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Investigating the Nucleation Effect of DMDBS on Syndiotactic Polypropylene from the Perspective of Chain Conformation

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Electronic Supplementary Information

Abstract The mechanism of nucleating agents (NAs) accelerating the crystallization of semi-crystalline polymers has received continuous attention due to the extreme importance in academic research and industry application. In this work, the nucleation effect and probable mechanism of 1,3:2,4-bis(3,4-dimethylbenzylidene)sorbitol (DMDBS) on promoting the crystallization of syndiotactic polypropylene (sPP) was systematically investigated. Our results showed that DMDBS could significantly accelerate the crystallization process and did not change the crystalline form of sPP. The *in situ* infrared spectra recorded in the crystallization process showed that in pristine sPP the tttt conformers decreased and the ttgg conformers increased subsequently. In sPP/DMDBS system, DMDBS could promote the increase of ttgg conformers rather than the decrease of tttt conformers. The further analysis by 2D-IR spectra revealed that ttgg conformers increased prior to the decrease of tttt conformers in the sPP/DMDBS system comparing with pristine sPP. Considering that ttgg conformers were basic elements of helical conformation of Form I crystal for sPP, we proposed a probable nucleation mechanism of DMDBS for sPP: DMDBS could stabilize the ttgg conformers which induced these ttgg conformers to pre-orientate and aggregate into helical conformation sequences as initial nuclei quickly and early to promote the sPP crystallization. Our work provides some new insights into the nucleation mechanism of NAs for sPP.

Keywords Syndiotactic polypropylene; Nucleating agent; Crystallization; Conformation

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INTRODUCTION

The nucleating agent (NA) is an important additive which could accelerate the overall crystallization of semi-crystalline polymers and improve the performances of products.^[1–3] For some widely used polymer materials, such as isotactic polypropylene (iPP), poly(L-lactic acid) (PLLA), etc., with respect to their relatively slow crystallization rate in the conventional process, the addition of NAs in matrix can advantageously shorten the processing time and lead to dramatically improved performances.^[4–8] Due to the extreme importance, exploration of the exact nucleation mechanism and development of highly effective NAs have been the most concerns in both the scientific research and industry application in the past decades. Up to now, two mechanisms including epitaxial crystallization and heterogeneous nucleation are generally accepted and used to explain the nucleation effect of NAs, especially on promoting iPP crystallization. The former mechanism, epitaxial crystallization, supposes that the nucleus could form on the substrates via epitaxial interaction for the dimensional matching between

lattice parameters of substrates and polymer.^[9,10] The latter mechanism, heterogeneous nucleation, suggests that the addition of NAs could provide many more sites with the surface which reduces the free energy barrier to primary nucleation.^[11–13] Furthermore, it was found that the polymer molecular conformation played an important role in the iPP crystallization process.^[14] Yan *et al.* revealed that crystallization occurred when the length of helix sequences exceeded a critical value in the crystallization process of iPP.^[15,16] Li *et al.* reported that the conformational ordering of iPP chains would take place before they packed into crystal lattice in the growth boundary layer.^[17,18] Moreover, during the flow-induced crystallization of iPP, Li *et al.* found that the short sequences of long iPP chains could adopt proper conformation in the flow field and the isotropic-nematic transition happened as the initiate of crystals when the concentration or length of these conformational ordering sequences surpassed a certain threshold.^[19,20] As for the iPP system containing NAs, Smith *et al.* found that NAs with cleft shape could affect the iPP chain conformation in the crystallization process via experimental measurements and molecular modeling. They proposed that these nucleators could bind and stabilize the chains in helical form, which would suppress the conformational transformation of iPP chain from helical to random and be beneficial to the crystallization

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process.^[21] Similarly, Myerson *et al.* used molecular dynamics to compare the *i*PP chain conformational change in the nucleation and crystallization process of *i*PP. They found that the orientation of chain backbone with helical conformation in the *i*PP-sorbitol system was larger than the orientation in pristine *i*PP, which could promote the crystallization of *i*PP.^[22] These pioneer works suggested that the nucleation action of NAs was related to their stable effect on the proper conformation, which was in favor of the crystallization process. Therefore, studying the effect of NAs on the polymer chain conformation provided us with an important sight of understanding the nucleation mechanism of NAs.

Syndiotactic polypropylene (sPP) is a class of polypropylene whose methyl-group shows prevalingly syndiotactic arrangement in the main chain, which is different from the commonly used *i*PP. It has lower crystallinity with small spherulites and stronger chain entanglement in the amorphous region,^[23–25] which makes it particularly suitable for the preparation of highly transparent films with puncture resistance or transparent pipes with better creep resistance. However, the commercial utilization of sPP was greatly limited for its slow crystallization rate during melt processing.^[26,27] Different from *i*PP which could be nucleated by many kinds of NAs, most commonly used NAs are not very efficient for sPP. Among various NAs investigated, it was reported that the sorbitol derivatives were relatively efficient in promoting the crystallization of sPP.^[28,29] Considering that there were few efficient NAs for sPP and few studies on the mechanism of NAs on promoting sPP crystallization, investigating the effect of sorbitol derivatives on the chain conformation of sPP in the crystallization process to gain new insights into the nucleation mechanism of such NAs is of great significance and helpful for developing high-efficiency NAs to promote the industrial development of sPP.

In this work, the effect of 1,3:2,4-bis(3,4-dimethylbenzylidene)sorbitol (DMDBS) on promoting the crystallization of sPP was systematically investigated by DSC, rheological measurement, and FTIR spectroscopy. From the perspective of chain conformation, the conformational changes of sPP chain in the crystallization of sPP with or without DMDBS were revealed by FTIR in combination with the two-dimensional correlation analysis proposed by Noda.^[30,31] For the sPP system containing DMDBS, the ttgg conformers would increase and aggregate into helical conformation sequences much quickly and early, which could perform as initial nuclei. Comparing with the homogeneous nucleation in pristine sPP, these abundant initial nuclei could promote the crystallization of sPP. Our work demonstrated that the nucleation action of DMDBS on accelerating the crystallization of sPP was due to its pre-orientation stable effect on ttgg conformers.

