S0032-3861(96)00353-9

Polymer Vol. 37 No. 23, pp. 5247–5253, 1996

0032-3861/96/\$15.00 + 0.00

Polymorphism of syndiotactic poly(*p*-methylstyrene): oriented samples

Claudio De Rosa*, Vittorio Petraccone, Gaetano Guerra and Carla Manfredi
Dipartimento di Chimica, Università di Napoli 'Federico II', Via Mezzocannone 4, 80134 Napoli, Italy
(Received 18 November 1995; revised 21 February 1996)

Possible routes for obtaining oriented fibres of the various known crystalline forms of syndiotactic poly(*p*-methylstyrene) are described. These routes include solvent diffusion and/or annealing on mesomorphic fibres. The X-ray fibre diffraction patterns show that form I, form II and all the clathrate forms are characterized by chains with helical s(2/1)2 conformation and repeating distance of ≈7.8 Å, while the mesomorphic form (form IV), form III as well as a new crystalline form (form V), are characterized by chains with *trans* planar conformation and repeating distance of ≈5.1 Å. Copyright © 1996 Elsevier Science Ltd.

(Keywords: syndiotactic poly(*p*-methylstyrene); polymorphism; oriented samples)

INTRODUCTION

The polymerization of styrene[1,2] and substituted styrenes[3–8] to fully syndiotactic polymers, in the presence of homogeneous catalytic systems, based on titanium or zirconium compounds and methylalumoxane, has been described.

The presence of a complex polymorphic behaviour[9–11] and the crystal structures of various modifications of syndiotactic polystyrene (s-PS)[12–18] have been reported. A complex polymorphic behaviour has been recently revealed also for syndiotactic poly(*p*-methylstyrene) (s-PPMS)[19–21]. This polymer does not crystallize by cooling from the melt or by annealing the amorphous phase while it readily crystallizes by casting or precipitation from solution as well as by solvent induced crystallization from the amorphous state[19]. On the basis of the X-ray diffraction patterns of unoriented samples of s-PPMS, three different crystalline forms and a mesomorphic form, as well as several clathrate forms (which include molecules of solvent) have been found[19]. The obtaining of crystalline and clathrate forms depends on the solvent, on the crystallization technique (e.g. casting, precipitation or induction by solvent from the amorphous state), or other parameters (e.g. temperature of casting, nature of the non-solvent in the precipitation)[19].

It has also been reported that by stretching all amorphous and semicrystalline (forms I and II and clathrates) s-PPMS samples, fibres are always produced in the mesomorphic form (form IV)[19]. For this reason oriented samples for the different crystalline and clathrate forms have not been available and their chain conformation was deduced only on the basis of *FT*i.r.[21] and solid state ^{13}C n.m.r.[20] studies on unoriented samples. According to these studies the chain conformations involved in the different forms are those found for s-PS (*trans* planar and s(2/1)2 helical).

In this paper possible routes for obtaining oriented fibres for the different crystalline and clathrate forms of s-PPMS, which involve solvent diffusion and/or annealing procedures on mesomorphic fibres, are presented. The availability of oriented crystalline samples and of their X-ray diffraction patterns (fibre spectra) is very helpful for the structural characterization of these crystalline and clathrate forms.

EXPERIMENTAL

s-PPMS was synthesized as described in ref. 19. The syndiotacticity of the polymer was evaluated by ^{13}C n.m.r.[8]; the fraction of *rrrr* pentads was higher than 95%.

Films of s-PPMS were obtained by casting procedures, generally conducted with 10% w.w. solutions.

The drawing of s-PPMS films was conducted with a Minimat apparatus with a strain rate of 0.1–0.2 min^{-1} at temperatures in the range of 120–150°C.

Wide angle X-ray diffraction patterns were obtained with nickel filtered Cu Kα radiation. The diffraction patterns of oriented samples were obtained with photographic cylindrical and flat camera, whereas those for unoriented samples were obtained with an automatic Philips powder diffractometer.

RESULTS AND DISCUSSION

Oriented clathrate forms by guest diffusion in mesomorphic fibres

The X-ray fibre diffraction pattern of the mesomorphic form, obtained by stretching a film in form I at 130°C, is reported in *Figure 1*. Broad equatorial

