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Effect of chain disentanglement on melt crystallization behavior of isotactic polypropylene

Xuehui Wang [a], Ruigang Liu [a], Min Wu [a], Zhigang Wang [b,*], Yong Huang [a,*]

[a] State Key Laboratory of Polymer Physics and Chemistry, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China
[b] Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China

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ABSTRACT

Isotactic polypropylene (iPP) with “disentangled” chains was generated through crystallization of iPP from its mineral oil solution. TGA test assured complete removal of mineral oil from iPP precipitates. Time sweep rheological measurements showed the modulus build-up with time indicating the formation of “disentangled” chains in iPP after the sample disentanglement treatment. The “disentangled” chains could preserve for a certain time before completely re-entangled during melting. Crystallization kinetics of iPP with “disentangled” chains was studied by using polarized optical microscope. The growth rate of spherulites in “disentangled” iPP was faster than that in the entangled one.

1. Introduction

Entanglements between macromolecular chains, being one of the basic consequences of their considerable chain lengths, play a very important role in the course of polymer processes, in which the substantial fragments of chains interpenetrate mutually. Some of the most significant examples of such processes are polymer crystallization, flow of molten polymers, and mechanical deformation of solid polymers.

Since the concept of chain reptation was founded by de Gennes [1,2], further theoretical developments were carried out by Edwards [3], Doi and Edwards [4], and Graessley [5] etc and much more research work focused on the role of chain entanglements on polymer viscosity [6–11], glass transition [12,13], and crystallization behaviors [14,15] etc. Among these studies, chain entanglements control the process of crystallization and determine the final structures of formed crystals. This is the same for all kinds of crystalline polymers including single crystals formed in dilute solutions, stacked lamellar crystals formed in melt and fiber crystals formed by drawing [16].

Several methods were reported to obtain isolated single- or pauci-chain polymer particles, for examples, through isolation of the polymer molecules from dilute solutions [17–24], controlled polymer synthesis [11,25] or molten polymer [26]. Bu et al. [14] prepared isotactic polystyrene with disentangled chains by freeze-drying method, in which the solution was rapidly frozen and the solvent was subsequently removed by sublimation, leaving isolated single- or pauci-chain collective particles. They found out that the collective particles crystallized much faster in both the cases of low and high supercoolings. Galeski et al. [26] proposed a method to obtain linear polyethylene with markedly reduced chain entanglement concentration from molten polymers, in which chain straightening in chain-extended samples, obtained under high pressure and temperature, through chain slippage in the *condis* mesophase, ensured a high level of disentanglement. They verified that disentanglement in chain-extended crystals was still maintained for a period of time after melting, which allowed one for the first time to study the role of chain disentanglement in a molten polymer on the crystallization kinetics and other properties.

In this study, iPP with “disentangled” chains is prepared through crystallization of iPP from its mineral oil solution. Rheological measurements on this iPP sample show that disentanglement can preserve for a period of time after melting. Crystallization kinetics study shows that the spherulites in iPP with “disentangled” chains grow much faster than that with entangled chains under the same supercooling conditions.

2. Experimental

2.1. Sample preparation

The isotactic polypropylene (iPP) sample was purchased from the Sigma–Aldrich Inc. Its mass-averaged molecular weight, M_w,

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* Corresponding authors.
E-mail addresses: zgwang@iccas.ac.cn (Z. Wang), yhuang@mail.ipc.ac.cn (Y. Huang).

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and molecular weight distribution, M_w/M_n, were 196,000 and 3.9, respectively, where M_n was the number-averaged molecular weight. The melt flow index of iPP was 35.0 g/10 min. The melting temperature, T_m, of iPP was about 163 °C (determined by differential scanning calorimetry, DSC, TA series Q200 at a heating rate of 10 °C/min). Mineral oil, the heavy grade, was purchased from the Sigma–Aldrich Inc. Mineral oil had the flash point higher than 110 °C and density of 0.86 g/cm^3. Reagent-grade *n*-hexane was purchased from the Beijing Chemical works and was used without further purification.

