Anionic Polyamides Modified with Poly(oxypropylene) by "One-Shot" RIM Technology: Structural and Morphological Characterization

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ABSTRACT: Anionic nylon 6 modified with poly(oxypropylene) up to 40% by weight and obtained by one-shot reaction injection molding ("one-shot" RIM) was characterized by wide-angle X-ray diffraction, transmission electron microscopy, differential scanning calorimetry, thermal gravimetric analysis, and Fourier transform infrared spectroscopy. Cross analysis by different techniques pointed out that the polymer contained only the α-form and the modifier had little, if any, influence on the crystallinity index, which was found to be about 40% when referred to the nylon 6 fraction only. Morphological changes at different modifier contents were ascribed to different block copolymer structures.

Introduction

Anionic polymerization of ϵ-caprolactam is very interesting in terms of short-time, low polymerization temperatures and low free monomer content at equilibrium if compared with hydrolytic polymerization.[1,2] In particular, by RIM technology it is possible to produce articles having a very complex shape in a single step from liquid components at relatively low viscosity. Moreover, a modifier such as an elastomer or a reactive macromer forming "in situ" an elastomeric product can be introduced in order to improve, for instance, the impact resistance of the material.[3] As a consequence of the interaction between the modifier, or its precursor, and the components of the system, different compositions, structures, and morphologies can be achieved.

The direct "one-shot" introduction in the RIM process of the reactants, including a macromer as precursor of an elastomeric fraction, at suitable polymerization conditions, allowed us to obtain good materials, comparable with products obtained via prepolymer anionic RIM polymerization.[4-6]

The main aim of the present study was the structural and morphological characterization of modified nylon 6 RIM samples, in order to point out the system peculiarities, also related to the modifier content.

Experimental Section

Materials. Nylon 6 RIM samples were prepared by a procedure developed in our laboratories and described in previous works.[4-6] Anionic polymerization of ϵ-caprolactam was performed "one shot" in a stainless steel mold at about 150 °C, introducing under stirring at 100 °C two streams, the former containing ϵ-caprolactam and the activator and the second containing the catalyst and the macromer as modifier. Sodium caprolactamate (CLNa) and hexamethylene diisocyanate (HDI) blocked with caprolactam were used as catalyst and activator, respectively. The macromer was Jeffamine D 2000, a linear poly(oxypropylene) of 2000 molecular weight terminated with amino groups. The samples, having a modifier content in the range of 0–40% by weight and molded as sheets 3 mm thick, were analyzed as made.

Instrumentation. Wide-angle X-ray diffraction (WAXD) was performed utilizing a Philips diffractometer with Bragg–Brentano geometry, working with Ni-filtered Cu Kα radiation (0.154 18 nm) and a proportional detector. Diffraction patterns were examined in the range between 5 and 40° (2θ), by steps of 0.01° (2θ) and time 2 s.

Differential scanning calorimetry (DSC) was performed by using a Perkin-Elmer DSC7 calorimeter: about 15-mg samples, placed in an aluminum sample pan, were analyzed in the temperature range between room temperature and 300 °C, at a heating rate of 20 °C/min under a nitrogen flow of 35 mL/min; some samples were analyzed in the range from −120 to +300 °C. Each sample was heated up to 245 °C (first scan), maintained at this temperature for 2 min, cooled to 150 °C at a cooling rate of 150 °C/min, held at this temperature for 3 min, and then heated from 150 up to 260 °C (second scan). Enthalpy (ΔH_m) and temperature of melting (T_m) data are referred to the first and second scans, while the glass transition temperature (T_g) is referred to the first scan.

Thermogravimetric analyses (TGA) were performed by using a Perkin-Elmer TGS2 apparatus and samples of about 15 mg by weight, in the temperature range between 50 and 600 °C, at a heating rate of 20 °C/min and under a nitrogen flow of 35 mL/min.

Thin sections, about 70 nm thick, were prepared at a temperature of −90 °C, utilizing a Reichert–Jung Ultracut E/FC4 ultracryomicrotome; then the sections were stained by exposure to vapors of a 2% RuO_4 aqueous solution to mark the poly(oxypropylene) phase;[7] the exposition times were established as a function of the achieved level of contrast. The morphological features of the sections were observed by means of a Philips EM 400 transmission electron microscope (TEM) working with a 80-keV acceleration voltage.

Sections 1 μm thick, transversally cut to the sheet thickness and placed on diaphragms with a hole of 500 μm in diameter, were investigated by a Fourier transform infrared spectrophotometer (FTIR). The absorption spectra were collected at room temperature by means of a Nicolet 740 spectrophotometer, equipped with a CsI beamsplitter and DTGS detector, in the wavenumber range between 5000 and 250 cm^{-1}. Each spectrum was the average of 128 scans at 8-cm^{-1} resolution.

