

Effects of Branches on the Crystallization Kinetics of Polypropylene-*g*-Polystyrene and Polypropylene-*g*-Poly(*n*-butyl acrylate) Graft Copolymers with Well-defined Molecular Structures*

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Abstract Effects of branches on the crystallization kinetics of polypropylene-*g*-polystyrene (PP-*g*-PS) and polypropylene-*g*-poly(*n*-butyl acrylate) (PP-*g*-PnBA) graft copolymers with well-defined molecular structures were systematically investigated by DSC. The Avrami equation was used to analyze the isothermal crystallization process, while the analysis of nonisothermal crystallization process was based on the Jeziorny-modified Avrami model and Mo model. The kinetics results of isothermal and nonisothermal crystallization verified the peculiar effects of branches on the crystallization process of PP backbones in PP-*g*-PS and PP-*g*-PnBA graft copolymers: on one hand, the interaction between branches (π - π interaction between PS branches, or dipole-dipole interaction between PnBA branches) restrained the mobility and reptation ability of the PP backbones, which hindered the crystallization process; on the other hand, the heterogeneous nucleation effect resulting from the branched structure and fluctuation-assisted nucleation mechanism (caused by microphase separation between the PS or PnBA rich phase and the PP rich phase) became more pronounced with increasing branch length, which facilitated the crystallization process.

Keywords: Polypropylene; Polypropylene-*g*-polystyrene graft copolymer; Polypropylene-*g*-poly(*n*-butyl acrylate) graft copolymer; Isothermal crystallization; Nonisothermal crystallization.

INTRODUCTION

Isotactic polypropylene (*i*PP) is one of the most widespread commercial polymers due to its outstanding physical and chemical properties. However, the lack of functional groups on PP chains has limited many end uses. In order to surmount this shortcoming, many efforts have been taken to introduce functional groups or segments onto PP's backbone^[1–4]. Particularly, PP-based graft copolymers have been attracting a lot of attention, due to their wide application fields such as compatibilizer, impact modifier, adhesion, coating, ionomer, antistatic agent, biocompatible material, stimulus-sensitive material and so on^[5]. Many methods have been developed to prepare PP-based graft copolymers, such as radical polymerization^[5–10], anionic polymerization^[11–16], coordination polymerization^[17, 18] and coupling reactions^[19, 20].

The physical properties of semi-crystalline polymeric materials strongly depend on their microstructure and crystallinity^[21]. Therefore, the study of polymer crystallization kinetics is significant from theoretical and practical points of view. There are many studies on the crystallization kinetics of grafted PP, such as maleic

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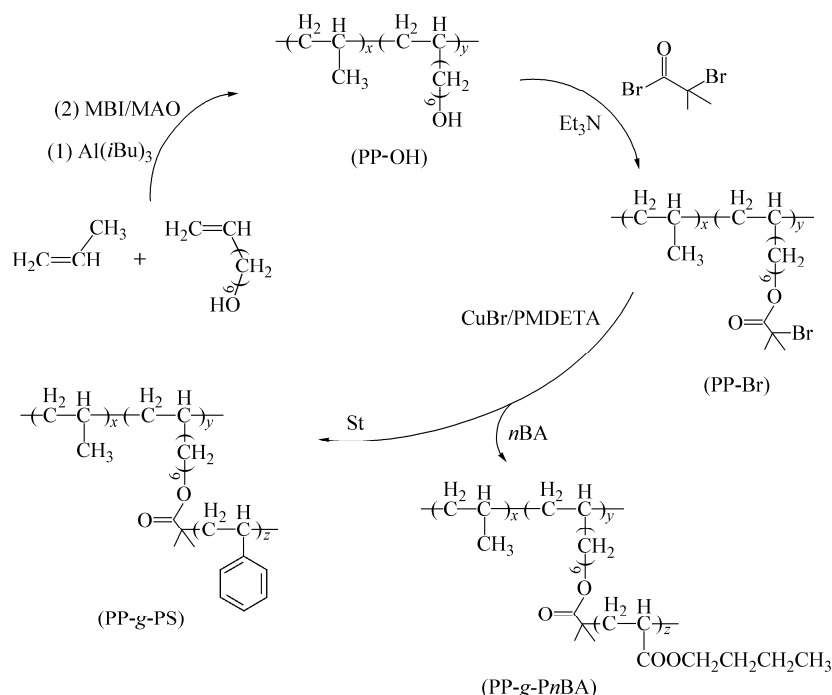
anhydride grafted PP^[21, 22]. Nevertheless, only a few studies have been reported on the crystallization kinetics of PP-based graft copolymers. The branches might endow the PP-based graft copolymers a very different crystallization behavior. Wu investigated the isothermal crystallization kinetics of PP-*g*-polydiphenylsiloxane (PP-*g*-PDPS), and demonstrated that the crystallization rate was influenced by the content of PDPS branches^[23]. In our previous work, we systematically studied the isothermal and nonisothermal crystallization kinetics of polypropylene-*g*-poly(ethylene-*co*-1-butene) (PP-*g*-EBR) graft copolymers with well-defined molecular structures, and found that the crystallization rate increased first and decreased then with increasing the branch level^[24].

Recently, we synthesized several polypropylene-*g*-polystyrene (PP-*g*-PS) and polypropylene-*g*-poly(*n*-butyl acrylate) (PP-*g*-PnBA) graft copolymers with well-defined molecular structures, basing on the same PP-Br macroinitiator, *via* a combination of metallocene-catalyzed polymerization and ATRP. The effects of PS or PnBA branches of the obtained graft copolymers on their thermal, rheological and foaming properties were investigated^[25]. In this study, the effects of branches on the isothermal and nonisothermal crystallization kinetics of PP-*g*-PS and PP-*g*-PnBA graft copolymers were systematically investigated using a differential scanning calorimeter (DSC).

EXPERIMENTAL

Materials

PP-Br sample was synthesized according to the method shown in Scheme 1. In the first step, poly(propylene-*co*-10-undecen-1-ol) copolymer (PP-OH) was obtained through the copolymerization of propylene with aluminum-capped 10-undecen-1-ol using the catalyst system of *rac*-Me₂Si(2-MeBenz[*e*]Ind)₂ZrCl₂ (MBI)/MAO. In the second step, the hydroxyl group in the resulting PP-OH copolymer was converted into the 2-bromoisobutyrate group by reacting with an excess amount of 2-bromoisobutyryl bromide in the presence of triethylamine.



Scheme 1 Synthesis route for PP-Br, PP-*g*-PS and PP-*g*-PnBA copolymers

Several PP-g-PS and PP-g-PnBA graft copolymers were synthesized based on the same PP-Br macroinitiator via ATRP. The details were shown in another paper^[25]. The nomenclature denotes the topology of the graft polymer which is described as PP- x g-P(S or n BA) y : The symbol x denotes the branch density (defined as the average number of branches per 10000 carbons in the PP backbone), and y denotes the branch length (defined as the average molecular weight of branches, kg/mol). The characteristics of PP-Br, PP-g-PS, and PP-g-PnBA samples are shown in Table 1.

Table 1. Summary of characterization results by SEC and DSC measurements for PP-Br, PP-g-PS, and PP-g-PnBA copolymers

Sample	St or n BA content ^a (wt%)	M_w^b (10^4 g/mol)	M_w/M_n^b	T_m^c (°C)	$\Delta H_{m,whole}^c$ (J/g)	$\Delta H_{m,PP}^{c,d}$ (J/g)
PP-Br	0	31.9	1.96	147.7	87.7	87.7
PP-7g-PS2.5	7.8	33.1	2.00	147.1	81.8	88.7
PP-7g-PS4.4	12.8	34.4	2.02	147.1	77.2	88.5
PP-7g-PS6.0	16.7	35.0	2.05	146.5	73.1	87.8
PP-7g-PnBA5.2	14.8	34.6	2.06	147.6	75.4	88.5
PP-7g-PnBA10.0	25.1	36.8	2.15	145.8	64.6	86.2
PP-7g-PnBA13.9	31.6	38.2	2.21	145.3	58.9	86.1

^a Weight fraction of St or n BA in the resulting graft copolymer, calculated from ¹H-NMR spectra;

^b Measured by SEC with a differential refractive index detector; ^c Determined by DSC measurements; ^d $\Delta H_{m,PP} = \Delta H_{m,whole} / \text{wt\% of PP in the obtained graft copolymer}$

Characterization

A differential scanning calorimeter (Mettler DSC 1) was used to analyze the isothermal and nonisothermal crystallization processes. The standard procedure for isothermal crystallization was as follows: the samples (about 5 mg) were melted at 200 °C for 5 min in order to eliminate thermal history; then they were rapidly cooled to the crystallization temperature and maintained at that temperature for the necessary time; finally they were reheated to 200 °C at a rate of 10 K/min. For dynamic nonisothermal crystallization, the samples were melted at 200 °C for 5 min and then cooled to room temperature at 5, 10, 20, and 30 K/min, respectively.

