

Reactive Copolymerization of Various Monomers Based on Lactams and Lactones in a Twin-Screw Extruder

In Kim, James L. White

Institute of Polymer Engineering, University of Akron, Akron, Ohio 44325-0301

Received 10 May 2004; accepted 20 July 2004

DOI 10.1002/app.21494

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The synthesis of polyamide–polyester-based diblock, triblock, and random block copolymers was carried out in a modular, corotating twin-screw extruder via reactive extrusion. ω -Lauryllactam (LA), ϵ -caprolactam (CA), and ϵ -caprolactone (CL) were used as monomers for the synthesis of the copolymers in the twin-screw extruder. Generally, CL was added downstream. Sodium hydride was the initiator, and *N*-acetylcaprolactam was the coiniciator. The syntheses of poly(LA-*b*-CL), poly(LA/CA-*b*-CL), and poly(LA-*b*-CA-*b*-CL) were attempted. Poly(LA/CA-*b*-CL) was a random LA–CA copolymer with a block of CL. The

simultaneous feeding of LA and CA with the initiator systems was added to the first hopper of the twin-screw extruder, and the addition of CL downstream to a second hopper (without the initiator) was used to form this block copolymer. The thermal, mechanical, rheological, and structural properties of the various copolymers were investigated and compared with those of the homopolymers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1875–1887, 2005

Key words: block copolymers; polyamides; reactive extrusion

INTRODUCTION

The copolymerization of ω -lauryllactam (LA) and other cyclic monomers such as ϵ -caprolactam (CA) and ϵ -caprolactone (CL) has been developed for many years. These copolymers, including CA-*ran*-LA,^{1,2} CA-*b*-CL,^{3,4} and LA-*b*-CA,^{5,6} were reported from 1970 to 1980. All these efforts on the copolymerization of lactams were carried out in batch reactors.

Investigations of the formation of block copolymers and random copolymers by anionic polymerization in twin-screw extruders have been reported only since the 1990s. Michaeli et al.⁷ reported the formation of block and random copolymers of styrene and isoprene in a twin-screw extruder. Block copolymers were produced by the upstream and downstream sequential feeding of monomers, whereas the simultaneous feeding of monomers produced a random copolymer.

More recently, in our laboratories, we have developed various polyamide-based copolymers, including block and random copolymers in a twin-screw extruder.^{8–11} These copolymers include poly(caprolactam-*ran*-lauryllactam),⁸ poly(lauryllactam-*block*-caprolactone),⁹ poly(caprolactam-*block*-caprolactone),⁹ poly(caprolactam-*block*-caprolactone-*block*-caprolactam),¹⁰ and poly(lauryllactam-*block*-caprolactone-*block*-lauryllactam).¹¹

The block copolymers consist of a hard polyamide block and a soft polyester block. The soft block contributes high toughness, elongation, and flexibility, whereas the crystalline hard amide blocks impart high strength, rigidity, chemical resistance, and high melting temperature.

In this article, we report on efforts to polymerize by reactive extrusion poly(LA-*b*-CL), poly(LA/CA-*b*-CL), and poly(LA-*b*-CA-*b*-CL).

EXPERIMENTAL

Materials

The monomers used to make the polyamide blocks were LA (EMS Chemie, Inc., Sumter, SC) and CA (DSM Chemicals North America, Inc., Augusta, GA). We obtained CL (ECEQ-tone monomer) from Dow Chemical Co. (Danbury, CT). Sodium hydride (Aldrich Chemical Co., Milwaukee, WI) was used as an initiator, and *N*-acetyl caprolactam (Aldrich Chemical) was used as a coiniciator to synthesize the copolymers. We also used commercial polyamide 12 (PA12; 1024U, Ube Nylon, Ube, Japan), poly(ϵ -caprolactone) (PCL; P767, Dow Chemical), and poly(ϵ -caprolactam) (PCA; DSM Chemicals North America) for a comparison study with thermal analysis [differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)], IR absorption, melt rheology, and mechanical properties.

Correspondence to: J. L. White.

Twin-screw extruder

All reactive extrusion studies were carried out with a Japan Steel Works Labotex 30 twin-screw extruder (Japan Steel Works, Ltd., Hiroshima, Japan). It was a modular, intermeshing, corotating twin-screw extruder with both right-handed-screw and kneading-disc-block elements. The corotating elements had self-wiping screw characteristics. This twin-screw extruder had barrel sections with electric heaters and water-cooling systems. The screw diameter was 30 mm, the center-line distance was 26 mm, and the active barrel length was 975 mm [length/diameter (L/D) = 32.5].

Block copolymerization in the twin-screw extruder

Because of the sensitivity of lactams to atmospheric humidity, we dried those materials at 100°C over 24 h *in vacuo* in an oven before the polymerization. We used argon gas to carry out reactive copolymerization in a twin-screw extruder.

Diblock copolymer poly(LA-*b*-CL) and triblock copolymer poly(LA-*b*-CA-*b*-CL) were produced by the sequential addition of monomers along the axis of the twin-screw extruder. For poly(LA-*b*-CL), CL was added at $L/D = 15$. For poly(LA-*b*-CA-*b*-CL), CA was added at $L/D = 15$, and CL was added at $L/D = 25$. CL and CA were preheated to 100°C. LA (3.045 mol, 600 g) was fed into the first hopper, 3.045 mol (344 g) of CA was fed into the second hopper, and 6.09 mol (695 g) of CL was fed into the third hopper. A second block copolymer with a similar composition was prepared in the same manner. These were designated poly(LA-*b*-CL)-1 and poly(LA-*b*-CL)-2.

A random copolymer was produced through the simultaneous feeding of two monomers into the first feed port to synthesize random block terpolymer poly(LA-*ran*-CA-*b*-CL). LA (4.260 mol, 840 g), 3.180 mol of CA (360 g), 0.125 mol of sodium hydride (3 g), and 0.097 mol of *N*-acetylcaprolactam (15 g) were tumble-mixed under argon gas to obtain a uniform distribution mixture in a drybox at room temperature. This mixture was fed into the first feed port of the twin-screw extruder at a first hopper feed rate of 1.3 kg/h with a feeder to synthesize a random copolymer (LA/CA). CL (6.090 mol, 695 g) was fed into the second hopper of a twin-screw extruder without any initiator or activator with a well-controlled liquid pump. Subsequently, a second copolymer of this type [poly(LA-*ran*-CA-*b*-CL)-2] was prepared with roughly the same LA/CA composition and 7.010 mol of CL (800 g).

The screw configurations used to synthesize various copolymers are shown in Figure 1. Screw configurations a and c had two kneading disc blocks, which were located before the second hopper, and a third kneading zone was located between the second hop-

per and the exit die. Screw configuration b had one more kneading disc block zone between the third hopper and the exit die for the third monomer's block copolymerization.

The temperature profiles investigated for reactive copolymerization in a twin-screw extruder are listed in Table I. The experimental conditions were carefully chosen to polymerize each of the sequential monomers successfully in the twin-screw extruder. The first feed port for LA should be below the crystalline melting temperature (T_m) of LA (150°C). The temperature of subsequent barrels should be higher than T_m of LA (150°C). We understand from Ha and White⁸ that the melting point of LA/CA random copolymer is less than 175°C.

We used different screw speeds of 50–150 rpm at a 1.3 kg/h feed rate for LA and CA and at 1.3 and 1.5 kg/h feed rates for CL in the reactive polymerization process because we sought to control the molecular weight of the caprolactone block copolymer.

The extruded products were crushed into granules or powder and dried before the characterization of the products.

Product characterization

The conversion of the monomer to the block copolymer was determined in the following manner. The block copolymer was boiled in distilled water or methanol to remove residual LA. After drying *in vacuo*, the copolymer was extracted with toluene in a Soxhlet apparatus to isolate the unreacted PCL and homopolymer of PCL, which was soluble in the toluene. The measured weight of the product after solvent extraction, divided by the initial weight of the block copolymer, was the degree of conversion.

The thermal transition behavior of the various block copolymers and block terpolymers were determined by DSC (Thermal Analyzer 9900, Dupont) from –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 N₂ was 35 mL/min.

The IR spectra of the products were measured in a PerkinElmer 16 PC-FTIR Fourier transform infrared (FTIR) spectrometer to determine the relative compositions of the copolymers. The samples for FTIR measurement were films prepared by compression molding.

