

# Structure, Mechanical, and Thermal Behavior of Nylon 6-Polyisoprene Block Copolymers Obtained via Anionic Polymerization

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**ABSTRACT:** The structure and physicomechanical properties of nylon 6 (N-6) modified with polyethylene oxide-polyisoprene-polyethylene oxide (PEO-PI-PEO) copolymers via activated anionic polymerization have been investigated by using differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), thermogravimetric analysis (TGA), dynamic mechanical analysis (DTMA), and by optical microscopy. This study deals with the influence that the

N-6/PI ratio and the length of the PI segments have on the physicomechanical behavior, thermal stability, and the structural changes of the block copolymers. Literature does not report on previous investigations of this kind. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3251–3258, 2004

**Key words:** block copolymers, crystallization, phase behavior

## INTRODUCTION

Elastification of nylon 6 (N-6) by introduction of the soft segment of polybutadiene,<sup>1–4</sup> butadiene-acrylonitrile copolymer diols,<sup>5</sup> and styrene-butadiene<sup>6</sup> has been reported in the literature in recent years. Activated anionic polymerization is a progressive method used to incorporate the flexible block segments into the main chain of N-6. In our case, telechelic oligomers based on polyethylene oxide-polyisoprene-polyethylene oxide (PEO-PI-PEO) block functionalized either with hexamethylene diisocyanate (HM, I) or with isophorone diisocyanate (IF, II) and successively blocked with 6-hexanelactam (HL) have been used to achieve elastification of N-6. The oligomers mentioned could act as a macroactivator (MA) and as a comonomer at the same time. The synthesis of PEO-PI-PEO telechelic oligomers and the corresponding block copolymers are reported in our previous work.<sup>7</sup>

By varying the concentration of the MA from 2 to 10 wt % and its molecular weight ( $M_n = 2500; 3500; 11,000$ ), a variety of block copolymers with a wide range of chemical and physical structure, morphologies, and mechanical properties can be obtained.

The aim of this work was to study the influence of the concentration and the chain length of soft PI block upon the mechanical properties and thermal behavior

as well as their effect on the structure and the morphology of the block copolymers obtained.

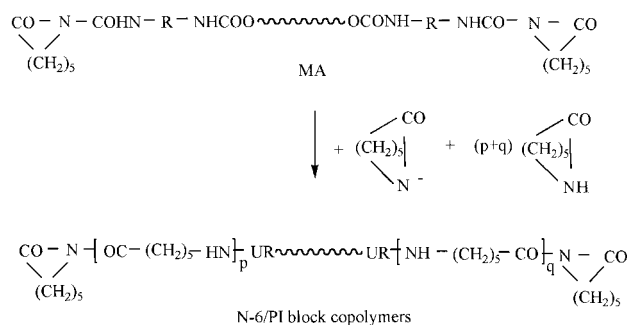
## EXPERIMENTAL

### Materials

6-Hexanelactam (HL; BASF) was dried in a desiccator on  $P_2O_5$  at 60°C in vacuum for 3 days. The initiator, sodium salt of hexanelactam (Na-HL), was synthesized and purified according to ref. 8. Hexamethylene diisocyanate (1,6-diisocyanatohexane) and isophorone diisocyanate (5-isocyanate-1-isocyanatomethyl-1,3,3-trimethylcyclohexane) (Merck) were used as received.

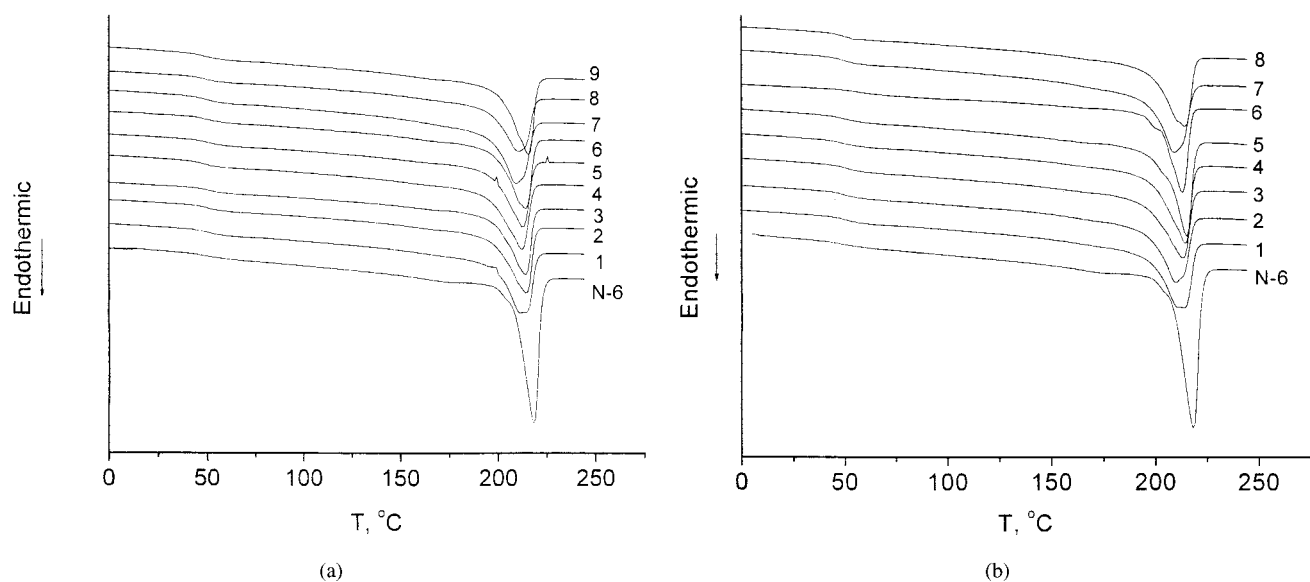
### Anionic polymerization

The polymerization was carried out in bulk at 180°C by using the ampoule technique. The prepolymer functionalized with diisocyanate and monomer HL



