# Anisotropic mechanical properties of uniaxially oriented electrically conducting poly(*p*-phenylene vinylene)

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The mechanical properties of uniaxially oriented poly(*p*-phenylene vinylene) film prepared by simultaneous thermal elimination and uniaxial extension of the poly(sulphonium salt) precursor have been measured both in the machine and transverse directions. The mechanical properties are anisotropic and dependent upon the degree of molecular orientation. Young's modulus varies between 2.3 and 37 GPa as a function of draw ratio in the machine direction and between 2.3 and 0.5 GPa in the transverse direction. The effect of chemical doping on mechanical properties has also been determined. A comparison between mechanical and electrical anisotropy in oriented samples has been made.

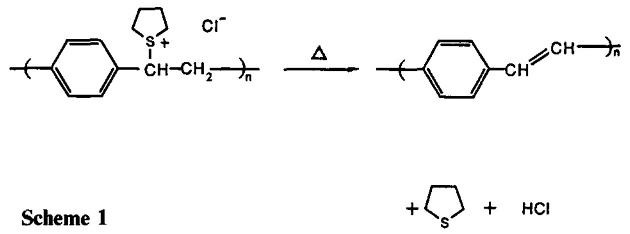
**(Keywords: mechanical properties; poly(*p*-phenylene vinylene); conducting polymer)**

## INTRODUCTION

Fully conjugated electrically conducting polymers have been the subject of extensive physical characterization, chiefly aimed at understanding the unique electrical, electrochemical and optical properties of these materials. Relatively few studies have addressed the mechanical behaviour of available conducting polymers. However, as new applications for these materials arise[1], it is expected that their load-bearing capability will assume greater importance.

The reported tensile properties for materials such as polyacetylene[2,3] and polypyrrole[4,5] are disappointing in comparison to what might be expected for a fully conjugated, rigid, linear macromolecule. Clearly, the mechanical performance of these materials is limited by their morphological structure. For instance 'Shirakawa' polyacetylene film consists of entangled mats of microfibrils[6], while electrochemically polymerized heterocycles form grainy films of irregular topology[7]. In contrast, excellent mechanical properties have been reported for solid-state polymerized poly(diacetylenes)[8]. Correspondingly, these materials possess a very highly ordered single crystalline morphology. However, the degree of order in these single crystals is such that it has entirely prevented chemical 'doping', which is necessary to impart high conductivity to this class of materials[9].

Poly(*p*-phenylene vinylene) (PPV) prepared from the water-soluble poly(sulphonium salt) precursor can be obtained in the form of dense, homogeneous, well ordered film[10]. A unique internal plasticization phenomenon, associated with the thermally induced transformation from the precursor to the conjugated product (*Scheme 1*), allows these materials to be efficiently and controllably oriented by means of a uniaxial stretching process[11]. It has been shown that the electrical properties of oriented PPV are anisotropic and strongly dependent upon the state of molecular orientation[11,12]. Conductivity is greatly enhanced parallel to the axis of orientation and may attain a value as high as $10^4\,\mathrm{S\,cm^{-1}}$ at high draw ratios (corresponding to an almost 100-fold increase as a result of stretching).



**Scheme 1**

The present paper reports the mechanical behaviour of PPV films prepared over a wide range of draw ratios and possessing variable molecular orientation. Tensile properties in both the machine and transverse directions have been examined and compared to the anisotropy of the electrical properties.

## EXPERIMENTAL

The PPV precursor, poly(xylylidene tetrahydrothiophenium chloride) ($M_w = 1.1 \times 10^6$, $M_w/M_n = 2.1$), was synthesized according to a previously published procedure[10]. Films ($56\,\mu m \times 15\,cm \times 120\,cm$) were cast under a stream of filtered air on large plexiglass sheets from concentrated aqueous polymer solutions (4 wt%). Films were stretched on a uniaxial web stretching apparatus[11]. In this process, precursor polymer film is passed over differentially driven heated rolls. As the temperature of the film is raised, the conversion (elimination) reaction proceeds, and the plasticizing effect of the volatile products allows considerable extensional deformation. The draw ratio is determined by the relative speeds of the heated rolls. The roll temperature is precisely controlled to avoid the formation of bubbles or the development of excessive tensile stress in the film. After stretching, PPV precursor films were annealed at constant

