

Explanation of the epitaxial deposition of nylon 66 on carbon fibres and its extension to isotactic polypropylene

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This work demonstrates epitaxial relationships between the crystal structure and growth faces of nylon 66 on high-modulus graphite fibres and explains observations in the literature. It also extends the concepts and applies them to the more complicated system of isotactic polypropylene (i-PP) on highly graphitic carbon fibre structures. The proposed arrangements are based upon matching a polymer's crystalline structure, along its growth face, to possible graphitic structure dimensions along carbon fibre surfaces. The matches involving substrates and overgrowths in both cases are nearly perfect, being within 5%, thus accommodating favourable low-energy positioning of the polymer's crystal structure. The relationship involving nylon 66 allows this polymer's chains to orient along fibre surfaces between graphite basal plane edges. This epitaxial relationship is consistent with the literature and is used to predict the orientation of crystalline i-PP chains when deposited on carbon fibres. To preserve a low-energy epitaxial relationship, the i-PP chains are suggested to be oriented some 78° across stepped graphite basal plane end surfaces and are most likely oriented at 78° to the fibre direction. Additional discussion, arising from complexities in the case of i-PP, concerns the relation between the number of possible polymer nucleation orientations and the nucleating ability of a given fibre surface. Copyright © 1996 Elsevier Science Ltd.

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Introduction

Transcrystalline growth of nylons and isotactic polypropylene (i-PP) on higher modulus, graphitic carbon fibres has been studied by a number of research groups^{1–5}. Using X-ray diffraction, nylon 66 chains were shown to orient along the fibre direction by Frayer and Lando². Bless and Lando³ have also shown (using Raman spectroscopy) that when considering the nucleating ability of two carbon fibres with the same modulus, nylon 66 orients upon fibres that exhibit asymmetric vibrations of basal plane edges, and does not orient on fibres lacking plane end vibrations. This special behaviour has never been adequately explained and is undoubtedly related to the possible epitaxial relations between the two materials.

In the case of i-PP, Hobbs⁴ postulated, using pictorial scale models, that certain higher modulus poly(acrylonitrile) carbon fibres, presumed to possess an exposed basal plane surface structure (without presenting plane ends), might support the epitaxial nucleation of i-PP on the wider basal plane surfaces of such fibres. Contrary to the work by Hobbs, Greso and Phillips⁵ have presented evidence showing that i-PP nucleation on graphitic, pitch-based carbon fibres occurs epitaxially along basal plane edges. However, to date, the dimensions involving epitaxial deposition of nylon on carbon fibres and the orientation of the i-PP chains relative to a fibre's direction, have not been determined. Data still have to be

reconciled with both the epitaxial relationships between polymer chains nucleating upon carbon fibre surfaces and the polymer chain orientations relative to a carbon fibre's draw direction.

After a brief introduction to epitaxy and the previous results prompting this investigation, this work involves a discussion of carbon fibre surfaces and a presentation of how a certain type of graphitic-like surface could accommodate the direction and epitaxial deposition of nylon 66 on carbon fibres. This model is then used as a basis for explaining the epitaxial deposition of i-PP that permits prediction of the i-PP chain direction on the surfaces of graphitic carbon fibres. Further discussion concerns the implications of the ways in which nylon 66 and i-PP are believed to nucleate on carbon basal planes.

Epitaxy

Epitaxy involves the deposition of one material on the surface of another so that the crystal structure of the depositing overgrowth material can develop at or near the lowest energy state possible at the crystallization temperature. It generally involves two surface dimensions for each material comprising the interface. Wittmann and Lotz have described the degree of disregistry, Δ_{eptx} , for the dimensions involving polymer nucleation on substrates as a percentage, per equation (1)⁶. In equation (1), d represents the distance between lattice planes or distances between molecules (or folded polymer chains) at the surfaces of the substrate and the overgrowth. For polymer molecules, Wittmann and Lotz determined the limit of acceptable epitaxial disregistries to be about 10%⁶. Thus, epitaxially coordinated interfaces should

