Interchain packing and unit cell of syndiotactic polypropylene

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We have examined the general validity and applicability of our newly proposed alternative interchain packing and unit cell for syndiotactic polypropylene, in relation to the long-standing original structural model. Whereas our recent evidence arose from single crystals in ultra-thin films, we now demonstrate the correctness of our structure for polycrystalline thick films, for bulk specimens obtained directly from the polymerization and for uniaxially oriented specimens. This removes any possible ambiguity that our structure might represent a special case arising from thin-film, substrate or epitaxial effects, or from thermal or mechanical treatments. We also remove any questions about chemical defects as originators of our alternative structure by demonstrating that our specimens have among the very highest syndiotactic contents, ordered-sequence distributions, melting temperatures, heats of fusion and crystallinities in the literature. Finally, by re-examining earlier X-ray evidence from other studies, we find consistent confirmation of our proposed structure. This structure consists of chains with a $(t_2g_2)_2$ conformation in a cell similar to the generally adopted one, but with close packing on (010) planes rather than *C*-centering. The molecular origin of our alternative structure arises from the helical handedness of the molecules. We show that these favour antichiral packing and that this requires close packing on (010) planes. The earlier *C*-centred unit cell requires exclusively isochiral packing and is not seen in a regular manner in any of our samples but only as a defect structure, with specimens grown at the highest temperatures being essentially defect free.

(Keywords: syndiotactic polypropylene; structure; chirality; crystallization; unit cell; orientation; electron diffraction; X-ray diffraction)

INTRODUCTION

Our knowledge of the crystal structure of syndiotactic polypropylene is based upon the pioneering research of Natta, Corradini, and co-workers[1–4] in the 1960s. That work covered specifically the synthesis[1], chain conformation[2], intra-molecular energetics[3], inter-chain packing[1,4] and finally the full crystal-structure determination[4] of this important polymer. The molecular conformation was shown[1–4] to be $(t_2g_2)_2$ which corresponds to an s(2/1)2 helix. The unit cell, based upon X-ray diffraction analysis of doubly oriented specimens, was reported as orthorhombic with $a=1.450$, $b=0.560$, $c=0.74$ nm, space group $C222_1$, and interchain packing as seen in *Figure 1a*[1,4]. Because of the helical conformation of the syndiotactic polypropylene (sPP) macromolecules, the question of accommodation or rejection of chains of opposite hand in the lattice arises. While this question was not explicitly addressed in earlier work, the space group reported ($C222_1$) implicitly requires that all chains in the lattice be of the same hand (isochiral).

To explore this question, we recently succeeded in growing highly regular single crystals of syndiotactic polypropylene and performing the first electron diffraction analysis of this polymer[5]. Crystals lacking regular crystallographic faceting had earlier been obtained by Marchetti and Martuscelli[6], but could not be examined by electron diffraction because of their sensitivity to electron beam damage. Our electron diffraction results were not consistent with the structure of *Figure 1a*, but led us to propose an alternative structure, which is depicted in *Figure 1b*. In both cases the molecular conformation and basic unit cell dimensions are the same; however, as seen in *Figure 1*, the interchain packing is substantially different. Using molecular models, we demonstrated the origin of these differences, namely: (a) For a *C*-centred unit cell (*Figure 1a*) all helices on a *bc* plane must be of the same hand, and so must also be the molecules depositing on successive 200 planes. Thus, the lattice must be fully isochiral, with molecules of opposite hand not tolerated. (b) For our alternative unit cell (*Figure 1b*), each *bc* facet could contain helices of either or both hands in a random or regular arrangement, but then the molecules on the successive 200 plane must be of opposite hand, leading to an antichiral packing on 010 planes.

In fact, all our crystals (which had been grown by slow cooling from the melt to ambient temperature) exhibited 010 and 210 reflections characteristic of our newly proposed packing, but they also displayed to varying degrees an *h*10 streak that implied defective structures

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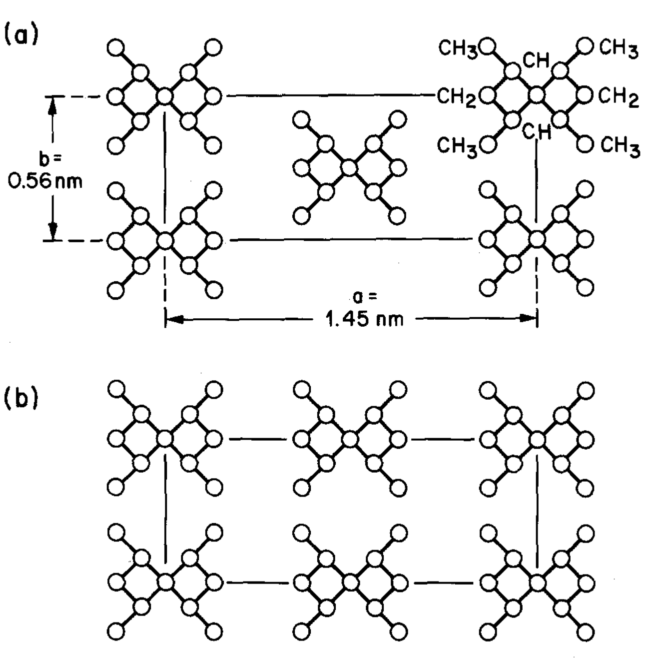

