

Effect of solvent on the polymorphism of poly(4-methylpentene-1): 1. Solution-grown single crystals

G. Charlet and G. Delmas

Chemistry Department, Université du Québec à Montréal C.P. 8888, Montreal, Quebec, Canada H3C 3P8

and J. F. Revol and R. St. J. Manley

Pulp and Paper Research Institute of Canada, 3420 University Street, Montreal, Quebec, Canada, H3A 2A7

The morphology and structure of poly 4-methylpentene-1 single crystals grown in a variety of solvent systems is studied by electron microscopy, electron and X-ray diffraction. Depending on the solvent, two different crystalline structures are identified. The usual modification I is formed in a xylene-amylacetate mixture. Modification III is grown in decalin and in a xylene-cyclohexane mixture. In a slowly cooled xylene solution, a mixture of single crystals of both structures is obtained. These results confirm earlier work and show that there is a definite dependence of the structure of the solution-grown polymer crystals on the crystallization temperature. Finally, a refined characterization of modification III single crystals is presented.

(Keywords: poly(4-methylpentene-1); single crystals; polymorphism; morphology; structure)

INTRODUCTION

Polymorphism is a prevalent feature of the higher polyolefins¹⁻³. Numerous studies have specified for some polymers, the conditions for obtaining the different modifications. These conditions are reviewed for polybutene-1⁴ and polypentene-1⁵. Most of the polymorphs of polyolefins are crystallized from solution and the formation of metastable crystalline structures is typically very sensitive to the solvent and thermal history of the solution⁶⁻⁸.

The relation between the occurrence of gelation in semi-dilute solutions of crystallizable polymers and the existence of new crystalline modifications prepared by subsequent drying of the gels is a subject of growing interest⁹⁻¹⁴. Recently, we have found¹⁵⁻¹⁷ that solutions of isotactic poly 4-methylpentene-1 (P4MP1) in a variety of solvents exhibit thermoreversible gelation. In an effort to elucidate the origin of gelation and to ascertain the possible role of new crystal forms, we have investigated the structure of the polymer crystallized from various solvents in a wide range of concentration. The results for crystals recovered from semi-dilute solutions and gels in alkanes, cycloalkanes, aromatics, tetraalkyltins, carbon tetrachloride and carbon disulphide will be given in a subsequent paper¹⁸.

In the present work, P4MP1 single crystals were grown in decalin, xylene, xylene-amylacetate and xylene-cyclohexane equivolume mixtures. Crystals grown in decalin^{19,20}, xylene^{19,21-27}, toluene²⁸, amylacetate²⁸ and the xylene-amylacetate mixture¹⁹ have already been reported to give modifications I, II or III depending on experimental conditions. All results have been compiled in order to make comparisons with earlier data and bring out the relationship between the formation of the different

polymorphs and the solvent and thermal history. In addition, a refined characterisation of P4MP1 modification III, using selected area electron diffraction in conjunction with the specimen tilting technique is presented.

EXPERIMENTAL

Materials

P4MP1 is the same as used in previous work¹⁵⁻¹⁷. This commercial ICI sample has an intrinsic viscosity of 2.8 dl g⁻¹ in decalin at 135°C. Its isotactic content, determined by ¹³C n.m.r. according to the procedure proposed by Neuenschwander²⁹, is higher than 95%. The solvents were of reagent grade or better and were used without further purification. Decalin and xylene were the commercial isomeric mixtures.

Preparation of single crystals

P4MP1 solutions in xylene, decalin, xylene-cyclohexane and xylene-amylacetate equivolume mixture (polymer concentration about 0.5 g l⁻¹) were prepared in sealed glass tubes by heating above the dissolution temperature, respectively at 120, 135 and 170°C, for at least 24 h in a thermoregulated oil bath. The solutions were then gradually cooled (initial cooling rate less than 15° h⁻¹) to room temperature by turning off the heater of the oil bath.

