polymer papers

X-ray diffraction, conformational analysis and stereoregularity of a crystalline poly(3-methyl-1,3-pentadiene)

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X-ray diffraction patterns of unoriented samples of a recently synthesized highly crystalline poly(3-methyl-1,3-pentadiene) show the presence of two polymorphic forms. For one of these forms a fibre pattern is presented and the identity period of the chain is determined. To obtain information on the type of tacticity of the polymer, geometric and energy analyses and Fourier transform calculations on isolated chain models have been performed. It is suggested that the experimentally observed chain axis repeat value is more easily accounted for by a 1,4-*cis*-syndiotactic structure.

(Keywords: syndiotactic 1,4-*cis*-poly(3-methyl-1,3-pentadiene); X-ray diffraction; conformational analysis; Fourier transforms)

INTRODUCTION

It has recently been found that, in the presence of the catalytic system Ni(acac)$_2$ – MAO (acac = acetylacetonato, MAO = methylalumoxane), the polymerization of several 1,3-alkadienes affords stereoregular polymers[1]. In particular, the (E)-isomer of 3-methyl-1,3-pentadiene polymerizes to a highly crystalline polymer, as shown by differential scanning calorimetry (melting temperature 97°C) and by X-ray diffraction experiments on unoriented samples[1]. The ^{13}C nuclear magnetic resonance (n.m.r.) spectrum of this polymer presents six sharp resonances, indicating a high stereoregularity[1]. However, the n.m.r. analysis has not enabled recognition of the type of stereoregularity.

A partially crystalline polymer of 3-methyl-1,3-pentadiene, containing mainly *cis*-1,4 units, was synthesized several years ago, in the presence of a catalyst consisting of a complex from TiCl$_4$ or VCl$_3$ and an organoaluminium compound[2,3]. However, the information on that polymer is poor and no information about its tacticity is available.

In this paper, X-ray diffraction patterns of unoriented samples of this highly crystalline poly(3-methyl-1,3-pentadiene) (P3MP) are presented, which show the presence of two polymorphic forms. For one of these forms a fibre pattern is also presented and the identity period of the chain is determined.

In order to obtain information concerning the type of tacticity of the polymer, two sets of analyses on isolated chain models have been performed.

Geometric and energy analyses on stereoregular chain models of different tacticity have been compared in order to evaluate the feasibility of the experimentally observed identity period. In addition, Fourier transform calculations for the minimum energy model chains of different stereoregularity (having the suitable identity period) have been compared with the distribution of the diffracted intensity on the layer lines.

EXPERIMENTAL

The polymer, synthesized as described previously[1], was supplied by the Dipartimento di Fisica, University of Salerno.

Oriented crystalline samples were obtained by drawing compression-moulded samples at almost 25°C.

Wide angle X-ray diffraction patterns were obtained with nickel-filtered CuKα radiation. The diffraction patterns of unoriented samples were obtained with an automatic Philips diffractometer, while those for oriented samples were obtained with photographic cylindrical and flat cameras.

CALCULATION METHODS

Conformational energy calculations

An analysis of the conformational energy has been performed on chains of isotactic and syndiotactic *cis*-P3MP. The calculation method is the same as used in the conformational analysis of a number of polymers, comprising polydienes[4–7].

The conformational energy has been evaluated as the sum of a bending term due to the bond angle deformation, a torsional term due to the intrinsic torsional potential

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around single bonds and a non-bonded term due to the interactions between atoms separated by more than two bonds. The non-bonded energy has been calculated only for distances less than the van der Waals distance for each pair of atomic species, while it has been taken as zero in the other cases. The methyl group has been taken as a single unit. The potential functions used are those of ref. 8.

The calculations have been made for a portion of polymer chain containing four monomeric units. According to the equivalence postulate[9], the geometric equivalence of successive constitutional repeating units has been imposed with the aim of obtaining results representative of the polymer chain in the crystalline field.

