

# Kinetics of the Solid-State Polymerization of Nylon-6

JIAN-JUN XIE

Institute of Polymer Science and Engineering, Xiangtan University, Hunan, 411105, People's Republic of China

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**ABSTRACT:** The kinetics of the thermally induced solid-state polymerization (SSP) of nylon-6 were examined in both a fixed-bed reactor and a rotary reactor. Factors such as the regulator content, the reaction temperature and time, the particle size, the type and geometry of the nylon-6 prepolymer, the nitrogen gas flow rate, the water content of the nitrogen gas flow, and the polymerization process were studied. The results showed that the regulator content, the reaction temperature and time, and the particle size were the primary factors, and that the others were negligible. Moreover, the SSP rate and number-average molecular weight ( $M_n$ ) increased with increasing reaction temperature and time and decreasing particle size. The SSP rate and  $M_n$  had maximum values with increasing regulator content in an experimental range of 0.03–0.07 wt %. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 616–621, 2002; DOI 10.1002/app.10341

**Key words:** nylon 6; solid-state polymerization; kinetics; number-average molecular weight; end-group concentration

## INTRODUCTION

The solid-state polymerization (SSP) of nylon-6 is achieved by the heating of low molecular weight polymer (prepolymer) pellets below their melting temperature but above their glass-transition temperature. Polycondensation occurs, and the condensation byproducts can be removed by the application of a vacuum or an inert gas. The synthesis of high-quality and high molecular weight polyesters and polyamides is important for type cords and engineering plastics. This process is commonly performed at a temperature close to the melting point of the polymer (10–40°C lower). Under these conditions, the polymer end groups are sufficiently mobilized for the reaction to take place. The main polycondensation reaction is an equilibrium reaction, and byproducts, such as wa-

ter, are removed so that the forward reaction will be favored. The polycondensation rate depends on both chemical and physical processes, and there are three possible rate-determining steps:

1. Chemical reaction control: A reversible chemical reaction that includes microlevel end-group diffusion.
2. Interior diffusion control: Diffusion of the volatile reaction byproducts in the solid polymer.
3. Surface diffusion control: Diffusion of the volatile reaction byproducts from the surface of the polymer pellets to the inert gas.

Depending on the process and operating variables, the polycondensation rate is controlled by one or more of these steps. It is important to examine the control mechanism of the SSP process not only for optimizing process parameters but also for improving product quality.

The main factors that affect SSP include the reaction temperature and time, the size and type of the particle, the initial molecular weight, the

Correspondence to: J.-J. Xie (xiejjun12@263.net).

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number and type of chain end groups, the catalyst employed, the crystallinity, and the technique used for the removal of byproducts. Pilati<sup>1</sup> and Fakirov<sup>2</sup> provided two excellent reviews of the work in this area. Models, mechanisms, and kinetics for poly(ethylene terephthalate) (PET) have been widely studied, but very little has been published about nylon-6. Zimmerman<sup>3</sup> showed a tendency to broader than normal molecular weight distributions and a formula for the kinetics in studying the polyamidation equilibrium in the solid phase. Gaymans et al.<sup>4</sup> studied the factors influencing nylon-6 polymerization in the solid state, such as the starting molecular weight, heat treatment, and remelting. Heat treatment had little effect, but the starting molecular weight had a strong effect on the reaction rate. The higher the starting molecular weight was, the faster the reaction was. Gupta and coworkers<sup>5,6</sup> proposed two models of the SSP of nylon-6 and verified them with the experimental data of Gaymans et al. Mallon and Ray<sup>7</sup> developed a particle model of solid-state polycondensation that considered the polymer crystalline fraction and the concentrated end groups and condensate in the amorphous fraction. Xie and coworkers<sup>8–11</sup> studied the factors influencing SSP for nylon-6, proposed two models with monofunctional and bifunctional regulators, and verified the models with their experimental data. In this article, we discuss the mechanism and kinetics of the SSP of nylon-6.

## EXPERIMENTAL

### Materials

$\epsilon$ -Caprolactam (commercial-grade), 6-aminocaproic acid (analytical-grade), and 2,2,2-trifluoroethanol (analytical-grade) were supplied by BASF (Italy). Sulfuric acid (95–98%), 0.02 mol/L HCl and NaOH standard solutions, and benzoic acid (Chemical Reagent Company, Shanghai, China) were analytical-grade. Commercial nylon-6 chips were supplied by the Ninth Chemical Fiber Factory (Shanghai, China) and the Chemical Fiber Factory (Xuzhou, China).

