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INTRINSICALLY CONDUCTIVE POLYMERS FOR ELECTROMAGNETIC INTERFERENCE SHIELDING

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Abstract

The main aims of the project were to research whether intrinsically conducting polymers could be synthesised and formulated to provide a range of readily processable product forms for transformation into shapes by either melt extrusion, solvent based coating or polyurethane reaction forming. The products needed to meet both the conductivity and environmental resistance targets set by the end user partners according to the aimed EMI shielding applications.

Polythiophene, polypyrrole and polyaniline routes have been studied. Polythiophene route had to be abandoned because of the low stability of such a conductive polymer.
Polyaniline based conductive thermoplastic blends were synthetised and studied according to their theological and electrical properties. Aging of such conductive materials was extensively studied in various degrading environments.

Polyaniline and polypyrrole based coatings were developed and polymer and latex synthetis were optimised. Polyaniline paints or thick coats of good electrical and mechanical quality have been achieved.

Demonstrators have been developed for each of the envisaged applications : cables, electrical boxes and acoustics.
Performances and aging of these demonstrators has been assessed by the industrial end-users involved in this research.

Introduction

The work described hereafter has been performed during the course of a BRITE-EURAM Project funded by the Commission of the European Communities.

The aim of the project was the development of new intrinsically conductive polymers for electromagnetic interference shielding.
The consortium had to study whether intrinsically conducting polymers could be synthesised and formulated to provide a range of readily processable product forms for transformation into shapes by either melt extrusion, solvent based coating or polyurethane reaction forming.

The products needed to meet both the conductivity and environmental resistance targets set by the end user partners. Further it was necessary to establish whether the chemical process for producing the product could be scaled up.
Stability of the produced ICP's submitted to degrading environments had to be extensively studied so that the long-term behaviour of products incorporating ICPs could be forecasted.

The industrial end-users involved in the projects had to manufacture demonstrators with the developed ICPs :
- a coaxial cable with a braided shield in combination with an ICP-filled extruded layer,
- a multiconductor low pass cable with ferrite coated conductors, the ferrite layer being coated itself with a thin ICP-lacquer layer,
- shielded boxes to be used as a container for electronics,
- and an acoustic antenna prototype made of a ICP shielded and PUR coated piezoelectric sensor.

Technical description and Results

I. Synthesis of intrinsically conductive organic materials

The technical approach taken in this project was to introduce processability into conducting polymers by either directly polymerizing functionalised monomers or by producing co-polymers containing alternating Mocks of conducting and processable material. In the first case the alkyl or alkoxy groups present should disrupt the structure of the final polymer so inducing processability whereas for the second group of materials processability will arise from the thermoplastic blocks.

1.1: Monomer Synthesis

Synthetic routes to various thiophene and aniline based materials containing pendant alkyl or alkoxy groups were developed.
It did not prove to be possible to produce polymers via the condensation of aromatic halides and quinoneimines etc. because of the highly air sensitive nature of the intermediates produced. Electropolymerisation may be a route for using these materials but this was outside the scope of the project and so this approach was not taken any further.

1.2:Oligomer Synthesis

As discussed above the proposed routes to aniline oligomers involving the coupling of electrophilic quinoimines with carbon nucleophiles were not successful owing to the high air sensitivity of the intermediates formed. However, it was possible to produce thiophene oligomers by a similar strategy. These molecules proved to be very useful models for the polymers to be described later and provided an insight into the nature of the chemistry required to successfully produce oligomers or polymers in one step, for example thiophene oligomers suitable for incorporation into a polyurethane system.

1.3:Polymer Synthesis

The initial objective in this area was to produce functionalised conductive polymers which because of their architecture could be easily blended with thermoplastics or reactive resins. Both thiophene and aniline polymers were produced using monomers synthetised in section 1.1.
Both of these materials required doping in a subsequent synthetic step to impart conductivity to the species formed. Of the materials produced in this initial stage the polyaniline based materials showed little processablity ie. they did not melt or dissolve in solvents, and they also had very low values of conductivity (of the order of 10-3 S/cm). Therefore the study of these systems was not taken any further.

In contrast the polythiophene materials showed good conductivities (up to 20 S/cm) and could easily be blended with thermoplastics. The problem encountered by the partners with these species was their poor long term conductivity stability. It is assumed that this relaxation in conductivity is related to the presence of pendant side chains associated with the polymer, evidence for this coming from the observation that the conductivity of polythiophene materials has far better long term stability when there are no side chains present. On the basis of these insights the final approach taken was to introduce functionality on the polymer counterion instead of the backbone itself. It was hoped that this approach would have the advantage of producing materials which were both processable and of high conductivity. The system which showed the best combination of these properties is a polymer which has the long chain sulphonic acid dodecylbenzene sulphonic acid (DBSA) as a counterion.

To optimise the conductivity of this material it is necessary to maximise its molecular weight. This because the charge carrying species may then travel further through a bulk sample along a polymer chain before it needs to 'hop' onto another one, a less favoured process energetically. The molecular weight of a polyaniline may be manipulated by the amount of oxidant added and the temperature of the reaction mixture.

The polymer molecular weight rises to a maximum as the amount of oxidant added is reduced. This is as would be expected for a free-radically induced polymerisation where a smaller number of reactive sites result in the polymer molecular weight being higher. Below this maximum there are presumably not enough free radicals generated to react with all of the monomer. In a similar manner reducing the temperature of the reaction mixture increases the molecular weight as the radical lifetime is increased. Keeping the temperature of the reaction mixture below 0°C also reduces the amount of polymer branching and prevents the formation of toxic by-products such as benzidene.

Effective doping of the polymer is also important to maximise its conductivity with the maximum in conductivity being reached when there is one dopant molecule for every two monomer units in the polymer chain. As the molecular weight of the polymer increases it becomes increasingly difficult for dopant molecules to penetrate the polymer coils. Consequently ICI found that forcing conditions were required to effectively dope the material.

Another important characteristic of the material is the particle size of the polymer produced. This parameter will significantly effect the percolation characteristics of the system because large spherical particles will have a high percolation threshold whereas for small needle shaped particles this value will be much lower. In a typical polyaniline synthesis spherical particles of size 50-100 µm are obtained. These particles are agglomerates and their size may be much reduced by conventional milling or grinding operations to the range 10-20 µm. However, these operations are messy and time consuming. ICI have found that if a surfactant is included in the reaction mixture much smaller particles are obtained (in the range 10-20 µm). The surfactant adsorbs onto the surface of the particles as they are formed and prevents agglomeration. Interestingly the particle morphology is also significantly altered as the particles are 'rice grain' shaped. As expected particles with this morphology have lower percolation thresholds when blended with thermoplastics than 'conventional polyaniline'.

