Morphology and structure of syndiotactic polystyrene

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Syndiotactic polystyrene with a high degree of stereoregularity and crystallinity has been prepared in the form of thin, electron-transmissible films. The morphology has been studied by transmission electron microscopy. The results were similar to those for isotactic polystyrene except for a significantly larger lamellar growth rate. High-energy electron diffraction gave the following structural data for syndiotactic polystyrene: space group $P\bar{6}2c$, $a=26.25(5)$ Å, $c=5.045(8)$ Å, $Z=18$ for the $-CH_2-CH(C_6H_5)-$ unit, $\rho_{th}=1.033\ \mathrm{g\,cm^{-3}}$. The macromolecular backbone chain is planar zigzag (4*1/1). Three macromolecules form clusters of two types of handedness. Ordering of these clusters results in a well pronounced superstructure ($a=\sqrt{3}a_b$), but partial ordering has also been observed and is probably caused by radiation damage and/or rapid crystallization.

(Keywords: syndiotactic polystyrene; morphology; structure; transmission electron microscopy)

INTRODUCTION

Though isotactic polystyrene (iPS) has been known since 1955[1] and many publications have appeared on its structure[2–4] and morphology[5–10], it was only recently that stereospecific polymerization succeeded in the preparation of syndiotactic polystyrene (sPS) with more than 98% stereoregularity and a high degree of crystallinity[11]. So far, neither crystal data nor morphological pictures on a microscopic scale have been reported on this novel material. It is the purpose of this paper to present results obtained by transmission electron microscopy (TEM) on the morphology and by high-energy electron diffraction (HEED) on the structure of sPS crystals grown in thin, electron-transmissible films.

EXPERIMENTAL

The raw material of sPS was produced and kindly supplied by Idemitsu Kosan Co. Ltd, Japan. For comparison of structural data, iPS was also investigated (Polyscience Inc., St Goar, FRG). The average molecular weights were in both cases $M_w \simeq 800\,000$. Thin unoriented amorphous films of the polymers were prepared on hot orthophosphoric acid (270°C) by putting a drop of a solution (0.5 wt% in *o*-xylene) onto the acid. After the solvent is evaporated the polymer spreads on the surface of the acid and is subsequently quenched to room temperature. Thin oriented films were made following the method of Petermann and Gohil[12]. Crystallization of sPS was achieved by annealing at 180 or 200°C for 5–10 min. For iPS, orthophosphoric acid was heated to 220°C and subsequent crystallization was carried out at 200°C for 1 h.

The morphological studies were done on a Philips EM 400T transmission electron microscope at 100 kV acceleration voltage in the defocus imaging mode[13]. High-energy electron diffraction (HEED) has been carried out on the same instrument with 100 kV acceleration voltage, spot size 5, camera length 575 mm, Scientia negative films, and Au as internal standard with $a=4.07856$ Å.

RESULTS AND DISCUSSION

Morphology of syndiotactic polystyrene

Isotactic polystyrene (iPS) has been used in a number of investigations as a model substance to study crystallization behaviour of thermoplastic polymers. The results obtained with syndiotactic polystyrene (sPS) are very similar with the exception of the lamellar growth rate being more than one order of magnitude higher than in iPS[6], but no precise crystallizaton data have so far been reported on sPS. In *Figure 1* lamellar crystals (dark lines) seen 'edge-on' (molecular direction in the plane of the film) are imaged in defocus contrast. The crystal thickness in the molecular direction is about 200 Å, while their width exceeds several micrometres. The crystals were grown from an amorphous film annealed for 5 min at 200°C. The lamellae emerge from a few nuclei and splay out. It is remarkable that single lamellae can be found belonging to several nuclei. Additionally, in some regions very small and dense-packed lamellae are observed (arrow in *Figure 1*). In future investigations, these morphologies will be investigated in more detail. The regions showing no contrast in the defocus image partly contain 'single-crystal' lamellae with chains oriented

