Influence of Shear on Crystallization Behavior of the β Phase in Isotactic Polypropylene with β-Nucleating Agent

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ABSTRACT: Wide-angle X-ray diffraction (WAXD) was used to investigate the effects of shear on the crystallization behavior of polypropylene (PP) with β-nucleating agent. The melt was subjected to shear at the shear rate from 0.5 to 60 s^{-1} for 5 s with a CSS450 shear stage. For the PP with low content of the additive, the formation mechanism of the β crystals is almost the same as that of pure isotactic polypropylene (*i*PP), viz., shear induces. Otherwise, for the samples with high content of the additive, the formation mechanism of the β form are nucleating agent induces. The results clearly show that shear restrains the formation of high β phase for the melt with additive.

Introduction

Most all of the semicrystalline polymers are subjected to intense flow fields when they are processed from melt. The microstructure formed during the process of polymer products determines the final properties. In recent years, the study of flow-induced crystallization has aroused a great interest of many scientists because it reveals the possibility of controlling and predicting the final morphologies and properties of the semicrystalline polymers in most of the transformation processes like injection molding or extrusion. Because of flow, the polymer chains are oriented in melt and can crystallize with different morphologies. Shear flow is often considered as a “weak” flow, but in polymer melts at different stages of processing, shear affects the overall crystallization kinetics[1−3] and modifies the polymer crystallization behavior and the resulting morphologies,[3−7] and even a shish-kebab structure has been observed in the deformed polymer matrix.[8,9]

Crystallization of polymers is of great technological importance due to the mechanical properties imparted, which ultimately result from the change in molecular conformation, and crystallization in semicrystalline polymers can have a dramatic impact on the mechanical properties and hence is important to final application. Isotactic polypropylene (*i*PP) is of polymorphic composition, having at least four modifications: α, β, γ, and smectic. The experimental observations suggested that the α modification is the thermodynamically stable one. So commercial polypropylene grades have crystallized mostly in α modification under the usual industrial thermal conditions. The β form is thermodynamically metastable and difficult to obtain under normal processing conditions. Therefore, β modification has been considered as laboratory curiosities. Among all the crystalline forms of isotactic polypropylene, the β crystals have many performance characteristics such as improved elongation at break and impact strength, so many research groups[1,2,4−8,10−31] have investigated and elevated the performance of the β-PP. Using special techniques can obtain the polypropylene with higher levels of β form, such as the temperature gradient method,[10,11] adding specific nucleating agent[12−27] or flow-induced crystallization,[1,2,4−8, 28−31]of which the effective and accessible method to obtain the PP with higher level of β-phase is the addition of some β-nucleating agents. Until now, only two classes of compounds have been mainly used as β-form nucleating agents: the first class is a minority of aromatic ring compounds, such as γ-quinacridone (Dye Permanent Red E3B), triphenodithiazine, and *N*,*N*′-dicyclohexylterephthalamide; the second class includes certain group IIA metal salts or their mixtures with some specific dicarboxylic acids, such as calcium salt of imido acids and compounds of calcium stearate and pimelic acid.[19] The chemical and structural features of the first class of β-nucleating agents have been investigated on occasion. The second class of the β nucleating agents system is complex, and it is difficult to determine which real nucleating agent is substantial in the system. This topic has been out of the range of our investigations.

In most of the polymer processing operations used to manufacture β-*i*PP, because of shear flow or other factors that affect the activity of the β-nucleating agent, it is difficult to obtain pure or nearly pure β-PP. In the present work, the influence of shear on the crystallization behavior of polypropylene with β-nucleating agent was studied by means of wide-angle X-ray diffraction and a polarizing optical microscope.

Experimental Section

Materials. The isotactic polypropylene homopolymer employed in this work was a commercial product of Aldrich Chemical Co., Inc. The M_w and M_n determined by gel permeation chromatography (GPC) were 339 869 and 74 492, respectively, and the *i*PP was used as received. The used β-nucleating agent was a mixture of lanthanum stearate (LaC) and $CaCO_3$.

