

## Synthesis by reactive processing of block copolymers of Nylon 6 / Poly (ether-esteramide)

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### Summary

Block copolymers of nylon 6 with 10, 15 and 20% of poly (ether-esteramide) as elastomeric phase were synthesized by reactive processing. These materials are obtained by the anionic polymerization of  $\epsilon$ -caprolactam in the presence of a linear prepolymer of poly (ether-esteramide) with a Grignard reagent. Differential Scanning Calorimetry (DSC), torque rheometry and formic acid test were used to characterize the obtained copolymers. The results showed that block copolymers of Nylon 6 were formed. The melting temperature and the crystallinity of the copolymer decreased when the elastomer phase content increased. Two Tg's appeared; the blocks of the copolymers were not miscible. We calculate the size of nylon 6 blocks for each composition. The physical-mechanical behavior was also studied. More flexible materials were obtained when the soft phase content in the copolymer was increased. The results of this work provide an important information for the synthesis of this kind of materials by reactive extrusion.

### Introduction

Nylon 6 is a thermoplastic material that shows a great spectrum of applications in the automotive, electrical and packaging industries[1]; that is the result of their unique combination of thermal and mechanical properties. However its relatively low impact resistance limits its use. One of the methods to diminish the fragility consists in the incorporation of an elastomer phase onto nylon chain by a reaction to form a copolymer[2]. By this way, it is possible to obtain materials that have a more wide range of applications, than Nylon 6, depending on the elastomer content of the product. The preparation of this kind of copolymers has been carried out by Reactive Injection Molding, RIM[3-5].

The research focused on the development of new polymeric materials has been accomplish technical requirements with existent polymeric materials by chemical modification, blending, reinforcing or other methods that modify properties. The use of processing equipment as reactors to achieve chemical modification of polymers has been largely used. The establishment of operation conditions to carry out successfully one kind of reaction by reactive processing is not as simple as it could appear.

Preliminary information is needed for the reaction and operation conditions in order to carry out efficiently the proposed reaction. This work was focused on gaining information to carry out the synthesis by reactive extrusion.

## **Experimental**

### *a) Materials.*

Monomer:  $\epsilon$ -caprolactam (UNIVEX); monomer/initiator: prepolymer of poly(ether-esteramide) and catalyst: Grignard of  $\epsilon$ -caprolactam (DSM RIM Nylon Inc.);

### *b) Block Copolymers Synthesis.*

The acyllactam end groups on the prepolymer of poly(ether-esteramide) are the initiation sites for the polymerization of the  $\epsilon$ -caprolactam in the presence of anionic catalyst.

#### *Experiments on Mixing Chamber.*

Block copolymers of nylon 6 with 10, 15 and 20% of poly(ether-esteramide) as elastomeric phase were synthesized on the mixing chamber of a torque rheometer (C. W. Brabender, PL-2000) equipped with "cam" rotors. The reaction was followed by recording the change of torque with reaction time.

The reagent was manually feed into the chamber; first the solid  $\epsilon$ -caprolactam was added and then the prepolymer of poly(ether-esteramide) was injected; the materials were finally mixed for 10 sec. Grignard reagent was added and the chamber was closed. Previously the Grignard catalyst was stored under  $N_2$  atmosphere and was maintained in a vacuum desiccator before its use. Finally, the melted material was taken out and it was chopped using a blade mill after cooling.

The operating conditions of the mixing chamber were optimized considering the results of rheograms, differential scanning calorimetry (DSC) and the physical appearance of the material. First of all the temperature and rpm's of the chamber at steady reaction time of 5 min were chosen. The reaction time was determined by the DSC analysis of samples obtained at different points on the torque-time curve.

### *c) Synthesis of Poly(ether-esteramide) and Nylon 6 Homopolymers.*

In order to have reference materials, of the two copolymer blocks, both homopolymers were also synthesized on mixing chamber, at 210°C and 40 rpm. Both materials were characterized by differential scanning calorimetry (DSC). The obtained results were compared with the results for the copolymer with 15% of poly(ether-esteramide) synthesized and characterized under the same conditions.

#### *Poly(ether-esteramide).*

The poly(ether-esteramide) shows high torque values at the used temperature for the copolymer synthesis (195°C), due to its elastomeric character, then these experiments were carried out at higher temperature (210°C) and at the same speed of 40 rpm. The chamber was feeded with 70 g of prepolymer and 17.5 g of catalyst and were let react up to obtain the maximum on the torque-time curve.

### *Nylon 6.*

On the other hand, for the synthesis of Nylon 6 it was used the prepolymer as initiator. The chamber was feeded with 69.12 g of solid caprolactam and then 0.88 g of prepolymer were injected and mixed during 10 s, finally 17.5 g of catalyst were added and the chamber was closed.

