# Highly conductive and stiff fibres of poly(2,5-dimethoxy-*p*-phenylenevinylene) prepared from soluble precursor polymer

Shizuo Tokito\*, Paul Smith †‡ and Alan J. Heeger†§\*\*

Institute for Polymers and Organic Solids, University of California at Santa Barbara, Santa Barbara, CA 93106, USA

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Fibres of poly(2,5-dimethoxy-*p*-phenylenevinylene), PDMPV, were prepared from a precursor polymer, poly[2,5-dimethoxy-*p*-phenylene (1-methoxyethylene)] which is soluble in organic solvents. Wet-spun precursor polymer fibres were drawn and converted to PDMPV in a temperature-controlled, continuous drawing system. X-ray diffraction patterns of the drawn PDMPV fibres indicated a high degree of molecular orientation with a mosaic spread less than 8°. Tensile drawing of PDMPV resulted in a dramatic improvement of the mechanical properties; at a draw ratio of 8, the modulus and strength were 35 GPa and 0.7 GPa, respectively. After doping (with iodine), the PDMPV fibres became highly conducting ( $\sigma = 1200 \text{ S cm}^{-1}$ ) while retaining excellent mechanical properties: the modulus decreased to 25 GPa and the tensile strength remained essentially unchanged. A strong correlation between the electrical conductivity and the mechanical properties was found.

(Keywords: polymer fibres; X-ray diffraction; electrical conductivity; tensile strength)

# INTRODUCTION

As a result of the intrachain  $\pi$ -bonding of the conjugated structure and the relatively strong interchain electron transfer interactions, the mechanical properties (Young's modulus and tensile strength) of conjugated polymers are potentially superior to those of saturated polymers, such as polyolefins. Moreover, because of these two features, it may be possible to achieve exceptional mechanical properties with aligned conjugated polymers at lower chain lengths than required for their saturated counterparts<sup>1</sup>. The same  $\pi$ -bonding leads to  $\pi$ -electron delocalization along the polymer chains and to the possibility of relatively high charge carrier mobility, which is extended into three-dimensional transport by the interchain electron transfer interactions<sup>2</sup>. Since the high density of redox sites within the  $\pi$ -electron system (essentially one per monomer) offers the additional advantage of a relatively high density of carriers through doping, high electrical conductivities are possible. Thus, conjugated polymers are of special interest because of the potential of a unique combination of electrical and mechanical properties<sup>3</sup>

This combination of properties has been demonstrated in recent findings by Akagi *et al.*<sup>4</sup>, who reported the Young's modulus (*E*) and tensile strength of *trans*polyacetylene films which had been stretched seven or eight times to be E = 100 GPa and tensile strength = 0.9 GPa. In addition, Machado *et al.*<sup>5</sup> reported that

0032-3861/91/030464-07 © 1991 Butterworth-Heinemann Ltd. oriented poly(p-phenylenevinylene) films (converted from the polyelectrolyte precursor polymer by heat treatment) attained E = 40 GPa and tensile strength = 0.5 GPa. Because these values approach the stiffness of high-performance polymers such as aramids, it seems clear that excellent mechanical properties are likely to be obtained with conjugated systems, provided that material with sufficient order and orientation can be produced.

As the electrical and mechanical properties are currently limited by defects and structural disorder, improvement in material quality that will enable the exploration of intrinsic properties has become an important goal of conducting polymer research<sup>3</sup>. It has been long recognized, however, that conjugated polymers tend to be insoluble and infusible. Thus, the question to be answered is whether processing methods can be developed that will lead to chain-extended and chain-aligned materials of sufficient quality. Significant progress has been made; the addition of long alkyl side chains $^{6-12}$  has opened opportunities for processing from solution or from the melt. However, the relatively bulky side chains decrease the  $\pi$ -electron density (and thus the carrier density) and the interchain coupling, making it more difficult to achieve the structural coherence needed to obtain high carrier mobility and exceptional mechanical properties.

