Continuous Polymerization of ω-Lauryl Lactam in an Intermeshing Corotating Twin-Screw Extruder

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ABSTRACT: This article describes the synthesis of poly(ω-lauryl lactam) by a reactive extrusion process. Anionic ring-opening polymerization was performed in an intermeshing corotating twin-screw extruder. We investigated the evolution of conversion of ω-lauryl lactam as a function of reaction time, screw speeds, different feed rates, and different screw configurations along the screw axis in a twin-screw extruder. For comparison with continuous polymerization in a twin-screw extruder, we studied polymerization in an internal mixer, which was considered a batch reactor. We found the final conversion of ω-lauryl lactam made in a twin-screw extruder was higher than in an internal mixer. Higher molecular weights are found at lower screw speeds and feed rates. Melt viscosities and mechanical properties of the polymers were measured. Residence time, molecular weights, and shear mixing have the main effect on the mechanical properties of products. The twin-screw extruder performance was interpreted in terms of commercial software. It was found that twin-screw extruder reaction rate was higher than those in the batch reactor and increased locally with screw speed and feed rate. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1605–1620, 2005

Key words: reactive extrusion; twin screw extruder; polyamide 12

INTRODUCTION

Since the discovery of rapid anionic polymerization of lactams in the 1950s, it has received considerable attention.[1–9] Kralicek and Sebenda[1–4] in the Institute of Macromolecular Chemistry in Prague and Mottos et al.[5–11] of Monsanto in the U.S.A. discovered massive cocatalytic influence of certain imides on the anionic polymerization of ε-caprolactam. If an equivalent amount of N-acetylcaprolactam was added to sodium ε-caprolactam, the rate of polymerization increased by several orders of magnitude. Even a small addition led to an immediate jump in the rate of polymerization.

This literature on lactam polymerization almost completely concerns ε-caprolactam. There has been little in the literature on the polymerization of other lactams.[12–15] Beyond the work of Ha and White,[15] there has been little information on the continuous reactive extrusion process of ring-opening polymerization of ω-lauryl lactam.

Research on polymerization ω-lauryl lactam was begun in the late 1950s and led to commercial production of lactam by Huls and Emser Werke in 1966 and Aquitaine Organico in 1971 based on ω-lauryl lactam produced from butadiene. Ube Kosan subsequently began producing 12-aminododecanoic lactam mono-

mer, made from cyclohexane rather than butadiene. They also commercially developed polyamide 12. Recently, the Swiss EMS Chemie Co. and Japan Ube founded a joint company (now Ems-Grivory) in 1992. They synthesize lauryl lactam and produce several grades of polyamide 12 from ω-lauryl lactam by a hydrolytic process under high temperature and pressure.

In the present article, it was our intention to make a fundamental study of reactive bulk polymerization of ω-lauryl lactam in an internal mixer as well as a twin-screw extruder. It involved comparison of evolution of conversion of their products, which could be synthesized in a batch reactor and twin-screw extruder, investigations of differential scanning calorimetry (DSC) measurement, thermogravimetric analysis (TGA) measurement, rheological properties, molecular weight, melt viscosity, and mechanical properties.

EXPERIMENTAL

Materials

The basic material used in this study was ω-lauryl lactam (LA), which was obtained from EMS Chemie Inc. (Sumter, SC). LA's appearance is a white flake. Its melting point is 150°C and boiling point is 280°C. The molecular weight is 197.

Sodium hydride (NaH) was used in this study as an anionic ring-opening polymerization initiator. This was obtained form Aldrich Chemical (Milwaukee, MI). Its

molecular weight is 24 and its density is 1.396. It reacts explosively with water and ignites spontaneously on standing in moist air. It is a gray-white power. *N*-acetyl-caprolactam $[(CH_2)_5CONCOCH_3]$ was used as a liquid in this study as an anionic ring-opening polymerization coinitiator. Its molecular weight is 155.2; its density is 1.094, and its boiling point is 134–135°C/26 mmHg. This was obtained from Aldrich Chemical.

A commercial polyamide 12 (PA 12) (Ube nylon 12 3024U, Japan), which is a homopolymer supplied by Ube, was also investigated. The polymer has a melting point at 174°C and is supplied in the form of spherical pellets. Because of the sensitivity of LA monomer to atmospheric humidity, we dried it at 80°C over 24 h in a vacuum oven before the polymerization.

Apparatus

Internal mixer

The polymerization of monomer was carried out in a Brabender Plasti-Corder laboratory internal mixer (PL 2000; C. W. Brabender Instrument Inc., NJ) to optimize the reaction parameters and to make a comparison with reactive extrusion. It has a chamber, tangential rotors, argon purging system, heaters, and a temperature control/monitor/record assembly. The chamber of the mixer holds up to 80 ml. The fill factor of raw materials was 0.75.

Twin-screw extruder

All reactive extrusion was carried out with a Japan Steel Works Labotex 30 twin-screw extruder (The Japan Steel Works, Ltd., Hiroshima, Japan). It is a modular intermeshing corotating twin-screw extruder which has screw and kneading disc block elements.

The corotating elements have self-wiping screw characteristics.[16,17] This twin-screw extruder has a barrel section with electric heaters and water cooling systems. The screw diameter is 30 mm; the center line distance is 26 mm, and an active barrel length is 975 mm (L/D = 32.5).

Reactive processing

Polymerization in an internal mixer

Monomer, initiator, and coinitiator were premixed in a dry box under purging argon gas, which is useful to avoid initiator being killed in open air. These were fed into the chamber of the internal mixer. The residence time in the internal mixer was usually measured after feeding the premixed monomer and initiator as well as coinitiator. It is necessary to determine the amount of monomer and initiator including coinitiator to see the optimum condition of polymerization.

Twin-screw extruder processing and residence time distribution

The residence time distribution and mean residence time for the various screw configurations were measured by introducing aluminum flakes (10 g) into the hopper of the twin-screw extruder by using polyamide 12 material. The sample was subsequently placed in a furnace and polyamide 12 was burned away.

The aluminum flakes were weighed in a Mettler AE200 balance to determine the concentration of aluminum flakes in each extruded sample. Residence time distribution functions were calculated by using the equation[18]

$$E(t) = \frac{C(t)}{\sum\limits_{0}^{\infty} C(t)\,\Delta t} \tag{1}$$

where t is time and $C(t)$ is the tracer concentration.

The mean residence time defined by

$$\bar{t} = \frac{\sum\limits_{0}^{\infty} t\,C(t)\,\Delta t}{\sum\limits_{0}^{\infty} C(t)\,\Delta t} \tag{2}$$

was calculated. A predetermined amount of monomer and initiator including coinitiator were premixed in a dry box and fed into the hopper.

In our polymerization experiments, we used two different screw configurations, which consist of (1) one set of kneading disc blocks and (2) three kneading disc blocks, respectively (see Fig. 1). Feed rates of 1 and 3 kg/h were used. Screw speeds of 50, 100, and 200 rpm were used in this study. Monomer and initiator were fed into the hopper. The machine was purged with nitrogen gas.

