Macromol. Symp. ***175**, 215–224 (2001)*

Crystal Structures and Order-Disorder Phenomena in Polymers

Claudio De Rosa and Finizia Auriemma*

Dipartimento di Chimica, Univerisità di Napoli “Federico II”
Via Mezzocannone 4, 80134 Napoli - Italy

SUMMARY: The crystal structure of various polymers, presenting symmetry breaking, is discussed. Owing to the presence of disorder, the crystal structure of polymers is generally described in term of ideal modifications, a limit ordered form, characterized by ideal three-dimensional order, and a limit disordered form, characterized by the presence of statistical disorder in the packing, while preserving the order in the parallelism of the chains. The real crystalline forms are generally intermediate between the limit ordered and limit disordered models. The occurrence of conformational disorder, which produce defects frozen in the crystals of syndiotactic polypropylene, is analyzed.

Introduction

The study of the crystal structure of polymers, performed with the traditional X-ray diffraction, generally leads to models of packing which describe the order in the long range. The local arrangement of the polymer chains, e.g. the order in the short range, is, generally, not accessible by X-ray diffraction. More recently, the use of electron diffraction and solid state ^{13}C NMR spectroscopy has allowed the direct observation of the local arrangement of the chains. New phenomena which control the mode of packing of polymers, like the symmetry breaking[1-4] and the frustration[5-7], the formation of non-equilibrium structures containing defects frozen in the crystals[8], have been revealed.

Various kinds of structural disorder may be present in polymer crystals. A general concept is that the polymorphic behavior and order-disorder phenomena can be described with reference to limit ordered and limit disordered models, that is, ideal fully ordered and fully disordered models. The real crystalline forms are generally intermediate between the limit ordered and disordered models, the amount of disorder being dependent on the conditions of crystallization and thermal and mechanical treatments.

In this paper we present some examples of crystal structures of polymers showing symmetry breaking and analyze a particular kind of conformational disorder which has been recently observed in syndiotactic polypropylene.

CCC 1022-1360/00/$ 17.50+.50/0

Symmetry breaking

The crystal structure of the most stable polymorphic form (form I) of syndiotactic polypropylene (s-PP) provides a first example of symmetry breaking. Powder samples or single crystals of s-PP crystallized at high temperatures are in a modification of form I close to the limit ordered structure, where right-handed and left-handed two-fold helical chains alternate along both axes of the orthorhombic unit cell⁹⁾.

The space group proposed for this structure is *Ibca* (figure 1A), according with the intensities of the reflections observed in the X-ray and electron diffraction patterns⁹⁾. This space group corresponds to a lattice having the highest symmetry compatible with the symmetry of the s-PP chain, because the local two fold rotation symmetry axes of the s(2/1)2 helical chains, perpendicular to the chain axis, are maintained in the lattice as crystallographic elements of symmetry. However, the electron diffraction pattern of single crystals of s-PP grown at very high temperature (140 °C) show the presence of the 001 reflection¹⁰⁾, which is extinct in the space group *Ibca*. This indicates that the symmetry of the space group should be lower than *Ibca*¹⁾. More generally, these data clearly indicate that low symmetries of the unit cell are revealed even for symmetric single crystals, by the asymmetry of the electron diffraction pattern. Moreover in the solid state ^{13}C NMR spectrum of annealed samples of s-PP in form I the resonance of the methyl carbons is split in a doublet¹¹⁾. This is a clear evidence that two different methyl carbons are present in the unit cell, and indicates that the symmetry of the lattice is lower than *Ibca*, for which all the methyl carbons are equivalent.

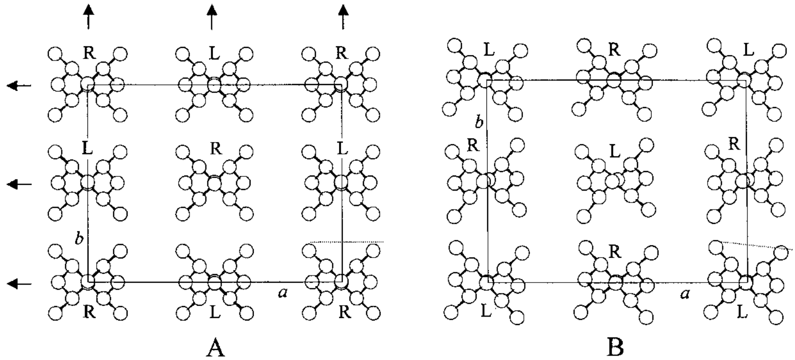

Figure 1: Models of packing in the form I of s-PP according to the space groups *Ibca* (A) and $P2_1/a$ (B). The arrows indicate the crystallographic twofold axes, present in A and lost in B. The dotted lines show that in B the chains are rotated by nearly 5° around the chain axes.