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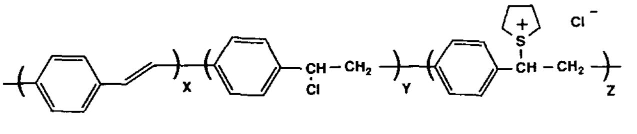
length at 250°C for 2 h under nitrogen to complete the elimination reaction. The details of PPV processing and sample preparation, including a description of the stretching apparatus, have been published elsewhere[11].

Mechanical testing was performed on an Instron Model 4202. Specimens were prepared to be 5.1 mm in width. The film thickness decreased with increasing draw ratio in the range of 5–30 $\mu$m. For specimens cut parallel to the machine direction a gauge length of 75 mm was used; for transverse specimens a gauge length of 12 mm was used (due to limitations of film width). A strain rate of 2% $\text{min}^{-1}$ ($3.3 \times 10^{-4}\,\text{s}^{-1}$) was used throughout. For each data point, five samples were tested, of which three were averaged.

Samples were characterized by elemental analysis (University of Massachusetts Microanalysis Laboratory) and infrared spectroscopy (Mattson Cygnus 100, fitted with gold wire grid polarizer). Chemical doping studies were performed using $SbF_5$ and $AsF_5$ Lewis acid dopants. Conductivity measurements were made using a standard evacuable four-probe apparatus and doping levels were determined gravimetrically. The details of chemical doping have been given elsewhere[10].

## RESULTS AND DISCUSSION

Initial efforts were aimed at determining the 'green' strength of the films, i.e. the mechanical behaviour of the films obtained directly after thermal stretching and before annealing. Elemental analysis and spectroscopic studies indicate that these materials are at an intermediate stage of conversion and are adequately described by the structure shown in *Scheme 2* with the fractional molar compositions $x, y, z$ approximately equal to 1, 2.25, 0.75.



**Scheme 2**

Typical stress–strain curves for these materials measured parallel to the machine direction are given in *Figure 1* for various draw ratios; additional data are listed in *Table 1*. The 'as stretched' materials exhibit classical yield behaviour at low and intermediate draw ratios. At draw ratios greater than five, however, purely elastic deformation is observed. The yield stress increases with draw ratio from 45 MPa for the unstretched (isotropic) material up to 150 MPa for a draw ratio of five. The attainable strain decreases rapidly with draw ratio from 50 to 2% upon increasing the draw ratio from one to ten. The tensile modulus increased substantially as a result of orientation, from 2.7 GPa for isotropic film to 16 GPa for film which had been stretched to ten times its initial length. Note that materials of low draw ratio yielded with the formation of a stable neck, which propagated at constant rate and constant stress until reaching the grips and fracturing.

The 'as stretched' materials also exhibited yield behaviour when stressed in the transverse direction. The anisotropy of yield stress was as high as six. In general, the tensile behaviour of these materials, particularly the dependence of yield stress upon draw ratio, is similar to that reported for other oriented ductile polymers[13] such as polypropylene[14] and polyethylene terephthalate[15].

In the preparation of conducting poly(*p*-phenylene vinylene) an annealing operation is required in order to convert the polymer completely to its conjugated form (*Scheme 1*). In the present case, annealing was performed under conditions of constant length and mild tension; no significant stress relaxation accompanied the process. An inert environment is required during annealing to prevent oxidation of vinylene units which are formed. Materials prepared in the present work were converted quantitatively to PPV with no significant oxidation. Typical elemental analyses were: C, 92.5; H, 5.7; S, 0.3; C, 0.7; O, 0.4% (theoretical: C, 94.1; H, 5.9%).