### Melt Polymerization of Nylon-6 Prepolymer Chips

Nylon-6 prepolymer was made from the melt polymerization of  $\epsilon$ -caprolactam under a dry nitrogen gas flow according to the usual method<sup>8,12</sup> in an aluminum fixed bed that had four glass tubes

with an automated temperature-controlled system thermostated to an accuracy of  $\pm 0.5^\circ\text{C}$ . The tube reactor was 2.5 cm in diameter and 25 cm long. The rod-shaped polymers taken off the broken tubes were turned on a lathe and cut first into spiral rods and then into chips. The weighed samples were extracted with 20 times their weight of freshly distilled water at  $90^\circ\text{C}$  under 1 atm for 16 h and then were filtered and dried to a constant weight via heating to  $105^\circ\text{C}$  under a high vacuum. The self-made prepolymer chips were only used for discussing the effect of the regulator content and the particle geometry for the SSP of nylon-6.

### SSP

The SSP for prepolymer chips and commercial chips of nylon-6 was conducted in the same apparatus, temperature-controlled under a dry nitrogen flow, as the melt polymerization. The rotary reactor was the same as that used by Chang et al.<sup>13</sup>

### Analyses

The relative viscosity ( $\eta_r$ ) of nylon-6 for the prepolymer chips and the SSP samples was determined in 95.7% sulfuric acid as a solvent at  $20 \pm 0.1^\circ\text{C}$  with an Ubbelohde-type viscometer. The concentration for the measurement of  $\eta_r$  for the SSP of the nylon-6 samples was 0.01 g/mL. The number-average molecular weight ( $M_n$ ), which could be used to determine the number-average degree of polymerization, was determined with the following equation:<sup>14</sup>

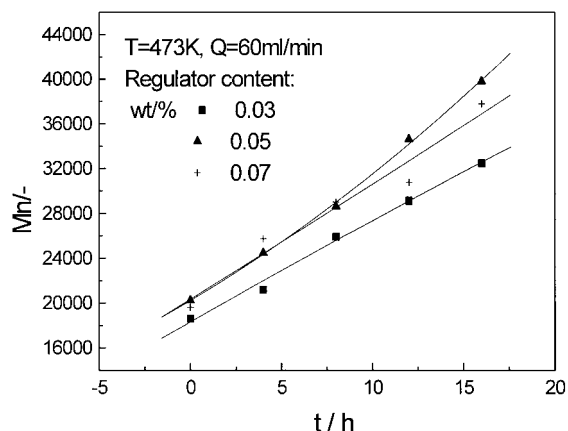
$$\bar{M}_n = 11500(\eta_r - 1) \quad (1)$$

Carboxy and amino end groups were determined by the titration of a 0.01 g/mL polymer solution in 2,2,2-trifluoroethanol at  $60^\circ\text{C}$  with 0.02 mol/L NaOH and HCl aqueous solutions, respectively.

## RESULTS AND DISCUSSION

### Effect of the Regulator Content

Figure 1 shows the effects of the different regulator contents on  $M_n$  at  $200^\circ\text{C}$  and nitrogen gas flow rate,  $Q_{\text{N}_2} = 60 \text{ mL/min}$ .  $M_n$  had a maximum value with the regulator content increasing from 0.03 to 0.07 wt % for the self-made prepolymer chips. This agrees with the results shown in Figure 2,



**Figure 1** Effect of the relative molecular mass regulator of the prepolymer on  $M_n$  for SSP in a fixed bed.

which displays the change in the end-group concentration with the progress of the reaction in the solid state. The reason is not clear and should be discussed in the future.

