

Anionic Copolymerization of Lauryl Lactam and Polycaprolactone for the Production of a Poly(ester amide) Triblock Copolymer

In Kim, James L. White

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

Received 13 December 2002; accepted 5 March 2003

ABSTRACT: This article examines the anionic polymerization of lauryl lactam into polyamide 12 and the copolymerization of lauryl lactam with a diisocyanate-end-capped polycaprolactone used to produce a poly(ester amide) block copolymer. The molecular weights of the polyester polyols used in the preparation of the diisocyanate-end-capped polycaprolactone were varied. The products were characterized with Fourier transform infrared spectroscopy and dif-

ferential scanning calorimetry, and the mechanical properties were measured in a mechanical tester. The influence of the polyol molecular weight was considered. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3797–3805, 2003

Key words: anionic copolymerization; block copolymers; polyamides

INTRODUCTION

Since its discovery in the 1950s, the rapid anionic polymerization of lactams has received considerable attention.^{1–10} However, the literature is almost entirely devoted to caprolactam. There is little on the polymerization of other lactams.^{11–15} Polyamide 12, based on lauryl lactam, is produced commercially. Atochem introduced a polyamide-based thermoplastic elastomer (TPE) in 1982, naming its product Pebax [poly(ether-block-amide) elastomer]. Dow Chemical Co. also developed poly(ether amide), poly(ester amide), and poly(ether ester amide). They were all based on condensation polymerization.¹⁶

In our own laboratories, Ha and White¹⁵ made poly(lauryl lactam) in a twin-screw extruder and a caprolactam/lauryl lactam random block copolymer. Kim and White¹⁷ synthesized a simple AB block copolymer of poly(lauryl lactam) and polycaprolactone (PCL) in a batch mixer and a twin-screw extruder. Lee and White^{18,19} made block ABA PCL and PCL polyethers in a batch mixer and a twin-screw extruder.

In this article, we present a study of the copolymerization of lauryl lactam and diisocyanate-end-capped PCLs of different molecular weights for the creation of a poly(ester amide) block copolymer (PESA). A schematic description of the preparation of the synthesized PESA is shown in Figure 1. Our intention was to make toughened polyamide 12 or a TPE.

EXPERIMENTAL

Materials

The monomer used to make polyamide 12 in this study was lauryl lactam (EMS Chemie, Inc. Sumter, SC). 4,4'-Diphenylmethane diisocyanate (MDI) and polyester polyols of different molecular weights (Lexorez 1100-220, 1100-110, 1100-45, and 1100-35) were obtained to make diisocyanate-end-capped PCL from Bayer (Pittsburgh, PA) and Inorex Chemical Co. (Philadelphia, PA), respectively.

Sodium hydride (Aldrich Chemical Co.) was used as an initiator and *N*-acetyl caprolactam (Aldrich Chemical, Milwaukee, WI) was used as a coinitiator to synthesize polyamide 12. Because of the sensitivity of lauryl lactam and polyester polyol to atmospheric humidity, we dried those materials at 80°C for 24 h in a vacuum oven before the polymerization. The materials are listed in Table I.

Apparatus and procedure

General procedure for the synthesis of diisocyanate-end-capped PCL

It was necessary to react an excess of MDI and PCL polyols of different molecular weights. Usually, a well-dried, 500-mL, three-necked, round-bottom, angled flask equipped with a water-cooled condenser with a capped CaCl₂ drying tube, a thermocouple, an N₂ inlet, and a mechanical stirrer was charged with 1 mol of polyester polyol and heated to 85°C. The polyester polyol was added to 2.1 mol of MDI under mechanical stirring over a period of 1 h while a nitrogen atmosphere was maintained.

Correspondence to: J. L. White.

TABLE I
Raw Materials Used to Synthesize Polyamide-12, Diisocyanate-End-Capped PCL and PESA

	Trade name	Chemical name and structure	Source	Functionality	Molecular weight
1	Initiator	Sodium hydride	Aldrich		24/mol
2	Coinitiator	<i>N</i> -acetylcaprolactam	Aldrich		155.2/mol
3	Lactam	Lauryl lactam	EMS		197/mol
4	MDI	4-4'-diphenylmethane diisocyanate	Bayer	2	250/mol
5	Polyol L 1100-220	Polyester polyol Hexanedionic acid, polymer with 2,2-oxybis	Inorex	2	500/mol
6	Polyol L 1100-110	Polyester polyol Hexanedionic acid, polymer with 2,2-oxybis	Inorex	2	1000/mol
7	L 1100-45	Polyester polyol Hexanedionic acid, polymer with 2,2-oxybis	Inorex	2	2500/mol
8	L 1100-35	Polyester polyol Hexanedionic acid, polymer with 2,2 oxybis	Inorex	2	3200/mol

of polymerized polyamide 12 in 200 mL of *m*-cresol (used as a solvent). We subsequently poured this into an excess amount of methanol under the condition of rapid agitation. Polyamide 12 was freed from unreacted monomers and oligomers by Soxhlet extraction for 12 h. 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.