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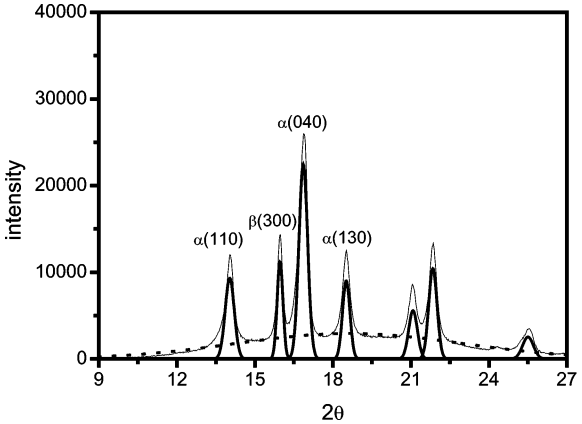

Figure 1. Peak-fit procedure of an example WAXD intensity profile for calculation of the contributions of amorphous and total crystalline phase (α phase and β phase) in the polymer melt after shear.

Sample Preparation. *i*PP and β-nucleating agent were mixed in a two-roll mill at 190 °C for 6 min and then molded into 1 mm thick sheets. The concentrations of the nucleating agent were 0.05, 0.08, 0.1, 0.3, 0.6, and 1 wt % and the samples were designated as PP1, PP2, PP3, PP4, PP5, and PP6, respectively. The pure *i*PP sample designated as PP0 was also prepared for comparison.

Shear Apparatus and Shear Method. A Linkam CSS-450 high-temperature shear stage (Linkam Scientific Instruments, Ltd., Tadworth, Surrey, U.K.) was used in this work. The stage can be designed to apply a variety of shear modes: step, steady, or oscillatory within a wide range of shear rates and strains. The mechanical design and electronics of the Linkam shear stage provided a precise control of the parameters for the shear experiment that included temperature, heating/cooling rates, and sample thickness. Recently, this apparatus has been used to study the behavior of orientation-induced crystallization of polymers in many research groups.[3,29,30,32,33]

All the samples were melted at 200 °C for 5 min to erase any thermal or mechanical history before the measurements. After the sample was melted entirely, the upper lid of the shear cell was adjusted to obtain the desired sample thickness of 40 μm; then cooled the sample down to 134 °C at a rate of -30 °C /min. As soon as the temperature reached the target value, a steady shear was applied to the melting sample for 5 s. Then the sample was kept at the fixed temperature until complete crystallization and investigated by ex situ WAXD. In situ rheo-optical experiments were performed with a Leica DMR Polarizing microscope equipped with a JVC color video camera (TK-C1381) and Linkam Optical Shearing Stage (CSS 450). Morphological changes during shear-induced crystallization were recorded by time-resolved optical measurements.

Wide-Angle X-ray Diffraction Measurements and Data Analysis. The WAXD measurements were carried out at room temperature with a Rigaku D/max 2000V PC diffractometer with curved graphite crystal filtered Cu Kα radiation source ($\lambda = 0.154$ nm) at 40 kV and 200 mA.

A typical averaged WAXD profile and the peak-fit procedure used to deconvolute the peaks with the Origin software are shown in Figure 1. In this WAXD profile, (110) at $2\theta = 14.1°$, (040) at 16.9°, (130) at 18.5° are the principal reflections of the α-crystals of *i*PP while (300) at about 16° is the principal reflection of the β-crystals, and they are considered as the marker peaks for α-crystals and β-crystals, respectively. After the amorphous background was extracted, the fitted crystal peaks and amorphous contribution peak are described by the Gaussian function. However, as shown in Figure 1, the fitted amorphous peak obtained by this procedure is always a little larger than the real amorphous peak.

