Long-Living Anions Could Dramatically Change the Overall Physical Properties of a Polyamide (Nylon 6) Synthesized by a Novel Process

Kyoungwan Oh, Hoyeon Kim, and Yongsok Seo*

ABSTRACT: We devised a novel strategy of two-stage anionic polymerization of (ε-caprolactam) in a twin screw extruder to control the generation of branched structures. Long-living anions of nylon 6 prepared in the first extrusion gave rise to a change in the molecular structure when they interacted with diamine added during the second extrusion. It has been found that the transfer of living anions between functional molecules having the same anion-forming groups affects the structural change of the resulting polymer molecule. The variation in chain structure has resulted in dramatic changes in the physical and dynamic properties of the polymer despite changes in molecular weight of less than 2 without forming a network structure. Tensile elongation and toughness at the optimum concentration of the additive were increased by 5 and 10 times, respectively, which was enough for the resulting polymer to be classified as a super-tough nylon without a toughener. It can be widely used as a matrix polymer for diverse composite materials.

1. INTRODUCTION

Most polymers synthesized through the step polymerization have a lower molar mass than those obtained through the radical polymerization.1,2 The characteristic rheological properties of such polymers are a low zero-shear-rate viscosity and a wide Newtonian viscosity plateau. Although the physical properties of step polymerized polymers, such as ductility, toughness, and durability, are adequate for their wide use in the film, fiber, textile and packaging industries, other physical properties must be improved to enhance their performance and expand their range of application. Increasing the molar mass of a polymer enhances almost all its physical properties; thus, numerous attempts have been made to fabricate polymers with higher molar mass.3 However, the molar masses of polymers synthesized through condensation polymerization cannot be increased indefinitely because their step-by-step growth means that the reactant viscosity increases progressively lowers the probability of chain growth.4 Given the limits on increasing the molar mass of such polymers, alternative strategies for improving their physical properties have been actively sought over the past decades.5,6 In this study, we report our recent success in overcoming these barriers for an exemplary polymer, a poly (ε-caprolactam) or so-called nylon 6 (polyamide 6, PA6), synthesized using the anionic ring-opening polymerization (AROP) method. This novel method is demonstrated here for the poly (ε-caprolactam), but can be easily applied to other polymers, not only those obtained through a condensation polymerization process but also those synthesized through anionic polymerizations and other condensation or radical polymerization methods.

As mentioned above, the molar mass of a polymer cannot be increased indefinitely, which requires a different approach that changes the molecular structure in a controllable manner. Entangled polymer melts can exhibit a wide range of relaxation time, which are related to their melt viscosities.7 The viscosity (η) of an entangled polymer melt increases strongly with increasing molar mass (M). Reptation theory with contour-length fluctuations and constraint-release effects predicts that the shear viscosity of an entangled linear polymer melt scales with its molar mass as $M^{3.4}$.7 A characteristic feature of polyamide 6 (PA6) is that it has active groups that can react with various functional groups of organic or polymeric materials. Thus, we attempted to improve the physical properties of PA6 by adding to the polymerization mixture a bifunctional molecule that can react with two PA6 molecules and thus double the molar mass.1,8,9 A diepoxy compound was synthesized as such a linking agent and was mixed with the commercially available PA6.1 The chain relaxation dynamics were found to vary over a few orders of magnitude as a result of the addition of the appropriate amount of the linking agent.
We attribute this unexpected result to the generation of three- or four-armed star polymer molecules. Although the zero-shear-rate viscosity was increased to a value greater than 200 times the viscosity of the linear chain, the mechanical properties were not noticeably improved. This outcome was ascribed to the low number of branched molecules.

To increase the number of branched molecules, we tried an alternative process: Instead of using commercially available PA6, we carried out the anionic ring-opening polymerization (AROP) of ε-caprolactam in an extruder. In our previous study, a diepoxide linking agent was added to the extruder in the reactive extrusion of ε-caprolactam. The resulting PA6 samples exhibited properties similar to those of the modified PA6; however, their molar masses were substantially lower than those of the commercial polymer because of the short reaction time in the laboratory scale extruder; their melt viscosities were consequently lower. In order to improve the physical properties as well as the molar mass, we tried an alternative method in this study: instead of mixing the reactants with the ε-caprolactam, we added it in the second extrusion. This simple process variation could dramatically change the whole physical properties of the produced polymers. This revolutionary change in physical properties was attributed to the long-living anions, which trigger a revival of the polymerization reaction in the second stage.