In terms of mechanical behaviour, the effect of annealing was substantial. Annealed materials did not exhibit sharp

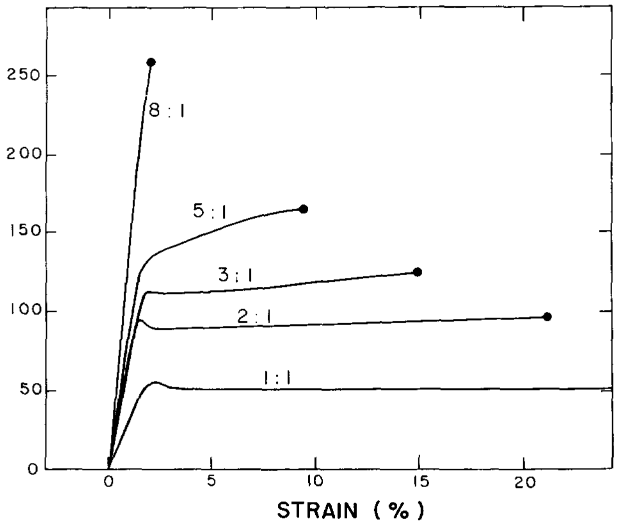


**Figure 1** Stress–strain curves for 'as-stretched' (unannealed) PPV precursor stretched to a series of draw ratios. Measurements were made in the machine direction

**Table 1** Tensile properties of 'As-stretched' PPV measured parallel to the draw direction

| Draw ratio | Modulus (GPa) | Yield stress (MPa) | Yield strain (%) | Tensile strength (MPa) | Elongation (%) |
|---|---|---|---|---|---|
| Isotropic | 2.7 | 45.2 | 3.3 | 48.2 | 38 |
| 1[a] | 3.5 | 60 | 2.5 | – | 53 |
| 2 | 8.1 | 114 | 1.8 | 116 | 20 |
| 3 | 9.1 | 129 | 1.9 | 140 | 14 |
| 4 | 8.6 | 112 | 1.4 | 157 | 13 |
| 5 | 10.6 | 152 | 1.4 | 181 | 9.3 |
| 6 | 11.8 | – | – | 223 | 2.9 |
| 8 | 14.2 | – | – | 256 | 2.1 |
| 10 | 15.5 | – | – | 271 | 2.1 |

[a] Materials of draw ratio 1 are not isotropic because the precursor elimination/stretching process involves a substantial volume change ($\approx$50%) and these materials are converted at constant length[11]

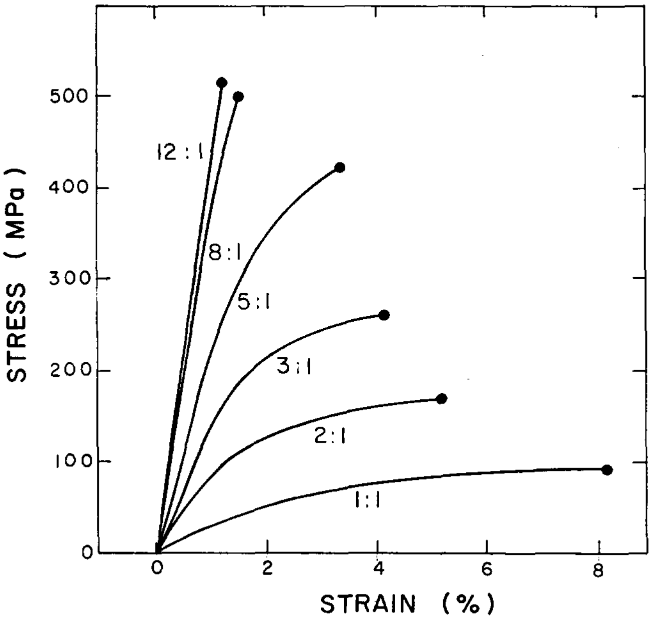


**Figure 2** Stress–strain curves for fully annealed PPV stretched to a series of draw ratios. Measurements were made in the machine direction

