

# In situ Formation and Compounding of Polyamide 12 by Reactive Extrusion

A. Wollny,<sup>1</sup> H. Nitz,<sup>1</sup> H. Faulhammer,<sup>2</sup> N. Hoogen,<sup>2</sup> R. Mülhaupt<sup>1</sup>

<sup>1</sup>Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie, Stefan-Meier-Strasse 31, D-79104 Freiburg i.Br., Germany

<sup>2</sup>Atofina, CERDATO, Route de Rilsan, 27470 Serquigny, France

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**ABSTRACT:** The anionic polymerization of lauryllactam was initiated at 270°C using sodium hydride as an initiator and *N,N'*-ethylene-bisstearamide (EBS) as an activator (NaH:EBS molar ratio of 2). Polymerization occurred in less than 2 min and was successfully performed in an internal mixer and a twin-screw extruder with corotating intermeshing screws (Werner & Pfleiderer ZSK 25). The content of residual monomer, as determined by thermogravimetric analysis, was lower than 0.5 wt %. Molecular weight, as measured by size exclusion chromatography, was governed by the lauryllactam:NaH molar ratio calculated on a  $M_n$  of 25 kg/mol at a constant NaH:EBS molar ratio of 2. Blends

were prepared *in situ* by polymerization of lauryllactam solutions of various polymers. When poly(ethylene-*co*-butylacrylate) (Lotryl<sup>®</sup>; Atofina) was dissolved in lauryllactam, rubber-toughened polyamide 12 blends were obtained. Mechanical properties of the injection-molded polymers were examined by stress-strain as well as notched Charpy impact tests at different temperatures. Blend morphologies were imaged by scanning electron microscopy (SEM). © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 344–351, 2003

**Key words:** reactive extrusion; anionic polymerization; polyamide 12; *in situ* blend formation

## INTRODUCTION

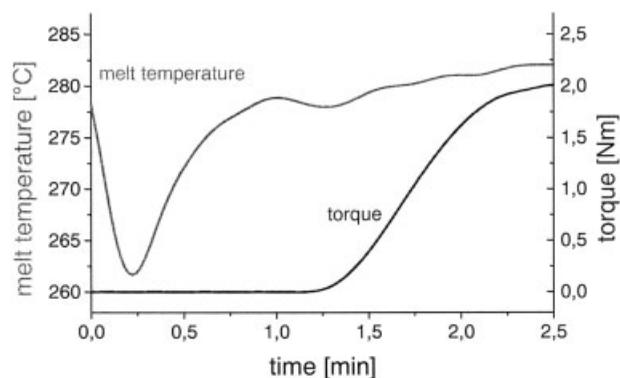
Anionic polymerization of  $\epsilon$ -caprolactam in the presence of strong bases was first described in 1939 by Ritter and Joyce of Du Pont.<sup>1</sup> However, about 20 years later, in 1956, it was the mechanistic studies of Mottus and coworkers on the polymerization mechanism of anionic lactam polymerization that attracted considerable attention in the literature and stimulated many groups to engage in research in this field.<sup>2</sup> The initiators of anionic lactam polymerization are the lactamate anions being formed by the reaction of a lactam with a strong base. Schwartz and Paul proposed the use of the alkaline and earth alkaline metals, especially sodium and potassium, and their oxides, hydroxides, hydrides, carbonates, and other reactive compounds of these metals, including organometallic reagents.<sup>3</sup> The disadvantage associated with using alkaline metals as initiators is the formation of a considerable amount of amine in the reaction mixture.<sup>4</sup> According to the patent literature, the most favored initiator after ethyl magnesium bromide is sodium hydride because the only side product in the reaction with lactam is hydrogen, which can be readily removed from the reaction mixture. A very large number of activators

were found in the literature reviewed by Sebenda<sup>5</sup> and Frunze.<sup>6</sup> A rough classification was made by distinguishing between activators based on lactams carrying an electronegative polar substituent on the nitrogen atom and activators producing such *N*-substituted lactams *in situ* during polymerization. Very effective activation in the presence of *N*-acyl lactams such as *N*-acetyl and *N*-benzoyl caprolactam has been very well known for many years.<sup>7,8</sup> Examples of the second class of activating compounds are isocyanates and carbodiimides, which were first described in 1956, by Schnell and Fritz.<sup>9</sup> Because of the toxicity of the isocyanates, isocyanate derivatives are often used. For example, the reaction between caprolactam and hexamethylenediisocyanate affords hexamethylenedicarbonylcaprolactam, which is a very effective activator but much less toxic to the isocyanate.<sup>10–12</sup> Examples of bifunctional activators using adipoyl-biscaprolactam were described by Ueda<sup>13</sup> and employing isophthalolyl biscaprolactam by Udipi et al.<sup>14</sup>

