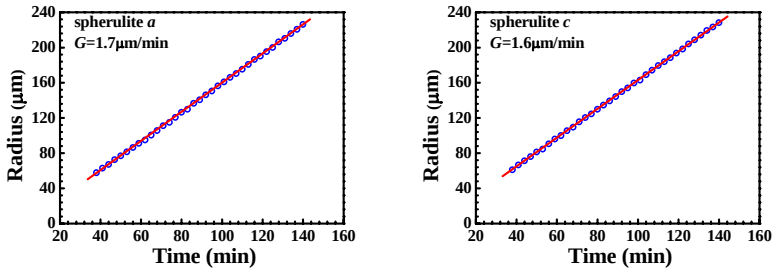


Fig. S57 Selected POM micrograph for PLLA during isothermal crystallization at 140 ^{o}C and 100 min. The four red arrows indicate the measured directions of the selected four spherulites, respectively.



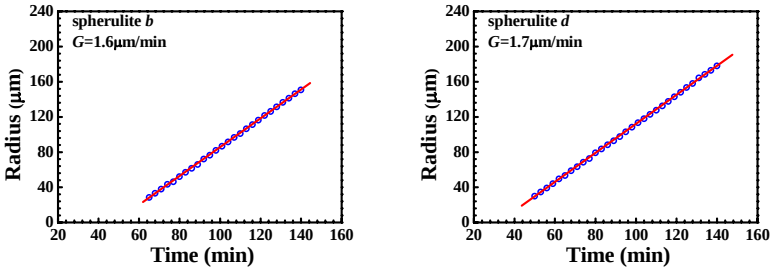


Fig. S58 Changes of radius of the selected four spherulites shown in Fig. S57 for PLLA during isothermal crystallization at 140 °C.

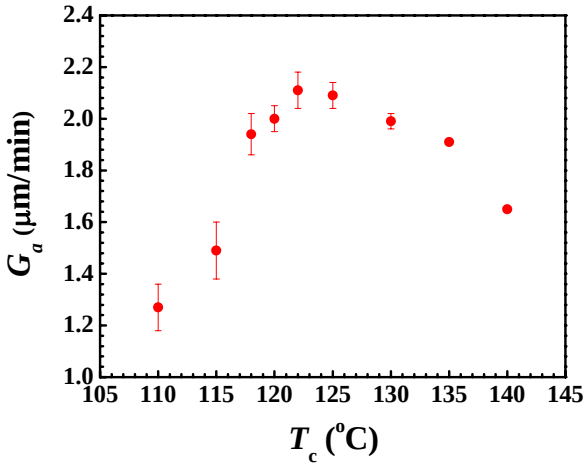


Fig. S59 Change of average spherulitic growth rate as function of isothermal crystallization temperature for PLLA film samples with free top surface prepared by solution cast.

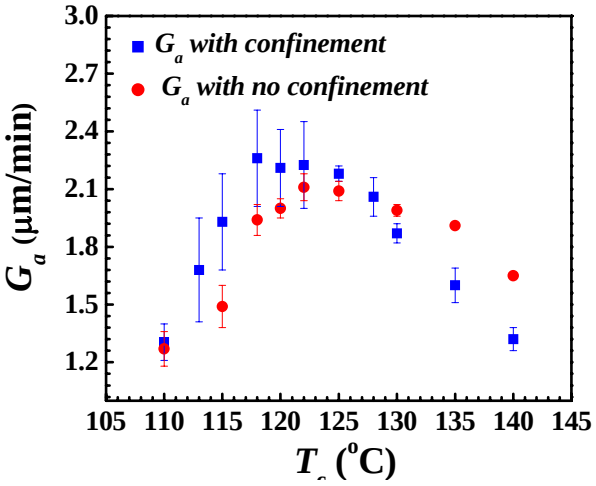


Fig. S60 Changes of average spherulitic growth rate as functions of isothermal crystallization temperature for PLLA film samples with surface confinement (between cover glasses) and with no surface confinement (solution cast), respectively.