Fourier transform calculations

The procedure for the calculation of the Fourier transforms is the same as that used for syndiotactic poly(1-butene)[10].

The square of the modulus ($|F(\xi, \varphi, \zeta)|^2$) of the Fourier transform was calculated for each model as a function of the cylindrical reciprocal lattice coordinates ξ and ζ for a fixed value of the third coordinate φ. The mean value with respect to φ, $\langle |F(\xi, \zeta)|^2 \rangle$, was obtained by averaging the results for 90 different rotations of the models around the chain axis.

The calculated intensities were multiplied by a thermal factor of the kind:

$$\exp(-B\xi^2/2)\exp(-B\zeta^2/2)$$

using an isotropic parameter $B = 8$ Å^2.

RESULTS AND DISCUSSION

X-ray diffraction analysis

The X-ray diffraction pattern of the as-prepared powder is shown in *Figure 1A*, and is identical to that shown in ref. 1. The X-ray diffraction pattern of a compression-moulded sample is shown in *Figure 1B*. Although the two patterns present some peaks with analogous relative intensities and positions (at $2\theta = 9.5$, 16.0 and 19.0°), the pattern of *Figure 1B* presents well defined additional peaks at $2\theta = 11.0$, 13.3 and 17.5°. This clearly indicates the presence of two different crystalline forms of P3MP, hereafter referred to as form I and form II.

Oriented samples of form II of the crystalline P3MP can easily be obtained by drawing of a compression-moulded film, and the corresponding photographic pattern (obtained with a cylindrical camera), is shown in *Figure 2*. The diffraction angles 2θ, the Bragg distances, d, and the reciprocal coordinates, ξ and ζ, of the reflections on the layer lines, l, as well as a qualitative evaluation of the relative intensities, are given in *Table 1*.

With reference to *Table 1*, it appears that form II shows the presence of two different layer lines, besides the equatorial layer line, whose ζ reciprocal coordinates are consistent with l indexes 1 and 2, for a repeating unit $c = 8.6$ Å. This value of c is confirmed by measurements on tilted fibre spectra. These data are consistent with a *cis*-1,4 structure, in which the chain repetition occurs after two monomeric units.

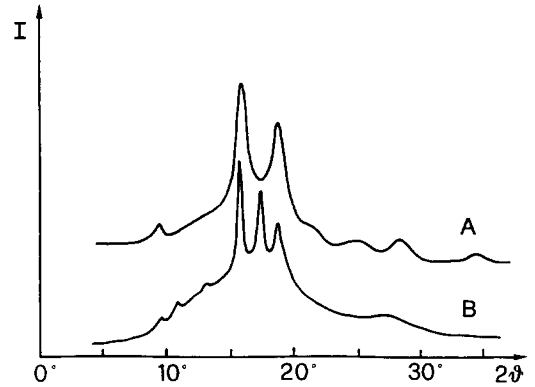

Figure 1 X-ray diffraction patterns of samples of P3MP: A, as-prepared powder; B, compression-moulded film

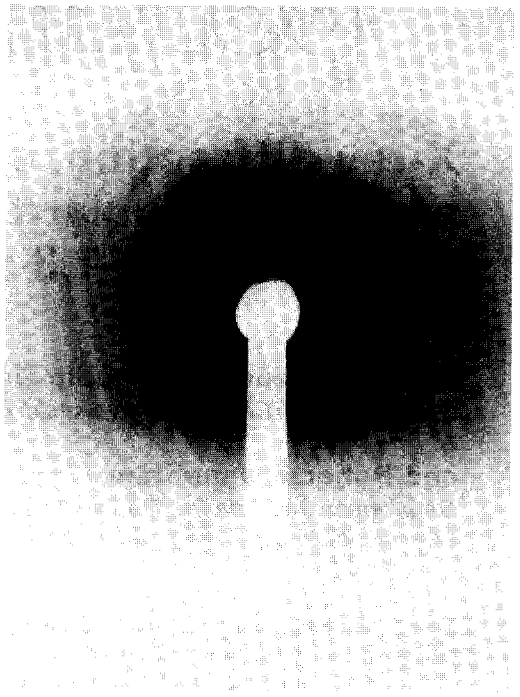

Figure 2 Photographic X-ray diffraction pattern (obtained with a cylindrical camera) of an oriented sample of form II of P3MP