---

* To whom correspondence should be addressed

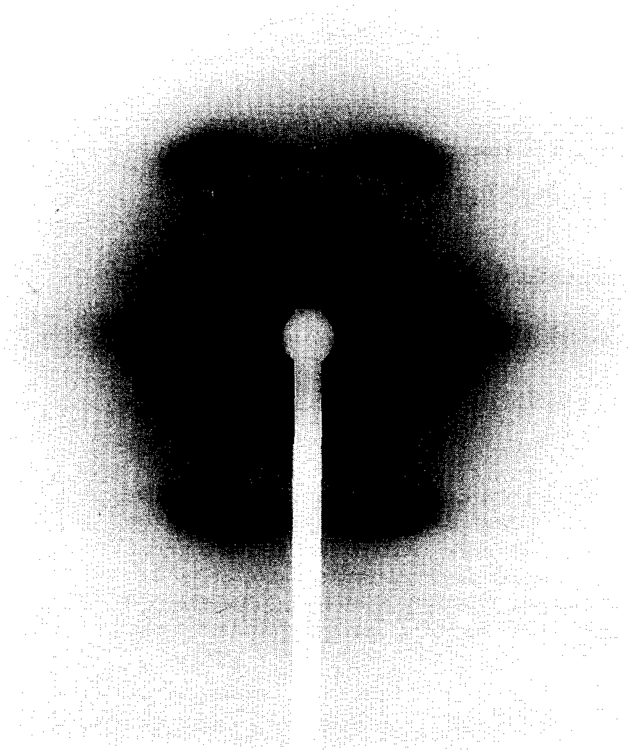

Figure 1 X-ray fibre diffraction pattern of a s-PPMS sample in the mesomorphic form (form IV), obtained by stretching at 130°C of a film in form I

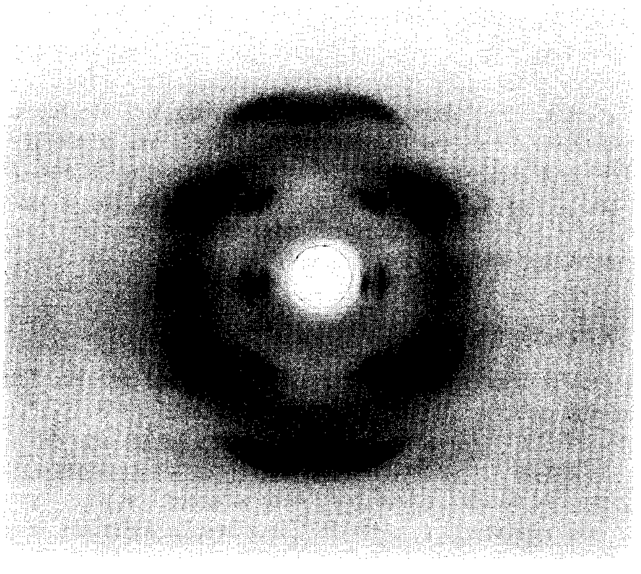

Figure 2 X-ray fibre diffraction pattern of a s-PPMS sample in the clathrate form including tetrahydrofuran

halos centred at $2\theta = 6.2^{\circ}$, 11.5° and 15.9° (Cu Kα), a meridional reflection at $\zeta = 0.39\,\text{Å}^{-1}$ and a strong reflection at $2\theta = 20^{\circ}$ (Cu Kα) on the first layer line ($\zeta = 0.20\,\text{Å}^{-1}$), are present. From these data a value of the chain axis of nearly 5.1 Å is obtained. This identity period is indicative of the presence of chains with *trans* planar conformation in the mesomorphic form.

The X-ray fibre diffraction pattern of a mesomorphic fibre after immersion for 1 min, under condition of fixed length, in tetrahydrofuran (THF), is reported in *Figure 2*. All the reflections observed in *Figure 2* are reported in

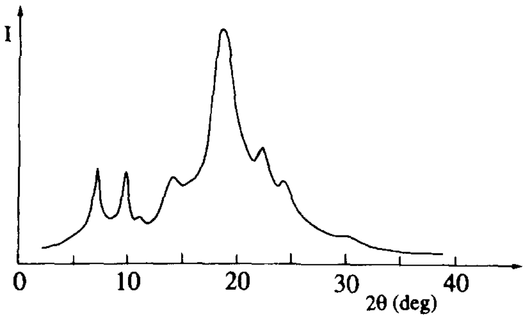

Figure 3 X-ray powder diffraction pattern of an unoriented s-PPMS sample in the clathrate form including tetrahydrofuran

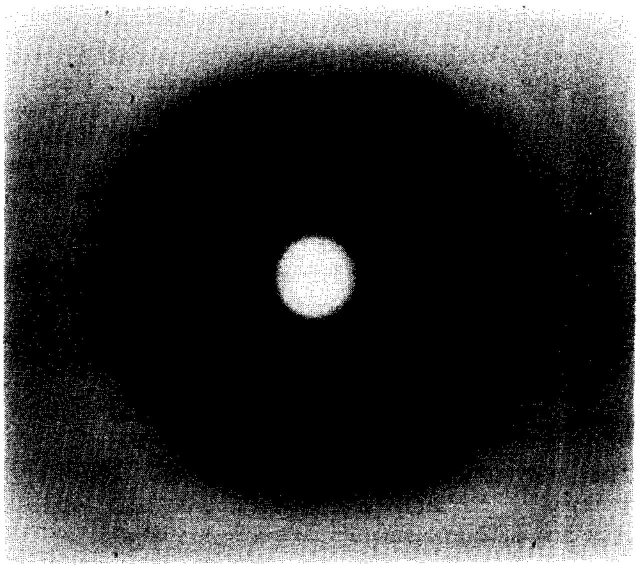

Figure 4 X-ray fibre diffraction pattern of a s-PPMS sample in the clathrate form including *o*-dichlorobenzene

