

# Investigations on the Simulation of the Reactive Extrusion of Nylon 6

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## SYNOPSIS

In this article, a novel simulation of the processing conditions of the anionic ring-opening polymerization of nylon 6 in a counterrotating twin-screw extruder by use of a modified Haake Rheometer run at elevated temperatures is described. Experimental results for several combinations of processing parameters are presented. General relations between processing parameters, conversion ratio, and molecular weight of the product are observed. These observations can be used in the eventual scaling up of investigations to an actual twin-screw extruder. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

More than 90% of commercial nylon 6 plastics are manufactured by condensation polymerization via epsilon-caprolactam dehydration.<sup>1</sup> The remainder is manufactured by monomeric cast molding (MC)<sup>2</sup> and reactive injection molding (RIM).<sup>3</sup> The conventional condensation-polymerized nylon 6 resin typically has the disadvantages of a low degree of polymerization, long polymerization period, low molecular weight, and wide molecular weight distribution due to a high viscosity in the later stage of the polymerization, which leads to poor transportation and mixing of heat and mass. These factors worsen the performance of nylon 6 resin and narrow its applications in industry. During recent years, the modern twin-screw extruder with multiple purposes has been used increasingly to overcome these problems and to manufacture better performing nylon 6 resins through a reactive extrusion process known as REX.<sup>4,5</sup>

Compared with condensation polymerization, the continuous reactive extrusion processing of nylon 6, in which the epsilon-caprolactam monomers are ring-opening polymerized directly, possesses three obvious advantages: (1) a short reacting time, generally sev-

eral minutes for REX rather than 10 h or more for the condensation polymerization; (2) no by-products coming out when the monomers are polymerized; (3) the ending nylon 6's molecular weight is several times that of condensation polymerization. Therefore, the nylon 6 product prepared through a reactive extrusion process has excellent properties and a lower cost, offering a profitable property-to-price ratio.<sup>6</sup> A number of companies in North America and Europe are now actively carrying out the investigation on this work and have been successful on the laboratory scale.<sup>4-6</sup> They will certainly continue to develop industrial applications for their findings, aiming at the establishment of the large scale production plants of continuous reactive extrusion process of nylon 6 plastics. But because of economic considerations, no details on experimental procedures or results on the reactive extrusion of nylon 6 have been published.

In order to simulate the operation conditions of the counterrotating twin-screw extruder, before buying an actual extruder, we designed a novel experiment for nylon 6 reactive extrusion with a modified Haake Torque Rheometer, and conducted a corresponding experimental study. In this article we describe this investigation. The influences of relevant factors on the anionic ring-opening polymerization of epsilon-caprolactam are discussed, and several experimental results, applicable to the scale up of nylon 6 reactive extrusion process to an actual twin-screw extruder, are presented.

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## EXPERIMENTAL

### Raw Materials and Chemical Reagents

The monomer used was Caprolactam  $\text{NH}(\text{CH}_2)_5\text{CO}$ , white crystalline powder, melting point:  $69.2^\circ\text{C}$ , from Toray, Japan. The chemical reagents used were sodium hydroxide of chemical purity grade, and newly distilled 2,6-toluene-diisocyanate (TDI), both from Shanghai No. 1 Chemical Reagent Factory.

### Haake Torque Rheometer

The Haake Torque Rheometer is usually used for compounding modification of plastics and simulation of process parameters during their molding. It is able to automatically measure and simultaneously record the relation curves between torque, temperature of plastic molten, and processing time. Its speed and temperature is adjustable, and it can be operated along with a small plastic processing device such as a banbury mixer, or a single or twin-screw extruder, as well as an afterprocess stretching device, etc.

Our experiment was conducted in a 60 g banbury mixer, which has four main features: (1) 50 mL mixing volume; (2) five options of rotors (the counterrotating roller type rotors were used in this work); (3) 5 kg loading weight; (4) three temperature pick up points and one torque pick up point. Because the initial monomeric molten of the caprolactam is less viscous, it is liable to leak out from the sealing surface of the mixer, which may be one of the main reasons why people have not been able to use it as polymerizing reactor so far. Therefore, we made a special well-sealed mixer and protected the system with Nitrogen in order to avoid the invasion of air into the anionic reacting system of caprolactam.

