Characterization of uniaxially drawn poly(4-methyl-pentene-1)

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For poly(4-methyl-pentene-1) (PMP41) of increasing uniaxial draw, X-ray diffraction analysis reveals a shift of diffraction peaks at lower 2θ angle and the concurrent generation of new peaks at higher angles. The corresponding crystal structure at lower draw ratio is a common tetragonal form and that at higher draw is orthorhombic. The heat of fusion of the perfect tetragonal crystal of undrawn PMP41, obtained by X-ray diffraction and d.s.c., is 4.4 kJ mol^{-1}. The crystallinity of drawn PMP41 increases with draw, up to ~90% for a draw ratio >30. The fraction of extended chains for a draw ratio of 10, calculated from the linear thermal expansion coefficient, is 26%. The modulus of drawn PMP41 is proportional to the fraction of extended chains.

(Keywords: uniaxial draw; poly(4-methyl-pentene-1); crystal structure; thermal expansion)

INTRODUCTION

By solid-state coextrusion, poly(4-methyl-pentene-1) (PMP41) has been successfully drawn uniaxially more than 30 times[1]. The maximum tensile modulus obtained is 3.6 GPa comparable to that reported for the chain axis direction of the perfect crystal, 6.7 GPa[2]. The change in morphology on draw includes the development of multiple melting peaks. Wide-angle X-ray scattering (WAXS) and infrared dichroism show the existence of highly oriented morphologies at higher draw.

Characterization studies on the most highly drawn PMP41, draw ratio 40, have been made by WAXS, linear expansion and differential thermal analysis and d.s.c. X-ray diffraction provided changes in crystal structure on draw. D.s.c. combining with X-ray diffraction gave the crystallinity at a succession of draw ratios. The linear thermal expansion coefficient, measured by thermomechanical analyser, was used to calculate the fraction of extended chains.

EXPERIMENTAL

The preparation of uniaxially-drawn poly(4-methyl-pentene-1) and its differential thermal analysis and wide-angle X-ray diffraction analysis have been reported[1]. The thermal expansion coefficient was measured by using a thermomechanical analyser, TMS-2, between −50°C to 150°C at a scanning rate of 10°C/min.

RESULTS AND DISCUSSION

Changes in crystal modification

As is well known, polymorphism is prevalent in the higher poly-α-olefins. For PMP41, five polymorphic forms have been reported[3]. The polymorph crystallized from solvents depends on the solvent and the thermal history of the solution. Modification I can also be obtained from the melt. Modification IV is hexagonal; the others are tetragonal. Modifications I, III and V exhibit strong peaks at a 2θ of 9°–10° and 12°–14°, moving to lower 2θ on transition from V to I[3].

PMP41 is also found to exhibit changes in crystal modification on uniaxial draw (*Figure 1*), i.e. the peak at a 2θ ~13° moves to lower values. Meanwhile, the peak at 2θ of ~21°–22° also moves lower with increasing draw ratio (see *Table 1*) and a new peak occurs at a 2θ ~35° (*Figure 1*). This new, possibly mixed, crystal structure is consistent with d.s.c. scanning curves in which a doublet melting point is observed for highly drawn PMP41[1].

It has been concluded that semicrystalline thermoplastics that can change crystal structure on draw, may possess ductilities well beyond the low level of natural draw ratios. For example, to the smectic modification for isotactic polypropylene[4], the monoclinic crystals for high density polyethylene[5] and all *trans* conformation for poly(ethylene oxide)[6]. An equivalent change in crystal structure on draw has been found here using X-ray analysis. On increasing uniaxial draw, increases are seen in both the height of layer lines and the distance between the reflection spots of the same layer (*Figure 2*). The determination of crystal structure for drawn PMP41 has been carried out by indexing flat-plate patterns. This procedure is based on the relationship between the position of the diffraction spots and the reciprocal lattice of the crystals[7,8]. The corresponding crystal structure for lower draw is tetragonal with $a=b=18.35$ Å and $c=13.52$ Å, the common form of PMP41. That for high draw is found to be orthorhombic with $a=17.70$, $b=8.85$ and $c=12.33$ Å (*Tables 2* and *3*). However, the morphology for highly drawn PMP41 is more likely to be a mixture rather than a single habit. The crystal structure for highly drawn PMP41, obtained by solid-state extrusion, is found to have no change in either the position of reflection spots or the distance between the reflection spots after annealing to near its melting point, 225°C (see *Figure 3*).