Results

Diffraction spectra in the range between 15 and 30° (2θ) of the sample of polyamide 6 (PA6) homopolymer (0% by weight of modifier) and of samples having 10 and 35% by weight contents of modifier are reported in Figure 1, where it can be seen that in all samples only the α-form is present, showing two main reflections α_1 and α_2 corresponding to the crystallographic planes (200) and (002 + 202).[8,9]

In Table I, the mean experimental values of the angular positions and the relative intensities of α_1 and α_2 for the samples having a different content of modifier are reported

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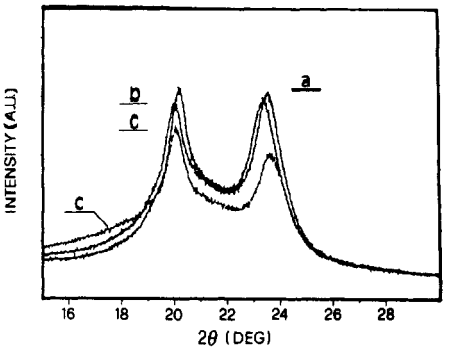

Figure 1. Wide-angle X-ray diffraction spectra of PA6 modified with (a) 0, (b) 10, and (c) 35% by weight of poly(oxypropylene).

Table I
Experimental WAXD Data for Nylon 6 RIM Modified with Poly(oxypropylene)

modifier (% by weight)	2θ, deg		(I/I0)	
	α_1	α_2	α_1	α_2
0	20.16	23.53	1.00	1.00
5	20.32	23.61	0.83	0.85
10	19.94	23.40	0.89	0.90
15	20.02	23.51	0.73	0.79
20	20.02	23.42	0.69	0.79
25	19.95	23.48	0.72	0.62
30	20.21	23.55	0.61	0.44
35	20.09	23.35	0.59	0.50
40	20.10	23.45	0.50	0.37

and compared with those of the PA6 homopolymer. Several measurements on the PA6 homopolymer sample gave a value of 0.15° (2θ) as the maximum variation of α_1 and α_2 peak positions. In the case of PA6 modifier samples, this variation increases up to 0.25° (2θ), as a function of poly(oxypropylene) content, indicating a micrononhomogeneity, probably due to a different modifier texture. On the other hand, WAXD instrumental error is less than 0.02° (2θ). Figure 1 and Table I show a decrease of the relative intensity of the reflections on an increase in the concentration of the modifier; the decrease is more evident for α_2, with a shift of the maximum peak positions independent of the poly(oxypropylene) content and furthermore an intensity decrease in the spectral region between α_1 and α_2.

A deconvolution in the 15–30° (2θ) range was performed on the collected spectra by utilizing a suitable profile fitting program[10] to point out the possible structural changes induced on the PA6 phase and to obtain information on the crystallinity index (CI). As input parameters for PA6 homopolymer deconvolution, experimental values of the maximum peak positions of α_1 and α_2 were introduced. As full width half-maxima (fwhm) of the α_1 and α_2 peaks and of the halo positions of the PA6 amorphous phase, δ, literature data were taken.[11,12] All the parameters were free to change up to obtaining the best profile fitting reported, for example, in Figure 2a.

In order to obtain information on the contribution due to the modifier to the amorphous phase of the systems, a rubberlike sample of poly(oxypropylene) with urea bridges was prepared by extending with 6.5% by weight of HDI. The experimental results, reported in Figure 2b, gave a spectrum showing amorphous features and a maximum centered at 20° (2θ) characterized by an asymmetric shape. From the deconvolution, a unique contribution to the amorphous halo, centered at 19.7° (2θ) and with fwhm 5.53° (2θ), was calculated (Figure 2b). The asymmetry of the halo was not considered as determinant for the CI calculation of the PA6–modifier systems.