RESULTS AND DISCUSSION

Effect of Branches on Isothermal Crystallization Kinetics of PP-g-PS and PP-g-PnBA Graft Copolymers

The isothermal crystallization thermograms of PP-Br, PP-g-PS and PP-g-PnBA copolymers at different crystallization temperatures are graphically presented in Fig. 1. When the crystallization temperature increased, the crystallization exothermal peak became broader obviously, and the time to reach the maximum degree of crystallization increased.

Analysis of isothermal crystallization based on the Avrami equation

The Avrami equation is well known for analyzing the isothermal crystallization of polymers. The relative crystallinity of a polymer at time t , $X(t)$, can be expressed as:

$$X(t) = 1 - \exp[-K(T)t^n] \quad (1)$$

where n is a constant whose value depends on the mechanism of nucleation and the form of crystal growth, and $K(T)$ is a rate constant containing the nucleation and growth parameters. Avrami equation in this simple form represents unimpeded spherical crystal growth^[26, 27]. $X(t)$ is equal to the ratio of the heat generated at time t (Q_t) to the heat generated at infinite time (Q_∞) according to the following equation:

$$X(t) = Q_t / Q_\infty = \int_0^t (dH / dt) dt \bigg/ \int_0^\infty (dH / dt) dt \quad (2)$$

where dH/dt is the rate of heat evolution. Eq. (1) can be changed to:

$$\lg[-\ln(1 - X(t))] = n \lg t + \lg K(T) \quad (3)$$

The graphic representation of $\lg[-\ln(1-X(t))]$ versus $\lg t$ will generate a straight line. Then the Avrami exponent n and crystallization rate constant $K(T)$ can be determined from the slope and intercept of the line, respectively.

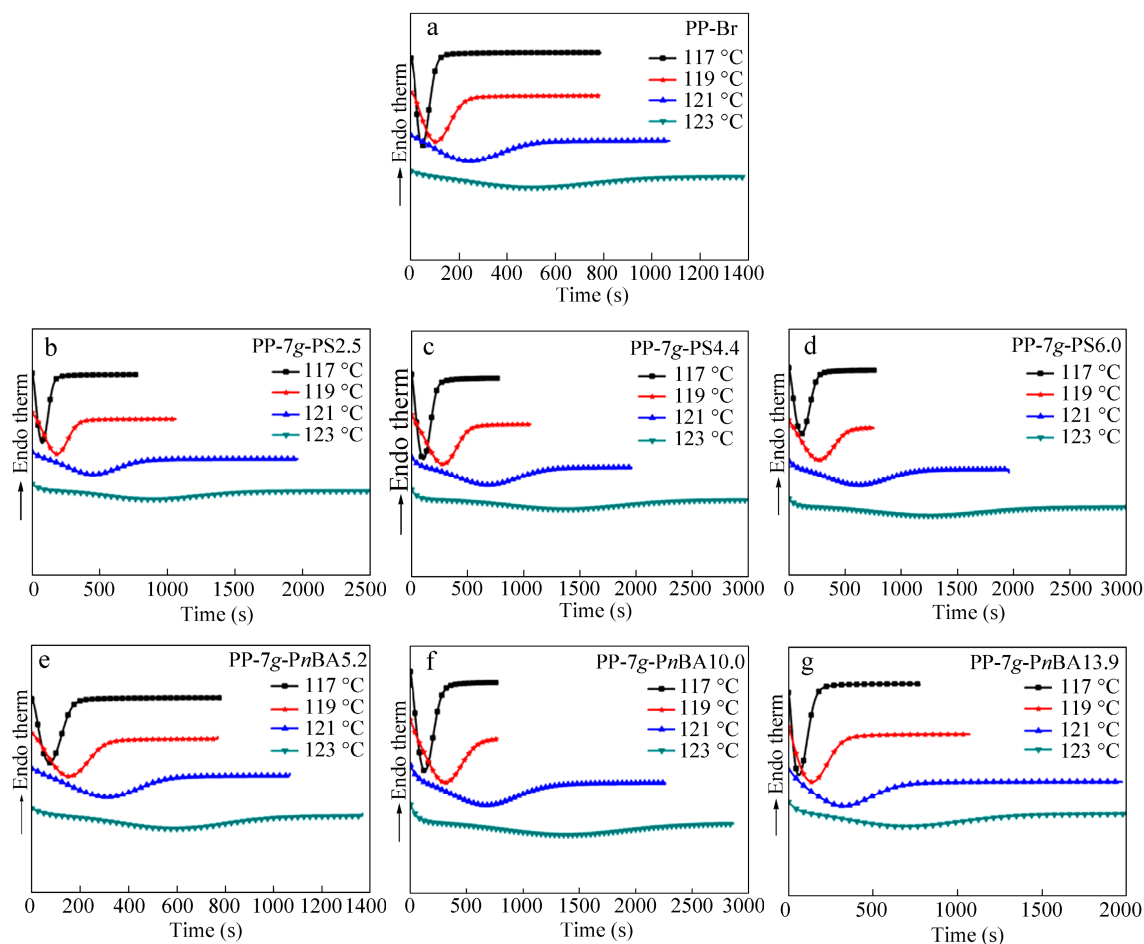


Fig. 1 Heat flow versus time during isothermal crystallization for (a) PP-Br, (b) PP-7g-PS2.5, (c) PP-7g-PS4.4, (d) PP-7g-PS6.0, (e) PP-7g-PnBA5.2, (f) PP-7g-PnBA10.0 and (g) PP-7g-PnBA13.9 at different temperatures

Development of relative crystallinity with time for isothermal crystallization of PP-Br, PP-g-PS, and PP-g-PnBA copolymers at different crystallization temperatures are plotted in Fig. 2. As can be seen, all the isotherms shifted to right along the time axis with increasing the crystallization temperature, indicating the crystallization rate was gradually decreased. The plots of $\lg[-\ln(1-X(t))]$ versus $\lg t$ are shown in Fig. 3. Each plot showed only the linear portion, which was followed by a gentle roll-off at longer times. The deviation from linearity in the later stage of crystallization is often attributed to secondary crystallization caused by the spherulitic impingement. From the slope and intercept of these plots, kinetic parameters of PP-Br, PP-g-PS and PP-g-PnBA copolymers were calculated (listed in Table 2). The value of $K(T)$ decreased with increasing crystallization temperature, which implied a decrease in the nucleation rate. The Avrami exponents of PP-Br, PP-g-PS and PP-g-PnBA copolymers fell in the range of 2.05–2.55 over the crystallization temperature range studied. The non-integral n value may reflect a mixed nucleation and crystal growth mechanism^[28].