Figure 1 Molecular-axis projections of the unit cell of syndiotactic polypropylene according to (a) the originally proposed structure[1,4] and (b) our newly proposed structure[5]

on *bc* planes and coexistence of both types of packing[5]. Moreover, we also observed streaked reflections at $b^* = (1.12\,\mathrm{nm})^{-1}$, which demonstrated a superstructure with a unit cell doubled along *b*; we interpreted this as implying localized alternation of helical handedness on each *bc* plane.

Nevertheless, because our findings arose from individual single crystals grown in ultra-thin films on mica substrates, the general validity of our conclusions still needs to be investigated, particularly in view of their differences from the widely accepted structure (*Figure 1a*). Thin-film effects are well known to influence crystallization and morphology of polymers (see, for example, Reference 7), and substrate effects to influence orientation (see, for example, Reference 8) and polymorphism (see, for example, Reference 9). We thus need to examine thicker films and bulk specimens. Moreover, the effects of mechanical orientation of our own sample must also be probed, since deformation was used to prepare the specimens in References 1 and 4. Such mechanically induced thermal changes are, of course, pervasive among polymers. In fact, for syndiotactic polypropylene, Natta *et al.*[10] have documented conformational changes from $(t_2g_2)_2$ to all-*trans* upon uniaxial drawing of a quenched specimen. Finally, the possible effects of configurational stereosequence on molecular packing also need to be addressed: could the differences between the two proposed structures (*Figure 1a* and *b*) have chemical origins (e.g. degree of syndiotacticity, sequence distribution, blockiness, or molecular weight)? There are certainly precedents for this in terms of chain defects and molecular length. In poly(vinylidene fluoride), incorporation of regiodefects in excess of ≈11.5 mol% favours crystallization of the β-phase (all-*trans*) over the common α-phase (tg^+tg^-)[11]. An even closer example is that of isotactic polypropylene, where low molecular weight samples yield the γ-phase instead of the dominant α-polymorph[12,13]. Note that both of these phases have the same chain conformation, $(tg)_3$, and differ only in packing. This is exactly analogous to the case we are exploring here for syndiotactic polypropylene.

In this paper, we describe our results from thick films, bulk samples and mechanically oriented specimens. In addition, we compare the chemical characteristics of our polymer and of others used in earlier work. Finally, we re-examine the published structural evidence from previous studies. As we will show, in all of these cases we find consistent and full support for our newly proposed interchain packing and unit cell.

EXPERIMENTAL

The samples of syndiotactic polypropylene used were the same as in our first report[5], where their synthesis and ^{13}C-nuclear magnetic resonance (n.m.r.) characterization were described in detail. For X-ray diffractometry, the specimens were examined in the reflection mode at 0.5° $2\theta\,\mathrm{min}^{-1}$ using Ni-filtered CuKα radiation from a 2 kW generator. Differential scanning calorimetry (d.s.c.) heating runs were made under dried N_2 at $5^\circ\mathrm{C\,min}^{-1}$ using data smoothing (because of minute amounts of sample) and baseline correction, following calibration with suitable melting-point standards. For electron microscope examination, thin or thick films (as required) were deposited onto freshly cleaved mica substrates by casting from appropriate concentrations of polymer solutions in toluene or trichlorobenzene. After evaporation of the solvent, the films were melted and then crystallized isothermally or cooled quickly to ambient temperature. After shadowing with Pt/C and backing with amorphous carbon, they were floated off their substrates and examined by electron diffraction and bright-field transmission electron microscopy at 100 keV.

Uniaxially oriented specimens could not be drawn macroscopically for examination by X-ray diffraction because of the minute amount of polymer available to us (the polymerization yield was only 0.16%[5]). To overcome this problem, we prepared uniaxially oriented films for investigation by electron diffraction as follows. Unoriented films ≈0.1 μm thick were cast from concentrated solution onto flexible, narrow substrates of fluorinated ethylene–propylene copolymer (Teflon FEP®). Following evaporation of the solvent and melting and recrystallization of the polymer, the substrates with the film adhering to them were manually drawn by ≈300%. The polypropylene film was then backed with a thick layer of poly(acrylic acid) from concentrated solution in water. After evaporation of the water, the glassy poly(acrylic acid) was peeled off, carrying the oriented polypropylene film with it. The latter was then backed with evaporated carbon, and, after re-dissolution of the poly(acrylic acid) in water, was placed on electron microscope grids for examination by electron diffraction.

