# Structural study on syndiotactic polystyrene: 3. Crystal structure of planar form I

**Yozo Chatani* and Yukio Shimane**
*Department of Material Systems Engineering, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan*

**and Toshikazu Ijitsu and Toshimitsu Yukinari**
*Central Research Laboratories, Idemitsu Kosan Co. Ltd, Kimitsu, Chiba 299-02, Japan*
*(Received 27 February 1992; revised 11 June 1992)*

The crystal structure of a planar zigzag form of syndiotactic polystyrene (planar form I) obtained by annealing as-cast samples from solutions (molecular compounds with the solvents) was studied by X-rays. Crystal data are as follows: orthorhombic system, space group $P2_12_12_1$ (no. 19), but finally Pbnm (no. 62), $a = 8.81$ Å, $b = 28.82$ Å, $c$ (chain axis) $= 5.06$ Å, eight monomer units (four chains) per unit cell. Planar form I is different in alignment of the planar zigzag chains from planar form II obtained by melt-crystallization, which belongs to the hexagonal system. Moreover, the crystal structure of planar form I is characterized by a 'stacking fault' in the molecular packing.

**(Keywords: syndiotactic polystyrene: X-ray diffraction; crystal structure; disordered structure; polymorphism)**

## INTRODUCTION

Since the successful synthesis of a highly syndiotactic polystyrene (sPS) was reported in 1986[1], the structure of sPS has been investigated by several workers[2–10]. In a previous paper[11], polymorphism in sPS has been reported. In particular, as-cast sPS samples from solutions with a variety of solvents are molecular compounds of sPS with the solvents used, in which the sPS chains assume a twofold helix of type $(\text{-TTGG-})_2$[12]. When the as-cast samples were annealed at high temperatures, above ~190°C, the molecular compounds underwent a transition to a planar zigzag form (planar form I) involving removal of the solvent (guest). This planar form, however, gave an X-ray diffraction pattern different from that of melt-crystallized sPS which is again a planar zigzag form (planar form II), indicating that both phases are different in molecular packing from each other: the unit cell of planar form II was reported to be hexagonal[6,10]. This study revealed that planar form I exhibits a rather rare type of disorder in molecular packing.

## EXPERIMENTAL

Syndiotactic polystyrene[1] with a weight-average molecular weight of $1.3 \times 10^6$ ($M_w/M_n = 2.8$) and a triad syndiotacticity greater than 99% was used. Uniaxially oriented samples of planar form I were prepared by annealing uniaxially oriented samples of the sPS–toluene molecular compound above 200°C according to a previous paper[11].

Nickel-filtered CuK$\alpha$ radiation was used throughout this study. *Figure 1* shows the X-ray fibre pattern of planar form I. The $d$-spacings of the reflections were measured with a cylindrical camera of diameter 100 mm and they were corrected with those of NaCl powder. The reflection intensities were obtained using the same camera by the multiple-film method and measured visually with an intensity scale. The equatorial reflections were again observed with a position-sensitive proportional counter system equipped with an arc-type probe. The meridional reflections for the uniaxially oriented sample were observed by the Norman method employing a Weissenberg camera.

The density of the sample was determined by the flotation method with densities of liquid media (NaCl aqueous solutions) measured using a pycnometer.

## STRUCTURE ANALYSIS

### Unit cell and space group

In the X-ray fibre pattern, 40 independent reflections were observed on the zero, first and second layer lines. In addition, two meridional reflections (very strong 002 and week 004 reflections) were observed in the Weissenberg photograph. All the observed reflections could be indexed in terms of an orthorhombic cell with cell constants $a = 8.81$, $b = 28.82$ and $c$ (chain axis) $= 5.06$ Å. The observed chain repeat of 5.06 Å is straightforwardly interpreted in terms of the fully extended zigzag chain, the chain repeat comprising two monomer units. Since the systematic absences of reflections ($h00$ when $h$ is odd, $0k0$ when $k$ is odd, and