EXPERIMENTAL

Materials

The sPP sample was pilot product produced by Petrochina Petrochemical Research Institute with weight-average molecular weight (M_w) of 130 kg·mol⁻¹ and a polydispersity index of 1.7. The microstructure of sPP chains was characterized by ¹³C-NMR and a fraction of fully syndiotactic pentad [rrrr] of

75% was determined according to the literatures.^[32,33] The nucleating agent Millad 3988 (Milliken Chemical, Belgium) was used as received, whose effective ingredient was 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (DMDBS).

Sample Preparation and Characterization

The samples with various contents of DMDBS (*x* wt%) were marked as sPP-*x*, which were prepared by melt-blending sPP and DMDBS using a Haake PolyLab OS mixer (ThermoFisher, Massachusetts) at 180 °C for 5 min at a rotation speed of 80 r·min⁻¹. Both the 0.5 mm-thick sheets for rheological experiments and 50 μm-thick films for FTIR measurements were melt-pressed at 180 °C under a pressure of 10 MPa for 5 min, and then cooled naturally to room temperature.

Differential scanning calorimetry (DSC). The thermal properties of the sPP samples were examined by a Mettler DSC-821e apparatus (Mettler Toledo Instruments Inc., Switzerland) with a temperature accuracy of ± 0.05 °C. The temperature scale of the DSC instrument was calibrated with indium (T_m = 156.60 °C and ΔH_m^0 = 28.45 J·g⁻¹) as a standard. All experiments were carried out in a nitrogen atmosphere with the sample weight of 5–8 mg. In the nonisothermal melt-crystallization process, the samples were firstly heated to 200 °C and held there for 5 min to erase previous thermal history; subsequently, they were cooled to 0 °C to record the crystallization exotherms and heated to 200 °C again to record the melting endotherms for further analysis. In the isothermal melt-crystallization process, they were cooled to the selected crystallization temperature (T_c) after erasing the previous thermal history by held at 200 °C for 5 min and then kept at this temperature to record the crystallization exotherms until the crystallization finished.

Wide-angle X-ray diffraction (WAXD). The WAXD measurement was conducted on Xeuss 2.0 System (Xenocs, Sassenage, France) with X-ray source consisting of a Cu K α (λ = 1.54 Å) microfocus tube and the distance from sample to detector being 149 mm. The samples for WAXD characterization were cooled down from 200 °C to 25 °C at 10 °C·min⁻¹ after complete crystallization.

Rheological measurement. All rheological measurements were performed using a Haake Mars III parallel-plate rheometer (ThermoFisher, Massachusetts) with a heated nitrogen stream for temperature control, and disk-shaped specimens (diameter 16 mm, thickness 0.5 mm) cut from melt-compression molded sheet were used. In the cooling process, small-amplitude oscillatory shear with strain amplitude of 1% and frequency of 1 rad·s⁻¹ was applied, and the temperature was subsequently decreased at a rate of 5 °C·min⁻¹ from 200 °C to 70 °C.

Fourier transform infrared spectroscopy (FTIR). All the FTIR spectra were recorded on a Nicolet 6700 spectrometer (ThermoFisher, Massachusetts) equipped with a hot stage in dry air atmosphere. The samples were prepared by being sealed between two ZnS tablets. The spectra were collected at a 2 cm⁻¹ resolution and 16 co-adding scans with a 2 min interval during the isothermal crystallization. The baseline correct processing of stretching vibration bands was performed by OMNIC 8.0 software.

Two-dimensional correlation analysis. Spectra recorded at an interval of 2 min were selected in certain wavenumber

ranges, and the generalized 2D correlation analysis was applied by 2DShige software (Shigeaki Morita, Kwansei Gakuin University, Japan). The final contour maps were plotted using Origin 8.5 software. In 2D correlation maps, red system-colored regions are defined as positive correlation intensities, while blue system-colored regions are regarded as negative correlation intensities.

RESULTS AND DISCUSSION

The Nucleation Effect of DMDBS for sPP Crystallization

The crystallization and melting behaviors of sPP incorporated with various contents of DMDBS were evaluated by DSC. The cooling curves are shown in Fig. 1(a) and the crystallization temperatures (T_c) of various sPP samples are summarized in Fig. 1(c). It could be found that the T_c value of the neat sample sPP-0 was at about 72.0 °C and it increased significantly to 73.4, 76.8, 79.0, and 79.4 °C for samples sPP-0.05, sPP-0.1, sPP-0.2, and sPP-0.5, respectively. At a fixed cooling rate (10 °C·min⁻¹), the higher T_c value of sample represents the much higher crystallization ability of polymer. The lowest T_c value of sPP-0 means the neat sPP performed the lowest crystallization ability and the increase of T_c values with the addition of DMDBS indicates that the crystallization ability of

sPP was enhanced by DMDBS.

Fig. 1(b) shows heating curves of various sPP samples, and it is found that there existed double melting peaks in the melting process of all the sPP samples. In the previous literatures,^[26] it has been reported that the low temperature melting endotherm (T_{ml}) corresponded to the melting of primary crystallites formed during cooling and the high temperature melting endotherm (T_{mh}) represented the melting of the re-crystallized crystallites formed during a subsequent heating scan. The melting temperatures (T_{ml} and T_{mh}) of sPP composites versus DMDBS loadings are also summarized in Fig. 1(c). It is clear that the T_{ml} value of sPP-0 was at about 115.2 °C and it increased to 116.5, 116.7, and 117.9 °C for sPP-0.05, sPP-0.1, and sPP-0.2, respectively, and kept constant at about 117.9 °C even the content of DMDBS was 0.5 wt% for sPP-0.5. It is well known that the higher T_m value denotes the crystallite with greater stability (i.e. thicker lamellae).^[28] The increase of T_{ml} values showed that DMDBS could improve the stability of primary crystals. Meanwhile, T_{mh} remained at about 129.0 °C in the concentration range of DMDBS studied from 0 wt% to 0.5 wt%. Furthermore, the crystallinities of sPP with various DMDBS contents were also determined by WAXD measurement and the data are listed in Fig. 1(d). It could be found that all the five samples had similar crystallinities of around 22% in the NA concentration range studied from 0 wt% to 0.5 wt%.