Table 1 Diffraction angles, 2θ, Bragg distances, d, and reciprocal coordinates, ξ and ζ, of the reflections on the layer lines, l, in the X-ray fibre patterns of form II

2θ	d	ξ (Å^{-1})	ζ (Å^{-1})	l	Intensity[a]
9.5	9.30	0.107	0.0	0	w
11.0	8.04	0.124	0.0	0	w
13.5	6.56	0.152	0.0	0	w
16.0	5.54	0.181	0.0	0	vs
17.7	5.00	0.200	0.0	0	s
19.5	4.55	0.220	0.0	0	s
26.5	3.36	0.297	0.0	0	m
29.5	3.03	0.330	0.0	0	m
41.5	2.18	0.460	0.0	0	w
50.0	1.82	0.548	0.0	0	w
17.7	5.02	0.157	0.122	1	m
19.3	4.61	0.179	0.122	1	s
21.4	4.16	0.207	0.122	1	w
22.8	3.91	0.107	0.233	2	vw
24.8	3.59	0.154	0.233	2	m
28.4	3.15	0.217	0.233	2	m
34.9	2.57	0.311	0.233	2	m
45.2	2.01	0.441	0.233	2	vw
50.5	1.81	0.502	0.233	2	vw
21.0	4.23	0.0	0.233	2	m

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

Regarding the tacticity relative to the tertiary carbon atoms, we recall that in the crystalline phase the two monomeric units in the repeating unit can be related both by a helical two-fold axis (coinciding with the chain axis) or by a glide plane (containing the chain axis). In the first case, the polymer chain symmetry corresponds to the s(M/N) line repetition group (in this particular case, c = 8.6 Å would indicate a s(2/1) line repetition group[6]) and the asymmetric carbon atoms of the monomeric units are of the same chirality (isotactic polymer). In the second case, the polymer chain symmetry corresponds to the tc line repetition group and the asymmetric carbon atoms along the chain are of alternate chirality (syndiotactic polymer)[7].

In the following section, geometric and energy analyses on isolated chain models are reported, in an attempt to infer the tacticity (1,4-*cis*-isotactic or 1,4-*cis*-syndiotactic) of this stereoregular polymer.

Geometric and energy analyses

For the sake of simplicity, we confine our analysis to particular model chains (having s(2/1) and tc symmetries) characterized by simple geometrical conditions on the internal parameters. In particular, with reference to *Figure 3*, we assume that $\tau_1 = \tau_4$, $\tau_2 = \tau_3$ and θ_3 equal to the torsional minimum (180° *trans* conformation). Under these conditions, the s(2/1) symmetry is realized only if $\theta_2 = -\theta_1$, while the tc symmetry is obtained only if $\theta_2 = \theta_1$ and we can calculate the chain axis repeat for the two possible symmetries as a function of only one torsion angle.

Figure 4 shows the trends of the chain axis repeats c as a function of θ_1 for two different values of $\tau_2 = \tau_3$ (125° and 127°) and for the s(2/1) and the tc line repetition groups (assuming $\tau_1 = \tau_4 = 111°$). These bond angle values are close to both experimental and calculated values generally obtained in a number of *cis* and *trans* polydienes. The curves of *Figure 4* clearly indicate that for each value of θ_1 the chain axis repeat corresponding to the tc symmetry is greater than that corresponding to the s(2/1) summetry*. Moreover, the curve corresponding to the tc line repetition group and to $\tau_2 = \tau_3 = 127°$ is very close to the experimental chain axis repeat (8.6 Å) for an anticlinal conformation of θ_1 ($\theta_1 = \theta_2 \simeq 240°$)†.