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involve dimensional matches of about 10% or less.

$$\Delta_{\text{eptx}} = 100(d_{\text{overgrowth}} - d_{\text{substrate}})/d_{\text{substrate}} \quad (1)$$

Wittmann, Lotz and co-workers⁷⁻⁹ demonstrated the validity of the equation by showing that polymer nucleation, in the absence of a thermal gradient or melt orientation, initiates epitaxially upon a compatible substrate. Using transmission electron microscopy, they proved this relationship in order to explain the occurrence of epitaxial nucleation of chain-folded, lamellar polyethylene (PE) on a number of different organic substrates and also on *i*-PP^{8,9}. Their work showing lamellar PE growth on oriented *i*-PP surfaces also demonstrated the distances between polymer chains to be the most important dimension involved in polymer epitaxy. Petermann and Xu¹⁰ and Lee and Schultz¹¹ have also observed this ordered morphology after nucleating PE on oriented *i*-PP films.

Thus, if the crystalline dimensions of a semicrystalline polymer's growth front are known, then one can predict polymer nucleation on an epitaxially compatible material by knowing the material's crystalline surface structure. Greso¹² has used this approach to facilitate finding a previously unrecognized nucleating agent for poly(ether ether ketone).

There is, however, one more constraint to consider when attempting to produce the epitaxial matches between the chain-folded crystal structure of a polymer on a substrate—in addition to the 10% limit on spacings between polymer crystal repeat distances. When addressing the observations noted by Peterman and Xu, concerning the temperature dependence of PE epitaxially nucleating on oriented *i*-PP¹⁰, Greso and Phillips determined that the dimensions of the contact area available for lamellar deposition is also an important factor in controlling whether or not epitaxy will occur between a substrate and a polymer overgrowth¹³. Using the lamellar thicknesses of *i*-PP and PE, found as a function of crystallization temperature, Greso and Phillips showed a clear correlation between the minimum length available for polyethylene deposition across *i*-PP lamellae and the temperature-dependent nucleation and appearance of a crosshatched growth of PE lamellae on oriented *i*-PP. Greso and Phillips⁵ subsequently demonstrated that this same phenomenon occurred in *i*-PP transcrystalline growth on graphite fibres. The amount of columnar growth of polymer lamellae, i.e. that growing perpendicularly away from the substrates¹⁴, increases very clearly with increasing carbon fibre crystalline domain size.

However, even though transcrystalline growth indicates the perpendicular growth of lamellae away from nucleation-favourable surfaces, it does not indicate how polymer chain stems initially orient against such a surface. The present work explains the relation between surfaces of carbon fibres and the transcrystalline growth of polymers for polymers that have two possible (distinct) types of growth face.

Graphite surfaces: basal plane edges

When considering how basal planes are exposed at the surface of graphitic carbon fibres, it is of interest to note the work of Greso and Phillips⁵, Liu and Loper¹⁵ and of Yamada and Tobisawa¹⁶. Using scanning electron

microscopy (SEM), Greso and Phillips showed that there is an apparent tendency for the planes of the higher heat-treated mesophase pitch fibres to stack in a manner similar to the edges of a slanted deck of playing cards, with the basal planes stacking perpendicular to the fibre direction. This type of pitched surface morphology has been shown to resemble the basal plane end morphology of slow-cooled Kish graphite (formed during steel manufacturing)¹⁵ and the graphitic morphology exhibited by synthetic graphite¹⁶. This basal plane edge morphology has been observed more closely by others, using scanning tunnelling microscopy/SEM¹⁷ and SEM¹⁸. Of interest here are the two different ways in which graphitic basal planes can terminate, thereby generating the exposed edges of interest to potential epitaxial developments.

Figure 1 shows the possible arrangements of basal plane edges together with the dimensions along basal planes of graphite. As shown, planes might end with either alternating or pitched slant associations, each having either one of two edge arrangements: zig-zag or niched (also known as 'arm chair'¹⁹). The graphite dimensions in Figure 1 are based upon the crystallographic data presented by Wyckoff for graphite²⁰. By using energy calculations for a number of planar polycyclic structures, Stein and Brown¹⁹ determined that, due to resonance stability, benzyl rings comprising niched surfaces are more stable than benzyl rings comprising zig-zag surfaces. Their work thus provides a fundamental basis for the existence of niched edges at basal plane ends.

