

NON-ISOTHERMAL CRYSTALLIZATION KINETICS OF POLY(PHENYLENE SULFIDE) WITH LOW CROSSLINKING LEVELS*

Fang-li Lou^a, Yi Xu^{a, b}, Huan Pang^a, Yan-hui Chen^a, Jia-zhuang Xu^a,
Zhong-ming Li^{a**} and Ai Lu^b

^a College of Polymer Science and Engineering and State Key Laboratory of Polymer Materials Engineering,
Sichuan University, Chengdu 610065, China

^b Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang 621900, China

Abstract Poly(phenylene sulfide) (PPS) with different crosslinking levels was successfully fabricated by means of high-temperature isothermal treatment (IT). The crosslinking degree of PPS was increased with IT time as revealed by Fourier-transform infrared spectroscopy and dynamic viscosity measurements. Its influence on the non-isothermal crystallization behaviors of PPS was studied by differential scanning calorimeter (DSC). The crystallization peak temperature of PPS with 6 h IT was 15 K higher than that of the one with 2 h IT at 30 K/min cooling rate. The non-isothermal crystallization data were also analyzed based on the Ozawa model. The Ozawa exponent m decreased from 3.5 to 2.2 at 232°C with the increase of the IT time, suggestive of intensive thermal oxidative crosslinking reducing the crystallite dimension as PPS crystal grew. The reduced cooling crystallization function $K(T)$ was indicative of the larger activation energy of crosslinked PPS chain diffusion into crystal lattice, resulting in a slow crystal growth rate. Additionally, the overall crystallization rate of PPS was also accelerated with the increase of crosslinking degree from the observation of polarized optical micrograph. These results indicated that the chemical crosslinked points and network structures formed during the high-temperature isothermal treatment acted as the effective nucleating sites, which greatly promoted the crystallization process of PPS and changed the type of nucleation and the geometry of crystal growth accordingly.

Keywords: Poly(*p*-phenylene sulfide); Crosslinking; Non-isothermal crystallization; Ozawa model.

INTRODUCTION

Poly(phenylene sulfide) (PPS) is a typical semi-crystalline polymer with very rigid molecular chains, of which the ultimate properties greatly depend on the microstructures, especially on the crystalline structure and morphology^[1, 2]. Therefore, this stimulated a growing research interest in the crystallization behavior of PPS in order to optimize the final performance. In the recent years, numerous studies have thus focused on the crystallization of PPS and its blends^[3–17]. The effects of molecular weight, branching agent content, end-group counter atom and thermal history on the isothermal crystallization kinetics of PPS were thoroughly studied, and usually explained by means of the Avrami equation^[3–5]. However, in industrial applications, crystallization usually goes through a non-isothermal process, so study on the non-isothermal crystallization is more practically significant. Lopez and co-workers utilized Ozawa theory to investigate the non-isothermal crystallization process of linear and branched PPS. The results indicated that the values of Ozawa exponent ranged from 2.3 to 3, manifesting a low dimensional growth of crystal, which was in good agreement with the investigation achieved

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** Corresponding author: Zhong-ming Li (李忠明), E-mail: zmli@scu.edu.cn

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by isothermal methods^[18]. According to the Ozawa model, Zhang *et al.* investigated the non-isothermal crystallization of PPS and polyamide 66 blends with a compatibilizer poly(ethylene-stat-methacrylate), and they claimed that the crystallization process was greatly influenced by the interactivity among the molecular chains^[19]. Minkova and Magagnini found that the non-isothermal crystallization of PPS was strongly accelerated by thermotropic liquid-crystalline co-poly(ester amide) Vectra-B950 without any change in the type of nucleation and the geometry of crystal growth^[20]. Rajan *et al.* studied the non-isothermal crystallization kinetics of PPS/liquid crystalline polymer blends^[21]. Their study revealed a notable reduction in the Avrami exponent, indicative of the nucleated process leading to rod-shaped growth with thermal nucleation.

