

Structure and Thermal Behavior of Nylon-6/Polytetrahydrofuran Triblock Copolymers Obtained via Anionic Polymerization

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ABSTRACT: The structure, crystallization, and phase behavior of nylon6-*b*-polytetrahydrofuran-*b*-nylon6 triblock copolymers synthesized via activated anionic polymerization have been studied. The composition, molecular weight of polytetrahydrofuran (PTHF) soft block, and type of polymeric activators (PACs) have been varied. Differential Scanning Calorimetry (DSC), Wide-Angle X-ray Diffraction (WAXD), Transmission Electron Microscopy (TEM), and Polarized Light Microscopy (PLM) experiments have revealed that in triblock copolymers only the nylon-6 component crystallizes while PTHF segments are amorphous. The soft blocks do not alter the spherulitic crystalline structure of nylon-6 and hard blocks crystallize in the α -modification. The degree of crystallinity decreases with increasing PTHF concentration. The phase behavior has been investigated by Dynamic Mechanical Thermal Analysis (DMTA). Two different glass transition temperatures (T_g) for all samples have been observed. This indicates that nylon-6 and PTHF segments are not molecularly miscible and the copolymers are microphase separated. The mechanical properties of the copolymers synthesized have been evaluated. Nylon-6 copolymers with soft block concentrations up to 10 w/w %, exhibit improved notched impact strength in comparison to the nylon-6 homopolymer, retaining relatively high hardness and tensile strength. All copolymers possess low water absorption and good thermal stability. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1448–1456, 2002; DOI 10.1002/app.10448

Key words: nylon; block copolymers; structure

INTRODUCTION

Nylon-6 is a widely used engineering thermoplastic having many important industrial applica-

tions because of its high strength, good thermal and chemical stability, good fatigue, and heat sag resistance. It has, however, a certain disadvantage in its low-notched impact strength. To improve the toughening properties of nylon-6, it is a common practice to either blend rubbers into the nylon-6 matrix or to introduce flexible soft segments into the nylon-6 main chains through an activated anionic copolymerization of hexanelac-

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tam (HL).^{1–3} The physical and mechanical properties of nylon-6 copolymers exhibit a strong dependence on the activator type, molecular weight, copolymer composition, as well as on the polymerization conditions. With increasing the soft block concentration a decreased hardness and tensile strength, accompanied by an increased tensile elongation and impact strength have been observed. The rate and amount of water absorption also increases.³ When a soft component is introduced into the rigid nylon-6 matrix, absorbing a large amount of impact energy, it acts as an effective stress concentrator and enhances both the crazing resistance and the shear yielding. At a low concentration of flexible component the obtained nylon-6 copolymers have a combination of high modulus and high impact strength. These copolyamides possess a better dimensional stability to moisture and temperature changes in comparison to the copolyamides containing higher concentration of soft block. Nevertheless, little attention has been paid to these systems.

Our study was focused on the effect that the structure, crystallization, and phase behavior have upon the mechanical properties of *in situ* polymerized nylon-6/PTHF block copolymers at low concentration of the soft block (2–10 w/w).

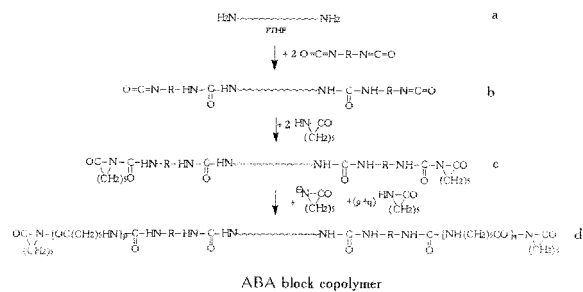
EXPERIMENTAL

Materials

Hexanelactam (BASF) was used after drying under vacuum at 60°C for 3 days. The initiator sodium salt of hexanelactam (NaHL) was synthesized according to ref. 4. Tetrahydrofuran (Merck) was purified by distillation followed by drying over sodium wire under reflux in the presence of traces of benzophenone until a persistent blue color was obtained. Hexamethylene diisocyanate—HM (1,6-diisocyanatohexane) and isophorone diisocyanate—IF (5-isocyanato-1-isocyanatomethyl-1,3,3-trimethyl-cyclohexane)(Merck) were used without further purification.