A space group with symmetry lower than *Ibca* can be obtained by removing the crystallographic twofold axes, so that the chains may rotate around their axes and translate along the chain axis. In the model of figure 1B the chains are slightly rotated around their axes and shifted along the chain axis[1]. The local two fold rotation axes of the chains, perpendicular to the chain axis, are therefore lost in the lattice and the symmetry is broken. The space group is monoclinic $P2_1/a$ and two of the four chains included in the unit cell are independent, e.g. not related by any element of symmetry (figure 1B). In the space group *Ibca* all the methyl carbons are equivalent (figure 1A), while two non equivalent methyl carbons are present in the model $P2_1/a$ (figure 1B). This model, therefore, accounts for the electron diffraction data and the splitting observed in the solid state NMR spectrum and corresponds to a local packing of the chains, e.g. it describe the order in the short range. Owing to possible different setting angles of the chains in different domains of the crystal, which diffract coherently, the model with higher symmetry *Ibca* may be considered, however, as an average model structure, suitable for the description of the order in the long range.

Form IV of s-PP has been obtained by exposing fiber samples of s-PP in the trans planar form III to vapours of organic solvents[12]. The crystal structure of form IV, as reported by Chatani et al.[12], is characterized by chains in $T_6G_2T_2G_2$ helical conformation packed in a triclinic unit cell (a_t = 5.72 Å, b_t = 7.64 Å, c_t = 11.60 Å, α_t = 73.1°, β_t = 88.8°, γ_t = 112.0°) according to the space group $P1$ (figure 2A). We have recently evidenced that the structure could be also described by an analogous model having higher symmetry[4]. In this alternative model, reported in figure 2B, the unit cell is monoclinic and centered on the C face with parameters a_m = 14.17 Å, b_m = 5.72 Å, c_m = 11.60 Å, β_m = 108.8°, the space group is $C2$[4].

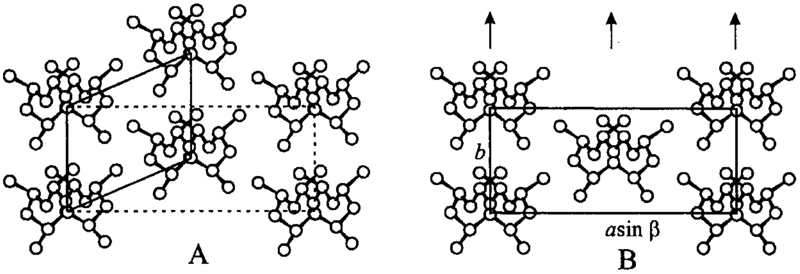

Figure 2: Models of packing in the form IV of s-PP according to the space groups $P1$ (A) and $C2$ (B). The arrows indicate the crystallographic two fold axes, present in B and lost in A. In the model A the continuous lines show the triclinic unit cell.

The monoclinic model presents a slightly lower packing energy than the triclinic model, whereas both models give the same good agreement between calculated and experimental X-ray diffraction patterns. In the monoclinic model (figure 2B) the local two fold rotation axes of the chain in the $T_6G_2T_2G_2$ conformation (which has indeed $t2$ symmetry), perpendicular to the chain axis, are maintained in the lattice as crystallographic symmetry (space group $C2$). In the triclinic model all the chains are rotated by the same amount (nearly 6.5°) around the chain axis with respect to the monoclinic structural model. The crystallographic two-fold rotation axes are lost as a consequence of this rotation and the symmetry is broken. Since clockwise and counter clockwise rotations are equivalent, the monoclinic model with higher $C2$ symmetry may be taken as descriptive of the order in the long range, or in other terms, it may describe an average structure of the form IV. The triclinic model (figure 2A) presents symmetry breaking (space group $P1$) and it is probably more properly descriptive of local situation of order, that is the symmetry, locally, is broken.