3. Isothermal crystallization processes of PLLA film samples with no surface confinement. The PLLA film samples with free top surface were prepared by pressing PLLA melts between two cover glasses and then removing the top cover glass.

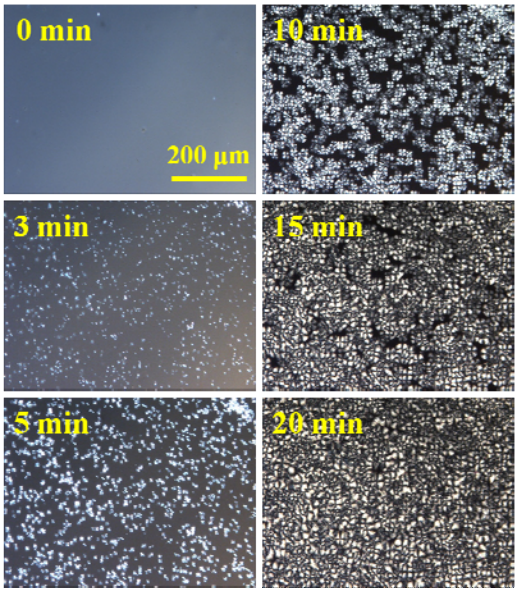


Fig. S61 Selected POM micrographs for PLLA during isothermal crystallization at 110 ^{o}C. The PLLA film sample was prepared by removing the top cover glass after pressing PLLA melts between two cover glasses. The scale bar represents 200 μm and is applied to all the micrographs.

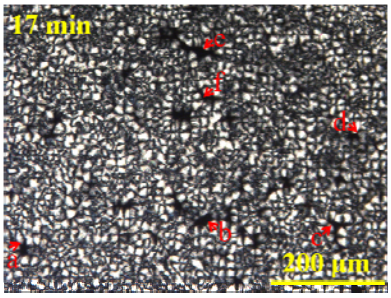


Fig. S62 Selected POM micrograph for PLLA during isothermal crystallization at 110 ^{o}C and 17

min. The six red arrows indicate the measured directions of the selected six spherulites, respectively.