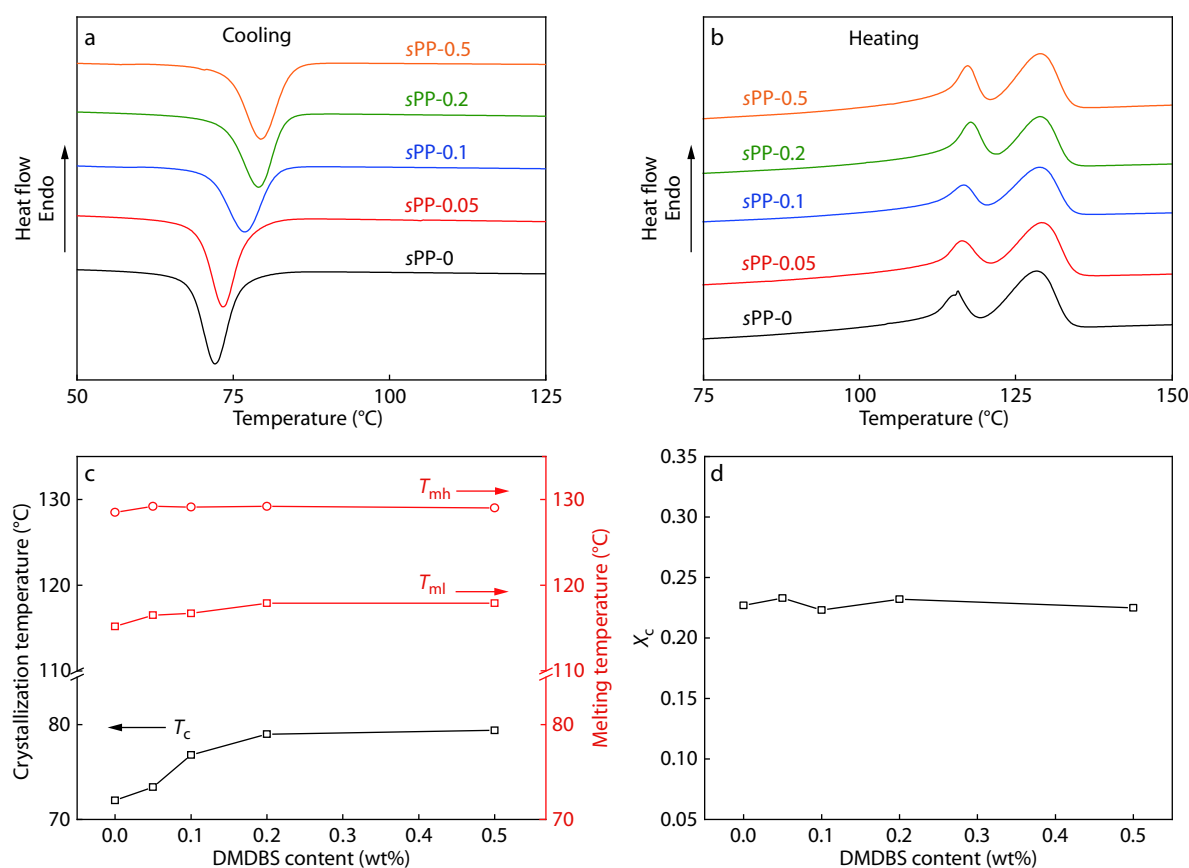


Fig. 1 DSC (a) cooling and (b) heating curves of various sPP samples. (c) Crystallization temperature (T_c) and melting temperatures (T_{ml} and T_{mh}) of sPP calculated from DSC curves. (d) The crystallinity (X_c) of sPP with various DMDBS contents determined by WAXD measurement.

This result indicates that the addition of DMDBS could promote the crystallization but have no obvious effect on the crystallinity of sPP.

The nucleation effect of DMDBS was further investigated by isothermal crystallization. Fig. 2(a) shows the DSC traces of various samples isothermally crystallized at 110 °C and it could be found that with the content of DMDBS increased from 0 wt% to 0.5 wt%, the DSC curves of samples became much more distinct. The Avrami equation is a widely used method for analyzing the crystallization kinetics including the half-time ($t_{0.5}$) of isothermal crystallization, the Avrami exponent n , and the crystallization rate constant k .^[34,35] Fig. 2(b) shows the plots of $\log[-\ln(1 - X(t))]$ versus $\log t$ of raw experimental data and fitted lines by Avrami equation. The kinetics parameters are listed in Table 1. The $t_{0.5}$ value is an important parameter to evaluate the crystallization rate of polymer. Generally, the shorter $t_{0.5}$ represents the faster crystallization of polymer.^[4] From Table 1, it is clear that $t_{0.5}$ values of sPP samples decreased with the increase of DMDBS, which indicates that the crystallization of sPP was promoted by DMDBS. The Avrami exponents (n values) of various sPP samples varied between ~ 3.17 and 3.70 , which is in good agreement with the values of ~ 3.06 to 3.79 found in an earlier study.^[29] These n values are very close, which means that DMDBS did not change the type of nucleation and growth geometries of sPP.