Each block copolymer was characterized in the following manner. The block copolymer was boiled with distilled water or methanol for the removal of residual lauryl lactam. This allowed the determination of the total poly(lauryl lactam) and PCL block copolymer. After drying *in vacuo*, the polymer was extracted with tetrahydrofuran (THF) or chloroform in a Soxhlet apparatus to isolate unreacted PCL as THF- or chloroform-soluble parts. The measured weight divided by the initial weight of the block copolymer was the degree of conversion.

The transition behavior of PESA was determined by differential scanning calorimetry (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 N₂ was 35 mL/min.

The infrared spectra of PESAs were measured with a Fourier transform infrared (FTIR) spectrometer (16 PC-FTIR, PerkinElmer, Norwalk, CT) to determine the chemical reactions of the reactants.

The dynamic mechanical thermal properties of the polyamide block copolymer, measured at 1 Hz with a 4°C/min temperature profile, were determined. An extension mode test from -50 to 250°C was performed.

The samples are prepared by compression molding at 200°C and were cut into dumbbell-shaped speci-

mens of ASTM D 638 Type V. The tensile properties were measured with an Instron model 4204 mechanical tester (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 AND DISCUSSION

Polymerization of lauryl lactam and copolymerization of lauryl lactam and diisocyanate-end-capped PCL in an internal mixer

The sodium hydride initiator and *N*-acetylcaprolactam coinitorator were separately premixed with the lauryl lactam monomer in a dry box under argon gas purging. Usually, this was done with 0.09 mol of the initiator to 1.0 mol of the monomer and 0.09 mol of the coinitorator to 1.0 mol of the monomer. The degree of conversion of lauryl lactam to polyamide 12 was determined as follows. We dissolved 5 g of polymerized polyamide 12 in 200 mL of the *m*-cresol solvent. We subsequently poured this into an excess amount of methanol under the condition of rapid agitation. Polyamide 12 was freed from the unreacted monomers and oligomers by Soxhlet extraction for 12 h. We then filtered and dried the precipitates in a vacuum-drying oven for 48 h at 100°C. Subsequently, the measured weight of the polymer divided by the initial weight of the monomer was taken as the degree of conversion. The conversion of lauryl lactam to polyamide 12 was 90%.

The polymerization of lauryl lactam and the copolymerization of lauryl lactam and diisocyanate-end-capped PCL were carried out in an internal mixer. Two different methods were used to feed materials into the internal mixer, and the torque as a function of time was recorded. A one-step process method in-

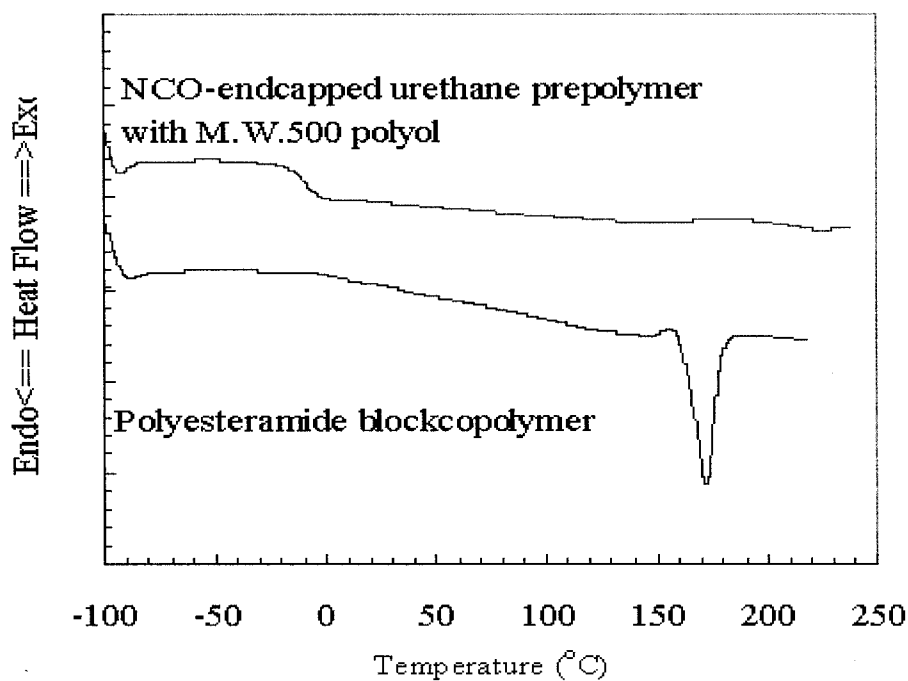


Figure 2 DSC thermogram characterization (20°C/min).

involved feeding all the reactants into the chamber of the internal mixer simultaneously. The second method involved feeding the reactants into the chamber of the internal mixer sequentially. The concept was that lauryl lactam was polymerized and then diisocyanate-

end-capped PCL was poured into the chamber of the internal mixer to react with the polymerized lauryl lactam.