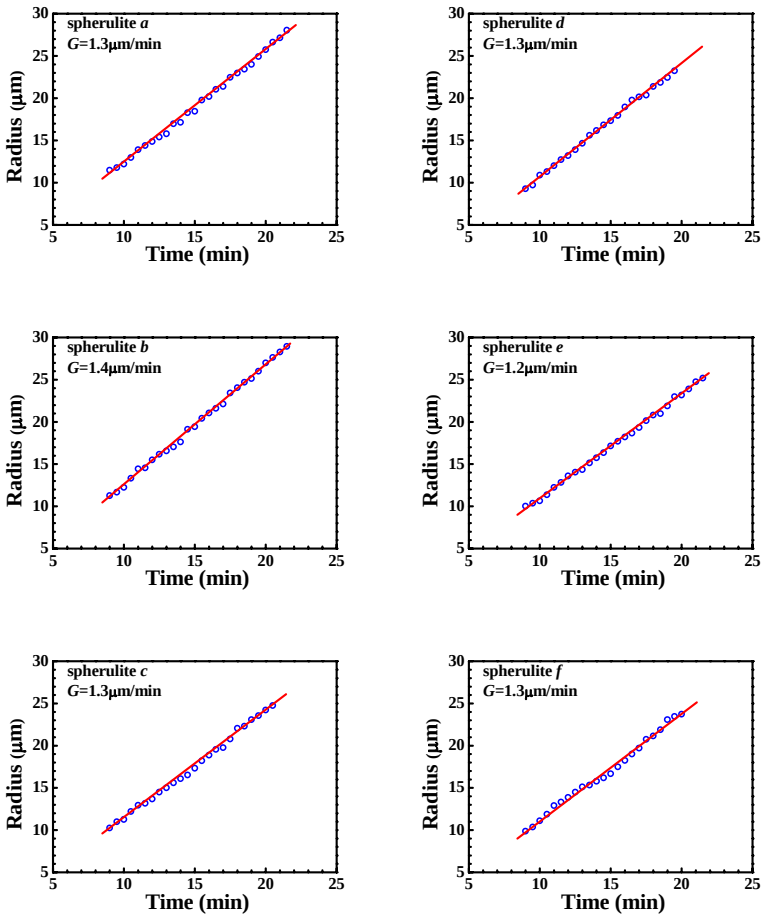


Fig. S63 Changes of radius of the selected six spherulites shown in Fig. S62 for PLLA during isothermal crystallization at 110 ^{o}C.

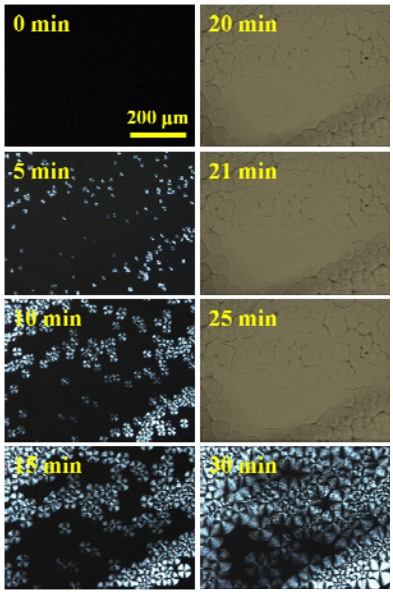


Fig. S64 Selected POM micrographs for PLLA during isothermal crystallization at 120 ^{o}C. The PLLA film sample was prepared by removing the top cover glass after pressing PLLA melts between two cover glasses. The micrographs at 20, 21 and 25 min were collected under bright field. The scale bar represents 200 μm and is applied to all the micrographs.

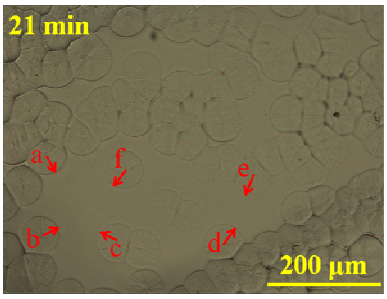
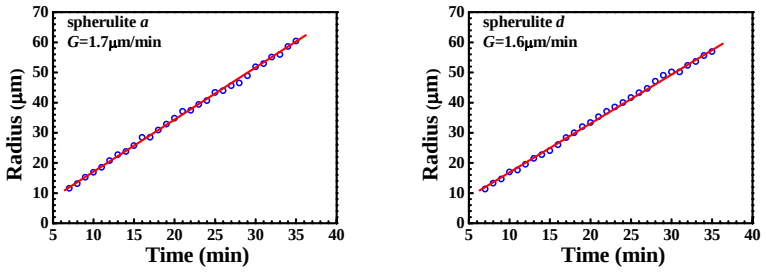


Fig. S65 Selected POM micrograph for PLLA during isothermal crystallization at 120 ^{o}C and 21 min. The six red arrows indicate the measured directions of the selected six spherulites, respectively.