Many studies show the thermal oxidative crosslinking reaction for PPS unavoidably takes place upon the melt process, due to the free radical reaction between oxygen and PPS molecular chains. This crosslinking reaction introduces chemically crosslinking points among the PPS molecules and thus reduces the freedom degree of their chain segments. The mobility of polymer chains plays an important role in the diffusion process of chain segments into crystal lattices. Therefore, the degree of crosslinking considerably affects the crystallization progress of PPS, which is directly related to their mechanical properties, for example, tensile strength and impact strength. However, very little attention has been paid to the effect of crosslinking happened during the heat treatment on the non-isothermal crystallization behavior of PPS. In this paper, we adopted different isothermal treatment (IT) time lengths to treat PPS in order to obtain different crosslinking levels in PPS, then investigated their non-isothermal crystallization behaviors by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The Ozawa model was further utilized to evaluate the non-isothermal crystallization kinetics of PPS. Moreover, the influence of crosslinking degrees on the nucleation and crystal growth was also discussed. The results obtained from this paper impart some importance for the industrial application of PPS.

EXPERIMENTAL

Materials and Sample Preparation

The PPS resin was obtained from Deyang Science and Technology Corp. (Deyang, China). Its molecular weight is $M_w = 48000$, $M_n = 21000$, and its polydispersity is about 2.29. The PPS resin was dried at 140°C for 4 h in order to remove the low molecular weight fraction, and kept in sealed plastic bags to minimize moisture absorption before use. Then, the samples were kept at a constant temperature of 260°C with different IT time (2, 4, and 6 h, respectively). The related information was shown in Table 1.

Table 1. The condition of isothermal treatment of PPS samples

Sample	IT temperature (°C)	IT time (h)	MFI (g/10min) (316°C, 5 kg)
PPS0	260	0	> 1000
PPS1	260	2	620
PPS2	260	4	376
PPS3	260	6	323

Fourier-transform Infrared Spectroscopy

In order to confirm the thermal oxidative crosslinking reaction, we employed Fourier transform infrared (FTIR) spectra to characterize the oxygen-containing groups of PPS samples. The FTIR spectra were obtained using a Nicolet-560 FTIR spectrometer (Nicolet Corp., USA). The PPS film (*ca.* 200 μm) for infrared analysis was fabricated by hot press at 280°C for 5 min at 10 MPa.

Rheological Measurements

Rheological experiments were performed on a Haake RheoStress 600 (RS600) using 25 mm diameter parallel plates. Dynamic frequency sweep was performed at constant stress in the stress-controlled mode. It was conducted under 310°C with the strain amplitude of 5%–20%, which guaranteed all the dynamic experiments to be in the linear viscoelastic regime.

Differential Scanning Calorimetry Studies

A Perkin-Elmer Diamond DSC was used to record non-isothermal crystallization exotherms of PPS samples. The temperature and melting enthalpy were calibrated with standard indium. To minimize thermal lag between the polymer sample and the DSC furnace, the samples were encapsulated into aluminum pans and weighed around (7.5 ± 0.1) mg. Each sample was used only once and all the runs were carried out under nitrogen atmosphere to minimize thermal degradation. The experiment started with heating the samples from 50°C to 320°C at a rate of 30 K/min, and kept at 320°C for 8 min, so as to erase the previous thermal history. The samples were then cooled to room temperature at different constant cooling rates (D) ($D = 5, 10, 15, 20, 30$ K/min, respectively) and the heat flow during crystallization was recorded as a function of time and temperature.

For non-isothermal crystallization, the relative crystallinity $X_c(T)^{[22]}$, as a function of temperature is defined as:

$$X_c(T) = \frac{\int_{T_0}^T (dH_c / dT) dT}{\int_{T_0}^{T_\infty} (dH_c / dT) dT} \quad (1)$$

where T_0 and T_∞ are the onset and end of crystallization temperature, respectively. dH_c/dT is the heat flow at temperature T . The relation between the crystallization time t and the sample temperature T_c can be formulated as:

$$t = \frac{T_0 - T_c}{D} \quad (2)$$

Ozawa extended the well-known Avrami model to describe the non-isothermal crystallization data of semi-crystalline polymers^[23–27]. Assuming that non-isothermal crystallization process may be composed of infinitesimally small isothermal crystallization steps, the equation is defined as:

$$\ln[-\ln(1 - X_c(T))] = K(T) - m \ln D \quad (3)$$

where $X_c(T)$ is the relative crystallinity at temperature T , D is the constant cooling rate, m is the Ozawa exponent and $K(T)$ is the cooling crystallization function that depends on the nucleation density and the spherulitic radial growth rate, for both instantaneous and sporadic nucleation. By plotting $\ln[-\ln(1 - X_c(T))]$ versus $\ln D$, a straight line should be obtained and the kinetic parameters, m and $K(T)$, can be calculated from the slope and the intercept, respectively.

