Uniaxial draw of poly(4-methyl-pentene-1) by solid-state coextrusion

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By using solid-state coextrusion, poly(4-methyl-pentene-1) has been successfully drawn uniaxially to more than 30 times at 150°C. Wide-angle X-ray and infra-red dichroism reveal a highly oriented structure. The maximum tensile modulus obtained is 3.6 GPa comparable with that of the perfect crystal of this polymer of 6.7 GPa. Thermal analysis was used to follow the changes in morphology on draw, including the development of multiple melting points in the poly(4-methyl-pentene-1).

(Keywords: draw; poly(4-methyl-pentene-1); coextrusion; thermal analysis)

INTRODUCTION

The process of solid-state extrusion has been developed in recent years[1-3]. In this process, the thermoplastic entering the die is solid, i.e. below T_m or just above T_g if the polymer is amorphous. The polymer that emerges from the outlet orifice of the extrusion die is rigid.

Despite the great interest in polymer drawing, few studies on poly(4-methyl-pentene-1) (PMP41) have been reported[4]. This is a commercial polymer that has the unusual property that the crystalline phase can be less dense than the noncrystalline phase ($d_{crys} = 0.830$ g cm^{-3}, $d_{noncrys} = 0.838$ g cm^{-3} at 20°C) in contrast with other semicrystalline polymers[5]. It is thus of interest to evaluate the deformation behaviour and compare the properties before and after the drawing for PMP41.

By using solid-state coextrusion[6-8], poly(4-methyl-pentene-1) has been drawn at 150°C to ribbons with draw ratios >30. The drawn PMP41 exhibits high chain orientation with morphology changes as revealed by thermal analysis, wide-angle X-ray diffraction, Fourier transform infra-red spectroscopy and by mechanical measurement.

EXPERIMENTAL

The PMP41 tested in this study was obtained from Aldrich Chem. Co., Cat. No. 19099-3, Melt Index 20. This powder was compression moulded at 250°C for 20 min into a sheet of 0.25 mm thickness, followed by cooling to room temperature. The moulded PMP41 was uniaxially drawn using the solid-state coextrusion[6-8]. In this study, the sheet was extruded at 150°C at the rate of 0.1 cm/min. The surrounding billet for coextrusion was polyoxymethylene. PMP41 of draw ratio >8 was obtained by two- and three-step repetitive extrusions. The highest draw ratio obtained to this time is near 35.

The thermal analysis instrument used was a computerized (TADS) Perkin–Elmer DSC-2 at a scanning rate of 20°C/min.

Tensile tests were carried out using an Instron testing machine, model TTM, at a cross-head speed of 1 cm/min at 23°C. The tensile modulus was calculated as the tangent to the stress–strain curve at a strain of 1%, and tensile strength is an average of four measurements.

The polarization infra-red spectra were recorded using an IBM IR-98 Fourier-Transform Spectrometer operated at 2 cm^{-1} resolution and equipped with a gold grid polarizer. The infra-red dichroic ratio for absorption band at 918 cm^{-1}, which is assigned to CH_3 rocking modes[11], for PMP41 extrudes, was obtained from the infra-red spectra recorded with the polarizer successively oriented parallel and perpendicular to the sample draw direction[9].

Photographs of the wide-angle X-ray diffraction patterns were recorded on flat film cassettes in a Statton type (Warhus) camera with Ni-filtered Cu radiation.

Azimuthal scans for crystal orientation function calculations were obtained by using a Siemens Model D500 wide-angle automated diffractometer. Crystallite orientation was determined by using Hermans–Stein orientation function[15,16]

$$f_{c,z} = \tfrac{1}{2}(3\langle\cos^2\phi_{c,z}\rangle - 1)$$

where $\langle\cos^2\phi_{c,z}\rangle$ is the mean square cosine, averaged over all the crystallites, of the angle between the c crystallographic axis and the draw direction z. With the Wilchinsky method[17] $\langle\cos^2\phi_{c,z}\rangle$ for drawn PMP41 can be calculated from the relationship