### *d) Characterization.*

#### *Thermal Analysis.*

The calorimetric measurement of copolymer samples were carried out using a DuPont thermal analyzer fitted with a DSC cell. The heating rate was 10°C/min from room temperature to 250°C under nitrogen atmosphere, and also, for T<sub>g</sub> determination of some samples, form -100°C to 100°C. The enthalpy and the transition temperatures for each sample were estimated in the second heating cycle.

#### *Mechanical Properties.*

The tensile properties were evaluated, in Type M-I specimens, according to ASTM D638 in an Instron tensile tester 4301 with a cell of 5 kN at 5 mm/min at room temperature. Before the tests, all the samples were dried according to ASTM D 4066 for polyamides.

The flexural properties in a system of three points were evaluated according the ASTM D790, procedure A, in an Instron tensile tester 4301 with a cell of 500 N at 0.7 mm/min and room temperature; specimens (50 by 10 mm) were tested flatwise on a 25 mm support span.

The hardness Shore D determination was carried out according to the ASTM D2240 for rigid materials, on plates of 6.4 mm of thickness and ambient temperature with a durometer PTC Instruments model 3071.

#### *Formic acid test.*

In order to qualitatively investigate the copolymer formation this test was carried out as follows: 0.1 g of sample was suspended in 5 ml of formic acid, which is a solvent for Nylon 6 and a non-solvent for the poly(ether-esteramide). The test tubes were shaken thoroughly and then left for 12 hours. The following samples were analyzed: Commercial Nylon 6, Brabender synthesized Nylon 6, poly(ether-esteramide), and copolymers with different concentration of poly(ether-esteramide).

## **Results and Discussions**

### *Block Copolymers of Nylon 6/Poly (ether-esteramide)*

#### *Operation Conditions.*

The high temperatures more than 180°C were necessary for polymerization due to the high viscosity of the prepolymer. The condition of 195°C and 40 rpm was the more adequate for the copolymer synthesis with different content of poly(ether esteramide). It was reported that to obtain that kind of materials we need 2 min of reaction time for RIM[2] and 10 min for cast molding[5] at temperature of 130-140°C.

### Torque Rheometry.

Figure 1 shows the result of torque rheometry of the synthesized copolymers. You can see that at the beginning the reagents are in melted state and do not show appreciable resistance to the deformation (low torque); however after the induction time of the reaction it shows a progressive increase on torque indicating the occurrence of polymer formation. The induction time gradually decreases as the prepolymer content increases. This is attributed to the presence of a higher number of initiation sites, since the prepolymer acts also as initiator in this reaction system. A higher torque is also observed at the same reaction time as the poly (ether-esteramide) content increase. It was expected by the elastomeric characteristics of this material.

### Differential Scanning Calorimetry (DSC).

Figure 2 shows the thermograms of the copolymer with 10% of elastomeric phase corresponding to the three points of the torque-time curve ( $t_1$ ,  $t_2$ ,  $t_3$ , Figure 1). Samples at the three different times (near the maximum torque) were taken in order to verify the copolymer formation. These samples were analyzed by DSC. The three analyzed samples at times near the maximum torque showed almost 90% of conversion. The thermograms shows only one melting peak whose maximum varies, from 209 to 217°C, with the reaction time. These results indicate that the samples did not show the presence of residual caprolactam ( $T_m = 70.04^\circ\text{C}$ ) and that the sample taken on time  $t_3$  have the melting temperature near the reported[2] for RIM copolymer (217°C). Longer times than this produce degradation that it is detected by a progressive reduction on torque and also by a yellowing of the product. With the obtained results on torque rheometry and DSC it was established the adequate reaction time as the correspondent to the maximum torque.

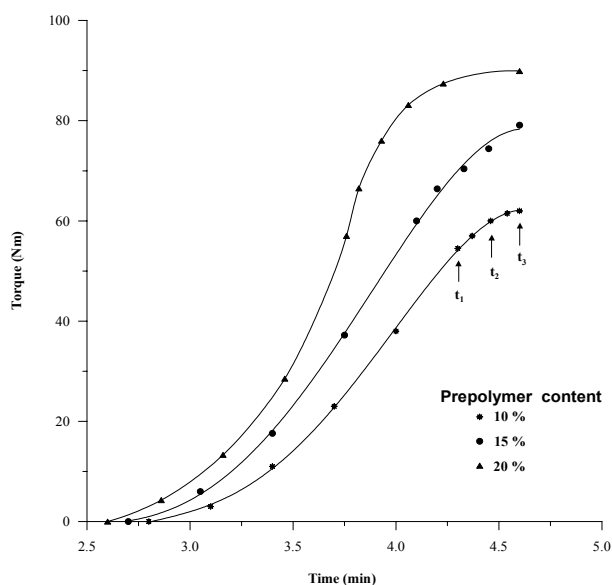


Figure 1. Rheograms of the block copolymers synthesis of Nylon 6 with different prepolymer content (\* 10, ● 15 and ▲ 20%). Operation conditions of mixing chamber: 195°C, 40 rpm.

