Electronic Supporting Information

How to regulate the isothermal growth rate of polymer spherulite without changing its molecular composition?

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Experiment section

Materials and Sample Preparation

Poly(butylene succinate) (PBS) and the copolymer of poly(butylene succinate-co-fumarate) (PBSF) were synthesized by a two-step reaction of esterification and polycondensation in the molten state, the detailed description can be seen in our previous work.[1,2] The basic information of the samples has been listed in Table S1.

The additive weight percentage of PBSF 40 and PBSF 60 was chosen as 1wt% in PBS matrix. Blend samples were dissolved in chloroform simultaneously and maintained for 3h at 50 °C to get a uniform solution. Then casting the solution in a glass disk to evaporate the solvent. The residual film was dried in vacuum at 50 °C until the solvent evaporated completely.

Equipment and Characterization techniques

Gel permeation chromatography system (Viscotek, M302 TDA) and ^{1}HNMR spectrometer (JEOL, ECA-400M) were used to determine the molecular weights (Mn and Mw) and composition of PBS and PBSF respectively.

Wide-angle X-ray diffraction (WAXD) analysis was carried out at room temperature using a Rigaku D/max2550HB+/PCX-ray diffractometer with Cu Kα radiation.

The crystallization behaviors of the samples were characterized by a differential scanning calorimeter (Shimadzu DSC-60) under a nitrogen atmosphere. Before measurements, indium and zinc standards were used for calibration. The natural crystallization (T_c) and melting temperature (T_m) of the samples in Table S1 were taken from the exothermal and endothermic peak at a cooling or heating rate of 10 °C/min on the DSC.

Self-nucleation experiment (SN) which was invented by Fillon[3] was performed according to the temperature profile in Figure S1. To obtain the crystallization temperature (T_c) after SN, four steps of thermal treatment should be following: (a) Elimination of the thermal history by heating the samples to 160 °C for 5 min. (b) Creation of a "standard" thermal history by cooling the samples to 35 °C at a rate of 10 °C /min. (c) Partially melting the samples for 5 minutes at a planned T_s. (d) Cooling the samples from T_s to 35 °C for crystallization following the full line in Figure S1. This procedure was repeated in various T_ss. The process of isothermal crystallization is identical in the step of (a)-(c), while the sample at step (d') should be cooled to pre-set temperature as soon as possible and maintain with it until the crystallization process was completed.

Leica polarized optical microscope (POM) (DM2500P) equipped with a Linkam THMS600 hot stage was used to obtain the crystal morphology and the spherulitic radial growth rates (G) of the samples. The measurement of spherulitic radial growth rate of the SN samples were following the procedure (a)-(d') in the Linkam THMS600 hot stage.

