Continuous Polymerization of Lactam–Lactone Block Copolymers in a Twin-Screw Extruder

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ABSTRACT: Continuous copolymerizations of ϵ-caprolactone with ϵ-caprolactam and ω-lauryl lactam were carried out in a modular intermeshing corotating twin-screw extruder. Sodium hydride (initiator) and *N*-acetyl caprolactam (coinitiator) were used to synthesize lactam–lactone copolymers in a twin-screw extruder. We consider the variables of feeding order and feed rate of comonomers on the reactive extrusion of lactam–lactone copolymers. It was observed that simultaneous feeding of both monomers with initiator and coinitiator in the first hopper produced a mixture of homopolymers. When we fed the lactam into the first hopper and caprolactone sequentially into the second hopper, we obtained the lactam–caprolactone block copolymers.

However, when we fed caprolactone first into the first hopper and the lactam into the second hopper, the extruded product was a mixture of poly(ϵ-caprolactone) and lactam monomer. We synthesized high molecular weight copolymers of poly(caprolactam-*b*-caprolactone) and poly(lauryl lactam-*b*-caprolactone) with different block lengths by sequential feeding of monomers. The block length of the block copolymer could be adjusted by controlling the feed rate of each monomer during reactive extrusion. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1429–1437, 2003

Key words: reactive extrusion; copolymerization; lactam; caprolactone; ring opening polymerization

INTRODUCTION

The use of twin-screw extruders as polymerization reactors has been the focus of increasing interest in the polymer industry because of their numerous advantages. There has been active research on polymerization by reactive extrusion since the 1960s. These efforts have included condensation polymerizations of polyurethanes[1–4] and polyetherimides,[5–8] and ring-opening polymerization of polylactams,[9–15] polyacetals,[16–19] and polylactones.[20–24] These efforts have almost exclusively concerned homopolymers.

Investigations of block copolymers and random copolymers have been conducted only since the 1990s. In 1993, Michaeli et al.[25,26] reported on the formation of block and random copolymers of styrene and isoprene in a twin-screw extruder. They performed an anionic living polymerization using *s*-butyllithium initiator. They reported that the sequential feeding of monomers produced a diblock copolymer, whereas the simultaneous feeding of monomers produced a random copolymer. More recently, Ha and White[27] described the formation of random copolymers of ω-lauryl lactam (LA) and ϵ-caprolactam (CA) in an intermeshing corotating twin-screw extruder.

In the present study, we describe the synthesis of block copolymers of lactams and lactones, specifically ϵ-caprolactam (CA)/ϵ-caprolactone (CL) and ω-lauryl lactam (LA)/ϵ-caprolactone (CL) block copolymers. There have been earlier syntheses of lactam–lactone copolymers,[28–32] including the introduction of a short block segment. However, the present study would appear to be the first synthesis of lactam–lactone block copolymers by reactive extrusion. An earlier report by the authors[33] described some of this work briefly in a conference abstract. We believe these block copolymers have potential as compatibilizing agents in polymer–polymer blends involving polyamides and polymers miscible with poly(ϵ-caprolactone) (PCL). It is well known that poly(ϵ-caprolactone) is miscible with a wide range of polar polymers such as polyesters and halogenated polymers.

EXPERIMENTAL

Materials

The basic monomers used in this study were ϵ-caprolactone (CL) (obtained from Union Carbide, now Dow Chemical), ϵ-caprolactam (CA) (obtained from Allied Signal, now Honeywell), and ω-lauryl lactam (LA) (obtained from Ube Industries). Sodium hydride (NaH) and *N*-acetyl caprolactam (*N*-acetyl CA) used in this study as an anionic initiator and coinitiator,

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Figure 1 (a) Experimental setup for continuous copolymerization using a JSW Labotex 30 modular intermeshing corotating twin-screw extruder. (b) Screw configuration for copolymerization of lactam and lactone in a twin-screw extruder.

respectively, were obtained from Aldrich Chemical Co. (Milwaukee, WI).

Apparatus

A Japan Steel Works (JSW) Labotex 30-mm twin-screw extruder was used as a chemical reactor for all reactive extrusions in this study. It is a modular-type intermeshing corotating twin-screw extruder. The screw diameter is 30 mm, the centerline distance is 26 mm, and the active barrel length is 975 mm (L/D = 32.5).

The experimental setup of the reactive extrusion process is shown in Figure 1(a). The barrel temperature was 230°C for CA–CL copolymerization and 200°C for LA–CL copolymerization. All polymerizations were carried out with a screw configuration that has two zones of kneading disk blocks before the second hopper, as shown in Figure 1(b), to allow more residence time and rigorous mixing of reactants before sequential feeding of the second monomer.

Procedure

All reactions were performed with purging dry nitrogen gas into the extruder. We carried out copolymerization of CL/CA and CL/LA in a modular intermeshing corotating twin-screw extruder. We investigated the influence of the feeding order of monomers into the hoppers. We fed two monomers simulta-

neously into the first hopper and sequentially into the first and second hoppers. This allowed the order of monomer addition to be optimized. For sequential copolymerization, the second monomer preheated to 150°C was fed into the second hopper with dry nitrogen gas at various feed rates.