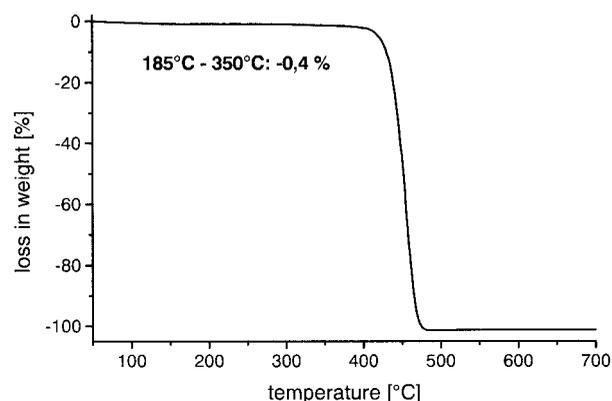
Activated anionic lactam polymerization proceeds sufficiently fast that it can be used in a reactive extrusion process. In 1968 Illing wrote the first description of the polymerization of lactams in a corotating twin-screw extruder. He used twin-screw extruder ZSK 53 for manufacturing polyamides 6 and 12 with a molecular weight of 70,000–100,000 g/mol at throughput rates of 27–43 kg/h.<sup>15</sup>

Recent studies of the anionic polymerization of caprolactam in a twin-screw extruder have been re-

Correspondence to: R. Mülhaupt (rolf.muellhaupt@makro.uni-freiburg.de).



**Figure 1** Development of torque and melt temperature during polymerization in the internal mixer.



**Figure 2** TGA curve of polyamide 12.

ported by Menges and Bartilla,<sup>16</sup> among others. They explored sodium caprolactamate as the initiator and acetyl caprolactam as the activator, using a 30-mm corotating intermeshing twin-screw extruder. Nichols and Tucker employed caprolactam magnesium bromide as the initiator and acetyl caprolactam as the activator, performing polymerization in a 20-mm counterrotating nonintermeshing twin-screw extruder.<sup>17</sup> Simulations and analysis of anionic lactam polymerization in twin-screw extruders were described by Kye and White<sup>18</sup> and by Michaeli et al.<sup>19</sup> The continuous polymerization of lauryllactam in a modular corotating twin-screw extruder was first described by Ha and White.<sup>20</sup> The resulting polyamide 12 had a residual monomer content of 3%–7%, and the molecular weight, depending on screw speed, varied from 19 to 22 kg/mol.

In the present article we present a new initiator/activator system<sup>21</sup> for the anionic polymerization of lauryllactam in a twin-screw extruder, thus producing polyamide 12 with much less residual monomer. Polymerization of lauryllactam polymer solutions was explored as a route to *in situ* polymer blend formation and rubber-toughened polyamide 12. The molecular weights, molecular weight distributions, residual monomer content, blend morphology, and mechanical properties of *in situ* polyamide 12 and polyamide 12 blends were investigated.

## EXPERIMENTAL

### Materials

Lauryllactam (LL) and *N,N'*-ethylene-bisstearamide (EBS) were supplied by Atofina. The lactam was used as received, and the EBS was used after drying for 24 h in vacuum at elevated temperatures. Sodium hydride (Aldrich, Steinheim, Germany) was used without further purification.

