

Starlike Nylon 6/Polyurethane Block Copolymers by Reaction Injection-Molding Process (RIM)

EDUARDO A. GONZÁLEZ-DE LOS SANTOS, ANGÉLICA S. LÓPEZ-RODRÍGUEZ,
MA. JOSEFINA LOZANO-GONZÁLEZ, FLORENTINO SORIANO-CORRAL

Centro de Investigación en Química Aplicada, Enrique Reyna # 140, Saltillo, Coahuila, CP 25100 Mexico

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ABSTRACT: Starlike block copolymers of Nylon-6 and polyurethane were synthesized using ϵ -caprolactam as a monomer, caprolactam magnesium bromide as a catalyst, and a star prepolymer of polyurethane. These copolymers were compared with the linear block copolymers of Nylon-6 and polyurethane. Such copolymers were obtained using the reaction injection-molding process (RIM) of ϵ -caprolactam at different contents of polyurethane (5–30 wt %). In increasing the content of the soft phase, in FTIR, a displacement was observed in the band at 1637 cm^{-1} , assigned to the amide I of the Nylon 6, to a higher wavenumber. This suggests a bigger interaction between the urethane group of the polyurethane and the amide group of the Nylon 6. Star block copolymers showed better mechanical properties compared with the linear ones. This behavior is attributed to the higher crystallinity and ramifications present in the materials. The structure and the thermal properties of the copolymers were studied using different techniques such as DSC, WAXS, DMA, and SEM. A decrease in the crystallinity when increasing the soft phase was also observed. Finally, physical tensile, impact, and hardness tests of the copolymers were carried out. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2483–2494, 2001

Key words: starlike polymer; block copolymer; Nylon 6/polyurethane; RIM; reactive processing; intramolecular interaction

INTRODUCTION

Block copolymers with an elastomeric sequence and terminal blocks of Nylon-6 have been developed because the high melting point of Nylon-6 (220–230°C) can improve the range of service temperatures of thermoplastic elastomers. On the other hand, the presence of soft central blocks

[polyurethane (PU)] improves significantly the impact strength of Nylon 6.^{1–7} The Nylon 6 block copolymers require the use of a catalyst and an activator for their formation. The activator contains terminal amide groups that allow the formation of Nylon 6. This can be carbamoyl caprolactam, acyl caprolactam, or prepolymers functionalized with terminal caprolactam groups.⁶ The catalysts most frequently used are caprolactam magnesium bromide, sodium caprolactamate, and potassium caprolactamate.⁸

Extensive research for obtaining Nylon 6 by modifying the functionality of the activator has been performed. Chang et al.⁹ obtained Nylon 6

Correspondence to: E. A. González-de los Santos (eduardo@polimex.ciqa.mx).

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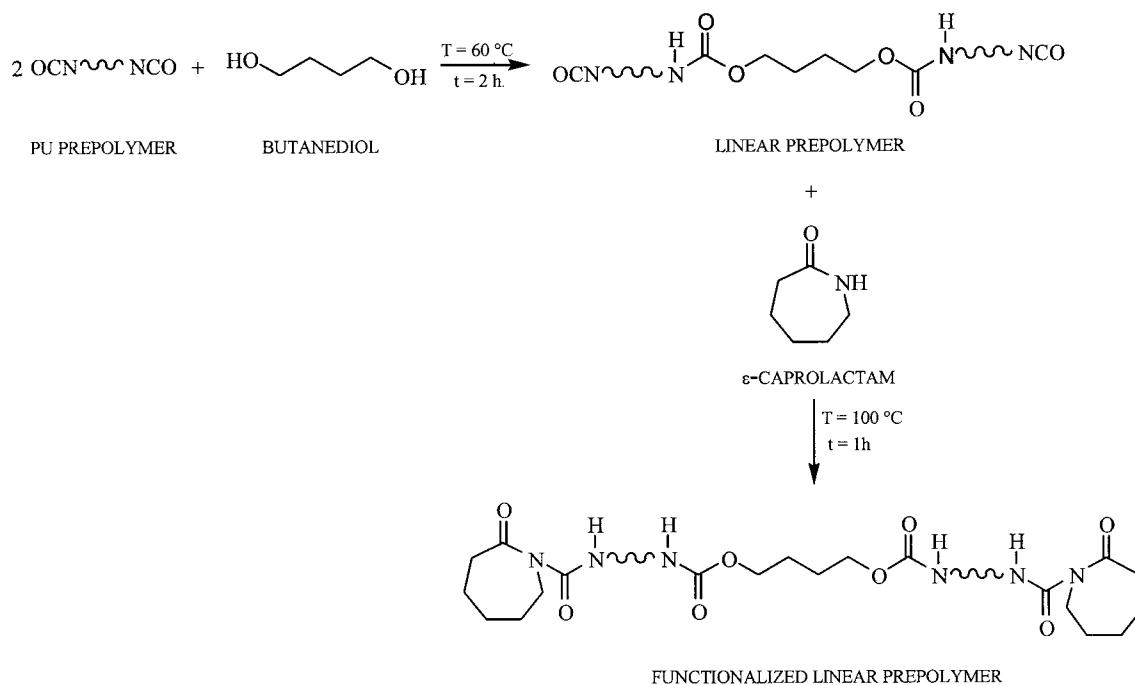


Figure 1 Synthesis of linear prepolymer using butanediol.

with a star structure from Desmodur L-2291A and caprolactam, using the reaction injection-molding (RIM) process. They studied the effect of the mold temperature, the molecular weight, and the polyol content using different catalysts. They reported that the catalytic activity using potassium caprolactamate was higher compared with sodium caprolactamate, and using poly(tetramethylene ether glycol), they obtained a higher impact strength. The objective of this research was to study Nylon 6/PU block copolymers using a trifunctional activator and to compare them with a linear copolymer. Further studies using higher-branched PU prepolymers will be published later.

