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Crystallographic structures on the sequential copolymer of ε-caprolactam and pyrrolidinone (nylon 4/6)

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Abstract

The structure and morphology of lamellar crystals of a sequential copolymer of poly(pirrolidinone) with poly(ε-caprolactam) (nylon 4/6 copolymer) has been studied by transmission electron microscopy, electron diffraction and X-ray diffraction. The results obtained indicate that at room temperature single crystals of this copolymer have an α-form structure which is also the most stable one for both related homopolymers. The crystallographic unit cell is monoclinic with $a = 9.60$ Å, b (chain axis) $= 14.80$ Å, $c = 8.06$ Å and $\beta = 67°$. The effects of temperature on the lattice spacings show that the characteristic 200 and 002 equatorial spacings converge with increasing temperature but do not meet prior to the melting temperature. In conclusion, the copolymer and the related homopolymers behave similarly with respect to their room temperature most stable crystal structure and behavior on heating. The second characteristic crystalline phase (γ-form) reported for even nylons could only be obtained by treating the polymer sample with iodine–potassium iodide solutions.

Keywords: Copolymer; Polyamides; Nylons

1. Introduction

Crystals of nylons 4 [1] and 6 [2] have been shown to be chain-folded. In these nylons the chains regularly fold back and forth to form hydrogen-bonded sheets, with the molecular chains alternating up and down within each sheet. Experimental results from electron and X-ray diffraction show that crystals of both nylons are found in monoclinic phases, with chains lying normal to the crystal surfaces and, with four chains passing through the unit cell. At room temperature, the lamellar single crystals of nylon 4 and nylon 6 present two strong diffraction signals at spacings around 4.4 Å (representing the projected interchain distance within a hydrogen-bonded sheet) and 3.7 Å (related to the intersheet distance), which are characteristic of many even nylons. Moreover, there is a common behavior between these two nylons when crystals are heated, because in both cases these two characteristic spacings move together with increasing temperature, and both nylons melt before the diffraction signals actually meet.

Polymorphism has been shown to be present in many of the even nylons. Thus, although the monoclinic α-phase is the usual phase found for even polymers with a low number of methylenes, a second phase (γ-form) is stabilized for a larger number of methylene units due to the improved Van der Waals interactions between methylenes. The γ-form [3] corresponds to a pseudohexagonal structure with a characteristic packing spacing at 4.15 Å. A shortening of the repeat unit (ca. 0.35 Å/amide group) with respect to the extended conformation is also characteristic because the amide groups are rotated ca. 60° off the sheet plane. In many even nylons the a phase can be systematically converted into the α-phase (or vice versa) or both can coexist in various proportions. In fact, using thermal, mechanical or different chemical treatments lead to polymorphic forms of nylon 6, coexisting the stable α-form and the unstable γ-form [4–7].

The structural study of aliphatic copolyamides is scarce. We could only find some works about synthesis and general properties of even/even statistical copolyamides obtained from mixtures of ω-laurolactam with ε-caprolactam and octanelactam (nylons 6/12 [8] and 8/12 [9] copolymers, respectively). On the other hand, in our laboratory we have reported the study of either alternating [10,11] and statistical [12] even/even copolyamides containing glycine (nylons 2/6 and 2/12). However, from the structural point of view these copolymers may deviate from other aliphatic

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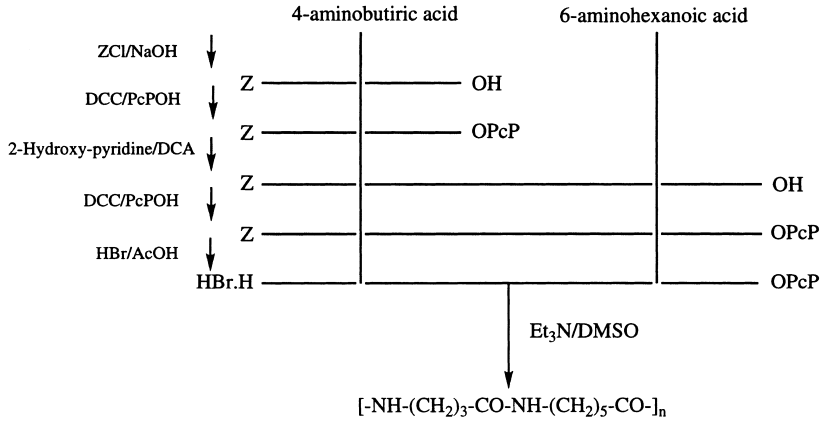