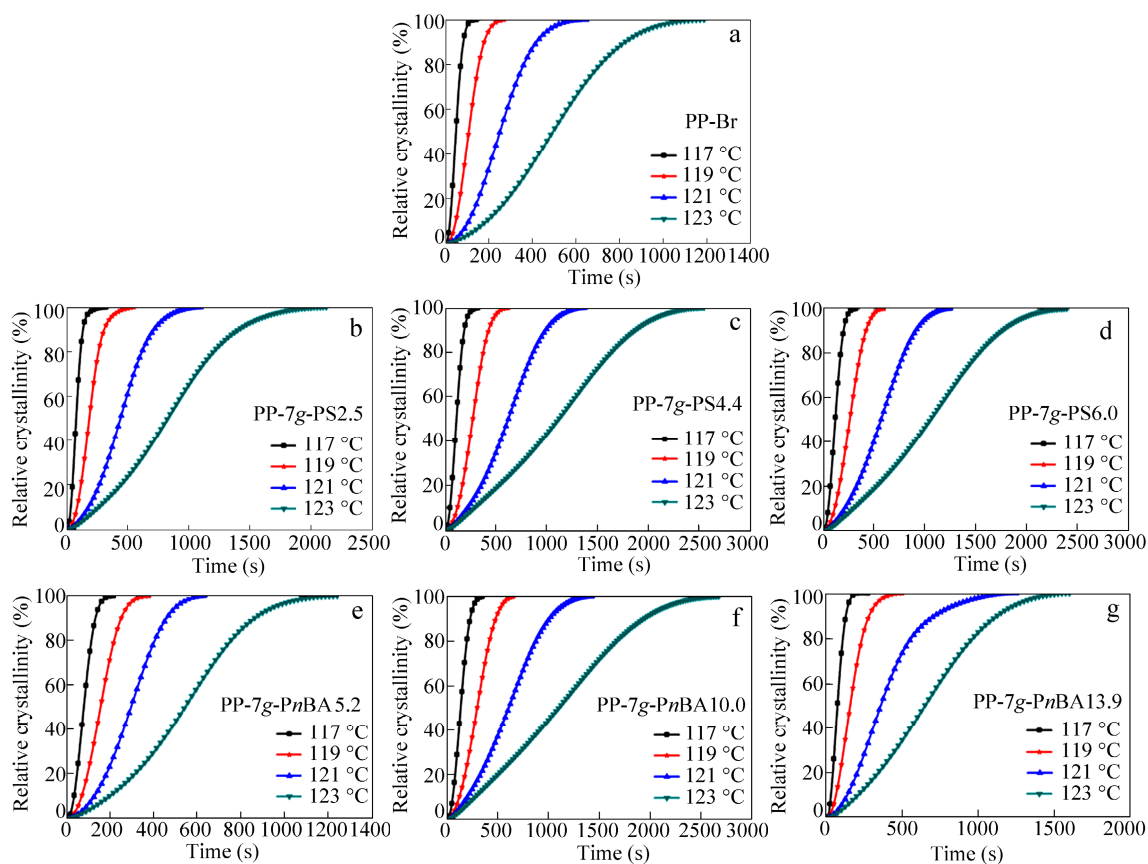
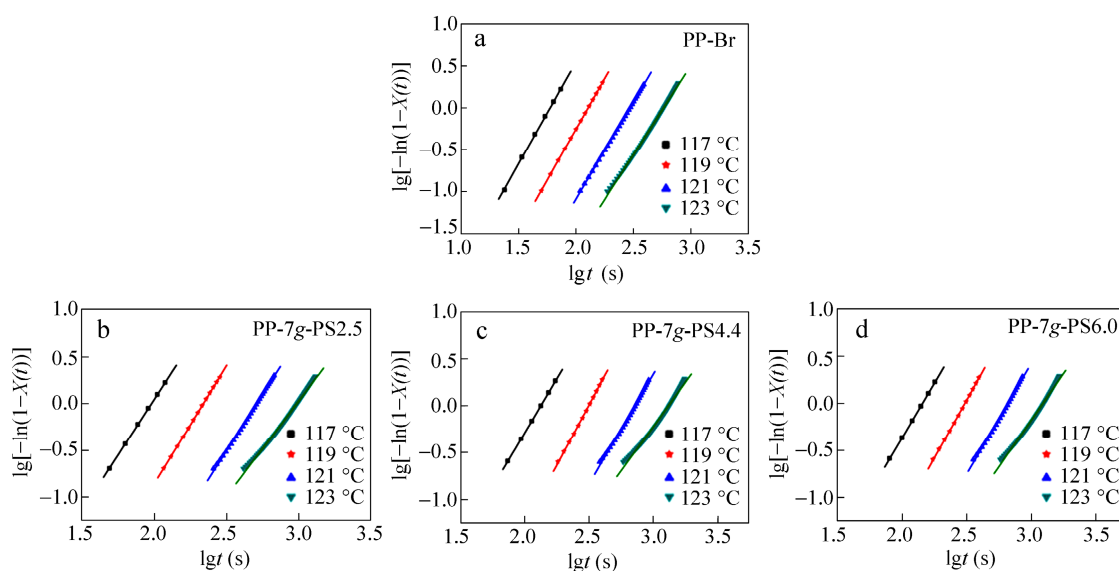


Fig. 2 Development of relative crystallinity with time for isothermal crystallization of (a) PP-Br, (b) PP-7g-PS2.5, (c) PP-7g-PS4.4, (d) PP-7g-PS6.0, (e) PP-7g-PnBA5.2, (f) PP-7g-PnBA10.0 and (g) PP-7g-PnBA13.9 at different temperatures



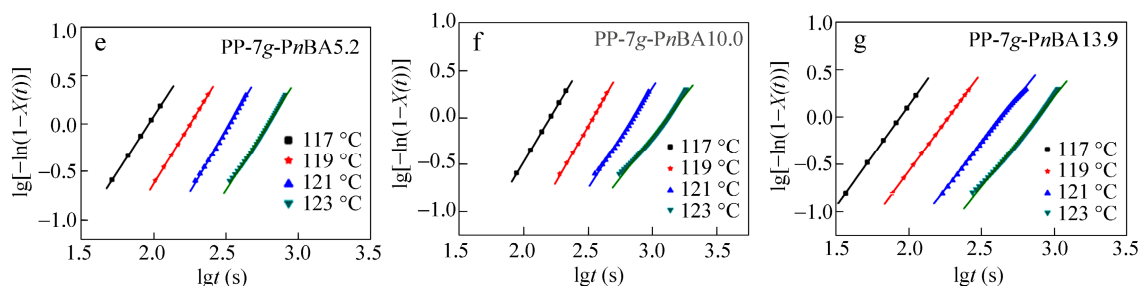


Fig. 3 Plots of $\lg[-\ln(1-X(t))]$ versus $\lg t$ for isothermal crystallization of (a) PP-Br, (b) PP-7g-PS2.5, (c) PP-7g-PS4.4, (d) PP-7g-PS6.0, (e) PP-7g-PnBA5.2, (f) PP-7g-PnBA10.0 and (g) PP-7g-PnBA13.9 samples

Table 2. Kinetic parameters and T_m^0 of PP-Br, PP-g-PS and PP-g-PnBA copolymers from the analysis of isothermal crystallization

Sample	T_c (°C)	n	$K(T)$ (s $^{-n}$)	$t_{1/2}$ (s)	T_m^0 (°C)
PP-Br	117	2.44	4.71×10^{-5}	51	158.4
	119	2.43	7.60×10^{-6}	110	
	121	2.26	2.57×10^{-6}	253	
	123	2.14	1.21×10^{-6}	494	
PP-7g-PS2.5	117	2.40	1.79×10^{-5}	82	155.1
	119	2.52	1.29×10^{-6}	189	
	121	2.31	5.36×10^{-7}	444	
	123	2.12	4.51×10^{-7}	828	
PP-7g-PS4.4	117	2.31	1.23×10^{-5}	115	155.8
	119	2.55	4.21×10^{-7}	274	
	121	2.34	2.01×10^{-7}	625	
	123	2.16	1.79×10^{-7}	1121	
PP-7g-PS6.0	117	2.31	1.25×10^{-5}	113	156.5
	119	2.46	7.82×10^{-7}	266	
	121	2.35	2.30×10^{-7}	574	
	123	2.15	2.19×10^{-7}	1057	
PP-7g-PnBA5.2	117	2.31	2.77×10^{-5}	80	156.2
	119	2.47	2.70×10^{-6}	156	
	121	2.58	3.04×10^{-7}	296	
	123	2.37	2.31×10^{-7}	542	
PP-7g-PnBA10.0	117	2.28	9.17×10^{-6}	137	158.2
	119	2.38	8.94×10^{-7}	299	
	121	2.30	2.52×10^{-7}	630	
	123	2.14	2.15×10^{-7}	1098	
PP-7g-PnBA13.9	117	2.24	4.50×10^{-5}	74	159.9
	119	2.21	7.46×10^{-6}	177	
	121	2.13	2.37×10^{-6}	368	
	123	2.05	1.19×10^{-6}	647	