In the beginning of the polymerization, the caprolactam molten are homogenously mixed because of the lower molten viscosity and strong agitation of the rotors. As the reaction continues, the system viscosity increases rapidly. The molten are not only sheared by the rotors, but also pressed by loading weight. The high viscosity reactant system is then forced to be well mixed, as the interfaces between different reactant molten are placed in frequent contact, similar to the situation exerted by shearing and kneading part in the counterrotating twin-screw extruder. The strong mixing effect of the rotors obviously far exceeds that which can be obtained by a hand-made glass agitator in a beaker.

The experimental procedure is to heat up and rapidly stir the activated caprolactam molten, and then immediately put the activated reactant system

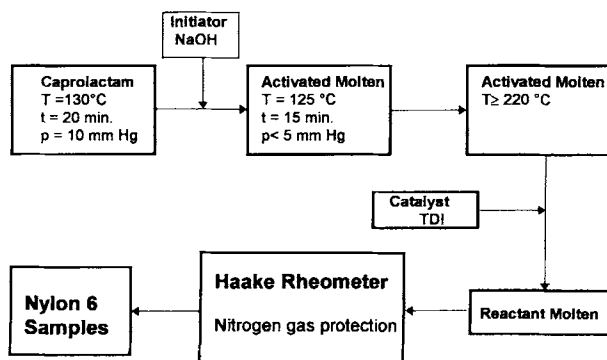
into a preheated, running, specially designed Haake Torque Rheometer to banbury, mix, and react. As soon as the desired process time is reached, the end product is taken out.

### The Preparation of the Activated Molten

Our experiment is greatly different from both MC and RIM processes at normal temperature in that the polymerization is completed at a temperature higher than the melting point of nylon 6, i.e.,  $220^\circ\text{C}$ . Fundamentally, the preparations of the activated molten are similar for both processes, but when used in reactive extrusion process, the preparation should be based on careful consideration of the repeatability of the experimental results. The quality of raw materials, the vacuum time, and the vacuum pressure were kept uniform for every batch. In addition, each batch of the activated molten were divided into several parts to banbury separately during experiment, in order to compare the experiment's repeatability.

### The Synthesis Process Procedure

The synthesis of nylon 6 consisted mainly of four steps. First, caprolactam monomer was heated to below  $130^\circ\text{C}$  and vacuumed in a beaker to remove water content. Then the initiator solution of NaOH was added to the monomer molten to make activated molten. The vacuuming was continued so as to expel residual water content from the molten. Next, the molten were heated over  $220^\circ\text{C}$  in the beaker, according to each scheduled experiment requirement (this initial polymerizing temperature was one of the variables investigated). Finally, the catalyst TDI was added and the reactant molten were immediately poured into a rheometer at setting reaction temperature. The synthesis process procedure can be simply described by the following flow chart:



### The Measurement of Conversion Ratio

Nylon 6 resins with NH and CO groups are strong polar polymers, which readily absorb moisture water from ambient air. Therefore, in order to obtain the dry weight of the samples, they were first pelletized, weighed, and then put into an oven to dry at 150°C until their weight no longer changed with time. This weight was denoted by  $M_0$ . The samples were then placed in an extractor filled with distilled water as a solvent, and left for 24 h in order to remove residual unpolymerized caprolactam monomers. The samples were then oven dried until their weight again became constant. The weight of the extracted samples is designated as  $M_*$ . The conversion ratio  $G$  is then

$$G = \frac{M_*}{M_0} \times 100\% \quad (1)$$

### The Measurement of Molecular Weight

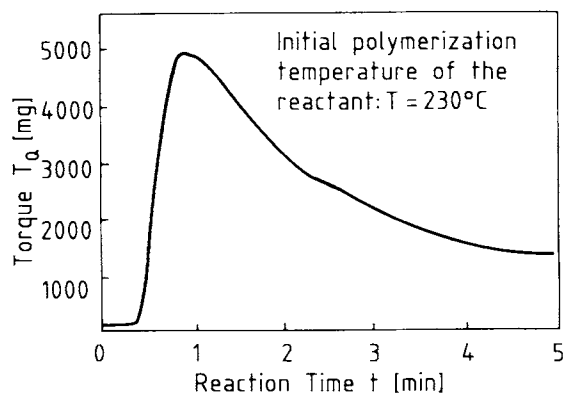
The molecular weight of the samples was determined through viscosity measurement using 93% sulfuric acid as a solvent to prepare nylon 6 dilute solution. The relative viscosity  $\eta_r$  was measured with an Ubbelohde viscosimeter as:

$$\eta_r = \frac{t}{t_0} \quad (2)$$

where  $t$ ,  $t_0$  are flow time of the dilute solution and solvent, respectively. The specific viscosity  $\eta_{sp}$  is defined as

$$\eta_{sp} = \eta_r - 1 \quad (3)$$

and the intrinsic viscosity  $\eta$  is given as



**Figure 1** The relation between torque and polymerization time (a).

$$\eta = \frac{-1 + \sqrt{1 + 1.4\eta_{sp}}}{0.75} \quad (4)$$

Therefore, the viscosity average molecular weight  $\bar{M}_\eta$  of the samples can be determined by the empirical (five-point method) eq. (5) according to data reduction:

$$\bar{M}_\eta = 113 (132.68 \eta - 5) \quad (5)$$

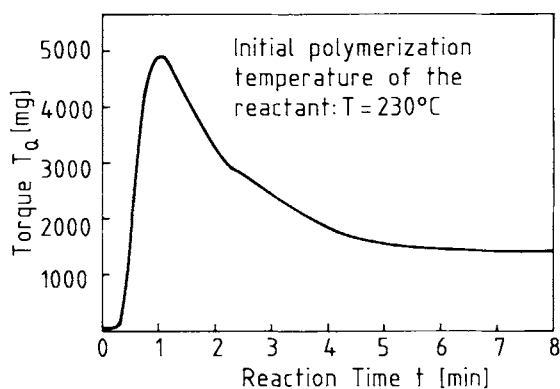
## RESULTS AND DISCUSSIONS

Our results and discussions on the experimental data of nylon 6 anionic ring-opening polymerization are based on mixing ratios of initiator (NaOH) and catalyst (TDI) to caprolactam (CL) of 0.14 g/100 g and 0.115 g/100 g, respectively. The polymerization time is taken as 5 min.

### The Relationship between Torque and Polymerization Time

Figure 1 shows the relationship between torque and polymerization time of the caprolactam activated molten under the initial polymerization temperature of 230°C. Because the torque of the system is related to its viscosity, the measured magnitude of the torque can be used to characterize the variation of the viscosity indirectly. In the first 20 s, the system viscosity is very low and almost constant. After 20 s, the viscosity increases very rapidly, and the polymerization approaches completion. Its torque climbs to a maximum value within approximately 1 min. After this, the extension of polymerization time primarily serves to increase conversion ratio, and has less effect on the magnitude of the molecular weight.

The operation conditions of Figures 1 and 2 are almost the same except for the difference of polymerization time. It can be seen clearly from both of them that as the polymerization time increases, the viscosity of the system at first drastically decreases, and then stabilizes, for about 5 min. This situation may be attributable to three reasons. One is that the polymerizing heat causes the system temperature to increase, and, thus, lowers the viscosity. Another is that at elevated temperatures the sodium ions in the remaining initiators result in thermal degradation. The third is that the shear action of the rotors leads a mechanical degradation. A combination of the above factors finally cause the significant drop of molecular weight and make the corresponding system torque decrease drasti-



**Figure 2** The relation between torque and polymerization time (b).

cally. The above results obtained in the Haake Torque Rheometer imply that when using a counter-rotating twin-screw extruder to perform nylon 6 reactive extrusion, it is necessary to strictly control the residence time of reacting molten in the barrel of the extruder so as to avoid severe thermal degradation.

Of course, a short residence time for an ascertained length of screw means a high screw speed, i.e., a higher shear rate. This gives rise to mechanical degradation. Therefore, in practice, one should attempt to balance these process conditions to obtain a suitable molecular weight. In addition, at elevated temperatures, the amount of the alkali initiator should be strictly controlled so as to reduce the amount remaining in the barrel and thereby limit the corresponding thermal degradation. If possible, some inhibitors could be put in from a lateral port of the barrel, to improve the thermal stability of the initiator and to avoid this degradation. Similar initiators currently available for conventional monomeric cast molding should, thus, be modified so as to be suitable for the reactive extrusion process at elevated temperature.