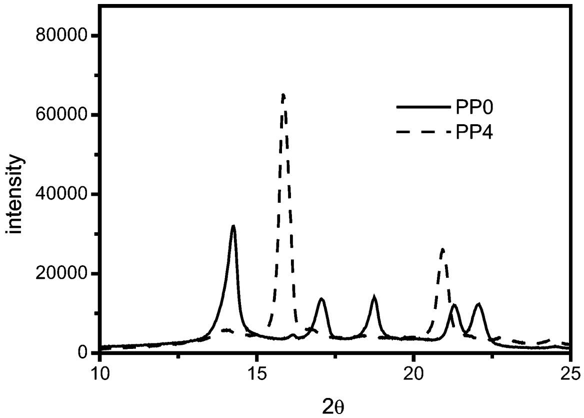

Figure 2. WAXD patterns of sample PP0 (neat *i*PP) and PP4 (with 0.3% additives) crystallize at 134 °C under quiescent condition.

The procedure we adopted to calculate the total crystalline fraction is the one that Hsiao et al described.[30] However, we modified the method to calculate the contribution from each crystalline phase (α and β-phase). This was given by

$$X_{\mathrm{all}} = 1 - \frac{A_{\mathrm{amorphous}}}{\sum A_{\mathrm{crystallization}} + A_{\mathrm{amorphous}}} \tag{1}$$

$$X_{\beta} = \frac{A_{\beta(300)}}{A_{\alpha(110)} + A_{\alpha(040)} + A_{\alpha(130)} + A_{\beta(300)}} \times X_{\mathrm{all}} \tag{2}$$

$A_{\beta(300)}$ is the area of the (300) reflection peak; $A_{\alpha(110)}$, $A_{\alpha(040)}$, and $A_{\alpha(130)}$ are the areas of the (110), (040), (130) reflection peaks, respectively; $A_{\mathrm{amorphous}}$ is the area of the amorphous peak.

Results and Discussion

Effect of the Nucleating Agent Concentration. Figure 2 shows the WAXD patterns of PP0 and PP4 crystallized at 134 °C under quiescent conditions. The WAXD pattern of PP0 shows five obvious peaks at 2θ of approximate values 14.2, 17.0, 18.7, 21.3, and 22.0°, respectively, which correspond to the (110), (040), (130), (131), and (111) reflections. These characteristic diffraction angles indicate that α-monoclinic crystals exist in PP0. In this WAXD diffraction pattern, there is a very tiny peak at about 16° which corresponds to the (300) reflection of β-hexagonal crystals, indicating few β-form crystals exist in PP0. In comparison with that of PP0, an obvious difference can be seen in the pattern of PP4. In this pattern, the (300) reflection of β-form crystals is clearly seen at 2θ of about 16°, and the intensity of the β peak is even greater than that any of the α-characteristic peaks. This assuredly indicates the presence of β-form crystals in the samples containing the β-nucleating agent. Figure 3 shows the crystallinity of β-form crystals in the samples containing different concentrations of the β-nucleating agent crystallized at 134 °C under static state. From Figure 3, it can be seen that there is little nucleating efficiency if the addictive is less than 0.05%, but the β-form crystallinity of the samples containing β-nucleating agent increases rapidly until the agent content is more than 0.1% and then slightly increases with continuously higher agent content. The higher the nucleating agent concentration is, the higher the β-form crystallinity becomes. This result clearly indicates that the additives used in this work have a prominent β-nucleating effect on *i*PP.

Effect of Shear. The variation of the shear rate affects the molecular chain orientation in the polymer melt, which in turn will influence the nature (habit and orientation) as well as the kinetic and thermodynamic

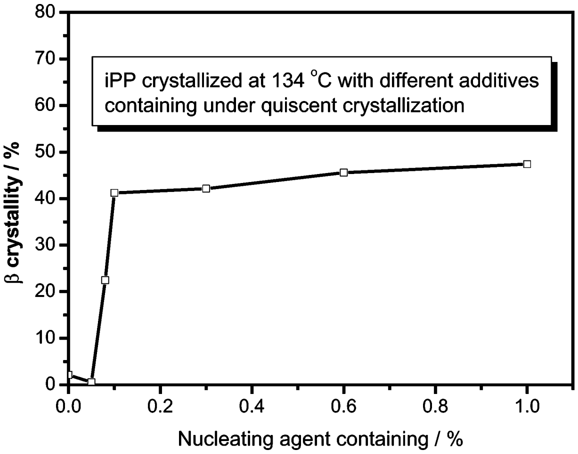

Figure 3. β-Form crystallinity of samples with different additives content at 134 °C at quiescent crystallization.