For sequential copolymerization, the first monomer (lactam or lactone) and initiator system (NaH and N-acetyl CA) were premixed with a predetermined ratio of monomer to initiator (5 mmol/mol of the monomer) at room temperature and then fed into the first hopper using various feed rates. Preheated comonomer was fed into the second hopper without initiator and coinitiator.

Characterization of products

The monomer conversion was evaluated by Soxhlet extraction with methanol, which dissolves monomers and oligomers. The yields of CL–lactam copolymers were evaluated by Soxhlet extraction using toluene, which dissolves homopolymer polycaprolactone (PCL). The monomer conversions and copolymer yields were determined by comparing the weight of the sample before and after extraction of monomers/oligomers and homopolymers, respectively.

The first step in characterization of polymerization products was generally by use of a differential scanning calorimeter (DSC; DuPont Thermal Analyzer

TABLE I
Homopolymerization of ε-Caprolactam (CA), ω-Lauryl Lactam (LA),
and ε-Caprolactone (CL) in a Twin-Screw Extruder

Monomer	Initiator system	Polymerization product	Reference
CA	NaH/N-acetyl caprolactam	Polyamide 6	13
LA	NaH/N-acetyl caprolactam	Polyamide 12	27
CL	Aluminum triisopropoxide Titanium-n-butoxide NaH	Polycaprolactone	24

9900, Boston, MA) at a scanning rate of 20°C/min before and after extraction. Because the two homopolymers are immiscible, one may readily determine which monomers are polymerized from the melting temperature obtained. After extraction of homopolymer PCL, one may characterize the presence of copolymer in polymerization products. The 200-MHz ^{1}H-NMR (Bruker Instruments, Billerica, MA) was also used in this study to investigate the existence of copolymer. Measurements with ^{1}H-NMR were conducted in suitable solvents containing TMS as internal standard.

We determined the number-average molecular weight (M_n) of lactam–caprolactone copolymers using a membrane osmometer (Model 231; Jupiter Instrument) with a cellulose acetate membrane, which is capable of measuring M_n above 10,000. The membrane was placed in the osmometer cell, which was filled with trifluoroethanol so that the membrane divided the cell into two halves. The polymer solution in trifluoroethanol with a known concentration c (g/L) was injected into half the cell and pure trifluoroethanol was injected into the other half of the cell. The pressure difference ΔP between the two halves of the cell was measured. The measurements were repeated for four different concentrations for each polymer sample. A plot of $\Delta P/c$ versus c was constructed by fitting a straight line to the data. We obtained $\Delta P/c$ at $c = 0$ g/L, $(\Delta P/c)_0$. The M_n was calculated from the following equation:

$$M_n = RT(\Delta P/c)_0 \tag{1}$$

where R and T denote the gas constant and absolute temperature, respectively.

The polydispersities of polyamides and their copolymers were determined by gel permeation chromatography (GPC) using m-cresol at 100°C. The GPC was calibrated with polystyrene standards. The universal calibration was applied using an on-line viscometer to detect intrinsic viscosity. The GPC was equipped with a Waters 510 pump (Waters Chromatography Division/Millipore, Medford, MA), three different columns, and a refractive index detector.

A Rheometrics mechanical spectrometer (Model RMS 800; Rheometrics, Poole, UK) was used in the oscillatory mode with a 25-mm parallel plate fixture. The complex melt viscosity [$\eta^*(\omega)$] of products polymerized with different initiator concentrations was measured to compare the relative degree of polymerization under nitrogen purging. Thermogravimetric analysis (TGA; DuPont Thermal Analyzer 9900) was used to study the thermal stability of the products. The rate of TGA scan temperature was 20°C/min.

An Instron test machine (Model 4204) was used to measure the mechanical properties of the polymerization products. The tensile property measurements were conducted at stretch rates of 50 mm/min (dL/dt) at room temperature. The polymer sheet for tensile bar was produced by a compression-molding press (Wabash Model 20) at 195°C. The tensile bar was prepared by compression cutting of the pressed sample sheets using a tensile bar–shaped cutter (specimen type V of ASTM D638). Our test specimens were dried in vacuum oven for 24 h at 45°C to remove the effect of humidity. The results cited are the mean values of five tests of each sample after discarding the maximum and minimum.

RESULTS

DSC characterization

It was possible to polymerize CA, LA, and CL individually in the twin-screw extruder. This could be done with various initiators, as described in various earlier studies from our laboratory.[13,24,27] This is summarized in Table I.