Therefore, there is a significant amount of evidence indicating that basal plane edges are at least niched and

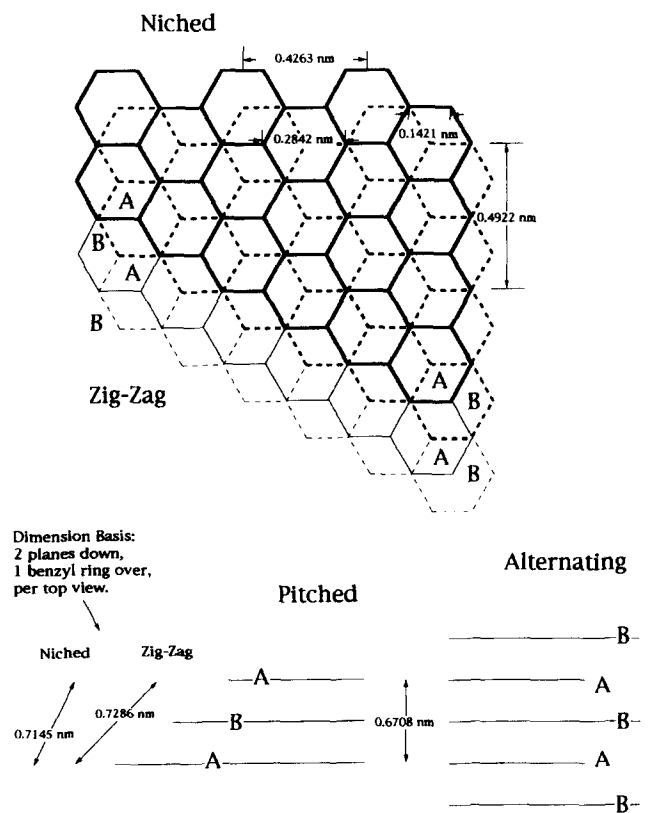


Figure 1 Different spatial arrangements between the various possible basal plane edges of graphite. The basal planes have arranged according to two alternative positions, A and B, corresponding to the highly crystalline case

are likely to be stepped or pitched. Thus, the arrangements of this type of basal plane morphology structure, and its dimensions, are assumed to be the energetically preferred carbon surface. This surface is used for comparing the surface dimensions of graphitic fibres with the growth face dimensions of nylon 66 and *i*-PP in order to determine the epitaxial arrangement and orientation of these polymers' chains along basal plane edge surfaces and fibre directions.

Polymer chain orientation on graphitic plane ends

Nylon 66. On the basis of work by Lovinger²¹, Figure 2 shows a representation of how graphite plane ends could epitaxially nucleate nylon 66. Because of the unusual manner in which nylon 66 grows positive spherulites, and since Khoury¹ has shown positive, birefringent crystal growth to be the preferred orientation of nylon 66 growing from the surfaces of carbon fibres, it is assumed here that nylon 66 crystalline growth involves Lovinger's positively birefringent direction of growth. The epitaxial dimensions for this nylon growth front (shown in Figure 2) on graphitic basal plane surfaces involve the distances between the hydrogen-bonded nylon sheets matched to the distance between the basal planes, as well as multiples of repeating distances along nylon 66 chain stems and along basal plane edges.

The envisaged relationship concerning the deposition of nylon 66 on a graphite surface involves placement of a nylon chain across the 'steps' at the ends of the

stacked basal planes that form the pitched or slanted morphology shown in Figure 2. In this case, the 0.369 nm distance between the nylon chains allows them to align between each graphite sheet while the single-chain length repeat distance is very close to being exactly four times the length of the repeat distance along the niched edge of the stacked basal planes. The percentage difference, Δ_{eptx} , between the substrate and overgrowth dimensions, shown in Table 1, is less than 5% and well within the allowable epitaxial limit of 10%.