---

*To whom correspondence should be addressed. Present address: Nanamatsu 1-16-24, Amagasaki, Hyogo 660, Japan

0032–3861/93/081625–05

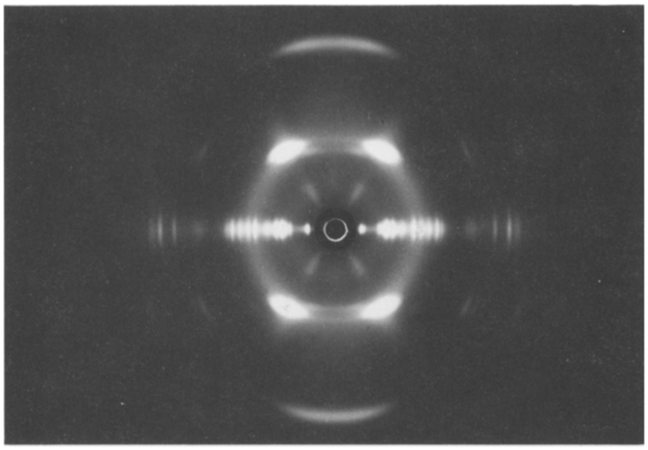

**Figure 1** X-ray fibre photograph for planar form I

$00l$ when $l$ is odd) were detected, the space group was assumed to be $P2_12_12_1$ (no. 19). As shown later, however, the resulting structure in this study was found to exhibit a higher symmetry of space group Pbnm (no. 62). This unit cell gives a calculated density of $1.08\,\mathrm{g\,cm^{-3}}$ comparable to the observed density of $1.09\,\mathrm{g\,cm^{-3}}$ when it contains eight monomer units (four polymer chains).

### *Molecular packing*

Based on the planar zigzag chains having the normal bond lengths and bond angles, many crystal structure models in the *ab*-projection, the plane group of which is pgg, were first examined by trial and error. However, despite getting only one plausible model which could fairly explain the observed intensities for $hk0$ reflections with $(h+k)$ even, that model never satisfied the reflection intensities for $(h+k)$ odd. Here we noticed a characteristic feature in the X-ray diffraction pattern, that is, the $hk0$ equatorial reflections with $(h+\mathrm{k})$ odd are rather broad as compared with the reflections with $(h+k)$ even. This feature is seen in *Figure 2*, which is the diffraction curve of the equator for the uniaxially oriented sample. The 1 2 0, 1 4 0 and 2 3 0 reflections appear solely, but they are evidently broad as compared with the reflections of $(h+k)$ even. Again, the intensities of $(h+k)$ odd reflections varied slightly from sample to sample, indicating that the molecular arrangement involves some kind of disorder, and the structure seemed to be pseudo *c*-centred or, if not, very close. This feature was independently observed by Katayama and co-workers by electron diffraction for single crystals of planar form I[9]. Therefore we had to consider a disordered structure as shown in *Figure 3*. In the figure, molecules indicated by full lines and by broken lines are statistically disposed in the unit cell. Here only molecules indicated by full lines or by broken lines, respectively, satisfy the symmetry of plane group pgg. However, from the aspect of intermolecular contacts, the alignment of the molecules along the *a*-axis must be regular in each array, but two types of alignment of the molecules as shown by full lines (F-array) and broken lines (B-array) are feasible. After trial-and-error procedure in structure factor calculation, the best positions of the two arrays were decided so that the B-array is related to the F-array by mirror operation about a plane at $x=1/4$ or $3/4$. However, if both arrays are to exist in equal probability, the structure must be of *c*-centre, and $(h+k)$ odd reflections disappear systematically. In practice, however, $(h+k)$ odd reflections appeared. The structure model was then refined by changing the appearance ratio of F:B. The discrepancy factor for all the observed equatorial reflections dropped to 14% when the appearance probabilities of F- and B-arrays were 70 and 30%, respectively, or vice versa. The reflection intensities of the layer lines, including the extremely strong 0 0 2, were also explained well when the benzene planes are on the planes at $z=1/4$ and $3/4$, and hence the methylene groups are on $z=0$ and $1/2$. The discrepancy factor for all observed reflections was 17%, where the thermal parameters were assumed to be $8.0\,\text{Å}^2$ for all the atoms including the hydrogen atoms. *Table 1* shows the atomic coordinates. The observed and calculated structure factors are compared in *Table 2*.

