Molecular orientation and conductivity in highly oriented poly(*p*-phenylene vinylene)*

J. Briers, W. Eevers, P. Cos and H. J. Geise†
University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium

and R. Mertens and P. Nagels
University of Antwerp (RUCA), Middelheimlaan 1, B-2020 Antwerp, Belgium

and X. B. Zhang and G. Van Tendeloo
University of Antwerp (RUCA), Department of Physics, Electron Microscopy, Groenenborgerlaan 171, B-2020 Antwerp, Belgium

and W. Herrebout and B. Van der Veken
University of Antwerp (RUCA), Department of Inorganic Chemistry, Groenenborgerlaan 171, B-2020 Antwerp, Belgium

Highly oriented films of poly(*p*-phenylene vinylene) (PPV) were prepared by uniaxial stretching during thermal conversion of a water-soluble sulfonium polyelectrolyte precursor polymer. The precursor films were stretched up to seven times their original length. Doping of the stretched PPV films was achieved by dipping into a 0.12 M solution of $FeCl_3$ in nitromethane. The d.c. electrical conductivity of these doped films was measured as a function of the doping time and as a function of the temperature between 80 and 300 K. Compared with the maximum conductivity obtained in unstretched PPV films doped with $FeCl_3$ ($\sigma_{dc} = 35\ \Omega^{-1}\ cm^{-1}$), the stretched films showed a higher conductivity ($\sigma_{dc} = 230\ \Omega^{-1}\ cm^{-1}$) when measured along the stretching orientation. The molecular structure and the changes caused by doping of stretched PPV films were studied by infra-red dichroism, transmission electron microscopy and electron diffraction.

(Keywords: poly(phenylene vinylene); conduction mechanism; molecular orientation)

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.

Poly(*p*-phenylene vinylene) (PPV) is an alternating copolymer of *p*-phenylene and acetylene. The synthesis and properties of the last two polymers have been extensively studied[1]. High-quality films of PPV can be prepared through thermal elimination of a sulfonium salt precursor polymer. Thermal elimination of this precursor under tensile stress produces stretched films with a high degree of molecular orientation. The mechanical as well as the electrical properties of oriented PPV are anisotropic and depend strongly on the degree of molecular orientation[2].

It has been shown[3] that PPV is a good electrical conductor upon doping with AsF_5 and SO_3. As an electron acceptor, $FeCl_3$ was previously reported to dope polyacetylene (PA) and poly(*p*-phenylene) (PPP)[4]. It has been proved[5] that high electrical conductivity in PPV can also be achieved by $FeCl_3$.

EXPERIMENTAL

Films of PPV were synthesized via pyrolysis of a water-soluble sulfonium polyelectrolyte, derived from *p*-xylene bis(tetrahydrothiophenium chloride), according to the Kanbe[6] and Wessling[7] procedure, later modified by Lenz *et al.*[8]. After drying in air, the free-standing yellowish-green transparent polymer films were converted to PPV by heat treatment at 300°C for 3 h under rigorous nitrogen conditions. This thermal treatment eliminates the tetrahydrothiophene moiety.

Highly oriented films of PPV were prepared by uniaxial stretching during thermal conversion of the sulfonium precursor polymer. The precursor films were stretched up to seven times their original length. The degree of chain alignment of the fully converted and stretched PPV films as a function of the draw ratio $\lambda = l/l_0$, where l_0 and l are the initial and final lengths, respectively, was studied by infra-red dichroism using a Bruker IFS 113v FTIR spectrophotometer fitted with an AgBr-grid polarizer. Doping of the unstretched and stretched films was accomplished by immersing them into a 0.12, 0.24 or a saturated 0.62 M solution of $FeCl_3$ in anhydrous nitromethane for various times (10 to 300 s).

A JEOL 100C (operating voltage 100 kV) and a CM 20 TEM (200 kV) were employed for electron diffraction (EC) and bright-field imaging; a JEOL 200CX (120 kV) was used for high-resolution (HRTEM) imaging.