2. RESULTS AND DISCUSSION

Diamine is expected to participate in the PA6 synthesis process because the amine group of diamine molecules can be attacked by the anions in the chain growing reactions in the extruder. Depending on the amount of diamine added, the PA6 molecules are cross-linked or form branched PA6. We tested this approach with the aim of improving the physical properties of the PA6 samples. The variation in the physical properties of the synthesized PA6 samples via single extrusion was similar to that observed for the samples prepared with the diepoxides. The mechanical properties of the samples produced with the two methods were similar; thus, we concluded that the reactivity of the diamine additive was similar to that of the diepoxide additive.

Although these PA6 samples synthesized via AROP of ε-caprolactam in the presence of additives (diepoxide or diamine) exhibit improved physical properties (similar to or better than those of commercial PA6, which has a molar mass more than twice that of our PA6 samples), their mechanical properties were not as dramatically improved as their rheological properties, probably because of their low molar mass. The AROP was performed in a laboratory-scale twin-screw extruder where the additives quench partly the living anion and can stop further growth of the chain. Thus, we altered the reaction scheme in order to increase the molar mass of the synthesized PA6 and improve the reaction with the diamine: PA6 was initially synthesized by performing the AROP of ε-caprolactam in the twin-screw extruder followed by the mixing of pelletized PA6 particles with the additives and a second extrusion process. Since some living anions were likely present (alive) in the pelletized particles, we expected that further reaction with the additive would occur and that the resulting product would exhibit a larger molar mass than that obtained via single-step extrusion.

The mechanism of the anionic polymerization of ε-caprolactam by AROP with the activator, terephthaloyl biscaprolactamate (TBC), proceeds as follows (Scheme 1): TBC reacts with sodium caprolactam anion and the caprolactam ring is opened. The living anion attacks an ε-caprolactam monomer, extracts a proton, and generates a next living anion that acts as a nucleophile in opening the ε-caprolactam ring of a dimer. A trimer with a living anion is formed, and the chain propagation process continues until the anions are quenched or all monomers are consumed. The caprolactam chain end groups of polymerized PA6 can react with the diamine chain extender and thus form a new PA6 repeating unit via ε-caprolactam ring-opening; alternatively, they directly associate to form a caprolactam by-product.

Some well-known side reactions involving the activator occur in the AROP of PA6, particularly branching reactions. In the initial stage of polymerization, active anions on living chains tend to react with activators rather than with monomers. As a consequence, bifunctional activators dangle on the side positions of linear PA6 chains and provide new growth sites for the formation of branched polymers. Furthermore, a Claisen-type condensation also produces a branched polymer chain. The occurrence of the branching reaction depends on the composition of the reactants, the structure of the activator, the reaction time, and the temperature. The use of a bifunctional activator rather than monofunctional one is known to promote Claisen type condensation reactions. In this study, the molar ratio of diamine content to initiator was limited less than 1.25 to exclude the possibility of cross-linking reactions.

Table 1 lists the viscosity—average molar mass, melting temperature, enthalpy of fusion, and crystallinity of PA6s that reacted with the diamine during the second extrusion. The increase in the molar mass obtained with this process indicates that living anions were still alive in pure PA6 polymerized after the first extrusion. The amine groups of PDA1 and EDA3 react with the caprolactam end groups of PA6, increasing the molar mass (Schemes 1 and 2). The caprolactam chain end groups of polymerized PA6 can react with the diamine chain extenders. Two living anions in two different chains can then react with one diamine group of a diamine molecule or, more likely, with the two amine groups on the same diamine.
Table 1. Molar Mass, Melting Temperature, Enthalpy of Fusion, and Crystallinity of PA6s that Reacted with the Diamine during the Second Extrusion