Synthesis and Sample Preparation

A series of nylon-6-*b*-polytetrahydrofuran-*b*-nylon-6 triblock copolymers (Scheme 1) were synthesized by activated anionic polymerization. The detailed synthetic route has been reported in our previous article.⁵ It includes at first the synthesis of PTHF diamine (Scheme 1a) as a precursor for



Scheme 1

polymeric activators (PACs), followed by a functionalization with diisocyanate (Scheme 1b). The polymeric activators were prepared *in situ* during the polymerization (Scheme 1c). The polymerizations were carried out with initiator NaHL (1 mol % to the monomer quantity) at 180°C for 2 h. The weight percentage of the PACs component was chosen to be 2, 5, and 10. PTHF with two different block lengths ($M_n = 2000$ and $4000 \text{ g}\cdot\text{mol}^{-1}$) were chosen. HM and IF diisocyanates were used as coupling agents. IF was used for the first time. For DSC, WAXD, TGA, TEM, and PLM, the samples were prepared using ampoules. The samples for DMTA, impact testing, hardness, tensile testing, and water absorption measurement were prepared by hand-mold casting in a rectangular mould ($80 \times 60 \times 6 \text{ mm}$).

Measurements

Differential Scanning Calorimetry

The melting and crystallization behavior of the nylon-6/PTHF samples was studied using a Perkin-Elmer DSC-7 in the 0–240°C range. Each sample was heated from 20 to 240°C at a rate of $20^\circ\text{C min}^{-1}$ before quenching to 0°C at a rate of $100^\circ\text{C min}^{-1}$. Finally, the sample was reheated to 240°C at a rate of $20^\circ\text{C min}^{-1}$. The melting temperature (T_m) was obtained as the maximum of the melting endotherm, while the glass transition temperature (T_g) was obtained from the inflection point of the second heating run. The DSC crystallinity (α_{DSC}) was calculated via the ratio between the measured and equilibrium heats of fusion ($\Delta H_f/\Delta H_f^\circ$). The equilibrium heat of fusion (ΔH_f°) is 230 J g^{-1} .⁶

Wide-Angle X-ray Diffraction

Wide-angle X-ray measurements were performed on a Dron 2 diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.54$) in the transmission mode at

room temperature. The voltage and tube current were 30 kV and 10 mA, respectively. Percentage crystallinity (α_{WAXD}) was calculated by a standard procedure.⁷

Thermal Gravimetric Analysis

Thermogravimetric analysis was carried out with a Perkin-Elmer TGA-7 thermal analyzer in the 40–600°C temperature range at a heating rate of 20°C min⁻¹ under a nitrogen flow of 35 mL min⁻¹.

Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal measurements were performed in a single-cantilever bending mode on a DMTA MKII, using a flat sample at a heating rate of 2°C min⁻¹. The operating temperature range was from -90 to 150°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 computer throughout the test.

Optical Microscopy

Polarizing microscopy (PLM) was carried out on an Opton Karl Zeiss apparatus, equipped with an Olympus camera. Slices of about 5 μm thick were used.

Transmission electron micrographs were obtained with a Philips TEM using an acceleration voltage of 80 kV. The surface of the slices was etched in a solution of 30% formic acid and viewed in reflected light.

Mechanical Properties

Tensile tests were performed on an "ZIP-PT-250M-2" testing machine with a crosshead speed of 25 mm min⁻¹ at room temperature. The cross-section dimensions of the samples were 3 \times 6 mm at a clamp distance of 100 mm. The initial modulus was calculated at 2% elongation.

Notched impact resistance was measured with a Sharpy pendulum on 50 \times 4 \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 \cdot s⁻¹. All mechanical tests were conducted after conditioning at 20°C and 65% relative humidity for 24 h.

Shore D Hardness

Hardness measurements of the block copolymers were measured on a Shore D hardness tester in accordance to ISO/R 868 standard.

Water Sorption

Water sorption was performed according to ISO 62 standard.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry

DSC analysis revealed the semicrystalline character of nylon-6 and the completely amorphous character of PTHF segments in the copolymers. The soft blocks do not crystallize whatever their nature and length. The melting transition (54°C) corresponding to pure PTHF diamine (Table I) has not been observed for all samples. This indicates that the PTHF segments, incorporated into the nylon-6 main chains, are in the amorphous state.

The DSC spectra (Fig. 1) show a smooth peak in the 60–130°C range at the first heating for all samples, and its disappearance at the second scan. This can be explained by the fact that the PTHF segments hinder the crystallization of nylon-6 segments and that some of the crystals formed during the polymerization are less perfect and smaller.¹ A very small depression in the melting temperature (T_m) of the nylon-6 component with the increase of PTHF content up to 10 w/w % for all copolyamides has been found (Table I). A reduction of the melting transition enthalpy (ΔH_p) and degree of crystallinity (α_{DSC}) have been also observed.