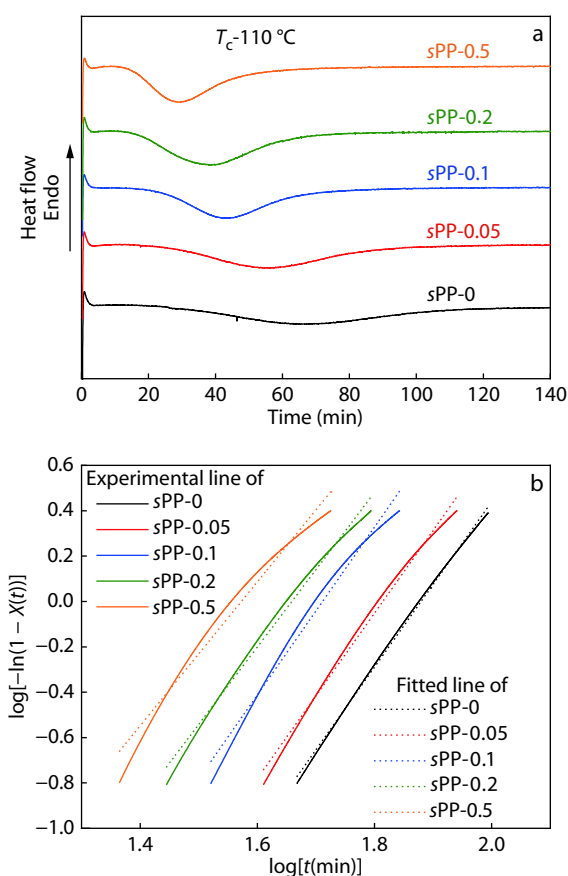


Fig. 2 (a) DSC curves of various sPP samples in the isothermal crystallization at 110 °C. (b) Plots of $\log[-\ln(1 - X(t))]$ versus $\log t$ for various sPP samples.

Table 1 Isothermal crystallization kinetics parameters for various sPP samples.

Sample	sPP-0	sPP-0.05	sPP-0.1	sPP-0.2	sPP-0.5
$t_{0.5}$ (min)	66.7	55.9	43.5	38.8	29.4
n	3.64	3.64	3.70	3.40	3.17
k (min^{-n}) $\times 10^7$	1.40	2.44	4.64	22.38	102.8

As expected, the crystallization rate constants k of sPP samples varied markedly depending on the addition of DMDBS at the given crystallization temperature. When the contents of DMDBS were 0 wt%, 0.05 wt%, 0.1 wt%, 0.2 wt%, and 0.5 wt%, the values of k could be obtained as 1.40×10^{-7} , 2.44×10^{-7} , 4.64×10^{-7} , 22.38×10^{-7} , and $102.8 \times 10^{-7} \text{ min}^{-n}$, respectively. The increase of the values of k indicates that the crystallization of sPP was accelerated by DMDBS.

The sPP crystallization with or without DMDBS was also characterized by rheological measurement. Fig. 3 shows the elastic modulus (G' in Pa) of sPP-0 and sPP-0.2 as a function of temperature upon cooling from 200 °C to 70 °C at $5^\circ\text{C}\cdot\text{min}^{-1}$. It is clear that G' of sPP-0 increased linearly and then a sudden sharp increase by a factor of 2 was observed at about 88.9 °C, while the sudden sharp increase of G' curve for sPP-0.2 was observed at about 93.5 °C (shown in the enlarged view of black rectangle from 80 °C to 100 °C in Fig. 3). The onset temperature (T_{onset}) of the sudden sharp increase represents the start of sPP crystallization. The higher T_{onset} for sPP-0.2 (at about 93.5 °C) showed that the crystallization of sPP-0.2 was promoted by DMDBS, which is in accordance with the result of DSC. In the enlarged view of black circle from 100 °C to 160 °C in Fig. 3, relatively small but distinct increase was detected on the curve of sPP-0.2 at about 134 °C before the crystallization occurred, while the small increase was absent in the curve of sPP-0. Therefore, this small increase on the G' curve of sPP-0.2 should be caused by the addition of DMDBS. In the previous studies of *i*PP/DMDBS system, it has been reported that DMDBS crystallized as thin fibrils from the *i*PP melt firstly and then these fibrils acted as NA to promote the *i*PP crystallization.^[36–39] Therefore, for the sPP/DMDBS system we investigated in this work, the nucleating ability of DMDBS for sPP may be also relevant to DMDBS

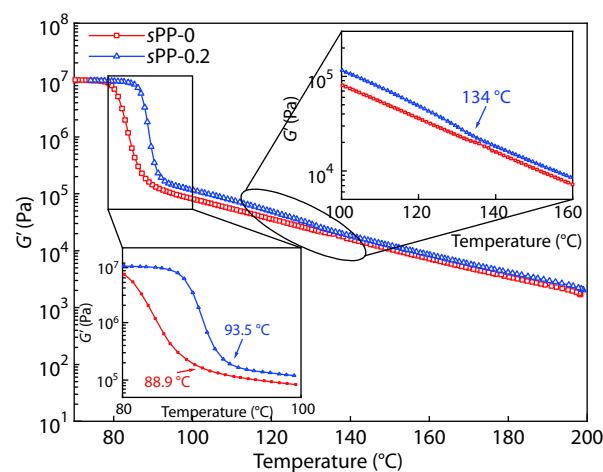


Fig. 3 Elastic modulus (G') as a function of temperature for sPP-0 and sPP-0.2.

thin fibrils. In summary, DMDBS was an effective NA for sPP which could not only promote the crystallization rate but also improve the stability of primary crystallites.

The Conformational Changes of sPP Chain in the Crystallization Process

In the previous works of sPP crystallization, Huang *et al.* reported that the development of sPP chain conformation was an important process in the crystallization process.^[40] Wang *et al.* revealed that in the isotropic state of sPP melt, the most common conformers were ttgg and tttt, corresponding to basic elements of helical and trans-planar zigzag conformations, respectively. They found that the existence of ttgg conformer might be the motivation for the formation of short helical conformation,^[41] which was in accordance with the helical structure of Form I crystal. Huang *et al.* proposed that partial chains among the amorphous component changed in conformation first, and then the crystallization occurred as the sPP chains formed unique helical conformations.^[42] These works revealed that the change of sPP chain conformation could determine the crystallization process of sPP, and studying the effect of DMDBS addition on the sPP chain conformation maybe give us much more useful information to understand the mechanism of DMDBS accelerating the crystallization behavior of sPP from the perspective of chain conformation.

