

Polyamide-6-*b*-Polybutadiene Block Copolymers: Synthesis and Properties

P. Petrov,¹ K. Jankova,² R. Mateva¹

¹Department of Polymer Engineering, University of Chemical Technology and Metallurgy, Kl. Ohridsky Boulevard 8, 1756 Sofia, Bulgaria

²Department of Polymers, Assen Zlatarov University, 8010 Burgas, Bulgaria

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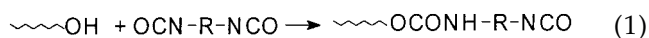
ABSTRACT: Polyamide-6 (PA6)/polybutadiene (PB) block copolymers were synthesized with macroactivators (MAs) based on hydroxyl-terminated polybutadiene functionalized with diisocyanates and having three *N*-acyllactam chain-growing centers per molecule. Two different diisocyanates, hexamethylene diisocyanate and isophorone diisocyanate, were applied as precursors for the MAs. The sodium salt of ϵ -caprolactam was chosen as an initiator. The influence of the MA type and concentration on the anionic ring-opening polymerization of ϵ -caprolactam at 180°C was studied. A large percentage of the gel fraction in the copolymers was estimated, indicating crosslinked macromolecules. The structure and phase behavior of the copolymers were investigated with differential scanning calorimetry, wide-angle X-ray scattering, thermogravimetric analysis, and dynamic

mechanical thermal analysis. In the copolymers, only the PA6 chains crystallized, and the crystallinity depended on the PB content. Different glass-transition temperatures for the PB blocks and PA6 blocks were observed, indicating microphase separation in the copolymers. The mechanical properties of the copolymers were studied by notched impact testing and hardness measurements. The impact strength increased linearly with the soft component concentration up to 10 wt % and reached values six times higher than those of the PA6 homopolymer. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 711–717, 2003

Key words: block copolymers; polyamides; polybutadiene; anionic polymerization

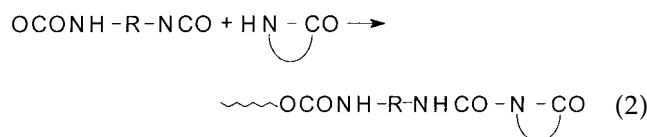
INTRODUCTION

The anionic polymerization of ϵ -caprolactam is a very useful method for producing articles in a single step from liquid components. When activators or macroactivators (MAs) are used for accelerating the process, the polymerization time is reduced to several minutes.^{1,2} Moreover, the use of MAs (especially elastomeric oligomers) allows the desired modifications of some polymer properties (e.g., improved impact resistance). MAs have been prepared preferentially by the functionalization of telechelic polyethers and liquid rubbers with reactive hydroxyl, amino, or carboxyl end groups.^{2–14} The functionalization is usually a simple reaction of the reactive groups of the telechelic oligomer with diisocyanates:



The chain-growing centers, having an *N*-acyllactam structure, can be formed in a separate step or directly

in the polymerization mixture (*in situ*) by the addition of caprolactam:



Usually, MAs are bifunctional compounds that promote the propagation of the polyamide-6 (PA6) chains in two directions. Therefore, ABA-type triblock copolymers with an elastomeric central block (B) and terminal PA6 blocks (A) can be obtained theoretically. During the anionic polymerization of caprolactam, well-known side reactions occur,^{4,14} and it has been proven that some of these reactions lead to the formation of multiblock $[-(\text{AB})_n-]$, branched, and crosslinked macromolecules. Boscolletto et al.⁹ confirmed that at lower MA concentrations, ABA structures are dominant, whereas at higher MA concentrations, the formation of $(\text{AB})_n$ -type structures are favored.

Obviously, the mechanical and physical properties of PA6 copolymers can be controlled by variations in the MA type and molecular weight, copolymer composition, and polymerization conditions.

In our research, hydroxyl-terminated polybutadiene [HTPB; number-average molecular weight (M_n)

Correspondence to: R. Mateva (rpm@uctm.edu).

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= 4830; number-average functionality (f_n) = 3.32] was chosen as a precursor for MA preparation. Hexamethylene diisocyanate (HM) and isophorone diisocyanate (IF) were used for the functionalization of HTPB. Our study was focused on the synthesis of PA6–polybutadiene (PB) copolymers with branched and crosslinked macromolecules. The influence of the type of PB-based MA and its content (2–10 wt %) on the polymerization kinetics and copolymer properties was investigated.