EXPERIMENTAL

Reagents

Caprolactam [$C_6H_{11}NO$] was dried under a vacuum at 40°C for 12 h. A poly(ether urethane) prepolymer with terminal isocyanate groups (Hysol of Mexico S.A., Mexico), formed from poly(propylene ether glycol) (PPG) and 4,4'-methylenebis(phenyl isocyanate) (MDI), average molecular weight $M_n = 750$, isocyanate content = 10.08 % (ASTM D 2572-87, ref. 10), 1,4 butanediol

[$HO(CH_2)_4OH$], glycerol [$OH(C_3H_5OH)OH$] (Aldrich Chemical Co., Milwaukee, WI), and a caprolactam magnesium bromide solution in caprolactam [$MgBrC_6H_{10}NO$] (DSM RIM Nylon Inc., The Netherlands).

Synthesis of Prepolymer

Linear Prepolymer

A reaction vessel equipped with a mechanical stirrer, thermometer, and N_2 atmosphere was charged with the poly(ether urethane) prepolymer and butanediol in a molar ratio of 2:1 (see Fig. 1). The reaction was carried out at 60°C with stirring for 2 h. Once the reaction was finished, the solution was heated at 100°C ; then, caprolactam in a molar ratio of 2:1 was added for the purpose of obtaining the linear activator. The reaction was carried out for 1 h.

Star Prepolymer

The poly(ether urethane) prepolymer was added to a reaction vessel equipped with a mechanical stirrer in a N_2 atmosphere. Then, glycerol was added in a molar ratio of 3:1. The reaction was carried out at 60°C for 1.5 h. Later, caprolactam was added in a molecular ratio of 3:1 and the

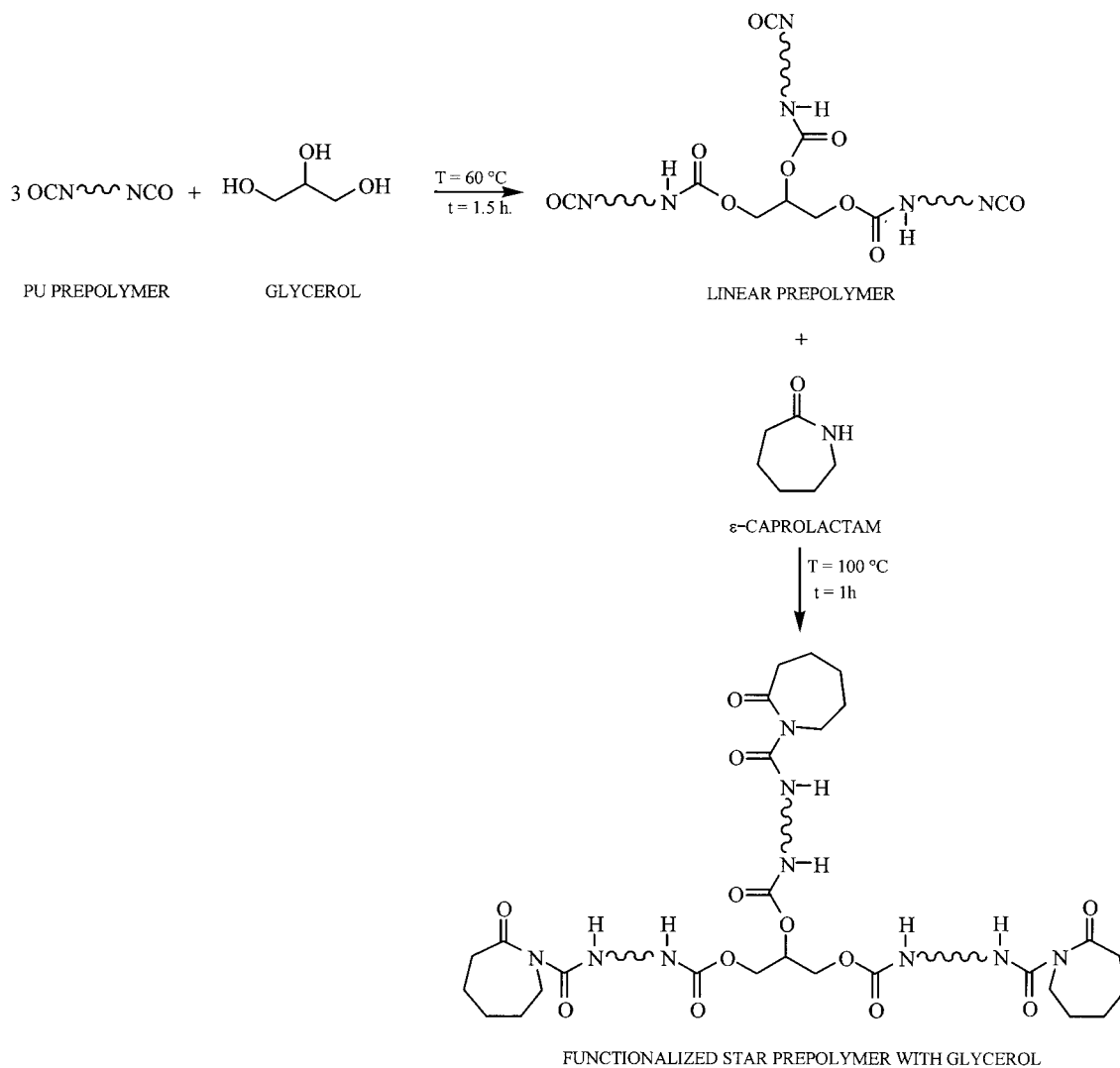


Figure 2 Synthesis of star prepolymer using glycerol.

temperature was increased to 100°C and the reaction was heated for 1 h to obtain the star activator (see Fig. 2).

Block Copolymerization

In the RIM, the activator and catalyst were dissolved in molten ϵ -caprolactam at 90°C. Once the prepolymer and catalyst were fully dissolved, both solutions were mixed and poured into a preheated mold at 170°C for 30 min, where polymerization occurred. The mold was cooled to 25°C and the Nylon 6/polyurethane block copolymer plaque was released from the mold. This polymerization procedure was used to produce all the linear and star Nylon 6/PU block copolymers showed in Table I.

Characterization of Activators

Infrared Spectroscopy (FTIR)

A Nicolet Magna-IR Model 550 spectrometer in a wavenumber interval 400 to 4000 cm^{-1} was used. The preparation of the sample was carried out, depositing a small quantity on a glass of potassium bromide (KBr).