Morphology Observation

The morphology of PPS with different heat treatment time was observed by polarized optical microscope (POM) with video attachment, which was connected to a hot stage (CSS450). Briefly, the samples were heated from room temperature to 340°C at 30 K/min, kept for 5 min to allow the PPS samples to melt completely, and then cooled to room temperature at 10 K/min for non-isothermal crystallization. The images of PPS crystal growth were taken at a given time during this period.

RESULTS AND DISCUSSION

Since the polymer backbone of PPS is composed of a series of alternating aromatic rings and sulfur atoms, PPS tends to undergo thermal oxidative crosslinking when it is heated to a high temperature. Hill *et al.* pointed out that the thermal crosslinking reactions in PPS would possibly take place above 210°C, with the presence of a large amount of C—O bonds among the PPS chains^[28]. As illustrated in Fig. 1, compared with neat PPS, a new peak at 1717 cm^{-1} assigned to the C=O stretching vibration appears, which suggests thermal oxidative crosslinking reaction does happen at the treatment temperature, *i.e.*, 260°C.

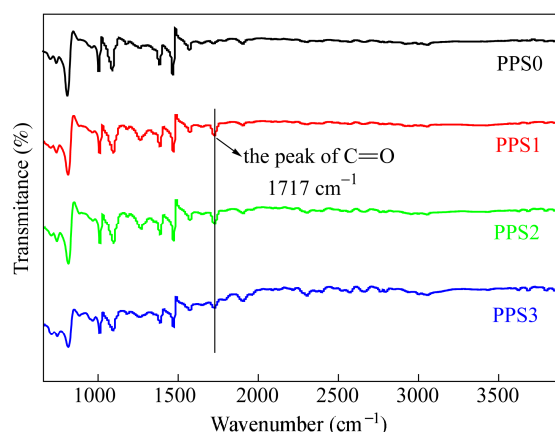


Fig. 1 FTIR spectra of PPS samples without and with different IT at 260°C

Figure 2 displays the complex viscosity (η^*) and storage modulus (G') versus frequency of PPS samples at different IT time at 310°C. From the observation of Fig. 2(a), η^* keeps rising as the IT time increases. Especially, η^* of PPS3 is 674 Pa·s, which is nearly 8.5 times larger than that of PPS0 (79.1 Pa·s) at 0.01 s⁻¹. The nodes among the PPS molecular chains are generated by the thermal oxidative crosslinking increase with the gradually prolonged IT time. They are prone to confine the flexibility of the PPS molecular chains, which gives rise to the further increased η^* . η^* exhibits a dramatic decrease during the frequency from 0.01 s⁻¹ to 0.1 s⁻¹ in PPS3 sample, indicative of an apparent shear thinning phenomenon. In general, the shear thinning is more pronounced in the solid-like materials such as crosslinking polymers and polymer composites than linear polymers because of the entangled macromolecular network. In addition, it can be observed from Fig. 2(b) that G' shows no plateau in the low frequency region, which implies that all the three PPS samples after IT do not form a complete network structure and the crosslinking level is rather low.

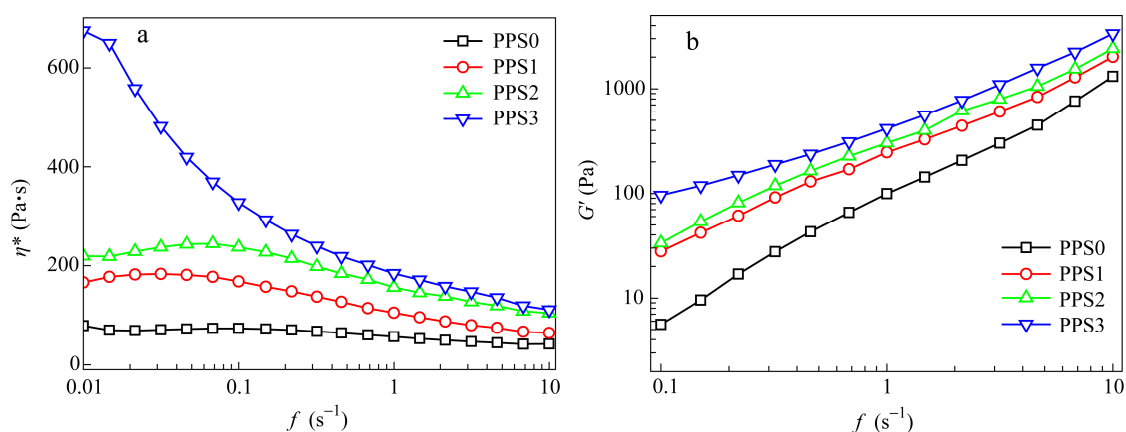


Fig. 2 (a) Complex viscosity (η^*) and (b) storage modulus (G') versus frequency for the PPS samples at 310°C