Table 1 Diffraction angles 2θ, Bragg distances d, reciprocal coordinates ξ and ζ and intensities of the reflections on the layer lines l observed in the X-ray fibre diffraction pattern of the clathrate form including tetrahydrofuran (*Figure 2*)

2θ (deg)	d (Å)	ξ (Å^{-1})	ζ (Å^{-1})	l	I_{obs}[a]
7.0	12.6	0.079	0	0	s
9.6	9.19	0.109	0	0	s
11.0	8.04	0.124	0	0	vvw
13.75	6.44	0.155	0	0	vw
15.5	5.72	0.175	0	0	vvw
18.0	4.93	0.203	0	0	m
21.25	4.18	0.239	0	0	w
25.5	3.49	0.286	0	0	vvw
29.25	3.05	0.327	0	0	vvw
30.75	2.91	0.344	0	0	vvw
13.6	6.51	0.082	0.130	1	m
18.2	4.87	0.158	0.130	1	mw
19.2	4.63	0.172	0.130	1	s
20.7	4.29	0.193	0.130	1	w
22.3	3.98	0.215	0.130	1	m
24.5	3.63	0.243	0.130	1	vw
26.7	3.34	0.270	0.130	1	vvw
29.7	3.01	0.305	0.130	1	vvw
22.3	3.99	0.	0.246	2	m
24.0	3.70	0.100	0.251	2	s
27.1	3.28	0.173	0.251	2	vvw
29.3	3.05	0.212	0.251	2	vvw
31.4	2.85	0.246	0.251	2	vw

[a] s = strong, m = medium, w = weak, vw = very weak, vvw = very very weak

Table 2 Diffraction angles 2θ, Bragg distances d, reciprocal coordinates ξ and ζ and intensities of the reflections on the layer lines l observed in the X-ray fibre diffraction pattern of the clathrate form including *o*-dichlorobenzene (*Figure 4*)

2θ (deg)	d (Å)	ξ (Å^{-1})	ζ (Å^{-1})	l	I_{obs}[a]
8.4	10.56	0.095	0	0	vw
9.3	9.56	0.104	0	0	s
16.4	5.41	0.185	0	0	s
28.5	3.13	0.319	0	0	vw
31.2	2.86	0.349	0	0	vw
33.7	2.66	0.376	0	0	vw
15.4	5.75	0.118	0.128	1	vs
19.9	4.45	0.185	0.128	1	s
21.8	4.07	0.210	0.128	1	s
26.4	3.37	0.267	0.128	1	m
22.1	4.02	0	0.244	2	s
27.3	3.26	0.185	0.244	2	vw
29.4	3.03	0.222	0.244	2	vw

[a] s = strong, m = medium, w = weak, vw = very weak

Table 3 Diffraction angles 2θ, Bragg distances d, reciprocal coordinates ξ and ζ and intensities of the reflections on the layer lines l observed in the X-ray fibre diffraction pattern of form II (*Figure 6*)

2θ (deg)	d (Å)	ξ (Å^{-1})	ζ (Å^{-1})	l	I_{obs}[a]
9.7[b]	9.07	0.110	0	0	s
11.0	8.04	0.124	0	0	vvw
14.5	6.11	0.164	0	0	vw
18.3	4.86	0.206	0	0	mw
12.1	7.31	0.041	0.130	1	w
14.5	6.11	0.099	0.130	1	ms
17.9	4.95	0.154	0.130	1	s
21.5	4.13	0.204	0.130	1	ms
25.2	3.54	0.251	0.130	1	vvw
22.3	3.99	0	0.247	2	w
24.1	3.69	0.114	0.246	2	vw
26.9	3.31	0.175	0.246	2	vvw
29.6	3.02	0.222	0.246	2	vw

[a] s = strong, ms = medium strong, w = weak, mw = medium weak, vw = very weak, vvw = very very weak

[b] The strong reflection at $2\theta = 9.7°$ observed in the fibre spectrum is resolved into two reflections at $2\theta = 9.2°$ and $9.7°$ in the powder spectrum[19]

Table 1. The X-ray powder diffraction pattern of an unoriented sample of the clathrate form including THF[19] (obtained by casting procedure from THF solution at room temperature) is reported in *Figure 3*. A comparison between the positions and the intensities of the reflections in the fibre spectrum of *Figure 2* and in the powder spectrum of *Figure 3*, shows that there is the same clathrate structure in both samples.