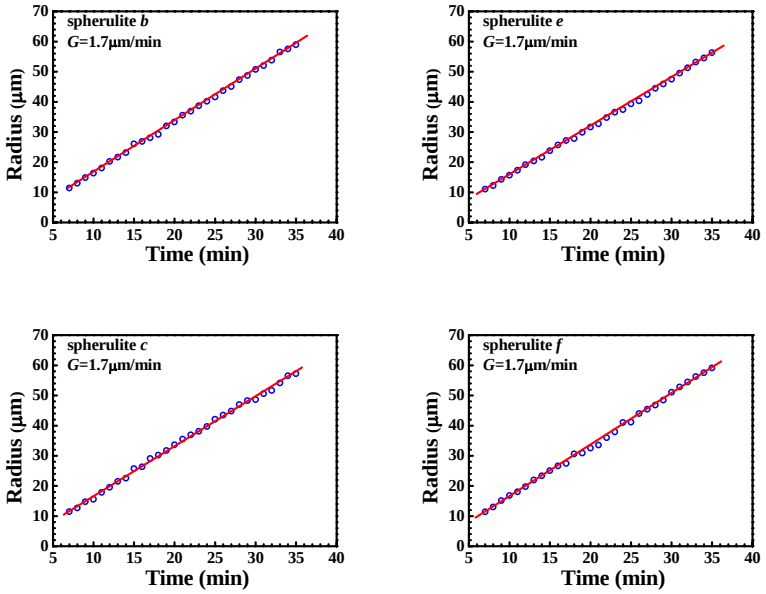


Fig. S66 Changes of radius of the selected six spherulites shown in Fig. S65 for PLLA during isothermal crystallization at 120 ^{o}C.

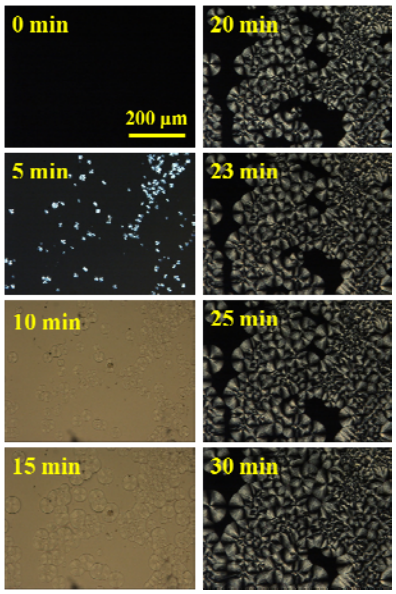


Fig. S67 Selected POM micrographs for PLLA during isothermal crystallization at 122 ^{o}C. The PLLA film sample was prepared by removing the top cover glass after pressing PLLA melts between two cover glasses. The micrographs at 10 and 15 min were collected under bright field. The scale bar represents 200 μm and is applied to all the micrographs.

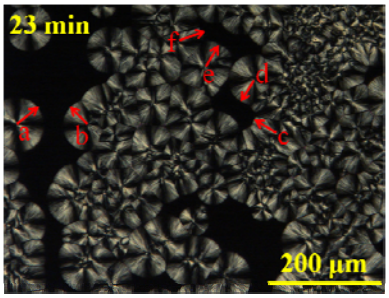


Fig. S68 Selected POM micrograph for PLLA during isothermal crystallization at 122 ^{o}C and 23 min. The six red arrows indicate the measured directions of the selected six spherulites, respectively.

