Fibres of poly(methoxy-2-ethyl-hexyloxy)phenylenevinylene prepared from the soluble, fully conjugated polymer

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Electrically conductive fibres were prepared of poly(methoxy-2-ethyl-hexyloxyphenylenevinylene), which is soluble in its conjugated form, employing a simple wet-spinning process, without the need of a precursor-conversion reaction. The enhanced processibility of the polymer, however, comes at the expense of a reduction in both mechanical and electrical properties in comparison with the unsubstituted parent polymer.

(**Keywords: conductive polymers; PPV derivatives; fibres; solution processing**)

Introduction

Conjugated polymers are emerging as a potentially important class of (semi)conducting organic materials. One family of conjugated macromolecules of particular interest are the phenylenevinylene polymers (PPV)[1–4], because of their relatively high electrical conductivities and presumed improved environmental stability over, for example, polyacetylene. Commonly, PPV, and some of its derivatives are synthesized and processed via a precursor route, in which a non-conjugated, soluble precursor polymer is processed and converted thermally and/or chemically into the final, intractable product[4,5]. The latter transformation often is a time consuming process in order to obtain complete conversion (ranging from a few hours to, according to ref. 4, up to 7 days at 300°C).

More recently, the synthesis was described of a substituted PPV, i.e. poly(methoxy-2-ethyl-hexyloxy-phenylenevinylene) (PMEHPV, *Figure 1*), which is soluble in common organic solvents in its conjugated form[6]. The relatively long side groups enable dissolution and processing of the polymer directly, in its conjugated form, with common processing methods, thus eliminating the precursor-conversion step. Here, we report on the electrical and mechanical properties of solution-spun fibres of this interesting conjugated polymer.

Experimental

Poly(methoxy-2-ethyl-hexyloxyphenylenevinylene) was synthesized according to the method in reference 6. The molecular weight of the polymer sample was 5×10^5, as derived from gel permeation chromatography measurements using polystyrene. A 3% w/v solution of the polymer was prepared at room temperature in tetrahydrofuran; and subsequently it was wet spun into hexane using laboratory extrusion equipment. The as-spun fibre was dried in a vacuum oven at room temperature. Typically, the dried fibres were of a diameter of ~170 μm.

Tensile drawing and mechanical testing of the fibres were performed with an Instron tensile tester (Model 1122) equipped with a constant temperature chamber. Fibres 15 mm long were drawn at an elongation rate of 5 mm min^{-1} at various temperatures. Tensile properties were tested at room temperature. The gauge length was 20 mm, and the rate of elongation was 10 mm min^{-1}. Thermogravimetric analysis and differential scanning calorimetry (d.s.c.) were carried out with a Mettler TA 3000 system at a standard rate of 10 K min^{-1}. Doping with iodine and conductivity measurements were performed simultaneously using a standard four-probe apparatus; doping levels were determined gravimetrically.

Results

Thermogravimetric analysis of PMEHPV (*Figure 2*) seems to indicate that the polymer is relatively stable at elevated temperatures, up to ~300°C. D.s.c. studies also showed no significant enthalpy changes up to this temperature. However, it was observed during the dissolution process that the present polymer sample was rather sensitive to thermal treatment, and at moderate temperatures yielded insoluble material.

Deformation studies of the as-spun, unoriented PMEHPV fibres indicated that the maximum draw ratio (λ_{max}) of the samples was 2.7, at ~65°C. A rapid decrease in λ_{max} was observed at higher temperatures, which is attributed mainly due to the above mentioned modest thermal stability.

Table 1 summarizes data of the mechanical and electrical properties of the as-spun and drawn PMEHPV fibres.