The DSC results confirm our expectations that the introduction of a small quantity of flexible PACs with different length will not decrease T_m drastically, and the copolymers will retain their thermal stability. On the other hand, the degree of crystallinity of the copolymers decreases compared to that of the nylon-6 homopolymer. The change in the chemical structure seems to be the main factor for this decrease.

The copolymers obtained with PACs having different molecular weight (PTHF₂₀₀₀ and PTHF₄₀₀₀) and concentration show small differences in T_m and α_{DSC} (Table I).

Wide-Angle X-ray Diffraction

As seen from the diffraction spectra in the 2.5–18° (θ) range of the copolyamide samples, having 2, 5, and 10 w/w % content of soft block, only the α -form is present. The two main reflections α_1 and α_2 correspond to the crystallographic planes (200)

Table I Influence of the PACs Type and Concentration on Some Parameters Characterizing Copolymers

Sample Code	ratio w/w%	T_g'' °C	T_m' °C	T_m'' °C	$\Delta H_f'$ Jg ⁻¹	α'_{DSC} %	$\Delta H_f''$ Jg ⁻¹	α''_{DSC} %	α_{WAXD} %	M_v 10 ⁻³	G %
PA:PTHF _I 2000	90:10	52.7	215.7	209.5	58.5	25.4	49.6	21.6	28.8	40	43
	95:5	52.4	216.8	209.4	57.2	24.9	50.9	22.1	30.3	100	40
	98:2	52.4	217.8	214.3	57.3	24.9	47.8	20.8	31.6	135	31
PA:PTHF _I 4000	90:10	54.1	217.4	209.0	52.3	22.7	39.2	17.0	28.9	50	41
	95:5	49.5	215.4	209.2	51.0	22.2	47.2	20.5	32.5	110	39
	98:2	54.3	219.6	211.5	54.8	23.8	38.0	16.5	34.9	200	31
PA:PTHF _H 2000	90:10	48.6	221.0	210.6	55.6	24.2	48.6	21.1	35.6	40	40
	95:5	50.7	221.1	214.6	60.2	26.2	50.7	22.0	36.2	120	38
	98:2	54.0	222.2	214.7	62.3	27.1	44.1	19.2	35.7	160	30
PA:PTHF _H 4000	95:5	50.4	215.7	207.8	51.2	22.3	40.4	17.6	33.3	100	34
	98:2	54.2	214.9	208.5	51.5	22.4	43.0	18.7	35.3	115	26
PA	—	48.9	224.2	214.9	—	—	—	—	44.0	—	—
PTHF _{DIAMINE}	—	—	54.0	—	—	—	—	—	—	—	—

T_g'' —glass transition temperature at second heating; T_m' —melting temperature at first heating; T_m'' —melting temperature at second heating; $\Delta H_f'$ —heat of fusion at first heating; α'_{DSC} —degree of crystallinity calculated from DSC analysis at first heating; $\Delta H_f''$ —heat of fusion at second heating; α''_{DSC} —degree of crystallinity calculated from DSC analysis at second heating; α_{WAXD} —degree of crystallinity calculated from WAXD analysis; M_v —viscometric molecular weight; G—gel fraction.

and (002+202)⁶ (Fig. 2 and Table II). These data are good proof that the crystals formed in the block copolymers are owed to the nylon-6 components.

A deconvolution in the 5–15° (θ) range has been performed by a profile-fitting program to point out the possible structural changes appearing in the nylon-6 phase and to obtain information about the degree of crystallinity. A small decrease of the intensity of the reflections with an increase in PTHF concentration has been observed. Evidently the degree of crystallinity of the block co-

polymers decreases with an increase in the concentration of soft segment (Table I). The reduction in crystallinity is attributed to the formation of PTHF domains in the copolymers, which inhibit the regular alignment of the polyamide chains.⁸

Thermal Gravimetric Analysis

The thermal decomposition temperatures (T_d) and the maximum decomposition rates (V_d^{\max}),