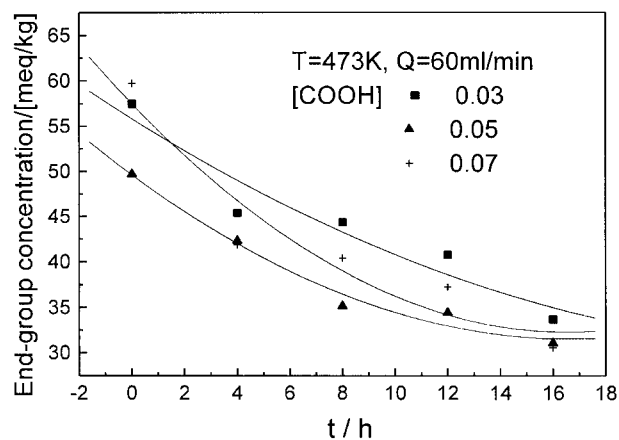
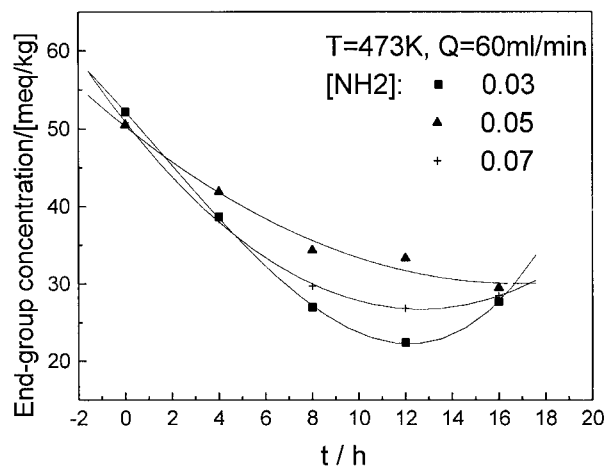
#### Effect of the Reaction Temperature and Time

Figure 3 shows the effects of the reaction temperature and time on  $M_n$  for the SSP of commercial nylon-6 chips.  $M_n$  increased with the reaction temperature and time. This agrees with the results of Huang and Walsh<sup>15</sup> for PET SSP. The higher reaction temperature accelerated the diffusion rate of the chain end groups and increased the reaction rate of SSP. Also, the longer reaction time increased the residence time and made the chain end groups of the longer distance diffuse to approach one another; this produced an easy reaction. Of course, the diffusion distance depended on the end-group concentration and its distribution. Initially, there was a homogeneous distribution. In the SSP, a change in the end-group distribution away from the homogeneous distribution was possible because some of the nearest end groups were reacting away while others remained frozen. The end groups of the longer distance diffused to approach one another and reacted when both the reaction temperature and time increased. Therefore,  $M_n$  increased. Meanwhile, the increase in the SSP reaction rate decreased with the reaction time increasing and the reaction temperature rising because the end-group concentration decreased with the increasing reaction time and rising reaction temperature. This was also verified by the results shown in Figure 4, which displays the change in the end-group concentra-

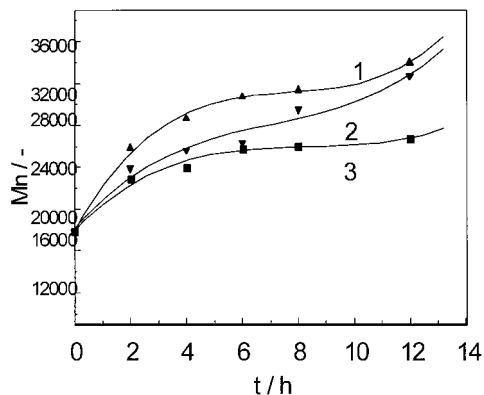
tion with the reaction temperature and time. The end-group concentration decreased with increasing temperature and time for the SSP of nylon-6.

#### Effect of the Nitrogen Gas Flow Rate

The effect of the gas flow rate on  $M_n$  at different reaction times and 200°C is shown in Figure 5. The gas flow rate hardly affected  $M_n$  and the SSP rate. The gas flow rate had a small effect on  $M_n$  at 4 h and  $Q_{N_2} < 100$  mL/min [Fig. 5(a)]. This could be experimental error because  $M_n$  had a distribution from the particle center to the particle surface and was maximum at the center of the particle for the SSP of poly(butylene terephthalate) (PBT).<sup>16</sup> The results of the end-group method also showed no change for  $M_n$  with the gas flow rate increasing from 50 to 200 mL/min [Fig. 5(b)], but



**Figure 2** Effect of the regulator contents on the end-group concentrations at 220°C and  $Q_{N_2} = 60$  mL/min in a fixed bed.