Scheme 1

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**Figure 1** (a) DSC thermograms of N-6/PI copolymers, obtained with different concentrations of MA based on HM: 1–3 (2, 5, 10 wt % of MA<sub>2500HM</sub>); 4–6 (2, 5, 10 wt % of MA<sub>3500HM</sub>); 7–9 (2, 5, 10 wt % of MA<sub>11000HM</sub>). (b) DSC thermograms of N-6/PI copolymers, obtained with different concentrations of MA based on IF: 1–3 (2, 5, 10 wt % of MA<sub>2500IF</sub>); 4–6 (2, 5, 10 wt % of MA<sub>3500IF</sub>); 7–8 (2, 5 wt % of MA<sub>11000IF</sub>).

were added to a glass reactor in nitrogen atmosphere and were molded at 120°C under continuous stirring for 20 min (the MAs were prepared directly in the polymerization mixture, i.e., *in situ*). After the homogenization of the mixture, the initiator (Na-HL) was

added under vigorous stirring, and the mixture was forced into the ampoules with N<sub>2</sub>. Block copolymers containing 2, 5, and 10 wt % MA were prepared with a constant initiator concentration of 1 mol % to the monomer quantity (Scheme 1).

**TABLE I**  
DSC Characteristics of the Block Copolymers Obtained

N-6/MA (w/w %)	Type of MA	$T_g^a$ (°C)	$T_m^b$ (°C)	$T_m^c$ (°C)	$\Delta H^d$ (J/g)	$\Delta H^e$ (J/g)	$\alpha^{n^f}$ (%)	$\alpha^{n^g}$ (%)
100	—	47.5	220.9	218.2	81.3	58.1	35.2	25.2
98/2	Ia	50.8	217.6	211.2	44.0	44.3	19.2	19.3
95/5		52.7	218.9	214.3	53.6	42.4	23.3	18.4
90/10	MA <sub>2500HM</sub>	50.0	219.3	213.9	53.6	38.3	23.3	16.7
98/2	Ib	48.4	214.6	212.9	40.6	38.6	17.6	16.8
95/5		50.3	213.7	212.6	45.5	40.0	19.8	17.1
90/10	MA <sub>3500HM</sub>	50.4	214.9	213.7	50.1	41.9	21.8	18.8
98/2	Ic	49.9	215.7	209	49.8	44.3	21.6	19.3
95/5		48.9	216.9	210	46.7	40.0	20.3	17.4
90/10	MA <sub>11000HM</sub>	49.8	216.1	215	53.4	43.4	23.2	18.9
98/2	IIa	50.8	218.4	213.8	46.9	44.1	20.4	19.2
95/5		50.3	217.7	209.6	53.6	42.6	23.3	18.5
90/10	MA <sub>2500IF</sub>	51.4	215.5	213.1	54.1	40.3	23.5	17.5
98/2	IIb	49.7	217.9	214.3	42.7	41.5	18.6	18
95/5		49.4	218.6	214.9	50.8	42.5	22.1	18.5
90/10	MA <sub>3500IF</sub>	54.3	215	212.9	52.1	36.2	22.6	15.7
98/2	IIc	52.2	217.6	214.9	44.8	35.3	19.5	15.3
95/5	MA <sub>11000IF</sub>	49.1	217.5	214.0	47.6	41.2	20.7	17.9

<sup>a</sup> Glass transition temperature at second scan.

<sup>b</sup> Melting temperature at first scan.

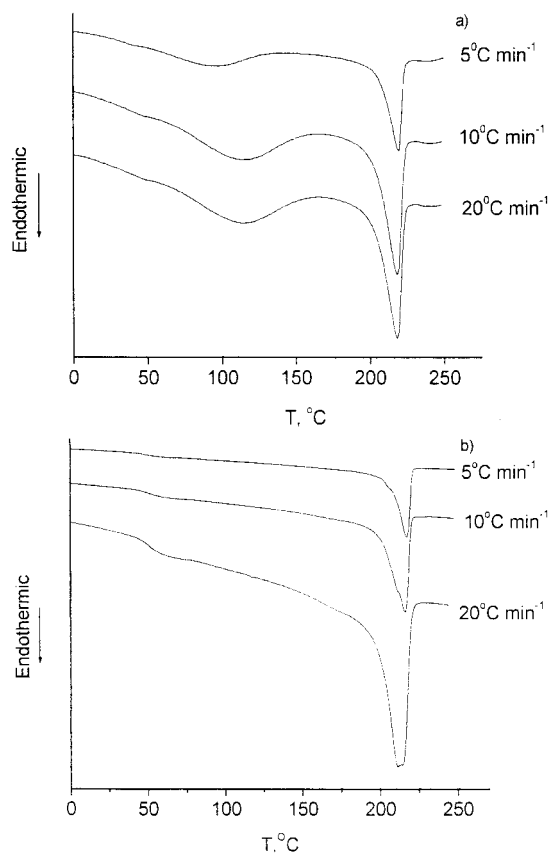
<sup>c</sup> Melting temperature at second scan.