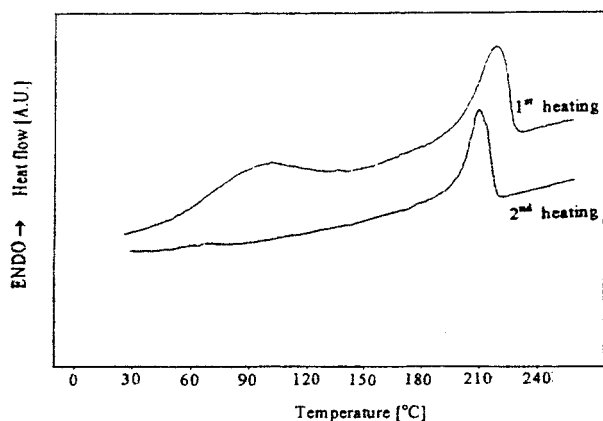


Figure 1 Differential Scanning Calorimetry of nylon-6/PTHF_{4000/IF} copolymer (90/10 w/w%): (a) first heating; (b) second heating.

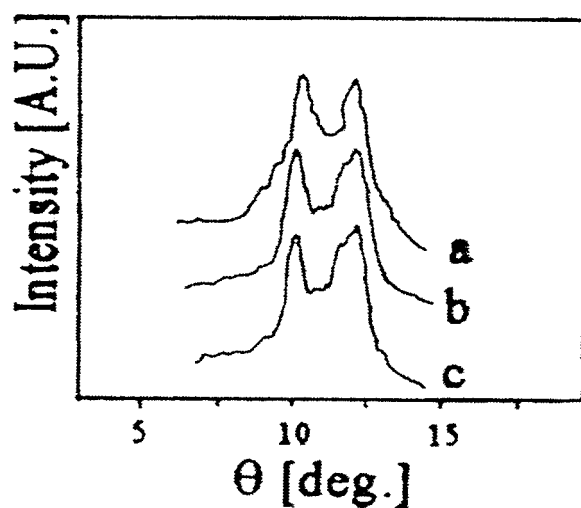


Figure 2 Wide-Angle X-ray Diffraction of nylon-6/PTHF_{4000/IF} copolymers: (a) 90/10 w/w%; (b) 95/5 w/w%; (c) 98/2 w/w %.

Table II Main WAXD Reflections of nylon-6/PTHF Copolymers

Sample Code	ratio w/w%	α_1 θ°	α_2 θ°
PA:PTHF _{I 2000}	90:10	10.07	12.01
	95:5	10.38	11.96
	98:2	10.24	12.04
PA:PTHF _{I 2000}	90:10	10.26	12.12
	95:5	10.19	12.08
	98:2	10.04	12.15
PA:PTHF _{H 2000}	90:10	10.14	12.02
	95:5	10.13	12.03
	98:2	10.03	12.05
PA:PTHF _{H 4000}	95:5	10.19	12.07
	98:2	10.15	12.09
PA	—	10.17	12.07

α_1 —reflection corresponding to the crystallographic plane (200); α_2 —reflection corresponding to the crystallographic plane (002 + 202).

for nylon-6/PTHF copolymers in nitrogen atmosphere (Table III), undergo small changes with increasing the concentration of soft segment. This can be explained by a similar thermal stability of nylon-6 and PTHF in nitrogen atmosphere. Nevertheless, noteworthy is the fact that the copolymers containing longer soft segments reveal T_d values slightly lower than those for copolymers with shorter soft blocks.

Dynamic Mechanical Thermal Analysis

From the loss tangent curve of nylon-6 homopolymer,¹⁰ three different relaxation peaks (labeled α ,

Table IV Glass Transition Temperatures of Some Nylon-6/PTHF Copolymers According to the DMTA Experiments

Sample Code	ratio w/w%	$T_{g\text{PTHF}}$ $^\circ\text{C}$	$T_{g\text{PA}}$ $^\circ\text{C}$
PA:PTHF _{I 2000}	90:10	-71.66	70.48
	95:5	-71.64	69.62
	98:2	-70.74	69.99
PA:PTHF _{I 4000}	90:10	-67.30	67.36
	95:5	-68.64	65.62
	98:2	-69.40	68.63

$T_{g\text{PTHF}}$ —glass transition temperature of PTHF-segments and $T_{g\text{PA}}$ —glass transition temperature of PA-segments according to DMTA analysis.

