

Effect of solvent on the polymorphism of poly(4-methylpentene-1): 2. Crystallization in semi-dilute solutions

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The structure of poly(4-methylpentene-1) (P4MP1) crystallized in semi-dilute solutions (polymer volume fraction between 0.02 and 0.08) in linear and branched alkanes, cycloalkanes, alkane-like compounds, aromatics, carbon tetrachloride and carbon disulphide is reported. As much as five different modifications can be recovered, depending on the solvent and the thermal history of the solution. The results are consistent with the existence of a wide variety of polymer conformations in solution, made accessible by the P4MP1 solubility over a large temperature range. From the observed effects of solvent and thermal history, the main parameter which determines the resulting polymer structure, appears to be the crystallization temperature. The four possible structures prepared in the lower cycloalkanes, as well as crystallizing from tetraalkyltins, structures often unexpected with regard to the correlation with the crystallization temperature, suggest that specific solvent effects, involving shape and size factors, could also affect the resulting polymer conformation at low temperature.

(Keywords: poly(4-methylpentene-1); structure; solvent effect; polymorphism)

INTRODUCTION

In a previous work¹, the morphology and structure of isotactic poly(4-methylpentene-1)(P4MP1) single crystals grown in decalin, xylene, xylene-cyclohexane and xylene-amylacetate equivolume mixtures, were studied by electron microscopy, electron and X-ray diffraction. Depending on the solvent, and in the case of xylene, on the thermal history of the solution, two different crystalline structures have been prepared, which essentially corroborated earlier results²⁻⁸. The usual modification I is formed in a mixture of xylene-amylacetate⁸. Modification III is grown in decalin^{6,7} and in a mixture of xylene and cyclohexane. A single crystal mixture of both structures is obtained from a gradually-cooled xylene solution, while either modification I^{2,6,7} or modification II³⁻⁵ were previously obtained. On the other hand, isothermal growth at 20 C and at temperatures higher than 50 C were reported³⁻⁵ to give modifications II and I respectively. These results point to a definite dependence of the structure of crystals grown from xylene on the crystallization temperature. They prompted us to determine the structure of P4MP1 obtained in a wider temperature range from solutions (polymer volume fraction ϕ_2 between 0.02 and 0.08) in a large variety of solvents: linear and branched alkanes C_nH_{2n+2} , cycloalkanes, tetraalkyltins, aromatics, carbon disulphide and carbon tetrachloride. The latter were selected in an extended domain of solvent quality, with the purpose of varying the temperature over which the polymer would crystallize. The dependence of the final polymer structure on the thermal history imparted to the solutions is also discussed in some typical cases.

EXPERIMENTAL

Materials

P4MP1 was the same highly isotactic sample as used in previous work^{1,9-12}. Unless specified, the as-polymerized ICI polymer, labelled N (for nascent), was submitted to melting and slow recrystallization under vacuum (specimen labelled M) prior to use. Except for the alkane-like compounds, the solvents were purchased from the Chemical Samples Co. or Aldrich Co. They were of reagent grade or better and were used without further purification. The tetraalkyltins were the same as used in ref. 11.

Sample preparation

The P4MP1 solutions were prepared in sealed glass tubes. Dissolution was achieved by heating the sealed tubes at the maximum heating temperature, T_{max} , for 8-24 h. The solutions were then cooled to room temperature either rapidly, by quenching in the air, or slowly at a rate of $2.5^\circ h^{-1}$ monitored by a programmed temperature air oven (SETARAM RT 3000 C, Lyon, France). The polymer was then recovered by slow drying of the precipitate or the gel at room temperature under atmospheric pressure, or, for the higher boiling solvents, under a forced draft of air.

Wide angle X-ray diffraction

The structure of the resulting polymer was identified by wide angle X-ray diffraction (WAXD) at 25 C under vacuum, using a Waurus camera and an ENRAF-NONIUS Diffractis 601 X-ray generator (CuK α , 40 kV,