We determined the molecular size distributions of the various block copolymers and terpolymers with gel permeation chromatography (GPC; 150C ALC/GPC001, Waters, Milford, MA). We used *m*-cresol as a solvent and measured the molecular weights of the products at 100°C.

The complex melt viscosity [$\eta^*(\omega)$] of the products was determined in the parallel-disc dynamic oscillation mode with the Advanced Rheometric Expansion

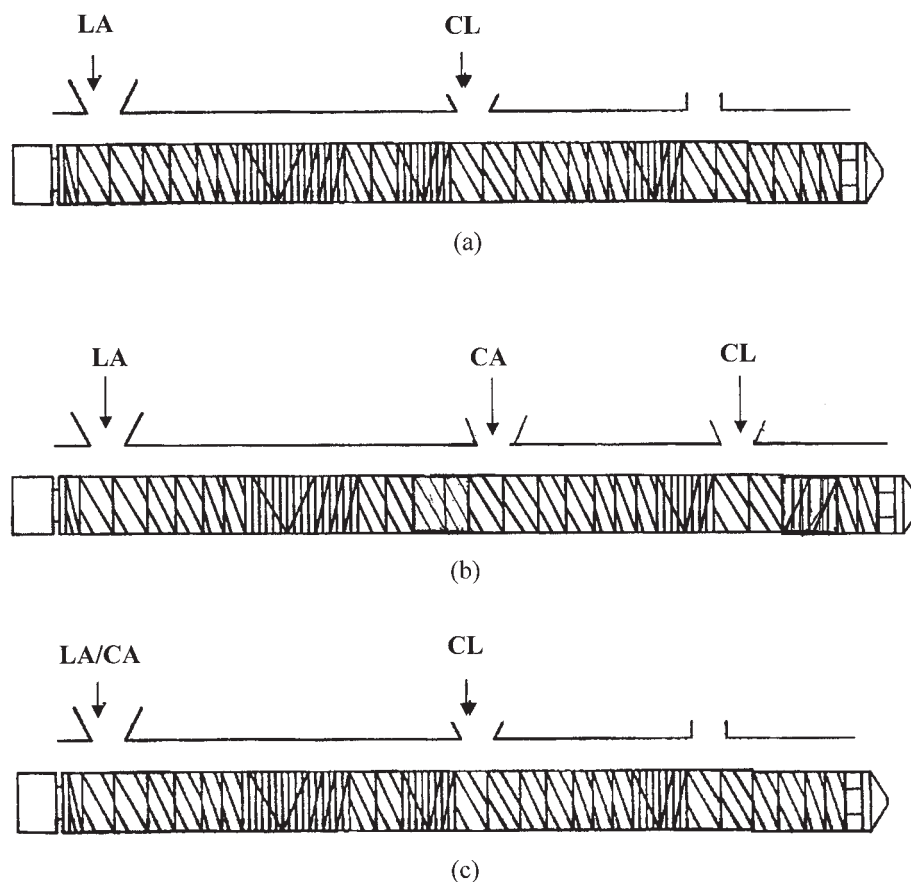


Figure 1 Modular screw configurations for reactive extrusion in a JSW Labotex 30 modular, intermeshing, corotating twin-screw extruder.

System (Rheometric Scientific, Inc., NJ) with low-pressure purging from a liquid nitrogen source.

To observe the mechanical properties of the products and their temperature dependence, we performed a dynamic mechanical thermal analysis (extension mode) at a 1-Hz frequency, at a 4°C/min heating rate, from -50 to 250°C. For further mechanical testing of the products at room temperature, we prepared samples by compression molding at 200°C and cut them into dumbbell-shaped specimens (ASTM D 638 type V). The tensile properties were measured with an Instron 4204 mechanical tester (Instron, Canton, MA) 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

Product conversion

The conversion of the poly(LA-*b*-CL) block copolymers was evaluated via Soxhlet extraction with toluene, which dissolved the residual monomers, oligomer, and homopolymer polycaprolactone. The intended composition for the 100 mol % conversion of poly(LA-*b*-CL) was about 51 mol % LA and 49 mol % CL. We found that the conversion of poly(LA-*b*-CL) was about 90% [poly(LA-*b*-CL)-1 = 89.9%, poly(LA-*b*-CL)-2 = 90.4%].

The intended composition for the 100 mol % conversion of poly(LA-*b*-CA-*b*-CL) was about 33.5 mol % LA, 33.5 mol % CA, and 33 mol % CL. Problems,

TABLE I
Temperature Profiles Investigated for Reactive Copolymerization in a Twin-Screw Extruder

	Zone 1 (°C)	Zone 2 (°C)	Zone 3 (°C)	Zone 4 (°C)	Zone 5 (°C)	Zone 6 (°C)	Zone 7 (°C)	Zone 8 (°C)
Poly(LA- <i>b</i> -CL)	100	195	195	195	195	195	195	210
Poly(LA- <i>b</i> -CA-CL)	80	210	215	215	215	215	215	215
Poly(LA- <i>ran</i> -CA-CL)	50	195	215	210	210	195	180	180

however, rose at the intended feed rates of 1.5 kg/h LA, 1.5 kg/h CA, and 1.5 kg/h CL. Unpolymerized monomer was found at the die. The monomer feed rates were modified to 0.5 kg/h LA, 0.5 kg/h CA, and 0.5 kg/h CL. The initiator concentration was maintained at 0.125 mol. The conversion of the poly(LA-*b*-CA-*b*-CL) triblock copolymer was about 81%.

The intended concentration of the poly(LA/CA) random copolymer was 55.0 mol %, and that of the PCL block was 45.0 mol % for poly(LA/CA-*b*-CL). The conversion of the synthesized poly(LA/CA-*b*-CL) terpolymers was about 90% according to the solvent-extraction method ($[\text{poly(LA/CA-}b\text{-CL)-1}] = 89.5\%$, $[\text{poly(LA/CA-}b\text{-CL)-2}] = 90.2\%$).

DSC

Figure 2(A)-1(b,c) shows the DSC traces of the virgin extruded poly(LA-*b*-CL)-1 block copolymer and extracted product. Two different melting peaks were observed in both the initial and extracted products. Moreover, the heat of fusion for the PCL block was reduced after the extraction of the oligomers, PCL, and PCL-dominant copolymer. One peak appeared at about 52.3°C for the PCL block, and the other appeared at about 174.8°C for the poly(ω -lauryllactam) (PLA) block. Figure 2(A)-2 shows that poly(LA-*b*-CL)-2 exhibited a trend similar to that of poly(LA-*b*-CL)-1.

Figure 2(B) shows that unextracted poly(LA-*b*-CA-*b*-CL) had two different T_m 's. One melting peak occurred at 49°C (19.67 J/g), and the other melting peak was at 143°C (30.96 J/g). There were three different T_m 's for extracted poly(LA-*b*-CA-*b*-CL). After the extraction of the monomer and polycaprolactone from the synthesized virgin poly(LA-*b*-CA-*b*-CL), the first melting peak was at 57.30°C (10.57 J/g), corresponding to the PCL block. The higher melting peaks were at 150 and 170°C, corresponding to PA12 and polyamide 6 (PA6), respectively. However, these were different and lower than the established T_m values of PA12 (180°C) and PA6 (210°C).

The measurements of DSC for both unextracted and extracted poly(LA/CA-*b*-CL) terpolymers revealed two different T_m 's, as shown in Figure 2(C)-1. For virgin extruded poly(LA/CA-*b*-CL)-1, one melting peak occurred at 54.21°C (11.18 J/g), and a second melting peak appeared at 135°C (28.7 J/g). After the extraction of the monomer and homopolymer from the synthesized virgin poly(LA/CA-*b*-CL)-1, one melting peak appeared at 54.2°C (11.18 J/g), and the other melting point was at 134.8°C (28.70 J/g). The peak at 54.2°C corresponded to the PCL block, and the other peak at 134.8°C corresponded to the PCA/PLA random copolymer block. Poly(LA/CA-*b*-CL)-2 had a DSC trace similar to that of poly(LA/CA-*b*-CL)-1.