With a mixture of monomers, the results are more complex. If we use a NaH/N-acetyl CA initiator system, which in our experience will polymerize both CL and lactams, and introduce it with both monomers into the first hopper of the twin-screw extruder, we obtain a product with the DSC scan shown in curve (a) of Figure 2 for the CA–CL system. The monomer conversion was more than 90%. Two melting peaks at 52 and 207°C are seen. These clearly correspond to PCL and polyamide (PA) 6. The PCL was removed from the extruded product by Soxhlet extraction using toluene, leaving a product with DSC scan (b) (Fig. 2). This indicates the product formed was a physical mixture of the two homopolymers.
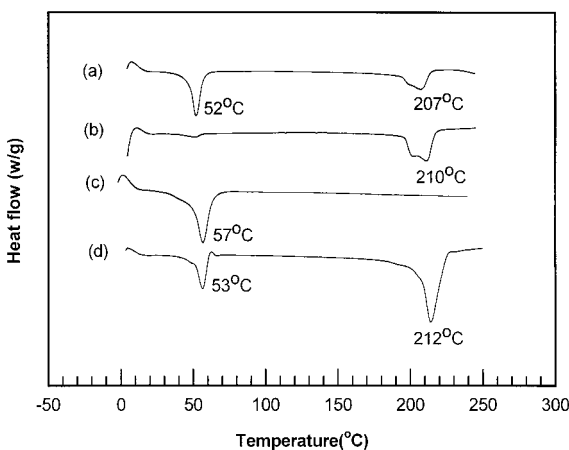
Figure 2 DSC curves for the synthesized products in a twin-screw extruder: (a) virgin extrudate by simultaneous feeding of CA (2 kg/h) and CL (2 kg/h) with initiator system; (b) after extraction of homopolymer PCL from extrudate in (a); (c) after extraction of monomer and oligomer from the extrudate obtained by CL/initiator feeding into the first hopper and CA feeding into the second hopper; (d) after extraction of homopolymer PCL, monomer, and oligomer from the extrudate obtained by CA/initiator feeding into the first hopper and CL feeding into the second hopper.

In a second experiment, CL and the initiator system were fed into the first hopper and CA was fed into the second hopper. The conversion of total monomers was only about 50%. We extracted the residual monomer by Soxhlet apparatus using methanol. The product after extraction had the DSC scan shown as curve (c) (Fig. 2), which demonstrates that the extruded product is a physical mixture of PCL and CA monomer. Neither block copolymer nor PA6 was produced when the CL with initiator system was fed into the first hopper and CA into the second hopper.

If CA and the initiator system are fed into the first hopper and CL into the second hopper, a product with DSC scan (d) (Fig. 2) is obtained. This product was not soluble in methylene chloride and toluene, suggesting it is a CA–LA block copolymer.

Similarly, we synthesized the LA–CL block copolymers by sequential feeding of monomers (LA/initiator system into the first hopper and CL into the second hopper). Figure 3 shows DSC traces of the virgin extruded product (a) and the PCL-extracted product (b). This indicates the presence of LA–CL block copolymer in the extruded products. After extraction of oligomers and PCL, two different melting peaks were observed. One peak was about 55°C for the PCL block and the other was about 175°C for the poly(ω-lauryl lactam) (PA12) block. However, when we first fed CL into the first hopper with the same initiator system and sequentially fed LA into the second hopper, the extruded product was a mixture of PCL and LA monomer. The CL was polymerized by NaH and N-acetyl CA before the second hopper. The monomer

conversion of CL reached 94%. However, the growing PCL anion did not initiate LA, which was fed into the second hopper. As a result, monomer conversion of LA was 0% and the block copolymer was not produced. Simultaneous feeding of both monomers into the first hopper caused a mixture of PCL and PA12. These results are the same as what we have observed in CL/CA polymerization. The results are summarized in Table II.

The occurrences of a mixture of PCL/PA12 by simultaneous feeding and block copolymer by sequential feeding (lactam into the first hopper) were also confirmed by ^{1}H-NMR characterization.

^{1}H-NMR characterization

In Figures 4 and 5, ^{1}H-NMR peaks of the products, which were produced by sequential and simultaneous feeding of monomers, are compared. We removed PCL, oligomers, and residual monomers before the NMR measurements. A mixture of $CDCl_3$ and trifluoroethanol was used as a solvent.

In Figure 4, the triplet peaks corresponding to around 3.2 and 4.1 ppm appeared because of the protons, which are marked as 1 and 2, respectively. Therefore, these peaks indicate the existence of PA6 block and PCL block in the extruded product after extraction of PCL. Figure 4 demonstrates the formation of block copolymer when we fed the monomers sequentially (CA into the first hopper and CL into the second hopper). The quadruplet peak around 3.9 ppm comes from the solvent we used.