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[†] To whom correspondence should be addressed

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RESULTS AND DISCUSSION

Infra-red dichroism

In order to obtain a value for the degree of orientation by infra-red dichroism, it is necessary that the value of the angle between the dipole transition moment and the chain axis is known for at least one of the infra-red-active modes. With this angle and the dichroic ratio, $R = A_{\parallel}/A_{\perp}$, where $A_{\parallel}$ and $A_{\perp}$ are the measured absorbances of the specific vibration with the incident radiation polarized parallel and perpendicular to the stretch direction z, the degree of orientation may be specified in terms of the 'Hermans orientation function'. This function is defined as:

$$f = (R-1)(R_0+2)/(R+2)(R_0-1)$$

where $R_0 = 2\cot^2\theta$, θ being the angle between the transition moment M of the specific vibration mode and the chain axis. The absorption at 555 cm^{-1}, assigned to a *p*-phenylene out-of-plane ring bend having a transition moment at 90°, is taken as the reference[9]. As can be seen from *Table 1*, the orientation function rapidly increases until $\lambda = 5$, and stabilizes at a value of $f = 0.96$ with increasing stretch ratio.

Electrical properties

The room-temperature electrical conductivity of $FeCl_3$-doped, unstretched and stretched ($\lambda = 4$) PPV films shows a fast initial increase with increasing doping time, followed by a slow increase to a maximum value $\sigma_{dc} = 35\,\Omega^{-1}\,cm^{-1}$ for the unstretched and $\sigma_{dc} = 230\,\Omega^{-1}\,cm^{-1}$ for the stretched films. The dopant concentration expressed as $y = [FeCl_4^-]/[C_8H_6]$ is considerably higher in the stretched ($y = 0.39$) than in the unstretched samples ($y = 0.071$) for equal doping time (60 s) and equal dopant solution concentration (0.12 M $FeCl_3$ in nitromethane).

The room-temperature conductivity for oriented films parallel ($\sigma_{\parallel}$) and perpendicular ($\sigma_{\perp}$) to the stretch direction shows an anisotropy $\sigma_{\parallel}/\sigma_{\perp}$ equal to 13 ($\lambda = 4$). This may be understood in terms of the relative contributions of intrachain and interchain transport of charge carriers, the latter being the rate-limiting step in the conduction mechanism.

The temperature dependence of the d.c. conductivity, measured between 80 and 300 K along the orientation direction, provide information about the conduction mechanism. For unstretched films, a plausible mechanism is variable-range hopping. The data obey Mott's formula in which $\log(\sigma T^{1/2})$ is proportional to $T^{-1/4}$ in three dimensions[10]:

$$\sigma_{dc} = \frac{3e^2\nu_0}{128\alpha^2}\left(\frac{T_0}{T}\right)^{1/2} N(E_F)\exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right]$$

Because of their morphology, stretched PPV films are non-continuous materials, but consist of fibrils separated by barriers due to interfibril contacts. Hence, a possible explanation for the conduction process in stretched–aligned films is fluctuation-induced tunnelling between highly conducting regions separated by potential barriers. The theoretical approach of Sheng[11] predicts a temperature dependence of the form:

$$\sigma(T) = \sigma_0 \exp[-T_1/(T+T_0)]$$

Table 1 Dichroic ratios and orientation function values for various draw ratios

Draw ratio, λ	Dichroic ratio, R	Orientation function, f
1	0.740	0.19
2	0.120	0.83
3	0.063	0.91
4	0.036	0.94
5	0.026	0.96
6	0.033	0.95
7	0.028	0.96