The iPP pellets were added into mineral oil at a mass concentration of 5 wt%, and the mixture was vacuumed long enough to remove air as much as possible which had resided in mineral oil. Then the mixture was put into a Julabo oil bath at 180 °C, held at this temperature for about 30 min to ensure that all of the iPP pellets were fully dissolved and a homogeneous solution was obtained. After that, oil bath was cooled down to room temperature gradually, allowing iPP to crystallize completely. At last, the mixture was poured into *n*-hexane, and the obtained iPP was precipitated, filtered, rinsed, and finally dried in vacuum. The iPP sample after this treatment (labeled hereafter as iPP$_{\text{disentangled}}$) appeared to be white powder, and was ready for further measurements. The original iPP sample was labeled hereafter as iPP$_{\text{commercial}}$.

2.2. Characterizations

Thermogravimetric analysis (Perkin–Elmer, Pyris 1 TGA) was applied to investigate whether the mineral oil was completely removed after iPP precipitation from its mineral oil solution. Gel permeation chromatography (GPC) analysis (Polymer Laboratories, PL-GPC220) was applied to measure the molecular weights and molecular weight distributions for both iPP$_{\text{disentangled}}$ and iPP$_{\text{commercial}}$. Rheological sweep measurements on iPP$_{\text{disentangled}}$ and iPP$_{\text{commercial}}$ were performed by using a Rheometer (TA Instruments Inc., Advanced Rheometer TA AR2000) to answer some crucial questions, such as possibility of iPP degradation after the oil treatment procedure, and formation of “disentangled” chains in iPP et al. Disk-shaped samples were prepared by vacuum compression molding with 1 mm in thickness and 20 mm in diameter at 180 °C. Afterward, they were melted on the rheometer at 180 °C prior to the frequency and time sweep processes, respectively. Frequency sweep measurements were performed starting from angular frequency of 500–0.01 rad/s. Time sweep measurements were performed at the fixed angular frequency of 350 rad/s to examine the modulus changes versus time. Note here for the frequency sweep measurement the sample (the “disentangled” melt) had been annealed at 180 °C for about 30 min in vacuum before the measurement, which ascertained the re-entanglement of the chains in the melt with no obvious thermal degradation effect, while for the time sweep measurement the sample (the “disentangled” melt) did not experience this vacuum annealing step because re-entanglement with time was intended to prove. Polarized optical microscopy (POM, Olympus BX51) was used to study the crystallization kinetics of iPP. The iPP specimens were placed between two cover glasses, maintained at 180 °C for a given annealing time (in the range of 0.5–30 min) on one hot stage, and then quickly moved to another hot stage with appointed temperatures for isothermal crystallization.

3. Results and discussion

The TGA curve of iPP$_{\text{disentangled}}$ is illustrated in Fig. 1, compared with those of mineral oil and iPP$_{\text{commercial}}$. The samples were heated from 25 to 650 °C at a heating rate of 20 °C/min. It is seen that mineral oil starts to decompose at about 200 °C, and nearly finishes decomposition at a temperature close to 400 °C; and iPP$_{\text{commercial}}$ starts to decompose at 350 °C, and finishes decomposition at 490 °C; whereas iPP$_{\text{disentangled}}$ starts to decompose at 330 °C and finishes decomposition at 480 °C. It can be obviously found that there is no any signal of decomposition for iPP$_{\text{disentangled}}$ at around 200 °C as mineral oil does, which indicates that mineral oil has been eliminated from iPP$_{\text{disentangled}}$ after the precipitation process by using *n*-hexane as an extracting agent. Furthermore, the curve of iPP$_{\text{disentangled}}$ fits quite well with that of iPP$_{\text{commercial}}$, indicating similar thermal degradation behaviors for these two samples.