The crystal structure of the α form of syndiotactic polystyrene provides another example of symmetry breaking. Electron diffraction patterns of single crystals of s-PS in the α form was reported by Greis and Petermann13). A hexagonal unit cell with axes $a = b = 26.26$ Å was proposed. Various models of packing have been proposed for this structure3,7,13,14). The most important feature, found by Greis et al.13), is that the trans planar chains are organized in triplets. The X-ray powder and fiber diffraction patterns3,14,15), as well as the electron diffraction pattern7,13) are basically accounted for by a trigonal packing of triplets of trans planar chains, according to space groups $P3c1$ or $P3$. Three independent triplets (not related by any element of symmetry) are included in the unit cell. The space group of highest symmetry for the limit ordered structure would be $P3c1$ if the local glide plane of the trans planar chains was maintained in the lattice as crystallographic symmetry (figure 3)14). The analysis of the electron diffraction pattern of the single crystals in the α form13) shows that the intensity of $hk0$ and $kh0$ reflections are different. This is a clear indications that the symmetry of the space group should be lower than $P3c1$3). These data still show that low symmetries of the unit cell are revealed even for symmetric single crystals, by the asymmetry of the electron diffraction patterns. The α form of s-PS forms, indeed, standard hexagonal single crystals7,13) but a low unit cell symmetry.

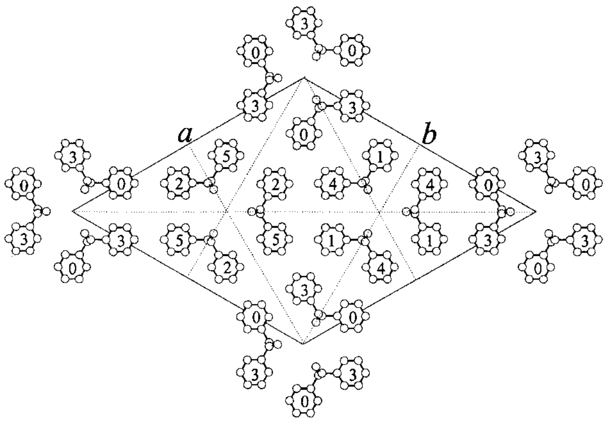

Figure 3: A preliminary model of packing in the α form of s-PS according to the space group $P3c1$. The dotted lines indicate the crystallographic glide planes coincident with the local glide planes of the chains.

The removal of the crystallographic glide plane symmetry produces a lowering of the space group symmetry from $P3c1$ to $P3$ 3). In the space group $P3$ the triplets of chains may rotate around the threefold axes3); in a refined model, the azimuthal orientation of the three independent triplets are found to be different7), the crystallographic glide plane is lost and the symmetry is broken. This model accounts for the different intensities of the $hk0$ and $kh0$ reflections observed in the electron diffraction pattern7). This limit ordered model, presenting symmetry breaking, should be thought as a local ordered arrangement of the chains; disorder in the setting angles of the triplets or opposite setting angles of triplets in different domains of the crystal, which diffract coherently, may produce higher symmetry packing modes, which can be taken as descriptive of the order in the long range.

The last example of symmetry breaking we present is the crystal structure of form III of isotactic poly(4-methyl-1-pentene) (i-P4MP). Electron diffraction patterns of single crystals of form III have been reported in 198416) but the crystal structure has been resolved only recently2). The square single crystals indicate that chains in four-fold helical conformation are packed in a tetragonal unit cell. The most simple mode of packing, typical of many isotactic polymers with chains in 4/1 helical conformation, is characterized by coordination number equal to four with every right handed chain surrounded by four left handed helices and *viceversa*. The space group of highest symmetry is $I4_1/a$, if the neighboring helices are anticlined; it is $I4_1cd$ if all the chains are isoclined. Many isotactic polymers with chains in 4/1 helical conformation, do, indeed, crystallize in tetragonal lattice according to the space groups $I4_1/a$ and $I4_1cd$[17,18].