Interestingly the dodecylbenzene sulphonic acid (DBSA) dopant also proved to be a very efficient plasticiser for the DBSA doped polyaniline. When polyaniline which had already been doped with a the required amount of DBSA to impart maximum conductivity was heated with more DBSA a solid complex was formed. Evidence for a further reaction taking place was obtained from DSC studies of mixtures of the doped polyaniline and DBSA which showed an exothermic peak at 140°C corresponding to the complexation reaction. Remarkably solid complexes were obtained for mixtures of doped polyaniline with up to three times the weight of DBSA. The complexes so formed are particularly interesting because, in comparison with normal doped polyaniline, they show flow behaviour. Capillary rheometry studies indicated that there was little decomposition of these 'melts' at temperatures below 200°C and their rheological nature was similar to that of plasticised **PVC.**

On heating this structure is broken down to give essentially a solution of polyaniline.DBSA in DBSA which while being highly viscous will still flow. On cooling the structure is reformed. The observation that such complexes will melt and flow is an important one because, if the correct processing conditions are achieved, blends with other thermoplastic polymers should give a continuous network of conductive material through the composite structure thus giving percolation at very low levels of conductive material. In addition the formation of what is essentially a solution in the polymer melt should allow, under the right conditions, polymer orientation to give much higher conductivities than those conventionally observed for polyaniline with a random chain orientation. Evidence for this hypothesis will be given in the next section.

1.4 : **Synthesis at Interfaces - coatings preparation**

The unique proper-ties of polyaniline.DBSA allow the direct formation of stable dispersions without the need for additional stabilisers. This approach has the advantage that the conductivity of the resulting coatings will be higher because there is no stabilising diluent present and because pre-synthesised purified polymer is used there are no problems associated with the removal of toxic by-products which are inevitably associated with ICP synthesis.

ICI discovered that if polyaniline in its emeraldine base form (of a suitable molecular weight and particle size) is simply stirred in toluene with sufficient DBSA to fully dope it a stable thixotropic dispersion is obtained which gives coherent rubbery films when the solvent is removed. The conductivity of these films is in the range 20-40 S/cm which is typical for solvent cast polyaniline films. (These latter articles are obtained by dissolving dedoped polyaniline in N-methylpyrollidone casting a film and then doping with aqueous acid).

The films obtained from ICI's dispersions have the useful properties noted above for a variety of reasons. Firstly it is obvious if the films are examined with a microscope that they consist of small particles of polyaniline.DBSA embedded in polyaniline.DBSA film. The latter part of the structure presumably arises by dissolution of the lower molecular weight polymer fragments in the solvent and it is the 'film' portion of the structure which gives the final films their good physical characteristics. It is to be expected that the structure of the polymer chains in the 'film' segments will be that described in the previous section for the plasticised polyaniline.DBSA compounds i.e. polymer chains surrounded by interdigitating surfactant molecules and X-ray studies have confirmed the presence of similar structures in the two material forms. The surfactant aggregation postulated for this structure will also give rise to the thixotropic nature of the dispersions as the forces involved in holding the surfactant structure together are relatively weak and are easily broken down by shearing.

If in the preparation of the dispersion an excess of DBSA is used the properties of the films obtained are much improved i.e. they are much less brittle and the amount of shrinkage on solvent evaporation is less. The presence of excess DBSA appears to increase the amount of polymer that is dissolved and thus there are fewer particles in these films which obviously reduce film strength and elasticity. Interestingly DSC studies on these latter films showed an exotherm at 140°C i.e. at the same temperature as noted for the further complexation of DBSA to polyaniline as noted for the plasticised formulations described in the previous

section, Annealing experiments were carried out on these films containing excess DBSA and significant increases in conductivity were observed for short times (2-3 reins) of up to 150 S/cm whereas at longer times the conductivity started to drop sharply.
However, if samples are cooled immediately after being annealed for 3 reins the high conductivity values are 'frozen in' and appear to be stable at room temperature for long periods.

The reason for this increase in conductivity appears to be greater order being built into the molecular structure of the system i.e. more of the aggregated structure described above is being built in. Evidence for this comes from X-ray studies which show the diffraction peak associated with alkyl chains of the DBSA becoming much sharper as the conductivity increases. Optical microscopy is also consistent with this proposal as the annealed samples are highly birefringent indicating significant molecular ordering.

1.5 : **Synthesis of latex and conducting paints**

1.5.1 **Polypyrrole**

Standard powder synthesis

In order to optimize the synthetic conditions for PPy standard powders or latexes, a systematic study was undertaken by LCR on several parameters such as stirring speed, presence and/or nature of a tensioactive agent, presence and/or concentration of a codoping agent, concentration of monomer, nature of solvent, etc.
The nature of the optimal solvent changes with the concentration of monomer. For $[Py]=10^{-1}$ M, methanol is the best solvent whereas for $[Py]=5.10^{-2}$ M water should be used as far as thermal stability is concerned. However, the best conductivity values are obtained in water ($[Py]=5.$ 10-2 M, 600 rprn, $\sigma= 14.4$ S/cm).

Higher concentrations of pyrrole lead to a higher weight loss and a lower conductivity :

- $[Py]=5.\ 10^{-2}$ M, w. I.-7-9% at 200C, $\sigma=14$ S/cm
- $[Py]=10^{-1}$ M, w.l.~9-12% at 200C, $\sigma< 10$ S/cm

An increase in the stirring speed results in an increased weight loss at high temperature and a decreased grain diameter (600 rpm: 300 nm; 300 rpm: 400 rim). The influence of the stirring speed on the conductivity is quite unclear.
To summarize shortly LCR's results, the best powders were obtained with: stirring speed -300-600 rpm and [Py]< 5.10-2 M.