The geometrical analysis, combined with the considerations about the torsional minimum of the angle θ_1, suggest that the tc line repetition group (corresponding to the syndiotatic polymer) should be preferred to the s(2/1) line repetition group (corresponding to the isotactic polymer) for a chain axis repeat of 8.6 Å.

In the conformational energy calculations, the bond and torsional angles relative to the lateral hydrogen atoms and methyl groups have been left variable while, for the sake of simplicity, the values of $\tau_1 = \tau_4$ and $\tau_2 = \tau_3$ (with $\theta_3 = 180°$) have been taken as fixed.

Figure 5 shows the conformational energy obtained for the two symmetries as a function of the values of the chain axis repeat and of the corresponding θ_1 values, for the case of $\tau_2 = \tau_3 = 127°$. The lowest energy for each symmetry has been reported as zero in *Figure 5*.

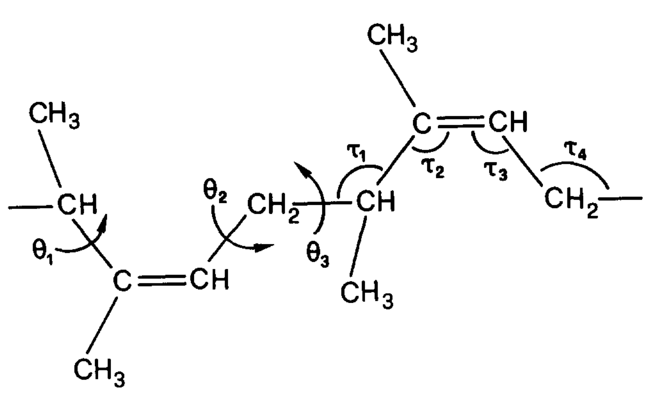

Figure 3 Scheme representing two constitutional repeating units of *cis*-P3MP indicating the torsion (θ_i) and bond (τ_i) angles referred to in the text. Torsion angles are defined with respect to the main chain

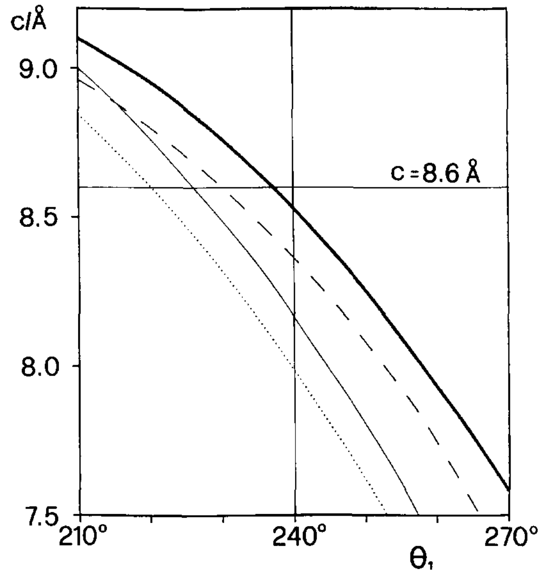

Figure 4 Chain axis repeat, c, of *cis*-P3MP as a function of torsion angle θ_1 for different symmetries and values of the bond angle $\tau_2 = \tau_3$ (τ_1 and τ_4 are fixed at 111°). ····, s(2/1), τ_2 = 125°; ——, s(2/1), τ_2 = 127°; – – –, tc, τ_2 = 125°; ▬, tc, τ_2 = 127°. The horizontal line corresponds to the experimentally observed c value

These calculations indicate that a chain axis of 8.6 Å for *cis*-P3MP is more easily accounted for by a tc symmetry (syndiotactic polymer). In fact, the value of 8.6 Å corresponds to the minimum conformational energy for the tc line repetition group, while the minimum conformational energy for the s(2/1) line repetition group is obtained for a chain axis repeat of 8.3 Å. It is worth noting that in both cases the conformational minimum energy is obtained for a value of θ_1 very close to the anticlinal conformation.