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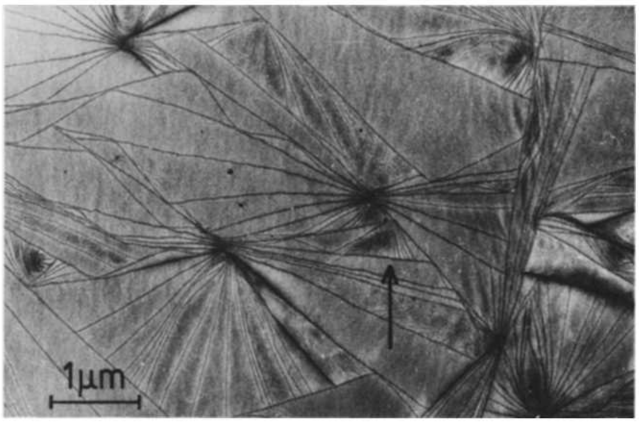

Figure 1 Electron micrograph of sPS lamellar crystals seen 'edge-on'. The film was crystallized for 5 min at 200°C

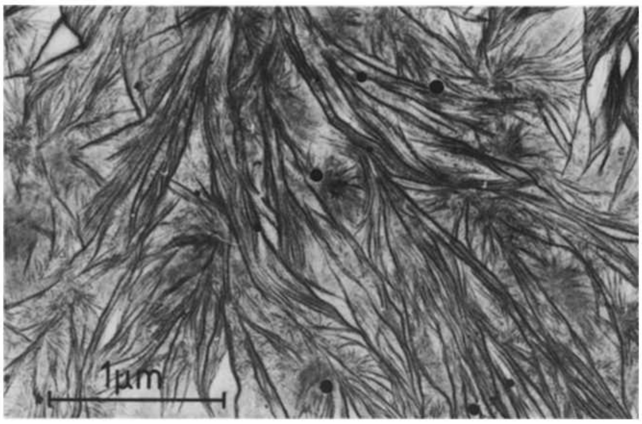

Figure 2 Electron micrograph of two-dimensional spherulites, grown for 5 min at 180°C

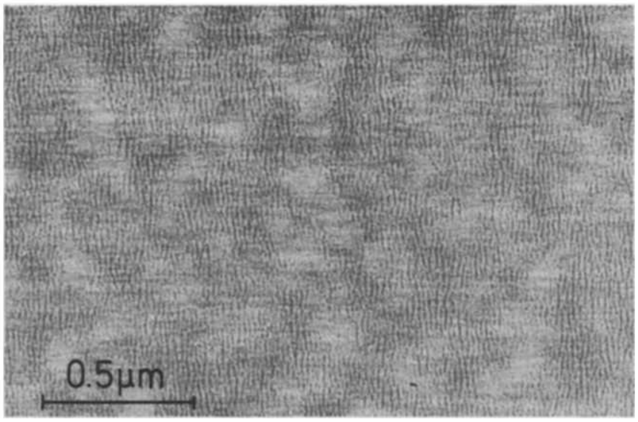

Figure 3 Electron micrograph of a highly oriented sPS film. The molecular direction is horizontal. Vertical lamellar and horizontal shish crystals can be seen

perpendicular to the plane of the film as revealed by dark-field contrast and electron diffraction (see *Figure 5*). The fine substructure in these regions results from the defocus imaging mode and may not have any relevance to the morphology[14]. Crystallizing the amorphous films at lower temperatures results in the occurrence of two-dimensional spherulites (*Figure 2*). Highly oriented structures were obtained by drawing a thin molten film from a hot (270°C) glass slide[12]. After drawing, shish-kebab structures are seen in the films (*Figure 3*) with a rather low shish content. Resulting from this particular preparation condition the lamellar crystal thickness is reduced to about 90 Å (in comparison to the above 200 Å), while the shish crystals can barely be seen (some dark horizontal lines). The molecules are oriented in the drawing direction, exhibiting a fibre symmetry (see *Figure 4*). It is noted that high crystallinity is obtained in these oriented films even without annealing.