A promising strategy for approaching the intrinsic mechanical and electrical properties is through the use of the versatile precursor route, involving the preparation of a processible polymer and subsequent conversion of the precursor polymer to the conjugated polymer<sup>6-13</sup>. The significant advantage of this route is that the (partly) saturated precursor polymers can be processed from solution before thermal conversion to the conjugated final product. The precursor polymers may, therefore, be drawn before and during the thermal conversion process to yield oriented, homogeneous conjugated polymers.

<sup>\*\*</sup> To whom correspondence should be addressed

<sup>\*</sup> Permanent address: Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga-shi, Fukuoka 816, Japan

<sup>†</sup> Materials Department, UCSB, Santa Barbara, CA 93106, USA ‡ Department of Chemical and Nuclear Engineering, UCSB, Santa

Barbara, CA 93106, USA

<sup>§</sup> Department of Physics, UCSB, Santa Barbara, CA 93106, USA

Poly(*p*-phenylenevinylene), PPV, can be prepared from a precursor polymer, a polyelectrolyte, which is soluble in water<sup>12,13</sup>. After doping with strong acceptors (AsF<sub>5</sub>, SO<sub>3</sub> and SbF<sub>5</sub>), the conductivity reported for PPV is in the range 10–40 S cm<sup>-1</sup> for unstretched films, and to 500–10000 S cm<sup>-1</sup> for highly oriented films<sup>12–14</sup>. Attempts to dope PPV with iodine gave conductivities<sup>15</sup> of only  $10^{-2}-10^{-3}$  S cm<sup>-1</sup>.

As noted above, Machado *et al.*<sup>5</sup> reported that highly oriented PPV films (converted from the polyelectrolyte precursor polymer by heat treatment) had attractive mechanical properties. However, they found that chemical doping with SbF<sub>5</sub> and AsF<sub>5</sub> resulted in significant embrittlement of the highly oriented PPV films, suggesting that such strong electron acceptors might react with conjugated polymer backbones and diminish the mechanical properties.

More recently, we succeeded in the preparation of moderately oriented poly(2,5-thienylenevinylene) fibres<sup>16</sup> from a precursor polymer which was soluble in organic solvents<sup>17,18</sup>. The PTV fibres had an X-ray orientation factor,  $f = (3 \cos^2 \theta - 1)/2 = 0.86$ . The orientation resulted in improvement of the mechanical and electrical properties by about a factor of 20 compared with those of unoriented PTV fibre<sup>16</sup>.

The dimethoxy derivative of PPV, poly(2,5-dimethoxy-p-phenylene vinylene), PDMPV, was prepared by a precursor route similar to that for PPV and exhibited conductivities as high as 200 S cm<sup>-1</sup> after iodine doping<sup>15</sup>. However, the commonly used aqueous solutions of the PDMPV precursor polymer tend to form gels, and the gradual elimination of the sulphonium group in the solid precursor cannot be avoided even at room temperature; both effects make subsequent processing into highly oriented films and fibres difficult. Recently, the Kyushu University group<sup>19</sup> succeeded in preparing a dense PDMPV film from a new precursor polymer which was soluble in common organic solvents, easily processible, and stable even at 100°C.

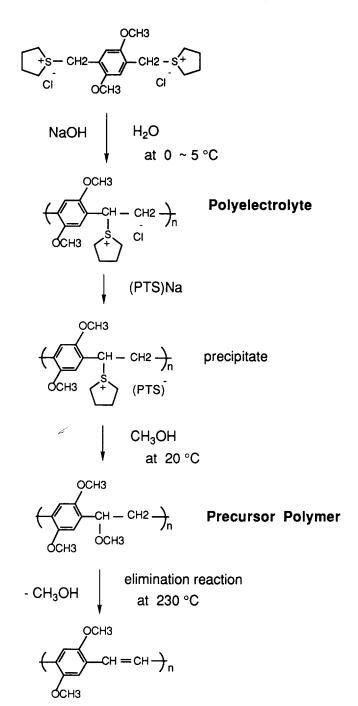
In this paper, we describe the preparation and characterization of highly oriented PDMPV fibres. The PDMPV precursor fibres were prepared from solution in organic solvents by wet spinning. They were subsequently drawn up to eight times before conversion to PDMPV fibre using a temperature-controlled, continuous drawing system, which enabled the reproducible preparation of high-quality fibres. The resulting oriented PDMPV fibres exhibited excellent mechanical properties (E = 35 GPa and tensile strength = 0.7 GPa) and high electrical conductivity ( $\sigma = 1200 \text{ S cm}^{-1}$  after iodine doping). More importantly, the mechanical properties were retained after doping; E decreased only to 25 GPa, and the tensile strength remained essentially unchanged. The mechanical properties and electrical conductivities of these fibres were determined as a function of draw ratio, and the results are presented in detail. We discuss the phenomena taking place during tensile drawing, and the relationship between mechanical properties and electrical conductivity in conjugated polymers.