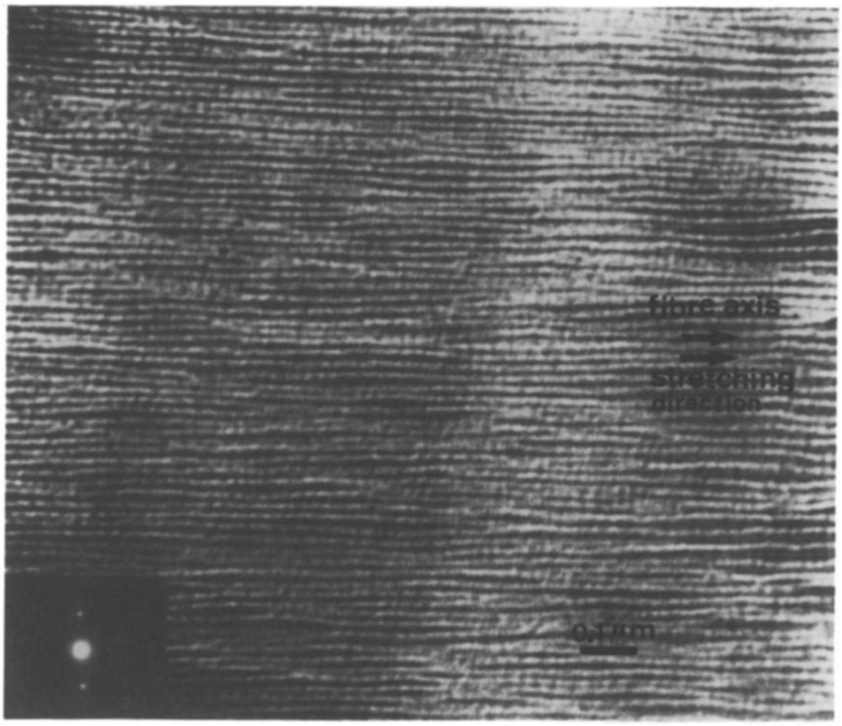
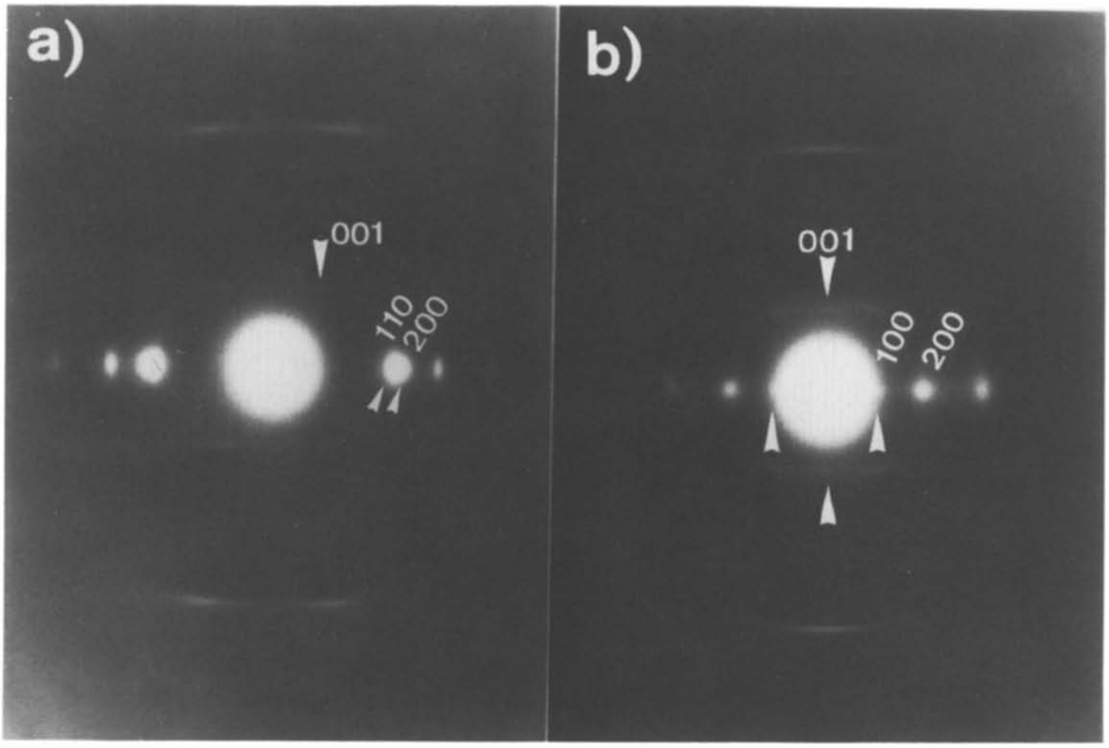


Figure 1 The morphology of undoped, stretched PPV showing well oriented fibrils with an average diameter of 200 Å. The corresponding diffraction pattern is inserted