When we fed both monomers simultaneously into the first hopper we obtained the results shown in
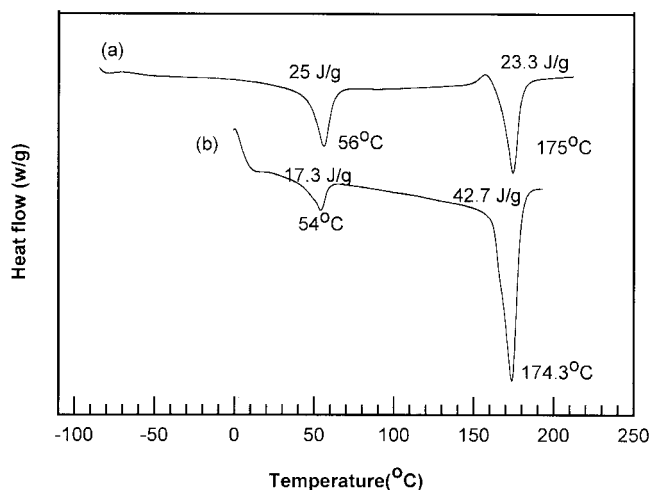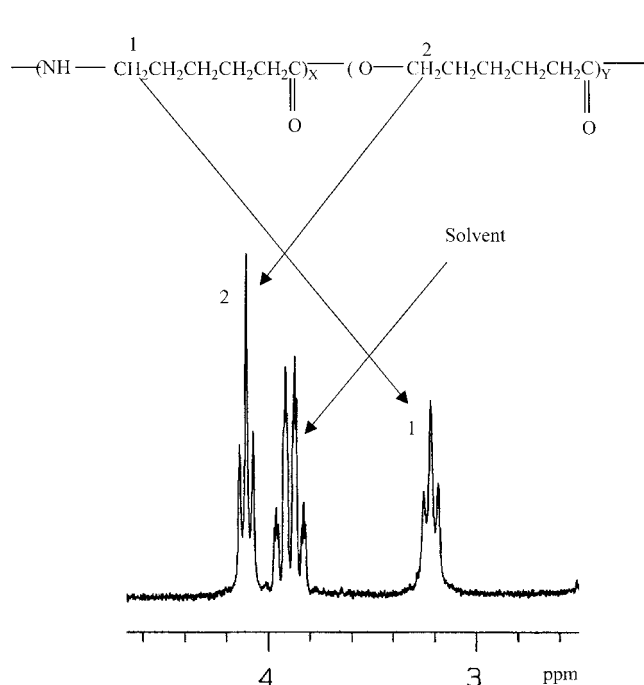

Figure 3 DSC curves for the synthesized products by sequential feeding of LA (1.5 kg/h) with NaH and N-acetyl caprolactam (equivalent 5.0 mmol/mol of LA monomer) into the first hopper and CL (1.5 kg/h) into the second hopper: (a) virgin extruded product; (b) after extraction of PCL and oligomers.

TABLE II
Comparison of Different Feeding Procedures of Lactam and Lactone

Feeding procedure[a]		Monomer conversion (%)		Copolymer yield (%)	Product
First hopper[b]	Second hopper	CL	Lactam		
CA and CL	No feeding	93	91	0	Mixture of PA6 and PCL
CA	CL	91	93	75	CA–CL block copolymer
CL	CA	94	0	0	Mixture of PCL and monomer CA
LA and CL	No feeding	96	94	0	Mixture of PA12 and PCL
LA	CL	95	95	82	LA–CL block copolymer
CL	LA	94	0	0	Mixture of PCL and monomer LA

[a] Feed rate: 2 kg/h for each monomer.
[b] NaH and N-acetyl caprolactam (5 mmol/mol of monomer) were fed into the first hopper.

Figure 5. The peak around 4.1 ppm, which should indicate a PCL block, was not clearly observed after extraction of PCL and oligomers. In the case of simultaneous feeding, it seems that the CA–CL block copolymer does not exist in the product but a mixture of PCL and PA6 is formed. The very small trace around 4.1 ppm may be considered as a small amount of copolymer or residual PCL after extraction.

It is demonstrated that the simultaneous feeding of monomers with both initiator and coinitiator forms a mixture of PCL and PA6. Meanwhile, the sequential feeding of monomers forms a block copolymer of CA and CL. This corresponds to the result of DSC characterization.

TGA characterization

Figure 6 shows the TGA results for PA6, PCL, and P(CA-b-CL) polymerized in a twin-screw extruder. Volatilization of the PCL block starts at 320°C. The PA6 block has a volatilization temperature of 450°C and completely degrades around 500°C.

Figure 7 also shows the TGA results for PA12, PCL, and P(LA-b-CL) polymerized in a twin-screw extruder. Volatilization for the PCL block starts at 320°C. The PA12 block has a volatilization temperature of 470°C and completely degrades around 520°C. In comparison with P(CA-b-CL) in Figure 6, the thermal degradation temperature of P(LA-b-CL) is about 20°C higher.
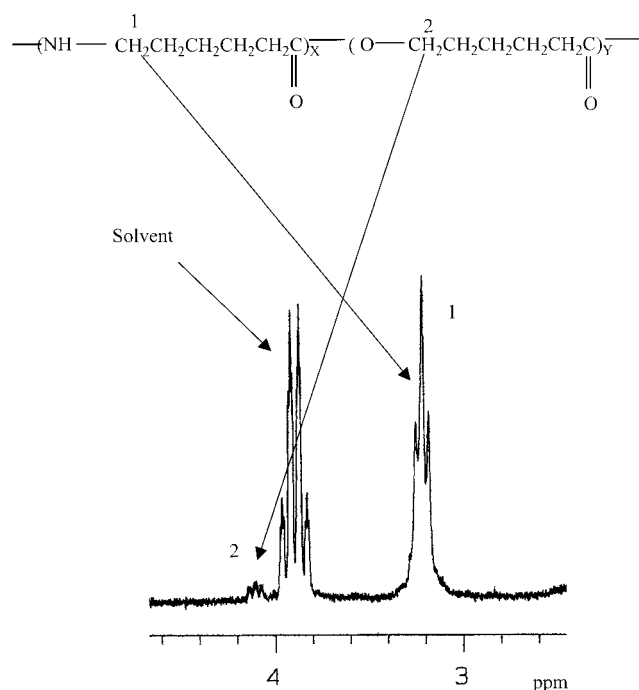

Figure 4 ^{1}H-NMR peak of the synthesized product by sequential feeding of CA (2 kg/h) with NaH and N-acetyl caprolactam (equivalent 5.0 mmol/mol of CA monomer) into the first hopper and CL (2 kg/h) into the second hopper.