Structural investigations on polystyrene

High-energy electron diffraction (HEED) from isotactic polystyrene (iPS) gave results in good agreement with the data of the X-ray study by Natta *et al.*[2]. Our geometric data are certainly more accurate owing to the use of gold as internal standard. The results are listed in *Table 1* and compared with the literature[2]. We refer to α-iPS to distinguish it from another phase or modification of iPS reported by Sundararajan and Tyrer[3] as β-iPS. *Table 2* displays indexed *d*-values of α-iPS. Also included are observed intensities though HEED intensities *per se* and in comparison with X-ray intensities are generally of little value. Nevertheless, the agreement for α-iPS is remarkable. A fibre pattern of α-iPS (with Au) is shown in *Figure 4*, while a [0 0 1] single-crystal pattern is reproduced in *Figure 5*.

Both figures also show the corresponding patterns of syndiotactic polystyrene (sPS) on exactly the same scale for better comparison. Indexing and evaluation of the diffraction data gave a hexagonal unit cell with hexagonal/trigonal symmetry and a well pronounced superstructure. The results are summarized in *Table 1*, while *Table 3* contains a listing of indexed *d*-values of both the basis and the superstructure. The observed intensities

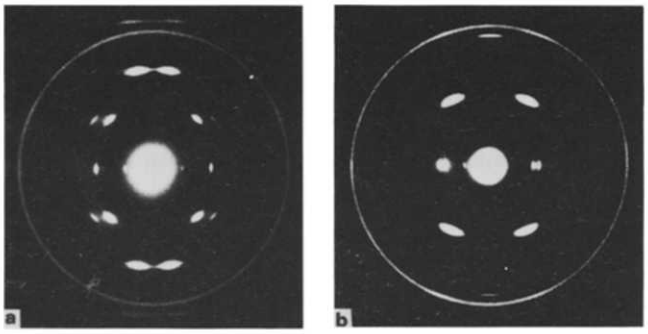

Figure 4 HEED fibre patterns of (a) α-iPS and (b) sPS, both with Au as internal standard

Table 1 Structural data of α-isotactic and syndiotactic polystyrene

Parameters	α-iPS[2]	α-iPS	$\text{sPS}_{\text{basis}}$	$\text{sPS}_{\text{super}}$
Space group	$R\bar{3}c$	$R\bar{3}c$	$P\bar{6}c2$	$P\bar{6}2c$
a_{hex} (Å)	21.9(1)	22.08(5)	15.16(3)	26.26(5)
c_{hex} (Å)[a]	6.65(5)	6.593(7)	5.045(8)	5.045(8)
Helix[b]	2*3/1	2*3/1	4*1/1	4*1/1
V (Å^3)	2762	2783	1004.1	3012.9
Z[c]	18	18	6	18
$V' = V/Z$ (Å^3)	153.5	154.6	167.4	167.4
ρ_{th} (g cm^{-3})	1.126	1.119	1.033	1.033
$k = V_0/V'$[d]	0.674	0.669	0.618	0.618

[a] Identity period of macromolecule

[b] Helix point net notation (4*1/1 is planar zigzag)

[c] Z is the number of $-CH_2-CH(C_6H_6)-$ units

[d] Packing density with molecular volumes V_0 after Wunderlich[15]

Table 2 Crystallographic data of α-isotactic polystyrene obtained by electron diffraction from single crystals (for lattice parameters, see *Table 1*)

hkl	d_{calc}	d_{obs}	I_{obs}	I^2
110	11.04	11.03	m	m
300	6.374	6.361	m	m
220	5.520	5.517	st	st
211	4.871	4.870	st	st
410	4.173	4.179	w	mw
131	4.132	4.136	m	ms
330	3.680	3.691	w	mw
321	3.652	3.687	w	mw
012	3.249	3.253	vs	vs
202	3.117	3.119	w	m
122	2.999	2.990	vw	mw
312	2.800	2.799	m	ms
113	2.155	2.176	m }	s
223	2.041	2.031	m }	