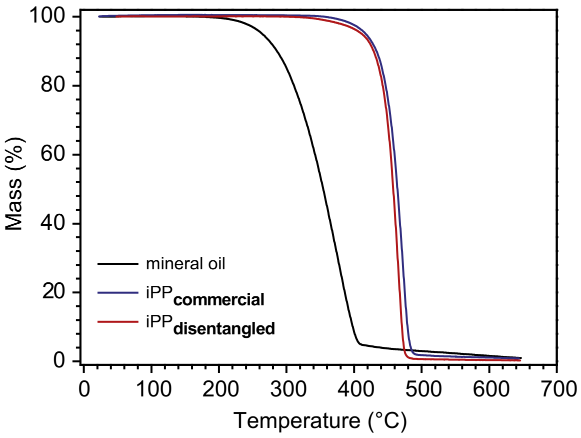

Fig. 1. TGA curves of mineral oil, iPP$_{\text{disentangled}}$ and iPP$_{\text{commercial}}$.

When iPP is thoroughly dissolved in mineral oil, its chains are expected to coil, so the entanglements of iPP chains in the solution are reduced significantly comparing with the melt state. Thus when iPP crystallizes from its mineral oil solution during cooling, it is obvious that the “disentangled” chains can be preserved. On the other hand, iPP crystallization can further reduce chain entanglements through the chain-folding crystallization process. This hypothesis can be proved by our investigations on iPP melt rheological behaviors and crystallization kinetics, which will be depicted in details in the following sections.

Frequency sweep measurements have been performed on iPP$_{\text{disentangled}}$ and iPP$_{\text{commercial}}$ to investigate whether iPP undergoes degradation during the sample disentanglement treatment. Fig. 2a shows the corresponding changes of storage modulus, G', loss modulus, G'', and viscosity, $[\eta^*]$, versus angular frequency for iPP$_{\text{disentangled}}$ and iPP$_{\text{commercial}}$ respectively. G', G'' and $[\eta^*]$ nearly superpose for iPP$_{\text{disentangled}}$ and iPP$_{\text{commercial}}$ respectively, and no obvious differences can be observed. It is considered that obvious deviations of G', G'' and $[\eta^*]$ should be observed if a large extent of degradation exists after the sample disentanglement treatment, while these kinds of deviations cannot at all be seen in Fig. 2a. The above result is well consistent with our GPC results, which indicate none of molecular weight decreases for iPP$_{\text{disentangled}}$. Our GPC results are summarized as follows: the values of M_w, M_n and M_w/M_n for iPP$_{\text{commercial}}$ are 196,000, 49,900 and 3.9, respectively, and the values of M_w, M_n and M_w/M_n for iPP$_{\text{disentangled}}$ are 199,000, 58,900 and 3.4, respectively. The results indicate that there are slight increases of M_w and M_n and slight decrease of M_w/M_n for iPP$_{\text{disentangled}}$ if compared with iPP$_{\text{commercial}}$, possibly due to loss of very short chains iPP into the mixture of mineral oil and hexane. Nevertheless, the mass-averaged molecular weight (M_w) of “disentangled” sample, an important rheology-relevant parameter, is maintained after the mineral oil treatment procedure.

In addition, the presence of the low frequency modulus upturns clearly suggests the formation of some networks in the melt state