Figure 3 shows the DSC curves obtained at different cooling rates for PPS samples with different IT time. The exothermic crystallization peaks are mono-modal. Their shape implies that, as already observed by Lopez and Wilkes for PPS, the secondary crystallization does not play an important role in these samples^[4]. From these curves, the peak temperature (T_p), the onset crystallization temperature (T_o) and the infinite crystallization temperature (T_∞), etc. can be obtained for the description of the non-isothermal crystallization behavior of PPS. The values of these parameters are listed in Table 2. As expected, T_o , T_p and T_∞ all shift towards the lower temperature when the cooling rate increases. This phenomenon is normally due to the limited crystallization time

caused by the fast cooling rate not allowing the polymer immediately to response and start to crystallize^[4], thus resulting in a delayed (decreased) crystallization temperature. As shown in Table 2, T_o , T_p and T_∞ all increase as the IT time increases at a given cooling rate. For example, at 30 K/min, T_p of PPS2 and PPS3 are *ca.* 7 and 15 K higher than that of PPS1.

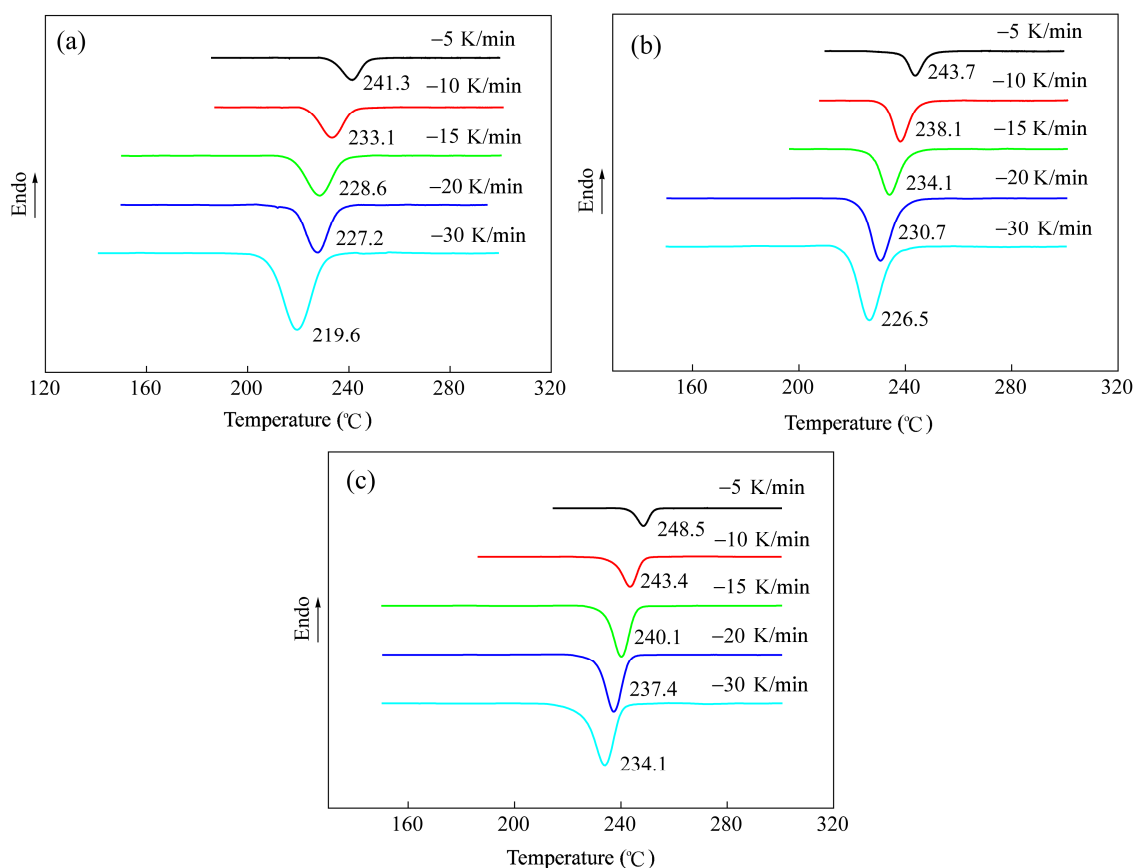


Fig. 3 DSC thermograms of PPS with different IT time at different cooling rates (a) PPS1, (b) PPS2 and (c) PPS3