### The Relationship Between Temperature and Reaction Time

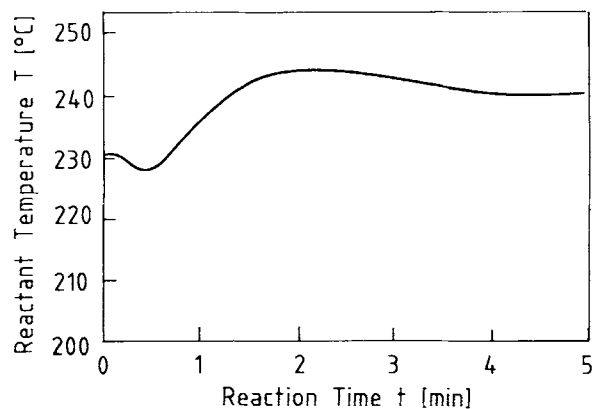
The anionic ring-opening polymerization of the caprolactam is a typical exothermal process. One can usually know the polymerization extent of the system, i.e., the change of conversion ratio, through the observation of the change of the system temperature, because conversion ratio and temperature variation curves of caprolactam are very similar to each other.

Figure 3 gives a typical relation of the temperature increase of the reactant system with reaction time

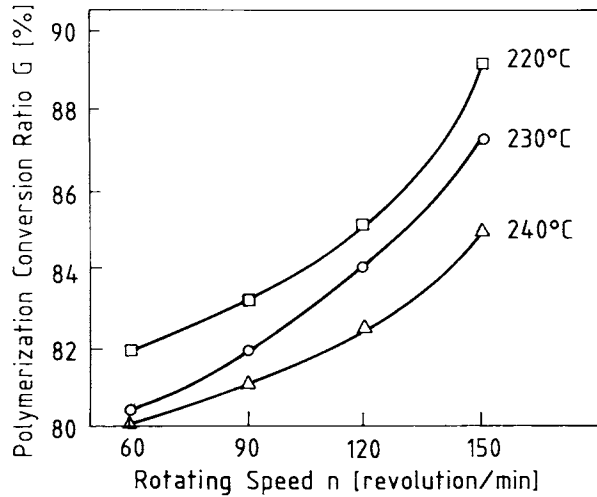
of nylon 6 anionic ring-opening polymerization obtained by a Haake Rheometer. During the experiment, the increase of system temperature gradually decreases with the increase of the initial polymerizing temperature of the reactant. For example, setting the rotating speed at 120 revolutions per minute (rpm), the temperature increase caused by reaction is 26°C if one starts at an initial temperature of 220°C, the temperature increase is 17°C for a starting initial temperature of 230°C, and 14°C for a starting initial temperature of 240°C. This shows that when one arranges the screw element configuration of a twin-screw extruder, the amount of heat exchange involved in every segment of the barrel should be considered carefully to fit with this temperature increase to maintain a suitable temperature profile in the barrel. Otherwise, it may influence the microstructural morphology and performance of the end product significantly.

### The Relationship between Conversion Ratio and Rotating Speed

Figure 4 indicates that at constant initial polymerization temperature, the higher the rotating speed, the higher the final conversion ratio. It contributes to the polymerizing area because the higher rotating speed leads to the faster variation of the rotor surface, making more contact opportunities between interfaces of the activated molten due to high mixing ratio of their surface area over volume, and, thus, reaching a completed polymerization. But the higher conversion ratio may be predicted only within a reasonable speed range. If the speed is over some suitable values, it may lead to a drop of the conversion ratio, as too high a speed will result in too high a shear rate exerted on reactant molten, giving more