It is interesting to note that nylon 66 might also be epitaxially associated with basal plane surfaces and not edges. In such an instance, the 0.369 nm distance between the chains could align along every third benzene ring (4.922 divided by 2 and multiplied by 3) to form a Δ_{eptx} of -0.07% and the 1.72 nm distance along the chain direction could align along four benzenoid rings in a normal position to form a Δ_{eptx} of 0.93%. However, there are three possible chain directions (or six, counting direction reversals) that might develop upon such a surface due to three-fold symmetry along the basal planes, each direction at 60° to any other direction. Alternatively, the pitched basal plane end orientation allows for only one possible nylon 66 chain direction and is therefore consistent with the findings of Bless *et al.*²², Bless and Lando³ and Frayer and Lando², who have shown, using X-ray diffraction, that the *c*-axes for nylon 66 can align along the fibre direction when fibres possess basal plane edges. Thus, a number of different nylon chain directions along carbon fibres would not show a

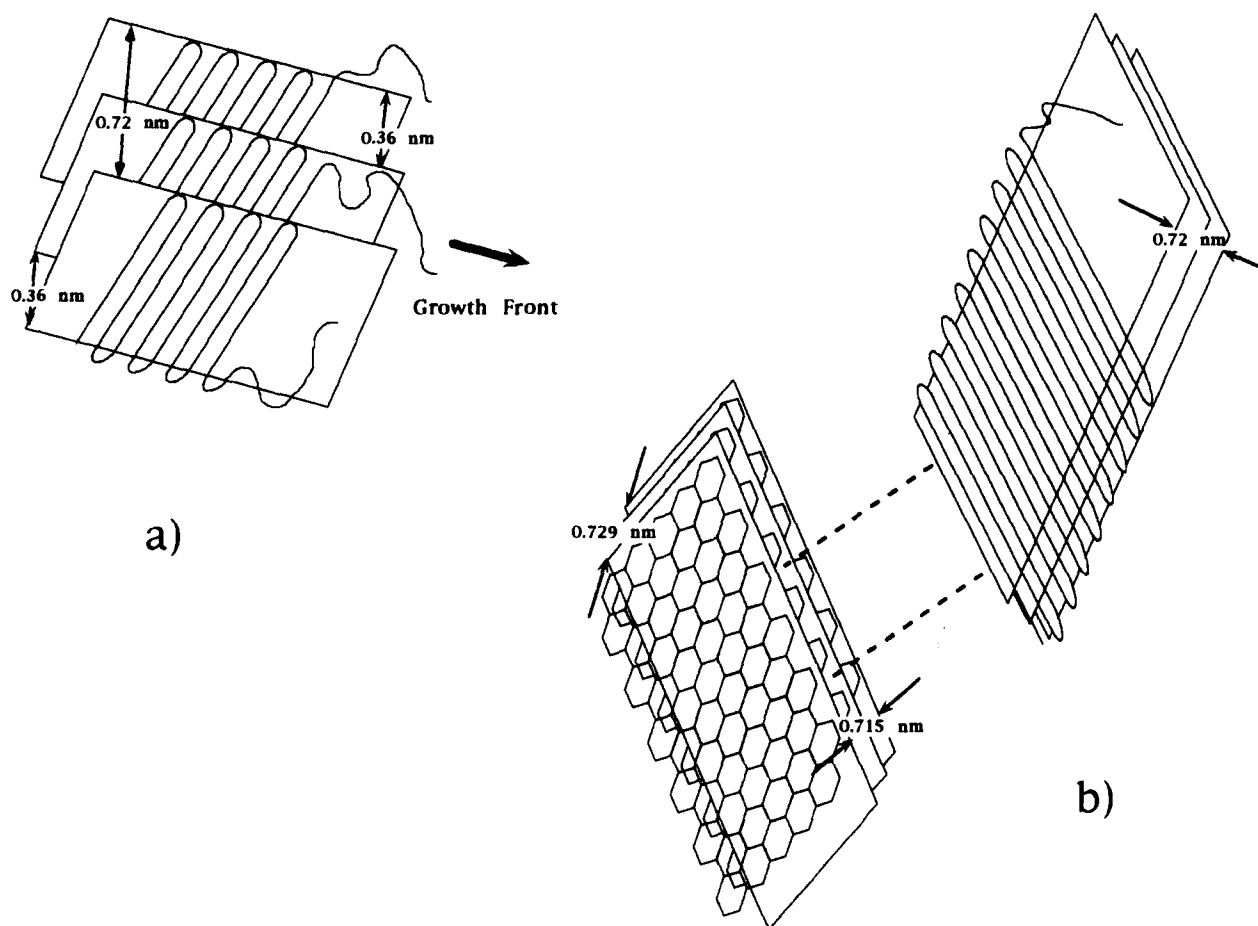


Figure 2 Nylon 66 orientation on basal plane edges. (a) Manner of growth for positively birefringent nylon 66, (b) one possible arrangement of lamellar nucleation in nylon 66 using pitched or stepped graphitic basal plane edges

Table 1 Epitaxial matches between graphite, nylon 66, and alpha *i*-PP

Substrate			Overgrowth	
Spacing (nm)	multiple × spacing	% Mismatch Δ_{eptx} (%)	multiple × spacing	Spacing (nm)
Graphite			alpha <i>i</i>-PP	
Niched				
0.832	1 × (0.832)	2.48	2 × $d(101)$	$d(101) = 0.4244$
0.4263	1.5 × 0.4263	4.93	1 × 0.671	$d(100)/\cos(12.2) = 0.671$
Graphite			Nylon 66	
Niched				
0.7145	1 × (0.7145)	3.40	2 × $d(010)$	$d(010) = 0.3694$
0.4263	4 × (0.4263)	0.87	1 × c	$d(011) = 1.720$

distinct X-ray orientation pattern. In order for the epitaxial nucleation of nylon 66 chains to occur solely along one direction, nylon 66 would have to nucleate on pitched basal plane ends that are normal to, and would have to span, the fibre direction.