Crystallization half-time, $t_{1/2}$, is defined as the time at which the degree of crystallization reaches 50% of its final extent. The larger the value of $t_{1/2}$, the lower the rate of crystallization. The relationship between $t_{1/2}$ and the crystallization rate parameter $K(T)$ is as follows:

$$K(T) = \ln 2 / t_{1/2}^n \quad (4)$$

The values of $t_{1/2}$ calculated from Eq. (4), listed in Table 2, were in good accordance with those obtained directly from Fig. 2, which suggests that the Avrami analysis accurately describes the isothermal crystallization of PP-Br, PP-g-PS and PP-g-PnBA copolymers. The $t_{1/2}$ for all samples increased with the increase of crystallization temperature. Moreover, at a given crystallization temperature, the $t_{1/2}$ values of PP-g-PS and PP-g-PnBA graft copolymers were larger than those of PP-Br, suggesting that crystallization rate decreased due to the introduction of PS or PnBA branches. Furthermore, at a given crystallization temperature, the $t_{1/2}$ value of PP-g-PS and PP-g-PnBA graft copolymers increased first and decreased then with the enhancement of branch length. This verified the peculiar effects of branches on the crystallization process of PP backbones in PP-g-PS and PP-g-PnBA graft copolymers: on one hand, the interaction between branches (π - π interaction between PS branches, or dipole-dipole interaction between PnBA branches) restrained the mobility and reptation ability of the PP backbones, which hindered the crystallization process; on the other hand, the heterogeneous nucleation effect resulting from the branched structure^[29–31] and fluctuation-assisted nucleation mechanism^[32, 33] (caused by microphase separation between the PS or PnBA rich phase and the PP rich phase) became more pronounced with increasing branch length^[24], which facilitated the crystallization process.

Equilibrium melting point

The equilibrium melting point (T_m^0) of a crystalline polymer is an important thermodynamic parameter for understanding its crystallization behavior. The T_m^0 is often determined by the Hoffman-Weeks linear extrapolation method^[34]. After isothermal crystallization at various T_c for enough time, T_m of the sample was obtained by reheating from T_c to 200 °C at a rate of 10 K/min. The T_m^0 can be obtained by linear extrapolation of the line of T_m versus T_c to intersect the line of $T_m = T_c$. The linear Hoffman-Weeks plots for PP-Br, PP-g-PS and PP-g-PnBA samples are illustrated in Fig. 4, and the determined values of T_m^0 are collected in Table 2. As can be seen from Table 2, the T_m^0 of PP-g-PS and PP-g-PnBA graft copolymers was lower than that of PP-Br, except the PP-7g-PnBA13.9 sample. Furthermore, one can note that the T_m^0 of PP-g-PS and PP-g-PnBA graft copolymers increased with the increase of branch length. The enhancement of branch length would increase the positional restriction imposed on the PP backbones by the branches, which lowered the melt entropy of the graft copolymer and consequently led to the increase of T_m^0 ^[35].

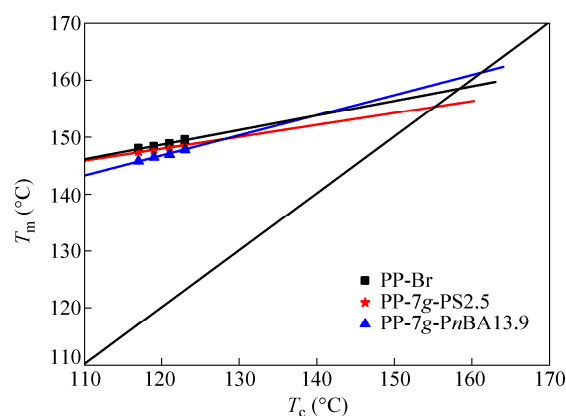


Fig. 4 Linear Hoffman-Weeks plots for PP-Br, PP-7g-PS2.5, and PP-7g-PnBA13.9 samples (The plots for the other samples were omitted for clarity)

Effect of Branches on Nonisothermal Crystallization Kinetics of PP-g-PS and PP-g-PnBA Graft Copolymers

From a technological point of view, nonisothermal crystallization conditions approach more closely to the practical conditions of polymers processing. Therefore, the investigation of nonisothermal crystallization kinetics of polymers is very important. The nonisothermal crystallization thermograms of PP-Br, PP-g-PS and PP-g-PnBA copolymers at different cooling rates are shown in Fig. 5. With increasing cooling rate, both onset (T_0) and peak (T_p) crystallization temperatures of PP-Br, PP-g-PS and PP-g-PnBA copolymers shifted to lower

temperatures. Meanwhile, the exothermic peak became broader with increasing the cooling rate, which was ascribed to the imperfect crystal structures formed at rapid cooling rates^[36]. The values of T_0 and T_p for the samples are collected in Table 3. As shown in Table 3, at a given cooling rate, T_p of PP-g-PS and PP-g-PnBA graft copolymers was lower than that of PP-Br. Moreover, at a given cooling rate, T_p of PP-g-PS and PP-g-PnBA graft copolymers decreased first and increased then with increasing branch length.

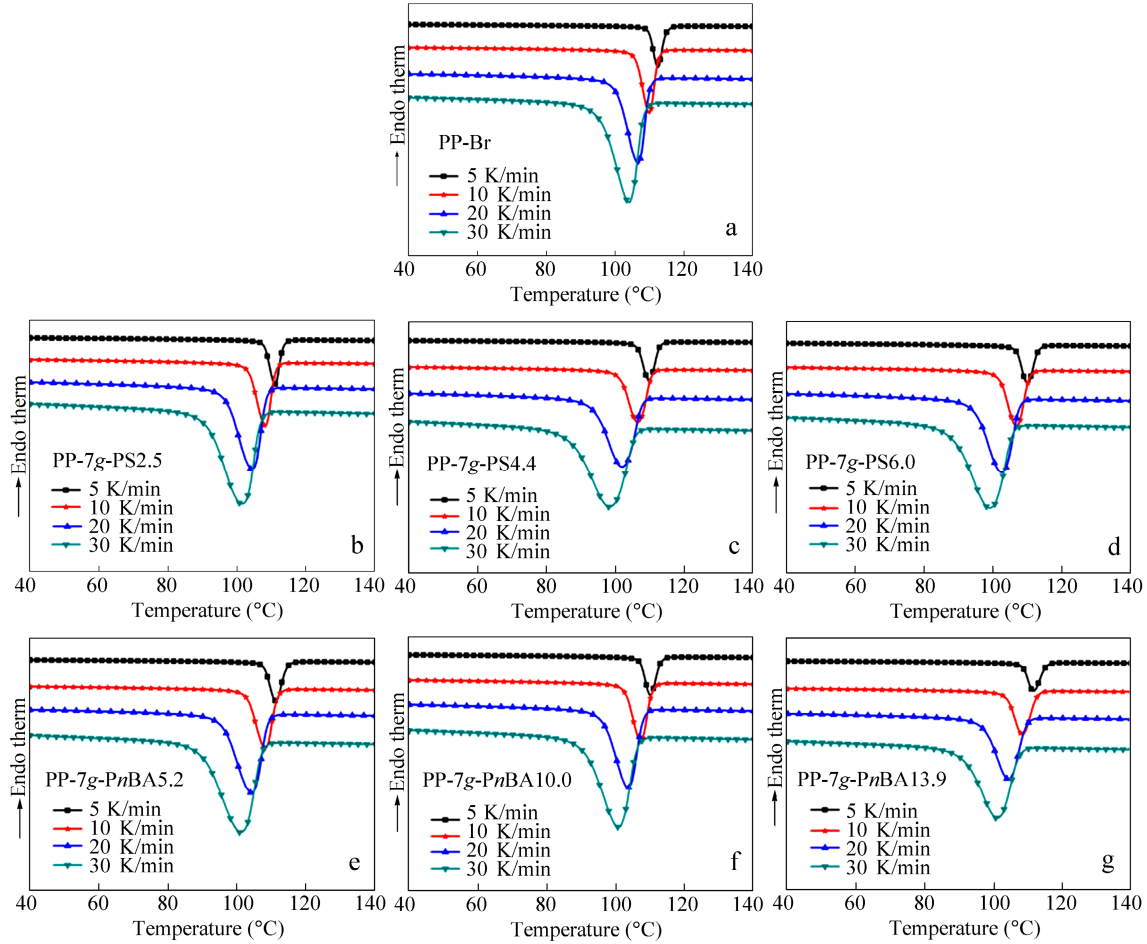


Fig. 5 DSC curves during nonisothermal crystallization at different cooling rates for (a) PP-Br, (b) PP-7g-PS2.5, (c) PP-7g-PS4.4, (d) PP-7g-PS6.0, (e) PP-7g-PnBA5.2, (f) PP-7g-PnBA10.0 and (g) PP-7g-PnBA13.9 samples