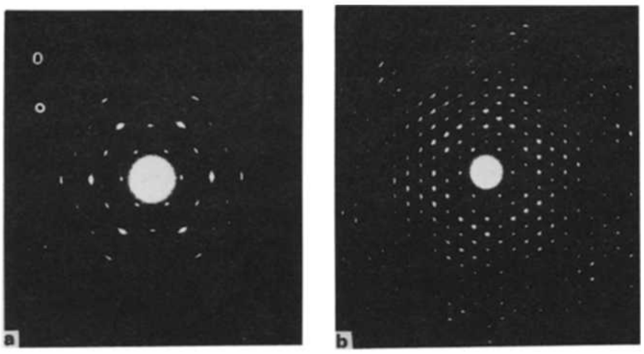

Figure 5 HEED patterns of [0 0 1] zones of (a) α-iPS crystallized at 200°C for 1 h and (b) sPS crystallized at 200°C for 5 min

are also included mainly to distinguish between basis and superstructure reflections.

Very interesting is the observation that different domains on the sPS films showed gradual development of the superstructure (see *Figure 6*; for indexing of [0 0 1] zones see *Figure 7*). It is, of course, also possible that the superstructure disappears with increasing radiation damage. It is important to confirm the basis/superstructure relation because it is this phenomenon which supports nicely our structural model deduced and described in the following section.

Corresponding to the theories of conformations of macromolecules with regular sequences of equivalent motifs[16,17], there exist two basic models for sPS. In the first case, a helix of type 4*2/1 could occur with a repeat distance of $\simeq 7.4$ Å as observed for syndiotactic polypropylene I ($-CH_2-CHCH_3-$)[18]. Secondly, a planar zigzag backbone chain is also possible (4*1/1 in point net notation) and has been found by Natta *et al.*[19] in a metastable crystalline modification. The latter case is also well documented for syndiotactic poly(vinyl chloride) ($-CH_2-CHCl-$), which shows a repeat distance of 5.10 Å[20].

Our HEED data of sPS gave $c = 5.045$ Å, which is identical to the repeat distance, indicating unambiguously a planar zigzag conformation. Such a macromolecule in its highest symmetry with parallel orientation of the benzene rings has a *c*-glide plane containing the chain carbon atoms. Perpendicular to the chain axis are mirror planes with the benzene rings residing on them and twofold rotation axes halfway between a pair of mirror planes. *Figure 8* shows two macromolecules in projection along the molecular axes. The enantiomorphous relation vanishes if one macromolecule is shifted by $c/2 = 2.522$ Å along the molecular axis.

From the packing theories for organic molecules and macromolecules by Kitaigorodsky[21] and in view of the hexagonal/trigonal diffraction geometry of sPS, it is obvious that three macromolecules are in close contact. There is no difference whether the zigzag chains are outside or inside of this triple unit. Therefore, we deal in the following only with the latter type of clusters. Again, there exist two enantiomorphous clusters as shown in *Figure 9*; this relation disappears by a shift of $c/2 = 2.522$ Å of one cluster along the *z* axis. The point-group symmetry for the cluster is $\bar{6}m2$. The smallest possible unit cell would contain one of these clusters with $Z = 6$ for ($-CH_2-CHC_6H_5-$) units. To predict the lattice parameter from packing theories, the following bond

Table 3 Crystallographic data of syndiotactic polystyrene obtained by electron diffraction from single crystals (for lattice parameters, see *Table 1*)

$h k l_b$	$h k l_s$	d_{calc}	d_{obs}	I_{obs}
	100	22.7	(*a*)	(*a*)
100	110	13.13	13.16	s
	200	11.37	11.36	vw
	210	8.595	8.60	w
110	300	7.580	7.587	vs
200	220	6.565	6.555	s
	310	6.307	6.287	m
	400	5.685	5.675	ms
	320	5.217	5.214	w
210	410	4.962	4.954	m
	101	4.925	4.942	vw
	201	4.611	4.608	m
	500	4.548	4.551	w
300	330	4.376	4.386	m
	211	4.351	4.341	vs
	420	4.294	–	0
	301	4.200	–	0
	510	4.084	4.095	w
	311	3.493	–	0
220	600	3.787	3.787	m
	401	3.776	–	0
	430	3.738	3.725	w
	520	3.641	3.661	w
	610	3.467	3.486	w
002	002	2.523	2.528	vs
004	004	1.261	1.260	s