Latex preparation

Standard Synthesis

Two tensioactive agents have been used: methylcellulose (MEC) and the sodium salt of polyvinylsulfonic acid (PVS).
The thermal stability of these latexes is better than the stability of standard powders under 300°C. However, their conductivity is lower:

- Best synthesis of powder: σ=1 4.4 S/cm
- Same conditions + PVS: σ= 6.3 S/cm

This effect stems from the presence of an insulating layer of surfacing agent at the surface

of the conducting polymer grains: this "coating" protects the grains from external attacks such as oxidation, but limits the intergrain contact which is mostly responsible for the macroscopic conductivity.
The presence of the surfactant improves the monodispersity of the grain size without affecting its average value. Regarding thermal stability, the stirring speed has no influence under 275°C, but at higher temperatures, thermal stability decreases with increasing stirring speed. The conductivity increases with stirring speed when PVS is used, but decreases when MEC is used. Lower pyrrole concentrations lead to higher conductivity values.

Codoped Latexes

It is well known that electrochemically prepared PPy is much more stable than the chemically prepared material. This effect partly stems from the nature and size of the doping agent. Diffusion of small anions such as Cl-, NO_3-, used to prepare "chemical" polypyrrole, will easily take place under heating, whereas for the large doping anions, used for "electrochemical" PPy, it will not . In terms of conductivity and thermal stability, the best results are obtained with paratoluenesulfonate or perfluoroalkylsulfonate anions. Polypyrrole latexes were thus synthesised in the presence of tetraethylammonium paratoluenesulfonate, in order to increase their conductivity and thermal stability.

The optimal synthetic conditions of such codoped latexes are:

- [Py]< 5.10^{-2}M
- Stirring speed < 500 rpm

The conductivity of the codoped material is 50% higher than the conductivity of the standard material. The grain diameter of codoped PPy is also bigger (600 rim).

Most of the influence of the synthetic conditions on the final properties of the material probably stems from the change in grain size. For example, the increased conductivity noted for a decreasing monomer concentration can be related to the formation of smaller grains, thus promoting a better electrical contact (better compacity, higher density). However, smaller grains lead to more grain boundaries which act as a barrier to the charge carriers and we might as well expect a decrease in conductivity. Several other effects can be presented either way. Some results can also not be explained today in the absence of a very complete physico-chemical study (opposite influence of MEC and PVS, for example). Extrapolations and predictions are therefore impossible and a general and systematic study has to be undertaken in order to clearly define the properties of the final product corresponding to a precise set of synthetic parameters.

Control of the polimerization kinetics of "Chemical" polypyrrole

The influence of the synthesis temperature on the conducting properties of polypyrrole prepared by the "chemical" method has been described in several papers. Lowering the temperature, in certain limits, leads to an increased conductivity. This phenomenon can be explained considering that as temperature is lowered, the reaction rate and thus the growth of the polymer chains are slowed down. This will in turn result in a more regular polymer backbone (with less a, b bonds between neighboring cycles, for example) and a higher conductivity.

However, control of the thermal homogeneity in the synthetic medium is difficult to achieve, especially for large volumes. For this reason, LCR investigated the possibility to replace the thermal control of the polymerisation kinetics by a redox control.
Chemical synthesis of polyheterocycles makes use of transition metal salts as polymerisation initiator, the potential of the redox couple $M^{n+}/M^{n'+}$ being higher than the oxydation potential of the monomer.
The polymerization kinetics at t=O is governed by the value of this redox couple, and since the high oxydation level cation is consumed by the reaction, the kinetics gets slower as it proceeds. Furthermore, according to Nernst's equation, the potential of the oxydative solution is proportional to log $([M^{n+}]/[M^{n'+}])$. Thus by adjusting the relative amounts of the oxidizing and reducing agents, it is possible to freely control the polymerization kinetics,
LCR has accordingly applied this approach to the polymerization of pyrrole with Fe^{3+} salts.

Controlled potential polymerization of pyrrole was performed for standard, codoped and latex synthesis.
The ferrous salt used was iron(II) chloride tetrahydrate. The $FeCl_3$ and pyrrole concentrations (1. 16 10^{-1}M and 5 10-2 M, respectively) are those *giving* the best materials in terms of conductivity. The $[FeCl_3]/[Pyrrole]$ ratio is constant at 2.3. The synthesis have been performed in 80 ml of deionized water. The monomer was added after complete dissolution of the ferric and ferrous salts. In the case of latexes (using the sodium salt of polyvinylsulfonic acid as surfactant), the monomer was thoroughly mixed with the PVS salt prior to introduction. Magnetic stirring (150 rpm) was used. The higher the Fe(II) ions concentration, the longer the time elapsed before the solution darkens. After 3 hours, the product is filtered, washed/centrifugated 3 times with deionized water and dried one night at 25°C under vacuum.

- Standard synthesis: polypyrrole conductivity starts from -3 S/cm for [FeII]=0, reaches an optimum (σ=5,8 S/cm) for [FeII]=6.3 10-2 M and then falls to approximately 4 S/cm for higher concentrations.
- Codoped materials: the conductivity is almost constant at -20 S/cm for all [FeII] concentrations.
- Latexes: conductivity of the latex increases linearly with the [FeII] concentration, going from 1.64 S/cm to 4.1 S/cm in this domain of concentration.

Discussion

The different behaviors of the three types of synthesis can be tentatively interpreted considering the polymerization mechanism involved.
First, as mentioned before, addition of ferrous chloride slows down the polymerization of pyrrole and, according to our hypothesis, will allow a more regular growth of the macromolecule, which will in turn present less chain defects. However, the growth of the chain also depends on the lifetime of the pyrryl radical-cation formed by the reaction between the ferric ion and the monomer. This radical can react in several ways with the impurities in the solution and lead to the formation of undesired products. These products can also be oxidized and incorporated in the growing polymer chain or, if this reaction takes place at the end of the polymer chain, stop its growth. In the case of standard synthesis, competition between homopolymerization and reaction with an impurity results in the presence of an optimum, corresponding to an “ideal” lifetime of the radical-cation.
In the case of latexes, the monomer being dissolved in PVS vesicles, polymerization only

takes place inside of these. Thus protected from hydrosoluble impurities, the radical can only react with the monomer. The slower the reaction, the better the linearity of the chain: conductivity will increase with increasing concentrations of [FeII] ions, as observed. The average value of the conductivity,' measured on a pressed pellet, will be lower than for a standard powder because of the presence of an insulating shell of surfacing agent around the conductive PPy grains.