### Processing

Preliminary experiments on anionic lauryllactam polymerization with the described initiator/activator system were carried out in an internal mixer (Haake PolyLab). The reaction mixtures were prepared in a 250-mL round-bottomed flask equipped with a magnetic stirrer and a nitrogen inlet. Typically, 48 mg (2 mmol) of sodium hydride and 593 mg (1 mmol) of EBS were dissolved at 160°C in 50 g (253.4 mmol) of molten lauryllactam in order to obtain a polymer with a  $M_n$  of 25 kg/mol. The polymerization reactions were performed in a Haake PolyLab twin-screw internal mixer equipped with a 60-mL mixing chamber. After stirring for about 30 min under an atmosphere of nitrogen and after the formation of hydrogen was terminated, the melt was poured into the 270°C preheated mixing chamber. Polymerization was performed at a rotational screw speed of 60 rpm. When the torque

**TABLE I**  
Polymerization Conditions for Reactive Extrusion

Experiment No.	Feed (kg/h)	Screw speed (rpm)	Torque (%)	Barrel temperature (°C)	Melt temperature (°C)	Pressure (bar)
1	3.3	100	14.6 ± 0.9	270	281	11.0 ± 0.7
2	3.2	200	20.0 ± 2.8	270	282	10.2 ± 1.3
3	3.3	300	23.8 ± 0.6	270	283	10.1 ± 0.7
4	4.2	200	19.1 ± 5.0	270	281	11.2 ± 1.7

TABLE II  
Results of Molecular Characterization of Polyamide 12

Experiment No.	Monomer content (%)	Viscosity	$M_p$ (kg/mol)	$M_w$ (kg/mol)	$M_n$ (kg/mol)	Polydispersity
1	0.15	1.37	26.2	36.4	18.7	1.95
2	0.16	1.32	23.7	32.0	16.4	1.95
3	0.17	1.28	20.8	31.7	15.0	2.10
4	0.32	1.38	26.5	34.2	19.1	1.80

reached a maximum, the samples were quickly recovered and quenched between metal plates.

The reactive extrusion polymerization was carried out in a Werner & Pfleiderer ZSK 25 twin-screw extruder with intermeshing corotating screws. The length:diameter ( $L:D$ ) ratio was 42,  $D = 25$  mm. Melting of the lactam was carried out in an electrically heated 10-L flask while being stirred under a nitrogen atmosphere using a mechanical stirrer. Prior to the polymerization reaction, sodium hydride and EBS were added to the lactam melt, resulting in a stable reaction mixture. For pumping the lactam melt, a gear pump with a heated pump unit was used. To control the mass flow of lactam into the extruder, the flask with the stirring unit was placed on a balance connected to a personal computer, which calculated the feed amount in kilograms per hour. Connections between the flask and pump and the pump and extruder were accomplished by heated metal tubes. A metal plate equipped with a nitrogen inlet closed the generally used solid feed in zone 0. The lactam melt was pumped in zone 1, after being heated at a temperature of 230°C. Zones 2–10 were heated to the polymerization and extrusion temperature of 275°C. The obtained strands were pelletized and dried at 80°C. The dried pellets were injection-molded into test bars according to DIN 53455. The different test specimens for tensile strength and notched impact strength were injection-molded on a Ferromatic Milacron K40. The temperature of the cylinder was 225°C–240°C and that of the mold was 40°C.

### Mechanical properties

The tensile modulus of the polymers was measured using a Zwick Z005. Notched impact Charpy strength measurements were performed at 23°C and –40°C according to ISO179/1A. The data were taken without preconditioning the samples.

### Polymer characterization

The residual monomer content in the polyamide was determined by means of gas chromatography (GC) using a Varian 3800 and by means of thermogravimetric analysis (TGA) using a Netzsch STA 409. Regarding the analysis by GC the polyamide was dissolved in 1,1,1,3,3,3-hexafluoroisopropanol, and the monomer content was calculated using a calibration function. For TGA all measurements were made under an atmosphere of nitrogen. The temperature was increased from 30°C to 750°C. The loss in weight from 185°C to 350°C was attributed to the amount of unreacted lauryllactam.

Size exclusion chromatography (SEC) was measured in a high-temperature SEC apparatus model (Waters 150-C ALC/GPC) using benzylic alcohol. The calibration was carried out by polyamide 12 standards.