For form III of i-P4MP, however, two experimental data indicate that the symmetry of the space group is lower than $I4_1/a$ or $I4_1cd$. Also in this case, although the square single crystals of form III of i-P4MP are highly symmetric, the packing presents low symmetry as revealed by the asymmetry of the electron diffraction pattern. Pradere et al.[19] have indeed observed different intensities of $hk0$ and $h\bar{k}0$ reflections in the electron diffraction patterns. Dark field imaging revealed that the square crystals are made of many small microdomains, which were considered by the authors to have the same molecular packing in the *ab* plane, but positioned in the crystal with opposite *c* axis direction[19]. The diffraction pattern obtained with larger selected area diffraction is symmetric, that is the intensities of $hk0$ and $h\bar{k}0$ reflections are equal[19]. That means that only using a small diffraction aperture, e.g. when very small area of the single crystal are selected, the presence of microdomains can be evidenced. These observations are a clear indication that the symmetry of the space group should be lower than $I4_1/a$ or $I4_1cd$. The solid state CPMAS ^{13}C NMR spectrum of form III of i-P4MP[20], reported in figure 4, gives the same evidence of a low symmetry of the packing.

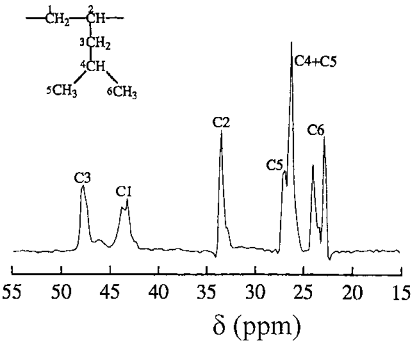

Figure 4:
Solid state CPMAS ^{13}C NMR spectrum of form III of i-P4MP.

The resonances of the methyl carbons show narrow splittings which can be traced back to packing effect. Two different kinds of methyl C6 and two different kinds of methyl C5 must be present in the unit cell. This also indicates that the symmetry of the space group should be lower than $I4_1/a$ or $I4_1cd$. The space group proposed for this structure, compatible with these observations, is $I4_1$[2], and the low symmetry of the packing comes from the fact that two of the four chains included in the tetragonal unit cell are independent, that is not related by any element of symmetry. The two independent chains have independent and different azimuthal orientations, so that different microdomains can be differentiated by different settings of the chains rather than by the relative *c* axis orientation. The model of packing is shown in figure 5[2,21].

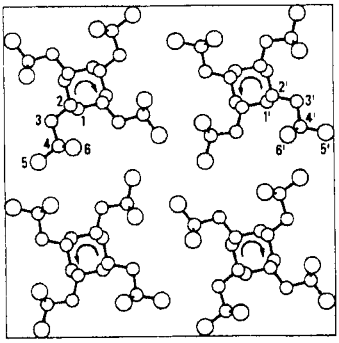

Figure 5: Model of packing in the form III of i-P4MP according to the space group $I4_1$.

Chains in 4/1 helical conformations are packed in the tetragonal unit cell with axes $a = b =$ 19.38 Å and $c = 6.98$ Å according to the space group $I4_1$[2]. The two independent chains are enantiomorphous and isoclined and their azimuthal settings are such to account for the asymmetry of the electron diffraction pattern. The model of figure 5 also accounts for the splitting of the methyl carbons resonances observed in the CPMAS spectrum of figure 4. The methyl carbons of the two independent chains C6 and C6' or C5 and C5', present, indeed, different chemical environments since the contact distances with the neighboring atoms are different[20].

The low symmetry model proposed for the crystal structure of form III of i-P4MP is descriptive of a very local packing of the chains, that is of local situation of order, which can be detected only by a direct observation of very small area of the diffracting crystals. When larger area are observed, for example by X-ray diffraction or by electron diffraction with large selected area aperture[19], since different microdomains having different setting angles of the chains may diffract coherently, only an average structure with higher symmetry can be seen. The high symmetry model with space group $I4_1/a$ accounts for the X-ray diffraction pattern and the symmetric electron diffraction pattern obtained with larger selected area aperture, therefore it could be taken as descriptive of the order in the long range or, in other terms, of an average structure.

Structural disorder

Various kinds and amounts of disorder can be present in the structure of polymers, depending on the conditions of crystallization. In some cases, modifications crystallized in special conditions (e.g. melt-crystallization at high temperatures or single crystals grown at high temperatures) are very close to the limit ordered model, but in many cases these limit ordered models are really ideal. The real crystalline forms are generally intermediate between the two ideal limit ordered and limit disordered models.