To make the SN experiment in Figure 3 easily understandable, P-60 had been chosen as an example. The T_c (black grid) in Figure 3 (c) was obtained by following the procedure (a)-(d), and the range of T_s is 113-145 °C. The G of P-60 SN at 133 °C was measured by following the procedure (a)-(c)-(d'), and the T_s was fixed in 133 °C. By repeating the procedure (a)-(c)-(d') and changing the isothermal crystallization temperature (98-103 °C) in (d'), the whole red dot in Figure 3(d) have been obtained. For the study of effect of PBSF 60 and SN method on the isothermal crystallization kinetics of PBS (Figure S4 (b)), the procedure was the same as (a)-(c)-(d') and executed in DSC.
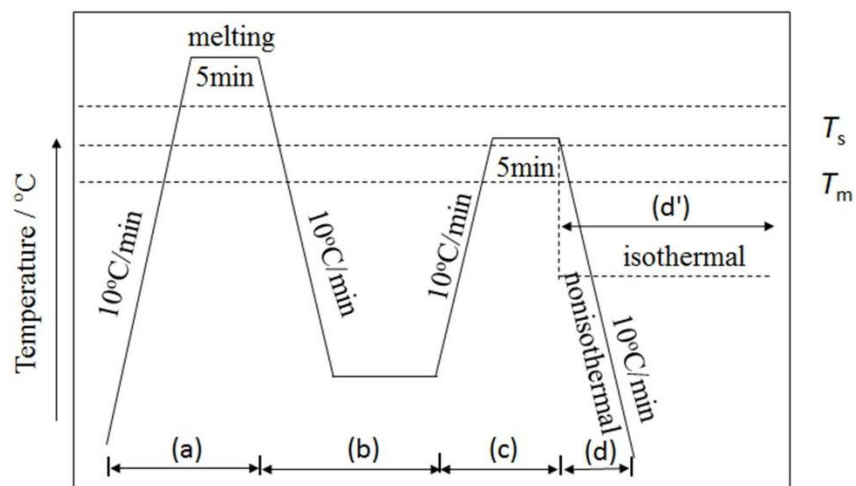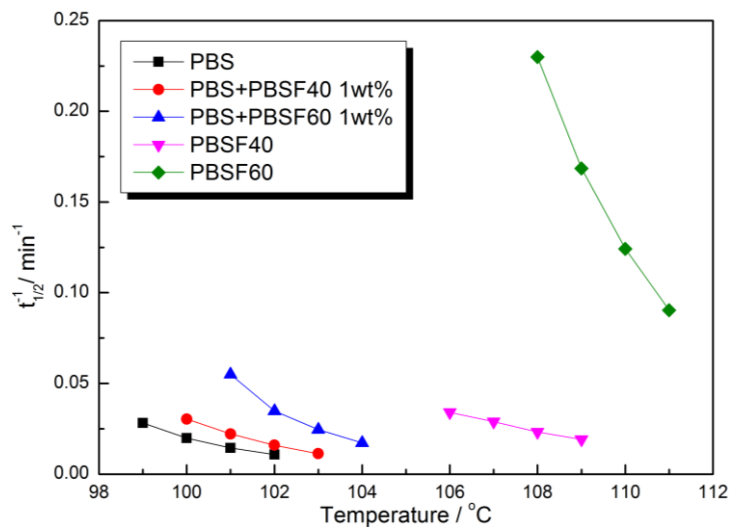
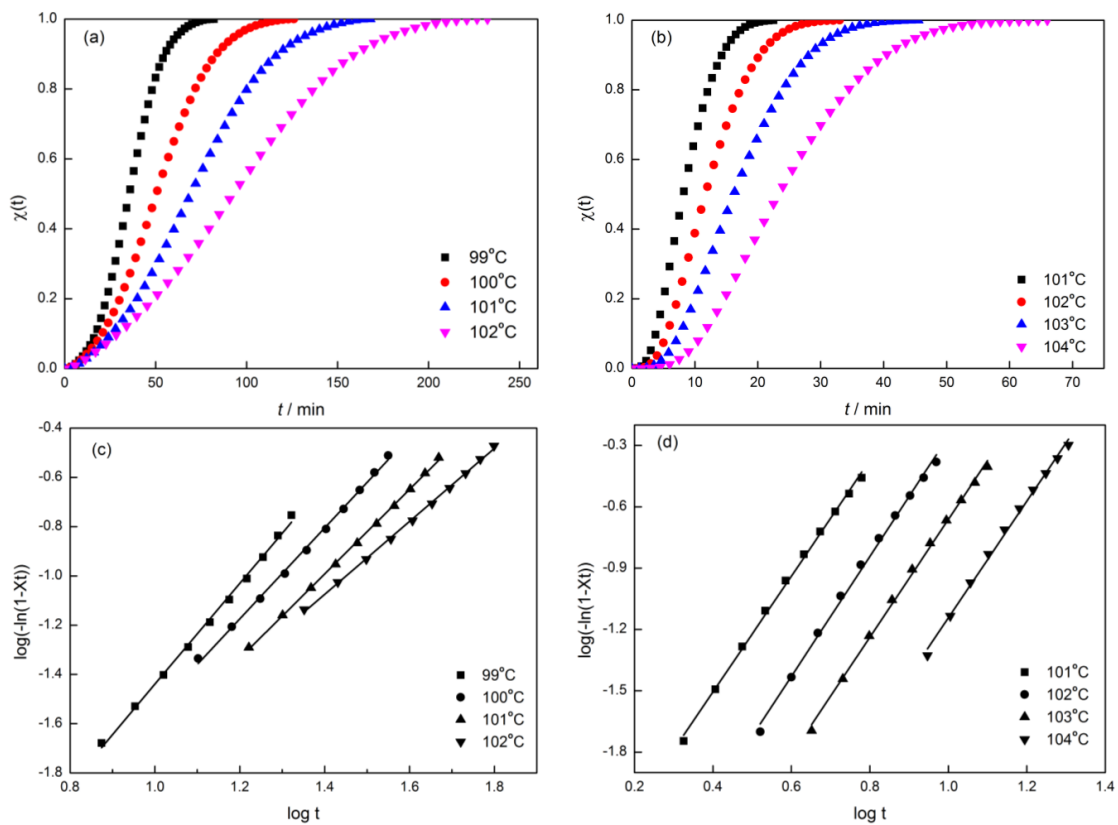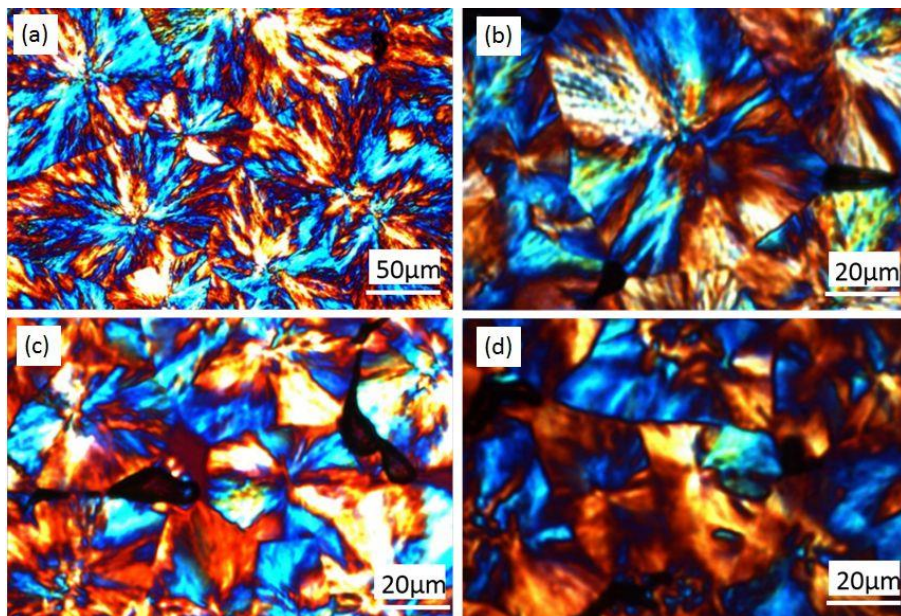**Figure S1.** Typical self-nucleating procedure.
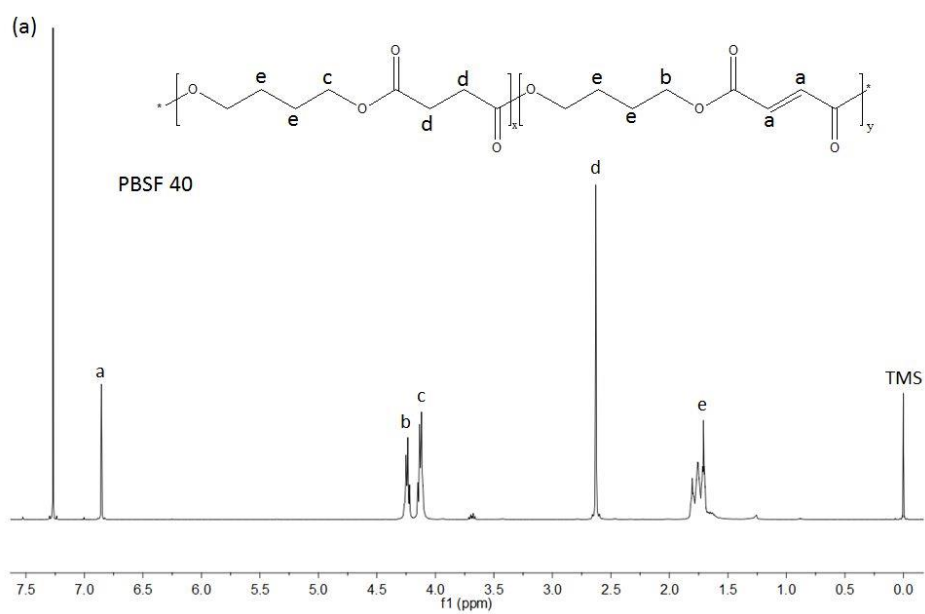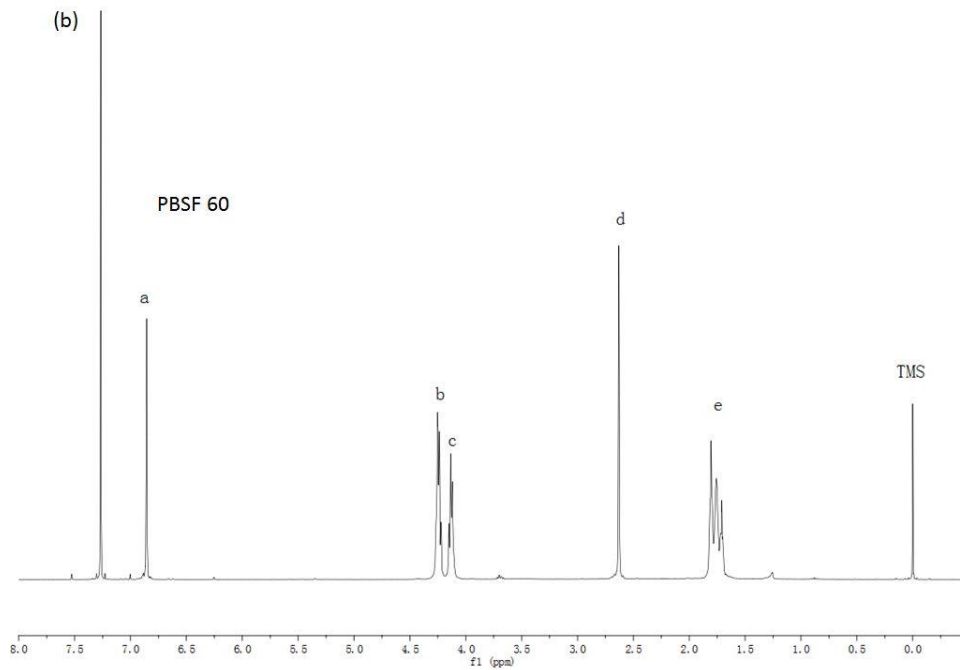
Figure S2. ^{1}H-NMR spectrum of (a)PBSF 40 and (b)PBSF 60 copolyester.

