Poly(ferrocenylene vinylene phenylene vinylene). A Photoactive Semiconductor

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Poly(ferrocenylene vinylene phenylene vinylene), a soluble conjugated aromatic polymer, can be doped with iodine to give an air-stable photoactive semiconductor.
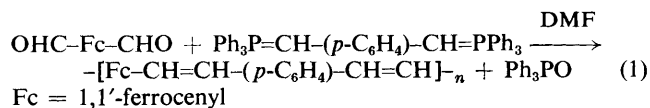
The conjugated chains which characterise conducting polymers are stiff causing these polymers to be insoluble, infusible materials. The major goal of a processible polymeric electrical conductor may be achieved by designing a flexible conjugated polymer chain. Our strategy is based on use of the 1,1'-ferrocenyl unit as a flexible conjugating linkage. Ferrocene and ferricinium picrate are organic insulators[1] with conductivities of 10^{-14} $(\Omega cm)^{-1}$ and 10^{-13} $(\Omega cm)^{-1}$, respectively,

however, Cowan[2] found that biferrocenyl $Fe^{2+}Fe^{3+}$ picrate has a much higher conductivity of 10^{-8} $(\Omega cm)^{-1}$. Sanechika et al.[3] reported that poly(1,1'-ferrocenylene) doped with iodine and tetracyanoquinodimethane (TCNQ) has a conductivity σ_{RT} of 10^{-2} to 10^{-4} $(\Omega cm)^{-1}$. We describe here poly(1,1'-ferrocenylene vinylene phenylene vinylene) (PFVPV) and its properties including conductivity.

Our synthesis is a modification of the Wittig condensation described by Hagihara and Sonogashira (equation 1).[4]

$$OHC\text{-}Fc\text{-}CHO + Ph_3P=CH-(p\text{-}C_6H_4)-CH=PPh_3 \xrightarrow{DMF}$$
$$-[Fc\text{-}CH=CH-(p\text{-}C_6H_4)-CH=CH]_n + Ph_3PO \quad (1)$$
$$Fc = 1,1'\text{-ferrocenyl}$$

Reaction in dimethylformamide (DMF) produced two fractions. Fraction 1 precipitates from the reaction mixture; it is purified by successive extractions with DMF, ethanol, and 50% ethanol (28% yield). A DMF-soluble fraction, 2 (26% yield) was isolated by pouring the reaction mixture into ethanol, dissolving the precipitate, and reprecipitating with ethanol. Of the other solvents tried, hexamethyl-phosphoramide (HMPA) was found to give the highest yield of polymer (ca. 68%). In this communication, only the polymers prepared in DMF will be described in detail.

Fractions 1 and 2 gave satisfactory elemental analyses which suggest low end group content. Fraction 1 is insoluble in all organic solvents, whereas fraction 2 is reasonably soluble in tetrahydrofuran (THF), marginally soluble in $CHCl_3$, and insoluble in hexane. Both materials are orange, thermally stable powders, with m.p. >400 °C (sealed tube). Gel permeation chromatography of fraction 2 in THF against a polystyrene calibration curve gave an estimated molecular weight of 3000. The insoluble fraction 1 probably has a higher molecular weight.

PFVPV is a strongly insulating material with resistivity greater than 10^{12} Ωcm. Upon oxidation (doping) with I_2, Br_2, and AsF_5, the polymers become semiconductors with room temperature conductivities ranging from 10^{-4} to 10^{-9} $(\Omega cm)^{-1}$ (Table 1). In all experiments but one, a pellet, formed from undoped polymer, was mounted between two platinum wires in a doping vessel. Dopant vapour pressure was controlled by immersing the dopant reservoir in a slush bath. Doping was continued until conductivity reached a limiting value. In one experiment (Table 1, samples 5 and 6), a sample of polymer powder and a pressed pellet mounted between two platinum wires were simultaneously exposed to iodine vapour until the conductivity of the pellet reached

its limiting value. The oxidized polymer powder was then pressed between stainless steel contacts and its conductivity measured at 1000 lb in^{-2}. The value obtained is about 8 times greater than that obtained by doping the polymer pellet. This may be due to more uniform doping of the powder or an effect of pressure. The colour of all the polymer samples turned black upon oxidation. Pressed pellets are noticeably inhomogeneously doped as shown by a skin effect.