Fourier transform infrared spectroscopy (FTIR), which is

sensitive to the chain conformation, was applied to trace the conformational change of sPP chains in the isothermal crystallization. Figs. 4(a) and 4(b) show the spectral changes in the wavenumber regions of 985–935 and 880–805 cm^{-1} as a function of time during the isothermal crystallization of sPP-0 and sPP-0.2 at 110 $^{\circ}\text{C}$. From Figs. 4(a) and 4(b), it is clear that five conformation sensitive bands of sPP chain were confirmed, which correspond to the different conformational structure of sPP, and the characteristic infrared vibrational assignments for sPP have been reported, as summarized in Table S1 (in the electronic supplementary information, ESI), to describe various conformations of the sPP chains. The bands at 811, 867, and 977 cm^{-1} correspond to the 4_1 helix conformation of sPP chains in form I crystal, while the bands at 826 and 963 cm^{-1} are associated with trans-planar conformation of sPP chains in mesophase or amorphous phase.^[43–46]

In Fig. 4(a), it is found that the intensities of the bands at 811, 867 and 977 cm^{-1} increased gradually with time, which indicates the helical conformation increased in sPP-0. Meanwhile, the intensities of the bands at 826 and 963 cm^{-1} decreased with time, which indicates that the trans-planar conformation decreased. The increase of helical conformation and the decrease of trans-planar conformation showed the transformation from melt to form I, which represented the occurrence of crystallization in sPP-0. In Fig. 4(b), the change of

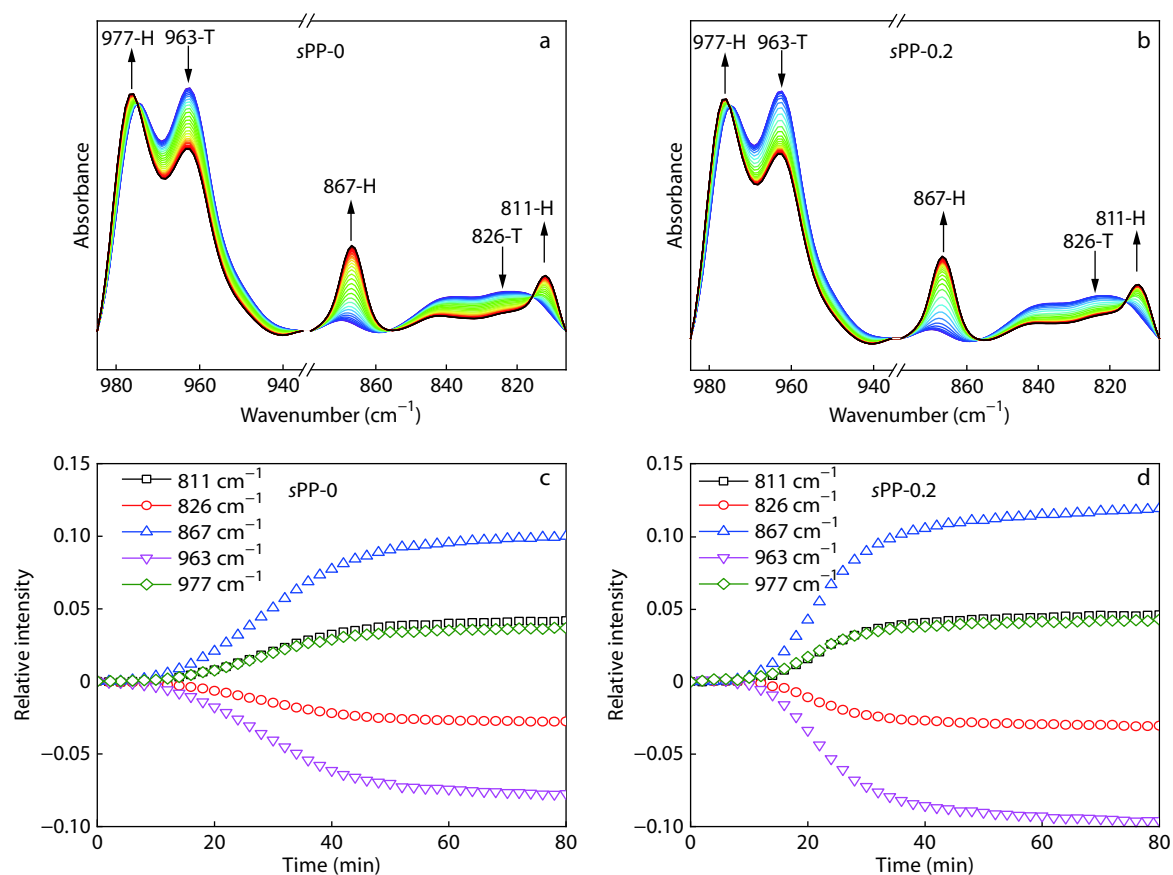


Fig. 4 Time-dependent FTIR spectra of (a) sPP-0 and (b) sPP-0.2 crystallized at 110 $^{\circ}\text{C}$ in the wavenumber regions of 985–935 and 880–805 cm^{-1} . Relative intensity of FTIR bands at 811, 826, 867, 963, and 977 cm^{-1} as a function of time during the isothermal crystallization of (c) sPP-0 and (d) sPP-0.2 at 110 $^{\circ}\text{C}$.

conformation sensitive bands of sPP-0.2 shows the similar phenomenon to sPP-0 where the helical conformation increased and the trans-planar conformation decreased. Thus, the formation of form I also occurred in sPP-0.2. The WAXD characterizations of samples after the crystallization have proved that both the crystalline structures of sPP-0 and sPP-0.2 were form I (see Fig. S1 in ESI).