Characterization of Copolymers

Differential Scanning Calorimetry (DSC)

A thermal analyzer (TA Instruments Model 2920) was used. A small sample was heated from 25 to 250°C in the first scan at 10°C/min. After cooling

Table I Proportions of Reagents Used in the Synthesis of the Linear and Star Copolymers

Nomenclature	Prepolymer ^a (wt %)	Caprolactam ^a (wt %)	Catalyst ^b (wt %)
Linear-5	5	95	10
Linear-10	10	90	10
Linear-20	20	80	10
Linear-30	30	70	10
Star-5	5	95	10
Star-10	10	90	10
Star-20	20	80	10
Star-30	30	70	10

^a Percentage by total weight.^b Percentage by weight.

to -50°C , the sample was reheated (second scan) up to 250°C at $10^{\circ}\text{C}/\text{min}$. From this analysis, the melting temperature (T_m) and cold-crystallization temperature (T_c) were recorded. The degree of crystallinity was calculated from the heat of melting.

Dynamic Mechanical Analysis (DMA)

The measurements were carried out in a TA Instruments Model DMA 983. The sample was analyzed in a temperature interval from -80 to 150°C at 5°C and 0.1 Hz of frequency.

Wide-angle X-ray Diffraction (WAXD)

X-ray measurements were performed on a Siemens instrument Model D5000, under the following operation conditions: 35 kW, 25 mA, $\lambda = 1.5 \text{ \AA}$, and scan speed of $0.4^{\circ}/\text{min}$.

Physical and Mechanical Testing

Izod notched impact strength was measured according to ASTM D 256, using an IZOD machine Model CSI-137D by the pendulum method at 23°C . The tensile tests were performed on an Instron machine series 4301 with a cell of 5 KN. The specimens were cut according to ASTM D 638 for the type of specimen I. Shore "D" hardness was determined using a PTC Instruments durometer Model 307 L according to the norm ASTM D 2240.

Scanning Electronic Microscopy (SEM)

The fracture obtained from the samples cooled with N_2 was recovered with gold-palladium and

analyzed in a scanning electronic microscope TOP-Con SM 510. To analyze the sample, secondary electrons were used with a work distance of 18 mm and 15 kW.

RESULTS AND DISCUSSION

Synthesis of Prepolymers: Infrared Spectroscopy (FTIR)

In the FTIR spectrum of the linear and star prepolymer, the wide band at 3300 cm^{-1} assigned to the hydroxyl group of the butanediol and glycerol disappeared [Fig. 3(a)]. On the other hand, the band corresponding to the isocyanate group of the prepolymer appears approximately at 2272 cm^{-1} . The narrow band around 3300 cm^{-1} is characteristic of the N—H group (urethane) and the band at 1539 cm^{-1} corresponds to the N—H flexion of the prepolymer. The band corresponding to the carbonyl group of the PU also appears around 1720 cm^{-1} . When adding the caprolactam for the synthesis of the activators, the disappearance of the band of the isocyanate group was observed mainly at 2272 cm^{-1} , and the presence of the carbonyl group corresponding to the ring of the caprolactam, at 1650 cm^{-1} [(See Fig. 3(b)].

Synthesis of Block Copolymers

Infrared Spectroscopy (FTIR)

The IR spectrum of the Nylon 6 block copolymers was studied mainly in the region of the amide I band of the Nylon 6, since the bands of the urethane group overlap with the bands of the amida