The data of *Table 1* correspond to a chain axis of nearly 7.8 Å, indicative of the presence in the clathrate including THF of chains with helical conformation of s(2/1)2 symmetry.

The X-ray diffraction pattern of oriented fibres of the clathrate form including *o*-dichlorobenzene (*o*-DCB), obtained by immersion of the mesomorphic fibre (under condition of fixed length) in *o*-DCB for 24 h, is shown in *Figure 4*. All the reflections observed in *Figure 4* are reported in *Table 2*. The X-ray powder pattern of an unoriented sample of the clathrate form including *o*-DCB[19] (obtained by casting procedure from *o*-DCB at room temperature) is reported in *Figure 5*. A comparison between the fibre pattern of *Figure 4* with the powder pattern of *Figure 5* shows that there is a same clathrate structure in both samples. Also for the clathrate including *o*-DCB, the data of *Figure 4* and *Table 2* correspond to a chain axis of nearly 7.8 Å, indicative of helical s(2/1)2 chain conformation.

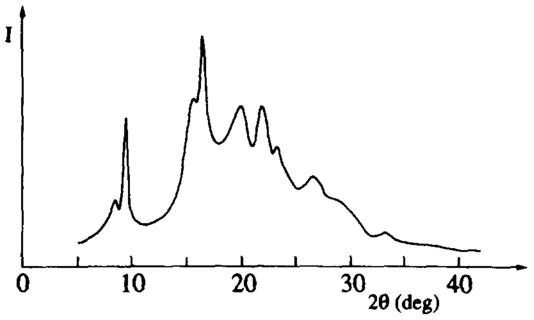

Figure 5 X-ray powder diffraction pattern of an unoriented s-PPMS sample in the clathrate form including *o*-dichlorobenzene

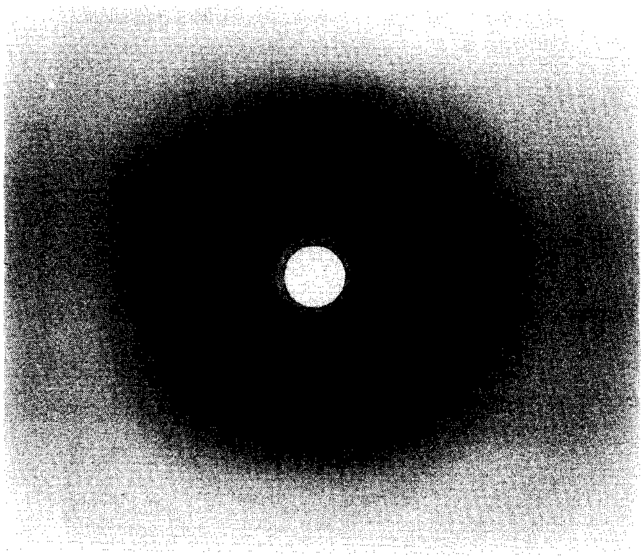

Figure 6 X-ray fibre diffraction pattern of form II of s-PPMS, obtained by annealing of oriented THF clathrate samples in the temperature range 70–80°C

Annealing of clathrate fibres: oriented crystalline forms I and II

Annealing of oriented samples in the clathrate forms represents a possible route to obtain oriented fibres of various crystalline forms of s-PPMS.

As described in ref. 19, the polymorphic behaviour of the clathrates upon thermal treatments is complex, being dependent on the type and the amount of the guest molecules. For instance, in unoriented samples, the THF clathrate is transformed into form II by annealing in the temperature range 90–150°C, whereas it is transformed into mesomorphic form IV by rapid heating up to 180°C[19].

The polymorphic behaviour of oriented samples of the THF clathrate is also more complex. Indeed annealing of the clathrate fibre, under condition of fixed length, in the temperature range 70–80°C (for 24 h) produces a fibre with low crystallinity whose X-ray diffraction pattern is shown in *Figure 6*. This pattern presents all the reflections typical of form II (by comparison with the powder patterns reported in ref. 19).