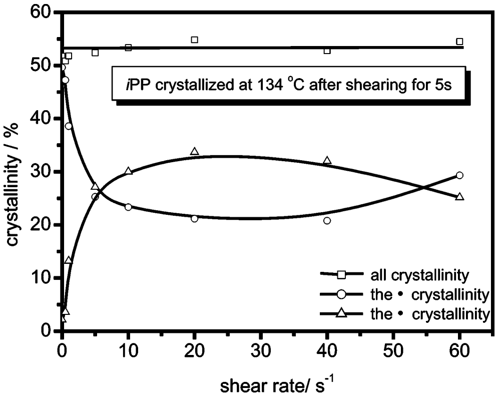

Figure 4. Shear rate dependence of crystallinity in the pure *i*PP.

behaviors. Shear was imposed on the samples having different nucleating agent concentration at 134 °C with various shear rates. Figure 4 shows the development of the crystalline (both α and β forms) phase in the *i*PP melt after shear as a function of shear rate. The percentage of the total crystalline phase (the sum of α and β crystals) in the polymer melt is also shown in Figure 4. The total crystallinity of *i*PP has not changed obviously with different shear rates. It is seen that the crystallinity of β crystals is particularly sensitive at low shear rates. With increasing shear rate, the crystallinity of β-form crystals increases rapidly and reaches a maximum when the shear rate is 20 s^{-1}. It is interesting to note that the crystallinity of the β form reduces slightly with continuously increasing shear rate. The crystallinity of the α form changes contrarily.

Figure 5 shows the polarized microscope morphology of the samples during crystallization process under the same conditions in Figure 4. It is noted that when shear rate is 0.5 s^{-1}, the number and the morphology of the crystals change little compared to those form under the quiescent crystallization. From Figure 4, we also see that the β-form crystallinity at shear rate of 0.5 s^{-1} is a little higher than that under quiescent condition. The reason for this result is that the effect of shear is faint, thus the number of oriented αnuclei is not high enough to induce many β crystals. When shear rate is 1 s^{-1}, the crystal density is much higher than that of the crystals form under static crystallization and the β crystallinity increases. This shows that the orient degree of α nuclei is higher than that formed under static crystallization. When the polymer is exposed to shear, the shear stress on the surface of the sample is much larger than that in the center. At a low shear rate, the effect of shear on the samples is only to act on the surface; therefore, the α-row nuclei first emerge only on the polymer surface and they could induce β crystals such as the results obtained by Hsiao.[30] Figure 5 shows that the density of α-row nuclei increases rapidly when the shear rate reaches 5 s^{-1}. However, when the shear rate exceeds 20 s^{-1}, with the strong shear effect, the observed α-row nuclei also form in the internal of the samples and increase with shear rate. Under this condition, the density of the α-row nuclei on the sample surface is too high and the growth rate of these nuclei is too fast, the crystals impact so quickly that the growth of the induced β crystals are restrained. Therefore, when the shear rate exceeds 20 s^{-1}, the crystallinity of β crystals decreases slightly with increased shear rate and the change trend of the α crystals is converse. This result is different with Hsiaos'.[29,30] Hsiao et al. found that the amount of β phase increased with shear rate and reached a plateau value above the shear rate of 60 s^{-1} because the amount of β phase was related to the amount of the oriented α nuclei. They explained it by critical orientation molecular weight (M^*). Under the imposed shear flow, only polymer molecules having a molecular weight above M^* can form oriented structures. The critical orientation molecular weight is a very sensitive quantity at low shear rate and reaches plateau above a shear rate of 60 s^{-1}.

