Aliphatic polyamides (nylons): Interplay between hydrogen bonds and crystalline structures, polymorphic transitions and crystallization

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Abstract
Aliphatic polyamides (nylons) constitute a family of polymers with outstanding properties and multiple applications. Despite the intensive research studies carried out with nylons, there are still multiple unsolved questions concerning crystallization processes, crystalline structures, polymorphic transitions, and crystalline morphologies. Constrains imposed by the strong intermolecular interactions affect the amorphous state, the rigid amorphous phase, the molecular folding, the morphology and obviously the crystalline structure. Some of these relevant points are discussed in the present work.

KEYWORDS
Brill transition, crystalline structures, crystallization, hydrogen bonds, polyamides, spherulites

INTRODUCTION
Aliphatic polyamides, commonly known as nylons, are usually obtained from polycondensation reactions between diamines and dicarboxylic acids or their derivatives (nylons XY or AA-BB type). Nylons can also be obtained by both the polycondensation of ω-amino acids and the ring opening polymerization of lactams (nylons X or AB-type).

Polyamides are semicrystalline thermoplastics with outstanding mechanical properties (e.g., mechanical strength, flexibility, toughness, and durability) and wide applications in distinct areas (e.g., automotive industry, textile sector where nylon was the world’s first synthetic fiber, sportswear products and even medical sector). Thus, nearly 10% of plastics used in modern vehicles correspond to different polyamides. For example, polyamides with more than 10 CH2 groups between adjacent amide groups have excellent properties like toughness, low water absorption, and good dimensional stability to be employed as automobile hoses. In general, nylons can be considered as fossil-based plastics, although nowadays great efforts have been focused on the production of bio-based polyamides as those based on castor oil as a natural source (e.g., nylon 11, Rilsan®), and those derived from cadaverine (e.g., nylons 54, 56 and 510), a natural diamine that can also be produced at large scale by biotransformation of lysine using recombinant Escherichia coli.5

Capability of amide groups to form strong intermolecular hydrogen bonding interactions is the main reason of the high thermomechanical performance of polyamides that contrasts with the weaker properties found for example in polyesters having similar repeat units (i.e., those derived by the simple change of the NHCO amide group by the OCO ester group). Thus, nearly 10% of plastics used in modern vehicles correspond to different polyamides. For example, polyamides with more than 10 CH2 groups between adjacent amide groups have excellent properties like toughness, low water absorption, and good dimensional stability to be employed as automobile hoses. In general, nylons can be considered as fossil-based plastics, although nowadays great efforts have been focused on the production of bio-based polyamides as those based on castor oil as a natural source (e.g., nylon 11, Rilsan®), and those derived from cadaverine (e.g., nylons 54, 56 and 510), a natural diamine that can also be produced at large scale by biotransformation of lysine using recombinant Escherichia coli.5

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Establishment of intermolecular hydrogen bonds is the main driving force that determines the peculiar crystalline structures and
morphologies of polyamides and even their complex structural polymorphism. Seguela\textsuperscript{6} has recently pointed out and discussed the relative difficulty of polyamides to render high degrees of crystallinity despite their high chain regularity, the establishment of strong intermolecular interactions and their usually limited molecular weights (i.e., in the case of polycondensation polymers).

Another specific phenomenon of polyamides resulting from the presence of H-bonds in the molten state is the so-called memory effect upon crystallization.\textsuperscript{6-9} Hydrogen bonds are weaker in the molten state, but some organized domains may persist.\textsuperscript{10} Therefore, a complete fusion usually requires keeping the sample for a significant time at some degrees above the melting point. Furthermore, the indicated domains can behave as homogeneous nuclei promoting crystallization upon cooling\textsuperscript{11} and giving also rise to a low melting entropy.\textsuperscript{12}