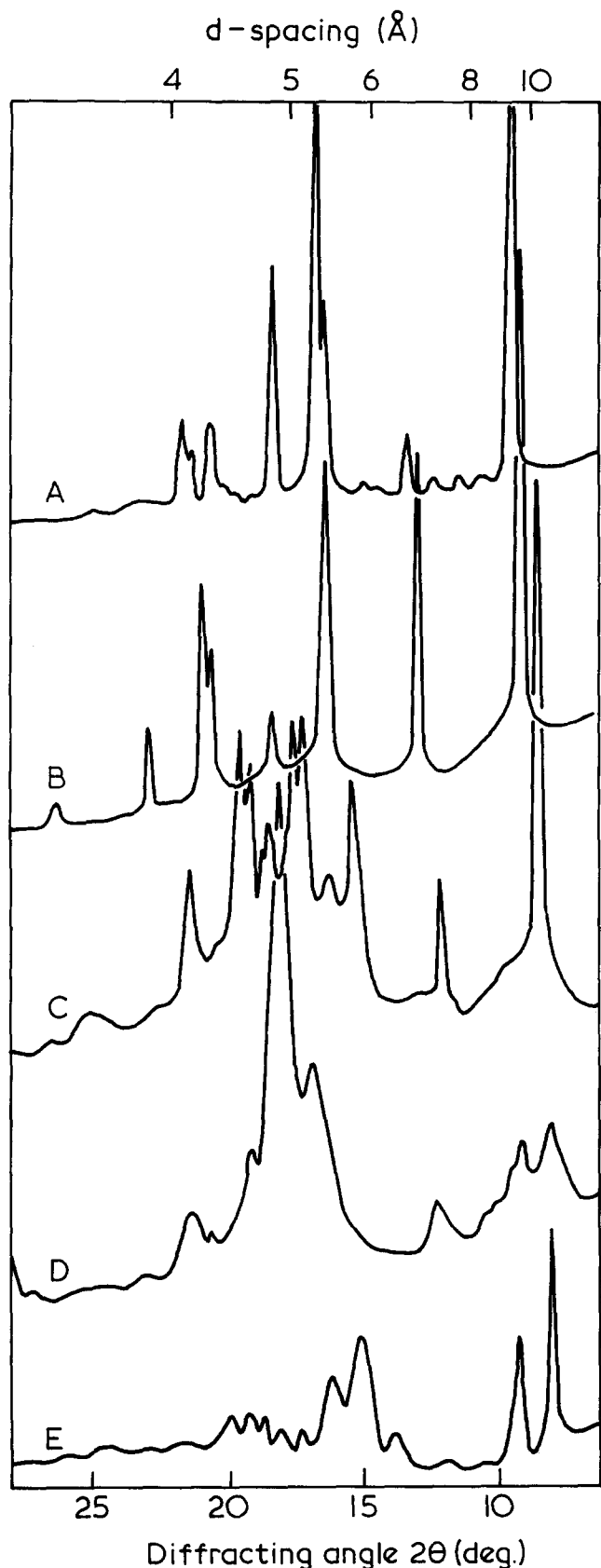


Figure 1 Wide angle X-ray diffraction diagrams of P4MP1 modifications I, (A), II (E), III (B), IV (D) and V (C)

20 mA, exposure time 30–90 min). High resolution WAXD diagrams were also recorded with a Guinier-Lenné camera operating in parafocus geometry and equipped with a quartz monochromator. The diffractograms of Figure 1 were obtained by microdensitometer

tracings of the X-ray films. The observed d -spacings, listed in Tables 2–6 were measured from the Guinier-Lenné WAXD patterns. The unit cell parameters a and c of modifications I–IV were calculated from the relation between the d -spacings and the Miller indices of the diffracting planes h, k and l :

$$\frac{1}{d^2} = \frac{f(h,k)}{a^2} + \frac{l^2}{c^2}$$

by a least square fit on linearized data¹³ using $(d^{-2} \cdot f(h,k)^{-1})$ and $(l^2 \cdot f(h,k)^{-1})$ as variables: $f(h,k)$ is $(h^2 + k^2)$ for tetragonal (modifications I, II and III) and $(h^2 + h \cdot k + k^2)$ for hexagonal (modification IV) crystals. This method, although it does not take into account the dependence of the accuracy of the d -spacings on the diffracting angle and the peak intensity, allowed a non-arbitrary calculation of a and c values which brings about the smallest differences (most generally less than 0.5%) between experimental and calculated lattice spacings.

