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Rheologically determined negative influence of increasing nucleating agent content on the crystallization of isotactic polypropylene

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ABSTRACT

Dibenzylidene sorbitol (DBS) exists in the form of fibril and usually acts as an effective nucleating agent to facilitate crystallization of polyolefin during manufacturing. In this research, the isothermal crystallization of isotactic polypropylene (iPP) containing different amounts of DBS was followed by dynamic rheometry, and described upon a viewpoint of viscoelastic property evolution. Since the adopted temperatures within the entire sample preparation and characterization process were below the melting point of DBS, the DBS additives played a role of only solid nucleating agent, thus the possible effect of a changed miscibility between iPP and DBS on the viscoelastic properties as change of temperature could be ignored. Although saturation of nucleating iPP was observed at 0.1% DBS concentration, a negative influence with further increasing DBS content on the crystallization of iPP was determined for the first time via time sweep of G' upon a single angular frequency and application of "inverse quenching" protocol within a wide range of angular frequency. Even more, a largely increased G' and viscosity were observed in the melt as decreasing the temperature of iPP containing 0.1% DBS, suggesting a strong quasi-solid like behavior before iPP crystallization. A complement for well understanding the crystallization of iPP containing nucleating agent was discussed based on the formation of the DBS fibrils' network, the interfacial tension between crystalline/amorphous phase, and the consistency of crystallizing lamellae. Our study demonstrates clearly that the crystalline characteristic upon saturation of heterogeneous nucleating is difficult to be detected by traditional means, but could be followed reasonably by rheological measurements which is much sensitive to the microstructural changes.

1. Introduction

To elucidate the crystallization mechanisms of semicrystalline polymers clearly, various techniques for in-situ assessing the crystallization process of molten polymer have been adequately developed. As it is well known that some physical or chemical characteristics are intimately connected with crystallization behavior, quantitatively or qualitatively estimated crystallization process can be performed through monitoring certain physical or chemical characteristic alteration. In a polymer crystallization process, the exothermic enthalpy, caused by macromolecular chains' configuration transition from random coils to ordered arrangement, may be measured by differential scanning calorimetry (DSC); the formation of periodic ordered structure is promptly detected by synchrotron-source wide- and small-angle X-ray scattering (WAXS and SAXS) [1] or small-angle light scattering (SALS) [2], in which the scattering signal will be significantly amplified when the periodic distance is n ($n = 1, 2, 3\ldots$) orders compared to the wavelength of incident ray; the morphological observation of crystallite growth can be conducted on polarized light microscope (PLM) because of obvious diffraction index difference between crystalline phase and amorphous phase; while the subtle framework of lamella in nanoscale can be obtained via real-time atomic force microscopic (AFM) detection [3], because the stiffness and modulus of crystallite are remarkably larger than that of melt phase. Moreover, the viscoelastic, rheological properties, such as viscosity, storage or loss (elastic or viscous) modulus and loss tangent, with high sensitivity to intrinsic microstructure and molecular conformation of polymer material, also can be utilized to characterize polymer crystallization behaviors.

Investigation of polymer crystallization through rheological approaches has attracted extensive attention in the past two decades, and some fruitful results were reported in literature. From a viewpoint of rheology, polymer crystallization is simplified as liquid-to-solid transition or biphasic system where rigid spherulites suspend in amorphous melt. Dynamic modulus and viscosity

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will proportionally increase with elevated solid-like degree (crystallinity). Commonly, evolving spectrum of elastic modulus G' upon quiescent isothermal (T_c) condition was to describe crystallization process and estimate crystallization kinetics. Khanna [4] proposed a relation for associating relative crystallinity $\alpha(t)$ with G', which continuously altered during isothermal nucleated crystallization of the polyamide and polypropylene melts. In a more detail study by Boutahar et al. [5], combined rheometry with calorimetry and optical microscopy, two different expressions were suggested for quantitatively calculating the transformed fraction from the dynamic moduli, corresponding to two cases that are suspension-like system for a pure polypropylene melt and colloid-like system for a nucleated polyethylene melt. Viscoelastic properties are highly sensitive to microstructural changes even at very low crystallinity. So rheological technique was used to explore the early stage of crystallization, where some traditional means, such as DSC, could fail because the low exothermic flux was unappreciable. Winter et al. have measured the viscoelastic mechanical properties at the early crystallization stage for a series of semicrystalline polymers, including polyolefins [6,7], thermoplastic elastomer [8], bacterial polyester [9], and poly(vinyl chloride) [10]. They suggested that, at the critical point for liquid-to-solid transition, the crystallizing melt behaves as a physical gel, where its relaxation modulus can be described as a power law and loss tangent is independent of low angular frequency. Acierno et al. [11] investigated the effect of poly(1-butene) molecular weight on the rheological parameters of the crystalline critical gel. Based on their research, it was claimed that the viscoelastic behaviors in the early stage of crystallization were dominated by the molecular character of the amorphous phase. Grizzuti et al. [12,13] developed an innovative rheological protocol, called “inverse quenching”, which allows one to obtain reliable viscoelastic properties developed during crystallization. For such “inverse quenching” technique, proceeding crystallization is temporarily stopped by elevation of temperature. The reliability of this rheological approach has been confirmed at least for the crystallization of polypropylene [12] and poly(1-butene) [13]. Shear-accelerated polymer crystallization kinetics was also estimated by rheological technique [14]. Recently, rheological investigation of shear-enhanced crystallization of isotactic polypropylene nucleated by multi-walled carbon nanotubes has been carried out by our group [15].

In order to realize fast crystallization and uniform distribution of spherulite size, heterogeneous additives, nucleating agents (NAs), are frequently introduced, which enable semicrystalline polymer melts to nucleate and crystallize in a convenient manner. Dibenzylidene sorbitol (DBS), acted as a kind of highly efficacious NA for nucleating polyolefin melts [16], has been extensively applied in both fields of academy and manufacturing. Some preliminary studies have shown that DBS substance possesses fibrillous profile [17,18], the fibrillar morphology offers a large specific area for producing a high nuclei density; and DBS fibrils could nucleate polyolefin crystallization via an epitaxial mechanism, as confirmed by the electronic microscopy [19] and AFM [20]. Especially, when the DBS concentration reaches a critical value, the DBS fibrils will self-organize into a three-dimensional network with decrease of temperature but before crystallization takes place, which has been experimentally approved by Shepard et al. [17] and Thierry et al. [19]. However, the critical value of DBS amount required for the formation of the DBS fibrils’ network was very low, about 0.1 wt% as reported by Shepard et al. [17]. The 3D DBS fibrils’ network may facilitate the subsequent process of nucleation and crystallization growth. Interestingly, an oriented deformation of DBS network could act as a template for anisotropic crystallization of polypropylene, and resulted in higher lamellar orientation level compared to the pristine polymer, as shown in the researches by Nogales et al. [21,22]. Kristiansen et al. [23] constructed experimentally a phase diagram for the binary polypropylene (PP)/DBS system, and demonstrated that the crystallization mode was dominated by DBS concentration. Liquid–liquid phase separation would occur during cooling the homogeneous binary melt when the DBS concentration was high, such as exceeding 1 wt%. Interestingly, in some publications [17,23,24], after melting the PP/DBS system upon a relatively high temperature (commonly higher than 240 °C that could induce DBS to be completely molten), an extra enhancement in viscoelasticity appeared before the occurrence of PP crystallization during the cooling process of homogeneous PP/DBS melt, which was regarded as a representation for DBS solidifying and crystallizing to fibrils and then solid DBS fibrils assembling into network superstructure.

The mechanism about polymer crystallization with the presence of nucleating agent is so complicated, and still remains many open topics to discussion. Although the nucleated crystallization behaviors have been widely studied through some traditional techniques, including DSC, PLM, X-ray scattering, etc., NA nucleated polymer crystallization followed by rheological technique was less demonstrated in the literature [4,5]. A principal understanding of such crystallization process, based on a viewpoint of rheological viscoelasticity, is by far unavailable. Furthermore, the role of NA amount or NA network in the crystallization of polymers needs to be elucidated unambiguously.