<sup>d</sup> Heat of fusion at first scan.

<sup>e</sup> Heat of fusion at second scan.

<sup>f</sup> Degree of crystallinity at first scan.

<sup>g</sup> Degree of crystallinity at second scan.



**Figure 2** (a–b) Dependence of the melting endotherm of N-6/PI copolymer, synthesized with MA<sub>2500HM</sub> (2 wt %) on the heating rate at first and second scan.

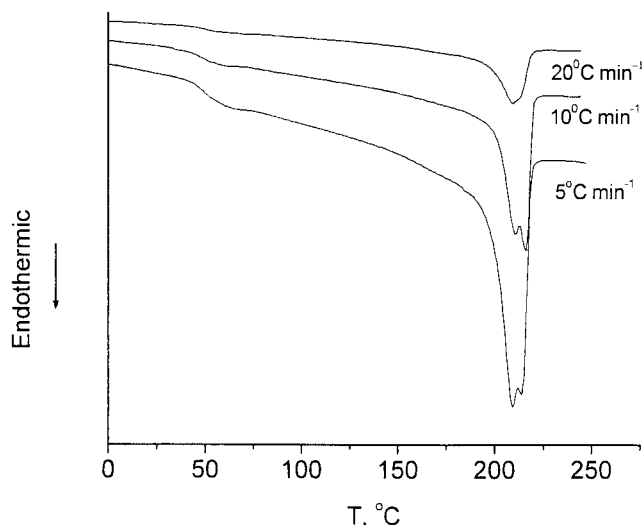
## Measurements

### Differential scanning calorimetry

The melting and the crystallization behavior of the extracted N-6/PI samples were studied by using a TA Instrument DSC Q100 in the temperature range between 0 and 240°C, at a heating rate 20°C min<sup>-1</sup> under a nitrogen flow of 50 mL/min. Each sample was heated up to 240°C (first scan) and quenched to 0 at a rate of 100°C min<sup>-1</sup>. Then, the sample was reheated to 240°C (second scan) at a rate of 20°C min<sup>-1</sup>. The melting temperatures ( $T_m$ ) were obtained as the maximum of the melting endotherms. The glass transition temperature ( $T_g$ ) was calculated at the inflection point from the second heating run. The degree of crystallinity ( $\alpha_{dsc}$ ) was calculated via the ratio between the measured and the equilibrium heats of fusion ( $\Delta H_f / \Delta H_f^0$ ). The equilibrium heats of fusion  $\Delta H_f^0$  was 230 J g<sup>-1</sup>.<sup>9</sup>

### Wide-angle x-ray diffraction (WAXD)

WAXD analyses was carried out with a TUR-62 diffractometer, digital output at constant time of 3 s, Cu $\alpha$  radiation (secondary graphite monochromatic) in re-



**Figure 3** Dependence of the melting endotherm of N-6/PI copolymer, synthesized with MA<sub>11000HM</sub> (2 wt %) on the heating rate.

flection mode. The degree of crystallinity as the ratio between the sum of integrated intensity of all crystal peaks and total integrated intensity was determined from the WAXD pattern. The  $d$ -spacing was calculated from the WAXD intensity curve by Bragg's equation for scattering angles at the intensity maximum.