Figure 5 ^{1}H-NMR peak of the synthesized product by simultaneous feeding of CA (2 kg/h) and CL (2 kg/h) with NaH and N-acetyl caprolactam (equivalent 5.0 mmol/mol of CA monomer) into the first hopper.
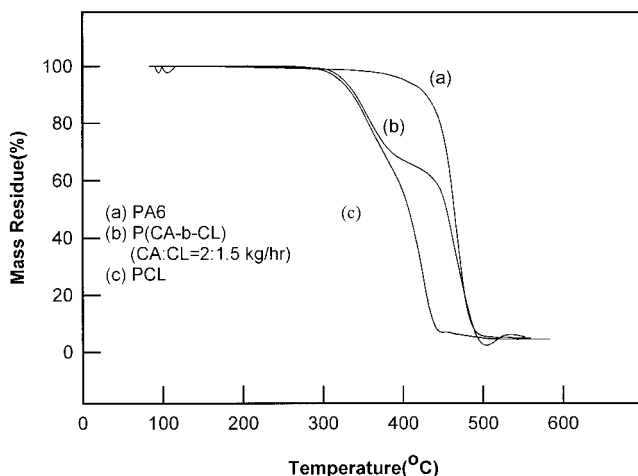
Figure 6 TGA measurements of the synthesized PA6, PCL, and P(CA-*b*-CL) in the twin-screw extruder.

Molecular characterization

Figure 8 shows two separate peaks in the GPC measurement for the product synthesized by simultaneous feeding, whereas there is a single peak for the product by sequential feeding. Figure 9 illustrates the difference of molecular weights between before and after feeding of CL into the second hopper. The overall shift of GPC peak after feeding of CL into the second hopper implies that the molecular weight increases when block copolymer is formed by sequential copolymerization.

The molecular characteristics of the synthesized products are summarized in Table III. The conversion of CA was almost completed before feeding of CL. To measure the molecular weight of the PA6 block, we removed a sample of the synthesized PA6 from the second hopper before feeding of CL and measured the molecular weight using a membrane osmometer. The M_n of homopolymer PA6 at the second hopper before
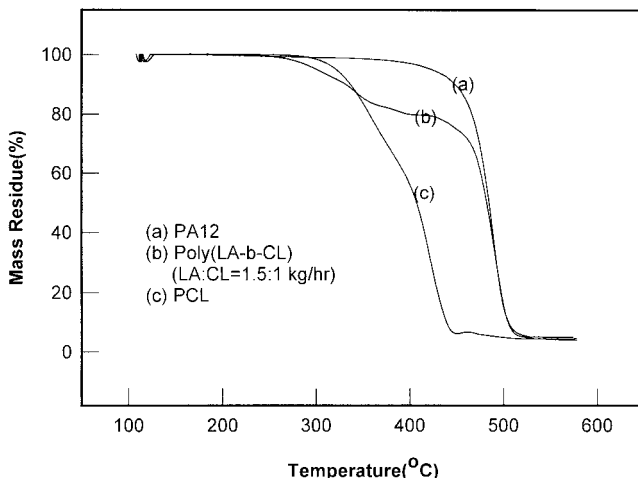
Figure 7 TGA measurements of the synthesized PA12, PCL, and P(LA-*b*-CL) in the twin-screw extruder.
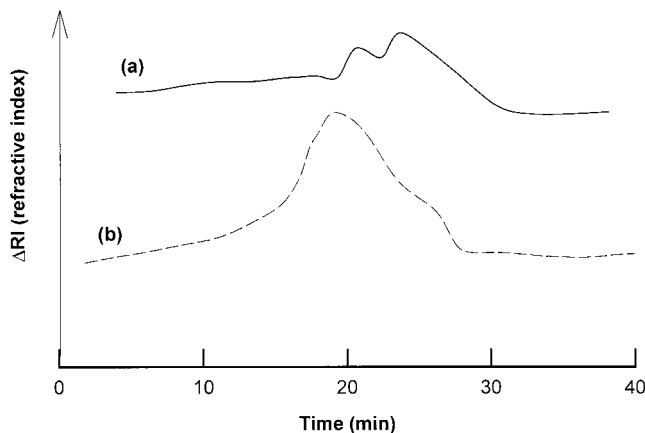
Figure 8 GPC peaks of the synthesized products of CA (2 kg/h) and CL (2 kg/h) in a twin-screw extruder: (a) simultaneous feeding of CA and CL with initiator and coinitiator into the first hopper; (b) sequential feeding of CA with initiator into the first hopper and CL into the second hopper.