The reaction temperature was 200°C, and the rotor speed was 100 rpm. The torque was increased during

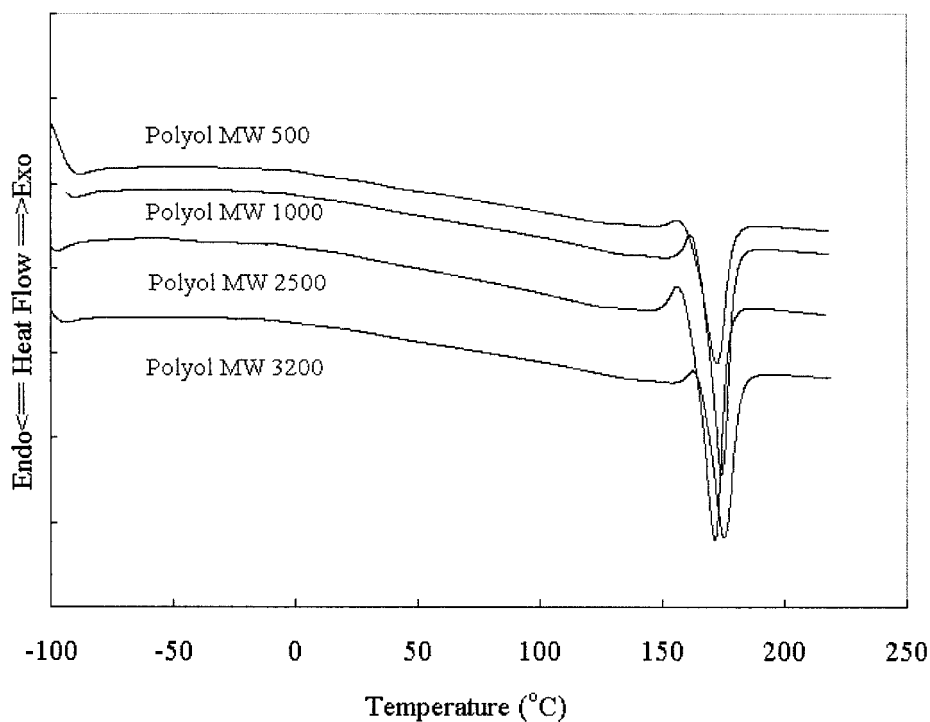


Figure 3 DSC thermograms of PESAs with NCO-end-capped PCL with prepolymers of various molecular weights.

