Materials for LED Devices

A thesis presented by Patricia Catherine Marr BSc., MSc.,

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DECLARATION

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LIST OF ABBREVIATIONS

δ	Chemical shift (Relative to TMS)
δ_i	Partial Positive or Negative Charge
Bipy	Bipyridine
Br, s, d, t, q, m	broad, singlet, doublet, triplet, quartet, multiplet.
CV	Cyclic voltammetry
Dec	Decomposed
DMSO	Dimethylsulphoxide
DTA	Differential Thermal Analysis
DSC	Differential Scanning Calorimeter
ECL	Electrochemiluminescence
EL	Electroluminescence
ether	Diethyl ether
h,min	hours, minutes
IR	Infra Red
LED	Light Emitting Diode
LEC	Light emitting Electrochemical Cell
LEP	Light Emitting Polymer
M	mol dm^{-3}
mmol	milimoles
mp	melting point
MeCN	Acetonitrile
MS	Mass Spectrum
NMR	Nuclear Magnetic Resonance
OEt	Ethoxide group
O^iPr	Isopropoxide group
OR	Alkoxide group
PA	poly(acetylene)
PPV	Poly(*p*-phenylenevinylene)
RT	Room Temperature
THF	Tetrahydrofuran
TGA	Thermogravimetric Analysis
TMS	Trimethylsilane
UV-Vis	Ultraviolet and Visible

ABSTRACT

2,5-Dialkoxy-substituted bromomethylbenzene monomers were prepared by alkylation of hydroquinone followed by chloro- or bromomethylation. They were then polymerised using the base-catalysed elimination of HBr (Gilch method) to give precursor polymers for the corresponding poly-p-phenylenevinylenes (PPVs). The electron-donating alkoxide groups promote the elimination of HCl. From the ^{1}H NMR data it was clear that with the exception of the R=MEH (MEH=2-ethylhexyl) polymer **5**, the precursor polymers had already partially converted to conjugated forms (20-40% from the ^{1}H NMR). This explained their low solubility and their absorption and emission spectra. The polymers generally show a trend towards longer wavelength absorption and emission as MeO groups are replaced by longer chain alkoxides. With the exception of the dimethoxy polymer **3** the amount of HCl elimination determined by TGA is higher than expected from the NMR results. The results are rationalised by proposing that polymer **5** with large, branched groups eliminated HCl less readily due to greater steric constraints for the back-bone rotation necessary prior to elimination. Polymers **1**,**2** and **4** contain more cross-links than the unencumbered **3** for the same reason. Attempted conversion of **5** into the fully conjugated form was unsuccessful as the steric barriers to rotation of the bulky groups in the solid state prior to elimination are too great.

Polymer precursors were immobilised inside a silica sol-gel and silica/organic polymer (ormosil) matrices. The luminescence properties of these materials are reported. Device manufacture was not attempted with these materials since the doping levels achievable were not sufficiently high in order to permit low turn-on voltages. The use of base to polymerise the monomer within the gel was also investigated. This resulted in the formation of PPV-type polymer within the gel after 15 min exposure to 1mol dm^{-3} NaOH solution. The polymerisation of the monomer in the gel imparted a degree of flexibility on the otherwise glassy TEOS gel. This method resulted in the formation of a free-standing, yellow luminescent composite. These composites were investigated using PL and thermal analysis.

Methods of immobilising luminescent inorganic materials were also investigated $[Ru(bpy)_3]Cl_3$, Coumarin and Al oxime were all successfully incorporated into TEOS TMOS and Flexigel.

Electrochemical LED devices were investigated. by using poly(1,4-phenylenevinylene) (PPV) polymerised within a TEOS matrix doped with lithium triflate. Molar ratio of triflate to TEOS was 1:20. lithium triflate was added with the precursor polymer prior to gelation. The monomer was converted to the conjugated PPV by subjecting the monomer in the aged gel to NaOH as before which resulted in a yellow composite material, with a higher degree of flexibility than TEOS under normal conditions and with conductivity in the order of 1x10^{-4} S cm^{-1}. Thin films of flexigel electrochemical LED materials containing $[Ru(bpy)_3]Cl_3$ have also been fabricated and their electrochemistry discussed.

"The most exciting phrase to hear in science, the one that heralds new discoveries, is not 'Eureka!' (I've found it!), but 'That's funny'."

Isaac Asimov

Chapter 1

Introduction

1.0.0 INTRODUCTION TO LIGHT EMITTING POLYMERS (LEPS)

Producing a plastic that can emit light would have seemed outlandish just two or three years ago. Even the idea that plastics can conduct electricity came as a surprise to most. Plastic is commonly thought of as the material that surrounds most electrical wires to keep the electricity away from us. This of course was uniquely the case until the mid-seventies, when a group of scientists stumbled across a polymer that behaved as a semiconductor. This discovery opened up a whole new field of science and of materials which have the electrical properties of a metal with the processability of plastics. The Achilles heel so far, however, is that plastics capable of conducting electricity as well as metals are much more expensive.

In polyethylene each of the four electrons assigned to each carbon is included in a σ bond. The passage of an electric current through a substance requires a free movement of electrons and therefore the lack of electron delocalisation in polyethylene prevents it conducting electricity.

The key to making conducting polymers is to provide electrons which are not so localised. Remove one hydrogen from each carbon and you leave the atoms with an extra electron, these electrons are free to form π bonds with their neighbouring carbons on the chain, the result is a sequence of alternating single and double bonds all the way down the polymer backbone. In this regular conjugated sequence the extra electrons can be induced to move along the polymer chain forming an electric current.

The first conducting polymer candidate, polyacetylene, (MacDiarmid, Shirakawa and Heeger, 1975) was found to be difficult to process and was by no means a superconductor. However their research group found that adding a small quantity of another (oxidising) material could increase the conductivity of the polymer. This was a major breakthrough and several other doping materials were tested. It was found that doping this polymer in a solution of iodine removed about 10% of the conducting electrons which left the polymer with some positively charged holes (polarons), and negatively charged counter ions lying beside them. With this set-up in effect, there are fewer electrons in the polymer, and those that remain can move more freely (unoccupied energy levels).

Such doping was found to raise the conductivity of the polymer by a factor of a million, but this increase was still not enough to bring it up to that of copper. For good conductivity it is essential to have many mobile carriers in the form of electrons, or conversely holes in an array of electrons. The number of electrons (carriers) is not a problem in conducting polymers. The restricting feature is the mobility of the carriers. The problem is caused by an intrinsic property of polymers. Polymer chains coil up like a mass of tangled string.[1]

No one polymer chain will extend completely across, making contact with both electrodes, therefore, carriers have to make many jumps between polymer chains. There are many points throughout the sample where the chains are in close contact, but the distances over which chains closely approach each other is short. This limits the macroscopic conductance of the polymer. When the chains are aligned, the overlap distance of neighbouring chains is large. This increases the macroscopic conductance quite substantially.[2]

MacDiarmid found that molecular order was increased by stretching the polymers out into a thin sheet, this forced chain alignment. The chains were also packed very tightly by increasing the crystallinity to create the closest possible arrangement of molecules. It is easy to see how this would allow electrons to jump effortlessly from chain to chain.[1]

The conductivity of MacDiarmid's polymer was increased a thousand fold by a novel approach. Instead of using chloroform as the solvent, fluorophenol was used which acted as a secondary dopant. The effect that caused a thousand fold increase in conductivity was later rationalised as follows. The solvent coats the negative iodide ions created by the primary dopant shielding the molecules of the polymer backbone from their influence. In the absence of the neutralising effect of the counter ions the positive molecules begin to repel each other; as they are bound together, the only way they can move apart is by straightening themselves out.

1.1.0 PHYSICS OF CONDUCTING POLYMERS

Consider the ethylene molecule [5]

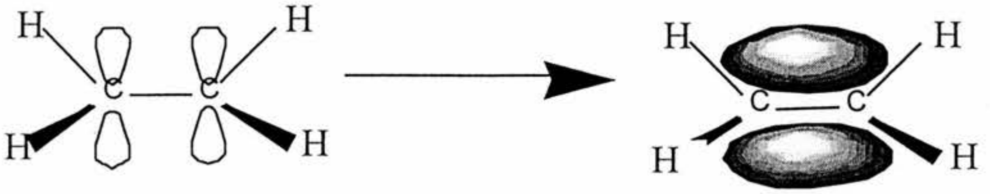


Figure 1 Diagram of orbital arrangement in ethylene

Here each carbon atom in the molecule forms 3 sigma bonds (2 C-H bonds and 1 C-C bond). This leaves each carbon atom with one unbonded valence electron. These final two electrons exist in Pz orbitals (sp^2 hybridisation) and form a carbon carbon π bond where the electrons in the bond are much less tightly bound to the carbon nuclei (Figure 1).

In ethylene molecule there exists a double carbon bond (1 σ bond and 1π). The electrons in these π bonds are less tightly bonded to the carbon nuclei, therefore they require less energy to be perturbed into excited states. In a solid state parlance, less energy is required to excite across the energy gap between the valence band and the conduction band.

Band theory is a useful model for describing the electronic structure in the solid state Figure 2 shows the band structure for a conductor an insulator and a semiconductor material. We can imagine that the bands are constructed from the overlap of the atomic orbitals of the constituent atoms. The discrete energy levels of the atomic orbitals merge into a wider energy band. In a conducting solid the empty band and the filled band are almost continuous, therefore it takes very little energy to excite the electrons from one band to another. These electrons can move freely through the solid and hence can carry an electric current. In an insulator there is a substantial gap between the filled and empty bands so the electrons are relatively immobile, the semiconductor is intermediate between the conducting and the insulating state where the band gap (Eg) is less than that in an insulating material.

In the early part of the century it was shown, that by measuring the energy E of the absorption maximum of a range of conjugated molecules, and plotting the energy against the reciprocal of the number (n) of conjugated repeat units, a linear relationship was found. By extrapolating this line it can be seen that $E = 0$ when $n = \infty$. If you interpret this E as band gap energy E_g between the valence and conduction bands in semiconductors $E_g = 0$ would imply metallic behaviour [5]. It was thought that if an organic material with a very large n could be made it would behave as a metal. This is where the polymers make their appearance, as they are organic materials with a very large number of repeat units.

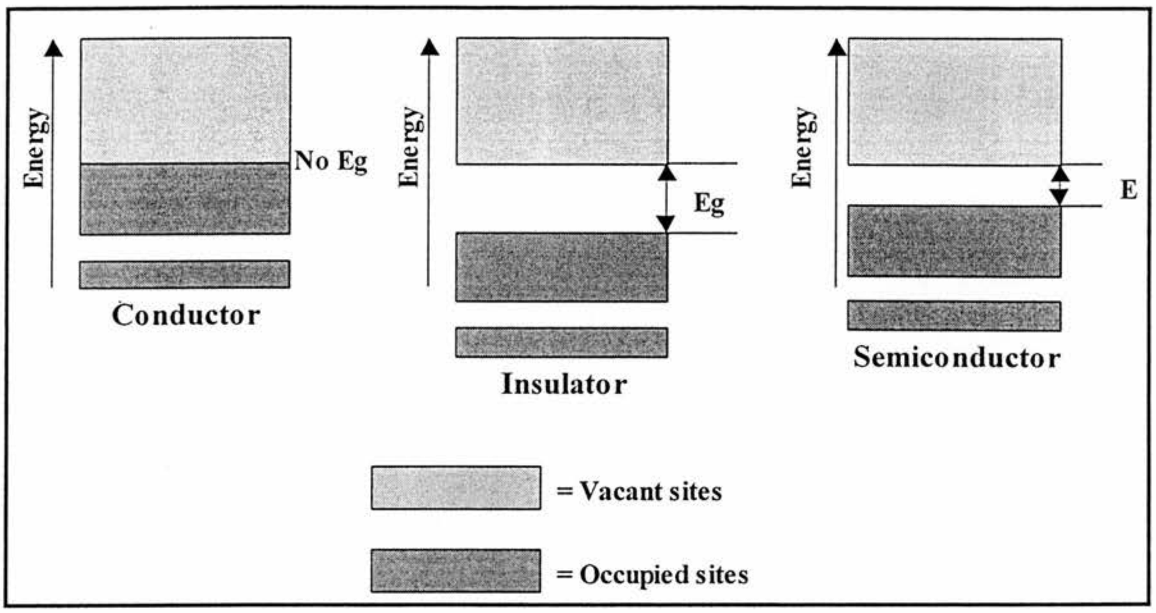


Figure 2 Schematic representation of the band structure for a metal an insulator and a semiconductor

Polyacetylene was thought to be the polymer which would behave best as a metal. It was first synthesised by Natta in 1950. However limited physics was carried out on this material, and it was found that contrary to expectations, this material behaved as a semiconductor and not as a metal. A polyacetylene film was synthesised from a modified Natta route and this material was also found to be intrinsically semiconductive with a band gap of 1.4 eV [3]

Arsenic pentafluoride and iodine were used to chemically oxidise (or dope section 1.2.1) the polyacetylene. This resulted in the conductivity being increased by as much as 11 orders of magnitude, which brought PA in line with the conductivity of mercury. This breakthrough has led to the emergence of many other conjugated polymers which are insulating/semiconductive but which become much more conductive on chemical oxidation or reduction.[4]

As previously mentioned PA was predicted to be of metallic character but was shown to be intrinsically semiconductive. Its physics can be explained best using quantum chemistry. By deriving the MO as linear combination of atomic orbitals (LCAO) we have:

$$\Phi k=\frac{1}{\sqrt{Nn}}\sum^{iakn}\phi_{n}$$

Equation 1

Φk =The molecular wavefunction

a =The carbon atom spacing

k =The wave vector

ϕn =Atomic wavefuncton

n =Number of atomic wavefunctions in the summation is made over.

N =denotes a particular carbon site.

Such a wavefunction Φk can then be used in Schrodinger's equation to calculate the energy states of the system (Figure 3). With increasing wavefunction overlap of the individual π wavefunctions with their neighbours, the resulting bands become broader and the gap between the bands decreases. In the limit of total overlap at infinite repeat unit number (the infinite polymer chain), the bands will merge producing metallic behaviour, that is, disappearance of the band gap (Figure 3).

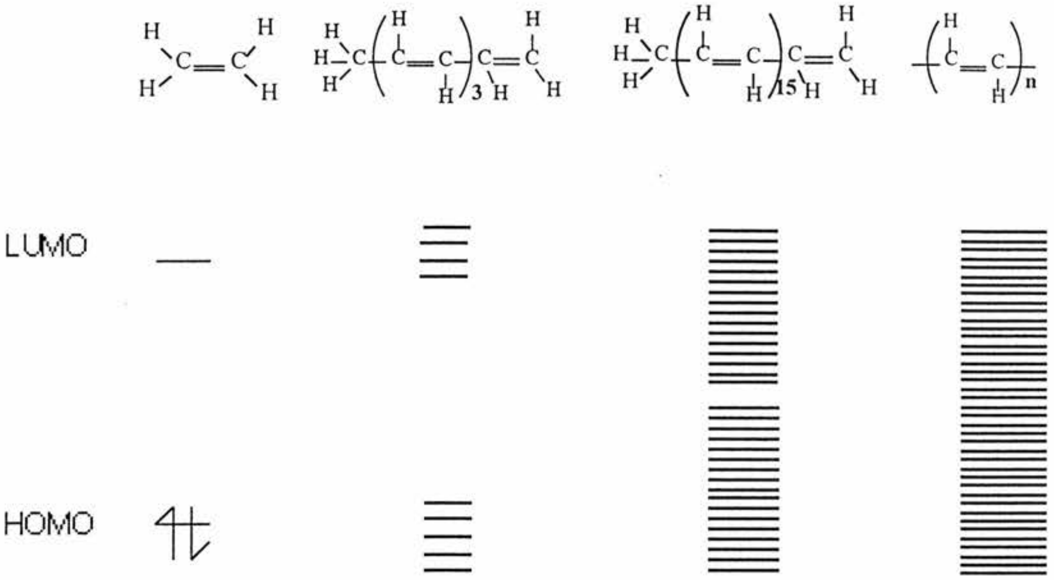


Figure 3 Diagramatical representation of theoretical band gap decrease in polyacetylene

The solution to Schrodinger's equation with such a wave function yields energy levels in the form:

$$\mathbf{E(k)^v = -2t \cos ka = -E_k} \qquad \textbf{Equation 2}$$

$$\mathbf{E(k)^c = 2t \cos ka = E_k} \qquad \textbf{Equation 3}$$

where t is the transfer integral which arises from the nearest neighbor terms in calculating the energy of the system, and is a direct measure of the π wavefunction overlap between neighboring carbon sites along the backbone, that is, the extent of delocalisation. The valence band is denoted by those states of negative energy. The conduction band by the positive energy states. Each carbon atom donates one π electron per site (per carbon atom), but Pauli's Exclusion Principle will allow two π electrons per site, one spin-up one spin down, so the energy band will be half-filled. All the negative sites are filled, but as the band structure is continuous, the system as a whole is metallic.

The above theory fails if one of the basic assumptions used is invalid, i.e. that single and double bonds are of equal length. In reality double bonds are slightly shorter than single bonds 0.03 - 0.04.Å. The average bond length being 1.4 Å. It is hard to see why such a difference causes a marked effect on the electronic properties. But essentially the energy of a half filled one-dimensional band system is lowered by localisation of the π electrons through the bond length alternation this is called a Peierls' distortion. There are however several other theories which try to explain the band gap value of 1.4 eV.[2]

1.2.0 SOLITONS IN POLY(ACETYLENE)

It is known that PA exists as a dimerised lattice and that a band gap between the valence and conduction band exists. If we plot the total energy per carbon atom (site energy) vs. U (the site displacement) we find that at

U = 0, the undimerised case, the site energy goes through a local maximum[5,6] (Figure 4).

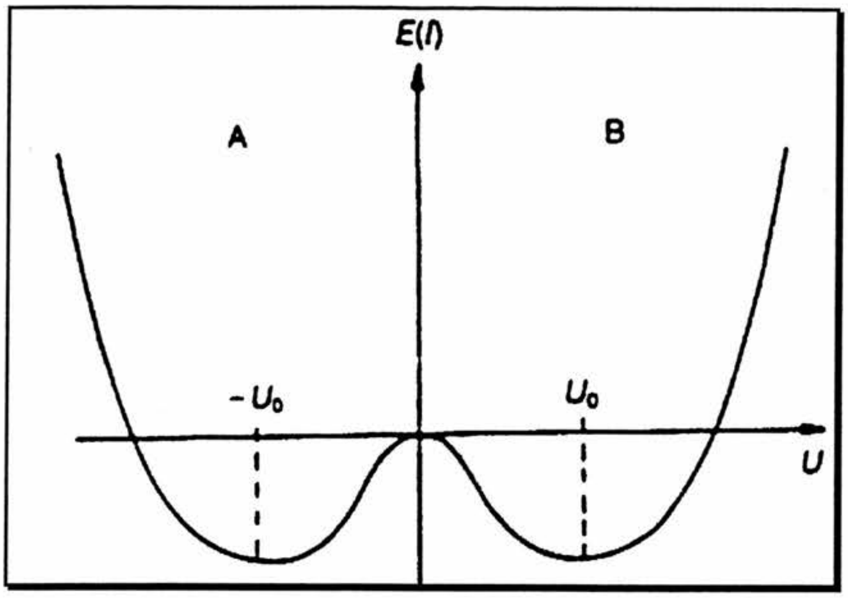


Figure 4 Plot of site energy Vs site displacement

This shows again that the poly acetylene system is unstable with respect to the Peierls transition. Also seen are two energy minima at U_0, which can be thought of as two phases of PA:

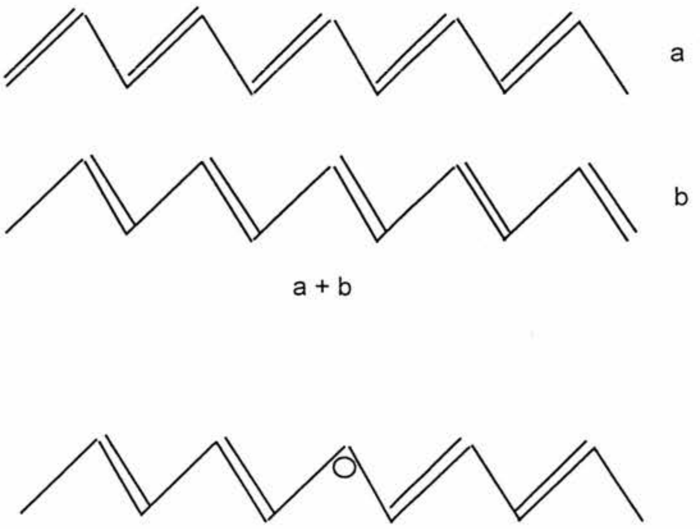


Figure 5 Soliton formation by the combination of two phases of PA which are represented by a + b

The resonance forms a + b are identical in terms of site energy but a points to the right and b points to the left. This a + b are identical degenerate ground states. Joining pieces of a + b together a bond mismatch occurs as one carbon site has too few π electrons to form a double bond. Although one unpaired π electron is present the system is neutral (i.e. the same no of protons as electrons). The system has one unpaired electron and therefore has spin 1/2. It is a neutral spin 1/2 entity. These topological defects are called solitons due to their non dispersive nature and the mathematical formalism from which they derive. The soliton in polyacetylene can be considered as an excitation from one geometric energy minimum a, to the other b. When the soliton moves up or down the chain it will convert phase a to b and *vice-versa* at little energy cost (Figure 5).

1.2.1 DOPING :- POLARONS, BIPOLARONS AND CHARGED SOLITONS

Real interest in conducting polymers grew when it was found that they could be made to conduct electricity when they had been doped. Doping of conventional semiconductors implies the use of small quantities of impurities (ppm scale) introduced into the crystal lattice. Conducting polymers often have as much as 1% - 50% by weight, of chemically oxidising or reducing material incorporated into them. Dopants are added to physically alter the number of π electrons on the polymer backbone leaving an oppositely charged counter ion alongside the polymer chain. This is achieved by a redox reaction. A π electron can be added or removed without causing alteration to the sigma backbone of the polymer so the charged polymer remains intact. Doping has a marked effect on the physical properties of the conducting polymer: the conductivity can be increased by as much as 11 orders of magnitude approaching the conductivity of copper.

During doping of a conjugated polymer, chain electrons are removed (p-type doping) or added (n-type doping). With polyacetylene altering the electronic structure of the backbone causes changes in the C - C bond lengths at the charged site. Such a species is termed a polaron if it is singly charged, and a bipolaron if it is doubly charged. In effect a polaron can be thought of as a radical ion associated with a lattice distortion. It is not necessary for the chain to be degenerate to support polarons and bipolarons with the result that the charge carriers in many of the conjugated polymers could take this form.[2,7] In poly(acetylene) bipolarons are unstable; instead polarons combine to form charged solitons.

1.3.0 *ELECTROLUMINESCENCE FROM SEMIONDUCTING POLYMERS*

The discovery in Cambridge of electroluminescence (EL) from semiconducting polymers came as a further surprise to the polymer world. electroluminescence occurs when a voltage is applied across a thin film of a semiconducting polymer. This bias excites the molecules in the polymer chain and the energy emitted as a result of that electronic stimulation is output in the form of light.[8] The polymer used in these initial studies was poly(*p*-phenylenevinylene) which will be discussed later (see section 1.5.0).

Patents ensued and the impetus had been provided for the development of light emitting polymers (LEP's) and devices thereof.[9] Electroluminescent polymers have been hailed as the next generation of materials for use in large area displays for which existing technology; cathode ray tubes and liquid crystals, are not entirely suitable.

The ideal LEP device would have numerous advantages over the existing inorganic devices in this class. Inorganic devices are fabricated using more expensive techniques such as chemical vapour deposition or sublimation and further to this these techniques do not lend themselves readily to the fabrication of large area devices for the manufacture of computer displays or TV screens. LEP devices can be fabricated from solution by dip or spin coating at ambient or near ambient conditions. Many potential applications of conjugated electroluminescent semiconducting polymers, have been foreseen, based on the combination of their electro-optical properties, mechanical strength, and easier processability; in the areas of optics and electronics for example, plastic lasers,[10] organic transistors.[11]

1.4.0 POLYMER LED DEVICES

Polymer LEDs were first made in the following manner. A 200 nm film of PPV was sandwiched between a transparent positive electrode of indium tin oxide and a negative electrode of aluminium (Figure 6). The negative electrode injects electrons into the film while the positive electrode pulls them out, a process which is equivalent to injecting positively charged holes. When an electron and a hole meet on the same part of the polymer chain this is the equivalent to an excited state (called an exiciton) which returns to the ground state by releasing a photon which we see as light. The interesting point is that these conjugated polymer LEDs do not require higher levels of conductivity. In fact, if the material is made will not emit light, because the hole transport is too rapid and there are not enough electrons present to form excitons (Figure 7).

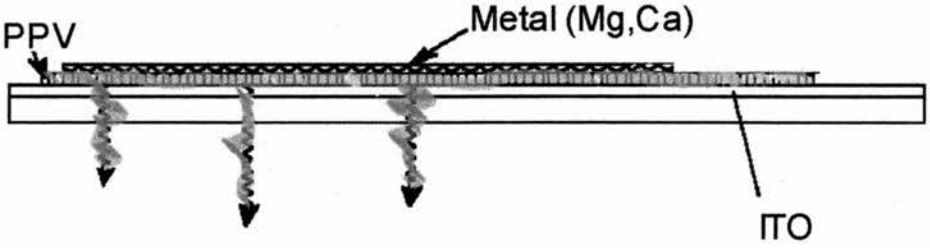


Figure 6 Schematic representation of a working polymer LED

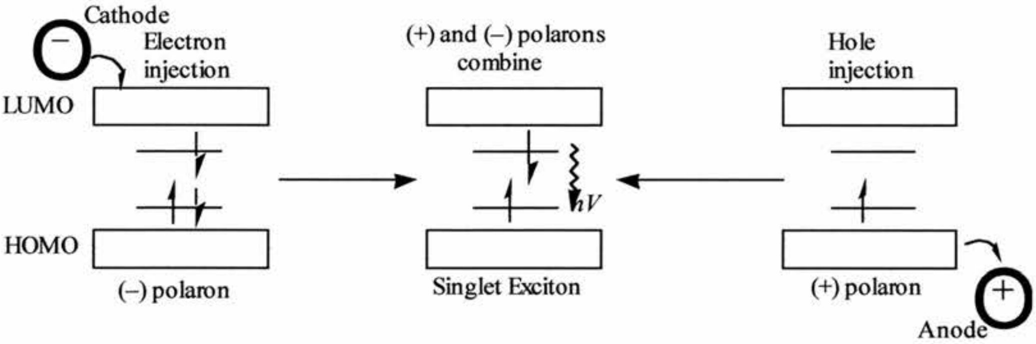


Figure 7 Diagram of polymer LED function

Colours vary with the band gap of the polymer, adjusting the conjugation length and the presence of electron donating / withdrawing group of the polymer backbone makes tuning the amount of energy the polymer requires to reach the excited state possible. Although most colours have been achieved the major problem with these systems is efficiency and longevity. The first LED devices that were made consumed large quantities of electricity and only returned a faint glow. Typically for every 10,000 electrons injected, only 1 photon was emitted (0.01%). A key breakthrough occurred in 1992 when a Cambridge group added another tier to the LED sandwich, the electron transport layer. This layer transports electrons with greater mobility than the light emitting layer and so eases the electron's passage from the negative electrode. While such a layer causes the electron's passage to be energetically favourable, it does so enough to make the hole's reverse trip energetically unfavourable. Since the change in work function impedes the progress of the holes, they must wait at the interface until they meet their electron partner. This causes fewer holes to be wasted and the addition of the transport layer increased the efficiency from 0.3% to 1.5% [1]. However a new polymer, poly(cyanoterepthalylidine), caused an increase from 1.5% to 4% efficiency, an efficiency comparable to that of inorganic LEDs. The added cyano groups increased the polymer's affinity for electrons and enabled it to serve as both a light emitting and electron transporting layer. A film of standard PPV was retained as a hole transport layer as it has always conducted holes very well.[17]

Polymeric LEDs continue to die young and the only clue to their failure is that there are microscopic black dots apparent after the device has failed. It is thought that these spots represent places within the polymer, where electrons and holes recombine and instead of emitting their energy as light, heat is emitted. Although the real reason for the spots is still unknown, it is apparent that when they form they continue to grow. Another theory is that each spot forms a kind of sinkhole that attracts more and more electrons with the consequence that no light emission is taking place. A dark spot on an LED not only ruins its display potential but it also stops electrons travelling far enough to light up other areas of the LED as well.

There are strong suspicions that the culprit could well turn out to be the electrodes themselves. These are made from highly reactive metals such as calcium or magnesium. On contact with water and air these metals may bleed ions into the polymer's light emitting layer, damaging the device. More theories include: (i) the light emitted by the device may be itself destroying it; (ii) the film may not be of uniform thickness causing thinner parts to attract too much current; (iii) Dust particles may be incorporated into the matrix (this could be eradicated by making the devices in a clean room). The amount of heat generated by the device could be limited by applying a pulsed current rather than a steady one.[1]

1.5.0 POLY (P-PHENYLENE VINYLENE) PPV'S

PPV's are seen as the most promising among the electroluminescent polymers. PPV is a bright yellow polymer, which emits green light at 551nm and 520 nm. The drawback of this material was that any direct polymerisation from the monomer led to a commercially unusable product, as once the material is fully conjugated it can not be disolved or mechanically altered. This all changed with the development of the soluble precursor route to PPV Figure 9 first by Wessling and Zimmerman[12,13] and was then subsequently modified by others.[14,15,16,]

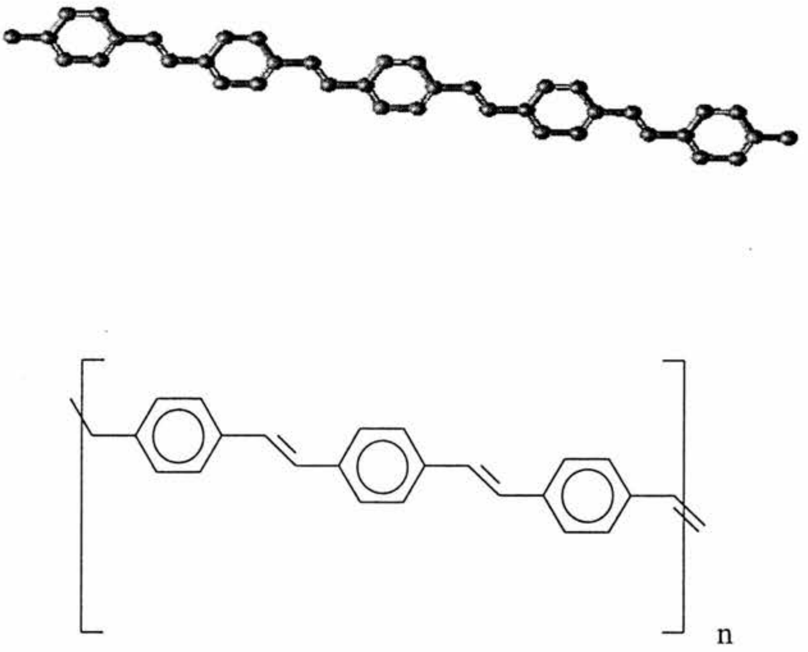
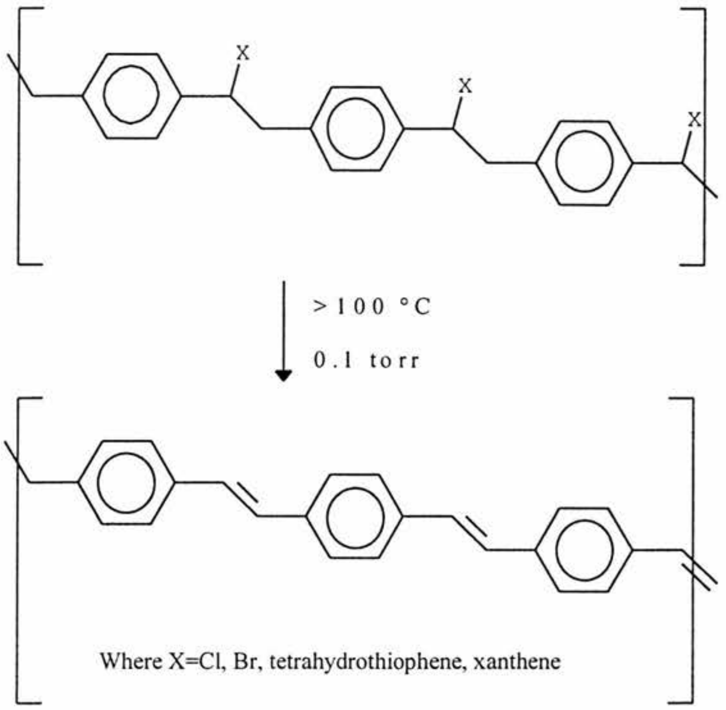


Figure 8 PPV

The Wessling precursor route involves the reaction of 1,4-bis(dichloromethyl)benzene with tetrahydrothiophene which forms the bis-sulphonium salt. Polymerisation is then induced to the precursor polymer stage by using less than 1eq of base to form the soluble precursor. The precursor polymer is then nutralised with acid and dialysed against distilled water to remove impurities and low molecular weight materials. The precursor polymer is then fabricated into thin films and the polymerisation is completed by heat treatment in the temperature range of 100-300°C in *vacuo* typically 10^{-6} mbar.[1,15] Structural variations in the precursor polymer in the sulphonium salt group or the type of counter ion in the polyelectrolyte have led to a variety of precursor polymers,which, in turn, have led to a variety of conjugated polymers that have tailored electronic or optical properties.[17]

The elimination step is the most important step, as incorrect conditions can lead to the formation of low EL efficiency PPV films. It has been found that preparation of films in a reducing atmosphere of nitrogen or hydrogen can inhibit the formation of carbonyl groups[18] and therefore improve the EL quantum efficiencies.[19] Performing the elimination step in such an atmosphere has the benefit of reducing the conversion temperature to that of approximately 100°C. This is sufficient to attain full conversion. This is important as it enables PPV films to be coated onto flexible substrates such as poly(etheylene terepthalate) (PET) or poly(propylene) (PP). Modified Wessling routes to PPVs have been used with varying success including the use of sulphinyl groups,[20,21,22] the use of a xanthate precursor polymer (which was soluble in organic solvents),[23] chemical vapour deposition (CVD).[24] Electropolymerisation,[25] and ring opening metathesis polymerisation (ROMP).[26]



Where X=Cl, Br, tetrahydrothiophene, xanthene

Figure 9 Soluble precursor route

1.6.0 *EFFECT OF SIDE CHAINS*

Conjugated polymers have inflexible chains leading to low solubility and difficulties in processing. The degree of conjugation has a direct effect on both the energy of the band gap and the solubility of the polymer. There are two ways of overcoming this problem:

(1) Saturated spacer groups placed in between each conjugated monomer unit of the polymer.