For codoped materials, the large size of the codoping agent (tosylate ions) governs all the transport phenomena: at the individual chain level, it defines the local geometry by its own symmetry and at the material level, it sets the interchain distances.
The thermal stability of the material synthesized withouts PVS or tosylate and having the highest conductivity was measured by following its evolution versus time at 68°C. After 70 hours, 50% of the initial conductivity is still present: whereas only 30°/0 residual conductivity is obtained for the standard material.

Naphtalene disulfonate-codoped polyprrole

The use of naphtalene mono- or disulfonate ions as codoping agents for polypyrrole is mentioned in the litterature. LCR has first investigated the influence of naphtalenedisulfonate (NDS) ions on the conductivity and thermal stability of PPy powders.

Experimental procedure

Ferric chloride $FeCl_3.6H_2O$ (2.5 g, 1.16 10^{-1} M) and Na_2NDS are dissolved in 80 ml of deionized water under stirring. Pyrrole monomer (268 mg, 5. 10^{-2}M) is added to the solution. After 3 hours, the product is centrifugated/washed three times with deionized water, and dried under vacuum at room temperature for 24 hours.

Results

The conductivity of the codoped material oscillates between 15 and 23 S/cm. An optimum is reached for an equal mass of codopant and ferric chloride.
The optimum product loses ~45% of its conductivity upon heating at 85*C for 25. 104s. After cooling, the loss is only *30°/0*. The origin of this behaviour (water uptake?) is currently under investigation.
As a general rule, the properties of NDS-codoped PPy are not significantly improved compared to Tosylate -codoped PPy.

Naphtalene 2-sulfonate codoped polypyrrole

The codoping agent is introduced in the acidic form (N2SH) during the synthesis of PPy powder. The best conductivity is obtained for the lowest N2SH concentration and its value is higher than the best one obtained with tosylate.

The thermal stability of the materials has also been assessed. The "best" product loses less than 20°/0 of its original conductivity afetr three days at 80°C in air. In the same conditions, tosylate-codoped PPy loses ~30%.

1.5.2 Polyaniline

Preparation of polyaniline latexes was undertaken, using the standard procedure, in the presence of an emulsifier. Potassium persulfate $K_2S_2O_8$ was used as polymerization initiator in an H_2O/HCl mixture. The stirring speed was varied between 100 and 300 rpm, the reaction time being -4 hours. MEC or PVS have been used as tensio-active agents.
The latexes were submitted to at least 3 washing(Deionized water)/ centrifugation (2000 rpm, 1 min.) cycles, and dried at 3 0°C under vacuum.
The influence of the stirring speed, aniline weight (1 %, 5%), nature (hJ.EC, PVS) and concentration (1, 5, 10* m(aniline)) of tensioactive agent was investigated.
The stirring speed has **no** influence on the thermal stability (evaluated by DSC and TGA) of the materials, but increasing the speed results in an increase in conductivity.

PANI/PVS latexes

The DSC spectra of PANI/PVS latexes exhibit two peaks at 100°C (water and/or HCl loss) and 21 0°C respectively. For **5°/0** Aniline, the area of the 2nd peak increases with decreasing percentages of PVS. It is thus likely that the amplitude of this peak is modulated by the protection of the grain by a PVS shell, defined by the PVS percentage during the synthesis.

For 1% aniline, the 2nd peak is weak or non-existing whatever the percentage of PVS.

The thermogravimetry experiments performed on the materials confirm the DSC results. Weight loss is observed at 100°C, 21 0°C and 400°C (degradation and rearrangement of the PANI chains). The weight loss at 210°C increases with decreasing percentages of PVS (for **5?4.** Aniline):

- 5g PVS: -25%
- 25g PVS: -17%
- 50g Pvs: -11'?40

For 1% aniline, the curves are identical for all the PVS percentages.
The conductivity of these latexes is : $1.78<\sigma<6.18$ S/cm. There is no straightforward correlation between the conductivity and the percentage of PVS.

PANI/MEC latexes

The TGA results obtained on PANI/MEC latexes are similar to those of PANI/PVS.
The conductivities are lower: $0.55<\sigma<3.46$ S/cm.
All the synthesis performed with 5% aniline are more stable than those with 1% aniline, but their conductivity is lower.

Interpretation : *as* mentioned before, the conductivity of the latex increases with increasing stirring speed and decreasing aniline concentration. These two parameters will reduce the grain size and thus lead to a higher compacity and therefore conductivity of the material.

DSC/TGA results can also be rationalized. Actually, for 5% aniline, increasing the PVS concentration results in a smaller weight loss at 2 10°C; for 1 % aniline, there is no peak at this temperature.
5% aniline synthesis will yield bigger grains which implies a higher quantity of PVS to

achieve a good encapsulation of the particle. For 10/0 aniline, the PVS content is always sufficient for a good coverage.

Thus, all the variations mentioned earlier can be explained on the basis of the size variation of the conducting particles.

Codoped PANI latexes

Tetraethylammonium paratoluenesulfonate was used as codoping agent in the optimal synthesis of standard PANI (PVS, 200 or 500 rpm) at a concentration of 0.5 M.

Contrarily to PPy, the conductivities of the codoped products are lower (0.31 <0< 4.5 S/cm). This unexpected effect might stem from the fact that the synthesis of PAM is performed in an acidic medium, the pH of which is lower than the pKa of paratoluenesulfonic acid. The paratoluenesulfonate anion will act as a base to form the acid, which can not be used as a dopant by the material.

Thermal stability was evaluated by measuring the evolution of the conductivity at high temperatures as a function of time. The measurements were difficult in the case of 5°/0 aniline products because a large amount of gaseous HCl was released, corroding the metal probes. 1% ANI synthesis lost 45% of its initial conductivity after 4000 min. at 76°C, and 5% AM synthesis lost 700/0 after 4000 min. at 90°C.

The TGA results however show that the weight loss at 21 O*C for 5% ANI codoped materials is smaller than for the standard ones.

2. Transformation Processes

2.1 : Conductive/Non-Conductive Polymer Blends

2.1.1 ICI's developments

Thermoplastic Blends

The first experiments carried out to determine the conditions required for forming conductive blends with thermoplastics were simple solution blending procedures. The technique used was to dissolve or disperse the conductive material in a solvent and blend this mixture with a solution of a thermoplastic material in the same solvent. Solvent was then removed from the system and the conductivity and morphology of the resulting material investigated. To produce conductive materials a continuous network of the conductive component of the blend is required.