Table 1. Shear Rate Dependence of β Crystallinity in the PP with Different Nucleating Agent Concentrations

shear rate (s^{-1})	β-crystallinity (%)			
	PP0	PP1	PP3	PP4
0	2.14	0.54	41.21	42.11
0.5	3.59	13.14	37.96	37.38
1	13.21	11.11	37.48	38.24
5	27.13	10.25	36.89	18.29
10	30.01	12.21	32.07	11.43
20	33.68	22.72	24.84	9.34
40	32.01	20.81	25.12	11.01
60	25.18	18.37	12.89	1.96

For high supercooled melt, the crystallization of *i*PP is controlled by its growth process,[34] but the formation mechanism of the nuclei for the shear induced is different from that for nucleating agent induced nucleating. Table 1 shows the β-form crystallinity of the PP with different nucleating agent concentrations and shear rates. The β form crystallinity of PP1 changes like that of PP0; viz., the crystallinity first increases with the shear rate and then decreases slightly when shear rate exceeds 20 s^{-1}. It is considered that in PP1 only few of the β crystals are induced by additives and the formation mechanism of most of the β crystals is the same as that of PP0 which is the pure *i*PP without nucleating agent, viz., shear-induced β -crystals. It is observed that the β-crystal crystallinity of PP1 is lower than that of PP0. We think that the dispersed additives in PP1 melt restrained the formation of the α-row nuclei after shear. So the amount of the oriented α crystals is reduced and the quantity of the induced β crystals is low. Table 2 shows the development of the total crystalline phase and the α phase of PP0 and PP1. The total crystallinity of PP0 is higher than that of PP1. In PP crystallization, the oriented α nuclei induce β crystals first, because of the higher growth rate of β crystals than that of the α crystals at 134 °C, the induced β crystals restrained the growth of the oriented α nuclei. When the shear rate is below 1 s^{-1}, we know that the