Generally, the melting point of DBS is well above that of polyolefin. For instance, the melting temperature of 1,3:2,4-di-*p*-methylbenzylidene sorbitol is within a range of 230–240 °C, whereas PP will be melted at about 165 °C. As to DBS, its molten temperature is simultaneously the decomposition temperature. In many practical cases of melt mixing PP and DBS, a melting temperature above 230 °C may induce obvious thermo-oxide degradation of PP and partial decomposition of DBS. Nevertheless, for experimental investigations, the binary PP/DBS system was commonly melted at a temperature equal to or higher than the melting point of DBS to obtain a homogeneous liquid melt. The case that crystallization began from a solid (DBS)-molten (PP) situation was merely considered though it is more suitable for the realistic dynamic melt processing. In our present study, the adopted temperatures during the entire processes of sample preparation and characterization were $\leq$210 °C, which was high enough for well melting PP crystals while preserving the solid state of DBS. The DBS additives played a role of only solid nucleating agent. The possible effect of a changed miscibility between iPP and DBS on the viscoelastic properties, such as emergence of liquid–liquid phase separation during cooling a homogeneous melt of PP/DBS when the DBS concentration was relatively high [23], could be excluded. Rheologically described crystallization of DBS nucleated polypropylene is the primary topic in this study. Quiescent isothermal crystallization of isotactic polypropylene compounded with different amounts of DBS (0–3 wt%) was followed by dynamic rheometry. In-situ monitoring of elastic modulus (G') evolution during crystallization proceeding was performed by obeying two strategies: (1) time sweep of G' under a single angular frequency (1 rad/s); (2) application of “inverse quenching” protocol to obtain viscoelastic properties within a wide range of angular frequency (0.05–100 rad/s). DBS content dependence on viscoelastic properties’ evolution during isothermal crystallization will be demonstrated clearly. The relation between rheological evolution and crystal morphology is established through combination of rheometry and optical microscopy. Finally, we would like to propose a hypothetical mechanism description to explain the observed specific rheological evolution depending on the DBS content, taken into account the formation of DBS fibrils’ network, the interfacial tension between crystalline/amorphous phase, and the consistency of crystallizing lamellae.

2. Experimental

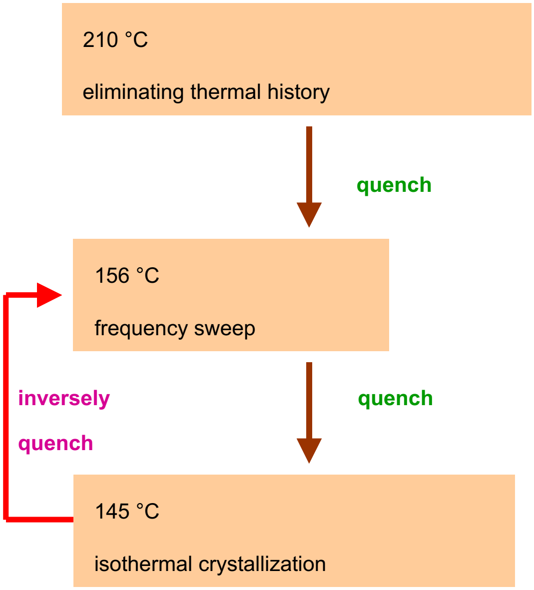
2.1. Materials and sample preparation

A commercially available isotactic polypropylene (iPP), trade marked as T30S (Yan Shan Petroleum, China), with $M_w = 39.9 \times 10^4$ g/mol and $M_w/M_n = 4.6$, was used as the base polymer. A kind of industrial DBS, 1,3:2,4-di-*p*-methylbenzylidene sorbitol (MDBS), has been kindly supplied by Shujin Chemical Co. Ltd, Nanjing, China. The molecular formula of MDBS can be seen in Ref. [17]. MDBS is a highly efficacious nucleating agent for accelerating polyolefin crystallization, while the recommended MDBS dosage is 0.1–0.3 wt% for polypropylene products to obtain optimal mechanical performances and optical transparency. The molten temperature of MDBS is about 230 °C, whereas partial thermal decomposition of MDBS will also take place at such temperature. In a concise manner, MDBS is abbreviated as DBS in rest of the text.

A masterbatch composed of 5 wt% DBS and 95 wt% iPP was melt-mixed in a TSSJ-2S co-rotating twin-screw extruder. Temperature of the extruder was maintained at 160, 190, 210, 210 and 195 °C from hopper to die and the screw speed was about 110 rpm. Through adding the fitted amounts of iPP to dilute the as-prepared masterbatch, a series of iPP samples within a wide concentration range of DBS (0, 0.02, 0.05, 0.1, 0.3, 1.0, 3.0 wt%) were melt-compounded again in the extruder. The highest content, 3 wt%, is substantially higher than the normally used one in industry. The adopted temperatures of extrusion processing are below the melting temperature of pure DBS. The reasons are: (1) low temperatures were beneficial for avoiding the possible thermo-oxide degradation of iPP and decomposition of DBS, especially, for the specimen with large amount of DBS (i.e. ≥ 3 wt%), substantial decomposition might happen when melt extrusion was performed upon the melting point of DBS; (2) uniform dispersion of DBS fibrils in iPP matrix could be realized via extrusion compounding though the processing temperature was lower than the melting point of DBS [17]. After pelletized and dried, the extruded specimens were compression molded under 200 °C and 15 MPa for 3 min, and then the compressed specimens were used to perform rheometric, calorimetric and optical microscopic characterizations.

2.2. Rheological measurements

All rheological measurements were performed on a Gemini 200 dynamic rheometer (Malvern Instruments Ltd, UK) using 2.5 cm diameter and 1.2 mm distance parallel plates. Before the measurements of isothermal crystallization, the testing samples were first heated to 210 °C for 5 min to eliminate the pristine crystalline structures; and then cooled quickly to the desired crystallization temperature at a rate of −20 °C/min. Two experimental protocols were adopted for monitoring rheological evolution during isothermal crystallization proceeded at 145 °C: (1) time sweep of elastic modulus (G') upon a single angular frequency of 1 rad/s; (2) application of “inverse quenching” protocol to obtain viscoelastic properties within a wide range of angular frequency (0.05–100 rad/s). The procedure of “inverse quenching” is presented in Scheme 1. After preheated at 210 °C, the molten sample was promptly cooled to 156 °C for conducting frequency sweep (the crystallinity was 0% at that moment), then successively cooled to 145 °C and crystallized at this temperature; after a duration of crystallization, the sample was again heated to 156 °C for frequency sweep (crystallization was stopped at such high temperature). This cycle was repeated for several times until a high transformed fraction was reached, and the total effect of successive crystallization circles could be reflected on the evolution of viscoelasticity. Moreover, all dynamic rheological experiments were performed upon low strain ($\leq 0.5\%$) for erasing the effect of shear deformation on crystallization.



Scheme 1. “Inverse quenching” protocol used in this study.

2.3. Differential scanning calorimetry

The calorimetric analysis of the as-prepared samples was conducted using a Perkin–Elmer pyris-I DSC, calibrated by indium. The slices, about 5 mg, were cut from the compression-molded samples. The slices were heated to a preset temperature (210 °C) at a rate of 100 °C/min and held at such temperature for 5 time to eliminate the initial thermal history, then (1) cooled down to 50 °C under a constant rate of −10 °C/min for nonisothermal crystallization or (2) cooled quickly (200 °C/min) to 145 °C and held at this temperature for isothermal crystallization.

2.4. Polarized light microscopy

Morphological observations of iPP crystallites’ growth were conducted on a Leica DMIP polarizing light microscope (PLM) equipped with a Linkam THMS 600 hot stage under crossed polarizers. The thin slices were cut from the compression-molded specimens, inserted between two microscopic cover glasses, melted at 210 °C and squeezed to obtain thin films. The slices were held at 210 °C for 5 min to achieve thermal equilibrium. Subsequently, the molten slices were rapidly cooled to expected crystallization temperature (145 °C) and then in-situ morphological observation of crystallization was implemented under isothermal condition.