feeding of CL was 33,900. After feeding of CL into the second hopper, the M_n of the extruded products was greater than 33,900. Therefore, it is considered that the molecular weight of PA6 block of P(CA-*b*-CL) is 33,900. The molecular weight of PCL block was obtained by subtracting 33,900, the molecular weight of PA6 block, from the total molecular weight of copolymer. The molecular weights of PCL blocks we produced were in the range of 11,200 to 20,900. The yield of block copolymer was around 75% after extraction of oligomer, PCL, and PCL-dominant copolymer. The
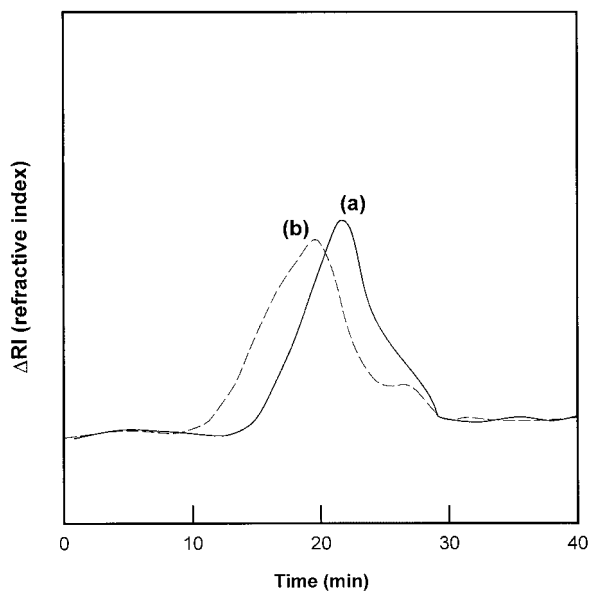

Figure 9 GPC peaks of the synthesized products with and without feeding of CL into the second hopper: (a) homopolymerization of CA (2 kg/h) without feeding of CL into the second hopper; (b) copolymerization by sequential feeding of CA (2 kg/h) into the first hopper and CL (2 kg/h) into the second hopper.

TABLE III
Molecular Weight, Polydispersity, and Copolymer Composition of the Synthesized Products of Lactam and Lactone in a Twin-Screw Extruder

Feed rate					Monomer conversion (%)	Copolymer yield (%)	Copolymer composition	
First hopper[a]	Second hopper	Product	M_n[b]	M_w/M_n[c]			M_n[b] PA6 block	M_n PCL block
2 kg/h CA	No feeding	PA6[d]	33,900	3.0	92 (84[d])	—	—	—
2 kg/h CA	No feeding	Mixture of PA6 and PCL	22,100 to 53,000	2.0 to 2.8	92	—	—	—
2 kg/h CL	—							
2 kg/h CA	1 kg/h CL	P(CA-b-CL)	45,100	2.8	91	73	33,900	11,200
2 kg/h CA	1.5 kg/h CL	P(CA-b-CL)	50,400	2.9	91	73	33,900	16,500
2 kg/h CA	2 kg/h CL	P(CA-b-CL)	54,800	2.7	90	75	33,900	20,900
1.5 kg/h LA	No feeding	PA12[d]	39,200	2.3	95 (90[d])	—	—	—
1.5 kg/h LA	1 kg/h CL	P(LA-b-CL)	65,600	2.2	96	83	39,200	26,400
1.5 kg/h LA	1.5 kg/h CL	P(LA-b-CL)	73,900	2.4	95	82	39,200	34,700
1.5 kg/h LA	3 kg/h CL	P(LA-b-CL)	87,200	2.1	73	64	39,200	48,000

[a] NaH and N-acetyl caprolactam (5 mmol/mol of monomer) were fed into the first hopper.
[b] Measured using membrane osmometer.
[c] Measured by GPC using m-cresol at 100°C calibrated by polystyrene standards.
[d] The sample taken from the second hopper.

polydispersity of the CA–CL block copolymers was about 2.0 to 3.0.

We also synthesized various molecular weights of LA–CL block copolymer. The conversion to PA12 taken from the second hopper was 90% before we fed the second monomer of CL. The M_n of homopolymer PA12 at the second hopper was 39,200 before feeding of CL. After feeding of CL into the second hopper, the M_n of the extruded products was greater than 39,200. Therefore, it is considered that the molecular weight of the PA12 block of P(LA-b-CL) is 39,200. The molecular weight of PCL block was also obtained by subtracting 39,200, the molecular weight of PA12 block, from the total molecular weight of copolymer. The molecular weights of PCL blocks we produced were in the range of 26,400 to 48,000. The yield of block copolymer was

in the range of 64 to 83%. The polydispersity of the P(LA-b-CL) was about 2.0 to 2.4.

Increasing the throughput of CL fed into the second hopper resulted in high molecular weight copolymer having a long PCL block. The block length was adjusted by controlling the throughput of monomers.

