Nonisothermal Crystallization Behaviors of Structure-Modified Polyamides (Nylon 6s)

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ABSTRACT: The morphological development and thermal properties of different polyamides with long-chain branches without forming a network structure were characterized by differential scanning calorimetry, polarized optical microscopy, and nonisothermal crystallization kinetics. The crystallization characteristics were analyzed using the nonisothermal kinetic equation proposed by Seo. Polarized optical microscopy and the Avrami exponent show the effect of the structural changes on the molecular ordering during the crystallization and early morphological development. The Avrami exponent, n, determined from the analysis of the nonisothermal crystallization kinetics, indicates a reduced heterogeneous nucleation for the modified polyamides. Structural changes (branching) of the polyamides impede crystallization, as indicated by the shift of the crystallization peaks to lower temperatures.

1. INTRODUCTION

Nylon is a condensation polymer with amide bonds in the backbone which consists of several different types of monomers in combination with one another. Its many outstanding properties such as exceptionally strong, durable, chemical-resistant, elastic, easy to wash, and relatively high abrasion resistance make it widely used for various purposes such as clothes, reinforcement in rubber materials such as car tires, a rope, or a thread, and a range of injection-molded parts for vehicles and machinery.1−3 It can be easily mixed with different variations with significantly different material properties.4

However, polyamides usually have a relatively low molar mass compared to other polymers synthesized by free-radical polymerization.5 This characteristic is common to all polymers synthesized by the step polymerization process. Because of their low molar mass, these melts generally have quite different rheological properties from other polymers. They show a wide Newtonian viscosity plateau over a wide range of shear rates and have very low melt viscosities.5,6 The result of this property is the lack of processibility in the extrusion process such as a blow molding process because of the low degree of shear thinning.7 Moreover, their weak strain-hardening gives rise to difficulties in processing operations where elongational properties dominate.5 The issue is then how can the rheological properties of these polyamides be controlled to easily meet the requirements under different processing conditions.6,7 One possible method to solve the characteristic rheological problem is to change the molecular weight and structure of the molecules in a controllable manner. The chain relaxation dynamics and the rheological properties of polymer melts vary significantly because of the resulting polymer chain entanglements.6 We reported a simple process of changing the molecular structure. This makes it easy to generate long-chain branches in a controllable manner without creating a network structure.6−8 By adding a linking agent, a branched structure can be created in the polyamide backbone. The relaxation dynamics and rheological properties of a polyamide [nylon 6 (Ny6)] melt were significantly improved by the formation of three-arm or four-arm (H) star polymer molecules, the branches of which were placed in the connecting molecules.6 Zero shear viscosity increased more than 200 times the linear chain viscosity without forming a network structure. The storage modulus and loss modulus at low frequencies increased more than 104 and 103 times compared to neat Ny6.6,8 These results may solve the rheological barriers of polyamide melts and open up new possibilities for a wide range of applications. We have also succeeded in synthesizing Ny6 by reactive in situ extrusion using a linking agent (a diepoxide or a diamine).7,9 The linking agent reacted with growing Ny6 chains during anionic polymerization in the extruder to produce branched Ny6 chains with branch structures without the formation of cross-linked molecules, which was accompanied by a remarkable improvement in physical and rheological properties.7,8

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Even though the produced or modified nylons exhibit significantly improved rheological properties, the introduction of the linking agent reduced both melt enthalphy and crystallinity.\textsuperscript{6}\textsuperscript{-9} This means that the crystallization of Ny6 was hindered by structure changes. The branched part of the Ny6 chains had low mobility because of its binding to the backbone, making it difficult to crystallize.\textsuperscript{7}\textsuperscript{-9} The crystallinity was then possibly affected by the branched structure.\textsuperscript{7}\textsuperscript{-9} This is different from the case of a commercial Ny6 modification.\textsuperscript{6}\textsuperscript{-9} In that case, the branch was a long chain involved in the crystallization in different layers, so the crystallinity does not decrease significantly. However, the branches produced in the reactive extrusion synthesis can be quite short enough to disrupt the main chain ordering. The crystallinity then decreases with the addition of the linking agent. The amount of the linking agent reduced both melt enthalphy and crystallinity.\textsuperscript{6,7} This means that the crystallization of Ny6 was significantly hindered by structure changes. The branched part of the Ny6 molecules, with an emphasis on the morphological changes occurring in Ny6.\textsuperscript{10}