| samples  | $T_m$ (°C) | $\Delta H_m$ (J/g) | $X_c$ DSC (%) | $X_c$ WAXD (%) | molar mass (g/mol) | zero-shear rate viscosity (Pa·s) |
|----------|------------|--------------------|---------------|---------------|-------------------|---------------------------|
| PA6      | 213.6      | 61.75              | 32.5          | 43.1          | 26,800            | 270                       |
| PDA1 0.25| 212.8      | 60.04              | 31.6          | 38.8          | 38,100            | 4660                      |
| PDA1 0.5 | 213.4      | 57.19              | 30.1          | 37.3          | 44,900            | 10,900                    |
| PDA1 0.75| 212.7      | 56.81              | 29.9          | 35.0          | 49,000            | 12,100                    |
| PDA1 1   | 213.4      | 54.72              | 28.8          | 32.2          | 52,500            | 33,600                    |
| PDA1 1.25| 212.9      | 50.54              | 26.6          | 29.3          | 50,400            | 25,000                    |
| EDA3 0.25| 212.8      | 60.23              | 31.7          | 39.2          | 39,200            | 5600                      |
| EDA3 0.5 | 213.2      | 57.95              | 30.5          | 37.4          | 45,700            | 7700                      |
| EDA3 0.75| 212.6      | 55.67              | 29.3          | 34.8          | 49,100            | 17,900                    |
| EDA3 1   | 213.1      | 54.15              | 28.5          | 32.1          | 52,800            | 40,100                    |
| EDA3 1.25| 213.0      | 49.78              | 26.2          | 29.4          | 51,800            | 30,000                    |

“a”The number after the diamines indicates the molar ratio of the diamine contents to the initiator. “b”Molar mass of PA6 resins were calculated by the Mark-Houwink equation of $[\eta] = k[M]^a$. The Mark-Houwink constants are $k = 22.6 \times 10^{-3}$ (mL/g) and $a = 0.82$ for nylon 6 at 25 °C in 90% formic acid solution.16,23 “c”The zero-shear rate viscosities were calculated by fitting the viscosity data with the Carreau equation (see the text).17

Scheme 2. Chemical Structures of (a) TBC, (b) p-Phenylenediamine (PDA1), and (c) 3-(4-Aminobenzoyloxy)phenyl 4-aminobenzoate (EDA3)

molecule (Scheme 1). Depending on the chain length of the reacting PA6, the molar mass of PA6 can be doubled. Both diamine groups of PDA1 and EDA3 show a similar trend in the molar mass, which implies that the living anions react similarly with these two diamines.

The general trend is similar to that observed for the single-step process found in our previous study, although the viscosity average molar mass is higher.8 The addition of excessive diamine results in quenching of the growing anions and the cessation of further chain growth in the single-step extrusion process. By contrast, in the two-step process, the living anions of the PA6 chain ends react with diamine molecules added during the first extrusion; thus, further anion transfer to other monomers or initiator species does not occur because most of them already reacted during the first extrusion process. It should be noted that the amounts of added diamine are much greater than the amounts added in the single-step process.10 Diamine molecules react first with a PA6 chain and then with another PA6 chain. If the amount of added diamine is less than or the same as the amount of initiator, the probability of the reaction of two PA6 chains with a diamine molecule increases. If the amount of added diamine is increased above this level, PA6 living anions react with diamine molecules to form diamine dangling chains rather than connecting two chains; thus, the average molar mass is reduced.9 Another reason for the production of high molar mass PA6 by the two-step process is that the PA6 molecules produced by the first extrusion have high molar mass because the growing PA6 chains react with the $\varepsilon$-caprolactam monomer.11 The maximum molar mass of the two-step PA6 molecules is nearly twice that of the pure PA6 molecules produced by the single-step process.