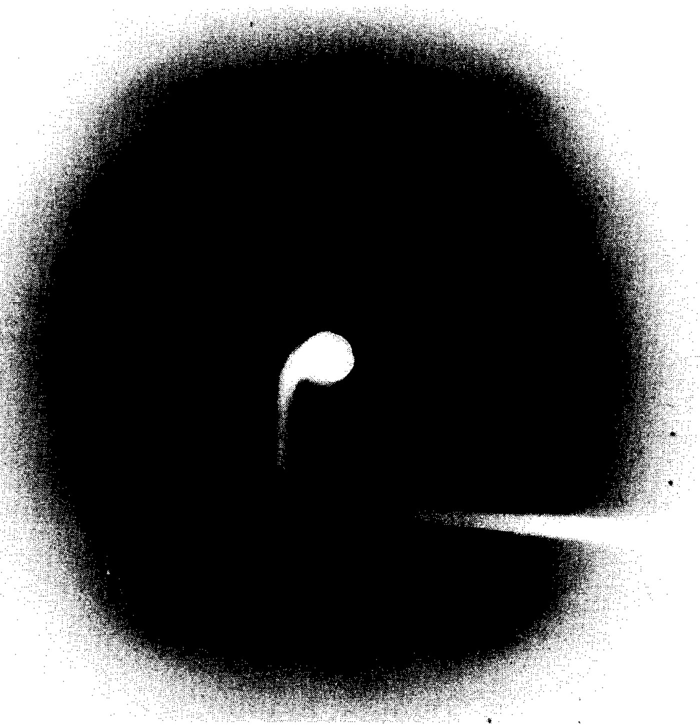

Figure 7 X-ray fibre diffraction pattern of the THF clathrate fibre annealed at 90°C (form I + form II)

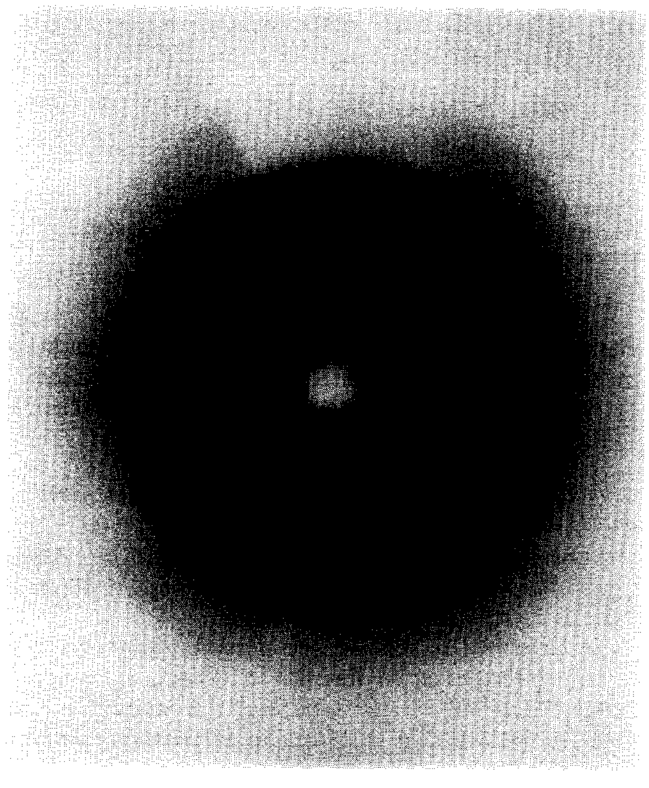

Figure 8 X-ray fibre diffraction pattern of the *o*-DCB clathrate fibre annealed at 100°C (form I + form IV)

After a successive annealing at 90°C, the X-ray diffraction pattern is still typical of form II but presents also some extra-reflections typical of form I (*Figure 7*). The reflections of form II (*Figures 6* and *7*) are reported in *Table 3* and correspond to a chain axis of nearly 7.8 Å. This indicates that form II is characterized by chains in a helical s(2/1)2 conformation.

Table 4 Diffraction angles 2θ, Bragg distances d, reciprocal coordinates ξ and ζ and intensities of the reflections on the layer lines l observed in X-ray fibre diffraction patterns of form I (*Figures 7* and *8*)

2θ (deg)	d (Å)	ξ (Å^{-1})	ζ (Å^{-1})	l	I_{obs}[a]
7.41	11.9	0.084	0	0	m
15.1	5.86	0.171	0	0	w
16.4	5.39	0.186	0	0	s
16.2	5.48	0.130	0.128	1	w
22.6	3.93	0	0.257	2	m

[a] s = strong, m = medium, w = weak

The polymorphic behaviour upon thermal treatments of the *o*-DCB clathrate in oriented samples is simpler. Annealing in the temperature range 100–160°C led to oriented samples including both form I and mesomorphic form (form IV). The X-ray diffraction pattern of the fibre annealed at 100°C is reported in *Figure 8*. The reflections of form I observed in the patterns of *Figures 7* and *8* are reported in *Table 4*.

Also for form I of s-PPMS a chain axis of nearly 7.8 Å, indicative of a s(2/1)2 helical conformation of the chain, is observed.