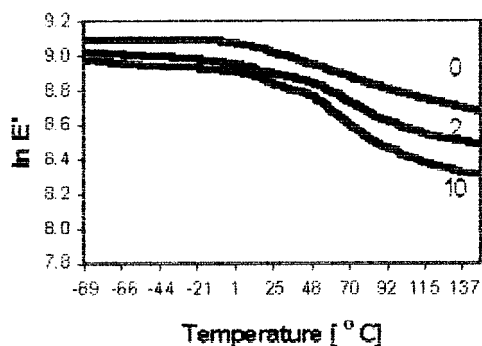
β , and γ) descending from higher to lower temperatures, can be seen. The transition occurring between 27–70 $^\circ\text{C}$,^{1,3,10} assigned to be the α -transition, reflects the onset of motion of large chain segments caused by the breaking of molecular bridging in the amorphous region. The β -transition at about -65 $^\circ\text{C}$ ^{1,10} is caused by a local segmental motion of amide groups in the amorphous region that are not hydrogen bonded to the other amide groups¹⁰ and several ethylene carbon groups.⁹ The γ -peak occurring at about -113 $^\circ\text{C}$ is caused by the well-known “crankshaft mechanism.”¹⁰ This peak reflects the onset of cooperative movement of methylene groups in the amorphous region.

It is well known that microphase separation as a consequence of the positive free energy of mixing between the polymer blocks is characteristic

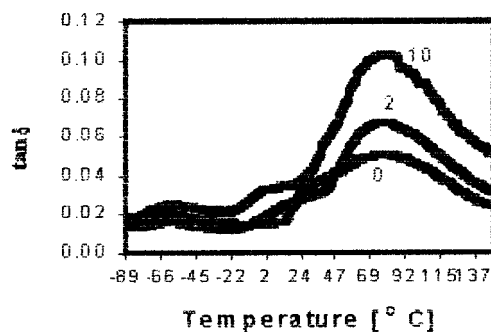
Table III Thermal Gravimetric Analysis of Nylon6/PTHF Copolymers

Sample Code	Ratio w/w%	$Td_{5\%}$ $^\circ\text{C}$	$Td_{50\%}$ $^\circ\text{C}$	Vd^{max} $^\circ\text{C}$ min^{-1}
PA:PTHF _{I 2000}	90:10	384.3	521.8	42.0
	95:5	402.3	540.8	41.6
	98:2	409.8	546.8	41.1
PA:PTHF _{I 4000}	90:10	364.9	498.5	32.3
	95:5	378.0	534.5	31.8
	98:2	401.8	519.0	27.8
PA:PTHF _{H 2000}	90:10	408.2	521.9	44.2
	95:5	412.9	505.5	37.8
	98:2	420.3	523.6	36.0
PA:PTHF _{H 4000}	95:5	390.0	517.7	32.9
	98:2	405.0	513.7	35.9

$Td_{5\%}$ —decomposition temperature at 5% weight loss; $Td_{50\%}$ —decomposition temperature at 50% weight loss; Vd^{max} —maximum decomposition rate.



a



b

Figure 3 Dynamic Mechanical Thermal Analysis of nylon-6 and nylon-6/PTHF_{2000/IF} copolymers (90/10 w/w % and 98/2 w/w %): (a) variation of dynamic elastic modulus, E' , with temperature; (b) variation of loss factor, $\tan \delta$, with temperature.

for most block copolymers.^{3,9,10} For the nylon-6/PTHF block copolymers, the peak occurring at about -65°C is assumed to be a result from the simultaneous occurrence of two relaxations, one caused by the α -relaxation of the soft block segments and the other caused by the β -transition observed for nylon-6. The elastic modulus (E') and loss factor ($\tan \delta$) are plotted against the temperature at a constant frequency of 1 Hz (Fig. 3). There are two T_g s for all copolymers. The lowest one, in the -71 to -67°C range, corresponds to the T_g of PTHF soft block, while the higher one, ranging from 60 to 70°C , corresponds to the T_g of nylon-6 hard blocks. These two distinct transition peaks indicate that, despite the formation of the triblock copolymer through covalent links, the amorphous nylon-6 and PTHF

chains are not molecularly miscible. Below the glass transition temperatures, the amorphous chain conformations are frozen into a rigid network, yielding a high value for the elastic modulus and low value for the loss tangent for all samples. The T_g is characterized by a large decrease in E' and a pronounced $\tan \delta$ peak. The $\tan \delta$ peaks for PTHF block are relatively narrow, and its T_g is not much affected by the different composition of the block copolymers. A downshift of the T_g of nylon-6 with increasing the concentration of the soft block has been reported.³ On the one hand, this can be due to a decreased domain size and crystallinity of hard blocks after the copolymerization, and on the other hand to the plasticizing effect of moisture. It is noteworthy that for all our copolymers, the main $\tan \delta$ peak at about 70°C gradually increases in magnitude without a significant shift in increasing the content of PACs up to 10 w/w %. From our point of view the microphase separation and the low concentration of PTHF in the copolymers are the reasons that the presence of soft component do not affect the T_g of nylon-6. The glass transition temperature marks the onset of long-range motion in amorphous polymer chain segments. The higher T_g means that more thermal energy will be required to dissociate the hydrogen bonds as a result from the better-ordered chain structure. The higher the hard block concentration, the higher the dynamic elastic modulus for the materials. The different length of PAC block does not change much the dynamic mechanical properties of nylon-6 copolymers.