Figs. 4(c) and 4(d) show the relative intensity of FTIR bands at 811, 826, 867, 963, and 977 cm^{-1} as a function of time during the isothermal crystallization of sPP-0 and sPP-0.2 at 110 $^{\circ}\text{C}$. It is found that the relative intensity of conformation sensitive bands of sPP-0 approached the platform at about 60 min, while the relative intensity of conformation sensitive bands of sPP-0.2 got close to the equilibrium at about 40 min. Therefore, the FTIR band intensity change ratios of sPP-0.2 were faster than that of sPP-0, which indicates that the conformational change of sPP was promoted by DMDBS.

For further analysis of the FTIR band intensity change ratios in the crystallization process, the peak position of the first order derivation of the FTIR band intensity profiles as a function of crystallization time is a proper parameter to describe the characteristic time of the change,^[40] which are shown in Fig. 5. In Fig. 5, the rough change ratios of conformation sensitive bands of sPP-0 and sPP-0.2 could be obtained as $963\text{ cm}^{-1} > 826\text{ cm}^{-1} \sim 977\text{ cm}^{-1} > 867\text{ cm}^{-1} \sim 811\text{ cm}^{-1}$ and $977\text{ cm}^{-1} \sim 867\text{ cm}^{-1} > 963\text{ cm}^{-1} > 826\text{ cm}^{-1} \sim 811\text{ cm}^{-1}$, respectively. It is found that the sensitive bands at 977 and 867 cm^{-1} started to change earlier than 963 and 826 cm^{-1} in sPP-0.2, while the sensitive bands at 963 and 826 cm^{-1} started to change earlier than 977 and 867 cm^{-1} in sPP-0. This result means that the change of helical conformation was earlier than trans-planar conformation in sPP-0.2, which is different from the change order in sPP-0. Therefore, it could be concluded that DMDBS could promote the change of helical conformation rather than trans-planar conformation.

From the analysis of original 1D FTIR spectra, we found that DMDBS could promote the conformational change of sPP chain, especially for the helical conformation. However, the change ratio sequences of conformation sensitive bands of sPP samples obtained from Fig. 5 were rough and the change order of some conformation sensitive bands was difficult to determine accurately, which limits the further analysis of the conformational change of sPP chain in the crystallization process. To obtain further useful and clear information of the conformational change of sPP chain, two-dimensional correlation (2DCOS) was considered for the analysis of FTIR spectra. 2DCOS is a mathematical analytical method first proposed by Noda,^[47] and it has been extensively applied to trace spectra fluctuations of diverse external perturbations such as temperature, time, and concentration.^[48,49] 2DCOS can capture the subtle information which is not obvious in 1D spectrum and improve the spectral resolution. Hence, both the FTIR spectra of sPP-0 and sPP-0.2 during isothermal crystallization from 0 min to 80 min with an interval of 2 min were used to perform the 2DCOS.

The 2D-IR correlation spectra were obtained including two types of spectra, 2D synchronous and asynchronous spectra. These correlation spectra were characterized by two independent wavenumber axes (ν_1 , ν_2) and a correlation intensity

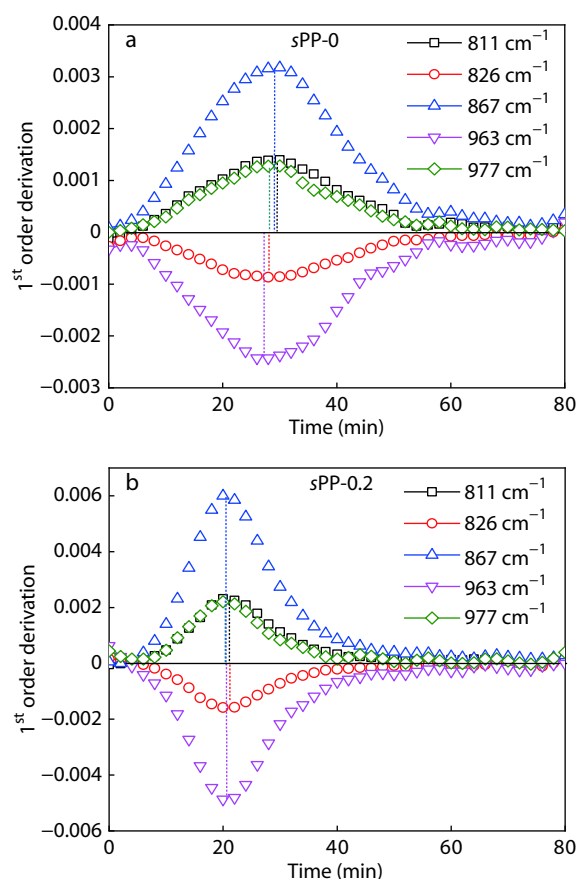


Fig. 5 The first order derivation of the FTIR band intensity as a function of time during the isothermal crystallization of sPP-0 (a) and sPP-0.2 (b) at 110 $^{\circ}\text{C}$.

axis. The correlation intensity in the 2D synchronous and asynchronous maps reflects the relative degree of in-phase or out-of-phase response, respectively. The warm colors (red) are defined as positive intensities, while the cool colors (blue) are defined as negative ones. The 2D synchronous spectra are symmetric with autopeaks along the diagonal line and cross-peaks ($\Phi(\nu_1, \nu_2)$) which are off-diagonal peaks, and the 2D asynchronous spectra are asymmetric with only off-diagonal cross-peaks ($\Psi(\nu_1, \nu_2)$). According to Noda's rule,^[31] when $\Phi(\nu_1, \nu_2) > 0$, if $\Psi(\nu_1, \nu_2)$ is positive (red-colored area), band ν_1 will vary prior to band ν_2 ; if $\Psi(\nu_1, \nu_2)$ is negative (blue-colored area), band ν_1 will vary after ν_2 . However, this rule is reversed when $\Phi(\nu_1, \nu_2) < 0$. Briefly, if the symbols of the cross-peak in the synchronous and asynchronous maps are the same (both positive or both negative), band ν_1 will vary prior to band ν_2 ; if the symbols of the cross-peak are different in the synchronous and asynchronous spectra (one positive, and the other one is negative), band ν_1 will vary after ν_2 under the environmental perturbation.