RESULTS AND DISCUSSION

A typical electron diffraction pattern from syndiotactic polypropylene single crystals grown isothermally at high temperature (105°C) is seen in *Figure 2*. All the reflections are sharp and characteristic of the *hk*0 reciprocal lattice plane. As in our initial study[5], the presence of *h*10 reflections with *h* only even (instead of only odd) contradicts the original packing scheme (*Figure 1a*) and supports instead our alternative model (*Figure 1b*). However, there is an important difference from the

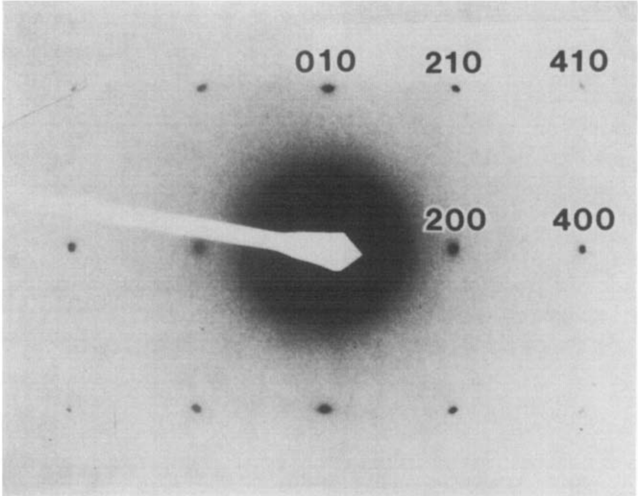

Figure 2 Single-crystal electron diffraction pattern from syndiotactic polypropylene crystallized isothermally from the melt at 105°C

single-crystal diffraction patterns that we presented previously, namely the essential absence of the *h*10 streak along *a** that was exhibited to varying degrees by our slowly cooled samples (see Figure 3 of Reference 5). The absence of substantial streaking is particularly recognizable in the 210 spots: to the extent that these depart from exact circularity, they do so by arcing circumferentially (i.e. with constant *d* spacing) rather than along *a** (i.e. with varying *d* spacing) as was seen in Figure 3a of Reference 5. This implies that the packing of *Figure 1a* is hardly detectable even as a defect structure when our specimens are crystallized at the highest temperatures, and that our alternative packing (*Figure 1b*) is adopted in an essentially regular manner. In a forthcoming publication[14] (which examines the variation of structure and morphology with temperature), we show that such defects are introduced progressively and increasingly as crystallization temperature is lowered. However, our structure (*Figure 1b*) remains dominant at all temperatures of crystallization; we have never observed the earlier packing of *Figure 1a* as a regular lattice in any of our crystals.

In interpreting our results on a molecular level, the electron diffraction pattern of *Figure 2* leads us to the conclusion that chains are stacked in the *a* direction in an antichiral manner dictated by steric requirements of their deposition directly atop a chain in the *bc* plane. We show this schematically in *Figure 3* (chain b). Isochiral deposition, on the other hand, would require a helix of the same hand (chain a) to crystallize in between two substrate molecules in a *C*-centred manner (again for steric reasons). We should note that even though all substrate helices are drawn in *Figure 3* with the same hand, this is neither necessary, nor in fact expected. We have drawn them this way only to be able to depict the deposition of isochiral chain *a* according to the original model[1,4].

Having examined the structure of single crystals grown on mica in ultra-thin ($\leqslant 50$ nm) films at high temperatures, we now begin to generalize our results by exploring thick, polycrystalline films grown from the melt, as well as uniaxially oriented ones prepared by mechanical drawing. For brevity, we discuss both of these cases together with the aid of *Figure 4*. The electron diffraction patterns of both the unoriented and the oriented polycrystalline samples are seen to consist of the same reflections; these are numbered in *Figure 4* and identified in *Table 1*. As expected, the strongest reflection in both cases is **1** (i.e. 200 of syndiotactic polypropylene), which becomes equatorial in the drawn specimen. Remarkably, the second strongest reflection is **3**, whose *d* spacing and equatorial disposition in *Figure 4b* identify it uniquely as 010 of syndiotactic polypropylene. This reflection is of course the major one prohibited by the symmetry of the earlier unit cell (*Figure 1a*) but required by our alternative structure (*Figure 1b*).

Conversely, the 110 reflection supports the earlier packing scheme of *Figure 1a*; to what extent is it present in our polycrystalline and drawn samples? Its spacing is consistent with reflection **4** in *Figure 4a* and *b*, and its intensity is substantially weaker than that of the 010 in the polycrystalline specimen and much more so in the oriented sample. The reason for this is that the 201 reflection, which occurs at almost exactly the same spacing as the 110 (see *Table 1*), migrates to the first layer in drawn films. Therefore, the intensity of reflection **4** in *Figure 4b* might bring us closer to a measure of the true presence of the 110 peak. However, even that would be a gross overestimate, because a third reflection is also superposed equatorially at this spacing (see *Table 1*): it is the second strongest reflection of isotactic polypropylene, i.e. the 040. While reasons for incorporation of the isotactic polymer within our sample will be discussed later, we should first point out that there is no uncertainty whatsoever about its presence in *Figure 4*.