Of equal or greater importance is the likelihood that the electron clouds, which exist above and below the conjugated bonds comprising basal planes (the detailed nature of which is generally related to the electrical conductivity of the particular graphite), could discourage plane surface nucleation in favour of plane edge nucleation should it be taking place in an area weak in electron cloud density.

If this approach is correct for nylon 66 and carbon fibres, it should be reasonable to assume that *i*-PP, or any other polymer showing transcrystalline growth on a highly graphitic (or higher modulus) carbon fibre, has some type of preferential epitaxial orientation across or along the ends of the basal planes at the fibre's surface. The reasoning presented for nylon 66 still applies to *i*-PP; however, the epitaxially constrained, estimated orientation of *i*-PP along basal planes is quite different.

Isotactic polypropylene. Using an unusual procedure, Lotz and Wittmann²³ showed that *i*-PP can be crystallized on a PE substrate with a (010) contact plane face and thus this contact face was assumed to prevail when placed in contact with pitched and niched basal plane ends. It is interesting to note that methyl groups protrude from this *i*-PP face. Assuming the (010) plane is in contact with basal plane edges, a representation of how *i*-PP methyl groups could nucleate on stepped graphite plane ends is shown in *Figure 3*.

The polymer chain orientation in *Figure 3* differs from those in *Figure 2* in that the nylon 66 chains are parallel to the graphite plane ends while the *i*-PP chains are oriented so that they lay somewhat perpendicular to the parallel basal planes. The *i*-PP chains are oriented in such a way because the ridges of methyl groups [that stretch across the adjacent *i*-PP chains at an angle of about 43° (ref. 23)] can fit 'into' the angled basal plane end ridges (that stretch across niched, basal plane surfaces). For this to be the case, it would require that the *i*-PP chains be oriented with the chain direction making an angle of about 78° to the carbon fibre direction. This also assumes that most of the basal plane edges along pitch-based carbon fibres are predominantly stacked and oriented so that the ends are stepped and span parallel to the fibre direction.