**Figure 3** The relation between system temperature and reaction time.



**Figure 4** The relation between conversion ratio and rotating speed, for three initial reactant temperatures.

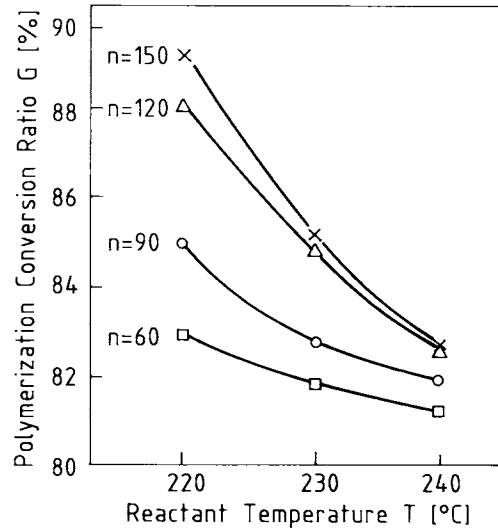
opportunities to break the macromolecular chains. This will inhibit further reaction of the molten and, thus, decrease the conversion ratio.

#### The Relationship between Conversion Ratio and Reactant Temperature

The relationship between conversion ratio and initial polymerization temperature of the reactant is shown in Figure 5. It is obvious that the conversion ratio decreases with the increase of the initial polymerizing temperature at the same rotating speed, because the anionic ring-opening polymerization of caprolactam is a typical exothermal process. Figure 6, reproduced from ref. 2, indicates an equilibrium relationship between nylon 6 polymer and caprolactam monomer in the later stage of the polymerization. When setting the initial polymerization temperature of the reactant at a higher level, the system temperature in the later stage of polymerization correspondingly goes up and the equilibrium point shifts back, resulting in a loss of conversion ratio of the end products. In the present experiment, the measured value of polymerization conversion ratio is in good agreement with that of Figure 6 for reactant temperatures over 220°C.

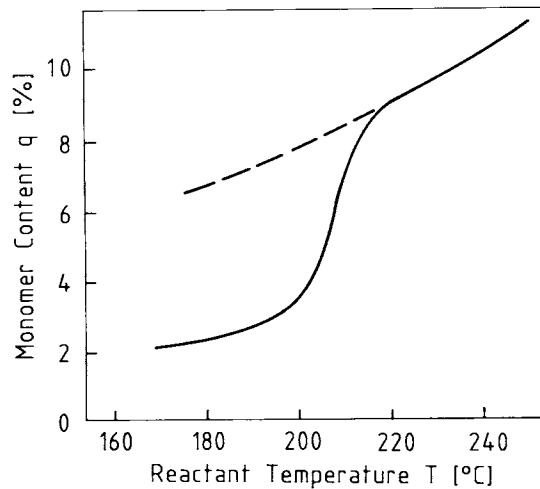
#### The Relationship between Molecular Weight and Reactant Temperature

Under the condition of the same rotating speed and reaction time, the molecular weight of the end products goes down with the increase of the initial polymerizing temperature, as shown in Figure 7.

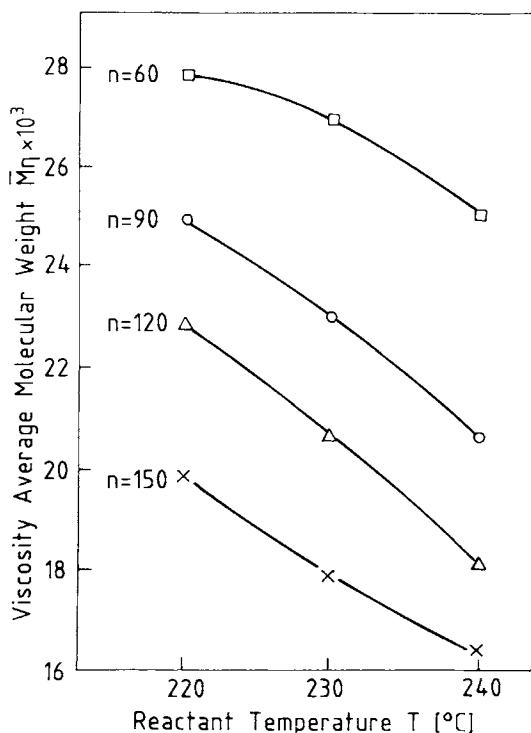


**Figure 5** The relation between conversion and initial reactant temperature, n: rotating speed (rev./min).

This may result from two reasons. One is the reverse movement of the polymerization equilibrium due to the higher initial temperature, terminating the growth reaction of the monomer too early. The second is that the increase of the temperature enhances the thermal and mechanical degradation and finally leads to a decrease of the molecular weight of the ending products. It can be predicted that the molecular weight of the polymer will be as high as 70,000 to 80,000, which approaches that of conventional monomeric cast nylon 6, if one takes sample at the peak time shown in Figure 1,