The same conclusion can be reached by considering minimization of the conformational energy as a function of all bond and torsion angles, for both 1,4-*cis*-isotactic and 1,4-*cis*-syndiotactic configuration, with the constraint of an identity period of 8.6 Å. In fact, it is found that the values of τ_1 and τ_2 corresponding to the minimum energy situations are very similar in the two cases ($\tau_1 \approx 111°$ and $\tau_2 \approx 127°$); however, the optimized θ_1 and θ_2 values

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*For the two symmetries the same value of c is obtained when θ_1 = 180°, because for this value $\theta_2 = -\theta_1$ and $\theta_2 = \theta_1$ degenerate in the same condition

†The same result is obtained for the other torsional minimum θ_1 = 120°

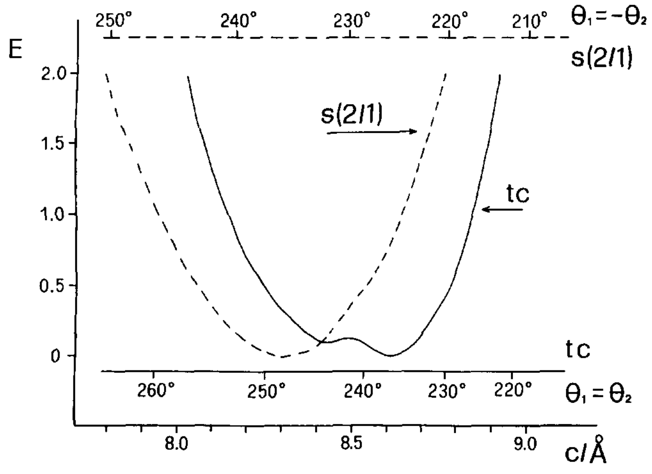

Figure 5 Curves of the conformational energy, E, of *cis*-P3MP as a function of the chain axis repeat, c, for two different symmetries corresponding to the bond angle $\tau_2 = 127°$. The values of the dihedral angles θ_1 and θ_2, for the s(2/1) and *tc* symmetries, corresponding to the c values on the abscissa, are indicated on scales at the top and bottom of the plot, respectively. The energies, reported in kJ (mol of monomeric unit)$^{-1}$, refer to chains having a succession of asymmetric carbon atoms: ...SSSS... for the s(2/1) symmetry and ...SRSR... for the *tc* symmetry. The values of the energy are referred to the minimum (assumed as zero) for each curve

are very close to the anticlinal value for the syndiotactic polymer while, for the isotactic polymer, they are further from the exact anticlinal value, by nearly 10° and 15°, respectively.

Fourier transform calculations

The isolated model chains for P3MP for the 1,4-*cis*-isotactic and for the 1,4-*cis*-syndiotactic polymers, obtained by energy minimization with the constraint of an identity period of 8.6 Å (described in the previous section), are shown in *Figures 6* and *7*, respectively.

The Fourier transforms of the two models, qualitatively compared with the reflections observed on the layer lines, are shown in *Figure 8*. It is immediately apparent that the two models, although of completely different stereoregularity, are characterized by very similar Fourier transforms.

Hence, the present comparison between Fourier transforms of isolated chains and observed diffraction intensities does not allow discrimination between models which are not only conformationally but also constitutionally different. In several cases this kind of comparison has instead allowed discrimination between different constitutions[11,12] and, for a polymer of a given constitution, between different conformations of the main chain[10,12–14] and in some cases even between different conformations of the lateral groups[10].