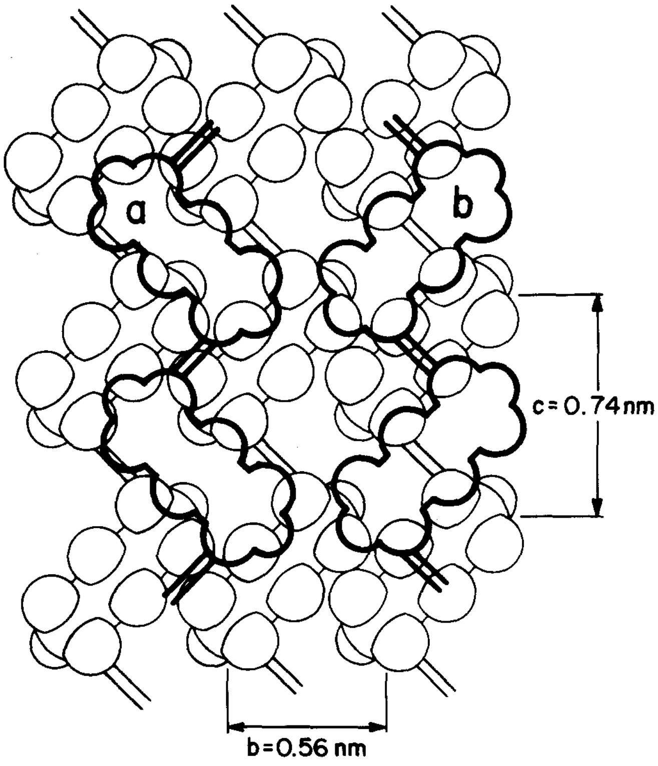

Figure 3 Schematic representation of the chiral origins of the two proposed modes of packing in syndiotactic polypropylene. The top surfaces of right-handed helices constituting a *bc* substrate are drawn with light lines in an *a* projection. Superimposed upon them with heavy lines are the bottom surfaces of (a) a right-handed and (b) a left-handed helix crystallizing atop this *bc* substrate. It is seen that for steric reasons helix a must deposit between substrate helices, while helix b must do so directly atop an underlying one

Table 1 Identification of reflections obtained in polycrystalline and uniaxially oriented specimens

Reflection	*d* Spacing (nm)	Intensity[a]	Location[b] (drawn)	Identity	Calc. *d* spacing (nm)
1	0.722	V.s.	eq.	200 sPP	0.725
2	0.630	V.w.	eq.	110 iPP	0.626
3	0.562	S.	eq.	010 sPP	0.560
4	0.523	V.w.	eq.	110 sPP	0.521
				201 sPP	0.518
				040 iPP	0.524
5	0.481	V.v.w.	eq.	130 iPP	0.478
6	0.430	M., broad	No orien.	210 sPP	0.443
				111 sPP	0.427
				111 iPP	0.417
				$\bar{1}31$ iPP	0.407
				041 iPP	0.406
7	0.361	M.	eq.	400 sPP	0.362
				310 sPP	0.365

[a] V.s., very strong; s., strong; m., medium; v.w., very weak; v.v.w., very very weak