Conducting polymers in their doped state do not generally disperse well in moderately polar thermoplastic hosts because of the very high surface energy associated with the ionic conducting polymer. Consequently it is necessary to reduce this surface energy which may be done by attaching alkyl chains to the polymer so that its charged nature is effectively masked; this approach also stabilises colloidal particles of the conducting polymer by providing steric stabilisation against flocculation etc.

A polymer which does possess alkyl chains to aid dispersion in the manner described above is polyaniline doped with DBSA whose synthesis was described in the previous section. As was also described previously it is possible to disperse or even dissolve this material in organic solvents (in direct contrast to conventional polyanilines) because of the alkyl groups present. Such dispersions were used to produce blends by solution mixing with PMMA and SBS.
For the polar PMMA high conductivites are observed up to that of the parent polymer at a 30 wt% loading of the conductive filler. In contrast for the non-polar SBS much lower conductivities are observed. Interestingly in both cases no classical percolation threshold is observed, indeed for the blends with PMMA a conductivity of 0.1 S/cm is obtained for only 12 wt % of polyaniline.DBSA within the blend. The reason for the difference in behaviour between the two host polymers is clearly seen when the blends are examined under the optical microscope. The blend with PMMA consists of well dispersed polyaniline.DBSA particles of size 1-10 mm throughout the whole sample forming a continuous network. In contrast the blend with SBS contains large agglomerates of conductive particles (of up 100 μm) surrounded by a continuous insulating layer of SBS. This difference in behaviour can only be explained in terms of the difference in surface energy between the two host polymers. The SBS has a low surface energy making interaction with the polyaniline unfavorable whereas PMMA has a higher surface energy resulting in a more favorable interaction.

In the synthesis section of this report methods for producing plasticised polyaniline.DBSA formulations were discussed. It was obviously of great interest to discover how these materials behaved in blending experiments. Initially solution blending experiments of the type described were carried out. It was noticeable during these studies that the plasticised polyaniline.DBSA materials were much more soluble in common organic solvents than their non-plasticised counterparts.

It is obvious from this figure that the plasticised material gives higher values of conductivity for equal loadings of conductive material. The reason for this is apparent when the blends are examined by microscopy; the unplasticised material forms particle agglomerates whereas the plasticised compound affords a continuous network of conductive material through the sample even at low loadings of the polymer component. This difference in behaviour can again only be explained in terms of polymer surface energies with the plasticiser being effective at reducing this parameter.

Similar blends were made with the plasticised polyaniline.DBSA and polar polymers such as PMMA; for these systems continuous networks of conductive polymer with no discernible particulate were discovered by microscopy in comparison to systems with no plasticiser in which the network was composed of particulate. The result of this was a slight increase in conductivity up to -20 S/cm.

Melt blending studies were also carried out on these plasticised formulations with to date limited success. Some good quality blends were obtained but the amount of plasticiser present appears to be critical in obtaining good melt blending behaviour. However, an extrusion trial on the plasticised polyaniline alone produced good quality lace. The melt rheology observed was similar to that for plasticised PVC indicating that this material should be suitable for processes such as wire coating etc.

Conductive Paint

The bulk of the paint dispersions were prepared in toluene. However, it was recognised that xylene would be considered a more ‘user friendly’ solvent. Polyaniline generated by the alternative preparative route and also Widnes plant batches were used in attempts to define a process for paint production in xylene.

The criteria for successful paint preparation in toluene from previous work were-

Use of low molecular weight polyaniline (IV‘s in the range 0.8-1 .2)
A molar equivalent of DBSA used as plasticiser with polyaniline
Fine particle size material was important, so ball milling was essential to generate a good dispersion.

The combination of small particle size distribution and low molecular weight suggests that there may be some solubilisation of the polymer during the dispersing/thickening phase at 95-100°C which would give added coherence to the film on deposition from solvent. With xylene as the dispersing solvent, the objective was to produce the same quality of paint dispersions as in toluene -yielding the same or better conductivity of a deposited film. It was also the intention to see if the ball milling stage could be eliminated since this would introduce an added complication into plant production of paint and whether the higher molecular weight material produced on the Pilot Plant could be converted to paint.

For the best dispersions in xylene, the optimum level of DBSA to polyaniline was 1:1, but the heating stage was critical in paint generation. In some cases the temperature was taken to 130°C with the onset of a viscosity rise taken as being significant. Even at high temperatures, there was little evidence of gelation, although on standing at room temperature, some paints did gel: these could be broken down, however, by shaking or stirring.

The conductivities of' films produced from polyaniline dispersions in xylene were, in general, poorer than those produced in toluene. However, there were certain exceptions when comparable values were achieved. There was some inconsistency along a sample and also from one side to the other. This could be partly attributed to the coarse particle size distribution of the particles although films deposited from ball milled polyaniline gave only values between 1-5 S/cm at best. This was attributed to the use of higher molecular weight polyaniline from the Pilot Plant batches. These experiments did not rule out xylene as a possible alternative to toluene but did suggest tight control on molecular weight and particle size distributions may be necessary.

2.1.2 **KBW's** developments

KBW introduced the concept of "counter-ion induced processability" for polyaniline by Prof. Heeger (Synth. Met. 48 (1992)'91 and ICSM '92).

KBW used the material "VERSICON" from ALLIED SIGNAL to start. To achieve counter-ion induced processability, they dedoped the polyaniline VERSICON and doped it with dodecyl benzene solphonic acid (DBSA) and campher sulphonic acid (CSA) as functionalizing dopants. In a first series of experiments, KBW estimated the optimum of dopant content. A value of max. 0.4 for the molar ratio of DBSA/Polyaniline is the best. The DBSA doped polyaniline, KBW synthesized, shows a conductivity which is greater by a factor 25 than the original VERSICON.

As pointed out by Heeger counter-ion induced processability lead to reduced disorder and therefore to higher quality intrinsic conductive polymers; it may be that again the value "n" is quite different in VERSICON and the DBSA doped polyaniline. To interpret this value on a molecular level, KBW tried to estimate the part of polyaniline which can be protonated (doped) by DBSA.

The quantification of "n" by solid-phase-NMR-spectroscopy was not successful, but the NMR shows, that the amount of conductive carriers is much higher in the DBSA doped polyaniline than in VERSICON. This is in agreement with the conductivity measurements.
DBSA doped polyaniline was solution blended with EVA to check up the stability of the conductivity : the conductivity is very stable for the produced samples.