2 POLYMORPHISM OF CONVENTIONAL NYLONS

First proposed crystalline structures of aliphatic polyamides correspond to nylons 66, 610 and 6 and were given by Bunn and his group.\textsuperscript{13,14} These structures were based on a sheet arrangement of hydrogen bonded molecular chains that adopted an all-trans minimum energy conformation. Hydrogen bonds were formed along a single direction since a correct geometry between NH and CO groups of neighboring chains could be established. This structure, \( \alpha \)-form, was characterized by X-ray fiber diffraction patterns showing two equatorial reflections at spacings close to 0.440 and 0.380 nm, which were associated to intrasheet and intersheet spacings, respectively. Sheets held together by weak van der Waals interactions and showed a progressive (triclinic unit cell) or recuperative (monoclinic unit cell) shift along the chain axis to minimize dipolar interactions between close amide groups. Accurate experimental information concerning molecular conformation, setting orientation of molecules and relative shifts between neighboring chains could be derived from the crystallographic resolution of small model compounds as performed for example in those constituted by suberamide or sebacamide units (Figure 1).\textsuperscript{15} Obviously, structures having this type of unidirectional hydrogen bonds display highly anisotropic mechanical properties.\textsuperscript{16}

The named \( \gamma \)-form is a second well-known structure of nylons that is also characterized by the arrangement of hydrogen bonds along a single direction.\textsuperscript{17} This structure was initially postulated for odd-odd nylons (i.e., those derived from diamines and dicarboxylic acids having an odd number of carbon atoms), but is also frequent in polyamides with long polyethylene sequences and even it is a second polymorphic form of nylon 6.\textsuperscript{18} This structure can be considered as the result of a near 60° rotation of amide groups from the typical sheet arrangement. Hydrogen bonds can be well established between parallel chains (when the polymer is directional) giving rise to a pseudohexagonal packing (equatorial reflection close to 0.415 nm) and a slightly shorter chain repeat length. CO and NH groups are nearly collinear in the \( \gamma \)-form in contrast with the slight deviation of linearity postulated for the \( \alpha \)-form (i.e., see that amide groups do not lie exactly in the zig-zag plane of molecular chains in Figure 1).\textsuperscript{14}

Therefore, it has been suggested that the \( \gamma \)-form has stronger hydrogen bonds than the \( \alpha \)-form, a feature that is in agreement with FTIR and NMR observations\textsuperscript{19} but that is controversial when computation data are considered.\textsuperscript{20} In general, thermodynamic stability between \( \alpha \) and \( \gamma \) forms is similar (i.e., nylon 6\textsuperscript{21}) and consequently one or the other form can be obtained depending on specific solvent (e.g., exposition to iodine solutions\textsuperscript{19}), thermal or mechanical treatments, processing conditions (e.g., spinning rate and postdrawing treatments\textsuperscript{22}), incorporation of fillers and nucleating agents,\textsuperscript{23} mixing with other polymers,\textsuperscript{24} and logically on the selected crystallization conditions (e.g., solvent, substrate and temperature for solution, epitaxial and melt crystallizations). Note also that the \( \gamma \)-form lacks a truly hexagonal symmetry since for example hydrogen bonds are established along a single direction and not along three directions at 60°. In addition, parallel and antiparallel chains exist in the unit cell and the previously indicated reflection can be split in two close reflections at spacings slightly higher and lower than 0.415 nm.

A mesomorphic form highly similar to the \( \gamma \)-form is also commonly found in nylons. This form has been described with different names in the literature (e.g., \( \alpha ' \), \( \delta \), \( \gamma ' \)) and usually appears when the...
polymer is fast cooled from the melt state. In this case, hydrogen bonds seem to be completely established but randomly distributed along the chain axis and according to three different crystallographic planes that gives rise to a hexagonal packing.\(^{25}\)

From an experimental point of view, it is difficult to distinguish between \(\gamma\) and \(\alpha\) forms since both are characterized by X-ray reflections around 0.415 nm. Quantification of the ratio between the two polymorphs is problematic since it depends on the appropriate choice of the deconvolution parameters. Nevertheless, the metastable \(\alpha\) form usually experiments a transition on heating towards the \(\alpha\) form at moderate temperatures (e.g., 100–120°C for nylon 6\(^{26,27}\)), which is not characteristic for the \(\gamma\) form. This transition could even be detected in the corresponding DSC heating runs.\(^{26}\) \(\gamma\) and \(\alpha\) forms of nylon 6 have clearly been distinguished from well differentiated FTIR bands\(^{27,28}\) and also from confocal Raman microspectroscopy.\(^{29}\) Thus, main distinction is obtained from the local scale conformation data derived from vibrational spectroscopy and not from the long-range order deduced from diffraction profiles.