Abbreviations:

Z=Benzyloxycarbonyl
PcP=Pentachlorophenyl
DCC=1,3-Dicyclohexylcarbodiimide
DCA=Dicyclohexylamine
Et_3N=Triethylamine
DMSO=Dimethylsulfoxide

Scheme 1.

copolyamides because of the particular nature of the nylon 2 or polyglycine. Thus, the glycine unit takes a particular conformation where a rotation of 120° between its NH and CO directions is derived. In this case, the standard structure of nylons with parallel sheets of hydrogen-bonded molecules is no longer present and every individual polymer chain is hydrogen-bonded to the six neighbouring molecules, creating a hexagonal lattice with an interchain distance of 4.15 Å.

The objective of the present investigation is to ascertain the crystalline character of the nylon 4/nylon 6 copolymer or, in other words to prove if the stable α-structure found in the related homopolymers is kept in the resulting sequential copolymer.

2. Experimental

A sample of nylon 4/6 with an intrinsic viscosity of 0.35 dLg^{-1}, measured in dichloroacetic acid at 25°C, was used in these experiments. This low intrinsic viscosity value hinders to get films and fibers. The polymer was synthesized by the ester-active method, being the reaction conducted in dimethylsulfoxide at room temperature. The total ester salt concentration was 1 mg mL^{-1} and 2.2 equiv. of triethylamine were added as proton acceptor. The monomer was synthesized in solution applying the widely known methodology developed in peptide synthesis [13] and outlined in Scheme 1. The *N*-carbobenziloxy-aminobutiric acid and the *N*-carbobenziloxy-aminobutiric pentachlorophenyl ester were prepared according to procedures published in the literature [14,15].

The melting temperature of the copolymer determined by differential scanning calorimetry was 227°C. It is interesting to note that this melting point is lower than those observed in the related homopolymers nylon 4 (267°C) and nylon 6 (230°C). The infrared spectrum of nylon 4/6 copolymer shows characteristic amide and methylene absorption bands: 3300 (amide A), 3066 (amide B), 2940 and 2868 (C–H), 1640 (amide I), 1542 (amide II), 690 (amide V) and 578 cm^{-1} (amide VI). These shifts agree with the characteristic bands reported for the α-form of the nylon 6 [16].

Morphologies of spherulites grown from the melt were observed by polarizing optical microscopes (Nikon Microflex AFX-DX equipped with a Nikon FX-35DX camera and Carl Zeiss Standard GFL). A first order red tint plate was used to determine the sign of spherulite birefringence under cross-polarization.

Crystallization experiments were carried out from dilute solutions (0.1% w/v) in 2-methyl-2,5-pentanediol at 110 and 120°C. Single crystals were also prepared by addition of six volumes of *n*-butanol to a dilute solution of the polymer in formic acid. This solution was held at 100°C overnight before cooling to 60°C.

The recovered crystals were also soaked in aqueous 0.1 M iodine and potassium iodide solutions for seven days at room temperature in order to get crystals in the γ-form [7]. The polymer was isolated by filtration and the iodine was then washed out of the sample via sodium thiosulfate solution and water before drying in a vacuum desiccator.

Samples for transmission electron microscopy were prepared by depositing drops of the crystal suspension in *n*-butanol onto carbon-coated grids and then shadowed with