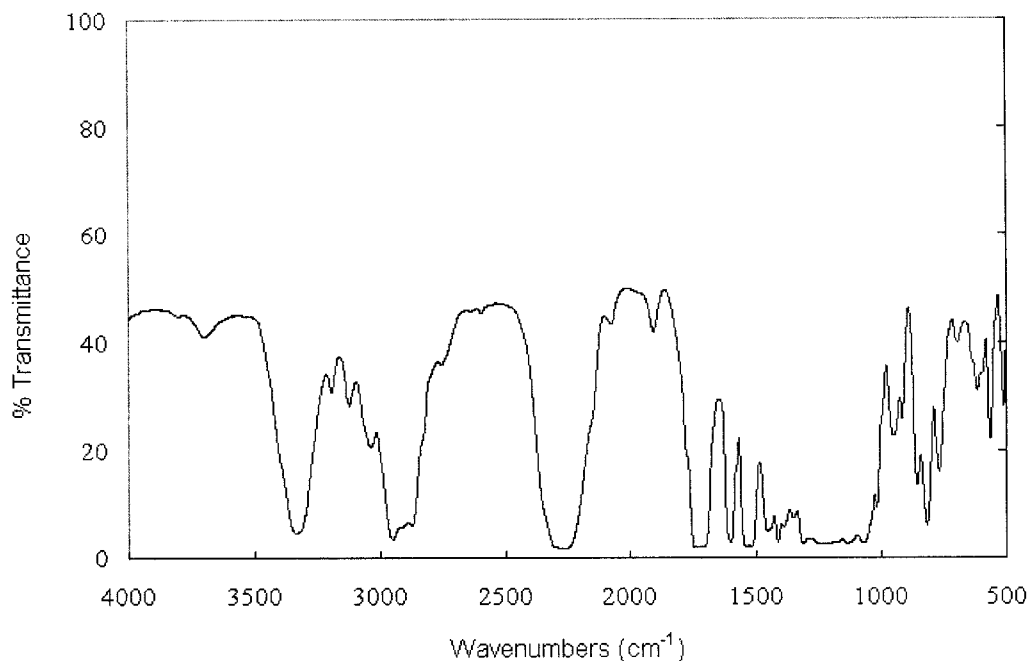


Figure 4 FTIR spectrum of an NCO-end-capped PCL prepolymer.

the polymerization; it then reached a steady state and subsequently decreased as the reaction continued. On the basis of the torque as a function of time during the polymerization of lauryl lactam, the reaction time to the polymerization of lauryl lactam was about 3 min in the one-step process. The torque increased during

the polymerization, reached a steady state, and then decreased as the reaction continued.

In the case of the copolymerization of lauryl lactam and diisocyanate-end-capped PCL, we first sought to make the block copolymer with the one-step process. The polymerization of the lactam did not proceed.

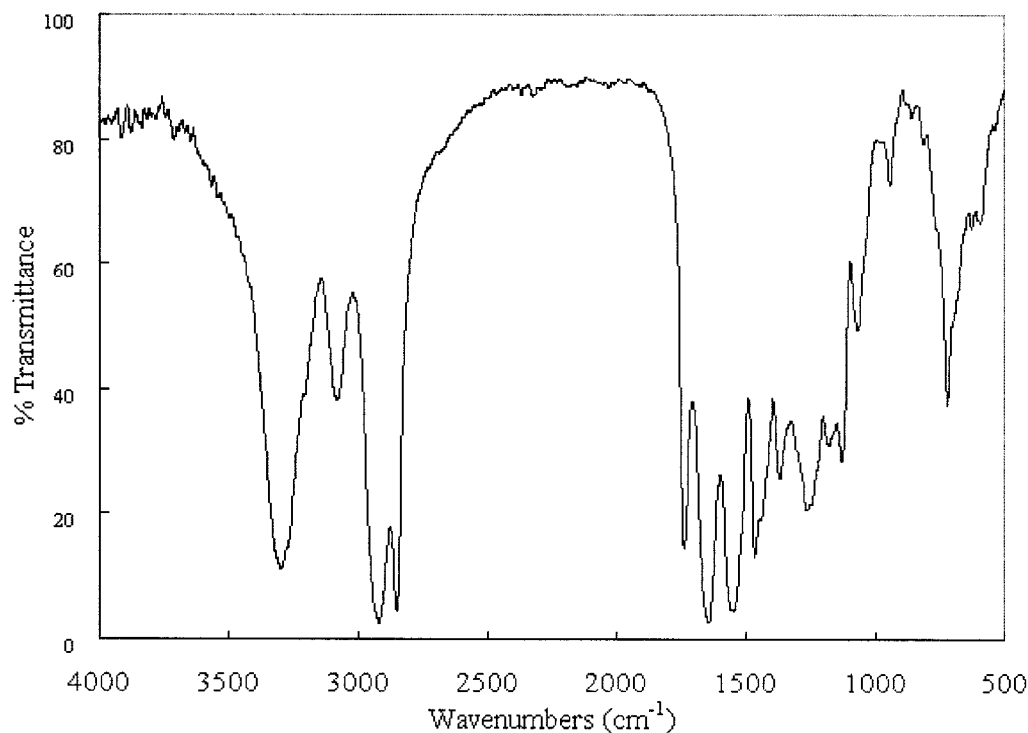


Figure 5 FTIR spectrum of PESA.