Probably, one of the most problematic points concerning the polymorphism of nylon corresponds to the prediction of the conditions at which structural transitions take place. This point is aggravated by the multiple names that the different crystalline structures have received along the time, the great diversity of conditions tested, and by the great variability of observed behaviors that probably needs to be properly categorized in order to discard non-representative differences. In general, a treatment with aqueous iodine-potassium iodide solutions favors the conversion of the \(\alpha\) form into the \(\gamma\) form,\(^{30}\) a process that could be reversed by exposition to phenol in the case of nylon 6. For this polymer, it has also been described that the weight fraction of the \(\gamma\) form decreased with increasing temperature and crystallization time.\(^{31}\) Transitions of nylon 12 have also extensively studied. This polymer mainly crystallizes in the \(\gamma\) form but the sheet structure can also be obtained by drawing at high temperature and high-pressure crystallization.\(^{32}\)

Polyamides having \(\alpha\) or \(\gamma\) structures crystallize in solution given rise to lath-like morphologies, which preferential growth direction becomes aligned to the single hydrogen bonding direction. This feature is clearly distinctive from the rhomboic crystals usually obtained with polyesters having similar repeat units but displaying only dipolar interactions.\(^{33}\) Lamellar chain folding could take place between anti-parallel chains belonging to the polyethylene sheets (i.e., between hydrogen bonded and non-hydrogen bonded chains for the \(\alpha\) and \(\gamma\) structures, respectively. Note that only in the first case hydrogen bonding and folding directions coincide).\(^{34}\) Interestingly the thickness of the lamellae of polyamides can be driven by the topology of hydrogen bonds as postulated by Dreyfuss et al.,\(^{35}\) although folds implying hydrogen bonds have also been proposed.\(^{36}\) It should also be pointed out that the low crystallinity of polyamides obtained from quiescent melt requires a high thickness of the amorphous layers in the lamellar stacks. Therefore, chains emerging from lamellar surfaces should follow a quite large trajectory before to have an opportunity to reenter in the lamellae, a feature that has low probability to occur just in the neighboring chain segment.\(^{6}\)

3 | STRUCTURES WITH DIFFERENT HYDROGEN BOND DIRECTIONS

Peculiar crystalline structures have been determined for nylons when they incorporate special chemical units where a single methylene group becomes placed between two amide groups. This is the case of nylons derived from monomethylenediamine, malonic acid, and glycine units due to their conformational preferences. In the first case, the monomethylen bisamide residue adopts a gauche conformation and, as a consequence, its two NH groups point out at 180° instead of the 0° expected for an all trans conformation. Structures with different hydrogen bonding directions were postulated depending on the number of methylene groups in the dicarboxylic unit (i.e., a single direction for an even number and three directions for a low odd number).\(^{37,38}\) More interestingly, hydrogen bonds were distributed along three directions in copolymides with regularly alternating glycine and \(\omega\)-amino acid units.\(^{39–41}\) The final molecular arrangement is related with the typical polyglycine II (PGII) structure,\(^{42}\) and represents a clear disruption of the standard structure of nylons based on the stacking of hydrogen bonded sheets. Trigonal or hexagonal lamellar morphologies (Figure 2A) were found for these copolymides depending on the parity of the \(\omega\)-amino acid. Small model compounds based on glycine residues linked to aminohexanoic acid\(^{43}\) and different dicarboxylates\(^{44}\) demonstrated that CONH-CH\(_2\)CO and NHCH\(_2\)-CONH torsional angles were close to 77° and –145°. Therefore, the incorporation of glycine units into both nylons X and nylons XY could induce new structures related to PGII.