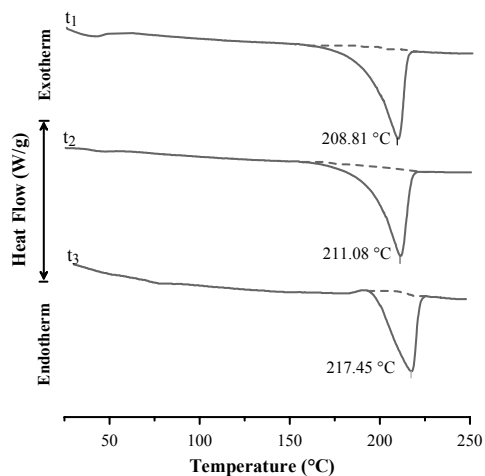


Figure 2. DSC of samples taken at different reaction times during the copolymer synthesis in the mixing chamber

Figure 3 shows the DSC analysis of the poly(ether-esteramide), copolymer with 15% of poly(ether-esteramide) and Nylon 6, chamber synthesized at 210°C and 40 rpm. It can be appreciated that the melting temperature of the copolymer only corresponds to that of nylon 6 blocks since the poly(ether-esteramide) is an elastomeric material[6].

On the other hand, Table 1 presents the glass transition temperatures ( $T_g$ ) of the same materials. It is observed that the copolymer shows two transitions widely separated: one below room temperature and the other above it. The first,  $T_{g1}$ , could be attributed to the poly(ether-esteramide) and the second one,  $T_{g2}$ , to the amorphous part of the Nylon 6 blocks. Some authors[2,6-7] suggest that the presence of these two transitions indicate the immiscibility of the copolymer components

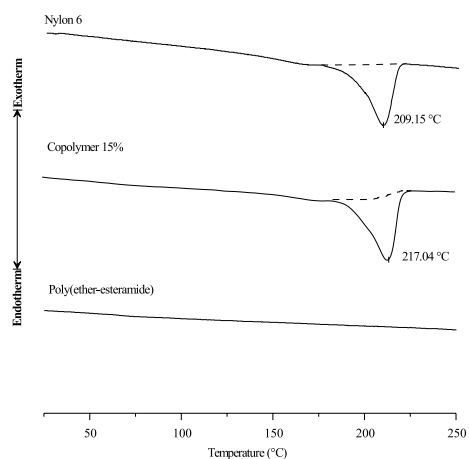


Figure 3. DSC thermograms of the second run of chamber synthesized Nylon 6, poly(ether-esteramide) and the copolymer with 15% of prepolymer content.

Table 1. Glass transition temperatures of chamber synthesized Nylon 6, poly(ether-esteramide) and the copolymer with 15% of poly(ether-esteramide) content.

Material	T <sub>g1</sub> (°C)	T <sub>g2</sub> (°C)
<b>Poly(ether-esteramide)</b>	-59.63	-
<b>Copolymer</b>	-71.20	47.61
<b>Nylon 6</b>	-	52.35

*Thermal analysis.*

Figure 4 shows the melting temperatures ( $T_m$ ) of the synthesized copolymers and a commercial Nylon 6. The melting temperatures found for the copolymers with 10 and 20% of poly(ether-esteramide) correspond to that reported by Hedrick and Gabbert[2] for the copolymers obtained by RIM. A linear decrease in the melting temperature was observed as the prepolymer content increases. It has been reported that this decrease could be produced by attractive interactions between the copolymer blocks[8], and also by the decrease on the size and perfection of the crystallites in the Nylon 6 block. Copolymerization usually lowers the melting point by shortening of the length of crystallizable sequences[9]. A decrease on the length of the nylon block produces a smaller lamellar thickness of crystals, consequently showing a lower melting point[10]. Nishi and Sakurai[11,12] have attributed the decrease of the melting point to the diluted effect of non-crystalline polymer, depending on the molar fraction of crystalline component of the copolymer.