### Thermogravimetric analysis (TGA)

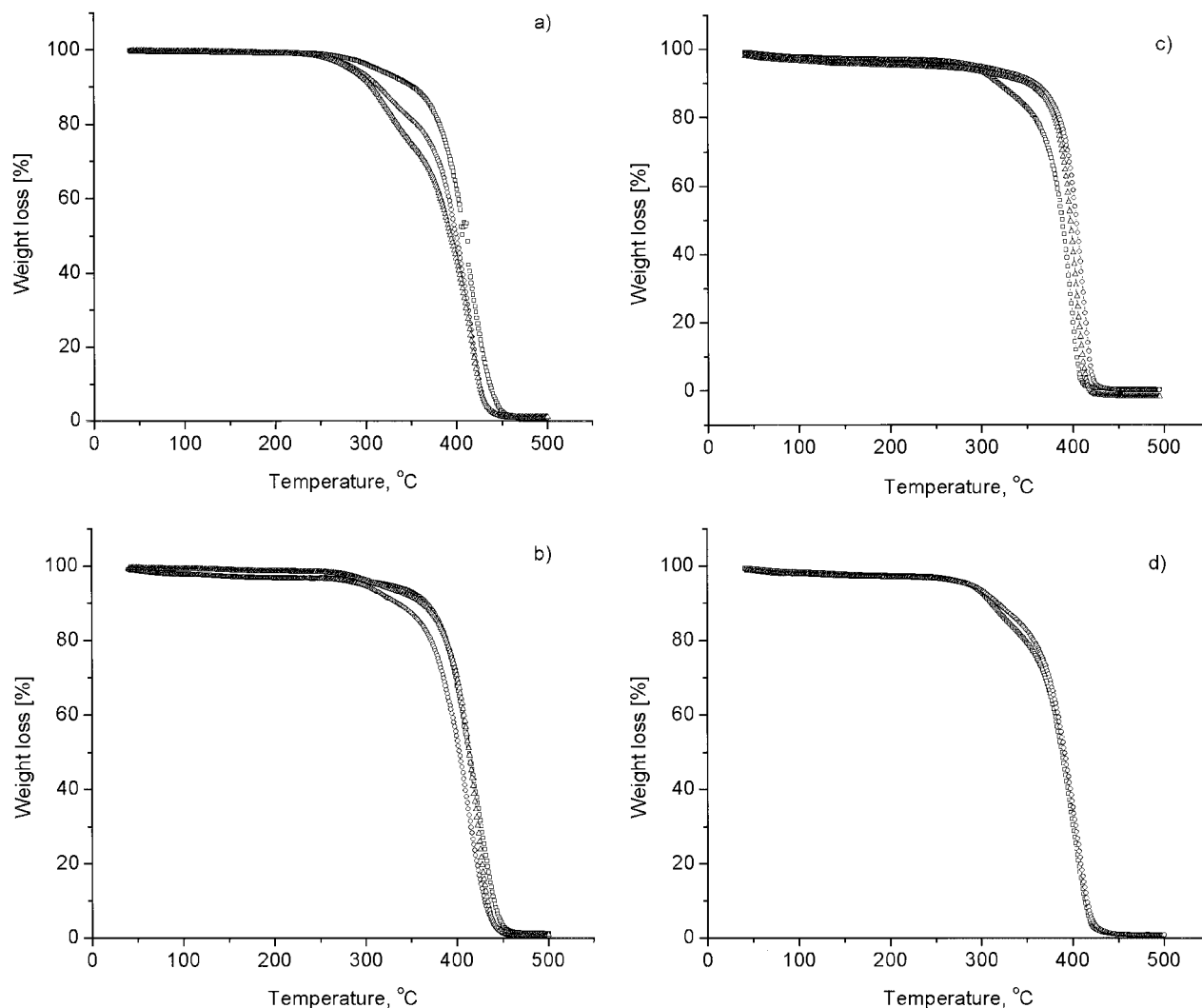
TGA was performed on a TA Instruments TGA 2050 in a temperature range between 40 and 600°C at a

**TABLE II**  
 $T_g$  Characteristics of the Block Copolymers Obtained

N-6/MA (w/w %)	Type of MA	$T_d^{5\% \text{ w.loss}}$ (°C)	$T_b^{\text{max}}$ (°C)
100	—	314.86	427.53
98/2	Ia	310.14	414.75
95/5		287.14	415.70
90/10	MA <sub>2500HM</sub>	300.00	417.61
98/2	Ib	296.69	397.61
95/5		281.18	391.89
90/10	MA <sub>3500HM</sub>	295.83	414.75
98/2	Ic	320.67	426.97
95/5		293.74	410.90
90/10	MA <sub>11000HM</sub>	311.97	421.41
98/2	IIa	283.13	397.89
95/5		296.48	411.13
90/10	MA <sub>2500IF</sub>	234.07	401.67
98/2	IIb	269.05	393.80
95/5		249.99	371.81
90/10	MA <sub>3500IF</sub>	277.53	395.70
98/2	IIc	272.97	395.37
95/5	MA <sub>11000IF</sub>	295.45	411.13

<sup>a</sup> Decomposition temperature at 5% weight loss.

<sup>b</sup> Maximum decomposition temperature.



**Figure 4** (a–d) TGA for N-6/PI block copolymers obtained with different MAs: (a) MA<sub>2500HM</sub>: □, 2 wt %; ○, 5 wt %; △, 10 wt %; (b) MA<sub>11000HM</sub>: □, 2 wt %; ○, 5 wt %; △, 10 wt %; (c) MA<sub>2500IF</sub>: □, 2 wt %; ○, 5 wt %; △, 10 wt %; (d) MA<sub>11000IF</sub>: □, 2 wt %; ○, 5 wt %; △, 10 wt %.

heating rate 10°C under a nitrogen flow of 40 mL min<sup>-1</sup>.

#### Dynamic mechanical analysis (DMTA)

The dynamic mechanical properties of the samples were measured with a torsional pendulum on a Rheometrics Scientific ARES. The test specimens 45 mm long, 12 mm wide, and 0.8 mm thick were cut from melt-pressed films. Torsional response data were obtained at 10°C intervals in the temperature range of -90 to 110°C at a constant frequency of 1 Hz.

#### Optical microscopy

The experiments were carried out on a polarizing optical microscope (Opton Karl Zeiss) equipped with an Olympus camera.