EXPERIMENTAL

Materials

ϵ -Caprolactam (BASF, Mount Olive, NJ) was dried in a desiccator over P_2O_5 at 60°C under vacuum for 3 days. The initiator, sodium salt of caprolactam (NaCl), was synthesized and purified according to ref. 15. Benzene (Merck, USA) was dried and distilled over calcium hydride. Sulfuric acid, HM, and IF (Merck) were used as received.

Synthesis

Synthesis of the prepolymer

The synthesis of HTPB was performed by the free-radical polymerization of butadiene and initiated by H_2O_2 in 1-butanol as a solvent. The detailed synthetic route has been reported elsewhere.¹⁶ H_2O_2 (113.8 g; Fluka, USA) was dissolved in 980 g of 1-butanol in a 5-L metal autoclave under a nitrogen atmosphere, and then 1410 g of butadiene was condensed under pressure. The stirring speed of the reaction mixture was 600 min^{-1} . The polymerization was carried out at 120°C for 4 h. The synthesized telechelic oligomer was HTPB (M_n = 4830; f_n = 3.32; yield = 60%), and it was used in the preparation of the MAs.

Functionalization of HTPB with diisocyanates

HTPB (1 mol) was dissolved in benzene in a 250-mL flask equipped with a stirrer, a reflux condenser, an argon purge, and a thermometer. The preparation was carried out at 50°C for 5 h. The reaction was monitored by IR spectroscopy to a constant value of the absorption peak of the isocyanate groups at 2086 cm^{-1} .

Synthesis of the PA6–PB block copolymers

The MAs were obtained directly in the polymerization mixture (i.e., *in situ*). The polymerizations were carried out in bulk with NaCl (1 mol % to the monomer quantity) as an initiator at 180°C for 2 h with an ampule technique. The monomer ϵ -CL, the prepolymer functionalized with diisocyanate, and the ampules were added to a glass reactor in a nitrogen atmosphere. The ϵ -CL and prepolymer were molten at

110°C and were stirred for 10 min (MA preparation). Then, the initiator, NaCl, was added with vigorous stirring, and after homogenization, the reaction mixture was forced into ampules with N_2 .

The samples for dynamic mechanical thermal analysis (DMTA), impact testing, and hardness measurements were prepared by a so-called hand-mold casting technique. In this case, after the homogenization, the reaction mixture was quickly transferred into a rectangular mold with internal dimensions of 80 mm \times 60 mm \times 6 mm.

The weight percentages of the MAs in the reaction mixture were 2, 5, and 10.

Analysis

Gel permeation chromatography was used to determine M_n 's and weight-average molecular weights of HTPB. The measurements were performed in tetrahydrofuran at 35°C in a 1 $cm^3 min^{-1}$ flow with a Waters 200 chromatograph (Milford, MA) equipped with four Ultrastyrigel columns (with pore sizes of 1 \times 10⁶, 2 \times 10⁴, 1 \times 10⁴, and 1 \times 10³ Å). The calibration curve was obtained with polystyrene standards in the molecular weight range of 470,000 to 180 g/mol. f_n was calculated from the M_n value and the hydroxyl content (X_{OH} ; wt %) with the following equation: $f_n = M_n \times X_{OH} / M_{OH} \times 100$, where M_{OH} is the molecular weight of the OH group.

The copolymer yield was followed by an interruption of the polymerization process at a certain stage and the removal of both the byproducts and the unreacted monomers via an extraction with benzene for 8 h in a Soxhlet apparatus.

IR spectra were obtained on a PerkinElmer 1600 (Fourier transform infrared) spectrophotometer (Shelton, CT) with KBr pellets. ¹H-NMR spectra were obtained on a Bruker apparatus (Billerica, MA) operating at 250 MHz with D_2SO_4 as a solvent and tetramethylsilane as an internal standard. Elemental analyses for C, H, and N were carried out on a PerkinElmer 2400 elemental analyzer.

The gel fraction was determined by the dissolution of the copolymer samples (0.2 wt %) in sulfuric acid (96%).