3. Results

3.1. Nonisothermal and isothermal crystallization evaluated by DSC

Crystallization behaviors of iPP nucleated by different amounts of DBS are first estimated by the traditional calorimetric approach, DSC. It should be clarified that DBS can only nucleate the most common monoclinic α-modification of iPP, whereas other types of crystal forms will not be introduced. Monoclinic α-type crystal form solely existed in the as-prepared samples is experimentally proved by the cooling or heating curves, where, for each calorimetric curve, a single narrow exothermic or endothermic peak is observed. A simple estimation of the effect of DBS content dependence on the nucleation efficiency is obtained through nonisothermal cooling crystallization approach, as shown in Fig. 1. The obvious improvement of crystallization temperature, T_c, indicates that DBS indeed

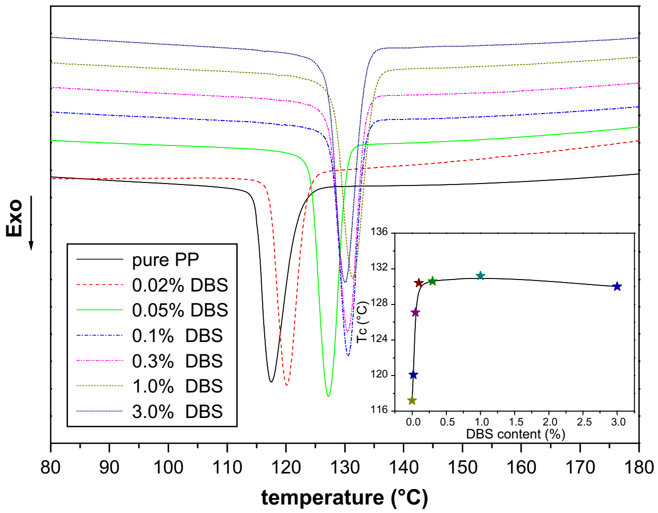


Fig. 1. Nonisothermal crystallization DSC thermograms of iPP containing different contents of DBS (inset: the crystallization temperaure, T_c, plotted as a function of DBS content).

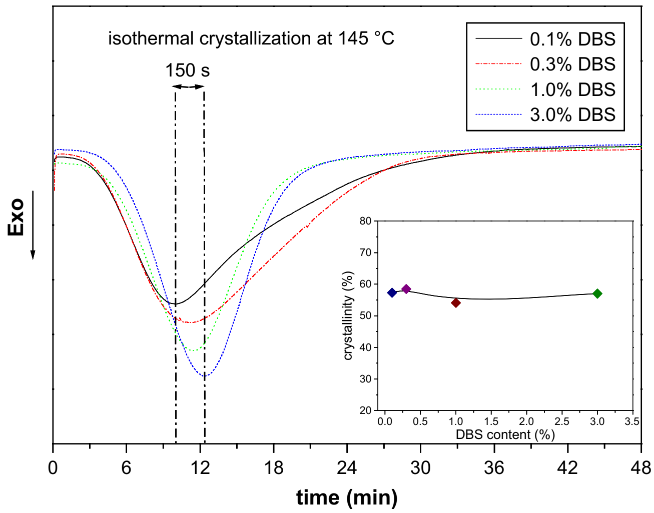


Fig. 2. Isothermal crystallization DSC thermograms of iPP containing different contents of DBS (inset: the crystallinity, X_c, plotted as a function of DBS content).

promotes the nucleation and crystallization of iPP. For a purpose of clarity, T_c is plotted as a function of DBS content, and presented in the inset of Fig. 1. When the DBS content is below 0.1%, T_c gradually increases with promotion of DBS amount, whereas, within a relatively high content range (0.1–3.0%), T_c is almost unchanged though for a precise observation T_c has a little decrease at the highest content of 3.0%. The latter phenomenon can be named as saturation of nucleation that has been often found in the case of excessive NA concentration [21,25]. The term of ‘saturation of nucleation’ means that the effect of NA amount on crystallization behavior of basal polymer is weak when the NA amount exceeds a critical value, namely NA amount dependence on crystallization kinetics of polymer is constant within a high concentration range of NA. So, in our study, the threshold NA content for appearing saturation of nucleation is roughly denoted as 0.1%.

Isothermal crystallization measurements were designated to conduct at 145 °C, at such high temperature self-nucleation of iPP would be substantially depressed, thus nucleation could be attributed to the effect of NA solely. It should be noted that, when the DBS content is below 0.1%, the low nucleation efficiency and weak thermal flux make exothermic crystallization peak to be hardly distinguished, the crystallization process doesn’t end within an examined duration of 1 h even the DBS content is 0.05%; otherwise, complete exothermic crystallization peak forms when the DBS content is $\geq$0.1%, as shown in Fig. 2. This phenomenon is in accordance with the expectation that, under a relatively high crystallization temperature, NA may play a crucial role in dominating nucleation process. Consequently, nucleation and crystallization will not fully proceed until the NA amount is adequate for saturation of nucleation. For the isothermal crystallization processes presented in Fig. 2, the first half (left side) of exothermic peak is commonly assigned to describe the nucleation through epitaxy of polymer chains onto DBS fibril surface, while the other half (right side) of peak is responsible for the crystallization growth via self-diffusion of macromolecules into crystal lattice. So the exothermic peak position (time) may be used to estimate nucleating kinetics. An appreciable delay in nucleating kinetics can be seen with increase of DBS content that the difference of exothermic peak time between 0.1% DBS and 3.0% DBS is about 150 s. This implies a negative effect of NA on polymer crystallization when the NA amount is very excessive. It should be noted that, in many cases, the slow down of nucleation rate observed via DSC after the amount of NA exceeds a threshold for nucleating saturation is not so obvious and usually can be ignored. The negative effect of nucleation may be due to inadequate mass supplication when the amount of nucleation site is extremely hugeous. A similar finding has been reported in Ref. [26] for high concentration carbon nanotubes’ nucleated polyamide crystallization. Moreover, one may note that the width of right side peak for iPP containing 1.0% and 3.0% NA is obviously broader than those containing the lower NA contents (0.1% and 0.3%), which indicates logically that a large nuclei density induces a shorter growth duration of spherulite comparing to the case that occurred upon a small nuclei density. Consequently, an interesting phenomenon for iPP crystallization upon NA amount exceeded nucleating saturation is suggested as that a relatively high NA concentration may depress the nucleating efficiency, otherwise, reduce the duration of spherulite growth (crystallization perfecting process). How can one estimate the whole crystallization behavior including nucleating and growth exactly? Rheological approach may offer other information to complete our understanding on such crystallization phenomenon.

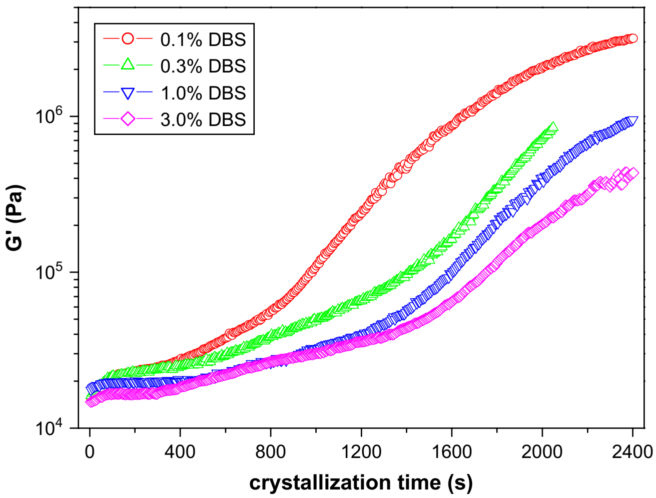
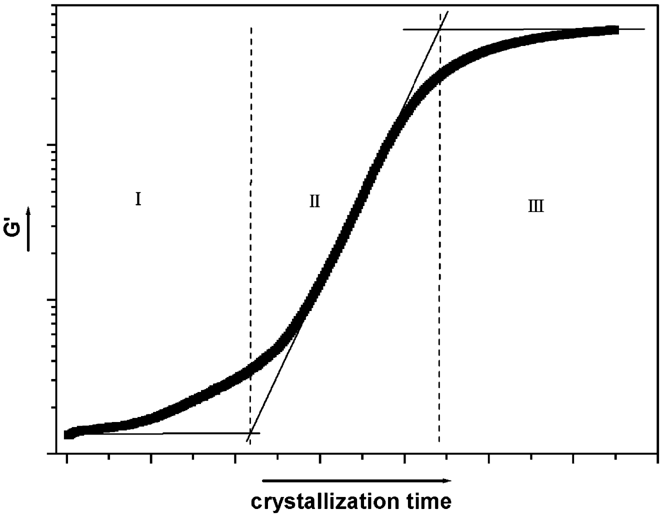


Fig. 3. Evolutions of elastic modulus as a function of crystallization time for iPP containing different contents of DBS (the temperature is 145 °C).



Scheme 2. Schematic illustration of rheologically assessed crystallization process.

3.2. *Isothermal crystallization followed by rheometry*

Sequentially, isothermal crystallization will be described, based on a viewpoint of rheological viscoelasticity. As mentioned in Section 2, two experimental protocols were adopted for monitoring rheological evolution during isothermal crystallization proceeded at 145 °C: (1) time sweep of *G*′ upon a single angular frequency (1 rad/s); (2) application of "inverse quenching" protocol to obtain viscoelastic properties within a wide range of angular frequency (0.05–100 rad/s).