Annealing of mesomorphic fibres: oriented crystalline forms III and V

As described in ref. 19 unoriented samples in form III of s-PPMS are obtained by annealing of form I or form IV at high temperature (e.g., 210°C). In order to obtain oriented fibres in form III, annealing at 210°C for 20 h, under condition of fixed length, of fibres in mesomorphic form have been performed. The X-ray fibre diffraction pattern of form III is shown in *Figure 9*.

All the reflections observed in the spectrum of form III of *Figure 9* are reported in *Table 5*. From these data a chain axis of nearly 5.1 Å, indicating a *trans* planar conformation of the chains in form III, is evaluated. The

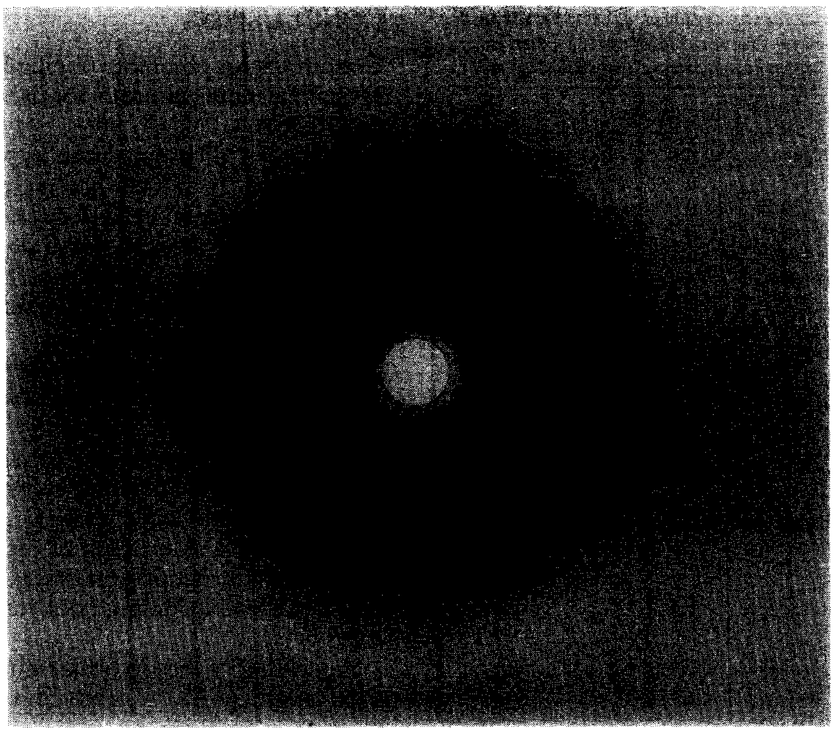

Figure 9 X-ray fibre diffraction pattern of form III of s-PPMS, obtained by annealing of the mesomorphic fibre at 210°C. Some reflections of form V are also present

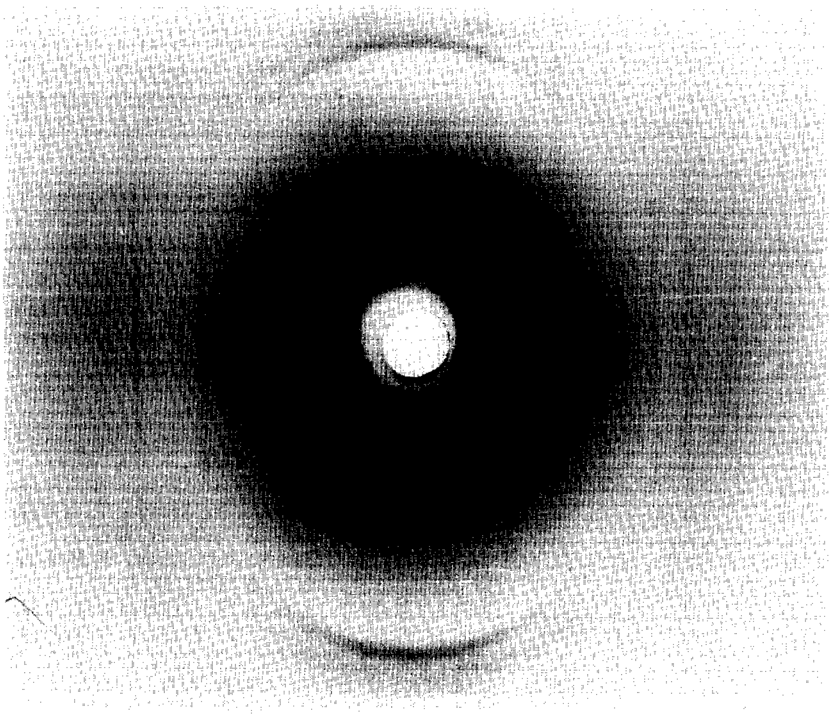

Figure 10 X-ray fibre diffraction pattern of form V of s-PPMS, obtained by annealing of poorly oriented amorphous samples at 180°C

crystal structure of the form III of s-PPMS has been recently solved and refined with the Rietveld method[22]. *Trans* planar chains are packed in an orthorhombic unit cell with axes $a = 13.36$ Å, $b = 23.21$ Å and $c = 5.12$ Å. The space group proposed is *Pnam*[22].