The melting and crystallization behavior of the PA6–PB samples was studied with a PerkinElmer DSC-7 from 0 to 240°C. Each sample was heated from 20 to 240°C at a rate of 20°C min^{-1} and was then quenched to 0°C at a rate of 100°C min^{-1} . A reheating run to 240°C was performed at a rate of 20°C min^{-1} . The melting temperature (T_m) was obtained from the endothermic maximum. The differential scanning calorimetry (DSC) crystallinity was calculated by the ratio of the measured and equilibrium heats of fusion ($\Delta H_f / \Delta H_f^0$). ΔH_f^0 was 230 J g^{-1} .⁹

Wide-angle X-ray measurements were performed on a Dron 2 diffractometer with Ni-filtered Cu K α radiation ($\lambda = 1.54$) in the transmission mode at room temperature. The voltage and tube current were 30 kV and 10 mA, respectively. The crystallinity percentage, determined by wide-angle X-ray diffraction, was calculated by a standard procedure.¹⁷

Thermogravimetric analysis (TGA) was carried out with a PerkinElmer TGA-7 thermal analyzer from 40 to 600°C at a heating rate of 20°C min⁻¹ under a nitrogen flow of 35 cm³ min⁻¹.

Dynamic mechanical thermal measurements were performed in a single-cantilever bending mode on an MKII dynamic mechanical thermal analyzer with a flat sample at a heating rate of 2°C min⁻¹. The operating temperature range was -90 to 140°C, and the frequency was 1 Hz. The storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$) for each sample were automatically recorded by a computer throughout the test.

The notched impact resistance was measured with a Charpy pendulum on 50 mm \times 4 mm \times 6 mm specimens at an average notch depth of 0.5 mm at room temperature. The distance of the supports was 40 mm, and the pendulum velocity of impact was 2.9 m s⁻¹.

Shore D hardness measurements of the block copolymers were performed on a Shore D hardness tester in agreement with ISO/R Standard 868.

RESULTS AND DISCUSSION

Synthesis of the PA6-PB block copolymers

Two MAs, MA₁ and MA₂, were synthesized on the basis of HTPB functionalized with HM or IF, respectively. The influence of the structure of the MAs on the anionic polymerization of ϵ -CL at 180°C was studied. So that MAs would be obtained with three *N*-acyllactam growing centers per molecule, f_n for HTPB was chosen to be approximately 3.

Different MAs for the anionic polymerization of ϵ -CL (including those based on PB^{2-4,7,12,13}) have been studied. Nevertheless, little attention has been paid to MAs with a functionality higher than 2.

To promote side reactions such as transamidation and Claisen-type condensation^{14,18} we chose a polymerization temperature of 180°C. This temperature and the functionality of the MAs ($f_n \sim 3$) favored the branching and crosslinking of the PA6 macromolecules. We believe that for processes in which articles are produced from initial monomers in a single step (i.e., reaction injection molding of nylon (NYRIM) technology), the presence of branched and crosslinked macromolecules will enhance some of the mechanical properties of the materials.

The copolymer syntheses were performed with 2, 5, and 10 wt % MA. It was impossible to homogenize the reaction mixture when 15 wt % MA was used.

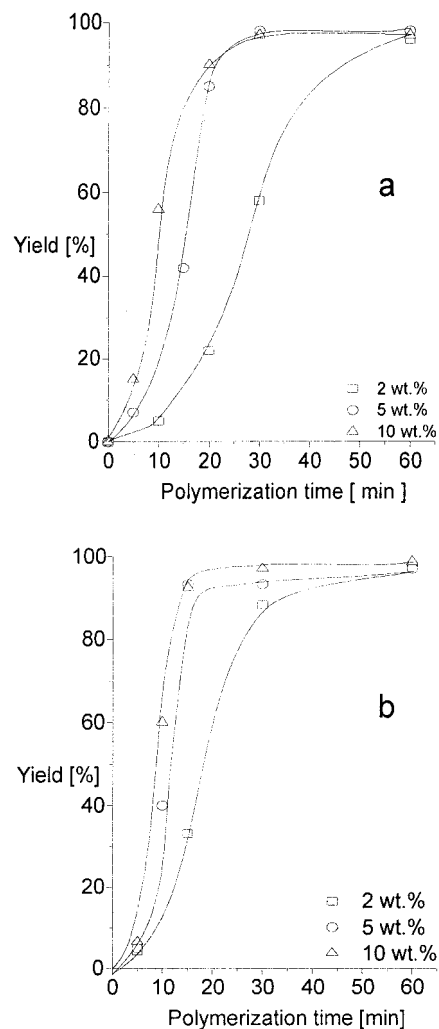


Figure 1 Yield versus the time of polymerization at different MA concentrations (at 180°C with 1 mol % NaCl as an initiator): (a) MA₁ and (b) MA₂.