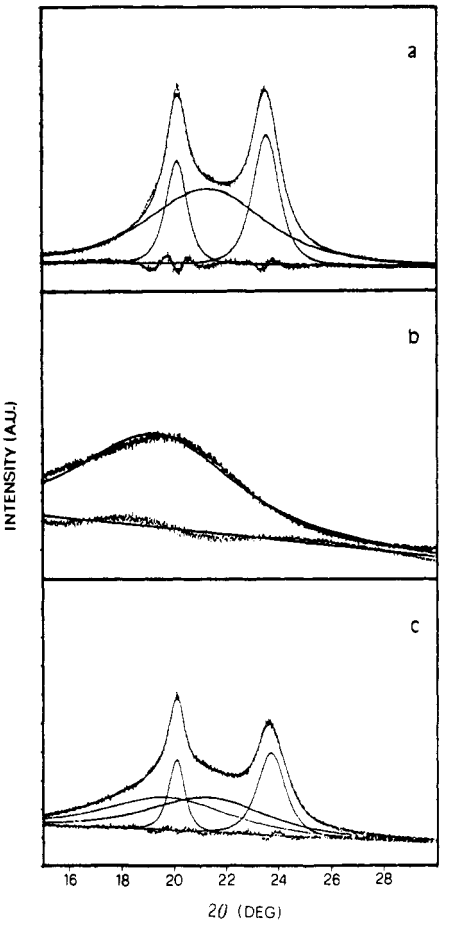

Figure 2. Diffraction spectra, deconvolutions, and differences between calculated and experimental spectra of samples: (a) PA6 homopolymer, (b) rubberlike poly(oxypropylene) with urea linkages, and (c) PA6 with 35% by weight of the modifier.

Table II
Curve-Fitting WAXD Results for Nylon 6 RIM Modified with Poly(oxypropylene)

modifier (% by weight)	2θ, deg			
	α_1	fwhm	α_2	fwhm
0	20.16	0.93	23.53	1.24
5	20.24	0.93	23.68	1.24
10	19.98	0.98	23.41	1.20
15	20.06	0.93	23.46	1.22
20	20.06	0.87	23.46	1.23
25	20.02	0.84	23.48	1.27
30	20.14	0.80	23.65	1.33
35	20.05	0.71	23.70	1.26
40	19.89	0.81	23.57	1.36

The input parameters utilized for all samples' deconvolution were the following: experimental value of the maximum peak position of α_1 and α_2 for each sample, free to change; calculated values of fwhm of the α_1 and α_2 peaks for PA6 homopolymer, free to change; calculated values of the maximum peak position and of fwhm for δ in the PA6 homopolymer sample, fixed; calculated values of maximum peak positions and of fwhm for the amorphous phase, J, for the rubberlike sample, fixed. The obtained experimental spectra and the deconvolution results for the sample with 35% by weight modifier are shown in Figure 2c.

In Table II all the calculated data from the deconvolutions are summarized. From these data it can be observed that α_1 and α_2 positions can vary in the range 0.2° (2θ) for all the samples. Bragg's peak areas and CI are reported in Table III. CI of PA6–modifier samples and of their corresponding PA6 phases were determined

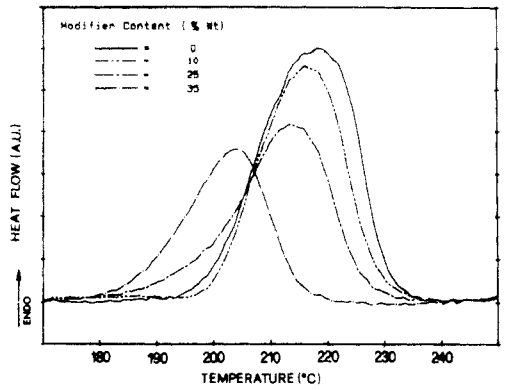

Figure 3. Differential scanning calorimetry of the PA6 homopolymer and of PA6 with 10, 25, and 35% by weight of the modifier.

Table III
Curve-Fitting WAXD Results and Calculated Crystallinity Index for Nylon 6 RIM Modified with Poly(oxypropylene)

modifier (% by weight)	area (%)				%	
	α_1	α_2	δ	J	CI_{Total}	CI_{PA6}
0	15.8	24.6	59.6		40.4	40.4
5	14.8	26.7	58.5		41.5	41.5
10	14.8	24.3	50.7	10.2	39.1	43.5
15	12.7	24.2	52.0	11.1	36.9	41.5
20	12.7	22.5	47.9	16.9	35.2	42.4
25	11.1	21.7	40.5	26.7	32.8	44.7
30	10.4	19.9	41.5	28.2	30.3	42.2
35	10.4	21.3	34.8	33.5	31.7	47.7
40	10.5	19.5	28.5	41.5	30.0	51.3

as follows: (i) ratio of the crystalline peak areas on the total sample area and (ii) ratio of the crystalline peak areas to the total area relative to the PA6 homopolymer contribution, CI_{PA6}. The analysis points out that, by increasing the modifier content, CI decreases. On the contrary, CI_{PA6} shows a near constant value of about 40% up to 30% by weight of modifier content, followed by an increase at higher modifier concentration. Such a CI_{PA6} increase for samples with modifier levels higher than 30% by weight could be related to an increase of X-ray absorption by the modifier amorphous phase.