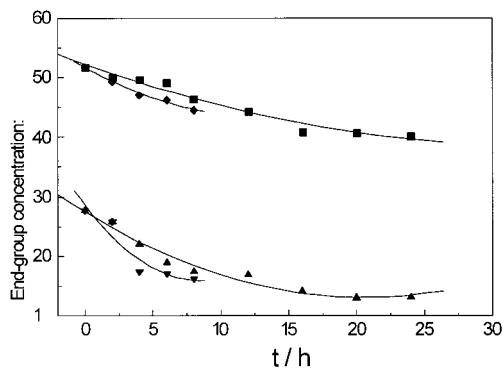


**Figure 3** Effect of different temperatures on  $M_n$  at  $Q_{N_2} = 60$  mL/min in a fixed bed: (1) 220°C, (2) 200°C, and (3) 190°C.

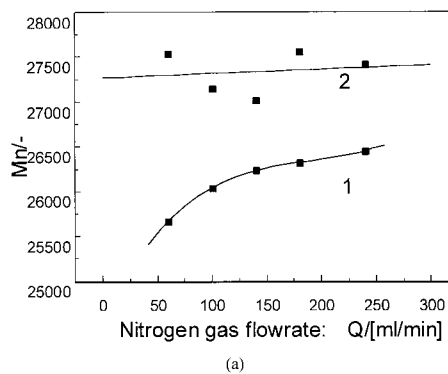
$M_n$  increased at  $Q_{N_2} = 240$  mL/min (which could also be experimental error). The results of the end-group-concentration measurements further verified that the aforementioned conclusion was correct because the end-group concentration did not change with the nitrogen gas flow rate increasing from 50 to 240 mL/min (Fig. 6). The SSP of nylon-6 was not an outside-diffusion-controlled process in the experimental range of the nitrogen gas flow rate. That is, the diffusion of the volatile reaction product (water) from the surface of the polymer to the inert gas was not controlled.

**Effect of the Particle Size**

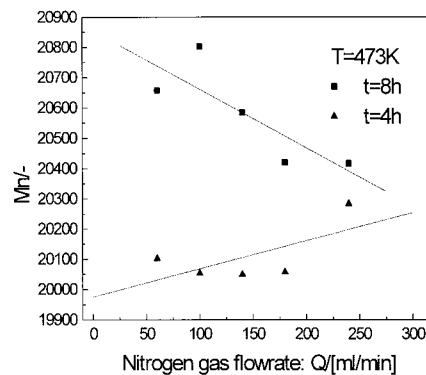
Figure 7 shows the effect of the particle size on the SSP rate and  $M_n$  at 190°C and  $Q_{N_2} = 60$  mL/min. The larger particles resulted in a lower SSP reaction rate and a lower value of  $M_n$ . Huang and Walsh<sup>15</sup> found for the SSP of PET that inte-



**Figure 4** End-group concentrations versus time at  $Q_{N_2} = 60$  mL/min in a fixed bed: (■) COOH and (▲)  $NH_2$  at 473 K and (◆) COOH and (▼)  $NH_2$  at 493 K.



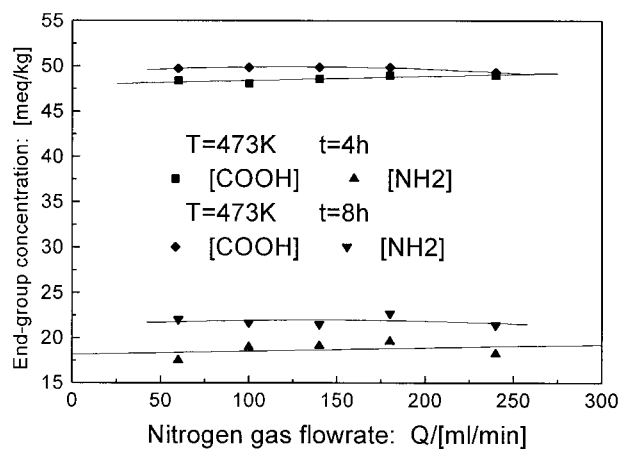
(a)