Table 2. Characteristic data of non-isothermal crystallization exotherms for the PPS samples

D (K/min)	PPS1			PPS2			PPS3		
	T_o (°C)	T_p (°C)	T_∞ (°C)	T_o (°C)	T_p (°C)	T_∞ (°C)	T_o (°C)	T_p (°C)	T_∞ (°C)
5	247.8	241.3	231.1	251.7	243.7	236.0	253.2	248.5	241.8
10	243.7	233.1	223.4	248.7	238.1	227.7	249.2	243.4	233.3
15	237.8	228.6	217.1	245.8	234.1	223.1	246.9	240.1	228.9
20	235.2	227.2	212.3	243.6	230.7	216.6	244.4	237.4	223.3
30	230.6	219.6	206.1	241.9	226.5	214.0	243.0	234.1	215.6

To further obtain the relevant non-isothermal crystallization kinetic information, the experimental data, as shown in Fig. 3, need to be presented as $X_c(T)$ according to the Eq. (1). $X_c(T)$ of the PPS samples as a function of temperature at different cooling rates is displayed in Fig. 4. Then, the curve of PPS1, PPS2 and PPS3 at the cooling rate 10 K/min chosen from Fig. 4 is present in Fig. 5(a), in order to compare the different crystallization rates of samples with different IT time. It is shown that PPS3 displays the fastest crystallization rate. Due to the IT, thermal oxidative crosslinking points form. They cannot be melted with increasing the temperature, so when the temperature starts to decrease, they can act as heterogeneous nucleation sites to generate the stable crystal nucleus formation and accelerate the crystal nucleation. As the IT time increases, more crosslinking points form,

which further accelerates the crystal nucleation rate as shown in Fig. 5(a). The crystallization rate of all the three samples can be further evaluated by their crystallization half-time ($t_{1/2}$) as depicted in Fig. 5(b). At the same crystallization time, PPS3 has the highest relative crystallinity during the non-isothermal crystallization process, but the relative crystallinity of the PPS1 composite is almost the same as that of PPS2. Moreover, the crystallization half-time ($t_{1/2}$) value of PPS3 (0.8 min) is the shortest among the PPS samples (1.4 min for PPS1 and PPS2), verifying the accelerated nucleating ability in PPS3. The overall crystallization rate is determined by two stages: the nucleation rate and crystal growth rate. For PPS3, the nucleation rate dominates the whole crystallization process, which gives rise to its shortest crystallization half-time value. However, when the thermal oxidative crosslinking level is relatively low in PPS2 compared to PPS3, its overall crystallization rate is comparable to PPS1. Although the nucleation stage of PPS2 can be accelerated by more crosslinking nodes, its crystal growth stage is restricted because the crosslinked PPS2 chain segments make the diffusion of molecular chain to the crystal lattice harder. This results in the same overall crystallization rate of PPS1 and PPS2.