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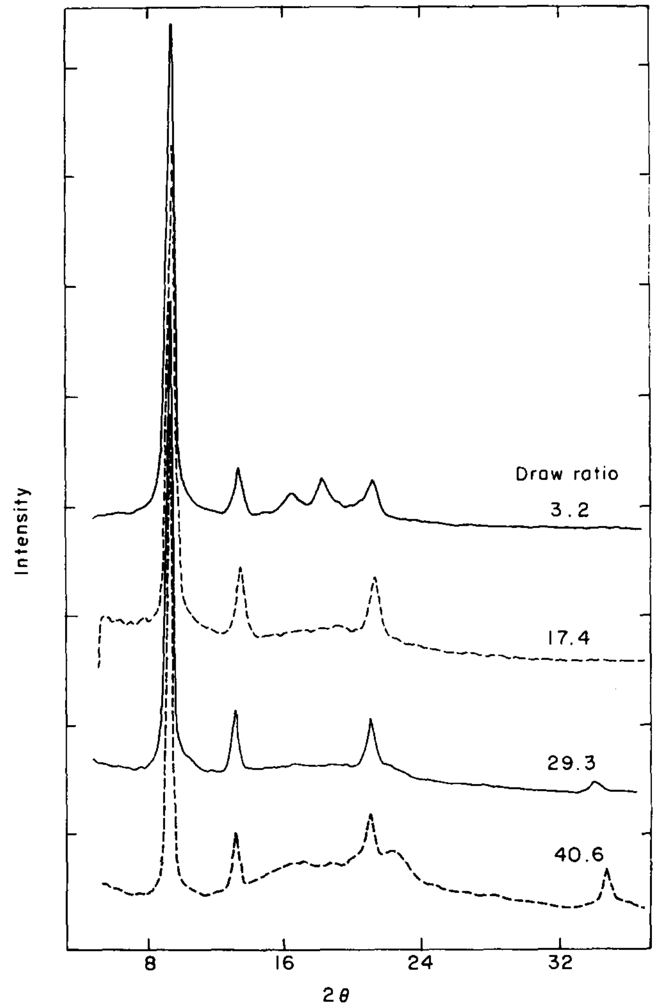

Figure 1 X-ray diffraction intensity curves for uniaxially-drawn PMP41 for several draw ratios

Table 1 Changes in 2θ at 21°–22° for crystals of PMP41 with increasing draw ratio

Effective draw ratio *EDR*	2θ angle	Lattice d-spacing (Å)
1.0[a]	21.54	4.12
2.3	21.44	4.14
3.2	21.33	4.16
10.0	21.21	4.18
11.6	21.18	4.19
17.4	21.12	4.20
33.4	21.09	4.21
40.6	21.10	4.21

[a] Undrawn

Degree of crystallinity

The X-ray diffraction intensity distribution curve of melt-crystallized and undrawn PMP41 is given in *Figure 4*. The diffraction curve is as reported[9] with a group of crystalline peaks. The most intense (200) reflection is at a 2θ angle between 6°–11° with a small amorphous halo beneath and a second group of peaks with the most intense (212) and (321) *et al.* reflections in the 2θ interval 16°–17°, also with an amorphous halo underneath. This crystal form is the common tetragonal.

Because the diffraction intensity exhibits no structure at angle of $2\theta > 40°$ for CuKα radiation[10], Ruland's procedure[11] is inappropriate for estimating the crystallinity. The crystallinity of undrawn PMP41 was thus determined from its diffraction curve (*Figure 4*) by the conventional procedure of subtracting the estimated area of the amorphous contribution from the total diffraction curve via a computer program on a PDP-11/34. The degree of crystallinity so obtained for undrawn PMP41, annealed at 150°C, is 65%. The heat of fusion obtained by d.s.c. is $2.86\,\mathrm{kJ\,mol^{-1}}$. Defining the fractional crystallinity by the heat of fusion[12],

$$\text{crystallinity} = \Delta H_1/\Delta H_2 \qquad (1)$$

gives a heat of fusion of the perfect crystal, ΔH_2, of $4.4\,\mathrm{kJ\,mol^{-1}}$.