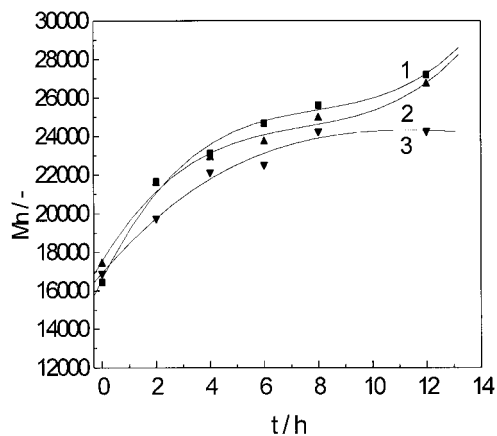
(b)

**Figure 5** Effect of the nitrogen gas flow rates on  $M_n$  at 200°C and different SSP times in a fixed bed: (a) viscosity method [(1) 4 and (2) 8 h] and (b) end-group method.

rior diffusion had more effect on the SSP reaction rate than surface diffusion when a large-particle sample was used and that at low reaction temper-

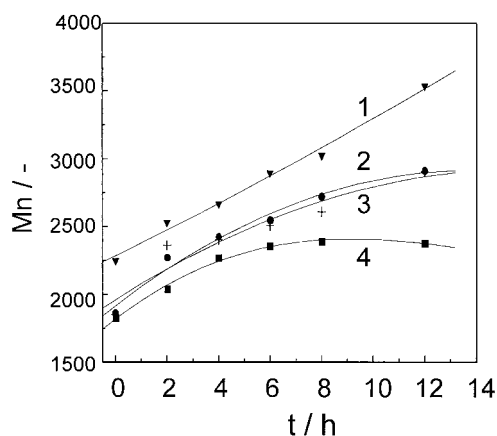


**Figure 6** Effect of the nitrogen gas flow rates on the end-group concentrations at different SSP times in a fixed bed.

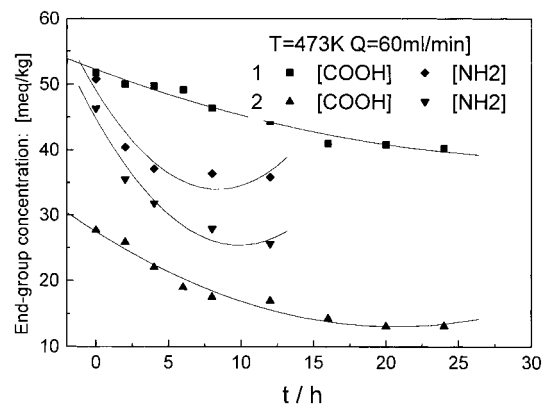


**Figure 7** Effect of the particle diameters on  $M_n$  at  $190^\circ\text{C}$  and  $Q_{\text{N}_2} = 60 \text{ mL/min}$  in a fixed bed. The equivalent diameters were (1) 0.98, (2) 1.2, and (3) 1.4 mm.

atures the SSP reaction rate for the large-particle sample was controlled first by chemical reaction, second by ethylene glycol (EG) diffusion from the solid polymer to the surface, and third by EG diffusion from the surface to the inert gas. At the experimental temperatures and nitrogen gas flow rates employed in this study, the water interior diffusion from the solid polymer to the surface was a controlled process for the SSP reaction rate in the experimental range used.



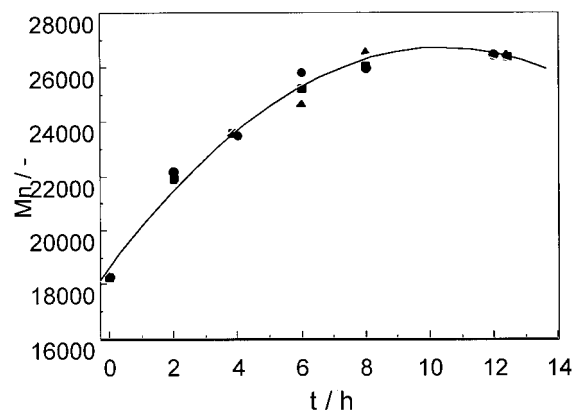
**Figure 8** Effect of the particle geometry of different prepolymer chips on  $M_n$  at  $190^\circ\text{C}$  and  $Q_{\text{N}_2} = 60 \text{ mL/min}$  in the rotary reactor: (1) chips from the Chemical Fiber Factory (Xuzhou, China), cylinder particle ( $\phi 1.50 \times 1.63 \text{ mm}$ , equivalent diameter = 1.4 mm); (2,3) self-made prepolymer, thin rectangular particle ( $2.0 \text{ mm} \times 4.0 \text{ mm} \times 0.5 \text{ mm}$ ); and (4) chips from the 9th Chemical Fiber Factory (Shanghai, China), cylinder particle ( $\phi 1.125 \times 1.82 \text{ mm}$ , equivalent diameter = 1.2 mm).