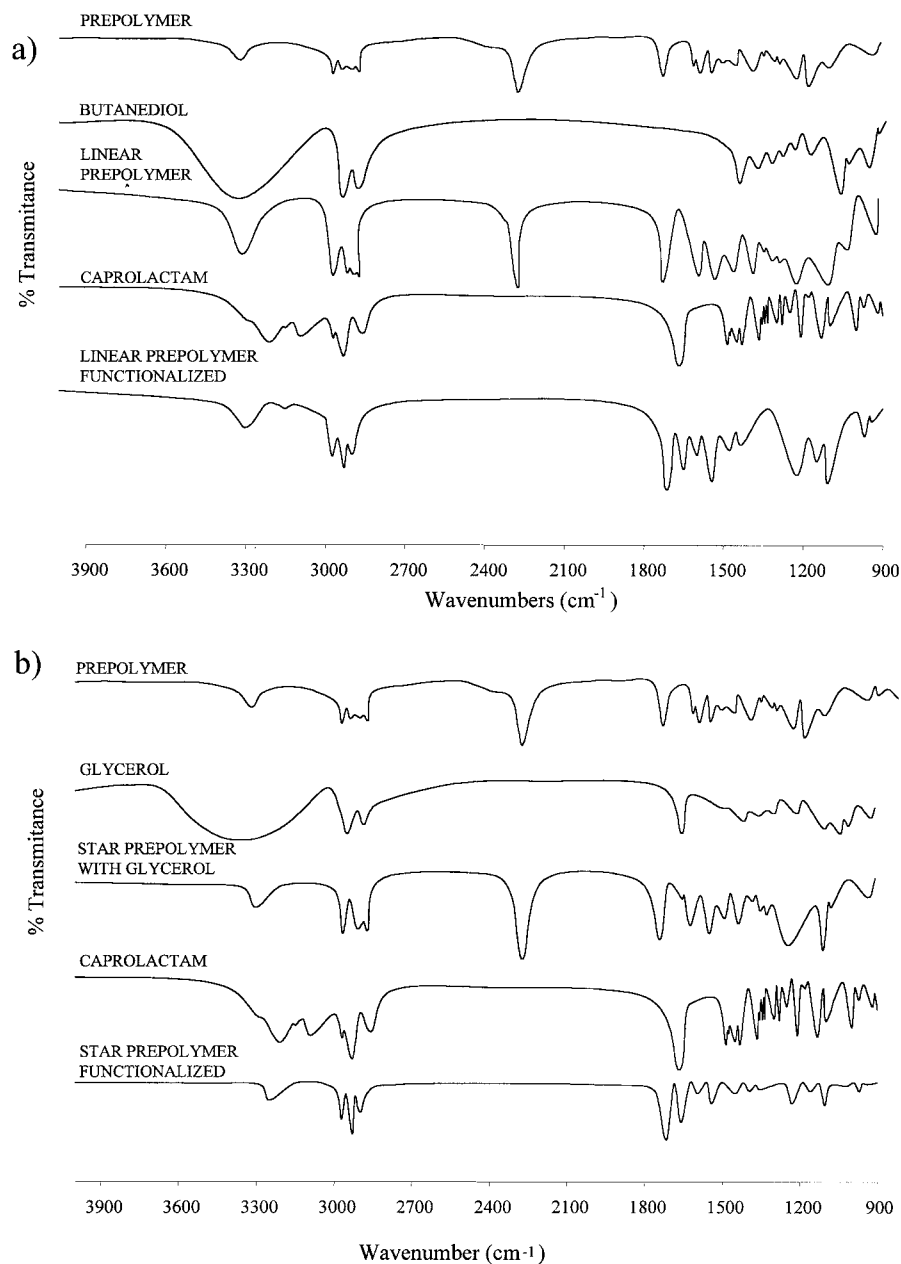


Figure 3 FTIR spectra of the (a) linear and (b) star prepolymers.

II of the Nylon 6 around 3300 and 1540 cm^{-1} . The band of the amide I of the Nylon 6 obtained by the RIM process appears at 1637 cm^{-1} . Seo and Ha suggested a decrease in the intermolecular interaction between the blocks of Nylon 6, due to the interaction between the blocks of Nylon 6 and PU.⁷ Thus, when the prepolymer content increases, as shown in Figure 4, the band of the amide I shifts to higher wavenumbers, decreasing the molecular interaction between the blocks of

Nylon 6 and, then, the crystallinity. The linear copolymers present a bigger displacement than that of the star copolymers because the interaction of the amide group exists with the urethane group caused by the linearity of the chains.

WAXD

In Figure 5(a,b), the diffraction spectrum is presented for the linear and star copolymers,

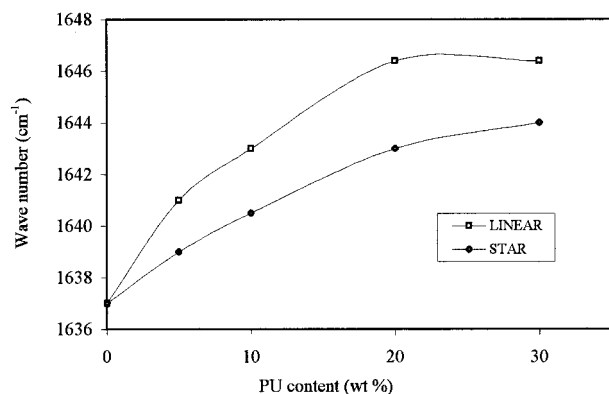


Figure 4 Analysis of the amide I region in linear and star Nylon 6/PU block copolymers.

respectively. It is well known that Nylon 6 presents two crystal structures (α and γ), depending on the thermal and processing conditions.¹¹ All samples presented two diffraction peaks around $2\theta = 20^\circ$ and $2\theta = 24^\circ$ that correspond to the α crystal structure. The intensity of the diffraction curve decreased when the prepolymer content increased. This suggests that the crystallization degree and the size of the crystal of the Nylon 6 block decreased as the prepolymer content increased. This is attributed partially to the interaction between the PU with the block of Nylon 6 and inhibits the crys-

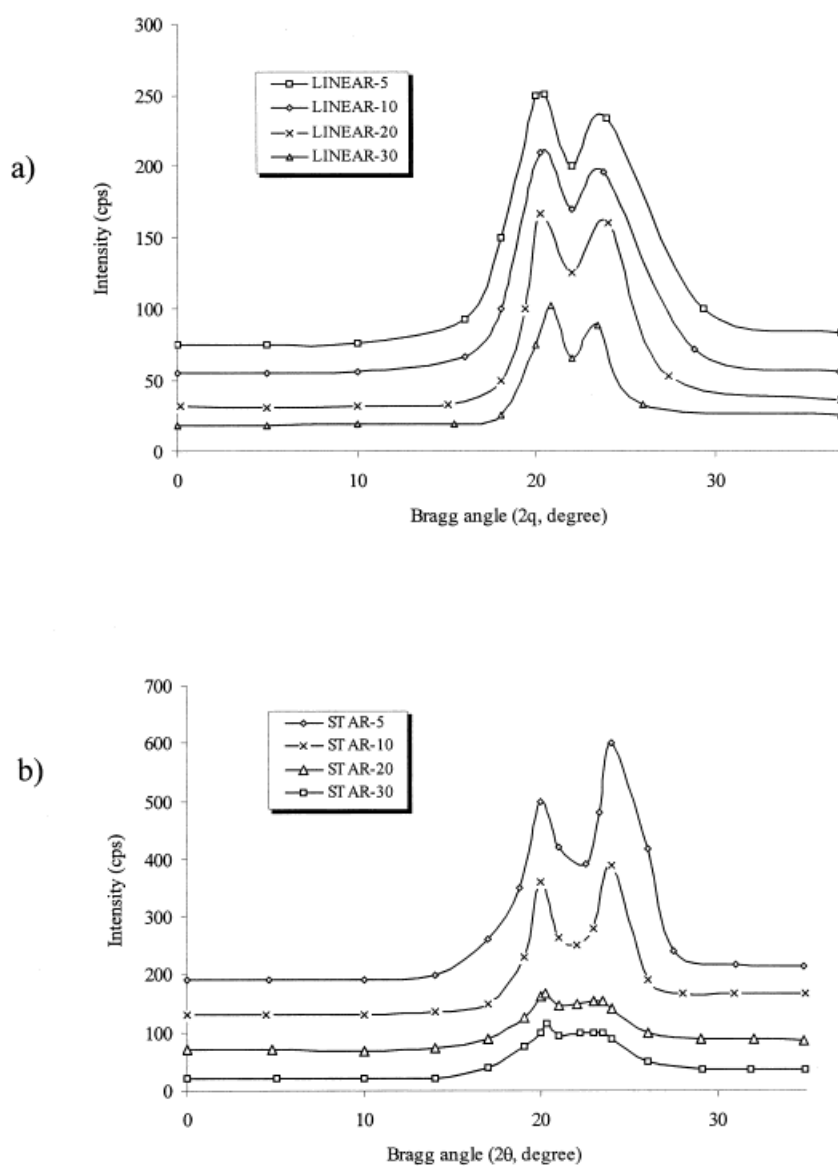


Figure 5 X-ray diffractograms of the (a) linear and (b) star Nylon 6/PU block copolymers.