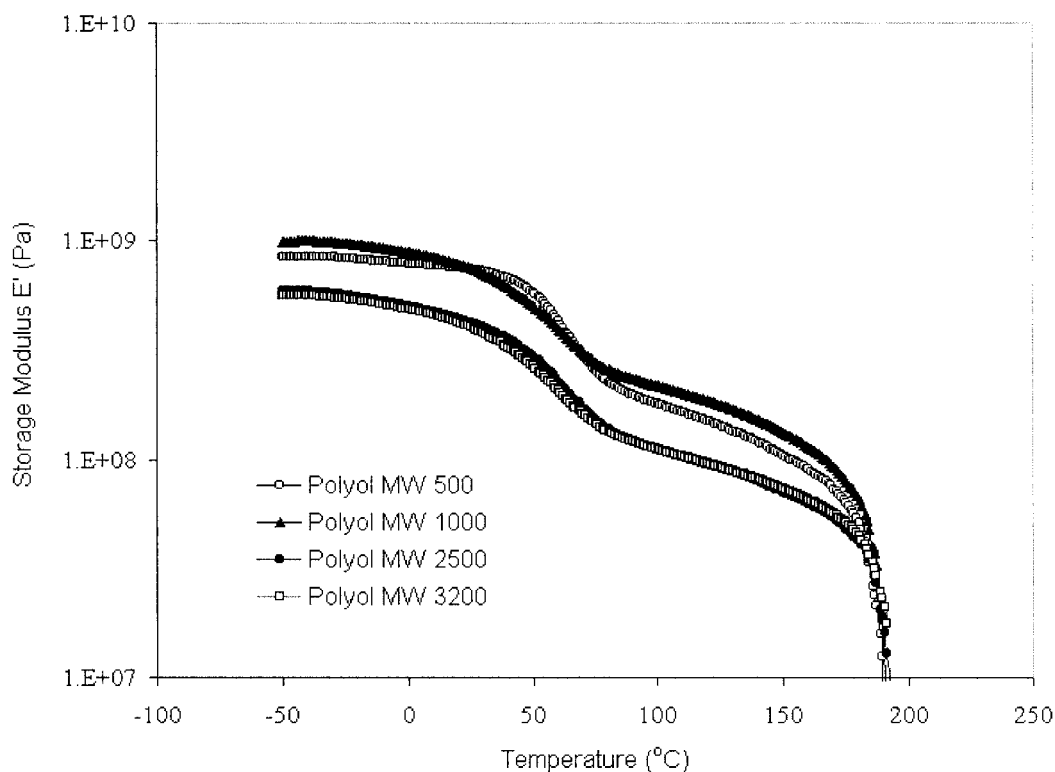


Figure 6 Dynamic mechanical behavior of PESAs with NCO-end-capped prepolymers with polyols of different molecular weights as a function of temperature.

Diisocyanate-end-capped PCL acted as an impurity during the polymerization of lauryl lactam in this one-step method.

When we tried to use sequential feeding, we could produce the copolymer as the torque increased during the lauryl lactam polymerization. The torque sud-

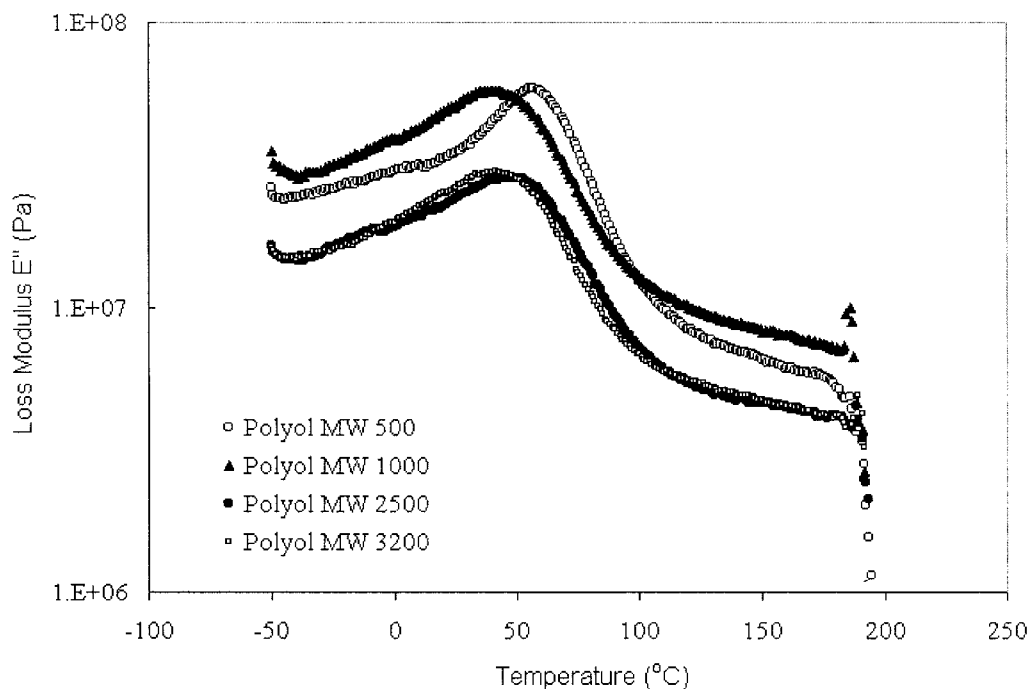


Figure 7 Dynamic mechanical behavior of PESAs with NCO-end-capped prepolymers with polyols of different molecular weights as a function of temperature.