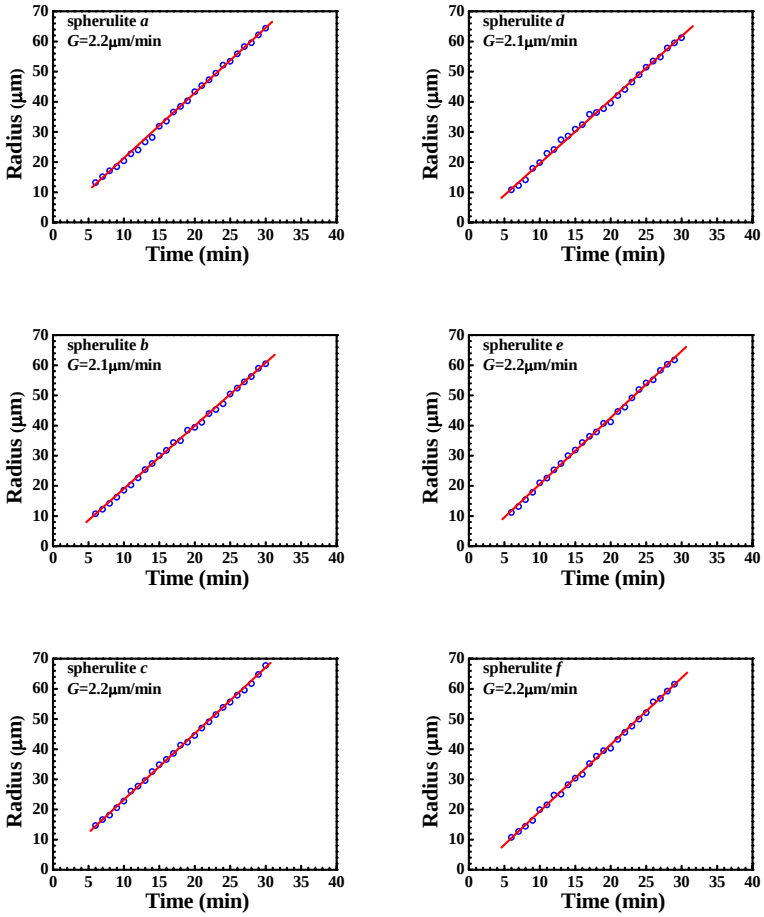


Fig. S69 Changes of radius of the selected six spherulites shown in Fig. S68 for PLLA during isothermal crystallization at 122 ^{o}C.

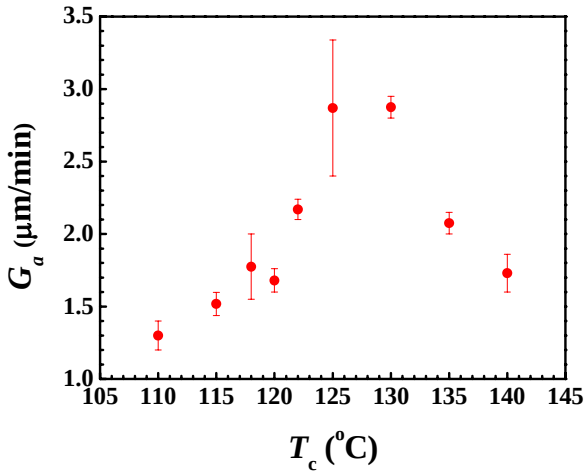


Fig. S70 Change of average spherulitic growth rate as function of isothermal crystallization temperature for PLLA film samples prepared by removing the top cover glass after pressing PLLA melts between two cover glasses.

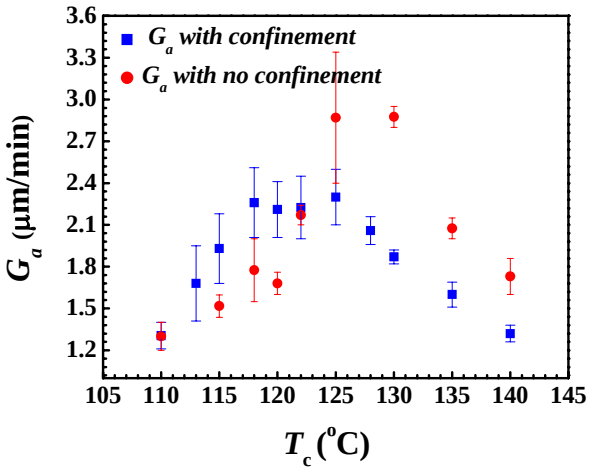


Fig. S71 Changes of average spherulitic growth rate as functions of isothermal crystallization temperature for PLLA film samples with surface confinement (between cover glasses) and with no surface confinement (by removing the top cover glass), respectively.