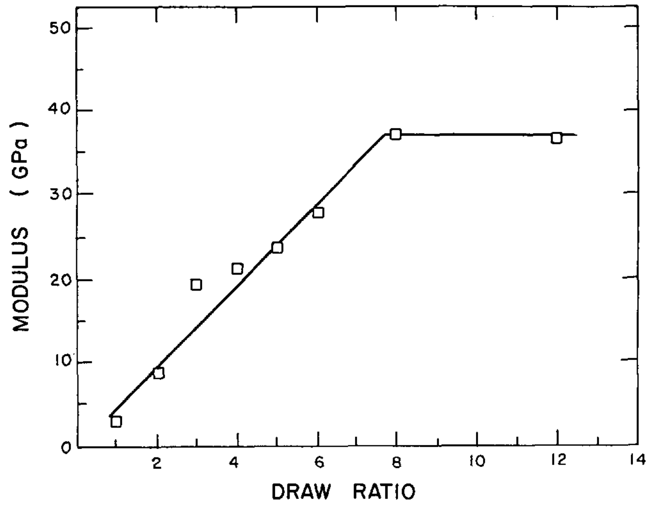


**Figure 3** Young's modulus in the machine direction for annealed PPV plotted as a function of draw ratio

yield points. They did, however, exhibit some plastic deformation, the extent of which decreased with increasing draw ratio (see *Figure 2*). Cyclic loading induced a measure of strain hardening in these materials. For instance, annealed films of draw ratio three experienced a 20% increase in tensile modulus after one deformation cycle to 4% strain. In general, moduli and tensile strengths increased significantly as a result of annealing; attainable elongation, however, was greatly reduced.

For measurements parallel to the machine direction, typical stress–strain curves are shown in *Figure 2* and averaged results are plotted in *Figures 3* and *4*. The increase in modulus with draw ratio is considerably more rapid, particularly at low and intermediate draw ratios, than has been commonly observed for various oriented flexible chain polymers (PET, PP, PE, Nylon)[16]. This is attributed to the unusually high efficiency of molecular orientation characteristic of the PPV stretching process. Studies have shown that, for PPV, molecular orientation at a given draw ratio significantly exceeds that predicted by the pseudo-affine deformation model, which is often considered an upper limit to orientation in the stretching of semi-crystalline polymers[11,12,17]. For PPV, Young's modulus increased from 2.3 GPa for unstretched material to 37 GPa in the highly oriented case. For comparison, the latter value is intermediate between 4.6 GPa, typical of highly drawn Nylon 6,6 fibres[16], and 150 GPa, typical of high performance polyaramid fibres (Kevlar)[18].

For polyacetylene prepared by the Shirakawa method, a tensile modulus of 0.2 GPa has been reported[2]. Presumably, this value increases somewhat with *cis* to *trans* isomerization and/or partial stretch alignment, but no details have been given. For polypyrrole prepared electrochemically, the mechanical properties have been shown to depend a great deal upon the method of preparation[4]; however, the highest reported modulus for this polymer is 2.4 GPa, which is equivalent to that of unstretched PPV in the present study. The properties of highly oriented PPV correspond most closely to those of single crystalline poly(diacetylene), for which a tensile modulus of 42 GPa has been reported[8]. The last-mentioned materials, however, are much more difficult to prepare and handle than PPV. It may also be interesting to note that oriented PPV exhibited significantly better mechanical properties than those reported for electrically conducting nickel phthalocyanine/Kevlar composite fibres[19].

In *Figure 4*, the stress and strain at failure are plotted for annealed PPV as a function of draw ratio. The ultimate strain decreases from about 9 to 1% with increasing draw ratio. The tensile strength, however, exhibits a maximum value of about 500 MPa occurring at a draw ratio of six.

The transverse properties of oriented PPV have also been measured. Previous studies of PPV oriented manually[12] or at constant stress[17] have reported tendencies of the oriented materials to fibrillate, reflecting poor transverse properties. However, the heated roll stretching process used in the present study has produced materials with improved transverse integrity. Stress–strain curves obtained in the transverse direction are shown in *Figure 5* and calculated properties are listed in *Table 2*. Young's modulus decreased with draw ratio from 2.3 GPa in the undrawn state to 0.5 GPa at a draw ratio of five. Tensile strength decreased only slightly, maintaining a value of about 30 MPa at a draw ratio of five; elongation increased slightly with draw ratio. Note that the transverse