SEM measurements of fracture surfaces were performed on a Philips XL30 FEG apparatus. Therefore, the samples were cooled down to the temperature of liquid nitrogen and broken. Before measuring sam-

TABLE III  
Polymerization Conditions for Blend Synthesis via Reactive Extrusion

Experiment No.	Lotryl grade	Lotryl	Feed (kg/h)	Screw speed (rpm)	Torque (%)	Barrel temperature (°C)	Melt temperature (°C)	Pressure (bar)
21	—	0%	4	200	12.6 ± 2.5	275	287.0	9.8 ± 0.7
22	35BA320	3%	4.2	200	15.0 ± 3.1	275	287.0	10.2 ± 0.9
23	35BA320	6%	4.2	200	13.4 ± 0.9	275	287.6	10.0 ± 0.6
24	35BA320	9%	4.2	200	12.9 ± 0.7	275	287.5	9.9 ± 0.5
25	35BA320	12%	4.2	200	13.6 ± 4.0	275	286.5	9.4 ± 1.4
41	—	0%	3.9	200	21.0 ± 1.2	275	286.7	—
42	28BA175	3%	4.0	200	17.2 ± 1.4	275	286.7	—
43	28BA175	6%	4.2	200	16.2 ± 1.6	275	287.2	—
44	28BA175	9%	4.2	200	17.9 ± 1.1	275	286.0	—
45	28BA175	12%	4.1	200	18.9 ± 1.8	275	286.7	—

TABLE IV  
Residual Monomer Content (TGA)  
of PA12 Lotryl Blends

Experiment No.	21	22	23	24	25	41	42	43	44	45
	35BA320					28BA175				
Monomer content (%)	0.49	1.23	1.51	2.20	3.02	0.97	1.39	0.93	0.56	1.32

ples, the surface of the samples were sputter-coated with palladium.

## RESULTS AND DISCUSSION

### Polymerization in an internal mixer

Preliminary experiments on the anionic polymerization of lauryllactam using sodium hydride as initiator and *N,N'*-ethylene-bisstearamide (EBS) as activator were performed in an internal mixer. A typical polymerization sequence is shown in Figure 1. The molten lauryllactam containing activator and initiator was fed into the preheated internal mixer. About 1 min was needed to heat the melt to the polymerization temperature of 270°C. The endothermic beginning of the reaction can be identified by declining temperature. Torque was increasing after approximately 1.25 min, reflecting the increasing melt viscosity, which reached a maximum after 2.5 min. Then polymerization was stopped by turning off the internal mixer and quenching the polymer melt between metal plates. The residual monomer content of the resulting polyamide 12 was measured by thermogravimetric analysis (TGA). A typical TGA trace is displayed in Figure 2. Weight loss from 185°C to 350°C was assigned to the content on unreacted lauryllactam, which is usually less than 0.5%.

The fast kinetics and slightly exothermal character of the polymerization reaction allowed the use of this system in a reactive extrusion process. The most important requirement for a polymerization reaction in an extruder is a high conversion rate at the given reaction time, which is limited by the average residence time and the evolution of the polymerization heat because of the limited cooling possibilities in the extruder. It should be noted that the polymerization enthalpy of ring-opening lactam polymerization was low.

### Polymerization in the twin-screw extruder

The polymerization reactions were carried out in a Werner & Pfleiderer ZSK25 twin-screw extruder with intermeshing corotating screws. The screw configuration of the modular screws consisted mainly of transporting elements and some mixing elements and was designed to achieve an average residence time of about 2 min. In a first series of experiments the poly-

merization reactions were carried out under different extrusion conditions. In general, the average residence time mainly was influenced by the feed of the monomer melt and the screw speed. As a consequence, we performed a series of polymerizations varying the screw speed from 100 to 300 rpm and the lactam feed from 3.5 to 6 kg/h, respectively, in order to determine the minimum residence time necessary for complete polymerization at higher feeding rates. During extrusion the resulting torque and the melt temperature and melt pressure at the die were recorded. The experimental conditions for these polymerizations are summarized in Table I.

As apparent from experiments 1–3, summarized in Table I, screw speed influenced the torque at a constant feed. The influence of the feed on the resulting torque, which was in the range of 20% for a feed of 3.2–5 kg/h, also was small. Therefore, further experiments were performed applying a screw speed of 200 rpm and an average feed of about 4 kg/h. The melt temperature and pressure were influenced by neither the feed nor the screw speed.