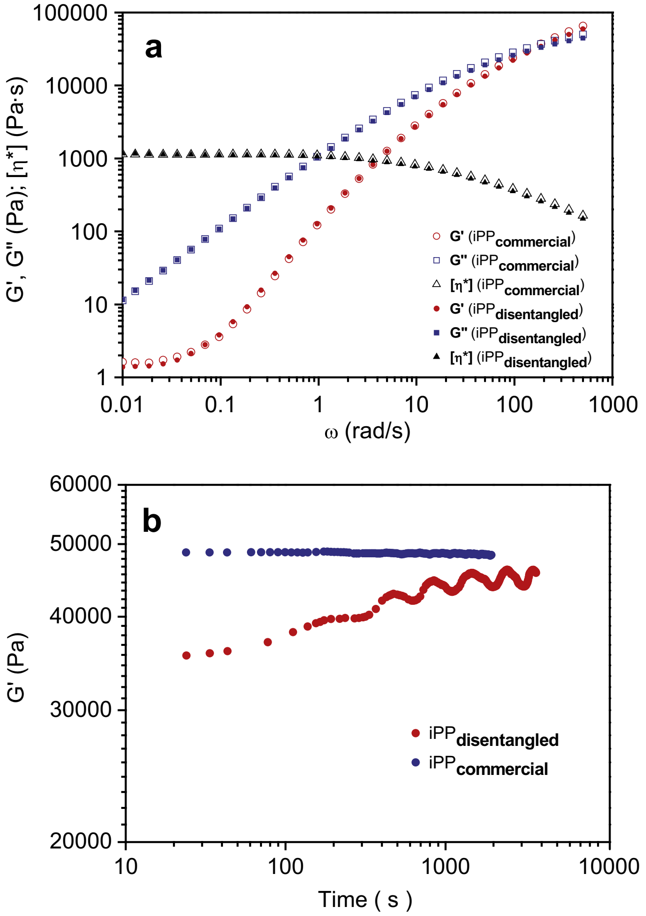

Fig. 2. Changes of storage modulus, G', loss modulus, G'', and viscosity, $[\eta^*]$, with frequency for iPP$_{\text{disentangled}}$ and iPP$_{\text{commercial}}$ (a); and build-up of storage modulus, G', with time for disentangled iPP melt compared with about constant storage modulus for entangled iPP$_{\text{commercial}}$ melt (b).

that may be initiated due to clustering of additives/catalysts in the samples. Since chain disentanglements only have large effect on G' at higher frequencies where storage modulus reaches over the plateau, so the slight upturns of G' at the low frequency region can be ignored in the aspect of disentanglement study in this work.

As reported by Rastogi et al. [11,27], the average molecular mass between entanglements, $<M_e>$, is inversely proportional to the entanglement density. This is related to the elastic modulus in the rubbery plateau region, G_N^0. Therefore, G_N^0 is an intrinsic property as it arises from the elastic response of the entangled polymer melt. Disentangled chains in crystals during rapidly heating will adopt a random coil conformation through the well-known “chain explosion” process [28], however, the chains are essentially disentangled at the beginning because entanglements formation unavoidably takes time. To further demonstrate the existence of “disentangled” chains in the iPP melt, build-up of the plateau modulus with time was examined by time sweep rheological measurements, and the results are shown in Fig. 2b. A fixed frequency of 350 rad/s in the plateau region for the iPP samples was chosen. As can be seen from Fig. 2b, at the beginning time, a lower plateau modulus is observed for iPP$_{\text{disentangled}}$. As iPP chains tend to mix by themselves and entanglements take place during melting, an increase in modulus of about 30% can be obviously observed within the 20 min period. The modulus then does not show obvious increase thereafter. The final modulus in the plateau for iPP$_{\text{disentangled}}$ is relatively comparable with that of iPP$_{\text{commercial}}$. On the contrary, for the entangled iPP$_{\text{commercial}}$ sample under the same experimental condition, no such build-up of modulus can be observed (see Fig. 2b). The obvious distinction of modulus changes with time between iPP$_{\text{disentangled}}$ and iPP$_{\text{commercial}}$ infers that the “disentangled” chains do exist in iPP$_{\text{disentangled}}$ after the sample disentanglement treatment.