TGA

The TGA trace for poly(LA-*b*-CL)-1 showed intermediate behavior between PA12 and PCL. However, the weight losses for both were found at lower temperatures than those of either PCL or PA12. We found that the unextracted poly(LA-*b*-CL)-1 product had faster weight loss than extracted poly(LA-*b*-CL)-1 when we measured the mass residues of the products as a function of temperature. This is presented in Figure 3(A)-1. Poly(LA-*b*-CL)-2 was similar to poly(LA-*b*-CL)-1.

Figure 3(B) shows that extracted poly(LA-*b*-CA-*b*-CL) started to volatilize at 260°C and was completely degraded at about 500°C, whereas our unextracted poly(LA-*b*-CA-*b*-CL) started to volatilize at about 220°C and was soon completely degraded at about 500°C with increasing temperature.

Figure 3(C)-1 shows that the volatilization temperature of PA6 was about 420°C, and it was completely degraded at about 470°C. The volatilization temperature of PA12 was about 440°C, and it was completely degraded at about 510°C. PCL volatilized at 320°C and was completely degraded at 420°C. Extracted poly(LA/CA-*b*-CL)-1 started to volatilize at 300°C and was completely degraded at about 500°C, whereas unextracted poly(LA/CA-*b*-CL)-1 started to volatilize at about 200°C and was soon completely degraded at about 500°C with increasing temperature. The rate of weight loss of unextracted poly(LA/CA-*b*-CL)-1 was faster than that of the extracted product. The trend for poly(LA/CA-*b*-CL)-1 in TGA was intermediate behavior between that of the polyamides (PA6 and PA12) and that of PCL. Synthesized poly(LA/CA-*b*-CL)-2 showed a trend similar to that of poly(LA/CA-*b*-CL)-1.

FTIR spectroscopy analysis

Figure 4(A)-1-(B)-3 shows that the absorption for the amide groups of PA6 and PA12 occurred at 3300 cm^{-1} , and the carbonyl groups of the polyamides existed at 1640 cm^{-1} . The absorption of the carbonyl stretching of PCL occurred at 1724 cm^{-1} . By normalizing the film thickness (x) of a sample, we could determine the composition of the block copolymer. From the relationship between the intensity of the transmittance light (I) and x of the sample, we could obtain the turbidity (τ). For τ of reference samples, we also measured FTIR spectra of homopolymers such as PA12 and PCL. Then, we compared τ values of the sample and homopolymers to calculate the content of each block segment with the following equation:

$$-\frac{dI}{dx} = \tau I \quad (1)$$

$$\tau = \frac{1}{x} \left(\ln \frac{I}{I_0} \right) = -\frac{1}{x} \ln \left(1 - \frac{\Delta I}{I_0} \right) \quad (2)$$

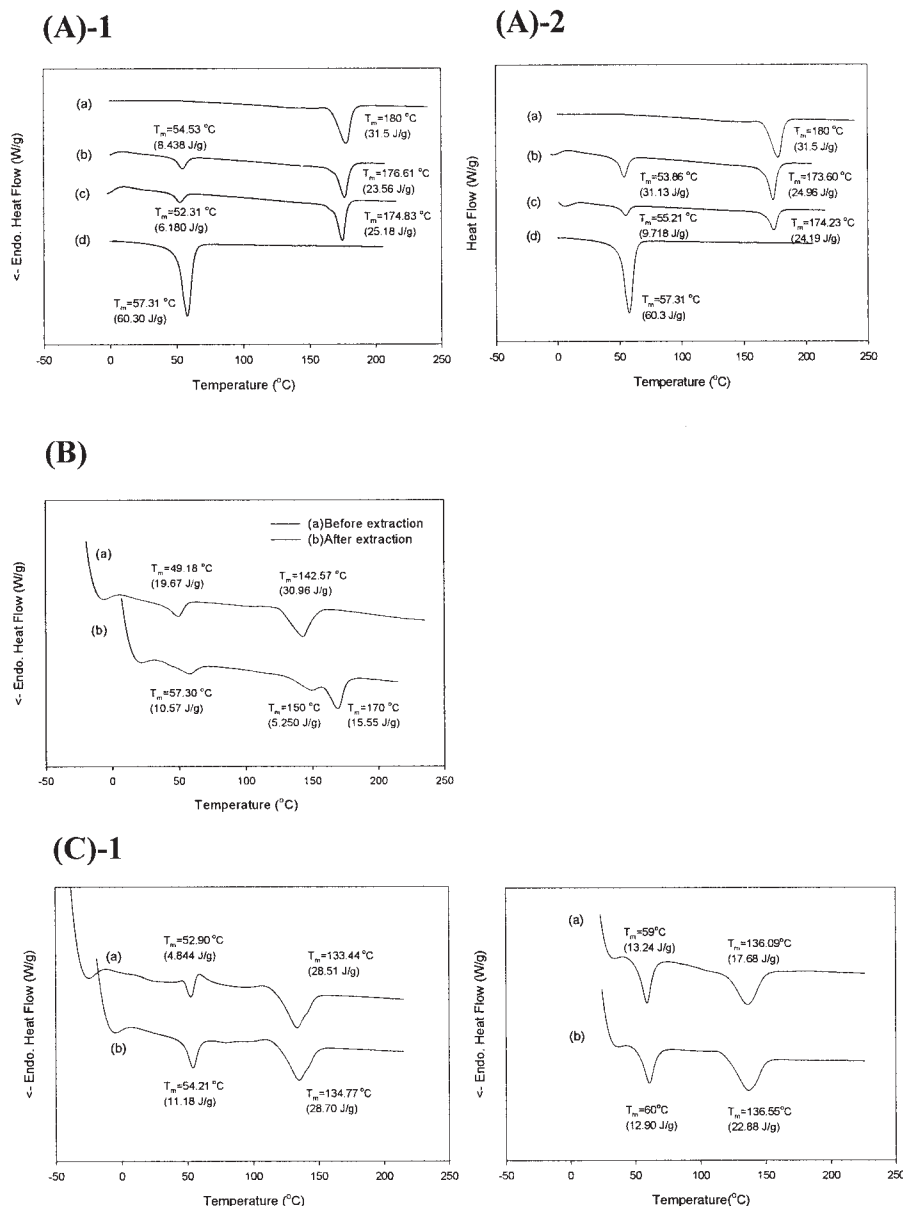


Figure 2 DSC measurements: [(A)-1] (a) PA12, (b) synthesized poly(LA-*b*-CL)-1 in the twin-screw extruder before the extraction-extruded product, (c) synthesized poly(LA-*b*-CL)-1 in the twin-screw extruder after the extraction-extruded product, and (d) PCL; [(A)-2] (a) PA12, (b) synthesized poly(LA-*b*-CL)-2 in the twin-screw extruder before the extraction-extruded product, (c) synthesized poly(LA-*b*-CL)-2 in the twin-screw extruder after the extraction-extruded product, and (d) PCL; [(B)] (a) synthesized poly(LA-*b*-CA-*b*-CL) in the twin-screw extruder before the extraction-extruded product and (b) synthesized poly(LA-*b*-CA-*b*-CL) in the twin-screw extruder after the extraction-extruded product; [(C)-1] (a) synthesized poly(LA/CA-*b*-CL)-1 in the twin-screw extruder before the extraction-extruded product and (b) synthesized poly(LA/CA-*b*-CL)-1 in the twin-screw extruder after the extraction-extruded product; and [(C)-2] (a) synthesized poly(LA/CA-*b*-CL)-2 in the twin-screw extruder before the extraction-extruded product and (b) synthesized poly(LA/CA-*b*-CL)-2 in the twin-screw extruder after the extraction-extruded product.

where I_0 is the intensity of the initial light beam, λ is the wavelength, and E is the extinction ratio ($\Delta I/I_0$).

On the basis of this relationship, the PA12 content in poly(LA-*b*-CL)-1 was about 45.4%, and the average PCL block content in poly(LA-*b*-CL)-1 was about 38.2%. We then characterized the FTIR results of the poly(LA-*b*-CL) copolymers with the FTIR results of various PA12/PCL blends. The τ values of poly(LA-

b-CL)-1 were close to the value of the 60/40 (w/w) PA12/PCL blend.

Similarly, we obtained FTIR results for poly(LA-*b*-CL)-2 and estimated its block contents. These were again calibrated with PA12/PCL blends. The estimated values of the PA12 block and PCL block of poly(LA-*b*-CL)-2 were close to the value of the 40/60 (w/w) PA12/PCL blend with respect to τ .