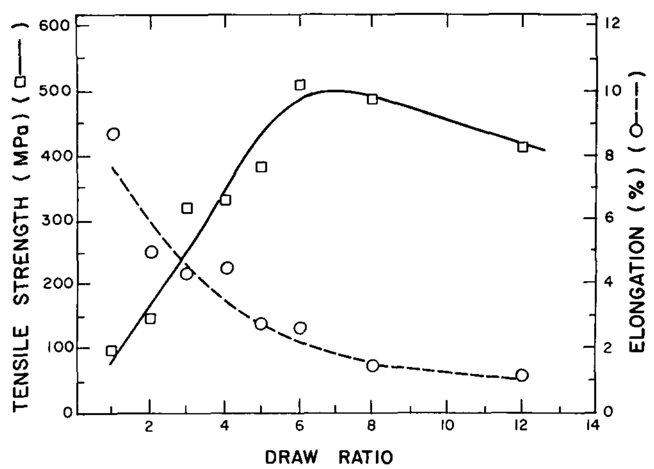


**Figure 4** Tensile strength (□) and ultimate elongation (○) measured in the machine direction for annealed PPV plotted as a function of draw ratio

properties of oriented PPV, although inferior to the properties in the machine direction, are comparable to those of many flexible chain polymeric materials.

The effect of chemical doping upon the mechanical properties of the material is of primary interest. Doping is required to impart high electrical conductivity to these materials. It also results in large dimensional changes and structural rearrangements within the material[20]. X-ray diffraction studies have shown, however, that doping does not disrupt chain alignment in oriented PPV. In *Table 3*, results are given showing the degree of doping, electrical conductivity and tensile properties of samples doped with arsenic pentafluoride and antimony pentafluoride.

It is well known that many conjugated polymers, including PPV, have very poor atmospheric stability in the doped state. In the present study, precautions were taken to minimize the air exposure of samples before tensile testing. Doped samples were transported in argon filled vessels, quickly mounted and tested within 15 min of total air exposure. Thus, although atmospheric degradation may be expected to alter the measured tensile properties, as has been reported for polyacetylene[2], the effect in the present study is expected to be minimal.

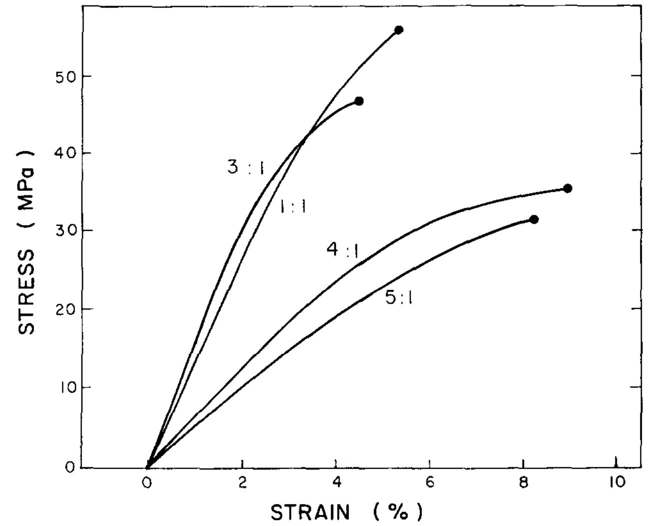


**Figure 5** Stress–strain curves for fully annealed PPV stretched to a series of draw ratios. Measurements were made in the transverse direction

**Table 2** Tensile properties of annealed PPV measured perpendicular to the draw direction

| Draw ratio | Modulus (GPa) | Tensile strength (MPa) | Elongation (%) |
|---|---|---|---|
| Isotropic | 2.33 | 41.2 | 2.1 |
| 1 | 1.49 | 51.1 | 4.6 |
| 2 | 0.83 | 30.1 | 3.9 |
| 3 | 1.23 | 37.4 | 4.0 |
| 4 | 0.54 | 36.0 | 6.0 |
| 5 | 0.47 | 31.7 | 7.7 |

For $AsF_5$ doping, conductivities in excess of 5000 S cm$^{-1}$ in the machine direction have been observed. Measurements of dopant weight uptake indicate a doping level of approximately one dopant molecule per PPV repeat unit. The effect of doping upon mechanical properties measured in the machine direction was chiefly embrittlement; the strain at break was reduced to approximately 1%. The modulus and strength were also reduced considerably (two to five times). For $SbF_5$ doping, uptakes were higher and conductivities were around 2000 S cm$^{-1}$. The resulting mechanical properties, however, were very similar to the $AsF_5$ doped material. In the transverse direction, mechanical properties were seriously compromised after doping, making sample mounting and subsequent measurement impossible.

