Crystalline Structure of Atactic Poly(acrylonitrile)

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ABSTRACT: Commercial poly(acrylonitrile) is an atactic polymer with a concentration of syndiotactic diads of 0.46–0.48[1,2] and shows a significant amount of crystallinity of about 30%.[3] An explanation that accounts for this apparent paradox is proposed in terms of the formation of crystals from mixed tacticity chains, in which the isotactic sequences are in a "shape emulating" conformation which enables them, as long as they are present in sequences of even numbers of monomer units, to cocrystallize with planar zigzag syndiotactic units. The model is similar to that recently proposed to account for the crystallinity in poly(vinyl chloride) (PVC).[4,5] The model is shown to be consistent with both the electron and X-ray diffraction data of PAN while, at the same time, providing an explanation of the comparatively high crystallinity and also a reason why it is significantly larger than PVC. The paper draws on the statistical basis developed in ref 5 and predicts a crystal thickness of 10 monomer units for PAN, a value similar to that in PVC but which is very difficult to measure from diffraction patterns because of the poor interchain register in the polymer.

Introduction

The nature of crystallinity in atactic poly(acrylonitrile) (PAN) has been the focus of some debate in recent years.[6–9] In fact, some authors have questioned whether the order found should be called crystallinity at all.[9] This paper marshals evidence and introduces new data to suggest that the crystal entities in PAN are composed of isotactic as well as syndiotactic sequences. This model is akin to the one recently proposed by the authors to account for the crystallinity observed in atactic poly(vinyl chloride) (PVC).[4,5]

In 1960 it was proposed that the principal crystalline phase in PAN was composed of syndiotactic sequences in their planar zigzag conformation.[7] Furthermore, it was suggested a second, isotactic, crystal phase must somehow be present to account for the fact that the radical polymerized polymer, which has a higher isotactic than syndiotactic diad content (measured to be 46–48%[1,2]), shows a significant amount of crystallinity. In assigning a crystal structure on the basis of an X-ray fiber pattern two assumptions were required: first, that all the chains regardless of configuration were arranged in the planar zigzag conformation and, second, that each phase was mutually exclusive of the other.

The X-ray fiber diffraction pattern of PAN is characterized by a single, strong equatorial reflection and few, if any, other sharp reflections especially in the off-equatorial zone.[8] Given favorable crystallization conditions, the intense equatorial line can be resolved into a doublet,[7,8] thus providing evidence that the structure is orthorhombic rather than hexagonal.[1] In determining the crystal structure for PAN, Stephani *et at.*[7] indexed the inner line of the doublet as 110 and the outer line as 200 and so determined the lattice parameters to be a = 10.2 Å, b = 6.1 Å, and c = 5.1 Å where $a/b > \sqrt{3}$. In addition, they noted that the inner reflection was more intense than the outer.

A subsequent electron diffraction study performed by Holland *et al.*,[8] while confirming an orthorhombic cell, demonstrated from a pattern of the [001] zone that the 200 and 110 reflections had been index previously the wrong way. The unit cell was found therefore to be a = 10.55 Å, b = 5.8 Å, and c = 5.08 Å where a/b was, in this time, $< \sqrt{3}$.

On the other hand, Lindenmeyer and Hoseman[9] have suggested that it is more appropriate to define the order in PAN using the concept of paracrystallinity. The main motivation behind their proposal appears to be that almost no off-equatorial diffraction peaks have been observed for PAN, thus indicating a distinct lack of interchain register and, second, that crystallinity has been estimated by Hinrichsen[3] as being as high as 28–34% using X-ray methods. Paracrystalline disorder, unlike that due to atomic vibrations, effectively distorts the crystal lattice and leads to a broadening of diffraction peaks, the degree of which rises with increasing scattering angle. Although the Lindenmeyer and Hoseman model goes some way to show how PAN crystals might be partially ordered, it does have questions unanswered as to the conformation and the configuration of the chains involved.

The diad tacticity (α = 0.46–0.48)[1,2] and crystallinity (28–34%)[3] of PAN indicate that both syndiotactic and isotactic units must somehow be incorporated in the crystal lattice. Attempts have been made to identify uniquely a helical or planar zigzag conformation but to no avail.[7,10] Mainly, these proposals have the difficulty that the trans–trans conformation of an isotactic sequence is energetically unfeasible or that the structures do not fit the unit cell dimensions known from diffraction work.