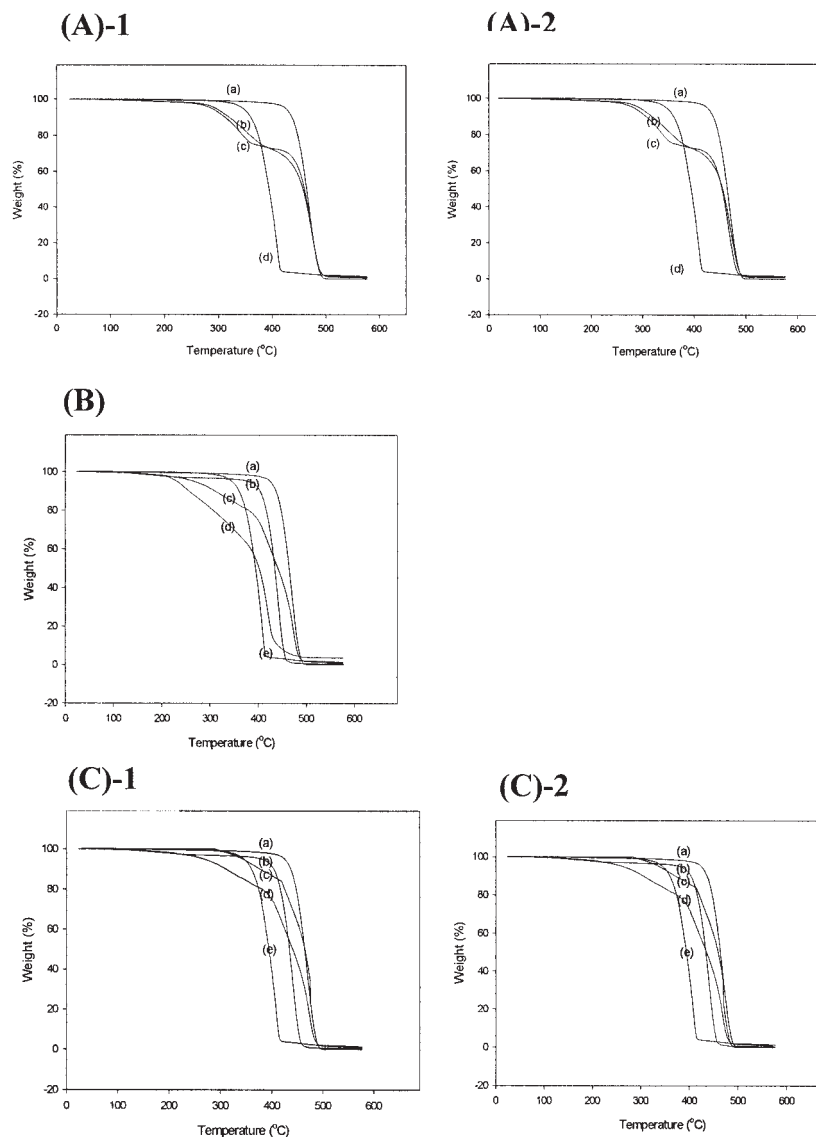


Figure 3 TGA measurements: [(A)-1] (a) PA12, (b) extracted poly(LA-*b*-CL)-1, (c) unextracted poly(LA-*b*-CL)-1, and (d) commercial PCL; [(A)-2] (a) PA12, (b) extracted poly(LA-*b*-CL)-2, (c) unextracted poly(LA-*b*-CL)-2, and (d) commercial PCL; [(B)] (a) PA6, (b) PA12, (c) extracted poly(LA-*b*-CA-*b*-CL), (d) unextracted poly(LA-*b*-CA-*b*-CL), and (e) commercial PCL; [(C)-1] (a) PA6, (b) PA12, (c) extracted poly(LA/CA-*b*-CL)-1, (d) unextracted poly(LA/CA-*b*-CL)-1, and (e) commercial PCL; and [(C)-2] (a) PA6, (b) PA12, (c) extracted poly(LA/CA-*b*-CL)-2, (d) unextracted poly(LA/CA-*b*-CL)-2, and (e) commercial PCL.

The value of random PA6 and PA12 in poly(LA/CA-*b*-CL)-1 was about 36.4%, and the average PCL content in poly(LA/CA-*b*-CL)-1 was about 39.3% with respect to τ . This again indicated that the absorbance of the blends was much lower than expected from the homopolymers according to additivity. Subsequently, we calibrated the FTIR results of poly(LA/CA-*b*-CL)-1 by preparing various PA6/PA12/PCL blends. Calibrating the FTIR results of the poly(LA/CA-*b*-CL)-1 terpolymer with the FTIR results of various PA6, PA12, and PCL blends, we found that poly(LA/CA-*b*-CL)-1 had about 20% LA, 20% CA, and 60% PCL. Similarly, we obtained FTIR results for poly(LA/CA-*b*-CL)-2, estimated its block contents, and calibrated them with PA6/PA12/PCL blends. We found that the

estimated values of the PA6/PA12 block and PCL block of poly(LA/CA-*b*-CL)-2 were close to the values of the 20/20/60 (w/w/w) PA6/PA12/PCL blend.

The value of the PA6 block and PA12 block was about 38.3%, and the average PCL block content in triblock poly(LA-*b*-CA-*b*-CL) was about 12.1%. The absorption values for poly(LA-*b*-CA-*b*-CL) were close to the τ values for the 40/40/20 PA6/PA12/PCL blend.

Molecular weight characterization

We estimated the molecular weight distribution of our block copolymers with GPC (150C ALC/GPC001, Waters).