Isothermal crystallization kinetics using the Avrami equation is usually applied for the crystallization kinetics.\textsuperscript{11} However, it is difficult to keep the molten sample in an amorphous state while it is being cooled to the crystallization temperature in an isothermal crystallization experiment. In addition, the normal crystallization process in commercial production is nonisothermal. The nonisothermal crystallization kinetics was theoretically investigated by Ozawa.\textsuperscript{12} However, it has an implicit drawback of comparing the conversions at fixed temperatures at different cooling rates which can lead to deviations from the predicted linear behavior.\textsuperscript{12\textsuperscript{-15}} We have devised a nonisothermal crystallization analysis scheme that can avoid the problem of the Ozawa analysis.\textsuperscript{14,15} The nonisothermal crystallization kinetics can use additional insights into the crystallite structures that occurs during the formation of nanocomposites.\textsuperscript{16\textsuperscript{-18}} Therefore, the objective of this study is to apply the nonisothermal analysis method to the crystallization behavior of modified Ny6 molecules, with emphasis on the morphological changes caused by the presence of long-chain branches.

2. DESCRIPTION OF THE NONISOTHERMAL CRYSTALLIZATION MODEL

Here, we briefly reiterate the nonisothermal analysis scheme.\textsuperscript{14,15} In the Ozawa equation, the time variable in the Avrami equation is replaced by the cooling rate term as follows

$$\ln[-\ln(1 - x_c(T, U))] = n K(T) - n \ln U$$

where \(n\) is the Avrami exponent, \(x_c(T)\) is the volume fraction of the polymer transformed at a temperature \(T\), \(U\) is the cooling rate, and \(K(T)\) is the so-called cooling function, which is only a function of temperature.\textsuperscript{14} The volume fraction of a polymer, \(x_c(T)\), can be easily obtained by converting the weight fraction of the polymer, \(x_w(T)\), using the density of the amorphous phase and the density of the crystallized phase.\textsuperscript{15}

Adopting the exponential dependence of the \(K(T)\) function (\(K(T) = aT + b\)), eq 1 can be expressed as a linear relationship between \(T_{\text{max}}\) and \(U\), that is, \(n \ln U = aT_{\text{max}} + b - \ln[-\ln(1 - x_c(T_{\text{max}}, U))]\).\textsuperscript{14-16} Therefore, eq 1 can be rewritten as

$$\ln[-\ln(1 - x_c(T, U))] = a(T - T_{\text{max}}) + \ln[-\ln(1 - x_c(T_{\text{max}}, U))]$$

All parameter values can be determined without resorting to any numerical process.\textsuperscript{17,18} Plotting of \(\ln[-\ln(1 - x_c(T, U))]\) versus \(T - T_{\text{max}}\) gives a straight line whose slope represents the parameter \(a\) value and plotting \(T_{\text{max}}\) versus \(\ln U\) presents a straight line with a slope of \(n/a\) and an intercept is \(\ln[-\ln(1 - x_c(T_{\text{max}}, U))] - b)/a\).

3. RESULTS AND DISCUSSION

A previous report introduced a novel strategy for controlling the polymer melt rheology and the chain relaxation dynamics.\textsuperscript{6} The modification process involves a linking agent that can connect two chains in a linear matter first to double its molar mass and then later generate three- or four-armed polymers.\textsuperscript{6}

Long-chain branches were easily generated in a controllable manner without the formation of a network structure (see the Supporting Information for the chemical structure of the linking agent and the reactions).\textsuperscript{6} This has resulted in unusually large improvements in the rheological properties of the polymer melt and thus its relaxation dynamics.