An examination was done of how processing conditions affected residual monomer content and chain length as well as molecular weight distribution of the resulting polyamide 12. The samples were characterized by size exclusion chromatography (SEC), solution viscosimetry, and gas chromatography (GC) in order to determine the content of residual lauryllactam. The residual monomer content, the viscosity, and the SEC data are listed in Table II.

It is apparent from Table II that the content of residual lauryllactam monomer was rather low, typically less than 0.2 wt %. Thus, with a feed of 3.5–5 kg, a sufficient residence time of the melt for complete polymerization could be assumed. Viscosity values for samples 1–4 were expected to be on the same order because these polymers were made from the same

TABLE V  
SEC Data of Homopolyamides

Experiment No.	$M_p$ (kg/mol)	$M_w$ (kg/mol)	$M_n$ (kg/mol)	Polydispersity
21	29.4	34.1	15.1	2.25
41 <sup>a</sup>	24.3	26.5	13.3	2.0

<sup>a</sup> Measured after injection molding.

TABLE VI  
Mechanical Data for Polyamide 12 Lotryl Blends

Experiment No.	Lotryl grade	Lotryl content	Young's Modulus (MPa)	Yield strain (%)	Yield stress (MPa)	Break strength (MPa)	Elongation at break (%)
19	35BA320	10%	756	15	31.3	47.72	297
21	—	0%	1240	5.6	40.1	50.2	277
22	35BA320	3%	1140	9.6	37.3	46.9	251
23	35BA320	6%	1036	10.8	35.6	45.7	255
24	35BA320	9%	837	13.5	32.6	47.4	276
25	35BA320	12%	574	18.4	27.6	45.0	291
41	—	0%	1397	5.2	42.0	41.7	182
42	28BA175	3%	1289	6.8	39.1	45.8	207
43	28BA175	6%	1254	9.8	38.0	46.4	219
44	28BA175	9%	1201	10.6	36.4	45.1	221
45	28BA175	12%	1127	11.4	34.6	42.3	198

batch. The differences between the experiments were within the error tolerance of the measurements.

The SEC data showed values all of which were in the expected order of magnitude. The amount of sodium hydride and EBS were adjusted in order to obtain polyamide molecular masses of 25 kg/mol. This value was found for  $M_p$ , the molecular weight at the peak maximum in the SEC curves. The polydispersity index was on the order of 2. Thus, it can be concluded that the anionic polymerization of lauryllactam in a twin-screw extruder at a screw speed of 200 rpm and with a feed of 3 to 5 kg/h resulted in high-molecular-weight polyamide 12 with a low monomer content (less than 0.2 wt %) and a narrow molecular-weight distribution. Therefore, all subsequent polymerization reactions were carried out under these experimental conditions.

#### Polyamide blends prepared by reactive extrusion

A convenient route to polyamide blends is to use lauryllactam as a reactive solvent.<sup>22</sup> Here lauryllactam was used as a solvent for an elastomer. After dissolving the elastomer in lauryllactam and adding the activator/initiator lauryllactam solution, polymerization was begun. During polymerization, phase separation occurred because of the incompatibility of the polyamide 12 with the blend component, thus producing polyamide 12–rubber blends in a single extrusion step. To toughen polyamide 12, two grades of Lotryl (Atofina), a copolymer of ethylene and butylacrylate—namely, 35BA320 and 28BA175—were used as elastomer component. Regarding the designation of the two Lotryl grades, the first two numbers indicate the butylacrylate content, 35% and 28%, respectively, and the second number represents melt viscosity.

The polymerizations experiments in the presence of Lotryl are summarized in Table III. First, about 1 kg of pure lauryllactam was polymerized to create a reference homopolyamide 12. Then the extrusion was

stopped, and the calculated amount of Lotryl was added, thus increasing the Lotryl content stepwise up to 12%. After stirring for at least 15 min, polymerization was continued. The results are summarized in Table III.

From Table III it can be seen that the feed in all cases was on the order of 4 kg/h. As apparent from the torque, melt temperature and pressure at the die (in the series from 41 to 45 the pressure was not recorded because of problems with the sensor), no significant changes for either the Lotryl grade or the content were observed. Characterization of the resulting polymer blends by their residual monomer content was carried out by thermogravimetric analysis (TGA), the results of which are shown in Table IV.