4. Hoffman-Weeks plot to obtain the equilibrium melting point for PLLA from DSC measurements

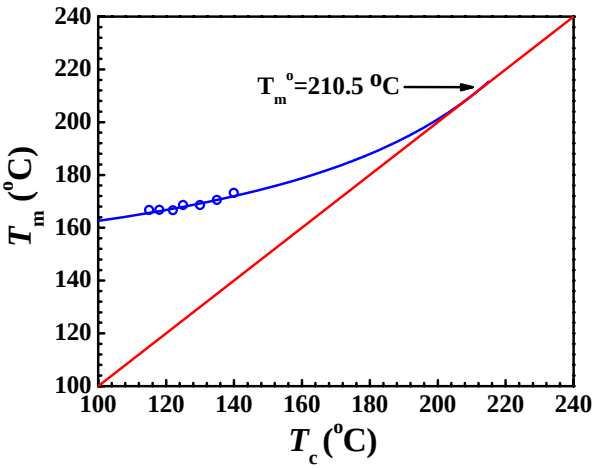


Fig. S72 Hoffman-Weeks plot to obtain the equilibrium melting point for PLLA from DSC measurements.

5. AFM height image of the surface of PLLA film sample. The sample was prepared by pressing PLLA melts between cover glasses and after crystallization at 110 °C for 30 min the top cover glass was removed for the AFM observation.

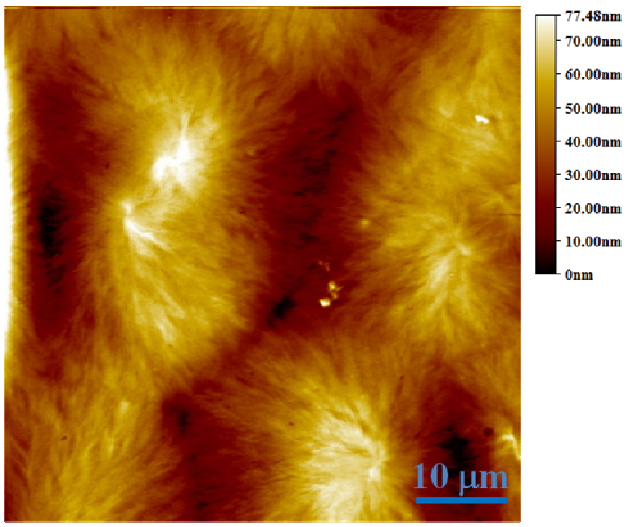


Fig. S73 AFM height image of the surface of PLLA film sample, indicating the gradually decreasing height radially from the spherulite center. The sample was prepared by pressing PLLA melts between cover glasses and after crystallization at 110 °C for 30 min the top cover glass was removed for the AFM observation.

6. Nucleus numbers formed during crystallization and film thicknesses for PLLA film samples covered with cover glass and uncovered solution cast PLLA film samples.

Table S1. Nucleus numbers formed during crystallization and film thicknesses for PLLA film samples covered with cover glass and uncovered solution cast PLLA film samples.

T_c (^oC)	N_{c1}	N_{c2}	l_c (μm)	N_{s1}	N_{s2}	l_s (μm)	N_{c1}/l_c	N_{c2}/l_c	N_{s1}/l_s	N_{s2}/l_s
140	13	15	28	2	7	46	0.46	0.54	0.04	0.15
135	14	17	32	7	11	54	0.44	0.53	0.13	0.20
130	17	20	33	20	24	46	0.52	0.61	0.43	0.52
125	49	56	25	25	41	40	1.96	2.24	0.63	1.03
122	168	181	31	85	95	49	5.42	5.84	1.73	1.94
120	90	100	30	46	67	41	3.00	3.33	1.12	1.63
118	229	242	23	121	131	38	9.96	10.52	3.18	3.45
115	672	770	27	411	415	38	24.89	28.52	10.82	10.92

Note: T_c stands for the crystallization temperature, N_{c1} stands for the nucleus number at the early stage of crystallization for PLLA films covered with cover glass, N_{c2} stands for the nucleus number at the late stage of crystallization for PLLA films covered with cover glass, and l_c stands for the corresponding film thickness; N_{s1} stands for the nucleus number at the early stage of crystallization for uncovered solution cast PLLA films, N_{s2} stands for the nucleus number at the late stage of crystallization for uncovered solution cast PLLA films, and l_s stands for the corresponding film thickness.