PAN is thus an example of a polymer which is virtually completely atactic but nevertheless displays considerable crystallinity, and one is drawn to a comparison with atactic PVC (as described previously in ref 5), which is also crystalline (about 10% for α = 0.55). In PVC, cocrystallization involves syndiotactic sequences in the usual planar zigzag conformation and isotactic sequences in a special conformation which largely emulates both the external shape and the axial repeat of the syndiotactic planar zigzag. Thus, mixed tacticity PVC sequences containing even-numbered runs of isotactic units were also found to be crystallizable. The conformation of a pair of such isotactic units sits in a subsidiary energy minimum when the conformation is −167°, −167°, +154°, +154°, −154°, −154°, +167°, +167° for an *siis* sequence. There is also some distortion of the backbone angles in concert

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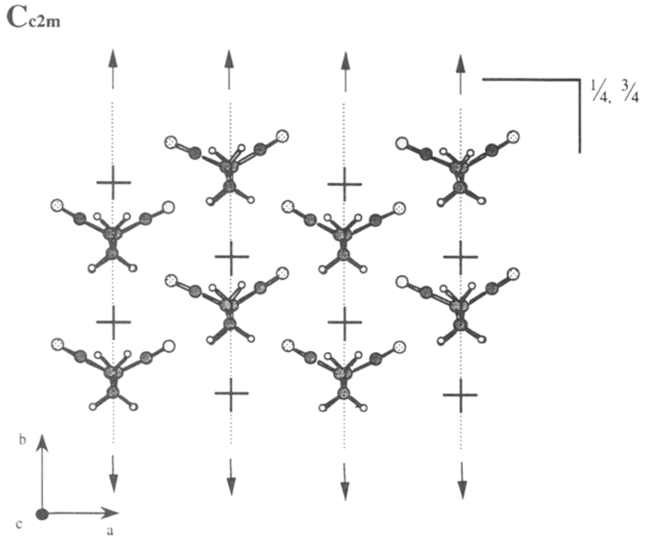

Figure 1. Crystal structure of syndiotactic PAN.

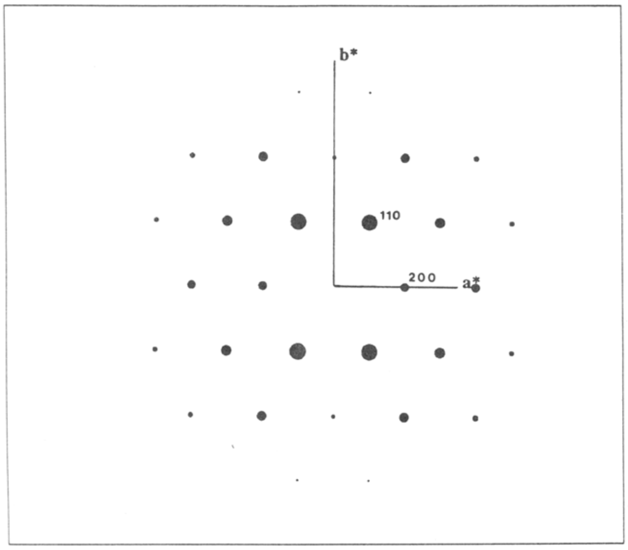

Figure 2. Electron diffraction pattern ([001] zone) as simulated by CERIUS for a syndiotactic chain filled lattice (unit cell dimensions as determined by Holland *et al.*[8]).

with the rotation angles. Such a model has been found to be consistent with measurements of tacticity (0.55), crystallinity (10%), and crystal thickness in the chain direction (13 monomer units) as well as specific variations in WAXD with tacticity.[5] This paper explores the possibility, first suggested in ref 5, that such a mixed tacticity isomeric crystal model may be appropriate to PAN too.[4,5]

Electron Diffraction Modeling of PAN

A crystal model was built for PAN, in accord with the space group *Cc*2*m* established in refs 5 and 7 using the unit cell parameters reported by Holland[8] and the electron diffraction simulated using CERIUS software. Figure 1 shows the structure projected onto the *a*–*b* plane and Figure 2 the electron diffraction simulated for the [001] zone.

In contrast to the experimental diffraction observed by Holland, the simulation shows the 200 to be much less intense than the 110 reflection. Possible reasons for this mismatch between observed and simulated diffraction are as follows: (a) The conformation of the chains are in error; for example, a reduction in the projected angle between the C≡N groups (Figure 1), drawing them toward the plane of the zigzag, would increase the intensity of 200. (b) The space group is in error, and the chains in centers of cells could be inverted or displaced on the *ab* projections, with the result that the structure factor for the 110 peaks is reduced.