The relative crystallinity as a function of temperature, $X(T)$, can be formulated as:

$$X(T) = \frac{\int_T^{T_0} (dH_c / dT) dT}{\int_{T_0}^{T_\infty} (dH_c / dT) dT} \quad (5)$$

where T is the crystallization temperature at time t ; T_0 and T_∞ are the initial and end crystallization temperatures, respectively; dH_c denotes the crystallization enthalpy released during an infinitesimal temperature range of dT . The development of relative crystallinity as a function of temperature during nonisothermal crystallization for PP-Br, PP-g-PS and PP-g-PnBA copolymers at different cooling rates is shown in Fig. 6. All these curves

showed the similar reversed S shape, indicating the existence of slow nucleation stage, fast primary crystallization stage, and slow secondary crystallization stage. Meanwhile, these curves shifted towards lower-temperature side as the cooling rate increased.

Table 3. Values of T_o , T_p , and $t_{1/2}$ at various cooling rates (ϕ) for PP-Br, PP-g-PS and PP-g-PnBA copolymers

Sample	ϕ (K/min)	T_o (°C)	T_p (°C)	$t_{1/2}$ (min)
PP-Br	5	114.9	112.5	1.22
	10	112.8	109.9	0.62
	20	110.3	106.8	0.38
	30	108.6	104.4	0.28
PP-7g-PS2.5	5	113.6	111.1	1.27
	10	111.3	108.3	0.67
	20	108.8	104.3	0.44
	30	107.1	101.2	0.34
PP-7g-PS4.4	5	113.0	109.9	1.43
	10	110.7	106.7	0.76
	20	108.0	102.1	0.51
	30	106.1	98.1	0.42
PP-7g-PS6.0	5	113.2	110.0	1.38
	10	110.7	106.9	0.71
	20	107.9	102.5	0.46
	30	105.9	99.1	0.37
PP-7g-PnBA5.2	5	114.5	111.3	1.42
	10	111.8	108.1	0.78
	20	109.1	104.3	0.45
	30	107.5	101.2	0.35
PP-7g-PnBA10.0	5	113.1	110.1	1.45
	10	110.8	107.4	0.83
	20	108.2	103.5	0.48
	30	106.5	100.6	0.36
PP-7g-PnBA13.9	5	115.3	111.6	1.36
	10	112.7	108.3	0.74
	20	109.7	104.2	0.45
	30	107.7	101.1	0.35

The crystallization temperature (T) can be converted to crystallization time (t) using the well-known relationship for nonisothermal crystallization processes:

$$t = \frac{T_o - T}{\phi} \quad (6)$$

where T is the crystallization temperature at time t , and ϕ is the cooling rate. Figure 7 shows the evolution of the relative crystallinity of PP-Br, PP-g-PS and PP-g-PnBA copolymers with the crystallization time. The crystallization half-time ($t_{1/2}$) obtained directly from Fig. 7 are listed in Table 3. As expected, the value of $t_{1/2}$ for all samples decreased with increasing cooling rate. At a given cooling rate, the $t_{1/2}$ value of PP-g-PS and PP-g-PnBA graft copolymers was larger than that of PP-Br. Furthermore, at a given cooling rate, the $t_{1/2}$ value of PP-g-PS and PP-g-PnBA graft copolymers increased first and decreased then with the increase of branch length.

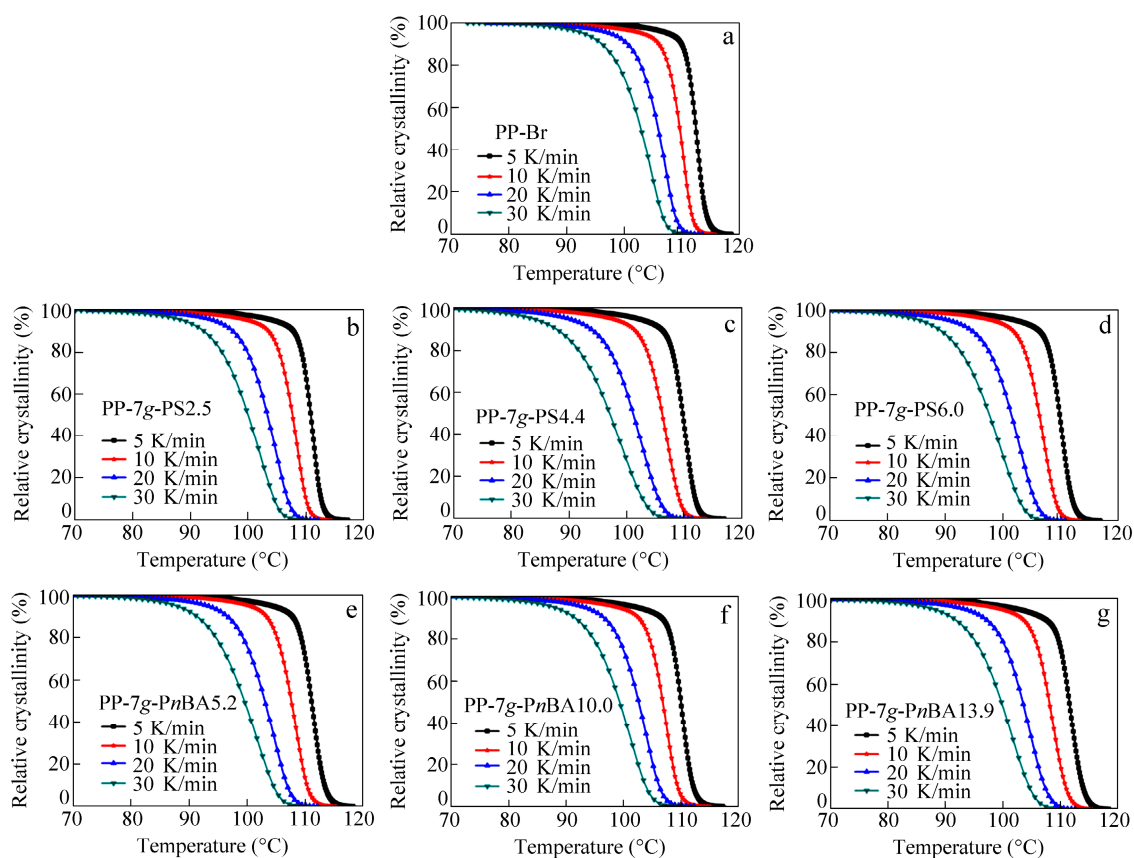
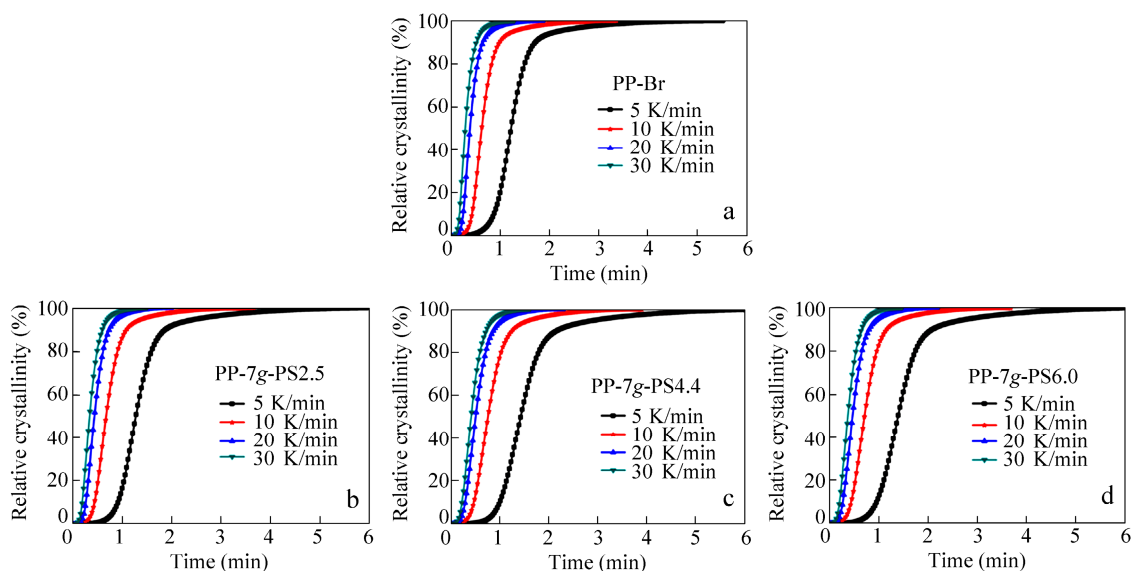