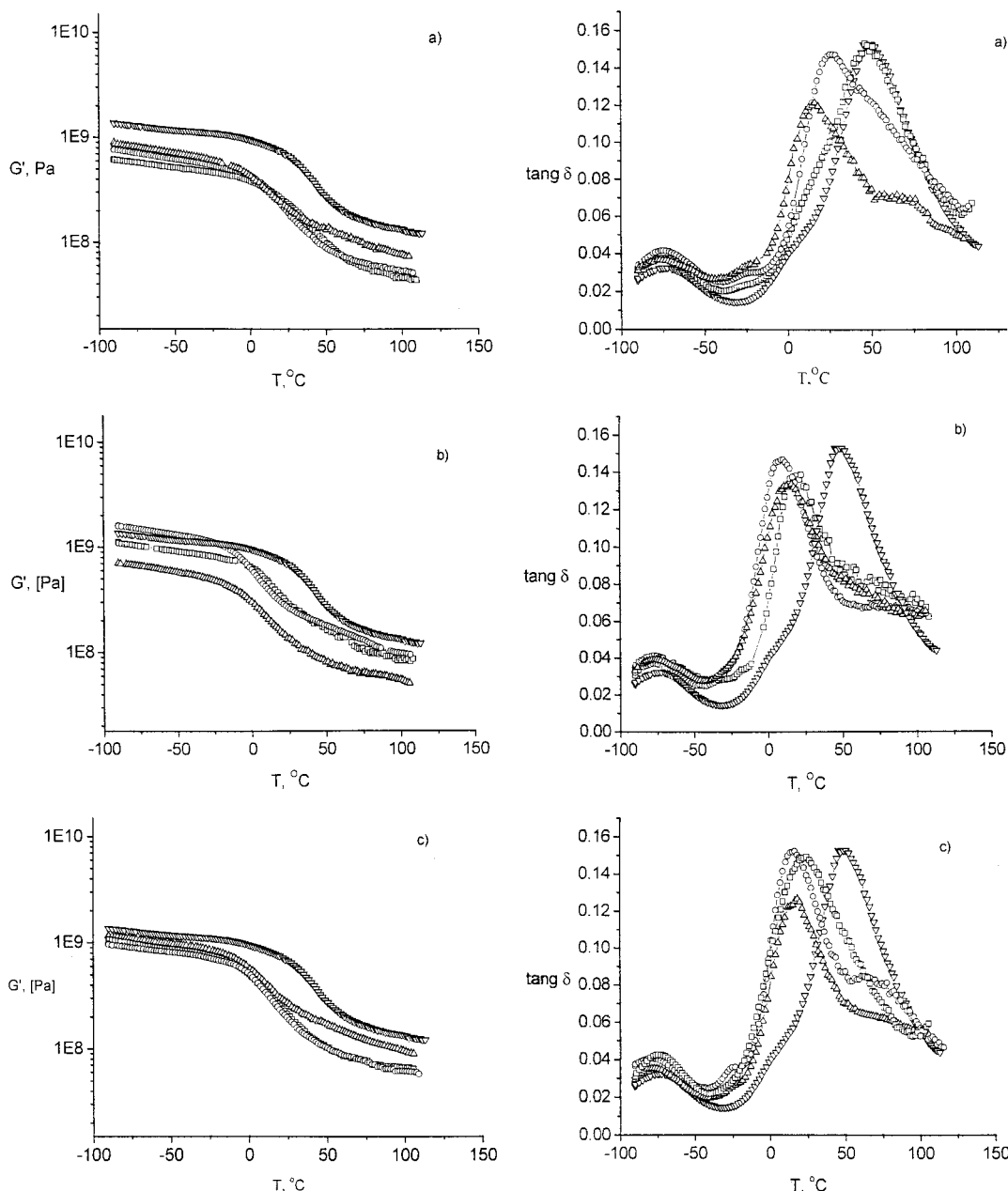
#### Mechanical measurement

Notched impact resistance of the samples was measured with a Sharpy pendulum at room temperature. The distance of the supports was 40 mm and the pendulum velocity of impact was 2.9 m s<sup>-1</sup>. Tensile tests were performed on a ZIP-PT-250M-2 testing machine at a crosshead speed of 25 mm min<sup>-1</sup> at room temperature.

## RESULTS AND DISCUSSION

#### Differential scanning calorimetry (DSC)

According to the DSC measurements, the melting peak of the N-6 homopolymer appears at 218°C and the melting peak of the N-6 component in the block copolymers is slightly shifted to a lower temperature range [Fig. 1(a, b)]. The  $T_g$  of the amorphous region of



**Figure 5** (a) Temperature dependence of the storage modulus ( $G'$ ) and  $\tan \delta$  of N-6 and N-6/MA<sub>2500HM</sub>:  $\nabla$ , N-6;  $\square$ , 2 wt %;  $\circ$ , 5 wt %;  $\triangle$ , 10 wt %. (b) Temperature dependence of the storage modulus ( $G'$ ) and  $\tan \delta$  of N-6 and N-6/MA<sub>3500HM</sub>:  $\nabla$ , N-6;  $\square$ , 2 wt %;  $\circ$ , 5 wt %;  $\triangle$ , 10 wt %. (c) Temperature dependence of the storage modulus ( $G'$ ) and  $\tan \delta$  of N-6 and N-6/MA<sub>11000HM</sub>:  $\nabla$ , N-6;  $\square$ , 2 wt %;  $\circ$ , 5 wt %;  $\triangle$ , 10 wt %.

N-6 in the block copolymers is not influenced by the content of the soft segment and it remains at about 48–50°C. The heat of fusion ( $H_f$ ) and the degree of crystallinity of the N-6/PI block copolymers are lower, if compared to N-6 homopolymer (Table I).