As already mentioned, the symmetry of the resulting structure is higher than that of the assumed $P2_12_12_1$, because all the atoms were found to be disposed at special *z*-positions, involving generation of centres of symmetry at (1/4, 0, 0) and other equivalent positions. Therefore the structure has the symmetry of space group Pbnm (no. 62) regardless of the disorder: only F or only B molecules

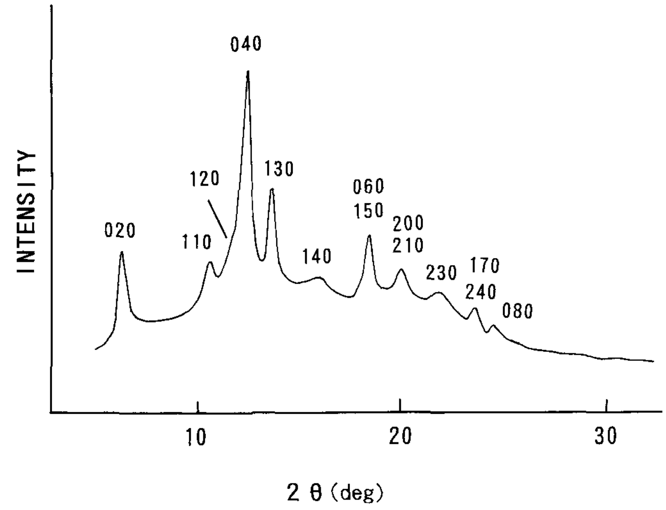

**Figure 2** X-ray diffraction curve of equator for planar form I

**Table 1** Fractional atomic coordinates[a]

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| C ($H_2$) | 0.148 | 0.061 | 0.000 |
| C (H) | 0.096 | 0.087 | 0.250 |
| C | −0.075 | 0.088 | 0.250 |
| C | −0.150 | 0.131 | 0.250 |
| C | −0.309 | 0.133 | 0.250 |
| C | −0.393 | 0.091 | 0.250 |
| C | −0.317 | 0.049 | 0.250 |
| C | −0.159 | 0.047 | 0.250 |
| C ($H_2$) | 0.148 | 0.061 | 0.500 |
| C (H) | 0.096 | 0.087 | 0.750 |
| C | 0.168 | 0.134 | 0.750 |
| C | 0.327 | 0.139 | 0.750 |
| C | 0.393 | 0.183 | 0.750 |
| C | 0.302 | 0.223 | 0.750 |
| C | 0.143 | 0.218 | 0.750 |
| C | 0.077 | 0.174 | 0.750 |

[a] The coordinates of the hydrogen atoms that have a C–H distance of 1.10 Å are omitted from this table. The atomic coordinates of the counterpart shown by broken lines in *Figure 3* are $(-x+0.5,\ y,\ z)$. When the space group Pbnm is adopted, the origin is shifted to $x=0.250$