The hypothesized contact dimensions [stretching across

the *i*-PP (010) plane], involving the *i*-PP (010) plane dimensions in contact with pitched and niched basal plane edges, are shown in *Table 1*. This comparison generates a Δ_{eptx} below 5%, thus being acceptable, but also indicates that the spacings between the rows of methyl groups on *i*-PP chains influence the preferred, initial contact between the depositing *i*-PP chains and the heterogeneous nucleating surface.

Prediction of polymer/fibre contact orientation

Considerations regarding the development of a good epitaxial contact between the fibre and the matrix for nylon 66 and *i*-PP concern the possible directions available to depositing chains. First, the turbostratic nature of carbon fibres necessitates the spreading apart of basal planes from 0.335 to 0.341 nm (ref. 24) and requires a more random association between alternating planes. The small distance difference, however, does not greatly alter the Δ_{eptx} values determined for epitaxial matches. Similarly, at least in the case of *i*-PP, if basal planes are of a pitched nature, each successive plane in a given stack could be recessed away from an adjacent layer; this arrangement would still provide a stepped association between basal plane niches, while only requiring an angular change between niche rows and the plane stacking direction. If this were the case, only the angle of the *i*-PP chains across the basal plane edges would change from the manner presented in *Figure 3*. This situation would not apply to nylon 66 since nylon 66 chains would not deposit in niche rows.

The second point concerns the greater potential for an interruption of the uniform deposition of polymer chains on a graphitic surface when more deposition directions are available to them. The single deposition direction available for nylon 66 contrasts with the two available to *i*-PP as depicted in *Figure 3*. However, both of these arrangements provide fewer than the three directions possible along the threefold symmetry of a basal plane surface described by Hobbs⁴. This is a concern because if polymer chains can orient in more possible arrangements on a carbon fibre surface, it would be more difficult to identify the polymer's chain direction. The one direction available to nylon 66 certainly facilitated the determination of the its chain direction relative to the carbon fibre direction. On the other hand, determining the *i*-PP chain orientation experimentally would be more difficult because the two non-perpendicular arrangements of *i*-PP chains, situated around edges of round fibres, would require using more sophisticated X-ray techniques.