Figure 1a shows the dependence of the complex viscosity on the frequency. Although their absolute values differ slightly, the PA6 molecules containing PDA1 or EDA3 exhibit similar behavior. There is no broad Newtonian plateau of low viscosity in the melt viscosity for PA6, but weak shear thinning behavior is observed in the measured frequency range. This is attributed to the formation of some branched molecules by Claisen-type condensation reaction induced by the high extrusion temperature.11 The viscosity values of other PA6/diamine compounds are, however, one or two orders higher than those of neat PA6 at low shear rates, although this difference decreases at high shear rates because of the strong shear thinning of diamine-added PA6. Notably, the viscosities of the PA6/diamine melts increased with increasing diamine/initiator molar ratio to reach 1, irrespective of the type of added diamine. This diamine concentration is 10 times greater than the maximum concentration in the single-step process that gives rise to the maximum viscosity.8,9 Above this concentration, the melt viscosity decreases. This phenomena is common to all PA6/diamine or PA6/diepoxide compounds produced through the reactive extrusion process for both single-step and two-step processes.12,20,21 We observed similar behavior in an earlier study when we mixed a commercial PA6 with a diepoxide.1
The viscosity of the modified PA6 is two orders of magnitude greater than that of pure PA6 despite a maximum two-fold change in molar mass. The zero-shear-rate viscosities in Table 1 were calculated by fitting the viscosity data with the Carreau equation and by using the Cox–Merz rule,
\[ \eta(\dot{\gamma})/\eta_0 = (1 + (\dot{\gamma}\tau_a)^n)^{-(n-1)/n}, \]
where \( \eta_0 \) is the zero-shear-rate viscosity, \( \dot{\gamma} \) is the shear rate, \( \tau_a \) is the characteristic time, and \( n \) is a parameter. The zero-shear-rate viscosity reaches its highest value when the diamine/initiator molar ratio is 1. No noticeable difference is observed between different diamine-added PA6s, although with EDA3 exhibits slightly enhanced physical properties, possibly because of the better reactivity of EDA3 stemming from its longer molecular length (Scheme 2). The highest zero-shear-rate viscosity is greater by a factor of 120 for PA6 with added PDA 1 and 150 for PA6 with added EDA3.

Another remarkable rheological property change is evident in the dynamic modulus (storage modulus (\( G' \)) and loss modulus (\( G'' \))) shown in Figure 2. Generally, \( G' \) characterizes the elastic solid-like behavior, whereas \( G'' \) characterizes the viscous liquid-like response. For linear polymer melts that exhibit linear viscoelastic (LVE) motion in the low-frequency region, the \( G' \) is proportional to the square of frequency (\( \omega^2 \)) and the loss modulus is proportional to the frequency (\( \omega \)). The power-law dependences of \( G' \) and \( G'' \) on \( \omega \) become weaker with the addition of the diamine but do not reach a steady plateau value; after reaching their maximum values upon the addition of diamine at a diamine/initiator molar ratio of 1, they decrease. Furthermore, the \( G' \) is larger than the \( G'' \) over the whole investigated frequency range, which indicates the occurrence of a molecular structural change in the PA6/diamine compounds. The viscosity—average molar mass of PA6/diamine was, at its maximum, less than twice that of pure PA6 (Table 1). This result implies that the melt viscosity will be, at most, less than 10 times that of pure PA6 according to the 3.4 power law for linear molecules. Actually, the zero-shear-rate viscosities of PDA1 and EDA3 are increased by factors greater than 120 and 150, respectively, at a diamine/initiator molar ratio of 1. This result demonstrates the occurrence of another change in molecular structure.

Two possible structural changes can explain the aforementioned drastic change in the viscosity as well as the changes in the \( G' \) and \( G'' \). Cross-linking reactions are known to occur in the anionic polymerization of \( \varepsilon \)-caprolactam when the monomer conversion is complete and if the reaction temperature exceeds 180 °C. However, the cross-linking reaction does not occur significantly for the following two reasons. First, almost no residue was observed after the 90% formic acid extraction. This result was also checked by performing a light scattering analysis of the polymer solutions, which detected no insoluble particles in the formic acid. Once the cross-linked PA6 molecules are produced, they are infusible in the melt; thus, their contribution to the viscosity is quite low according to the Einstein equation. Therefore, this result cannot be reconciled with the consequence of significant cross-linking. The other evidence telling against substantial cross-linking is the fact that the viscosity decreases beyond the optimum amount of diamine (diamine/initiator molar ratio = 1). If substantial cross-linking occurs, the viscosity should continuously increase with increasing diamine content.