Figure 1 shows the melt viscosities of various modified Ny6 as a function of frequency. Neat Ny6 melts show a broad
linking agent concentration. When the molar amount of the epoxy group in the sample was larger than that of the Ny6 amine group (over 1:1 ratio), the melt viscosities increased significantly higher than that of Ny6H (see the Supporting Information for the reaction between the linking agent and Ny6 molecules). Surprisingly, there is no apparent Newtonian plateau in these samples but only strong shear-thinning behavior is observed over the whole frequency range.6

The shear-thinning behavior of the modified Ny6 melts in Figure 1 could be well-explained using a simple Carreau equation using the Cox-Merz rule.10 The zero shear rate viscosity obtained from the Carreau model (Table 1) increased

Table 1. Viscosity Molar Mass Calculated from the Mark–Houwink Equation

| molar ratio between the epoxy group of the linking agent and the amine group of nylon6 | viscosity molar mass (g mol⁻¹) after the reaction | zero shear rate viscosity (Pa·s) from the Carreau equation |
|---|---|---|
| 0.0 (Ny6M) | 2.82 × 10⁴ | 200 |
| 0.0 (Ny6H) | 3.24 × 10⁴ | 540 |
| 0.2 (sample 1) | 3.38 × 10⁴ | 1600 |
| 0.4 (sample 2) | 3.76 × 10⁴ | 2500 |
| 0.6 (sample 3) | 3.97 × 10⁴ | 3.33 × 10⁴ |
| 1.0 (sample 4) | 4.54 × 10⁴ | 7.24 × 10⁴ |
| 1.25 (sample 5) | 4.91 × 10⁴ | 8.85 × 10⁴ |
| 2.0 (sample 6) | 4.97 × 10⁴ | 10.9 × 10⁴ |
| 2.25 (sample 7) | 4.18 × 10⁴ | 9.07 × 10⁴ |

“Standard deviation is less than ±2%.

with the addition of the linking agent (DEPPB, (4,4′-di(2,3-epoxypropyloxy) phenyl benzoate)) concentration. After reaching the peak of 1.09 × 10⁵ Pa·s for DEPPB (2), it decreased to 9.07 × 10⁴ Pa·s for DEPPB (2.25). The peak melt viscosity was more than 200 times that of the Ny6H melt. The intrinsic viscosity was measured and the molar mass was calculated using the Mark–Houwink equation (Table 1). Like the melt viscosity, the viscosity average molar mass reached the maximum when the molar ratio of the reactive functional groups was 2 (DEPPB(2)) and then it decreased. The viscosity average molar mass of DEPPB(2) was about 1.6 times that of Ny6H. Assuming the melt viscosity to follow the 3.4 power law (η ∼ M³⁴), this small molar mass change (1.6 times) can increase the melt viscosity by less than 5 times of Ny6H.19 Hence, it verifies that a significant increase in the melt viscosity of DEPPB(2) with strong shear thinning without the appearance of Newtonian plateau is inconsistent with the increase in the linear molar mass because of the linking agent. Neither was it due to the cross-linking reaction because the reacted extrudates could be reprocessed many times without showing any signs of solidification in the extrusion (Figure 3 of ref 6). Also, one of the reactants must have three functional groups on the molecules to proceed the cross-linking reaction, but the linking agent, DEPPB, has two functional groups and the Ny6H molecule has a monoamine group at the end of the chain. The other chain end of Ny6H terminates with the ε-caprolactam polymerization initiator. Therefore, no cross-linking reaction occurs.17 Also, light scattering analysis of the polymer solution did not detect any particles insoluble in formic acid.9 According to the Einstein equation, even if cross-linking occurred, the amount of cross-linked particles could not increase the melt viscosity so much.19 All these observations implicate that the cross-linking reaction or gelation cannot be the reason for unexpectedly high melt viscosity at low shear rates and the strong shear thinning.9

Figure 2 shows the thermal degradation characteristics of all nylons by thermogravimetric analysis (TGA). The medium viscosity-grade Ny6M exhibits earlier degradation behavior than Ny6H and modified nylons because of its low molar mass and hence low thermal properties. The modified nylons demonstrate two different degradation trajectories. Modified nylons of linear molecules (no. 2 and 3) follow the trajectory of Ny6H, but others (no. 4–7) of high melt viscosity having the nonlinear molecular structure (branching) show better degradation behavior because of the enhanced molar mass and the different molecular structures (Figure 1 and Scheme S11). On the other hand, in the latter group of samples, the 5 wt % degradation temperature (Table 2) increased slightly. This is consistent with the change in molar mass (Table 1). The starting temperature of degradation did not change noticeably. The molar mass of the branched molecules increased but was not sufficient to delay the onset of the degradation of the modified nylons. It is also consistent with the change in zero shear rate viscosity in different samples (Table 1).