Fig. 6 shows the 2D synchronous and asynchronous spectra in the isothermal crystallization process of sPP-0. According to the Noda's rule for the determination of sequence order described before, the final sequence order in the sPP chains conformational change could be described as $963\text{ cm}^{-1} > 826\text{ cm}^{-1} > 977\text{ cm}^{-1} > 867\text{ cm}^{-1} > 811\text{ cm}^{-1}$ (the de-

termination details of sequential order of sPP-0 have been listed in Table S2 (in ESI), and ">" means earlier than or prior to). According to the assignments of bands shown in Table S1 (in ESI), this sequence order could also be described as CH₃ rock (trans-planar in interfacial) > CH₂ rock (trans-planar in mesophase or amorphous) > CH₃ rock (helical in interfacial) > CH₂ rock (helical in crystalline) > CH₂ rock (helical in crystalline). This sequence order could be interpreted as that the trans-planar conformation changed prior to the helical conformation in the crystallization process. In the study of variations of regular conformation structures in sPP melt, Wang *et al.* revealed that the changes of helical and trans-planar conformations were related to the changes of their basic element conformers ttgg and tttt, respectively.^[41] Thus, we can investigate the development of tttt and ttgg conformers during the crystallization by comparing the changes of trans-planar and helical conformations. From the sequence order obtained based on Fig. 6, it could be found that the decrease of trans-planar conformation was earlier than the increase of helical conformation, which suggests that the transformation of conformers tttt was prior to the aggregation of ttgg conformers. Therefore, it could be concluded that in the crystallization process of pristine sPP, the tttt conformers would trans-

form firstly, and then the ttgg conformers could increase to go beyond a certain threshold and aggregate into helical structures as homogeneous nuclei in melt to induce the crystallization.

Fig. 7 shows the 2D synchronous and asynchronous spectra in the isothermal crystallization process of sPP-0.2 and the final sequence order in the sPP chains conformation transformation could be described as 977 cm⁻¹ > 867 cm⁻¹ > 963 cm⁻¹ > 826 cm⁻¹ > 811 cm⁻¹ (the determination details of sequential orders of sPP-0.2 have been listed in Table S3 (in ESI), and ">" means earlier than or prior to) or CH₃ rock (helical in interfacial) > CH₂ rock (helical in crystalline) > CH₃ rock (trans-planar in interfacial) > CH₂ rock (trans-planar in mesophase or amorphous) > CH₂ rock (helical in crystalline). This sequence order could be interpreted as that the helical conformation changed prior to the trans-planar conformation in the crystallization process. We have known that the changes of ttgg and tttt conformers could be investigated by analyzing the development of trans-planar and helical conformations during the crystallization. The sequence order obtained based on Fig. 7 shows that the increase of helical conformation was prior to the decrease of trans-planar conformation. This result suggests the aggregation of ttgg conformers was

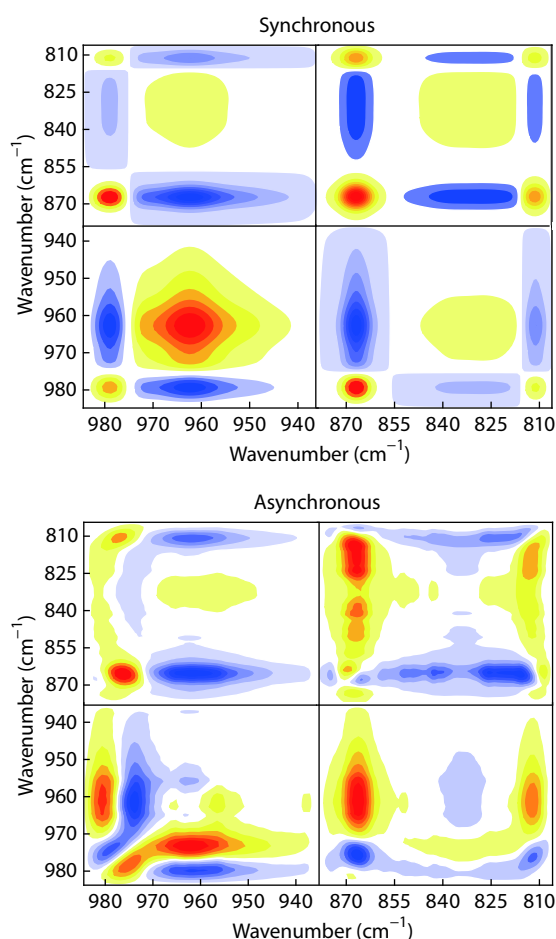


Fig. 6 2D synchronous and asynchronous spectra of sPP-0 calculated from the spectra obtained during isothermal crystallization at 110 °C from 0 min to 80 min.

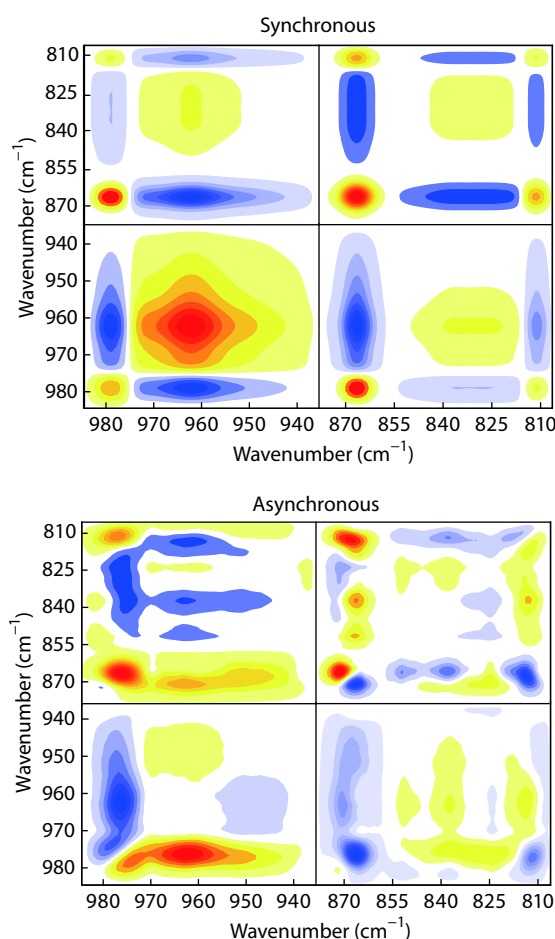


Fig. 7 2D synchronous and asynchronous spectra of sPP-0.2 calculated from the spectra obtained during isothermal crystallization at 110 °C from 0 min to 80 min.