KBW applied these methods for dedoping/doping procedures, also to produce several boxes for TS.ASM with the ICP "EDRAN" from SOLVAY.

2.2 : **Transformation** processes

2.2.1 : **Preparation** of the **ICP's filled matrix**

KBW were interested in highly conductive polyaniline to improve the transfer impedance of coaxial cables. Typical values of > 500 S/cm were estimated to be reached by simulations.
Different molecular weight polyanilines were supplied from ICI and were solution blended in EVA. Indeed, the highest conductivities were found with the highest molecular weight polyaniline.

First processing experiments were made by a Brabender mixing chamber to study the processing of supplied polyaniline. The selection of the polymer matrix and the processing temperature were the most important factors influencing the morphology of polyaniline blends. By optical microscopic analysis, it was shown that in conductive blends a high degree of conductive pathways was formed. In non-conductive blends conductive islands of polyaniline were separated by the polymer matrix.

A first rule was formulated to design conductive polyaniline blends; a highly polar polymer matrix and a high viscosity of the polymer matrix at processing temperature are the most important factors. A further check of this rule was done with different polymers; but only with chlorinated polyethylene (CPE) and chlorsulphonated polyethylene (CSM) blends with conductivities in the range of the incorporated pure polyaniline were obtained.

2.2.2 : **Thermoplastic processing**

Using the procedures described in section 2.1 polyaniline.DBSA was blended with a plasticised chlorinated polyethylene using a twin screw extruder. A good quality lace was obtained which could be chipped without further problems. A quantity of two kilograms of material were made which had a conductivity of 4 S/cm, very similar to that observed in the Brabender experiments.

2.2.4 : **Coating preparation**

2.2.4.1 **ICI's developments**

As described previously it is possible to produce a polyaniline paint with conductivities up to 150 S/cm by simply dispersing polyaniline of a suitable molecular weight and particle size in toluene. Paints produced by this process appeared to us to be the only way to supply the partners with materials of high enough conductivity to be effective in their applications. Paints produced by the above method could be readily applied to substrates by simple dip coating procedures to give coherent tough and flexible coatings. Problems were encountered with the initial samples with material flaking off the substrate with time. This difficulty was partially overcome by including excess DBSA in the formulation which had the effect of plasticizing the material to make it more rubbery and to dissolve more of the polyaniline itself.

2.2.4.2 **LCR's developments**

One of the main advantages expected from the use of ICP is the possibility to easily coat surfaces, especially those which can not be properly shielded using standard techniques [sputtering, metallization . ..).

TS.ASM was especially interested in the shielding of a polyurethane box, used as a container for a piezoelectric sensor.

In the course of the project, several types of PPy coatings have been tested. Standard synthesis, codoped synthesis, latex synthesis, controlled redox potential synthesis have been tried.

Preparation of the samples:

Plates :

In a 500 ml container, ferric chloride was dissolved in 200 ml of deionized water (together with ferrous chloride and tetraethylammonium paratoluenesulfonate). The PU plate was then immersed in the solution and, after 10 minutes, the monomer was added. The solution was then stirred for 30 seconds. After 4 hours, the plates were withdrawn from the reaction medium, washed gently in deionized water and left to dry in air one night.

Concerning EMI shielding effectiveness, an attenuation of -12 dB of electrical field in far field conditions has been obtained between 1 and 18 GHz with the produced plates.

Pu containers :

The standard solution is prepared by dissolving $FeCl_3$. $6H_2O$ (9.4 g) in 300 ml of deionized water. The boxes are filled with the adequate solution. Pyrrole monomer (1.005g) is then added and rapidly mixed. After 3 hours, the containers are emptied, gently rinsed twice with deionized water and left to dry in air. A set of four PPy-coated PU boxes has been prepared and given to TS.ASM for shielding measurements (see corresponding report for results, in section 3).

3. Environmental Resistance and Ageing

The objective of’ this section was to determine the behaviour of conducting polymers when they were exposed to various degrading environments like UVs, water, temperature.
During the ageing procedures, evolution of electrical and mechanical properties has been studied : conductivity, Young modulus, elastic limit, tensile strength have been evaluated at different stages of the ageing tests.
These tests have been performed on polypyrrole and polyaniline polymers, polythiophene exhibiting a too short lifetime to be correctly studied.

PPy coatings :

TS.ASM received PU plates coated with polypyrrole from LCR. PPy was doped either by the FeCl3 + Tosylate system or by the FeCl3 + N2SH system.
the PPy coated samples have been submitted to a dry atmosphere at a temperature of 60°C. Conductivity has been measured all along the ageing procedure which lasted about 40 days. This led to the determination of a half lifetime close to about 200 hours for both dopant/codopant systems.

Thermoplastics/PANI blends :

TS.ASM made several plates with this material thanks to a compression moulding procedure, Similar tests were performed also by KBW and same conclusions were found.
The produced material has been submitted to the following ageing procedures :

- ageing at room temperature during 2500 hours
- ageing in dry air at 60”C during 2500 hours
- outdoor exposure (sun and rain) during 2500 hours
- exposure to water saturated atmosphere, at 60°C during 1000 hours
- immersion in water at 25°C during 1100 hours
- UVs exposure in a closed chamber at 23*C during 2500 hours.
- ozone exposure

All along the different ageing procedures, electrical conductivity measurements have been performed.
Moreover, all along the immersion in water at 25*C and the exposure to water saturated atmosphere at 60°C, the weights and the thicknesses of the samples have been controlled in order to evaluate :

water uptakes by the specimens
dopants or plasticizer losses from the specimens.

Conclusions :

After 2500 hours of exposure in dry air at 20°C or 60°C, PVC/PANI samples do not exhibit any decrease in conductivity.
They even show an improvement of their conductivity close to 20% after having been submitted to dry air at 60°C.
Conductivity of PVC/PANI specimens is not decreased by an exposure to UVs at room temperature. Their conductivity is also stable at the tested concentrations of ozone.
Howewer, samples exposed to water saturated atmosphere at 60°C or immersed in water at

25°C exhibit a strong decrease of their conductivity versus time.

TS.ASM observed a lowering of water pH during samples ageing : this prooves that there is a loss of doping agent which could explain the decrease in conductivity.