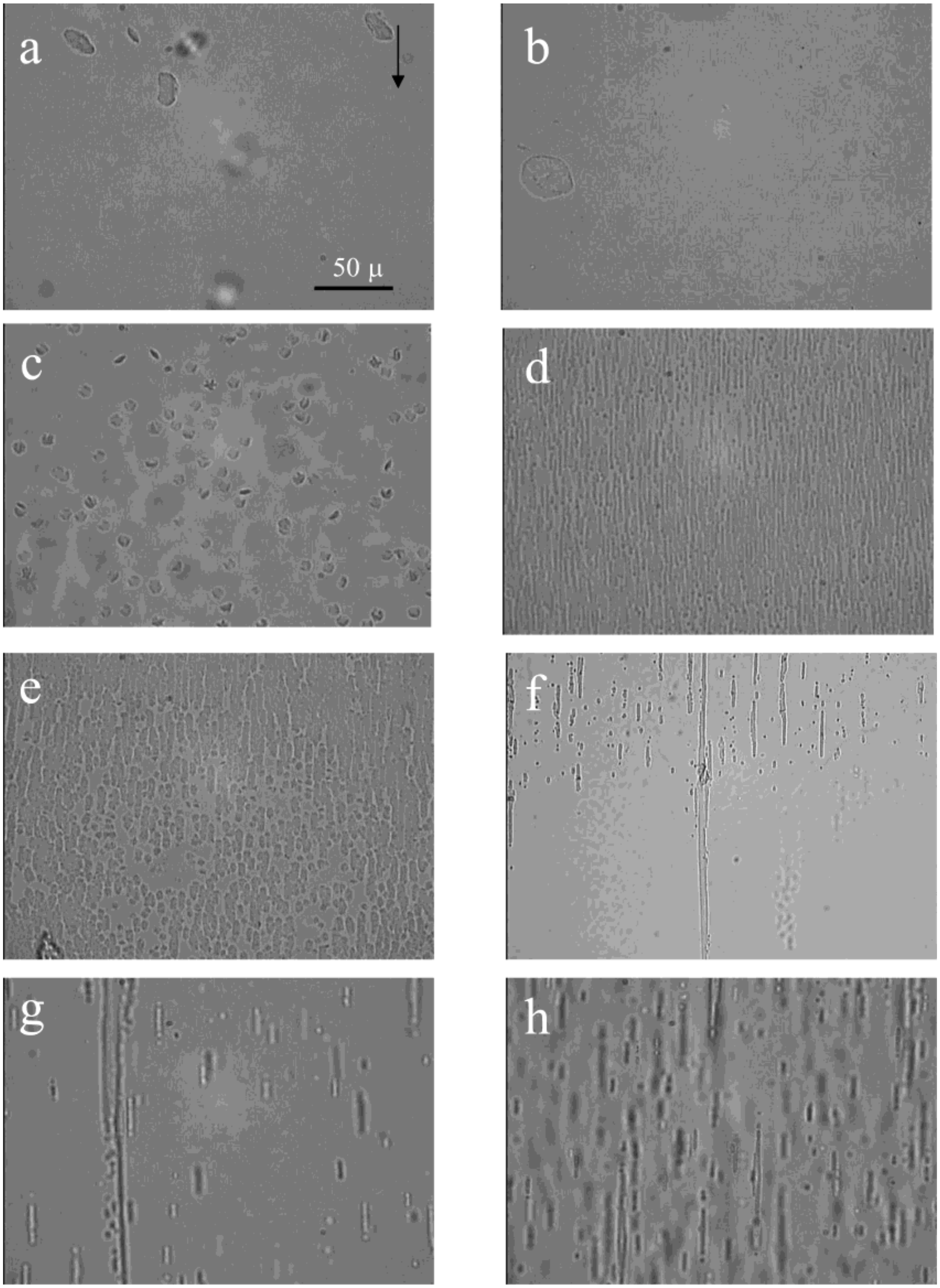

Figure 5. Polarizing photos of the pure *i*PP crystallized after shear at 134 °C. Shear rate is as follows (s^{-1}): (a) 0; (b) 0.5; (c) 1; (d) 5; (e) 10; (f) 20; (g) 40; (h) 60.

orientation degree of α nuclei is low. As shown in Table 2, the α crystallinity of PP0 is higher than that of PP1. When the shear rate increases, the density of α row nuclei increases. The α-phase crystallinity of PP1 is higher than that of PP0 when the shear rate reaches 5 s^{-1}. This indicates that the oriented α crystals of PP1 is fewer because of the dispersed additives in the polymer melt. Some of the dispersed additives induce the β crystals, but the content of the additive in PP1 is much lower than those in PP3 and PP4, and the β crystals content induced by nucleating agent in PP1 is much lower. After the application of shear, some polymer chains orient along the flow direction and then form the oriented α nuclei. The oriented α nuclei are the crucial factor to induce β crystals after shear. In PP1 the dispersed additives may disturb the formation of the α-row nuclei that causes the oriented α nuclei in PP1 to be fewer than that in PP0. So the induced β crystals obtained by α-row nuclei in PP1 are fewer too. The growth rate of β crystals is faster than that of α crystals at 134 °C; therefore, these induced β crystals restrain the growth of α crystals. In PP0, the oriented α crystals are larger, the induced β crystals are also larger, and the restrained degree of the growth of α crystals is much

Table 2. Total Crystalline Phase and α-Crystalline Phase Developed in PP0 and PP1 with Shear Rate from 0.5 to 60 s^{-1} for 5s

shear rate (s^{-1})	all crystallinity of PP0 (%)	all crystallinity of PP1 (%)	α-crystallinity of PP0 (%)	α-crystallinity of PP1 (%)
0	51.76	41.75	49.62	41.21
0.5	50.86	42.38	47.27	29.24
1	51.8	42.53	38.59	31.42
5	52.4	41.72	25.27	31.47
10	53.35	40.74	23.34	28.53
20	54.84	43.35	21.16	20.63
40	52.79	40.48	20.78	19.67
60	54.51	45.78	29.33	27.41

larger than that in PP1. So α-crystal crystallinity in PP0 is lower than that in PP1 at these shear rates. When the shear rate exceeds 20 s^{-1}, the α crystallinity of PP0 is close to that of PP1. The results of Table 2 confirm that the growth mechanism of β crystals in PP1 is almost the same as that in PP0. The existence of the additives in PP1 restrained the formation of the shear-induced β crystals.