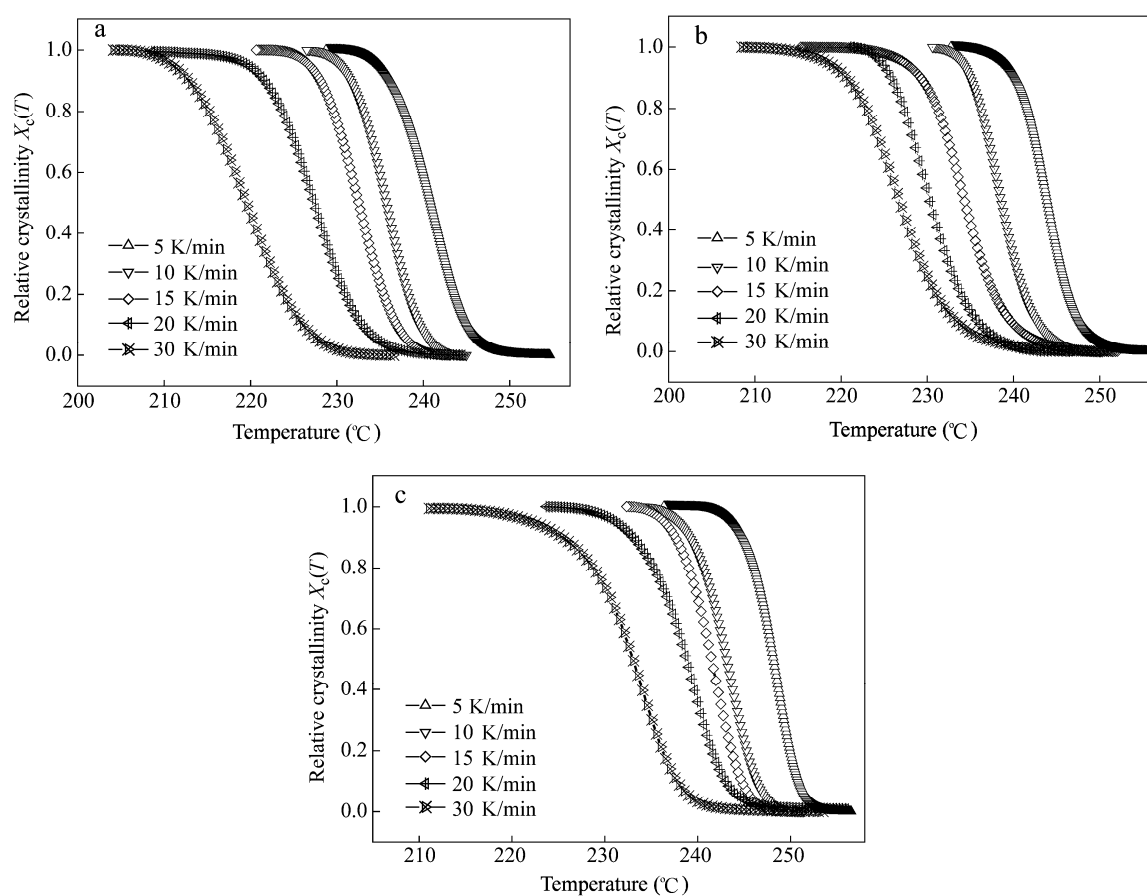


Fig. 4 Plots of relative crystallinity versus temperature for crystallization of PPS with different IT time: (a) PPS1, (b) PPS2 and (c) PPS3

In order to reveal the effect of different crosslinking degrees on the nucleation and the geometry of crystal growth, we adopted the Ozawa model. Based on the $X_c(T)$ data of PPS2 in Fig. 4, we further do a double logarithmic plot of $\ln[-\ln(1 - X_c(T))]$ versus $\ln D$ at a fixed temperature (Fig. 6). Two adjustable parameters, $K(T)$ and m , are obtained by a linear regression. Table 3 summarizes the m and $K(T)$ values as well as the corresponding correlation coefficient r^2 for all of the samples. According to Table 3, r^2 is in the range of 0.85–1.00, which suggests that the Ozawa model has a satisfactory fit to the experimental data of these samples.