Fig. 6 Development of relative crystallinity with temperature for nonisothermal crystallization of (a) PP-Br, (b) PP-7g-PS2.5, (c) PP-7g-PS4.4, (d) PP-7g-PS6.0, (e) PP-7g-PnBA5.2, (f) PP-7g-PnBA10.0 and (g) PP-7g-PnBA13.9 samples



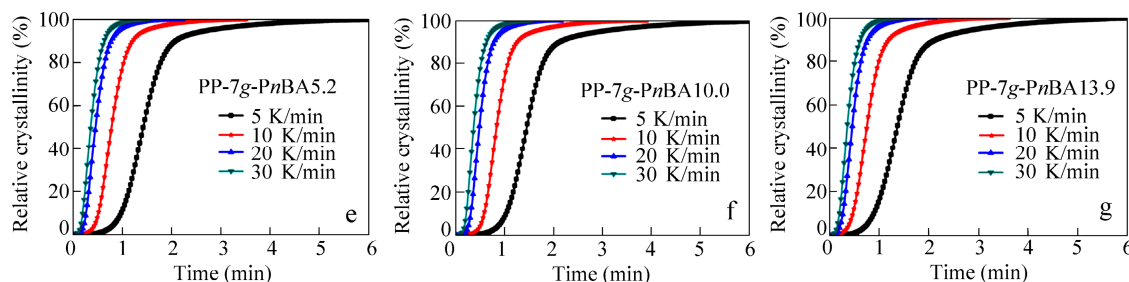


Fig. 7 Development of relative crystallinity with time for nonisothermal crystallization of (a) PP-Br, (b) PP-7g-PS2.5, (c) PP-7g-PS4.4, (d) PP-7g-PS6.0, (e) PP-7g-PnBA5.2, (f) PP-7g-PnBA10.0 and (g) PP-7g-PnBA13.9 samples

Analysis of nonisothermal crystallization based on Jeziorny-modified Avrami model

Assuming that the crystallization temperature is constant, the Avrami equation can be directly used to describe the kinetics of nonisothermal crystallization. In this case, the Avrami equation is expressed as:

$$1 - X(t) = \exp(-Z_t t^n) \quad (7)$$

or

$$\lg[-\ln(1 - X(t))] = \lg Z_t + n \lg t$$

where $X(t)$ is the relative crystallinity, the exponent n is a mechanism constant depending on the type of nucleation and the growth dimension, and Z_t is the growth rate constant involving both nucleation and growth rate parameters. Considering the nonisothermal character of the process investigated, Jeziorny suggested that Z_t should be corrected to obtain the corresponding rate constant at a normalized cooling rate, Z_c , as follows^[37]:

$$\lg Z_t = \frac{\lg Z_c}{\phi} \quad (8)$$

Figure 8 presents the plots of $\lg[-\ln(1 - X(t))]$ versus $\lg t$ for PP-Br, PP-g-PS and PP-g-PnBA copolymers at various cooling rates. All the plots possessed two distinct regions related to primary and secondary crystallization stages. The Avrami parameters (n and Z_c) of the two stages can be determined from the slope and intercept of the plots, respectively. The calculated values of n_1 , n_2 , Z_{c1} , and Z_{c2} are summarized in Table 4 (the subscripts 1 and 2 denote the primary and secondary crystallization stages, respectively). The value of n_1 , under the experimental cooling rates, for PP-Br, PP-g-PS and PP-g-PnBA copolymers ranged between 3.16 and 5.40, implying spherulitic crystal growth. Additionally, the n_1 value of all the samples decreased with increasing the cooling rate, which might be due to the fast crystallization rate that resulted in high supercooling and prevented spherulites from being fully developed^[36, 38]. Moreover, for the secondary crystallization, the corresponding values of n_2 were smaller than those of n_1 . Generally, the mode of spherulites growth at the second stage is transformed into the lower dimensional space extension, which is attributed to the effect of slower crystallization or the further perfection of crystal caused by spherulitic impingement or to the reorganization of initially poorly crystallized macromolecules or small and metastable crystals^[39].

As shown in Table 4, at a given cooling rate, the Z_{c1} values of PP-g-PS and PP-g-PnBA graft copolymers were smaller than those of PP-Br. Moreover, at a given cooling rate, the Z_{c1} of PP-g-PS and PP-g-PnBA graft copolymers decreased first and increased then with the enhancement of branch length. In comparison to Z_{c1} , the Z_{c2} of all the samples remained almost a constant value (about 1.0). The variation in both branch level and cooling rate had little influence on the value of Z_{c2} . Similar phenomenon was observed in PP-g-EBR^[24] and long chain branched polyethylene (LCBPE) samples^[36].