Earlier reported heats of fusion for pure PMP41 crystals are in a divergent range from 9.9 to $19.7\,\mathrm{kJ\,mol^{-1}}$ [13–16]. A recent fusion enthalpy for modification I, the tetragonal form, has been reported to be 5.0 or $7.6\,\mathrm{kJ\,mol^{-1}}$, depending on the method[3]. Thus, the corresponding heat of fusion is 4.9 and $7.5\,\mathrm{kJ\,mol^{-1}}$, respectively. A more recent value of heat of fusion is $5.2\,\mathrm{kJ\,mol^{-1}}$ [25]. The heat of fusion of the perfect crystal obtained by Equation (1) is close to that of $4.9\,\mathrm{kJ\,mol^{-1}}$ from ref. 3 and $5.2\,\mathrm{kJ\,mol^{-1}}$ from ref. 25.

The corresponding changes in crystallinity of drawn PMP41 were obtained using Equation (1) with heats of fusion measured by d.s.c. The PMP41 uniaxially-drawn 30 times gives the highest crystallinity ~90% (*Figure 5*). The orientation due to drawing involves the local shearing of crystals and segments in amorphous regions parallel to the chain axis. Due to the low heat of fusion, a quasi-melting process due to shearing easily occurs and results in 'recrystallization', confirmed by the relationship in *Figure 5*.

Table 2 Lattice spacing of PMP41 with draw ratio of 5.0

Miller indices	Lattice d-spacing (Å) d_{obs}[a]	d_{calc}[b]
200	9.18	9.18
220	6.45	6.49
311	5.38	5.33
212	5.19	5.21
321	4.71	4.76
411	4.24	4.23
420	4.04	4.10
203	3.87	4.05

[a] Observed d-spacing, measured from X-ray diffraction patterns

[b] Calculated d-spacing, using tetragonal form and $a=b=18.35$, $c=13.52$. These parameters of unit cell calculated from observed d-spacing

Table 3 Lattice spacing of PMP41 with draw ratio of 33

Miller indices	Lattice d-spacing (Å) d_{obs}[a]	d_{calc}[b]
200	8.86	8.85
210	6.32	6.26
202	5.20	5.06
301	5.12	5.32
311	4.54	4.56
401	4.02	4.16
220	3.99	3.96
203	3.86	3.73

[a] Observed d-spacing, measured from X-ray diffraction patterns

[b] Calculated d-spacing, using an orthorhombic crystal form, $a=17.70$, $b=8.85$, $c=12.33$. These parameters of unit cell calculated from observed d-spacing