X-ray diffraction

The crystal suspensions were filtered, dried and collected in a special glass capillary. Wide angle X-ray diffraction (WAXD) at 25°C or as a function of temperature were performed with a Guinier-Lenné camera

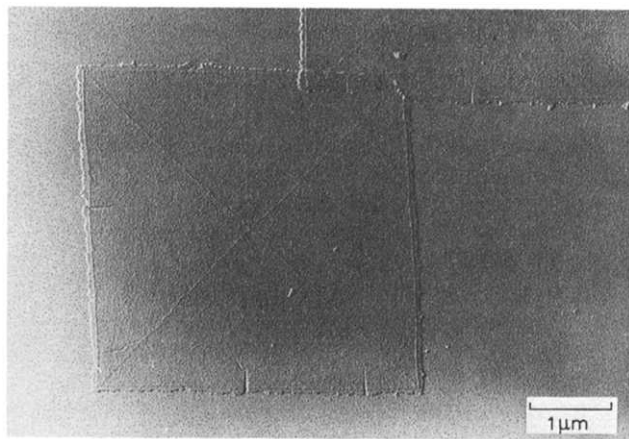


Figure 1 Electron micrograph of a P4MP1 single crystal grown in xylene. After polymer dissolution at 120°C for 24 h, the solution (0.03 g.dl⁻¹) was gradually cooled to room temperature

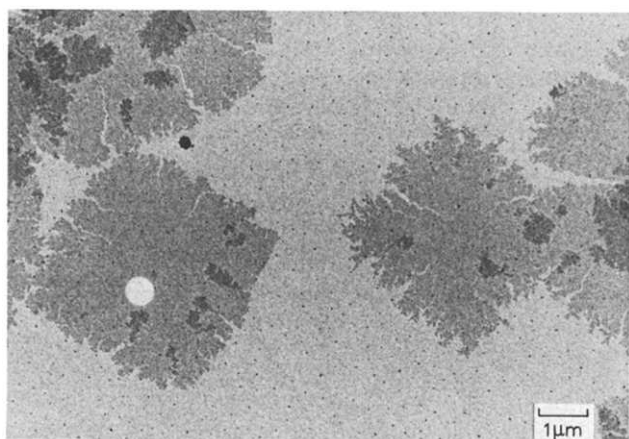


Figure 2 Electron micrograph of a P4MP1 single crystal grown in decalin. After polymer dissolution at 135°C for 24 h, the solution (0.05 g.dl⁻¹) was gradually cooled to room temperature

(Enraf-Nonius Diffractis 601 generator, CuK_α radiation, 40 kV, 20 mA) operating in parafocus geometry and equipped with a quartz monochromator. When required, the temperature and film displacement could be linearly programmed. The diffractograms of Figure 5 were obtained by microdensitometer tracings of the X-ray films. The unit cell parameters of P4MP1 modifications I and III were calculated according to the procedure described in ref. 18.

Electron microscopy

The P4MP1 single crystals were collected on carbon-coated microscope grids and observed with a Philips EM-400T electron microscope, operated at 80 kV for normal imaging and 120 kV for electron diffraction. When required, Pt/C or Au shadowing was performed, gold being chosen for electron diffraction calibration. Measurements on tilted crystals were carried out with a special rotation specimen holder, allowing tilt angles from -60 to +60°.

Differential scanning calorimetry

Solid-solid and melting endotherms were observed with a differential scanning calorimeter (Perkin Elmer DSC-2C) using a heating rate of 10° min⁻¹.

RESULTS AND DISCUSSION

Description of the single crystals and their corresponding electron diffraction patterns

A typical P4MP1 single crystal grown in a gradually cooled xylene solution is shown in Figure 1. The crystal consists of a four-sectored square lamella, several microns in width and about 100–150 Å in thickness. It has well-defined faces, although some imperfections (picture frame type crystal and cracks) are observed. In xylene-cyclohexane and xylene-amylacetate equivolume mixtures, perfect square crystals are obtained, indistinguishable from those prepared in xylene. These features are essentially the same as described by other authors for P4MP1 grown in xylene^{19,21–23}, xylene-amylacetate²⁴, amylacetate²⁸, tetralin¹⁹ and toluene²⁸.

P4MP1 single crystals crystallized in decalin display a curious morphology, as shown in Figure 2. The general shape resembles a square, but the contours exhibit finely serrated edges, due to the successive development of small sectored lateral outgrowths, usually observed for dendritic crystals formed at high supercooling. In the same solvent but using a different thermal history (isothermal growth at 45°C instead of gradual cooling), Nakajima *et al.* obtained¹⁹ non-planar multilayered crystals of circular shape and also composed of many small lamellae.