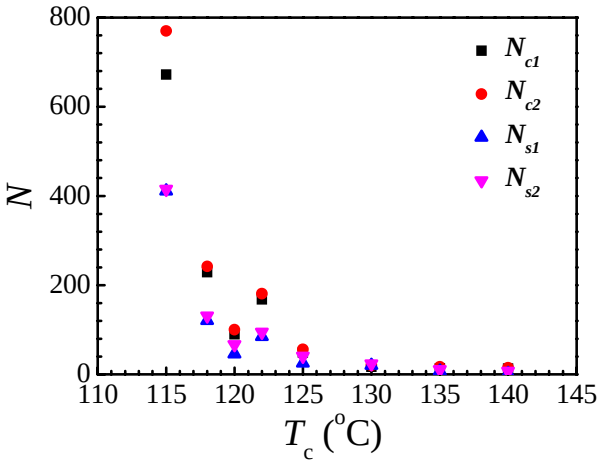


Fig. S74 Changes of nucleus number with crystallization temperature for PLLA film samples covered with cover glass and uncovered solution cast PLLA film samples, respectively.

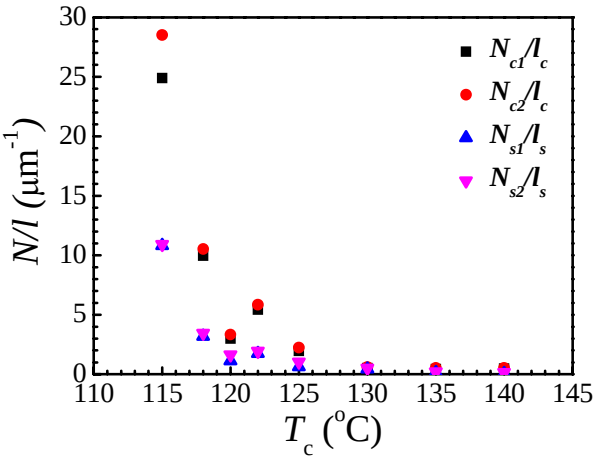


Fig. S75 Changes of nucleus number normalized by film thickness with crystallization temperature for PLLA film samples covered with cover glass and uncovered solution cast PLLA film samples, respectively.