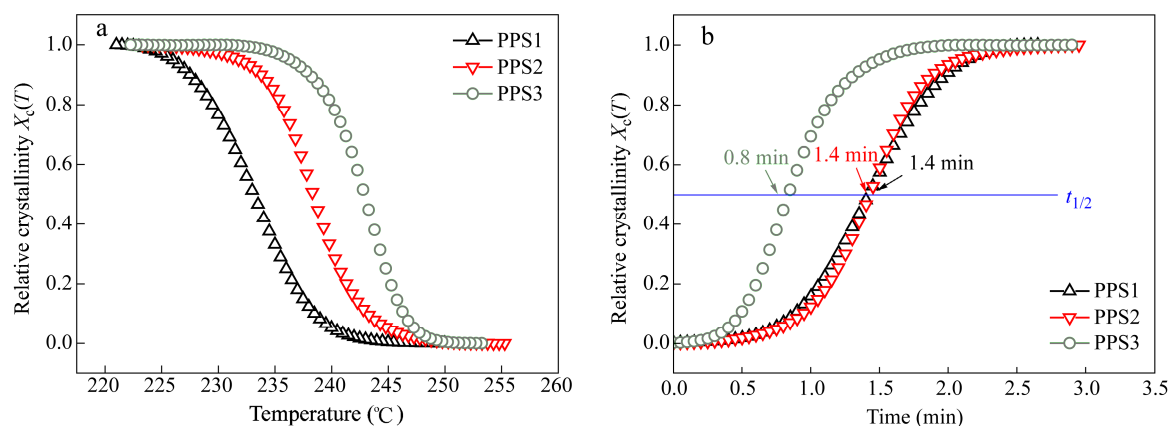


Fig. 5 Plot of the relative crystallinity as a function of temperature (a) and time (b) for PPS samples with different IT time at the same cooling rate of 10 K/min

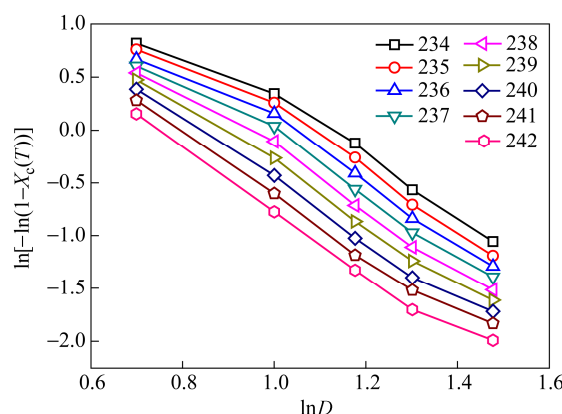


Fig. 6 Plots of $\ln[-\ln(1 - X_c(T))]$ versus $\ln D$ for PPS2 at various temperatures

Table 3. Non-isothermal crystallization kinetics for the PPS samples based on Ozawa model

PPS1				PPS2				PPS3			
T (°C)	m	$K(T)$ (K min ⁻¹)	r^2	T (°C)	m	$K(T)$ (K min ⁻¹)	r^2	T (°C)	m	$K(T)$ (K min ⁻¹)	r^2
226	3.1	3.6	1.00	230	2.8	3.7	1.00	234	1.9	2.57	0.97
228	3.3	3.8	0.95	232	2.7	3.2	0.99	236	2.3	2.93	0.97
230	3.2	3.2	0.98	234	2.4	2.7	0.99	238	2.2	2.63	0.98
232	3.5	3.3	0.95	236	2.6	2.6	0.99	240	2.2	2.44	0.99
234	3.1	2.8	0.97	238	2.7	2.5	1.00	242	2.6	2.49	1.00

Generally, the Ozawa exponent m is within 1.8 to 3.5 for these three samples. Specifically, it ranges from 3.1 to 3.5 for PPS1 within the temperature range of 226–234°C, from 2.4–2.8 for PPS2 within the temperature range of 230–238°C, and from 1.9–2.6 for PPS3 within the temperature range of 234–242°C. In other words, the Ozawa exponent m decreases with the increase of the IT time. Rajan *et al.* reported similar results for PPS/LCP blends^[29]. This result is indicative of intensive thermal oxidative crosslinking reducing the dimension of PPS crystals. Namely, for PPS1 sample, the PPS crystals manifest a typical three dimensional spherulitic growth. With the prolonged IT time, the PPS crystal growth dimension becomes lower. When the crosslinking level is the highest, the PPS3 sample displays a nearly two dimensional crystal growth. The cooling crystallization function, $K(T)$, represents the crystal growth rate because of the instantaneous nucleation of PPS. As exhibited in Table 3, we find that $K(T)$ decreases with increasing the IT time (within the temperature range investigated), illuminating the crystal growth rate of PPS is reduced as the crosslinking increases, especially for the shorter IT

treated samples. These results also verify the low crystal growth rate of IT treated PPS samples in Fig. 5(b).