In this last regard, a more random orientation of

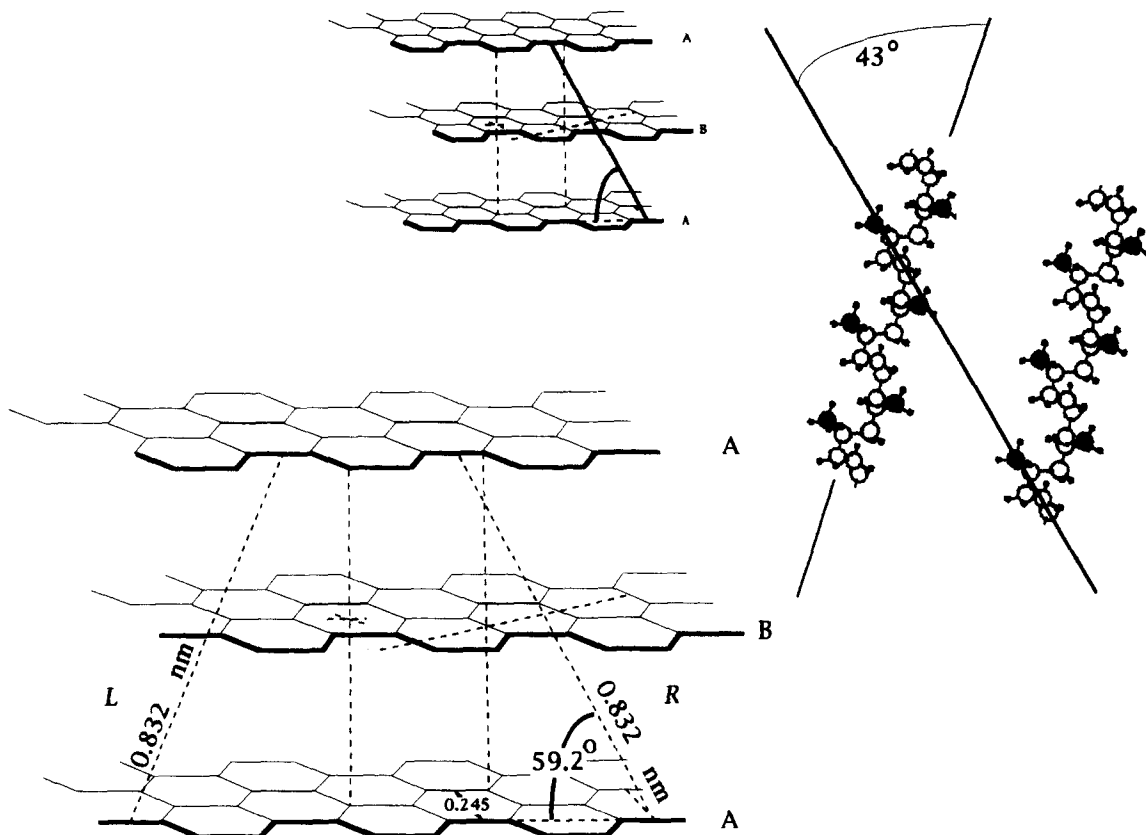


Figure 3 Orientation schematic of *i*-PP chains upon graphite basal plane edges. The ridges of methyl groups on the polymer helices are proposed to fit epitaxially on trenches in the niched basal plane edges that are relatively staggered, similar to steps in a staircase. Methyl groups may fix an *i*-PP chain within graphite trenches according to either the **L** or **R** orientations shown, depending on initial chain orientation. The space between the *i*-PP chains is shown in exaggerated form

polymer chains along a surface might be more desirable by permitting applied and localized interfacial stresses to dissipate prior to reaching a carbon reinforcement. For *i*-PP, the semi-cross transcrystalline orientation of the van der Waals' bonded polymer chains, relative to the fibre direction, would encourage reorientation of chains relative to the direction of stress. This could potentially result in a different mode of failure than occurs in polymers showing transcrystalline orientation such as nylon 66 chains, where the orientation is predominantly along the fibre direction.

An additional aspect to be considered is associated with the nucleating ability of a surface that provides one chain deposition direction compared with a surface that provides more than one such direction. Assuming both a unidirectional case and a multi-deposition case existed for a given polymer, and that epitaxial registrations in one direction for the unidirectional case and identical epitaxial registrations in at least two directions across a different substrate for the multi-directional case were available, and by further assuming that only epitaxy was involved in determining whether a nucleating agent was effective or not, which of the two surfaces would make a better nucleating agent? Answering this question might provide at least some general insight into the performance of nucleating agents. Seemingly, a surface providing a greater number of possible initial chain deposition directions would be more conducive for nucleation because of the lesser amounts of time and energy required for epitaxial orientation during nucleation. However, as noted earlier, the possibility of several deposition directions would also hinder

the growth of crystals once the initial deposition had taken place.

Summary

This work has elucidated the possible directions of epitaxially grown nylon 66 and *i*-PP chains on basal plane ends of higher modulus carbon fibres. The manner in which nylon 66 nucleates epitaxially is consistent with literature observations and involves only one direction: that with individual chains fitting between individual and pitched graphitic basal planes.

The way in which *i*-PP could epitaxially nucleate on graphitic basal planes involves two directions on pitched basal planes, both involving placement of methyl groups into niches along the 'arm chair' arrangement of basal plane ends. In addition, considerations of the possible ways in which a polymer chain could nucleate relative to the fibre direction of graphitic carbon fibre were discussed. It was noted that knowing such orientations could provide a basis for understanding the interfacial properties that influence fracture in semicrystalline polymer matrix composites.

A question was also raised and comments were made concerning whether a greater number of directions involved in nucleation of polymer chains would increase the nucleating ability of a given surface.

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