The X-ray fibre diffraction pattern of a poorly oriented amorphous sample annealed (under condition of fixed length) at 180°C, is shown in *Figure 10*. The reflections observed in the spectrum of *Figure 10* do not correspond to those of the known crystalline forms of s-PPMS, therefore a new crystalline form (thereafter called form V) is obtained. All the reflections observed in the spectrum of form V of *Figure 10* are reported in *Table 6*. These data correspond to a chain axis of nearly 5.1 Å and indicate the presence of chains in *trans* planar conformation for form V.

Table 5 Diffraction angles 2θ, Bragg distances d, reciprocal coordinates ξ and ζ and intensities of the reflections on the layer lines l observed in the X-ray fibre diffraction pattern of form III (*Figure 9*)

2θ (deg)	d (Å)	ξ (Å^{-1})	ζ (Å^{-1})	l	I_{obs}[a]
7.75	11.4	0.088	0	0	vs
10.4	8.53	0.117	0	0	vw
13.25	6.68	0.150	0	0	m
14.0	6.33	0.158	0	0	m
15.0	5.91	0.169	0	0	vw
16.75	5.29	0.189	0	0	w
17.75	5.00	0.200	0	0	w
23.25	3.83	0.261	0	0	vw
26.0	3.43	0.292	0	0	vvw
28.0	3.19	0.314	0	0	vw
18.2	4.87	0.063	0.196	1	vw
20.2	4.39	0.117	0.196	1	s
21.3	4.17	0.138	0.196	1	vvw
35.0	2.56	0	0.391	2	w

[a] vs = very strong, m = medium, w = weak, vw = very weak, vvw = very very weak

Table 6 Diffraction angles 2θ, Bragg distances d, reciprocal coordinates ξ and ζ and intensities of the reflections on the layer lines l observed in the X-ray fibre diffraction pattern of form V (*Figure 10*)

2θ (deg)	d (Å)	ξ (Å^{-1})	ζ (Å^{-1})	l	I_{obs}[a]
5.01	17.6	0.057	0	0	ms
5.74	15.3	0.066	0	0	ms
6.19	14.3	0.070	0	0	w
6.63	13.3	0.075	0	0	w
7.15	12.4	0.081	0	0	s
8.35	10.6	0.094	0	0	s
9.0	9.83	0.102	0	0	vw
9.75	9.07	0.110	0	0	w
10.5	8.42	0.119	0	0	ms
11.1	7.97	0.125	0	0	w
11.9	7.49	0.134	0	0	mw
12.3	7.20	0.139	0	0	ms
12.7	6.94	0.144	0	0	m
13.1	6.73	0.149	0	0	m
13.7	6.44	0.155	0	0	ms
14.3	6.19	0.162	0	0	m
15.0	5.91	0.169	0	0	s
15.6	5.68	0.176	0	0	ms
16.1	5.49	0.182	0	0	s
16.6	5.34	0.187	0	0	w
18.1	4.90	0.204	0	0	ms
18.9	4.68	0.214	0	0	ms
19.7	4.50	0.222	0	0	w
21.0	4.23	0.236	0	0	mw
21.2	4.19	0.239	0	0	w
22.1	4.02	0.249	0	0	w
22.5	3.94	0.254	0	0	vw
23.5	3.79	0.264	0	0	vvw
24.0	3.71	0.270	0	0	vvvw
25.4	3.50	0.286	0	0	m
26.3	3.38	0.296	0	0	m
27.2	3.27	0.306	0	0	m
28.7	3.10	0.322	0	0	m
31.7	2.82	0.355	0	0	vvw
34.5	2.60	0.385	0	0	vw
36.0	2.49	0.401	0	0	vw
36.8	2.44	0.410	0	0	vw
38.3	2.35	0.426	0	0	vw
41.7	2.16	0.463	0	0	w
20.5	4.34	0.120	0.197	1	vs
35.2	2.54	0	0.394	2	m

[a] vs = very strong, s = strong, ms = medium strong, m = medium, w = weak, vw = very weak, vvw = very very weak, vvvw = very very very weak

CONCLUSIONS

Conditions for obtaining oriented samples of the various crystalline and clathrate forms of s-PPMS have been described.