**Table 2** Observed ($F_o$) and calculated ($F_c$) structure factors

| *hkl* | $F_o$ | $F_c$ | *hkl* | $F_o$ | $F_c$ |
|---|---|---|---|---|---|
| 020 | 28 | 27.2 | 101, 111 | 108 | 117.2 |
| 110 | 24 | 20.8 | 121 | – | 3.0 |
| 120 | 33 | 32.7 | 041, 131 | 71 | 94.6 |
| 040 | 63 | 65.4 | (051) | – | 0.0 |
| 130 | 48 | 44.9 | 141 | – | 1.0 |
| 140 | 24 | 25.2 | 151, 061 | 19 | 15.5 |
| 150, 060 | 45 | 50.1 | (201) | – | 0.0 |
| 200, 210 | 33 | 28.5 | 211 | – | 0.5 |
| 160 | – | 7.2 | 161 | – | 0.4 |
| 220 | – | 1.2 | 221 | – | 4.9 |
| 230 | 34 | 28.8 | (071) | – | 0.0 |
| 240, 170 | 40 | 41.6 | 231 | – | 0.4 |
| 080, 250 | 28 | 34.3 | 241 | – | 2.6 |
| 180 | – | 7.4 | 171 | – | 1.4 |
| 260 | – | 2.1 | 081 | – | 4.3 |
| 190 | – | 4.6 | 251 | – | 1.7 |
| 270 | – | 3.3 | 181 | – | 0.3 |
| 310, 0109, 320 | 23 | 24.1 | 261 | 17 | 7.4 |
| 330, 280, 1100, 340 | 24 | 29.2 | 191, 271, 301, 311 | 39 | 38.6 |
| 350, 290 | 17 | 15.6 | 0101 | – | 1.6 |
| 360 | – | 6.1 | 321 | – | 2.8 |
| 1110 | – | 0.6 | 331, 281 | 27 | 29.5 |
| 2100, 0120, 370 | 40 | 41.2 | 1101 | – | 0.0 |
| 1120 | – | 6.3 | 341 | – | 0.7 |
| 380 | – | 1.6 | (0111) | – | 0.0 |
| 2110 | – | 7.9 | 351 | – | 4.3 |
| 400, 410 | 49 | 54.7 | 291 | – | 0.8 |
| 420 | – | 13.4 | 361 | – | 2.5 |
| 390 | – | 18.0 | 1111 | – | 5.1 |
| 1130, 430, 2120, 440 | 38 | 54.1 | 2101 | – | 9.7 |
| 0140 | – | 14.2 | 0121 | – | 3.3 |
| 450 | – | 0.6 | 371 | – | 4.8 |
| 3100 | – | 0.2 | 1121 | – | 2.5 |
| 1140, 460, 2130 | 23 | 16.2 | 381 | – | 0.2 |
| 3110, 470 | 19 | 9.3 | 2111 | – | 4.6 |
| 480, 1150, 2140, 3120 | 28 | 25.9 | (0131) | – | 0.0 |
| 490 | – | 1.2 | (401) | – | 0.0 |
| 0160 | – | 1.6 | 411 | – | 4.9 |
| 3130 | – | 4.9 | 421 | – | 3.8 |
| 1160, 2150, 510, 4100, 520 | 22 | 11.9 | 391, 1131, 431, 2121, 441 | 37 | 40.3 |
| 530 | – | 4.7 | 0141 | – | 4.7 |
| 540 | – | 3.7 | 451 | – | 0.4 |
| 4110 | – | 0.1 | 3101 | – | 2.2 |
| 3140 | – | 5.6 | 1141 | – | 0.1 |
| 550 | – | 2.3 | 461 | – | 3.4 |
| 2160 | – | 10.6 | 2131 | – | 1.1 |
| 1170 | – | 4.7 | 3111 | – | 2.9 |
| 560 | – | 1.6 | 471 | – | 0.5 |
| 4120$^a$ | – | 2.5 | (0151) | – | 0.0 |
| 0220, 6100, 5150, 1220, | 27 | 26.3 | 481 | – | 1.8 |
| 4180, 3200 |  |  | 1151, 2141, 3121 | 26 | 14.3 |
| 6110 | – | 1.1 | 491 | – | 1.0 |
| 5160 | – | 1.3 | 0161 | – | 0.4 |
| 710, 2220, 720, 6120, | 23 | 20.4 | 3131, 1161, 501, 2151, 511 | 30 | 24.8 |
| 4190, 730 |  |  | (052) | – | 0.0 |
| (011)$^b$ | – | 0.0 | 142 | – | 0.2 |
| 021 | 14 | 10.1 | 152, 062 | 14 | 21.8 |
| (031) | – | 0.0 | 202 | – | 3.6 |