Rheological properties

Figure 10 shows complex melt viscosities of PA6 and PCL synthesized in the JSW Labotex 30 modular co-rotating twin-screw extruder. Of the two homopolymers, PA6 (T_m = 215°C) has a much higher melt viscosity than that of PCL (T_m = 58°C) at 230°C. The zero shear melt viscosity of PA6 at 230°C was about 900 Pa·s, whereas that of PCL was about 15 Pa·s.
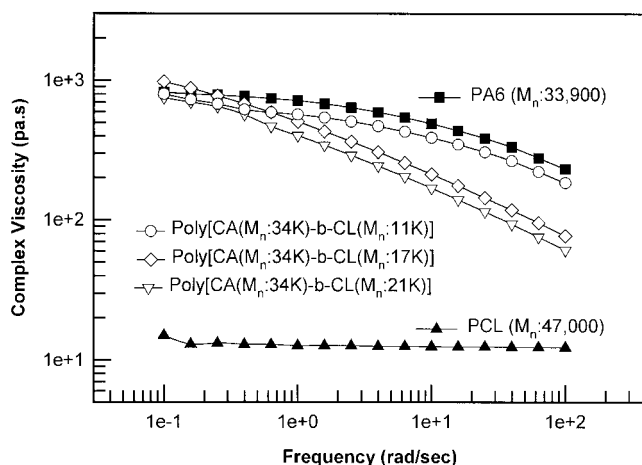

Figure 10 Complex viscosities of the synthesized PA6, PCL, and P(CA-b-CL) measured at 230°C as a function of frequency.
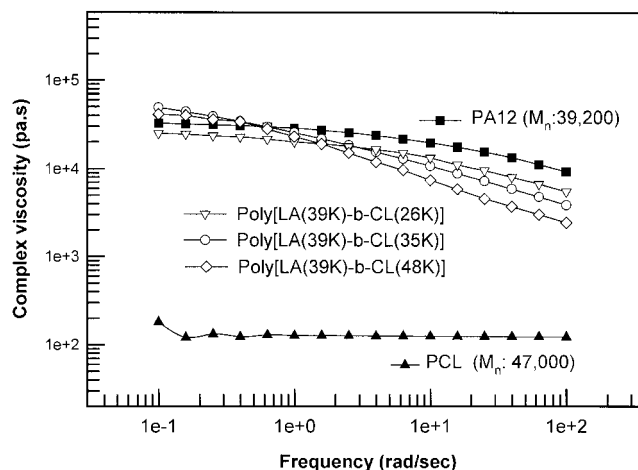

Figure 11 Complex viscosities of the synthesized PA12, PCL, and P(LA-b-CL) measured at 200°C as a function of frequency.
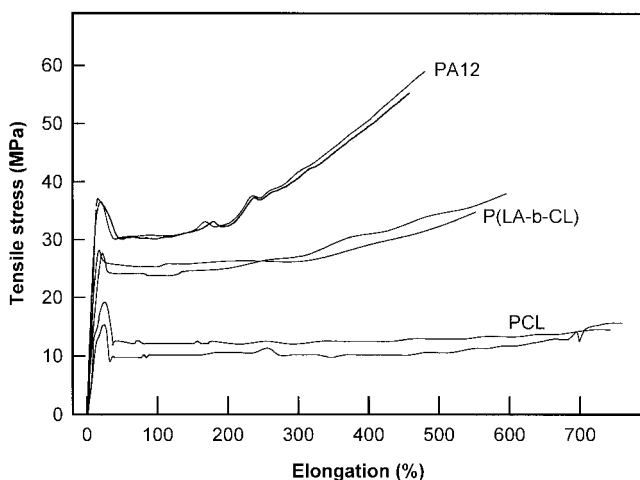
Figure 12 Engineering stress–elongation curves of PA12 (M_n: 39K), PCL (57K), and P[LA (39K)–CL (35K)] produced by reactive extrusion.

We also compared complex melt viscosities of CA–CL block copolymer with those of PA6 and PCL (Fig. 10). The zero shear melt viscosities of P(CA-*b*-CL) and PA6 appeared to be similar.

Figure 11 shows complex melt viscosities of the PA12 and PCL polymerized by reactive extrusion. PA12 (T_m = 175°C) has a much higher melt viscosity than that of PCL (T_m = 58°C) at 200°C. The zero shear melt viscosity of PA12 at 200°C was about 30,000 Pa·s, whereas that of PCL was about 110 Pa·s. We also compared the complex melt viscosities of LA–CL block copolymer with PA12 and PCL (Fig. 11). The P(LA-*b*-CL) having a high molecular weight PCL block has a slightly higher melt viscosity at low frequency than that of PA12.

As the frequency is increased, the melt viscosities of P(CA-*b*-CL) and P(LA-*b*-CL) are placed between poly(lactams) and PCL. The lactam–CL block copolymers have more non-Newtonian behavior than that of homopolymers. The longer PCL block of the lactam–CL block copolymer resulted in a lower melt viscosity at high frequency, as shown in Figures 10 and 11.

Mechanical properties

The engineering stress–elongation curves of PA12 and PCL synthesized by reactive extrusion are shown in Figure 12. PA12 has a higher tensile strength and lower elongation than those of PCL. The tensile strengths of PA12 and PCL were about 57 and 15 MPa, respectively. The elongations of PA12 and PCL were 460 and 760%, respectively.

We also compared the stress–elongation curve of P(LA-*b*-CL) with those of PA12 and PCL. P(LA-*b*-CL) exhibits an intermediate behavior in the stress–elongation curve between those of PA12 and PCL.