[a] Background of central spot (see *Figures 4* and *5*)

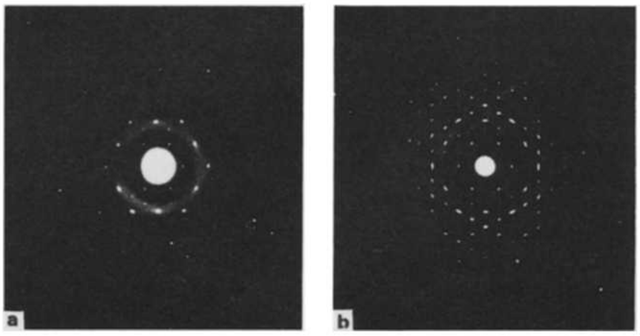

Figure 6 Gradual development of the sPS superstructure demonstrated on [0 0 1] zones

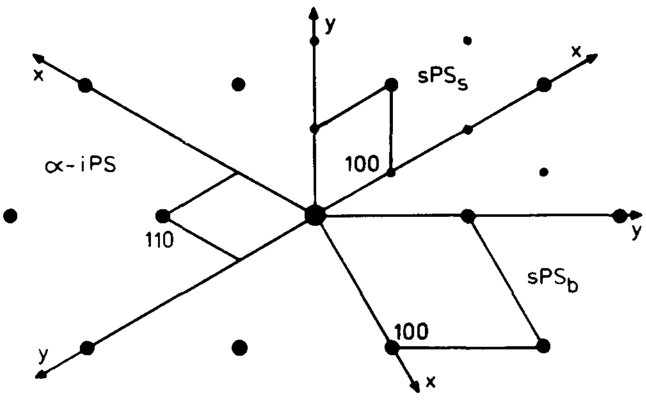

Figure 7 Indexing of [0 0 1] zones of polystyrene

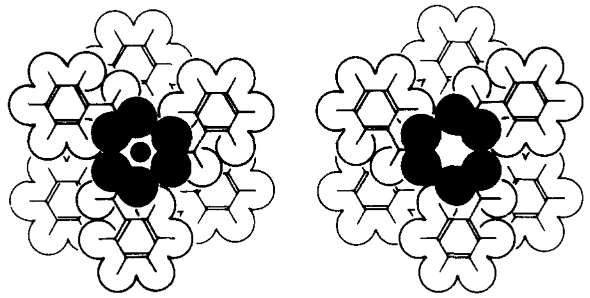