[b] Equatorial

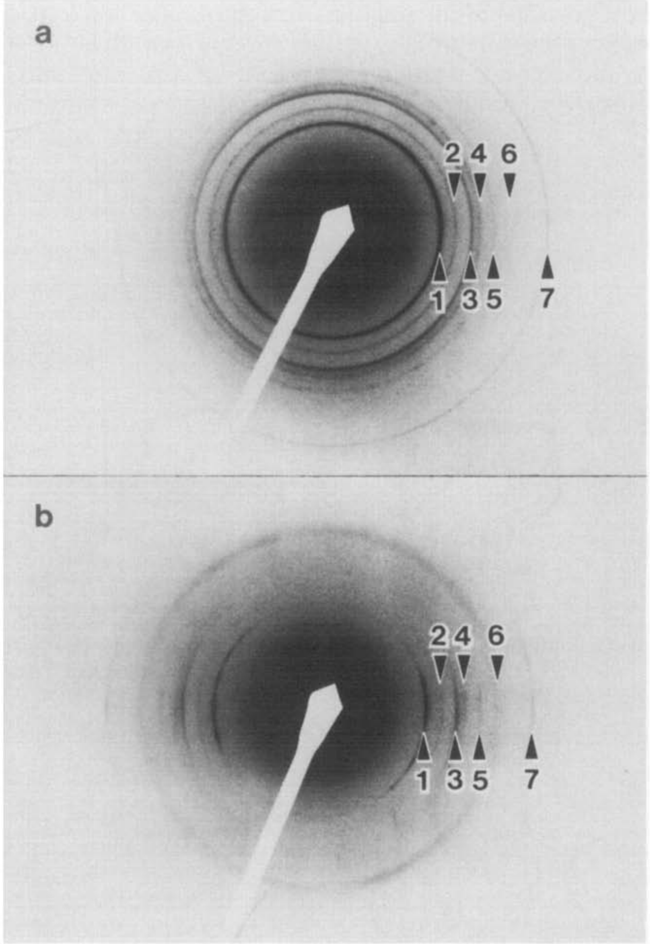

Figure 4 Electron diffraction patterns of polycrystalline, melt-grown films of syndiotactic polypropylene: (a) before; (b) after uniaxial orientation by mechanical drawing. Numbered reflections are identified in *Table 1*

This is so because reflections **2** and **5** in this figure occur at spacings inconsistent with any of the peaks expected of the syndiotactic polymer (see *Table 1*). Accordingly, we conclude that both in polycrystalline samples crystallized from the melt as thick films and in mechanically deformed samples, the presence of the 110 reflection is at best extremely weak (if not questionable). This, coupled with the high intensity of the 010, confirms the validity of our packing model to such specimens.

We now move on to the structure of the specimen as obtained directly from the polymerization reaction. This removes any possible effects of subsequent melting and recrystallization, as well as of the substrate. The X-ray diffractogram of such a specimen is given in *Figure 5* (curve a). As before, peaks are observed that are not expected of the syndiotactic polymer. This becomes clearer when curve b, arising from a highly isotactic polypropylene (iPP), is drawn to scale (i.e. using its 110 peak to normalize the intensity to that observed in curve a). The fact that isotactic polypropylene is produced in small amounts by our syndiospecific catalyst is not surprising; it is in fact consistent with several previous studies[15–18]. The prevailing interpretation[18] of this has been that the polymeric chains are stereoblocks consisting primarily of long syndiotactic sequences, with much shorter isotactic sequences and other defect structures. Our polymer had been prepared[5] using a standard syndiospecific catalyst system and procedures as in the previous studies, and a substantial amount of isotactic component was detected at the pentad level using ^{13}C-n.m.r. (see Figure 1 of Reference 5). As we describe elsewhere[14], separate crystals of isotactic polypropylene can be discerned in our samples and are in fact commonly grown with a quasi-epitaxial relationship to their syndiotactic counterparts.

By digitally subtracting curve b from curve a in *Figure 5*, we can obtain an estimate of the actual peak intensities in the X-ray diffractogram of pure syndiotactic polypropylene. As is seen in *Figure 5* (curve c), this subtraction is not perfect (some residual intensity remains at the location of the 130 iPP peak, and the baseline drops somewhat abruptly at ≈22° 2θ). This is most likely to be attributable to different crystallinities of the isotactic polymer in the samples yielding curves a and b. Nevertheless, despite its imperfections, curve c clearly demonstrates a strong presence with high intensity for the 010 and 210 peaks of syndiotactic polypropylene, coupled with a