**Table 2** *continued*

| *h k l* | $F_o$ | $F_c$ | *h k l* | $F_o$ | $F_c$ |
|---|---|---|---|---|---|
| 2 1 2 | – | 1.0 | (0 12 2) | – | 0.0 |
| 1 6 2 | – | 5.3 | 3 5 2 | – | 5.9 |
| 2 2 2 | – | 8.3 | 2 9 2 | – | 4.6 |
| (0 7 2) | – | 0.0 | 3 6 2 | – | 4.4 |
| 2 3 2 | – | 0.7 | 1 11 2 | – | 10.9 |
| 2 4 2 | – | 2.8 | 2 10 2 | – | 15.2 |
| 1 7 2 | – | 5.3 | 0 12 2 | – | 0.6 |
| 0 8 2, 2 5 2 | 18 | 10.8 | 3 7 2 | – | 0.1 |
| 1 8 2 | – | 5.8 | 1 12 2 | – | 1.8 |
| 2 6 2 | – | 9.5 | 3 8 2 | – | 1.6 |
| (0 9 2) | – | 0.0 | 2 11 2 | – | 2.8 |
| 1 9 2, 2 7 2 | 24 | 27.3 | (0 13 2) | – | 0.0 |
| (3 0 2) | – | 0.0 | 4 0 2, 4 1 2 | 21 | 19.2 |
| 3 1 2 | – | 0.5 | 4 2 2 | – | 4.2 |
| 0 10 2 | – | 7.7 | 3 9 2 | – | 6.3 |
| 3 2 2 | – | 5.3 | 1 13 2 | – | 10.0 |
| 3 3 2, 2 8 2 | 22 | 24.2 | 4 3 2 | – | 0.8 |
| 1 10 2 | – | 1.2 | 2 12 2, 4 4 2 | 24 | 27.1 |
| 3 4 2 | – | 4.1 | 0 14 2 | – | 1.0 |

[a] As for the equator, there are 39 non-observed reflections between 4 12 0 and 0 22 0. Although these non-observed reflections are omitted in the table for simplicity, the calculated structure factors for these reflections are $<8.7$