It is well known that the chain mobility plays a very important role during polymer crystallization. Large-scale conformational chain rearrangements are required to shift small fragments of chains to suitable positions and incorporate them into growing crystals. Therefore, the mobility of a macromolecule with respect to its neighbors is crucial in polymer crystallization and requires a careful consideration in description of nucleation and growth of polymer crystals. In this work, the crystallization kinetics from melts of iPP$_{\text{disentangled}}$ and iPP$_{\text{commercial}}$ was studied by means of polarizing optical microscope to examine the effect of disentanglement on iPP crystallization. Fig. 3 shows the optical micrographs of spherulites in iPP$_{\text{disentangled}}$ and iPP$_{\text{commercial}}$, which grow during isothermal crystallization at 135 °C. As can be seen from Fig. 3, the amount of nuclei in iPP$_{\text{disentangled}}$ is much more than that in iPP$_{\text{commercial}}$, which is mainly due to the effect of disentanglement in iPP$_{\text{disentangled}}$. This result is consistent with the research works of Hikosaka and Yamazaki [25,29–31]. In their studies,

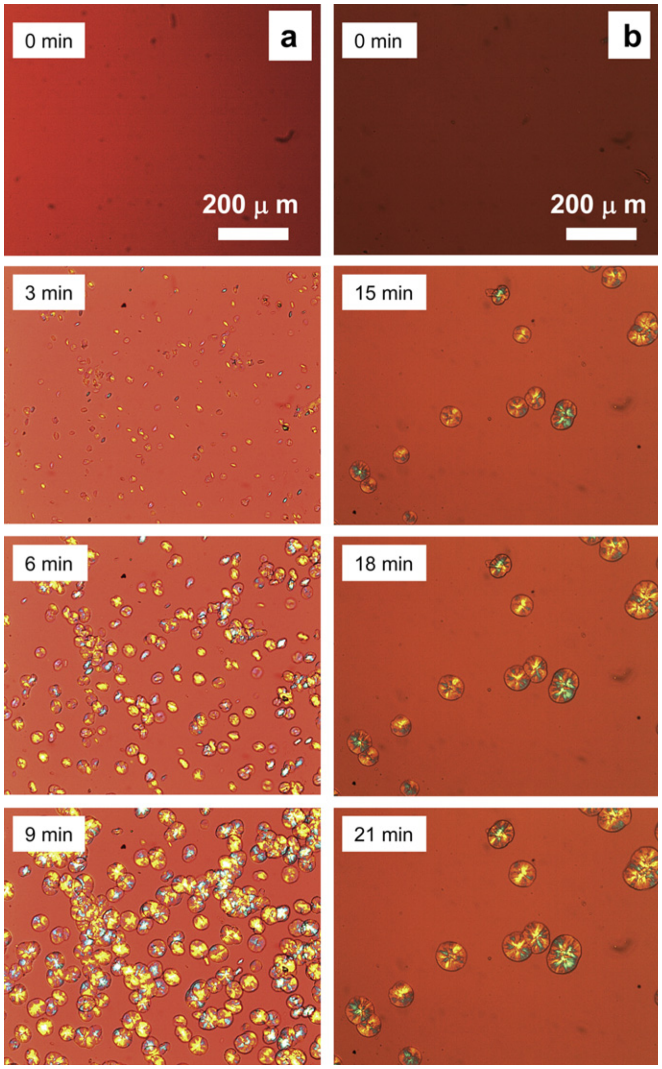

Fig. 3. Polarized optical micrographs of iPP$_{\text{disentangled}}$ and iPP$_{\text{commercial}}$ indicating the growths of spherulites during isothermal crystallization at 135 °C. Note the samples were kept in the melt state (180 °C) for 2 min before quenching to 135 °C and the time remarked in the micrographs indicates the isothermal crystallization time at 135 °C.