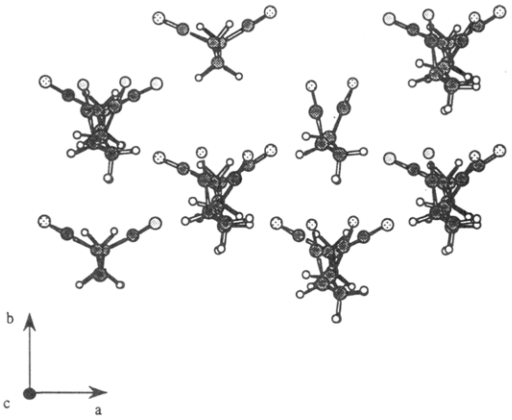

Figure 3. Representation of a PAN crystal lattice composed of syndiotactic and isotactic chains.

Simulated electron diffraction, from a lattice constructed of PAN chains with "drawn-in" nitrile groups, was indeed found to be very similar to the observed experimental electron diffraction. However, construction of such a chain with projected angles of 80° either involved bond angles, between the backbone and the side groups, being severely deformed or, when produced by twisting of the backbone, resulting in atom overlaps. In both of these constructions, the drawn-in conformation was found to be unstable and its existence is therefore unlikely.

PAN lattices were also built with similar crystal motifs to the lattice of PVC (*i.e.*, where the space group was *Pcam* and the center chain had been inverted), so that the diffraction could be simulated. Although it was found that the intensity of the 200 and 110 reflections do vary in relation to one another, when the middle chain was displaced in the *b* direction in the *ab* plane, two other more dominant reflections were also noted, the 010 and 210 reflections. However, neither of these reflections has been observed experimentally. The 010 reflection results when the center chain is displaced in the −*b* direction and 210 in the +*b* direction from the central position. One or another peak is thus always present in the simulation when the chains are arranged in the way.

The possibility that PAN sequences might emulate the shape of the syndiotactic chains has already been suggested.[5] In such an isotactic conformation, the C≡N groups of the crystallizable chains are indeed drawn toward the plane of the zigzag, and they give a conformation which corresponds to a local energy minimum.[5] A representation of a projection of a mixed tacticity structure is shown in Figure 3. The backbone bond torsional settings for shape emulating sequences are 160°, 160°, −160°, −160° with less bond angle distortion than for PVC.

In simulations of the Holland PAN lattice some of the syndiotactic units were replaced by shape emulating isotactic units. The resulting diffraction patterns for crystals comprising 50 and 100% isotactic sequences (each of which contain an even number of monomer units) are shown in Figures 4 and 5, respectively. In both these simulations the 200 peaks are noted to be as intense, if not more intense, than the 110. These simulations give a much better correlation with the experimental evidence than the first electron diffraction simulation. It is, however, difficult to compare the intensities of electron diffraction spots in an absolute way, and for this reason X-ray powder

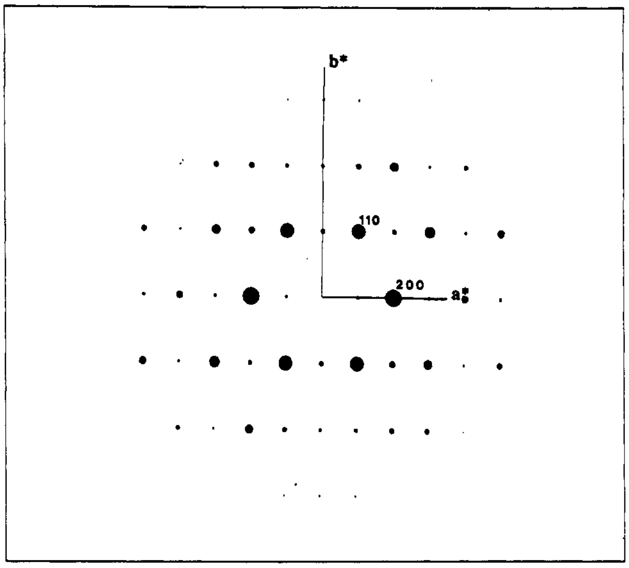

Figure 4. Electron diffraction ([001] zone) as simulated by CERIUS for a lattice that contains 50% isotactic and 50% syndiotactic sequences (unit cell dimensions as determined by Holland *et at.*[8]).