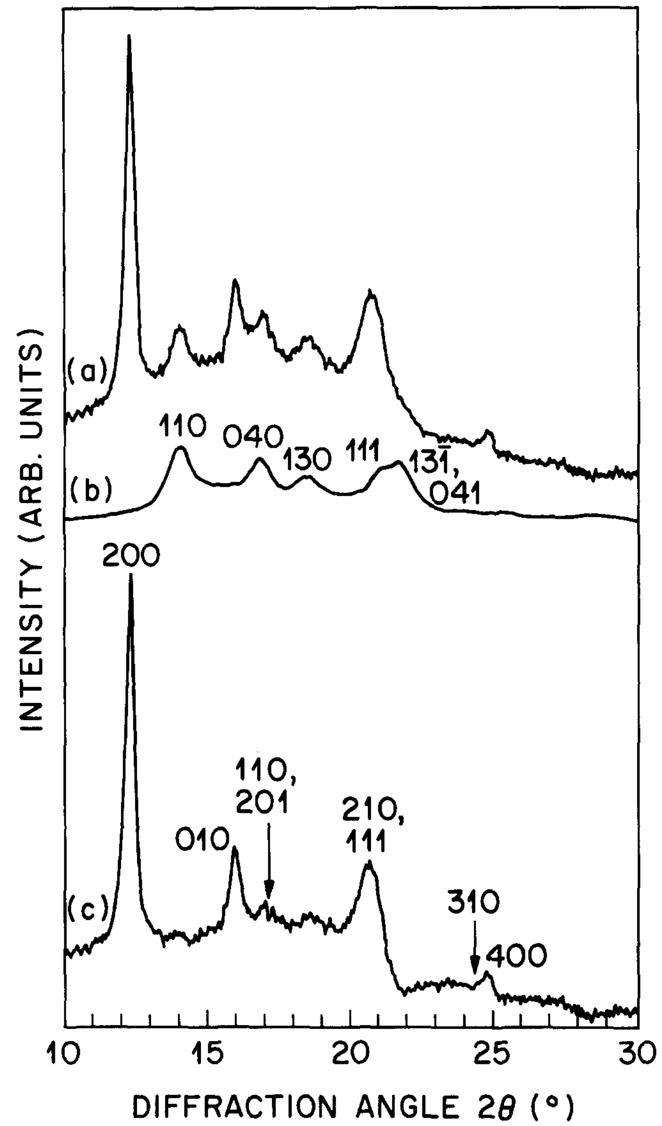

Figure 5 (a) X-ray diffractogram of syndiotactic polypropylene as obtained directly from the polymerization. (b) X-ray diffractogram of isotactic polypropylene normalized to the intensity of its 110 peak in curve a. (c) Digital subtraction of curve b from curve a

composite 110/201 peak that is only slightly above the baseline. Taken together, these results lead us once again to the adoption of the packing scheme of *Figure 1b* as the correct one for our syndiotactic polypropylene.

The final question now remains: are our samples in some way chemically different from those examined in earlier studies, to an extent that would lead to polymorphism as in, for example, α and β poly(vinylidene fluoride)[11] or α and γ isotactic polypropylene? We will show that this is not so. Ogawa and Elias[18] have obtained a variety of syndiotactic polypropylene samples under different polymerization and fractionation conditions, have examined their chemical structure using a number of techniques and have compared their structural results with those of other workers. The polymer which they found to combine the highest crystallinity and syndiotacticity was one obtained by extraction with hexane (designated 7-HX)[18]. That polymer had a racemic dyad content of 0.735, while ours[5] had 0.769. The syndiotactic and isotactic triad fractions for the earlier polymer[18] were 0.646 and 0.176, compared with 0.698 and 0.159 for ours. Thus we find no reason for concern as regards the stereochemical content and sequence distribution of our specimens.

With respect to crystallinity and molecular weight, we show in *Figure 6* d.s.c. melting curves for our sample, both as obtained from the polymerization reaction and after melting and slow recrystallization. The main peak in the 131–134°C region is attributable to the syndiotactic component, and the lower one at ≈123°C to its low molecular weight fraction rejected during slow crystallization. The much smaller peak around 150°C probably represents a separate isotactic fraction. We emphasize here that, even though previous studies[15–18] generally attribute the presence of isotactic and syndiotactic sequences to stereoblock chains, we have shown in this and other[5,14] work that separate crystals of the two isomers are in fact obtained. This implies that chains of each type are produced individually during synthesis, and that the resulting sample is primarily an intermolecular (rather than an intramolecular) blend. Moreover, we infer that the degree of syndiotacticity of our sample (and presumably of the earlier ones, as well) must actually be significantly higher than given above.

The melting temperatures observed for our syndiotactic polypropylene in *Figure 6* are among the highest reported (131.7 and 133.2°C for the as-polymerized and melt-recrystallized samples, respectively, *versus* 130°C for the highest crystallinity and syndiotacticity fraction in Reference 18, 131°C in Reference 19, and 132°C in Reference 20). The same is true for the heats of fusion of our syndiotactic polymer (1562 and 1764 J mol^{-1} for curves a and b in *Figure 6*, compared with 1360 J mol^{-1} in Reference 18 and 1234 J mol^{-1} in Reference 21). From