$$\langle\cos^2\phi_{c,z}\rangle = 1 - 2\langle\cos^2\phi_{200,z}\rangle$$

where $\cos^2\phi_{200,z}$ is determined experimentally by the

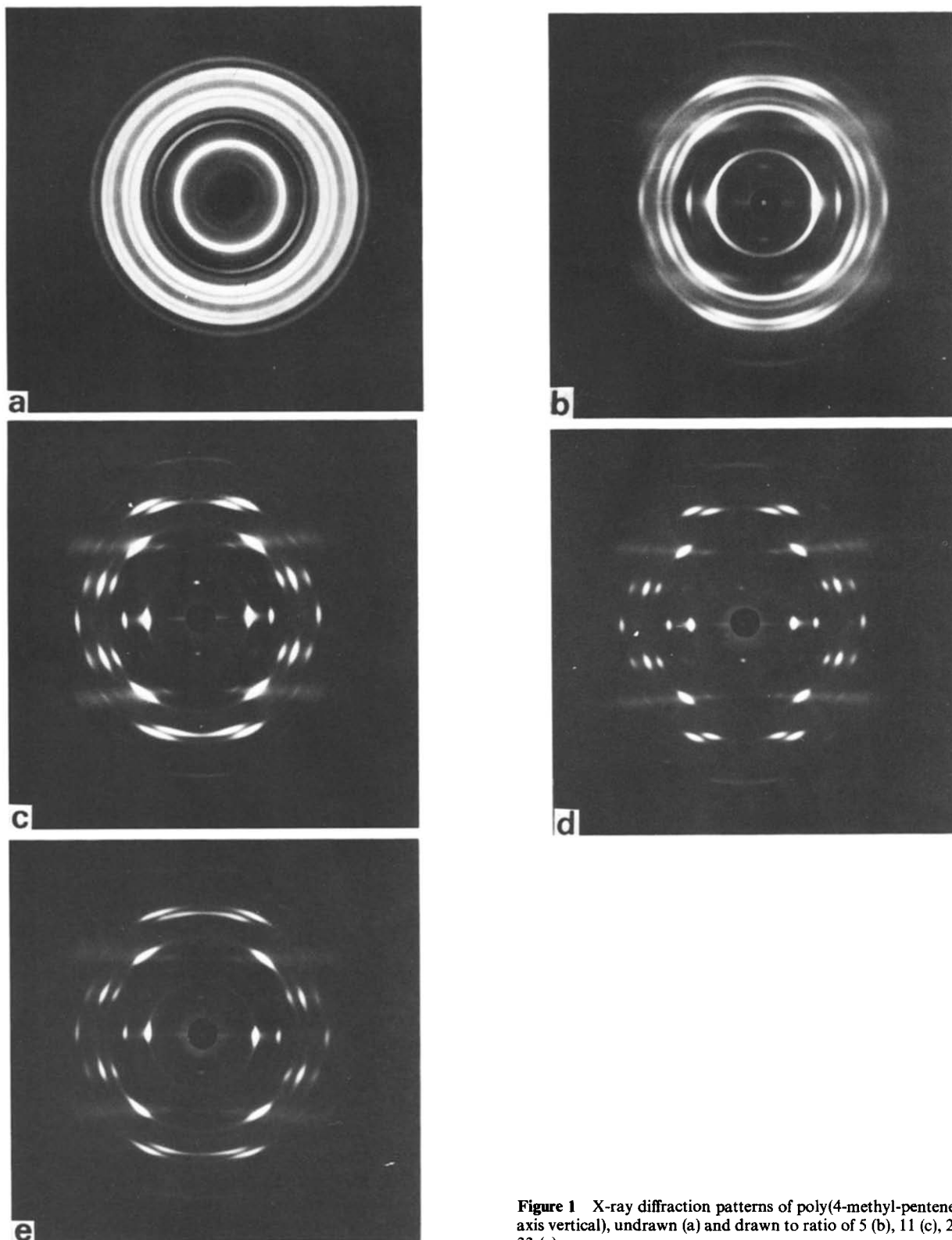*Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, People's Republic of China.

relationship

$$\cos^2\phi_{200,z} = \frac{\displaystyle\int_0^{\pi/2} I(\phi)\sin\phi\cos^2\phi\,d\phi}{\displaystyle\int_0^{\pi/2} I(\phi)\sin\phi\,d\phi}$$

Details of the Wilchinsky method can be found in the treatment by Alexander[18].