For the specimens containing 0.1–3.0% DBS, evolutions of *G*′ with crystallization time, obtained via single frequency–time sweep, are plotted in Fig. 3. Similar to the isothermal DSC measurements, at low DBS content (0–0.05%), the alteration of *G*′ with time is unobvious, especially, for 0% and 0.02%, *G*′ is almost unchanged within the whole testing duration. However, for samples containing DBS content within a range for saturation of nucleating iPP, the spectrums of *G*′ development as a function of time sensitively relate to the microstructural changes during isothermal crystallization. A typical rheologically described crystallization process could be divided into three successive stages, as schematically illustrated in Scheme 2: (1) slow increment of *G*′ in the nucleation-controlled induction period; (2) abrupt increases of *G*′ in the fully proceeded growth period; (3) leave-off of *G*′ at the last stage of crystallization. It should be reminded that DBS content dependence on the crystallization behaviors is unremarkable in either nonisothermal or isothermal DSC measurements when the DBS content is within a range for saturation of nucleation. Interestingly, development of *G*′, however, strongly depends on the DBS

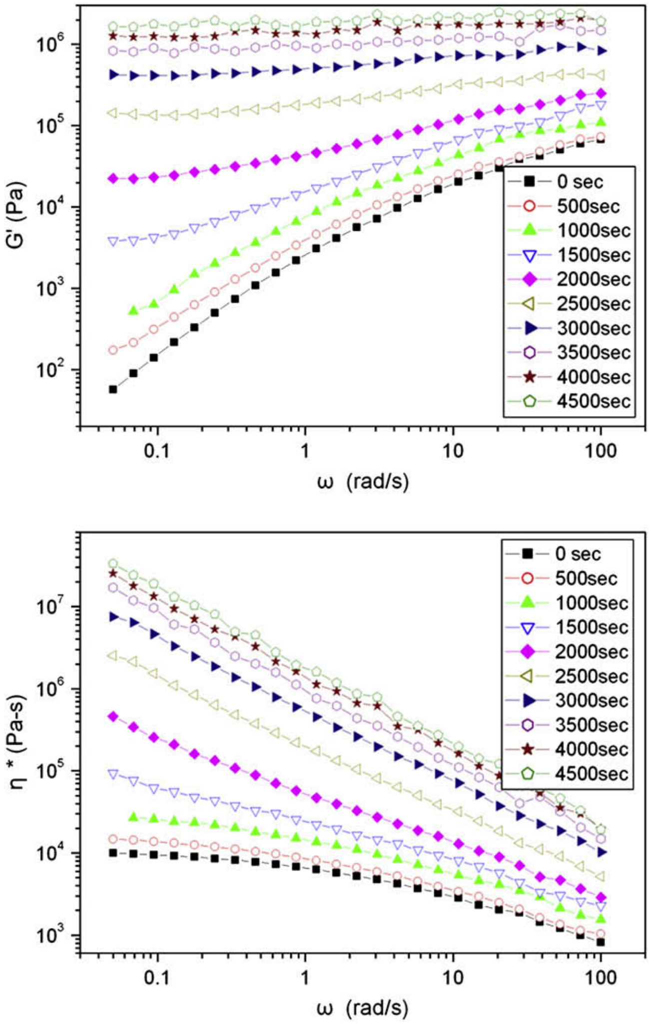


Fig. 5. Evolution of *G*′ vs. ω and η^* vs. ω spectrum as a function of crystallization time for 0.05% DBS (rheological measurements and isothermal crystallization conducted at 156 °C and 145 °C, respectively, and the indicated crystallization times represent the total annealing time at 145 °C during the successive cycles).

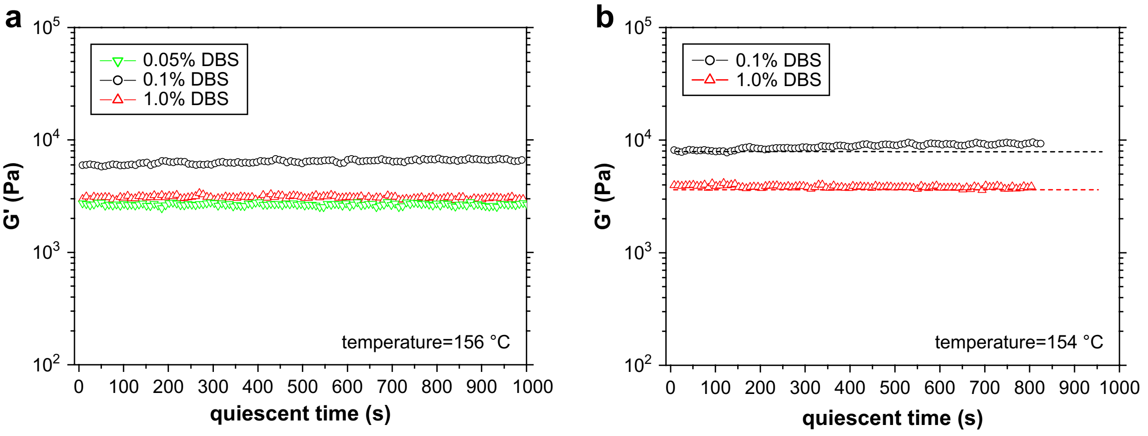


Fig. 4. Time dependence of elastic modulus upon quiescent condition at (a) 156 °C and (b) 154 °C (the dashed lines in (b) are drawn to guide the eyes).

content in the rheological measurements, indicating that rheometry has a much higher sensitivity than traditional DSC approach to estimate polymer crystallization characteristics. During the isothermal crystallization process, increment of G' is obviously depressed by the increase of DBS content. For example, the onset of the abrupt increase of G' for sample containing 0.1 wt% DBS occurs at crystallization time around 800 s, while it becomes 1400 s for sample containing 3.0 wt% DBS. The G' at the crystallization of 2400 s, on the other hand, is as high as 3×10^6 for sample containing 0.1 wt% DBS, but only 3×10^5 for sample containing 3.0 wt% DBS. Thus increasing NA amount seems to play a strongly negative influence on the rheologically described crystallization kinetics. It seems that there exists a conflict about the crystallization period between Fig. 2 and 3. As indicated in Fig. 2, crystallization stops at about 1800 s for all four samples (the thermal exchange is hard to be detected after 1800 s). Whereas, Fig. 3 shows that the G' still increases remarkably even crystallization time exceeds 1800 s. At the last stage of crystallization (after 1800 s), the spherulite growth rate is very slow and the thermal exchange becomes weak. The structural development of crystallization perfecting will last for a significantly longer time than 1800 s. Obviously, rheological technique has a high sensitivity for following the crystallization perfecting process at the last stage of crystallization. Tiny change in crystalline structure may induce significant improvement in the rheological properties. While a mechanism discussion about largely increased G' with crystalline structure evolution will be demonstrated in Section 4.2.

For single frequency–time sweep, rheological properties are available merely at a certain frequency, and the time of measurement is limited (below 2400 s), namely the appreciable crystallinity is restricted because the sensitivity of melt rheological response may decrease or the adhesive force between the sample and the testing parallel-plate becomes weak at a higher solid-phase fraction or crystallinity. Fortunately, the "inverse quenching" approach can overcome these two shortcomings. The detailed mechanism description and the reliability of "inverse quenching" protocol have been reported in the literature [12,13]. The most important one for this technique is to designate an appropriate temperature for measuring rheological properties at which the crystallization process is stopped simultaneously the formed crystallite can be maintained. Such a measurement temperature, T_{iq}, is assigned at 156 °C. The T_{iq} of 156 °C is below the T_m of α-type crystal form for 10°, and no obvious melting occurs under this T_{iq}, confirmed by PLM observation. Also the rheological property under 156 °C is constant, indicating that no microstructural transition takes place during the quiescent process, as shown in Fig. 4(a). When the

