Highly-conducting Poly(2-n-butoxy-5-methoxy-1,4-phenylene vinylene)

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Orientated free-standing films of poly(2-n-butoxy-5-methoxy-1,4-phenylene vinylene) are easily prepared *via* a water-soluble precursor polymer and reach conductivities as high as 2160 S cm^{-1} when doped with $FeCl_3$ and 590 S cm^{-1} when doped with I_2.

Poly(1,4-phenylene vinylene) (PPV) and its derivatives can be readily prepared in high molecular weight by a two-step synthesis originally described by Wessling and Zimmerman.[1—4] High molecular weight films of poly(2,5-dimethoxy-1,4-phenylene vinylene) (PDMPV) are known to be easily doped with I_2 or $FeCl_3$, producing electroconductivity as high as 10—10^2 S cm^{-1}.[3,4] This is in contrast to PPV which cannot be doped with the same dopants. A stronger dopant such as AsF_5 is required to dope PPV.[5] The two electron-donating methoxy substituents appear to facilitate PDMPV doping.

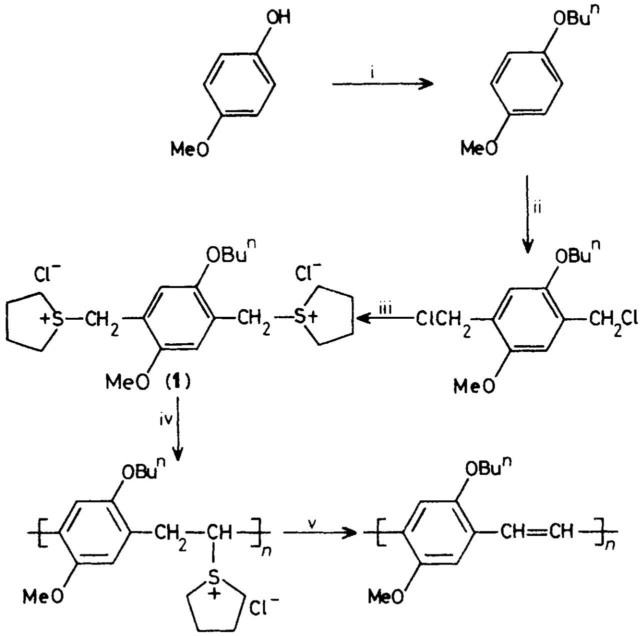
PDMPV films, however, possess one drawback in that they cannot be obtained in a uniaxially orientated form because the precursor polymer films are hardly stretched. Uniaxial orientation is known significantly to improve electroconductivity along the stretching direction.[2,3,5]

In contrast, it was found that a slight structural modification

Table 1. Conductivities of doped PBMPV.

Draw ratio[a] L/L_0	Dopant[b]	Doping time/min	Degree of doping dopant/repeat unit	Conductivity /S cm^{-1}
1	I_2	25	0.57	110
	$FeCl_3$	5	0.44	240
	$Fe(ClO_4)_3$	2	0.54	75
3.6	I_2	25	0.78	590
	$FeCl_3$	5	0.47	2160
	$Fe(ClO_4)_3$	2	0.59	370

[a] Thicknesses of unstretched (L/L_0 = 1) and stretched (L/L_0 = 3.6) films were 58 and 52 μm, respectively. [b] Structures of doping species were assumed to be I_3^-, $FeCl_4^-$ and ClO_4^-.



(2)

Scheme 1. *Reagents and conditions:* i, Bu^{n}Br, KOH/MeOH; ii, MeOH/HCl, dioxane/reflux; iii, C_4H_8S, MeOH, 50 °C; iv, OH^-; v, heat/vacuum, 200 °C.

of PDMPV giving an unsymmetrical structure can facilitate stretching of the precursor polymer films prior to the final thermal elimination in the second synthetic step.[6] When we polymerized the bis-sulphonium salt of 1,4-bis(chloromethyl)-2-n-butoxy-5-methoxybenzene (**1**) at 10 °C in an aqueous NaOH solution, the resulting polyelectrolyte precursor polymer films (**2**) cast from aqueous solution after dialysis using a dialysis tube having a molecular cut-off of 12 000, could be stretched at 110–150 °C up to a draw ratio of about 4 (Scheme 1).

The stretched precursor films were then transformed into the final polymer films of poly(2-n-butoxy-5-methoxy-1,4-phenylene vinylene) (PBMPV). Thermal elimination was conducted under vacuum at 200 °C for 20 h. These polymer films were then doped at room temperature either with I_2 in the vapour phase (10^{-5} mmHg) or in a nitromethane solution of $FeCl_3$ or $Fe(ClO_4)_3$ (0.2 M).

Electroconductivities of the doped films were measured by the four-probe method and Table 1 summarizes the results. A rapid conductivity increase was observed on exposure of the films to different dopants. Conductivities of as high as 590 S cm^{-1} were measured on the I_2-doped stretched films, and 2160 S cm^{-1} on the $FeCl_3$-doped films. The $Fe(ClO_4)_3$-doped films exhibited a little lower conductivity. The polymer films lost integrity when they were kept longer than 2 min in a solution of $Fe(ClO_4)_3$ in nitromethane (0.2 M). The degree of doping presented in Table 1 was obtained from the weight gain after doping. A blank test was run using only nitromethane in the absence of ferric salts and the weight gain was found to be nil. I.r. spectra of the polymer films obtained prior to doping revealed that the C=C bonds in the vinylene units are in the *trans* form. We believe that optimization of the synthetic process, the film preparation method and the stretching condition of the films can further improve conductivity.

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