Another point of difference is that all linear polymers were totally degraded at 600 °C, whereas a small amount (less than 4 wt %) of samples (no. 4–7) remained at that temperature. At the temperature going over 400 °C, the C–C bonds of the nylon backbone spontaneously break to yield two shorter chains furnished with a terminal radical. It can be conjectured that some cross-linking reactions between degrading radicals might happen at that degradation temperature, although we did not investigate further details.

As mentioned in our previous study, the crystallinity decreased slightly with the chain structure modification.
DSC scan curves are presented in Figure 3. All curves were recorded after cooling the melts at 240 °C with various cooling rates. The main difference between different cooling rates is in the characteristic onset and peak crystallization temperature which are related to the associated enthalpy change and the peak-broadening effect in the modified Ny6 compared to neat Ny6 (Ny6H). The onset temperatures of the modified Ny6 were lower than those of neat Ny6H. This means that the degree of supercooling necessary for the crystallization was larger for all modified Ny6’s. This consequence is attributed to the slowing down of the crystallization by the branching structure which hinders chain ordering in the crystallization process. All of the samples exhibit a single crystallization exotherm.

As the cooling rate goes up, the polymer melt has less time for crystallization. Thus, the exotherm peaks appear at lower temperature. $T_{\text{max}}$ of the modified Ny6s is also lower than those of the neat Ny6H at low cooling rates because they need more time for chain ordering. One exception is the sample 2 which has a larger molar mass than pure Ny6 (H or M) but still relatively low zero shear rate viscosity because it does not have branching arms in the Ny6 molecule backbones yet (Table 1). A high melt viscosity restricts the movement of the molecules, but the arrangement of local molecules through the hydrogen bonds improves with the molecular weight, which makes the simple chain arrangement for crystallization easier. In the case of other modified polymers, the change in the chain structure (branching) disrupts the arrangement of the chain

Figure 3. DSC curves of nonisothermal crystallization at different cooling rates.

Figure 4. Evolution of $T_{\text{max}}$ as a function of $\ln(U)$.
molecules. The thermograms also show that the curves are symmetric around $T_{\text{max}}$, which implies that crystallization occurs as much after $T_{\text{max}}$. This exemplifies that the dynamic restriction (high melt viscosity) is less critical than the structural ordering effect (participation of the branching moiety in crystallization). Because of the restriction in the chain conformation, it takes more time for the modified molecules to become ordered.

A linear variation of the maximum temperature crystallization isotherm, $T_{\text{max}}$, with the logarithm of the cooling rates ($\ln U$) is displayed in Figure 4. It shows predicted linear behavior when the cooling rate is low ($<5^\circ\text{C}/\text{min}$) which is in agreement with other cases. $T_{\text{max}}$ decreases as the cooling rate increases because less time is available for the crystallization process at higher cooling rates. The relative crystallinity development of neat Ny6 and modified nylons is shown in Figure 5 (vs temperature) and Figure 6 (vs time). As the cooling rate increases, a large portion of the relative crystallinity occurs after the most rapidly increasing point in the heat flow curve where the kinetics change to a slower process. More branching was produced with the addition of more linking agent which induces higher viscosity, slower chain movement, and slower crystallization. It reduces the crystallinity of the sample, creating an amorphous phase. The crystallinity change was not so remarkable when the branch length was long enough to participate in another crystalline lamella (Figure 3B of ref 6). However, when the branching length was not long, decrease in crystallinity with branching

Figure 5. Development of relative crystallinity, $x_\alpha$, as a function of temperature at different cooling rates.