In the light of the above results and reports of the doped polymer structure[20,21], it appears that the added dopant molecules located between polymer chains contribute no appreciable load bearing capacity in the chain direction and merely increase the average cross-sectional area per chain, thereby lowering the modulus. Doping also results in embrittlement, which may be attributed to expected chemical defects (scission; crosslinking) introduced by the powerful oxidizing ability of the dopants used. In the transverse direction, the effect of doping is even greater because of the lateral separation of chains required for the accommodation of dopant ions[20,21].

In *Table 4*, the first-order orientation function, determined from the infrared dichroism of the 558 cm$^{-1}$ infrared absorbance[11,17], is given for PPV for a series of draw ratios. Also shown are the mechanical anisotropy before doping (ratio of moduli in the machine and transverse directions) and the electrical anisotropy after $SbF_5$ doping (ratio of conductivities in the machine and transverse directions). The fact that the two types of anisotropy are similar over a range of draw ratios and orientation functions may suggest that in the present case anisotropy arises from similar structural features (e.g. orientation, crystallite size, shape and perfection, inter-chain interactions).

In summary, similarly to the electrical properties, the mechanical properties of PPV can be varied over a wide range through control of molecular orientation. It is expected that the available range of mechanical properties for PPV can be further expanded by the preparation of polymer blends[22].

## CONCLUSIONS

The mechanical properties of PPV prepared by thermal stretching of the poly(sulphonium salt) precursor are anisotropic and highly dependent upon the degree of

**Table 3** Tensile properties and electrical conductivity of chemically 'doped' PPV measured parallel to the draw direction

| Draw ratio | Dopant | Dopant uptake (wt%) | Conductivity (S cm$^{-1}$) | Modulus (GPa) | Tensile strength (MPa) | Elongation (%) |
|---|---|---|---|---|---|---|
| 5 | $AsF_5$ | 167% | 5000 | 11.6 | 87.1 | 0.8 |
| 5 | $SbF_5$ | 620% | 1850 | 9.2 | 111 | 1.3 |
| 10 | $AsF_5$ | 161% | 6390 | 4.4 | 64.9 | 1.5 |
| 10 | $SbF_5$ | 330% | 2320 | 7.1 | 46.0 | 0.7 |

**Table 4** Mechanical and electrical anisotropy of oriented PPV

| Draw ratio | Orientation function[a] | $E_{\parallel}/E_{\perp}$[b] | $\sigma_{\parallel}/\sigma_{\perp}$[c] |
|---|---|---|---|
| Isotropic | 0 | 1 | 1 |
| 1 | 0.17 | 1.9 | 4.1 |
| 2 | 0.73 | 11 | 12 |
| 3 | 0.84 | 16 | 20 |
| 4 | 0.94 | 39 | 34 |
| 5 | 0.95 | 50 | 58 |

[a] Determined from i.r. dichroism of PPV 558 cm$^{-1}$ absorbance
[b] Young's moduli of annealed sample before doping
[c] Electrical conductivity after $SbF_5$ doping to maximum conductivity

molecular orientation attained (draw ratio). For drawn samples, values for the Young's modulus as high as 37 GPa and tensile strength up to 500 MPa have been measured in the machine direction. These properties approach those of many high performance fibres. At low and intermediate draw ratios ($\leqslant 5$) samples also maintain good mechanical strength in the transverse direction. Chemical doping reduces the tensile modulus and tensile strength, and limits the attainable strain to about 1%.

## ACKNOWLEDGEMENT

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