RESULTS AND DISCUSSION

Effect of solvent on the structure of P4MP1 from semi-dilute solutions

Table 1 gives the structure of P4MP1 crystallized from solutions containing polymer volume fractions ϕ_2 between 0.02 and 0.08 in a large variety of solvents. After heating at T_{max} chosen high enough to allow complete dissolution of the polymer within one day, the solutions were cooled at 2.5° h^{-1} to room temperature. Depending on the solvent, as much as four different crystalline structures are prepared. In high-boiling solvents, like the normal alkanes (with $n \geq 9$), a branched dodecane and a branched decane, P4MP1 crystallizes into the ordinary modification I (also obtained from the melt). In lower linear ($n = 5-7$) and branched ($n = 6-9$) alkanes, as well as in carbon tetrachloride and cycloalkanes containing 6–10 carbon atoms, modification III, already prepared from more dilute solutions in decalin^{6,7} and xylene³⁻⁵ is recovered. Normal octane appears as an intermediate solvent, in which a mixture of both structures is crystallized. Modification II, previously grown at 20°C from dilute xylene solutions³⁻⁵ is present as a minor component in the mixed structure crystallized in carbon disulphide solutions. As already reported¹⁰, modification IV, previously obtained¹⁴ by annealing modification I above 200°C under 4500 atmospheres, is prepared from cyclopentane solutions. A fifth crystalline structure of P4MP1, modification V, recently crystallized⁹ from concentrated cyclohexane gels (ϕ_2 about 0.30) can be obtained in cyclohexane and carbon tetrachloride, if a different thermal history is imparted to the solutions, as discussed later (Table 7). The WAXD patterns of modifications I, II, III, IV and V are given in Figure 1. The corresponding lattice spacings are listed and compared with literature data in Tables 2–6 respectively. For clarity, a brief review of other appellations of P4MP1 polymorphs in the literature is also presented in appendix to this article.

It appears from the above results that P4MP1 can have a surprisingly high number of different solid-state conformations and that its crystallization into a given structure depends strongly on the nature of the solvent. The structure of the crystallizing polymer is likely to be

Table 1 Effect of solvent on the structure of P4MP1 from semi-dilute (ϕ_2 between 0.02 and 0.08) solutions. After dissolution at T_{max} , the solutions were cooled at 2.5° h^{-1} to room temperature where the solvent was evaporated. Different modifications may be prepared in some solvents by changing the polymer or solution thermal history, as shown in *Table 7*

Solvent	T_m^∞ ($^\circ\text{C}$) ^a	T_{max} ($^\circ\text{C}$)	Polymer structure
<i>n</i> -hexadecane	185	190	
<i>n</i> -dodecane	162	165	
2,2,4,6,6-pentamethylheptane	161	165	I
xylene + amylacetate (V/V)	157	165	
4-propylheptane	145	165	
<i>n</i> -nonane	140	165	
<hr/>			
<i>n</i> -octane	132	165	I + III
<hr/>			
2,2,4-trimethylpentane	133	165	
2,3,3,4-tetramethylpentane	126	165	
3,4-dimethylhexane	126	135	
<i>n</i> -heptane	124	135	
bicyclopentyl	123	155	
2,4-dimethylpentane	120	165	
<i>trans</i> bicyclo 4,4,0-decane	119	165	
2,3-dimethylpentane	112	165	
3-ethylpentane	110	165	III
2,3-dimethylbutane	107	165	
<i>n</i> -pentane	102	135	
bicyclo 4,3,0-nonane	101	135	
cyclooctane	95	135, 165	
bicyclo 3,3,0-octane	92	155	
cycloheptane	82	85	
xylene + cyclohexane (V/V)	79	135	
carbon tetrachloride	70	85	
cyclohexane	69	85	
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carbon disulphide	59	85, 135	II + III
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cyclopentane ^b	42	85	IV

^a Melting temperature of P4MP1 at infinite dilution (dissolution temperature). The measurements were performed according to the procedure described in ref. 11, on a highly crystalline polymer prepared by annealing sample N at 220°C for 20 h under vacuum

^b From ref. 10.

Table 2 Lattice spacings of P4MP1 modification I

Miller indices <i>hkl</i>	Lattice <i>d</i> -spacings (\AA)		<i>I</i> ^c
	<i>d</i> _{obs} ^a	<i>d</i> _{calc} ^a	
200	9.28 ₈	9.33 ₀	100
210	8.33 ₃	8.34 ₅	1
201	7.70 ₉	7.70 ₄	4
211	7.12 ₃	7.12 ₁	3
220	6.57 ₂	6.59 ₈	12
112	6.06 ₇	6.06 ₄	3
221	5.92 ₆	5.94 ₁	2
311	5.41 ₂	5.41 ₇	35
212	5.29 ₁	5.28 ₅	84
321	4.83 ₇	4.84 ₀	45
400	4.65 ₁	4.66 ₅	1
312	4.40 ₉	4.46 ₅	5
401		4.41 ₅	
113	4.30 ₀	4.30 ₃	19
411		4.29 ₆	
420	4.17 ₂	4.17 ₃	12
322	4.10 ₀	4.12 ₅	20
203		4.09 ₁	
313	3.61 ₅	3.06 ₄	5
422	3.56 ₈	3.56 ₀	
440	3.31 ₅	3.29 ₉	1