The other topological structure that can explain the drastic rheological behavior change is branching: the melt viscosity of a branched polymer increases exponentially with the number of entanglements per arm. \( \eta_0 \approx (M_e/M_a)^{3/2} \exp ((aM_e/M_a)) \) where \( M_a \) is the arm’s molar mass, \( M_e \) is the entanglement molar mass, and \( a \) is a constant independent of the number of arms, \( f \) (3 to 33 give the same results). The growing caprolactam anion can attach to the amine group of a diamine. Connecting two living PA6 molecules into one through the same amine group in a diamine molecule or through different amine groups on the same diamine molecule can increase the molar mass twice. Thereafter, another anion can attack the secondary amine in the latter case or the left primary amine in the former case (Scheme 1). The result is the formation of three-armed molecules. Branched PA6 molecules can be easily generated through the reaction in the extruder and through the

Figure 2. (a) Storage modulus and (b) loss modulus of PA6/PDA1 blends. (c) Storage modulus and (d) loss modulus of PA6/EDA3 blends.
use of a bifunctional activator. The exponential increase in relaxation time of branched molecules means that the melt viscosities of the branched molecules also increase exponentially. A larger stress is then necessary to disentangle the PA6 molecules, which causes a large increase in the $G'$ and a smaller increase in the $G''$. The $G'$ is greater than the $G''$ over the whole frequency range (Figure 2), which is another indication that a branched structure is formed. For general polymer melts, the $G''$ value is larger than the $G'$ value in the linear viscoelastic region. This result indicates that the PA6/diamine compounds have properties similar to those of a viscoelastic solid, which is attributable to the high level of entanglement of the branched chains. In addition, $G'$ and $G''$ have similar slopes, which also indicates the presence of a highly entangled state similar to that of a network.

The DSC scanning results for the PA6/diamine mixture are shown in Table 1. Although the enthalpy of fusion ($\Delta H_m$) and crystallinity ($X_c$) are reduced by the introduction of the diamines, the melting temperature does not change. Thus, the crystallization of PA6 is hampered by the branching structure. If the cross-linking reaction predominates, the degree of crystallinity is expected to decrease rapidly with the addition of diamine. However, the observed reduction in crystallinity was not so remarkable. To investigate the crystalline structure, we also conducted a wide angle X-ray diffraction (WAXD) analysis (Figure 3 A). The WAXD patterns for the PA6/EDA3 compounds show two peaks at $2\theta = 20$ and $23^\circ$. These peaks correspond to the reflections of the $\alpha$-crystalline planes (200) and (002) + (202) respectively. No other peaks such as the $\gamma$ crystalline peak at $2\theta = 21.5^\circ$ are evident. The crystallinity decreases with the increasing amount of added EDA3 (Table 1). This result is consistent with the outcomes reported for the single-step process. The newly synthesized PA6/diamine compounds exhibit the same crystalline structure as PA6. This is an additional merit of the synthesized polymers in that they can be recycled as normal PA6 to reduce their environmental impact because they have the same melting point as well as the same structure without cross-linking.

The mechanical properties of the PA6/diamine compounds are displayed in Figure 4. The PA6 samples with added diamines exhibit similar trends. All of the mechanical properties are enhanced by the addition of diamines. The modulus and tensile strength of linear polymers generally decrease with decreasing crystallinity. However, the modulus
and tensile strength of all the synthesized PA6s are enhanced by the addition of diamines. This behavior is attributed to their increase in molar mass as well as to the increase in the number of branches on the molecules, which promotes increased chain entanglements. These results are in partial agreement with the mechanical properties of PA6 synthesized by the single-step process. However, the mechanical properties of PA6 synthesized via the single-step process and those of PA6 synthesized via the two-step processes differ markedly. The enhanced molar mass of the PA6 compounds synthesized through the two-step process results in their modulus and tensile strength being 20–50% greater than those of PA6 synthesized through the single-step process.