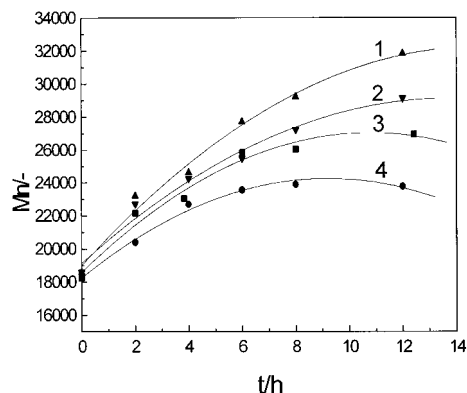
**Figure 9** Effect of the particle geometry on the end-group concentrations at  $220^\circ\text{C}$  and  $Q_{\text{N}_2} = 60 \text{ mL/min}$  in the rotary reactor: (1) chips from the 9th Chemical Fiber Factory, cylinder particle ( $\phi 1.125 \times 1.82 \text{ mm}$ , equivalent diameter = 1.2 mm), and (2) chips from the Chemical Fiber Factory, cylinder particle ( $\phi 1.50 \times 1.63 \text{ mm}$ , equivalent diameter = 1.4 mm).

#### Effect of the Particle Type and Geometry

Figures 8 and 9 give the values of  $M_n$  and the end-group concentrations, respectively, versus the SSP time for the different nylon-6 prepolymer chips in the rotary reactor. The particle geometry of the prepolymer had little effect on the SSP rate and  $M_n$ . The particle size, however, had an important effect on the SSP rate and  $M_n$  (Fig. 8). The particle size for curves 2 and 3 (self-made rectangular chips) was obviously smaller than that for curves 1 and 4 (cylinder chips). It can be inferred that the former was a chemical-controlled process



**Figure 10** Effect of the water content of nitrogen gas flow on  $M_n$  at  $190^\circ\text{C}$  and  $Q_{\text{N}_2} = 60 \text{ mL/min}$  in a fixed bed: (■) pure  $\text{N}_2$  saturated by water, (●) pure  $\text{N}_2$ , and (▲) pure  $\text{N}_2$  dried by silica gel.



**Figure 11** Effect of the different polymerization methods on  $M_n$  at 190°C and  $Q_{N_2} = 60$  mL/min: (1) fixed-bed reactor and 0.03 wt % regulator content, (2) rotary reactor and 0.03 wt % regulator content, (3) fixed-bed reactor and chips from the 9th Chemical Fiber Factory, and (4) rotary drum reactor and chips from the 9th Chemical Fiber Factory.

and the latter was an interior-diffusion-controlled process.

#### Effect of the Water Content of the Nitrogen Gas Flow

The effect of the water content of the nitrogen gas flow on the SSP reaction rate and  $M_n$  is shown in Figure 10. The water content of the nitrogen gas flow did not affect the SSP reaction rate and  $M_n$  for three experimental conditions: pure  $N_2$  saturated by water, pure  $N_2$ , and pure  $N_2$  dried by silicon gel. It can be inferred from the results that the water content produced by the SSP of commercial nylon-6 chips was lower than that required by outside diffusion controlled from the polymer surface to the inert gas. This further verifies that the SSP of nylon-6 was not an outside-diffusion-controlled process in the experimental temperature ranges used.

#### Effect of the Polymerization Process

Figure 11 shows the effects of the different polymerization processes on the SSP rate and  $M_n$ . The SSP rate and  $M_n$  in the rotary reactor were lower

than the SSP rate and  $M_n$  in the fixed-bed reactor for the same nylon-6 chips under the experimental temperature-controlled conditions. This can be explained by the temperature effect: the reaction temperature of the particle inside the rotary reactor was about 5°C lower than that in the fixed-bed reactor. Moreover, the reason that  $M_n$  with the longer polymerization time slightly decreased may be the oxidation of the nylon-6 chips with the increasing reaction time.

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