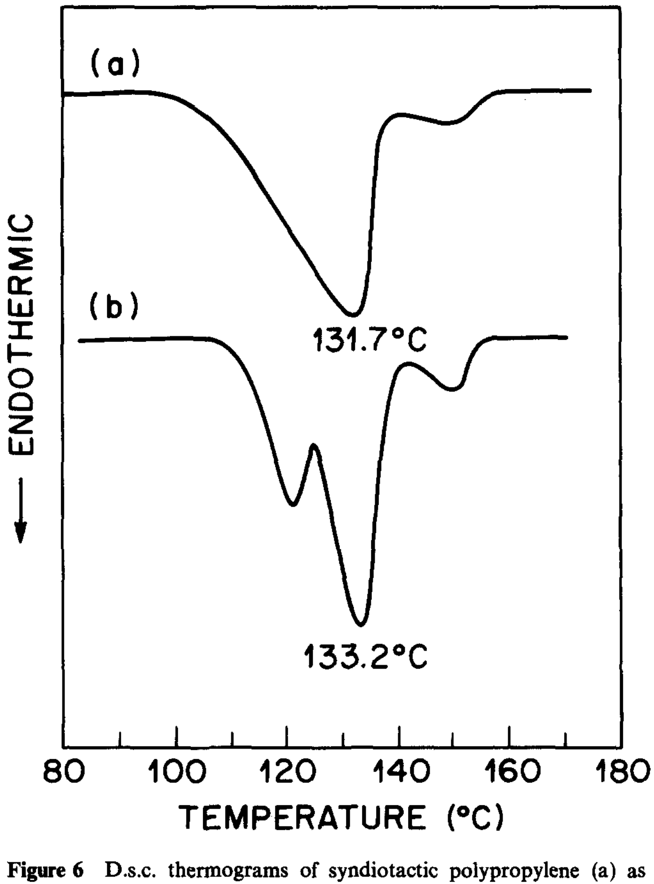

Figure 6 D.s.c. thermograms of syndiotactic polypropylene (a) as obtained directly from the polymerization and (b) after melting and slow cooling (1.2°C min^{-1}) to room temperature

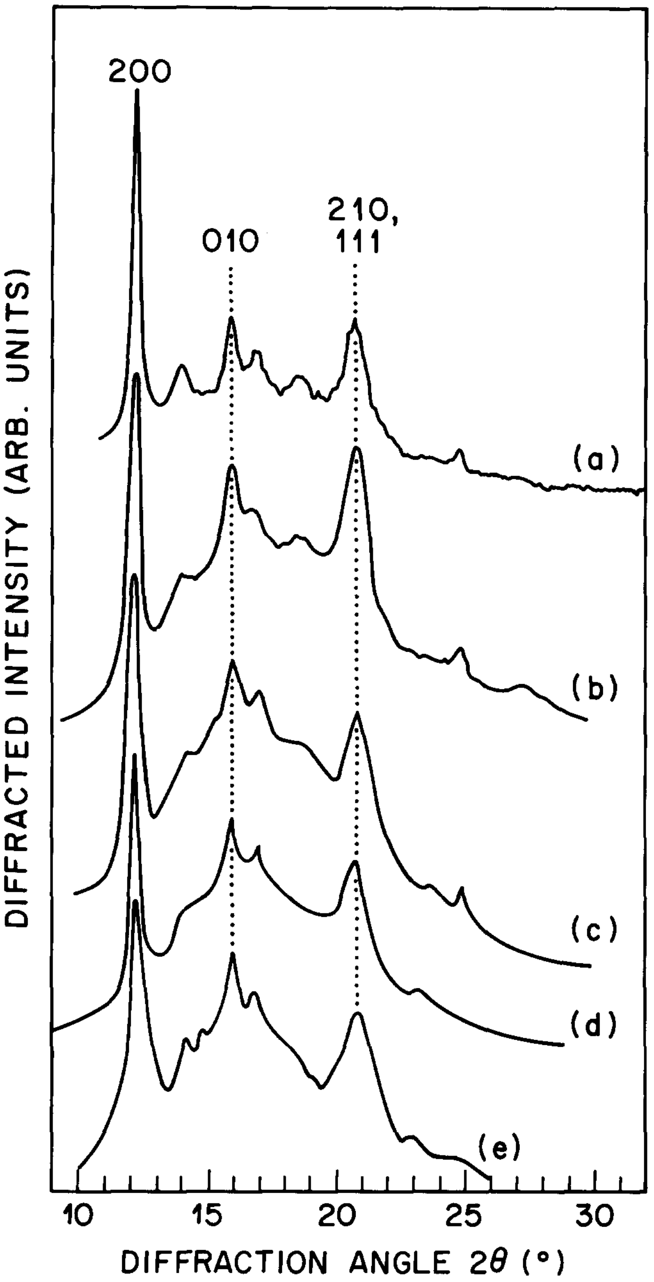

Figure 7 Comparative X-ray diffractograms of syndiotactic polypropylene: (a) this study; (b) Reference 18 (sample 7-HX); (c) Reference 20; (d) Reference 23; (e) Reference 22. Curves b–e are reprinted with permission of the publishers (see Acknowledgements)

all of these we conclude that our specimens not only are not significantly different in chemical characteristics from those used in other studies, but also have among the very highest syndiotacticities, chain regularities and crystallinities reported for syndiotactic polypropylene.

As the final step in demonstrating the generality and validity of our crystal structure (*Figure 1b*), we now examine X-ray evidence from the literature. The various diffractograms are seen in *Figure 7*, together with that of our own sample (curve a). An additional diffraction pattern from Reference 21 was not included, because it exhibited only minimal crystallinity (but is consistent with those seen in *Figure 7*).