Product characterization

The degree of conversion of LA to polyamide 12 was determined as follows. We dissolved 5 g of polymerized polyamide 12 in 200 ml of *m*-cresol. We subsequently added this into an excess amount of methanol under a condition of rapid agitation, using Soxhlet extraction for 12 h. Unreacted monomer and oligomers were removed from the polyamide 12 in this manner. We then filtered and dried the precipitates in a vacuum-drying oven for 48 h at 100°C. The weight of the polymer divided by the initial weight of the monomer was taken as the degree of conversion.
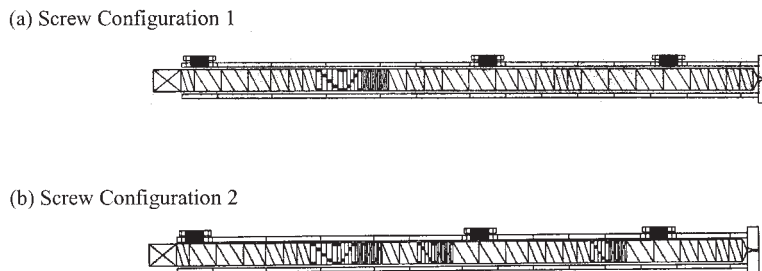
(a) Screw Configuration 1

(b) Screw Configuration 2

Figure 1 Screw configurations used for reactive extrusion in a twin-screw extruder. (a) Screw Configuration 1 (b) Screw Configuration 2.

The thermal transition behavior of products was determined by DSC (9900 thermal analyzer; DuPont, New Castle, DE) in the temperature range of -100 to $250°C$. A heating rate of $20°C/min$ was used. The sample weight was about 10 mg, and the flow rate of N_2 was 35 mL/min.

TGA (Thermal Analyzer 9900, DuPont) was used to investigate thermal stability of the products. The scanning rate was $20°C/min$ and the initial weights of the samples were $\sim$ 15–20 mg. The temperature range investigated was $25–600°C$. The flow rate of N_2 was set at 30 ml/min. A 5% weight loss was considered to be indicative of decomposition temperature.

The complex shear viscosity $[\eta^*(\omega)]$ of products was determined in the parallel disc dynamic oscillation mode using the Advanced Rheometric Expansion System (ARES; Rheometric Scientific Inc., NJ) with low-pressure purging from a liquid nitrogen source. The temperature was $190°C$.

An Instron test machine (Canton, MA) is used to measure the tensile mechanical properties of products. The samples are prepared by compression molding at $200°C$ and were cut into dumbbell-shaped specimens of ASTM D 638 Type V. The tensile properties were measured with an Instron model 4204 mechanical tester at room temperature and a crosshead speed of 10 mm/min with a 1-KN load cell. For each sample, at least five specimens were tested.

RESULTS

Polymerization in an internal mixer

The polymerization of LA was carried out in an internal mixer (Brabender Plasti-Corder) under argon gas. The initiator and coinitiator were sodium hydride and *N*-acetylcaprolactam, respectively. The temperature and torque were recorded as a function of time during the polymerization.

Figure 2 shows temperature and torque measurement for anionic ring-opening polymerization of LA in an internal mixer as a function of time. The reactants were fed at room temperature into the chamber of the internal mixer, which was at $200°C$ at the be-

ginning of the process. The material temperature was increased to $125°C$ when the reactants were first introduced into the chamber. The temperature then increased above the set temperature and subsequently gradually decreased to the set temperature. The temperature reached a stable state after 130 s. It remained substantially constant throughout the reaction. The torque gradually increased with time and then reached a maximum at 130 s.

Figure 3 shows the experimentally observed conversion as a function of time at different temperatures. We found 300 s was sufficient time to reach 90% conversion at $200°C$. We found increasing the temperature results in high conversion of LA at $[M]/[I] = 35$, 100 rpm, in an internal mixer.

Figure 4 shows the effect of concentration ratios $[M]/[I] = 35, 100, 1000$ at $200°C$ on conversion as a function of time. The reaction begins after about 1 min. We found increasing initiator concentration led to shorter time to reach final conversion.

Polymerization in a twin-screw extruder

The residence time distributions for modular intermeshing corotating twin-screw extruder were experimentally determined. We used a commercial polyamide 12 (Ube 1024®) at a barrel temperature at $200°C$, and screw speed of 200 rpm to determine residence time distribution in a twin-screw extruder. These results are shown in Figure 5. The mean residence time at 1 and 3 kg/h were 427 and 206 s, respectively, as determined by using delta function input of aluminum flakes into the first hopper after the machine achieved steady state.[18]

To investigate the effect of residence time in the twin-screw extruder, the evolution of polymerization conversion was investigated at different locations along the screw axes. To further investigate conversion of polymerized samples along the screw axis during continuous reactive polymerization, we carried out screw pulling experiments at various conditions at a screw speed of 200 rpm, feed rate of 1 and 3 kg/h, and a processing temperature of $200°C$. This was for Screw Configuration 2.
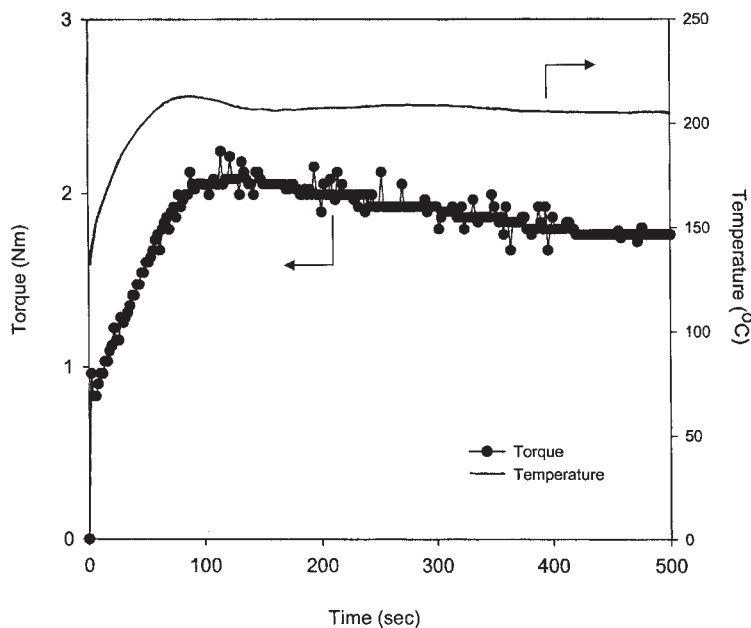
Figure 2 Temperature and torque measurements for anionic ring opening polymerization of ω-lauryl lactam at 200°C in Plasti-corder internal mixer.

After reaching steady conditions, the twin-screw extruder was stopped and subsequently cooled down to room temperature. We then reheated the machine until we could pull out screws from the barrel. This enables us to measure conversion as described earlier along the screw axis.

Figure 6 shows the level of conversion of LA along the screw axis, which we obtained for samples removed from cooled down screw. This experiment was variously performed with screw speeds of 50, 100, 200 rpm, a feed rate of 1 kg/h, and a barrel temperature of 200°C. The degree of conversion increased rapidly and was completed in the first kneading disc block region, which ranged between ~ 10 and 15 in L/D ratio.