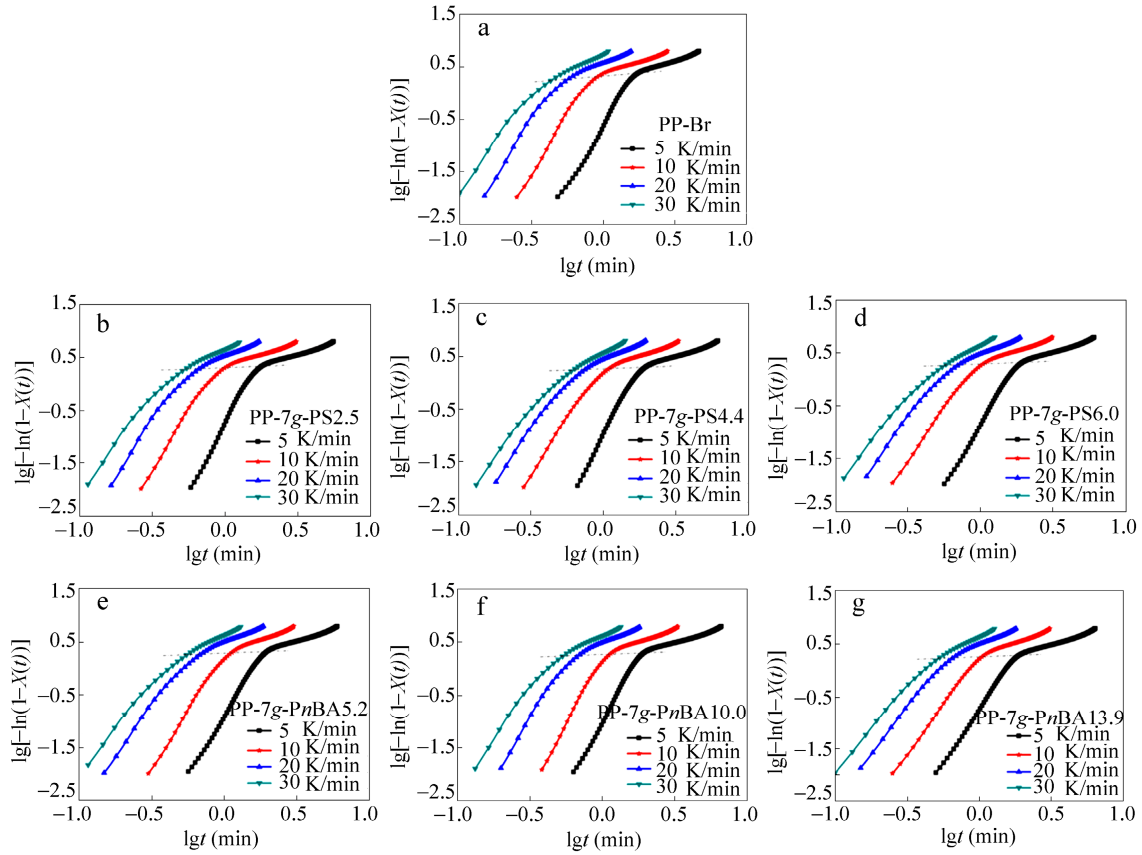


Fig. 8 Plots of $\lg[-\ln(1-X(t))]$ versus $\lg t$ for nonisothermal crystallization of (a) PP-Br, (b) PP-7g-PS2.5, (c) PP-7g-PS4.4, (d) PP-7g-PS6.0, (e) PP-7g-PnBA5.2, (f) PP-7g-PnBA10.0 and (g) PP-7g-PnBA13.9 samples at different cooling rates

Analysis of nonisothermal crystallization based on Mo model

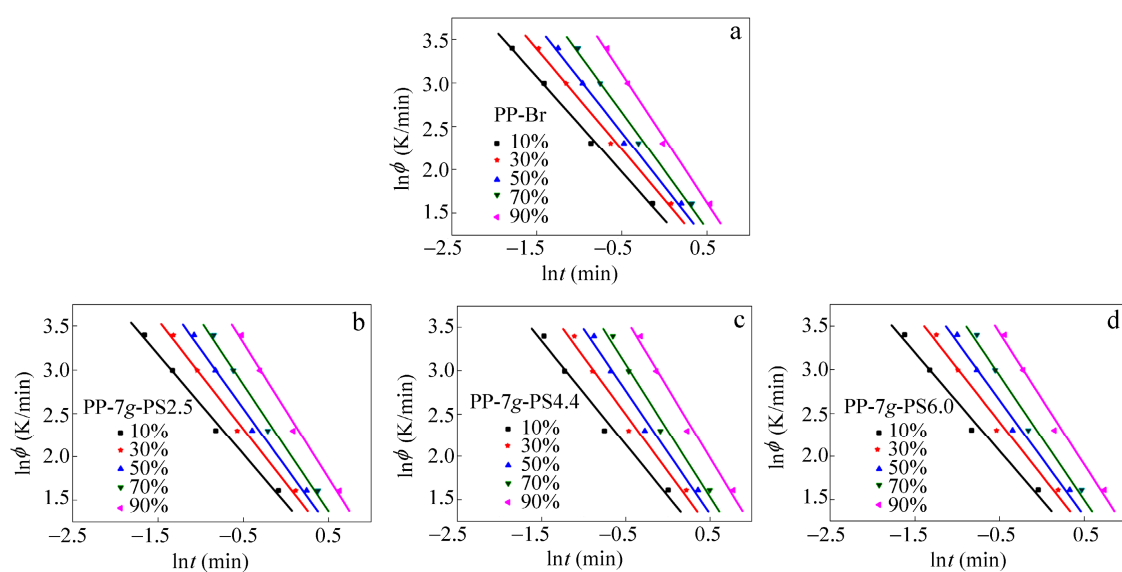
Aiming at finding a method to describe exactly the nonisothermal crystallization process, Mo and coworkers^[40] proposed a novel kinetics equation by combining Avrami equation with Ozawa equation as follows:

$$\ln \phi = \ln F(T) - \alpha \ln t \quad (9)$$

where $F(T) = [K(T)/Z_t]^{1/m}$ refers to the necessary value of cooling rate to reach a defined relative crystallinity at unit crystallization time; $\alpha = n/m$, the ratio of Avrami exponent n to Ozawa exponent m . Under different relative crystallinity, the plots of $\ln \phi$ versus $\ln t$ for PP-Br, PP-g-PS and PP-g-PnBA copolymers are shown in Fig. 9. The kinetic parameters α and $F(T)$ can be determined from the slope and intercept of the lines, respectively (listed in Table 5). It can be seen from Table 5 that the value of $F(T)$ increased systematically with increasing relative crystallinity, indicating that at unit crystallization time, a higher cooling rate should be required in order to obtain a higher relative crystallinity. At a given relative crystallinity, the larger the $F(T)$ value, the higher the cooling rate is needed within unit crystallization time, and the slower the crystallization process. It can be found that at a given relative crystallinity, the $F(T)$ values of PP-g-PS and PP-g-PnBA graft copolymers were larger than that of PP-Br. Furthermore, at a certain relative crystallinity, the value of $F(T)$ of PP-g-PS and PP-g-PnBA graft copolymers increased first and decreased then with the increase of branch length. These results are consistent with those obtained from the Jeziorny-modified Avrami approach, further confirming the aforementioned peculiar effects of PS and PnBA branches on the crystallization process of PP backbones in PP-g-PS and PP-g-PnBA graft copolymers.

Table 4. Nonisothermal crystallization kinetic parameters for PP-Br, PP-g-PS, and PP-g-PnBA copolymers from Jeziorny-modified Avrami analysis

Sample	ϕ (K/min)	n_1	Z_{c1}	n_2	Z_{c2}
PP-Br	5	4.79	0.753	0.87	1.080
	10	4.60	1.190	0.89	1.091
	20	4.12	1.192	1.03	1.068
	30	3.53	1.141	1.23	1.058
PP-7g-PS2.5	5	5.40	0.706	0.85	1.060
	10	4.39	1.141	0.88	1.080
	20	3.86	1.149	1.09	1.062
	30	3.39	1.114	1.23	1.051
PP-7g-PS4.4	5	5.32	0.631	0.89	1.024
	10	4.06	1.076	0.94	1.064
	20	3.57	1.106	1.14	1.052
	30	3.32	1.088	1.39	1.044
PP-7g-PS6.0	5	4.79	0.671	0.87	1.035
	10	3.89	1.099	0.92	1.074
	20	3.48	1.121	1.08	1.056
	30	3.16	1.097	1.45	1.051
PP-7g-PnBA5.2	5	4.65	0.662	0.87	1.039
	10	4.40	1.071	0.99	1.070
	20	3.73	1.142	1.05	1.059
	30	3.31	1.110	1.27	1.050
PP-7g-PnBA10.0	5	5.17	0.626	0.83	1.036
	10	5.12	1.054	0.94	1.065
	20	4.02	1.134	1.08	1.058
	30	3.36	1.104	1.20	1.049
PP-7g-PnBA13.9	5	4.22	0.710	0.87	1.024
	10	3.83	1.075	0.97	1.068
	20	3.60	1.137	1.09	1.059
	30	3.27	1.109	1.30	1.051