Calorimetric curves, relative to the second scan in the temperature range between 170 and 250 °C, are drawn in Figure 3 for the PA6 homopolymer and for PA6 with 10, 25, and 35% by weight of the modifier. The analysis of the curves points out that the endotherm maximum is centered at 219 °C, corresponding to T_m for the PA6 homopolymer, whereas by increasing the modifier content both T_m values and the areas of the melting peak corresponding to ΔH_m decrease. Moreover, shifts of the initial and final temperatures of the melting peak curve to values lower than the PA6 homopolymer sample are observed. No exothermal features and broadening of melting peak are present, contrary to that observed by Gardlund and Bator[13] in the case of nylon–polyurea block copolymers. The ΔH_m and T_m experimental values exhibit a decreasing trend at both the first and second scans, as shown in Table IV. Some differences in T_m values are due to the imposed thermal history, while the T_m decrease can be related to the reduction of the PA6 crystallite lamellar thickness (L), as described by the Thomson–Gibbs equation.[14] In the simplified form the Thomson–Gibbs equation can be written as

$$T_m = T_m^\circ\{1 - [2\gamma/L\Delta H_m^\circ\rho_c]\} \quad (1)$$

where T_m° is the melting temperature of an infinitely large crystal, γ is the specific surface free energy, L is the lamellar thickness, and ΔH_m° and ρ_c are the heat of fusion and the density of 100% crystalline PA6, respectively. In the calculation the values T_m° = 543 K, γ = 80 mJ/m^2, ΔH_m° = 230 J/g, and ρ_c = 1.235 g/cm^3, were used.[14] In Table IV, calculated L values from the calorimetric second scan vary in the range between 5.9 and 4.6 nm and show a decreasing trend, as a function of poly(oxypropylene) concentration, in good agreement with data obtained by Lindberg and Bertilsson.[15]

CI_{PA6}, the crystalline fraction of the polyamide at different modifier contents, was calculated by means of the equation

$$CI_{PA6} = \Delta H_m/[\Delta H_m^\circ(1 - \phi_r)] \quad (2)$$

where ΔH_m is the enthalpy of melting for the samples, and ϕ_r is the volume fraction of the soft phase determined by using ρ_{PA6} = 1.144 g/cm^3 and ρ_{soft} = 0.996 g/cm^3. Calculations relative to the first and second scans (Table IV) indicate a change between 41 and 34% and between 20 and 17%, respectively, as a function of the modifier content. The last two columns of Table IV refer to T_g values of PA6 and rubber phases for some samples. T_g values were determined as the middle height of enthalpic variation along the calorimetric curve, because the two transitions occur in a rather wide temperature range also for a heating rate of 30 °C/min. T_g decrease for the PA6 phase, and T_g-enhanced values for the rubber phase were observed by increasing the modifier percentage. These data were confirmed and found in good agreement with compressive and loss moduli as a function of temperature from dynamic-mechanical thermal analyses (DMTA) performed at 1 Hz and 3 °C/min showing a T_g inward shift.[16] T_g shift of the polyamide is more evident and points out a preferential sensitivity to the presence of the modifier. These facts would indicate both a good phase separation and the possible presence of very short blocks in the copolymer.[15]

The thermogravimetric analysis confirmed a good thermal stability of the PA6–modifier system without significant weight loss under 300 °C. Moreover, the rubberlike sample exhibited a better thermal stability than PA6 homopolymer having the maximum decomposition rates at about 360 and 320 °C, respectively; therefore, an improved thermal stability in the range from 330 to 400 °C for PA6–modifier samples is justified.

TEM micrographs (Figure 4) show some morphological features of the samples. Figure 4a indicates, for the sample with 25% by weight of the modifier, a continuous and regular texture of the soft phase, containing PA6 as an inclusion. Regions of preferential agglomeration of the soft phase are not evident, while a good polyamide interpenetration into the rubber phase is observed at higher magnification (Figure 4b). From image analysis the mean thickness in texture segments is 25 nm, about twice that measured for a sample with 15% by weight of the modifier. It is worth noting that the 15% by weight modifier sample showed also a closer texture. A thickness larger than that postulated by Van der Loos,[17] for the case of the poly(oxypropylene glycol)-based prepolymer, can be explained both by the "one-shot" process and by different chemical functional groups of the modifier. In fact increasing the concentration of the modifier chain extension of the soft segments via substituted urea linkages becomes more probable owing to reaction between aminic end groups of the macromer and isocyanate groups of HDI. Moreover, it is possible to distinguish the PA6 lamellae having a dimension of about 12 nm,[18] running nearly perpendicular to the texture segments of the rubber phase. On the

Table IV
Experimental DSC Data, from the First and Second Scans, for Nylon 6 RIM Modified with Poly(oxypropylene)

modifier (% by weight)	$\Delta H_m{}^a$ (J/g)	$T_m{}^a$ (°C)	$\Delta H_m{}^b$ (J/g)	$T_m{}^b$ (°C)	L^b (nm)	$CI_{PA6}{}^a$	$CI_{PA6}{}^b$	$T_{g,PA6}{}^a$ (°C)	$T_{g,soft}{}^a$ (°C)
0	95	220	45	218	5.9	41	20	63	
5	87	218				40		62	−62
10	82	218	37	216	5.7	39	18		
15	68	211				35		55	−59
20	64	211				35			
25	58	211	29	213	5.4	35	18	47	−57
35	46	206	24	204	4.6	34	17		
100									−64

[a] First scan. [b] Second scan.