We also did experiments at 3 kg/h feed rate. We found again lower screw speeds gave slightly higher conversion and again all conversion occurred in the first kneading disc block. We compared conversion along the screw at different feed rates. This is shown in Figure 7. Compared to Figure 6, we found that high
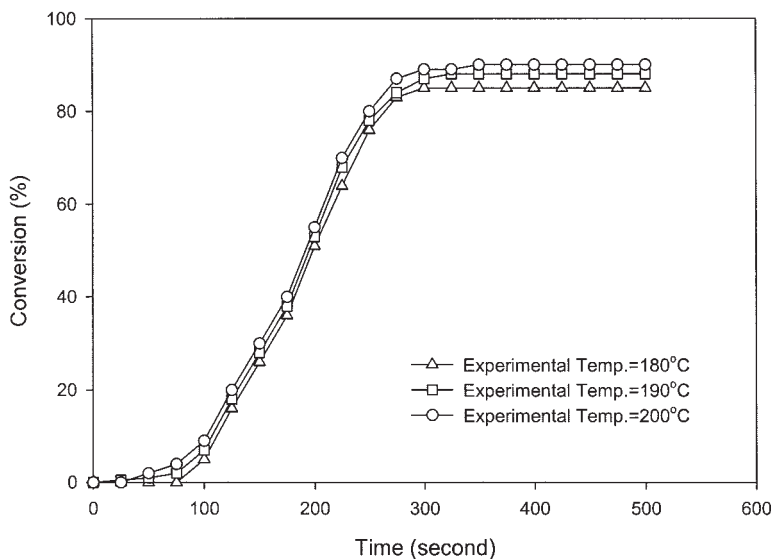

Figure 3 Evolution of conversion of ω-lauryl lactam as a function of reaction time in an internal mixer at 180, 190, and 200°C with 100 rpm at $[M]/[I] = 35$.
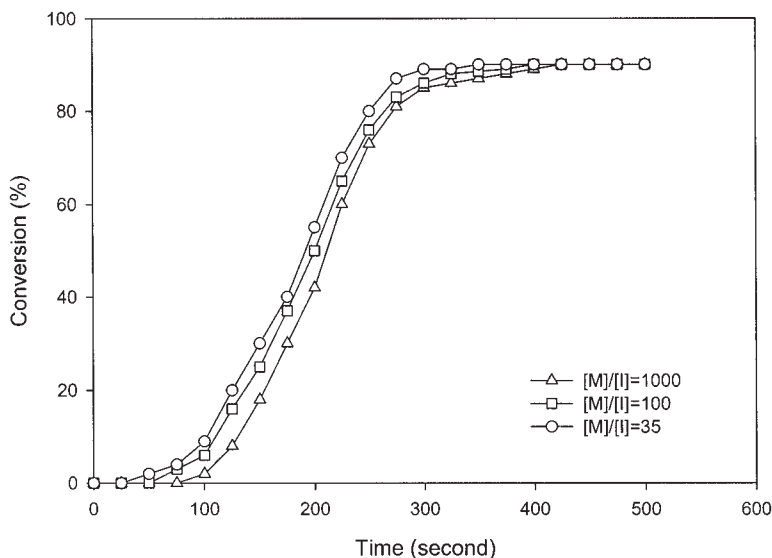
Figure 4 Evolution of conversion of ω-lauryl lactam as a function of reaction time in an internal mixer for different $[M]/[I]$ = 35,100, and 1000 at 200°C, 100 rpm.

feed rates gave lower conversion at the same screw position. Lower screw speeds at same feed rate gave slightly higher conversion and more likely all conversion was immediately following the first kneading disc in the first.

Thermogravimetric analysis

The polymerization products produced by ring-opening polymerization in batch reactor and in a twin-screw extruder were evaluated by TGA, as shown in Figure 8. It is compared to commercial polyamide 12. The products produced in a batch reactor began to exhibit weight loss at $\sim$ 200°C.

The products polymerized in a twin-screw extruder at 200°C of barrel temperature, screw speed of 200 rpm, and 1 kg/h feed rate showed very similar thermal traces as commercial polyamide 12. It was found that our twin-screw polymerized polyamide 12 had only a slightly lower percentage of mass residue over
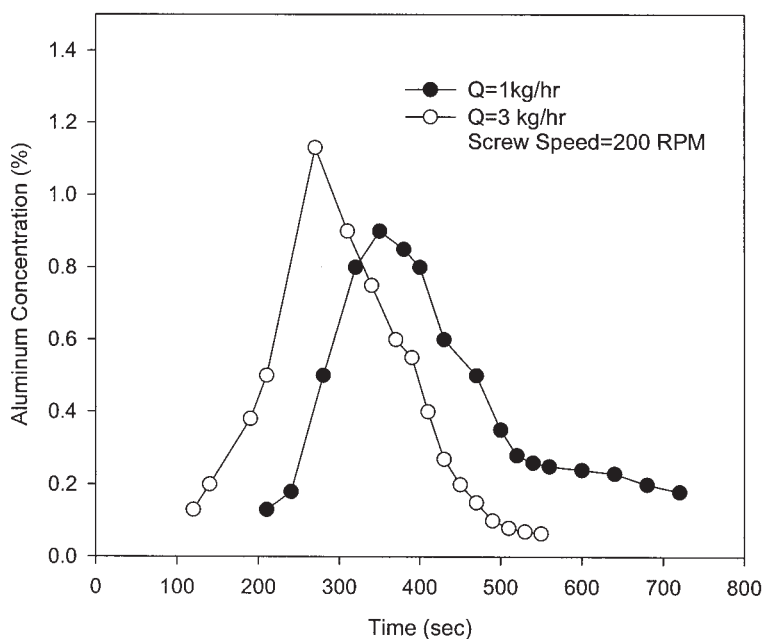

Figure 5 Residence time distribution of polyamide 12 at Q = 1 and 3 kg/h, screw speed of 200 rpm, and barrel temperature of 200°C in a modular corotating twin-screw extruder.
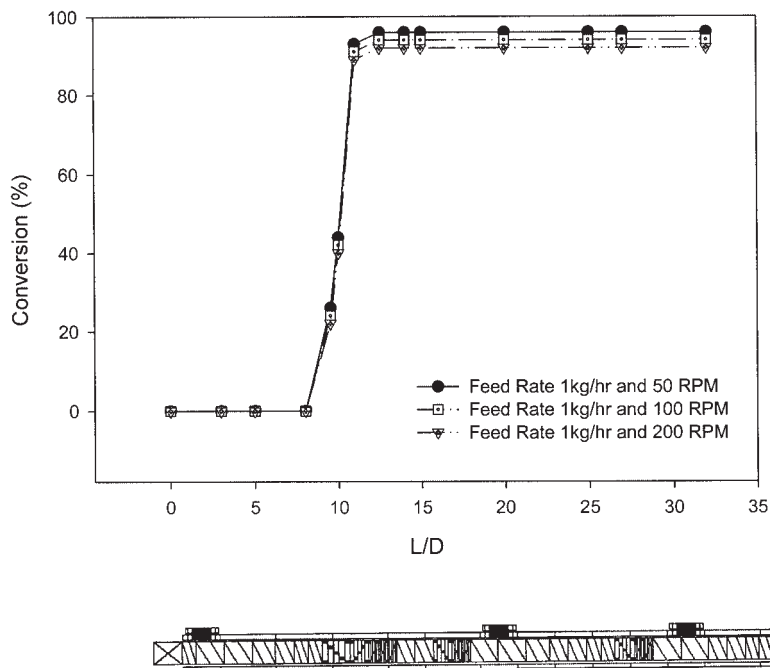
Figure 6 Evolution of conversion of ω-lauryl lactam along the screw axis at different screw speeds at 200°C, and feed rate of 1 kg/h.

300°C when compared to commercial polyamide 12 in TGA. The difference of mass residue of polymerized polyamide 12 and commercial polyamide 12 is very small. That means the final product polymerized contains a very small amount of monomer and oligomers.

Although some volatiles are seen at 280°C, complete degradation occurs at 420°C.