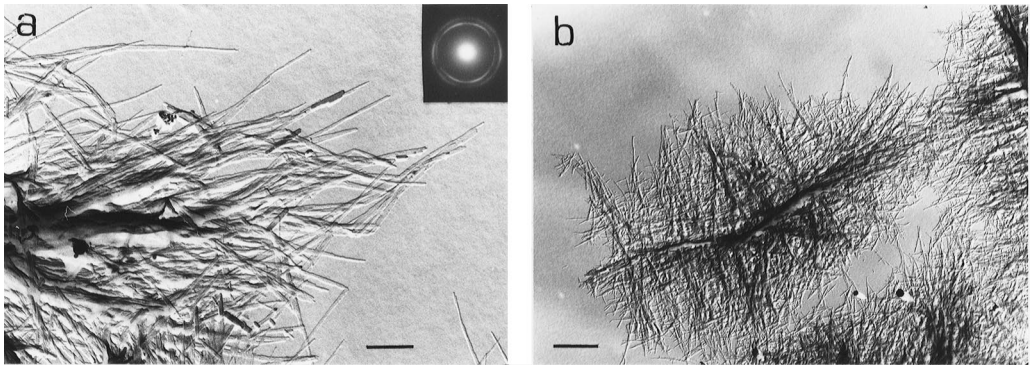

Fig. 1. Lamellar crystals of nylon 4/6 obtained from 2-methyl, 2,5-pentanediol solution at 110°C (a) and at 120°C (b). Note the influence of the temperature on the morphology. Scale bar = 1 μm. A twinned electron diffraction pattern of the crystals is shown as an inset of (a).

Pt–carbon pellets at an angle of 15°. A Philips EM-301 electron microscope operating at either 80 or 100 kV for imaging and diffraction modes, respectively was used.

Crystal mats to be studied by X-ray were prepared by slow filtering and the pattern was recorded under vacuum at room temperature in a modified camera (W.R. Warhus, Wilmington, DE) with a Ni-filtered Cu K_α radiation. X-ray diffraction patterns were recorded at room temperature and at various higher temperatures, up to the melting point, using a hot stage temperature controller. Patterns were internally calibrated with gold or calcite for electron or X-ray diffraction, respectively.

3. Results and discussion

Different morphologies were obtained depending on the crystallization conditions. Thus, nylon 4/6 crystallizes from 2-methyl-2,5-pentanediol solution at 110°C as multilayered lath-shaped crystalline lamellae (Fig. 1(a)) or with a dendritic habit (Fig. 1(b)) when the crystallization temperature is higher (120°C). This dendritic morphology was also observed when crystals were obtained by precipitation methods and is similar to the morphology obtained for nylon 6,4 [17], where the sample appears to be made up of groups of very small needlelike crystals roughly oriented in two directions at right angles.

Table 1
Observed and calculated diffraction spacings d_B (Å) for copolymer 4/6

Index[a]	Calculated	Observed	
		X-ray diffraction[b,c]	Electron diffraction
010	14.80	14.79 m	–
021	5.24	5.29 w	–
200	4.42	4.42 s	4.42 vs
002	3.71	3.71 s	3.71 vs
$\bar{2}02$	2.41	2.39 w	2.40 w
$\bar{1}61$, 261	2.19, 2.18	2.19 w	–

[a] On the basis of a monoclinic unit cell: $a = 9.60$ Å, $b = 14.80$ Å, $c = 8.60$ Å and $\gamma = 67°$.

[b] Abbreviations denote intensities: vs: very strong; s: strong; m: medium; w: weak.

[c] The values shown correspond to a mat pattern.

The same electron diffraction pattern was obtained irrespective of the crystal suspension preparation. Fig. 1(a) shows also the usual electron diffraction diagram obtained from the nylon 4/6 lamellar crystal. Diffraction signals are arched which indicate that the diffraction did not occur from an isolated but rather a group of single crystals. Moreover, a composed diagram is obtained in all cases which is in full agreement with the existence of a twinned structure with the composition plane being the 001 plane. The spacings measured in the electron diffraction pattern are summarized in Table 1.

Unfortunately, the X-ray diffraction pattern from the sedimented mat of nylon 4/6 lamellar crystals have a high degree of disorientation (Fig. 2(a)). However, in agreement with the electron diffraction pattern, the characteristic reflections of the α-phase appear to be equatorial, at spacings of 4.42 and 3.71 Å. Medium or weak intensity reflections at 32, 22.0, 16.3, 10.6, 9.2, 7.7 and 6.4 Å are also observed. They agree with the 2nd to 9th orders of a 64 Å basic spacing, attributed to the lamellar thickness. The fact that so many orders of diffraction are observed indicates that the lamellar width is fairly constant, as happens in other nylons [18]. Comparison of the d_{010} value and the lamellar thickness (deduced from both X-ray diffraction and the shadow of the crystals in the electron micrographs) shows that there are only four crystallographic repeats along the chain direction, in agreement with the study on the long spacing of polyamides reported by Dreyfuss [19]. A spacing of 2.19 Å related to some *h*6*l* reflections is also characteristic and points out to an extended conformation that will enhance the intensity of the 6th layerline. All experimental data agree (Table 1) with unit cell of parameters $a = 9.60$ Å, $b = 14.80$ Å, $c = 8.06$ Å and $\beta = 67°$. Note the spacing at 5.29 Å (Fig. 2(a)), indexed as the 021 reflection which is an indication of a unit cell constituted by two sheared sheets as postulated in the α form of nylon 6. On the other hand, the *c* parameter is equivalent to the sum of the length of both nylons 4 and 6 repeat units. In fact, the resulting unit cell fall between the dimensions of those reported for nylons 4