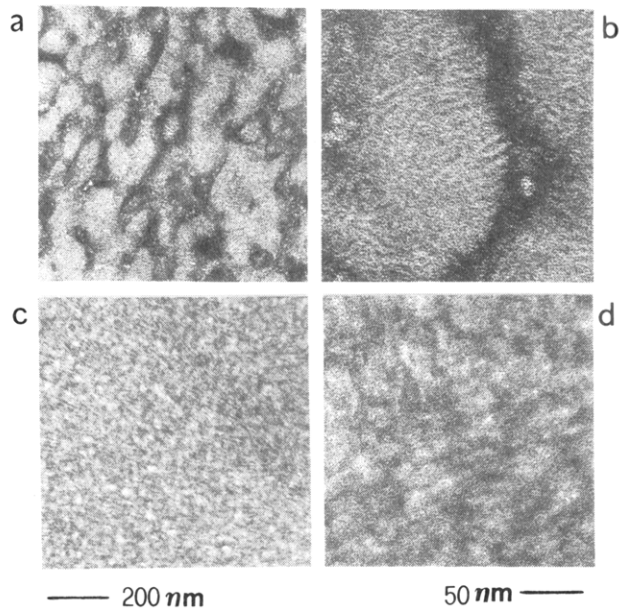

Figure 4. TEM micrographs at different magnifications of PA6 with (a) and (b) 25% by weight and (c) and (d) 40% by weight of poly(oxypropylene).

contrary, for the sample PA6–40% modifier an extremely fine distribution and high cocontinuity between polyamide and the rubber phase is observed, as reported in Figure 4c; at higher magnification (Figure 4d) it is difficult to distinguish clearly the two phases in the sample. However, lamellae of about 10 nm in dimension can be discerned. This fine mixing between the phases suggests the presence of a random block copolymer, A_mB_n, as also reported by Kurz,[19] although referring to a slightly different system.

Fourier transform infrared spectra in the 4000–500-cm^{-1} range of samples with 0, 5, and 25% by weight of the modifier are shown in Figure 5a–c: neither corrections nor manipulations were made on the spectra. The most important features of the spectra are the lowering of the absorption band intensities of the polyamide and the appearance of the poly(oxypropylene) COC stretching vibration mode, centered at 1109 cm^{-1}, with the increase of the modifier content. In Table V the vibration description of the main absorption bands and the relative wavenumbers of the samples are reported. The absorption peak positions are constant independent of the modifier percentage. Figure 6 shows the FTIR spectra in the range between 3500 and 2800 cm^{-1}. The detailed analysis of the band at 3300 cm^{-1} can point out both non-hydrogen-bonded (free) and hydrogen-bonded NH stretching modes. In these spectra the free NH band, as a weak shoulder at 3440 cm^{-1}, due to amidic and/or unreacted terminal groups, is absent: this fact witnesses for the good mixing achieved during the anionic polymerization carried out in the present work. From analysis of the spectra, the hydrogen-