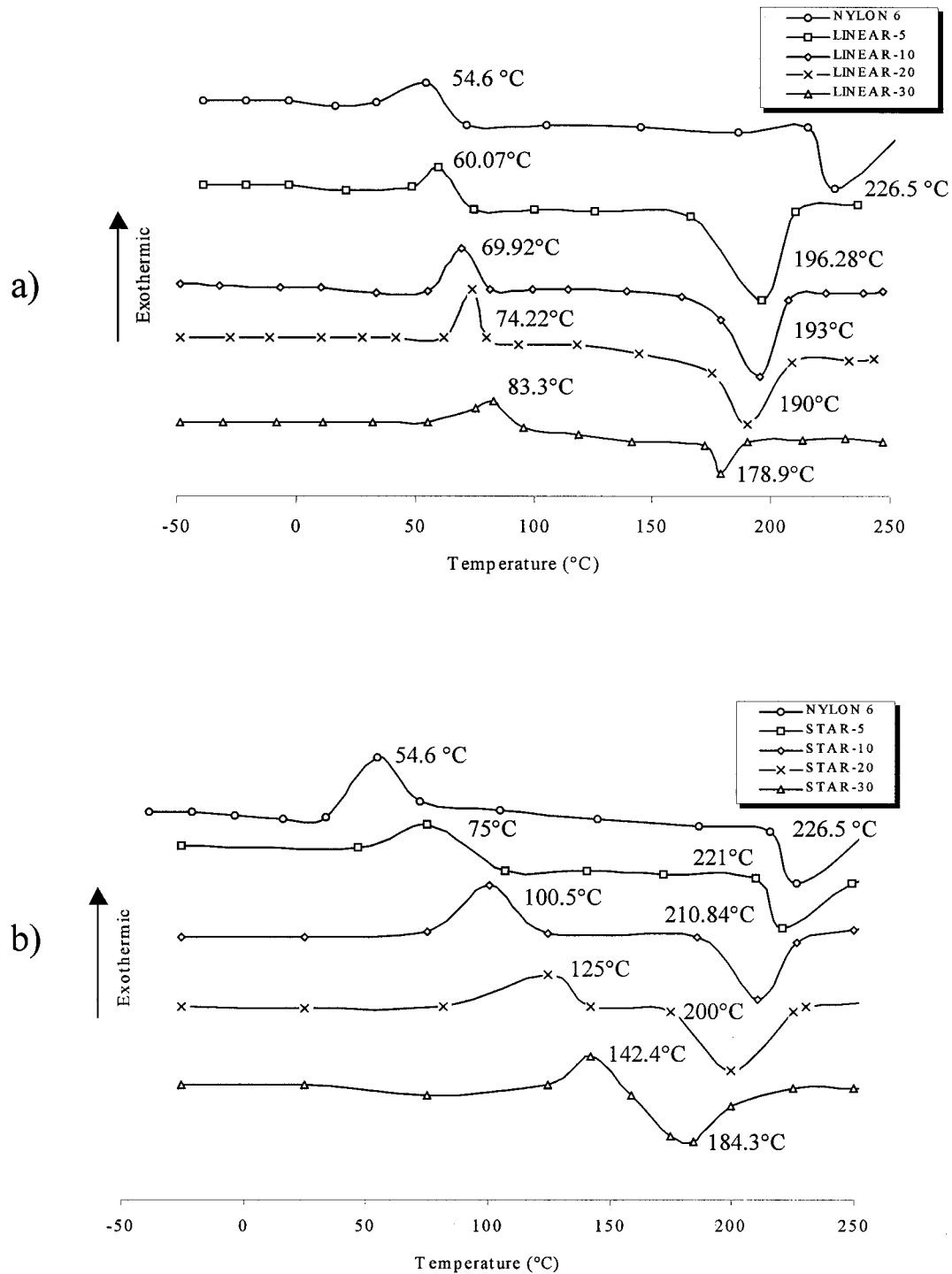


Figure 6 DSC thermograms of the (a) linear and (b) star Nylon 6/PU block copolymers.

tallization of Nylon 6. This decrement can also be caused by the decrease in the content of caprolactam in the formation of Nylon 6 when the rubber phase increased. Kim and Hong¹¹

also observed the same behavior when synthesizing Nylon 6/poly(ethylene glycol) block copolymers with the use of different linear activators.

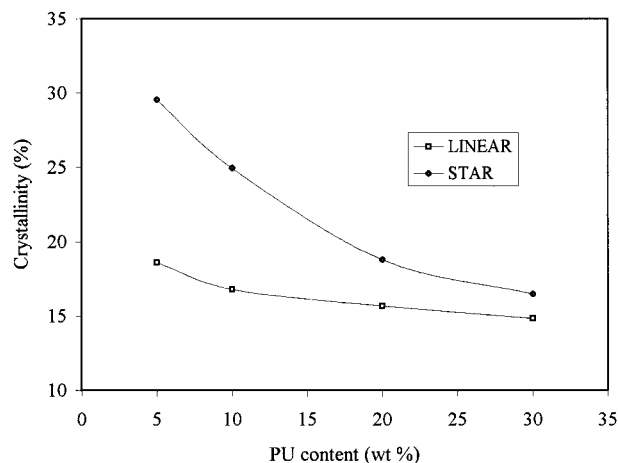


Figure 7 Crystallinity grade of linear and star Nylon 6/PU block copolymers obtained for DSC.