Optical Microscopy

It is evident from the photographs (Figs. 4–6) that the copolymers contain amorphous phase (dark domains) and crystalline phase. The morphology of the copolymers is similar to that of the pure nylon-6 sample. The spherulitic texture can be observed in both cases. Generally, PTHF crystallizes at a very low rate, in comparison to nylon-6. Thus, PTHF blocks in these copolymers hinder the crystallization of nylon-6 segments [Fig. 4(a) and (b)]. With increasing the content of PTHF, the tendency of the interaction between different blocks and the organization in separated phases increase, respectively. The crystallites are organized in domains, not very large in size. These formations also can be seen on EM photographs [Fig. 4(c) and (d)]. The copolymer with 2 w/w % PTHF-2000/HM has more perfect crystal

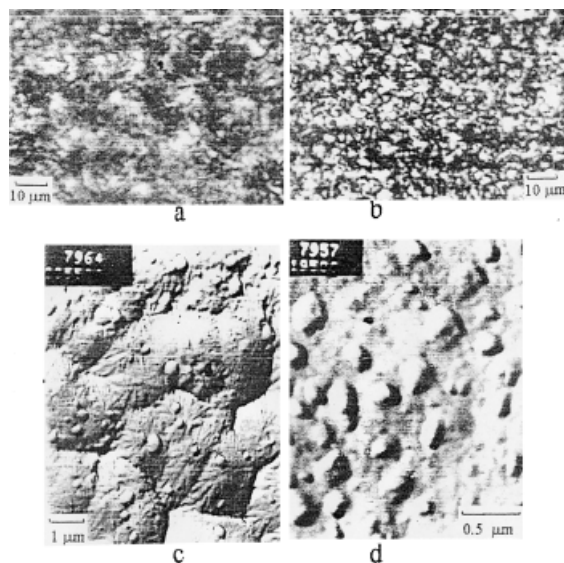


Figure 4 Morphology of nylon-6/PTHF₂₀₀₀/HM samples taken with polarizing (a,b) and electron (c,d) microscopes at copolymers ratio: (a) 98/2 w/w %; (b) 90/10 w/w %; (c) 95/5 w/w %; (d) 90/10 w/w %.

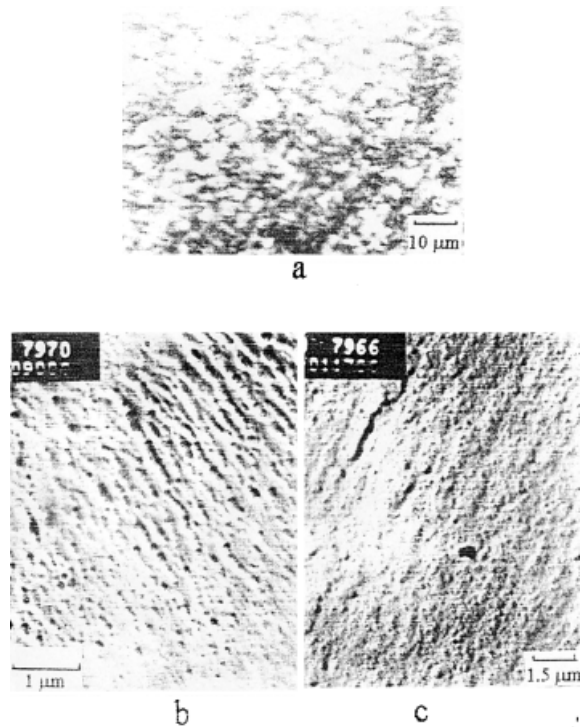


Figure 5 Morphology of nylon-6/PTHF₄₀₀₀/HM samples taken with polarizing (a) and electron (b,c) microscopes at copolymers ratios: 98/2 w/w %; 90/10 w/w %; 95/5 w/w %.