# EXPERIMENTAL METHODS AND TECHNIQUES

# Preparation of precursor polymer

The preparation of the precursor polymer and conversion to the conjugated polymer are summarized in

Scheme 1. Synthesis of the precursor polymer was carried out essentially according to the procedure reported by Momii et al.<sup>19</sup>, starting with the preparation of the monomer, 2,5-dimethoxyphenylene-1,4-dimethylene-bis-(tetrahydrothiophenum chloride), shown in Scheme 1. The monomer (0.4 M) was dissolved in distilled water and an equimolar amount of NaOH solution was added at 0-5°C under nitrogen flow. After reacting for 5 min, the solution formed a transparent gel-the polyelectrolyte precursor polymer. The gel was then redissolved in excess distilled water followed by the addition of p-toluene sulphonic acid sodium salt (1.0 M), to precipitate the polymer as a polycation salt with p-toluene sulphonic acid as the counter anion. The polycation salt was extracted, dissolved in methanol, and allowed to react with methanol at 20°C, while stirring, for 50 h to



Scheme 1 Synthesis of poly(2,5-dimethoxy-p-phenylenevinylene) from precursor polymer soluble in organic solvents

yield the methoxy substituted precursor polymer hereafter referred to as PPDMV (see *Scheme 1*) in the form of a powdery precipitate, which was subsequently filtered and vacuum dried. The resulting precursor polymer was purified by reprecipitation from chloroform solution into hexane.

The chemical structure of the precursor polymer was confirmed to be that shown in *Scheme 1* by i.r. spectroscopy.

D.s.c. measurements of the polymer were carried out using a Mettler DSC 30, with the sample under nitrogen. The d.s.c. thermogram of the precursor polymer indicated a glass transition at 110°C, well separated in temperature from the  $\approx 195^{\circ}$ C needed for thermal elimination of the methoxy leaving groups (*Scheme 1*).

#### Fibre spinning

Purified precursor polymer was dissolved in chloroform. The solution was spun using a high-precision syringe pump (Sage Instruments, model 355). The viscous solution was pumped at 13 dm<sup>3</sup> min<sup>-1</sup> through a 0.5 mm diameter needle into hexane; the resulting PPDMPV fibre was taken up onto a bobbin at a speed of 300 mm min<sup>-1</sup>. We found that with the methods used in this study, the most uniform PDMPV precursor fibres were obtained using a polymer concentration of about 5 wt%. After drying in a vacuum oven overnight, a uniform pale-green precursor fibre was obtained with a diameter of about 50  $\mu$ m.

# Drawing and conversion

The drawing of the precursor fibre and conversion to PDMPV was carried out using a temperature-controlled, continuous drawing tube furnace system described in detail elsewhere<sup>16</sup>. The draw ratio was varied by changing the relative speed of the two motors as the polymer fibre passed through the tube furnace. The total residence time was about 5 min. The temperature of the tube furnace was controlled with a programmable temperature controller (Omega, CN-2020). Nitrogen gas was bubbled through hydrogen chloride and introduced into the tube furnace during drawing to catalyse the conversion, acid catalyst (such as hydrogen chloride) played an important role in the elimination reaction of methoxy leaving groups of the precursor polymer<sup>17,19</sup>.