The conversion curves show that both MAs were active compounds and accelerated the anionic polymerization of ϵ -CL in proportion to their concentrations (Fig. 1). Under the same conditions, the polymerization of ϵ -CL initiated only with NaCl (without an activator) proceeded with an induction period, and the polymer was obtained in 1 h. The yields of all the PA6-PB copolymers were high (97–98%). The equilibrium polymer–monomer ratio was reached in a shorter time with MA₂ than with MA₁. These results are in good agreement with our previously published results,^{14,18} which showed that activators and MAs based on IF accelerated the polymerization of ϵ -CL faster than those based on HM.

The PA6-PB copolymers were purified by extraction in benzene (a solvent good for both CL and HTPB), and their composition was established by elemental analysis (Table I). Good agreement was obtained between the calculated and experimental values. In addition, the products extractable in benzene

TABLE I
Some Characteristics of PA6–PB Copolymers Obtained with MA₁ and MA₂

MA type	MA content [wt %]	Copolymer yield [%] ^a	PA6 calculated [%] ^b	PA6 found [%] ^c
MA ₁	2	97.6	95.65	96.5
	5	98.2	93.29	94.2
	10	97.8	88.02	88.9
MA ₂	2	97.9	95.94	97.1
	5	97.8	92.92	93.4
	10	98.2	88.38	89.2

^a Copolymer yield at final polymerization time (120 min)

^b Calculated by assuming that all of the initial PB was present in the copolymer.

^c Calculated by elemental analysis measurements (nitrogen content).

were studied by ¹H-NMR. The proton signals typical for PB (i.e., $\delta = 5.0$ and 5.5 ppm¹⁹) were not observed. Consequently, one can conclude that the extractable species were only ϵ -CL and ϵ -CL-based oligomers.

The aforementioned experimental results provide good proof that MA₁ and MA₂ behaved as activators and that *N*-acyllactam groups initiated the propagation of ϵ -CL. Therefore, the obtained copolymers contained short PB blocks incorporated into the PA6 main chains.

The formation of crosslinked macromolecules and the content of the gel fraction in the copolymers with the polymerization time were investigated. An increase in the gel fraction content with the polymerization time was observed. The gel fraction also increased with increases in the MA contents (Fig. 2).

Physical and mechanical properties of PA6–PB block copolymers

DSC measurements with a series of copolymers having 2, 5, and 10 wt % MA₁ and MA₂ were performed (Fig. 3). The experiments revealed a single endotherm in the melting region of PA6. Evidently, only PA6 chains crystallized in the copolymers, whereas PB chains remained in the amorphous phase. The T_m 's of the copolymers were 214–216°C (Table II). This indicates that the presence of a small amount of the soft blocks did not decrease the T_m 's of the copolymers and that they retained the characteristic high T_m of PA6. The copolymer crystallinity was calculated from ΔH_f . The data indicate a small decrease in the crystallinity with an increase in the MA concentration (Table II).

Wide-angle X-ray scattering (WAXS) was used to investigate the crystalline structure of the PA6–PB copolymers (Fig. 4). Three main reflections in the 2θ range of 5–36 were observed. These reflections were attributed to the two PA6 α -form reflections at 20.4–20.6 and 23.4–24.2 and to the PA6 γ -form reflection at

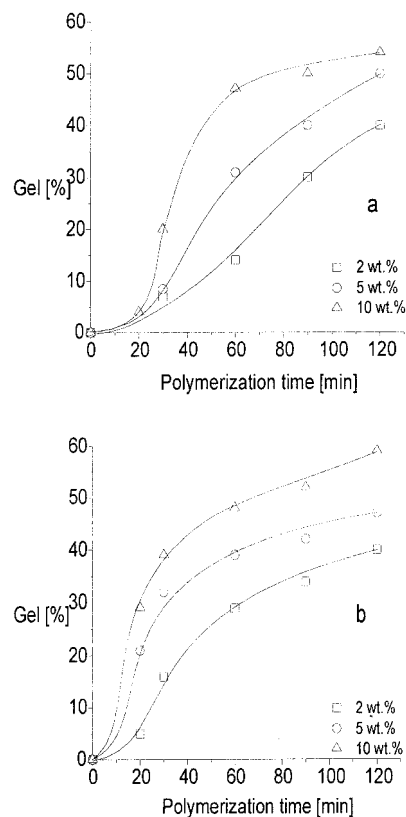


Figure 2 Gel fraction versus the time of polymerization at different MA concentrations (at 180°C with 1 mol % NaCL as an initiator): (a) MA₁ and (b) MA₂.