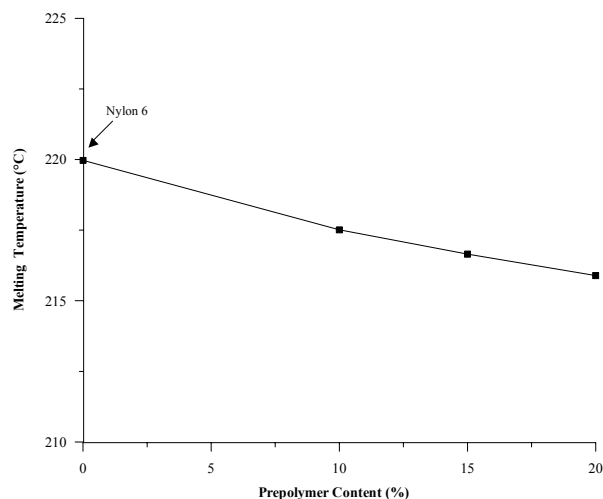


Figure 4. Effect of elastomeric phase content on the melting temperature of the copolymers.

The melting enthalpy ( $\Delta H_m$ ) was used to calculate the crystallinity, considering that the copolymers were synthesized on the same way and the thermal history was similar, by a heating-cooling program. The differences in crystallinity could be directly related to the composition.

Table 2 shows the melting enthalpy of the copolymers. It was found that  $\Delta H_m$  decreased as the poly(ether-esteramide) content increased. This decrease in  $\Delta H_m$  is partly due to the lower content of nylon blocks. The obtained values were normalized dividing by the weight fraction of caprolactam ( $x_w$ ) that was used in the polymerization. The ratio  $\Delta H_m/x_w$  is a better representation of the nylon crystallinity in the block copolymers.

The  $\Delta H_m$  value of 230 J/g, for a 100% crystalline Nylon 6 as proposed by Wunderlich[13] was used to calculate the crystalline fraction ( $x_c$ ). Some decrease on the crystallinity was observed as the prepolymer content increase, due to the rupture of the crystalline packing of Nylon 6 by the presence of poly(ether-esteramide), this is an elastomer that inhibit the regular alignment of the chains[8, 14] which produce a reduction on the size or perfection of polymeric crystals.

Table 2. Crystallinity as a function of the poly(ether esteramide) content.

Content (%)	$\Delta H_m$ (J/g)	$x_w$ Nylon (Weight fraction)	$\Delta H_m/x_w$ (J/g)	$x_c$ (%)
10	48.12	0.90	53.47	23.25
15	44.81	0.85	52.72	22.92
20	44.01	0.80	55.01	23.91

$x_c$  Crystallinity %

#### *Molecular weight of Nylon 6 block.*

Using nylon 6 melting temperature and the proposed Flory[15] theory of depression on the melting point it is possible to estimate the block length of Nylon 6 in the copolymer. This theory establish that in a copolymer formed from crystallizable A units and non-crystallizable B units, exists a decrease on the melting point of the crystallizable units.

The following equations relate the number average polymerization degree  $X_n$  to the melting temperature depression:

$$\frac{1}{T_m} - \frac{1}{T_{m_0}} = \frac{R}{\Delta H_u} \frac{2}{X_n} \quad [1]$$

$$M_n = M_0 X_n \quad [2]$$

where  $X_n$  is the number average polymerization degree,  $R$  is the gas constant of 1.987 cal/mol K,  $\Delta H_u$  is the enthalpy of fusion, 4300 cal/mol for the  $\epsilon$ -caprolactam[16],  $T_{m_0}$  is the initial melting temperature,  $T_m$  melting temperature of the copolymers and  $M_0$  is the molecular weight of the repetitive unit of Nylon 6. With the melting temperatures obtained by DSC and the weight fraction of the prepolymer,  $T_{m_0}$  of the synthesized

copolymers was obtained by extrapolating to zero on the graph of  $T_m$  vs  $1-x_w$  where  $x_w$  is the weight fraction of the crystallizable component. Substituting the known values on the equation and using the  $T_{m_0}$  obtained, the  $X_n$  value of Nylon 6 blocks on the copolymers for each poly(ether esteramide) content was calculated. Table 3 shows the results of  $T_{m_0}$  and the calculated size of Nylon 6 blocks.

In general, with the increase of the poly(ether esteramide) content, a decrease in the molecular weight of the Nylon 6 blocks was observed. This is mainly due to the decrease in the available amount of monomer for the formation of the Nylon 6 blocks. Kurz[7] also observed the same behavior in block copolymers of Nylon 6/poly(ether-esteramide) obtained by mass polymerization using a polypropylen-ether diol as a soft segment. Kurz also showed that these materials have an alternate block structure as was previously proposed by Hedrick and Gabbert[2] and they reported molecular weight of Nylon 6 block of 4700 and 3400 for copolymers with elastomeric phase 8.9 and 18.3%.