The cross-sectional area of the fibres was calculated from the weight of 200 mm length specimens and the density ( $\approx 1260 \text{ g dm}^{-3}$ ). The latter was measured by the flotation technique using acetone and carbon tetrachloride.

### Characterization

Mechanical properties were measured at room temperature using an Instron tensile tester (model 1122). The gauge length was 10 mm. A crosshead speed of 10 mm min<sup>-1</sup> was maintained throughout these experiments. Wide-angle X-ray diffraction (WAXD) photographs of the fibres were obtained using Ni-filtered CuK<sub> $\alpha$ </sub> radiation (Phillips X-ray generator, model PW1729) and a flat-film camera. The sample-to-film distance was 40 mm. The morphological features of the fibres were examined by scanning electron microscopy (Stereoscan 90, Cambridge Instruments).

The PDMPV fibres were doped by exposure to the vapour pressure (about 135 Pa) of iodine at room

temperature. The saturation doping level was not determined. Electrical measurements were carried out using the conventional four-probe method with a constant current source (Lake Shore Cryotronics) and a digital multimeter (Keithley Model 195A). The electrical conductivity was monitored *in situ* during the doping; measurements were continued over a period of about 1 h until the conductivity reached the steady state value. The actual dimensions of the fibre sample were measured after doping for determination of the conductivity.

# EXPERIMENTAL RESULTS

### Drawability of precursor polymer fibre

Uniform pale-yellow fibres of the precursor polymer were wet-spun from chloroform solutions into hexane. The dried fibres were drawn in nitrogen (without acid catalyst) using a conventional drawing apparatus with two grips. *Figure 1* shows the maximum draw ratio of the precursor fibre as a function of temperature. The draw ratio gradually increased with temperature reaching a maximum value of 12 at 150°C, which is above the glass transition temperature ( $T_g = 110^{\circ}$ C).

#### Drawing and conversion

Precursor polymer fibres (diameter about 50  $\mu$ m) were drawn and converted simultaneously by using a temperature-controlled continuous drawing system<sup>10</sup>. Deformation of the precursor fibre was found to occur primarily at a distance of about 30 mm from the entrance to the tube furnace where the temperature was measured to be about 120°C; i.e. slightly above the glass transition temperature.

Parameters critical to the optimization of the drawingconversion process are the temperature of the tube furnace and the conversion time. The temperature of the tube furnace was varied from  $150^{\circ}$ C to  $300^{\circ}$ C. The mechanical properties and electrical conductivity were measured for PDMPV fibres prepared at various temperatures. The optimum temperature for conversion to PDMPV was found to be  $230^{\circ}$ C. The fibres prepared at temperatures below  $200^{\circ}$ C were only partially converted to PDMPV.

The draw ratio was varied at  $230^{\circ}$ C by changing the relative speed of the two motors. The maximum draw ratio in the continuous drawing system was found to be 8, close to the maximum draw ratio of the non-converted

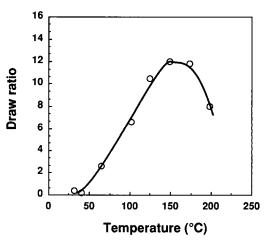


Figure 1 Drawability of the PPDMPV precursor polymer fibre at various temperatures

precursor polymer fibres as shown in *Figure 1*. Typical drawing-conversion times were approximately 6 min. The maximum winding speed was  $25 \text{ mm min}^{-1}$ , which was dictated by the length of the conversion furnace (150 mm).

# Surface features, structure and orientation

Figure 2 shows a SEM micrograph of a drawn PDMPV fibre (draw ratio 8). The cross-section was round, and the surface was smooth and uniform.