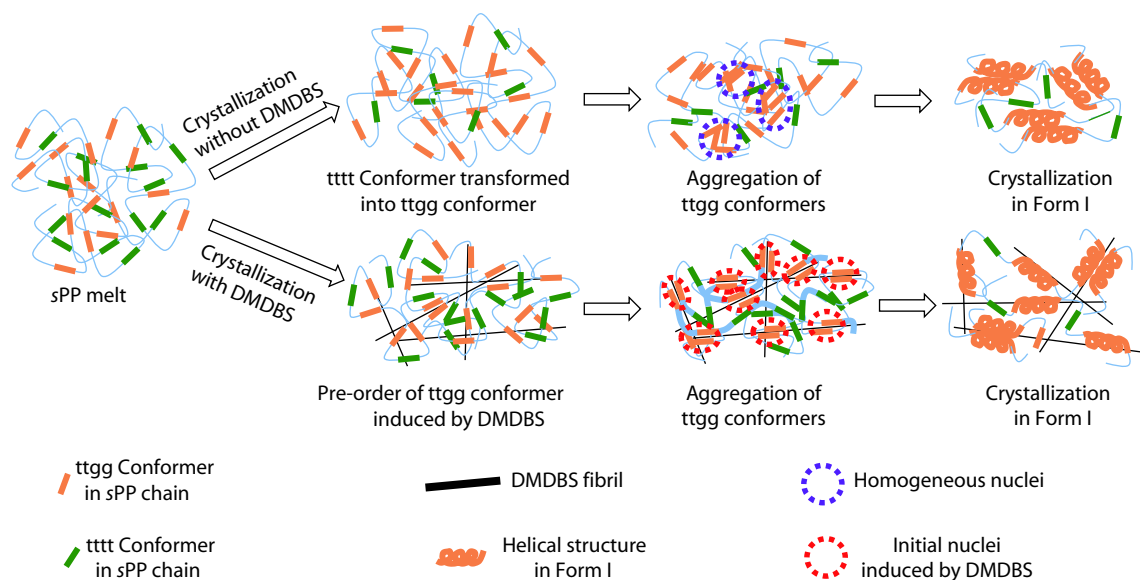
earlier than the transformation of tttt conformers. Thus, it is reasonable to conclude that the addition of DMDBS could make the ttgg conformers aggregate into helical structures much earlier and more quickly, which promoted the crystallization of sPP-0.2.

The Possible Mechanism of DMDBS Promoting the Crystallization of sPP

In the study of the structure changes in the crystallization process of *i*PPS, it was found that the order of conformational change in the nucleation period and the subsequent crystallization growth process were same.^[50] According to the Hoffmann and Lauritzen (HL) theory of polymer crystallization, it was known that the nucleation and crystal growth were two continuous processes in polymer crystallization.^[51] It could be reasonable to speculate that the sequence orders of the sPP chains conformational change in the nucleation and crystal growth processes were also same. In other words, the change sequence order of chain conformation in the nucleation process, which was the first process, could determine the sequence order of chains conformational change in the whole crystallization process, just like dominoes. Therefore, the details of chains conformational change in the nucleation process

could be obtained by the analysis of 2D-IR correlation spectra of sPP-0 and sPP-0.2, and a schematic diagram of nucleation and crystallization process of sPP with or without DMDBS is proposed in Scheme 1.

In the isotropic sPP melt, the most common conformers in the melt were ttgg and tttt conformers. In the nucleation process of the pristine sPP, the tttt conformers would transform into ttgg conformers firstly, which could make the content of ttgg conformers increase and go beyond a certain threshold; then, these ttgg conformers could aggregate together and form helical conformation, which performed as homogeneous nuclei in the melt. These homogeneous nuclei would induce the crystallization of pristine sPP. As DMDBS was added in sPP, it would crystallize as thin fibrils during the cooling of sPP melt and perform a stable and pre-orientation effect on the ttgg conformers. This effect would make the ttgg conformers pre-orientate and aggregate as initial nuclei immediately in the nucleation process, which was prior to the transformation from tttt conformers to ttgg conformers. Compared with the homogeneous nuclei formed by sPP chains themselves in the pristine sPP, much more initial nuclei could form quickly and early in the existence of DMDBS and promote the crystallization process of sPP.



Scheme 1 The nucleation and crystallization process of sPP with or without DMDBS.

CONCLUSIONS

In this work, the effect of DMDBS on promoting the crystallization of sPP was systematically investigated. The results of DSC and rheological measurement revealed that the efficient nucleating ability of DMDBS for sPP may be relevant to the DMDBS thin fibrils. By comparatively analyzing the 2D-IR spectra of sPP-0 and sPP-0.2, it was found that in the nucleation process of pristine sPP, the tttt conformers would transform to ttgg conformers firstly and increase the concentration of ttgg conformers. After the concentration of ttgg conformers surpassed a certain threshold, they could aggregate into helical structures as homogeneous nuclei and the crystallization of pristine sPP

occurred. When DMDBS was added in sPP, it could perform a stable effect on the ttgg conformers, which would induce the ttgg conformers pre-orientation and aggregate as initial nuclei immediately. Therefore, more initial nuclei could form more quickly and earlier comparing with the homogeneous nucleation process in pristine sPP, which promotes the crystallization of sPP.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at

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