7. DSC heat flow curves for obtaining the glass transition temperatures for PLLA crystallized at different conditions

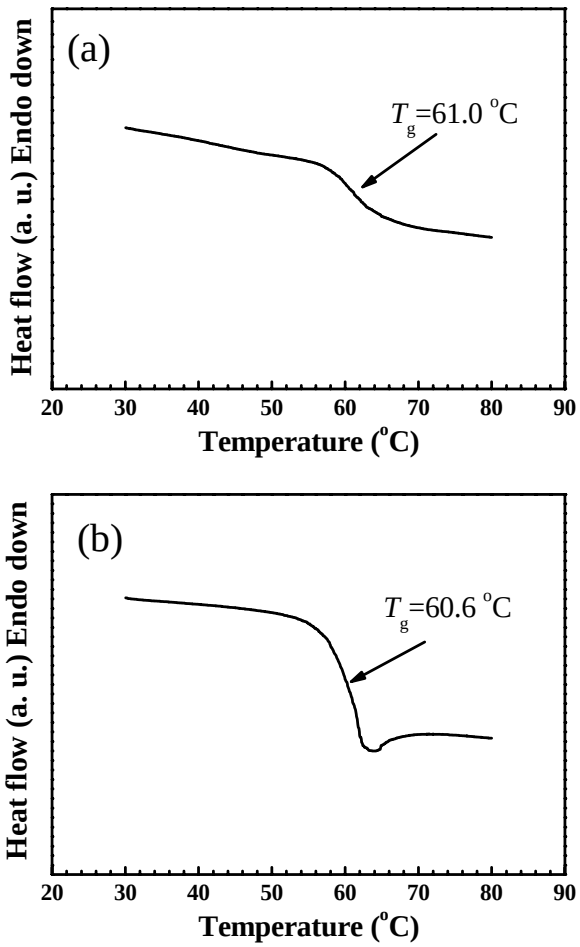


Fig. S76 (a) DSC heat flow curve during the first heating scan with a heating rate of 10 °C/min for PLLA sample, which had crystallized between cover glasses for certain times when the spherulites began to impinge upon each other at 135 °C. (b) DSC heat flow curve during the second scan with a heating rate of 10 °C/min for PLLA sample from (a), which were then remained at 180 °C for 5 min and then quenched to 30 °C at a cooling rate of 50 °C/min.

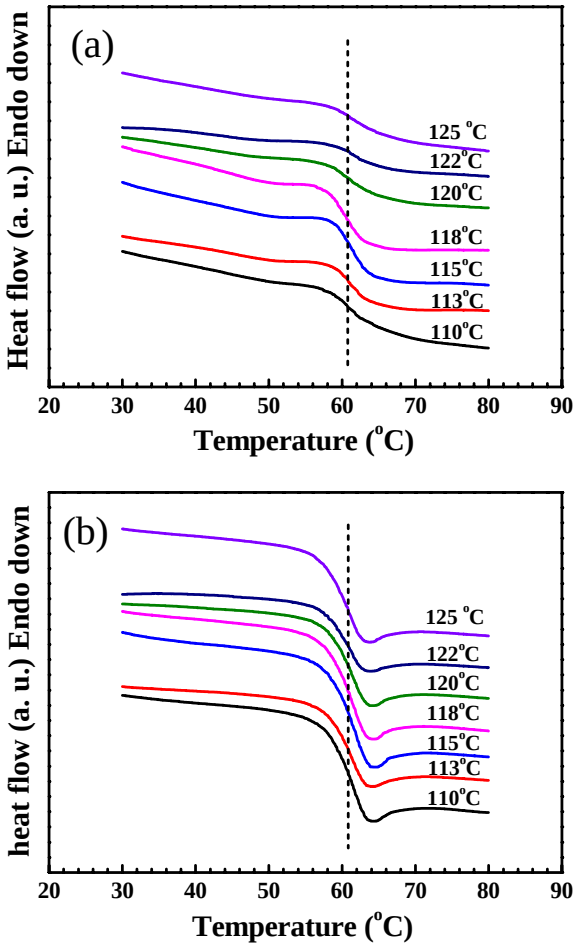


Fig. S77 (a) DSC heat flow curves during the first heating scan with a heating rate of 10 °C/min for PLLA samples with free top surface (obtained from solution cast), which had crystallized for certain times when the spherulites began to impinge upon each other at different temperatures. (b) DSC heat flow curves during the second scan with a heating rate of 10 °C/min for PLLA samples from (a), which were remained at 180 °C for 5 min and then quenched to 30 °C at a cooling rate of 50 °C/min. The used crystallization temperatures are marked above the curves.

Table S2. T_g values for PLLA film samples with free top surface (obtained from solution cast), which had crystallized for certain times when the spherulites began to impinge upon each other at different temperatures. T_{g1} values are obtained from the heat flow curves shown in Fig. S77a,

and T_{g2} values are obtained from that shown in Fig. S77b.

T_c (°C)	T_{g1} (°C)	T_{g2} (°C)
110	**60.9**	**61.6**
113	**60.8**	**61.3**
115	**61.4**	**61.7**
118	**60.5**	**61.3**
120	**61.1**	**61.4**
122	**61.6**	**60.8**
125	**61.4**	**61.1**