(2) Using long alkyl side chains on each of the monomer units.[27, 28, 29]

The effects of these strategies are as follows:

(1) The saturated spacer group approach alters the band gap of the polymer. This leads to a change in the wavelength emitted and therefore the colour of light emitted by the polymer.

(2) The use of long alkyl chains increases the interaction of the polymer with the solvents thereby increasing the solubility of the polymer and improves its processability. This method also allows the alkyl chains to insulate the polymer backbones against their affect on one another, decreasing the interchain annihilation of holes and electrons which affects the electroluminescence of the polymer adversely.[30]

Poly[(2,5-dialkoxy-1,4-phenylene)vinylenes] with one or two long solubilising alkyl chains dissolve in organic solvents.[31] Electroluminescence efficiency initially increases as the alkoxy chain length increases up to a limiting length. The efficiency decreases with a further increase in chain length.[32] Although mono and dialkoxy substituted PPV's can be made by the Wessling route,(10-14) The method by Gilch[33] is the preferred route. The mechanism shortens the Wessling preparation by two steps and proceeds by a base promoted 1,6-elimination of 1,4-bis(halomethyl)benzene derivatives.[34, 35] The most significant development in this area came from the synthesis of what has come to be known as MEH-PPV [36, 37] (poly(2-methoxy,5-(2'-ethylhexoxy)-p-phenylenevinylene). The branched ethyl-hexyl chain has been shown to have a favourable effect on the solubility of the polymer and is known to dissolve in tetrahydrofuran (THF), chloroform and xylene.

Electroluminescent devices have been made from MEH-PPV and 1.0% efficiency has been achieved. Addition of a hole blocking layer of poly(methylmethacrylate) (PMMA) via Langmuir-Blodgett techniques with aluminium cathodes has resulted in efficiencies of up to four times greater efficiencies. Adding a layer of acid doped polyaniline (PANi) (a known conducting polymer) in conjunction with the ITO layer reduces the drive voltage of the device and causes a considerable increase in the device efficiency.[38] Flexible electroluminescent devices have been fabricated by placing the active polymer onto PANi coated poly(ethyleneterephthalate) (PET).[31] Further advancements have been made with the recent introduction of poly(ethylenedioxythiophene) in conjunction with the ITO glass or by itself as the anode.[39, 40] Electroluminescent alkyl substituted PPVs other than MEH-PPV have been similarly prepared. [37, 41, 42, 43] If less than one equivalent of base is used, an α–halo precursor polymer can be obtained which can then be thermally converted in the Wessling manner. If the film formation is undertaken by CVD or through addition of excess base, incomplete conversion to a partially conjugated polymer occurs which may have advantages in increasing luminescence efficiency.

So far the drawbacks of perfect device fabrication have been many. These polymers prefer to be oxidised rather than reduced. This has had the effect that metals with a low work function such as calcium are needed in order to pump the electrons into the system. However, the weakest link in a polymer LED device is the metal contact. Metals such as calcium degrade easily under atmospheric conditions limiting the devices to use in inert atmosphere, which in turn limits the commercial potential of the devices. A replacement for these highly reactive metals must be found, the energy barrier for hole injection into the device will have to be lowered. This problem is being investigated through the use of copolymers.

The formation of statistical copolymers has been investigated and it was found that EL efficiencies were significantly increased for alkoxy substituted PPVs that show interrupted conjugation. This is not an isolated phenomenon, similar results have been found for other statistical copolymers having interrupted conjugation.[44, 45] It is important to get the balance right since shortening of the conjugated segments improves fluorescence yields and electroluminescence efficiency. On the other hand too many interuptions in the conjugation will lower the charge carrier mobility.

Improvements in electroluminescence efficiencies have also been reported resulting from the blending of conjugated polymers. Mixtures of MEH-PPV and poly(3-hexylthiophene) (both red electroluminescent polymers) have shown an increase in LED efficiency (1.7%) with a blend of 1 weight % of poly(3-hexylthiophene) to MEH-PPV. The cathode used in this case was a calcium cathode. Spectral studies of the system showed that the emitted light was originating from both polymers, although their combined efforts surpassed the individual luminescence efficiencies of each polymer singly. [46]

Still, the drawback of electroluminescent polymer devices is their short working lifetime, and this has hindered their popularisation. This is in part because of the polymers sensitivity towards oxidative degradation.[47] It has been shown that photo-oxidation produces carbonyl defects on the polymer chain.

These are believed to have the ability to quench fluorescence.[48, 49] Improvements to the design of devices, perhaps by methods of encapsulating the polymer in a suitable matrix, may put an end to problems caused as a result of oxidation and photo-oxidation of the polymers.

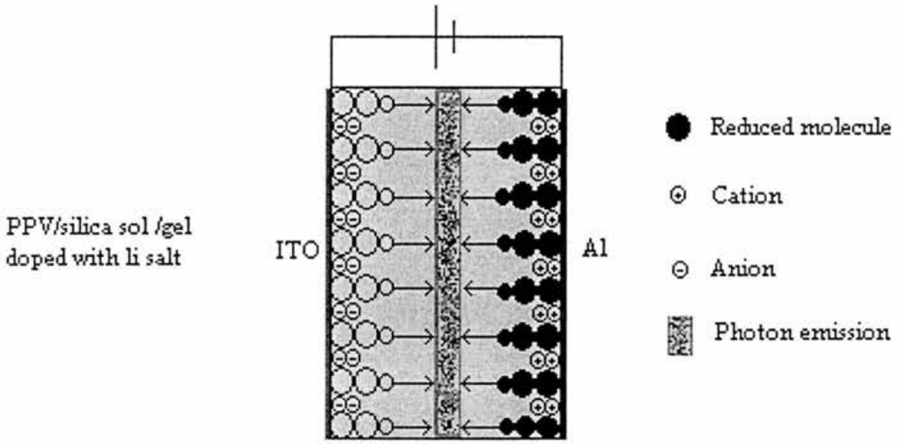


Figure 10 Electrochemical LED

Light emitting electrochemical cells (LECs) have recently been discovered.[50] These devices are fabricated from a blend of PPV and poly(ethyleneoxide) with a lithium salt (lithium trifluoromethanesulfonate, *commonly referred to as* lithium triflate) as the ion transporter.

A voltage applied in excess of the bandgap energy for PPV induces *p*- and *n*-doping of the regions adjacent to the anode and cathode respectively. A *p-n* junction is formed within the active layer, where positive and negative charge carriers combine with emission of a photon within the compensated *p-n* junction

(Figure 10). A two-colour LEC based on PPV and MEH-PPV[51] has been made which is tunable. Emission of red and green is available simply by changing the applied voltage.[52]

1.7.0 SOL-GEL CHEMISTRY AND PROCESSING

Most ceramic materials are made by traditional solid state chemistry in which control of ceramic growth is not usually approached from the molecular level. In contrast planned synthesis of organic polymers whose properties are controlled on a molecular level is commonplace within materials chemistry. Molecular control and the processing of ceramic materials provide an interesting opportunity to marry together the different areas of materials research namely solid state and polymer chemistry. Around the turn of the century attention was focused on colloidal sols, i.e. submicroscopically homogenous suspensions of solid particles in a liquid which can be manipulated chemically to form a gel.

The manmade synthesis of polysilicate gels from alkoxide precursors followed soon after the preparation of silicon tetrachloride ($SiCl_4$) in 1824. Publications in 1845 and 1846 showed that tetraethylorthosilicate could yield solutions that could be dried over time to produce optically pure materials.[53]

Sol-gel processes have been well studied and developed in the field of materials science since they are well-suited to preparing materials and to designing devices with specific properties.[54, 55] Sol-gels lend themselves to low temperature synthesis which permits the incorporation of organics and polymers within the pore structure (see section 1.7.2).

Sol-gel chemistry is divided into two main classes, depending on the nature of the precursor molecules:-

1. The inorganic precursor route involves the dispersion of the colloidal particles in a liquid to form a sol which upon catalysis, manipulation of pH or concentration undergoes gelation.

2. The alkoxide route appears to be the more versatile of the two.[56] The most important step in this route is the formation of an inorganic polymer by hydrolysis reactions during which the molecular precursor is transformed into a highly crosslinked solid in a one pot procedure.

Hydrolysis of tetraalkoxysilanes in an organic solvent such as alcohol leads to the formation of products with silanol functions. These form a colloidal dispersion of particles in a liquid i.e., a sol (by condensation polymerisation). The continuation of this process gives a continuous solid skeleton enclosing a continuous liquid phase, i.e. a gel. This transformation is considered the sol-gel transition and the gel point is described as the point in time (reaction) when the last link of the continuous network is formed.[57] The solid network is initially supple and allows further condensation and bond formation. This further reaction induces contraction of the network and expulsion of the liquid from pores, a process known as ageing. Drying of the gel by evaporation under ambient conditions gives a dried gel known as a xerogel.[55]

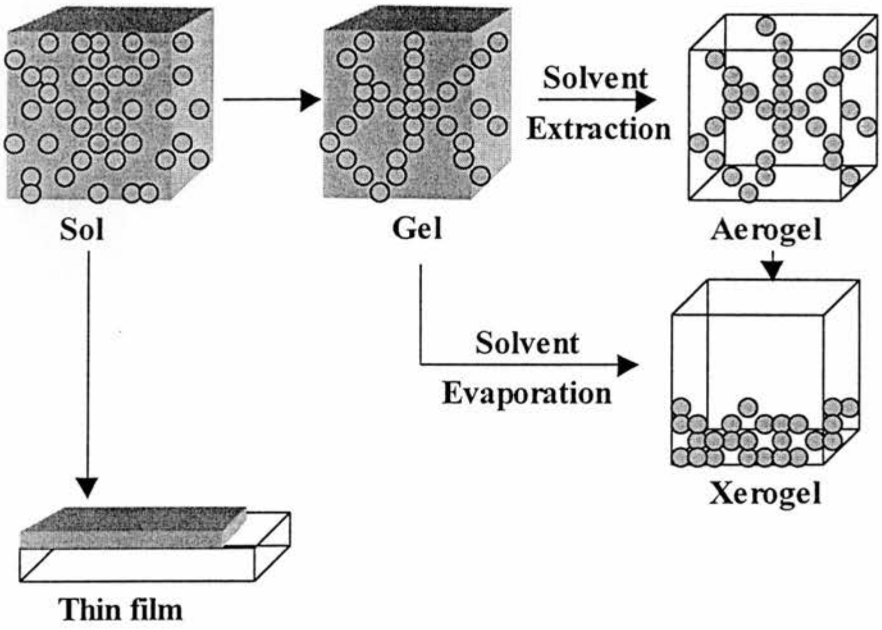


Figure 11 Sol-gel scheme of preparation

These materials are of use because of their high porosity and surface energy and are also used in the preparation of dense ceramics.[56] The advantage of the molecular approach lies in the fact that the materials can be processed in a number of ways such as monoliths, films, fibres and monosized particles or powders directly from the gel state (Figure 11). On a functional group level the synthesis of silicate gels can be described by three reactions, independent of whether a mineral acid or a base is used to catalyse the reaction. Alcohols such as ethanol are used to homogenise the mixture since alkoxysilanes are immiscible with water.

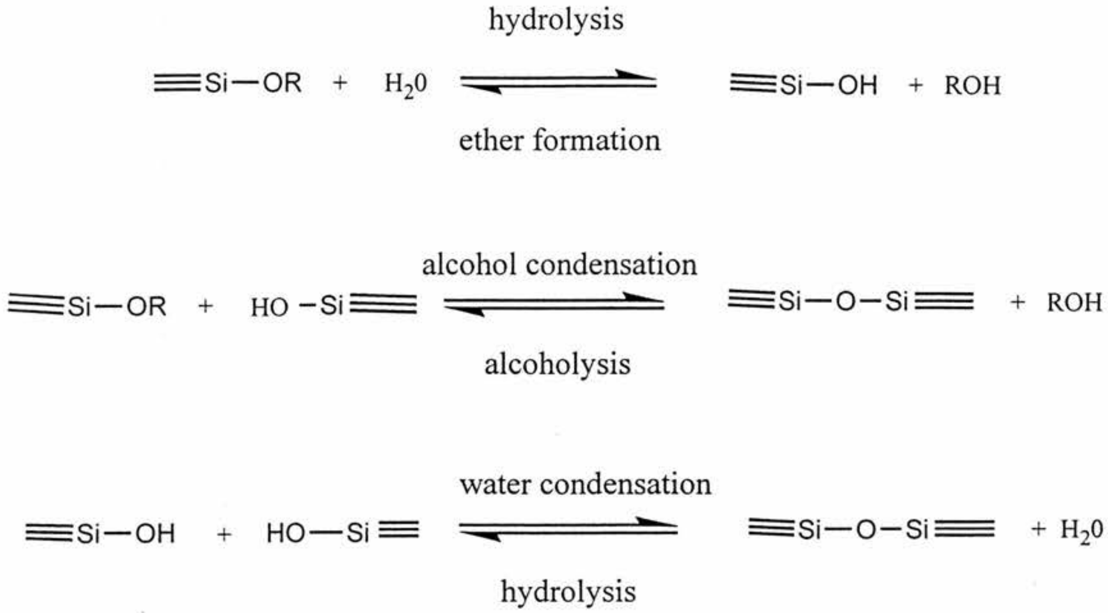


Figure 12 Basic Sol-gel reactions

1.7.1 REACTION MECHANISMS

The general mechanisms of sol-gel preparation of alkoxysilanes is well known.[58] It involves a nucleophilic attack by water at the silicon centre: the detailed mechanism is dependent on the choice of catalyst used, which may be: acidic, basic, or nucleophilic.

(1) Acid catalysis

There are two steps involved in acid catalysis: (i) reversible protonation of the alkoxy group which gives it a better leaving character: (ii) nucleophilic substitution by water or by silanol via a pentacoordinate intermediate. (Figure 13).

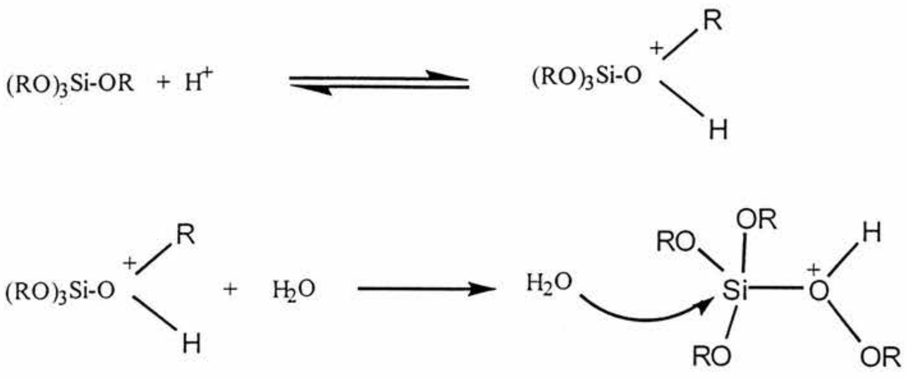


Figure 13 Acid catalysis [59]

(2) Basic catalysis

There are two steps involved in this mechanism also: (i) The nucleophilic hydroxide ion reacts with the alkoxysilane by nucleophilic substitution via the formation of a pentacoordinate intermediate and elimination of the alkoxide RO⁻; (ii) The catalyst forms by reaction with water; however, it is possible that the bases could act as nucleophilic catalysts (Figure 14).

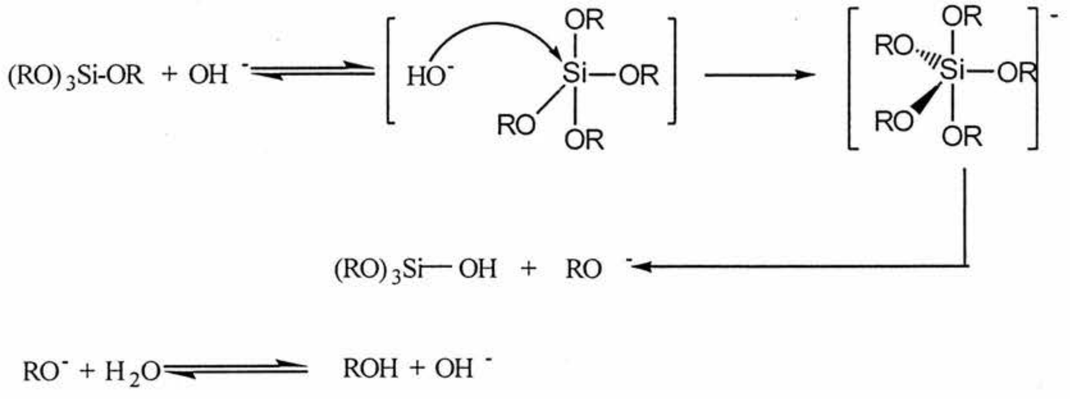


Figure 14 Basic catalysis [59]

(3) Nucleophilic catalysis

Nucleophilic catalysts such as F$^-$, HMPA, N-methylimidazole and N,N-dimethylaminopyridine coordinate to the alkoxysilane giving rise to a pentacoordinate silicon intermediate that is more reactive toward nucleophilic substitutions than the tetracoordinate species. The nucleophile coordinates to this pentacoordinate intermediate, leading to a hexacoordinate intermediate or transition state, which subsequently gives rise to the formation of alcohol and silanol and the catalyst is reformed (Figure 15).

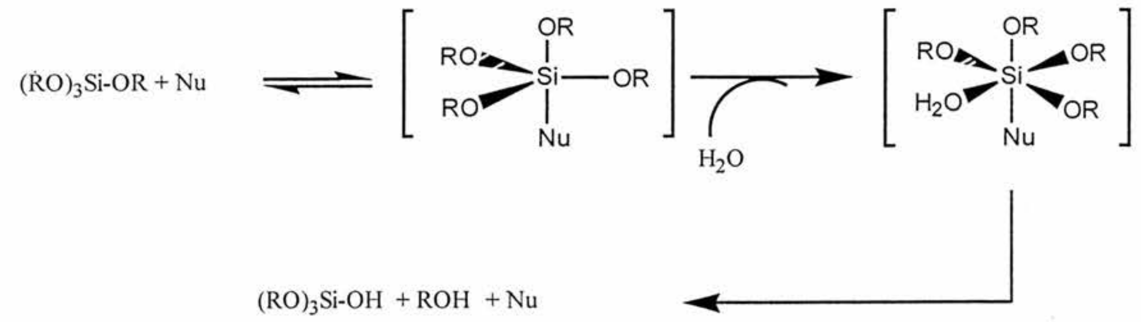


Figure 15 Nucleophilic catalysis [59]

However, these mechanisms are only the tip of the iceberg. Many simulations have been done based on different hypotheses. However, every small change in the experimental conditions (temperature, solvent concentrations, nature and concentration of catalyst) and external factors such as pressure, or sonication drastically modifies the texture, surface area, size and distribution of pores, density, processability etc [59]. The rate and the extent of hydrolysis is most influenced by the strength and concentration of the acid or base catalyst. The effect of temperature and solvent were found to be of lesser importance.

Hydrolysis of a solution of tetraalkoxysilanes, in an organic solvent such as alcohol, leads to the formation of products with silanol functions, which form a sol. These colloidal particles of silica are sometimes referred to as clusters. The clusters (colloidal particles of silica) continue to grow until the clusters collide then links are formed between the clusters. It is the aggregation of these clusters which eventually leads to the formation of a gel network. The network spans the whole of the container within which it is held and the the sol takes on an elastic solid appearance. This is known as the gel point. This is defined as the moment when the last link is formed in the chain of bonds that constitutes the spanning cluster, spanning from one side of the containment vessel to the other. (see Figure 11). The clusters are not completely connected to each other at this time but on ageing but all the clusters become interconnected to form the network structure and this is indicated by the increase in the stiffness of the gel and its shrinkage and eventual transition into a glassy state. The ageing process occurs in a series of steps which have been described as polymerisation, shrinkage coarsening and phase transformation.

Polymerisation as the name suggests is the continuation of bond formation increasing the connectivity of the network. This occurs via condensation reactions as described in section 1.7.0. These reactions have been followed by NMR and Raman spectroscopy and indicate that this process continues long after gelation has occurred.[60, 61] These condensation reactions also result in shrinkage and progressive strengthening and stiffening of the gel during ageing. These events depend in the same way on the physical reaction conditions as gelation itself i.e. temperature, pH, concentration and composition of the reaction media.

1.7.2 APPLICATIONS OF SOL-GEL MATERIALS

The high porosity of a dried gel is one of the most desirable of its features. The low refractive index (RI) of these materials makes them ideal for optics applications and their surface area makes them useful as catalytic substrates. This is particularly the case for supercritically dried sol-gels (aerogels). The high porosity of these gels and their low thermal coefficient also makes them suitable for thermally insulating windows.[55] The ability to prepare macropores or micropores makes it possible for gels to contain optically active molecules polymers to produce composites. This along with the optical purity and conductivity properties makes these materials of interest in many different areas of materials research. Advantages and disadvantages of the sol-gel process can be seen in table 1. [55]

For example silica-based composite materials with superior thermal stability and mechanical properties have been prepared with [$Tb(bpy)_2^{3+}$] and tetraethylorthosilicate by the sol-gel method and was found to be an excellent green emitting material which was heat stable to 150 °C The relative intensity was found to be higher than that of existing inorganic complexes used in luminescent lamps.[62] Encapsulation of laser dyes such as rhodamines and coumarins has been achieved; these hybrids show optical gain and laser action.[63]

Advantages
Better homogeniety from raw materials
Better purity from raw materials
Lower temperature of preparation
New non-crystalline solids outside the range of normal glass formation
New crystalline phases from new non-crystalline solids
Better glass products which arise from the special properties of the gel
Special products such as films.
Disadvantages
High cost of raw materials
Large shrinkage during processing
Residual fine pores
Residual hydroxyl and carbon
Health hazards of organic solvents
Long processing time

Table 1 Advantages and disadvantegs of sol-gel processing

1.7.3 INORGANIC / ORGANIC HYBRIDS:- COMPOSITE MATERIALS

Inorganic–organic hybrid materials of sol-gel materials, otherwise known as **Or**ganically **Mo**dified **Si**lica (ORMOSILs) have become of interest over the last few years. This area of research spans a huge range of interests including inorganic oxides as fillers for organic polymers to the incorporation of organic molecules covalently bound to silica.

The field of inorganic organic hybrid materials is still a new field and therefore the potential of these materials have not yet been fully explored. Some of the applications which have been explored are hybrid gels of polysiloxanes with phenylene bridges have been used as the matrix for the quantum confinement of semiconductor particles of CdS or nanosized CdS similarly nanoclusters of Cr^{0} have been formed in situ by complexation of $Cr(CO)_3$ groups onto the phenylene bridges of polysiloxanes. The incorporation of inorganic ions into silica gels and glasses is of the utmost interest for many technological applications including solid-state lasers and phosphors. Sol-gel processing is attractive for synthesising these materials as it is a low temperature method of creating glasses and ceramics. These hybrid materials would have favourable physical properties. The silica network provides good mechanical resistance, good thermal stability as well as good optical properties [63,59].

1.8.0 PROGRAMME OF RESEARCH

Overall aims

The general aims of this project were to synthesise and evaluate new composite materials for the electronics industry. The approach taken for this project was by using the information gained from the individual evaluation of the component parts of the composite (substituted PPVs and Sol-gel). To that end the synthesis and characterisation of organic luminescent polymers and inorganic polymers formed by the sol gel route were undertaken before the composite materials were formed and adapted for use as materials suitable for LED devices.

Chapter 2: Synthesis and characterisation of alkoxy substituted PPVs

Following on from the recent intense interest in the field of electroluminescent polymers. The main objectives of this project are to understand better the synthesis and structure-property relationships of alkoxy substituted PPVs, to gain an insight into their action and to use the information gained from these findings to design new materials with new or enhanced properties for use in technological applications.

The objectives of this section of the project were:

- The synthesis and characterisation of some alkoxy substituted PPVs via a precursor route.

- To gain structural information on the polymers in their precursor state and also in their fully conjugated state.
- To study the photochemistry and light emission characteristics of each polymer.
- To fabricate LEDs in conjunction with The University of Durham and to study lifetimes and quantum yields of this group of polymers. Any working devices could then be used to answer other questions such as the stability of the polymers and to allow further work in the field of improving efficiency and device lifetime by chemical and mechanical alterations.

Chapter 3: Preparation of PPV/sol-gel composites.

The main aim of this work is to develop a new class of LED devices based on emissive polymers and metal complexes so as to overcome the inherent efficiency limitations of organic devices. The polymers/complexes are to be immobilised in sol-gel processed silica glass. The sol-gel method provides a relatively quick, simple, low temperature method of doing this. Immobilised luminescent materials are believed to be more durable than thin molecular films. The glass is also thought to help in the preservation of the luminescent properties of the embedded materials.[63]

The objectives of this section of the project were:

- To prepare composite materials from alkoxy substituted PPVs and sol-gel derived ceramics.
- To evaluate the photochemical behaviour of the polymers within differing sol-gel derived materials.
- To study the effect of the sol-gel matrix on the stability of the polymers.
- To investigate the methods of thin film formation and device fabrication of these hybrid materials.
- To optimise the formulation of these materials for potential technological applications.

Chapter 4: Electrochemical LED Materials

Another area of continuing interest is the solid dye laser. Various laser dyes, of polymer materials, have been incorporated into silica materials in search of the solid dye laser. A fair amount of success has been obtained in the visible part of the spectrum. Encapsulation of laser dyes such as rhodamines and coumarins in sol-gel materials has been achieved and these hybrids show optical gain and laser action.[63]

Some concerns have been expressed over the efficacy of sol-gels as matrices for composite LED devices. Sol-gel processed silica has the same properties as glass. Although it has been shown that these properties have many useful attributes which impart beneficial properties to the encapsulated material, there may also be drawbacks to this kind of material. The primary concern seems to be that the matrix may not be adequately conductive. It is possible that these problems could be eradicated by drawing from the field of solid electrolytes. Lithium ion conducting solid electrolytes continue to be an active area of research due to the considerable progress made in the fields of lithium secondary batteries, electrochromic devices and electrochemical sensors, gel electrolytes and plasticised polymer electrolytes [63, 64, 65]

The objectives of this section of the project were:

- To prepare conducting sol-gel materials.
- To evaluate the conductivity by electrochemical means.

To prepare conducting sol-gel/PPV composite.

- To expand the possibilities of sol-gel derived luminescent materials by the incorporation of luminescent dyes.
- To prepare conducting sol-gel/luminescent dye composite.
- Preparation of electrochemical LED.

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Chapter 2

Synthesis and characterisation of PPVs

2.0.0 INTRODUCTION

Poly-*p*-phenylenevinylenes (PPVs) are seen as the most promising candidates among the conjugated polymers for the active layer in light emitting polymer (LEP) diodes.[1] In addition, the synthesis of PPVs is a well-known and versatile procedure, usually following the soluble precursor polymer route. Structural variations in the precursor polymer in the sulphonium salt group or the type of counter ion in the polyelectrolyte have led to a variety of precursor polymers, which, in turn, have led to a variety of conjugated polymers that have tailored electronic or optical properties. In particular, the nature of the polymer substituents has been shown to tune the band-gap of the polymer [2-9] and so change the wavelength of the emitted light. PPVs with alkoxide substituents, for example, have a band-gap shifted from ca. 2.3 eV (green light emission) to 2.1 eV (orange light emission). [10,11]

The use of large, bulky substituents appears to influence the photophysics of the PPV. They may have the effect of stiffening the polymer backbone, leading to a reduction in the amount of non-radiative decay and an increase in quantum efficiency of luminescence.[12] On the other hand the non-radiative singlet exciton decay in MEHPPV(poly(2-methoxy,5-(2'-ethyl-hexoxy)-p-phenylenevinylene), polymer (R=2-ethylhexyl, R'=Me)) is faster than in PPV due to the lower degree of crystallinity in the former[13] or perhaps non-radiative decay through side-chain vibrational decay. There is also thought to be an influence of substituents on the alignment of neighbouring chains.[14],[15] The alkyl chains serve to prevent the interchain quenching of intrachain triplet excitons[16], a phenomenon which is particularly evident in CN-PPV[17]. Time-resolved luminescence measurements from MEH-PPV show a marked dependence on the intensity of the excitation light: at low energies long-lived PL from interchain excitons is observed.[18]

Finally, the introduction of substituents may have a desirable effect on LED fabrication methods. Solubilising alkyl or alkoxide substituents on the monomer tend to increase the solubility of the final PPV so that it can be prepared directly in its fully conjugated form without the need for purification of the precursor polymer and the post-spinning baking step. Soluble conjugated polymers can be studied both in solution and in the solid state. Thus MEH-PPV luminesces strongly in solution and behaves much like a laser dye.[19] Lasing behaviour is observed in the solid state.[20] The solubility allows doping (e.g. with C_{60}) for efficient quenching of the exciton emission,[21] and the solubility also lends itself to the fabrication of blends prepared with other soluble polymers, leading to much enhanced device efficiency in many cases[22], inorganic sol-gel solutions[23,24] and the polyelectrolyte composite blends used in the new electrochemical devices.[25] One of the biggest drawbacks remaining for polymeric LEDs is their short working lifetime. To be useful in flat panel displays a polymeric LED would need a lifetime of several thousand hours, but so far most devices have fallen short of this goal.

PPVs **1-5** (Figure 4-8) were prepared, these polymers show considerably enhanced solubility compared to PPV. These were prepared from the bis-halomethyl monomers by the so-called chlorine precursor route (CPR)[26,27] or Gilch route[28, 29, 30] which involves the base-induced elimination of HX-). This route has been used extensively to make PPVs and derivatives[31A-E] and has recently been reviewed.[32] This route was chosen because of the simple halogen leaving groups involved in order to facilitate the characterisation of the products spectroscopically and thermally.

Of the polymers discussed here, only the dihexyloxy derivative **2** [26] and dimethoxy derivative **3** [33] have previously been reported, the latter prepared by a different route. Polymer **5** carries the same 2-ethylhexyloxy substituents as used in the, widely used and well known MEHPPV (poly(2-methoxy,5-(2'-ethyl-hexoxy)-p-phenylenevinylene), first reported by Heeger and also prepared by the chlorine precursor route from the methoxyalkoxydibromo-xylene monomer.[34] Since there is a need for the greater understanding of these polymers in solution and during the preparation procedure[35] we also report gel-permeation chromatography (GPC), thermal gravimetric analysis (TGA) and NMR data for the polymers.

2.1.0 TECHNIQUES (INSTRUMENTS USED)

2.1.1 THERMAL ANALYSIS

The story of thermal analysis starts back in the sixteenth century with the first account of thermometry. However the practical calorimetry was not defined until the eighteenth century with the advent of thermometric scales. This sparked off interest in the area with Lavoisier and Laplace, Fourier and Joule all contributing to our modern understanding of the subject. Thermal methods of analysis are now used in a wide variety of applications from quality control to geology. The International Confederation for Thermal Analysis and Calorimetry

(ICTAC) definition of thermal analysis is as follows: a group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample in a specified atmosphere, is programmed. The programme may involve heating or cooling at a fixed rate of temperature change, or holding the temperature constant, or any sequence of these[36].

2.1.3 SIMULTANEOUS THERMAL ANALYSIS

Thermal analysis techniques have been used for a wide range of materials analysis, not least of these being in the domain of polymeric materials. Thermal analysis as a tool has been used not only in research but in a wide variety of applications such as product development quality control and assurance as well as for purity testing product and furthermore as an analytical vessel for applications such as comparison studies.

With regard to polymer materials research effects such as glass transition temperature, degree of crystallinity, extent of cure, specific heat capacities, thermal stability, pyrolysis and oxidative decomposition can be measured accurately and speedily, which facilitates the tailoring of these materials to specific applications. When you consider that the processing of such materials will involve heating, cooling or ageing it is of primary importance to understand the effect such conditions will have on the materials. Commonly used techniques in the determination of a materials thermal behaviour are differential scanning calorimetry and thermogravimetry. These techniques have been reigning champions among the thermal methods used to study polymeric materials. However, the STA technique of simultaneous analysis is becoming an invaluable tool as it has many advantages over the single methods and is contributing to a better understanding of how materials will behave during processing (Figure 1).

This type of instrumentation has numerous advantages over the two parent techniques even when separately or even side by side [37]:

(1) No loss of sensitivity or resolution due to small sample size (1 - 10 mg)

(2) No problem of sample inhomogenity

(3) Accurate correlation of observed effects

(4) Weight measurement validates quantitative measurements from DSC experiments: Phase changes, melting and purity measurements can sometimes be associated with decomposition or volatilisation. These can immediately be detected. If a weight loss occurs prior to the reaction of interest, the true sample weight at the onset of this reaction will be known and any quantitative calculations will be valid.

(5) Detection of moisture content: (a) moisture levels can be detected also by observing weight losses over the appropriate temperature range and (b) the level of moisture may affect the physical properties for example this method ensures that the phase change value that is obtained for a glass transition is that of a sample of known moisture content.

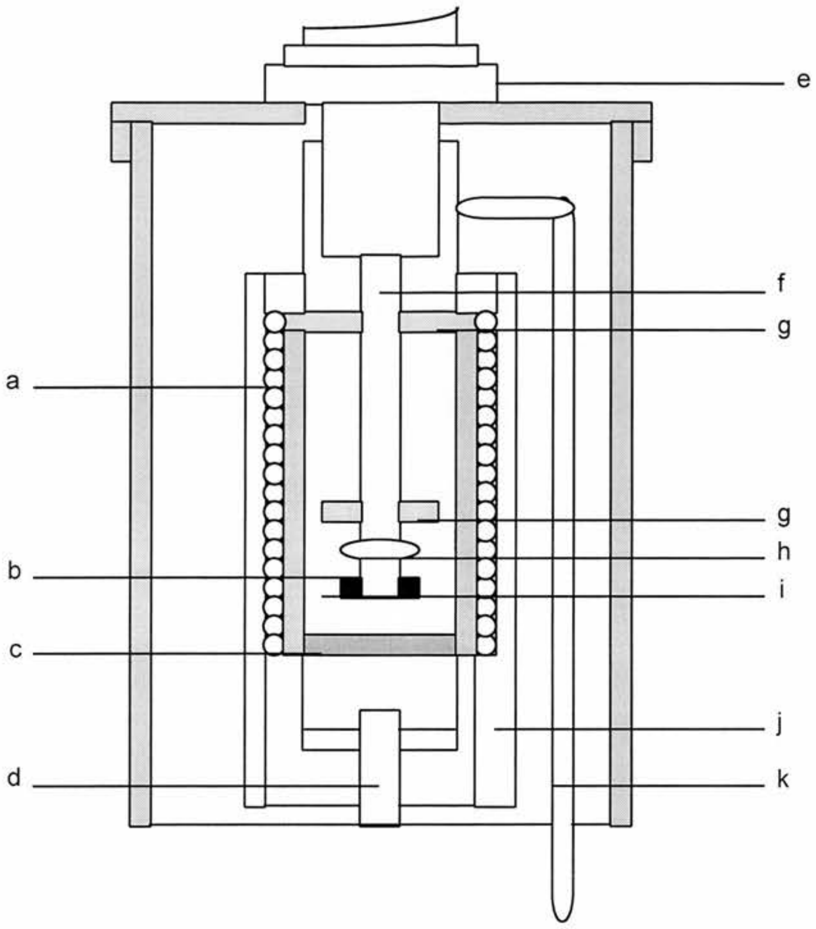


Figure 1

a = Mineral insulated graded heating element

b = sample and reference crucibles.

c = Fixed compartment divider with gas flow ports.

d = Gas entry tube.

e = Water cooled cold finger.

f = Ceramic hangdown protector tube.

g = Movable baffle plates with gas ports

h = Four bore ceramic hangdown suspended from electronic microbalance

i = Rigid heat flux TG - DSC plate

j = Liquid nitrogen cooling jacket

k = Side branch gas exit pipe.