Table 3. Molecular weight of Nylon 6 block on copolymers with different content of poly(ether esteramide).

Content (%)	$T_{m_0}$ (°C)	$X_n$	$M_n$
10		140	15789
15	219.14	91	10251
20		69	7820

#### *Mechanical Properties.*

Table 4 shows the effect of concentration of the elastomeric phase on mechanical properties of the copolymers. It is observed that Young's modulus, tensile strength at break and hardness decrease as the content of poly(ether-esteramide), that acts as initiator on the copolymerization reaction, increases. The Young's modulus decrease is attributed to the formation of Nylon 6 blocks of lower molecular weight as a result of more initiation sites available on the reaction medium, that produce a reduction in the stiffness of the material. While the tensile strength at break showed lower values due to the presence of higher content of elastomeric phase causing that the material yields at lower stress. In the same way, the hardness was also modified with the incorporation of the soft segment.

#### *Formic acid test.*

After several hours, the test tubes containing the samples of Nylon 6 showed a persistent clear solution. On the other hand, a persistently turbid solution was observed in the tubes containing the copolymers. This result strongly suggests the presence of a copolymer, as has been reported for other systems[17], due to the dissolution of the Nylon 6 blocks while the poly(ether esteramide) phase remains insoluble.



Table 4. Mechanical properties of the different synthesized copolymers.

Poly (ether- esteramide Content (%)	Young Modulus (Mpa)		Tensile Strength at Break (Mpa)	Hardness
	Tensile	Flexural		
Nylon 6 <sup>a</sup>	3000	-	58.9-68.7	-
10	2152.0 ± 236.5	2651.9 ± 176.8	57.8 ± 3.5	68 ± 3
15	2083.2 ± 179.6	2533.2 ± 96.6	55.8 ± 3.0	66 ± 3
20	1867.2 ± 77.9	2402.3 ± 95.7	41.1 ± 2.9	61 ± 3

## Conclusions

The characterization of the reactive processing synthesized materials indicates that block copolymers of Nylon 6/poly (ether-esteramide) were obtained.

It was found that melting temperature and crystallinity of the synthesized copolymers decreased when the elastomeric phase content increased according to the reduction in the size of Nylon 6 blocks. The size of nylon 6 blocks for each composition was calculated and showed a decrease as the poly(ether esteramide) content increased.

Two Tg's were detected corresponding to the two, not miscible, blocks of the copolymer.

More flexible materials were obtained when the soft phase content in the copolymer was increased.

The results of this work set the foundation for the synthesis of this kind of materials by reactive extrusion.

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## References

- 1 W. J. Sichina and A. Bizet; ANTEC, (1994), 2146.
- 2 R. M. Hedrick and J. D. Gabbert; *91st National AIChE Meeting*, Detroit MI (1981).
- 3 C. W. Macosko; *RIM Fundamentals of Reaction Injection Molding*, Hanser Publishers, Munich (1989).
- 4 V. Geenen and A. Arnold; European Patent 3 200 70 B1 (1993).
- 5 M. J. Lozano; PhD Thesis, University of Bradford, England (1995).

- 6 S. W. Tsui and A. F. Jonhson; *Journal of Material Science*, 23, (1995), 5967.
- 7 J. E. Kurz; *Polymer Process Engineering*, 3, (1985), 7.
- 8 S. W. Seo and W. S. Ha; *Journal of Applied Polymer Science*, 48, (1993), 883.
- 9 L. Nielsen; *Mechanical Properties of Polymers and Composites*, John Wiley and Sons, New York (1977).
- 10 R. G. Nelb, A. T. Chen and K. Onder; *Thermoplastic Elastomers-A Comprehensive Review*, Hanser Pub., Munich(1987).
- 11 T. Nishi and T. T. Wang; *Macromolecules*, 8, (1975), 909.
- 12 K. Sakurai, G. Amador and T. Takahashi; *Polymer*, 39, (1998), 4089.
- 13 B. Wunderlich; *Macromolecular Physics*, Vol 3, Academic, New York (1980).
- 14 S. W. Seo and W. S. Ha; *Journal of Applied Polymer Science*, 54, (1994), 1997.
- 15 P. J. Flory; *Principles of Pölymer Chemistry*, Cornell University Press, Ithaca, New York (1953).
- 16 Brandrup, J. and E. H. Immergut; *Polymer Handbook*, Interscience, New York, (1966).
- 17 W. H. Jo, C. D. Park and M. S. Lee, *Polymer*, 37, (1996), 1709.