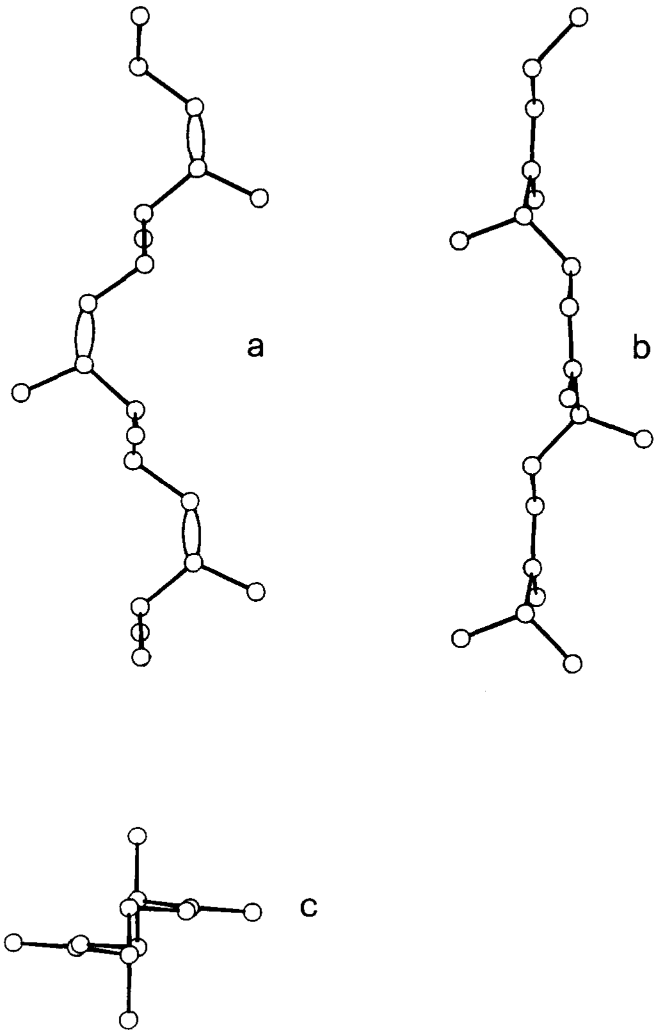

Figure 6 Isolated model chain with an identity period of 8.6 Å, with 1,4-*cis*-isotactic structure: (a) and (b) are two different side views; (c) is a projection along the chain axis

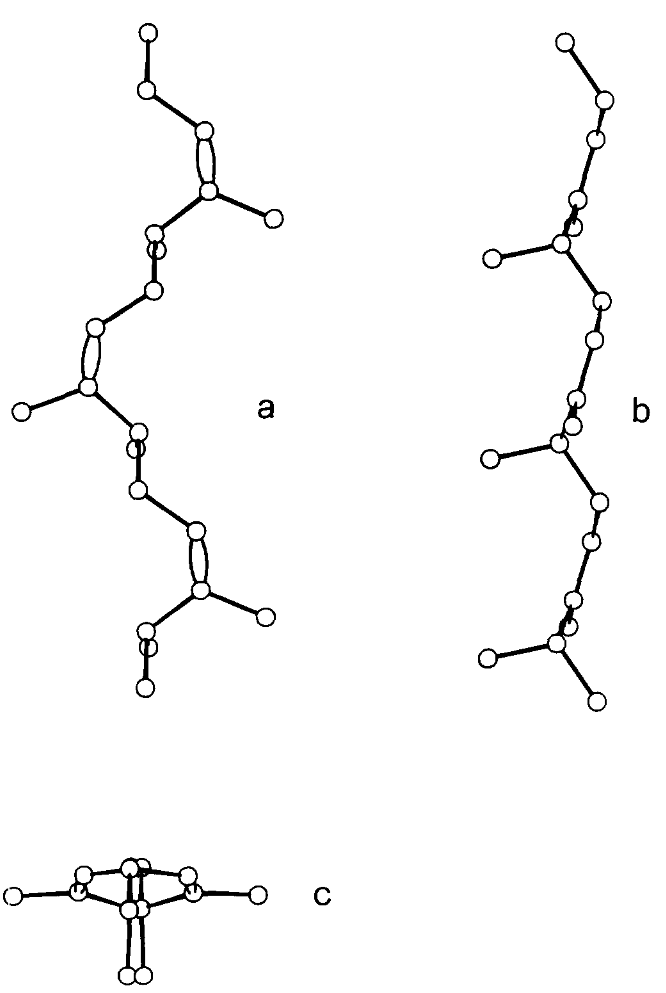

Figure 7 Isolated model chain with an identity period of 8.6 Å, with 1,4-*cis*-syndiotactic structure: (a) and (b) are two different side views; (c) is a projection along the chain axis