RESULTS AND DISCUSSION

It has been suggested that temperature over which extrusion draw can succeed is an interval above a reversible crystalline transition T_c and below the melting point T_m[4]. Other mechanisms may also be operative such as chain translation via changes in crystal structure. Our solid-state extrusion of PMP41 at 150°C is lower than a reported reversible crystal transition of 160°C[4,10]. The wide-angle X-ray diffraction patterns for this extrudate shows structure and high crystal orientation (*Figure 1*).

Figure 1 X-ray diffraction patterns of poly(4-methyl-pentene-1) (fibre axis vertical), undrawn (a) and drawn to ratio of 5 (b), 11 (c), 20 (d) and 33 (e)

The crystal structure for undrawn PMP41 is tetragonal. The crystal orientation function in *Figure 2* shows that the orientation function increases rapidly to near unity and then flattens at high draw ratio. This means that at higher draw ratios orientation is not a sensitive measure for evaluating the anisotropy of drawn polymers.
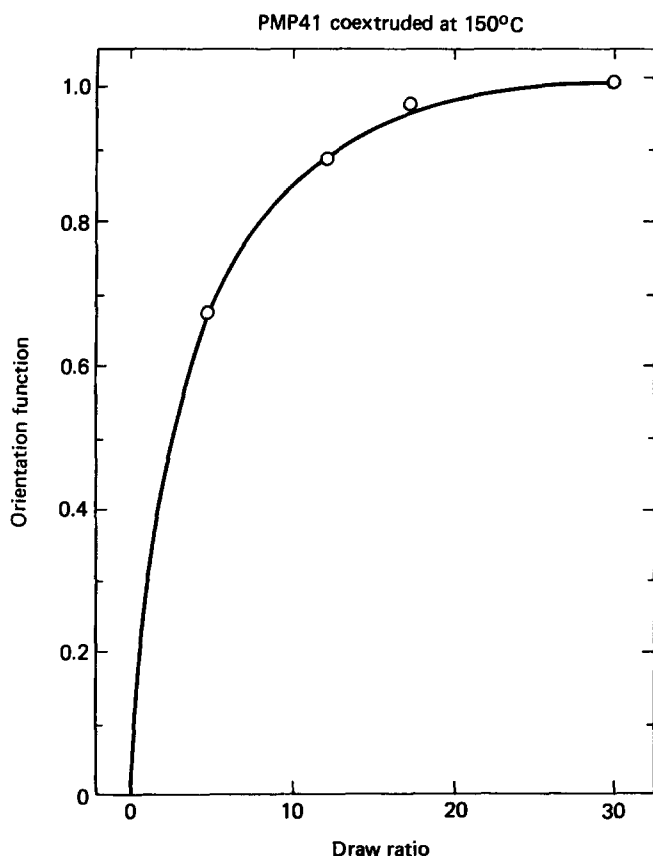

PMP41 coextruded at 150°C

Figure 2 Crystal orientation function vs. draw ratio for uniaxially drawn poly(4-methyl-pentene-1)
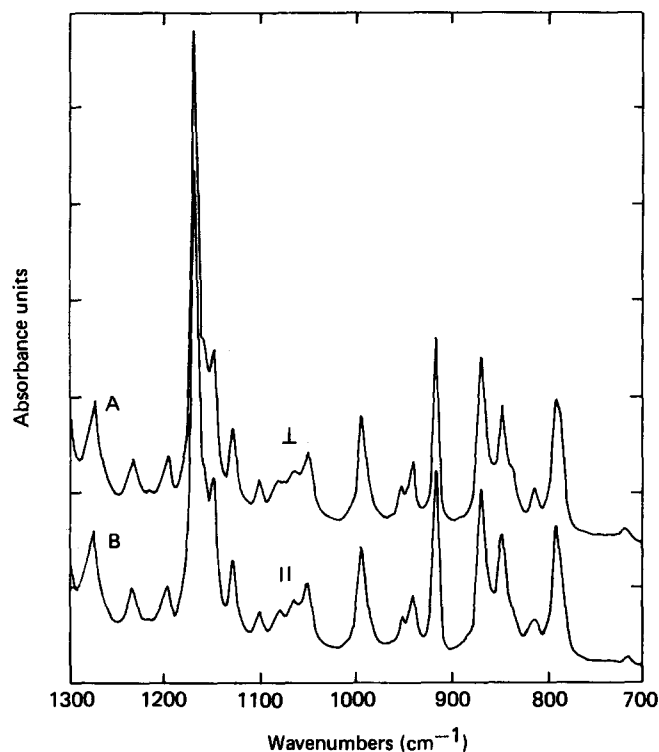