Information on the molecular orientation in the fibre was obtained by WAXD. Figure 3 shows WAXD patterns of an undrawn PDMPV fibre (Figure 3a) and PDMPV fibre with draw ratio of 8 (Figure 3b). The undrawn fibre (prepared by conversion of the precursor fibre held at constant length) exhibited three diffuse Debye-Scherrer rings and one equatorial reflection in the WAXD pattern. This pattern shows that the undrawn PDMPV fibre was of low crystallinity, but showed some degree of orientation in the as-spun fibres. The relatively sharp equatorial

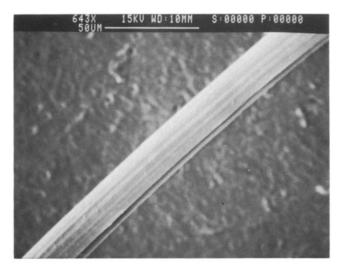


Figure 2 SEM of a PDMPV fibre with  $\lambda = 8$ 

reflection corresponds to a *d*-spacing of 1.76 nm. By contrast, the 8 times drawn PDMPV fibre exhibited four equatorial reflections and two clear meridional reflections. *Table 1* lists the observed reflections and the corresponding *d*-spacings. The equatorial and meridional reflections correspond to repeat lengths of approximately 1.76 nm and 0.68 nm, and an intra-chain repeat distance of approximately 0.63 nm (with higher order reflections in each case). The 0.63 nm spacing of the meridional reflection (first layer line) of PDMPV is identical to that observed in highly stretched PPV films, reported by Gagnon *et al.*<sup>21</sup> and Bradley *et al.*<sup>22</sup>.

The WAXD pattern of PDMPV fibre doped with iodine is shown in *Figure 3c*. The heavily doped PDMPV fibre exhibited a well defined layer line with a spacing of 0.63 nm (the same as the spacing in the undoped PDMPV fibre) and no significant increase in the mosaic spread of the equatorial reflections. The additional sharp circular reflection in *Figure 3c* is due to small crystallites of the inorganic impurities formed during doping. These data demonstrate that the high degree of molecular orientation is maintained even after chemical doping. Similar observations were reported recently for PPV by Masse et al.<sup>23</sup>.

A quantitative measure of the degree of orientation may be obtained from the angular half-width at halfheight of the intensity distribution. From the X-ray pattern of *Figure 3b*, we estimated the angular half-width

 Table 1
 Observed X-ray reflections and corresponding d-spacings for PDMPV

	Number	$2\theta$ (deg)	Spacing (nm)	Intensity
Equatorial	1	5°	1.76	strong
	2	13°	0.68	strong
	3	$20^{\circ}$	0.44	weak
	4	$26^{\circ}$	0.34	strong
Meridional	1	14°	0.63	strong
	2	28°	0.32	strong

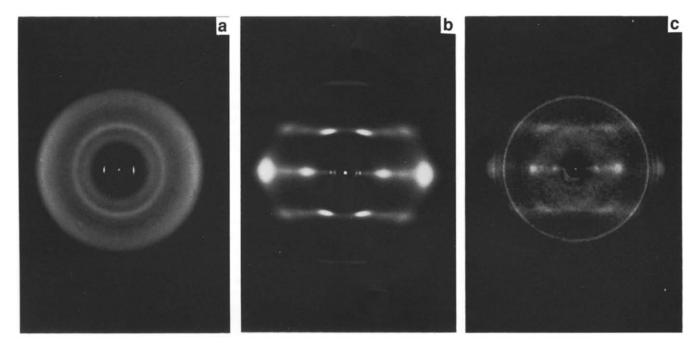


Figure 3 WAXD patterns: (a) undrawn PDMPV fibre; (b) PDMPV fibre with  $\lambda = 8$ ; (c) PDMPV fibre with  $\lambda = 8$  after doping with iodine

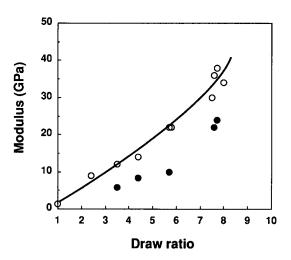
at half-height for the strong equatorial reflections to be about  $8^{\circ}$ . This angular spread corresponds to an orientation function:

$$f = \langle (3\cos^2\theta - 1) \rangle / 2 \approx 0.96$$

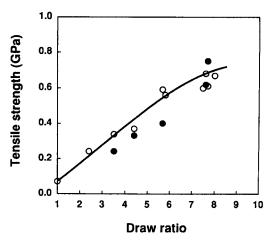
where the brackets imply an average over the experimental distribution as indicated in the X-ray pattern. The orientation function for the drawn fibres is, thus, comparable to that reported for oriented PPV films<sup>21-24</sup>.