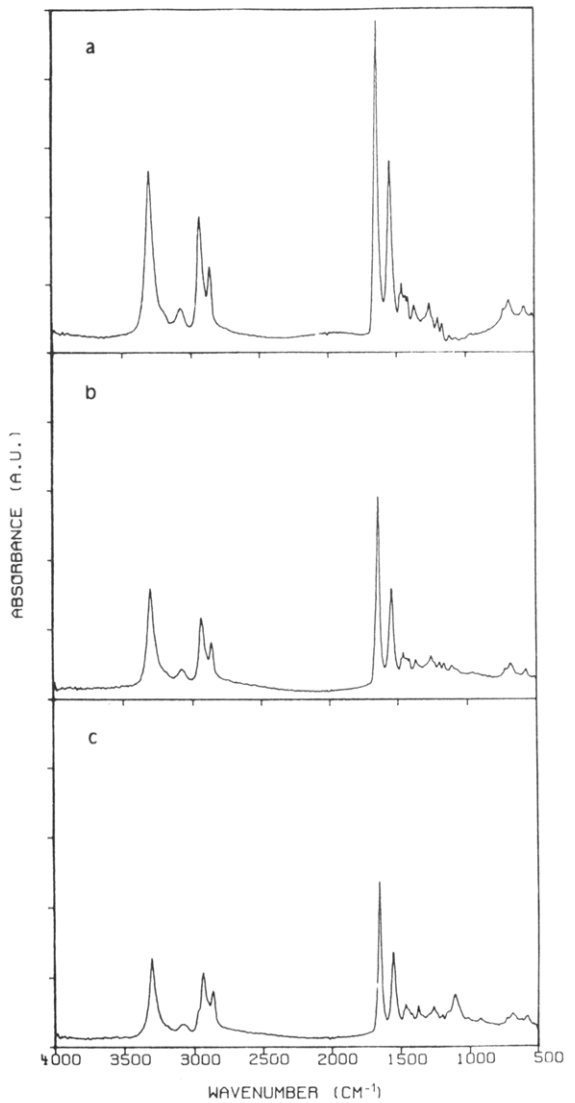

Figure 5. FTIR spectra in the wavenumber range between 4000 and 500 cm^{-1} of PA6 samples with (a) 0, (b) 5, and (c) 25% by weight of the modifier.

bonded NH stretching band presents a maximum at 3300 cm^{-1} and fwhm of about 51 cm^{-1} for all the examined specimens. Both asymmetric and symmetric CH_2 stretching modes, at 2935 and 2862 cm^{-1}, respectively, due to polyamide absorption and the CH_2 and CH_3 vibration modes, due to poly(oxypropylene), are evident. In fact, the poly(oxypropylene) modes determine a band deformation with appearance of a shoulder at 2968 cm^{-1}: it is prominent in the case of the sample with 25% by weight of the modifier. These absorptions also determine a change in the ratio between NH stretching and symmetric CH_2 stretching modes. In Figure 7, the IR spectra in the range between 1800 and 1000 cm^{-1} are reported: the strong

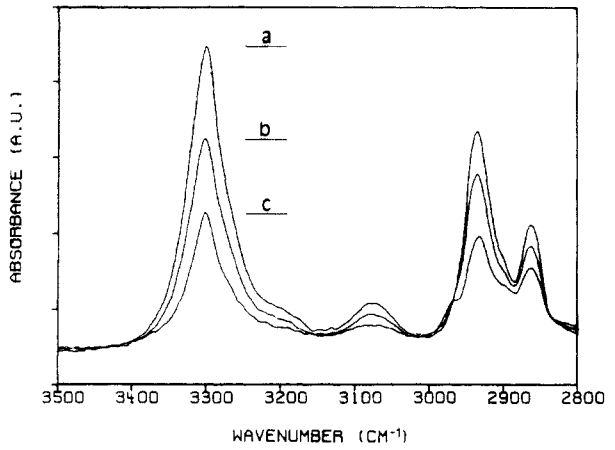

Figure 6. FTIR spectra in the 3500–2800-cm^{-1} range of PA6 samples with (a) 0, (b) 5, and (c) 25% by weight of the modifier.

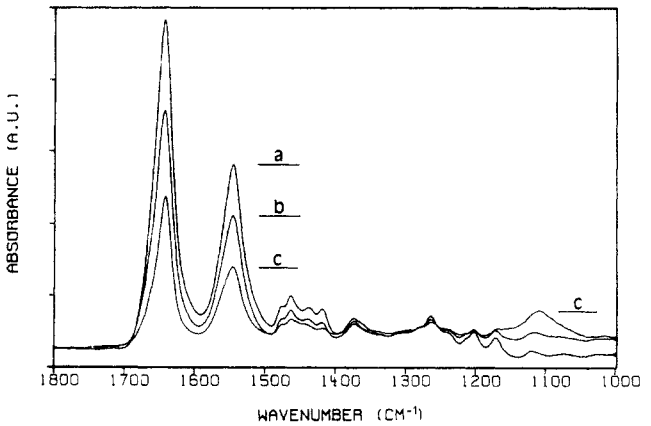

Figure 7. FTIR spectra in the 1800–1000-cm^{-1} range of PA6 samples with (a) 0, (b) 5, and (c) 25% by weight of the modifier.

Table V
Characteristic Infrared Bands of Polyamides

vibration description	wavenumber (cm^{-1})
hydrogen-bonded NH stretch	300
NH stretch connected to amide II	3073
CH_2 asymmetrical stretching	2936
CH_2 symmetrical stretching	2862
amide I	1642
amide II	1546
amide V	728
amide VI	688
ν(COC) of poly(oxyprolylene)	1110

absorption peaks at 1642 and 1546 cm^{-1} are due to amide I and amide II vibration modes, respectively; the positions of amide II, V, and VI (see Table V) allow the identification in the samples of the presence of only the α-form.[20,21] Particular attention was directed to the amide I absorption band and its large contribution due to C=O stretching vibration: as for the NH stretching region (Figure 6) free and hydrogen-bonded carbonyl groups are distinguishable also in amide I. In fact, as widely reported by Coleman and co-workers,[22,23] this absorption band is considered as produced by three bands associated to hydrogen-bonded carbonyl groups in ordered crystalline domains, hydrogen-bonded carbonyl groups in disordered amorphous domains, and non-hydrogen-bonded (free) carbonyl groups. In order to quantify the contribution of each of the three vibration modes and to obtain information on polyamide crystallinity when different percentages of the modifier are present, spectrum deconvolutions were performed by using the FOCAS program[24] in the range between 1700 and 1626 cm^{-1}. A base-line correction from 1900 to 900 cm^{-1} and a Gaussian band shape were assumed. The contributions