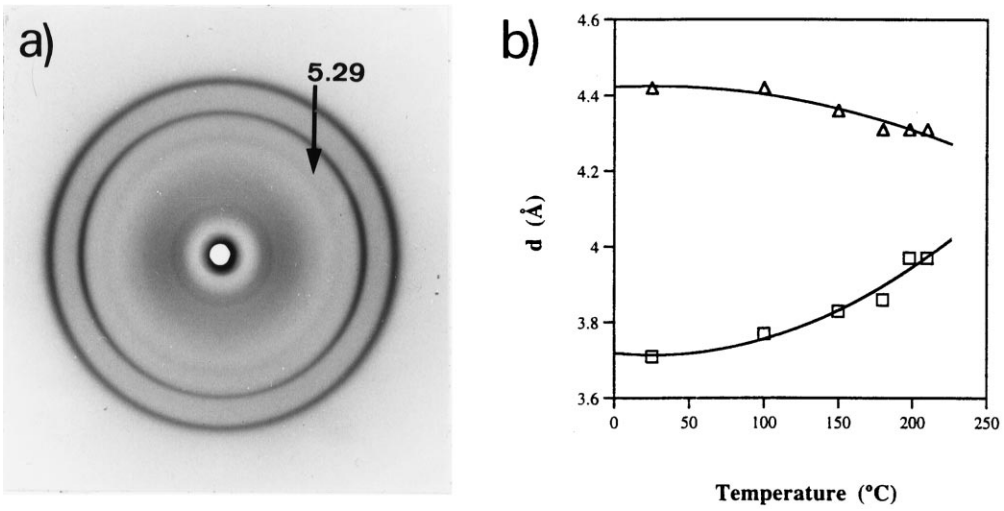

Fig. 2. (a) Wide-angle X-ray diffraction pattern from a mat of sedimented crystals of nylon 4/6 which were obtained at 110°C. Two equatorial reflections at 4.42 and 3.71 Å can be observed. (b) Graph showing the variations in spacing of the two equatorial X-ray diffraction signals on heating nylon 4/6 crystals from room temperature.

[1] ($a = 9.71$ Å, $b = 12.25$ Å, $c = 8.31$ Å and $\beta = 63°$) and 6 [2] ($a = 9.56$ Å, $b = 17.24$ Å, $c = 8.01$ Å and $\beta = 67.5°$).

A distortion of the α form is produced when the temperature increases, since the spacings of the equatorial diffraction signals vary (Fig. 2(b)). Similar to other nylons, as the temperature increases the 4.42 Å spacing decreases whereas the 3.72 Å spacing increases. At higher temperatures the lattice spacings almost converge to a single reflection but two distinct spacings can always be identified. An identical behavior was seen for nylons 4 [1] and 6 [20].

Spherulites (Fig. 3) grown from the melt at different temperatures, between 180 and 200°C, showed that a positive birrefringence was developed in most cases and so, hydrogen bonds were established in the radial directions. However, at 195°C a small amount of negative spherulites together with positive spherulites could be observed. In all cases, the X-ray diffraction pattern of the different spherulitic films showed again the characteristic signals of the α-form.

The γ-form was difficult to obtain since only appeared after a iodine–potassium iodide solution treatment. Thus, new signals at spacings of 14.00, 7.00 and 4.15 Å (Fig. 4(b)) which agree with a monoclinic unit cell of parameters $a = b = 4.79$ Å, c (chain axis) $= 14.00$ Å and $\gamma = 120°$ could be observed. The c parameter indicates a shortening around 0.4 Å per amide group from the extended conformation, as is usual in other nylons.