# Mechanical properties

The room temperature Young's modulus and the tensile strength of PDMPV fibres are shown versus draw ratio in Figures 4 and 5. The undrawn PDMPV fibre exhibited relatively poor mechanical properties. The modulus and tensile strength were 1.3 GPa and 0.07 GPa, respectively. The modulus of the PDMPV fibres increased linearly with the draw ratio (see Figure 4). Similarly, the tensile strength was initially linear with draw ratio as shown in Figure 5. At higher draw ratios, however, the strength appeared to approach an upper limit, which is probably due to the modest molecular weight of the present polymer. Figures 4 and 5 reveal that fibres which had been drawn to 8 times their initial length had a Young's modulus as high as 35 GPa and a



**Figure 4** Young's modulus as a function of the draw ratio for PDMPV fibre  $(\bigcirc)$  and for PDMPV fibre doped with iodine  $(\bigcirc)$ 



**Figure 5** Tensile strengths as a function of the draw ratio for PDMPV fibre  $(\bigcirc)$  and for PDMPV fibre doped with iodine  $(\bigcirc)$ 

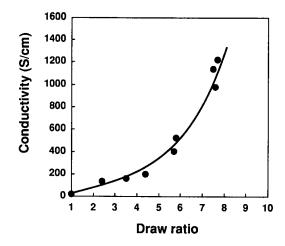


Figure 6 Electrical conductivity as a function of the draw ratio of PDMPV fibre

tensile strength of 0.7 GPa. The effects of doping on the mechanical strength are also displayed ( $\oplus$  in *Figures 4* and 5). The sample dimensions were measured after doping and used for the determination of the conductivity. The data presented in these graphs indicate that doping caused only a moderate reduction of the modulus and essentially no loss of tensile strength.

#### Electrical conductivity

The conductivities of PDMPV fibres doped with iodine were measured at room temperature. The conductivity increased rapidly after exposure to iodine vapour, approaching maximum values after about 1 h. Figure 6 shows the conductivity plotted against draw ratio. The undrawn PDMPV fibre exhibited a conductivity of  $20 \text{ S cm}^{-1}$ , with a gradual increase of conductivity seen up to a draw ratio of 5. At draw ratios greater than 5, the conductivity increased dramatically, as reported for stretched films<sup>21</sup> (although different in detail, because in Gagnon *et al.* the unstretched films were already about 30% converted). At a draw ratio of 8, the conductivity was  $1200 \text{ S cm}^{-1}$ , 60 times higher than that of the undrawn material.

# DISCUSSION

As is commonly observed for most polymers, the mechanical properties of the PDMPV fibres were found to improve significantly with the draw ratio and increased degree of orientation. Although qualitatively similar results<sup>16</sup> were obtained for poly(2,5-thienylenevinylene), PTV, the orientation function (f = 0.86) did not reach such a high value as in the PDMPV fibres (f = 0.96), and the values for the modulus and tensile strength of PTV were correspondingly lower (7 GPa and 0.5 GPa, respectively)<sup>16</sup>. Thus, in spite of the higher draw ratios achieved for PTV (as high as 20), the degree of orientation (and the corresponding values for the modulus and the tensile strength) was not as high as for PDMPV.