Table IV summarizes the tensile test results of poly(lactams), PCL, and lactam–lactone block copolymers. The tensile strengths and elongations of the block copolymers were in the range between those of PA and PCL. Specifically, the tensile strength of P(CA-*b*-CL) in different compositions and molecular weights was of the order of 35 to 43 MPa, whereas the tensile strength was 15 MPa for PCL and 59 MPa for PA6. The elongations of P(CA-*b*-CL) were in the range of 420 to 550%. The tensile strength of P(LA-*b*-CL) we produced is of the order of 28 to 42 MPa, whereas the tensile strength is 15 MPa for PCL and 57 MPa for PA12. The elongation to break of P(LA-*b*-CL) is about 510 to 650%.

The elongation of the block copolymer is increased with an increase in PCL block length attached to the polyamide block, whereas the tensile strength is decreased by PCL block length. In comparison with the mechanical properties of CA–CL block copolymer in Table IV, LA–CL block copolymer exhibits higher elongation and similar tensile strength with that of CA–CL block copolymer.

DISCUSSION

Goodman and coworkers[28–31] reported the polymerization of random copolymers of CL with CA or LA in a batch glass reactor. The random copolymers of lactams and CL were produced by simultaneous copolymerization of a mixture of CL and lactam without a

TABLE IV
Mechanical Properties of Polyamides, PCL, and Poly(lactam-*b*-CL) Produced by Reactive Extrusion

Polymer	Number-average molecular weight (PA block : PCL block)	Tensile strength (MPa)	Elongation to break (%)
PA6 (PCA)	33,900	59	270
PA12 (PLA)	39,200	57	460
PCL	47,000	15	760
P(CA-*b*-CL)	45,100 (34K : 11K)	43	420
P(CA-*b*-CL)	50,400 (34K : 16K)	38	490
P(CA-*b*-CL)	54,800 (34K : 21K)	35	550
P(LA-*b*-CL)	65,600 (39K : 26K)	42	510
P(LA-*b*-CL)	73,900 (39K : 35K)	36	580
P(LA-*b*-CL)	87,200 (39K : 48K)	28	650

substantial amount of coinitiator such as *N*-acetyl CA and hexamethylene diisocyanate. They confirmed a random copolymer having a slight blocklike character by finding only a single melting point of the copolymer. They reported that sodiocaprolactam (Na–CA) was employed as the source of catalytic lactamate anions and CL served as both coinitiator and comonomer.[28] They also argued that a random structure was attributed to the occurrence of base-catalyzed amide–ester interchange reactions. They did not use a particular coinitiator like *N*-acetyl CA because the comonomer of CL also served as coinitiator. Their reaction time to obtain a random copolymer was up to 6 h.

We used the *N*-acetyl CA as a coinitiator to reduce the reaction time because of limited residence time in a twin-screw extruder. In the presence of *N*-acetyl CA, it is considered that CL is unable to serve as a faster activator than *N*-acetyl CA, as described by Goodman and coworkers.[28] Therefore, a system of initiator (NaH)/coinitiator (*N*-acetyl CA) polymerizes the lactams before sodiocaprolactam reacts with CL. At the same time, NaH would polymerize CL separately. It is considered that there is no chance that CL reacts with sodiocaprolactam for copolymer in the presence of a significant amount of *N*-acetyl CA. As a result, the synthesized product by simultaneous feeding of monomers was characterized as a mixture of polyamide and PCL rather than a copolymer, as indicated in Figures 2 and 5.

We produced block copolymer by sequential feeding of monomers. Once the polymerization of lactam occurred before feeding of CL into the second hopper, the growing polyamide anion may initiate the ring-opening polymerization of CL for the formation of a block copolymer. However, when we polymerized CL first and fed lactam sequentially into the second hopper, the copolymer could not be produced. This indicates that the growing lactone anion is incapable of rapidly initiating the ring-opening polymerization of lactam in a few minutes during reactive extrusion. Therefore, the final product we obtained was a mixture of PCL and a lactam monomer (CA or LA).

The monomer conversion and yield of copolymer are slightly higher for the LA–CL system than for the CA–CL system (Table III) because CA is more hydrophilic than LA. This readily leads to a side reaction with moisture during the reactive extrusion.

CONCLUSIONS

We observed that the simultaneous feeding of monomers with initiator (NaH) and coinitiator (*N*-acetyl caprolactam) in the first hopper of the twin-screw extruder produces a mixture of homopolymers. We synthesized high molecular weight P(CA-*b*-CL) and P(LA-*b*-CL) by the sequential feeding of the monomers. Although the block copolymers can be produced by sequential addition of monomers, the order of monomer addition must be considered. In the reactive extrusion process, the growing reactive species must be capable of initiating quickly the second monomer fed into the second hopper for the block copolymerization. Only when we fed the lactam (CA or LA) into the first hopper and the CL sequentially into the second hopper did we successfully obtain lactam–CL block copolymers (CA–CL and LA–CL block copolymers). The respective block lengths of the copolymer can be adjusted by controlling the feed rate of each monomer during reactive extrusion.

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