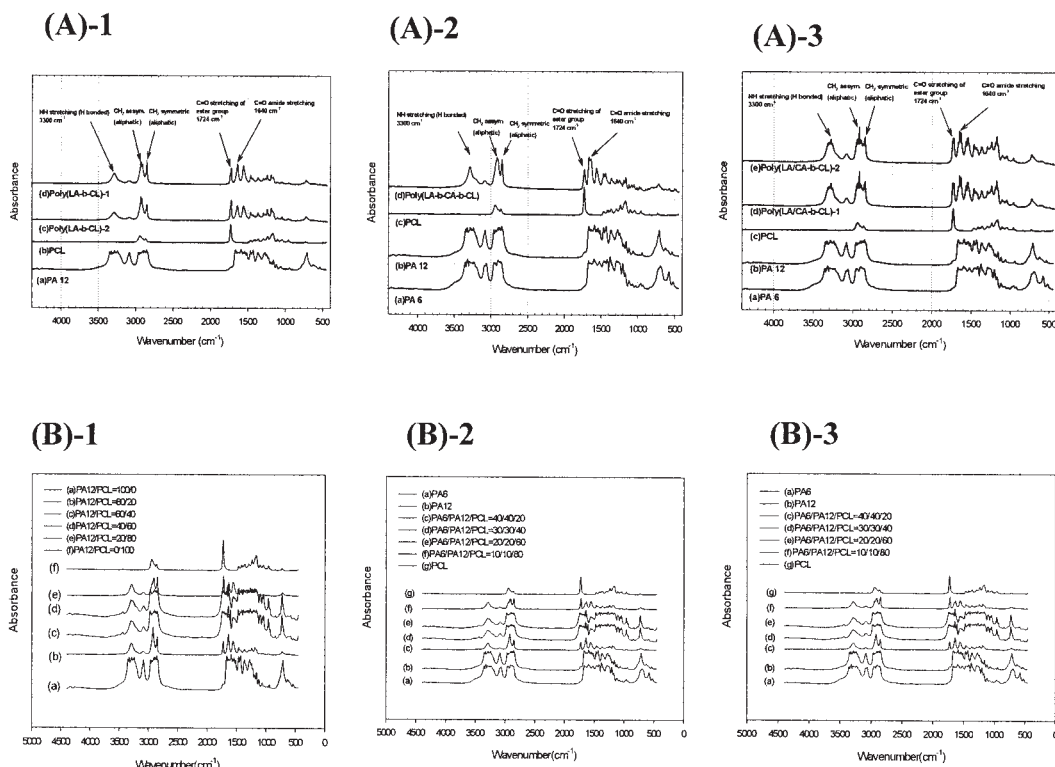


Figure 4 FTIR measurements measured at room temperature (PerkinElmer 16 PC-FTIR): [(A)-1] (a) PA12, (b) PCL, (c) poly(LA-*b*-CL)-2, (d) poly(LA-*b*-CL)-1, and (e) poly(LA/CA-*b*-CL)-2; [(A)-2] (a) PA6, (b) PA12, (c) PCL, and (d) poly(LA-*b*-CA-*b*-CL); [(A)-3] (a) PA6, (b) PA12, (c) PCL, (d) poly(LA/CA-*b*-CL)-1, and (e) poly(LA/CA-*b*-CL)-2; [(B)-1] (a) PA12, (b) 80/20 PA12/PCL, (c) 60/40 PA12/PCL, (d) 40/90 PA12/PCL, (e) 20/80 PA12/PCL, and (f) PCL; [(B)-2] (a) PA6, (b) PA12, (c) 40/40/20 PA6/PA12/PCL, (d) 30/30/40 PA6/PA12/PCL, (e) 20/20/60 PA6/PA12/PCL, (f) 10/10/80 PA6/PA12/PCL, and (g) PCL; and [(B)-3] (a) PA6, (b) PA12, (c) 40/40/20 PA6/PA12/PCL, (d) 30/30/40 PA6/PA12/PCL, (e) 20/20/60 PA6/PA12/PCL, (f) 10/10/80 PA6/PA12/PCL, and (g) PCL.

Figure 5 shows GPC peaks for poly(LA-*b*-CL)-1, poly(LA/CA-*b*-CL)-1, and poly(LA-*b*-CA-*b*-CL). The polydispersity indices were about 1.6. The ordering of the positions of the peaks in Figure 5 suggests that the radius of gyration should be in the following order: poly(LA/CA-*b*-CL) > poly(LA-*b*-CL) > poly(LA-*b*-CA-*b*-CL). This is probably the order of the molecular weights. We return to the question of molecular weight values in the Discussion section.

$\eta^*(\omega)$

We measured the $\eta^*(\omega)$ values of synthesized poly(LA-*b*-CL), poly(LA-*b*-CA-*b*-CL), and poly(LA/CA-*b*-CL) in the same manner as those of previous copolymers at 190°C.

Figure 6(A) illustrates that PCL showed Newtonian behavior over the whole frequency range (10^{-1} to 10^2 rad/s), and its zero-shear melt viscosity was about 150 Pa s at 190°C, whereas PA12 showed non-Newtonian behavior at the same temperature, and the zero-shear melt viscosity of PA12 was about 45,000 Pa s at 190°C. PA12 ($T_m = 180^\circ\text{C}$) showed higher melt viscosity than PCL ($T_m = 55^\circ\text{C}$) at 190°C.

In Figure 6(A), the low-shear melt viscosities of poly(LA-*b*-CL)-1 and poly(LA-*b*-CL)-2 appear to be similar to that of commercial PA12. They showed an intermediate trend between those of PA12 and PCL as the frequency was increased. The melt viscosity of poly(LA-*b*-CL)-1 was higher than that of poly(LA-*b*-CL)-2.

In Figure 6(B), the shear melt viscosities of poly(LA/CA-*b*-CL)-1 and poly(LA/CA-*b*-CL)-2 are shown to be intermediate between those of PA12 and PCL. The zero-shear melt viscosity of poly(LA/CA-*b*-CL)-1 was higher than that of poly(LA/CA-*b*-CL)-2.

In Figure 6(C), the melt viscosity of poly(LA-*b*-CA-*b*-CL) is shown to be intermediate between those of the two polyamides (PA6 and PA12) and PCL. However, its melt viscosity at a high frequency became lower than that of the PCL homopolymer.

Mechanical properties

Figure 7(A) shows that the bending storage modulus (E') of poly(LA-*b*-CL)-1 was about the same as that of PA12 and higher than that of PCL.

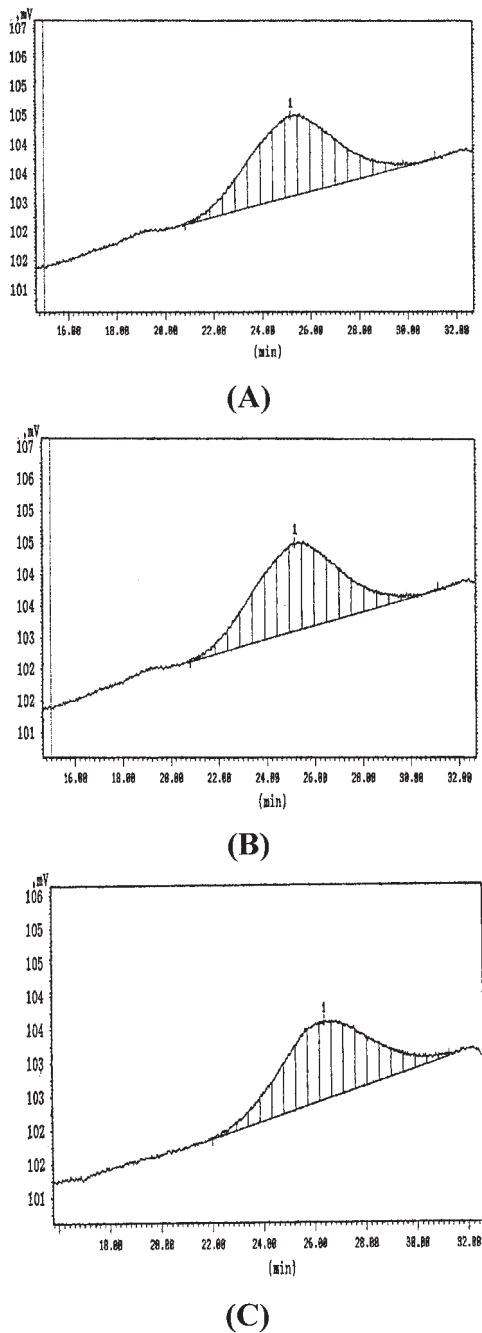


Figure 5 GPC traces of the block copolymers: (A) poly(LA-*b*-CL)-1, (B) poly(LA/CA-*b*-CL)-1, and (C) poly(LA-*b*-CA-*b*-CL).

In Figure 7(B), α peaks for poly(LA/CA-*b*-CL) can be observed at about 135°C, and this agrees with the DSC results for T_m 's. In Figure 7(C), E' of triblock poly(LA-*b*-CA-*b*-CL) seems complex. Its values were lower than those of the polyamides (PA6 and PA12) and higher than those of PCL. However, E' of poly(LA-*b*-CA-*b*-CL) was much lower than those of the polyamides. Generally, E' of poly(LA-*b*-CA-*b*-CL) decreased more with increasing temperature than those of the homopolymers.

Figure 8(A) shows that the tensile strengths to break of PA6 (60 MPa) and PA12 (70 MPa) were higher than that of PCL (20 MPa). The elongations to break of PA6 (300%) and PA12 (350%) were lower than that of PCL (770%). PA12 had a yield stress of 85 MPa, and PCL had a yield stress of 22 MPa. The poly(LA-*b*-CL) block copolymers showed yield behavior and necking in the tensile tests.