21.4–22.0. The crystalline structure of the PA6 homopolymer has been well investigated.^{20–22} It has been confirmed that for PA6, the α form is more stable than the γ form. However, the PA6–PB copolymers, depending on the copolymer composition, contained a certain amount of the γ form (Table III). According to the WAXS measurements, a decrease in the copolymer crystallinity with an increase in the PB concentration was estimated. It can be concluded that the presence of the PB microdomains inhibited the regular crystal-

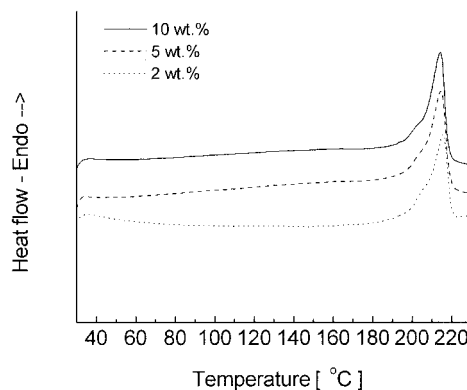


Figure 3 DSC for PA6–PB copolymers obtained with MA₂ (second heating).

TABLE II
 T_m and Crystallinity of PA6–PB Copolymers
Measured by DSC

MA type	MA content (wt%)	T_m' [°C] ^a	α'_{DSC} (%) ^b	T_m'' [°C] ^c	α''_{DSC} (%) ^d
MA ₁	2	215	25	214	22
	5	215	21	214	20
	10	214	18	213	18
MA ₂	2	216	27	215	21
	5	215	24	215	20
	10	214	19	214	19

^a Melting temperature at first heating.

^b Crystallinity calculated from DSC analysis at first heating.

^c Melting temperature at second heating.

^d Crystallinity calculated from DSC analysis at second heating.

lization of PA6 chains, and a dependence of the copolymer crystallinity on the MA content was observed as a result.

TGA confirmed the good thermal stability of the copolymers. A significant weight loss below 320°C was not observed (Table IV and Fig. 5).

Copolymers containing various amounts of the MAs exhibited only negligible differences in their decomposition temperatures (T_d 's) and maximum decomposition rates. In addition, the values were similar to the glass-transition temperature (T_g) and maximum decomposition rate of the PA6 homopolymer.

The dynamic mechanical properties of the PA6–PB copolymers were studied by DMTA. E' and $\tan \delta$ were plotted against the temperature at a constant frequency of 1 Hz (Fig. 6). Two main relaxations in the investigated temperature interval (from –90 to 140°C) were observed. The lowest one was attributed to the α relaxation of PB soft blocks (the temperature at the

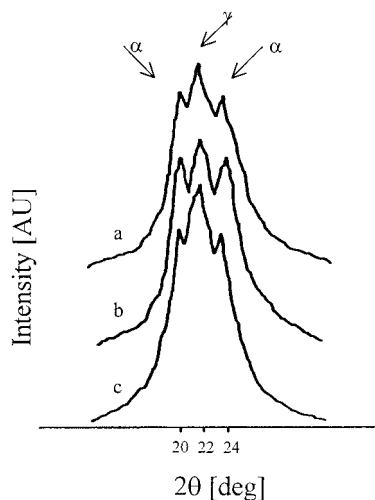


Figure 4 WAXS for PA6–PB copolymers obtained with MA₁: (a) 10, (b) 5, and (c) 2 wt %.

TABLE III
Main WAXS Reflections of PA6–PB Copolymers

MA type	MA content (wt %)	α_{WAXS} (%) ^a	α form (%)	γ form (%)
MA ₁	2	36	24	12
	5	33	24	9
	10	28	18	10
MA ₂	2	37	23	14
	5	34	24	10
	10	29	21	8

^a Crystallinity calculated from WAXS measurements.