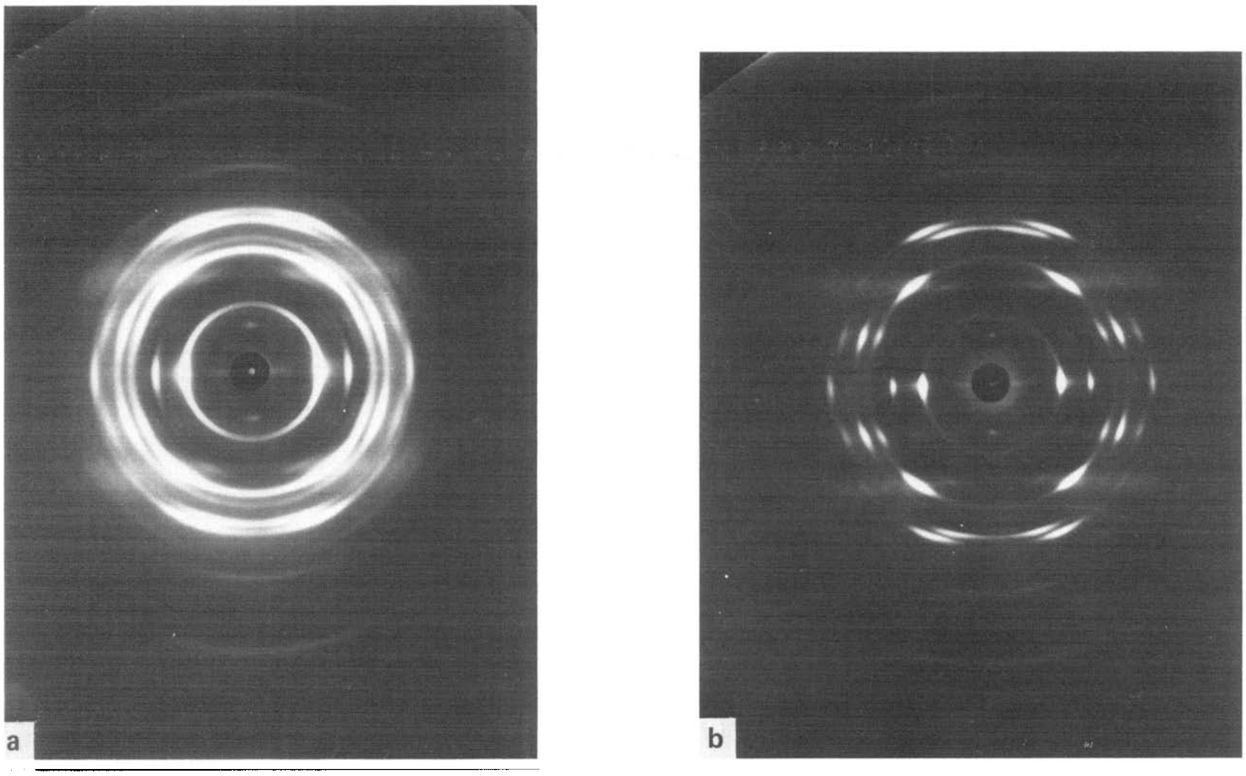

Figure 2 X-ray diffraction patterns for PMP41 for two draw ratios 5 (a) and 33 (b) (fibre axis vertical)