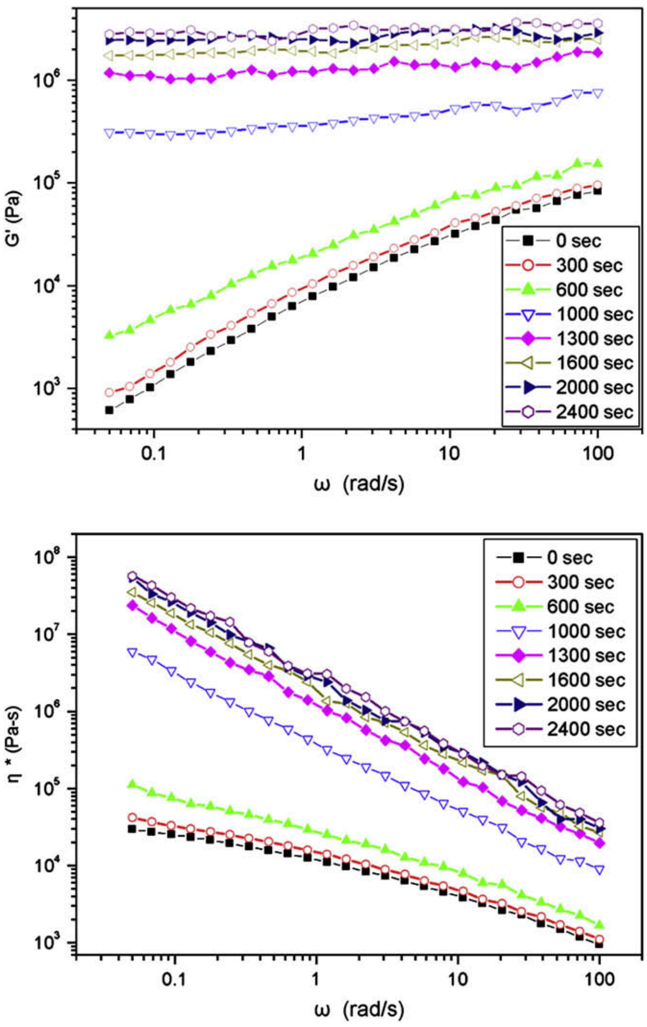


Fig. 6. Evolution of G' vs. ω and η^* vs. ω spectrum as a function of crystallization time for 0.1% DBS (rheological measurements and isothermal crystallization conducted at 156 °C and 145 °C, respectively, and the indicated crystallization times represent the total annealing time at 145 °C during the successive cycles).

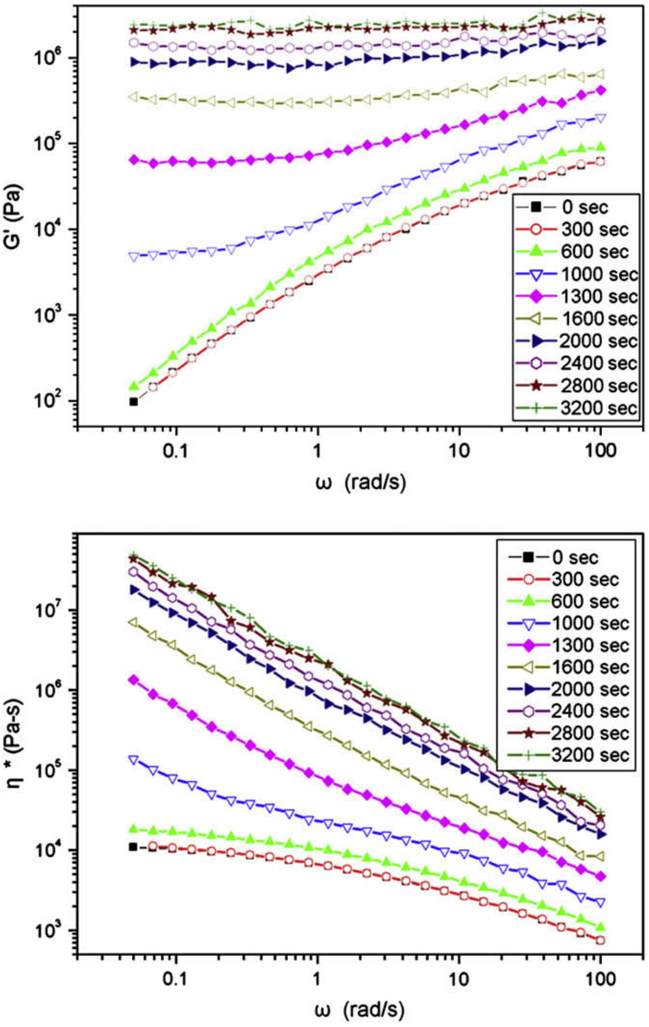


Fig. 7. Evolution of G' vs. ω and η^* vs. ω spectrum as a function of crystallization time for 1.0% DBS (rheological measurements and isothermal crystallization conducted at 156 °C and 145 °C, respectively, and the indicated crystallization times represent the total annealing time at 145 °C during the successive cycles).

temperature decreases merely to 154 °C, an appreciable alternation is observed for the sample containing 0.1% DBS, as shown in Fig. 4(b). It is valuable to note that the T_{iq} of 156 °C in our study is approximate to the T_{iq} in the study by Grizzuti and Acierno [12], which was 158 °C for estimating iPP crystallization. Three DBS contents, 0.05%, 0.1% and 1.0%, are chosen to implement inversely quenched rheological experiment, which represent before, threshold and excessive situation of nucleating saturation, respectively. In Figs. 5–7, G' vs. ω and η^* vs. ω (ω is within a range of 0.05–100 rad/s) are plotted as a function of the total crystallization time at 145 °C during successive heating–cooling cycles. These spectrums of frequency-dependent rheological properties are obtained via frequency-sweep at 156 °C after isothermal crystallization at 145 °C for a certain time. It should be emphasized that these G', η^* vs. ω curves (within a wide ω range) are useful for determining qualitatively the liquid-to-solid transition of melt feature.

With increase of crystallization time, the liquid-like rheological behaviors gradually develop to solid-like characteristics. At the initial stage of crystallization, G' is well dependent on ω within the whole frequency range, especially, in the low frequency regime, $G' \propto \omega^2$; then a nonterminal behavior appears in that a plateau of G' vs. ω generates at the low frequency regime; when the transformed fraction is high at the late crystallization stage, a well-defined solid-like behavior is found that G' is almost independent of ω within the whole frequency range. As to η^*, for the first stage, a flat of η^* vs. ω exists in the low frequency regime, which indicates the viscosity at zero shear rate; subsequently, a stress yield behavior is detectable, which is described as the rapid decrease of viscosity especially within the low frequency regime [12]; finally, within the whole frequency range, η^* is inversely proportional to ω, according to the exponential relation of $\eta^* \propto \omega^{-0.5}$. In order to quantitatively evaluate the kinetics of solidification and crystallization under different DBS contents, we would like to define a critical time of well-solidified state at which G' begins to be independent of ω within the whole frequency range. The threshold time for generation of well-solidified state is at about 1000 s for 0.1% DBS, while it is 1600 s for 1.0% DBS, indicating a faster kinetics of solidification and crystallization at 0.1% content than at 1.0% content. This result is in well accordance with the directly monitoring G' under single frequency–time sweep mode that increment of DBS content plays a negative effect on facilitating crystallization kinetics. For the case of 0.05% DBS, the DBS amount is inadequate for saturation of nucleation, in consequence the critical time of well-solidified state is slowest among these three contents, at about 2500 s. Compared to the single frequency–time sweep directly at 145 °C, the "inverse quenching" technique can obviously elongate the appreciable time of measurement, for example at 1.0% DBS content, which may be due to an improvement of liquid-like viscoelasticity by increasing the temperature from 145 °C to 156 °C while keeping the crystallinity unchanged.