α -relaxation maximum was equal to T_g), and the higher one corresponded to the α relaxation of PA6 hard blocks. The T_g 's of the copolymers are collected in Table IV. The presence of two distinct α relaxations indicated that the PA6 blocks and PB blocks were incompatible and, therefore, microphase-separated as a result of the positive free energy of mixing.^{11,23} However, a shoulder in the $\tan \delta$ peaks at about 20–30°C appeared. It can be attributed to the presence of a mixed phase between PA6 and PB, which was a result of the possible formation of copolymers with very short blocks. The $\tan \delta$ peaks of PB were similar to one another, and the T_g 's of PB were not much affected by the different copolymer compositions. In contrast, the $\tan \delta$ peaks of PA6 shifted to lower temperatures with increasing PB contents (Table IV and Fig. 6). A gradual increase in the magnitude of the peaks was also estimated. This can be explained by the influence of the soft blocks on the PA6 chain relaxation.

At very low temperatures, below T_g , the macromolecules were frozen, and all the samples showed high and similar values of the elastic modulus. At certain temperatures, the curves became divergent. In fact, the higher the soft block concentration was in the copolymers, the lower the value was of the corresponding E' .

TABLE IV
 T_g and T_d Values of PA6–PB Copolymers According to DMTA and TGA

MA type	MA content (wt %)	T_g^{PB} [°C] ^a	T_g^{PA6} [°C] ^b	$T_{d5\%}$ [°C] ^c	V_d^{max} (°C min ⁻¹) ^d
MA ₁	2	–66	66	324	34
	5	–67	64	320	27
	10	–68	60	318	26
MA ₂	2	–66	72	325	37
	5	–69	66	320	35
	10	–70	58	319	30

^a Glass transition temperature of PB blocks.

^b Glass transition temperature of PA6 blocks, according to DMTA.

^c Decomposition temperature at 5% weight loss.

^d Maximum decomposition rate.

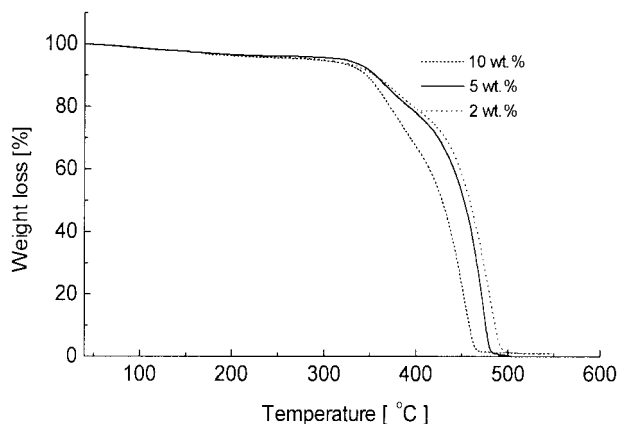


Figure 5 TGA for PA6–PB copolymers obtained with MA₂.

The mechanical properties of the PA6–PB copolymers containing small amounts of PB were studied by notched impact testing and hardness measurements.

Generally, the incorporation of a small amount of the soft component into PA6 increased the impact

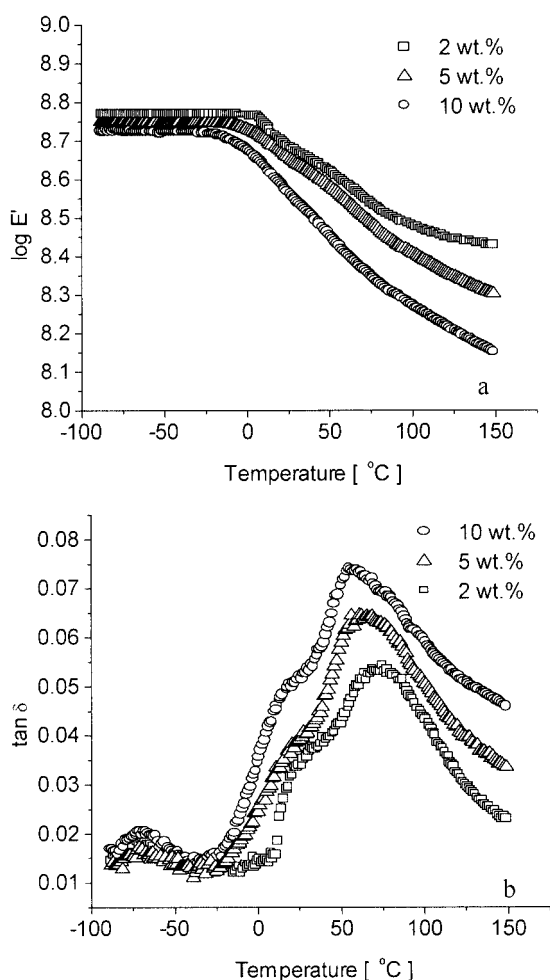


Figure 6 DMTA for PA6–PB copolymers obtained with MA₂: (a) variation of E' with temperature and (b) variation of $\tan \delta$ with temperature.