Figure 3 Polarized infra-red spectra for undrawn poly(4-methyl-pentene-1), (A) perpendicular and (B) parallel to the drawn axis
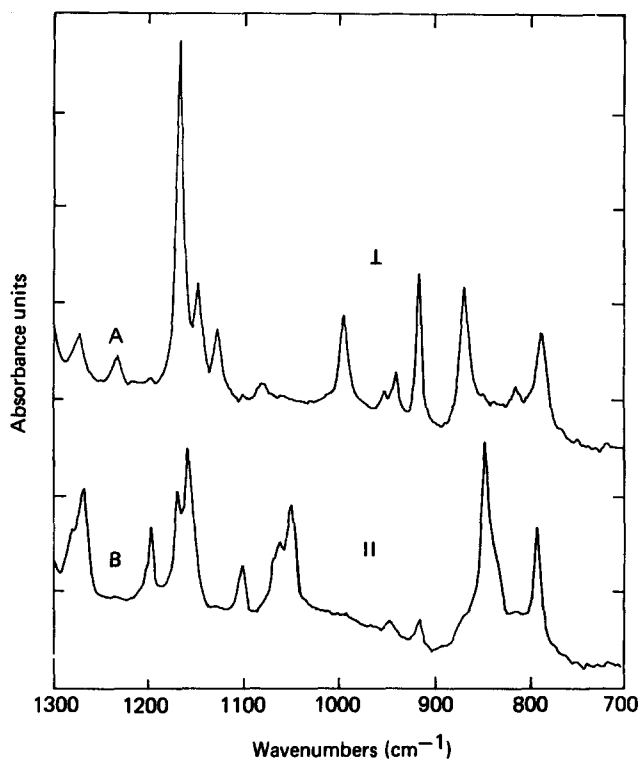

Figure 4 Polarized infra-red spectra for poly(4-methyl-pentene-1) of draw ratio 33, (A) perpendicular and (B) parallel to draw axis

To obtain the degree of orientation in both crystalline and amorphous phases for the uniaxially drawn PMP41, the infra-red dichroic rate for the absorption band at $918 \, cm^{-1}$ was determined. This band is rocking mode of two CH_3 groups in both crystalline phase and amorphous phase[11]. *Figures 3* and *4* are polarization i.r. spectra for PMP41 of unity (undrawn) and 33.4 draw ratio, respectively. For the undrawn PMP41 the polarization spectra are equivalent in the parallel and perpendicular directions and the same as that recorded without polarizers[11] (*Figure 3*). Significant changes are observed in the polarization spectra parallel and perpendicular directions to draw (*Figure 4*). The band chosen, $918 \, cm^{-1}$, for the dichroic ratio shows that dichroic ratio increases markedly with draw apparently approaching a limit above 5 (*Figure 5*).

From X-ray analysis (*Figure 2*) and i.r. dichroism (*Figure 5*), it is found that the orientation of polymer segments either in crystalline phase or in amorphous phase are saturated at higher draw ratio. This means that, in this case, the anisotropy for drawn polymers cannot be evaluated only by orientation of polymer segments. The molecular extension is thus necessary to evaluate the anisotropy for drawn polymers.