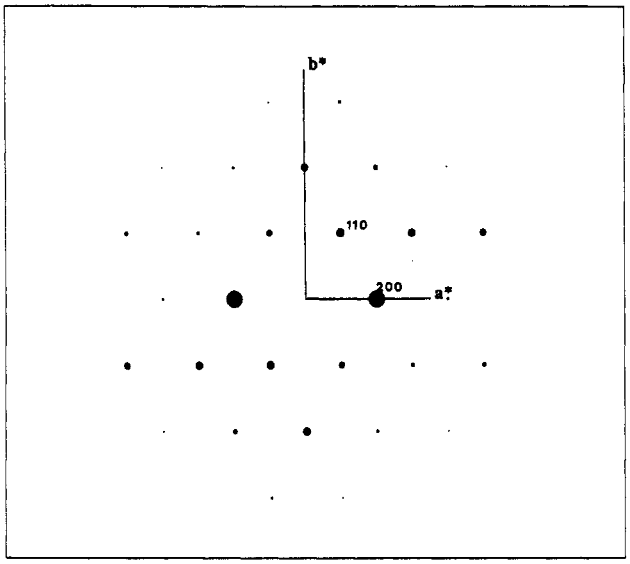

Figure 5. Electron diffraction pattern ([001] zone) as simulated by CERIUS for a lattice composed of shape emulating isotactic sequences (unit cell dimensions as determined by Holland *et al.*[8]).

diffraction patterns were also simulated for which the available experimental intensity data may be expected to be more reliable. Before considering the intensity issue in more detail we should point out that while the presence of a proportion of shape emulating isotactic sequences in the crystal is but one way of arriving at the observed intensity ratio, it has the major attraction that it also provides the basis for accounting for the high crystallinity observed in the predominantly atactic polymer.

X-ray Diffraction Modeling of PAN

WAXD (powder pattern) were also simulated for the same models of the syndiotactic (planar zigzag units), isotactic (shape emulating), and 50/50 mixed tacticity crystals (Figure 6). The tacticity greatly affects the intensity ratio of the 110 and 200 peaks, in accordance with the electron diffraction values. The advantage of the WAXD prediction is that it can be compared with experimental data.

Joh[11] succeeded in resolving the 110 and 200 reflections on X-ray powder diffraction scans of similar polymer samples and crystallization protocol as used by Holland[8] in his electron diffraction study. A value for the ratio of 200 and 110 peak intensities determined from the former experimental diffraction profile was found to be 1.5.

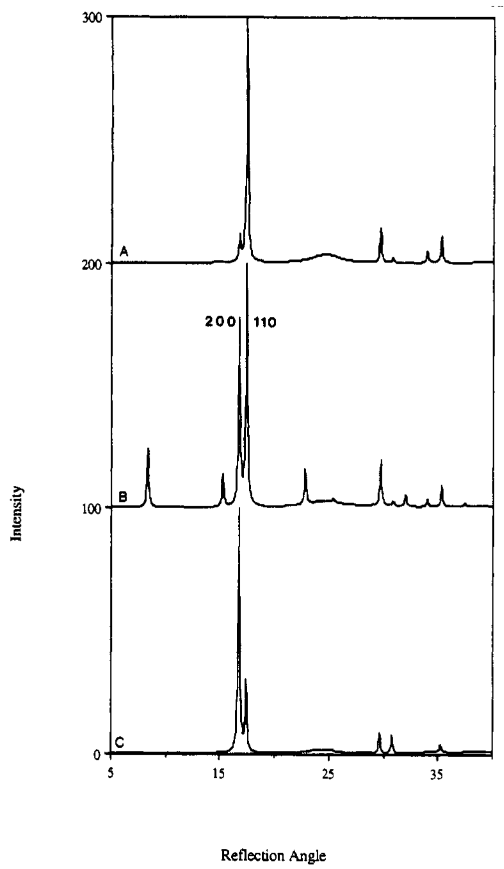

Figure 6. Simulation of the X-ray diffraction pattern of PAN for a series of different tacticity lattices: (A) syndiotactic, (B) tacticity = 0.5, (C) isotactic.