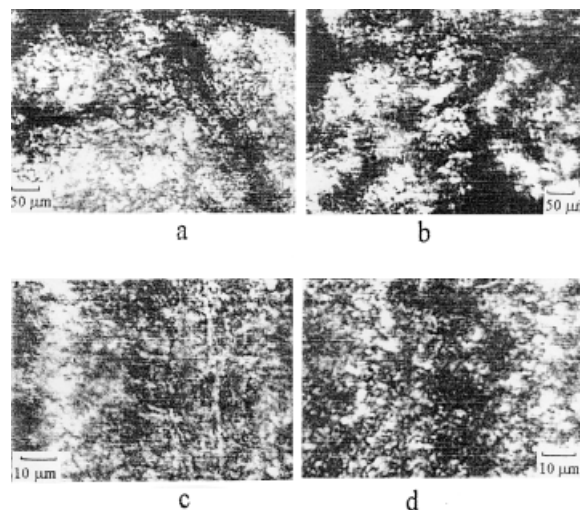


Figure 6 Morphology of nylon-6/PTHF₂₀₀₀/IF (a,b) and nylon-6/PTHF₄₀₀₀/IF (c,d) samples taken with polarizing microscope at copolymers ratios: (a) 95/5 w/w %; (b) 90/10 w/w %; (c) 95/5 w/w %; (d) 90/10 w/w %.

structure, larger spherulites, and higher percent of crystal phase (according to WAXD; Table I) than those of the copolymer containing 10 w/w % PTHF-2000/HM. The superstructure of copolymers obtained with PTHF-4000/HM is more uniform in comparison to nylon-6 /PTHF 2000/HM [Fig. 5(a)–(c)]. The formation of a more perfect crystal structure is facilitated by the higher molecular weight of copolymers (Table I).

Nylon-6/PTHF_{IF} copolymers are slightly different from those obtained with PTHF/HM. In all copolymers (with different content of PTHF and different M_v) structures with a higher degree of organization cannot be observed. The incorporation of PTHF/IF into the main chain decreases the

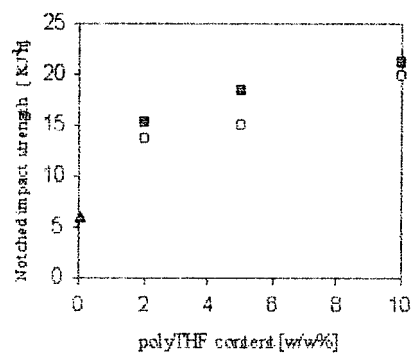
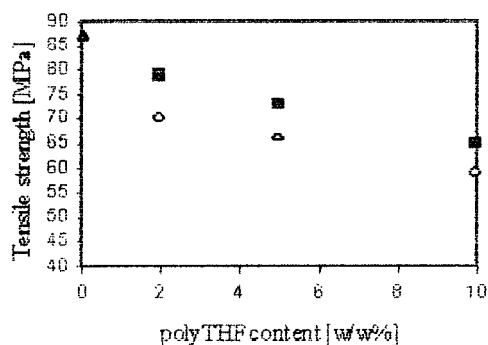
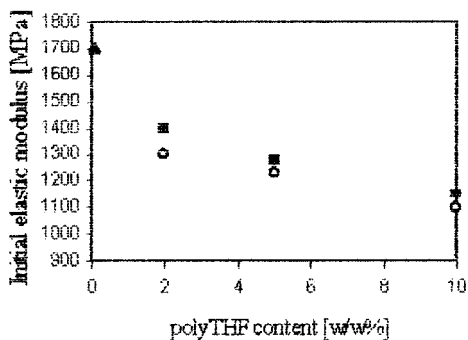


Figure 7 Notched impact strength vs. concentration of soft segments in nylon-6/PTHF copolymers: PTHF₄₀₀₀/IF (■); PTHF₂₀₀₀/IF (○); nylon-6 homopolymer (▲).