Electron diffraction diagrams of all these crystals exhibit very well-defined spots, indicating that they are perfect single crystals. Depending on the solvent, two kinds of patterns were observed. Figure 3 shows the electron diffraction diagram of single crystals grown in the xylene-amylacetate mixture. The image is properly oriented with respect to the diffraction pattern and the circle represents the irradiated area. The pattern displays diffraction spots located at the intersections of a square lattice and represents the typical reciprocal lattice of the equatorial (*hkO*) planes of P4MP1 modification I; this corroborates previous work in the same solvent²⁴. The pattern may be consistently indexed using a tetragonal unit cell having the following parameters^{30,31}: *a* = 18.70 Å and *c* = 13.68 Å. The *a** axis is parallel to the side of the crystal (as illustrated in Figure 3). Wide angle X-ray diffractograms of unoriented mats of these crystals

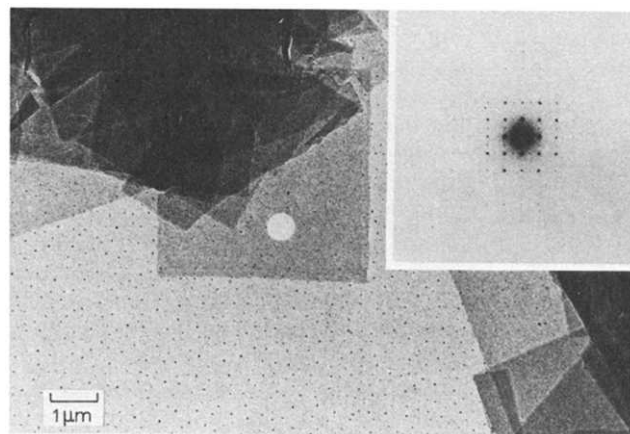


Figure 3 Electron micrograph and electron diffraction diagram of P4MP1 single crystals grown in the xylene-amylacetate equivolume mixture (dissolution at 170°C, gradual cooling to room temperature). The image is properly oriented with respect to the diffraction pattern and the circle represents the irradiated area. The four innermost and strongest reflections correspond to the 200 planes. The general features of both image and diffraction diagram are consistent with those reported in the literature²⁴

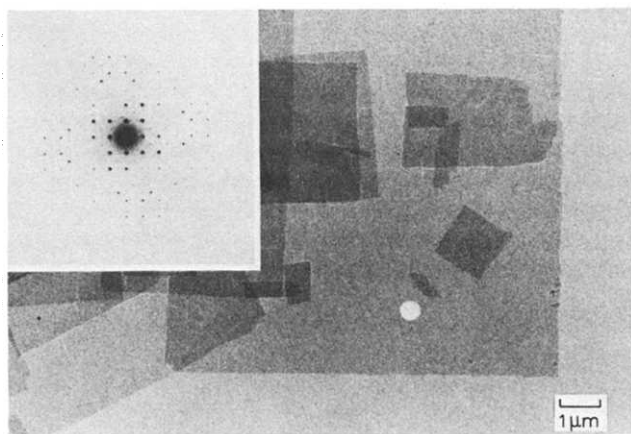


Figure 4 Electron micrograph and electron diffraction pattern of P4MP1 single crystals grown in the xylene-cyclohexane equivolume mixture (dissolution temperature: 135°C, gradual cooling to room temperature). The image is properly oriented with respect to the diffraction diagram and the circle represents the irradiated area

gave diagrams characteristic of modification I, as shown in Figure 5, curve A.

Electron diffraction patterns of crystals grown in the xylene-cyclohexane mixture are different. A typical diagram is shown in Figure 4, properly oriented with respect to the corresponding image. The diffraction spots are still located at the intersections of a square lattice and the a^* axis is here again parallel to the crystal side, but the symmetry is different from that of modification I single crystals. Indeed, the only symmetry element is a four-fold axis perpendicular to the lattice plane and passing through the central spot. In addition, if the spots are assumed to represent the reciprocal lattice of the equatorial planes, as is usual in the case of lamellar polymer single crystals, indexing using modification I unit cell parameters is impossible. The pattern is thus representative of a different crystalline structure of the polymer. The same pattern is observed for the specimens grown in decalin, indicating that the latter, although ill-defined in shape, have a well-defined lattice. A typical WAXD diagram of crystals grown in decalin or xylene-cyclohexane is given in Figure 5, curve B.

Crystals grown in xylene display one or the other type of electron diffraction patterns presented in Figure 3 and 4. Their X-ray line profiles consist of rings of both diagrams A and B (Figure 5). Therefore, gradual cooling leads to a mixture of single crystals of both structures.