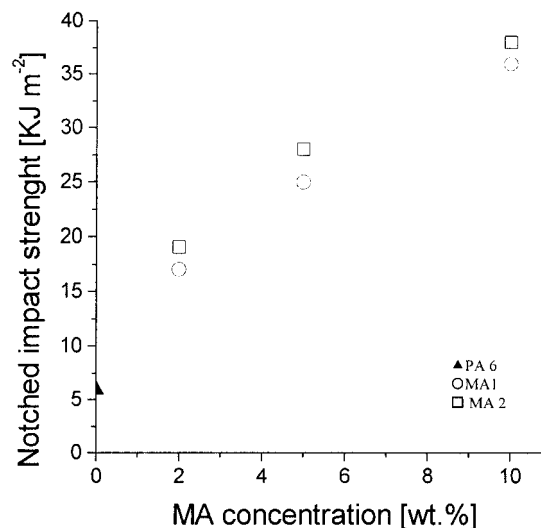


Figure 7 a_n versus the MA concentration.

strength of the material, which retained its other valuable properties, such as rigidity, toughness, and a high melting point.^{3,23}

The notched impact strength (a_n) of the PA6–PB copolymers with 2, 5, and 10 wt % of the soft component was studied (Fig. 7). The results obtained were compared to the impact strength of the PA6 homopolymer. The incorporation of only 2 wt % PB increased the impact strength of the copolymer threefold. A linear dependence of a_n on the soft block concentration (up to 10 wt %) was observed. The copolymers with 10 wt % PB exhibited six times better impact resistance than the PA6 homopolymer. The soft PB component (existing in the viscoelastic state) dissipated the impact energy better than hard PA6, and this led to an enhanced impact resistance of the copolymers in comparison with the PA6 homopolymer.

The influence of soft PB on the copolymer hardness was studied by Shore D hardness measurements (Fig. 8). Usually, the copolymer hardness depends on the hard component content. Therefore, all samples containing 90–98 wt % PA6 showed only a slight hardness decrease (10–30%) in comparison with the PA6 homopolymer.

CONCLUSIONS

MAs with three *N*-acyllactam growing centers per molecule were prepared *in situ*. They were based on HTPB functionalized with HM and IF. The MAs accelerated the polymerization of ϵ -caprolactam in proportion to the concentration and led to the formation of PA6–PB block copolymers. A large percentage of the gel fraction in the copolymers indicated the presence of crosslinked macromolecules. A decrease in the copolymer crystallinity with increasing MA concen-

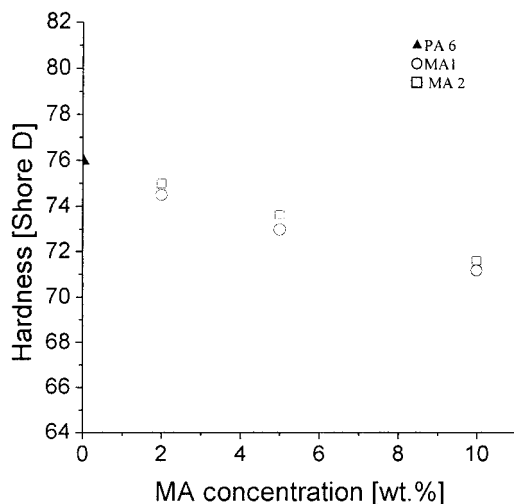


Figure 8 Shore D hardness versus the MA concentration.

tration was found by DSC and WAXS measurements. Different T_g 's of PB and PA6 blocks were found by DMTA, and this indicated microphase separation in the copolymers, which resulted in the formation of PB microdomains. The incorporation of soft PB blocks into PA6 main chains improved a_n of the copolymers without significant changes in their hardness and high T_m . The PA6–PB copolymers containing 10 wt % of the soft component had an impact resistance six times better than that of the PA6 homopolymer.

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