In general, the monomer content in the blends was slightly higher compared to the reference homopolyamide 12. This occurred because gas chromatography represents a more accurate method compared than TGA. However, the blends prepared on the extruder had a more similar monomer content than those prepared in the internal mixer. For the 35BA320 series a linear increase in monomer content with growing Lotryl content could be observed. This can be explained

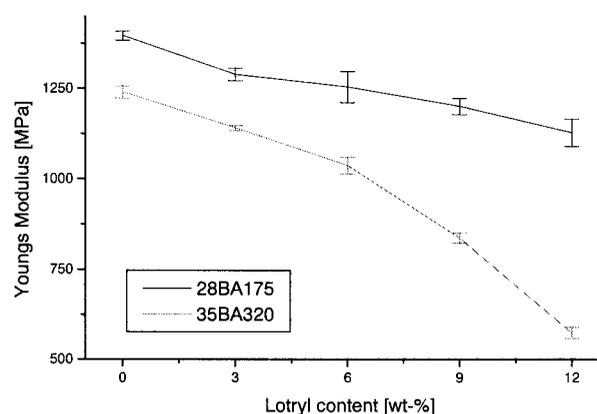


Figure 3 Young's modulus as a function of Lotryl content.

TABLE VII  
Results of Notched Impact Strength Tests

Experiment No.	21	22	23	24	25	41	42	43	44	45
Lotryl grade			35BA320					28BA175		
Content	0	3	6	9	12	0	3	6	9	12
Strength at 23°C (KJ/m <sup>2</sup> ) break type	6.4 (c)	7.0 (c)	11.4 (c)	14.4 (c)	41.1 (p)	6.5 (c)	7.4 (c)	10.2 (c)	12.8 (c)	16.6 (p)
Strength at -40°C (KJ/m <sup>2</sup> ) break type <sup>a</sup>	7.1 (c)	6.7 (c)	6.7 (c)	6.4 (c)	5.8 (c)	7.0 (c)	6.9 (c)	7.0 (c)	7.2 (c)	7.3 (c)

<sup>a</sup> Break type: (c) complete, (p) partial.

by an increasing number of side reactions at higher concentrations using the richer Lotryl-grade butyl acrylate. SEC studies were performed to verify if the obtained molecular weights were on the same order so that the mechanical data could be compared. SEC measurements were only applicable to the two homopolyamides because the blend components would falsify the molecular weights. The results of the TGA and the SEC data are shown in Table V.

As is apparent from Table V, the obtained molecular weights for both experiments were in the same order of magnitude within the error tolerance of the measurements. The amount of initiator/activator was calculated for a value of 25 kg/mol. This molecular weight was found for Mp, the molecular weight at the peak maximum in experiment 41. For the series starting with experiment 21, a slightly higher molecular weight was obtained. This can be explained by the eventual side reactions of the sodium hydride with impurities, or it also could be an error in measurement because of the high-temperature SEC of the polyamides in general showing higher error tolerances.

To examine the influence of the Lotryl content on the mechanical properties, strain-stress and impact Charpy tests were performed, both at room temperature and at -40°C, on injection-molded test specimens. The results of the tensile strength tests are listed in Table VI. The Young's modulus as a function of the Lotryl content is displayed in Figure 3.

From comparing the mechanical properties of Lotryl grades 28BA175 and 35BA320, it can be stated that 28BA175 exhibited better mechanical properties. The Young's modulus as well as the yield stress remained at higher levels and showed less decrease with increasing Lotryl content for 28BA175, which contained a lower amount of butylacrylate (28%), showed a lower melt index, and seemed to affect the mechanical properties of polyamide 12 less than 35BA320. Another possible explanation for the decrease in the mechanical properties of the 35BA320 blend is the increasing monomer content. For the elongation at break no general trend could be observed. To verify if the polyamide Lotryl blends showed improved impact strength at lower temperatures, impact Charpy strength tests were performed in order to compare the low-temperature impact strength of the different blends. Results of the notched impact tests are summarized in Table VII.