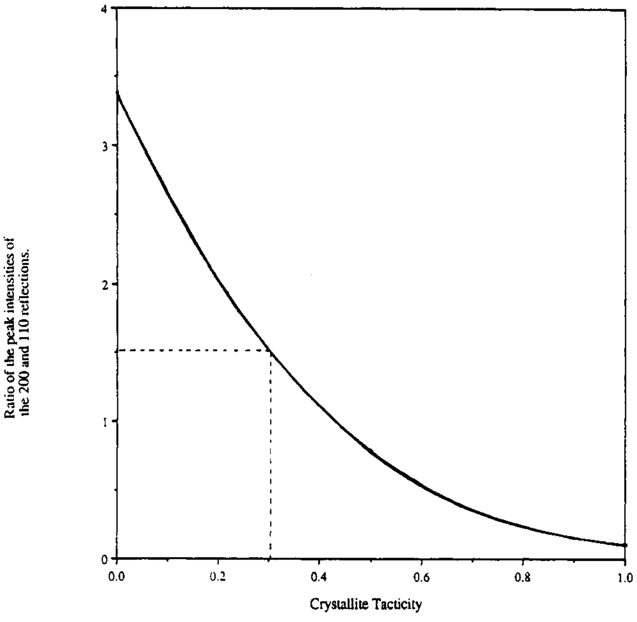

Figure 7. Like PVC,[5] the ratio of the 200 to 110 PAN peak intensities is seen to be related to the tacticity of the crystallite.

Values obtained from the simulated patterns calculated for different proportions of shape emulating isotactic and syndiotactic crystals are plotted in Figure 7. For the experimental ratio of 1.5, the graph (Figure 7) indicates the crystal tacticity to be 0.32. At first sight, it is perhaps strange that the crystals appear to be more isotactic than the mean value for the polymer (0.46–0.48% syndiotactic

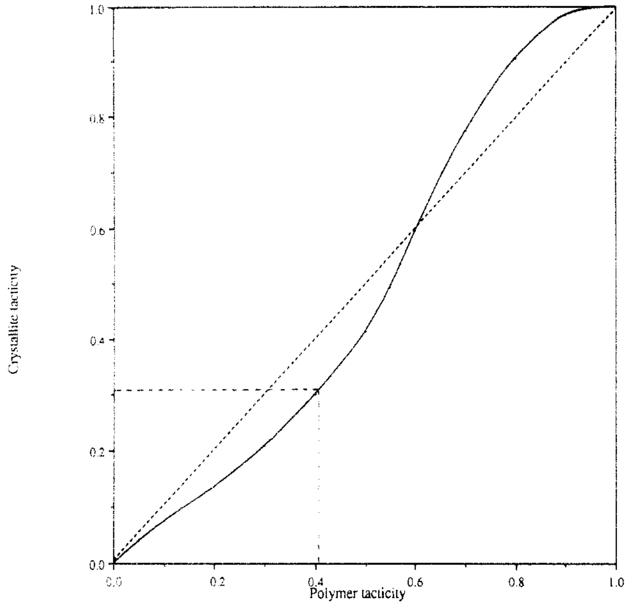

Figure 8. Relationship between the crystalline tacticity and the polymer tacticity, calculated in the same way as described for PVC in ref 5.

diads). However, a statistical analysis,[5] based on the assumption that it is the *sis* and *siiis*, *etc*., sequences which are noncrystallizable, gives the relation between crystal and polymer tacticity (reproduced as Figure 8). Given this relationship, a crystal tacticity of 0.32 corresponds to an overall polymer tacticity of 0.42 which is not far from the measured tacticity (0.46–0.48% syndiotactic diads).[1,2]

At this stage we must return to the predicted intensity for the mixed tacticity crystals shown in Figures 4 and 6. In each case extra reflections are apparent. They correspond to a doubling of the unit cell and have the appearance of "superlattice" reflections. We interpret their appearance in terms of the limited model size (2 cells × 3 cells in the plane normal to the chains). The result is that there is not necessarily an equal number of shape emulating isotactic sequences at the corners of the orthorhombic cells as at the centers, despite a 50/50 proportion overall.

It is intriguing to note that several authors have also observed such peaks in the experimental diffraction of PAN (see ref 5 for details) and have chosen to interpret their presence in terms of doubling of the unit cell parameters. The modeling work reported here suggests that the additional peaks are associated with an energetically based preference shown by the isotactic sequences for the centers or corners of the unit cell.