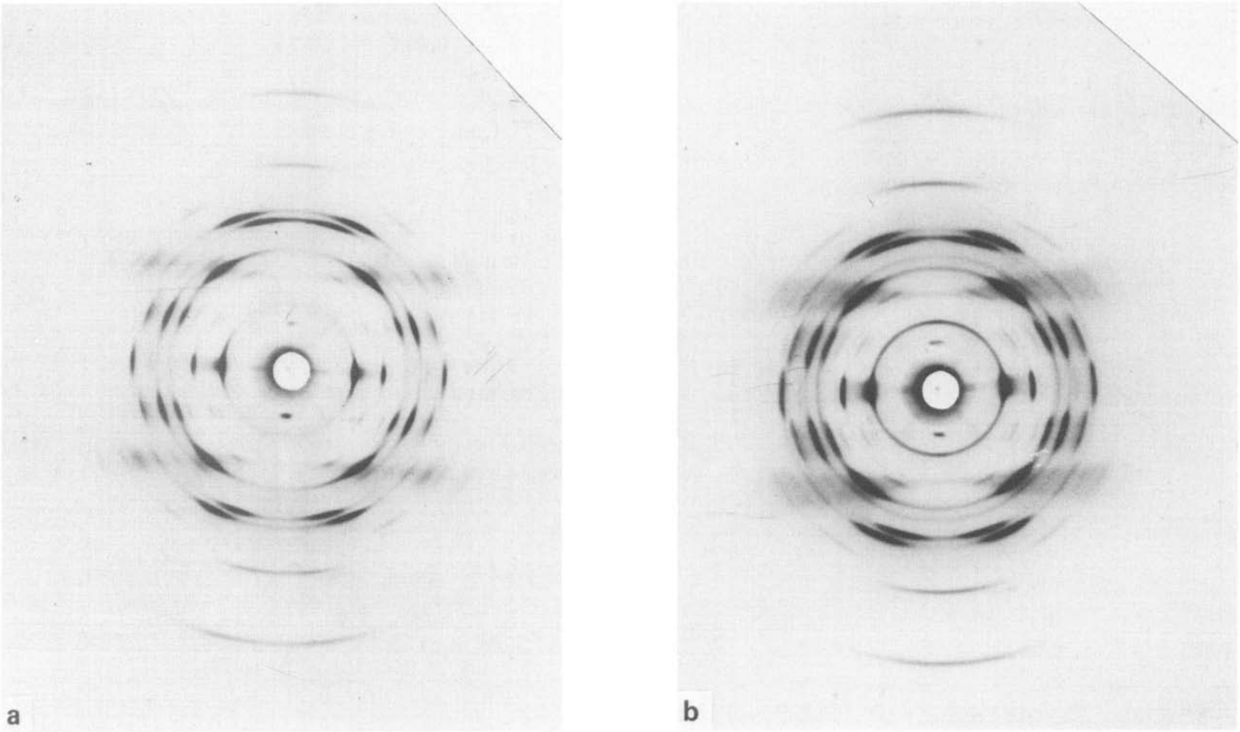

Figure 3 X-ray diffraction patterns for PMP41 of draw ratio of 31 after annealing at 225°C (a) and unannealed (b) (fibre axis vertical)

Extension of the chains on draw

The linear thermal expansion coefficient, α, can be used with a model to calculate the fraction of extended chains for uniaxially-drawn polymers[17]. A negative coefficient along the chain c-axis, viz polyethylene, is explained by an increase with temperature in torsional vibration of the planar zigzag[18,19]. Bending has also been shown to be important[20].

A positive linear thermal coefficient in the chain direction for undrawn PMP41 has been reported[21]. The value of 2.47×10^{-4} °C^{-1} at 20°C–120°C was obtained from *Figure 4* of ref. 21. For uniaxially drawn PMP41, chain components have been oriented and pulled to extension, giving a reduced expansion coefficient in the draw direction. The linear thermal expansion coefficients found here for PMP41 in the drawn direction at draw

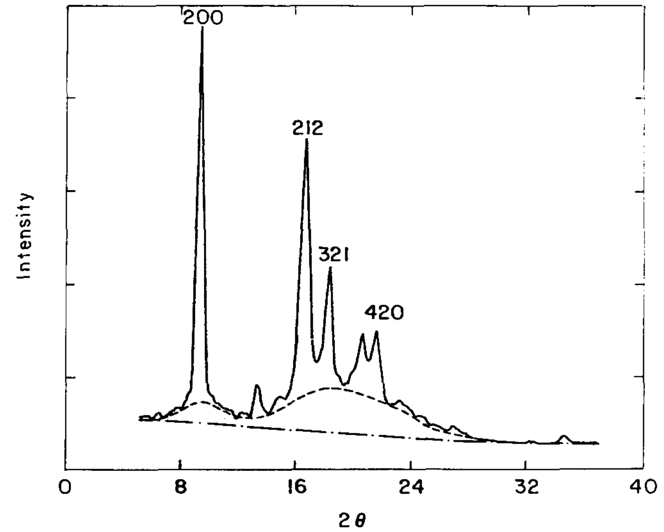

Figure 4 X-ray diffraction intensity curve for undrawn PMP41 after annealing at 150°C, melt-crystallized