^a Observed *d*-spacings, measured from the WAXD pattern of *Figure 1* curve A

^b Calculated *d*-spacings, using $a = 18.66 \text{ \AA}$ and $c = 13.65 \text{ \AA}$. These lattice dimensions were estimated from the observed spacings, indexed according to Bassi *et al.*²⁰ and Kusanagi *et al.*²¹ by the linearization method outlined in the text

^c Observed intensity of the WAXD reflections (arbitrary scale), estimated from the relative areas of the X-ray peaks of *Figure 1* curve A

Table 3 Lattice spacings of P4MP1 modification II

Lattice-spacings (\AA)		<i>I</i> ^b
Ref. 3-5	this work ^a	
9.57 ₉	9.50 ₇	very strong
8.46 ₂	8.44 ₃	strong
6.64 ₁	6.64 ₄	medium
	5.92 ₆	medium weak
5.45 ₅	5.43 ₆	medium strong
	5.11 ₁	medium
4.85 ₃	4.77 ₇	weak
	4.62 ₄	weak
	4.46 ₈	weak
4.29 ₈	4.32 ₆	weak
	2.20 ₇	weak

^a Observed *d*-spacings, measured from the WAXD pattern of *Figure 1B*.

^b Observed intensity (this work)

determined by its conformation in the dissolved state. The extensive work by Pino and his group¹⁵⁻¹⁷ on polymers chemically similar to P4MP1, but optically active, such as poly(*S*)3-methylpentene-1, poly(*S*)4-methylhexene-1 (P(S)4MH1) or poly(*S*)5-methylheptene-1, leaves little doubt about the existence, in solutions of the most stereoregular polyolefins, of helical main chain sections spirialized in both screw senses. With regard to P4MP1, circumstantial evidence of the presence of helices in solution has been given by measurements¹⁸ of the molar

optical rotation of copolymers of 4-methylpentene-1 and chiral units. This hypothesis has been also advanced to explain the occurrence of gelation in P4MP1-cycloalkane systems^{10,12} and the unusual results of an extensive thermodynamic study involving viscosimetry^{9,12} and calorimetry^{9,19}. The existence of helices in polyolefin solutions strongly depends on temperature, as seen from the large temperature coefficient of the optical rotation of P(S)4MH1 in solution¹⁵⁻¹⁷. If it is assumed that not only

the helical content of the chains, but also the conformations of these helices are a function of temperature, then the main factor determining the resulting structure must be the crystallization temperature of the polymer. In the above experiments, the cooling rate was chosen very low (2.5° h⁻¹) and therefore, the temperature at which the polymer crystallizes is certainly very close to the *equilibrium* crystallization temperature. The latter is not available for all the solvents used, but a relative estimation is provided by the melting temperature of the polymer at infinite dilution (dissolution temperature), T_m^∞ , measured on annealed P4MP1 samples, by using the procedure outlined in ref. 11. As seen in Table 1, the resulting polymer structure correlates quite well with the values of T_m^∞ . In solvents in which the polymer dissolves above about 135°C, P4MP1 crystallizes into modification I. When T_m^∞ lies between 133 and 69°C, modification III is obtained. In n-octane, P4MP1 dissolves at 132°C, a temperature which lies at the limit between the above two ranges, since a mixture of structures I and III is recovered. The mixed structure II + III, recovered from carbon disulphide solutions ($T_m^\infty = 49^\circ\text{C}$), can be also prepared from

Table 4 Lattice spacings of P4MP1 modification III (taken from ref. 1)