Without an experimental measurement of crystal thickness (difficult because of the lack of a sufficient longitudinal register in the chains to give meridional peaks suitable for line-broadening analysis) we cannot predict a crystallinity from our model in the same way that has been carried out for PVC.[5] We can, however, estimate an approximate crystallite thickness in the chain direction given that crystallinities between 28 and 34% have been measured for samples of commercial PAN[3] and that diad syndiotacticity is known to be 0.46–0.48.[1,2] The continuous curves in Figure 9 are plots of the calculated crystallinity as a function of the overall polymer tacticity for three different crystal thicknesses. They have been determined using the relationship already introduced in Figure 6 in the context of PVC, although in this instance the graph has been extended to include tacticity values of less than 0.5. The box on the graph represents the published range of experimental measurements of crystallinity (28–34%)[3] and the overall chain tacticity (0.46–0.48)[1,2] for PAN. Note that these data are commensurate for a mean crystal thickness of 10 monomer units. Three monomer units less than that measured in PVC[12] (13 monomer units).

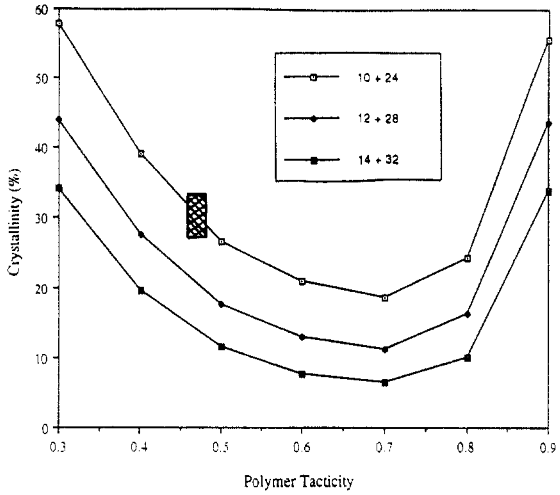

Figure 9. Degree of PAN crystallinity as a function of crystallite thickness in the chain direction calculated according to a method described in 5. The crystallinity values include a contribution from chain folding (where $N = 2N + 4$). By plotting the amount of crystallinity which has been measured experimentally (28–34%[3]) and the known tacticity of this polymer (0.46–0.48), the crystal thickness of a PAN crystallite can be deduced to be 10 monomer units. Key: sequence length (monomer units).

Figure 9 also suggests a reason why the amount of crystallinity in PAN is observed to be higher than in PVC. As the measured diad tacticity of PAN is lower than PVC (0.46–0.48 versus 0.55), the polymer is more isotactic. As it is *sis* which is the most frequently occurring noncrystallizable sequence (at least for mid-range and high tacticity), the minimum amount of crystallinity for a mixed tacticity lattice is predicted for a polymer with a diad tacticity of 0.6–0.7. The fact that the tacticity of PAN is further from this minimum than in the case of PVC provides an intrinsic explanation of the higher crystallinity found in PAN.

Conclusions

(1) In comparing the experimental and simulated electron diffraction patterns, it is clear that the crystals in PAN are not formed from syndiotactic sequences alone. The intensity ratio of the 200 and 110 diffraction peaks in experimental patterns is far greater than can be accounted for readily by a "syndiotactic only" PAN structure.

(2) A much better match was found between the experimental and simulated diffraction when the PAN crystal lattice was constructed from isotactic as well as syndiotactic sequences, the isotactic sequences being set in a conformation which emulates the shape of the syndiotactic planar zigzag conformation.

(3) In simulating the X-ray powder diffraction patterns and comparing the experimental 200 and 110 peak intensities, the PAN lattice is found to be more isotactic than syndiotactic.

(4) Using the I_{200}/I_{110} values, determined from the experimental X-ray powder diffraction, the crystallite and polymer tacticities were estimated. The estimated polymer tacticity (0.42) was found to be close to the diad tacticity of a radical polymerized PAN sample (0.46–0.48) as measured by NMR.[1,2]

(5) On the basis of this model for PAN crystallization and taking into account the experimental values of crystallinity and tacticity, the crystallite thickness in the

chain direction was estimated to be 10 monomer units, similar to that of PVC.

(6) A consequence of the model is the prediction that polymers with tacticities lower than 0.5 will have a higher crystallinity (for a given crystal thickness) than those with tacticities above 0.5. The model thus provides an explanation as to why PAN is more crystalline than PVC, despite both polymers having similar crystal structures which are more normally associated with the packing of syndiotactic planar zigzag chains.

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