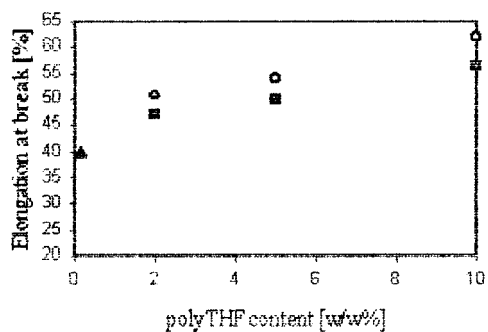
degree of crystallinity (Table I). Figure 6(a) illustrates the structure of a copolymer with 5 w/w % of PTHF-2000/IF. The distribution of amorphous and crystal phases is not very regular, and they are not comparable in size. With increasing the amount of PTHF/IF-2000 to 10 w/w %, the tendency of localization of amorphous and crystal phases in bigger domains is observed [Fig. 6(b)]. A more ordered crystal structure can be observed



a



b



c

Figure 8 Tensile strength (a), initial elastic modulus (b), and elongation at break (c) vs. concentration of soft segments in nylon-6/PTHF copolymers: PTHF_{4000/IF} (■); PTHF_{2000/IF} (○); nylon-6 homopolymer (▲).

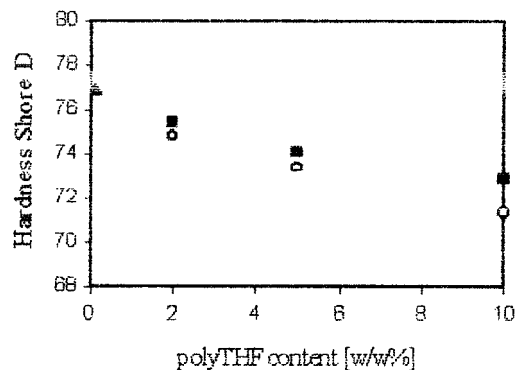


Figure 9 Shore D hardness vs. concentration of soft segments in nylon-6/PTHF copolymers: PTHF_{4000/IF} (■); PTHF_{2000/IF} (○); nylon-6 homopolymer (▲).

after the copolymerization of HL and PTHF-4000/IF [Fig. 6(c) and (d)]. The distribution is quite homogeneous, and a mosaic structure consisting of alternating crystal and amorphous domains is formed.

Mechanical Properties

The impact strength of nylon-6/PTHF copolymers increases with increasing soft block concentration (Fig. 7). Compared to the nylon-6 homopolymer, 2.5-fold higher values even at 2 w/w % of PTHF have been measured. This phenomenon can be attributed to the incorporation of soft segments into the hard nylon-6 matrix, serving as inhibitors of craze propagation. The copolymers having longer soft block exhibit an impact resistance that is a bit better than that of copolymers with a shorter PTHF block.

Tensile tests show a relatively small decrease in the tensile strength and elastic modulus, accompanied by an increase in tensile elongation with increasing PTHF concentration up to 10 w/w % [Fig. 8(a)–(c)].

As expected, a little decrease in the hardness values (Fig. 9) with the increase in concentration of the soft segments has been observed. In a triblock copolymer of A-B-A type the hardness depends on the concentration of hard blocks.

Water Sorption

Triblock copolymers nylon-6/PTHF show better water resistance compared to previously published results.² This phenomenon can be explained by the content of crosslinked macromolecules in our copolymers.⁵ The increased PTHF content and amorphous phase of the copolymers

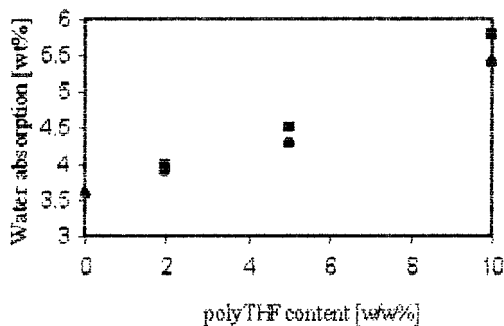


Figure 10 Water absorption vs. concentration of soft segments in nylon-6/PTHF copolymers: PTHF_{4000/1F} (■); PTHF_{2000/1F} (○); nylon-6 homopolymer (▲).

respectively lead to an increase in water sorption (Fig.10).

CONCLUSION

The structures and phase behavior of nylon-6/PTHF triblock copolymers with a low concentration of soft segments ($M_n = 2000$ and 4000 gmol^{-1}) have been studied. It has been established that the incorporation of PTHF into nylon-6 main chain lead to an improvement of the notched impact strength without significant changes in the tensile strength, elastic modulus, elongation at break, hardness, thermal and water resistance for all copolymers in comparison to the nylon-6 homopolymer. A decrease in the degree of crystallinity with increasing PTHF concentration has been observed. In the triblock copolymers only the nylon-6 component crystallizes while the PTHF phase is amorphous independent of its

length. Two different glass transition temperatures have been measured by DMTA, showing a microphase separation between nylon-6 and PTHF segments in the block copolymers.

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