When we also compared TGA results of polymerized polyamide 12 in a twin-screw extruder with that in an internal mixer, it was found that the product in
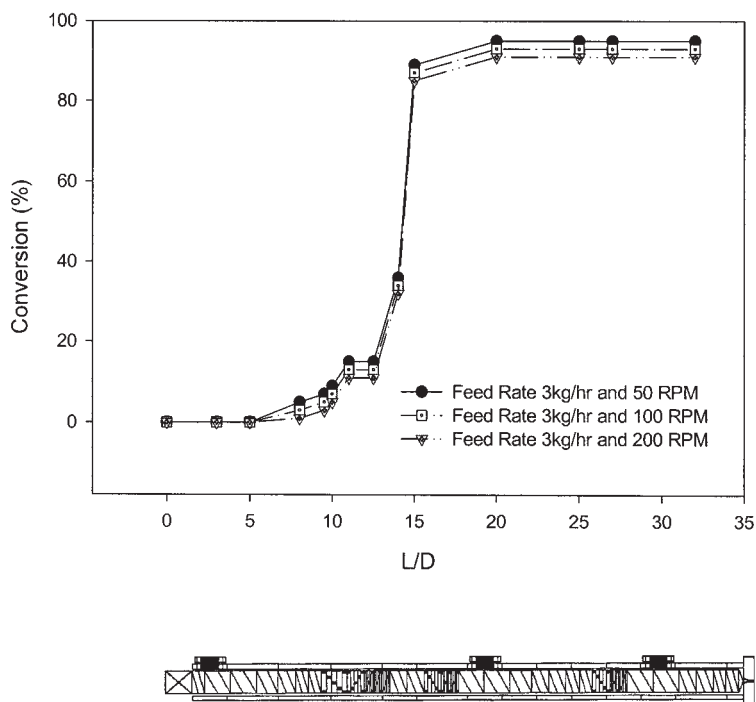

Figure 7 Evolution of conversion of ω-lauryl lactam along the screw axis at different screw speeds at 200°C, and 3 kg/h.
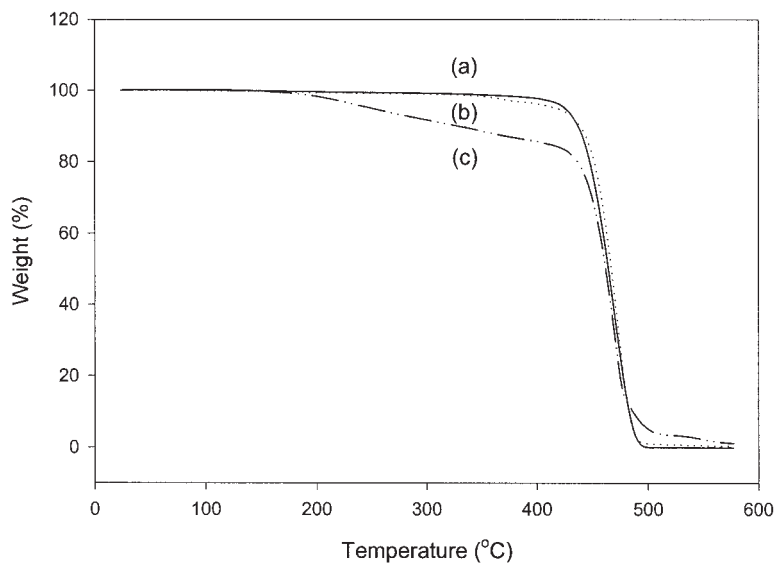
Figure 8 Thermogravimetric analysis of (a) commercial PA 12 (Ube 1024®) (—), (b) PA 12 synthesized in a twin-screw extruder (· · ·), and (c) PA 12 synthesized in a batch reactor (—..).

a twin-screw extruder exhibited higher mass residue (%) than that in an internal batch mixer over the entire range of temperature (25–600°C).

Differential scanning calorimetry

Figure 9 shows a DSC scan of LA monomer and polyamide 12 products synthesized in an internal mixer (batch-type reactor) and a twin-screw extruder (continuous reactor) as well as a commercial polyamide 12 (Ube 1024®). The samples were heated to 250°C and then quenched to below room temperature (<25°C) under nitrogen gas. The temperature was then raised at 20°C/min to 250°C. The crystalline melting point of LA monomer was ~ 156°C. The polyamide 12 products, which were synthesized in a batch-type internal mixer and a twin-screw extruder, respectively, exhibited different crystalline melting points and heats of fusion [T_m in batch = 174°C (ΔH = 25.83 J/g); T_m in twin screw extruder = 178°C (ΔH = 28.65 J/g)]. The commercial polyamide 12 was found to have a crystalline melting point at T_m = 180°C and heat of fusion of ΔH = 31.64 J/g.
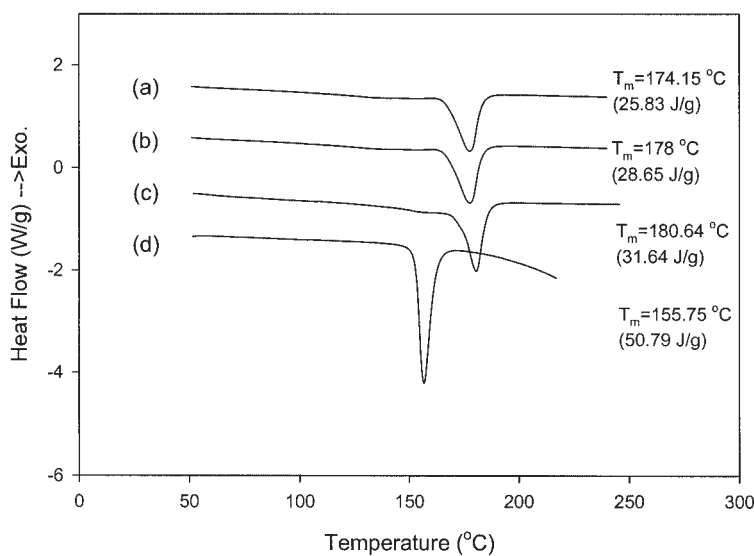

Figure 9 Differential scanning calorimetry (DSC) measurement of (a) PA12 synthesized in a batch reactor, (b) PA12 synthesized in a twin-screw extruder, (c) commercial PA12 (Ube 1024®), and (d) ω-lauryl lactam.

TABLE I
Viscosity Average Molecular Weights of PA12 Synthesized in Internal Mixer and Twin-Screw Extruder

Reactor type		$[\eta]$		Average molecular weight (MW)
Internal mixer		1.032		10,800
Commercial PA12		1.237		14,000
	Feed rate	**Screw speed (rpm)**	**$[\eta]$**	**Average molecular weight (MW)**
	1 kg/h	50	1.532	19,000
		100	1.298	15,000
Twin-screw extruder		200	1.175	13,000
	Feed rate	**Screw speed**	**$[\eta]$**	**Average molecular weight (MW)**
	3 kg/h	50	1.475	18,000
		100	1.237	14,000
		200	1.111	12,000

Intrinsic viscosity

The intrinsic viscosity was measured and used to estimate molecular weight. The empirical equation used to describe the intrinsic viscosity/molecular weight relationship, the Mark–Houwink equation, is

$$[\eta] = KM^a \qquad (3)$$

where a and K are constants for a specific polymer/solvent/temperature system. We measured intrinsic viscosities to determine viscosity average molecular weight of synthesized products, notably polyamide 12, by using a Ubbelohde viscometer. The solvent used in this experimental study was m-cresol. All measurements were made at 25°C. The Mark–Houwink constants for the polyamide 12 and m-cresol system were found by Griehl and Zarate,[19] $K = 1.55 \times 10^{-3}$ and $a = 0.70$ at a temperature of 25°C. They used an osmometer to measure their molecular weights, which were unfractionated samples.