The change in the β crystallinities for PP3 and PP4 in Table 1 shows the same trend, and they are different from those of PP0 and PP1. In the samples having the high content of β-nucleating agent, the formation mechanism of β crystals is nucleating-agent-induced. For the samples with high nucleating agent concentration under quiescent condition, the higher the content of β-nucleating agent added, the larger the proportion of the β crystals formed. After shear, the β-phase crystallinity decreased with the increasing shear rate. It was constrained to form oriented α-row nuclei after shear because of the high concentration of β-nucleating agent dispersed in the *i*PP. The nucleating agent supplied the nuclei surface to molecule chains to form the β nuclei, so the formation mechanism of β nuclei with high concentration additives is different from that induced by shear. However, shear may greatly accelerate the α-nucleating and crystal growth rate. The crystallinity of the α form increases with shear rate because the number of the active α nuclei which were induced by shear increases rapidly. α crystals restrain the growth of β crystals, and the crystallinity of β crystals decreases rapidly with the increased shear rate. This shows that the imposed shear restrains the growth of β crystals. Although the change trend is different among the samples with low and high contents of agent, it is clear that shear restrains the formation of high β crystallinity of PP with nucleating agent. Varga[21] also found that sheets in pure β-PP were formed at low takeoff rates, and the high shear rate restrained the formation of pure β-PP.

To ensure the shear effects on the samples with the additives and the nucleation function of the additives after shear, we held the samples of PP4 which completely crystallized after shear at 200 °C for 5 min to reheat to erase the history of the first crystallization and then cooled them to 134 °C at −30 °C/min to crystallize them for the second time under quiescent conditions. Figure 6 shows that the β-form crystallinity of the second crystallization has not changed compared to the crystallinity of the original isothermal crystallization sample, which crystallized under static conditions. This result indicates that the nucleating property of the additives has not changed after shear. So we can determine that the reason for the decreased β crystallinity is related to the shear; viz., shear has a negative impact on the production of the β form of the samples containing β-nucleating agent.

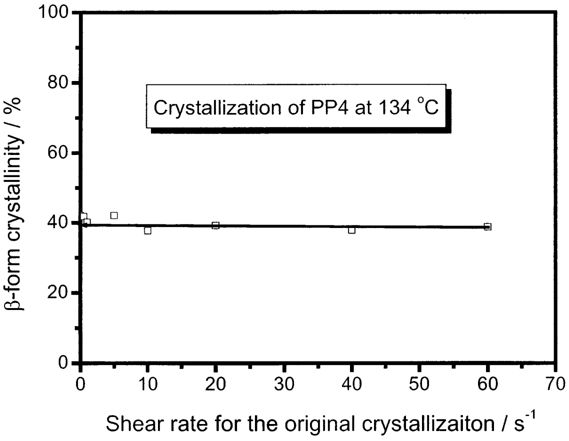

Figure 6. β phase crystallinity of sheared PP4 after heating to melt state.

Conclusions

In this work, we investigated a series of *i*PP samples containing a β-nucleating agent, and WAXD was used to study the shear-induced crystallization behavior of these samples. Our major conclusions can be summarized as follows:

1. The β-phase crystallinity of PP0 and PP1 increases rapidly until the shear rate reaches 20 s^{-1} and then decreases slightly with the shear rate increasing continuously. The formation mechanism of β crystals is shear-induced crystallization. The amount of β crystals is related to the amount of oriented α crystals formed at different shear rates. The reason that the β-phase crystallinity of PP1 is lower than that of PP0 is that the dispersed additives restrains the formation of oriented α nuclei and then causes the induced β-phase crystallinity to decrease.

2. With the application of shear, the samples of PP3 and PP4 (higher contents of additives than that of PP1) show that the β-phase crystallinity decreases compared to that of the static crystallization. The higher the shear rate is, the lower the β-phase crystallinity is. The reason for this result is that the shear accelerates the nucleation and the growth of the induced α crystals, the nucleating mechanism of which is different from the β crystals, where the nucleating agent lies on the nuclei surface, and this acceleration may restrain the growth of the β phase. So the β phase crystallinity is related to the shear rate. The high shear rate prevents the formation of a high proportion of β-PP.

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