The thermal analysis was carried out on a Rheometric scientific STA 625. The instrument specifications are as follows.

Instrument	STA 625
TA facility	TGA - DSC
Temperature range	-125°C to 625°C With autocool facilities
Furnace	Specially profiled alumina tube, non inductively wound
Furnace winding	Sheathed NiCr
Furnace cooling	With Liq N_2
TGA mass ranges	0 - 50 0 - 100 0 - 200 0 - 400mg
inc. Automatic Tare	17mg 35mg 75mg 150mg
TGA readability	0.5mg 1mg 2mg 4mg
Max. balance capacity	3.5g
DSC sensitivity	< 5mw
Crucible size	50 - 100ml
Crucible material	Aluminium

Table 1 Technical Specification for STA 625

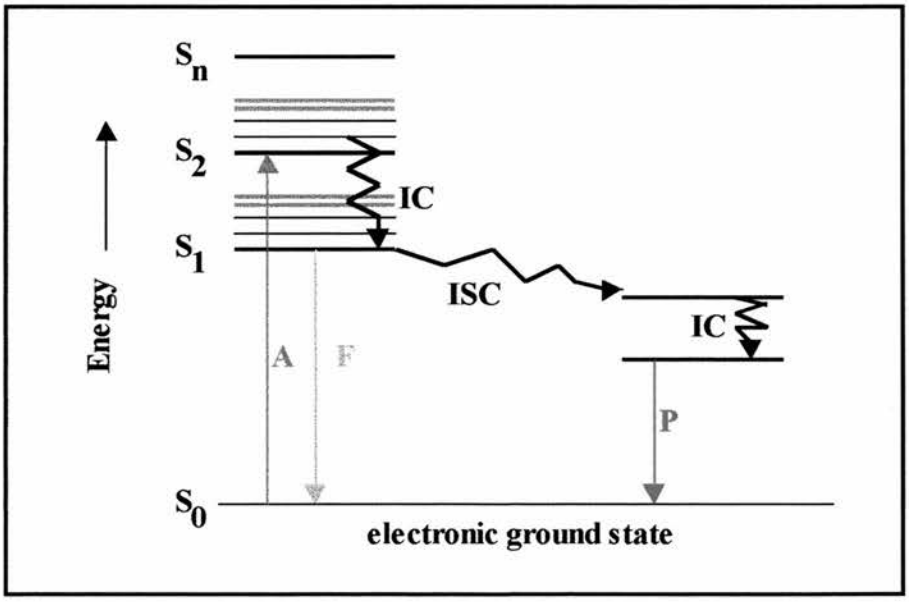
The samples in powder form (8 - 17 mg) were analysed at a heating rate of 10°C min. (unless otherwise stated) to 600°C and the runs were conducted in a dynamic nitrogen flow rate of 44 ml min^{-1}.

2.1.4 PHOTOLUMINESCENCE SPECTROSCOPY

Photoluminescence (PL) spectroscopy can be described as the recording of fluorescence or emission spectra and excitation spectra of the polymers. Usually, the excitation spectrum has the same form as the absorption spectrum, since the more light that is absorbed by the molecule the greater the number of photons that will be emitted.

Figure 2 Jablonski diagram illustrates the basis of PL spectroscopy. The sample is exposed to light from a source and absorbes a photon of radiation which is depicted as process **A** on Figure 2. This correspondes to an electron being excited to a higher energy level. After the initial absorption S_o-S_2 (Figure 2) the upper vibrational states undergo radiationless decay by giving up energy as heat to the surroundings **IC**. A radiative transition fluorescence **F** then occurs from the ground vibrational state of the excited energy level to the ground state. In phosphorescence the singlet excited state undergoes intersystem crossing **ISC** to a triplet state prior to slow radiative emission.

The distribution of wavelength-dependent intensity that causes fluorescence is known as the fluorescence excitation spectrum, and the distribution of wavelength-dependent intensity of emitted energy is known as the fluorescence emission spectrum.



S_0=ground state S_1,$S_2$and S_n=excited states IC=internal conversion
ISC=Intersystem crossing A=absorption F=fluorescence P=phosphorescence

Figure 2 Jablonski diagram

Fluorescence detection has two major advantages over other light-based investigation methods: high sensitivity and high speed.

Sensitivity is an important issue because the fluorescence signal is proportional to the concentration of the substance being investigated. Whereas absorbance measurements can reliably determine concentrations only as low as several tenths of a micromole, fluorescence techniques can accurately measure concentrations one million times smaller pico- and even femtomolar. Quantities less than an attomole ($<10^{-18}$ mole) may be detected.

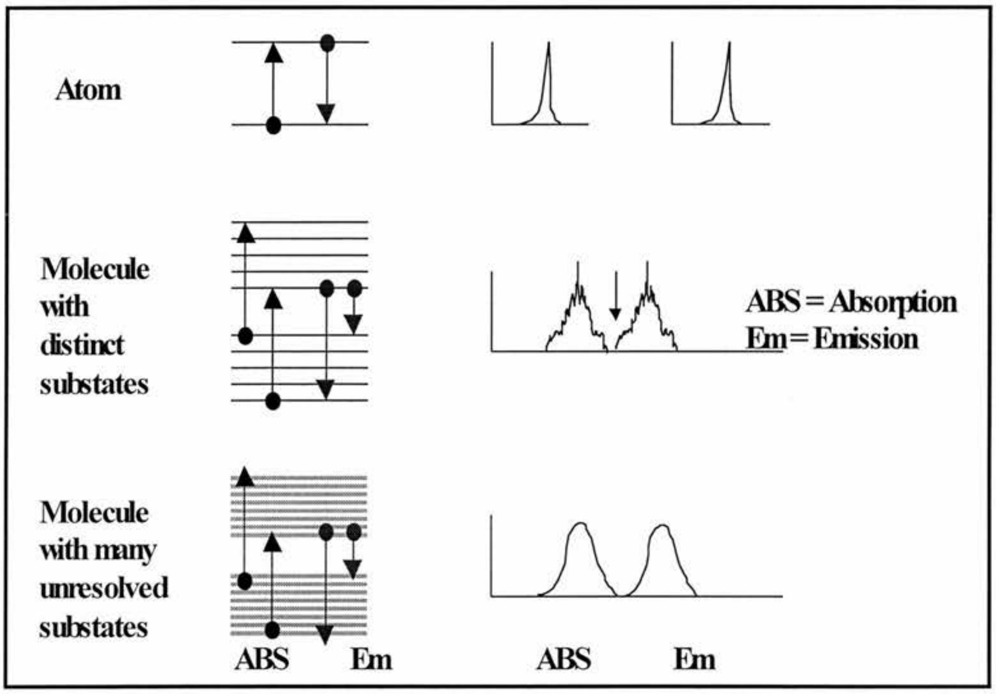


Figure 3 Characteristic absorption and emission patterns of atoms and molecules

This can be very useful, if as in this case, the absorption spectrum is difficult to measure, or if it is in the solid state. Note that only the emission spectra of atoms give sharp peaks. Electronic transition states are well defined and so their absorption and emission spectra are very narrow band frequencies (Figure

3 upper diagram). The excitation spectra of molecules although usually giving much broader peaks (when compared to the excitation spectra of atoms) can sometimes display vibrational fine structure (sometimes termed vibronic, or phonon sidebands) because the transition states are less defined (Figure 3 middle diagram). The third case is with molecules in solution, a broad band is observed each absorption and emission corresponds to a single electronic transition (Figure 3 lower diagram)

2.2.0 *SYNTHETIC ROUTES TO ALKOXYSUBSTITUTED PPV'S*

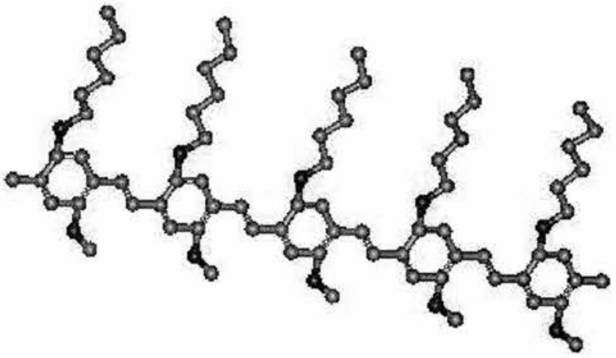


Figure 4 OMeOHEX PPV [1 (pcm37)]

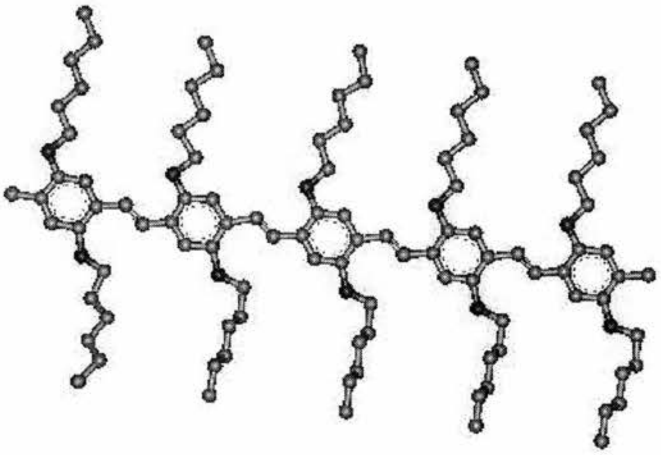


Figure 5 OHEX OHEX PPV 2 (pcm38)

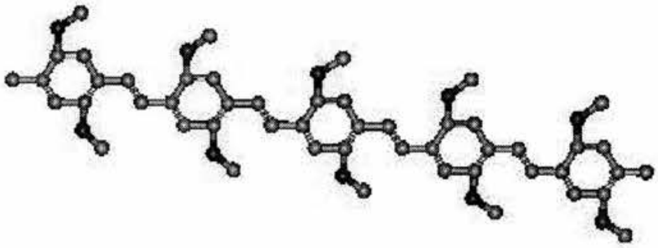


Figure 6 OMeOMe PPV 3 (pcm39)

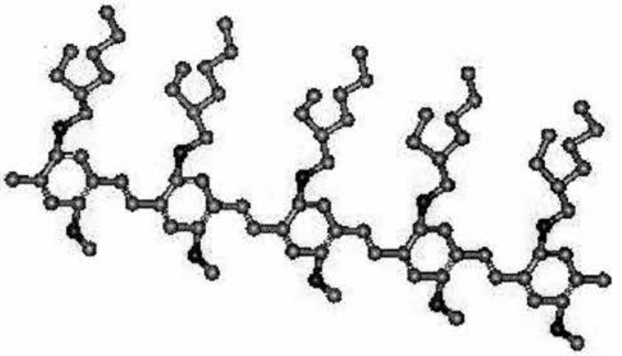


Figure 7 OMEH OMe PPV 4 (pcm52)

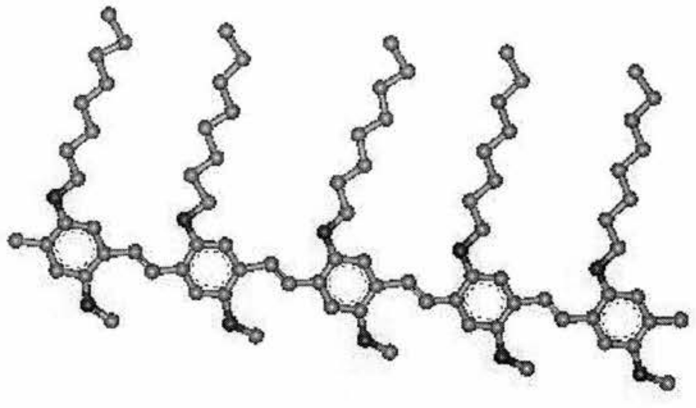


Figure 8 Ooct OMe PPV 5 (pcm51)

2.2.1 MODIFIED WILLIAMSON SYNTHESIS

The mono and diaryloxylated aromatic monomer building blocks were synthesised by the modified Williamson synthesis shown in Figure 10. Firstly, an aryloxide was prepared by the action of a base on the alcohol, then reacted with an alkyl halide to produce the ether. Figure 9 shows all the ethers synthesised that were used successfully in polymerisation reactions. Other ethers were made but were not successfully used to form polymers.

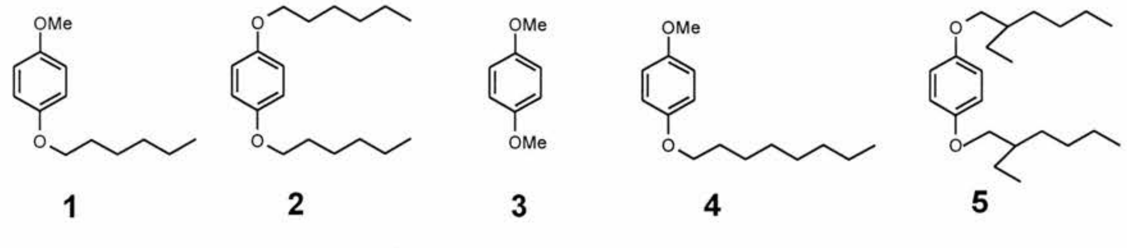


Figure 9

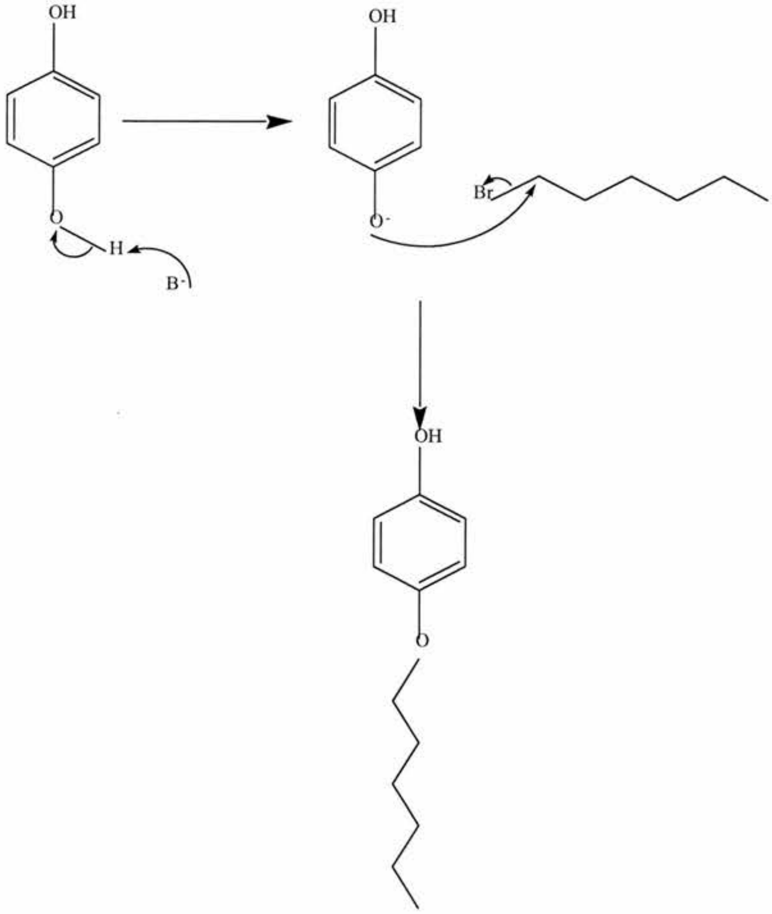


Figure 10 Modified Williamson synthesis

Figure 10 is the general mechanism used to synthesise all of the molecules, except in the preparation of 1-methoxy-4-hexyloxybenzene and 1-methoxy-4-octyloxybenzene, where *p*-methoxyphenol was used as the starting material rather than hydroquinone. These reactions and the product purification proved straightforward. The materials produced were of high quality and free from impurity, as shown by the NMR values.

The halomethylation reaction was used to convert the alkylphenols and benzenes produced by the Willamson synthesis. Halomethylation of an aromatic system is usually achieved by reaction of the aryl system with formaldehyde via a Friedel-Crafts alkylation reaction in the presence of HCl. The reaction is believed to begin by protonation of the formaldehyde, effectively creating a carbocation that is readily attacked by the electron rich π system of the aromatic ring.

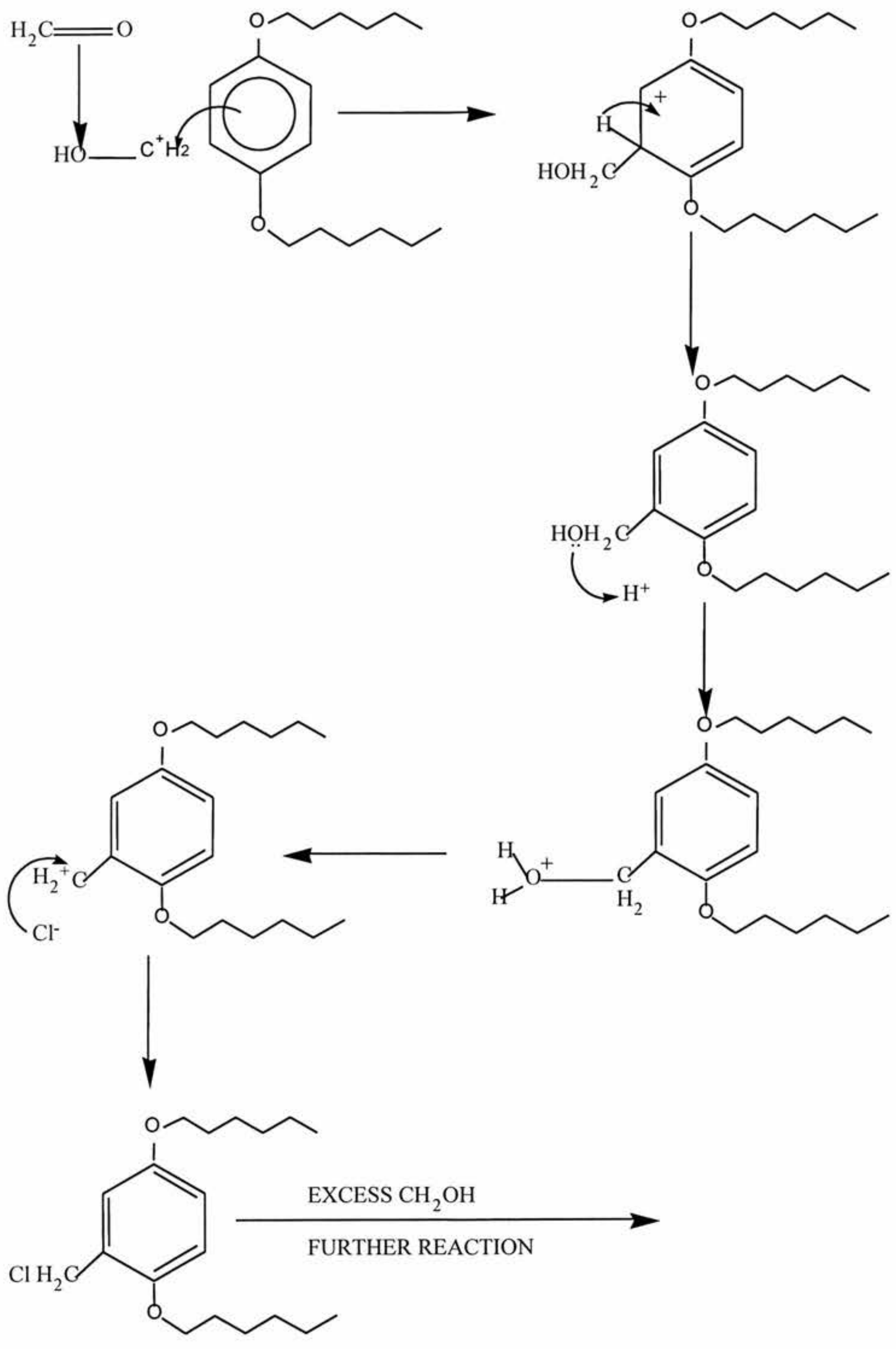
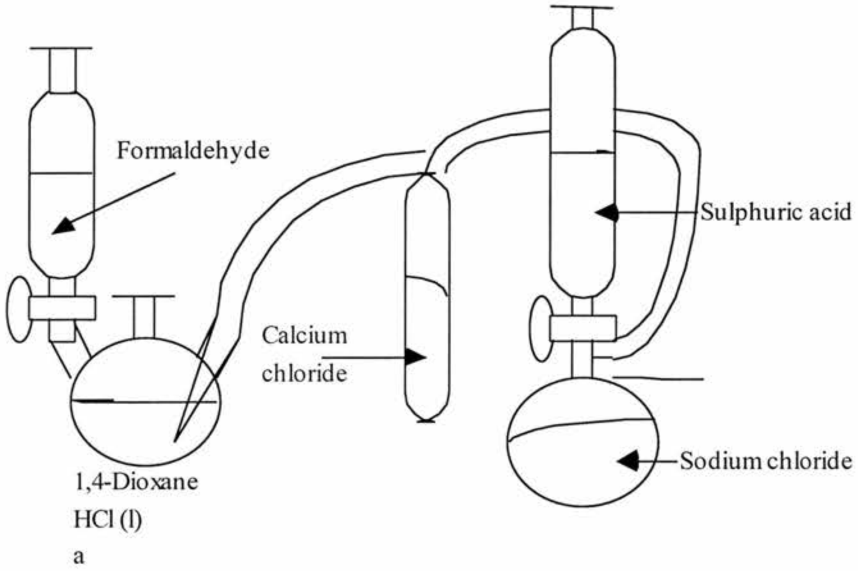


Figure 11 Halomethylation

In the presence of a Lewis acid catalyst aromaticity is regained following deprotonation of the ring, and the alcohol is formed. The OH group can then be substituted by a chloride ion, in the presence of excess formaldehyde, and in relatively concentrated solutions, the para disubstituted product is obtained as the major product. This reaction mechanism can be seen in Figure 11.

A number of difficulties were encountered while carrying out this reaction. The first two successful attempts were made using a gas-generating apparatus which employed sulphuric acid and hydrochloric acid to generate the gaseous HCl. On optimising the conditions for the chloromethylation reaction a change was made in the HCl generator used in the reaction, to a more convenient apparatus which is described as follows.



where a = mono and di alkyl substituted aromatics

Figure 12

This HCl gas generator involves the reaction of H_2SO_4 on NaCl which forms HCl (g) cheaply and simply. Figure 12 shows the experimental setup for a typical chloromethylation reaction. This is combined with a HCl generator in order to produce the gas *in situ.* The practical procedure for this apparatus involves adding sulphuric acid dropwise from a dropping funnel onto sodium chloride which releases the HCl gas. It should be noted that for 5 hours of gas generation a $1dm^3$ round bottomed flask should be employed. The sodium chloride should be added in batches as the sodium sulphate formed forms a hard impenetrable layer over the sodium chloride and prevents further reaction. In addition to this severe fizzing can occur if the flask contains too much NaCl. The HCl gas produced then passes through a drying tube filled with calcium chloride before being bubbled through the reaction vessel. This method of HCl generation, however, is not easily regulated and if used in conjunction with a paraffin bubbler it must be carefully monitored as suck back can occur with only a few seconds of unregulated gas flow.

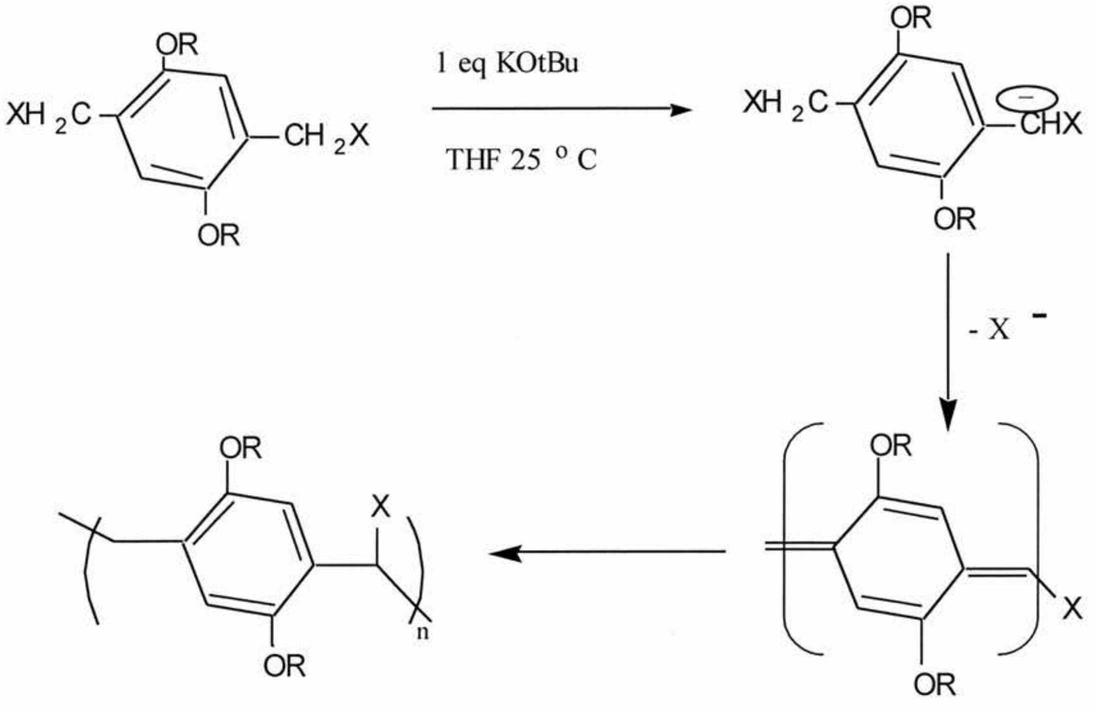
No difference should have been observed in the reaction between the two methods of gas generation, so the optimisation of the chloromethylation reaction was set to again. Purification of the starting materials and increasing the concentration of the attacking nucleophile had no effect. No chloromethylation had taken place. For experimental details see section 2.4.17

Eventually amethod by Swatos and Gordon [26,38] was employed which involved the use of mineral acids, paraformaldehyde and heat (95-110°C) This method was more successful in chloromethylation. This suggests that the presence of a mineral acid helps the reaction and that the old apparatus was letting through gaseous sulphuric acid which was promoting the reaction. The new generator was producing pure HCl gas and was therefore not as successful. The method by

Swatos and Gordon[26] was therefore employed in the subsequent chloromethylation reactions. These compounds were also bromomethylated using the same procedure substituting the HCl gas and liquid with HBr (Supplied by Aldrich) with the same success.

2.2.3 POLYMERISATION TO PRECURSOR

Base induced polymerisation to precursor polymer is shown in Figure 13



Where X=Cl, Br

Figure 13

2.2.4 POLYMERISATION TO PARTIALLY CONJUGATED PPV

The polymerisation reaction to give the precursor polymer was carried out by the method by Swatos and Gordon[26]. This procedure was very easy to duplicate and the products produced were found to be most soluble in decreasing order chlorobenzene, DMF, THF benzene, toluene and chloroform. The final step of the synthesis conversion of the precursor polymer to the fully conjugated polymer (100°C 0.1 torr. Figure 14) was omitted at this time in order to maintain solubility for characterisation purposes.

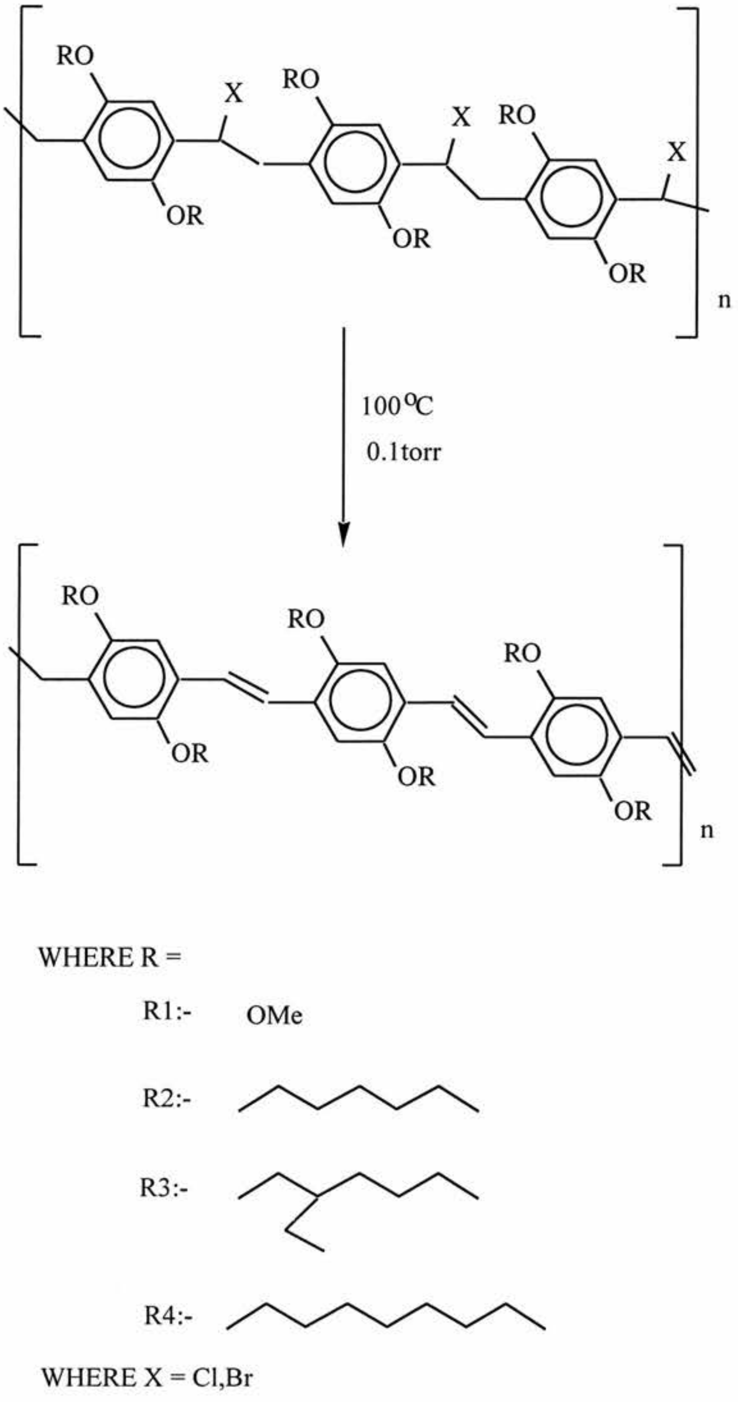


Figure 14

2.3.0 *SPECTROSCOPIC STUDIES OF PPV'S*

NMR traces were obtained using deuterated chloroform. Figure 15-19 and show the signals obtained from the 300MHz NMR.

The NMR spectra show as certain peaks characteristic of either the precursor polymer or the conjugated PPV **Error! Bookmark not defined.** which enable us to estimate the degree of conversion of the polymers. By comparing the ratio of the intensity of the OC*H* protons in the region 3.5-4.0ppm (which is present in both precursor and conjugated PPV) to CH*Cl* and C*H*OCH_3 in the region of 4.5-6.0 ppm (only present in the precursor polymer) an estimate of the ratio of the total polymer **:** unconverted polymer was obtained. By comparing the OC*H* signals near 6.7ppm gives an estimate of the total polymer **:** converted polymer Table 2 tabulates the the estimated conversion.

SPECIES PRESENT	*SIGNALS OBSERVED*
OCH	3.5-4.0ppm
CHCl	5.3-5.7ppm
CH_2	2.9-3.3ppm
OMe	4.6ppm
Phenyl H^1s	<7ppm
Cis double bonds	6.7ppm
Conjugated phenyl or vinyl	<7.2ppm

Some of the C-Cl groups can be substituted by OMe groups during the purification procedure to give a peak near 4.6 ppm. The spectrum of polymer **1** was somewhat unusual in having a larger than expected peak at 4.5 ppm; this may be due to water present in the sample as has been observed before in other PPV precursor polymers.

Thus it appears that **1** and **4** are mostly converted, **2** and **3** are partially converted, while **5** seems to be largely in the precursor form, while the rest are intermediate in their degree of conjugation.

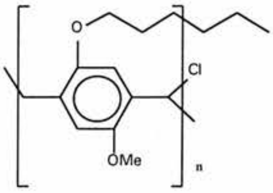
PRECURSOR POLYMER			**ESTIMATED % CONVERSION**
R	**R'**	**Code**	
OHex	OMe	**1** PCM 37	39
OHex	OHex	**2** PCM38[a]	
		#1	30
		#2	23
OMe	OMe	**3** PCM 39	25
OOct	OMe	**4** PCM 51	38
OMEH	OMEH	**5** PCM 52	<5 [b]

a # referes to batch number; b No peaks above 7.2 ppm (conjugation)

Table 2 Estimates of the degree of conversion from NMR data

These results were somewhat surprising since less than one equivalent of base (0.75 equiv) was used in each reaction. In the reaction where less base was used, for batch #2 of polymer **2** which was prepared using an older source of $KOBu^t$, the degree of conjugation was lower than expected. But overall the results point towards spontaneous HCl elimination, presumably promoted by the alkoxide groups which increase the electron density on the monomer. The degree of elimination. Swatos and Gordon[26] remarked on spontaneous elimination, but did not determine the degree of elimination quantitatively. They also noted that there was some gelation (cross-linking) of the sample in less polar solvents such as NMR solvents ($CDCl_3$). For a somewhat different polymer (2,3-diphenylPPV) the as-obtained polymer was 5% converted.[27] The most plausible explanation for the lower degree of conversion to the conjugated form is that the larger groups in **5** are sterically hindering the attack of base and/or the rotation of the precursor polymer chain that is necessary before the leaving groups can be eliminated according to the accepted E2 mechanism of the reaction.