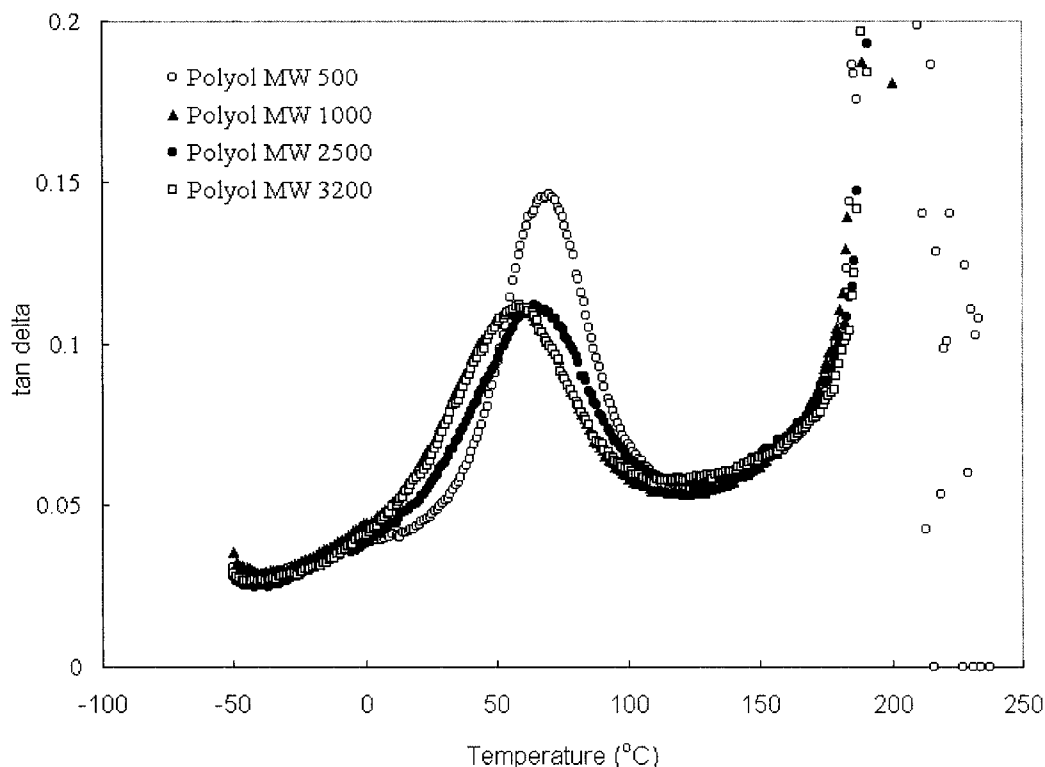


Figure 8 Dynamic mechanical behavior of PESAs with NCO-end-capped prepolymers with polyols of different molecular weights as a function of temperature.

denly decreased when diisocyanate-end-capped PCL was poured into the chamber. Finally, the torque increased after a few seconds. This was apparently due to the chemical reaction of polyamide 12 and diisocyanate-end-capped PCL.

Product characterization

The conversion of the block copolymer was determined as follows. The block copolymer that formed was boiled with distilled water or methanol, and the conversion of lauryl lactam was determined. After drying *in vacuo*, the polymer was extracted with THF or chloroform in a Soxhlet apparatus to isolate the unreacted PCL as THF- or chloroform-soluble parts. The measured weight divided by the initial weight of the block copolymer was the degree of conversion. The copolymer yield was about 70%. We found that the sequential feeding led to a better formation of linear chains from the various segments for the preparation of the block copolymers. The conversion to PESA decreased with the increasing molecular weight of the polyester polyol used in the diisocyanate-end-capped PCL.

We designated a PESA with diisocyanate-end-capped PCL with a polyol with a molecular weight of 500 as PESA500. Similarly, we used PESA1000, PESA2500, and PESA3200.

The transition behavior of the diisocyanate-end-capped PCL and block copolymer after extraction was determined with a DuPont 9900 differential scanning calorimeter. This is shown in Figure 2. The crystalline melting temperature (T_m) of the block copolymer was about 170°C. T_m of polyamide 12 was generally 180°C. Therefore, it existed between T_m of polyamide 12 and T_m of diisocyanate-end-capped PCL. Therefore, PESA was definitely formed by the chemical reaction. The thermal properties of the block copolymers with diisocyanate-end-capped PCL including polyols of different molecular weights are shown in Figure 3.

The melting temperature of the hard polyamide segment decreased as the molecular weight of the soft polyester segment (PCL) decreased. The FTIR spectra of (1) unreacted diisocyanate-end-capped PCL and (2) PESA that we synthesized are shown in Figures 4 and 5, respectively.