The DSC thermograms of the block copolymers show one smooth peak at the first heating that always appears in the 80–120°C temperature range at different heating rates. The peak disappears at the second scan [Fig. 2(a, b)]. It is probably due to the presence of small and imperfect crystallites.<sup>10</sup>

It has been observed that in the case of the N-6/polyisoprene (PI) block copolymers having the longest soft segment the splitting of the endothermic peak occurs at a heating rate of 5 and 10°C min<sup>-1</sup>, whereas at a higher heating rate appears a single melting endothermic peak (Fig. 3). The splitting of the endothermic peak at a low scan rate is due to the recrystallization.<sup>11</sup>

DSC data of the N-6/PI block copolymers show that their  $T_m$ 's do not change significantly with increase in soft-segment content up to 10 wt %. The reason is that the PI segments are located in the

**TABLE III**  
Glass Transition Temperatures of the Block Copolymers, According DTMA Analysis

N-6/MA (w/w %)	Type of MA	$T_g^{N6}$ [°C] <sup>a</sup>	$T_g^{PI}$ [°C] <sup>b</sup>	$T_g^{N6-PI}$ [°C] <sup>c</sup>
100	—	50	—	—
98/2	Ia	49	-74	—
95/5		25	-74	-25
90/10	MA <sub>2500HM</sub>	19	-74	—
98/2	Ib	23	-75	—
95/5		15	-75	—
90/10	MA <sub>3500HM</sub>	15	-75	—
98/2	Ic	25	-76	—
95/5		25	-77	-28
90/10	MA <sub>11000HM</sub>	19	-77	—
98/2	IIa	26	-75	—
95/5		20	-76	—
90/10	MA <sub>2500IF</sub>	23	-76	—
98/2	IIb	31	-75	—
95/5		35	-75	—
90/10	MA <sub>3500IF</sub>	23	-75	-20
98/2	IIc	25	-77	—
95/5	MA <sub>11000IF</sub>	25	-77	-20

<sup>a</sup> Glass transition temperature of nylon 6 block.

<sup>b</sup> Glass transition temperature of PI blocks.

<sup>c</sup> Glass transition temperature of nylon 6 and PI blocks.

amorphous region of the block copolymers.<sup>12</sup> All copolymers have a degree of crystallinity lower than that of to N-6 homopolymer because of the structural changes.

### TGA

The decomposition temperatures at 5% weight loss and the maximal decomposition temperatures vary in

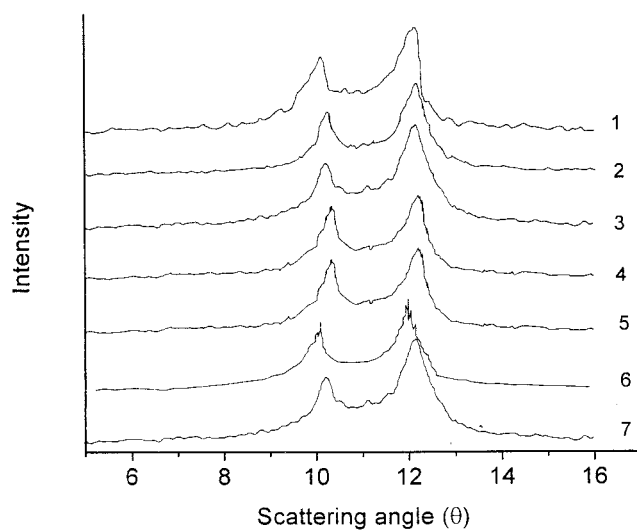
**TABLE IV**  
WAXD Parameters of the Block Copolymers Obtained

N-6/MA (w/w %)	Type of MA	$\alpha_{waxd}$ <sup>a</sup> (%)	$d(200)$ <sup>b</sup> (Å)	$d(002 + 200)$ <sup>c</sup> (Å)
100	—	39	4.447	3.734
98/2	Ia	34.2	4.478	3.765
95/5		34	4.348	3.643
90/10	MA <sub>2500HM</sub>	28.5	4.348	3.643
98/2	Ib	32	4.412	3.734
95/5		31	4.348	3.703
	MA <sub>3500HM</sub>			
98/2	Ic	33	4.478	3.76
95/5		31	4.434	3.734
90/10	MA <sub>11000HM</sub>	25.1	4.390	3.688
98/2	IIa	35	4.369	3.688
95/5		34	4.306	3.643
90/10	MA <sub>2500IF</sub>	27	4.369	3.658
98/2	IIb	33.8	4.369	3.718
95/5		32.9	4.369	3.703
90/10	MA <sub>3500IF</sub>	25.9	4.369	3.673
98/2	IIc	31	4.369	3.673
95/5	MA <sub>11000IF</sub>	30.7	4.390	3.688

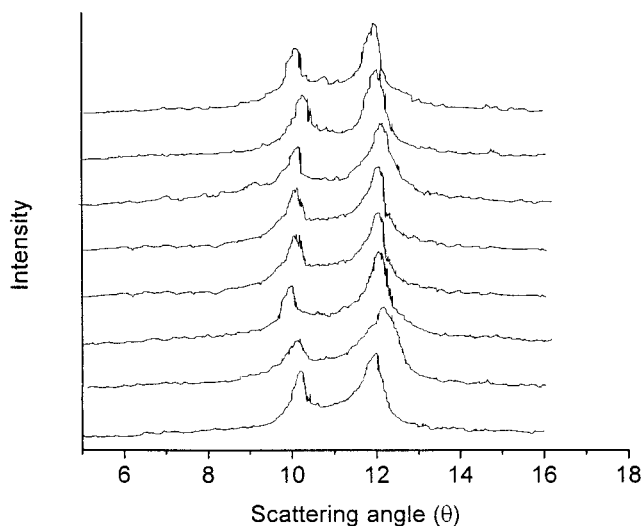
<sup>a</sup> Degree of crystallinity.

<sup>b</sup>  $d_{200}$  spacing.