DSC

The analyses of DSC for the linear and star copolymers, respectively, are shown in Figure 6(a,b). For the linear copolymers, an endotherm is observed between 170 to 196°C, which indicates the melting temperature (T_m), besides an exotherm between 60 and 83°C that is known as the cold-crystallization temperature (T_c), which is related to the disorder of the molecules.^{5,12,13} This temperature is observed above the temperature of the glass transition temperature (T_g), due to a quenching from the melting state in all the samples. In general, a decrease in the melting temperature (T_m) was observed with increase of the prepolymer content, because of a decrement in the crystal size of the Nylon 6 homopolymer,

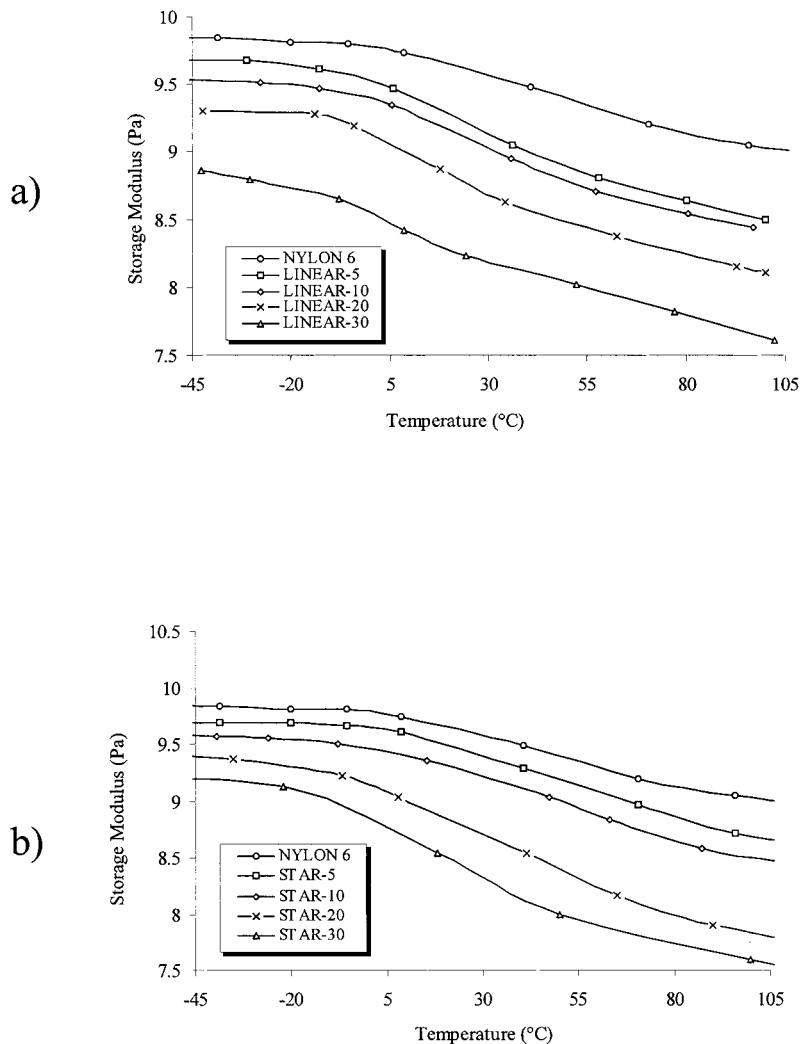


Figure 8 Storage modulus of the (a) linear and (b) star Nylon 6/PU block copolymers.

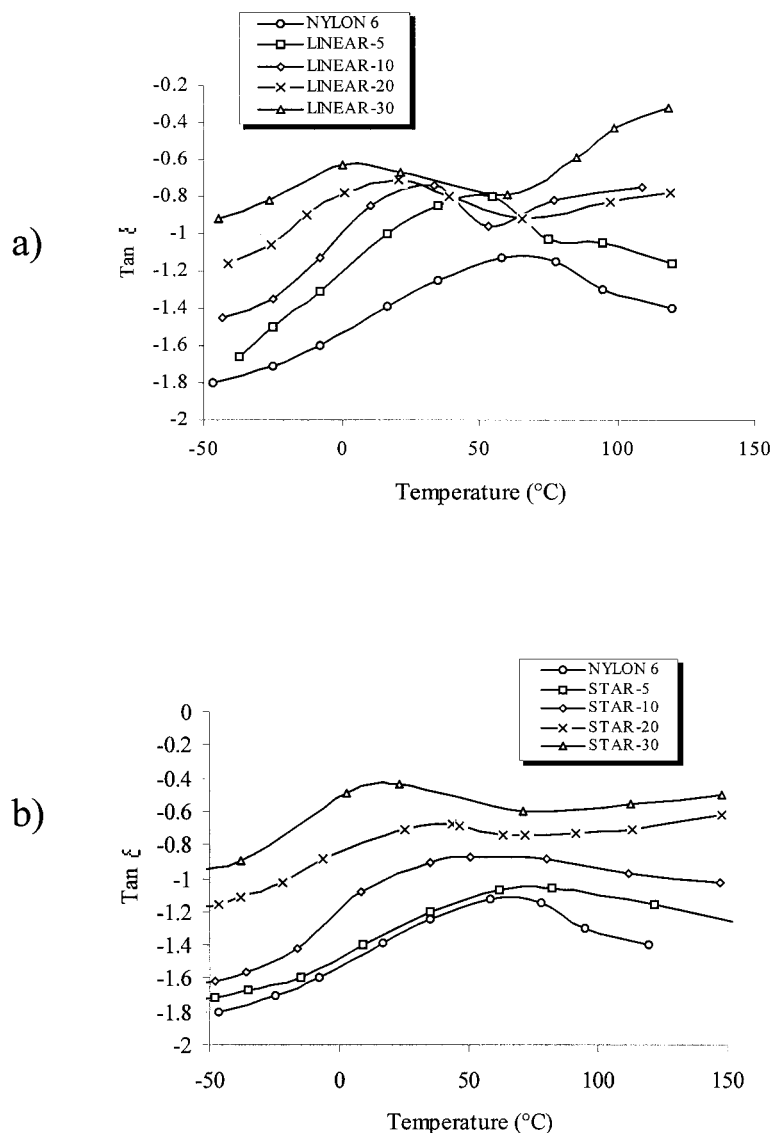


Figure 9 Loss $\tan \delta$ of the (a) linear and (b) star Nylon 6/PU block copolymers.

caused by the addition of the soft segment, that limits the growth in the length of crystalline chains.¹⁴ Also, as the prepolymer content (soft phase) increased, the centers of the chain initiations also increased; then, the blocks of Nylon 6 will be small. Additionally, the interaction between the urethane groups in the prepolymer and the amide groups of Nylon 6 through hydrogen bonds, as was observed by infrared spectroscopy, influences the decrease of the melting temperature.

