Influence of Oscillatory Shear on Crystallization of Isotactic Polypropylene Studied by Dynamic Mechanical Analysis

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Introduction. Isotactic polypropylene (iPP) has several modifications, including monoclinic (α), hexagonal (β), and triclinic (γ) phases. Commercial grades of iPP usually crystallize into α-iPP while the β-form is difficult to be obtained due to its metastable nature. In consideration of high ductility of the β crystals, many researchers are interested in the topics related to β-PP. Varga et al. carefully summarized the preparation, formation mechanisms, and characterization techniques of β-iPP.[1,2]

Investigation of the influence of shear on crystallization of polymers has become important because the knowledge might be useful for tuning the morphologies and properties of the polymers during processing. Leugering and Kirsch were the pioneers in this field paying particular attention to the promotion effect of shear stress on the formation of β-modification in iPP.[3] They carried out the shear process by shifting the cover plate over the PP melt between two glass plates. Afterward, many groups conducted investigations on shear-induced β-form iPP mainly by fiber pulling.[4−7] Recently some new techniques were introduced, like rheo-SAXS (small-angle X-ray scattering) and rheo-WAXD (wide-angle X-ray diffraction),[8−10] rheooptical,[11,12] shear-controlled orientation in injection molding,[13] rheometer,[14,15] and rheo-SALS (small-angle light scattering).[16]

The nucleation mechanism of β-crystal in sheared iPP melt is generally interpreted as follows.[17−21] That is, the molecular chains are extended and oriented in the direction of shear, so that some ordered structures form and act as α-nuclei. Then, the nucleation sites for the growth of β-crystals are generated on the oriented α-crystal assemblies. Besides, the amount of β-crystals is dependent on the amount of oriented α-crystals in the sheared iPP melt.[8,9]

In this work, isothermal crystallization of iPP and the influence of oscillatory shear are investigated with dynamic mechanical analysis (DMA) measurements. Conventional DMA instruments are so designed that the melting points of crystalline polymers have to be the ceiling test temperatures. One cannot yield information about the mechanical loss and modulus variation of a polymer during melting or crystallization. The machine used in our lab is Mettler-Toledo DMA/SDTA861, which provides precise measurements of shear rigidity ranging from 10 to 10^8 N/m and is competent for the current research. In the chosen experimental method, two identical samples are clamped symmetrically between two outer fixed parts and the central moving part providing the oscillatory force. The design makes it possible to trace the real-time dynamic mechanical properties of iPP melt, which is directly related to the development of the crystallization under shear. Therefore, this communication aims to show the feasibility of the DMA measurements in studying oscillatory shear-induced crystallization of iPP.

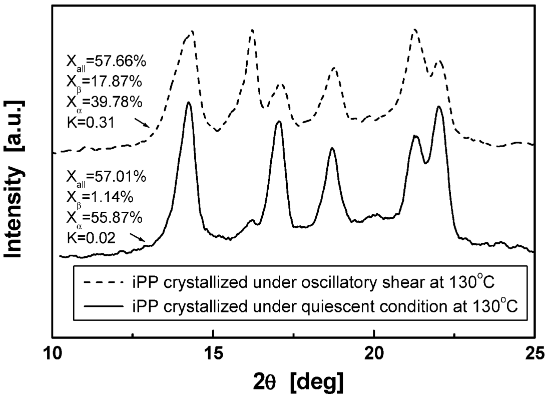

Figure 1. WAXD patterns of iPP samples crystallized under different conditions at 130 °C (X_{all}: total crystalline fraction; X_α: crystallinity of α-crystal; X_β: crystallinity of β-crystal; K: proportion of β-modification).

Results and Discussion. Details of the material and the characterization are given in the Supporting Information. The differences between the present work and previous studies of shear-induced crystallization of iPP include: (i) Here the shear is periodically offered by the DMA up and down, whereas the conventional methods provide single-directional shear. (ii) The shear can be imposed with various shear rates at the same time under multifrequency scanning mode. (iii) The samples are subjected to continuous oscillatory shear during the entire crystallization, while the other techniques usually apply shear at the early stage of crystallization.