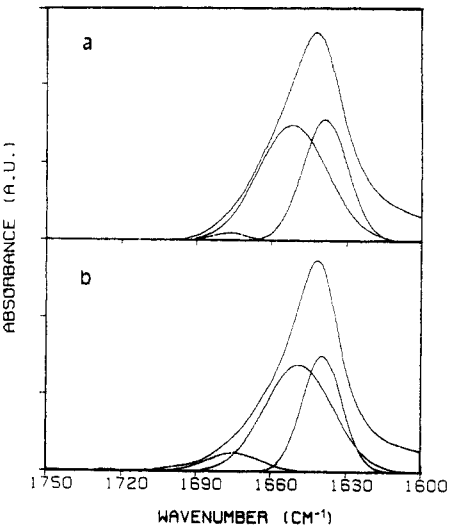

Figure 8. FTIR spectra and deconvolutions in the amide I wavenumber region of samples (a) PA6 homopolymer and (b) PA6 with 25% by weight of the modifier.

due to the poly(oxypropylene) absorption band, COC at 1109 cm^{-1}, were subtracted from the spectra of the PA6–modifier samples, although poly(oxypropylene) does not present intense bands in the examined spectral range. Fourier self-deconvolution in FOCAS software was utilized to evaluate the positions of the peaks. Position, number, and fwhm of the peaks were derived from literature data obtained for polyamides and copolyamides at room temperature.[21-23] Position, fwhm, and intensity were free to change during the optimization process. Parts a and b of Figure 8 show spectra and deconvolution results for PA6 homopolymer and PA6–25% by weight modifier. In Table VI curve-fitting results for the different samples are reported. It can be observed that, by increasing the content of the modifier, the area percentages of hydrogen-bonded carbonyl groups relative to ordered and disordered domains do not change noticeably. On the contrary, the area percentages, related to free carbonyl groups, seem to be influenced by modifier contribution levels and assume values of 2% for the homopolymer up to 7%, as a maximum, for PA6 samples with high modifier content. This procedure allowed us to evaluate a value in the 36–40% range of the crystallinity index for PA6 fractions in the samples. It is worth noting that fwhm's relative to hydrogen-bonded carbonyl groups associated to ordered and disordered domains are not in the 1:2 ratio as reported in ref 23 for PA6 homopolymer samples, while the ratio tends to be similar in the case of samples at higher poly(oxypropylene) content.

Discussion and Conclusion

The characteristics of the copolymers obtained in ϵ-caprolactam anionic polymerization by a standard RIM process using a prepolymer derived from a linear macromer (particularly a polyether) with reactive terminal groups, have been widely studied.[3]

Our system differed from the above common procedure, being the anionic RIM polymerization performed "one shot" by mixing all the components, monomer, catalyst, activator, and macromer, at the same time; the last component, the macromer, acts as a precursor of the modifier. In principle, this system should give less ordered materials than a standard RIM via prepolymer, from both a compositive and a structural point of view. However, it is believed that in RIM systems in which a preordered prepolymer reacts to give a block copolymer with A–B–A

Table VI
Curve-Fitting Results of the Amide I Region of Nylon 6 RIM Modified with Poly(oxypropylene)

modifier (% by weight)	hydrogen bonded: ordered ν (cm^{-1})	ordered fwhm (cm^{-1})	ordered A_0 (%)	hydrogen bonded: disordered ν (cm^{-1})	disordered fwhm (cm^{-1})	disordered A_d (%)	hydrogen non-Bonded: free ν (cm^{-1})	free fwhm (cm^{-1})	free A_f (%)
0	1639	21	40	1652	33	58	1677	17	2
5	1639	21	39	1652	33	57	1678	25	4
15	1639	19	36	1649	32	57	1675	25	7
25	1638	19	36	1649	32	57	1675	25	7
40	1637	19	39	1648	34	55	1675	24	6