Stretching of amorphous as well as semicrystalline (forms I and II and clathrates) samples produces fibres in the pure mesomorphic form (form IV).

Diffusion of solvent, for instance *o*-dichlorobenzene or tetrahydrofuran, in the mesomorphic oriented fibres induces the formation of oriented samples for the different clathrate forms.

Suitable thermal treatments of oriented clathrate samples allow us to obtain oriented fibres of form I and II of s-PPMS.

In particular, annealing of oriented THF clathrate samples in the temperature range of 70–80°C produces fibres in form II while at 90°C gives fibres with mixed forms II and I. Annealing of oriented *o*-DCB clathrate samples (in the temperature range 100–160°C), produces oriented fibres including both form I and mesomorphic form IV.

Annealing of mesomorphic fibres, under condition of fixed length, at 210°C produces transition into form III, whereas annealing at 180°C of a poorly oriented amorphous sample gives fibres of a new crystalline form, which has been called form V.

The X-ray fibre diffraction patterns of the various crystalline and clathrate forms show that form I, form II and all clathrate forms are characterized by chains with helical $s(2/1)2$ conformation and identity period of ≈ 7.8 Å, whereas mesomorphic form (form IV), form III and form V are characterized by chains with *trans* planar conformation and identity period of 5.1 Å.

ACKNOWLEDGEMENTS

Financial supports from the 'Ministero dell'Università e della Ricerca Scientifica e Tecnologica', from the 'Progetto Strategico Tecnologie Chimiche Innovative' of C.N.R. and from Montell Technology S.p.a. are gratefully acknowledged.

REFERENCES

1 Ishihara, N., Seimiya, T., Kuramoto, M. and Uoi, M. *Macromolecules* 1986, **19**, 2465

2 Zambelli, A., Longo, P., Pellecchia, C. and Grassi, A. *Macromolecules* 1987, **20**, 2035

3 Resconi, L., Albizzati, E., Giannini, U., Giunchi, G. and Mazzocchi, R. *Italian Patent Application* 1986, 22827 A

4 Ishihara, N., Kuramoto, M. and Uoi, M. *European Patent Application* 1987, 0224097 A1

5 Ishihara, N., Kuramoto, M. and Uoi, M. *Macromolecules* 1988, **21**, 3356

6 Pellecchia, C., Longo, P., Grassi, A., Ammendola, P. and Zambelli, A. *Makromol. Chem., Rapid Commun.* 1987, **8**, 277

7 Grassi, A., Pellecchia, C., Longo, P. and Zambelli, A. *Gazz. Chim. Ital.* 1987, **20**, 2035

8 Grassi, A., Longo, P., Proto, A. and Zambelli, A. *Macromolecules* 1989, **22**, 104

9 Immirzi, A., De Candia, F., Iannelli, P., Vittoria, V. and Zambelli, A. *Makromol. Chem. Rapid Commun.* 1988, **9**, 761

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 De Rosa, C., Guerra, G., Petraccone, V. and Corradini, P. *Polym. J.* 1991, **23**, 1435

13 De Rosa, C., Rapacciuolo, M. T., Guerra, G., Petraccone, V. and Corradini, P. *Polymer* 1992, **33**, 1423

14 Auriemma, F., Petraccone, V., Dal Poggetto, F., De Rosa, C., Guerra, G., Manfredi, C. and Corradini, P. *Macromolecules* 1993, **26**, 3772

15 Corradini, P., De Rosa, C., Guerra, G., Napolitano, R., Petraccone, V. and Pirozzi, B. *Eur. Polym. J.* 1994, **30**, 1173

16 Chatani, Y., Shimane, Y., Ijitsu, T. and Yukinari, T. *Polymer* 1993, **34**, 1625

17 Chatani, Y., Shimane, Y., Inagaki, T., Ijitsu, T., Yukinari, T. and Shikuma, H. *Polymer* 1993, **34**, 1620

18 Chatani, Y., Inagaki, T., Shimane, Y. and Shikuma, H. *Polymer* 1993, **34**, 4841

19 Iuliano, M., Guerra, G., Petraccone, V., Corradini, P. and Pellecchia, C. *New Polym. Mat.* 1992, **3**, 133

20 Guerra, G., Iuliano, M., Grassi, A., Rice, D. M., Karasz, F. E. and McKnight, W. J. *Polym. Commun.* 1991, **32**, 430

21 Guerra, G., Dal Poggetto, F., Iuliano, M. and Manfredi, C. *Makromol. Chem.* 1992, **193**, 2413

22 De Rosa, C., Petraccone, V., Dal Poggetto, F., Guerra, G., Pirozzi, B., Di Lorenzo, M. L. and Corradini, P. *Macromolecules* 1995, **28**, 5507