Miller indices <i>hkl</i>	Lattice d-spacings (Å)		<i>I</i> ^c
	<i>d</i> _{obs} ^a	<i>d</i> _{calc} ^b	
200	9.64 ₁	9.68 ₈	100
220	6.83 ₂	6.85 ₀	52
211	5.43 ₉	5.43 ₇	91
400	4.83 ₈	4.84 ₄	12
301	4.74 ₁	4.74 ₁	4
420	4.33 ₅	4.33 ₂	33
321	4.26 ₁	4.25 ₉	45
411	3.89 ₈	3.89 ₈	18
341	3.39 ₁	3.38 ₈	7
251	3.20 ₀	3.19 ₈	2
710	2.73 ₅	2.74 ₀	1
361	2.67 ₃	2.66 ₅	1
730	2.54 ₈	2.54 ₄	2
801	2.27 ₉	2.28 ₈	
542		2.28 ₇	
702	2.16	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	1.93 ₈	
1020	1.90 ₃	1.90 ₀	

^a Observed *d*-spacings, measured from the WAXD pattern of Figure 1 curve C

^b Calculated *d*-spacings, using $a = 19.38 \pm 0.02$ Å and $c = 6.98 \pm 0.01$ Å. These lattice dimensions were estimated from the observed spacings, indexed according to Kawasaki and Takayanagi^{4,5} and Charlet *et al.*¹ by the linearization method outlined in the text

^c Observed intensity of the WAXD reflections (arbitrary scale), estimated from the relative areas of the X-ray peaks of Figure 1 curve C

Table 6 Lattice spacings of P4MP1 modification V

Lattice <i>d</i> -spacings (Å) ^a	<i>I</i> ^b
10.35 ₂	very strong
7.32 ₂	medium strong
5.79 ₂	strong
5.48 ₇	weak
5.18 ₁	strong
5.04 ₁	strong
4.81 ₉	medium
4.61 ₈	strong
4.55 ₀	medium strong
4.16 ₆	medium strong
3.56 ₃	weak
3.17 ₈	very weak

^a Observed *d*-spacings, measured from the WAXD pattern of Figure 1E.

^b Observed intensity (visual estimation)

Table 5 Lattice spacings of P4MP1 modification IV

Miller indices	Lattice <i>d</i> -spacings (Å)			<i>I</i>
	Unoriented specimen <i>d</i> _{obs} ^a	<i>d</i> _{obs}	fibre ^b <i>d</i> _{calc}	
110	11.01 ₀	11.12	11.09	strong
200	9.59 ₃	9.60	9.60	medium
210	7.30 ₃	7.30	7.26	strong
310	5.30 ₉	5.33	5.33	strong
211	4.92 ₈	4.94	4.92	very strong
301	4.62 ₈	4.63	4.63	medium
410	4.17 ₂	4.20	4.19	medium weak
311		4.19	4.17	medium
401		3.87	3.90	very weak
220		3.67	3.63	very weak
411		3.57	3.55	weak
600		3.20	3.20	weak
202	3.17 ₃	3.17	3.16	strong
511		3.06	3.07	weak
212		3.00	3.04	medium weak
303	2.11 ₀	2.11	2.11	very weak

^a Observed *d*-spacings, measured from the WAXD pattern of Figure 1 curve D

^b From Ref. 10. Modification IV was tentatively indexed using an hexagonal unit cell, with dimensions $a = 22.17 \pm 0.14$ Å and $c = 6.69 \pm 0.02$ Å. The observed intensities *I* were visually estimated from the fibre pattern

Table 7 Effect of thermal history parameters on the crystalline structure of P4MP1 recovered from solutions (θ_2 between 0.02 and 0.08) in selected solvents

Solvent	T_m^∞ ($^\circ\text{C}$) ^a	Polymer structure ^b			
		low supercooling conditions		high supercooling conditions	
		low ^c T_{\max}	slow cooling ^d	high ^c T_{\max}	rapid ^d cooling
n-octane	132		I + III		III
xylene	132		I		III
toluene	110		I		III
benzene	107		I		III
cyclooctane	95		III		II + III
cycloheptane	82	III		II + III	
carbon tetrachloride	70	III		V	
cyclohexane	69	III		V	
tetraethyltin	146		II + III		II
tetramethyltin	120		II + III		II

^a Melting temperature of P4MP1 at infinite dilution¹¹

^b Crystalline conformation of the polymer after slow drying of the gel or precipitate at room temperature under atmospheric pressure

^c After dissolution at $T_{\max} = 85$ or 135°C for less than 24 h the solutions were cooled to room temperature at 2.5°h^{-1}

^d After dissolution at 165°C (tetraalkyltins) or 135°C (hydrocarbons and carbon tetrachloride) for less than 24 h, the solutions were either slowly (2.5°h^{-1}) or rapidly (by quenching in the air) cooled to room temperature

cycloheptane and cyclooctane solutions, when submitted to a different thermal history, as reported later. From *Table 1*, it can be predicted that solvents which dissolve P4MP1 in the $42\text{--}70^\circ\text{C}$ range should allow crystallization into modification II. Investigation of such solvents is currently carried out. For much lower dissolution temperatures, modification IV (T_m^∞ about 40°C) is prepared.