NMR of **1**



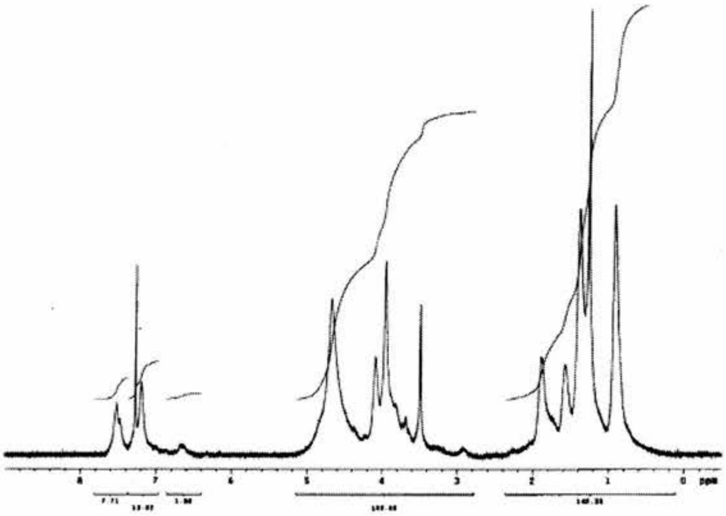
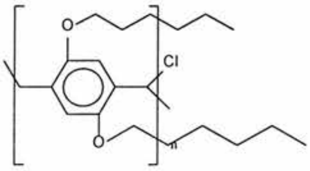


Figure 15

NMR of 2



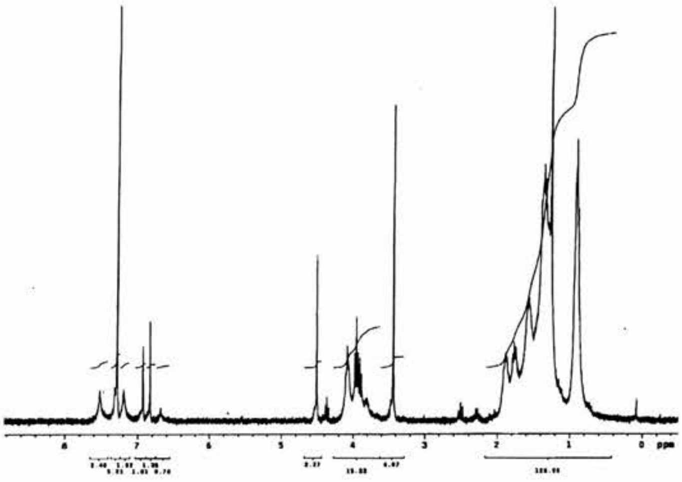
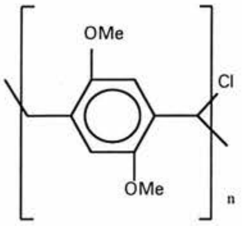


Figure 16

NMR of 3



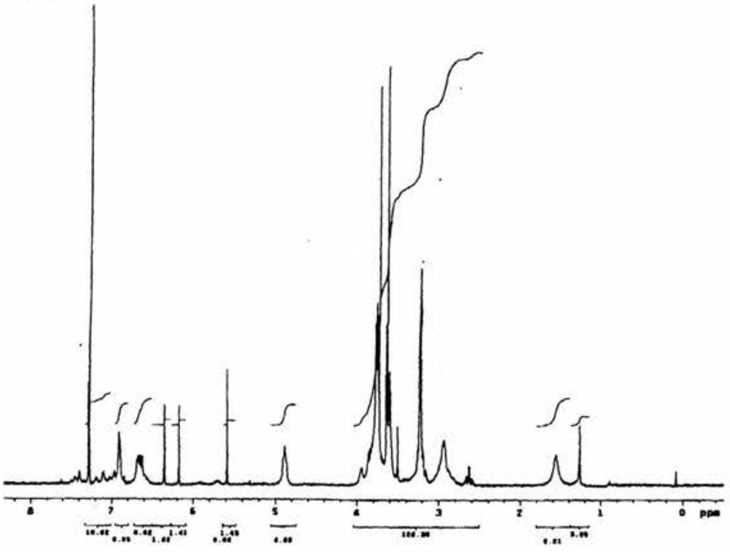
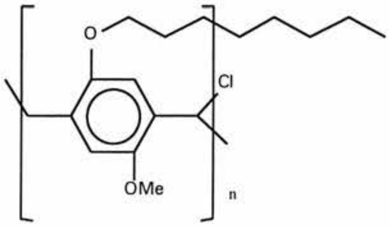


Figure 17

NMR of 4



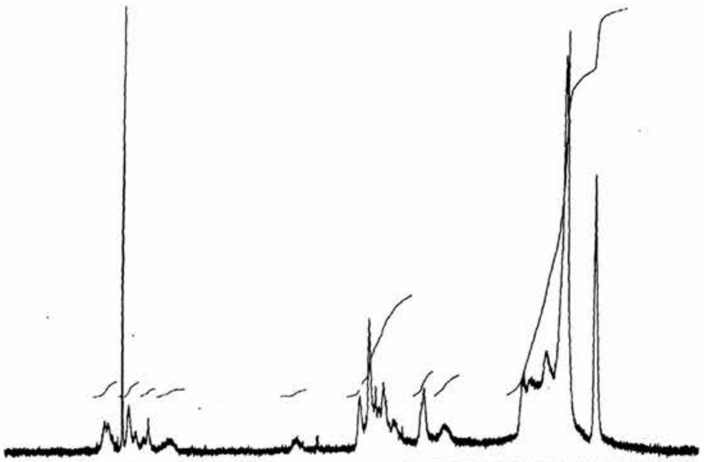
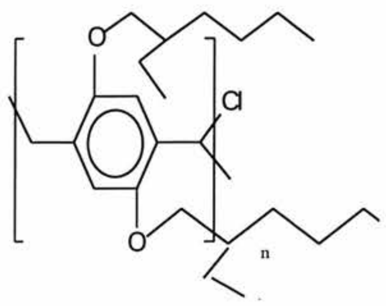


Figure 18

NMR of 5



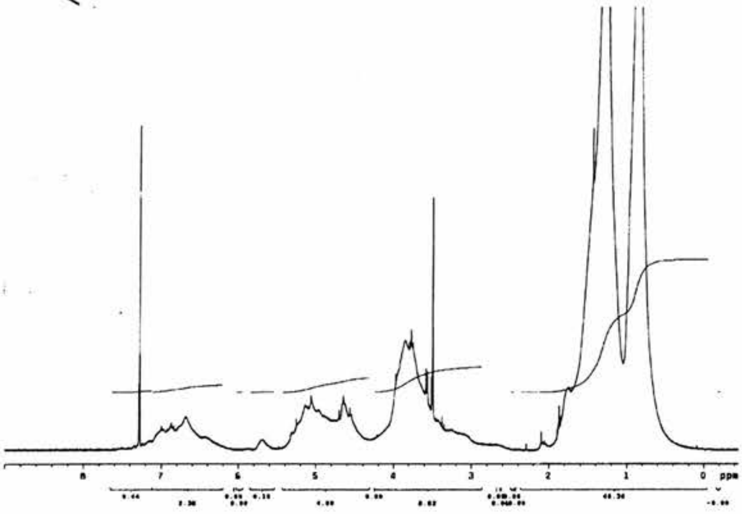


Figure 19

The FTIR spectra of the freshly prepared polymers cast as films on NaCl plates cast from CH_2Cl_2 showed in some cases characteristic bands due to conjugated PPV groups. Thus the spectra of **1**, **2** and **4** in particular contained bands at 965 and 838 cm^{-1} (assigned to the trans-vinylene and *p*-phenylene out-of-plane CH bends, respectively)[39]. In addition there were bands due to the CH stretch of the trans-vinylene group at 3024 cm^{-1}.

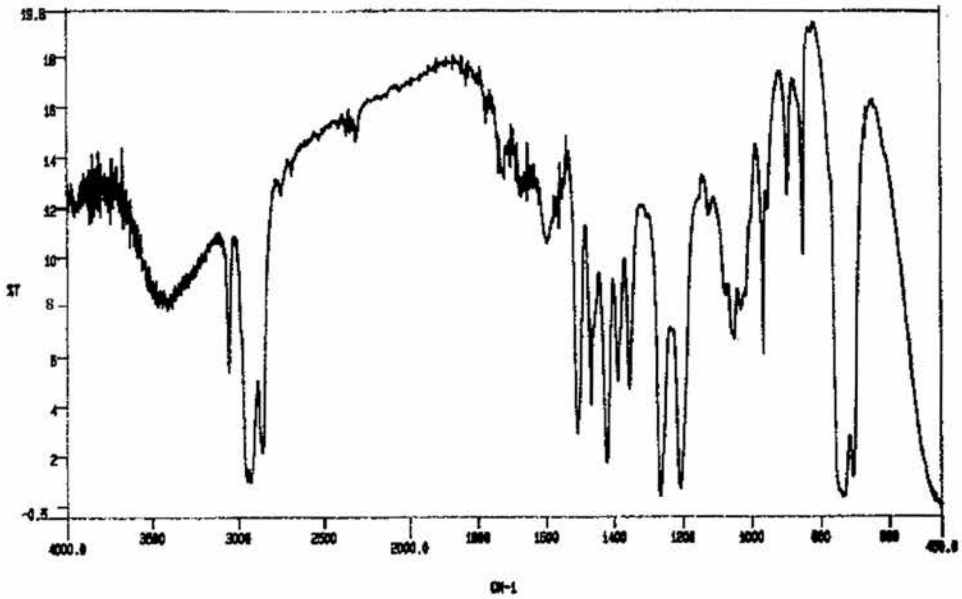


Figure 20

2.3.1 UV / VIS SPECTROSCOPY

UV Vis spectroscopy was carried out on Perkin Elmer UV/VIS lambda 14 / lambda 19, and a Philips PU 8720 UV/VIS scanning spectrophotometer. Both solution and solid state spectra were obtained Figures 20 and 21 . The results of both sets of experiments are tabulated in Tables 3 and 4.

We were interested to see whether electronic spectroscopy provided further evidence for greater conjugation in some of the polymer samples and to see how the side groups affect the optical properties of the polymers. Conversion of PPV precursors gives $\pi-\pi^*$ absorption in the visible region of the spectra. The position of this absorption as well as the relative peak heights of the features at 325 and 375 nm bands (assigned to stilbene and distyrylbenzene moieties, respectively) give information about the degree of conversion.[40,41] These studies and others[42] on the elimination reaction from tetrahydrothiophenium precursors show that in the initial stages of the conjugated units appear to form as blocks rather than randomly. In other words, there is selective elimination in order to delocalise the charge over more than two benzene rings. The conjugated segments are well-defined since the absorption bands often show vibronic structure which would be smeared out if a range of conjugation lengths was present.

Precursor polymer			**Absorption λ_{max}/ nm**	
R	**R'**	**Code**	**chloro-benzene**	**thin film**
OHex	OMe	**1** PCM 37	490	500
OHex	OHex	**2**PCM38 #1 #2	420 ^{a,b} 505	- 464
OMe	OMe	**3** PCM 39	380	380-500 br,sh
OOct	OMe	**4** PCM 51	465	490
OMEH	OMEH	**5** PCM 52	300, 360	360

Table 3

Precursor polymer			**Emission λ_{max} / nm**		
R	**R'**	**Reference number (Code)**	**chloro-benzene**	**DMF**	**thin film**
OHex	OMe	**1** (PCM 37)	580	560	590
OHex	OHex	**2**(PCM38) #1	-	518	c
		#2	587	-	585
OMe	OMe	**3** (PCM 39)	507	520	525
OOct	OMe	**4** (PCM 51)	550	540	580
OMEH	OMEH	**5** (PCM 52)	-	545	d

Table 4 a # refers to different batches; b From photoluminescence excitation(PLE) spectrum ; c film too thin; d no emission observed.

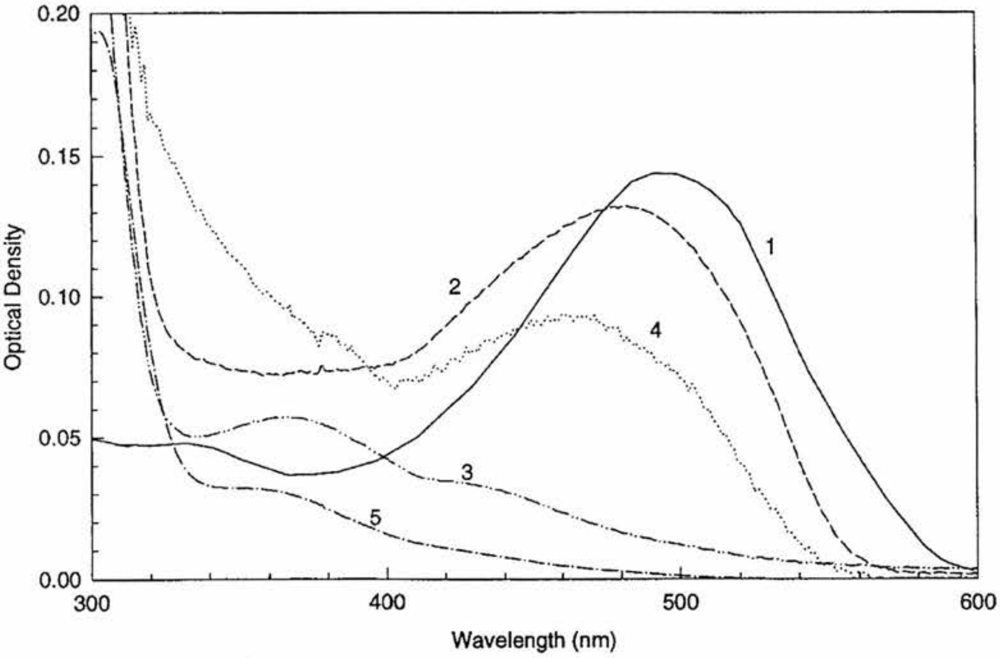


Figure 21 Absorption spectra of solutions of polymers 1-5

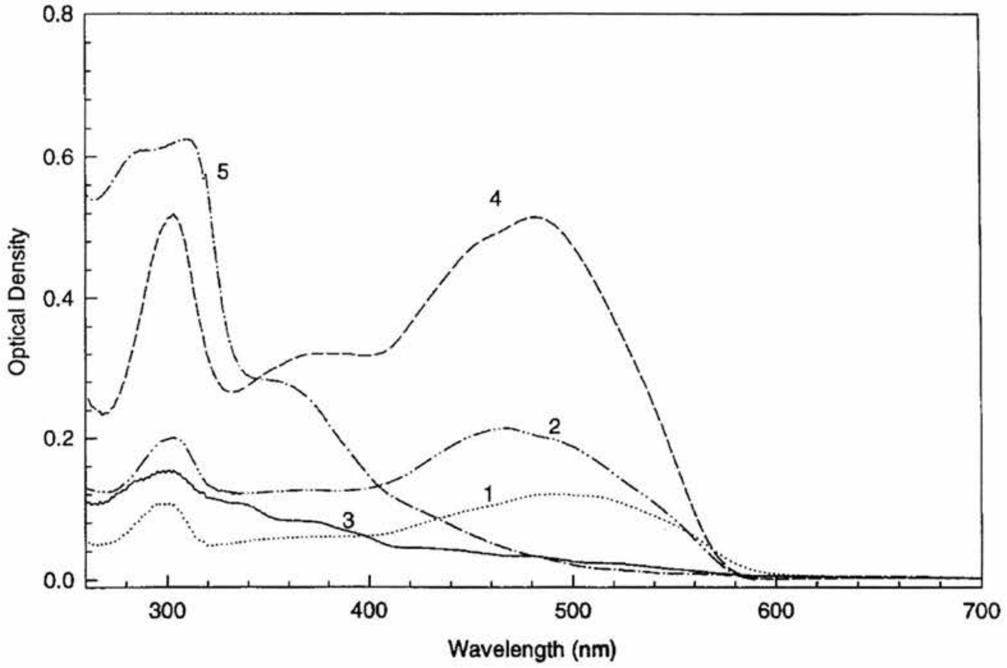


Figure 22 Absorption spectra of spin-coated films of polymers 1-5

The absorption spectra of both solutions and spin coated films are shown in Figures 20 and 21, and tabulated in tables 3 and 4. The data for polymer **2** in the Figures refers to the second batch. The polymers appear to divide into two groups. **1**, **2** (second batch) and **4** have strong absorptions in the visible peaking in the range 460-500 mn, and indicating the presence of some long conjugated segments in the polymers. In contrast for **3**, **5**, and **2** there is only weak absorption in the visible range, and the spectra are dominated by features in the near ultra violet, suggesting that these polymers are only weakly conjugated.

There are several factors that need to be considered to understand the observed spectra: inductive effects, degree of conversion, steric effects, and solubility. The inductive effect of alkoxide substituents explains the red-shift of absorption of **1**, **2** and **4** with respect to unsubstituted PPV. However, the differences in inductive effect between the alkoxide substituents used here would only have a small effect (of order a few nm) on the absorption spectra.

We consider that differences in the degree of conversion are a major factor in explaining the different spectra. The NMR data shows that polymers **1** and **4** have a relatively high degree of conversion, whilst polymer **5** is unconverted. This is consistent with the trends observed in the spectra. Steric effects can also affect the degree of conjugation of polymers. Bulky side groups can cause a twist between rings, thereby reducing the extent of electron delocalisation. We do not see any evidence for steric effects on the spectra of polymers **1-4**. However, we propose that steric hindrance in **5** is so severe that it prevents the elimination reaction, hence explaining the NMR and optical data.

It is more difficult to explain the results for polymer **2** and **3** which show quite different properties despite having similar degrees of conjugation by NMR. We believe that these differences stem from the low solubilities of polymer **2**(batch #1) and polymer **3**. The low solubility may lead to selective dissolution of polymer chains with only small conjugation lengths. Alternatively, during the reaction with base, rapid precipitation of the polymer chains in some way hinders the formation of long, conjugated segments.

Meier et al have carried out work on dialkoxy PPV oligomers, they consider the role of steric, inductive and solubility effects on optical spectra. [43] They found that torsion of the polymer backbone due to the steric effects of bulky side-groups is demonstrable in molecular modelling calculations, but not readily reflected in the absorption spectra of the polymers, They attributed this to problems in determining accurate spectroscopic data when the solubility of the polymer was low. Only by using soluble oligomers of controlled length could an accurate λ_{max} for the polymer be estimated by extrapolation. For dialkoxyPPVs (in particular the diisopropyl PPV this was estimated to be 486 nm.[44]

2.3.2 PHOTOLUMINESCENCE SPECTROSCOPY

Measurements were recorded on a Perkin Elmer LS50 fluorimeter. Spectra from the samples were recorded from solution, and on thin films, at the University of Durham under the guidance of Dr. I. Samuel and Mr. M. Halim.

The photoluminescence (PL) spectra of solutions and films of the polymers were measured, and the results are shown in Figures 23 and 24. The data for polymers **1**and **2** shows vibronic structure, and peaks at 590 nm in the film, which is the same value as for MEH-PPV. Note, however, that the emission maximum is at longer wavelength than previously reported (415 nm) for poly(diethoxy) PPV (35% eliminated) prepared by the Weissling route. This shows that our polymers have conjugated segments, which are longer than stilbene units.[42] The main features of the spectra for **1,2** (second batch) and **4** are similar, although the peaks are slightly blue-shifted for **4**. These are the three samples which showed strong visible absorption and hence relatively high conjugation. Polymer **3** shows an unusually broad PL spectrum peaking at 525 nm. No PL was detected from **5**. The main features of the solution PL spectra are the same as those of the films.

Conjugated polymers consist of segments with a wide distribution of conjugation lengths. All these segments contribute to the absorption. However, in emission, there is transfer of excitations to well-conjugated segments. This is why the absorption and PL spectra are not mirror images of each other. It means that the most-conjugated segments can dominate the PL. The presence of some well-conjugated segments explains the similarity of the PL spectrum of some of the polymers to MEH-PPV. The very broad spectrum of **3** must arise from a very wide distribution of conjugation lengths, with only a very low concentration of well conjugated segments. A low concentration of well-conjugated segments is consistent with the tail of the absorption of **3** which goes into the visible region.

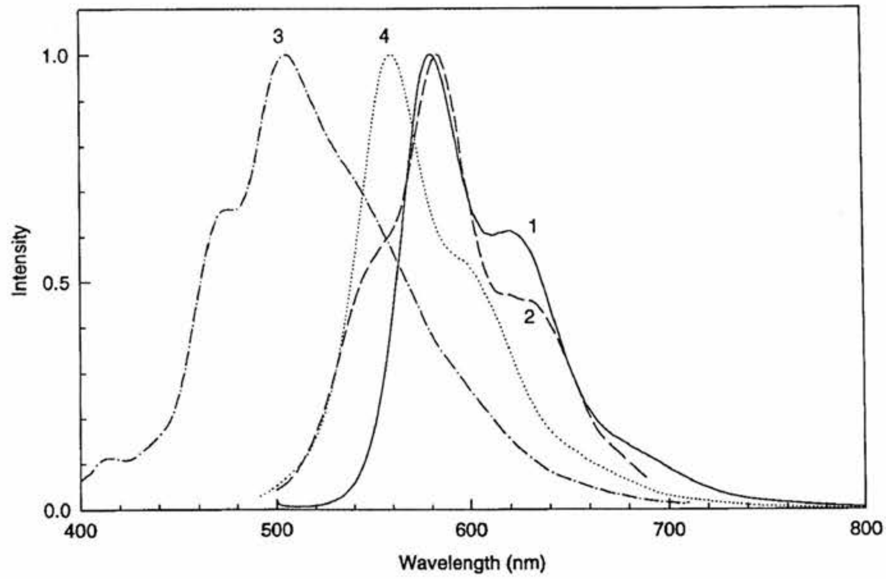


Figure 23 PL on solutions of polymers

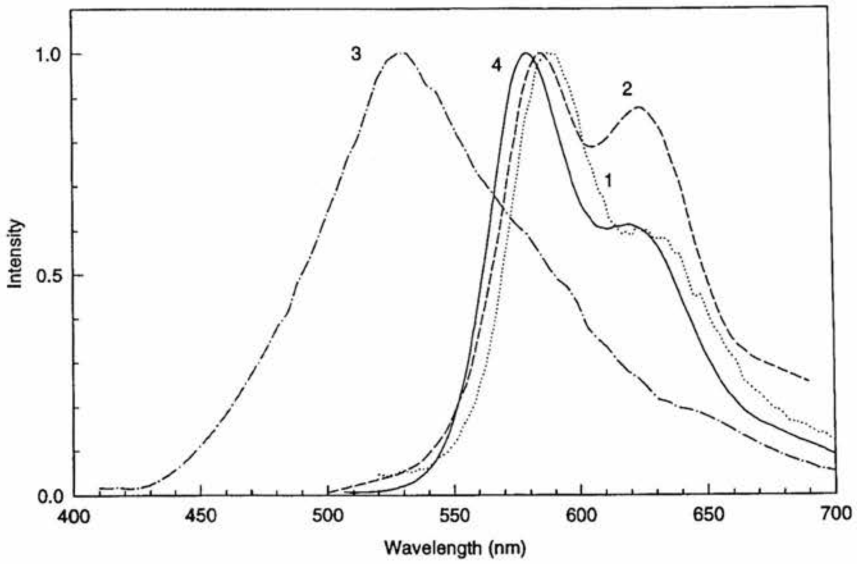


Figure 24 PL spectra of spin-coated films of polymers 1-5

As a comparison study PPV (unsubstituted) was prepared using the same method (Gilch). In the normal PPV PL and absorption spectra the presence of vibronic structure is thought to indicate the presence of a narrow distribution of conjugation lengths. Literature shows PPV has a λmax of 540 [45]. The PL of our PPV material (Figure 25) showed no vibronic structure in the emission spectra. This suggests that our PPV Figure 20 λ_{max} 500 was not fully conjugated and had a broad distribution of differing chain lengths. This is because the PPV made by this route is so insoluble that it drops out if solution on the formation of relatively short chain lengths.

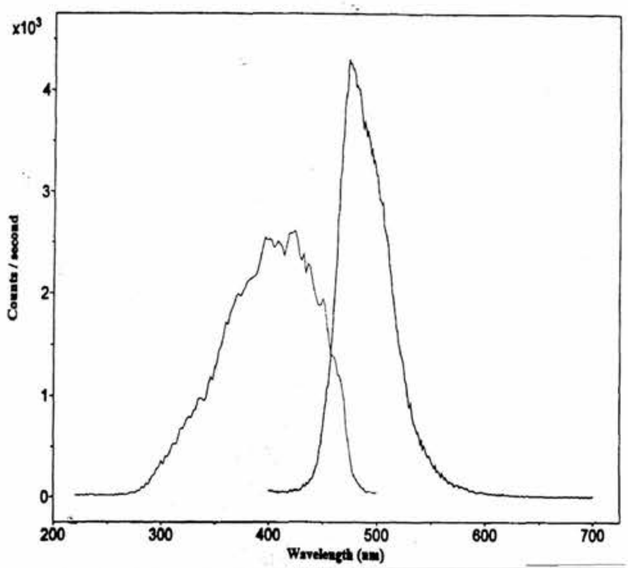


Figure 25 PL of Solid PPV

2.3.3 GEL PERMEATION CHROMATOGRAPHY (GPC)

A single solution of each sample was prepared by adding 10 cm^3 of solvent (THF) to 20 mg of sample and leaving overnight to dissolve. The following day the solutions were warmed in a water bath for 30 mins. to aid polymer dissolution and a small amount of 1,2 dichlorobenzene, was added in the solvent as an internal marker for flow rate correction purposes. The samples were then mixed thoroughly and part of each solution filtered through a 0.2 micron polyamide membrane. The filtrates were then transferred to glass sample vials which were placed in an autosampler.

Chromatographic conditions

Columns: PLgel 2 x Mixed bed-B, 30 cm, 10 microns
Solvent: THF
Flow rate: 1.0 ml/min
Temperature: Ambient
Detector: refractive index

The GPC system was calibrated with polystyrene and the results obtained (Table 4) are expressed as polystyrene equivalent molar masses, traces for polymers **1-5** shown in Figure 26- 30

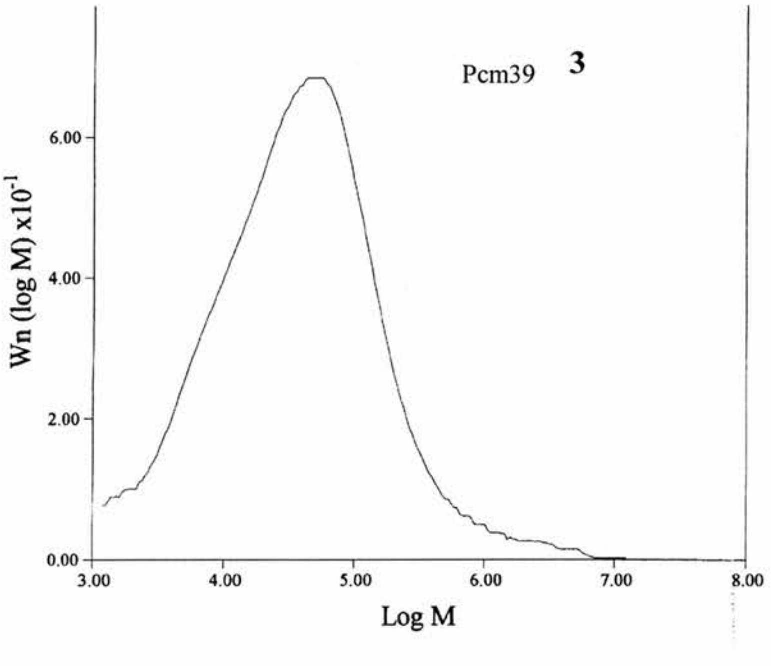


Figure 26

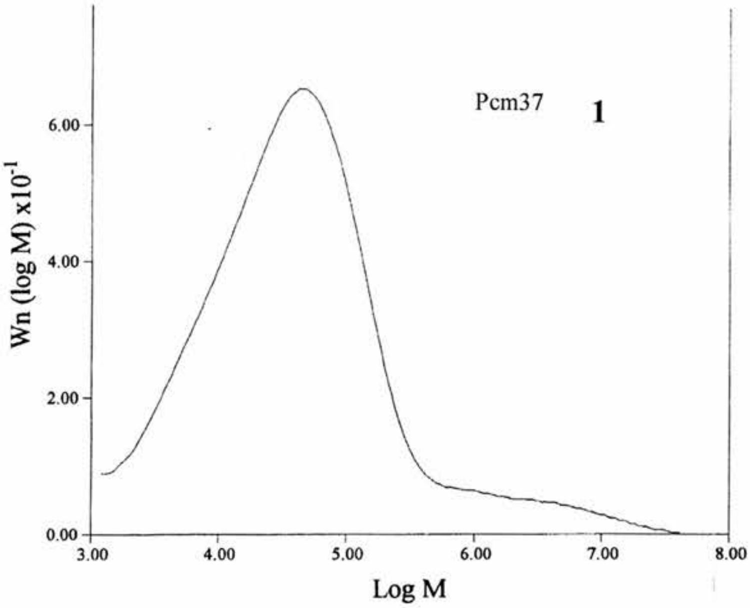


Figure 27

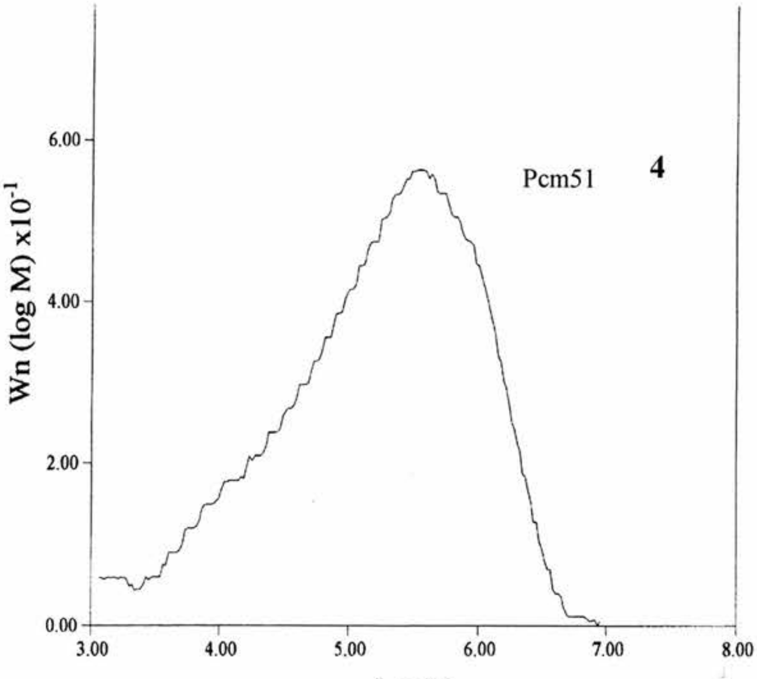


Figure 28

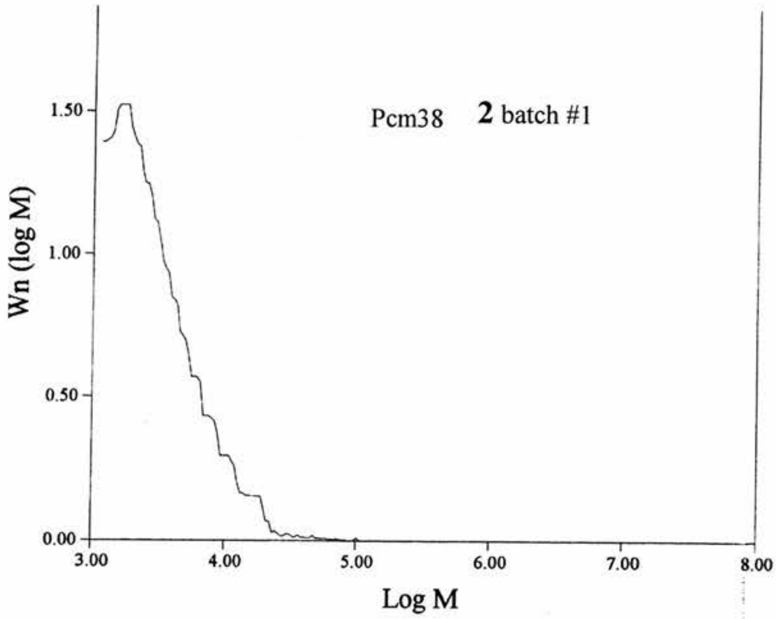


Figure 29

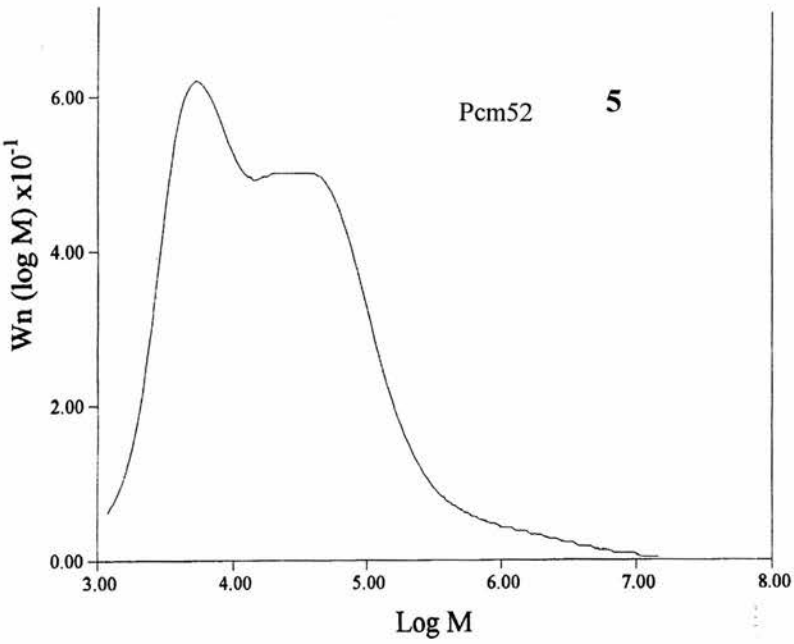


Figure 30

Using either THF or $CHCl_3$ as solvent, most samples were found to contain insoluble material except **5** (PCM 52) which has two highly solubilizing groups. The low chromatogram peak areas for **2** (PCM38) and **4** (PCM 51) suggests a lower solubility so the results may not be representative of the polymers as a whole. Polymer **2** was re-synthesized and this batch (#2) was found to be much more soluble. The lower solubility of **4** compared to **1** despite their structural similarity and similar molecular weight could be related to the greater degree of conjugation in polymer **4**. All of the samples were found to contain a proportion of low molecular mass material which is found generally in materials prepared in this manner. The polydispersity data indicates a large distribution of chain lengths in most cases. The very large values for polymer **4** are characteristic for a highly branched polymer, consistent with its tendency to gel in solution. Overall, while the data for the two solvents show subtle differences the overall trends are the same.

			THF			$CHCl_3$		
R	**R'**	**Reference number**[a]	M_w	M_n	$\frac{M_w}{M_n}$	M_w	M_n	$\frac{M_w}{M_n}$
OHex	OMe	**1** PCM 37	495 000	14 100	35.1	97 550	17 050	5.7
OHex	OHex	**2** PCM38						
		#1	4 715	2 480	1.9	11 000	4 030	2.7
		#2	930 000	13 700	68	-	-	-
OMe	OMe	**3** PCM 39	147 500	14 250	10.3	14 300	25 550	5.6
OOct	OMe	**4** PCM 51	497 500	29 800	16.7	417 500	27 050	15.4
OMEH	OMEH	**5** PCM 52	130 000	8 925	14.6	32 800	8 230	4.0

[a] # refers to different batches

Table 5 GPC data for polymers 1-5 in THF and $CHCl_3$

2.3.4 THERMAL ELIMINATION REACTION

Conducting polymer precursors are used in the fabrication of organic light emitting diodes. These precursors are applied to the LED substrate by spin coating, but little is known about how to control the viscosity in this process. On heating the polymer precursor it goes through an elimination reaction in order to form conjugated segments. Our precursor polymers **1-5** were expected to become fully conjugated when exposed to 100 °C and 0.1 mm of Hg. Under ambient pressure, analysis of the TGA/DSC curves shows weight loss in the 100-600 °C region. The first weight loss occurred up to 250 °C and is assumed to be associated with HCl elimination to form the conjugated polymer.