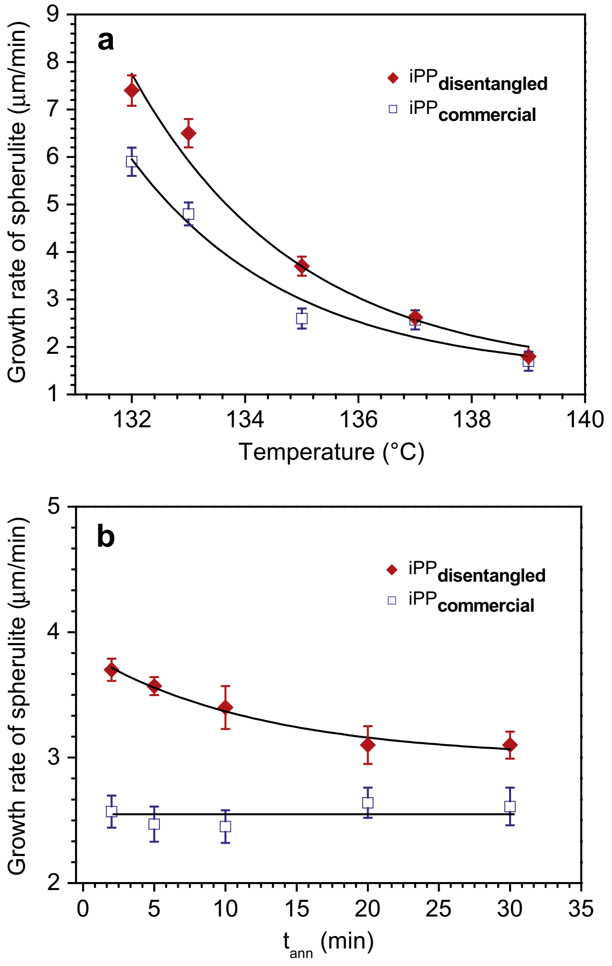

Fig. 4. Changes of growth rate of spherulites during isothermal crystallization with temperature, T_c, for $iPP_{disentangled}$ and $iPP_{commercial}$. Note the samples were kept in the melt state (at 180 °C) for 2 min before quenching to T_c (a); and changes of growth rate of spherulites at $T_c = 135$ °C with the annealing time, t_{ann}, (at 180 °C) for $iPP_{disentangled}$ and $iPP_{commercial}$ (b).

they found that the nucleation rate of polyethylene is a very sensitive detector of entanglements because the nucleation is a rearrangement process of chains to the crystalline lattice through disentanglement process, and the nucleation rate can be significantly suppressed with the increase of entanglement density.

Fig. 4a further shows the changes of growth rate of spherulites versus isothermal crystallization temperature, T_c, in the range of 132–139 °C for $iPP_{disentangled}$ and $iPP_{commercial}$. Note that iPP with M_W of 196,000 shows only one form of crystals when crystallized at above 130 °C [32], eliminating the complex issue of several crystal forms that iPP might bear. From Fig. 4a, an increase in the growth rate of spherulites for $iPP_{disentangled}$ over that of $iPP_{commercial}$ is clearly observed. As mentioned above, the lower the number of entanglement along the chain is, the higher the growth rate is. So the faster growth rates of spherulites for $iPP_{disentangled}$ are apparently a consequence of chain disentanglement, which is preserved in the melt after melting the $iPP_{disentangled}$ crystals (at 180 °C for 2 min). As the spherulite growth is sensitive to the disentanglement concentration in the melt, the growth rates of spherulites may be also applied to trace the reconstitution of entanglements in the melting process of iPP. Fig. 4b shows the growth rates of spherulites in $iPP_{disentangled}$ during isothermal crystallization at 135 °C, before which the samples were kept in the molten state (at 180 °C) for different annealing time (t_{ann}, 2–30 min). A decrease of the growth rate of spherulites for $iPP_{disentangled}$ with t_{ann} is apparently seen with the rate decreasing and reaching constant after about 20 min annealing time. The time needed for reconstitution of entanglements is in agreement with the result obtained on the basis of modulus build-up by the rheological study.

4. Conclusions

In this study, through crystallization of iPP in its mineral oil solution “disentangled” iPP could be prepared. TGA test assured none of mineral oil residue in the iPP sample after extraction and precipitation. Modulus build-up during time sweep in the rheological measurement provided a strong evidence to support the existence of “disentangled” chains. Crystallization kinetics of the “disentangled” iPP showed faster growth rates of spherulites than that of the entangled iPP. Disentanglement could be preserved for a period of time during melting, which allowed us to study the role of chain disentanglement on the crystallization behavior and eventually on other application properties of iPP.

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