Takayanagi *et al.*²⁵⁻²⁷ reported that two new structures of P4MP1, labelled as modifications II and III, can be crystallized from xylene solutions, respectively by isothermal growth at 20°C or continuous cooling. Modification III was later prepared¹⁹ from decalin by isothermal growth between 45 and 55°C. The similarity of the preparation conditions between these reports and the present work suggests that the single crystals grown from gradually cooled xylene-cyclohexane and decalin solutions should have the structure of either modifications II or III. The nature of our crystals will only be specified and compared with these previous findings after the following characterization presented below.

Characterisation of crystals grown in the xylene-cyclohexane mixture

The electron diffraction pattern of the crystals grown in decalin and the xylene-cyclohexane equivolume mixture

is sufficiently well-resolved to allow measurements of the reciprocal unit cell parameters a^* , b^* and γ^* . It is obvious from Figure 4 that $\gamma^* = 90^\circ$ and $a^* = b^*$. The equivalence of the a^* and b^* axes as well as the existence of a four-fold symmetry axis passing through the origin and perpendicular to the plane of the lamella, indicate that the unit cell should be tetragonal. From gold calibrated patterns, the a parameter is determined to be 19.44 ± 0.04 Å. The fibre period c cannot be evaluated by the usual methods using oriented samples, because stretching invariably induces a transformation to modification I before sufficient orientation is achieved. However, an indirect determination can be performed by tilting the single crystals around the a^* axis. At two definite values of the tilt angle α , new series of diffraction spots are observed, as illustrated in Figure 6. From the values of a and α , these reflections are indexed as $h31$ (with h even) and $h21$ (with h odd) for $\alpha = 42^\circ$ and $\alpha = 54^\circ$ respectively. The c parameter is then calculated to be 6.8 ± 0.2 Å. The WAXD d -spacings, measured with the Guinier-Lenné camera, were used to refine these calculations. The final unit cell is proposed to be tetragonal with the following parameters $a = 19.38 \pm 0.02$ Å and $c = 6.98 \pm 0.01$ Å. Calculated and observed d -spacings are compared in Table 1.

The close similarity between the above unit cell dimensions and those proposed by Takayanagi *et al.*^{26,27}, namely $a = 19.36$ Å and $c = 7.05$ Å confirms that P4MP1 also crystallizes into the tetragonal modification III from slowly cooled xylene-cyclohexane and decalin solutions.

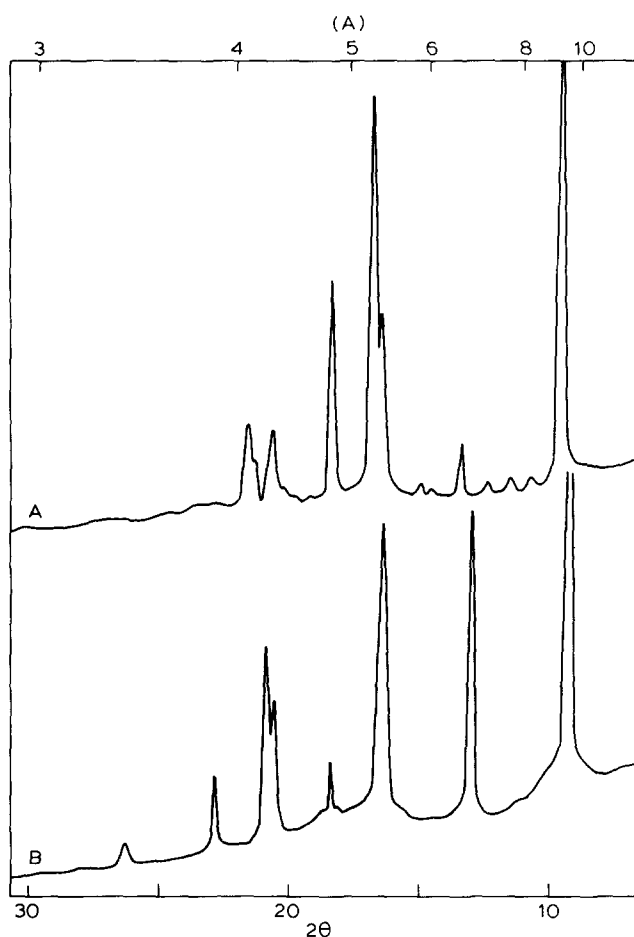


Figure 5 Curve A: wide angle X-ray diffraction pattern of P4MP1 modification I. Curve B: wide angle X-ray diffraction pattern of P4MP1 modification III