Isothermal crystallization and DMA measurements of iPP melt were simultaneously performed at 130 °C. Afterward, the WAXD spectrum of the resultant sample was compared with that crystallized under quiescent condition in differential scanning calorimetry (DSC) apparatus (Figure 1). Clearly, five distinct peaks appear in the spectra of the two samples at $2\theta = 14.2°$, 17.0°, 18.8°, 21.4°, and 22.0°, which correspond to the (110), (040), (130), (111), and (−131) reflections,[9] respectively, and indicate the existence of the α-form crystals. In the WAXD pattern of the sample crystallized under oscillatory shear, however, there is a strong peak at 16.2° corresponding to the (300) reflection of β-crystal, which is rather weak in the spectrum of the sample crystallized under quiescent conditions. It implies that the former is rich in β-form crystals and the latter only contains a few β-crystals. The above results demonstrate that the oscillatory shear can effectively induce the

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Table 1. Structure Parameters of the Crystals Developed in iPP

							unit cell of α-iPP (Å)		
sample	shear rate (s^{-1})	h_{110} (nm)	h_{040} (nm)	h_{130} (nm)	h_{300} (nm)	$I_{(110)\alpha}/I_{(040)\alpha}$	*a*	*b*	*c*
I[a]	0.53−2.67	12.998	19.128	18.385	24.768	2.83	6.22	20.23	6.46
II[b]	0	19.610	20.797	20.064	14.600	1.26	6.54	21.07	6.51

[a] I: iPP crystallized under oscillatory shear at 130 °C. [b] II: iPP crystallized under quiescent conditions at 130 °C.

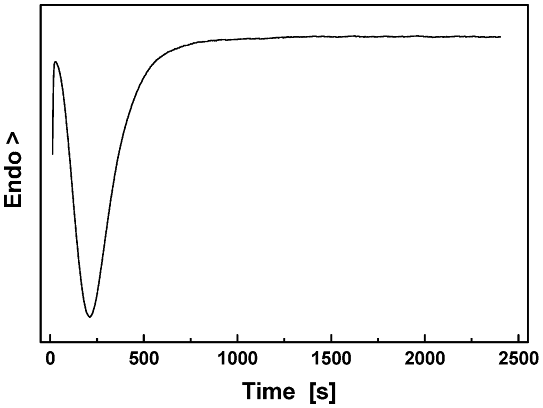

Figure 2. DSC isothermal crystallization thermogram of iPP at 130 °C.

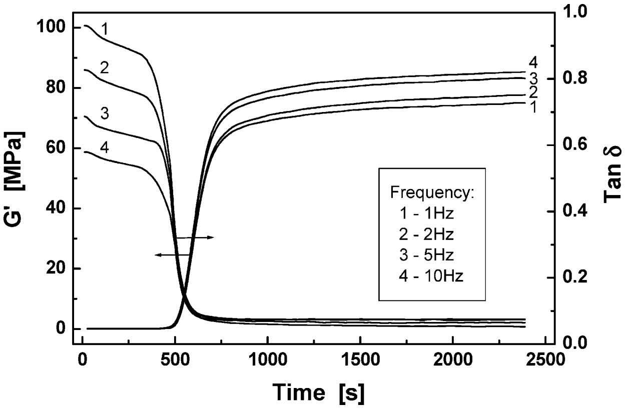

Figure 3. Time dependence of storage shear modulus, *G*′, and loss factor, tan *δ*, of iPP crystallized at 130 °C under oscillatory shear.

formation of *β*-form iPP during the isothermal crystallization. Quantitative descriptions indicate that there is no obvious difference in the total crystallinity of the two samples, confirming the aforesaid growth mechanism of *β*-crystals. Because a larger amount of oriented α-crystals formed under oscillatory shear, the *β*-crystallinity became significantly higher, but the shear did not increase the amount of the crystallizable chain segments on the whole.

Table 1 examines the crystal structures formed during shear-induced crystallization. Obviously, the crystallite dimensions of the three characteristic planes of α-phase, h_{110}, h_{040}, and h_{130}, decrease due to the oscillatory shear, while the dimension of (300) plane of the *β*-form crystal, h_{300}, increases. It means the *β*-crystals obtained under oscillatory shear are more perfect than those crystallized under quiescent conditions. Besides, it is found that the unit cell dimensions of α-crystals are sensitive to the oscillatory shear. The reduction in the *a*- and *b*-axis is more prominent than that in the *c*-axis. The results coincide with the above variation trend of the crystallite dimensions. Rybnikar[22] proposed that the $I_{(110)\alpha}/I_{(040)\alpha}$ ratio characterizes the relationship between the orientation of the *a* and *b* axes. According to his criteria, it is known that the α-crystals in the iPP crystallized under quiescent conditions is isotropic, whereas the *a*-axis of the α-crystals in the iPP crystallized under oscillatory shear is oriented in the shear direction. This again evidences the growth mechanism of *β*-crystals in more detail.