D.s.c. scanning curves were obtained at a rate of 20°C/min for extrudates obtained at a series of specific draw ratios, as shown in *Figure 6*. A sample of unity draw ratio, i.e. without draw, was also heated at 150°C for 1.5 h so that all samples in *Figure 6* have the same thermal history. *Figure 6* shows that, on increasing draw ratio, the melting curves are wider and more complex. The area under the melting peaks also becomes larger, which means increasing the crystallinity for drawn PMP41. For draw ratios > 30, the melting peak is a doublet, a feature not noted by Aharoni *et al.*[4] in their ratios for PMP41 of ≤ 14.
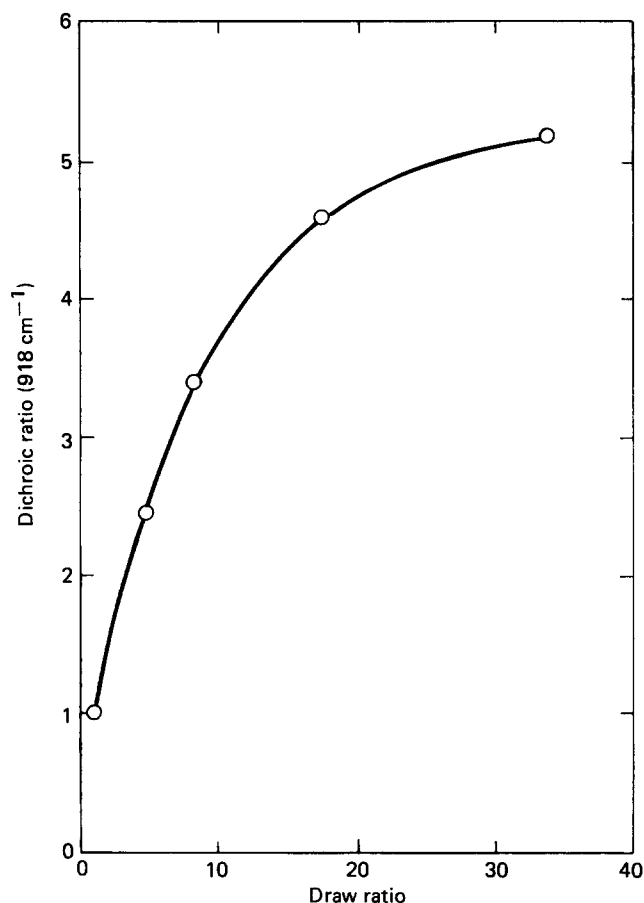
Figure 5 Infra-red dichroic ratio (A_I/A_{II}) for the absorption at 918 cm^{-1} vs. draw ratio for poly(4-methyl-pentene-1)

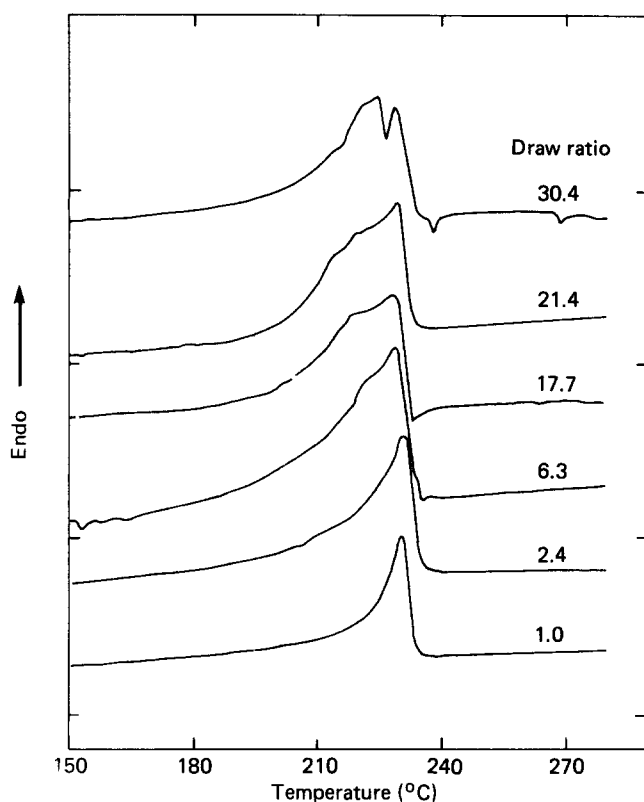subsequent dual melting points do increase with increasing draw.