In conclusion, the α-form is the most stable structure found in the nylon 4/6 copolymer as might have been expected for an even nylon with low number of methylenes. In fact both, the monoclinic structure and the behavior on heating observed in the copolymer are very similar to those reported for the related homopolymers nylons 4 and 6.

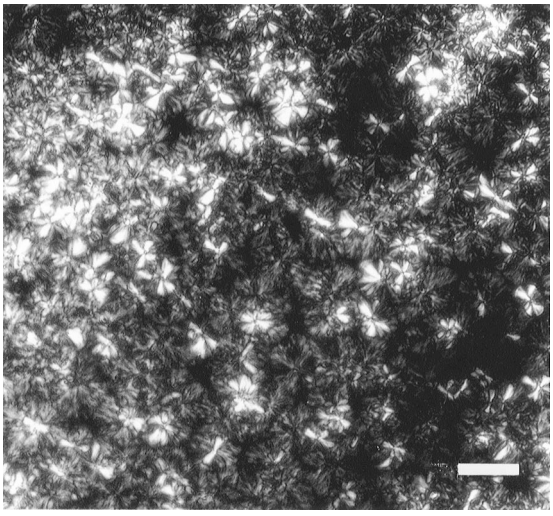

Fig. 3. Photomicrograph of nylon 4/6 positive spherulites growth at 195°C after fusion of the polymer. Scale bar 50 μm.

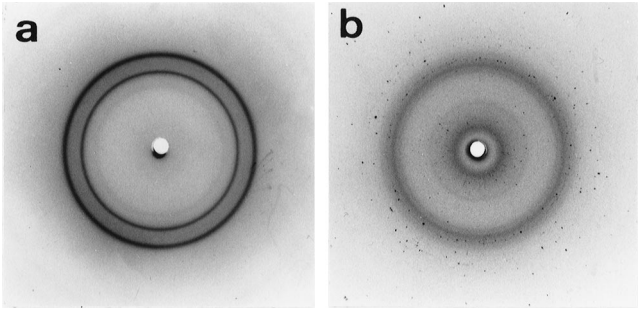

Fig. 4. (a) Wide-angle X-ray diffraction pattern from the polymer powder where the characteristic diffraction signals of the α-phase are observed. (b) X-ray diffraction pattern from the sample after the iodine-potassium iodide solution treatment. In this case weak signals arising from the α-form are also observed.

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References

[1] Bellinger MA, Waddon AJ, Atkins EDT, Macknight WJ. Macromolecules 1994;27:2130.
[2] Holmes DR, Bunn CW, Smith DJ. J Polym Sci 1955;17:159.
[3] Kinoshita Y. Makromol Chem 1959;33:1.
[4] Tsuruda M, Arimoto H, Ishibashi M. Chem High Polymers (Jpn) 1958;15:619.
[5] Ziabicki A, Kedzierska K. J Appl Polym Sci 1959;2:14.
[6] Ziabicki A. Kolloid Z 1960;167:132.
[7] Vogelson DC. J Polym Sci A 1963;1:1055.
[8] Kehayoglou AH. Eur Polym J 1983;19:183.
[9] Kehayoglou AH, Arvanitoyannis I. Eur Polym J 1990;26:261.
[10] Puiggalí J, Muñoz-Guerra S, Subirana JA. Polymer 1994;35:1291.
[11] Bermudez M, Puiggalí J, Muñoz-Guerra S. Macromolecules 1994;27:6325.
[12] Franco L, Xenopoulos A, Subirana JA, Puiggalí J. J Polym Sci, Polym Chem 1995;33:727.
[13] Gross E, Heienhofer J. The peptides, vol 1. New York: Academic Press, 1981.
[14] Bergmann M, Zervas L. Chem Ber 1932;65:1192.
[15] Kovacs J, Giannotti R, Kappor A. J Am Chem Soc 1966;88:2282.
[16] Abu-Isa I. J Polym Sci A 1971;9:199.
[17] Jones N, Atkins EDT, Hill MJ, Cooper SJ, Franco L. Macromolecules 1996;29:6011.
[18] Subirana JA, Aceituno JE. Macromol Symp 1996;102:317.
[19] Dreyfuss P. J Polym Sci, Polym Phys 1973;11:216.
[20] Brill RJ. Prakt Chem 1942;161:49.