3.3. Relation between rheological evolution and crystal morphology

In this section, we will correlate rheological evolution with crystal morphology changes during isothermal crystallization through association of rheometry and optical microscopy. The data

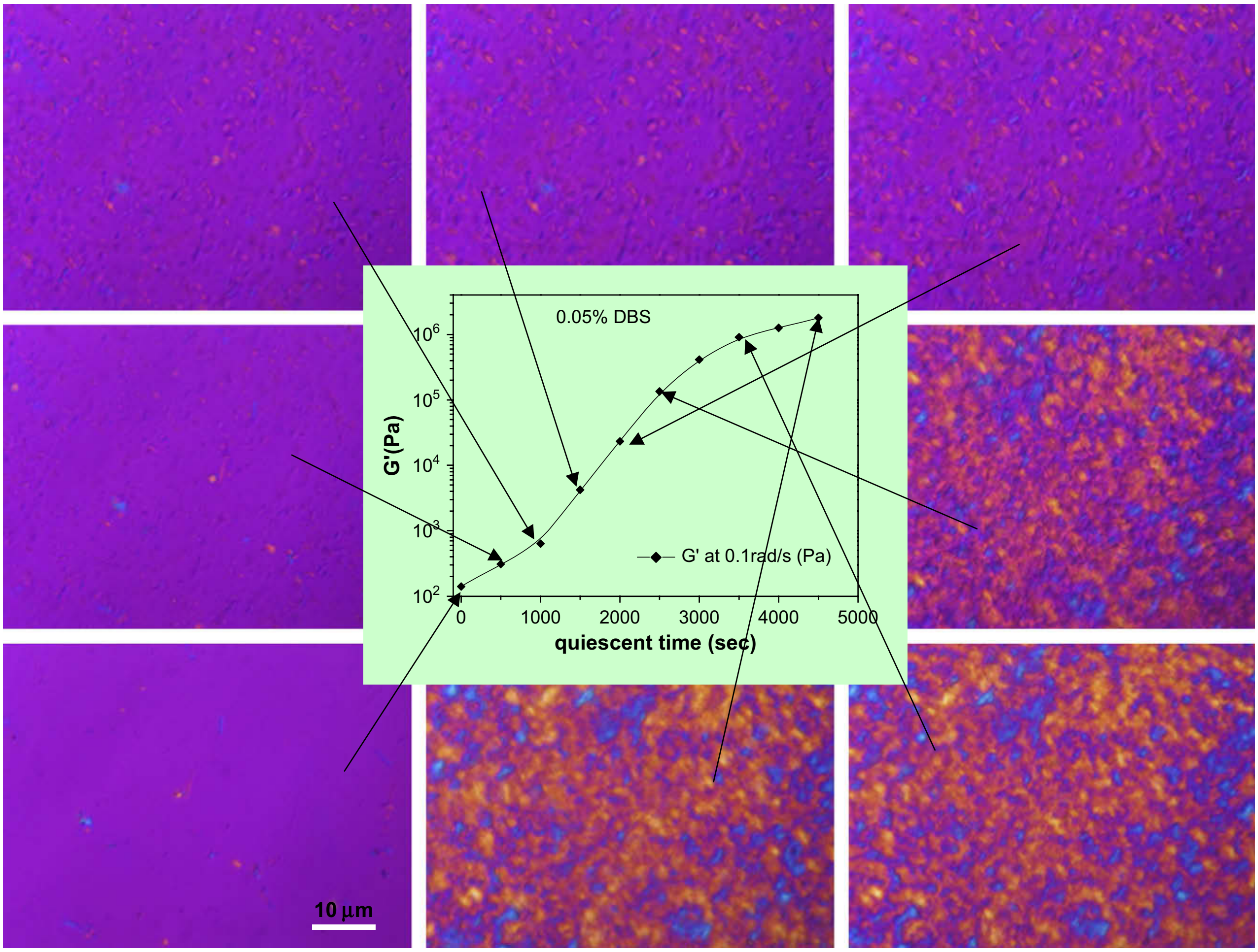


Fig. 8. Relation of elastic modulus and crystalline morphology as a function of crystallization time for 0.05% DBS.

of G' at 0.1 rad/s are picked out from the spectrums of G' vs. ω obtained through the "inverse quenching" technique, and plotted as a function of isothermal crystallization time, as shown in Figs. 8–10 selecting samples containing 0.05%, 0.1% and 1.0% DBS content as example. For a convenient purpose, crystallization morphology is observed directly at 145 °C after the expected crystallization time. A suspension-like crystallization mode is observed from the optical microscopy for samples containing of 0.05% and 0.1% DBS content: numerous individual nuclei with anisotropic profile are dispersed in the continuous melt phase, and gradually develop to crystallites until the impingement between each other. Especially, for sample containing 0.1% DBS content, many obvious threadlike primary nuclei are found at the very early stage of crystallization. It can be expected that these anisotropic primary nuclei generated from that small amount of PP chains epitaxially crystallized on the DBS fibrils or bundles. Otherwise, when the DBS content is at 1.0%, crystallization proceeding takes a colloid-like mode that the crystalline phase instantaneously occupies the whole melt region. The relations between rheological behavior and crystal morphology at two kinds of critical time, the turn point for abruptly increasing G' and the threshold time for generation of well-solidified state, are given more attention. For the DBS content of 0.05%, the trend of abruptly increasing G' is unobvious, and the turn point is constrainedly considered at 1000 s, where the crystalline fraction is still low and a majority of crystallites are separated from each other. So a percolated network of interacting crystallites does not establish at the critical time for rapid increment of G' when the NA content is low. The turn point of abruptly increasing G' is 300 s and 600 s for the 0.1% content and the 1.0% content, respectively. It is indicated that, within a content range of nucleating saturation, the induction period is shorter for the low content than for the high content. In both cases, the crystalline fraction is high. In the specimen containing 0.1% DBS, most crystallites contact with each other though the crystalline regions still act as dispersed phase in the continuous melt phase; for the specimen with 1.0% DBS, the whole observed area is changed to crystalline phase. In consequence, in these two cases, the network consisted of interacting crystallites will be established at the critical time for rapid increment of G'. At the threshold time for generation of well-solidified state, for three contents of 0.05%, 0.1% and 1.0%, the whole observed areas are all crystalline phase. The difference in morphological characteristic between three contents is ambiguous. Thus it seems that rheological measurement could provide us not only the information about crystallization kinetics, but also about the formation of crystallites' network and well-solidified state during the crystallization process. In-between, it is the perfection period, which causes the largest increase of G'.

4. Discussion

4.1. The role of formation of DBS network in the iPP crystallization

As demonstrated in the former sections of calorimetric and rheological measurements, in a range of relatively high NA content for saturation of nucleating iPP, a negative influence of NA content on facilitating iPP nucleation and crystallization has been

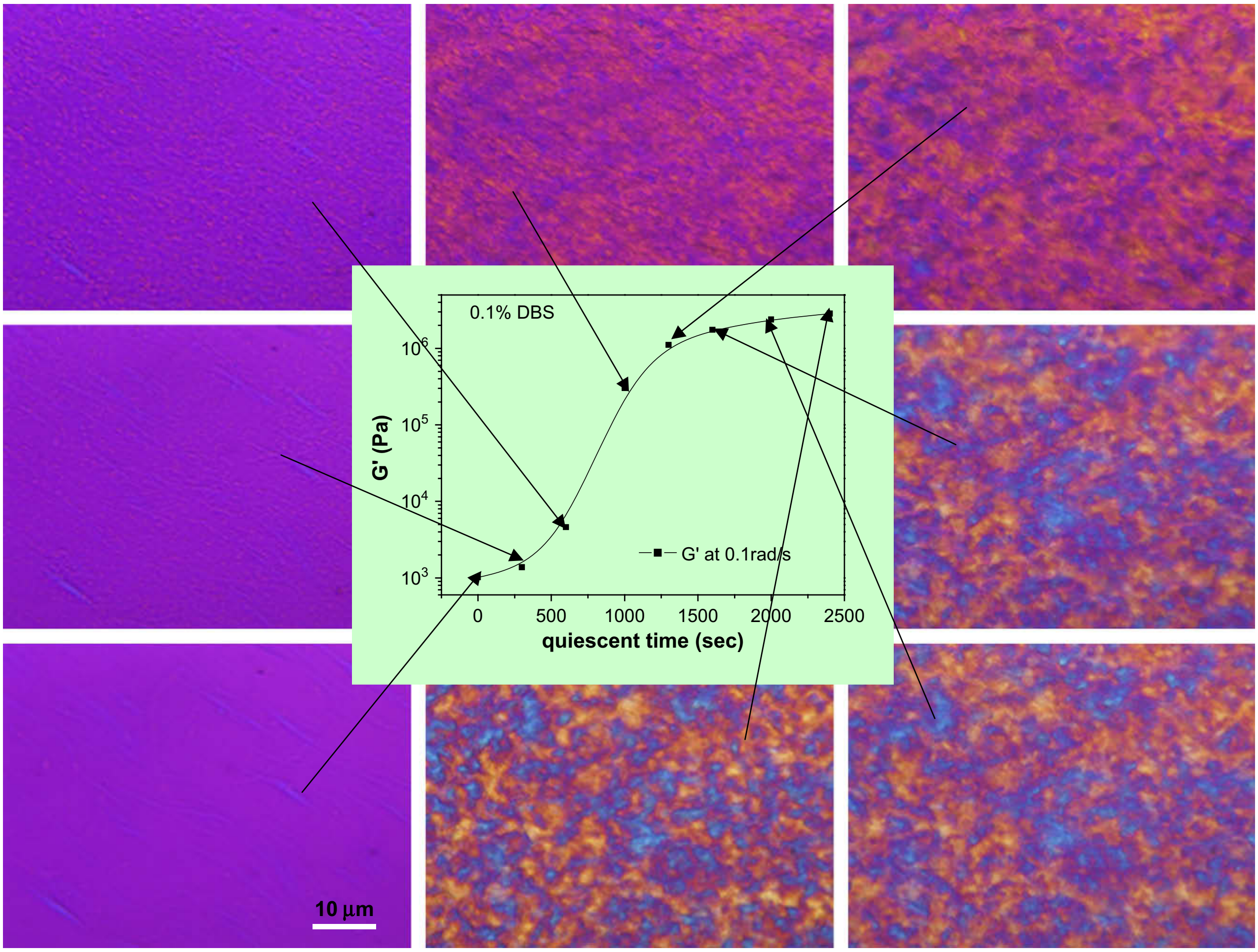


Fig. 9. Relation of elastic modulus and crystalline morphology as a function of crystallization time for 0.1% DBS.