As shown in Figure 4, the functional group of isocyanate (—N=C=O—) showed strong and broad stretching at 2270 cm^{-1} , alkane CH_3 showed absorption at 3000–2850 cm^{-1} , and N—H showed absorption at 3500–3100 cm^{-1} in the unreacted urethane prepolymer. Otherwise, the absorption of isocyanate disappeared at 2270 cm^{-1} , strong alkane CH_3 showed absorption at 3000–2850 cm^{-1} , and aromatic CH_2 showed bending at 3150–3050 cm^{-1} . In amide spectral analysis, carbonyl group (C=O) absorption occurred

TABLE II
Tensile Properties of PESA with Diisocyanate-End-Capped PCL with Polyols of Different Molecular Weights and Pebax

PESA with diisocyanate-end-capped PCL with different molecular weights	Tensile strength (MPa)	Elongation at break (%)	1% secant modulus (MPa)
PESA500	55	80	600
PESA1000	45	85	467
PESA2500	43	95	477
PESA3200	32	105	467
Pebax	30	300 ^a	Not applicable

^a Depending on the elastomer content.

at approximately $1680\text{--}1630\text{ cm}^{-1}$, and amide (NH or NH_2) absorption could be seen at $3350\text{--}3180\text{ cm}^{-1}$ and occurred around $1640\text{--}1550\text{ cm}^{-1}$.

We concluded that the chemical reaction between polyamide and diisocyanate-end-capped PCL took place during the reaction because of the absence of diisocyanate, the end group of diisocyanate-end-capped PCL, in the FTIR spectrum of PESA by a comparison of the FTIR results of the unreacted diisocyanate-end-capped PCL.

Dynamic mechanical thermal analysis was used to determine the viscoelastic properties of the materials under various temperature conditions. These properties were described by the storage modulus (E') and the loss modulus (E''). E' describes the elastic behavior of a material, and E'' describes that part of the deformation energy that is transformed

into heat. The E' , E'' , and $\tan \delta$ values of PESAs were measured at 1 Hz and $4^\circ\text{C}/\text{min}$ from -50 to 250°C . The dynamic mechanical moduli and loss tangent curves of PESAs as a function of temperature under bending are shown in Figures 6–8. The E' and E'' values of PESA500 were the highest among the polyester block copolymers. The α peak, related to T_m of the hard segment in Figure 8, was about 200°C , and the β peak of PESA was 50°C . The highest level of bending for $\tan \delta$, related to the damping properties and dimensional stability of PESAs, was found for PESA500. The tensile mechanical properties of the PESAs that we synthesized were measured with an Instron model 4204 mechanical tester at room temperature and a crosshead speed of $10\text{ mm}/\text{min}$ with a 1-KN load cell. The results are given in Table II.

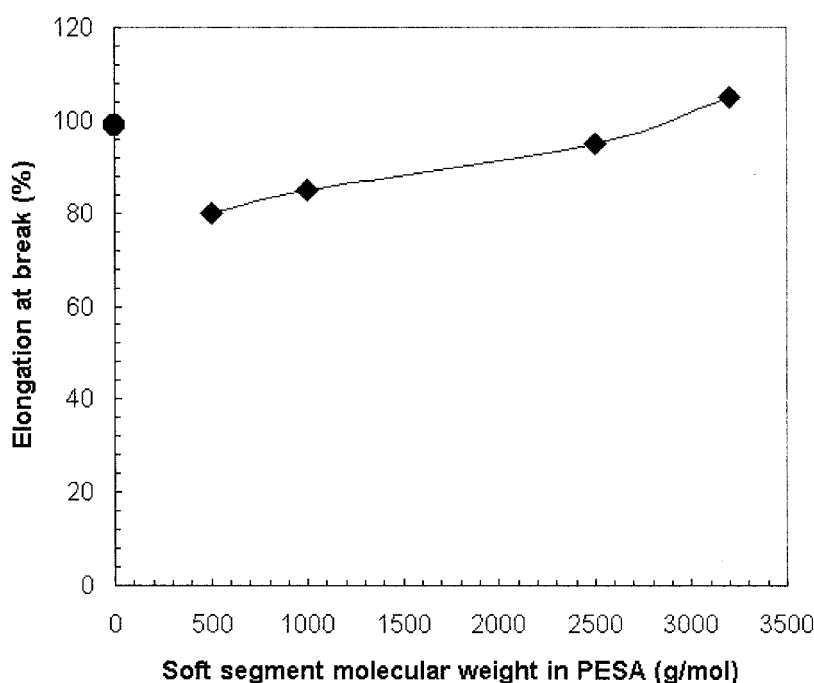


Figure 9 Elongation at break versus the soft-segment molecular weight in PESA and polyamide 12.