<sup>c</sup>  $d_{(002+200)}$  spacing.



(a)



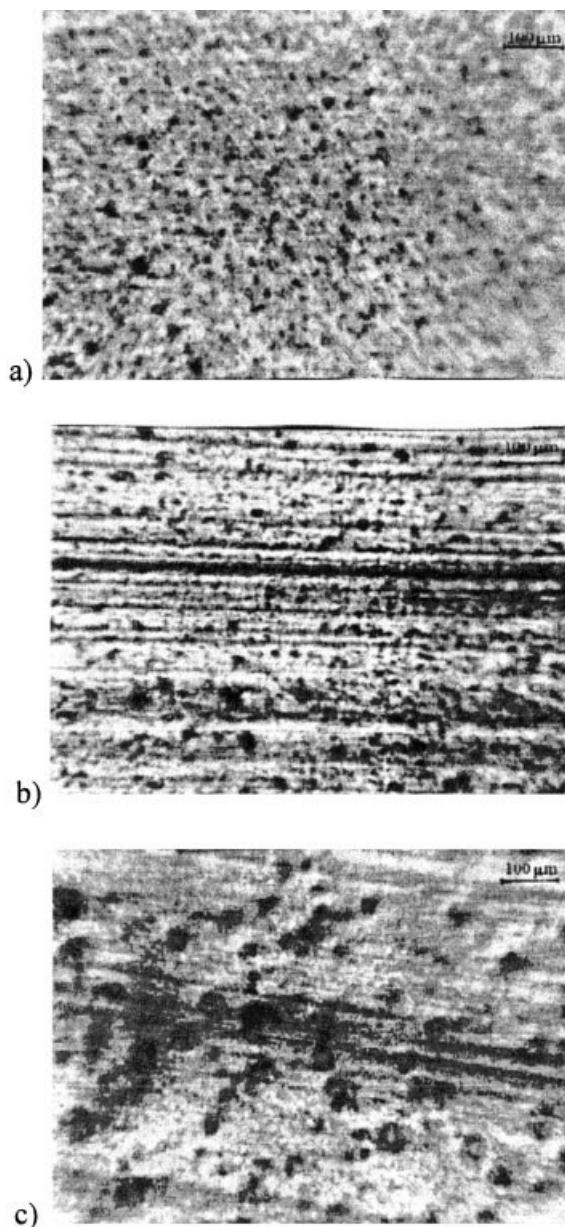
(b)

**Figure 6** (a) WAXD intensity curves of N-6/PI copolymers, obtained with different concentration of MA based on HM: 1–3 (2, 5, 10 wt % of MA<sub>2500HM</sub>); 4–5 (2, 5 wt % of MA<sub>3500HM</sub>); 6–7 (2, 10 wt % of MA<sub>11000HM</sub>); (b) WAXD intensity curves of N-6/PI copolymers, obtained with different concentrations of MA based on IF: 1–3 (2, 5, 10 wt % of MA<sub>2500IF</sub>); 4–6 (2, 5, 10 wt % of MA<sub>3500HM</sub>); 7–8 (2, 5 wt % of MA<sub>11000IF</sub>).

the region from 280 to 320°C and from 380 to 420°C, respectively (Table II). The samples obtained with MA based on IF have a little lower decomposition temperature in comparison to MA based on HM. All samples exhibit a good thermal stability up to 300°C [Table II and Fig. 4(a–d)].

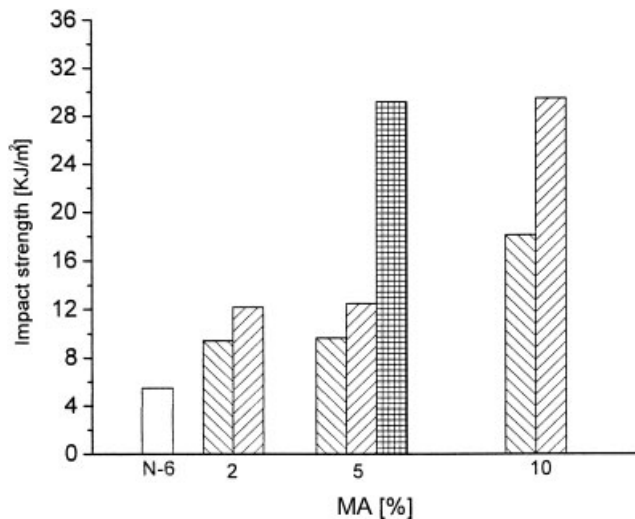
### DTMA

The influence of the length of soft block and the concentration (2, 5, and 10 wt %) on the storage