Several conclusions can be drawn with certainty by comparison of the diffractograms in *Figure 7*. First, our specimen (curve a) clearly has the highest crystallinity among those seen in this figure, including the high crystallinity and syndiotacticity one (sample 7-HX) of Reference 18 (curve b). This confirms our d.s.c. results described above. Second, all samples appear to contain significant amounts of isotactic polypropylene (visible primarily in the peaks and shoulders at ≈14° 2θ, which arise from the strongest reflection, the 110, of iPP). However, the most important conclusion from *Figure 7* is the clear and general presence of strong reflections characteristic of our new unit cell, namely the 010 and 210. While the 210 overlaps the 111 peak, the latter cannot constitute the bulk of the observed intensity because of the concomitant weakness of its zeroth layer counterpart (the 110); this is especially clear when the isotactic contribution is subtracted (see again *Figure 5c*). In any case, there is not the slightest ambiguity about the 010 peak in all X-ray traces of *Figure 7*. No other potential reflections of either structure[4,5] are possible at the observed 2θ angle of 15.8°: the closest peaks on either side would occur at 13.42° (101) and 16.96° (110). Therefore, from this comparative examination of published X-ray diffractograms we find consistent support for our proposed interchain packing and unit cell in the preceding literature.

CONCLUSIONS

Our newly proposed alternative unit cell for syndiotactic polypropylene takes full account of the chirality of the chains and shows that they favour close packing on (010) planes in an antichiral manner. The earlier *C*-centred unit cell[1,4] requires fully isochiral packing and is not seen in a regular manner in any sample that we studied. We find it only as a defect structure in our prevailing packing, and essentially absent at the highest crystallization temperatures (105°C). We demonstrated the generality of our new interchain packing not only for single crystals in ultra-thin films, but also for polycrystalline specimens, as-polymerized samples and uniaxially oriented films. This removes any possible ambiguity that our structure may represent a special case induced by substrate effects, thermal or mechanical treatments. By comparing our polymer with others used in the literature, we found it to have among the very highest syndiotacticities, ordered-sequence lengths, melting points, heats of fusion and crystallinities, thus removing any possible questions about its crystal structure on the basis of its chemical structure. Finally, by re-examining other published X-ray diffractograms, we find consistent experimental evidence supporting our structure in all of those previous studies.

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REFERENCES

1 Natta, G., Pasquon, I., Corradini, P., Peraldo, M., Pegoraro, M. and Zambelli, A. *Rend. Acc. Naz. Lincei* 1960, **28**, 539
2 Corradini, P. *Rend. Acc. Naz. Lincei* 1960, **24**, 8
3 Natta, G., Corradini, P. and Ganis, P. *Makromol. Chem.* 1960, **39**, 238

4 Corradini, P., Natta, G., Ganis, P. and Temussi, P. A. *J. Polym. Sci. C* 1967, **16**, 2477

5 Lotz, B., Lovinger, A. J. and Cais, R. E. *Macromolecules* 1988, **21**, 2375

6 Marchetti, A. and Martuscelli, E. *J. Polym. Sci. A-2* 1974, **12**, 1649

7 Keith, H. D., Padden, F. J., Jr., Lotz, B. and Wittmann, J. C. *Macromolecules* 1989, **22**, 2230

8 Lovinger, A. J. *Am. Chem. Soc. Polym. Prepr.* 1980, **21**(2), 253

9 Lovinger, A. J. *Polymer* 1981, **22**, 412

10 Natta, G., Peraldo, A. and Allegra, G. *Makromol. Chem.* 1964, **75**, 215

11 Lovinger, A. J., Davis, D. D., Cais, R. E. and Kometani, J. M. *Polymer* 1987, **28**, 617

12 Morrow, D. R. and Newman, B. A. *J. Appl. Phys.* 1968, **39**, 4944

13 Lotz, B., Graff, S. and Wittmann, J. C. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 2017

14 Lovinger, A. J., Lotz, B. and Davis, D. D. *Macromolecules*, in press

15 Zambelli, A., Natta, G., Pasquon, I. and Signorini, R. *J. Polym. Sci. C* 1967, **16**, 2485

16 Elias, H.-G. and Dietschy, H. *Makromol. Chem.* 1967, **105**, 102

17 Zambelli, A., Pasquon, I., Signorini, R. and Natta, G. *Makromol. Chem.* 1968, **112**, 160

18 Ogawa, T. and Elias, H.-G. *J. Macromol. Sci. Chem.* 1982, **A17**, 727

19 Boor, J., Jr. and Youngman, E. A. *J. Polym. Sci., Polym. Lett. Edn.* 1965, **3**, 577

20 Inagaki, H., Miyamoto, T. and Ohta, S. *J. Phys. Chem.* 1966, **70**, 3420

21 Boor, J., Jr. and Youngman, E. A. *J. Polym. Sci., Polym. Chem. Edn.* 1966, **4**, 1861

22 Natta, G., Pasquon, I. and Zambelli, A. *J. Am. Chem. Soc.* 1962, **64**, 1488

23 Zambelli, A., Natta, G. and Pasquon, I. *J. Polym. Sci. C* 1963, **4**, 411