The lower the molecular weight was of the polyol in the diisocyanate-end-capped PCL, the higher the modulus and tensile strength were of PESA. The mechanical properties of PESAs with diisocyanate-end-capped PCLs with polyols of different molecular weights are shown in Table II. The elongation at break versus the soft-segment length is plotted in Figure 9.

PESA500 exhibited not only the highest tensile strength and 1% secant modulus but also the lowest elongation at break of the PESA series. PESA3200 had the highest elongation at break. Compared with Pebax, which consisted of a polyamide 12/polytetramethylene glycol/polyamide 12 block copolymer produced Elf Atochem, PESAs synthesized in our study showed higher tensile strengths and lower elongations to break. This was, to some degree, due to their lower elastomer content.

CONCLUSIONS

PESAs can be made by sequential feeding into the chamber of an internal mixer. This sequential feeding method is better because it avoids the hindrance of diisocyanate-end-capped PCL in the polymerization of lauryl lactam to polyamide 12 and leads to the formation of linear chains from various segments to make PESAs. FTIR revealed a chemical reaction between polyamide 12 and diisocyanate-end-capped PCL.

The E' value of PESA500 was the highest among the polyester block copolymers according to dynamic mechanical analysis results. DSC results showed that the melting temperature of the hard polyamide segment decreased as the molecular weight of the soft polyester segment (PCL) decreased.

When diisocyanate-end-capped PCL with a lower molecular weight polyol was used to make PESAs for the purpose of toughening TPEs, higher tensile properties were exhibited. PESA500 had the highest level,

with respect to the dynamic mechanical properties, as a function of temperature. We also compared the mechanical properties of a commercial polyamide 12 TPE and our synthesized PESAs. The tensile strength of the PESAs that we made ranged from 32 to 55 MPa. The PESAs synthesized in our study showed higher tensile strength. The elongation at break versus the soft-segment molecular weight in the PESAs and polyamide 12 is shown in Figure 9. The elongation at break of polyamide 12 was 100%. The range of the elongation at break of the PESAs was 80–105%.

References

1. Mottos, E. H.; Hedrick, R. M.; Butler, J. M. U.S. Pat. 3,017,391 (1962).
2. Butler, J. M.; Hedrick, R. M.; Mottos, E. H. U.S. Pat. 3,017,392 (1962).
3. Sbenda, J.; Kralicek, J. Chem Listy 1958, 52, 758.
4. Petres, G. H.; Pospychala, H. C. U.S. Pat. 2,793,959 (1957).
5. Schwartz, E.; Paul, M. Ger. Pat. 1,052,112 (1958).
6. Gee, K. H.; Small, P. A.; Zeichy, E. L. Brit. Pat. 944,307 (1962).
7. Darnell, W. T.; Fisher, C. F.; Maier, R. E. U.S. Pat. 3,309,343 (1967).
8. Foster Grant Co. Brit. Pat. 986,678 (1965).
9. Garbert, J. D.; Hedrick, R. M. Polym Process Eng 1986, 4, 359.
10. (a) Udipi, K.; Dave, R. S.; Kruse, R. L.; Stebbins, L. R. Polymer 1997, 38, 927; (b) Udipi, K.; Dave, R. S.; Kruse, R. L.; Stebbins, L. R. Polymer 1997, 38, 939; (c) Udipi, K.; Dave, R. S.; Kruse, R. L.; Stebbins, L. R. Polymer 1997, 38, 949.
11. Brassat, B.; Reinking, K.; Hechelhammer, W.; Zygan, H. Ger. Offen. 2,235,462 (1974).
12. Ivanova, S. L.; Kdrashev, V. V.; Korchagina, M. A. Int Polym Sci Technol 1974, 1, T76.
13. Malkin, A. Y.; Ivanova, S. L.; Korchaging, M. A. Vysokomol Soedin A 1977, A19, 224.
14. Biensan, M.; Potin, P. U.S. Pat. 4,067,861 (1978).
15. Ha, S. K.; White, J. L. Int Polym Process 1998, 13, 136.
16. Foy, P. R.; Jungblut, C.; Deleens, G. E. U.S. Pat. 4,331,786 (1982).
17. (a) Kim, B. J.; White, J. L. J Appl Polym Sci 2003, 88, 1429; (b) Kim, B. J.; White, J. L. Soc Plast Eng Annu Tech Conf Tech Pap 2000, 46, 224.
18. Lee, B. H.; White, J. L. Soc Plast Eng Annu Tech Conf Tech Pap 2000, 46, 229.
19. Lee, B. H.; White, J. L. Polym Eng Sci 2002, 42, 1710.