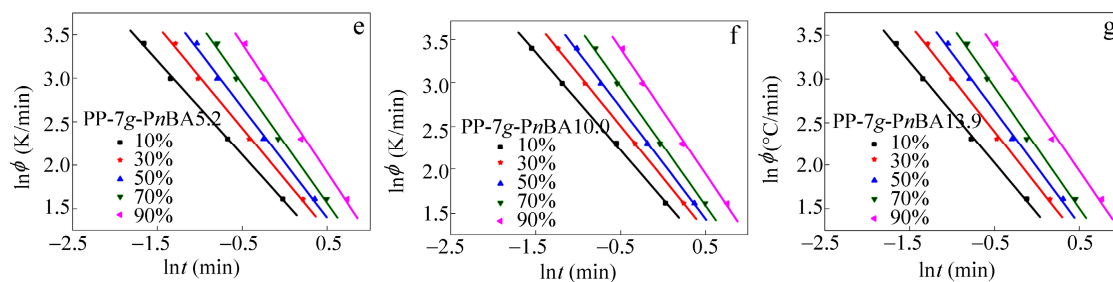


Fig. 9 Plots of $\ln\phi$ versus $\ln t$ for nonisothermal crystallization of (a) PP-Br, (b) PP-7g-PS2.5, (c) PP-7g-PS4.4, (d) PP-7g-PS6.0, (e) PP-7g-PnBA5.2, (f) PP-7g-PnBA10.0 and (g) PP-7g-PnBA13.9 at various relative crystallinity

Table 5. Nonisothermal crystallization kinetic parameters for PP-Br, PP-g-PS and PP-g-PnBA copolymers from Mo and Kissinger analysis

Sample	X_t (%)	α	$F(T)$	ΔE (kJ/mol)
PP-Br	10	1.10	4.14	-274.74
	30	1.16	5.22	
	50	1.24	6.07	
	70	1.34	7.30	
	90	1.48	10.59	
PP-7g-PS2.5	10	1.15	4.30	-220.72
	30	1.25	5.45	
	50	1.36	6.55	
	70	1.46	8.18	
	90	1.56	12.61	
PP-7g-PS4.4	10	1.20	4.66	-184.15
	30	1.33	6.20	
	50	1.44	7.75	
	70	1.54	9.99	
	90	1.62	16.37	
PP-7g-PS6.0	10	1.14	4.45	-199.43
	30	1.24	5.89	
	50	1.34	7.21	
	70	1.44	9.12	
	90	1.52	14.30	
PP-7g-PnBA5.2	10	1.09	4.84	-219.29
	30	1.18	6.27	
	50	1.28	7.59	
	70	1.38	9.46	
	90	1.48	14.20	
PP-7g-PnBA10.0	10	1.13	5.26	-228.48
	30	1.20	6.71	
	50	1.29	7.97	
	70	1.38	9.73	
	90	1.45	14.52	
PP-7g-PnBA13.9	10	1.16	4.24	-210.44
	30	1.24	5.86	
	50	1.31	7.22	
	70	1.40	9.04	
	90	1.42	14.11	

Crystallization activation energy

Considering the influence of different cooling rates (ϕ) on the nonisothermal crystallization process, Kissinger reported that the activation energy ΔE could be determined by the subsequent equation^[41]:

$$\frac{d[\ln(\phi/T_p^2)]}{d(1/T_p)} = \frac{-\Delta E}{R} \quad (10)$$

where R is the ideal gas constant, and T_p is the crystallization peak temperature. The plots of $\ln(\phi/T_p^2)$ versus $1/T_p$ with good linear relations for PP-Br, PP-g-PS, and PP-g-PnBA copolymers are presented in Fig. 10. ΔE can be calculated from the slopes of these lines, and the values are summarized in Table 5. It can be found that the magnitude of ΔE of PP-g-PS and PP-g-PnBA graft copolymers was smaller than that of PP-Br. The magnitude of ΔE for PP-g-PS sample decreased first and increased then with the enhancement of branch length, while the magnitude of ΔE for PP-g-PnBA sample increased first and decreased then with increasing the branch length. Generally, the ΔE consists of the transport activation energy (ΔE^*) and the nucleation activation energy (ΔF). ΔE^* refers to the activation energy required to transport molecular segments across the phase boundary to the crystal growth surface, while ΔF refers to the free energy of formation of crystal nuclei with a critical size^[42]. On one hand, the interaction between branches (π - π interaction between PS branches, or dipole-dipole interaction between PnBA branches) restrained the transport of macromolecular segments of PP backbones to the crystal growth surface, and consequently increased the ΔE^* ; on the other hand, the branched structure and fluctuation-assisted nucleation mechanism performed the function of heterogeneous nucleation, which decreased the ΔF . The changing trend of ΔE for PP-g-PS and PP-g-PnBA graft copolymers depended on the different contribution of increasing branch length to the decrease of ΔF and the increase of ΔE^* .

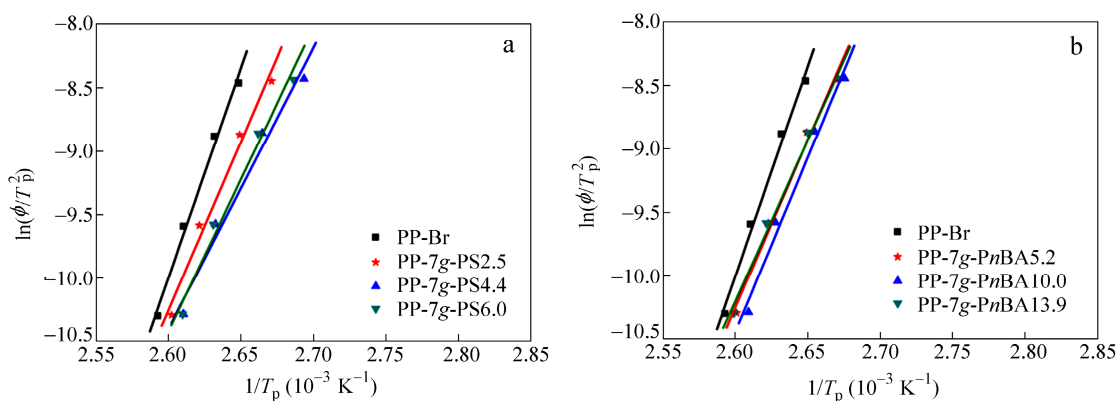


Fig. 10 Plots of $\ln(\phi/T_p^2)$ versus $1/T_p$ for (a) PP-Br and PP-g-PS samples, and (b) PP-Br and PP-g-PnBA samples

CONCLUSIONS

The isothermal and nonisothermal crystallization kinetics of PP-Br, PP-g-PS and PP-g-PnBA copolymers with well-defined molecular structures was investigated systematically by DSC. The Avrami equation was used to analyze the isothermal crystallization process. At a given crystallization temperature, the crystallization half-time ($t_{1/2}$) of PP-g-PS and PP-g-PnBA graft copolymers, larger than that of PP-Br, increased first and decreased then with the increase of branch length. These results verified the peculiar effects of branches on the crystallization process of PP backbones in PP-g-PS and PP-g-PnBA graft copolymers: on one hand, the interaction between branches (π - π interaction between PS branches, or dipole-dipole interaction between PnBA branches) restrained the mobility and reptation ability of the PP backbones, which hindered the crystallization process; on the other hand, the heterogeneous nucleation effect resulting from the branched structure and fluctuation-assisted nucleation mechanism (caused by microphase separation between the PS or PnBA rich phase and the PP rich phase) became more pronounced with increasing branch length, which facilitated the crystallization process.

The analysis of nonisothermal crystallization based on the Jeziorny-modified Avrami model showed that, under the experimental cooling rates, the Avrami exponent n_1 of PP-Br, PP-g-PS and PP-g-PnBA copolymers

ranged between 3.16 and 5.40. Furthermore, at a given cooling rate, the Z_{c1} of PP-g-PS and PP-g-PnBA graft copolymers decreased first and increased then with the increase of branch length. The Mo model could precisely describe the nonisothermal crystallization process of PP-Br, PP-g-PS and PP-g-PnBA copolymers, and the results obtained from Mo model were consistent with those obtained from the Jeziorny-modified Avrami approach. These results further confirmed the aforementioned peculiar effects of branches on the crystallization process of PP backbones in PP-g-PS and PP-g-PnBA graft copolymers. The magnitude of activation energy (ΔE) of PP-g-PS and PP-g-PnBA graft copolymers was smaller than that of PP-Br. Moreover, the magnitude of ΔE for PP-g-PS sample decreased first and increased then with the enhancement of branch length, while the magnitude of ΔE for PP-g-PnBA sample increased first and decreased then with increasing the branch length.

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