sequences, transfer reactions to amidic or ester groups can lead to block copolymers of the A_nB_m type so that more than one block B is present among the A polyamide chain blocks. Moreover, the reaction of the modifier precursor with the activated ϵ-caprolactam involves polyamide chain shortening. Therefore, the modifier presence could influence negatively the possibility of the polyamide chains to give ordered sequences or could give rise to rough phase separation with a loss in performance of the material. In the case of the PA6 homopolymer system and with modifier concentration up to 40% by weight the diffractometric analysis reveals a semicrystalline system in which a structural disorder corresponds to an increase of the modifier content. If the contribution of the soft phase is subtracted from the total amorphous fraction, the evaluated crystallinity index (CI) remains near constant. This indicates that there is no effect of the modifier on the possibility of polyamide to crystallize. The correctness of the calculated peak deconvolution and the assignment of crystalline and amorphous fractions is confirmed by the good agreement between the area percentage of the modifier halo and the nominal weight content (Table III). It is worth noting that the intensities at the maximum peak positions of α_1 and α_2 are at the constant ratio of about 1.0: this value is in agreement with Hirami's data[25] for the 140 °C crystallization temperature. This fact suggests that the modifier does not affect the hydrogen bond in the crystalline lattice. The change of the interplanar distance, d, and in consequence of the chain packing index (ICP) as defined by Murthy, cannot be considered on the basis of the shifts of α_1 and α_2 angular values owing to measurement of the variability in the range of 0.4° (2θ). On the other hand, the roughly calculated ICP assumes fairly high values, varying in the range between 0.62 and 0.69, and it could mean "an energetically lower and more stable nylon-6 lattice".[26] The α_1-fwhm calculated values point out an increase of the crystallite size perpendicular to the (200) plane; at the same time a fwhm increase of the α_2 peak relative to (002 + 202) planes occurs. Owing to high ICP values, not lower than the value for the PA6 homopolymer, and the crystallite size increase in the direction of axis a of the unit cell, a corresponding size decrease in the direction of axis b is expected. On the other hand, the lowering of the melting temperature, measured by means of calorimetric analysis, suggests a thinner thickness of PA6 lamellae in the direction of chain folding. The lamellae dimension was calculated by the Thomson–Gibbs equation, where a value of 80 mJ/m^2, representing the high surface free energy of the polymer, was assumed as a constant, while the modifier content varied. This choice can be justified by the direct TEM observation of the decrease of the lamellae thickness with the modifier concentration. The lowering of the melting temperature could be explained by Flory's equation[27] due to the dilution effect. However, the degree of polymerization of a few units, as calculated by this equation, appears uncorrect in considering the low values. This is not a surprise: in fact the choice of both $T_m°$ and $\Delta H_m°$ values as input in the equation can be ambiguous when the system is far from equilibrium conditions.[15] From both experimental evidence and the performed deconvolutions on WAXD and FTIR spectra, a crystallinity value of about 40%, at least up to 25% by weight of the modifier inside their respective variability, was estimated.

At higher modifier concentrations data obtained by the two techniques diverge. In the case of WAXD, CI rises to 51%, probably due to the different X-ray absorptions, whereas CI by FTIR of the sample with 40% by weight of the modifier maintains its constant value of about 40%.

On the other hand, CI by first-scan calorimetric analysis presents values, normalized for the rubber volume fraction, in the range between 41 and 36%. Second-scan running was also performed to equalize possible different thermal histories and to get appropriate values of melting temperature as input in the Thomson–Gibbs equation. In this case lower CI values in the range between 20 and 17% were obtained; such values were due to a lower crystallization extent for this preparation procedure, in agreement with Borggreve's data obtained for a similar system in analogous conditions.[28] In addition to the high CI value (40%) of the as-molded samples, the occurrence of good mixing and complete reaction was confirmed by the IR spectrum on the basis of the lack of appreciable absorption coming from the NH_2 stretching band due to unreacted species.

A further confirmation can be derived from FTIR analysis. As previously described, CI was determined by amide I absorption band decomposition into three contributions due to hydrogen-bonded carbonyl groups to ordered and disordered domains and non-hydrogen-bonded carbonyl groups. The presence of the modifier produces a slight increase of the contribution relative to the free carbonyl groups and a shift of the three maxima to lower wavenumbers than those of the PA6 homopolymer. This fact could indicate well-defined and stable bonds at higher modifier content.

TEM observations have shown a regular continuous texture of the soft phase extending throughout the nylon phase. However, with the highest amount of poly(oxypropylene) a high-phase continuity between the soft and the PA6 phases was observed. These morphological features confirm that a copolymer with a triblock A–B–A structure is present at low modifier concentrations, as proposed by Van der Loos.[17] At higher concentrations of modifier random block PA6–modifier copolymers with a structure of the A_mB_n type are more probable according to the T_g lowering of PA6 as a consequence of the reduced molecular weight of polyamide segments. All experimental data point out large phase separation.

Therefore, it was concluded that modified nylon 6, when obtained by the "one-shot" RIM process, is comparable with modified nylon 6 produced by the more common RIM technique via prepolymer reaction, from both the morphological and structural point of view.

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