These results confirm that the differences in the structure of P4MP1 crystallized in various solvents are mainly due to different crystallization temperatures. The large variety of modifications is a consequence of the unusually low enthalpy of fusion of the P4MP1 modification I crystal (estimated to be 60 or 90 J.g^{-1} , depending on the method¹¹) which allows crystallization of the polymer in a very large temperature interval: more than 200°C below the melting point, as estimated from the T_m^∞ range.

Effect of the solution thermal history on the resulting polymer structure

The dependence of the recovered P4MP1 structure on the crystallization temperature can also be verified in a given solvent by changing the solution thermal history. Such parameters as the cooling rate or the maximum heating temperature, T_{\max} , should alter the crystallization temperature. Very likely, a high T_{\max} and/or a rapid cooling to room temperature promotes a higher supercooling of the polymer than a low T_{\max} and/or a slow cooling. Indeed, high heating temperatures induce complete melting of the polymer nuclei, which, at lower temperature, delays considerably an isothermal recrystallization. In a continuously cooled solution, this promotes crystallization at lower temperature than in the presence of nuclei. The dependence on the cooling rate is obvious, quenching inducing crystallization at higher supercooling than slow cooling.

The effects of the solution thermal history are described in *Table 7* for n-octane, aromatics, cycloalkanes, carbon tetrachloride and tetraalkyltins. High supercooling conditions promote a general shift of the resulting structures towards those prepared at lower crystallization

temperature in the equilibrium (low supercooling) conditions of *Table 1*: in n-octane, modification III is crystallized instead of the mixture I+III. Solutions in aromatics lead to modification III instead of I. Cycloheptane and cyclooctane give the mixture II+III instead of III and tetraalkyltins, II instead of the mixed structure II+III.

In cyclohexane and carbon tetrachloride, high supercooling allows the recovery of the new modification V, while modifications II or IV were expected from the data of *Table 1*. In the case of cyclohexane, the effects of thermal history of both initial polymer and solution have been studied in greater detail. The same drastic dependence on T_{\max} is observed using either the nascent polymer, sample N, or sample M, prepared from sample N by slow recrystallization from the melt. However, the highest maximum temperature which allow crystallization into modification III are respectively 85° and 135°C for samples M and N, so that there exists a range of T_{\max} ($110\text{--}135^\circ\text{C}$) where the resulting P4MP1 structure only depends on the previous history of the polymer specimen. This effect must be considered in view of the gelation properties of the two materials in lower cycloalkanes¹². Upon heating at 70°C , mixtures of sample N and cyclohexane ($0.03 \leq \phi_2 \leq 0.15$) turn to clear rigid gels, which are stable at temperatures far above the solvent boiling point. In the same conditions, a fluid solution is obtained from sample M. The gelation phenomenon was attributed to the persistence at high temperature of network junctions, originating from crystalline remnants of fibrillar nature and possibly including some solvent molecules. These junctions have been found to persist for a long time above the gel-solution transition. Therefore, they could act as nuclei and induce crystallization in solutions of sample N, heated at 120°C for instance, at a higher temperature than in the corresponding sample M solutions, yielding modification III instead of V.

The P4MP1 structure obtained in cyclopentane was also found¹⁰ to depend on the maximum heating temperature. When dissolution is performed at 135 instead of 85°C , mixtures of modifications II, III and V, which all, after *Table 1*, presumably crystallize at higher

temperature than modification IV, are unexpectedly recovered. However, this does not alter the validity of the structure-crystallization temperature correlation, since, under high supercooling conditions, neither crystallization nor gelation occur over several weeks at room temperature. Therefore, in contrast with all other systems, the polymer was recovered by slow drying of the homogeneous solution and experienced crystallization upon concentrating the solution at 25°C.