This conversion occurred over a very broad temperature range and it was not possible to determine accurate weight losses due to the conversion process. Much greater weight loss beginning at 400 °C is associated with exothermic peaks (DSC) which can be related to the loss in mass expected from degradation products (e.g. loss of alkoxy groups, since polymer **5** with the largest groups showed the largest weight loss).These results showed that the weight loss from the precursor polymer incorporated the loss of HCl and the weight loss associated with the onset of degradation. The experiments were therefore repeated *in vacuo* to obtain a more accurate weight loss calculation and to see how the polymer behaved under the recommended reaction conditions for the thermal elimination reaction[26]. The results are shown in Table 6, and the trace for polymer **2** is reproduced in Figures 30 and 31. The observed weight loss expressed as a fraction of the maximum theoretical weight loss due to HCL for the mass of sample used = x. The % conversion that has already occurred before heating (i.e. in the as-prepared polymer) is then (1-x).100% and this is also listed in Table 6

Reference number[a]	**Max. theoretical weight loss (%)**	**Temperatue range of HCl loss(°C)**	**Measured weight loss (%) in vacuo**[b]	**% conversion in as-prepared sample**	**Degradation temperature (N_2/in vacuo[b])**
1	14	110-200	7 ± 2	58	367/284
2[a]					
#1	11	120-170	11	0	384/275
#2				-	
3	19	110-180	12	46	411/267
4	13	100-200	5 ± 2	71	406/287
5	9	100-200	7	24	374/283

a # refers to different batches b Error in weight loss measurement is ± 1% except where otherwise stated. Larger errors are associated with weight loss occurring over a broad temperature range. Errors in conversion estimates are greater.

Table 6 TGA/DTA (in vacuo) for polymer samples

From the data it is clear that **1** and **4** have undergone a similar degree of conversion to the conjugated form during polymerisation, whereas **5** shows a much lower conversion. With the exception of the dimethoxy polymer **3** the conversions determined by TGA are higher than expected from the NMR results. This can be reconciled by assuming that **1**, **4** and **5** contain cross-links which, although arising from HCl loss, do not lead to conjugated double bonds. The data suggests that polymer **2** has undergone much less conversion which is rather surprising given that the spectroscopic data suggesting that its degree of conversion is similar to polymer **3**. We propose that **2** is anomalous due to the presence of low-molecular weight material (oligomers or trapped solvent) as indicated by the GPC data. This low molecular weight material is removed at a similar temperature to that at which the HCl is eliminated.

In most precursor polymers dimethyl sulphide or tetrahydrothiophene Figure 31 is the leaving group, and it has been proved by TGA/mass spec and elemental analysis that upon heating the polymer precursor the leaving group is quantitatively eliminated in order to form the fully conjugated polymer. For these polymers the thermally induced conversion of the precursor polymer into the conjugated polymer occurs in a complex sequence of reactions rather than in a single step[46] and is also dependent on the nature of the counter ion [39,47] Our polymers have the advantage of a single conversion process to the fully conjugated form. Our assumption that the polymers are converted to the fully conjugated form is justified by these literature precendents and the degree of internal consistency with the spectroscopic data on the precursor polymers.

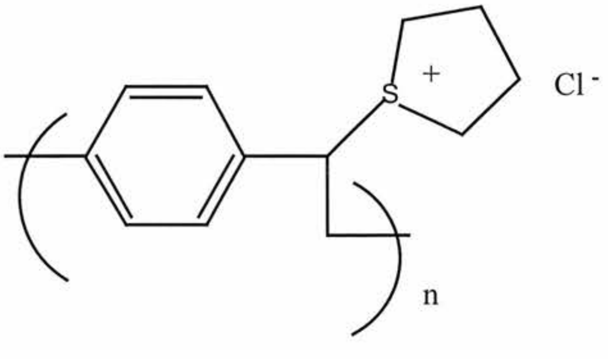


Figure 31

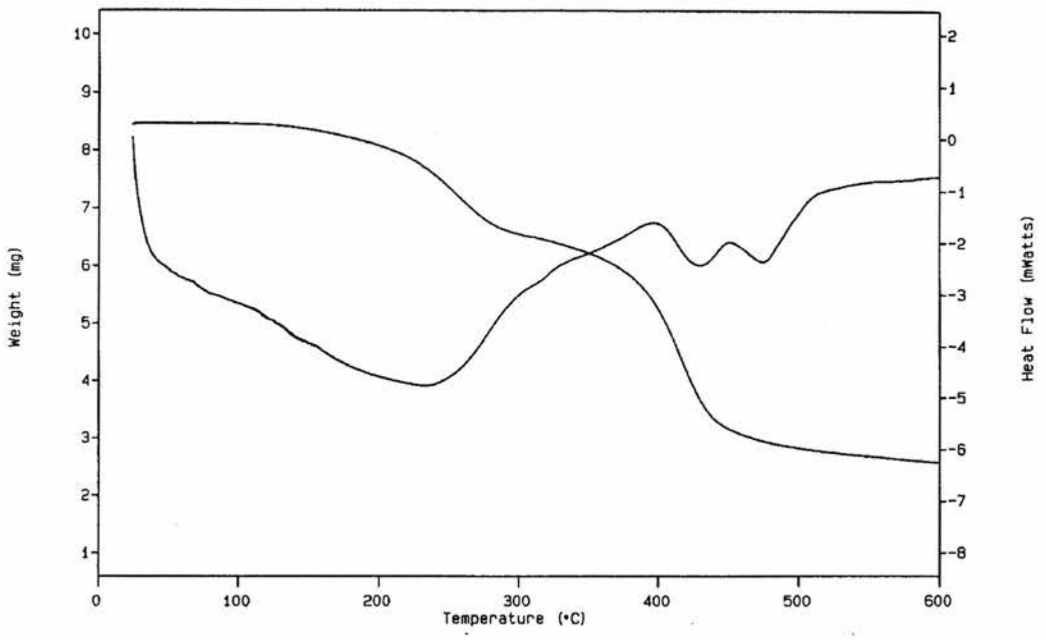


Figure 32 polymer 2 STA(TG + DSC)

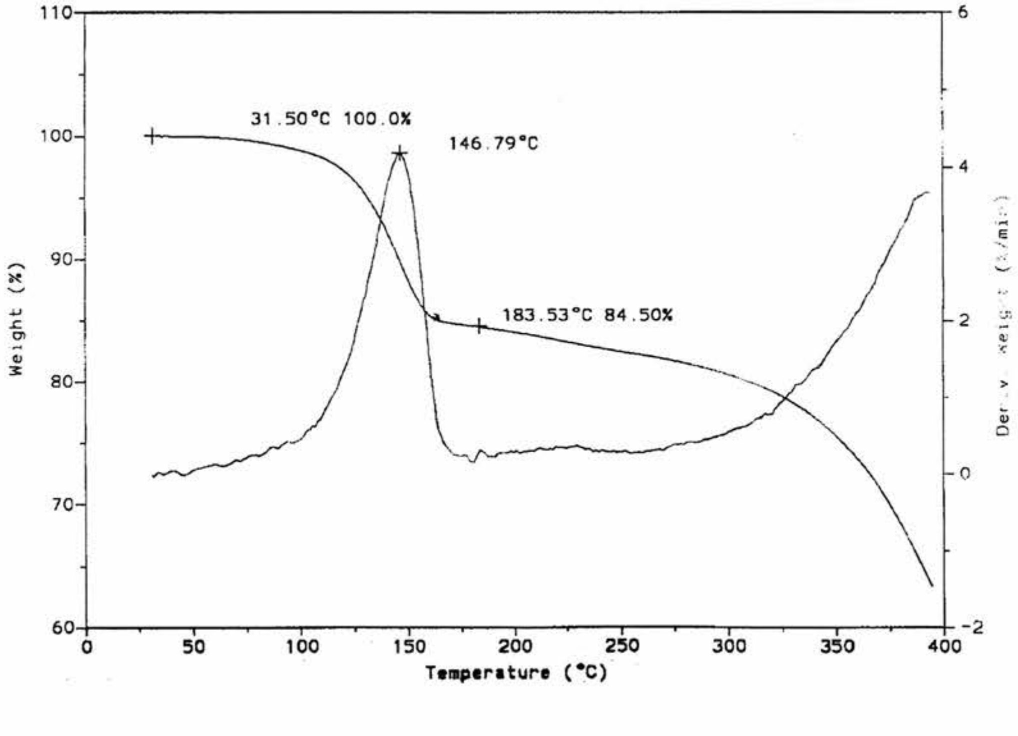


Figure 33 polymer 2 TGA under vacuum

2.3.5 CONCLUSIONS

Dialkoxy-substituted bis-chloro or bromomethyl benzene monomers prepared by alkylation of hydroquinone followed by chloro- or bromomethylation may be polymerised by the base catalysed elimination of HCL or HBr (Gilch method) to give the corresponding alkoxy-substituted PPV precursors. The ^{1}H NMR data showed that, with the exception of the R=MEH (MEH=2ethylhexyl) polymer **5**, the precursor polymers had already partially converted to conjugated forms (20-40% from the 'H NMR). This explained their low solubility and their absorption and emission spectra. Presumably, the electron-donating alkoxy groups promote the elimination of HCI or HBr.

The absorption spectra can be explained in terms of the degree of conversion and conjugation length, inductive effects, solubility, and steric factors. The solution spectroscopic data for polymers **2** and **3** were controlled not only by their degree of conjugation but also by the absence of long, conjugated segments. A wide distribution of conjugation lengths with only a low concentration of well-conjugated segments was the most likely explanation for the very broad emission observed in the PL spectrum of **3**. The conjugation length appeared to be related to the lower solubility of polymers **2** and **3** which affects either the solubility of chains containing such conjugated segments or in some way hinders the formation of these segments during the elimination reaction.

With the exception of **2** and **3** the TGA of the polymers showed that the amount of HCI or HBr elimination undergone by the polymer prior to analysis was higher than expected from the NMR results. This was reconciled by assuming that the polymers contain cross-links which, although arising from HCI or HBr loss, do not lead to conjugated double bonds. Cross-linking will be detrimental to the processing properties of the polymers. Steps to be taken to prevent conversion of the other polymers would include: (i) conducting the reaction in the absence of light (ii) reducing the amount of potassium tertiary butoxide used in the reaction; (iii) using an alternative base; (iv) reducing the reaction temperature. Preliminary spectroscopic studies of the reaction at O °C showed no change in absorption of the reaction mixture over a 24 h period. A similar experiment was attempted at – 78 °C which resulted in a small amount of white precipitate being formed which turned into the conjugated polymer on exposure to light.

We propose that the low-temperature elimination of HCI is affected by steric constraints along the precursor polymer backbone. Polymer 5 with large, branched groups eliminated HCI or HBr less readily due to greater steric constraints for the back-bone rotation necessary prior to elimination. Polymers 1, 4 and 5 contain more cross-links than the unencumbered 3 for the same reason, i.e. it is easier to eliminate HCI or HBr through interchain cross-linking reactions than by interchain double bond formation. Unfortunately, the most soluble and promising polymer from a device point of view 5 does not thermally convert smoothly into the fully conjugated, emissive form in the solid state for these same steric reasons.

2.4.0 EXPERIMENTAL

2.4.1 1,4-DIHEXYLOXYBENZENE AND 4-HEXYLOXYPHENOL

To a solution of hydroquinone (20 g, 0.18 mol.) in methanol (100 cm^3) was added a solution of potassium hydroxide (21.06 g, 0.36 mol.) in methanol (120 cm^3) at room temperature. After 5 min stirring, a mixture of *n*-Hexyl bromide (118 g, 0.72 mol.) in acetone (200 cm^3) was added slowly to the reaction mixture. This mixture was refluxed for 9 hours. It was then concentrated by evaporation of solvents, diluted with water and extracted into dichloromethane (500 cm^3). The dichloromethane extracts were dried over magnesium sulphate and evaporated to dryness under reduced pressure to yield a dark brown viscous liquid which on cooling solidified to form dark brown slightly translucent crystals which had an oily residue trapped between the crystal layers. *n*-hexyl bromide was distilled off under reduced pressure and the product was recrystallised from light petroleum, yielding a dark brown solid (33.66 g, 76.16%) ^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.85 (m, 6 H), 1.25 - 1.9 (m, 17 H), 3.85 (t, J = 7Hz, 4 H), 6.8 (s, 4 H). This NMR indicated that the product formed was a mixture of both mono and dialkylated species. This represented itself as shoulder peaks on the singlet and the triplet. This preparation was repeated several times to obtain sufficient monosubstituted phenol.

2.4.2 PURIFICATION (SEPARATION OF MONO AND DISUBSTITUTED SPECIES)

A solution of the product in aqueous sodium hydroxide (2 M, 200 cm^3) was stirred for 30 min in order to ensure complete conversion of the monosubstituted phenol into the salt form. Separation of the disubstituted product was accomplished by extraction into dichloromethane. The dichloromethane extracts were dried over magnesium sulphate and the solvent was removed under reduced pressure and then under high vacuum to afford cream/yellow coloured crystals (25.96 g).^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.85 (m, 6 H), 1.2 - 1.55 (m, 12 H), 1.65 - 1.90 (m, 4 H),3.85 (t, J = 7Hz, 4 H) 6.85 (s, 4 H). The monosubstituted phenol was released from solution by addition of HCl (2 M 200 cm^3). The monosubstituted product was extracted into dichloromethane and the extracts were dried over magnesium sulphate and the solvent evaporated under reduced pressure and then under high vacuum to afford a dark brown solid (4.40 g). ^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.85 (m, 3 H), 1.2 - 1.5 (m, 6 H), 1.7 (m, 2 H), 3.85 (t, J = 7Hz, 2 H), 6.8 (s, 4 H).

2.4.3 2,5-BIS(CHLOROMETHYL)-1,4-HEXYLOXYBENZENE

To a solution of 1,4 -dihexyloxybenzene (25.96 g, 0.092 mol.) in dioxane (180 cm^3) was added conc. HCl (20.5 cm^3) at room temperature. HCl gas was bubbled through the solution for 15 mins.. after which formaldehyde (3 x 10 cm^3) portions were added slowly over 30 min for one and a half hours. HCl gas was bubbled through the mixture continuously for three and a half hours. After that time the HCl gas flow was stopped and conc. HCl (95 cm^3) was added to the reaction mixture. The resulting solution was cooled whereupon the product was obtained.(6.03 g, 17.5%) ^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.85 (t, J = 7Hz, 6 H) 1.2 - 1.55 (m, 12 H), 1.7 - 1.9 (m, 4 H), 3.85 (t, J = 7Hz, 4 H), 4.5 (s, 4 H), 6.8 (s, 2 H).^{13}C NMR ($CDCl_3$, TMS) d_c: 14.03 (2 C), 22.6 -31.5 (8 C), 68 -69 (4C), 112 (2C), 126.6 (2 C), 150.4 (2 C).

2.4.4 1-METHOXY-4-HEXYLOXYBENZENE

To a solution of *p*-methoxyphenol (57.4 g, 0.46 mol.) in methanol (120 cm^3) was added a solution of potassium hydroxide (31.24 g, 0.56 mol..) in methanol (160 cm^3) at room temperature. After 5 min stirring, a mixture of *n*-hexylbromide (200 g, 0.92 mol.) in acetone (200 cm^3) was added slowly to the reaction mixture. This mixture was refluxed for 2 hours. It was then concentrated by evaporation of solvents, diluted with water and extracted into dichloromethane (500 cm^3). The dichloromethane extracts were dried over magnesium sulphate and evaporated to dryness under reduced pressure to yield a dark brown viscous liquid which on cooling solidified to form dark brown slightly translucent crystals which had an oily residue trapped between the crystal layers. *n*-Hexylbromide was distilled off under reduced pressure and the product was isolated using an air condenser (lebig condensor with warm air replacing the water in the outer layer) and recrystallised from methanol. This yielded a white/pink solid (77.13 g, 80.61%) ^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.88 (t, J = 7 Hz, 3 H), 1.3 -1.9 (m, 8 H), 3.77 (s, 3 H), 3.87 (t, J =7 Hz,2 H), 6.85 (s, 4 H).

2.4.5 2,5-BIS(CHLOROMETHYL)-1-METHOXY-4-HEXYLOXYBENZENE

To a solution of 1-methoxy-4-hexyloxybenzene (24.4 g, 0.117 mol.) in dioxane (172 cm^3) was added conc. HCl (28 cm ^{3}) at room temperature. HCl gas was bubbled through the solution for 15 min. Formaldehyde (3 x 10 cm^3) portions were added slowly over 30 min for 1 1/2.h. HCl gas was bubbled through the mixture continuously for 3 1/2 h. After that time the HCl gas flow was stopped and conc. HCl (128 cm^3) was added to the reaction mixture. The resulting solution was cooled whereupon (31.5 g, 87.8%) of product was obtained.^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.85 (t, J = 7Hz, 3 H),1.3 -1.9 (m, 8 H), 3.8 (3H s), 3.95 (t, J =7Hz 2 H), 4.53 (s, 2 H), 4.55 (s, 2 H), 6.85 (s, 2 H).

2.4.6 1-(2-ETHYLHEXYLOXY)-4-HEXYLOXYBENZENE

To a solution of hexyloxy phenol (10 g, 0.05 mol.) in methanol (60 cm^3) was added a solution of potassium hydroxide (4 g, 0.1 mol.) in methanol (80 cm^3) at room temperature. After 5 min stirring, a mixture of 2-ethylhexylbromide (19.44 g, 0.1mol) in acetone (100 cm^3) was added slowly to the reaction mixture. This mixture was refluxed for 9 hours. It was then concentrated by evaporation of solvents, diluted with water and extracted into dichloromethane (200 cm^3). The dichloromethane extracts were dried over magnesium sulphate and evaporated to dryness under reduced pressure to yield a dark brown viscous liquid which on cooling solidified to form dark brown slightly translucent crystals which had an oily residue trapped between the crystal layers. This residual 2-ethylhexylbromide was distilled off under reduced pressure and the product was recrystallised from light petroleum, yielding fine white needle-like crystals. (3.9 g, 22.5%).^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.85 (m, 4 H), 1.25 (m, 8 H), 1.7 (m, 3H), 3.85 (m, 2H), 6.75 (m, 4H). This suggests that only starting material has been recovered.

2.4.7 1,4-DI-(2-ETHYLHEXY)OXYBENZENE AND 1-(2-ETHYLHEXYL)-OXYPHENOL

To a solution of hydroquinone (17 g, 0.153 mol.) in methanol (100 cm^3) was added a solution of potassium hydroxide (17.2 g, 0.36 mol.) in methanol (120 cm^3) at room temperature. After 5 min stirring, a mixture of 2-ethylhexylbromide (44.72 g, 0.23 mol.) in acetone (200 cm^3) was added slowly to the reaction mixture. This mixture was refluxed for 9 hours. It was then concentrated by evaporation of solvents, diluted with water and extracted into dichloromethane (200 cm^3). The dichloromethane extracts were dried over magnesium sulphate and evaporated to dryness under reduced pressure to yield a dark brown viscous liquid which remained a dark brown oily liquid on cooling. 2-ethylhexyl bromide was distilled off under reduced pressure and the product was recrystallised from light petroleum, yielding a dark brown viscous liquid (23.32 g, 45.6%).

2.4.8 PURIFICATION (SEPARATION OF MONO AND DISUBSTITUTED SPECIES)

A solution of the product in aqueous sodium hydroxide (2 M 200 cm^3) was stirred for 30 mins. in order to ensure complete conversion of the monosubstituted phenol into the salt form. Separation of the disubstituted product was accomplished by extraction into dichloromethane. The dichloromethane extracts were dried over magnesium sulphate and the solvent was removed under reduced pressure and then under high vacuum to afford a dark brown viscous liquid . (15.84 g).^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.85 (m, 10 H), 1.25 (m, 14 H), 1.65 (m, 2 H), 3.7 (m, 4 H) 6.7 (m, 4 H). The monosubstituted phenol was released from solution by addition of HCl (2M 200 cm^3). The monosubstituted product was extracted into dichloromethane and the extracts were dried over magnesium sulphate and the solvent evaporated under reduced pressure and then under high vacuum to afford a dark brown oily liquid. (4.40 g). ^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.85 (m, 5 H), 1.25 (m, 10 H), 3.75 (d, 2 H), 6.7 (m, 4 H).

2.4.9 1,4-DIHEXADECYLOXYBENZENE AND 4-HEXADECYLOXYPHENOL

To a solution of hydroquinone (20 g, 0.18 mol.) in methanol (100 cm^3) was added a solution of potassium hydroxide (21.06 g, 0.36 mol.) in methanol (120 cm^3) at room temperature. After 5 min stirring, a mixture of hexadecyl bromide (98.9 g, 0.324 mol.) in acetone (200 cm^3) was added slowly to the reaction mixture. This mixture was refluxed for 10 hours. It was then concentrated by evaporation of solvents, diluted with water and extracted into dichloromethane (500 cm^3). The dichloromethane extracts were dried over magnesium sulphate and evaporated to dryness under reduced pressure the product was recrystallised from light petroleum to afford a light brown solid. (10.25 g, 10.2%). ^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.85 (m, 6 H), 1.25 - 1.9 (m, 33 H), 3.85 (t, J = 7Hz, 4 H) 6.8 (s, 4 H). This NMR indicated that the product formed was a mixture of both mono and dialkylated species. This represented itself as shoulder peaks on the singlet and the triplet.

2.4.10 PURIFICATION (SEPARATION OF MONO AND DISUBSTITUTED SPECIES)

A solution of the product in sodium hydroxide (2 M 200 cm^3) was stirred for 30 min in order to ensure complete conversion of the monosubstituted phenol into the salt form. Separation of the disubstituted product was accomplished by extraction into dichloromethane. The dichloromethane extracts were dried over magnesium sulphate and the solvent was removed under reduced pressure and then under high vacuum to afford cream coloured crystals (5.57 g).^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.85 -1.9 (m, 58 H), 3.25 (m, 2 H) 3.85 (m, 2 H), 6.6 (s, 4 H). The monosubstituted phenol was released from solution by addition of HCl (2M 200 cm^3). The monosubstituted product was extracted into dichloromethane and the extracts were dried over magnesium sulphate and the solvent evaporated under reduced pressure and then under high vacuum to afford a cream coloured solid (0.30 g). ^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.4 - 1.8 (m, 43 H), 3.8 (m, 2 H), 6.65 (m, 4 H).This experiment was repeated until adequate amounts of the disubstituted product was obtained.

2.4.11 1,4-DI-(2-ETHYLHEXY)OXYBENZENE AND 1-(2-ETHYLHEXYL)-OXYPHENOL

To a solution of hydroquinone (28.4 g, 0.258 mol.) in methanol (150 cm^3) was added a solution of potassium hydroxide (30.18g, 0.516 mol.) in methanol (200 cm^3) at room temperature. After 5 min stirring, a mixture of 2-ethylhexylbromide (100 g, 0.517 mol.) in acetone (200 cm^3) was added slowly to the reaction mixture. This mixture was refluxed for 12 hours. It was then concentrated by evaporation of solvents, diluted with water and extracted into dichloromethane (200 cm^3). The dichloromethane extracts were dried over magnesium sulphate and evaporated to dryness under reduced pressure to yield a dark brown viscous liquid which remained a dark brown oily liquid on cooling. 2-Ethylhexylbromide was distilled off under reduced pressure and the product was recrystallised from light petroleum, yielding a dark brown viscous liquid (41 g, 81%).

2.4.12 PURIFICATION (SEPARATION OF MONO AND DISUBSTITUTED SPECIES)

A solution of the product in sodium hydroxide (2M 400 cm^3) was stirred for 30 mins., in order to ensure complete conversion of the monosubstituted phenol into the salt form. Separation of the disubstituted product was accomplished by extraction into dichloromethane. The dichloromethane extracts were dried over magnesium sulphate and the solvent was removed under reduced pressure and then under high vacuum to afford a dark brown viscous liquid (15.84 g).^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.85 (m, 10 H), 1.25 (m, 14 H), 1.65 (m, 2 H), 3.7

(m, 4 H) 6.7 (m, 4 H). The monosubstituted phenol was released from solution by addition of HCl (2M 400 cm^3). The monosubstituted product was extracted into dichloromethane and the extracts were dried over magnesium sulphate and the solvent evaporated under reduced pressure and then under high vacuum to afford a dark brown oily liquid. (4.40 g). ^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.85 (m, 5 H), 1.25 (m, 10 H), 3.75 (d, 2 H), 6.7 (m, 4 H). Although both the mono and disubstituted species gave the correct NMR profiles the products themselves remained dark brown oils. The further purification of these compounds was carried out using Krugelrohr distillation, which yielded a much cleaner orange/yellow oil.

2.4.13 2,5-BIS(CHLOROMETHYL)-1-HEXYLOXYPHENOL

To a solution of hexyloxyphenol (17.8 g, 0.092 mol.) in dioxane (180 cm^3) was added conc. HCl (20.5 cm^3) at room temperature. HCl gas was bubbled through the solution for 15 mins. Formaldehyde (3 x 10 cm^3) portions were added slowly over 30 min for one and a half hours. HCl gas was bubbled through the mixture continuously for three and a half hours. After that time the HCl gas flow was stopped and conc. HCl (95 cm^3) was added to the reaction mixture. The resulting solution was cooled the oily product was isolated by extraction into dichloromethane. The product was evaporated to dryness to yield a dirty brown sludge. This material was not acceptable for further study and so the experiment was repeated using a purified sample of hexyloxyphenol. The hexyloxyphenol was purified by distillation using an air condenser to fine white crystalline needles. The experiment was then repeated with (5.1 g 0.26 mol) hexyloxyphenol in a scaled down reaction, whereupon a crystalline product was obtained. (5.3 g, 69.7% crude). After recrystallisation from methanol 1.32g 17.32% of this material was recovered which showed no peak between 4.6 - 4.8 ppm in the ^{1}H spectrum, which corresponds to CH_2Cl.

2.4.14 2,5-BIS(CHLOROMETHYL)-1,4-HEXADECYLOXYBENZENE

To a solution of 1,4-hexadecyloxybenzene (5 g, 0.00877 mol.) in dioxane (21.5 cm^3) was added conc. HCl (4 cm^3) at room temperature. HCl gas was bubbled through the solution for 15 mins. formaldehyde (3 x 2 cm^3) portions were added slowly over 30 min for one and a half hours. HCl gas was bubbled through the mixture continuously for three and a half hours. After that time the HCl gas flow was stopped and conc. HCl (25 cm^3) was added to the reaction mixture. The resulting solution was cooled and the product was filtered off.(4.36g 58.9% crude) the product was recrystallised from methanol (1.68 g, 22%). ^{1}H NMR showed no CH_2Cl peaks. This experiment was repeated several times with subtle changes to the procedure with no change in the NMR see section 2.2.1.

2.4.15 METHYLATION OF HEXYLOXYPHENOL

Hexyloxyphenol (0.077 g, 4mmol) was added to a stirred solution of powdered potassium hydroxide (0.897 g, 0.016 mmol) in DMSO (8 mls.). methyl iodide (1.133g 8 mmol was then added. The mixture was stirred continuously for thirty minutes, at which time the solution was poured into water (30 cm^3) and extracted with dichloromethane. The extracts were washed with water, dried and then evaporated to dryness^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.82 (m, 3H), 1.22 (m, 6H), 1,65 (m, 2H), 3.68 (s, 3H), 3.82 (t , J = 6.8Hz, 6H), 6.8 (s, 4H).^{13}C NMR

($CDCl_3$, TMS) δ_c: 153.90 (1C), 155.56 (1 C), 115.61 (2C),114.80 (2C), 68.77 (1C), 55.71 (1C), 31.65 (1C), 29.42 (1C), 25.78 (1C), 22.64 (1C), 14.06 (1C).

2.4.16 2,5-BIS(CHLOROMETHYL)-1,4-DIMETHOXYBENZENE

To a solution of 1,4-dimethoxybenzene (5 g, 0.0361 mol.) in dioxane (21.5 cm^3) was added conc. HCl (4 cm^3) at room temperature. HCl gas was bubbled through the solution for 15 mins. formaldehyde (3 x 2 cm^3) portions were added slowly over 30 min for one and a half hours. HCl gas was bubbled through the mixture continuously for three and a half hours. After that time the HCl gas flow was stopped and conc. HCl (25 cm^3) was added to the reaction mixture. The resulting solution was cooled and the product was filtered off .The product was recrystallised from dichloromethane/methanol (4.13 g, 48%). ^1H NMR ($CDCl_3$, TMS) δ_H: 3.85 (s, 6H), 4.62 (s, 4H), 6.85 (s, 2H).

2.4.17 2,5-BIS(CHLOROMETHYL)-4-DI-(2-ETHYL HEXYLOXY)BENZENE

To a solution of 1,4-di-(2-ethylhexyloxy)benzene (5.14 g, 0.0149 mol.) in dioxane (21.5 cm^3) was added conc. HCl (4 cm^3) at room temperature. HCl gas was bubbled through the solution for 15 mins. formaldehyde (3 x 2 cm^3) portions were added slowly over 30 min for one and a half hours. HCl gas was bubbled through the mixture continuously for three and a half hours. After that time the HCl gas flow was stopped and conc. HCl (25 cm^3) was added to the reaction mixture. The resulting solution was cooled and the product was filtered off. (4.36

g, 58.9% crude) the product was recrystallised from methanol ^{1}H NMR ($CDCl_3$, TMS) d $_H$: 'H NMR ($CDCl_3$, TMS) δ_H: 0.85 (m, 10 H), 1.25 (m, 14 H), 1.65 (m, 2 H), 3.7 (m, 4 H) 6.7 (m, 4 H). NMR showed that only starting material was present this experiment was repeated a further three times under modified conditions only starting material was found in all cases.

2.4.18 1-METHOXY 2-ETHYLHEXYLOXY BENZENE

2-ethylhexyloxyphenol (3.5 g, 0.01568 mol.) was added to a stirred solution of powdered potassium hydroxide (3.5 g, 0.0627 mol.) in DMSO (30 cm^3). Methyl Iodide (4.44 g, 0.0448 mol,1.95 cm^3) was then added. The mixture was stirred continuously for thirty minutes, at which time the solution was poured into water (30 cm^3) and extracted with dichloromethane. The extracts were washed with water, dried and left to crystallise (1.26 g, 34.23%).^{1}H NMR ($CDCl_3$, TMS) δ_H:0.88 (t , J=7Hz, 3 H), 1.25-1.9 (m, 10 H), 3.77 (s, 3 H), 3.87 (d, 2 H), 6.75 (m, 4H).

2.4.19 2,5-BIS(CHLOROMETHYL)-1,4-DI (2-ETHYL HEXYLOXY) BENZENE

To a solution of 1,4-di-(2-ethylhexyloxy) benzene (5 g, 0.0361 mol.) in dioxane (21.5 cm^3) was added conc. HCl (4 cm^3) at room temperature. HCl gas was bubbled through the solution for 15 mins. formaldehyde (3 x 2 cm^3) portions were added slowly over 30 min for one and a half hours. HCl gas was bubbled through the mixture continuously for three and a half hours. After that time the HCl gas flow was stopped and conc. HCl (25 cm^3) was added to the reaction mixture. The resulting solution was cooled but the product obtained did not crystallise. The product was isolated by extraction into methanol and left to crystallise in the fridge. No crystals were obtained. NMR of the oily product showed impurities present and the product was distilled under vacuum but the product decomposed on heating. This procedure was repeated with 2.8 g of the starting material and the product obtained showed no CH_2Cl peaks in the ^1H NMR, which indicates that only the starting material had been recovered.

2.4.20 POLYMERISATION OF 2,5-BIS(CHLOROMETHYL)-1-METHOXY-4-HEXYLOXYBENZENE

To a flame-dried septum-capped flask was added (5 g, 0.024 mol.) of 2,5-bis(chloromethyl)-1-methoxy-4-hexyloxybenzene in 100 cm^3 of THF. To a second flask prepared in an identical manner to the first one was added (2.00 g, 0.018 mol.) of potassium tertiary butoxide also in 100 cm^3 of THF. The contents of both flasks were degassed by bubbling nitrogen through the solutions for 30 mins.. The potassium *t*-butoxide solution was added to the monomer solution by injection through the rubber septa. The reaction mixture was left to stir for 2 hours. Poly(1-methoxy-4-hexyloxy)PPV was obtained by precipitation into methanol isolated by centrifuge and cleaned by repeatedly redissolving in THF and reprecipitating into methanol and isolation by centrifuge.

2.4.21 POLYMERISATION OF 2,5-CHLOROMETHYL-1,4-METHOXYBENZENE

To a flame-dried septum-capped flask was added (2 g 0.0085 mol.) of 2,5-bis(chloromethyl)-1-methoxy-4-hexyloxybenzene in 80 cm^3 of THF. To a second flask prepared in an identical manner to the first one was added (0.71g, 0.0064mol.) of potassium tertiary butoxide also in 80 cm^3 of THF. The contents of both flasks were degassed by bubbling nitrogen through the solutions for 30 mins. The potassium *t*-butoxide solution was added to the monomer solution by injection through the rubber septa. The reaction mixture was left to stir for 2 h. The polymer was obtained by precipitation into methanol isolated by centrifuge and cleaned by repeatedly redissolving in THF and reprecipitating into methanol and isolation by centrifuge.

2.4.22 POLYMERISATION OF 2,5-BIS(CHLOROMETHYL)-1,4-HEXYLOXYBENZENE

To a flame-dried septum-capped flask was added (1 g, 0.0026 mol.) of 2,5-bis(chloromethyl)-1-methoxy-4-hexyloxybenzene in 50 cm^3 of THF. To a second flask prepared in an identical manner to the first one was added (0.218g, 0.0020 mol.) of potassium tertiary butoxide also in 50 cm^3 of THF. The contents of both flasks were degassed by bubbling nitrogen through the solutions for 30 mins. The potassium *t*-butoxide solution was added to the monomer solution by injection through the rubber septa. The reaction mixture was left to stir for 2 h. Poly(1,4-hexyloxy)PPV was obtained by precipitation into methanol isolated by centrifuge and cleaned by repeatedly redissolving in THF and reprecipitating into methanol and isolation by centrifuge.