The most obvious difference is observed in the tensile elongation results. PA6 synthesized in single-step exhibits elongation less than twice that of pure PA6, but the elongation of PA6 synthesized in two-steps is enhanced by a factor of nearly five. As a consequence, the energy to break (or tensile toughness) was surprisingly large: 10 times greater than that of pure PA6. This remarkable improvement in the elongation and, thus, in the mechanical properties can be explained by the branches participating in cocrystallization with other crystalline lamellars (Figure 3B). Duvall et al. demonstrated that the interfacial strength between nylon 6,6 and polypropylene can be substantially increased if the long chain branch on the compatibilizer (maleic anhydride grafted polypropylene) participates in the cocrystallization of the polypropylene phase. The strong hydrogen bonding between PA6 molecules and branches indicates that branch moieties can participate in another lamellar crystalline phase as long as their branch length is sufficiently long (Figure 3B). In the case of the PA6 compounds prepared through the single-step process, the chains before the living anion transfer to the monomer have relatively short chain length as well as wide molar mass distribution, whereas the PA6 compounds prepared through the two-step process have relatively long and more uniform branches because all the PA6 moieties were synthesized in the first extrusion. These long PA6 chains form branched moieties that can be incorporated into another crystalline lamellar phase. The resulting cocrystallized molecules connect with otherwise separated crystalline lamellar (Figure 3B), which leads to large increase in elongation and especially high tensile toughness. The overall effect of the molar-mass enhancement and branch formation is to produce chain entanglements and induce cocrystallization both of which result in substantially improved mechanical properties. No noticeable difference is observed between different amine-added PA6s, although EDA3 added one exhibits slightly enhanced mechanical and rheological properties, possibly because of the better reactivity of EDA3.

3. CONCLUSIONS

A two-step process, in which the second extrusion consists of PA6 pellets containing living anions and a small amount of diamines, was successfully carried out to synthesize new PA6 molecules with dramatically improved rheological and mechanical properties. The added diamine molecules react with the living anions on the PA6 molecules synthesized in the first extrusion process. The addition of the diamine molecules not only increases the PA6 molar mass by connecting two PA6 molecules but also leads to the formation of branched molecules. We have shown that these effects are not due to the cross-linking. It has been found that the increased molecular weight and branching lead to drastic improvements in both the rheological properties and the mechanical properties of PA6. The rheological properties reach their optimal values at a diamine/initiator molar ratio of 1. The zero-shear-rate viscosity of PA6, prepared with the added PDA1 and EDA3, is 120 and 150 times higher than that of pure PA6, respectively. The storage modulus ($G'$) and loss modulus ($G''$) at low shear rates increased by factors greater than 100 and 30, respectively, compared to those of pure PA6. Another important feature of this two-step process is that the rheological properties can be finely tuned by varying the amount of the diamine added.

The mechanical properties of the synthesized PA6 were also significantly enhanced with increasing diamine addition until the diamine/initiator molar ratio reached 1. The most notable change was that observed in the elongation results. The chain entanglement and cocrystallization of branched moieties, which connect separate crystalline lamellar phases increase the elongation by a factor of four to five compared to pure PA6. The overall tensile toughness is enhanced by a factor of 7 to 10 compared to pure PA6. The newly synthesized PA6 has the same chemical structure as linear PA6 without cross-linking, which means that it can be recycled as normal PA6. Although a two-stage extrusion process was used in this study, a single extrusion process in which the diamine is added through the second hopper in the long extruder used in the industry is expected to give similar or better results because of the presence of more living anions in the extruder. Due to its superior physical properties, the newly synthesized PA6 material can be used for high-performance composite materials.