Table I shows the viscosity average molecular weights of all products as a function of different screw speeds during reactive extrusion under the following conditions with $[M]/[I] = 400$, feed rate of 1 and 3 kg/h, and screw speed of 50, 100, and 200 rpm as well as internal mixer. We found lower molecular weights
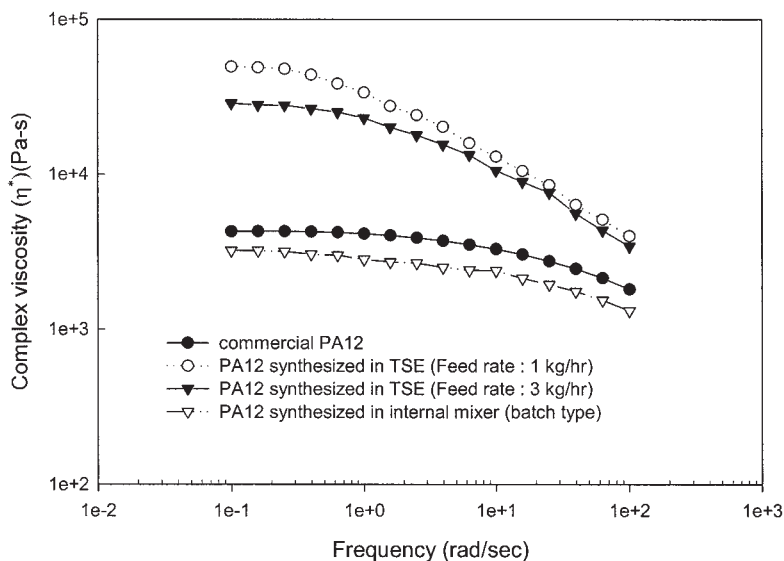

Figure 10 Comparison of complex melt viscosities of product in an internal mixer and in a twin-screw as extruder as a function of frequency sweep at 190°C.

TABLE II
The Mechanical Properties of Polyamide 12 Synthesized in an Internal Mixer, in a Twin-Screw Extruder, and Commercial Polyamide 12

Types of reactor for polymerization of ω-lauryl lactam	Screw speed (rpm)	Young's modulus (MPa)	Tensile strength at break (MPa)	Elongation (%)
Internal mixer		462 ± 1.0	56 ± 1.5	272 ± 10
Commercial polyamide 12		460 ± 1.0	55 ± 1.0	300 ± 5
	50	455 ± 2.0	65 ± 1.4	330 ± 10
Twin-screw extruder	100	453 ± 2.0	60 ± 1.3	337 ± 10
	200	450 ± 2.0	58 ± 1.3	342 ± 10

occur with higher screw speeds. For comparison, we also measured the molecular weight of commercial polyamide 12.

The average molecular weight of polyamide 12 synthesized in an internal mixer was about 10,800, while the average molecular weights of polyamide 12 synthesized in a twin-screw extruder was in the range of 13,000–19,000, depending on the experimental conditions such as various screw speeds and feed rates. Lower screw speed and lower feed rates result in higher molecular weights.

The viscosity (or perhaps better number) average molecular weights of commercial polyamide 12 (MW: 14,000) measured average molecular weight of polyamide 12 synthesized in a twin-screw extruder was higher (MW: 14,000 and 19,000).

Melt viscosity

We measured complex melt viscosities of polyamide 12 synthesized in an internal mixer and twin-screw extruder as well as commercial polyamide 12 as a function of frequency sweep at 190°C. We compared the complex melt viscosities of the products in an internal mixer with that of in a twin-screw extruder as shown in Figure 10.

The value of complex viscosity of products in a twin-screw extruder is higher than that in an internal mixer over the whole range of frequencies (10^{-1}–10^2 s^{-1}).

Comparing this data to commercial polyamide 12, our twin-screw extruder products showed higher melt viscosity, while the internal mixer showed lower values than commercial polyamide 12.

Mechanical properties

The mechanical properties of all products including commercial polyamide 12 are summarized in Table II. Figure 11 shows a comparison of tensile properties of synthesized polyamide 12 as a function of different screw speeds in a twin-screw extruder. We compared the tensile results with a different screw speed during reactive extrusion polymerization.
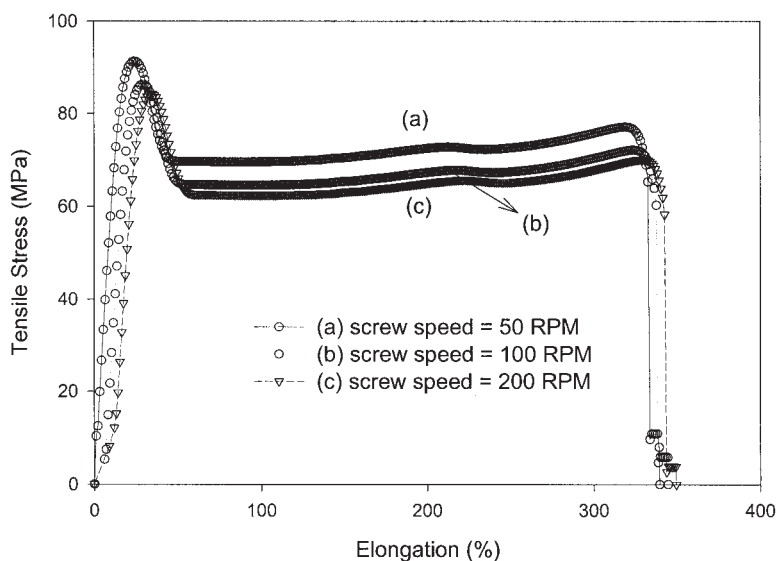

Figure 11 The results of tensile properties of synthesized product polyamide 12 as a function of different screw speeds in a twin-screw extruder.

TABLE III
Material Parameters Used for Calculation by Akro Co.
Twin Screw® Software

Parameters	Units	Value
Physical parameters of monomer and polymer		
Density of monomer	g/cm³	0.772
Density of polymer	g/cm³	1.010
Thermal conductivity	W/m K	0.23
Specific heat	KJ/kg K	2.35
Feed temperature	°C	25
Melting temperature of monomer	°C	150
Melting temperature of polymer	°C	173.72
Heat of fusion of polymer(monomer)	J/g	33(50)
Rheological parameters		
Consistency index (K) of polymer	KPa s^n	2.5
Consistency index (K) of monomer*		0.01
Consistency index (K) of product in the L/D = 8–15 ($\eta = K\dot{\gamma}^n$)		0.189
		$\overset{\sim}{3.015}$
Power law index (n) of polymer	—	0.6756
Power law index (n) of monomer	—	1
Temperature sensitivity, b	1/°C	0.015
Reference temperature	°C	200
Extruder Parameters		
Barrel temperature	°C	150,200
Screw temperature*	°C	120,170
Heat transfer coefficient, barrel*	W/m² K	200
Heat transfer coefficient, screw*	W/m² K	100

The Young's modulus for PA12 synthesized in an internal batch mixer had value of 460 MPa. The product PA12 synthesized in a twin-screw extruder exhibited 450–455 MPa. Commercial PA12 exhibited a value of 460 MPa. These are all essentially the same.

The tensile strength of the synthesized polyamide 12 in a twin-screw extruder was in the range of 58–65 MPa and the elongation at break was 330–342%. The tensile strength at maximum decreased and the elongation at break was increased with increasing screw speed.

The tensile strength of polyamide 12 made in an internal batch mixer was 56 MPa and the elongation to break was 272%. The tensile strength of polyamide 12 synthesized in a twin-screw extruder was 58–65 MPa and the elongation to break was 330–342%. The commercial polyamide 12's tensile strength was 55 MPa and the elongation to break was 300%. The tensile strengths are about the same. The elongation to break of the twin-screw extruder products was higher.