Figure 6. Development of relative crystallinity, $x_\alpha$, as a function of time at different cooling rates.
was quite evident.\textsuperscript{8,9} The melting temperatures of the Ny6H and Ny6M were 224 and 220 °C, respectively. The melting temperatures of the modified nylons were 3−4 °C lower which indicates that the modified nylons have a thinner lamellar thickness of the Ny6 chains because of the structure change.\textsuperscript{18} Modified nylons show peak broadening compared to neat nylons because of the retardation of chain relaxation and movement by the high viscosity.

The plot of ln[−ln(1 − x(T))] versus $T - T_{\text{max}}$ provides a straight line with a slope of n/a(Figure 7). Calculated Avrami constant values from Figures 4 and 7 are listed in Table 3. The calculated values of the Avrami exponent, n, for neat Ny6H were between 5.2 and 5.7 with an average value of 5.4. This value is close to the characteristic value for the heterogeneous nucleation.\textsuperscript{11} Ny6H is a polyamide of high viscosity grade that includes unknown catalysts or chemicals for the molar mass increase which is considered to act as the heterogeneous nuclei. This can be proved by the morphological observation later. In contrast, the Avrami constant of Ny6M shows the n value between 3.2 and 4.4 with an average value of 3.7, of

| cooling rate (°C/min) | Ny6M | Ny6H | sample 2 (DEPPB (0.4)) | sample 4 (DEPPB (1.)) | sample 5 (DEPPB(1.25)) | sample 7 (DEPPB(2.25)) |
|----------------------|------|------|------------------------|------------------------|------------------------|------------------------|
| 1                    | 4.44 | 5.73 | 4.18                   | 3.86                   | 3.81                   | 3.71                   |
| 2                    | 3.71 | 5.44 | 4.37                   | 4.09                   | 3.93                   | 4.08                   |
| 4                    | 3.20 | 5.22 | 4.45                   | 4.29                   | 4.09                   | 4.13                   |
| average              | 3.78 | 5.46 | 4.33                   | 4.08                   | 3.94                   | 3.97                   |
which the crystallization mechanism is the normal three-dimensional growth rate and slow down of the nucleation rate. The modified nylons all show the Avrami constant values between 3.7 and 4.4, close to that occurred by the solid sheaf growth in three-dimensional space with athermal nucleation.\textsuperscript{18} As the cooling rate increases, the Avrami index decreases. If the cooling rate becomes faster, then less time is allowed for a molecule to be relaxed and ordered. For the heterogeneous crystallites at high cooling rates, crystallization occurs at an earlier stage than that for low cooling rates. In the early stage of Ny6M, the Avrami constant values are close to 3 which means that more Ny6M molecules participate in three-dimensional growth at slow cooling rates. On the other hand, Ny6H molecules have high Avrami constant values because of heterogeneous nucleation. The Ny6H crystallites formed in the early stage do not have enough space to be fully ordered and grow. Thus, the size of the hedrite decreases significantly compared to that of Ny6H, as shown below.

Figure 8 shows the crystalline morphology by polarized optical microscopy. Ny6M melt forms large spherulites with slightly twisted lamellae.\textsuperscript{23} In contrast, the crystal structure of Ny6H consists of smaller ones of hedrites. The photomicrographs clearly reveal that the Ny6M has a larger, more developed spherulitic structure which is consistent with a lower rate of nucleation, yielding a lower, “overall” crystallization rate. This morphology difference can elucidate the Avrami constant difference. Because of excessive heterogeneous nucleation sites for Ny6H, the crystallites did not grow as large as those for Ny6M. The half-crystallization time ($t_{1/2}$) values increase with the cooling rate because of faster growth and crystallization (Table S1 in the Supporting Information). It increases more rapidly for Ny6H than Ny6M because of heterogeneous nucleation. The morphological appearance of modified nylons is similar to Ny6H but much smaller than that. Because of the rheological property restriction (much higher viscosity) and branching structure, the crystallite could not grow so large as Ny6H. Also, the branching structure seriously hinders the homogeneous nucleation. This morphological appearance is in agreement with the Avrami constant n values. The less crystallite formation and slow growth definitely slow down the crystallization speed and/or nucleation rate. Thus, the Avrami constant values of modified nylons are around 4 decreased from that of Ny6H (ca. 5.4).