With regards to their T_m^∞ , aromatic solvents and tetraalkyltins should promote crystallization into modifications III and I or III, respectively. Upon slow cooling, however, modifications I and II+III are respectively obtained, which indicates that the use of T_m^∞ may not be valid when the solvent nature changes (i.e. when dealing with different homolog series, such as saturated hydrocarbons and tetraalkyltins).

In aromatics, the polymer supercoolability could be indeed lower than in alkanes. In the case of xylene, the dependence on the crystallization temperature, which manifests itself as a dependence on the cooling rate, was already reported for dilute solutions^{1,3-5}. For instance, a mixture of single crystals of structures I and III was prepared¹ by gradual cooling. However, the addition of a co-solvent to xylene (amylacetate or cyclohexane) gave crystallization into a pure structure (modifications I or III, respectively). Identical results are obtained in semidilute solutions, as shown in Table 1, and are easily understood by the effect of the co-solvent on T_m^∞ . Furthermore, the crystalline structure grown in the solvent mixtures were found to no longer depend on thermal history parameters. When compared to the data of Tables 1 and 7, the recovery³⁻⁵ of modification II by isothermal growth in xylene at 20°C is rather surprising. It could be due to a lower stereoregularity of the polymer used, which reduces its crystallizability and thus, the actual crystallization temperature.

For tetraalkyltins, the use of T_m^∞ to estimate the crystallization temperature could be less appropriate than for alkane solvents because of kinetic (slower crystallization rate) or thermodynamic (higher attainable supercooling) factors. Alternatively, the unexpected structures of P4MP1 from tetraalkyltin solutions may emphasize specific solvent effects. Obviously, such effects are taken into account in T_m^∞ , but possibly to a different extent depending on the solvent nature. The tetraalkyltins are indeed the most globular and isotropic solvents, which may affect the conformational equilibrium in solution. This hypothesis is supported by the results obtained in solvents which dissolve P4MP1 at low temperature ($T_m^\infty < 100^\circ\text{C}$). In the latter case, the greater dependence on solvent of the resulting polymer structure, which is emphasized by the larger number of possible structures, is indicative of a larger sensitivity of the polymer helices to the solvent size and shape. The recovery of modification IV by such different routes as growth from cyclopentane and annealing modification I under high pressure¹⁴ also suggests the existence of such effects, since crystallization into a dense structure from a solution in a high free-volume solvent like cyclopentane, chemically similar to P4MP1, is quite unexpected. It can be explained if the cyclopentane molecules are assumed to stabilize a dense solution conformation of P4MP1, which would act as a precursor of modification IV. Similar effects were already discussed with regard to the phenomenology of P4MP1-cycloalkane gels^{12,19}.

CONCLUSION

The structure of P4MP1 crystallized in semi-dilute solutions depends on the solvent and, in some cases, on the thermal history imparted to the solution. The recovery of as much as five different modifications is well-explained by a drastic dependence of the polymer structure on the crystallization temperature (which may vary in a range which extends over more than 200 degrees below the melting temperature, due to the low fusion enthalpy of the P4MP1 crystal) and indicates the existence of various helical conformations in solution. The proposed correlation with the crystallization temperature is fairly consistent with literature results on dilute solutions¹⁻⁵, but cannot explain all observations on highly concentrated systems⁹, where other factors, e.g. the high viscosity of the medium, could play a determining role.

The larger variety of polymer structures is obtained at low crystallization temperatures, i.e. in low boiling solvents such as lower cycloalkanes. The profusion of crystalline modifications, the dramatic dependence of the recovered structure on thermal history as well as the occurrence of gelation¹² in these solvents are taken as strong indications that specific solvent effects, involving shape and size factors, play an important role in the conformational equilibrium in solution.

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APPENDIX 1:

Summary of appellations of P4MP1 crystalline modifications in the literature

Appellation in consideration of chronologic order	Reference of discovery	Other denominations in the literature ^a
II	3	VI ¹⁰
III	3-5	II ¹⁰
IV	14	high pressure modification, ¹⁴ III ¹⁰ , V ^{10,12}
V	9	II ⁹ , IV ¹⁰

^a In previous works^{9,10,12}, P4MP1 polymorphs were not properly labelled because two papers from Japanese laboratories^{4,5} escaped our attention. Also, at this time, the identity of modification IV and the structure prepared by Hagesawa *et al.*¹⁴ was ignored because very few details about the unit cell or the lattice spacings were given. It is only after the high pressure structure was prepared in our laboratory that the identity was definitely recognized