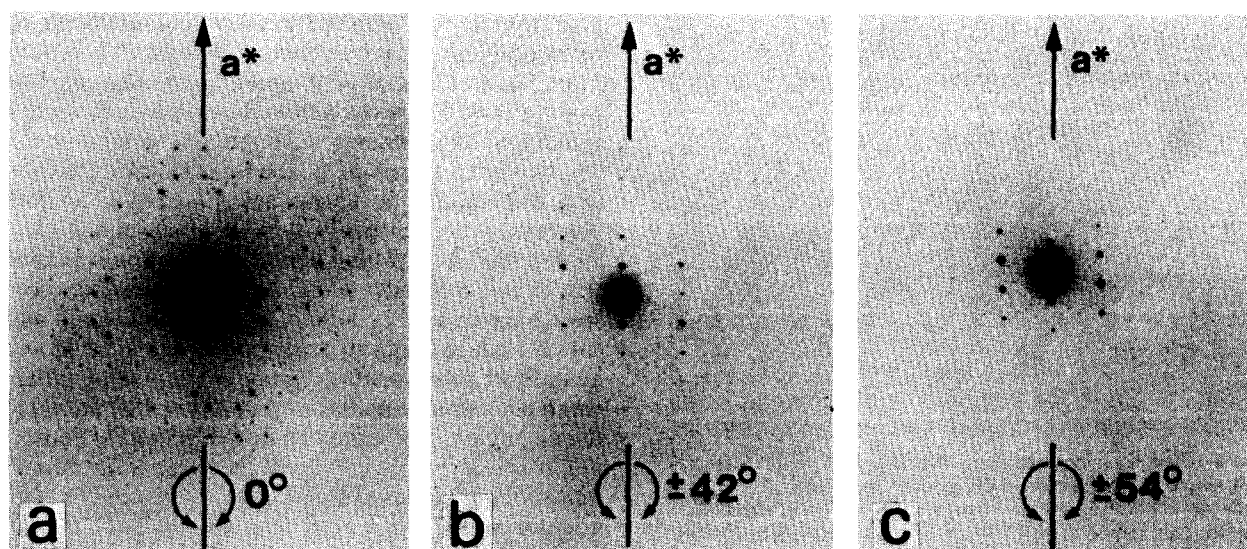


Figure 6 Electron diffraction diagrams of P4MP1 modification III single crystals obtained by tilting the lamella around the a^* axis. At two definite values of the tilt angle α (42 and 54°), new series of diffraction spots are observed

Table 1 Lattice spacings of P4MP1 modification III

Miller indices hkl	Lattice d -spacings (Å)			
	electron diffraction d_{obs}^a	d_{obs}^b	d_{calc}^c	I^d
200	9.70	9.64 ₁	9.68 ₈	100
220	6.87	6.83 ₂	6.85 ₀	52
211	5.39	5.43 ₉	5.43 ₇	91
400	4.87	4.83 ₈	4.84 ₄	12
301	4.67	4.74 ₁	4.74 ₁	4
420	4.37	4.33 ₅	4.33 ₂	33
321	4.25	4.26 ₁	4.25 ₉	45
411		3.89 ₈	3.89 ₈	18
440	3.43			
341	3.41	3.39 ₁	3.38 ₈	7
251		3.20 ₀	3.19 ₈	2
710	2.75	2.73 ₅	2.74 ₀	1
361	2.67	2.67 ₃	2.66 ₉	1
730	2.56	2.54 ₈	2.54 ₄	2
800	2.43		2.42 ₂	
820	2.36		2.35 ₀	
801		2.27 ₉	2.28 ₈	
542			2.28 ₇	
702		2.16 ₇	2.16 ₉	
831			2.15 ₇	
732		2.06 ₂	2.05 ₆	
921		2.01 ₆	2.01 ₂	
1000	1.94	1.94 ₁	1.93 ₈	
1020	1.90	1.90 ₃	1.90 ₀	

^a Observed d -spacings, measured from electron diffraction patterns of Figs. 4 and 6

^b Observed d -spacings, measured from the WAXD pattern of Figure 5 curve B.

^c Calculated d -spacings, using $a = 19.38 \pm 0.02$ Å and $c = 6.98 \pm 0.01$ Å; the unit cell parameters were calculated from the observed d -spacings by the linearization method outlined in ref. 18.