The lower degree of orientation obtained at a higher draw ratio found for PTV is indicative of the importance of chain relaxation during the tensile drawing and conversion process. In this context, the most important difference between the PDMPV and PTV precursor polymers is the temperature gap between the glass transition temperature  $(T_g)$  and the conversion temperature  $(T_{con})$ . For PPDMPV,  $T_g \approx 110^{\circ}$ C and  $T_{con} = 195^{\circ}$ C; for PPTV,  $T_g \approx 50^{\circ}$ C and  $T_{con} = 188^{\circ}$ C. Thus, although the conversion temperatures are approximately equal for the two systems, the glass transition temperature of the PPTV precursor polymer is much lower. Consequently, the PPTV precursor polymer was processed at temperatures  $T_p$  (= 240°C) relatively high above  $T_g$  ( $T_p - T_g \approx$ 190°C)<sup>16</sup>, leading to more rapid molecular motion and more extensive chain relaxation (before conversion) than in PPDMPV ( $T_p = 230^{\circ}$ C) for which ( $T_p - T_g \approx 120^{\circ}$ C).

To investigate these differences more quantitatively, the temperature dependence of the modulus of PPDMPV precursor polymer was compared with that of the PPTV precursor polymer. In both cases, Young's modulus was measured using strips of film  $(20 \text{ mm} \times 1 \text{ mm}, \text{thickness})$ 20  $\mu$ m). The measurements were carried out between room temperature and 140°C. The results are shown in Figure 7. The PPTV precursor exhibited a sharp drop in modulus at 50°C (at the glass transition) and decreased to 1 MPa at 70°C. At temperatures above 120°C, the modulus fell below 1 MPa. For the PPDMPV precursor, the sharp drop in modulus took place at 110°C (again at the glass transition) although it was still 10 MPa at 130°C. To convert the precursor polymer to the conjugated polymer on the timescale characteristic of the continuous drawing process (about 5 min) 140°C is probably necessary, even in the presence of acid catalyst. Therefore, the PPDMPV precursor fibre was converted immediately after, or simultaneously with drawing without major relaxation. To achieve analogous experimental conditions for PPTV, a different temperature profile would be required including two regimes such that the precursor is drawn at a relatively low temperature  $(\sim 50-60^{\circ}C)$  and then rapidly converted at higher temperature ( $\sim 150^{\circ}$ C).

Next, we attempt to estimate the theoretical axial Young's modulus of PDMPV from modulus/draw ratio data presented in *Figure 4*. The theoretical Young's modulus of flexible chain polymers can be derived from modulus/draw ratio data with the following equation<sup>25</sup>, if tensile drawing occurred in the affine mode:

$$E = [E_{\rm h}^{-1} + (3\pi/4)\lambda^{-3/2}(E_{\rm u}^{-1} - E_{\rm h}^{-1})]^{-1}$$
(1)

where E and  $\lambda =$  the experimental modulus and draw ratio, respectively;  $E_{\rm h}$  and  $E_{\rm u} =$  the moduli of the perfectly oriented and the unoriented polymer, respectively. As indicated above, tensile drawing of the amorphous

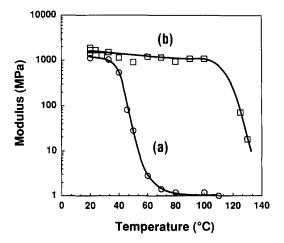
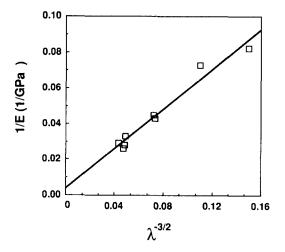


Figure 7 Temperature dependence of Young's modulus for PDMPV: (a) PPTV precursor fibre; (b) PPDMPV precursor fibre



**Figure 8**  $E^{-1}$  vs  $\lambda^{-3/2}$  for comparison with equation 1; the extrapolation of  $E^{-1}$  as  $\lambda \to \infty$  yields an estimate for the theoretical modulus of PDMPV of 250 GPa

PPDMPV precursor polymer fibre occurred before and during conversion with only moderate molecular relaxation. Thus, the conditions of affine deformation for validity of equation (1) appear to be satisfied during the tensile drawing; and we used this expression to obtain an extrapolated value for  $E_{\rm h}$  for the converted polymer from the experimental data. Figure 8 shows  $E^{-1}$  plotted against  $\lambda^{-3/2}$ . Extrapolating to infinite draw ratio,  $\lambda^{-3/2} \rightarrow 0$ , the axial modulus for perfectly oriented PDMPV was estimated to be as high as 250 GPa. This value is remarkably high, in view of the relatively large cross-sectional area of the PDMPV macromolecule.