Figure S3. Dependence of the inverse crystallization half time ($1/t_{1/2}$) on temperature.

Figure S4. Development of relative crystallinity as a function of time for (a) PBS, (b) P-60 SN at 133 °C; Corresponding Avrami plots of (c) PBS, (d) P-60 SN at 133 °C.

Figure S5. Spherulitic morphologies of (a) pure PBS, (b) P-60, (c) P-60 after SN treatment at 133 °C, and (d) P-60 after SN treatment at 136 °C then crystalized at 102 °C.
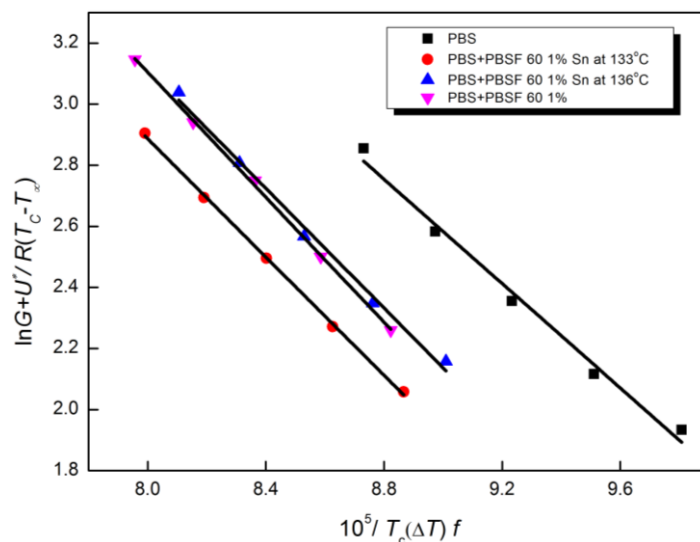
Figure S6. Plots of $\ln G + U^*/R(T_c - T_\infty)$ vs $10^5/T(\Delta T)f$ for different samples by using the empirical values of $U^* = 1500$ cal/mol and $T_\infty = T_g - 30$ K.

Table S1. Fundamental physical properties of PBS, PBSF 40, and PBSF 60.

Samples	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_m (J·g^{-1})	BF content	$M_n \times (10^4)$	$M_w \times (10^4)$	PDI
PBS	-40.0	77.5	114.5	68.7	0	3.17	8.04	2.5
PBSF 40	-35.8	87.7	121.4	68.8	36.4	0.86	3.32	3.8
PBSF 60	-31.4	94.7	127.6	71.7	55.6	0.73	1.65	2.3

T_g: Glass transition temperature

T_c: The peak temperature of the exothermic on the DSC cooling curve at the cooling rate of 10°C/min

T_m: The peak temperature of the endotherm on the DSC heating curve at the heating rate of 10°C/min

PDI: Polydispersity index.

Table S2. Avrami exponents of neat PBS and PBSF60-nucleated PBS at various temperatures

Samples	Crystallization temperature (°C)	n	k (min^{-n})	$t_{1/2}$ (min)
Neat PBS	99	2.04	3.29×10^{-4}	35.5
	100	1.85	4.08×10^{-4}	50.5
	101	1.71	4.12×10^{-4}	69.3
	102	1.48	7.16×10^{-4}	92.6
PBS+1 wt% PBSF 60 without SN	101	2.66	3.51×10^{-4}	18.2
	102	2.69	8.42×10^{-5}	28.8
	103	2.63	4.19×10^{-5}	40.7
	104	2.34	4.72×10^{-5}	58.2
PBS+1 wt% PBSF 60 SN at 136 °C	101	2.86	1.65×10^{-3}	8.8
	102	2.98	4.53×10^{-4}	12.5
	103	2.98	1.61×10^{-4}	17.8
	104	2.70	1.24×10^{-4}	24.9
PBS+1 wt% PBSF 60 SN at 133 °C	101	2.84	2.29×10^{-3}	8.2
	102	2.93	6.46×10^{-4}	11.6
	103	2.88	2.88×10^{-4}	16.2
	104	2.85	1.01×10^{-4}	23.3

Table S3. Crystallization parameters for neat PBS and PBSF 60-nucleated PBS

Specimens		universal empirical		
	PBS	PBS+PBSF60 SN at	PBS+PBSF60 SN at	PBS+PBSF60

			133 °C	136 °C	
T_m^0 / °C	130.20	133.32	132.79	133.48
K_g^{II}	0.85×10^5	0.97×10^5	0.98×10^5	1.02×10^5
G_0^{II}	10.27	10.63	10.96	11.29

1. H.-M. Ye, R.-D. Wang, J. Liu, J. Xu, B.-H. Guo, *Macromolecules*, 2012, **45**, 5667-5675.

2. Y.-R. Tang, D.-W Lin, Y. Gao, J. Xu, B.-H. Guo, *Ind. Eng. Chem. Res*., 2014, **53**, 4689-4696.

3. B. Fillon, J.-C. Wittmann, B. Lotz, A. Thierry, *J. Polym. Sci. Part. B. Polym. Phys.,* 1993, **31**, 1383-1393.