DISCUSSION AND INTERPRETATION

Batch reactor polymerization

Rapid reaction rates and high conversion was achieved with sodium hydride as initiator and *N*-acetylcaprolactam as coinitiator. The rates of rapid reaction time and conversion is in qualitative agreement with the results of literature.[12,14,15]

The degree of conversion of LA was measured as a function of residence time in the internal mixer. These was 93% conversion at a processing temperature of 200°C as shown in Figure 3. We found that 300 s was sufficient time to reach 90%. The major reaction occurred after 60–80 s.

Twin-screw extruder interpretation

We measured residence time distributions for modular intermeshing corotating twin-screw extruder experimentally. The mean residence time for polyamide 12 at a feed rate of 1 kg/h and screw speeds of 200 rpm was 427 s. At 3 kg/h, it was 306 s. However, we were unable to directly experimentally determine residence time along the screw axis in a twin-screw extruder during the reactive extrusion process itself.

We have sought to compare our experiments with commercial Akro-Co-Twin software for twin-screw extruders.[20,21] Kye and White[22,23] experimentally investigated differential residence time distribution in a ZSK30 twin-screw extruder using polyamide 6. They also tried to apply it to ε-caprolactam polymerization. Their observations of residence time suggest that introducing kneading disc blocks and decreasing the screw speeds at constant through rate increase the residence time. The residence time increased associated with increasing levels of fill. This problem has also been considered by Kim and White[24] and Cha.[25]

In our study, it is also important to understand the variation of conversion along the screw axis during reactive extrusion. Table III summarizes the material parameters for polyamide 12 used in a calculation by AkroCo Twin Screw® Version 3. We used LA monomer ($T_m = 150$°C) material parameters from the hopper prior to the first kneading disc block (L/D = 0–7).

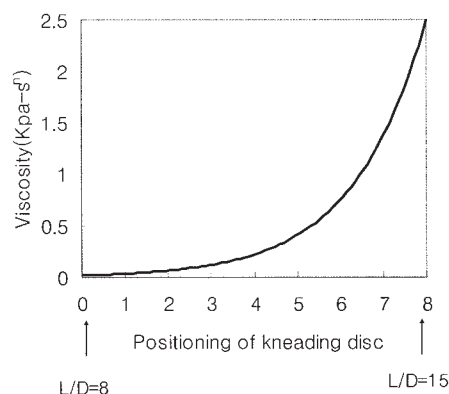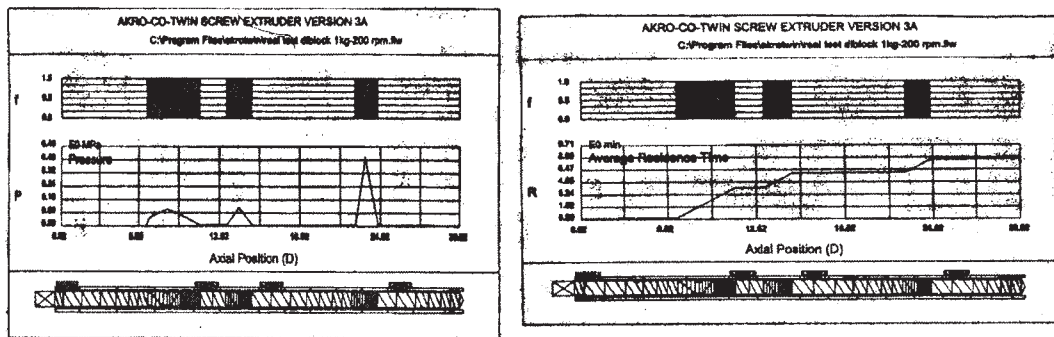**Figure 12** Correlation of increased viscosity for positioning of kneading disc block in the L/D = 8–15 during reactive polymerization of ω-lauryl lactam.
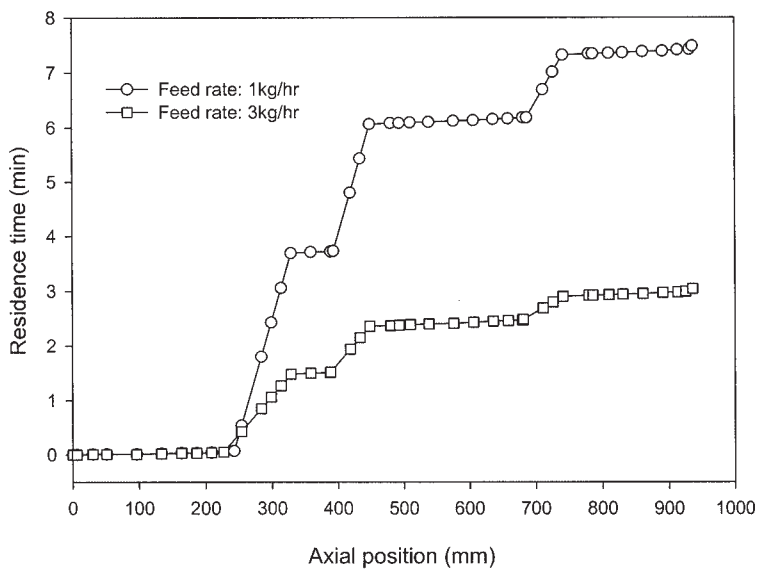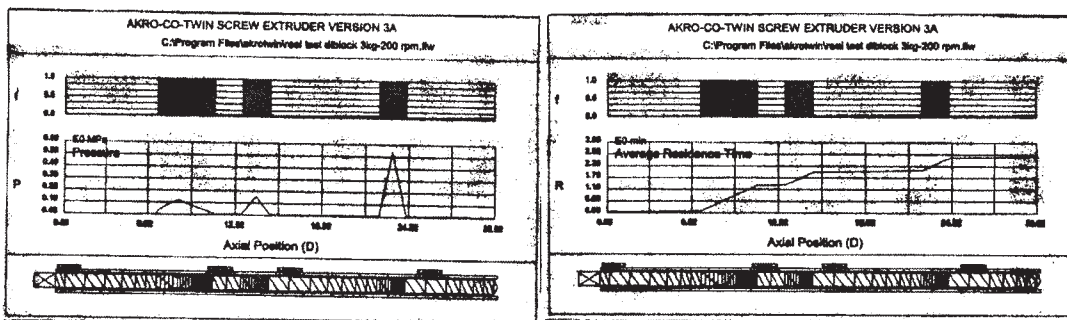
(a)

(b)