Conformational preferences of malonamide residues (i.e., CONH-CH\(_2\)CO and NHCH\(_2\)-CONH) torsional angles in the 100°–140° interval) cause that consecutive amide groups of a nylon XY chain rotate near 120° respect to the chain axis.\(^{45,46}\) Therefore, new structures with two defined hydrogen bonding directions were postulated for the first time. This significant feature was again demonstrated by the resolution of small model compounds having malonamide units.\(^{46–48}\)

Similar structures with two hydrogen bonding directions have also been postulated for nylons having longer polymethylene sequences and odd dicarboxylic or diamine units (i.e., those named as even-odd and odd-even nylons, respectively). These polyamides usually crystallize in solution giving rise to diffraction patterns with equatorial reflections close to the characteristic ones reported for conventional nylons (e.g., even-even) with a sheet structure. The peculiarity of the presence of an odd diamide unit lies in the fact that only 50% of hydrogen bonds can be established if the molecular chain adopts an extended conformation (Figure 2C). Therefore, a slight conformational deviation and a more significant change on the packing arrangement was postulated as explained in the caption of Figure 2C.

New structures with two hydrogen bonding directions have specifically been reported for different odd dicarboxylic acid derivatives (e.g., nylons 65,\(^{49,50}\) 125,\(^{51}\) 47,\(^{52}\) 49,\(^{53}\) 69,\(^{54,55}\) 89\(^{56}\) and 129\(^{56}\) that are constituted by glutarate, pimelate and azelate residues) as well as for odd diamine derivatives (e.g., nylons 56\(^{57,58}\) and 510\(^{59}\) based on cadaverine). Polyoxalamides can be considered as nylons derived from a
two-carbon dicarboxylic acid. Probably, the high rigidity of the planar oxalamide unit (NHCOCONH) imposes greater constrains in the hydrogen bonding geometry and consequently experimental results attained with nylon 92 (note that is another example of an odd-even sequence) may be the clearest evidence of the indicated structures with two hydrogen bonding directions.60 This geometry was also extrapolated to odd-odd nylons (e.g., nylon 55) where the rhombic lamellar morphology (Figure 2A, bottom) could be well explained.61 Finally, it should be pointed out that similar models have also been formulated for copolyamides based on diaminobutane and odd dicarboxylic acids with highly different lengths (e.g., glutaric and azelaic acids).53

4 | BRILL TRANSITION: RECENT ADVANCES

Polyamides can show on heating and just before fusion a solid state crystalline transition, which is known as the Brill transition.62,63 This structural change was firstly described with conventional nylons and consisted in a change from their sheet structure to a pseudohexagonal arrangement.64 The Brill temperature ($T_B$) was defined as the lowest temperature at which intersheet and intrasheet distances between neighboring chains become equal. Despite the multiple investigations carried out, the nature of this transition remains unclear. Some relevant points are the followings: (a) A hysteresis effect on heating and cooling is observed (i.e., $T_B$ is detected at a lower temperature in the cooling run).65 (b) A significant peak associated to the transition is rarely detected, that is enthalpies are practically negligible. Nevertheless, small endothermic peaks have explicitly been reported in some cases.65,66 (c) The transition is strongly dependent on the molecular structure and crystallization conditions (i.e., $T_B$ can vary over a great temperature range for a given nylon). (d) Interactions between amorphous (i.e., folds, rigid amorphous and amorphous components) and crystalline phases may have a relevant role in the transition.68,70 Some distinct explanations on the Brill transition have been formulated67,70,71: (a) Anisotropic thermal expansion, (b) Existence of a first-order transition together with second-order elements and (c) Thermally induced mobility of aliphatic moieties. Probably, this is the most accepted explanation since the conformational disorder caused by libration motion of aliphatic segments can justify the observed pseudohexagonal packing. In fact, several experimental evidences supported a high chain mobility and large amplitude torsional motions at high temperatures in the crystalline phase of nylons.72 Some authors have suggested a simple rotation of amide groups from a single direction (i.e., the sheet-like arrangement) to three different directions. However, this interpretation was contradictory with NMR experiments that indicated the scarce change of amide mobility and therefore the stability of the initial hydrogen bonding arrangement.73–76 In any case, an isotropic distribution of H-bonds before fusion has not been unambiguously demonstrated.77
Reverse Brill transitions have been observed for different nylons (e.g., nylon 4678) when they were submitted to a mechanical stretching. In this case, the single reflection associated to an initial \( \gamma \)-form was split in the two characteristic reflections of the sheet structure. A conformational change that leads to the extended molecular conformation seems logical, but uncertainties concerning disruption and reforming of hydrogen bonds when amide groups became untwisted require explanations at a molecular level.