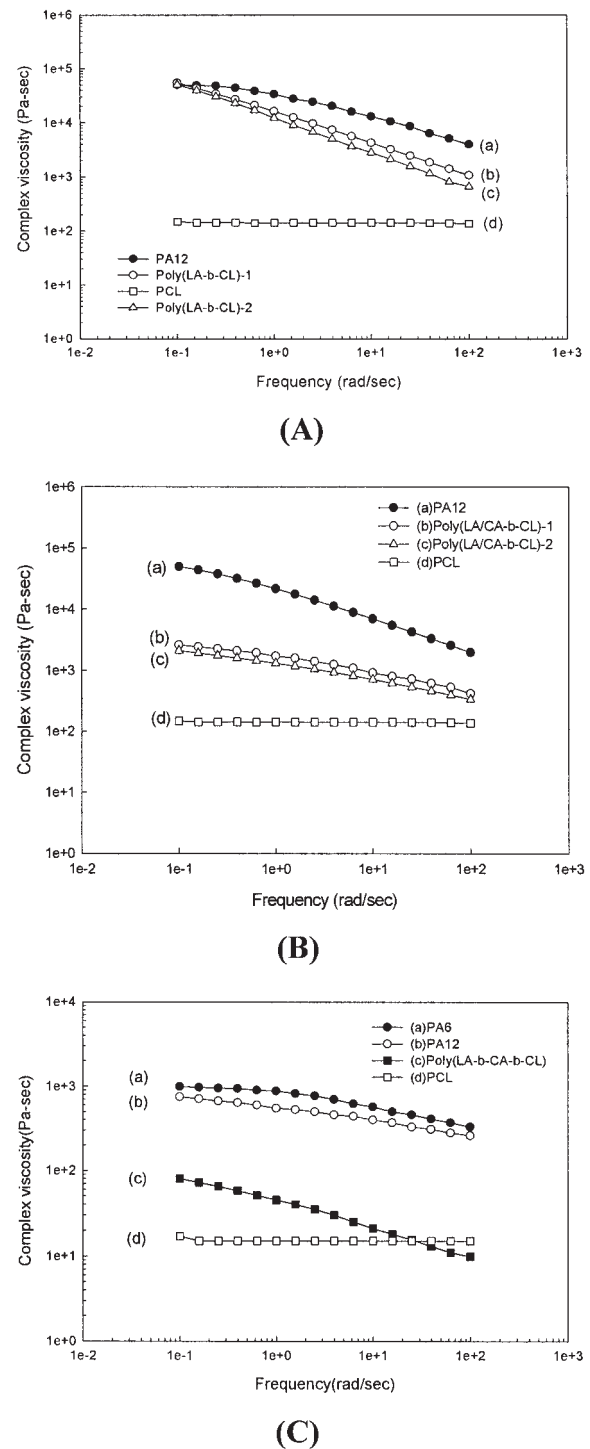


Figure 6 $\eta^*(\omega)$ measured at (A,B) 190 and (C) 230°C.

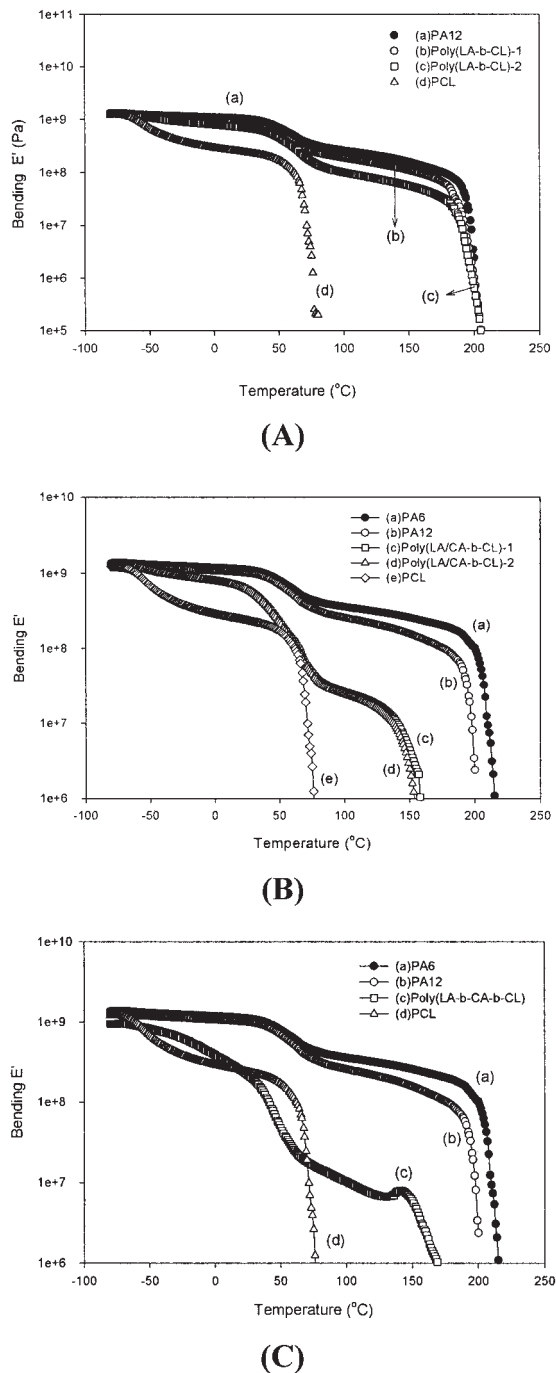


Figure 7 E' as a function of temperature.

Poly(LA-*b*-CL)-1 exhibited a yield stress of 48 MPa, and poly(LA-*b*-CL)-2 exhibited a yield stress of 38 MPa. The tensile strength to break was 42 MPa for poly(LA-*b*-CL)-1 and 43 MPa for poly(LA-*b*-CL)-2, whereas that for PA12 was 70 MPa, and that for PCL was 20 MPa. The elongation to break was 380% for poly(LA-*b*-CL)-1 and 480% for poly(LA-*b*-CL)-2, whereas that for PA12 was 350%, and that for PCL was 770%. Comparing the tensile properties of the poly(LA-*b*-CL) block copolymers synthesized in a

twin-screw extruder in this study with the homopolymers (PA12 and PCL), we found the mechanical properties of the poly(LA-*b*-CL) block copolymers to be intermediate.

The poly(LA/CA-*b*-CL)-1 terpolymer exhibited a yield stress of 25 MPa, and poly(LA/CA-*b*-CL)-2 showed a yield stress of 27 MPa, whereas PA12 had a yield stress of 85 MPa, and PCL had a yield stress of 22 MPa. The tensile strength to break of the poly(LA/

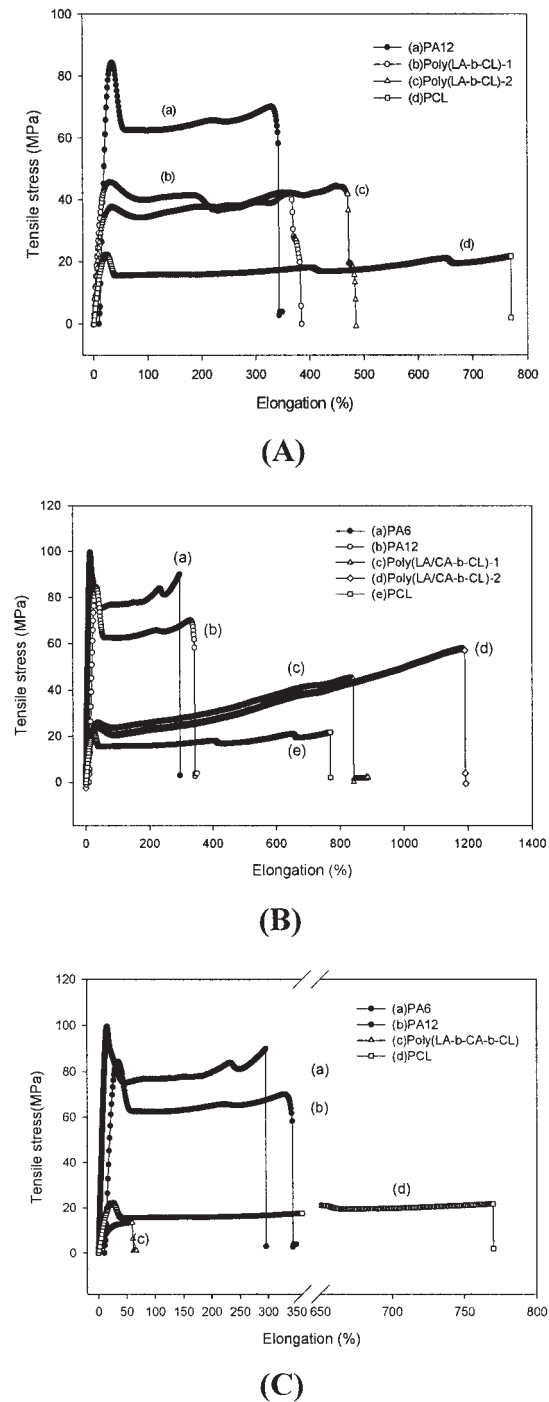


Figure 8 Tensile properties.