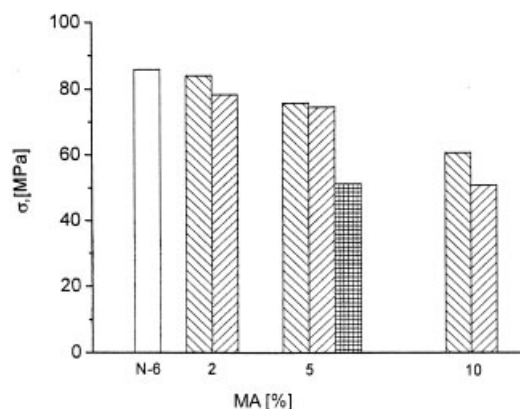
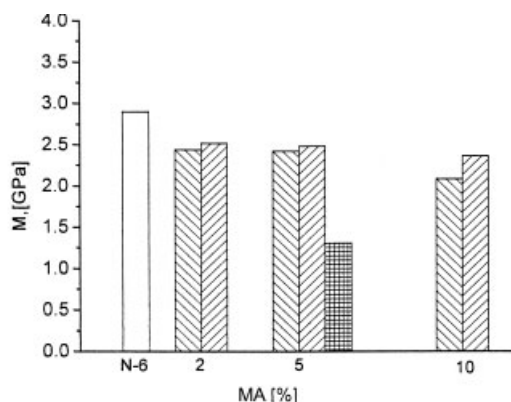
**Figure 7** (a–c) The optical microscopy observation of the N-6/MA based on HM: (a) MA<sub>2500HM</sub> (5 wt %), (b) MA<sub>3500HM</sub> (5 wt %), and (c) MA<sub>11000HM</sub> (5 wt %).

modulus ( $E'$ ) and  $\tan \delta$  is demonstrated in Figure 5(a–c) and Table III. The storage modulus for all block copolymers decreases with the incorporation of PI blocks into the main N-6 chain. As seen from Figure 5(a–c), the  $\tan \delta$  curve for the N-6 homopolymer exhibits two transitions:  $\alpha$ , at 50°C, due to the motion of large chain segments; and  $\beta$ , at -70°C, due to the segmental motion of amide groups in the amorphous region, which are not hydrogen bonded. The  $\tan \delta$  curves of the N-6/PI block copolymers show two glass-transition temperatures ( $T_g$ ): at -75 to -77°C and at 15–50°C. The lower ones belong to the  $T_g$  of the soft polyisoprene segments, and the



**Figure 8** Influence of the content and the length of MA on the impact strength: □, N-6; ▨, N-6/MA<sub>2500HM</sub>; ▩, N-6/MA<sub>3500HM</sub>; ▧, N-6/MA<sub>11000HM</sub>.

higher ones are attributed to the hard N-6 segments. With increasing content of the soft segments up to 10 wt %, the  $T_g$  due to a hard N-6 segments shifts to



**Figure 9** (a–b) Influence of the content and the length of MA on the elastic modulus and the tensile strength: □, N-6; ▨, N-6/MA<sub>2500HM</sub>; ▩, N-6/MA<sub>3500HM</sub>; ▧, N-6/MA<sub>11000HM</sub>.

a lower temperature probably because of the plasticizing effect of the soft segments, which increases the mobility of the molecular chain in the block copolymers.<sup>13</sup> The magnitude of the  $\tan \delta$  peak decreases with increasing the content of the soft segment. It is well pronounced at 10 wt % of MA. This could be explained by the influence of the soft segments on the relaxation of N-6 chains. A shoulder at  $-20^\circ\text{C}$  has been observed for some of the samples comprising a higher content of soft segment (Table III). The availability of two  $T_g$  peaks in all samples proves that the obtained N-6/PI copolymers are block ones. Moreover, that reveals that N-6 and PI segments are incompatible.

### WAXD

WAXD has been used to investigate the crystalline structure of N-6/PI copolymers. In all samples, only  $\alpha$  form is presented, which is characterized by the two main reflections,  $\alpha_1$  and  $\alpha_2$ , corresponding to the crystallographic planes (200) and (002 + 202)<sup>14</sup> [Fig. 6(a, b)].

The degree of crystallinity decreases with increasing the content of the soft segment because of the incorporation of PI blocks into the main chain of the copolymer (Table IV). The  $d$ -spacings ( $d_{200}$  and  $d_{002+200}$ ) in the block copolymers characterized for the N-6 crystal lattice decrease slightly with increasing the content of the soft segment and this shows that molecular chains of the N-6 domains in the copolymers are packed into a stable conformation.

### Optical microscopy

As is seen from the polarizing microscopy photographs, the dispersing phase of PI is distributed uniformly in the continuous polyamide matrix. The distribution of copolymers with shorter length of the soft segments is more uniform than that of the copolymers possessing the longest soft segments [Fig. 7(a–c)]. The photographs also show that with increasing the length of the soft segment, the domains of PI get larger in size.

### Mechanical properties

The notched impact strength of the N-6/PI block copolymers compared to N-6 increases in dependence of the content and the length of the soft segments (Fig. 8). The best impact strength values are achieved at the highest concentration of the soft segment (10 wt %). This is due to the fact that the soft segments dissipate the impact energy better than the hard N-6 does. The

increasing length of the soft segments also leads to better values of the impact strength.

The tensile strength and the elastic modulus decrease with the increasing content of the soft segment [Fig. 9(a, b)].

## CONCLUSION

Significant improvement of the impact strength, at insignificant decreasing of the tensile strength and the elastic modulus of N-6/PI block copolymers, has been achieved by the introduction of soft PI segments into the main chain of nylon 6. The concentration and the length of these segments have a marked effect upon the mechanical parameters of the materials.

The DTM measurements showed that the copolymers have two glass transition temperatures, which indicate the presence of block copolymers. It has been established that the microphase separation occurs because of the incompatibility of N-6 and PI blocks. The block copolymers with shorter length of the soft PI segments have a more uniform distribution than those comprising the longest soft segments.

The introduction of the soft segments does not significantly affect the  $T_m$  of the copolymers and they exhibit a good thermal stability.

The investigations show that macroactivators based on polyisoprene could be used successfully for the modification of N-6.

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