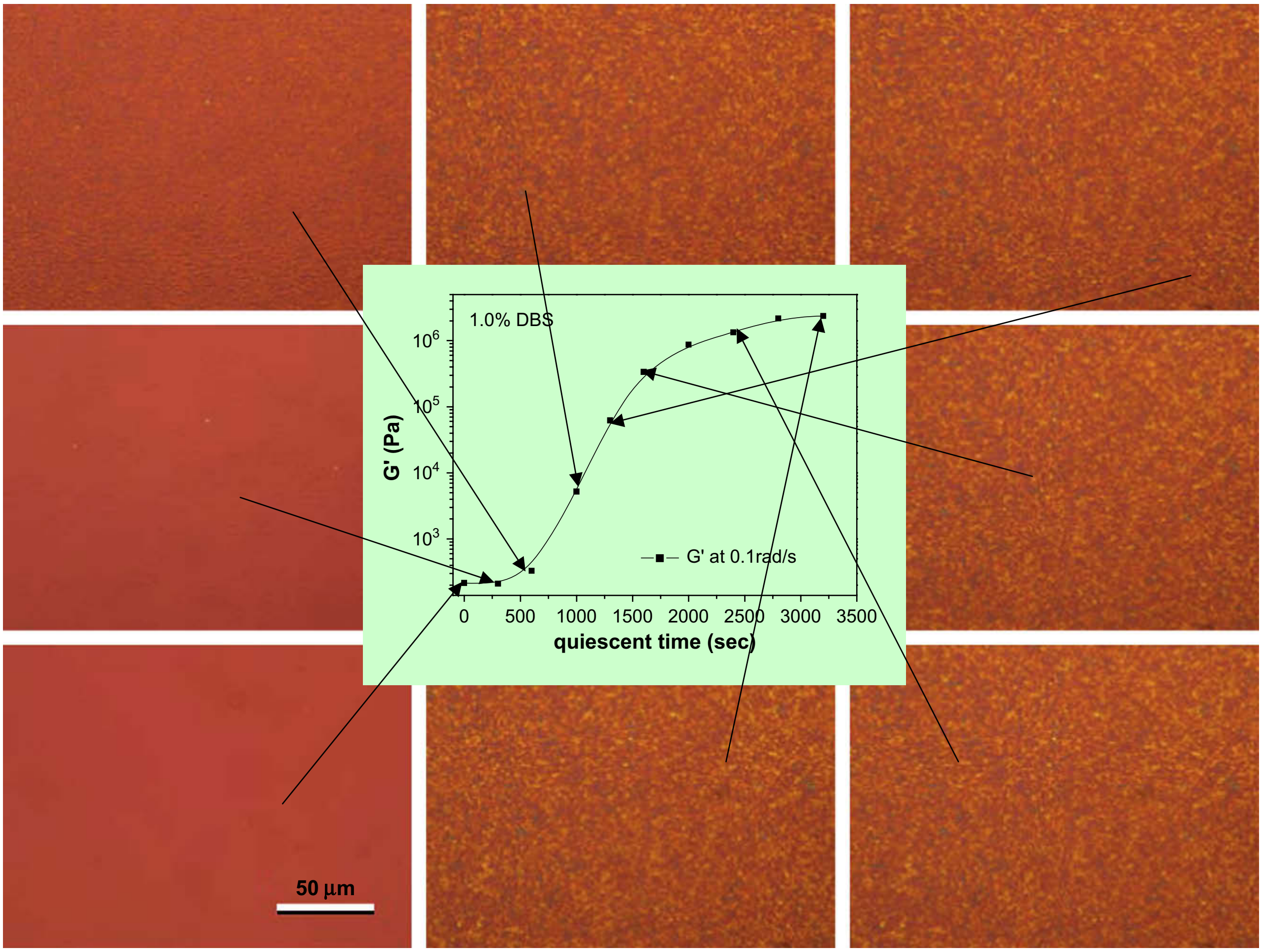


Fig. 10. Relation of elastic modulus and crystalline morphology as a function of crystallization time for 1.0% DBS.

unambiguously approved. However, compared to the calorimetric approach, the rheological technique follows the development of melt viscoelastic features during crystallization proceeding for roundly estimating the negative effect of NA amount dependence on nucleating iPP crystallization. The quantitative estimations using rheological approaches distinctly show that the crystallization or solidification kinetics is faster for the 0.1% content than for the 1.0% content; simultaneously, the increment magnitude of G' in the sample containing 0.1% DBS is dramatically larger than in the sample with higher content. Subsequently, these two interesting issues will be profoundly discussed as follows.

It has been well confirmed that the DBS fibrils may self-assemble into the network superstructure with decreasing temperature, even when the DBS content was relatively low (−0.1%) [17,19]. However, in our present study, the claimed DBS network is obviously different to the DBS network generated from assembly of cooling molten DBS. Throughout the whole investigation process, the melting temperature was lower than the melting point of DBS, implying that the DBS phase always exists in fibrillar form. Contrasting to the molten iPP matrix, the un-molten DBS fibrils are regarded as solid-like phase to buildup a framework analogous to the network structure consisted of inorganic particles with high aspect ratio. We would like to also name such framework structure composed by the un-molten DBS fibrils as network superstructure. Logically, the DBS network will be extremely useful for aiding iPP nucleation and crystallization due to the improvement of solid-like elasticity in melt and the decrease of macromolecular mobility through confined effect of this network. Otherwise, the network of DBS fibrils will not impact evidently the viscoelastic properties of iPP melt when the temperature is substantially higher than the T_m of iPP, which is shown in Fig. 11. As shown in Fig. 11, the frequency-dependent moduli, G' and G'', for various DBS contents, are almost superposed together, measuring under 190 °C. This result indicates that at a relatively high temperature the addition of DBS will not alter the microstructural characteristics of melt even though a largest amount of DBS (3%) is introduced. Evolutions of temperature-dependent rheological properties are shown in Fig. 12 for three DBS contents, 0.05%, 0.1% and 1.0%. The lowest temperature for testing is set at 156 °C, where crystallization of iPP will not take place, and thus the effect of DBS self-assembled network could be evaluated clearly. The low frequency of 0.1 rad/s is adopted because the rheological properties at a relatively low frequency will be more sensitive to microstructural changes. Obviously, the rheological properties are significantly enhanced for 0.1% DBS especially at 175 °C an abrupt increment is found, whereas the improvement of rheological properties through decreasing temperature is very limited for the contents of 0.05% and 1.0%. This phenomenon distinctly differs from the cases that the homogeneous PP/DBS melt was cooled from a temperature equal to or above the DBS melting point [17,23,24]. In those cases that both of iPP and DBS were all molten, the extra enhancement of viscoelastic properties found before appearance of iPP crystallization was positively proportional to the DBS amount. Nevertheless, since the DBS additives did not melt in our study, the phase-state transform of DBS would not take place with decreasing temperature. The enhancement of rheological properties is hypothesized as that the DBS fibrils' network aids