^d Observed intensity of the WAXD reflections (arbitrary scale), calculated from the relative areas of the X-ray peaks of Figure 5 curve B.

In contrast with previous findings²⁷, the single crystal morphology is not circular but square (Figure 4).

III-I solid-solid transition

Single crystals of modification III mounted on an electron microscope grid were annealed at 100°C for several hours and then cooled to room temperature for observation. The morphology of the resulting crystals is shown in Figure 7. The perfect square shape is retained and the only apparent change is the presence of cracks inside the lamellae. Electron diffraction reveals that these crystals have the modification I structure. Therefore, an

irreversible solid-solid transition from III to I has occurred. The presence of cracks may be attributed to the collapse of the unit cell in the equatorial plane from $a = 19.38$ Å (4_1 helix²⁷) to $a = 18.70$ Å (7_2 helix^{30,31}).

In order to ascertain the nature of the III-I transition, an unoriented sample of modification III crystals was heated in the Guinier-Lenné camera and its WAXD diagram recorded as a function of temperature between 45 and 95°C. Figure 8 shows that the III-I transition takes place discontinuously at $73 \pm 2^\circ\text{C}$, in agreement with previous measurements^{20,25-27}. By differential scanning calorimetry, the transition exhibits a solid-solid charact-

er, as shown in Figure 9. In addition to the melting peak at 238°C (heat of fusion: $40 \pm 1 \text{ J.g}^{-1}$), a small endotherm associated with the III-I transition is observed between 55 and 68°C (heat of transition: $2.3 \pm 0.4 \text{ J.g}^{-1}$). Annealing of modification III crystals in the course of the much slower heating in the Guinier-Lenné camera ($20^\circ \text{ day}^{-1}$) than in the d.s.c. ($10^\circ \text{ min}^{-1}$) is probably responsible for the higher transition temperature measured by X-ray diffraction than by calorimetry.

Comparison with literature data

The preceding structural observations are summarized and compared with literature results in Table 2. The structure of P4MP1 single crystals recovered from xylene strongly depends on the growth temperature. Upon isothermal crystallisation above 50°C, crystallisation into the usual modification I occurs^{19,22,23,25-27}, while modification II is favoured²⁵⁻²⁷ at 20°C. In contrast, modification III is formed either pure²⁵⁻²⁷ or mixed with modification I, upon slow cooling to room temperature. The apparent discrepancies between the results from gradually-cooled solutions can be attributed to differences in the cooling rate. For example, the observation of modification I alone by Keller *et al.*²¹ and Nakajima *et*

*al.*¹⁹ is probably due to a much slower cooling rate, actually slow enough to allow complete crystallisation of the polymer above 50°C. The formation of modification II instead of modification III upon infinitely rapid cooling to room temperature, i.e. by isothermal growth at 20°C suggests that either form III crystallizes below 50 and above 20°C, or other factors such as the tacticity, and therefore the crystallizability, of the polymer samples used could also intervene. The latter point is substantiated in a subsequent paper¹⁸. In contrast, addition of a co-solvent to xylene induces a structure which does not depend on

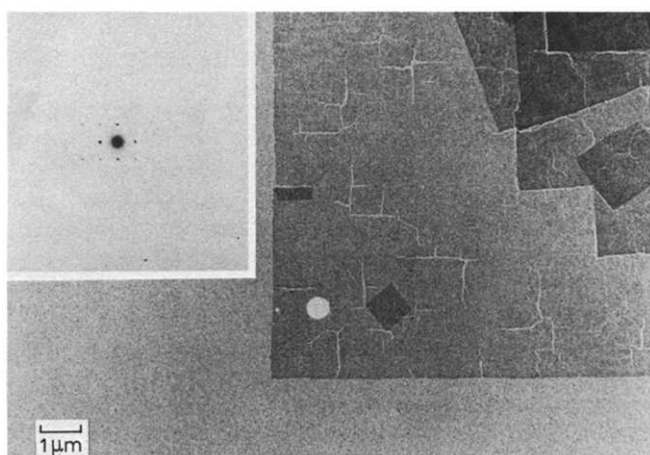


Figure 7 Electron micrograph of P4MP1 modification III single crystals annealed at 100°C