[b] Reflections in parentheses disappear theoretically for the space group Pbnm

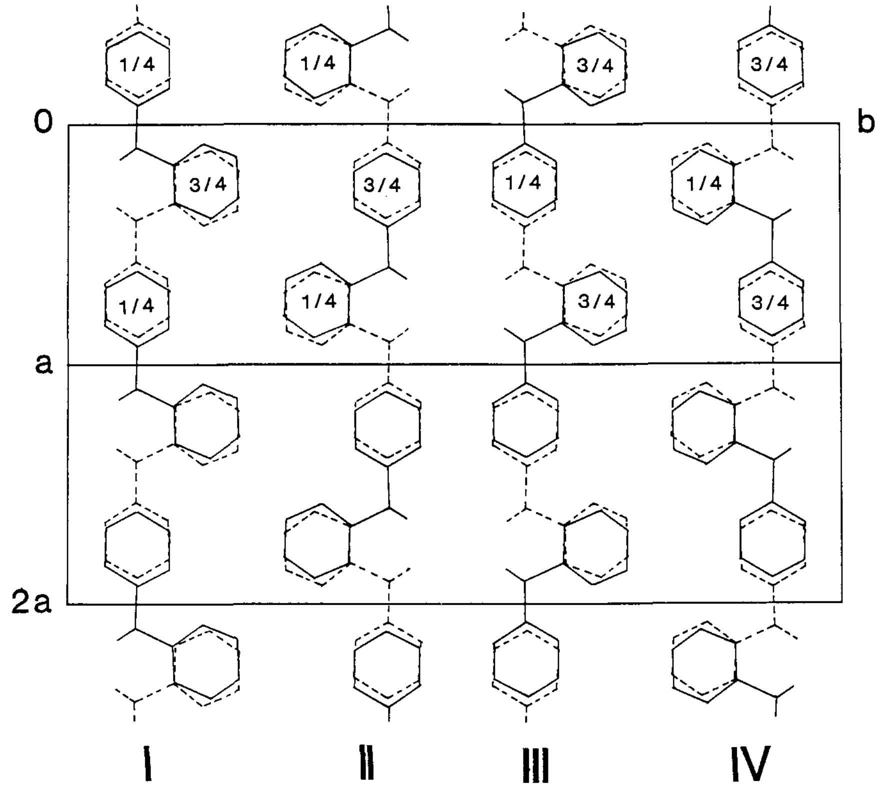

**Figure 3** Crystal structure of planar form I viewed along the chain axis. For molecules shown by full lines and broken lines, see text

themselves construct the structure having the symmetry of space group Pbnm. The space group Pbnm exhibits systematic absences of reflections for $0kl$ when $(k+l)$ is odd, $h0l$ when $h$ is odd in addition to the systematic absences in $P2_12_12_1$. In fact, in *Table 2*, reflections in parentheses, which satisfy the above conditions, give zero values and were not in practice observed.

## RESULTS AND DISCUSSION

Planar form I obtained by annealing as-cast samples from solutions (the molecular compounds with solvents) involves in any event a disorder concerning the molecular packing that is classified as a 'stacking fault'.

Many isotactic vinyl polymers are well known

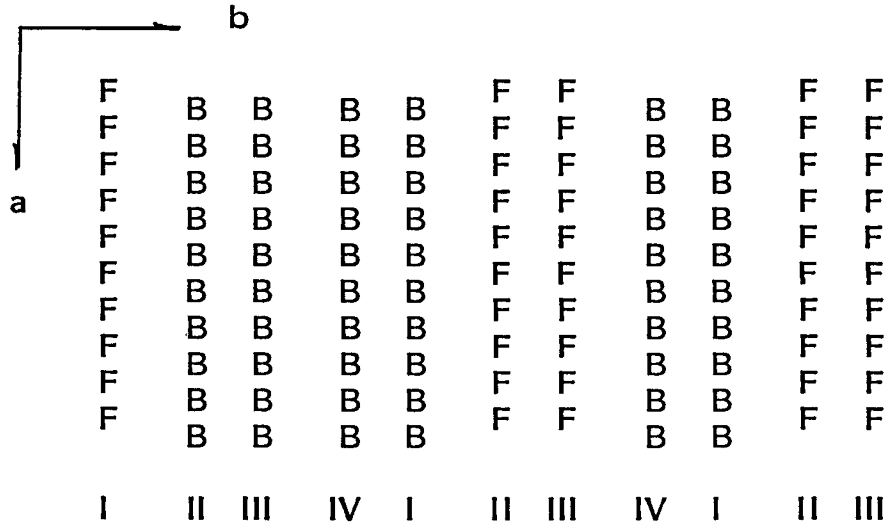

**Figure 4** Schematic representation of stacking fault in planar form I. F and B correspond to polymer chains shown by full lines and broken lines, respectively, in *Figure 3*