A particular kind of disorder has been found in samples of syndiotactic polypropylene having a relatively low degree of stereoregularity (fully syndiotactic pentad content [*rrrr*] = 86%)[8,22]. The chains present conformational disorder which produces defects frozen in the crystals[8]. The X-ray diffraction patterns and the corresponding solid state ^{13}C NMR spectra of samples of s-PP crystallized in forms I and II are reported in figure 6.

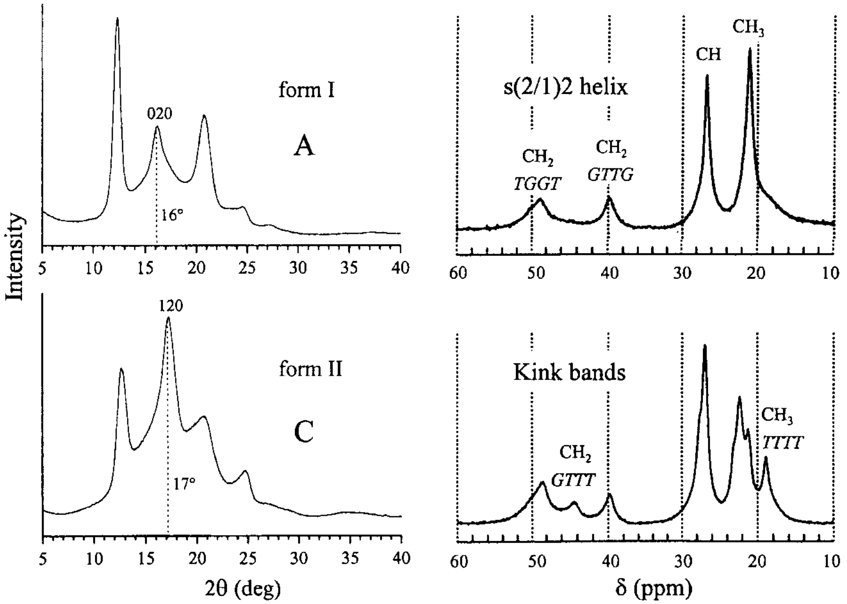

Figure 6: X-ray powder diffraction patterns of s-PP samples in the form I (A) and form II (C), and the corresponding solid state ^{13}C NMR CPMAS spectra (B) and (D), respectively.

Samples of s-PP which present X-ray powder diffraction pattern typical of the stable form I (figure 6A) show the usual solid state ^{13}C NMR spectrum, typical of the regular twofold helical conformation (figure 6B). Samples of s-PP which present X-ray powder diffraction pattern typical of the isochiral form II[23,24] (figure 6C) show a different solid state ^{13}C NMR spectrum with additional resonances in the region of the methylene and methyl carbon resonances (figure 6D). These additional resonances have been explained by assuming the presence of conformational disorder characterized by the presence of trans planar portion of chains in a prevailing twofold helical conformation[8,22]. A possible model of disorder is shown in figure 7B.

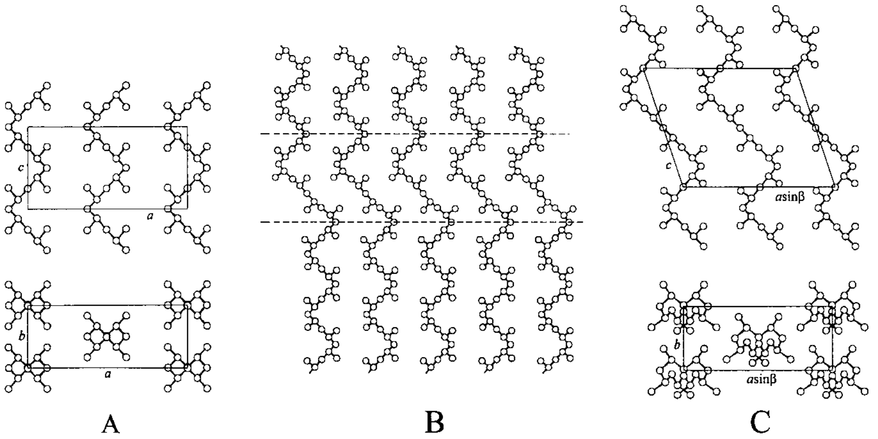

Figure 7: Models of packing in the limit ordered forms II (A) and IV (C) of s-PP and model of a conformationally disordered modification, presenting kink bands (B), intermediate between the limit ordered models of form II (A) and form IV (C).