Figure 2 shows the isothermal crystallization thermogram of iPP conducted in DSC. Since the temperature profile of the experiment is the same as that set for the shear-induced crystallization in DMA, the cooling rate (14 °C/min) that simulates the fastest one of the DMA machine might not be adequately fast, leading to the absence of induction period. On the basis of these data, it is interesting to see that under the oscillatory shear the polymer melt did not start to crystallize when the temperature reached 130 °C (Figure 3). It presents a striking contrast to the case of static crystallization. Having been cooled to 130 °C in the DMA configuration, the iPP was still in the melting state and exhibited rather low viscosity and modulus. The shear modulus was slowly raised due to crystallization after the temperature had been held at 130 °C for over 270 s. This means that the induction period became much longer than that for the static crystallization.

Hsiao et al.[9] reported that the oriented α-crystals appeared immediately (<30 s) in the sheared melt of iPP after application of shear at shear rate of 10 s^{-1}, which is much faster than the case of quiescent crystallization. Subsequently (>45 s), growth of *β*-crystals was observed. Other groups[14−16] also observed that the shear imposed on iPP melt enhanced the crystallization and shortened the entire crystallization. The results imply that the inception of the crystallization in the sheared iPP melt is ahead of the quiescent crystallization, which is contrary to our findings. In fact, the opposite observations can be attributed to the different shear modes. In the works cited above, the shear is single-directional and the duration of shear is short. Under these circumstances the iPP molecules in the melt would easily be oriented, forming primary ordered structures. Immediately after cessation of the applied shear, some of the ordered structures can be stabilized and evolve into primary nuclei. In the present work, however, the oscillatory shear would simultaneously lead to orientation and disorientation of the molecules in the iPP melt because of the reciprocating movement of the vibrating clamp. The ordered structures generated at the early stage and even the crystal formation might have been disturbed.

As shown by Figure 3, the storage modulus of the iPP melt begins to increase rapidly when the sample was kept at 130 °C for over 420 s, suggesting that the crystals growth is accelerated at this time. With increasing time, it appears that the increase of the modulus reaches a plateau at about 1000 s, meaning the majority of the crystallization has been completed.

Besides modulus, the spectra of loss factor, tan *δ*, of iPP crystallized at 130 °C under oscillatory shear were also collected (Figure 3). Since the iPP sample was still in the melt state at the beginning, the entire macromolecules were movable and the internal friction among the chains has to be high. During the crystallization, the growth of crystals and the formation of ordered structures would restrain the movements of the molecular chains and segments, leading to reduction in tan δ. When the crystallization time was 1000 s, the values of tan δ are almost constants, corresponding to the completion of crystallization. Although the time dependence of tan δ coincides with that of G' on the whole, the former is more informative. Besides the drastic decrease in tan δ initiated at about 300 s, the gradual reduction of tan δ within the range 0−300 s should reflect the formation of ordered precursors at the early stage of crystallization, which can hardly be revealed by the development of storage shear modulus.

Conclusions. DMA is an effective technique for investigating shear-induced crystallization of polymers. Compared to the conventional single-directional shear, the oscillatory shear mode of DMA helps to reveal much more information concerning the crystallization in terms of mechanical performance. Development of modulus and tan δ accompanying the crystallization can be simultaneously monitored. Under continuous oscillatory shear, the β-crystal of iPP can be obviously induced during the isothermal crystallization. Furthermore, the a-axis of α-crystal is orientated to the shear direction. The size of the unit cell of α-crystal in the iPP crystallized in DMA became smaller than that obtained under quiescent conditions, while the crystallite dimension of β-crystal was increased. Unlike previous works on shear-induced crystallization of iPP, the oscillatory shear provided by DMA prolonged the induction period of iPP crystallization probably due to the disturbance of the early stage of crystallization.

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Supporting Information Available: Experimental details and DSC melting thermograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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