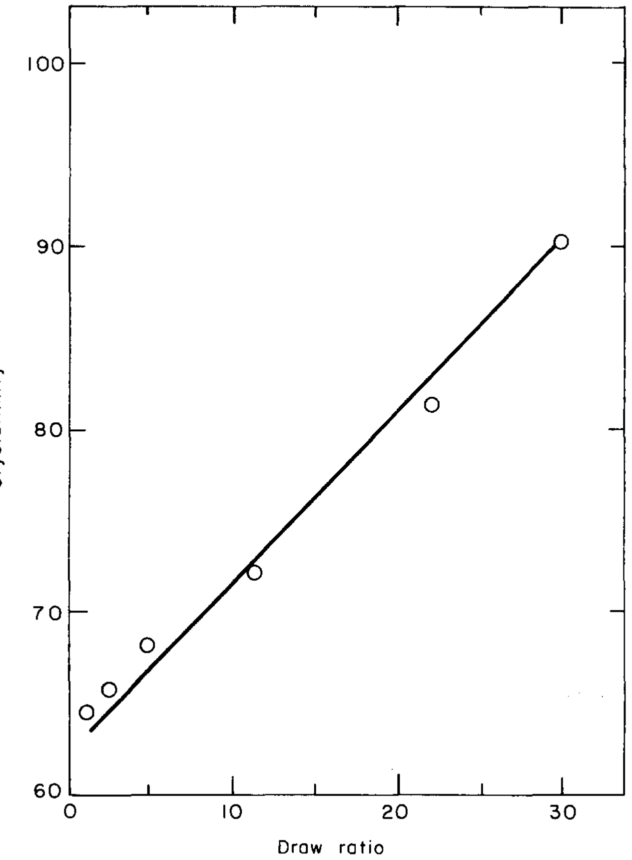

Figure 5 Crystallinity of drawn PMP41 vs. the draw ratio

ratio of 10 and 21 are -1.3×10^{-5} and -1.54×10^{-4} °C^{-1} for 60°C–120°C, respectively.

From the previous work of Capiati and Porter[17], the fraction of extended chains under uniaxial drawing is

$$\frac{A_e}{A_T}=\frac{(L_f/L_T)[\alpha_T E_T(1/E_f-1/E_a)+\alpha_a-\alpha_f]+\alpha_T E_T/E_a-\alpha_a}{(L_f/L_T)[\alpha_e E_e(1/E_f-1/E_a)+\alpha_a-\alpha_f]+\alpha_e E_e/E_a-\alpha_a} \tag{2}$$

where

$$L_f/L_T=\frac{\phi A_T-A_e}{A_T-A_e}$$

and E is the modulus, α the linear thermal expansion coefficient and ϕ the volume fraction of crystals; the subscripts, e, f, a, T denote extended chains, folded-chain crystals, amorphous and total, respectively.

Since the expansion coefficient of extended chains, α_e, and that of folded chains, α_f, are not equivalent in the case of drawwn PMP41 (*Table 4*), Equation (2) becomes

$$\frac{A_e}{A_T}=\frac{[\phi\alpha_T E_T/E_e+(1-\phi)\alpha_T E_T/E_a-(1-\phi)\alpha_a-\phi\alpha_f]-\frac{A_e}{A_T}(\alpha_T E_T/E_e-\alpha_f)}{[\phi\alpha_e-(1-\phi)\alpha_e E_e/E_a-(1-\phi)\alpha_a-\phi\alpha_f]-\frac{A_e}{A_T}(\alpha_e-\alpha_f)} \tag{3}$$

Taking the parameters in Equation (3) for uniaxially drawn PMP41 with draw ratio of 10 in *Table 4*, the fraction of extended chains, A_e/A_T, is 26%. The ratio of moduli of drawn PMP41 with draw ratio of 10 to that in the chain direction, E_T/E_e, is 33%. That A_e/A_T is coincident with E_T/E_e indicates that the modulus of drawn PMP41 is proportional to the fraction of extended chains.

Table 4 Parameters in Equation (3) for PMP41 of draw ratio 10

Definition	Value	Reference
ϕ, volume fraction crystals	0.71	This work
E_T, tensile modulus	2.23 GPa	1
α_T, expansion coefficient along *c*-axis	-1.3×10^{-5} °C^{-1}	This work
E_e, modulus in chain direction	6.7 GPa	2
α_e, expansion coefficient along extended chains	-1.54×10^{-4} °C^{-1}	This work, DR21
α_f, expansion coefficient of folded chain in chain direction	2.47×10^{-4} °C^{-1}	21
E_a, modulus of amorphous	800 MPa	23
α_a, expansion coefficient of amorphous	2.08×10^{-4} °C^{-1}	24

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