The most common goal of draw is the enhancement of tensile properties in the draw direction. Not unexpectedly, for PMP41, these properties increase, but modestly, with draw ratio (*Figure 8*). The measured tensile modulus of 1.0 GPa for undrawn PMP41 obtained is in the mid-range of those published for this polymer, 0.8–1.2 GPa.[12] The tensile modulus measured for highest
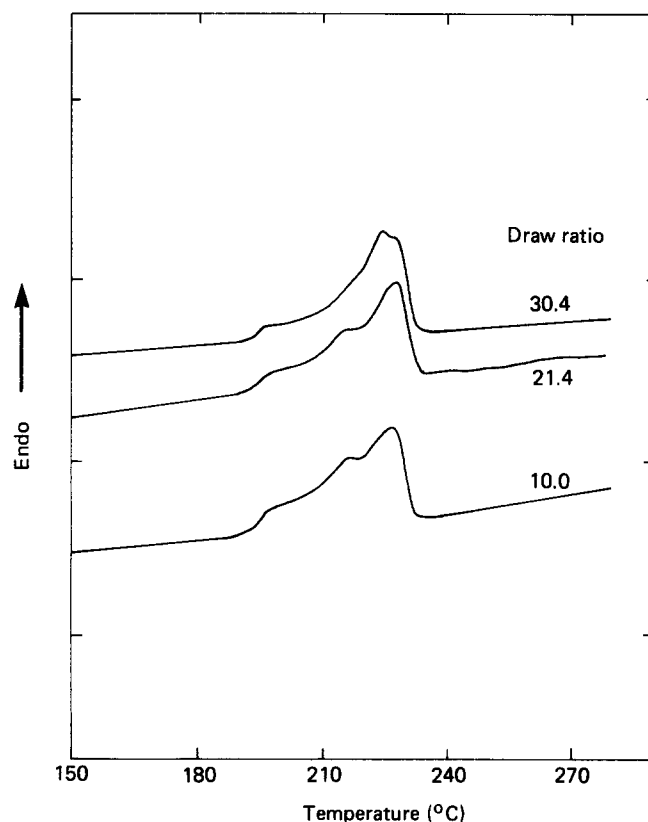

Figure 7 D.s.c. scans of poly(4-methyl-pentene-1) drawn and annealed at 190°C and 210 min

Figure 6 D.s.c. scans of uniaxially drawn poly(4-methyl-pentene-1)

The melting point T_m is not increased by draw; a small decrease is noted (*Figure 6*). For further evaluation, the extrudates were annealed at 190°C for 20 min. The d.s.c. scanning curves are shown in *Figure 7*. The single and
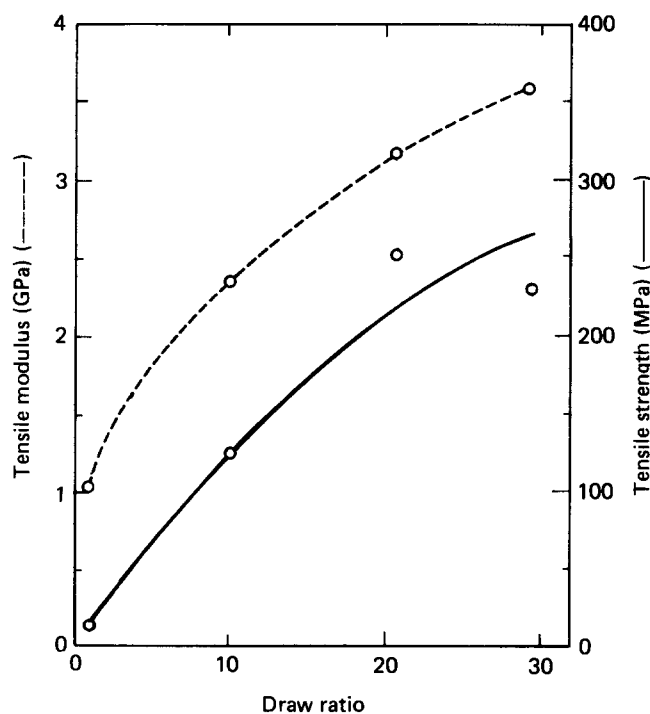

Figure 8 Increase in tensile modulus and strength for poly(4-methyl-pentene-1) on uniaxial draw

drawn PMP41 ($\sim$30 times) is 3.6 GPa. Sakurada et al.[13] estimated a maximum elastic modulus of 6.7 GPa for PMP41 measured from the (001) crystal plane and taking the internal rotations as a nearly ideal *trans–gauche* conformation. The maximum tensile strength obtained here for drawn PMP41 is $\sim$1/3 the expected maximum strength[14].

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