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### Highly Conducting Poly(P-Phenylene Vinylene) Prepared From Sulfonium Salt

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## HIGHLY CONDUCTING POLY(p-PHENYLENE VINYLENE) PREPARED FROM SULFONIUM SALT

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**Abstract** Highly conducting poly(p-phenylene vinylene), PPV, has been obtained via pyrolysis of the soluble precursor polymer derived from p-xylylene bis(diethyl sulfonium bromide) which is processed to film. The highly oriented PPV film is obtained by stretching the precursor film up to ten fold at a higher temperature. The films show extremely high conductivity of 2780 S/cm and 491 S/cm by doping AsF<sub>5</sub> and SO<sub>3</sub>, respectively, with high electrical anisotropy.

### INTRODUCTION

Poly (p-phenylene vinylene), PPV, tested as conducting polymer so far was prepared in the form of powder by Wittig olefin synthesis or dehydrohalogenation reaction and their electrical conductivities were reported as at most 3 S/cm by AsF<sub>5</sub> doping<sup>1,2</sup>. On the other hand, it has been also known that PPV is formed by sulfonium salt process<sup>3,4</sup> which can be processed into film. However, no information has been reported on electrical conductivity of the latter products so far. The authors have found out that PPV film by sulfonium salt process shows extremely enhanced conductivity, especially at a stretched forms.

### EXPERIMENTAL

PPV film was prepared via a procedure by Kanbe<sup>3</sup> and Wessling<sup>4</sup>. P-xylylene bis(diethyl sulfonium bromide) was polymerized by condensation in an aqueous alkaline medium to give a polyelectrolyte of

sulfonium salt. PPV precursor film was prepared by casting, and subjected to stationary heat treatment at a temperature between 100°C and 300°C in an inert atmosphere. Stretching of the film was carried out during the heat treatment up to ten fold. The doping was carried out at a pressure of ~3mmHg of SO<sub>3</sub>, ~350mmHg of AsF<sub>5</sub> or ~1mmHg of I<sub>2</sub> vapour.

## RESULTS AND DISCUSSION

PPV films obtained by sulfonium salt process were pale yellow to orange and transparent. The films were prepared in thickness of 5 to 15 μm. The elimination reaction proceeds by splitting of hydrogen bromide and diethyl sulfide as shown in Equation (1). The product PPV has a configuration of all trans form which is confirmed by IR spectrum.

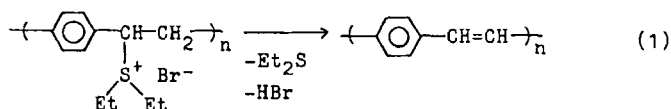


Table 1 shows the results of elemental analyses of the polymers produced at various heat treatment temperatures. Films treated at 200°C, still contain sulfur, show excellent flexibility and fairly high conductivity. In the film treated at 300°C, however, no sulfur was detected showing the substantial completion of the elimination reaction. The PPV

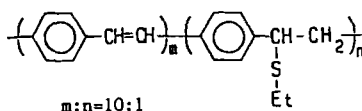
TABLE 1. Elimination reaction of precursor polymers to PPV  
-Elemental analyses of the products-

Temp. (°C)	Heat Treatment (Hr.)	Elemental Analysis S(%)	Conductivity SO <sub>3</sub> Doped (S/cm)
100	0.5	4.4	3.8x10 <sup>-4</sup>
200	0.5	3.1	0.24
200	2.0	2.7**	0.56
300*	0.5	<0.5	0.8

\* C:93.7(94.1), H:6.1(5.9)

( ):calculated values

\*\* Proposed structure of S-containing polymer



polymers prepared at 200 °C are estimated to have ethylthioether side group by the mass analysis of gas evolved during heat treatments in which  $m/e$  values of 108 and 110 evidently correspond to EtBr. The conjugation is estimated to be not so long as about  $m/n=10$ .