4. MATERIALS AND METHODS

4.1. Materials. ε-Caprolactam used in this study was obtained from Capro Corporation (Korea). All other chemicals (sodium hydride, terephthaloyl chloride, triethylamine, pyridine, resorcinol, p-phenylenediamine (PDA1), 4-nitrobenzoyl chloride, and activated Pd-carbon (10%)) were purchased from Aldrich (see Scheme 2 for chemical structures). We synthesized terephthaloyl biscaprolactam (TBC) by reacting terephthaloyl chloride with caprolactam in benzene. 3-(4-Aminobenzoyloxy) phenyl 4-aminobenzoate (EDA3) and sodium caprolactam was synthesized by the same method as we reported.

4.2. In Situ Polymerization by Reactive Extrusion. The reactant mixture consisted of ε-caprolactam, sodium caprolactam, TBS, and diamines, which were used as monomer, initiator, activator, and additives, respectively. The monomer: initiator:activator molar ratio was optimized as 50:1:0.5 in preliminary experiments for both high polymer yields and short polymerization times. The reactant mixtures were fed into a twin screw extruder (BA-19, Bautech) while argon was flowing to prevent quenching of active anions due to moisture during polymerization. The temperature profile from the feeding zone to the die were set to 140/180/200/220/230/240 °C and the screw speed to 50 rpm. The extruded PA6 was pelletized and dried under vacuum at 60 °C for a sufficient time before the second extrusion. A certain amount of a diamine was mixed with the dried PA6 pellets for the second reaction stage in the extruder. The second reaction condition was set in the same way as the first extrusion. The molar ratio of diamine content to initiator was varied as 0.25, 0.5, 0.75, 1, and 1.25 for each sample.

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4.3. Characterization. Differential scanning calorimetry (DSC 823e, METTLER TOLEDO) was used to analyze the thermal properties of PA6/diamine compounds. Under a nitrogen atmosphere, the sample was first heated from 25 to 280 °C at 10 °C/min, cooled to 25 °C, and heated to 280 °C at the same heating rate. The degree of crystallinity ($X_c$) was calculated using the following equation.

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_{100}} \times 100$$

where $\Delta H_m$ is the specific enthalpy of melting and $\Delta H_{100}$ is the enthalpy of melting with 100% crystalline nylon 6, 190 J/g.22

A wide angle X-ray diffractometer (WAXD, d8 Advance, BRUKER MILLER Co.) was used to analyze the crystalline order of the produced PA6. Before the measurement, pelletized PA6 particles were hot pressed at 240 °C and cooled to room temperature to obtain a film. The spectra with Cu Kα radiation were recorded at 25 °C with a diffraction angle (2θ) of 5°–40°. Intrinsic viscosity [$\eta$] was measured, and the viscosity average molecular weight was calculated using the Mark–Houwink equation. The Ubbelohde viscometer was used to check the time for polymer solution to pass through the capillary with 90% formic acid at 25 °C. The molecular weight of PA6 resin was calculated as $[\eta] = k[M]^{a}$ with the Mark–Houwink constant, $k = 22.6 \times 10^{-3}$ (mL/g) and the power-law index, $a = 0.82$ for nylon 6 at 25 °C in a 90% formic acid solution.23

The rheological properties were measured using the Advanced Rheometric Expansion System (ARES, Rheometric Scientific). The samples were prepared by injection molding at 240 °C in a mold of 25 mm diameter and 1 mm thickness. Dynamic moduli (storage modulus ($G'$), loss modulus ($G''$)), and complex viscosity were measured between parallel plates at 250 °C with an applied strain of 10% in the linear viscoelastic range and angular frequency from 0.05 to 500 rad/s.

AUTHOR INFORMATION

Corresponding Author
Yongsok Seo – RIAM, School of Materials Science and Engineering, College of Engineering, Seoul National University, Seoul 08826, Korea; orcid.org/0000-0001-9560-797X; Phone: +82-2-880-9085; Email: ysseo@smu.ac.kr; Fax: +82-2-885-9671

Authors
Kyoungwan Oh – RIAM, School of Materials Science and Engineering, College of Engineering, Seoul National University, Seoul 08826, Korea
Hoyeon Kim – RIAM, School of Materials Science and Engineering, College of Engineering, Seoul National University, Seoul 08826, Korea

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c01962

Author Contributions
*K.O. and H.K. contributed equally to this work.

Notes
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