2.4.23 1,4-DIOCTYLOXYBENZENE AND OCTYLOXYPHENOL

To a solution of hydroquinone (20 g, 0.18 mol.) in methanol (100 cm^3) was added a solution of potassium hydroxide (21.06 g, 0.36 mol.) in methanol (120 cm^3) at room temperature. After 5 min stirring, a mixture of n-octyl bromide (118 g, 0.72 mol.) in acetone (200 cm^3) was added slowly to the reaction mixture. This mixture was refluxed for 9 h. It was then concentrated by evaporation of solvents, diluted with water and extracted into dichloromethane (500 cm^3). The dichloromethane extracts were dried over magnesium sulphate and evaporated to dryness under reduced pressure. to yield a dark brown viscous liquid which on cooling solidified to form dark brown, slightly translucent crystals which had an oily residue trapped between the crystal layers. *n*-Octylbromide was distilled off under reduced pressure and the product was recrystallised from light petroleum.

2.4.24 PURIFICATION (SEPARATION OF MONO AND DISBSTITUTED SPECIES)

A solution of the product in sodium hydroxide (2 M, 200 cm^3) was stirred for 30 min in order to ensure complete conversion of the monosubstituted phenol into the salt form. Separation of the disubstituted product was accomplished by extraction into dichloromethane. The dichloromethane extracts were dried over magnesium sulphate and the solvent was removed under reduced pressure and then under high vacuum to afford white needles (35 g, 58%) .^{1}H NMR ($CDCl_3$, TMS) δ $_H$: 0.80 - 1.8 (m, 30 H), 3.85 (s, 4 H), 6.65 (s, 4 H). The monosubstituted phenol was released from solution by addition of HCl (2M 200 cm^3). The monosubstituted product was extracted into dichloromethane and the extracts were dried over magnesium sulphate and the solvent evaporated under reduced pressure and then under high vacuum to afford a dark brown solid (3.28 g). ^{1}H NMR ($CDCl_3$, TMS) δ $_H$: 0.80 - 1.8 (m, 15 H), 3.85 (s, 2 H), 6.65 (s, 4 H).

2.4.25 1-METHOXY-4-OCTYLOXYBENZENE

To a solution of *p*-methoxyphenol (28.7 g, 0.23 mol.) in methanol (100 cm^3) was added a solution of potassium hydroxide (15.62 g, 0.28 mol.) in methanol (140 cm^3) at room temperature. After 5 min stirring, a mixture of *n*-octyl bromide (88.83 g, 0.46 mol.) in acetone (150 cm^3) was added slowly to the reaction mixture. This mixture was refluxed for 4 hours. It was then concentrated by evaporation of solvents, diluted with water and extracted into dichloromethane (500 cm^3). The dichloromethane extracts were dried over magnesium sulphate and evaporated to dryness under reduced pressure. To yield a cream coloured viscous liquid which on cooling solidified to form small slightly translucent crystals which had an oily residue trapped between the crystal layers. *n*-Octylbromide was distilled off under reduced pressure. The product was isolated using an air condenser. and recrystallised from methanol. This yielded white crystals (32.84 g, 60.50%) ^{1}H NMR ($CDCl_3$, TMS) δ $_H$: 0.85 (s, 3 H), 1.2 (m, 10 H), 1.65 (m, 2 H), 3.65 (s, 3 H), 3.75 (t, J =7 Hz,2 H), 6.85 (s, 4 H).

2.4.262,5-BIS(CHLOROMETHYL)-1-METHOXY-4 OCTYLOXYBENZENE

To a solution of 1-methoxy-4-octyloxybenzene (27.6 g, 0.117 mol.) in dioxane (172 cm^3) was added conc. HCl (28 cm^3) at room temperature. HCl gas was bubbled through the solution for 15 min. Formaldehyde (3 x 14 cm^3) portions were added slowly over 30 min for one and a half hours. HCl gas was bubbled through the mixture continuously for three and a half hours. After that time the HCl gas flow was stopped and conc. HCl (128 cm^3) was added to the reaction mixture. The resulting solution was cooled whereupon the product was obtained however the NMR shows that only starting material was present..^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.85 (s, 3 H), 1.2 (m, 10 H), 1.65 (m, 2 H), 3.65 (s, 3 H), 3.75 (t, J =7 Hz,2 H), 6.85 (s, 4 H).

2.4.272,5-BIS(CHLOROMETHYL)-1,4-DIOCTYLOXYBENZENE

To a solution of 1,4-octyloxybenzene (39.07g, 0.117 mol.) in dioxane (172 cm^3) was added conc. HCl (28 cm ^{3}) at room temperature. HCl gas was bubbled through the solution for 15 min. Formaldehyde (3 x 14 cm^3) portions were added slowly over 30 min for one and a half hours. HCl gas was bubbled through the mixture continuously for three and a half hours. After that time the HCl gas flow was stopped and conc. HCl (128 cm^3) was added to the reaction mixture. The resulting solution was cooled whereupon the product was obtained. This procedure yielded only starting material. ^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.80 - 1.8 (m, 30 H), 3.85 (s, 4 H), 6.65 (s, 4 H).

2.4.28 2,5-BIS(CHLOROMETHYL)-1-METHOXY-4-OCTYLOXYBENZENE

To (11.99 g, 0.05 mol.) of 1-methoxy-4-octyloxybenzene was added 27 cm^3 of conc. HCl, 24.25 cm^3 phosphoric acid (85%), 33 cm^3 glacial acetic acid and 10.5 g of paraformaldehyde. The mixture was heated under reflux at 95 - 100 ^{o}C HCl gas was bubbled through the mixture continuously for 5 h. After that time the HCl gas was stopped and the reaction was maintained at 110^{o}C for a further 4 h. The reaction was then stopped and the mixture was left to cool The product precipitated out upon cooling and was isolated by filtration neutralised and recrystallised from hexane (12.25 g, 73.7%).^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.85 (s, 3 H), 1.2 (m, 10 H), 1.65 (m, 2 H), 3.8 (s, 3 H), 4.0 (t, J =7 Hz,2 H), 4.75 (s, 2 H), 4.8 (s, 2 H), 6.85 (s, 2 H).

2.4.29 2,5-BIS(CHLOROMETHYL)-1,4-DIOCTYLOXYBENZENE

To (16.7 g, 0.05 mol.) of 1,4-dioctyloxybenzene was added 27 cm^3 of conc. HCl, 24.25 cm^3 phosphoric acid (85%), 33 cm^3 glacial acetic acid and 10.5g of paraformaldehyde. The mixture was heated under reflux at 95 - 100^{o}C HCl gas was bubbled through the mixture continuously for 5 h. After that time the HCl gas was stopped and the reaction was maintained at 110^{o}C for a further 4 h. The reaction was then stopped and the mixture was left to cool the product precipitated out upon cooling and was isolated by filtration neutralised and recrystallised from hexane NMR showed only starting material was recovered. ^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.80 - 1.8 (m, 30 H), 3.85

(s, 4 H), 6.65 (s, 4 H).

2.9.30 2,5-BIS(CHLOROMETHYL)-1,4-DI-(2-ETHYLHEXYLOXY)BENZENE

To (16.7 g, 0.05 mol.) of 1,4-di(2-ethylhexyloxy)benzene was added 27 cm^3 of conc. HCl, 24.25 cm^3 phosphoric acid (85%), 33 cm^3 glacial acetic acid and 10.5 g of paraformaldehyde. The mixture was heated under reflux at 95 -100 ^{o}C HCl gas was bubbled through the mixture continuously for 5 h. After that time the HCl gas was stopped and the reaction was maintained at 110 ^{o}C for a further 4 h. The reaction was then stopped and the mixture was left to cool the product precipitated out upon cooling and was isolated by filtration neutralised and recrystallised from hexane (17.85 g, 83%)^1H NMR ($CDCl_3$, TMS) δ_H: 0.85 (m, 4 H), 1.25 (m, 16 H), 1.6 (s, 2 H) 3.7 (m, 4 H), 4.8 (s, 4H), 6.85 (s, 2H).

2.9.31 POLYMERISATION OF 2,5-BIS-CHLOROMETHYL-1-METHOXY-4-OCTYLOXYBENZENE

To a flame-dried septum-capped flask was added (5 g, 0.021 mol.) of 2,5-bis(chloromethyl)-1-methoxy-4-octyloxybenzene in 100 cm^3 of THF. To a second flask prepared in an identical manner to the first one was added (1.76g, 0.016mol.) of potassium tertiary butoxide also in 100 cm^3 of THF. The contents of both flasks were degassed by bubbling nitrogen through the solutions for 30 mins. The potassium *t*-butoxide solution was added to the monomer solution by injection through the rubber septa. The reaction mixture was left to stir for 2 hours. Poly(1-methoxy-4-octyloxy)PPV was obtained by precipitation into methanol isolated by centrifuge and it was purified by repeatedly redissolving in THF and reprecipitating into methanol and isolation by centrifuge.

2.4.32 POLYMERISATION OF 2,5-BIS(CHLOROMETHYL)-1,4-DI-(2-ETHYLHEXYLOXY)BENZENE

To a flame-dried septum-capped flask was added (16 g, 0.019 mol.) of 2,5-chloromethyl1,4-di-(2-ethylhexyloxy)benzene in 100 cm^3 of THF. To a second flask prepared in an identical manner to the first one was added (1.58g, 0.014 mol.) of potassium tertiary butoxide also in 100 cm^3 of THF. The contents of both flasks were degassed by bubbling nitrogen through the solutions for 30 mins. The potassium *t*-butoxide solution was added to the monomer solution by injection through the rubber septa. The reaction mixture was left to stir for 2 hours. Poly(1,4-di-(2-ethylhexyloxy)PPV was obtained by precipitation into methanol isolated by centrifuge and cleaned by repeatedly redissolving in THF and reprecipitating into methanol and isolation by centrifuge.

2.4.33 POLYMERISATION OF 2,5-CHLOROMETHYL-1-METHOXY-4-HEXYLOXY BENZENE.

To a flame-dried, septum-capped flask was added (1 g, 0.00313 mol) of 2,5-chloromethyl-1-methoxy-4- hexyloxy benzene in 100 cm^3 of THF. To a second flask prepared in an identical manner to the first one was added (0.3425g, 0.00235 mol.) of potassium tertiary butoxide also in 100 cm^3 of THF. The contents of both flasks were degassed by bubbling nitrogen through the solutions for 30 min The potassium *t*-butoxide solution was added to the monomer solution by injection through the rubber septum. A portion of the reaction mixture 2 cm^3 was extracted and monitored over a 12 h period by UV/VIS spectroscopy. The remaining mixture was left to stir for 2 h. On precipitation into methanol the polymer turned from white to yellow. This procedure was also carried out at 0°C and at -78°C. The same results were found for the procedure at 0 °C. at -78°C the reaction yielded starting material.

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Chapter 3

Preparation of PPV/sol-gel composites

3.0.0 INTRODUCTION

The main aim of this chapter is to develop a new class of LED devices based on emissive polymers and metal complexes to overcome the inherent efficiency limitations of organic devices. The polymers/complexes were chosen for immobilisation in sol-gel processed silica glass.

Thin films of hybrid material can be made in a sandwich configuration between two electrodes across which an electric field can be applied. Electrons and holes pass through the film *via* specially conducting molecules (charge transport layers) so as to reach the immobilised material within the film. When these electrons and holes meet at the luminescent material they annihilate each other to emit light Figure 1.

The sol-gel method provides a relatively quick, simple, low temperature method of Immobilising luminescent materials. These composites are believed to be more durable than thin molecular films. The glass, besides being an optically transparent matrix, is also thought to help in the preservation of the luminescent properties of the embedded materials as is explained below.[1, 2]

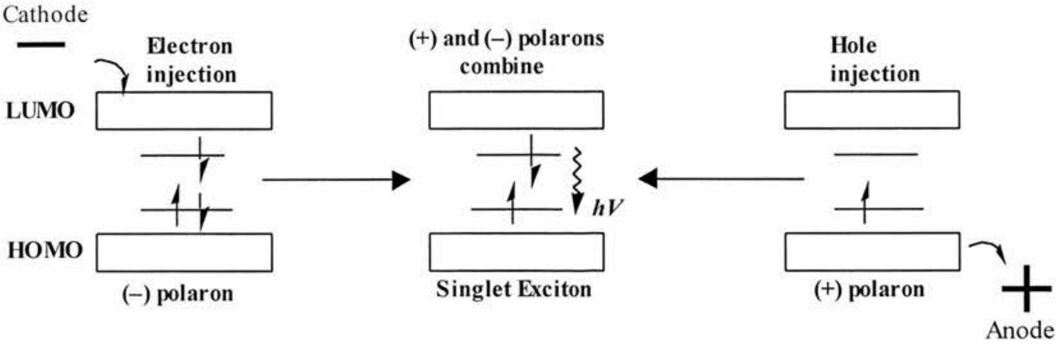


Figure 1

Current polymer LEDs have several limitations. Polymer LEDs work but they do not yet have the performance to rival conventional LEDs, and devices are fragile. Device lifetimes are shorter than desired. After device failure, microscopic black dots are apparent in the polymer material. Several theories have been postulated to account for the black spots.

(i) The light emitted by the device itself may be causing photo-decomposition and/or photooxidation.

(ii) The film may not be of uniform thickness thus causing thinner parts to attract more current and cause degradation of the polymer.

(iii) Dust particles may act as insulating areas which cause localised resistive heating.

The concepts raised here are discussed in greater detail in Chapter 1 (Introduction).

In this chapter we describe the development for incorporating light emitting species into a sol-gel matrix. This new class of LEDs is based on the symbiotic relationship of an intimately mixed silica/luminescent species for both photoluminescence and electroluminescence applications.

The advantages of such composite materials are as follows:

* The sol-gel method provides a relatively quick method of immobilisation.

- * Greater processability of sol-gels compared to polymer materials: facile preparation of thin films and lower cost due to low temperature processing.
- * Greater durability: inorganic silica glasses are inherently more thermally stable than polymers. Sol-gel glasses will resist deterioration through crystallisation.

Polymeric LEDs are generally made by spin-coating the polymer onto an indium tin oxide (ITO) substrate, and attaching electrodes to the glass. Sol-gel/polymer hybrids have the advantage that the polymer is already encased in glass and does therefore not need to be spin-coated onto glass. The device can be made simply by spin-coating the performed material with ITO and depositing the metal contacts directly onto the free-standing hybrid material.

There has been an interest recently in the encapsulation of luminescent polymers in sol-gel materials to eliminate the problems of the long-term stabilities of LEPs and increase the luminescence intensity and efficiency. Chang and Whang[3] have synthesised interpenetrating networks (IPNs) of PPV and silica via the sol-gel route. This work showed that the preparation of these PPV sol-gel composites is possible and merits further investigation. These IPNs did not phase-separate and could be used as the emissive layer in LED devices.

3.1.0 TECHNIQUES (INSTRUMENTS USED)

The background to thermal analysis and photoluminescence methods were discussed chapter 2 sections 2.1.2 and 2.1.4 respectively. In the remaining sections we describe special techniques used for the sol-gel composite materials.

3.1.1 SPIN COATING: INTRODUCTION TO SOL-GEL THIN FILM PRODUCTION

For electrochemistry and device applications thin film construction is necessary. Sol-gel cast thin films form crackless ceramics upon drying (thickness<0.5 μm). This can be explained in that the energy required to form cracks in a solid comes from the relief of stress in a volume proportional to the size of the original flaw. Since the energy invested in growing the crack is proportional to the surface area created, in thin films the surface to volume ratio becomes a barrier to the growth of the crack. It has been shown[4] that the energy release rate for such flaws is approximately proportional to the thickness of the film. Therefore as the thickness of the film approaches zero the stress intensity falls bellow the critical intensity of the material. It appears that this point is reached at approximately 1μm for most films using the technique of spin-coating.[5]

Spin-coating is divided into four stages[6] (1) deposition; (2) "spin up"; (3) "spin off"; and (4) evaporation. These stages are shown in Figure 2

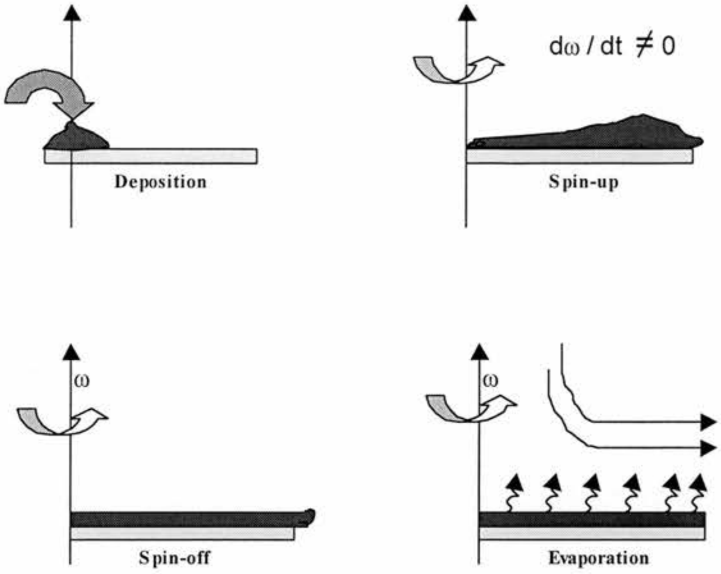


Figure 2 Spin-coating onto glass substrates

As excess of liquid is dispensed on the surface during the deposition stage. In “spin-up” the liquid flows radially outwards, as governed by the centrifugal forces. The excess liquid flows to the edges and leaves the surface as droplets. The thinner the film the greater the resistance to flow. Then evaporation takes over as the concentration of the non-volatile components increases and becomes the primary mechanism of thinning.

3.1.2 SOLID STATE NMR

Solid-state ^{13}C MAS NMR spectra were obtained on a Brüker 500 MSL spectrometer with a wide-bore Oxford superconducting magnet.

Using this NMR technique we investigated the structural aspects of the composites. ^{13}C was taken as the nucleus of choice as ^{1}H spectra have lower resolution due to dipolar broadening. Figure 3 shows the guidelines used in the interpretation of the general spectral signals found in solid state ^{13}C NMR.

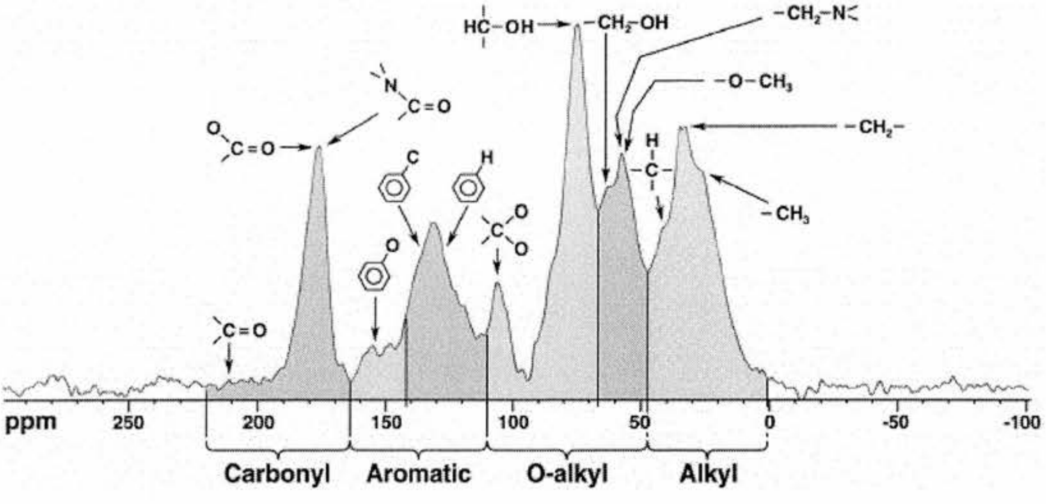


Figure 3 General spectral signals found in Solid State C^{13} NMR
http://www.waite.adelaide.edu.au/NMR/

3.2.0 SOL-GEL PREPARATION

Sol-gel processing is best described as follows. Hydrolysis of tetraalkoxysilanes in an organic solvent such as alcohol leads to the formation of products with silanol functions. Which form colloidal dispersion of particles in a liquid i.e., a sol (by condensation polymerisation). The continuation of this process gives a continuous solid skeleton enclosing a continuous liquid phase i.e., a gel. This transformation is considered the sol-gel transition and the gel point is described as the point in time (reaction) when the last link of the continuous network is formed.[7] The solid network is initially supple and allows further condensation and bond formation. This further reaction induces contraction of the network and expulsion of the liquid from pores, a process known as ageing. Drying of the gel by evaporation under ambient conditions gives a dried gel known as a xerogel [8] (Figure 4).

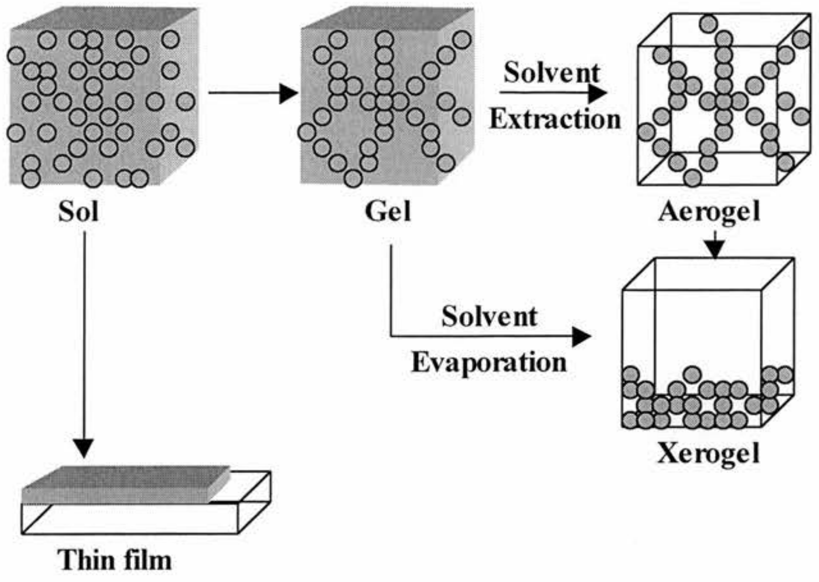


Figure 4 Sol-gel Processing

3.3.0 SYNTHETIC ROUTES TO PPV/SOL-GEL COMPOSITES.

Many different routes were investigated in order to find the optimum method of PPV incorporation.

- Dispersion.
- Monomer (Gilch) incorporation and polymerisation after gelation.
- Derivatisation.
- Preparation of composites using polymer dissolved in drying control agent.
- Preparation of composites using "Flexigels".

3.3.1 DISPERSION

The TEOS and TMOS gels were made according to literature[9] as shown schematically in Figure 5. A solution of polymer dissolved in chloroform (which is not soluble in the sol-gel mixture) was added to the sol at the second mixing stage Figure 5. In this method the polymer precipitated on addition of the polymer/chloroform solution to the sol. Solid aggregates were formed within the glass structure and homogeneity was not achieved. When the polymers were added in dichloromethane solutions the final glass was coloured with the polymer but it also contained specks of precipitated polymer. Excitation under UV at 365 nm showed weak emission from the glass with stronger emission from the precipitated polymer.

3.3.2 MONOMER INCORPORATION (GILCH) AND POLYMERISATION AFTER GELATION.

In these experiments 2,5-bischloromethyl-1,4-dimethoxybenzene and 2,5-bischloromethyl-1-methoxy-4-hexyloxybenzene monomer were added to the initial mixture of the sol-gel precursor in alcohol. The reaction was catalysed with HCl in the usual way. However, after 90 min a solution of base in alcohol was added. The base was thought to have two effects: (1) polymerisation of the monomer within the gelling solution; and (2) catalysis of the sol-gel process. In one experiment potassium hydroxide in ethanol was used. In another potassium *t*-butoxide was the base added. In each case the amount of base added was one equivalent w.r.t. monomer. In the first experiment addition of KOH in EtOH caused gelation to occur instantaneously. The products of all three reactions were opaque glasses; however, on heating at 200 °C for 10 min the material became yellow. This may indicate that polymerisation is occurring after the formation of the gel and that somehow the formation of the gel is inhibiting the polymerisation reaction, perhaps at the precursor polymer stage (loss of one HCl per monomer).

The inhibition may be due to the restraining nature of the base-catalysed sol-gel, which has a dense ceramic type network as opposed to the more polymeric skeletal structure of an acid catalysed gel (chapter 1).

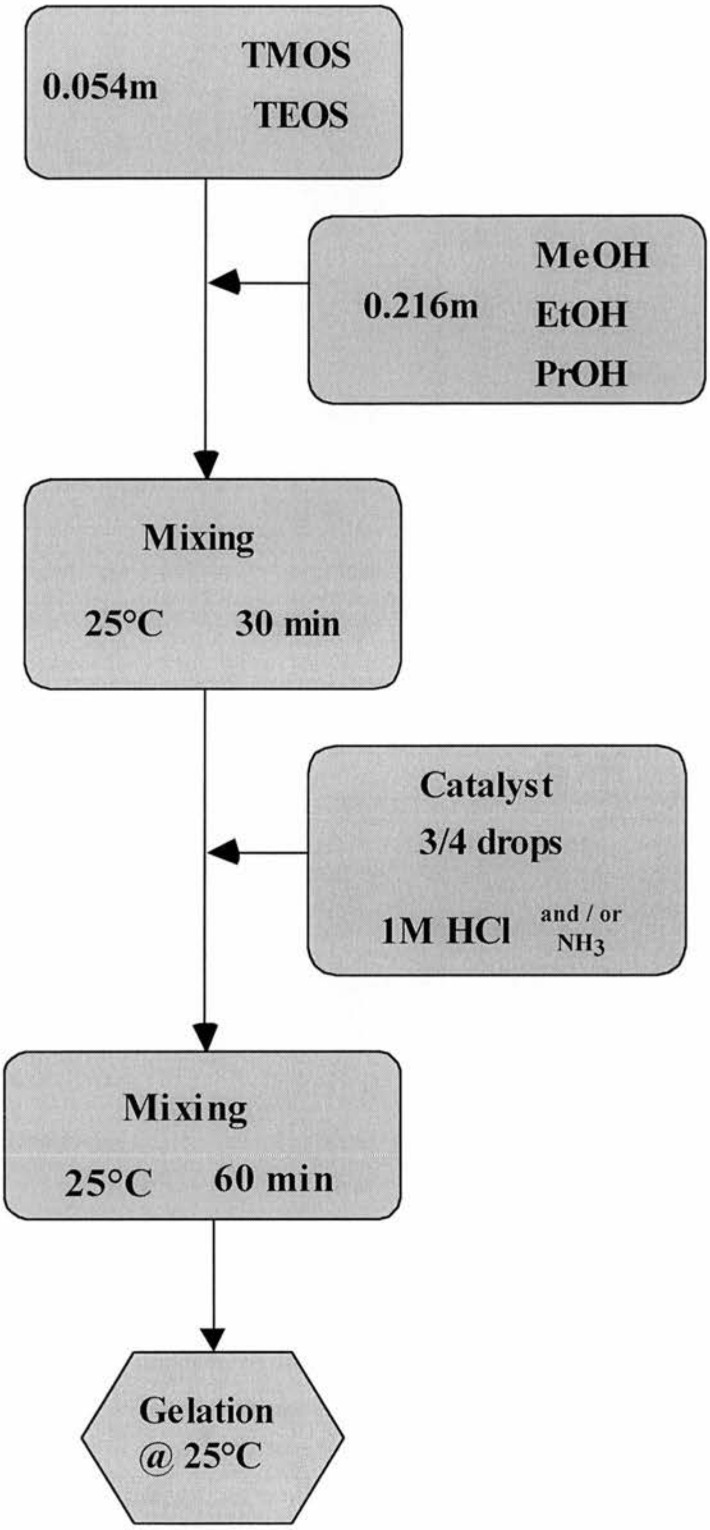


Figure 5 Schematic representation of Sol-gel Processing

Silicon precursor	:	Alcohol	:	Water	:	Catalyst
1	:	4	:	4	:	0.07

3.3.3 DERIVATISATION

The aim of these experiments was to form a gel suitable for coating by protecting the free OH groups in the gel, thus making the material soluble in solvents such as hexane. The alkyl substituted PPV polymers (prepared as discussed in chapter 2) are soluble to some extent in hexane. Adding the polymer solution to the derivatised gel when dip coated onto glass on evaporation form a homogenous thin film of composite material. Prakash *et.al.*[10] made organosilyl derivatised silica sols from (TMSCl) trimethylchlorosilane for sol-gel structural determination by NMR. These gels were made, by using acid followed by base catalysis. The mixture was made up according to the following ratios which Prakash , *et.al.*[10] had used for their preparation of derivatisied gels.

Silicon precursor : Alcohol : Water : HCl Catalyst

1 : 3.8 : 1.1 : 7×10^{-4}

The addition of ammonium hydroxide after 90 min changed the ratios of the mixture to:

Silicon precursor : Alcohol : Water :	HCl/NH_3 catalyst
1 : 3.8 : 1.1 :	$7 \times 10^{-4} / 2 \times 10^{-3}$

Gelation and ageing was carried out 50 °C.

Trimethylsilyl chloride (TMSCL) was used to create organosilyl derivitised silica sols by functionalising the surface of the colloidal silica. TMSCL proved to be a difficult chemical to work with as it is very moisture sensitive. Even after rigorous drying of the gel at 200 °C unwanted products formed within the gel from the presence of water. This method[11] did not produce a sol suitable for dip coating. On evaporation of the solvent a fine opaque residue was formed which was not homogeneous. An alternative derivatisation agent, trimethylsilylimadazole, was chosen as it was not as moisture sensitive as TMSCl. The procedure proved to be easier than before, although no more successful at producing a homogenous thin film.

3.3.4 PREPARATION OF COMPOSITES USING POLYMER DISSOLVED IN DRYING CONTROL AGENT.

It was apparent from all previous experiments for the preparation of TEOS and TMOS sol-gels that on drying and ageing the gels were somewhat brittle and prone to cracking. Any attempts to form thin films by spin-coating or dip-coating in the laboratory failed to produce anything robust. The use of a so-called drying control additive was employed to slow down the evaporation of alcohol and thus reduce the strain within the network due to capillary forces, allowing the film to be formed without cracking. [12] One class of drying control additive is an aprotic solvent that does not form hydrogen bonds, thus making the hydroxide ions more nucleophilic. For example the polar aprotic solvent DMF (dimethylformamide) does not bond to the silicate nucleophile involved in the condensation reaction.

However, due to their polarity the anionic reactants are stabilised with respect to the activated complex, slowing down the gelation reaction to some extent. DMF yields gels with larger pores (see Table 2) which become even larger after ageing at elevated temperatures ($\approx 150^{\circ}$C). Gels made with DMF do not crack at drying rates which would destroy gels prepared in the usual manner. DMF also had the added advantage of being a solvent for the PPV polymers. Free standing thin films of a polymer/glass hybrid were made by dissolving the polymer in DMF and then adding the solution of polymer in DMF to the matrix as a drying control agent. [13, 14]

3.3.5 PREPARATION OF COMPOSITES USING FLEXIGELS

This method was adapted from very recent work aimed at preparing free standing polymer/gel composite thin films for ion-selective electrodes.[15] This method employs the sol-gel process to prepare organic/inorganic polymer materials of network structure Figure 6. These materials are sometimes referred to as ormosils (organically modified silicates). Similar materials have been prepared by de Zea Bermudez *et. al.* [16] Light-emitting fabrics could be formed from spinning these materials which could be useful for future applications.

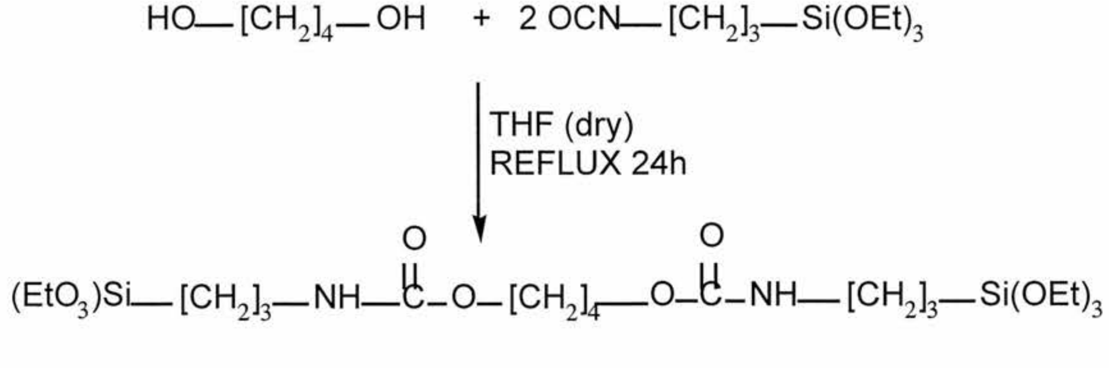
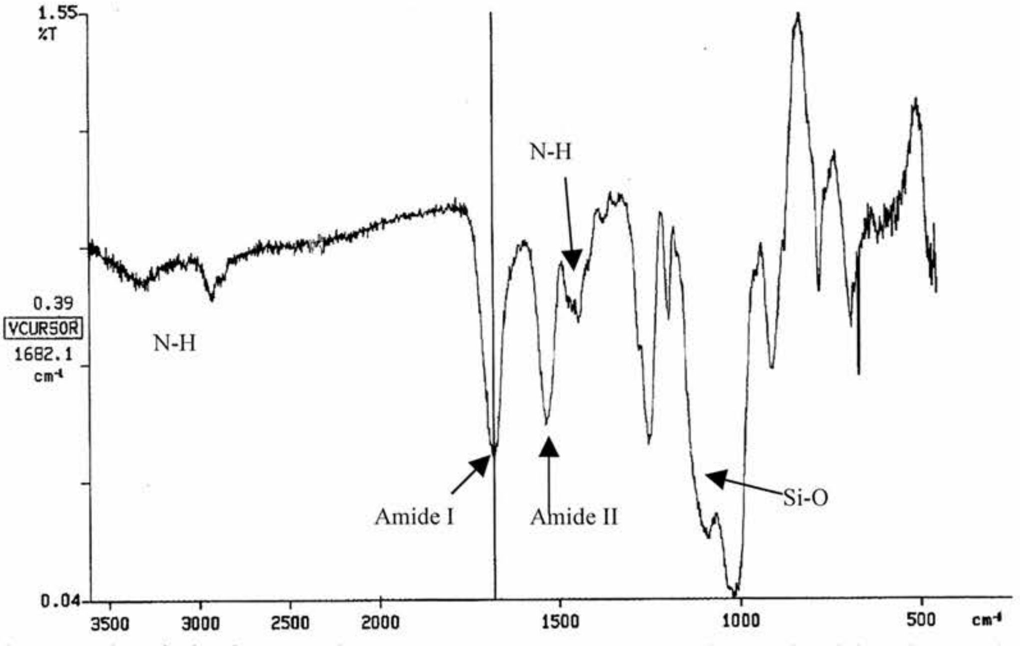


Figure 6 Preparation of Flexigel

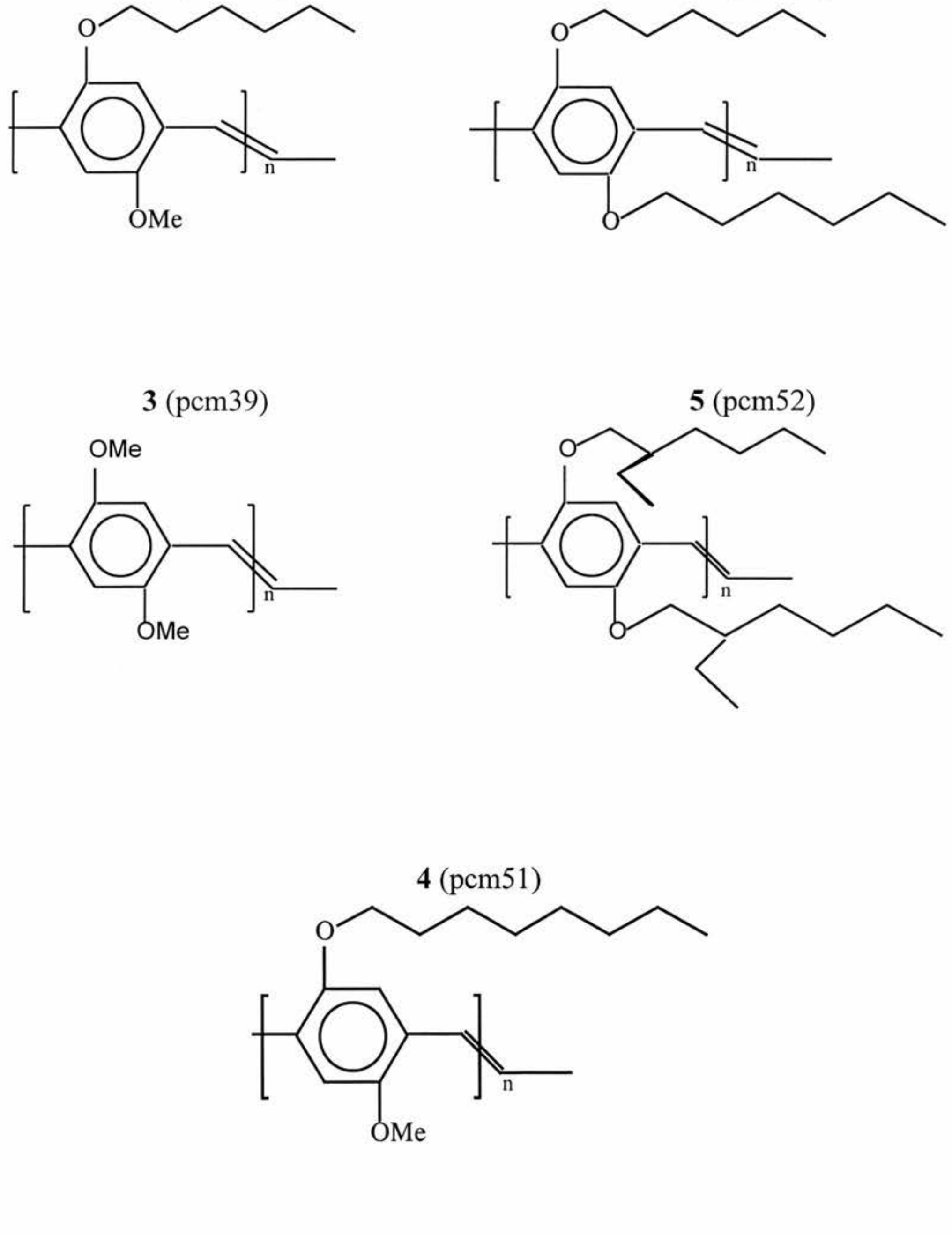
A mixture of 1,4-butandiol and 3-isocyanopropyl were refluxed together in THF for 24 h under nitrogen. The mixture was cooled and the THF was removed by rotary evaporation. The product was solubilised in approx. 200 cm^3 of DMF and filtered to remove any residual undissolved product. The gelling mixture was deposited onto a Teflon sheet and left to evaporate and gel.

