

Solubilization of Poly-(*p*-phenylene sulphide) Complexes in Strong Acids

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The first examples of solutions of conductive complexes of poly-(*p*-phenylene sulphide) in a variety of strong acids are reported.

A serious limitation of presently known conducting polymer complexes is their relative lack of conventional processibility.

Recently, a number of methods have been reported to increase processibility, including the grafting of polyacetylene

Table 1. Solubility of PPS complexes in acidic media.

Acid	PPS solubility	Colour of solution	Conductivity/S cm ⁻¹ of cast film	Hammett acidity (<i>H</i> ₀) ^a (100% acid)
FSO ₃ H	High	Blue-green	6 × 10 ⁻³	-15.6
FSO ₃ H-AsF ₅	High	Blue	8 × 10 ⁻³	
CF ₃ SO ₃ H	Low	Green	—	-14.6
CF ₃ SO ₃ H-AsF ₅	High	Blue	6 × 10 ⁻³	
CF ₃ SO ₃ H (electrolysed)	High	Blue	10 ⁻³	
H ₂ SO ₄ (98%)	Very low	Pale green	—	-11.9
Oleum (15%) (fuming sulphuric)	High	Blue	—	
H ₂ SO ₄ -AsF ₅	High	Blue	—	
HBr-AlBr ₃	Nil	—	—	
HClO ₄ (70%)	Nil	—	—	-13.0

^a From ref. 10.

to soluble polymers¹ and the formation of composites with processible polymers.²

Poly-(phenylene sulphide) and its derivatives³⁻⁵ were the first conventionally processible polymers to be shown to form highly conductive complexes. These polymers are both melt and solution processible in their virgin state, but they lose this processibility after being acceptor-doped (oxidized). Recently, however, a novel technique has been developed which allows the polymer to be solubilized in its doped (conductive) state. Frommer *et al.*⁶ have shown that a solution of the complexed polymer is formed when poly-(*p*-phenylene sulphide), PPS, is combined simultaneously with liquid AsF₃ and gaseous AsF₅. Highly conductive films of the polymer may be cast from these solutions by vacuum evaporation of the solvent. Here we describe the extension of this method to strong acid dopants and solvents.

Strong acids (HClO₄,⁷ H₂SO₄,⁷ HF,⁸ and ClSO₃H⁹ in particular) have been known to function as dopants for polyacetylene for some time, but the actual form and composition of the dopant in these cases is not well understood. Various mechanisms are possible by which charge is transferred to the polymer chain, including protonation of the chain,⁸ complexation with hydronium (H₃O⁺) ion,⁷ or electron transfer in an oxidative process.

We have found that a number of acids act as dopants and subsequently solvents for PPS (Phillips Petroleum; RytonTM, V-1 grade) at room temperature and below (Table 1). For entries where conductivity results are listed, films were cast by vacuum evaporation of the acid, and their conductivity measured by a d.c. 4-probe technique. In no case was this conductivity found to be stable in the presence of water (or water vapour). Opaque green-black conductive films were rapidly changed to transparent non-conductive films by exposure to water.

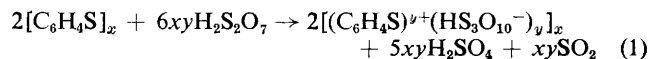
In cases where Table 1 lists the solubility as high, no solubility limit was apparent; as a given solution was concentrated by solvent removal, a continuous increase in viscosity occurred until a solid film was cast. No precipitate was ever observed as a result of solvent removal, although non-conductive precipitates of the polymer could readily be formed by the addition of water.

Only the strongest acids appear to be capable of solubilizing PPS. All the successful acids qualify as superacids.¹⁰ The two successful Brønsted acids in Table 1, FSO₃H and oleum, both have acidities of < -15 on the Hammett acidity scale.¹⁰ The other acid systems which solubilize PPS are all Brønsted-Lewis superacids with even greater acidities.

Acidity alone, however, is evidently not the sole criterion for a successful solvent-dopant system. The HBr-AlBr₃ mixture does not dope or dissolve PPS even though this system is considered a powerful superacid which is reportedly¹¹

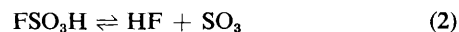
capable of completely protonating benzene. The failure of this system strongly suggests that the polymer is not complexed *via* any form of protonation, but by a direct electron transfer oxidation. Each of the acid systems which dope and dissolve PPS is a strong oxidant as well as a strong acid. The importance of the presence of a strong oxidant is well illustrated by the data for CF₃SO₃H, a superacid which is considered to be non-oxidizing;¹² however, electrolysis of a PPS-CF₃SO₃H mixture between two platinum electrodes results in the complete dissolution of the PPS. In this case, the PPS is presumably oxidized directly by electrochemical means or by a product of the electrolysis [most likely (CF₃SO₃)₂ or SO₃].¹³ A similar increase in oxidation activity resulting in the dissolution of the PPS can be obtained by the addition of AsF₅ or SbF₅ to the CF₃SO₃H, but the addition of PF₅ shows no effect.

Oleum, which also readily forms dissolved PPS complexes, contains various polysulphuric acids and SO₃ which are strong oxidants. For example, reaction (1) between H₂S₂O₇ and PPS is possible, with the oxidized polymer then being



soluble in the acid mixture.

In contrast to CF₃SO₃H, FSO₃H apparently does not require the addition of a separate oxidant. One possible oxidation mechanism in this system involves the dissociation (2) which produces the oxidizing agent SO₃.¹⁴



Finally one must consider the possibility of chemical side reactions which may lead to modification of the polymer backbone (*i.e.*, covalent bond formation). Such chemical modification may result in improved conductivity as has been previously observed for PPS treated with AsF₅ or SbF₅.^{4,5} Some types of reaction, however, are detrimental to conductivity as has been previously shown for poly-(*p*-phenylene) treated with SO₃¹⁵ or H₂SO₄.¹⁶ In this case, sulphonation of the phenyl rings occurs which renders PPP soluble but non-conductive. Similar reactions are likely to occur with PPS.

In addition to sulphuric acid, fluorosulphonic acid is a good sulphonating agent for organic compounds.¹⁷ Similar irreversible chemical changes suggesting sulphonation have been observed with both SO₃ and FSO₃H in earlier *e.s.r.* experiments with the PPS oligomer, Ph-S-C₆H₄-S-Ph.¹⁸ Also, *i.r.* analysis of PPS after treatment with FSO₃H followed by washing with water showed a very strong broad absorption

composed of several lines centred around 1200 cm^{-1} in addition to new lines at 1057 and 1015 cm^{-1} , a spectrum which is consistent with hydrated sulphonic acid groups.¹⁹ The i.r. spectrum also showed distinct evidence for changes in various phenyl ring vibrations which are typical of an altered ring substitution pattern (*i.e.*, other than *para*-disubstituted). A weak line at 898 cm^{-1} could be associated with isolated hydrogen atoms on sulphonated phenyl rings but no evidence was found for a line at 850 cm^{-1} previously associated with isolated hydrogen on intramolecularly bridged phenyl rings.⁴ The i.r. evidence, therefore, suggests that intramolecular bridging of phenyl rings which has previously led to high conductivities⁴ is largely supplanted by sulphonation.

In summary, the solubilization of PPS in acidic media requires the simultaneous action of a strong acid and a strong oxidant. The oxidant presumably oxidizes the polymer to the polymeric cation which then dissolves in the acid. The acid must be sufficiently strong to stabilize the strongly electrophilic polymeric cation which is readily attacked by any medium with appreciable basic properties.

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