As is apparent from Figure 4, the impact strength of the blend containing 35BA320 at -40°C was not influenced by the concentration of Lotryl. However, the impact strength at ambient temperature showed a strong increase, of 300%, when the amount of Lotryl was increased from 9% to 12%. For the 28BA175 blend, at -40°C the impact strength again was independent of the Lotryl content. At ambient temperature a nearly linear correlation between the Lotryl content and the impact strength was found. Up to a 9% concentration,

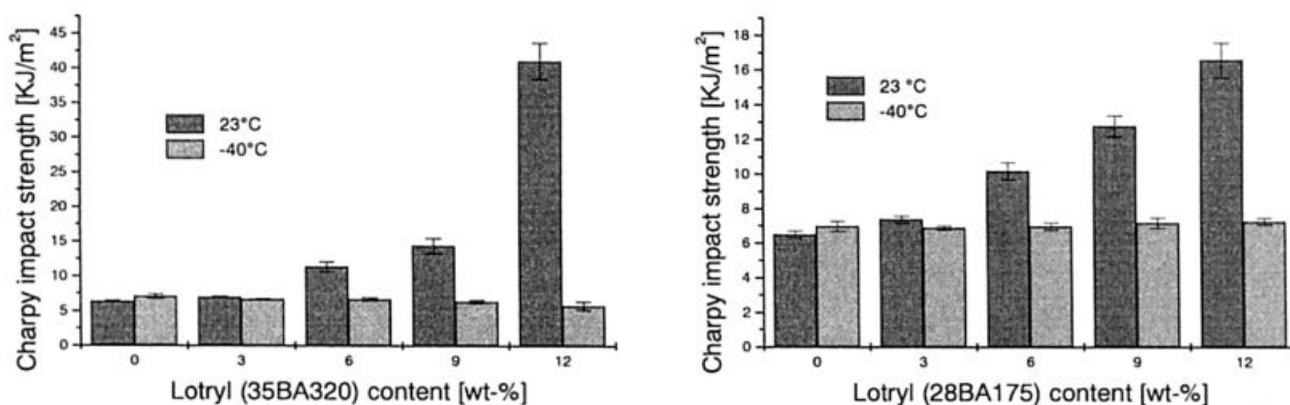
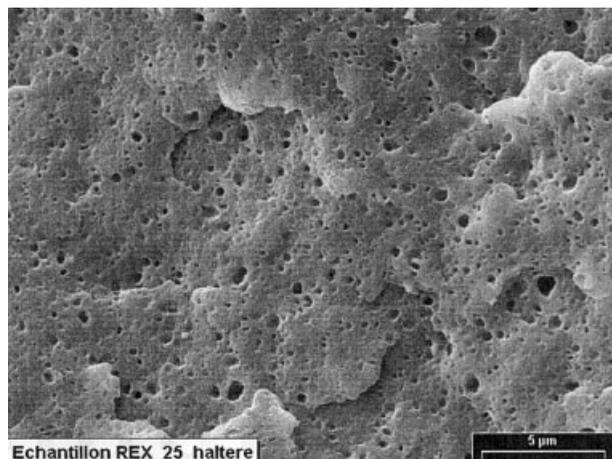


Figure 4 Notched Charpy impact strength of the Lotryl blends at different concentrations.



**Figure 5** SEM micrograph of sample 25 containing 12% 35BA320.

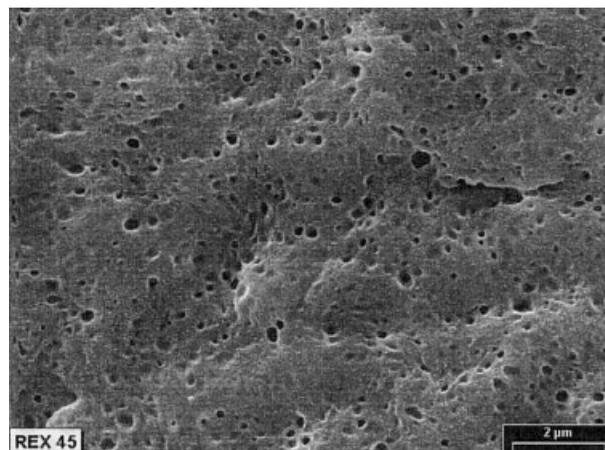
no significant differences could be observed in the impact strength of the two blends, but for 12% Lotryl the 35BA320 grade showed much better impact strength than did the 28BA175 grade. Better mechanical properties were observed for the 28BA175 grade, but the improvement in impact strength at ambient temperature was better for the 35BA320 grade. Detailed studies on the fracture and failure behavior of these *in situ* polymerized polyamide-12 blends using instrumented high-speed impact-bending tests have been described elsewhere.<sup>23</sup>