The star copolymers showed a higher melting temperature than that of the linear copolymers. This behavior could be attributed to less interac-

tion between urethane groups and amide groups and to the higher crystallinity of the star copolymers. In analyzing the cold-crystallization temperature (T_c), this is shown to increase with the increment in the prepolymer content. This increase of T_c causes a greater difficulty in the formation of crystals in the Nylon 6 blocks due to the interaction with the PU prepolymer. Also, for the star-shape copolymers, there is an entanglement effect. The interaction phenomena also interfere with the formation of Nylon 6 crystals and, in general, it decreased the crystallinity; the above was observed by X-ray analysis and was demonstrated by calculation of the crystallinity degree

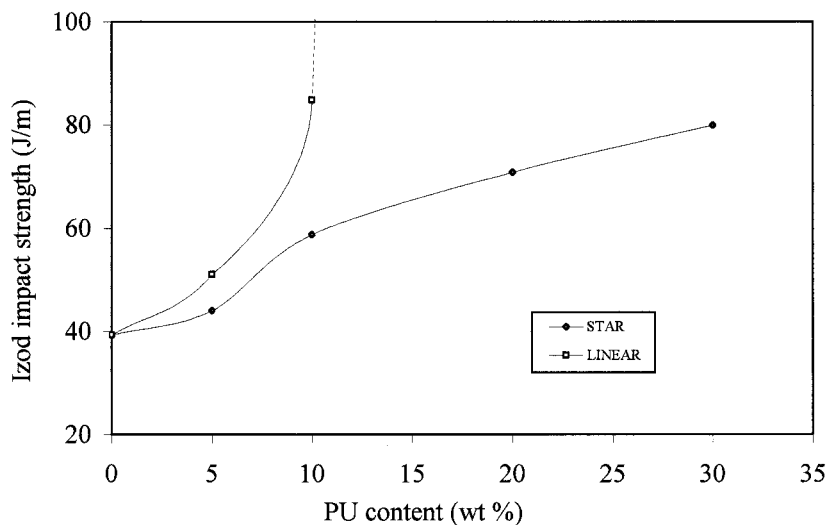


Figure 10 Influence of PU content on the impact strength of the linear and star Nylon 6/PU copolymers.

using the heat of melting (Fig. 7). The linear copolymers presented a lower degree of crystallinity.

DMA

The behavior corresponding to the storage module E' of the linear and star copolymers is shown in Figure 8. A decrease in the storage modulus with the increment of the rubber phase is observed. Higher values are obtained in the storage module E' for the star copolymers. This is attributed to the increment in the entanglement of the star prepolymers generating crosslinking, causing a

greater rigidity of the materials. Also, the star copolymers are more crystalline than are the linear ones (see Fig. 7).

The curves of $\tan \delta$ for the linear and star Nylon 6/PU block copolymers are shown in Figure 9(a,b), respectively. The presence of a single glass transition temperature is observed, near the T_g of the Nylon 6 (54°C). The T_g of the PU around -38°C is not observed. A single T_g in the block copolymers indicates a single phase, suggesting the existence of an interaction between the blocks of Nylon-6 and PU, as was observed in the infrared spectroscopy. A decrease was also observed in

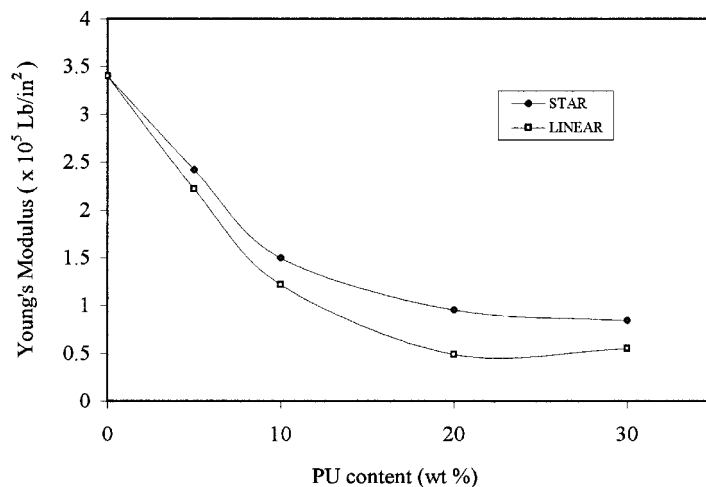


Figure 11 Young's modulus of linear and star Nylon 6/PU block copolymers.

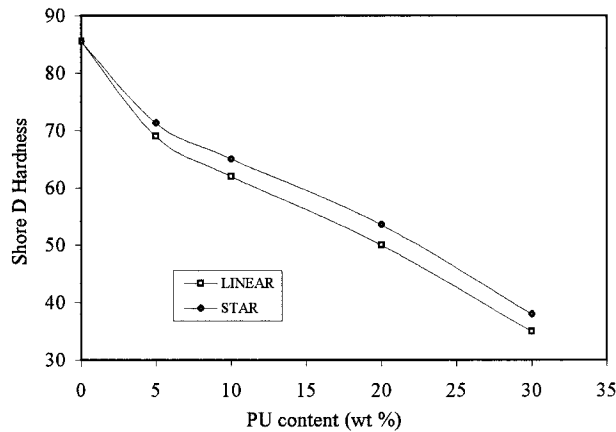


Figure 12 Shore D hardness of linear and star Nylon 6/PU block copolymers.

the glass transition temperature with an increase in the prepolymer content. In all samples, this behavior is generated by the addition of the rub-

ber phase; the properties of the PU predominate in the copolymer and, therefore, it decreases the rigidity of the materials. Higher values of T_g in the star copolymers are obtained. This suggests the presence of ramifications that allow a lower mobility of the chains of Nylon 6, and so for the molecules to flow, high temperature is required.