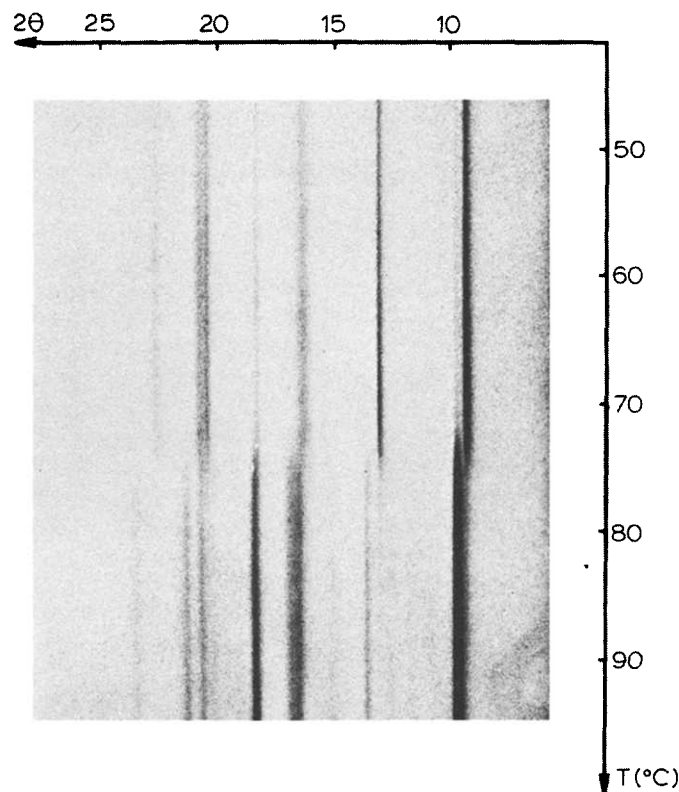


Figure 8 Wide angle X-ray diffraction diagram of unoriented modification III heated in the Guinier-Lenné camera between 45 and 95°C (heating rate: $20^\circ \text{ day}^{-1}$). Modification III transforms into modification I at $73 \pm 2^\circ \text{C}$

Table 2 Structure of P4MP1 single crystals as a function of the solvent and the thermal history of the solution

Solvent	Thermal history ^a	Single crystal structure	Reference
n-hexadecane	Isothermal growth between 130 and 144°C	I	19, 20
tetralin	Isothermal growth above 94°C	I	19, 20
amylacetate	Isothermal growth at 110°C	I	28
xylene + amylacetate	Gradual cooling	I	this work
xylene ^b	Isothermal growth above 50°C	I	24
	Isothermal growth above 50°C	I	19, 22, 23, 25-27
	Gradual cooling	I	19, 21
	Gradual cooling	III	25-27
xylene + cyclohexane	Gradual cooling	I or III	this work
	Isothermal growth at 20°C	II	25-27
	Gradual cooling	III	this work
toluene	Isothermal growth at 70 and 79°C	I	28
decalin	Isothermal growth at 45, 50 and 55°C	III	19, 20
	Gradual cooling	III	this work

^a In all cases where gradual cooling was imparted to the solution, the cooling rate is not constant and determined by the temperature gradient
^b Commercial isomeric mixture, except in Ref. 19 where *p*-xylene was used

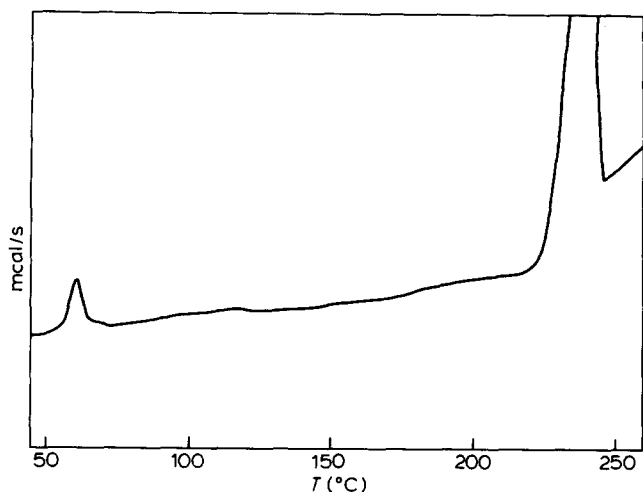


Figure 9 D.s.c. trace of P4MP1 modification III, heated at $10^{\circ}\text{min}^{-1}$. The two endotherms at $55\text{--}68^{\circ}\text{C}$ ($2.3 \pm 0.4 \text{ J.g}^{-1}$) and 238°C ($40 \pm 1 \text{ J.g}^{-1}$) are associated with the III-I solid-solid transition and melting of modification I, respectively

the thermal history of the solution. In decalin, modification III is grown from dilute solutions by isothermal crystallisation¹⁹ and by slow cooling to room temperature, so that no dependence on thermal history is apparent. However, highly concentrated solutions (polymer volume fraction about 0.3) were found³² to lead to the modification I structure.