FTIR was used to determine the extent of gel formation. The absence of a peak at 2250 cm^{-1} (NCO absorption) showed that the polymer had fully formed. i.e. no residual isocyanate [17]. The spectra also showed amide bands due to the urethane linkage: –CONH- **amide I** 1680-1630 , **amide II** 1515-1570. Other significant peaks include N-H bending at ~1600 also 3000-3500, and Si-O at ~1000 cm^{-1}.



3.4.0 SPECTROSCOPIC STUDIES OF COMPOSITES

The sol-gel composite materials contained the polymers discussed in Chapter 2 and are shown schematically in Figure 7.


1 (pcm37)

2 (pcm38)

3 (pcm39)

5 (pcm52)

4 (pcm51)

Figure 7

3.4.1 PHOTOLUMINESCENCE SPECTROSCOPY

Measurements were recorded on a PE luminescence spectrometer in solution, in TEOS gels, and in flexigels respectively Fig 8-10, at the University of Durham under the guidance of Mr. M. Halim and Dr. I. Samuel. Some further photoluminescence measurements were made at Edinburgh University with the help of Dr. Zoë Pikramenou on a PTI (Photon Technology International Inc.) QM-1 fluorimeter, which is of modular but conventional layout.[18] Performing an adsorption sweep chose the correct excitation wavelength. The wavelength chosen was equal to or less than the maximum of the main adsorption band of the composite samples. The PL spectra recorded for the PPV polymers (partially conjugated alkoxy-polymers discussed in Chapter 2) are shown in Table 1. As reported in Chapter 2 polymers **1**,**4**,and **5** showed the longest wavelength emission due to longer conjugated segments and the presence of longer alkoxy chains than the methyl (Figure 8). Polymer **2** of which batch #1 was used in this work has anomalous properties due to a low molecular weight.

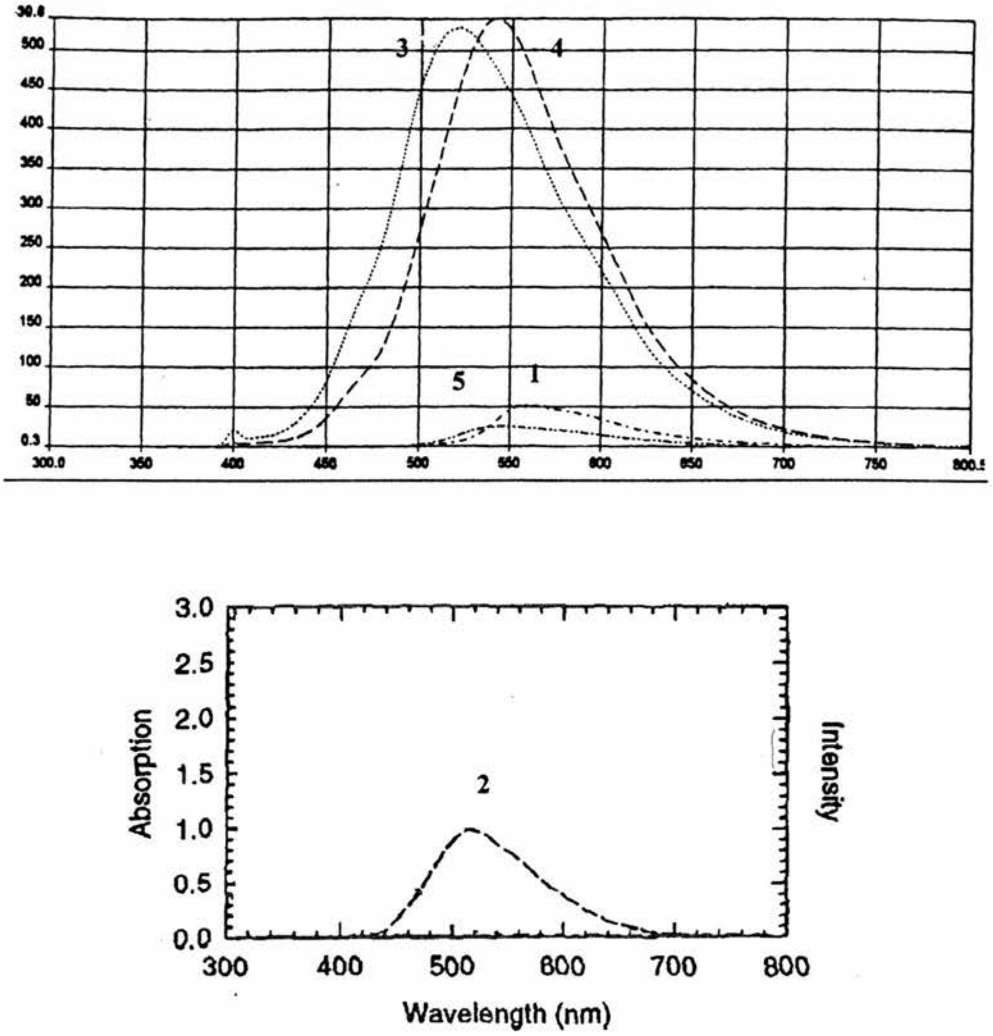


Figure 8 PL of polymers in Solution (DMF)

When the PL spectra of these polymers trapped inside TEOS (rigid glass matrix) gels were taken (Figure 9) it was noted that the majority of the λ_{max}^{em} values were shifted to lower values. This behaviour has also been reported for unsubstituted PPVs in TEOS gels prepared by heating the gels containing the Wessling type precursors.[3]

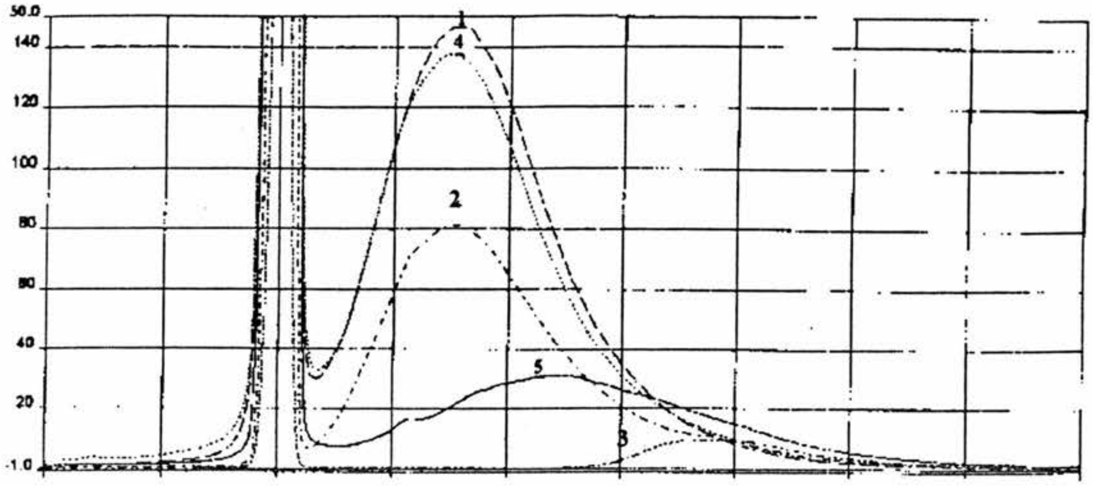


Figure 9 PL of polymers in TEOS

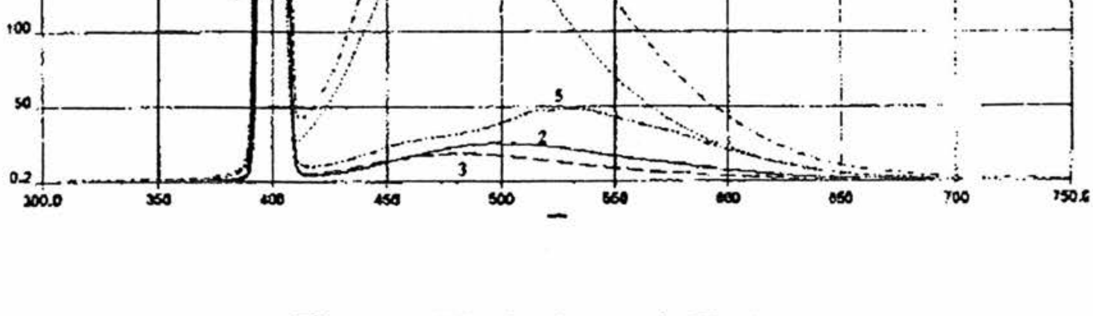


Figure 10 PL of polymers in Flexigel

precursor polymer R1	**precursor polymer R1**	**Reference number (code)**	**Solution DMF λ max. (em) nm**	**TEOS λ max. (em) nm**	**FLEXIgel λ max. (em) nm**
OHex	OMe	**1** (PCM 37)	560	480	500
OHex	OHex	**2** (PCM 38)	518	475	495
OMe	OMe	**3** (PCM 39)	520	590	480
OOct	OMe	**4** (PCM 51)	540	475	485
OMEH	OMEH	**5** (PCM 52)	545	525	525

Table 1

The photoluminescence results show that the wavelength of the light emitted from the gels is characteristic of, and thus originating from, the encapsulated polymer. The results also show broadening of this PL band and shifts in λ_{max}em to higher energy compared to PL of the polymers dissolved in DMF. This could be due to:

(i) The gel may be preventing the polymer from further movement by freezing its conformation because of the restrictive nature of the smaller pore sizes.

(ii) The gel is providing a range of environments, perhaps through a range of pore sizes.

Explanation (i) seems to hold the greatest merit as the emission is very close to that expected for a single stilbene conjugated segment [19]. Chang and Whang [3] also observed a shift in the PL λ_{max}em of PPV polymers when the sol-gel environment was changed from a rigid glass to a more flexible glass. This agrees with the results for three of our polymers. Their assertion that the gel exerts its greatest influence during conversion of their precursor polymers after gellation is questionable since our pre-formed polymers show similar shifts in PL λ_{max}em. We therefore believe that the gel is imposing restriction on the conformation of the polymer regardless of whether the polymer was added to the gel pre-formed or prepared *in situ* after gellation.

The exceptions to the PL broadening and shifts in λ_{max} to higher energy are intriguing. Polymer **3** dimethoxy-substituted PPV, (from the evidence gathered in chapter 2 appears to be more sterically hindered) than the others and this is reflected in the surprising shift to longer wavelength. This is due to further conversion of the polymer chains containing longer segments during thermal treatment of the gel. Alternatively, it may be due to an effect of the polar environment on the emission. A bathochromic shift of 10-20 nm would indeed be expected as a result of a polar environment stabilising the more polar π-π^* excited state. Polymer **5** (di-2-ethylhexyloxy substituents) is the least conjugated of the five polymers as inferred by spectroscopic studies in chapter 2. Perhaps this accounts for its anomalous behaviour as its spectrum is less affected by the gel.

The PL from the flexible polyurethane ormosil (flexigel) Figure 10 show the same general trends. Indeed it is suprising that the softer Flexigel does not show λ_{max}em values closer to those gained from solution. It is possible that a more relevent parameter than Chang and Whang's [3] "hardness" index is the pore size and/or surface area. Literature values for BET porosity and surface area on TEOS, TMOS and "Flexigel". [9, 15] suggest that this is the case. Table 2.

GEL TYPE	SOLVENT	SURFACE AREA	PORE SIZE
TEOS	Ethanol	160 m^2/g	34Å
	Methanol	180 m^2/g	36Å
	Isopropanol	285 m^2/g	18Å
TMOS	Methanol	169 m^2/g	36Å
	Ethanol	305 m^2/g	39Å
FLEXIGEL	DMF	8.3 m^2/g	17Å

Table 2 Table of Literature BET data for dried sol-gel materials [9,15]

PL spectroscopy of the composite materials showed that luminescence occurred within the free-standing films due to homogeneous incorporation of polymeric luminescent material. However, the efficiency of these hybrid materials as LED devices depends on the amount of light-emitting material incorporated in the sol-gel matrix. Currently, the problem is one of loading. Ideally, for LED devices of this type the loading should approach 50% w/w. The polymers used in these studies were as shown in Figure 7. These polymers are only soluble in chlorobenzene to a limit of 10% w/v. This is not enough to approach the 50% w/w necessary for devices of this type. Chang and Whang [3] reported doping levels of 30 and 40 mol%. They found that devices could be made from these concentrations, and that the lifetime and EL efficiencies of these devices were improved in comparison with that of pure PPV because the thermal vibration of the polymer chain was reduced. They also suggested the possibility of tuneable composite LEDs as the photoluminescence wavelength covered a wide range depending on the components and composites used in the synthesis. The solubility of these polymers in polar solvents such as alcohols and water has to be increased in order to approach the theoretical loading necessary. Increasing the solubility of the polymers can be addressed by one of two methods:

(i) Preparation of water-soluble (Wessling type) precursor polymers and addition to the sol-gel matrix.

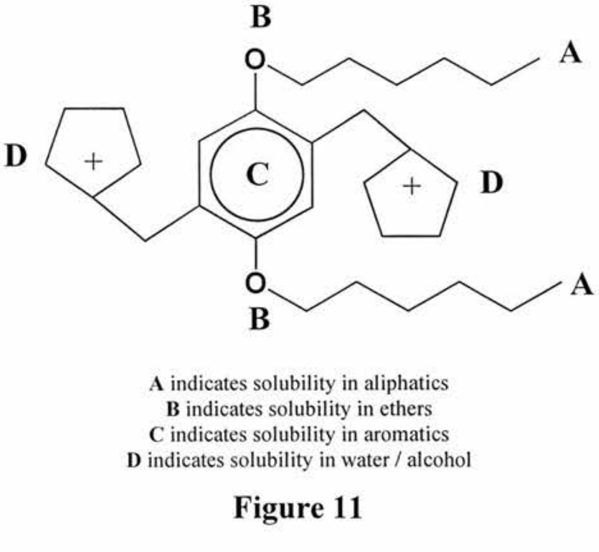
(ii) Polymerisation of water-soluble monomers directly to PPV within the sol-gel matrix via chemical means.

The strategy(ii) was pursued as described in section 3.5.0 (Other synthetic routes to PPV/sol-gel).

3.5.0 OTHER SYNTHETIC ROUTES TO PPV/SOL-GEL

Following on from the method used by Chang and Whang[3] which involved the formation of the Wessling type water-soluble monomer for the incorporation of PPV polymers into sol-gel derived glasses, we attempted to prepare Wessling monomers from three of our alkoxy substituted monomers: firstly the 2,5-bis-chloromethyl-1,4-dihexyloxybenzene, 2,5-bis-chloromethyl-1-hexyloxy-4-methoxybenzene and 2,5-bis-chloromethyl-1-octyloxy-4-methoxybenzene (section 3.7.11, 3.7.12 and 3.7.14).

Crude products were obtained for all three of these monomers; however, they were oily and non-crystalline. The component groups on the monomers are soluble to some extent in a wide range of solvent environments thus making crystallisation difficult (Figure 11). The difficulty encountered in crystallising these compounds and the associated stench from tetrahydrathiophene (THT) does not make for an easily fabricated usable product. It was then decided to prepare the dimethyl sulphide monomer used first by Gagnon *et.al.*[19]



A indicates solubility in aliphatics
B indicates solubility in ethers
C indicates solubility in aromatics
D indicates solubility in water / alcohol

Figure 11

3.5.1 PREPARATION OF COMPOSITES USING P-XYLENE BIS (DIMETHYLSULPHONIUM CHLORIDE)

TEOS gels were made as shown schematically in Figure 16 the monomer (*p*-Xylene bis (dimethylsulphonium chloride)) was added in equal molar quantities w.r.t. TEOS. The viscous sol was applied to prewashed glass slides, and after three days a clear gel formed. At this time the gel-coated slides were dried and subjected to heat treatment. The slides were then heated (100 °C at 0.1 torr) in order to convert the monomer into polymer in accordance with the literature. [20, 21] Instead, the gel bubbled which was due to the loss of alcohol and organic products. The monomer did not convert into the polymer within the gel matrix the material. Instead, it changed its appearance from a clear solid into a white opaque solid. It was thought that the gel matrix was too restrictive i.e it inhibited polymer formation. A higher temperature 200 °C was used on the second attempt. This resulted in even more damage to the gel material and decomposition of the organics to give charred black material.

The methodology used for the synthesis of the PPV precursors was based on the Swatos and Gordon methodology, which was discussed in chapter 2. There we showed that the use of base to polymerise the monomer to the precursor, resulted instead in the formation of a high degree of conversion to conjugated PPV. Thus it was decided that the monomer in the gel could be treated in the same manner to produce a fully conjugated polymer by the base induced polymerisation of the monomer within the gel. The synthesis was similar to that used previously, the only difference being the addition of the monomer with the alcohol to the alkoxysilane (Figure 12). The result was that the polymer formed within the gel on 30 min immersion in 1 mol dm^{-3} NaOH solution.

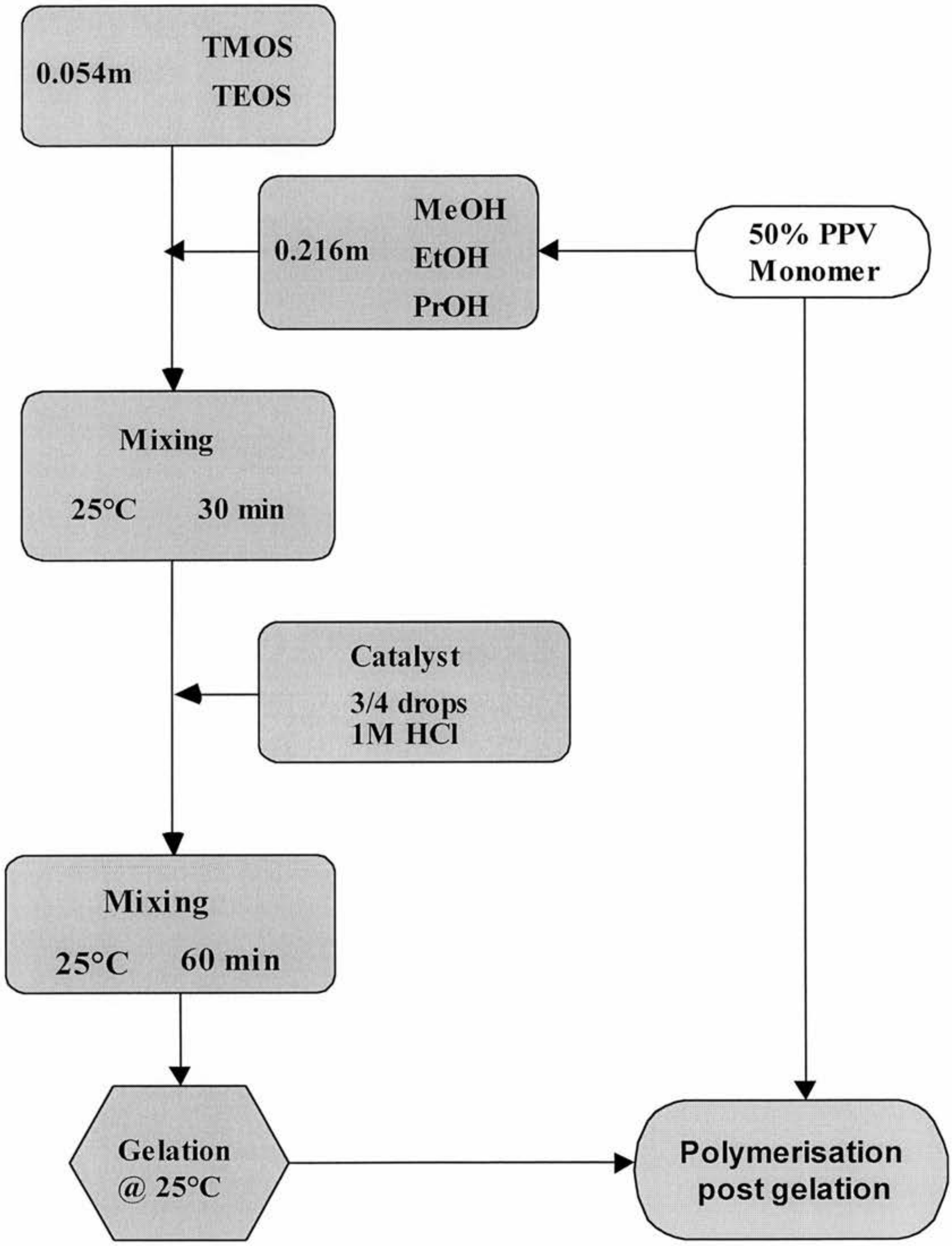


Figure 12

3.5.2 SPECTROSCOPY OF BASE POLYMERISED PPV/SOL-GEL COMPOSITES.

These base-polymerised materials were investigated using PL, FTIR and solid-state NMR in order to determine if the polymer had actually formed within the gel structure.

3.5.3 FTIR

FTIR spectra of the TEOS film before (Figure 13) and after base treatment (Figure 14) were recorded after the sols were cast onto NaCl plates and placed into a dessicator to dry and age. Samples of dried gels were also pressed into disks with KBr, and these proceed to give the best spectra of the two methods.

The spectra of the PPV/gel composites show that characteristic bands due to the aromatic CH stretch of conjugated PPV have appeared above 3000 cm^{-1} at 3024 cm^{-1}. Other characteristic bands expected at 965 and 835 cm^{-1} (due to out-of-plane CH deformation of vinyl and phenyl groups, respectively) were obscured, however, by the broad Si-O peak (900-1100 cm^{-1}).

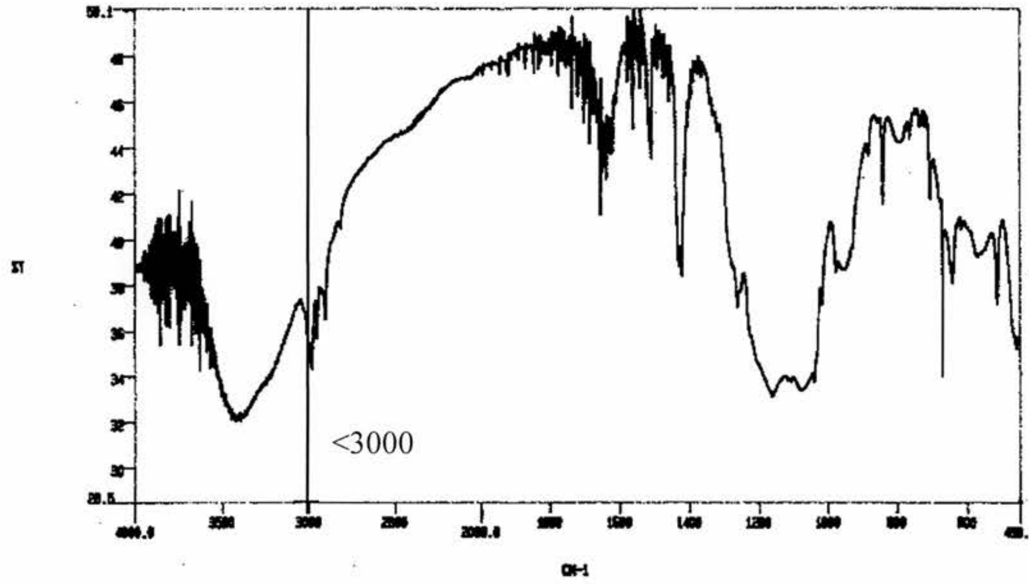


Figure 13

FTIR of TEOS/monomer gel before base polymerisation of the monomer within the gel

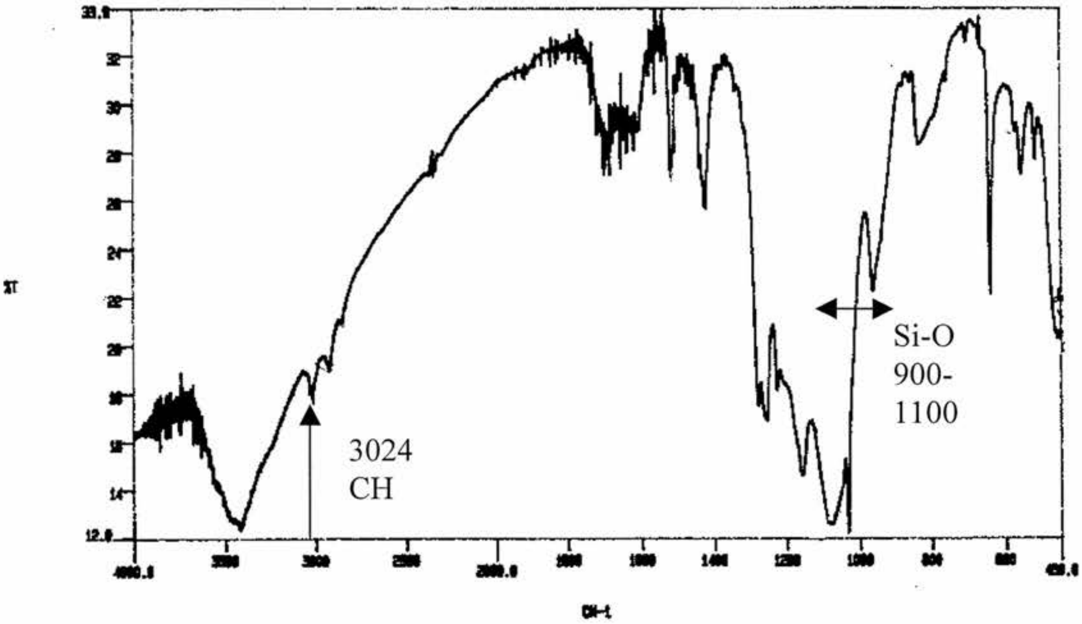


Figure 14

FTIR of TEOS/monomer gel after base polymerisation of the monomer within the gel to form PPV

3.5.4 PHOTOLUMINESCENCE SPECTROSCOPY

The PL and excitation spectra of the TEOS/PPV film is shown in Figure 15. Surprisingly its emission maximum at longer wavelength indicating a large degree of conjugation has occurred, in fact the λ_{max}em for the TEOS/PPV composite approaches that of high-quality PPV produced by the Wessling route (λ_{max}em 550 nm). Even more remarkable is the presence of structure in the excitation spectrum of the TEOS/PPV composite. The presence of vibronic structure is thought to indicate the presence of a narrow distribution of conjugation lengths, which is what one would expect if elimination did not occur randomly but was more favourable, adjacent to an existing conjugated segment [22]. This may be an effect of the gel matrix enclosure but its exact mode of operation is as yet unclear.

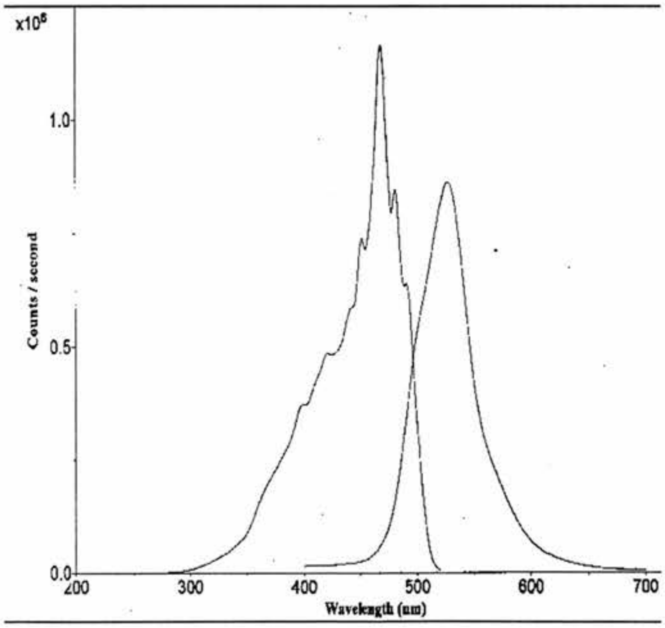
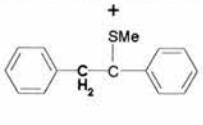
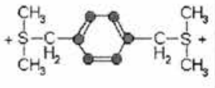
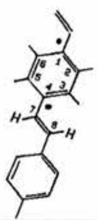


Figure 15 PL of PPV Polymerised in TEOS

3.5.5 SOLID STATE NMR

Solid-state ^{13}C MAS NMR were obtained on a Brüker 500 MSL spectrometer with a wide-bore Oxford superconducting magnet. Samples were spun at between 6 and 8 kHz in 7 mm diameter zirconia rotors with Kel-F caps in a MAS probe.

The three samples TMOS, TMOS+MONOMER and TMOS +PPV (spectra shown in Figures 18-20) were made in ethanol were very different in texture and composition. The blank TMOS gel could not be ground finely enough to facilitate tight packing. The monomer (p-xylene(dimethylsulphonium chloride)) in the TMOS gel sample had a waxy texture, which did not easily lend itself to rotor packing. The third sample polymer (PPV) in TMOS gel was slightly more elastic than the blank gel and caused its own electrostatic charging problems with respect to packing. Table 3 shows the peak assignments for TMOS, TMOS + monomer, and TMOS + PPV.

Samples	**Species observed in solid state NMR (chemical shift δ ppm)**							
	CH_3CH_2OH (ethanol)	OCH_3 (methanol)	CH_3CH_2OH (ethanol)	SMe_2		CH_3OSi (sol-gel)	**MONOMER** 	**PPV** 
TMOS (blank)	24.5	61.8	66.2	----	----	69.1	----	----
TMOS + Monomer	25.3	40-44	45	28.0	48	47.7	130.5 132.7**	----
TMOS + PPV	24.4	40-44	45	28*	50	46.5	----	128.6*** 137.2***

*Large decrease in peak height
** Aromatic protons (refer to text)
***Vinyl and aromatic polymers (refer to text)

Table 3

For comparison purposes, Figure 18 shows the ^{13}C SS NMR of TMOS gel. The peaks were observed due to ethanol and CH_3OSi. In the spectrum of TMOS + monomer (Figure 19), peaks were observed for ethanol, SMe_2 and CH_3OSi. The aromatic region in the TMOS/monomer spectrum (110-170 ppm.) shows the expected behaviour for the monomer, that is two signals corresponding to two equivalent aromatic carbon regions represented in blue and red in Figure 16.

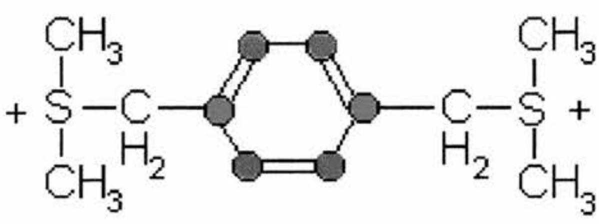


Figure 16

In the spectrum of TMOS + monomer after base treatment (Figure 20), peaks were observed for ethanol, SMe_2 (much less prominent) and CH_3OSi. The aromatic region in the polymer resulting from base treatment of the monomer/gel composite showed peaks in the expected region. The aromatic carbon peaks were broader and shifted downfield w.r.t the monomer which is indicative of conjugated polymer formation.