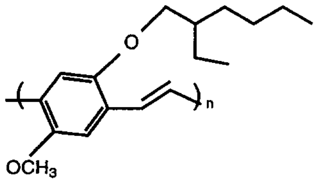

Figure 1 Structure of poly(methoxy-2-ethyl-hexyloxyphenylene-vinylene

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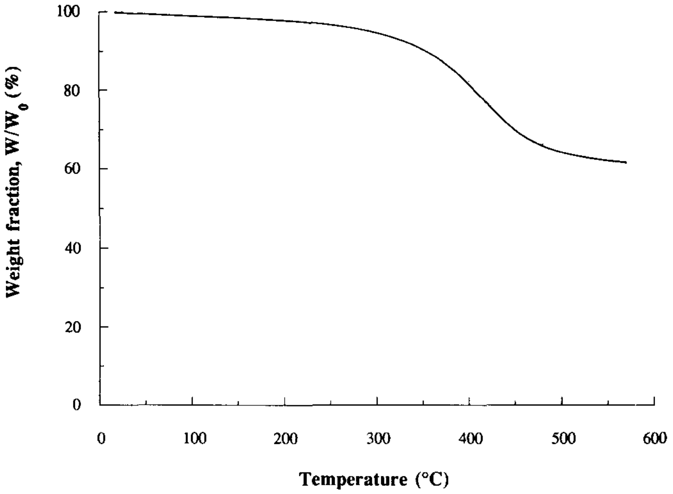

Figure 2 Thermogravimetric analysis of PMEHPV, recorded at 10 K min^{-1} under nitrogen

The mechanical properties of the undrawn fibres, before doping, were quite close to values that have been previously reported for PPV films[5]. As is commonly observed, tensile drawing is seen to significantly enhance the modulus and the tensile strength of the polymer fibres, while reducing their elongation at break. The improved mechanical properties evidently were due to enhanced macromolecular orientation; as shown in the wide-angle X-ray diffraction patterns in *Figures 3a* and *b* for the as-spun and the drawn fibres, respectively. The diffraction pattern of the undrawn fibre (*Figure 3a*) is fairly diffuse, which indicates that the as-spun material was only slightly crystalline. The diffraction pattern of the drawn fibre (*Figure 3b*), by contrast, shows significantly enhanced order with preferred orientation of the chain axis parallel to the stretching direction. The efficiency of the molecular orientation through tensile drawing of the present polymer is considered to be unusually high. For purposes of comparison, the orientation function f $[=\langle(3\cos^2\theta-1)\rangle/2]$ of PPV processed via the precursor route, and drawn to a ratio (λ) of 2, was reported[7] to be around $f=0.5$ and at a λ of 12, $f>0.95$. Similar results were previously obtained for poly(dimethoxyphenylenevinylene) fibres, also derived from a precursor polymer[8]. By contrast, we observed that for the present samples, which were drawn only to a λ of 2, the angular half width of the equatorial reflection was $<\sim 13°$ (*Figure 3b*), which corresponds to an orientation function in excess of $f=0.92$. We attribute this remarkably effective chain orientation to the rigidity of the conjugated PPV chain backbone. Nevertheless, despite this efficient drawing process, the mechanical as well as the electrical properties of the oriented PMEHPV fibres were modest in comparison with those of the unsubstituted PPV[7]. This, of course[9], is due to the relatively large pendant solubilizing side groups in this polymer (cf. *Figure 1*). Once more, we observe that enhanced processibility through side-chain derivatization is accomplished at the expense of a reduction of the macroscopic properties of the material.

The X-ray diffraction patterns of *Figures 3a* and *b* indicate that the substituted PPV fibres did not possess a highly ordered structure. Only two relatively strong reflections were observed in these diffraction studies. The intense equatorial reflection in *Figure 3b* corresponds to