Interestingly, the transformation of even-even nylons has recently been described as a two-step process with an intermediate state based on a pleated/rippled sheet structure (i.e., similar structures to those postulated by Pauling and Corey\(^79,80\) for protein sheet structures).\(^69\) Note that the rippled sheet arrangement is characteristic of the named PGI structure of polyglycine (i.e., nylon 2).\(^81\) These two steps appear merged in most nylons, being consequently difficult to experimentally separate the two events.

It should be pointed out that highly complex transitions have also been described with nylons having the two-hydrogen bonding structure. Specifically, in this case, intermediate structures (Figure 3) have been observed before to reach \( T_B \). A gradual evolution of the twisting between amide groups was suggested.\(^53\) In fact, great uncertainties exist between the integrity of hydrogen bonds during the heating process, being less and less accepted the initial hypothesis based on a disruption of initial bonds and the establishment of new random bonding distributions along three directions.\(^63,74\)

New hypotheses about the Brill transition of even-even and even nylons indicate that the intrasheet hydrogen bonds are basically preserved during heating, although some intersheet hydrogen bonds are eventually formed at temperatures close to fusion, justifying the final pseudohexagonal arrangement.\(^67\)

FIGURE 3  (A) Evolution during heating of the WAXD profiles of melt crystallized nylon 49. Inset shows a different orientation of the 3D representation to clarify the temperature evolution of the main reflections. (B) Evolution of the spacings of the main reflections during the cooling run. Full and empty symbols indicate well-defined and intuited reflections, respectively. The temperatures at which structural transitions occur are indicated with vertical lines. Reflections corresponding to three different structures (I, II and III) are indicated with red, green and blue symbols. Reproduced from Reference [53] with permission

5  |  CRYSTALLIZATION FROM THE MELT: SPHERULITES AND HYDROGEN BONDING

Crystallization from the melt under a non-oriented temperature gradient lead to a radial growth of lamellar crystals in all directions from central nucleation sites. These aggregates, named spherulites, display variable diameters (from micrometers to millimeters) and textures (e.g., fibrillar and ringed) depending on the specific crystallization conditions (e.g., degree of undercooling, cooling rate, polymer structure and presence of nucleating agents). The anisotropic character of lamellar crystals led to a characteristic birefringence that is detected when spherulites are viewed between crossed polarizers in an optical microscope (i.e., typical Maltese cross pattern). Positively and negatively birefringent spherulites can be distinguished (when visualized using a red tint plate) depending on the direction of the major refractive index (radial or tangential for positive or negative birefringence, respectively). Usually, the direction with the higher refractive index coincides with the molecular chain orientation (i.e., the spherulite tangential direction according to the radial disposition of the constitutive lamellae).

Polyamides may be in some cases an exception to this general behavior since the refractive index becomes superior in the direction where hydrogen bonds are established. In this way, spherulites of even and even-even nylons having a typical sheet structure with a single hydrogen bonding direction (i.e., the \( \alpha \) form) may display a positive or a negative birefringence depending on the disposition of sheets (i.e., positive for radial and negative for tangential).\(^32,83\) Systematic observations indicated that a negative birefringence was only observed when crystallization was performed under a very low undercooling degree,\(^84\) a result that
differs from the usual negative birefringence of related polyesters (i.e., similar repeat units but unable to form hydrogen bonds due to the change of NHCO groups by COO groups). Despite the extensive investigations that have been performed, there are still different concerns relative to the optical properties of nylon spherulites that need to be clarified.

a. The model postulated for Lovinger\textsuperscript{82,83} cannot explain how a slight change on the crystallization temperature has a dramatic effect on the orientation of constitutive sheets of polyamides having the conventional $\alpha$ form. Therefore, a higher complexity for the lamellar stack model seems to be required.