A note of caution is needed regarding the use of equation (1). This relation was developed for tensile drawing of flexible chain molecules that, unlike the present system, do not undergo chemical changes. The conversion from the precursor PPDMPV to the conjugated PDMPV is most likely associated with a change in chain stiffness, which may render the deformation process more efficient than in the affine case. This change may cause self-extension, an interesting and useful phenomenon in itself, but one that would lead to an over-estimate of the theoretical axial Young's modulus.

In our previous studies of PTV fibres, we observed a strong correlation between the mechanical properties and the electrical conductivity<sup>16</sup>. It was pointed out that the modulus and tensile strength were associated with both intra-chain interactions (e.g. strength of chemical bonding, chain conformation, etc.) and inter-chain interaction (e.g. van der Waals forces, inter-chain transfer interactions, chain conformation, etc.). In conjugated polymers, these same features (band-like conduction within a polymer chain and electron transfer between polymer chains) determine the carrier mean free path, and thus electrical conductivity. Therefore, we anticipate a general relationship between the conductivity and the tensile strength (and/or modulus). For drawn PDMPV fibres *Figure* 9 shows the relationship between Young's modulus and electrical conductivity and Figure 10 shows the relationship between the tensile strength and electrical conductivity. In both cases, a strong correlation is observed, suggesting that major improvements in electrical conductivity can be anticipated as the materials are further improved so that the mechanical properties approach their intrinsic values. However, until a more

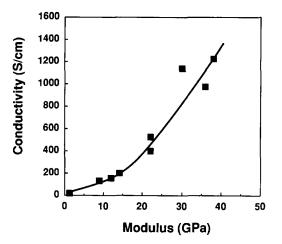


Figure 9 Electrical conductivity as a function of Young's modulus for PDMPV fibre

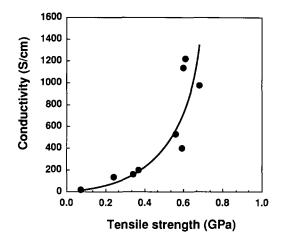


Figure 10 Electrical conductivity as a function of the tensile strength for PDMPV fibre

quantitative understanding of the relationships implied by *Figures 9* and *10* is attained (i.e. analogous to equation (1)), extrapolation to the intrinsic electrical conductivity is not possible.

### CONCLUSION

In this study, we successfully demonstrated the preparation of oriented fibres of PDMPV with a Young's modulus of 38 GPa and a tensile strength of 0.7 GPa. These values represent quite impressive mechanical properties, exceeding those of e.g. tyre-cord and approaching those of medium-performance fibres. They are similar to the values obtained for highly stretched PPV film<sup>5</sup>, and they are comparable with those of stretched *trans*-polyacetylene films<sup>4</sup>.

Although clearly very important in the context of potential applications, measurements of the mechanical properties of conjugated polymers doped to achieve high electrical conductivity are not common in the literature. In most known cases, the mechanical properties are degraded by chemical doping. The mechanical properties of the present PDMPV fibres, however, retained their excellent mechanical properties even after iodine doping: the modulus decreased only to 25 GPa, and the tensile strength remained essentially unchanged. The retention of mechanical properties has its origin partly in the orientation of the macromolecules within the fibre. The WAXD patterns of doped PDMPV indicate that even after doping, the PDMPV chains within the fibre maintain a high degree of molecular orientation.

Fibres with significant mechanical properties will be required for a variety of potential applications as electrical conductors. The results for PDMPV fibres, as reported here, provide hope that such applications may be realistically anticipated. More generally, these results imply that attempts to attain sufficient quality (chain extension and chain alignment) to approach the intrinsic electrical and mechanical properties of conducting polymers is a realistic goal.

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