**Figure 6** The equilibrium level of caprolactam monomer and nylon 6 polymer at different polymerization temperatures.



**Figure 7** The relation between molecular weight and initial temperature of the reactant.

i.e., polymerizing reaction time of 1 min rather than that of 5 min.

### The Relationship Between Molecular Weight and Rotating Speed

The results shown in Figure 8 demonstrate that the molecular weight drastically drops off with the increase of rotating speed. The explanation for this is that the shear rate increases with rotating speed, causing intense mechanical degradation and a drop in the molecular weight.

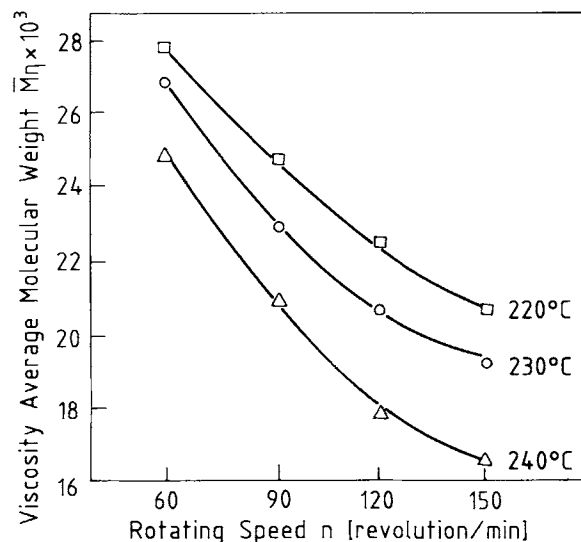
### CONCLUSIONS

In accordance with the above discussions and analysis, the following conclusions have been drawn:

1. The modified Haake Torque Rheometer used in our study is a closed system, and works at a high shear rate and elevated temperature. These conditions are substantially similar to those of nylon 6 polymerization in the reaction segment of a counterrotating twin-screw extruder. Our experimental results, then, can serve as a reference for the actual environ-

ment of the twin-screw extruder. Therefore, the simulation of nylon 6 reactive extrusion using a rheometer as a reactor is a simple and practical laboratory method of characterizing large-scale production. It also provides both an effective and economically feasible method for the simulation of reactive extrusion of other polymers with cyclized monomer molecular structure, such as nylon 10, nylon 12, their associated copolymers, etc.

2. The polymerizing rate of nylon 6 anionic ring opening is quite fast. Generally, the period to complete the polymerization is under 1 to 2 min. Undue extension of polymerizing time will cause an intense thermal degradation, resulting in severe reduction of the molecular weight. It is concluded that the control of the residence time in the barrel of a twin-screw extruder during reactive extrusion processing of nylon 6 is crucial.
3. In the later stage of the anionic ring-opening polymerization of nylon 6, there is an intense thermal degradation that is dependent on initiator type, residence time, and polymerizing temperature. In order to depress the thermal degradation caused by the initiator, one should add an inhibitor to improve the thermal stability of the initiator from a lateral port along the extruder barrel.
4. The conversion ratio of the monomeric caprolactam increases with increasing rotating speed, and decreases with increasing the ini-



**Figure 8** The relation between molecular weight and rotating speed, for three initial reactant temperatures.

tial polymerizing temperature within a definite speed range.

5. The molecular weight of the end product decreases with increasing rotating speed and decreases with increasing temperature, given the same compound and polymerization time.

One of the authors (Z. G. Yang) is now working as a guest scientist in the Institute of Polymer Research in Dresden. He appreciates the financial support by both the Excellent Youth Science and Technology Venus Program of Shanghai, Contract No.93QE14004, and the Foundation of the Institute of Polymer Research in Dresden for this work.

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