Figure 9 Enantiomorphous pair of sPS clusters

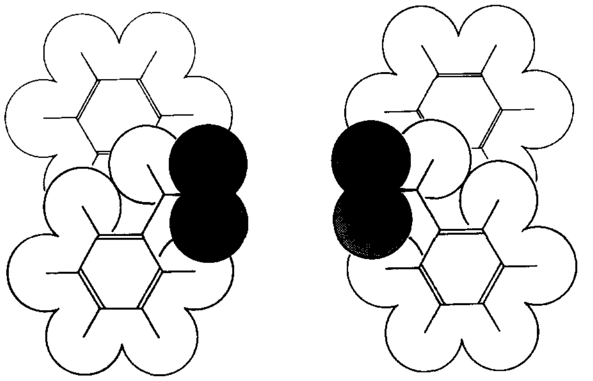

Figure 8 Enantiomorphous sPS units in projection along the molecular axes

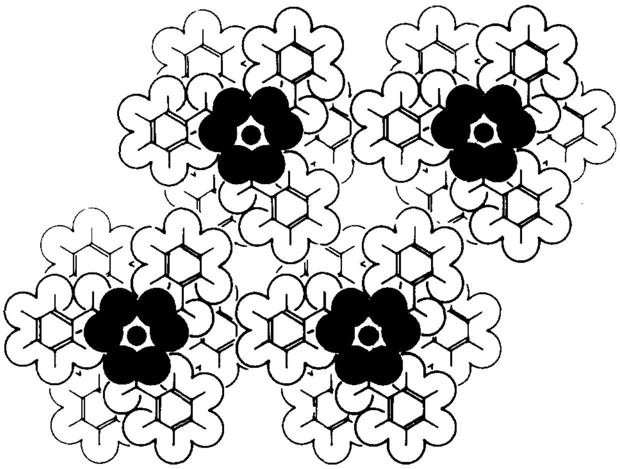

Figure 10 Basis structure of sPS

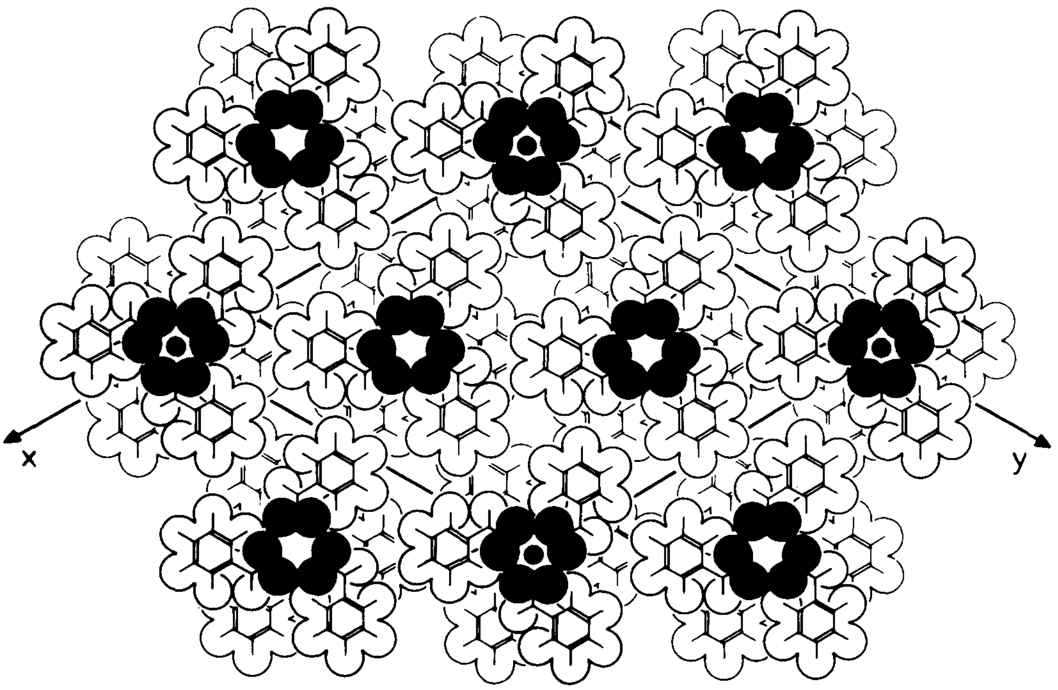

Figure 11 Superstructure of sPS

lengths and van der Waals' radii have been used:

$C(sp^3)–C(sp^3) = 1.534$ Å $\quad C(sp^3)–C(sp^2) = 1.501$ Å

$C(sp^2)–C(sp^2) = 1.400$ Å $\quad C(sp^3)–H(\sigma) = 1.102$ Å

$C(sp^2)–H(\sigma) = 1.086$ Å $\quad r_H(–C(sp^3)) = 1.26$ Å $(= c/4)$

$r_H(–C(sp^2)) = 1.26$ Å $\quad r_C(sp^2) = 1.70$ Å

Taking into account that penetration of the three macromolecules of one cluster allows overlapping of benzene hydrogen atoms only and that the same principle is valid also for the mutual penetration of clusters, a lattice parameter of $a \simeq 15.5$ Å is derived (see *Figure 10*)—in good agreement with the actual basis parameter $a_b = 15.16$ Å. Packing of screws, however, is especially close if screws of opposite handedness are in contact (1:1). In the case of hexagonal packing, this is not fully possible but a relation of 1:2 is an optimal compromise. Consequently, the most stable structure would be a superstructure with one cluster of one kind of handedness and two of opposite handedness (see *Figure 11*). Solid dots in *Figures 9–11* indicate clusters of alternative handedness. The lattice parameter would be $a_s = \sqrt{3}a_b = 26.26$ Å as actually observed. It should be noted again that the process of ordering occurs by small shifts of clusters along the z axis only and not by rotations of entire molecules or clusters. The appearance of ordered domains is expected to be influenced by crystallization rate and is a topic of our current investigations.

The space group with the highest symmetry is $P\bar{6}c2$ for the basis structure and for the superstructure $P\bar{6}2c$, which is the minimal subgroup of $P\bar{6}c2$ of the same class (so-called H-cell). In our earlier paper[22] we referred to $P3c1$ and $P31c$, allowing a symmetry reduction due to small tilts of benzene rings. After inspection of the actual model of sPS it is obvious that the slightest tilts of benzene groups would cause unacceptable strain. Thus, we now prefer the hexagonal space groups.

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REFERENCES

1 Natta, G., Pino, P., Corradini, P., Danusso, F. and Mantica, E. *J. Am. Chem. Soc.* 1955, **77**, 1700
2 Natta, G., Corradini, P. and Bassi, I. W. *Nuovo Cim. Suppl.* 1960, **15**, 68
3 Sundararajan, P. R. and Tyrer, N. J. *Macromolecules* 1982, **15**, 1004
4 Atkins, E. D. T., Keller, A., Shapiro, J. S. and Lemstra, P. *Polymer* 1981, **22**, 1161
5 Overbergh, N., Berghmans, H. and Smets, G. *J. Polym. Sci. (C)* 1972, **38**, 237
6 Edwards, B. C. and Phillips, P. J. *Polymer* 1974, **15**, 351
7 Overbergh, N., Berghmans, H. and Reynaers, H. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 1177
8 Overbergh, N., Girolamo, M. and Keller, A. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 1475
9 Petermann, J., Gleiter, H. and Miles, M. *J. Polym. Sci.–Phys.* 1979, **17**, 55
10 Petermann, J. and Gohil, R. M. *J. Macromol. Sci.–Phys. (B)* 1979, **16**, 177
11 Ishihara, N., Seimiya, T., Kuramoto, M. and Uoi, M. *Macromolecules* 1986, **19**, 2465
12 Petermann, J. and Gohil, R. M. *J. Mater. Sci.* 1979, **14**, 2260
13 Petermann, J. and Gleiter, H. *Phil. Mag.* 1975, **31**, 929
14 Thomas, E. L. and Hull, I. H. (Eds.), 'Structure of Crystalline Polymers', Elsevier Applied Science, London, 1984
15 Wunderlich, B., 'Macromolecular Physics', Academic Press, New York, 1973, Vol. I
16 Natta, G. and Corradini, P. *J. Polym. Sci.* 1959, **39**, 29
17 Natta, G. and Corradini, P. *Nuovo Cim. Suppl.* 1960, **15**, 9
18 Natta, G. *J. Polym. Sci. (C)* 1967, **16**, 2477
19 Natta, G., Peraldo, M. and Allegra, G. *Makromol. Chem.* 1964, **75**, 215
20 Natta, G. *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis. Mat. Nat.* 1961, **31**, 17
21 Kitaigorodsky, A. I., 'Molecular Crystals and Molecules', Academic Press, New York, 1973
22 Greis, O., Asano, T., Xu, Y. and Petermann, J. *Z. Kristallogr.* 1988, **182**, 58