Concerning samples submitted to water saturated atmosphere, we could determine a half lifetime of about 800 hours, and for immersion in water at 25*C, this half lifetime should be close to 1200 hours.

This decrease in conductivity seems to be directly correlated to the water uptake exhibited by the samples exposed to humidity and reversible.

As a matter of fact, samples which have been immersed in water at 25*C have been submitted to a drying procedure (90 hours in vaccum at room temperature) by the end of the trial. We have then observed a strong decrease of the weight of the samples and an improvement of the conductivity levels of roughly 20°/0.

This experiment seems to proove that PVC/PANI blends exposed to humidity exhibit a water uptake which provokes reversible losses in conductivity.

Samples exposed to outdoor environment (sun and rain) do not show any coherent decrease of their conductivity. This is probably due to a destructive interference between the conductivity improving effect of temperature and the conductivity lowering effect of water. PVC/PANI are indeed black and their temperature can rise up to 70°C when they are directly exposed to the sun.

4. Demonstration

4.1 : Cables

KBW has realized the following demonstrators :

- Demonstrator *N° 1* : a coaxial cable with a braided shield in combination with a ICP-filled extruded layer.
- *Demonstrator N°* 2: a multi-conductor low pass cable with ferrite coated conductors, the ferrite layer being covered itself with a thin ICP-lacquer layer.

The first demonstrator did not show any significant improvement of the EMI shielding effectiveness.

The attenuation performance of demonstrator n°2 has been measured on a length of 10 m in the frequency range of 1 MHz to 100 MHz.
KBW made a complete investigation concerning the EMC-behaviour of this cable used as an interconnection cable between a frequency inverter driving an AC-Motor. Frequency converters are working with very high switching speeds (e.g. a few nanoseconds) thus generating on the connection cable a very high level of EMI.
KBW measured such a test set up in an anechoïc chamber. The aim of the measurement was to compare a conventional shielded cable with the improved cable.

The essential results are :
- an improvement of approx. 14 d13 is realized in the frequency range of 0,3 to 5 MHz,
- in the frequency range of 30 MHz to 1 GHz, the RF-noise is reduced by approx. 6 dB.

KBW decided to make this product commercially available.

4.2 : Boxes

SDC performed EMI shielding effectiveness measurements on the box realized thanks to SOLVAY's EDRAN and supplied by KBW. These measurements have been performed according to the microwave test method.
A level of -35 dB, increasing with the frequency, is observed in the microwave domain.

4.3 : Acoustic antenna

Coated PU demonstrators :

With the conductive materials supplied by the Partners, TS.ASM manufactured and tested several coated polyurethane (PU) acoustic sensors.
These PU boxes were made of a material referenced ELPU 3563 which is a highly performing material for acoustic applications and were coated with :
- PANI thick coat by ICI (3 boxes referenced ICI1 to ICI3)
- PPY doped with $FeCl_3$ by LCR (1 box referenced LCR1)
- PPY doped with $FeCl_3$ and $FeCl_2$ codopant by LCR (1 box referenced LCR2)
- PPY doped with $FeCl_3$ and Tosylate (NEt4TS) codopant by LCR (1 box ref. LCR3)
- PPY doped with $FeCl_3$ and Naphtalene disulfonate (NDSNa2) by LCR (1 box ref. LCR4).

A planar pressure sensor made of piezoelectric polymer PVDF has been inserted in each manufactured coated PU box. The obtained acoustic sensor was submitted to shielding effectiveness measurements in TS. ASM laboratories.

These measurements have been performed for both magnetical and electrical fields, in near fiel conditions and in the frequency range 10 kHz -10 MHz.

As a reference, we consider the case of a classical EMI shielding made of a brass grid (typically mesh : 5 mm x 5 mm _ 0.8 mm) usually used to protect sensors and electronics from EM emissions.

Results of the measurements performed for E field are gathered in the table given in Table 4.3.1. For H field, according to theory, no significative attenuation was found with the ICP's shielding boxes.

Frequency (MHz)	**0.01**	0.05	**0.1**	0.5	1	5	**10**
Brass grid	23	30	41	34	5	<5	<5
ICI1	>38.2	43.4	43.9	47	44.1	32,4	19.9
ICI2	>38.2	44	42.9	48.4	35	35.3	12.3
ICI3	>38.2	48.6	46,3	48.3	50.4	37.4	18.4
LCR1	>37.7	31.8	28.6	16.8	11.2	2.1	-
LCR2	23.5	18.4	16	7.4	5.1	2.9	0.1
LCR3	>37.7	41.8	40.4	30.8	24.1	11.6	4.6
LCR4	>37.7	37.8	34.4	21.7	15.8	8.4	5.1

Table 4.3.1: Shielding Effectiveness for E field in dB

Data obtained show that both PANI and PPy coating solutions are very interesting in comparison with the mettalic grid solution, especially concerning high electrical frequencies. PANI coating solution appear to be more reproducible and more efficient than PPy coatings.

Conclusions :

The PANI coated boxes supplied by ICI allow to solve the problem of electrical field shielding in acoustics. As a matter of fact, this technology leads to SE values close to 46dB (this value of SE has to be achieved according to the calculations made on the basis of standard RF exposure conditions observed in a Radar beam).

PPy coating solution is interesting for low frequencies.

Thicknesses of PANI layer are very low. Consequently, acoustical performances of the boxes are not affected by the presence of the EMI shielding paint.

Nevertheless, coating adhesion on the PU surface is not sufficient to ensure an environmental resistance of the EMI shielding against mechanical stresses.

Conductive / Non-conductive polymer blends :

Two demonstrators have been realized with thermoplastic/ICP blends :

- a demonstrator based on a PANI/PVC blend purchased outside the Partnership
- a demonstrator based on PVC/ICP material supplied by KBW to TS.ASM.

These demonstrators are made of a conductive box containing a PVDF pressure sensor moulded into acoustic soft PUR.

Both demonstrators have been submittted to the shielding effectiveness measurement procedure in E field conditions.

A reference sensor was made of a PVDF pressure sensor moulded with polyurethane.

Results are gathered in Table 4.3.2.