These effects of concentration and cooling rate show that the crystalline structure of P4MP1 drastically depends on the crystallisation temperature. This point is further discussed in Part 2 of this work¹⁸.

REFERENCES

- 1 Wunderlich, B. in 'Macromolecular Physics', vol. 1, Academic Press, New York, 1973
- 2 Hannay, N. B. in 'Treatise on Solid State Chemistry', vol. 3, Plenum Press, New York, 1976
- 3 Tadokoro, H. in 'Structure of Crystalline Polymers', John Wiley & Sons, New York, 1979
- 4 Holland-Moritz, K. and Sausen, E. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 1
- 5 Holland-Moritz, K., Sausen, E., Djudovic, P., Coleman, M. M. and Painter, P. C. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 25
- 6 Danusso, F. and Gianotti, G. *Makromol. Chem.* 1963, **61**, 139
- 7 Geacintov, C., Schotland, R. S. and Miles, R. B. *J. Polym. Sci.* 1964, **C6**, 197
- 8 Gallegos, B. J. *J. Polym. Sci.* 1965, **A3**, 1982
- 9 Girolamo, M., Keller, A., Miyasaka, K. and Overbergh, N. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 39
- 10 Atkins, E. D. T., Isaac, D. H., Keller, A. and Miyasaka, K. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 211
- 11 Atkins, E. D. T., Isaac, D. H. and Keller, A. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 71
- 12 Atkins, E. D. T., Keller, A., Shapiro, J. S. and Lemstra, P. J. *Polymer* 1981, **22**, 1161
- 13 Sundararajan, P. D., Tyrer, N. J. and Bluhm, T. L. *Polym. Bull.* 1982, **6**, 286
- 14 Sundararajan, P. D., Tyrer, N. J. and Bluhm, T. L. *Macromolecules* 1982, **15**, 286
- 15 Charlet, G. and Delmas, G. *Polym. Bull.* 1982, **6**, 367
- 16 Charlet, G. *Ph.D. thesis*, McGill University, Montreal, Canada, 1983
- 17 Charlet, G., Phuong-Nguyen, H. and Delmas, G. *Macromolecules* 1984, **17**, 1200
- 18 Charlet, G. and Delmas, G. *Polymer* 1984, **25**, 1619
- 19 Nakajima, A., Hayashi, S., Taka, T. and Utsumi, N. *Kolloid Z. Z. Polym.* 1969, **234**, 1097
- 20 Nakajima, A., Hayashi, S. and Taka, T. *Kolloid Z. Z. Polym.* 1969, **233**, 869
- 21 Franck, F. C., Keller, A. and O'Connor, A. *Phil. Mag.* 1959, **4**, 200
- 22 Bassett, D. C., Dammont, F. R. and Salovey, R. *Polymer* 1964, **5**, 579
- 23 Woodward, A. E. *Polymer* 1964, **5**, 293
- 24 Khoury, F. and Barnes, J. D. *J. Res. Nat. Bur. Std. (US)* 1972, **76A**, 225
- 25 Tanda, Y., Kawasaki, N., Imida, K. and Takayanagi, M. *Rept. Prog. Polym. Phys. Jpn.* 1966, **165**, 9
- 26 Takayanagi, M. and Kawasaki, N. *J. Macromol. Sci.-Phys.* 1967, **B1**, 741
- 27 Kawasaki, N. and Takayanagi, M. *Rept. Prog. Polym. Phys. Jpn.* 1967, **10**, 337
- 28 Morrow, D. R., Richardson, G. C., Kleinman, L. and Woodward, A. E. *J. Polym. Sci. A2* 1967, **5**, 493
- 29 Neuenschwander, P., private communication, 1982
- 30 Bassi, I. W., Bonsignori, O., Lorenzi, C. P., Pino, P., Corradini, P. and Temussi, P. A. *J. Polym. Sci.* 1971, **A2**, 193
- 31 Kusanagi, H., Takase, M., Chatani, Y. and Tadokoro, H. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 131
- 32 Aharoni, A., Charlet, G. and Delmas, G. *Macromolecules* 1981, **14**, 1390