To compare the resulting morphologies of the blends, scanning electron microscopy (SEM) studies on the specimens were carried out. Therefore, cryo-fractures with subsequent extraction of the Lotryl using xylene were undertaken. The SEM micrographs for the blends containing 12% of the 35BA320 grade and the micrograph of the sample containing 12% of the 28BA175 grade are shown in Figures 5 and 6, respectively.

The distribution of the particle sizes in the two SEM micrographs was analyzed by image analysis. The distributions of the sizes of the Lotryl particles are shown Figures 7 and 8, in which no significant differences in average particle size can be seen. The sample showing better mechanical properties using the acrylate-poorer Lotryl grade 28BA175 apparently had an average particle size about half that of the rubber particles using 35A320.

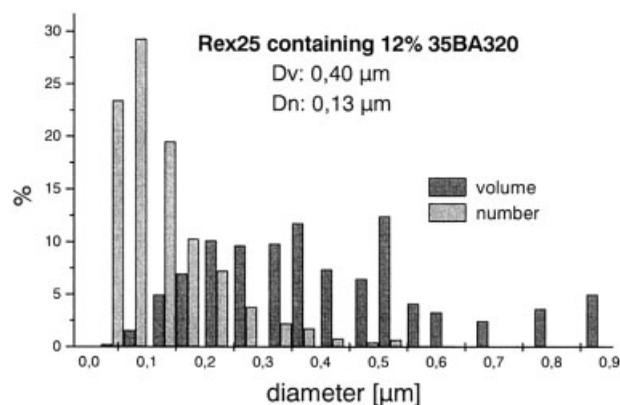
## CONCLUSIONS

In this study it was shown that the anionic polymerization of lauryllactam can be performed in the presence of sodium hydride as initiator and *N,N'*-ethylene-bisstearamide (EBS) as activator (NaH:EBS molar ratio of 2). Using a twin-screw extruder afforded high-molecular-weight polyamide 12 containing a remark-

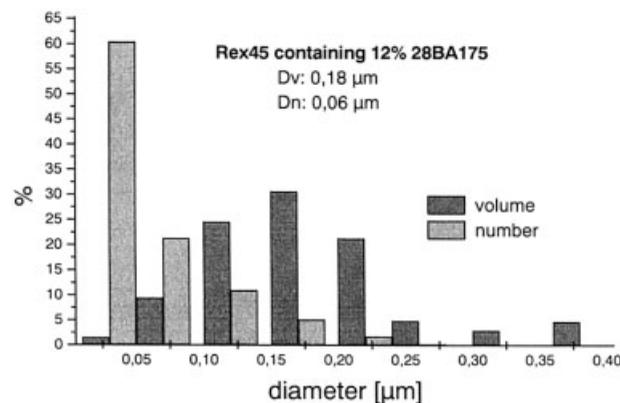


**Figure 6** SEM micrograph of sample 45 containing 12% 28BA175.

ably low residual monomer content, typically less than 0.5 wt %. At 170°C the lauryllactam solution of Na-lauryllactam and EBS was stable for more than 1 week but initiated rapid polymerization at 270°C to produce high-molecular-weight polyamide 12 in very high yields in less than 2 min. Most conventional



**Figure 7** Particle size distributions of sample 25 containing 12% 35BA320.



**Figure 8** Particle size distributions of sample 45 containing 12% 28BA175.

initiator/activator systems initiate polymerization as soon as the lactam monomer melts, thus causing feed problems and oligomer formation, which can adversely affect mechanical properties and broaden molecular weight distributions. In addition to lauryllactam, caprolactam solutions of various polymers also can be employed to produce blends in a single extrusion step. The *in situ* compounding was demonstrated for lauryllactam solution of an elastomer such as Lotryl. The *in situ* polyamide 12–Lotryl blends exhibited improved impact performance. This polymerization system is very versatile and can also be used for liquid injection and *in situ* composite formation.

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