Frequency (MHz)	**0.01**	**0.05**	**0.1**	**0.5**	1	**5**	**10**
INCOBLEND box	48,3	64.5	55.4	42.9	37.7	31.2	**25**
PVC/ICP box	32.6	32.7	32.6	32.8	33	33.5	**14.7**

Table 4.3.2: Shielding effectiveness for E-field in dB

These demonstrators have also been tested in acoustical tank in order to check if the conductive box was compliant with the acoustical performances to be achieved on the sensor. These tests led to successful results, especially for the Incoblenb based box : both demonstrators exibited sensitivities close to the sensivity obtained on the reference sensor.

Conclusions

All the synthesis tasks have been successfully completed. Highlights include the synthesis of end functionalised thiophene oligomers and polyaniline-surfactant complexes that form ordered morphologies with enhanced conductivity.
The environmental performance of polyaniline and polythiophene products supplied by ICI were assessed by the partners. Polythiophene failed to meet the stability requirements. This unfortunately resulted in the most promising approach to providing a conductive polyurethane having to be abandoned.

High conductivities are only achievable when continuous conducting morphologies are achieved. This was found to be the case and high conductivity (>100S/cm) coatings that could be formed into both coatings on substrates and self supporting films were successfully produced. It was discovered that polyaniline / surfactant complexes having an extended molecular conformation is the key to achieving high conductivity. Significant progress has been made towards applying the same effect in producing a melt extrudeable polyaniline and a product with a melt rheology similar to that of plasticised PVC has been demonstrated.

The coating formulation developed has achieved the highest conductivities reported using commercially acceptable solvents (toluene and xylene) provided the coating is heat treated. This product was recommended by ICI as being useable to fabricate all of the demonstrators and most likely to meet the conductivity and hence EMI shielding requirements and environmental resistance.

In spite of the problems faced to reach a high volume conductivity of ICP-compounds and the lack of ICP-material, KBW could realize the different demonstrators.
The conductivity of 1 to 5 S/cm is not high enough to realize their main goal : cables with an extrudable shield. The reached conductivity is not high enough to assure an interesting performance at low frequencies; conductivities of 500 S/cm and more are to be reached in order to realize shielding performances as requested by the industry under the stringent requirements of the EMC-Directive of the EU.
Notwithstanding this failure, KBW could improve the performance of their ferrite loaded low pass cables, opening new applications to these special cables, e.g. in the field of connection cables between a three phase AC-Motor and a frequency inverter.

LCR'S work proved that ICPS synthesized by the “chemical” route (as opposed to the electrochemical route, which was not relevant for the project), either as powders or as latexes, can be obtained with significantly enhanced properties compared to the standard materials. The use of a codoping agent, for powders or latexes as well, is an easy way to reach better conductivities (up to a few dozens of Siemens/cm) and thermal stabilities. The codoping technique LCR used provides an easy access to a family of polypyrroles, and to a lesser extent of polyanilines, and is quite general. The mechanisms responsible for the stabilization of the materials is quite unclear at the moment, but as a rule of thumb, “large” aromatic monosulfonate anions yield the best products. Control of the kinetics of the polymerization reaction via the redox potential of the synthetic medium has also been effected. This

technique is especially interesting for latexes, giving increased conductivities.
The research LCR have performed on the several possible ways to improve the conductivity and thermal stability of PPy have led to the conclusion that the use of a codoping agent is a crucial point. Aromatic sulfonic acids yield the best materials. The “best” codoping agent identified today is naphtalene 2-sulfonic acid. Conductivities nearing 30 S/cm can easily be obtained with a low content of N2SH. The thermal stability of this product is significantly enhanced, compared to the standard chlorine-doped PPy.

ICP deposited on top of insulating substrates (polyurethane plates or boxes) has poor mechanical properties which have prevented ageing studies. However, interesting shielding values could be reached in the high frequency domain,

Thanks to the conductive coatings synthesized by ICI (PANI) and LCR (PPy), TS.ASM made a set of shielded acoustical sensors which allowed a validation of the interest of such a technology for electrical RF field shielding. Long-term ageing of these coated sensor boxes in normal conditions (room temperature) has been studied and exhibited satisfying resistance for both coating techniques.

In spite of the impossibility to synthetise a ICP/Polyurethane blend of sufficient performances, TS.ASM could manufacture two shielded acoustical sensor boxes thanks to the ICP/thermoplastic blend delivered by KBW and purchased to the Zippering Kessler Company (Incoblend).
These two demonstrators exhibited highly performing E-field shielding potential, especially concerning the Incoblend based box. Their acoustical performances were also checked and revealed to be satisfactory.

Thanks to the PANI/PVC blends purchased by the end of the project, TS.ASM was able to manufacture samples in order to perform an extensive study of the ageing behaviour of PANI/thermoplastics blends.
This study was based on the monitoring of both mechanical and electrical properties of PANI/PVC samples submitted to various damaging environments (UVs, water, vapour, temperature . ..). It proved that PANI/thermoplastics blends exhibit satisfactory environmental resistance when they are kept away from water.

Ageing of PPy coatings was much more difficult to study because of the highly brittle aspect of such conductive layers. Nevertheless, temperature effects have been examined and half-lifetime for different temperatures were determined.

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BE 4577

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“INTRINSICALLY CONDUCTIVE POLYMERS FOR ELECTROMAGNETIC INTERFERENCE SHIELDING’.

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ICI has reported the work of the project at two international conferences which has also been published and is preparing to publish a full paper. The conditions that can lead to an explosion during synthesis scale up have been reported through the safety literature.

Publications

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- S J Davies, T G Ryan, C J Wilde "Melt Extrudable Cable Screens" Polymat '94 Preprints, 388, 19-22 September 1994, Imperial College, London

Conference Presentations

-Oral presentation by S J Davies on “Processable Forms of Conductive Polyaniline” at the International Conference on Science and Technology of Synthetic Metals (ICSM ‘94), Seoul, Korea,

- Oral presentation by S J Davies on “Melt Extrudable Cable Screens” at Polymat ’94, 19-22 September 1994, Imperial College, London

Abbreviations

TS.ASM : Thomson Sintra Activités Sous-Marines

ICI ICI Materials Wilton Research Center

KBW : Kabelwerk Eupen AG

LCR Thomson CSF / Laboratoire Central de Recherches

SDC : Thomson CSF / Division Systèmes Defense et Contrôle

I(2P Intrinsically conductive polymer

PANI : Polyaniline

PPy Polypyrrole

DBSA : Dodecylbenzene sulphonic acid

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