CA-*b*-CL) terpolymers was 45 MPa for poly(LA/CA-*b*-CL)-1 and 57 MPa for poly(LA/CA-*b*-CL)-2, whereas for PA6 it was 89 MPa, for PA12 it was 70 MPa, and for PCL it was 20 MPa. The elongation to break of poly(LA/CA-*b*-CL)-1 was 840%, and that of poly(LA/CA-*b*-CL)-2 was about 1200%, whereas that of PA6 was 300%, that of PA12 was 350%, and that of PCL was 770%. In comparison with PA6, PA12, and PCL, the tensile properties, tensile stress, and elongation of poly(LA-*b*-CL) and poly(LA/CA-*b*-CL) random block terpolymers were intermediate between those of PA12 and PCL, whereas the elongation to break of poly(LA/CA-*b*-CL) random block terpolymers were greater than those of the homopolymers. Poly(LA/CA-*b*-CL) was generally superior to poly(LA-*b*-CL). Comparing different poly(LA/CA-*b*-CL) random block terpolymers, we found that poly(LA/CA-*b*-CL)-2 exhibited lower yield strength, higher tensile strength, and higher elongation to break than poly(LA/CA-*b*-CL)-1.

Figure 8(c) shows that the tensile strength to break of poly(LA-*b*-CA-*b*-CL) was about 14 MPa; its tensile modulus was 67.3 MPa, and its elongation to break was about 70%. In comparison with the tensile properties of the homopolymers, poly(LA-*b*-CL), and poly(LA/CA-*b*-CL), the triblock copolymer poly(LA-*b*-CA-*b*-CL) showed a much lower tensile modulus, tensile strength, and elongation.

DISCUSSION

Polymerization in twin-screw extruders

A twin-screw extruder is a continuous reactor. It has a relatively short mean residence time (a few minutes) in comparison with a batch reactor during polymerization. Goodman and Vaschon¹² used *N*-sodiocaprolactam (C₆H₁₁NONa) as an initiator. Their reaction time for a random copolymer of CA and CL was up to 6 h in a batch reactor. Therefore, it is necessary to find a better initiator system for obtaining high conversions and molecular weights of the product in a twin-screw extruder.

We have described the homopolymerization of both LA⁸ and CA¹³ and their random copolymerization,⁸ as well as the same lactam-lactone copolymers.^{9-11,15} We used NaH and *N*-acetylcaprolactam as initiators. Problems with insufficient residence times arose during the effort to make the poly(LA-*b*-CA-*b*-CL) triblock terpolymer.

Several researchers have studied homopolymerization through the reactive extrusion of CL.^{14,16-18} Wautier and coworkers^{16,17} described the reactive extrusion of CL in patents. They reported that the degree of conversion of CL was about 99%. Vergnes and et al.¹⁹ investigated the polymerization of CL in a twin-screw extruder. Experiments were performed to determine the influence of the processing conditions (feed rate,

screw speed, barrel temperature, and initiator concentration). They reported that a lower feed rate at the same barrel temperature created a longer residence time and led to a high conversion of CL in a twin-screw extruder. They also observed that the residence time decreased when the screw speeds increased for the same operating conditions. Recently, Kim and White²⁰ described extensive experimental investigations for the bulk polymerization of CL both in an internal mixer and in a twin-screw extruder. They obtained a high 95% conversion of PCL with sodium hydride as an initiator. In our laboratories, we have made extensive studies of the polymerization of polyamides in twin-screw extruders.

Studies of the copolymer composition

We found that block copolymers showed different crystalline melting peaks that corresponded to individual block melting points from the results of DSC measurements for poly(LA-*b*-CL), poly(LA-*b*-CA-*b*-CL), and poly(LA/CA-*b*-CL). The diblock copolymer poly(LA-*b*-CL) exhibited two different crystalline melting peaks of about 55 and 175°C, which corresponded to those of the two pure block components. The terpolymer poly(LA/CA-*b*-CL) showed two different crystalline melting peaks. The DSC results for our poly(LA/CA-*b*-CL) corresponded to pure PCL and an LA/CA random copolymer. In a study using the simultaneous addition of CA and CL, Goodman and Vaschon¹² concluded that they had produced a random copolymer with little blockiness because it had a single melting point.

The triblock copolymer poly(LA-*b*-CA-*b*-CL) that we synthesized exhibited three different crystalline melting peaks. However, the polyamide block T_m 's were lower than the homopolymer melting points. To determine the reason, we prepared PA6/PA12 blends of various compositions and investigated the DSC traces for those blends. These are presented in Figure 9. By investigating the DSC measurements of PA6/PA12 melt blends of various compositions, we found that the polyamide blends were partially miscible systems and exhibited some T_m depression. The DSC results for the polyamide blends argued for the partial miscibility of the polyamide blocks for our poly(LA-*b*-CA-*b*-CL). However, the levels of depression of T_m were much greater, and this suggested that the LA and CA blocks were not pure. There may have been a gradient LA/CA region in the backbone.

Comparing the FTIR results for the copolymer with those for the neat polymers, we obtained a composition that did not add up to 100%. This observation also occurred for blends of polyamides and polycaprolactone. We believe that this was due to hydrogen bonding between the polyamide and polyester chains. This led to problems with the FTIR

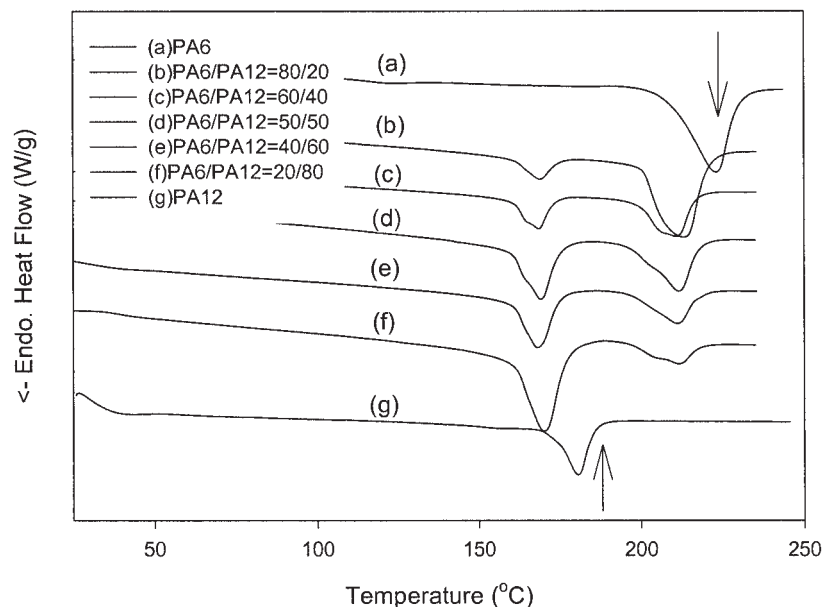


Figure 9 DSC measurements of PA6/PA12 blends of various compositions.

results for the block copolymer and for the polyamide and polycaprolactone blends. This problem was resolved by a comparison of the spectra of the copolymers with those of appropriate blends. We summarize this in Table II.

Molecular weights

According to the concentrations of the monomers and initiator of the polymers, the number-average molecular weights (M_n 's) should have been 47,700 for

poly(LA-*b*-CL)-1, 49,000 for poly(LA-*b*-CL)-2, 56,600 for poly(LA/CA-*b*-CL)-1, 58,000 for poly(LA/CA-*b*-CL)-2, and 25,000 for poly(LA-*b*-CA-*b*-CL). The low molecular weight of triblock copolymer poly(LA-*b*-CA-*b*-CL) was due to the low feed rates (0.5 kg/h) of LA, CA, and CL at the same initiator concentration (0.125 mol). We used these reduced feed rate conditions for the triblock copolymerization of poly(LA-*b*-CA-*b*-CL) because we were unable to obtain a fully polymerized product under the same experimental conditions (1.3 kg/h feed rates for LA, CA, and CL)

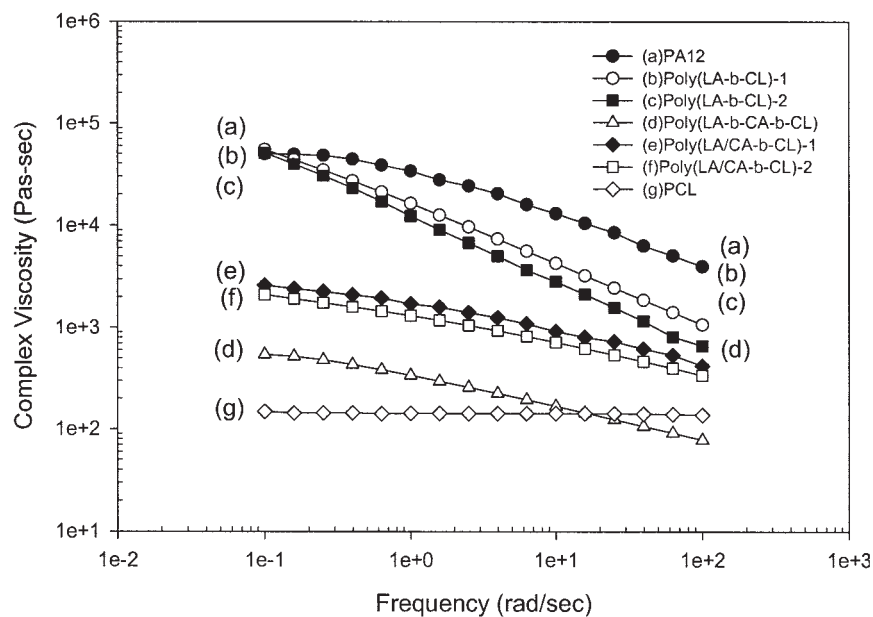


Figure 10 Comparison of complex viscosities measured at 190°C.