b. Conventional nylons exhibiting polymorphism (e.g., nylon 6) crystallize from the melt according to kinetic conditions since thermodynamic differences are low. Therefore, the applied cooling rate becomes determinant since it can favor either the slow growing of the $\alpha$ form or the fast growing associated to the $\gamma$ form.\textsuperscript{6,85} Note that spherulites should have a predominant $\gamma$ structure, at high temperatures, which can be susceptible to be transformed into an $\alpha$ phase on cooling. Changes on the hydrogen bonding direction (from intersheet to intrasheet) may occur but scarce discussion is nowadays available about the correlation between changes on the birefringence sign and the directions where hydrogen bonds are established.

c. New interpretations concerning negatively birefringent spherulites from even-even polyamides must be considered. These hypotheses formulated by Lotz et al.\textsuperscript{86} indicate the existence of scrolled lamellae that lead to hydrogen bonds established along an oblique direction to the spherulite radius. Moreover, spherulites seem to be complex since two crystalline entities with competitive properties (e.g., birefringence and unit cell orientation) are involved: the scrolled lamellae that are firstly formed and the subsequently crystallized in-filling material.\textsuperscript{86}

d. Odd-even nylons display a peculiar temperature dependence of the birefringence sign since it changed in the sequence positive-negative-positive when crystallization temperature was decreased (Figure 4).\textsuperscript{58} By contrast, conventional nylons showed a change from negative to positive birefringence with decreasing temperature. Furthermore, some reversibility of the birefringence sign with temperature has also been described for some even-odd nylons.\textsuperscript{52} Non-isothermal experiments showed also changes on birefringence during cooling and heating rates that were dependent on the corresponding rate.\textsuperscript{50,52} These features are peculiar and may be consequence of the constrains imposed by the two-hydrogen bonding geometry or even by the existence of complex structures as pointed out in the previous point.

FIGURE 4   (A) Optical micrographs of nylon 56 spherulites isothermally crystallized at the indicated temperatures. (B) Optical micrograph of a nylon 56 spherulite that was isothermally crystallized at three successive temperature steps, which reveals the clear change of birefringence. Low birefringent regions are hardly distinguished when black and white micrographs are taken (see the intermediate zone in the inset). Copyright 2010. Reproduced with permission from Elsevier

6 | PERSPECTIVE AVENUES AND CONCLUSIONS

Despite the high commercial applications of polyamides and the intensive research work that has been performed about the improvement of their properties (e.g., development of nanocomposites through addition of nanoclays) and also on the preparation of bio-based materials, there are several unsolved aspects that affect the crystallization process and the derived crystalline structures. It is relevant that most of the problematic issues were firstly studied in the middle-end of the past century, but in general hypothesis concerning molecular arrangements and in particular, hydrogen bonding intermolecular interactions are still being reformulated.

The relatively low crystallinity of polyamides, the role of hydrogen bonds in the amorphous phases and the relation between the rigid amorphous phase and the crystalline domains need special attention as well as the folding of molecular chains in the lamellar stacks. Geometrical restrictions of hydrogen bonds may affect the lamellar...
thickness, and the development of long loose loops in the lamellar surface may have a clear influence on the capability of polyamides to crystallize in a determined crystalline structure (i.e., α or γ form).

Efforts are also needed to unify the denominations of the different crystalline structures, trying also to discern the conditions (e.g., undercooling degree, cooling rate, annealing treatment) that favor a determined structure in function of the characteristics of the repeat unit (e.g., parity and length of the polymethylene sequences). Thermal transitions between polymorphs require greater attention and specially the role of mesophases.

The crystallographic resolution of small model compounds has provided useful information about new structures with three and two hydrogen bonding directions. These appear in polyamides having particular residues (e.g., glycine and malonamide) and also on polyamides with constraints derived from the peculiar hydrogen bonding geometry. The study of the morphology of lamellar crystals appears also as a fundamental tool to discern about the intermolecular interactions.

Surprisingly, the knowledge of the nature of the Brill transition is still in an embryonic state, although some of the formulated hypotheses can be discarded. The idea of a complex process involving intermediate states is attractive for conventional polyamides as well as for structures displaying multiple hydrogen bonding directions.

Typical spherulites developed from the melt state show different optical properties depending on the crystallization temperature. The sign of birefringence and its relation with the crystalline structure and the interplay between morphology and the establishment of strong intermolecular hydrogen bonds.

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