The defective region is clustered in planes and forms kink bands; it is characterized by chains in T_6G_2 conformation (figure 7B). Portions of helices in the regular twofold conformation, all having the same chirality are packed according to the limit ordered model of form II (space group $C222_1$)[23,24] and are connected by portion of chains in trans planar conformation. The most important feature is that a substantial parallelism among the local chain axes is maintained, so that the presence of these defects does not reduce too much the crystallinity. These kink bands may be regarded as stacking faults cutting the chain axes, but preserving a substantial parallelism of the chains. In this model (figure 7B), in the defective regions the chains are packed as in the form IV of s-PP (figure 7C), while in the ordered regions the chains are packed as in the form II (figure 7A). This suggests that, depending on the condition of crystallization, there exists a continuum of conformationally disordered modifications of s-PP containing kink bands, intermediate between two limit structures, the limit ordered form II and the limit ordered form IV (figure 7).

Acknowledgements

The financial support of the "Ministero dell' Università e della Ricerca Scientifica e Tecnologica" of Italy (PRIN 1998) is gratefully acknowledged.

References

1. C. De Rosa, F. Auriemma, P. Corradini *Macromolecules* **29**, 7452 (1996).
2. C. De Rosa, A. Borriello, V. Venditto, P. Corradini *Macromolecules* **27**, 3864 (1994).
3. C. De Rosa *Macromolecules* **29**, 8460 (1996).
4. F. Auriemma, C. De Rosa, O. Ruiz de Ballesteros, V. Vinti, P. Corradini *J. Polym. Sci. Polym. Phys. Ed.* **36**, 395 (1998).
5. B. Lotz, S. Kopp, D. Dorset *C. R. Acad. Sci. Paris* **319**, 187 (1994).
6. T. Okihara, L. Cartier, G. O. R. Alberda van Ekenstein, B. Lotz *Polymer* **40**, 1, (1998).
7. L. Cartier, T. Okihara, B. Lotz *Macromolecules* **31**, 3303 (1998).
8. F. Auriemma, C. De Rosa, O. Ruiz de Ballesteros, P. Corradini *Macromolecules* **30**, 6586 (1997).
9. B. Lotz, A. J. Lovinger, R. E. Cais *Macromolecules* **21**, 2375 (1988).
10. A. J. Lovinger, B. Lotz, D. D. Davis, F. J. Padden *Macromolecules* **26**, 3494 (1993).
11. P. Sozzani, R. Simonutti, M. Galimberti *Macromolecules* **26**, 5782 (1993).
12. Y. Chatani, H. Muruyama, K. Noguchi, T. Asanuma, T. Shiomura *J. Polym. Sci. Polym. Phys. Ed.* **29**, 1649 (1991).
13. O. Greis, Y. Xu, T. Asano, J. Peterman *Polymer* **30**, 590 (1989).
14. C. De Rosa, G. Guerra, V. Petraccone, P. Corradini *Polymer J.* **23**, 1435 (1991)
15. Z. Sun, R. L: Miller *Polymer* **34**, 1963 (1993).
16. G. Charlet, G. Delmas, F. J. Revol, R. St. J. Manley *Polymer* **25**, 1613 (1984).
17. G. Natta, P. Corradini, I. W. Bassi *Makromol. Chem.* **33**, 247 (1959)
18. P. Corradini, P. Ganis *Nuovo Cimento, Suppl.* **15**, 96 (1960).
19. P. Pradere, J. F. Revol, R. St. J. Manley *Macromolecule* **21**, 2747 (1988).
20. C. De Rosa, D. Capitani, S. Cosco, *Macromolecule* **30**, 8322 (1997).
21. C. De Rosa, F. Auriemma, A. Borriello, P. Corradini *Polymer* **36**, 4723 (1995).
22. F. Auriemma, R. Born, H. W. Spiess, C. De Rosa, P. Corradini *Macromolecules* **28**, 6902 (1995).
23. C. De Rosa, P. Corradini *Macromolecule* **26**, 5711 (1993).
24. C. De Rosa, F. Auriemma, V. Vinti *Macromolecules* **31**, 7430 (1998).