4. CONCLUSIONS

Nonisothermal crystallization analysis of neat Ny6s (Ny6H of high viscosity grade and Ny6M of medium viscosity grade) and modified nylons (modified Ny6H) provides some important information: the structural variation as well as the heterogeneous nuclei decides the crystalline structures of these nylons. The Avrami exponent of the Ny6H was close to 5.4 indicating that the crystallites follows the crystallization process of the heterogeneous nucleation, whereas that of the Ny6M was close to 4, indicating the kinetics of the normal three-dimensional growth rate and slow down of nucleation.\textsuperscript{20,21} All the modified nylons of Ny6H show the Avrami constant values between 3.8 and 4.4, which are close to that occurred by the solid sheaf growth in three-dimensional space with athermal nucleation because of crystallization hindrance by the branching point.\textsuperscript{22}

The morphology looked differently for Ny6H and Ny6M. Ny6M melt forms large spherulites with slightly twisted lamellae, whereas the crystal structure of Ny6H consists of smaller ones of hedrites. For Ny6H, the crystallites did not grow so large as those in Ny6M because of excessive heterogeneous nucleation sites while the crystalline morphology of Ny6M was that of large spherulites with slightly twisted lamellae. This morphology difference can elucidate the Avrami constant difference. The half-crystallization time ($t_{1/2}$) values increase with cooling rates because of faster growth and crystallization (see Table S1). It increases more rapidly for Ny6H than Ny6M because of heterogeneous nucleation. On the other hand, the crystallite morphologies of modified nylons look similar to that of Ny6H but in much smaller sizes. The rheological restriction (much higher viscosity) and the branching structure prevent the crystallite growth from being as large as that of Ny6H. Also, the branching structure inhibits the homogeneous nucleation. This morphological appearance is in agreement with the Avrami constant value difference. The less crystallite formation and slow growth definitely slow down the crystallization speed and/or nucleation rate. The Avrami constant values of modified nylons were around 4, decreased from that of Ny6H (ca. 5.4). The nonisothermal crystallization analysis provides the clue of morphological development as well as molecular ordering and relaxation of the modified nylons. Thermal stability of the modified nylons was better than that of pure Ny6H because of the increased molecular weight.

5. EXPERIMENTAL PART

5.1. Materials. Ny6H was a Kolon product (KN171, Korea). The number average molar mass ($M_n$) was found to be 24,200 g mol$^{-1}$ with a polydispersity index of 3.5. This molar mass was much higher than $M_n$ of Ny6 (2233 g mol$^{-1}$).\textsuperscript{24} It is a high viscosity-grade Ny6. For a comparison, we also used another Ny6 of medium viscosity grade, Ny6M (KN111, $M_n = 20,000$ g mol$^{-1}$, $\eta_{rel} = 2.45$ in 96% H$_2$SO$_4$), also a Kolon product. The high viscosity-grade Ny6H (KN171) was used to produce the modified Ny6 in order to prepare high viscosity nylons. Details of the process were fully explained in the previous study.\textsuperscript{6}

5.2. Characterization. TGA was performed on a TA instrument under a nitrogen atmosphere with a heating rate of 20 °C/min in a temperature range of 50–650 °C. Differential scanning calorimetry (DSC) was performed on a METTLER-TOLEDO DSC832e under a nitrogen atmosphere with a heating rate of 10 °C/min in a temperature range of 50–240 °C. To examine nonisothermal crystallization, the samples were melted at 240 °C for 5 min to eliminate the previous thermal history and then cooled at different cooling rates. A polarized optical microscope (Olympus BX-51) equipped with a METTLER-TOLEDO FP82 HT hot stage and a digicam II camera was used to record the growth of the crystallites.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04082.

Reaction of the linking agent (DEPPB) with nylon 6 molecules half-crystallization time $t_{1/2}$ (PDF)

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Notes
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