Doping with iodine gave the best and most interesting electrical properties. It results in the highest conductivity, up to 10^{-4} $(\Omega cm)^{-1}$. The doped samples are stable in air; their resistance actually decreases after prolonged exposure to air. All iodine doped materials undergo an instantaneous twofold increase in conductivity when illuminated with a 75 W tungsten lamp. Sample 2 loses iodine under dynamic vacuum with a concomitant decrease in conductivity. Redoping
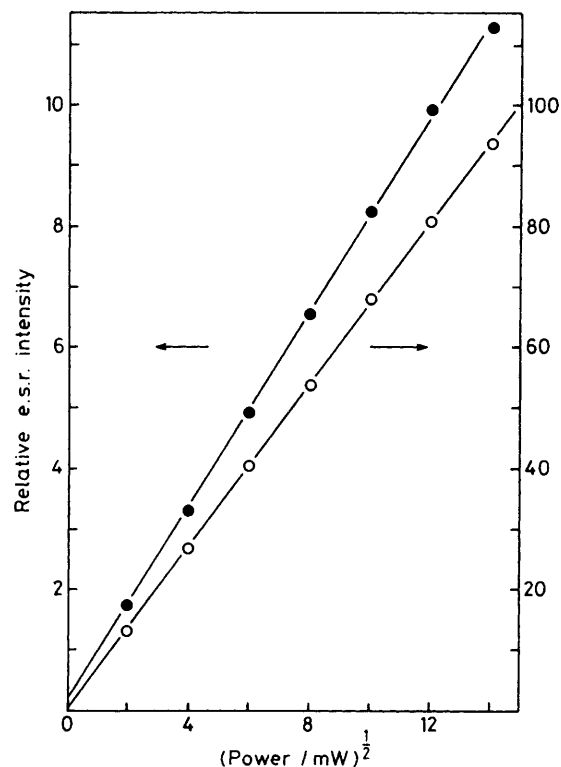

Figure 1. E.s.r. saturation characteristics of iodine doped PFVPV: (○) fraction 2, (●) fraction 1.

Table 1. Properties of doped poly(ferrocenylene vinylene phenylene vinylene).

Sample number	Solvent	Fraction	Dopant	Temperature of dopant reservoir/°C	Doping time/days	$\sigma/$ $(\Omega cm)^{-1}$ [d]	Dopant uptake[a]
1	DMF	1	I_2	-23	4	10^{-4}	0.75
2	DMF	2	I_2	-23	7	2.5×10^{-5}	—
3	DMF	1	I_2	-23	3	5×10^{-5}	—
4	DMF	2	I_2	-23	3	3×10^{-7}	—
5	HMPA	[b]	I_2	0	2	2×10^{-6}	0.45
6	HMPA[c]	[b]	I_2	0	2	1.6×10^{-5}	0.45
7	DMF	1	AsF_5	-95	0.25	2.5×10^{-9}	1.5
8	DMF	1	Br_2	-63	1	5.0×10^{-8}	3.1
9	DMF	2	Br_2	-63	1	4.0×10^{-9}	0.70
10	DMF	1	Br_2	-110 to 78	3	2.0×10^{-7}	3.3
11	DMF	2	Br_2	-110 to 78	3	2.0×10^{-9}	0.54

[a] By weight uptake given as mol of I, Br, AsF_5 per structural unit. The values should be divided by three for halogen dopants since they are known to exist as I_3^- and Br_3^- in doped polyacetylene. [b] Only insoluble polymer was obtained from polymerizations in HMPA. [c] The polymer powder was doped before pressing into a pellet. [d] Two-probe measurements do not allow an estimate of surface conductivity contribution.

restored the lost conductivity, showing iodine doping of PFPVP to be reversible. For an unknown reason it is more difficult to remove the iodine from the polymer obtained in HMPA. The most highly doped polymer contains 0.75 mol of iodine per structural unit or 0.25 mol of I_3^- per structural unit. Since the surface layer only was doped the actual dopant content may be higher than the values given in the last column of Table 1. In general, the higher molecular weight fraction gives greater conductivity than the lower molecular weight fraction similarly doped.

AsF_5 is a poor dopant and its use was not pursued further. PFVPV takes up large amounts of bromine, as much as 3.3 mol of Br per structural unit or about 1 mol Br_3^- per structural unit. The resulting effect on conductivity is small.

The two fractions of PFVPV show different e.s.r. characteristics. Fraction 2 gave an intense e.s.r. signal with free electron g values and a symmetrical lineshape upon iodine doping. The signal has a linewidth of 250 G at 77 K and 100 G at 300 K, and cannot be saturated at available Klystron power (Figure 1). Horsfield and Wassermann[5] gave $g_{||} = 3.15$ and $g_\perp = 1.82$ for ferricinium picrate. Therefore, the signal cannot be attributed to spin localization in the ferricinium system. The e.s.r. signal may be interpreted as arising from a delocalized unpaired spin the linewidth of which is broadened by hyperfine interaction with the protons, quadrupole interaction with the dopant, and spin orbit interaction with the ferricinium ion. Though iodine doped fraction 1 exhibits higher conductivity than fraction 2, its e.s.r. intensity is only one-tenth that of the latter. There is no relationship between unpaired spin concentration and conductivity in polyacetylene or other doped aromatic polymers.[6] At 77 K the e.s.r. spectrum is asymmetrical resembling the Dysonian lineshape with A/B ca. 2.1. A possible interpretation is the presence in these samples of small metallic domains separated by large enough distances to prevent charge carrier percolation.

References

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