Figure 13 (a) Computed fill factor and residence time along the length of screw axis of screw configuration under feed rate of 1.0 kg/h. (b) 3.0 kg/h at screw speed of 200 rpm, and processing temperature 200°C by Akro-co-Twin® software. (c) Residence time along the length of screw axis of screw configuration under feed rate of 1.0 kg/h and screw speed of 200 rpm, and processing temperature 200°C by Akro-co- Twin® software.
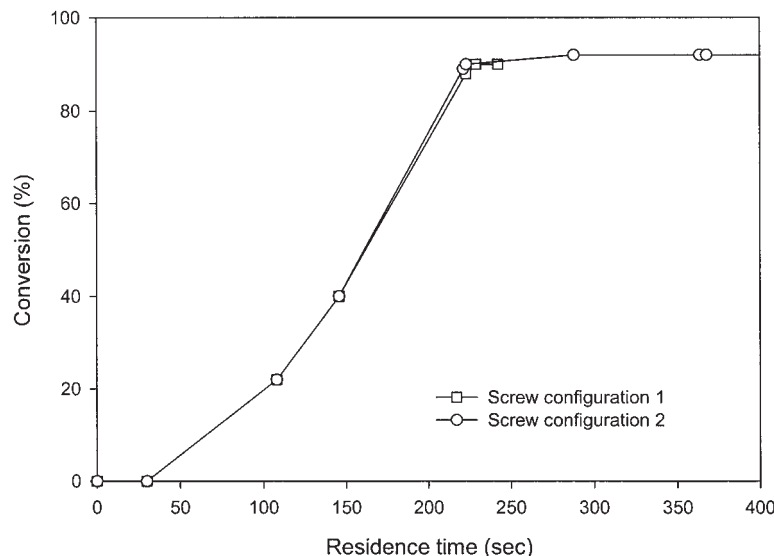
(a) Screw Configuration 1
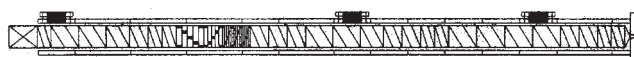
(b) Screw Configuration 2

Figure 14 Comparison of conversion with two screw configurations as a function of residence time at 1 kg/h, 200 rpm. (a) Screw Configuration 1 (b) Screw Configuration 2

In this region, the melted monomer is a Newtonian fluid and we used the monomer material parameters. The power law index was taken as 1; consistency index is 0.01 KPa s, and temperature sensitivity was 0.015°C^{-1}. During the reactive extrusion of LA, polymerization rapidly increased in the L/D = 8–15 and is completed in the L/D = 16–32. We considered intermediate material parameters in the L/D = 8–15 region. We chose an exponential equation for increasing viscosity of product along the screw axis in the L/D = 8–15 as shown in Figure 12. After L/D = 8–15, we used polyamide 12 material parameters to calculate residence time. The power law index was taken as 0.675; the consistency index was 2.5 KPa s, and temperature sensitivity was 0.015°C^{-1}. This Akro-Co-Twin model enables us to compute fill and starvation along the screw axis. These are presented in Figure 13. When the screw speed is 200 rpm and the feed rates are 1 and 3 kg/h, the starvation region is located from L/D = 0 to 6.52 (residence time 0–30 s) and a fully filled region formed at the first kneading disc block zone (L/D = 9.45–11, residence time = 31–220 s) in Screw Configuration 1, which has only one kneading disc block.

We can use the above methods to correlate conversion with residence time of LA in the twin-screw extruder. The polymerization reaction seems to be occurring at the first kneading disc block from the results of Figure 7. Figure 14 shows a comparison of conversion with screw configuration as a function of residence time from Akro-Co-Twin. Screw Configuration 1 has one kneading disc block range of L/D = 9.45–11 (residence time = ~ 31–220 s) obtained using Akro-Co-Twin software. The conversion of LA with Screw Configuration 1 in reactive extrusion reached about 90% at the first kneading disc block zone and then it was constant to the exit die. Screw Configuration 2 has three kneading disc blocks and pumping elements. The first kneading disc is located in the range of L/D = 9.45–11 (residence time = ~ 31–220 s) obtained using Akro-Co-Twin software; the second kneading disc is located in a range of L/D = 12.52–15 (residence time = ~ 223–326 s), and the third kneading disc block zone is located in the range of L/D = 22.5–24.5 (residence time = ~ 369–430 s) obtained using Akro-Co-Twin software.

The conversion of LA with Screw Configuration 2 reached ~ 90% at the first kneading disc zone and ~ 92% after the second kneading disc block. Subsequently, its value is constant though the end of the screw. Screw Configuration 2 exhibits higher levels of
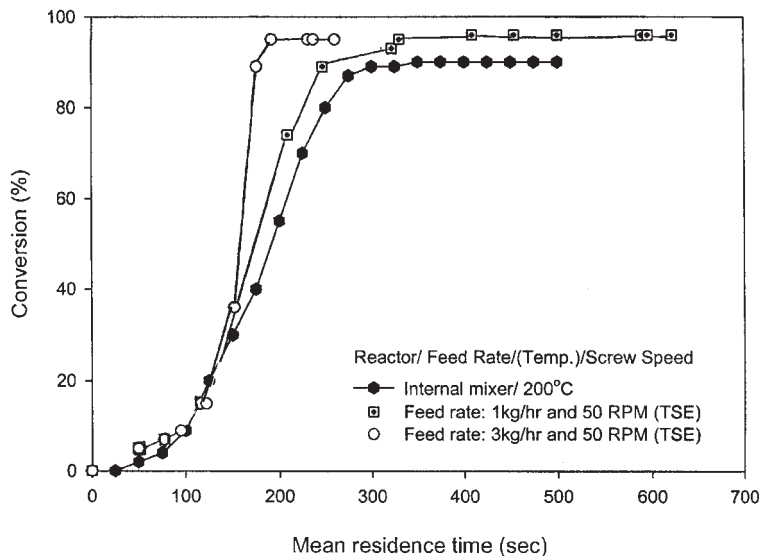
Figure 15 Dependence of conversion with different feed rate at same screw speed, 50 rpm, as a function of mean residence time in an internal mixer and twin-screw extruder.

fill than Screw Configuration 1 at the same screw speed.

Twin-screw extruder reaction rates

The available reaction time for LA in a twin-screw extruder depends on residence time in a twin-screw extruder. The residence time in a twin-screw extruder is related to screw speed and feed rate. We have investigated the effect of screw speed and feed rate on conversion of LA along the screw axis, as shown in Figures 6 and 7. We found that lower screw speed and feed rate gave higher conversion. We have now com-

puted residence time along the screw. The data are represented in Figures 15–17. This shows conversion as a function of residence time along the screw axis. It would appear that reaction rates increased locally with the screw speed and feed rate. However, total conversion was higher with lower screw speeds and feed rate.

Comparison of batch reactor and twin-screw extruder

When we compare the final degree of conversion of LA in an internal mixer and the twin-screw extruder,
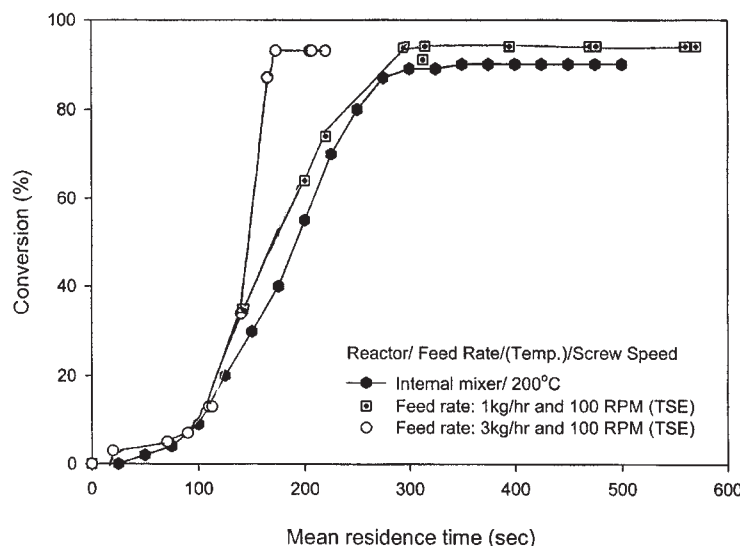