The morphology of the non-isothermally crystallized PPS with different IT time at a predetermined cooling rate of 10 K/min is presented in Fig. 7. It could be observed that, at 250°C, the PPS crystals do not appear due to the high ambient temperature (Figs. 7a1, 7b1 and 7c1). As the crystallization temperature decreases, the dense PPS crystals first can be observed in PPS3 at 245°C (Fig. 7c2). When temperature decreases to 230°C, a few large PPS crystals appear in PPS1, while the largest crystal density is present in PPS3. That is, the more the nuclei are, the smaller the crystals are. This phenomenon is consistent with the DSC results, verifying the un-melted chemically crosslinked points or network structure among PPS chains play a role of heterogeneous nucleation agent in accelerating the stable crystal nucleus formation in the non-isothermal crystallization of PPS. Furthermore, observed from Fig. 7(a4), PPS1 forms the spherulites (obvious Maltese cross), and the diameter of the spherulites can reach about 30 μm (230°C). With the increased crosslinking degree, one can see that no obvious spherulites can be observed (Figs. 7c1–7c4)). This phenomenon is ascribed to the formation of numerous small nuclei among the PPS chains, the reduced mobility of their chain segments and difficult PPS chains diffusion during the crystal growth stage. All these factors are contributed to the reduction of the apparent crystallite size.

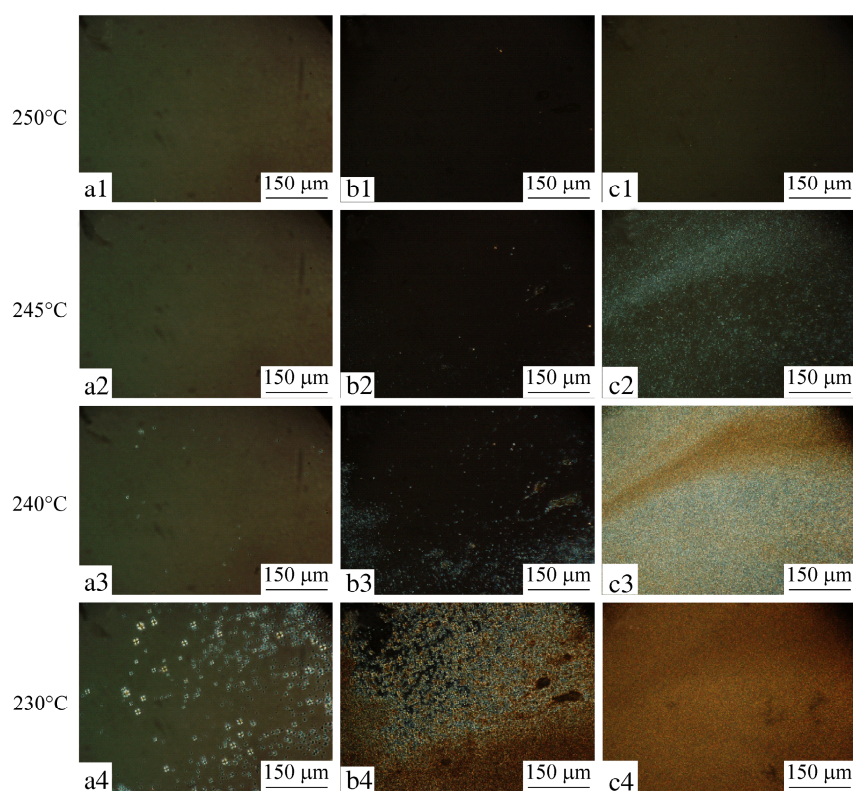


Fig. 7 Non-isothermal crystallization polarized optical micrographs at a cooling rate of 10 K/min for the PPS samples (a1–a4) PPS1, (b1–b4) PPS2 and (c1–c4) PPS3

CONCLUSIONS

Through tailoring IT time, we fabricated PPS samples with different low thermal oxidative crosslinking levels. FTIR and dynamic viscosity measurements both revealed that the degree of thermal oxidative crosslinking of PPS became stronger with the increase of IT time. The effect of crosslinking on the non-isothermal crystallization of PPS was investigated by DSC. The DSC results showed that the crosslinking can improve the heterogeneous nucleating ability of PPS, namely enhanced nearly 15 K in T_p from PPS1 to PPS3 at 30 K/min.

The Ozawa exponent m decreased with the IT time, which was suggestive of a lower dimension for PPS crystal growth. The reduced values of $K(T)$ suggested the lower crystal growth rate for PPS samples with the prolonged IT time. Moreover, observed from POM images, the overall crystallization rate of PPS was also accelerated due to the presence of crosslinking. These results indicated that the chemical crosslinked nodes and network structure acted as the effective nucleating sites, which promoted the overall crystallization rate of PPS and changed the type of nucleation and the geometry of crystal growth accordingly.

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