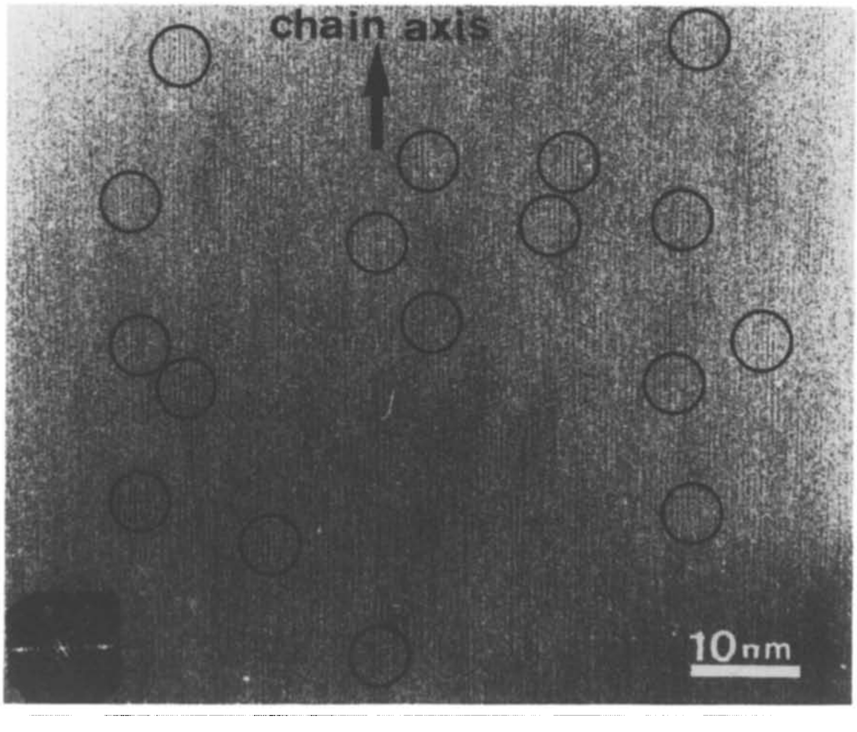


Figure 3 High-resolution TEM of doped PPV with the corresponding Fourier transform pattern inserted. Areas with a high degree of crystallinity are indicated with a circle

Satisfactory fits are obtained over the entire temperature range (80–300 K). The width of the potential barrier w is found from the expression:

$$w = \frac{T_1}{T_0} \frac{2\hbar}{\pi(2m\Delta E)^{1/2}}$$

Typical barrier parameters obtained from our analysis of the Sheng equation are: $w = 31$ Å and $\Delta E = 0.0116$ eV ($= 1.858 \times 10^{-21}$ J). The height of the potential barrier, ΔE, in the Sheng model corresponds to the charging energy $U = e^2/2C$ of this barrier. Using the formula for the capacity $C = \varepsilon_0 A/w$ with $\varepsilon_0 = 8.9 \times 10^{-12}\ \mathrm{C^2\ J^{-1}\ m^{-1}}$ we calculated the surface of the potential barrier A corresponding to the surface of a fibril section and found for the fibril radius $R = 280$ Å.

Morphology

The TEM bright-field image of a uniaxially stretched undoped PPV film, shown in *Figure 1*, sectioned with a microtome, shows the fibrillar morphology of the specimen. The fibres are well oriented in the stretching direction. The photograph shows an average diameter of the microfibrils of about 200 Å, which corresponds well with the fibril radius resulting from the Sheng model.

It was possible to identify a large number of local orientations in the morphological picture and to measure their angular deviations from the reference direction. The deviations range from -7 to $+8°$, with a maximum misorientation between the fibres of 15°. This is consistent with the HREM results of Masse *et al.*[12], who found similar values for the local angular deviations of individual crystallites in undoped PPV having an orientation function of $f = 0.96$.

Crystalline structure

The electron diffraction patterns (EDP) of pristine and doped PPV are shown in *Figures 2a* and *2b*. The seven sharp equatorial reflections (a^*–b^* plane perpendicular to the c direction) indicate that the lateral packing of neutral PPV chains is regular. The diffuse intensities of the longitudinal layer lines, symmetrically distributed along the c direction, imply that PPV chains are shifted in the axis direction in a paracrystalline structure. In the EDP of doped PPV a new reflection appears on the first layer, indicating that the c^* axis coincides with the c axis. It is clear that the molecular orientation remains the same after doping with $FeCl_3$. However, the unit cell of the crystalline structure has changed from monoclinic to orthorhombic with an increase of the lateral spacings caused by the dopant ions. The chemical repeat length (z direction) remains unchanged at 6.6 Å after doping. The experimental result supports the model in which stacked polymer chains are separated by planes containing dopant anions[13]. The unit-cell dimensions are: $a = 7.9$ Å, $b = 6.0$ Å, $c = 6.6$ Å and $\alpha = 123°$ for neutral PPV, and $a = 10.8$ Å, $b = 6.7$ Å and $c = 6.6$ Å for doped PPV.

A high-resolution image of a thin section of doped PPV is shown in *Figure 3*. This micrograph allows us a direct observation of the molecular packing in the oriented crystals. Two strong reflections in the corresponding computer Fourier transform pattern (inset in *Figure 3*) correspond to the 5.4 Å lateral spacing, consistent with the EDP of the doped PPV.

CONCLUSIONS

PPV becomes a good electrical conductor upon doping with $FeCl_3$. Stretched films show a high degree of orientation and crystallinity, proved by i.r. dichroism, EDP and HRTEM. TEM pictures of fibrillar samples confirm the fibre dimensions arising from the Sheng model of electrical conductivity.

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