Figure 16 Dependence of conversion with different feed rates at the same screw speed, 100 rpm, as a function of mean residence time in an internal mixer and twin-screw extruder.
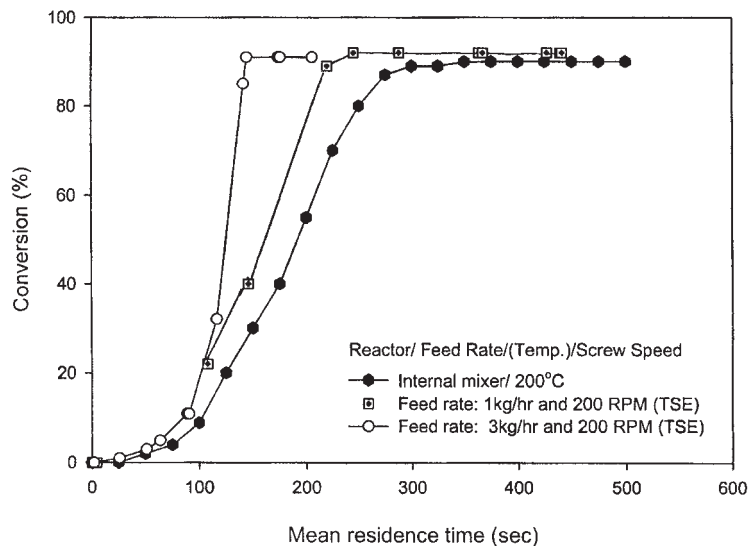
Figure 17 Dependence of conversion with different feed rate at same screw speed, 200 rpm, as a function of mean residence time in an internal mixer and twin-screw extruder.

we found that the total conversion in the twin-screw extruder (∼ 93%) is slightly higher that that in an internal mixer (∼ 90%). The polymerization was carried out in an internal mixer and in the twin-screw extruder with the same argon gas purge condition. However, the polymerization in the internal mixer is still more open to air than the polymerization in the twin-screw extruder, which essentially sealed and pressurized most of its volume. In this situation, initiator and coinitiator may interact moisture in the air in the internal mixer. This would cause moisture to kill the initiator and coinitiator, and the efficiency of initiator and coinitiator is decreased.

When we made calculations of residence times in the twin-screw extruder, we found the internal batch mixer needs much more reaction time to reach the same final high conversion (over 93%) of the twin-screw extruder. This is shown in Figure 17. The twin-screw extruder as a chemical reactor has better performance than the internal batch reactor based on our experimental results. This might be explained that the twin-screw extruder has superior mixing elements such as kneading disc blocks, making it capable of better distributive and dispersive mixing than internal mixer during reactive extrusion. Lee and White[26] investigated the polymerization ε-caprolactam in twin-

Figure 18 Dependence of conversion with different screw speeds at a feed rate of 1 kg/h as a function of mean residence time in an internal mixer and twin-screw extruder.
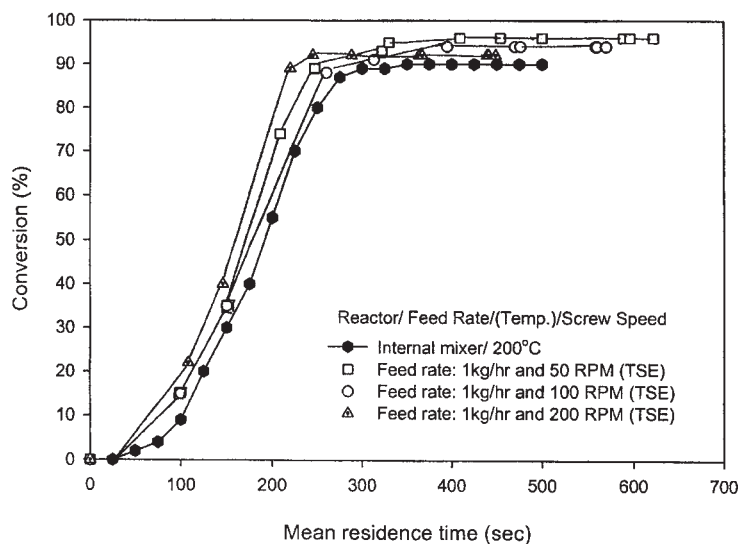
Figure 19 Dependence of conversion with different screw speeds at a feed rate of 1 kg/h as a function of mean residence time in an internal mixer and twin-screw extruder.
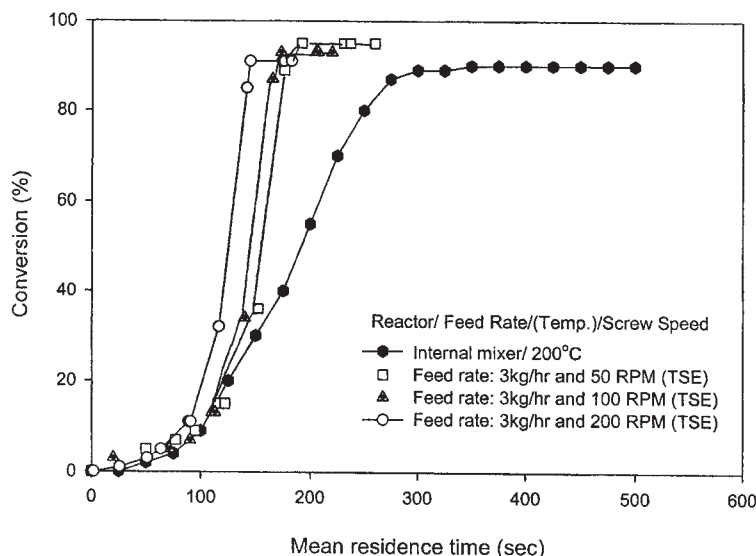
screw extruders. They found that the polymerization rate of twin-screw extruders with proper mixing elements is much higher than the internal mixer at low mixing times. Higher conversion was obtained in twin-screw extruders than an internal mixer for the same mean residence time considered. This is similar to what we have found.

Comparison to other earlier work

Introducing kneading disc blocks and decreasing screw speeds at constant feed rate increased the residence time. Decreasing feed rate at a constant screw speed also increased the residence time. This is a similar observation suggested by earlier investigators.[24,27,28]

Vergnes and coworkers[29] investigated polymerization of ε-caprolactone in a twin-screw extruder. Experiments were performed to find the influence of processing conditions (feed rate, screw speed, barrel temperature, initiator concentration). They reported lower feed rates at the same barrel temperature creates longer residence time and leads to high conversion of ε- caprolactone in a twin-screw extruder. They also observed that residence time decreased when the screw speeds increased for the same operation conditions. They found conversion is higher at higher barrel temperature.

In the present study, the conversion of our product polyamide 12 also exhibited higher conversion at lower feed rate (1 kg/h) at the same screw speeds and temperature. We found that higher screw speed gives lower conversion at the same feed rate and temperature. We also observed higher experimental temperature leads to higher conversion (see Fig. 3). Our results are in good agreement with Vergnes and coworkers's

results.[29] Lee and White[26] polymerized ε- caprolactam in an internal mixer and in different twin-screw extruders. They compared the conversion of ε-caprolactam made in internal mixer and twin-screw extruders and analyzed DSC measurements to compare commercial polyamide 6. They found that final conversion of poly(ε- caprolactam) made in twin-screw extruders is higher than that in an internal mixer as well as their products have almost same crystalline melting temperature compared to commercial polyamide 6 (Capron 8200; Honeywell). This agrees with our observations for the polymerization of LA.

Generally, variables that produce higher residence time, conversion, and molecular weight give products higher tensile strength.[22] Based on our tensile test results, the tensile strength was decreased and elongation at break was increased with increasing screw speed. The tensile strength and elongation to break of product made in twin-screw extruders exhibited higher values than commercial polyamide 12.

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