Important finding was that the precursor PPV film can be stretched to a high extent during thermal treatment and conductivity of the film doped by  $\text{SO}_3$  is markedly enhanced as shown in Figure 1. Although the conductivity of non-stretched film was nearly 1 S/cm, the value of a stretched one with stretching ratio ( $l/l_0$ ) of 10 reached at 491 S/cm. And uniaxially stretched films exhibited so large electrical anisotropy ( $\sigma_{\parallel}/\sigma_{\perp}$ ) as 100 at  $l/l_0=10$ , which is extraordinarily large compared with 16 of stretched polyacetylene<sup>5</sup>.

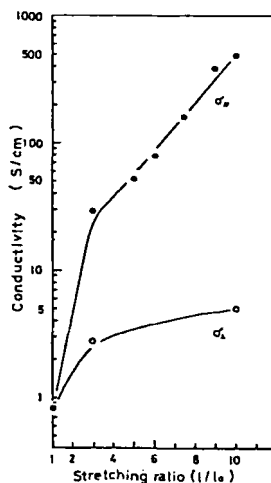


FIGURE 1. Effect of stretching of PPV film on electroconductivity. Thermal treatments and stretching were carried out at 200°C.

Electroconductivities of doped PPV films were measured for three kinds of dopant in comparison with those reported<sup>1,2</sup> (TABLE 2). Unexpectedly high conductivity, 2780 S/cm, was observed in the stretched film doped with  $\text{AsF}_5$ . Such high conductivity in one dimensional conjugated polymers has never been reported except for polyacetylene. The conductivity of unstretched PPV film, 39 S/cm, is also higher than those reported values of PPV. On the contrary,  $\text{I}_2$  doped PPV has low conductivity as  $10^{-2}$  S/cm. The film of 2,5-dimethoxy-PPV ( $\text{CH}_3\text{O}$ -PPV) was successfully prepared by sulfonium salt process and has also higher conductivity than reported product<sup>2</sup>.

TABLE 2. Electroconductivity of PPV doped by AsF<sub>5</sub>, SO<sub>3</sub> and I<sub>2</sub>.

Polymer	Method	Configuration	Shape	Conductivity(S/cm)		
				AsF <sub>5</sub>	SO <sub>3</sub>	I <sub>2</sub>
PPV	Wittig	cis/trans	powder	3.0*	-	3.8x10 <sup>-9</sup>
PPV	Dehydro-chlorination	trans	powder	0.7*	2.2x10 <sup>-5</sup>	3.7x10 <sup>-7</sup>
CH <sub>3</sub> O-PPV	"	trans	powder	10 <sup>-4</sup> *	1.7x10 <sup>-3</sup>	-
(unstretched)						
PPV	Sulfonium salt	trans	film	39	6.4	<10 <sup>-3</sup>
(stretched 1/1 <sub>0</sub> =9)						
PPV	"	trans	film	2780	420	1.2x10 <sup>-2</sup>
CH <sub>3</sub> O-PPV	"	trans	film	-	1.5	-

\* reported values<sup>1,2</sup>

The molecular orbital calculations<sup>6</sup> of conjugated polymers has been carried out for polyacetylene, poly-p-phenylene and PPV and the magnitude of conductivity of the doped polymers has been explained by the difference of band width of polymer molecules. The present work, however, revealed that the conductivity of PPV reached at the same level as that of polyacetylene, and the conjugation length seemed to be not so long. This result implies that not only primary structure but also higher order structure of conjugated polymer is important to electroconductivity.

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#### REFERENCES

1. G.E.Wnek et al., Polymer, **20**,1441(1979).
2. K.D.Gourley et al., Macromolecules, **17**,1025 (1984).
3. M.Kanbe et al., J.Polym.Sci.,A-1, **6**,1058 (1968).
4. R.A.Wessling et al., U.S.Patent 3,401,152 (1968).
5. Y.W.Park et al., J.Polym.Sci.,Polym.Lett.Edn., **17**,195(1979).
6. J.L.Bfedas et al., J.Chem.Phys., **76**,3673 (1982).