to exhibit disorder in molecular arrangement; these disorders are exclusively due to random occupation of one site by either of two kinds of helical polymers that have the same helical sense but differ in directional quality, i.e. up- and down-senses[13–15]. Therefore it can be said that the disorder in planar form I is of a rather rare type. As shown in *Figure 3*, the molecules shown by full lines (F) and by broken lines (B) are arranged randomly in the crystal lattice as a whole (the crystals consisting of only F molecules and only B molecules are equivalent to each other). However, the alignment of the molecules along the *a*-axis, for example array I, must be regular, because, since the benzene rings of F and B molecules in the array occupy almost the same position, random alignment of F and B molecules brings about molecular collision between the neighbouring molecules. Thus, each array must consist of only F molecules (F-array) or only B molecules (B-array). The fault must therefore take place in stacking of two such types of arrays along the *b*-axis. Here again additional restrictions on the stacking fault will be considered, namely, on the boundary between array II and array III (and equivalently between array IV and array I), both arrays may preferably be of the same sense (F–F or B–B), because the shortest $CH_2$---$CH_2$ carbon distance at this boundary is 3.96 Å for the F–F pair (or B–B pair), while the distance is too short (3.52 Å) for the F–B pair (or B–F pair). On the other hand, as is seen in *Figure 3*, on the boundary between array I and array II (and between array III and array IV) the molecules come into contact through benzene---benzene with C---C distances greater than 4.01 Å. This implies that there is no great difference in intermolecular interactions between the F–F pair and F–B pair. Therefore it is most likely that the stacking fault takes place exclusively on the boundary between array I and array II (and between array III and array IV). An example of the statistical molecular arrangement is shown in *Figure 4*. If such faults take place at random, the probabilities of two senses are equally 50%, the resulting structure being *c*-centred. Therefore reflections with $(h+k)$ odd must disappear systematically. However, there is a slight difference in the benzene---benzene contact for the F–F pair and the F–B pair: the shortest benzene hydrogen---benzene hydrogen distance is 2.4 Å for the F–F pair, but 2.1 Å for the F–B pair. This difference seems to explain the X-ray result that the appearance ratio of F:B (or B:F) is not 50:50 but 70:30.

We first assumed that the space group is $P2_12_12_1$, and finally accepted Pbnm. Strictly speaking, the atomic positions might vary, more or less, depending on the irregularity in the sequence of arrays (F–F and F–B). Again, the reflection intensities and the broadness of the reflections with $(h+k)$ odd vary depending on the sample history. However, if the benzene rings are disposed, on average, on the planes of $z=1/4$ and $3/4$, and the methylene groups are on the planes at $z=0$ and $1/2$ as decided in the structure determination, we can accept a higher symmetry Pbnm regardless of the disorder.

## REFERENCES

1 Ishihara, N., Seimiya, T., Kuramoto, M. and Uoi, M. *Macromolecules* 1986, **19**, 2464
2 Chatani, Y., Fujii, Y., Shimane, Y. and Ijitsu, T. *Polym. Prepr. Jpn* (*Engl. Edn*) 1988, **37**, E428
3 Shimane, Y., Ishioka, T., Chatani, Y. and Ijitsu, T. *Polym. Prepr. Jpn* (*Engl. Edn*) 1988, **38**, E452
4 Immirzi, A., De Candia, F., Inannelli, P., Vittoria, V. and Zambelli, A. *Makromol. Chem. Rapid Commun.* 1988, **9**, 761
5 Vittoria, V., De Candia, F., Iannelli, P. and Immirzi, A. *Makromol. Chem., Rapid Commun.* 1988, **9**, 765
6 Greis, O., Xu, Y., Asano, T. and Peterman, J. *Polymer* 1989, **30**, 590
7 Kobayashi, M., Nakaoki, T. and Ishihara, N. *Macromolecules* 1989, **22**, 4377
8 Kobayashi, M., Nakaoki, T. and Ishihara, N. *Macromolecules* 1990, **23**, 78
9 Tsuji, M., Tosaka, M., Okihara, T., Kawaguchi, A. and Katayama, K. *Polym. Prepr. Jpn* (*Engl. Edn*) 1989, **38**, E876
10 Guerra, G., Vitagliano, V. M., De Rosa, C., Petraccone, V. and Corradini, P. *Macromolecules* 1990, **23**, 1539
11 Chatani, Y., Shimane, Y., Inoue, Y., Inagaki, T., Ishioka, T., Ijitsu, T. and Yukinari, T. *Polymer* 1992, **33**, 488
12 Chatani, Y., Shimane, Y., Inagaki, T., Ijitsu, T., Yukinari, T. and Shikuma, H. *Polymer* 1993, **34**, 1620
13 Natta, G. and Corradini, P. *Makromol. Chem.* 1955, **16**, 77
14 Natta, G. and Corradini, P. *Nuovo Cimento* 1960, **15**, 40
15 Sakakihara, H., Takahashi, Y., Tadokoro, H., Oguni, N. and Tani, H. *Macromolecules* 1973, **6**, 205