TABLE II
Block Copolymers Synthesized by Reactive Polymerization in a Twin-Screw Extruder

Product	Conversion (%)	Crystallinity of polyamides (%)	Block compositions by FTIR			Thermal transitions by DSC		M_n by the Benoit method	Mechanical properties	
			Polyamide (%)	PCL (%)	T_m of PCL (°C)	T_m of polyamide (°C)	Young's modulus (MPa)		Tensile strength (MPa)	Elongation (%)
			Polyamide (%)	PCL (%)	T_m of PCL (°C)	T_m of polyamide (°C)		Young's modulus (MPa)	Tensile strength (MPa)	Elongation (%)
			Polycaprolactone (%)							
Poly(LA- <i>b</i> -CL)-1	90-91	78	45	38	52	175	43,000	230	42	380
			60	40						
Poly(LA- <i>b</i> -CL)-2	91-92	75	38	41	55	175	44,000	193	43	480
			40	60						
Poly(LA/CA- <i>b</i> -CL)-1	90-91	38	36	39	54	135	51,000	138	45	842
			20	60						
Poly(LA/CA- <i>b</i> -CL)-2	91-93	30	36	40	60	137	52,000	130	57	1200
			20	60						
Poly(LA- <i>b</i> -CA- <i>b</i> -CL)	80-81	27	36	12	57	150	20,250	67	14	78
			40	20						

for diblock copolymerization and random block terpolymerization.

We could have used Benoit et al.'s²¹ method based on a universal $[\eta]M$ ($[\eta]$ = intrinsic viscosity; M = molecular weight) curve with polystyrene standards to determine the molecular weights. This would have been speculative or worse because we could not expect the molecular weight to simply depend on the radius of gyration r_g^2 for a block copolymer when the solvent interacted differently with the two solvents. However, putting this objection aside and proceeding, we found M_n 's of 52,000, 44,000, and 20,300 for poly(LA/CA-*b*-CL), poly(LA-*b*-CL), and poly(LA-*b*-CA-*b*-CL). The poly(LA-*b*-CA-*b*-CL) molecular weight was lower than those of poly(LA-*b*-CL) and poly(LA/CA-*b*-CL), which corresponded to all of our other observations.

Melt viscosity and mechanical properties

The melt viscosities and mechanical properties of poly(LA-*b*-CL) and poly(LA/CA-*b*-CL) were promising. The viscosities were close to those of PA12, and the elongation to break was as large as or larger than that of PA12. They seemed reasonable. Poly(LA-*b*-CA-*b*-CL) had a low molecular weight that led to a low viscosity and poor mechanical properties.

Our copolymers exhibited non-Newtonian melt viscosity at 190°C. The melt viscosity of poly(LA-*b*-CL)-1 was higher than that of poly(LA-*b*-CL)-2. This was perhaps due to poly(LA-*b*-CL)-2 having a longer PCL block than poly(LA-*b*-CL)-1. Kim and White⁹ also argued that longer PCL block of diblock copolymer poly(LA-*b*-CL) led to a reduction in the block copolymer melt viscosity. The melt viscosities of poly(LA/CA-*b*-CL)-2 were lower than those of poly(LA/CA-*b*-CL)-1. This might also be explained by poly(LA/CA-*b*-CL)-2 having a longer PCL block than poly(LA/CA-*b*-CL)-1.

The mechanical properties and thermoplastic elastomer characteristics of the block copolymers improved with increasing molecular weights, and the modulus was apparently affected by the polyamide crystallinity level. This is clear from Table II.

CONCLUSIONS

We have described the syntheses of various types of copolymers (diblock, triblock, and random block terpolymers) by reactive extrusion. These copolymers were synthesized continuously in a twin-screw extruder with the upstream and downstream addition of monomers and with the simultaneous and sequential feeding of monomers.

Sodium hydride as an initiator and *N*-acetylcaprolactam as a coinitiator were good for reactive extrusion. These initiator systems in only a few minutes led

to a good conversion (90%) and successful copolymerization. The molecular weight of the PCL block copolymer could be controlled by the feed rate in a twin-screw extruder during reactive polymerization.

The polydispersity index of the synthesized copolymer measured by GPC was less than 2 because the molecular weight distribution of the copolymer was narrow. The mechanical properties and thermoplastic elastomer characteristics of the block copolymers improved with increasing molecular weights, and the modulus seemed to be affected by the polyamide crystallinity level. From an estimate of the compositions of the synthesized polyamide–polyester copolymers, we found that the synthesized copolymers could be adjusted if we controlled the feed rate of each monomer during reactive extrusion.

References

1. Lewis, E. F. U.S. Pat. 3,616,475 (1971).
2. Kubota, H.; Nowell, J. B. *J Appl Polym Sci* 1975, 19, 1521.
3. Kobayashi, F. *Jpn. Pat.* 66-714410 (1972).
4. Werner, B. H.; Hayes, R. U.S. Pat. 3,758,631 (1973).
5. Frunze, T. M.; Korshak, V. V.; Kovriga, V. V.; Ivanova, S. L.; Kuznetsova, I. G.; Kurashev, V. V.; Shleifman, R. B.; Kotel'nikov, V. A.; Dubovik, I. I. *Plast Massy* 1976, 1, 14.
6. Frunze, T. M.; Kotel'nikov, V. A.; Ivanov, M. P.; Valkova, T. V.; Kurashev, V. V.; Davtyan, S. P. *Polym Sci USSR* 1981, 23, 2902.
7. Michaeli, W.; Hocker, H.; Berghaus, U.; Frings, W. *J Appl Polym Sci* 1993, 48, 871.
8. Ha, S.; White, J. L. *Int Polym Process* 1998, 12, 136.
9. Kim, B. J.; White, J. L. *J Appl Polym Sci* 2003, 88, 1429.
10. Lee, B. H.; White, J. L. *Polym Eng Sci* 2002, 42, 1724.
11. Kim, I.; White, J. L. *Soc Plast Eng Annu Tech Conf Tech Pap* 2003, 49, 1653.
12. Goodman, I.; Vaschon, R. N. *Eur Polym J* 1984, 20, 529.
13. Kye, H.; White, J. L. *J Appl Polym Sci* 1994, 52, 1249.
14. Narayan, R.; Krishnan, M.; DuBois, P. U.S. Pat. 5,540,929 (1996).
15. Kim, I.; White, J. L. *J Appl Polym Sci* 2003, 90, 3797.
16. Wautier, H. U.S. Pat. 5,468,837 (1995).
17. Wautier, H.; Detournay, L.; Kaszacs, M. U.S. Pat. 5,656,718 (1997).
18. Narayan, R.; Krishnan, M.; Snook, J. B.; Gupta, A.; DuBois, P. U.S. Pat. 5,801,224 (1998).
19. Vergnes, B.; Poulesquen, A.; Gimenez, J.; Cassagnau, P.; Michel, A. *Int Polym Process* 2001, 16, 31.
20. Kim, B. J.; White, J. L. *Int Polym Process* 2002, 17, 33.
21. Benoit, M.; Grubisic, F.; Rempp, R. *J Polym Sci Part B: Polym Lett* 1967, 5, 753.