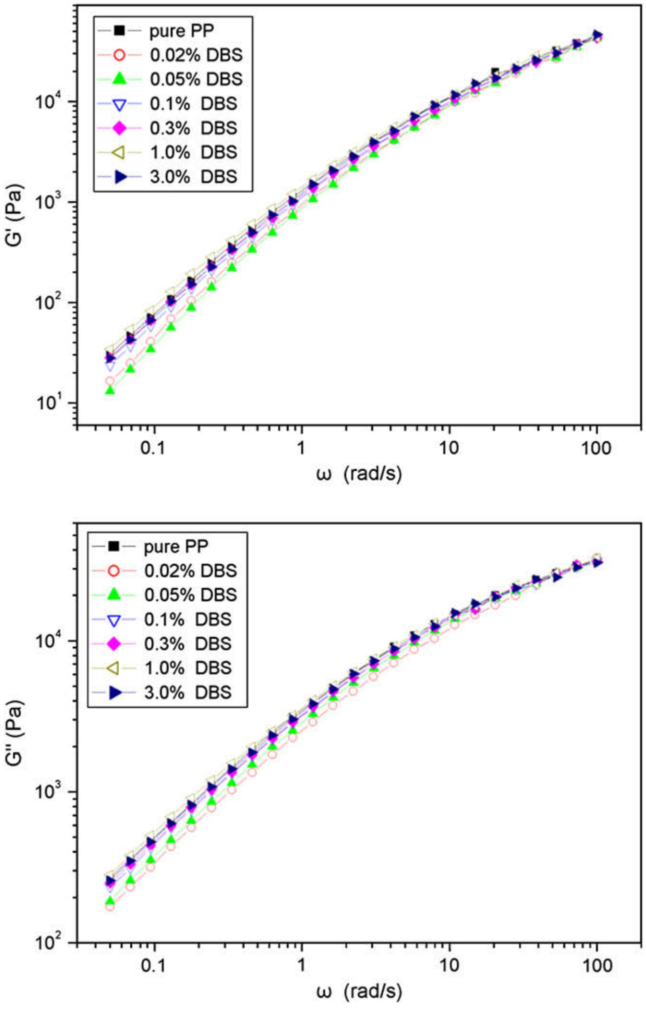


Fig. 11. Frequency dependence of viscoelastic moduli at 190 °C for iPP containing different contents of DBS.

the construction of local ordering mesophase before PP crystallization. It seems to imply that 0.1% is an optimum content for the formation of the DBS network among these three contents. Although a good explanation for this phenomenon is by far unavailable, it can be used to state the cause of NA content dependence on crystallization kinetics reasonably. In the melt with high solid-like elasticity, such as for the sample with 0.1% DBS, the mobility of macromolecular chains is low. The isothermal crystallization conducted at a relatively high temperature, 145 °C, is a nucleation-controlled process, and thus the chains with low mobility are easy to generate stable nuclei for facilitating the further crystalline growth. So the rheologically estimated kinetics of nucleation and crystallization or solidification is fast in the sample containing 0.1% DBS.

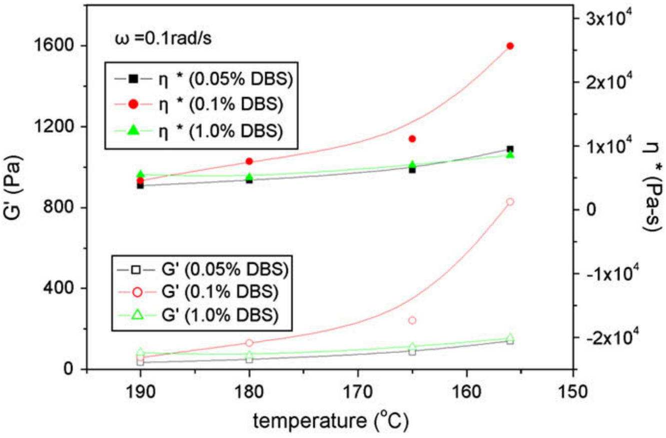


Fig. 12. Evolutions of rheological properties at 0.1 rad/s with decrease of temperature for iPP containing 0.05%, 0.1% and 1.0% DBS (the solid lines are drawn to guide the eyes).

4.2. *The negative effect of DBS content on* G′

In the single frequency–time sweep measurements shown in Fig. 3, the elevated magnitude of *G*′ is inversely proportional to DBS content, and after crystallization conducted for 2400 s the rheological property is substantially decreased with increasing DBS content. One may argue that the obvious difference for crystallinity existed between various DBS contents. As shown in Fig. 2, for the DSC estimated isothermal crystallization process, the majority of crystalline exothermic peak will form within a duration of 2400 s, and the crystallinity calculated from integrated peak area is plotted as a function of DBS content in the inset of Fig. 2. Within the DBS content range of 0.1–3.0%, the crystallinity lies in a narrow range of 55–58%. So the crystallinity difference between various DBS contents may not be the important reason for tremendous difference in elastic modulus. In some researches about rheologically estimated phase separation behaviors of molten polymer/polymer blends [27–29], with phase separation proceeding, *G*′ could increase or decrease depending on the resulted morphologies. The interfacial tension often plays a crucial role to determine evolution of *G*′ during phase separation progressing. An analogy exists between polymer crystallization and polymer/polymer phase separation. In a polymer crystallization process, the second phase, crystalline phase, generates from the amorphous melt phase. With the continuous increase of crystalline phase the gradually increased phase separation level is expected. For the sample containing 0.1% DBS, the distinct interface between crystalline phase and melt phase can form because crystallization proceeds as a suspend-like mode, where the individual crystallites dispersed in the amorphous phase are visible. Strong interfacial tension will exist at the well-defined phase interface, thus induces remarkable increment of elastic modulus. Nevertheless, the sample with 1.0% DBS crystallizes as a colloid-like mode, the crystalline/amorphous interface is ambiguous because the whole melt phase will be occupied by the crystalline phase instantaneously, and the boundary between these two phases is weak or unclear. With crystallization proceeding, the interfacial tension is promoted, but its increased magnitude is low, resulting in a limited enhancement in viscoelastic properties. Moreover, a question should be clarified that at the last stage of crystallization the original region with amorphous melt has completely transformed to the crystalline phase, even the DBS content is 0.1% the crystalline/amorphous interface is ambiguous, and thus the effect of interfacial tension on *G*′ may become weak. At this crystallization stage, rheological properties may be dominated by the system consistency or the connectivity among crystallites or lamellae [13]. Even at the last stage, iPP mass will not be totally transformed into crystal phase, and about 45% iPP mass can persist as amorphous melts, approved by the insertion of Fig. 2. Obviously, in most cases, the formed crystallites and lamellae connect with each other via the residual amorphous mass. For various DBS contents, the fractions of residual amorphous mass are almost same. So the connectivity among crystallites or lamellae will become weak if the amount of crystallite is huge, which resulted in decreased rheological properties at high DBS content though the crystallinity is almost unchanged with increase of DBS content. Since the liquid–solid phase separation occurring during the crystallization process also attributes to the improvement of measured G', it may be confused that how one can quantitatively evaluate the crystallization kinetics through the measured G'. At the current research stage, the influence extent of phase separation on the G' increase is indeed unable to be quantified. We still believe that rheological technique is meaningful to be used for the iPP/DBS system crystallization study, because: (1) whatever the liquid–solid phase separation is induced by crystallization can refer to the intrinsic features of crystallization behavior; (2) rheological approach can offer some special information about structure/morphological change what is unavailable for the conventional means used to investigate polymer crystallization; (3) crystallization kinetics can be quantified by some traditional techniques, such as DSC and XRD, while rheology may act as a good complement of these traditional means for understanding the polymer crystallization mechanism fully and profoundly. Finally, the negative influence of NA content on the rheological modulus found in our research is in accordance with or can be used to explain partially the decreased trend of polyolefin mechanical strength and modulus with increasing NA content, when the NA content reached a relatively high level [30].

5. Conclusions

In this study, rheological approaches have been used to follow the isothermal crystallization of iPP containing various contents of DBS. The relation between rheological behavior and crystalline morphology has been demonstrated in detail for two crystalline modes: suspend-like mode for the samples with low content DBS and colloid-like mode for the samples with high content DBS. For polymer crystallization study, rheological approach can be used as a good complement for traditional calorimetric technique, which offered viscoelasticity information for roundly estimating the NA content dependence on nucleating iPP crystallization, when the NA content was within a range for saturation of nucleation. Interestingly, a negative effect of DBS content on facilitating iPP crystallization has been rheologically determined. The rheologically described kinetics for nucleation and crystallization or solidification is inversely proportional to the DBS content, simultaneously, the increment magnitude of G' during crystallization becomes lower with increase of the DBS content.

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