Physical and Mechanical Testing

Impact, tension, and hardness tests of the linear and star Nylon 6/PU copolymers were carried out. The results are shown in the Figures 10–12, respectively. The impact strength increases with increase in the PU content. For linear copolymers, the material is softer at low concentrations of the rubber PU percentage; however, for starlike copolymers, the material maintains its integrity with a reasonable increment in the impact strength. When increasing the rubber phase, a decrease is manifested in the Young's modulus.

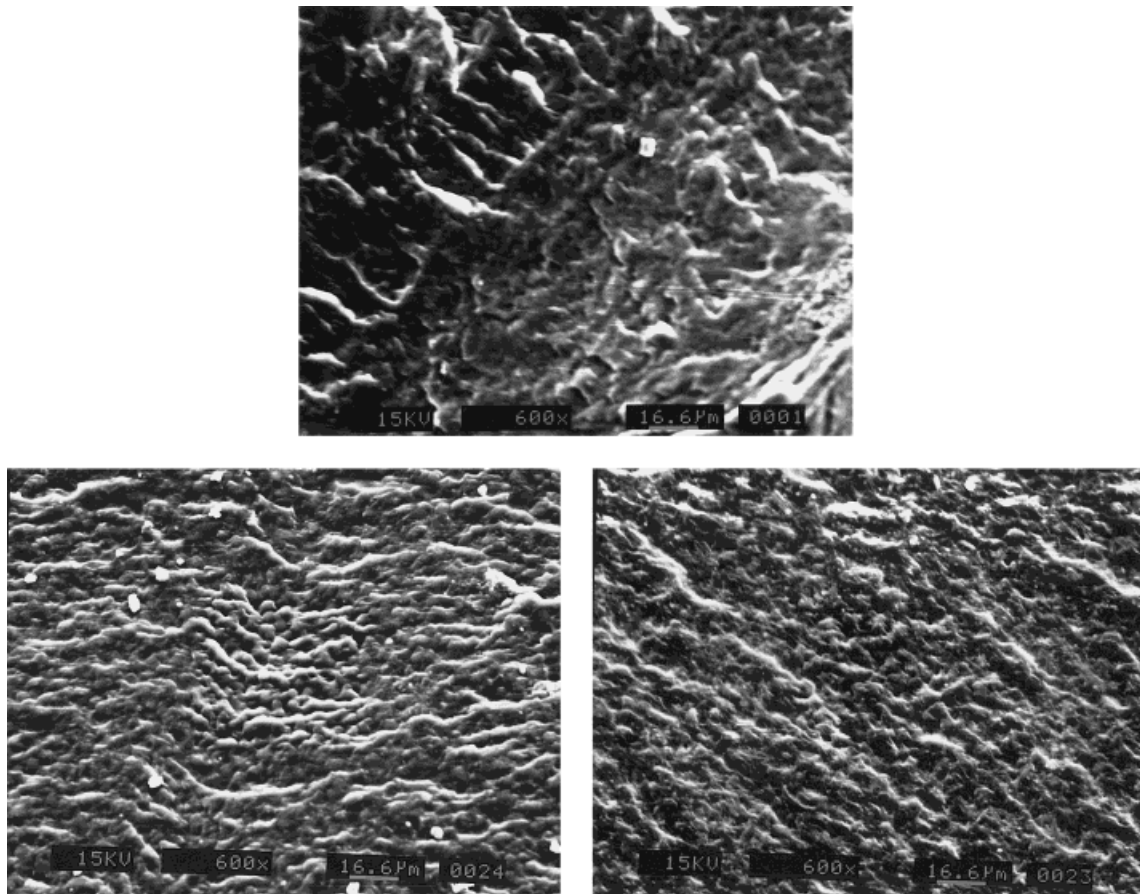


Figure 13 Micrographs of (a) Nylon 6, (b) linear-10 copolymer, and (c) star-10 Nylon 6/PU block copolymer.

This behavior indicates that an increase the chains' flexibility for PU also can be attributed to a decrease in the crystallinity and a decrease of the rigidity of the materials. In comparing the different copolymers, higher values were observed in the star copolymers; it is probably due to the presence of higher crystallinity and branching, which causes an increment in the rigidity of the material. The hardness decreases with the increment in the prepolymer content. This is attributed also to the addition of the rubber phase, for the interaction between the amide and urethane groups destroys the formation of crystals. The increment in the functionality of the prepolymer suggests an increase in the hardness of the block copolymers.

SEM

In Figure 13, the micrographs of the Nylon 6, linear-10, and star-10 copolymers can be observed. The presence of a single phase for the different copolymers is evident. This indicates that the rigid and rubber phases in the copolymer are compatible. Interaction between the blocks of Nylon 6 and PU observed by FTIR are confirmed as well as the presence of a single glass transition temperature for the analysis of DMA.

CONCLUSIONS

We synthesized Nylon 6/PU block copolymers using linear and starlike prepolymers. All the copolymers presented better impact strength compared with Nylon 6. In general, the star copolymers have a better mechanical property balance than that of the linear copolymers. Both copolymers show the α crystalline form characteristic of Nylon 6 blocks. The intensity of the peaks corresponding to the α crystal decrease when the PU content increased. This suggest a decrease in the crystallization degree and the crystal size, due to the presence of the rubber phase that avoids the intermolecular interactions between the amide groups of Nylon 6. This behavior was also ob-

served in the analysis of infrared spectroscopy and in the crystallinity degree calculated by DSC. From the DMA, a single glass transition temperature was observed (T_g), which indicates the presence of a single phase. Also confirmed by SEM analysis are the interactions between the amide groups of Nylon 6 and the urethane groups of PU. Further studies of these branched PU prepolymers will be published soon.

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