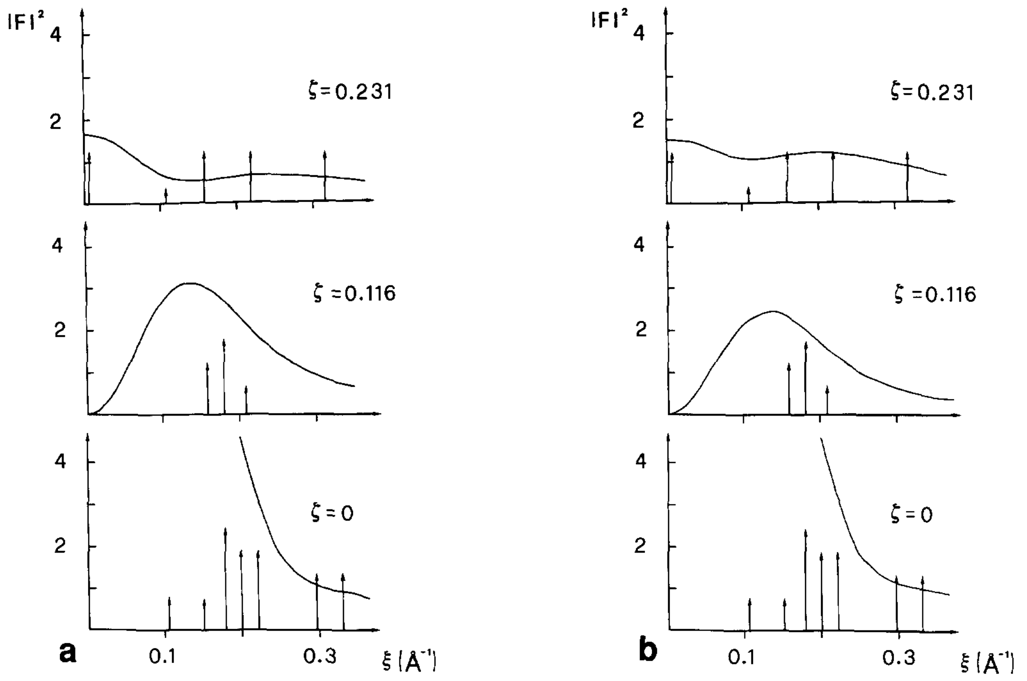

Figure 8 Results of the calculations of Fourier transform, at the indicated values of ζ ($Å^{-1}$), on the isolated stereoregular model chains, with identity period of 8.6 Å: (a) 1,4-*cis*-isotactic and (b) 1,4-*cis*-syndiotactic structure. A qualitative comparison with the observed X-ray diffraction intensities for form II of P3MP is also reported

CONCLUSIONS

Two polymorphs of a crystalline P3MP have been observed, and fibre patterns have been obtained for one of them, indicating an identity period of 8.6 Å.

The type of stereoregularity of this polymer (1,4-*cis*-isotactic or 1,4-*cis*-syndiotactic) cannot be established on the basis of comparisons between the diffraction intensities and Fourier transform calculations for isolated chain models. However, on the basis of geometric and energy considerations, it is suggested that the experimentally observed *c* value is more easily accounted for by a 1,4-*cis*-syndiotactic structure. A definitive decision on the type of stereoregularity of the polymer requires a complete structural analysis of at least one of the two forms. Studies in this direction are in progress in our laboratories.

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