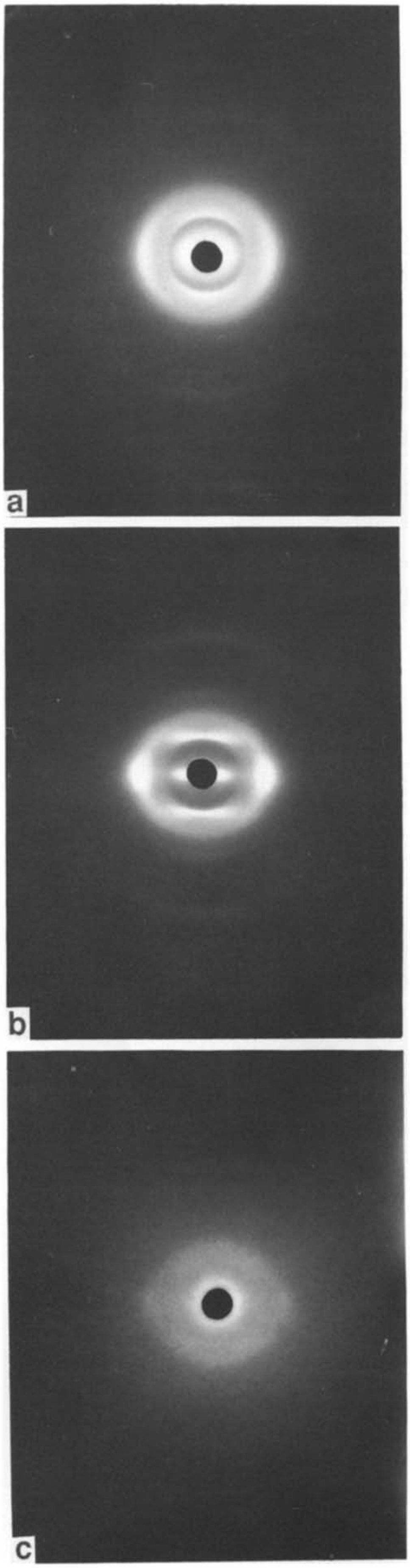

Figure 3 Wide-angle X-ray diffraction patterns of PMEHPV fibres: (a) as-spun; (b) drawn to $\lambda=2$; (c) drawn to $\lambda=2$ and doped with iodine for ~ 2 h

Table 1 Mechanical and electrical conductivity of solution-spun PMEHPV fibres

	Modulus (GPa)		Strength (MPa)		Elongation at break (%)		Conductivity ($S\,cm^{-1}$)	
λ	Undoped	Doped	Undoped	Doped	Undoped	Doped	Doped	Dopant uptake (mol%)
1	2.6	0.6	56	33	61	45	13	75
2	7.9	2.5	180	83	3	7	70	52

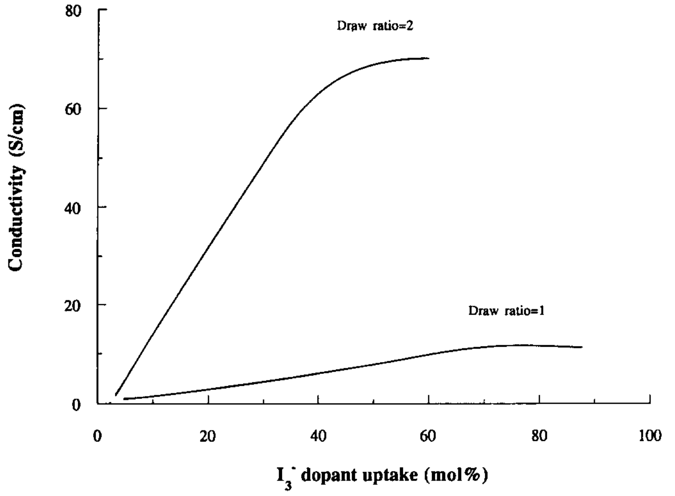

Figure 4 Conductivity *versus* dopant uptake (mol%)

a *d*-spacing of 4.1 Å between the macromolecules. The relatively intense meridional reflection is indicative of a repeat distance of 6.59 Å along the PMEHPV macromolecular axis. The latter value is essentially identical to that previously reported for PPV (cf. refs 4 and 10), which has the same backbone structure. *Figure 3c* shows a wide-angle X-ray diffraction pattern of the drawn fibre after doping with iodine. This pattern is rather diffuse in comparison to *Figure 3b*, which is indicative of the significant loss of order that occurred upon doping. Unlike, for example, in I_3^--doped polyacetylene[11], the scattering from the counter ions is not well defined, which indicates the lack of regularity in their packing. This reduced order, not surprisingly, was accompanied by a significant reduction in the mechanical properties of the PMEHPV fibres (cf. *Table 1*). The above observations are in accordance with results reported for unsubstituted PPV[7].

Figure 4 depicts the electrical conductivity as a function of the dopant uptake. The trend is a familiar one with the conductivity increasing to an optimum level and then levelling off, or even reducing with further dopant uptake.

In summary, we demonstrated that a soluble derivative of the conjugated polymer PPV can readily be processed into electrically conductive products via a standard solution spinning/drawing technique, without the need of a precursor-conversion reaction. This enhanced processibility, however, comes at the expense of a reduction in both mechanical and electrical properties in comparison with the unsubstituted parent polymer, as is expected.

Acknowledgements

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