Published spectra of annealed PPV show two main peaks [23]. The peak at 125 ppm has two peaks with two well-defined shoulder peaks which have been ascribed to the 4 carbons (a), (b), (c) and (d).(see Table 4 and Figure 17 [23])

(a) 136 ppm	C1 and C4
(b) 131 ppm	C2and C5
(c) 127 ppm	C7 and C8
(d) 124 ppm	C3 and C6

Table 4

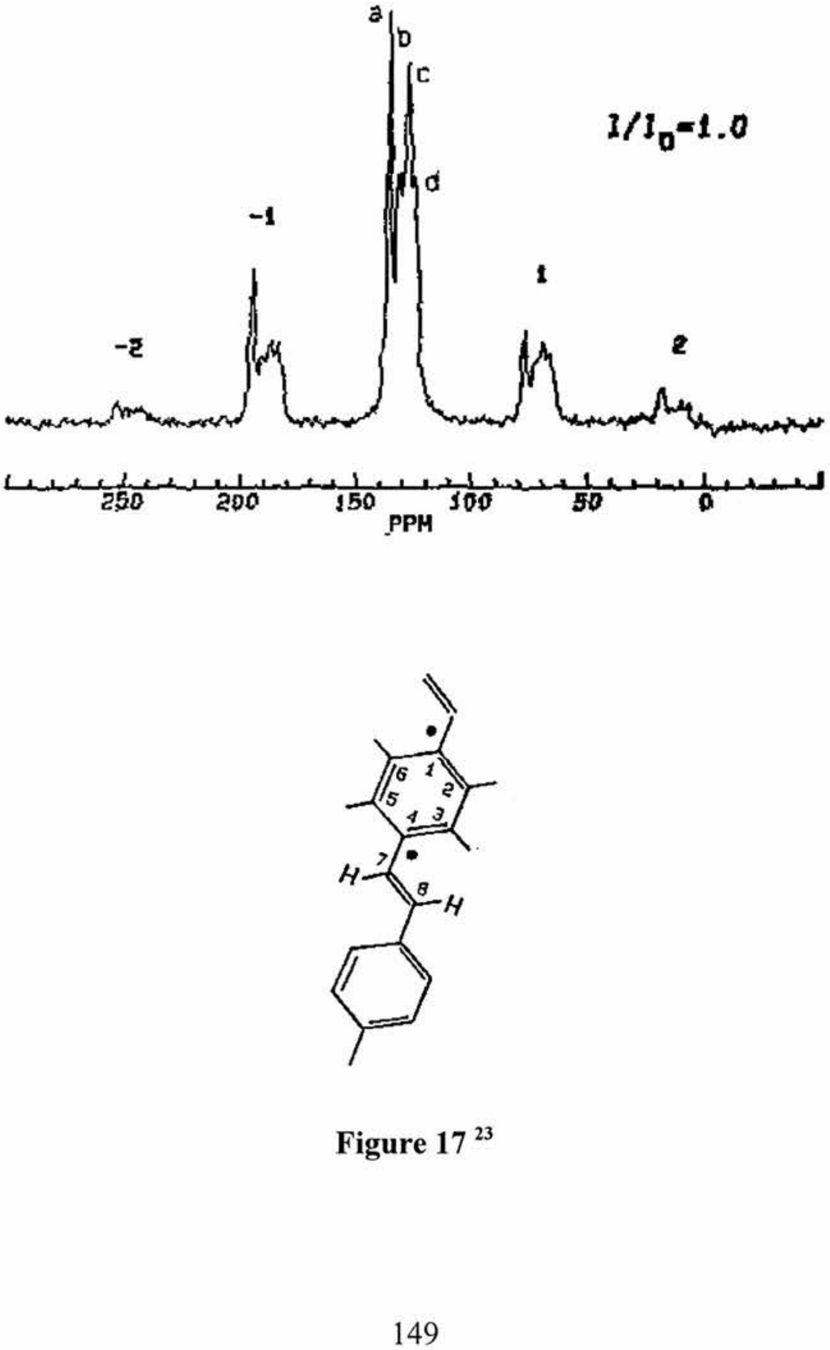


Figure 17[23]

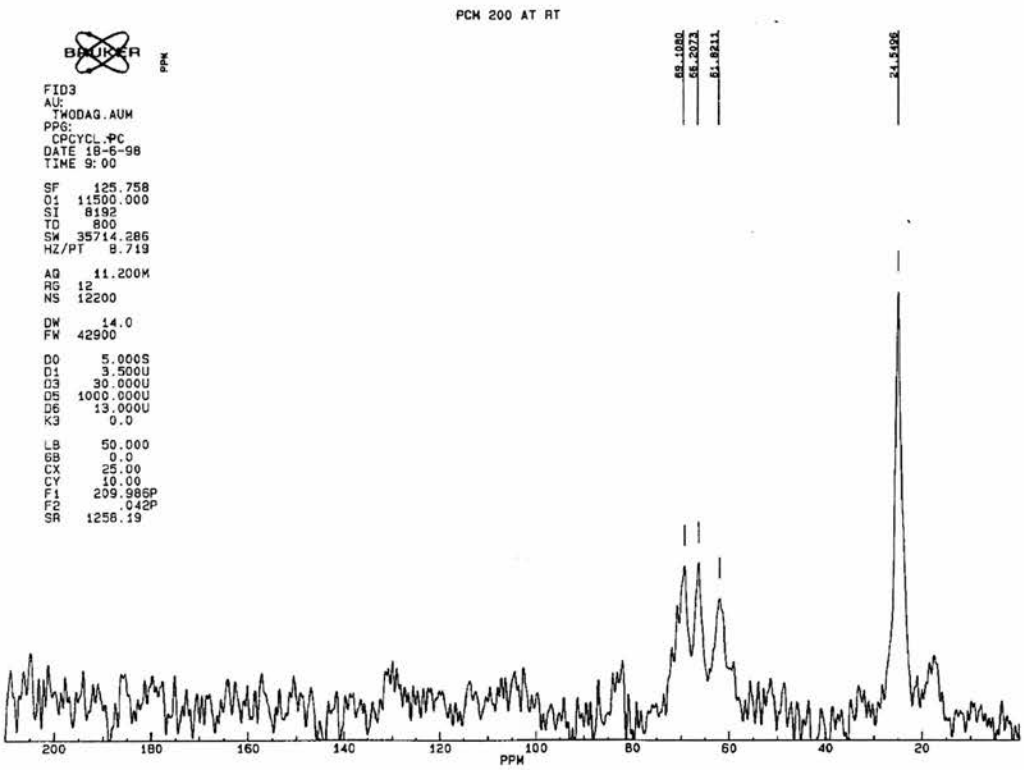


Figure 18 Blank TMOS GEL

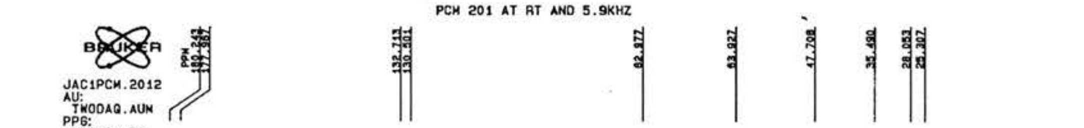
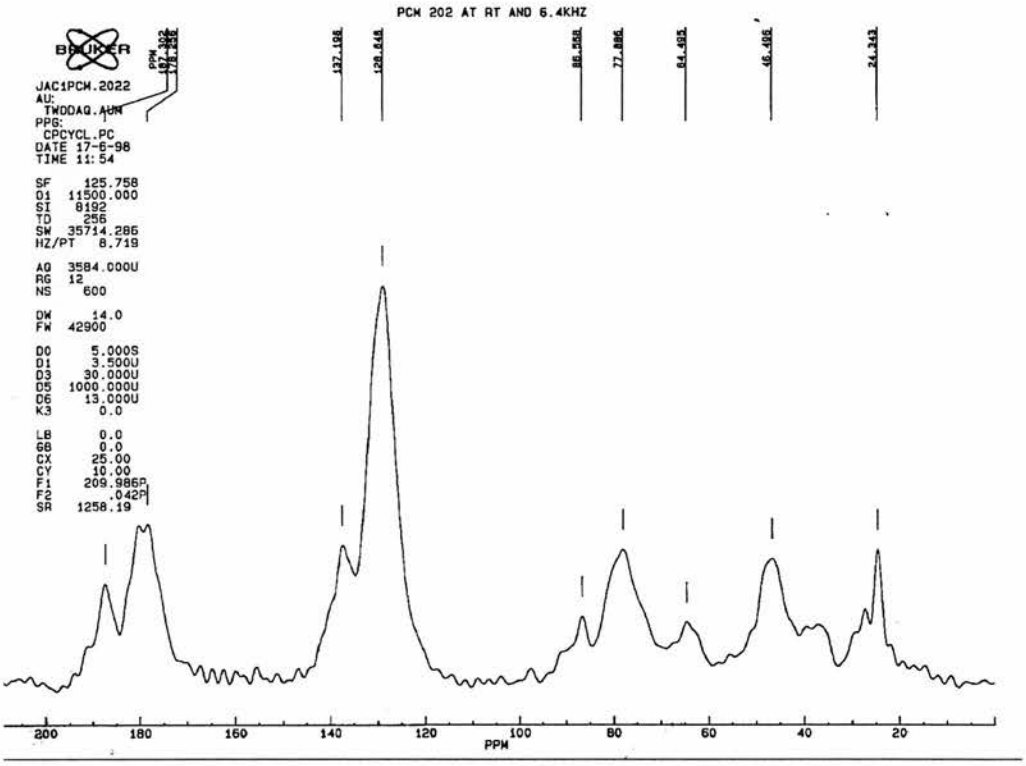


Figure 19 TMOS+ *p*-xylene(dimethylsulphonium chloride)



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JAC1PCM.2022
AU:
 TWDDAQ.AUN
PPG:
 CPCYCL.PC
DATE 17-6-98
TIME 11:54

SF      125.758
O1    11500.000
SI     8192
TD      256
SW    35714.286
HZ/PT     8.719

AQ   3584.000U
RG   12
NS      600

DW       14.0
FW   42900

D0       5.000S
D1       3.500U
D3      30.000U
D5    1000.000U
D6      13.000U
K3       0.0

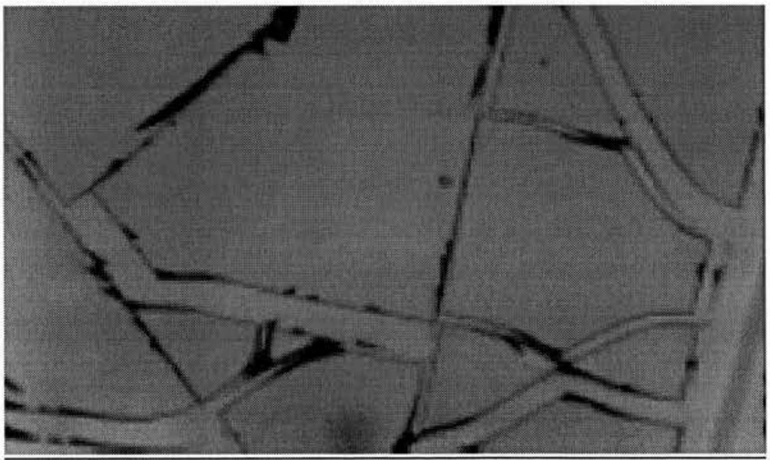
LB       0.0
GB       0.0
CX      25.00
CY      10.00
F1     209.986P
F2        .042P
SR    1258.19
```

Figure 20 TMOS/PPV composite prepared from base polymerisation of TMOS/monomer gel

3.6.0 PREPARATION OF SOL-GEL THIN FILMS (AVOIDING FRACTURE)

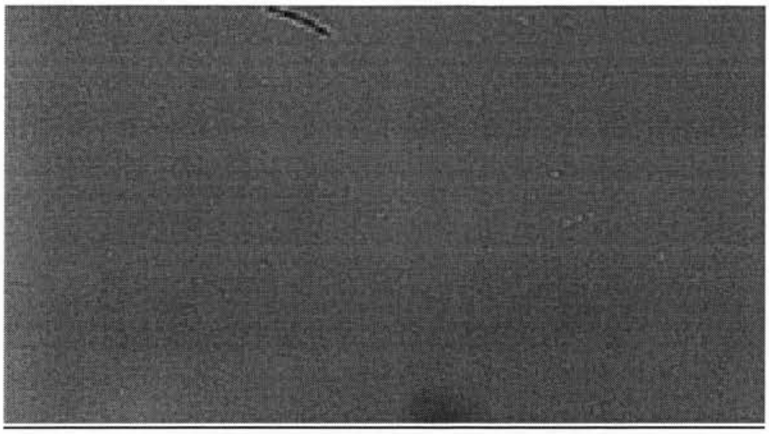
The technique of spin-coating is the chosen method for this experiment. Thin film fabrication and spin coating is discussed in section 3.1.1. The fabrication of TEOS/composite thin films was attempted and the results shown in Table 5.

When the thin films produced from the monomer incorporated gels were exposed to NaOH the gel peeled off the glass slide on washing with distilled water. The polymerisation (using NaOH $_{aq}$) of the monomer in the gel imparted a large degree of flexibility on the otherwise glassy TEOS gel. It is thought that the formation of the polymer chain within the sol-gel matrix is responsible for the flexibility. This method resulted in the formation of a free-standing, yellow, luminescent flexible composite films but did not adhere to the glass surface.



magnification X 150

Figure 21



magnification X 150

Figure 22

stage 1 RPM/time sec	stage 1 RPM/time sec	stage 1 RPM/time sec	result
200/4	500/20	3500/4	small cracks **Fig 21**
200/4	500/20	3500/4	small cracks
200/4	500/20	3500/4	small cracks
200/4	500/40	3500/4	large cracks
200/4	500/40	3500/4	no cracks
200/4	500/40	3500/4	no cracks **Fig 22**
200/4	500/40	3500/4	non uniform
200/4	500/40	3500/4	non uniform

Table 5

Spin-coating of flexigel/PPV monomer material onto a glass substrate (home made spin-coating apparatus see section 3.7.16) produced crackless films which adhered well to the glass substrate. However, these films did not allow conversion of the PPV monomer into polymer, either by heat or chemical treatment.

The flexigel was unstable in the presence of NaOH and eventually dissolved after 12 h. The solution became yellow with time after the dissolution which suggests that the monomer could not polymerise in the gel due to restriction of the monomer within the more densely packed flexigel matrix. An alternative explanation is that the NaOH failed to penetrate through the matrix. On ageing the gels became slightly coloured. The gels were exposed to heat under literature values for conversion (100 °C 0.1torr). On excitation with UV at 365 nm a weak blue/green emission was observed.

3.7.0 CONCLUSIONS

Various methods of polymer encapsulation in sol gels were attempted. Encapsulation of substituted PPV's and PPV in sol-gel materials, such as TEOS, TMOS and FLEXIGEL at room temperature was successful. The use of drying control agents such as DMF facilitated the room temperature addition of substituted PPV polymers into sol-gels. Spectroscopic studies on these materials showed interesting shifts in λ_{max} em of the polymers which depended on the nature of the host material used (Table 1).

High concentrations of luminescent polymer in gels were not obtainable by this method. Polymerisation post gelation was successful in producing the required concentration of polymer (50% w/w) in hard type gels such as TEOS and TMOS. The FLEXIGEL did not support this encapsulation method. The method of polymerisation of the monomer within the gel required the submersion of the gel in an aqueous solution of NaOH, this caused the FLEXIGEL to dissolve before conversion of the polymer could take place, rendering the material useless.

An insight into the processing of thin films for LED devices was provided by the preparation of thin films of the new composites. The preparation of thin films of these materials by spin-coating was shown to be highly dependent on the spinning speed. Spin-coating is the normal method of fabricating polymer LED devices and therefore this illustrates the possibility of applying these composites in the production of LED devices.

3.7.0 EXPERIMENTAL FOR COMPOSITES

3.7.1 ENCAPSULATION OF PRECURSOR IN TETRAETHYLORTHOSILICATE DERIVED GLASS. (HYDROLYTIC SOL-GEL METHOD A)

To 11.24 g (0.54 mol) of tetraethylorthosilicate (TEOS) was added 6.9 g (0.216 mol) of methanol at room temperature. After 30 min stirring 3 drops of 1M HCl were added as a catalyst. The mixture was stirred for a further 60 min at room temperature. During this time a solution of polymer in chloroform was added slowly. The mixture was covered with Nescofilm. A gel formed after 36 h. On drying and ageing (5 days in ambient conditions) the gel shrank >50% in linear dimensions and became hard and glassy.

3.7.2 PREPARATION OF TETRAETHYLORTHOSILICATE GELS FOR DERIVATISATION

To 13 g (0.624 mol) of tetraethylorthosilicate (TEOS) was added 11.04g (0.345 mol) of methanol at room temperature. After 10 min stirring drops of 1M HCl were added as a catalyst. The mixture was stirred for a further 60 min after which 4 drops ammonium hydroxide (33% w/w) were added in 10 cm^3 of ethanol. The mixture was stirred for 10 min. The mixtures were covered with Nescofilm. The mixture was incubated at 50 $^{\circ}$C. Gelation occurred after 17 h. On drying and ageing (5 days in ambient conditions) for 51 h the gel shrank >50% in linear dimensions, and became hard and glassy.

3.7.3 POLYMERISATION OF MONOMER WITHIN SOL-GEL MATRIX (I)

To 13 g (0.624 mol) of tetraethylorthosilicate (TEOS) was added 10.92 g (0.237 mol) of ethanol which contained 0.65 g 0.5% w/w w.r.t. TEOS of 2,5-bis-chloromethyl-1,4 dimethoxybenzene at room temperature. After 30 min stirring, 3 drops of 1M HCl were added as a catalyst. The mixture was stirred for a further 90 min at room temperature, after which a solution of potassium hydroxide in ethanol (0.39g in 10 cm^3, 1 equivalent w.r.t. monomer) was added. A gel formed almost instantaneously on addition of KOH in ethanol. The mixture was covered with Nescofilm, and incubated at 50 °C. On drying and ageing (5 days at 50 °C) the gel shrank >50% in linear dimensions, and became hard and glassy and opaque.

3.7.4 POLYMERISATION OF MONOMER WITHIN SOL-GEL MATRIX (II)

To 13 g (0.624 mol) of tetraethylorthosilicate was added 10.92 g (0.237 mol) of ethanol which contained 0.65 g 0.5% w/w w.r.t. TEOS of 2,5-bis-chloromethyl-1,4-dimethoxy benzene at room temperature. After 30 min stirring 3 drops of 1M HCl were added as a catalyst. The mixture was stirred for a further 90 min at room temperature, after which time a solution of potassium *t*-butoxide (0.5 g, 10 cm^3,1 equivalent w.r.t.. monomer) in ethanol was added. The mixture was covered with Nescofilm and incubated at 50 °C. The mixture formed a gel overnight. On drying and ageing (5 days at 50 °C) the gel shrank >50% in linear dimensions. and became hard and glassy and opaque.

3.7.5 POLYMERISATION OF MONOMER WITHIN SOL – GEL MATRIX (III)

To 13 g (0.624 mol) of tetraethylorthosilicate was added 30 cm^3 of ethanol which contained 0.65 g 0.5% w/w w.r.t. TEOS of 2,5-bis-chloromethyl-1,4 dihexyloxy benzene at room temperature. After 30 min stirring 3 drops of 1M HCl were added as a catalyst. The mixture was stirred for a further 90 min at room temperature, after which time a solution of potassium *t*-butoxide 0.19 g 10 cm^3 (1 equivalent w.r.t. monomer) in ethanol was added. The mixture was covered with Nescofilm. and was incubated at 50 °C. The mixture gelled overnight. On drying and ageing (5 days at 50 °C) the gel shrank >50% in linear dimensions. and became hard and glassy with a faint yellow hue. Yellow spots were observed within the matrix.

3.7.6 DERIVATISATION OF TEOS GEL WITH TRIMETHYLCHLOROSILANE (TMSCl)

The gel was prepared as in section 3.7.1 The gel was ground to a fine powder, washed first with ethanol and then with hexane. The gel was then dried at 100 °C in *vacuo* for 5 h. The dried sample was weighed (2.53 g) and it was then added to 10 cm^3 of dry toluene. 50 cm^3 of TMSCl was added under nitrogen and the mixture was refluxed for 5 h. After sonication for 1h the solid was filtered off. The soluble gel was isolated by extraction into hexane in a Soxhlet apparatus; however, the filtrate did not gel during evaporation of the solvent, but instead left a white powder.

3.7.7 DERIVATISATION OF TEOS GEL WITH TRIMETHYLSILYLIMADAZOLE

The sol-gel was prepared as in experiment 3.7.1. It was ground to a fine powder and washed first with ethanol and then with hexane. The gel was then dried at 100 °C in *vacuo.*, for 5 h.. The dried sample was weighed (0.53 g) and it was then added to 5 cm^3 of dry toluene. 5 cm^3 of trimethylsilylimadazole (TMSI) was added under nitrogen and the mixture was refluxed for 5 h, before sonication in 20 cm^3 of hexane for 1h. The solid was filtered off. The filtrate was cast onto glass slides the gel did not reform on curing, but instead left a fine white powder residue.

3.7.8 SOL - GEL PREPARATION OF FREE STANDING THICK FILMS.

To 11.24 g (0.54 mol) of tetraethylorthosilicate was added 12.96 g (0.216 mol) isopropyl alcohol at room temperature. After 30 min stirring 3 drops of 1M HCl were added as a catalyst. The mixture was stirred for a further 60 min at room temperature. The mixture was covered with Nescofilm. A gel started to form after 36 h.. At this point a solution of precursor polymer (10 cm^3, 0.1% w/w w.r.t TEOS) in DMF was added. The polymer gel mixture was deposited onto a Teflon sheet and a glassy film formed. This experiment was carried out several times with incorporation of the following. polymer **1**(PCM 38), **2**(PCM 51), **3**(PCM 37), **4**(PCM 39), and **5**(PCM 52). See fig 6 for structural details.

The same procedure was used for encapsulation of polymers **1-5** in tetramethylorthosilicate.

3.7.9 PREPARATION OF FLEXIBLE ORGANIC/INORGANIC HYBRID GELS

A mixture of 3.08 g (34 mmol)1,4-butanediol and 3-isocyanoatopropyl triethoxysilane 16.9 g (68 mmol) were refluxed together in THF for 24 h under nitrogen. The mixture was cooled and the THF was removed by rotary evaporation. The product was solubilised in approx. 200 cm^3 of DMF and filtered to remove any residual undissolved product. The gelling mixture was deposited onto a Teflon sheet and left to evaporate and gel.

3.7.10 INCORPORATION OF PRECURSORS INTO FLEXIGEL MATRIX.

5 cm^3 of gelling solution was added to 1 cm^3 of 1% polymer solution in DMF this was repeated for the four other polymers. The samples were homogeneously mixed. A 0.5 ml portion of the mixture was pipetted onto a Teflon sheet which was placed in an oven at 50 °C for 12h after which time the samples had gelled, and could be peeled off the Teflon sheet.

3.7.11 PREPARATION OF SULPHONIUM SALT MONOMER (I)

To 0.5 mol 2,5-bis(chloromethyl)-1,4-dihexyloxybenzene was added 3 eq of tetrahydrothiophene (THT). The mixture was stirred and heated at 50 °C for 24 h. On completion of the reaction, the solution was added dropwise into cold petroleum ether (40-60) After two days 0.05g of an oil was isolated. ^{1}H NMR

($(CD_3)_2$ CO))δ_H: 0.85 (m, 6 H), 1.2-1.55 (m, 12 H), 1.62 - 1.85 (m, 4H), 1,88 - 2.6 (m, 2H), 3.24 - 3.4 (m, 2H), 3.8 - 4.1 (m, 4 H), 4.4 (m, 2H), 6.85 (s, 4H).

This procedure was repeated using 0.38 g (0.01mol) of 2,5-bis(chloromethyl)-1,4-dihexyloxybenzene with the same result.

3.7.12 PREPARATION OF SULPHONIUM SALT MONOMER (II)

To 2.4 g (0.007 mol) 2,5-bis(chloromethyl)-1-methoxy-4-hexyloxy benzene was added 3 eq (1.76 g) of THT. The mixture was stirred and heated to 50 °C for 24 h. On completion of the reaction the solution was added dropwise into cold acetone. After two days, no product was isolated and the solvent was evaporated under reduced pressure, and then under high vacuum to afford a light brown oil. ^{1}H NMR (($(CD_3)_2$ CO)) δ_H: 0.88 (t, J = 7 Hz, 3 H), 1.3 -1.9 (m, 8 H), 1,88 - 2.6 (m, 2H), 3.24 - 3.4 (m, 2H),3.77 (s, 3 H), 3.87 (t, J =7 Hz,2 H), 6.85 (s, 4 H).

3.7.13 2,5-BIS(CHLOROMETHYL)-1,4-DIOCTYLOXYBENZENE

To (3.9 g, 0.01 mol) of 1,4-dioctyloxybenzene was added 5.4 cm^3 of 48% HBr, 4.85 cm^3 phosphoric acid (85%), 6.6 cm^3 glacial acetic acid, and 2.1 g of paraformaldehyde. The mixture was heated under reflux at 95-100°C. HBr gas was bubbled through the mixture continuously for 5 h. After that time the HBr bubbling was stopped, and the reaction was maintained at 110°C for a further 4 h. The reaction was then stopped and the mixture was left to cool. The product precipitated out upon cooling and was isolated by filtration neutralised and recrystallised from hexane. NMR showed that only starting material was recovered. ^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.80 - 1.8 (m, 30 H), 3.85 (s, 4 H), 6.65 (s, 4 H).

3.7.14 PREPARATION OF SULPHONIUM SALT MONOMER (III)

To 2.4g (0.007 mol) 2,5-bis(chloromethyl) 1-octyloxy-4-methoxy benzene was added 3 eq (1.76g) of THT. The mixture was stirred and heated to 50 °C for 24 h. On completion of the reaction, the solution was added dropwise into cold acetone. After two days no product was isolated the was solvent was removed under reduced pressure at first and then under high vacuum (0.1 torr). The product was isolated and it was a light brown oil. ^{1}H NMR ($(Cd_3)_2CO)$) δ_H: 0.85 (s, 3 H), 1.2 (m, 10 H), 1.65 (m, 2 H), 1,88 - 2.6 (m, 2H), 3.24 - 3.4 (m, 2H),3.65 (s, 3 H), 3.75 (t, J =7 Hz,2 H), 6.85 (s, 4 H).

3.7.15 POLYMERISATION OF SULPHONIUM SALT MONOMER

2,5-bis(thiophenium-methyl)-1,4-dihexyloxybenzene of 0.075 g (0.156 mmol) was dissolved in water:pentane (1:2) which was argon purged at 0 °C. Then 0.22cm^3 (30 mmol) of tetraethylammonium hydroxide in 10 cm^3 of water which had also been purged with argon was added. The solutions were added together and stirred for 2 h after which time a white precipitate had formed which was isolated, suspended in cold H_2O and neutralised with conc. HCl. The product was isolated by filtration. However, its NMR spectrum showed that only starting material was present.

3.7.16 PREPARATION OF P-XYLENE(DIMETHYLSULPHONIUM CHLORIDE)

To a solution of 6.56g 0.75M of α,α'-Dichloro-*p*-xylene in 50 cm^3 methanol/ water (80:20) at 50 °C was added 6.9g (2.25M) of dimethyl sulphide. The mixture was heated under reflux for 6 h. The mixture was concentrated by evaporation and the product was isolated by triturating in liquid nitrogen cooled acetone and was extensively dried under vacuum. To afford a white solid ^1H NMR ($CDCl_3$) d_H: 0.85 (s, 12H), 3.1 (s, 4H), 7.8 (s, 4H).

3.7.17 POLYMERISATION OF P-XYLENE(DIMETHYLSULPHONIUM CHLORIDE)WITHIN A TEOS MATRIX

To 0.101g (0.000489 mol.) of tetraethyl orthosilicate was added 0.0624g (0.001956 mol.) methanol at room temperature, 0.135g (0.00048m) of p-xylene(dimethylsulphonium chloride). After 30 min stirring 3 drops of 1M HCl were added as a catalyst. The mixture was stirred for a further 60 min at room temperature 2 drops of DMF was added as a drying control additive. The mixture was covered with Nescofilm and gellation occurred after 3 days. Just prior to gellation the gelling liquid was pippetted onto glass slides to form a film after gellation the films were subjected to a variety of conditions to convert the monomer to the conjugated polymer. (a) 380°C for 3 h resulted in bubbling of the gel and decomposition of the organics (b) 200°C for 2h had the same effect. (c) 150°C in *vacuo* for 3h. the gel bubbled and turned from clear to opaque yellow/white (d) The gel was soaked in 1N NaOH and the gel turned from clear to bright yellow. The gel was then washed with distilled water to remove any excess base. The gel peeled off the glass slide and remained flexible. The same procedure was carried out with TMOS for the solid state for the FTIR and NMR work (where methanol read ethanol)

3.7.18 PREPARATION OF A SPIN-COATING APPARATUS

A spin-coating apparatus was fabricated using an overhead variable speed (30-200 rpm) mechanical stirrer mounted upside down so that the rotating side faced up. A flat chuck was obtained from the St Andrews departmental mechanical workshop. On fitting the flat chuck to the mechanical stirrer glass slides could be attached and spun at the desired rpm.

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Chapter 4

Electrochemical LED Materials

4.0.0 INTRODUCTION (INCORPORATION OF LUMINESCENT MATERIAL INTO SOL-GELS)

Sol-gel technology is a very useful approach for developing room temperature phosphorescence optical sensors which exhibit a high physical rigidity that enhanced relative intensities and triplet lifetimes of the immobilised luminescent species.[1]

Inorganic–organic hybrid materials of sol-gel materials, otherwise known as **Or**ganically **Mo**dified **Si**lica (ORMOSILs) have become of interest over the last few years. This area of research spans a huge range of interests including inorganic oxides as fillers for organic polymers, and the incorporation of organic molecules covalently bound to silica.

The field of inorganic organic hybrid materials is still new; therefore, the potential of these materials has not been fully explored. Some of the applications which have received attention include hybrid gels of polysiloixanes with phenylene bridges, as the matrix for the quantum confinement of semiconductor particles of CdS or nanosized CdS. Similarly nanoclusters of Cr^o have been formed *in situ* by complexation of $Cr(CO)_3$ groups onto phenylene bridges of polysiloxanes. The incorporation of inorganic ions into silica gels and glasses is of the utmost interest for many technological applications including solid-state lasers and phosphors.[2]

Silica based composite materials prepared by the sol-gel method have been doped with $[Tb(bpy)_2{}^{3+}]$ and were found to be excellent green emitting material. These materials were found to have superior thermal stability, heat stable to

150 °C and they were found to be higher than that of existing inorganic complexes used in fluorescent lamps.[3] Quenching problems have been associated with sol-gel systems. Luminescence has been quenched by hydroxyl groups and water. Two strategies have been developed to overcome this: vigorous drying of the sol-gel at high temperatures and the use of chelating ligands such as 2-6-pyridinedicarboxylate which helps to isolate the active metal centre[4].

Another area of continuing interest is the solid-state dye laser. In pursuit of this goal various laser dyes, have been incorporated into silica materials. A fair amount of success has been obtained in the visible part of the spectrum. Encapsulation of laser dyes such as rhodamines and coumarins in sol-gel materials has been achieved and these hybrids show optical gain and laser action.[5] UV absorbing dyes (PTP, Exalite 351, and PBD) have been used to dope sol-gel silica by diffusion. Laser emissions for PTP, Exalite 351, and PBD doped silica samples peaked at 342 nm, 352 nm, and 364 nm. The laser output at 342 nm was the shortest wavelength yet reported for solid-state dye lasers [6].

Numerous silylated coumarin dyes have also been incorporated within silanol-terminated, polydimethylsiloxane (Polyceram MW 400-700) hosts using the sol-gel process to form crack-free, polishable monoliths.[7] The use of silylated laser dyes allows for covalently bonding the laser dyes to their hosts, and these materials showed significant improvement in the photo and thermal-stability of the silylated dye Polyceram compared to that of the unsilylated dye Polyceram at a dye:Si mole ratio of $10^{(-4)}$:1. The improved stability is attributed to the immobilisation and higher degree of caging of the dye [7].

4.0.1 ELECTROCHEMILUMINESCENCE

Chemiluminescence is the emission of light caused by a chemical reaction i.e. a chemical reaction, which results in the formation of a product molecule in the excited state, which radiatively decays to the ground state. When this phenomena is achieved by the electrochemical route to the excited state (by electron transfer in solution) it is referred to as electrochemiluminesence (ECL). For example the reaction between anion and cation radicals of 9,10-diphenylanthracene (DPA) in acetonitrile, with the resulting blue emission from DPAs first excited singlet state.

$$\mathrm{DPA}^{\bullet +}\ \mathrm{W} + \mathrm{W}\ \mathrm{DPA}^{\bullet -} \longrightarrow {}^{1}\mathrm{DPA}\ ^{*} + \mathrm{DPA}$$

ECL from inorganic systems was first studied in aromatic radical ions but ECL was reported[8] from inorganic complexes such as tris(2,2'-bipyridyl) ruthenium(II) $[Ru(bpy)_3]^{2+}$. Studies of this complex showed that ECL was generated from the reduction of $[Ru(bpy)_3]^{3+}$ to $[Ru(bpy)_3]^{2+}$. This reaction produces an orange luminescence (λ_{max}^{em} 594nm) which is strong enough to be visible in a slightly darkened room. Further studies[9] on the reaction suggested that the light emitting species in the reaction was the $[Ru(bpy)_3]^{2+*}$ triplet. The existence of this triplet was confirmed by cyclic voltammetry, which showed that the excited triplet is formed from the charge transfer between $[Ru(bpy)_3]^{3+}$ and $[Ru(bpy)_3]^{1+}$ which are formed as the result of a redox reaction. The charge transfer between $[Ru(bpy)_3]^{3+}$ and $[Ru(bpy)_3]^{1+}$ is sufficiently energetic (ΔG° -2.7 eV) to produce the triplet which is 2.04 eV above the ground state [10, 11] Figure 1. Recently a solid state analogue of an electroluminescent system called a light "emitting cell" (LEC) has been pattented[19]. This system is discussed in the next section.

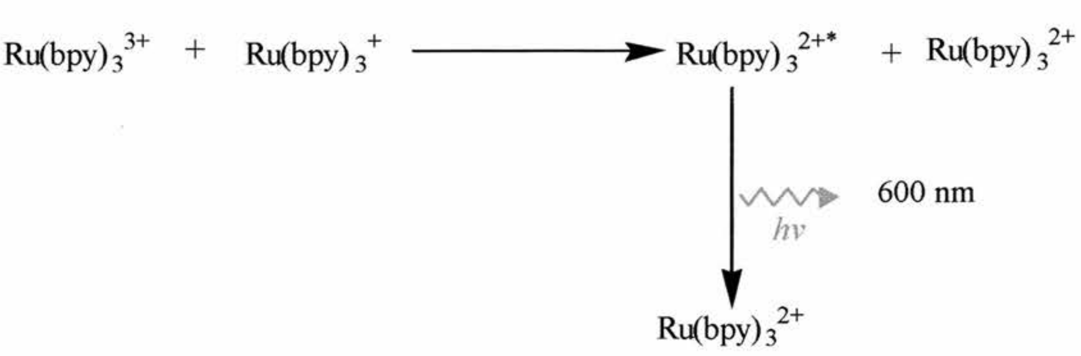


Figure 1

4.0.2 SOL-GEL COMPOSITES AS MATERIALS FOR LIGHT EMITTING ELECTROCHEMICAL CELLS (LECS)

Recall now concern over the efficacy of sol-gels as matrices for composite LED devices which was detailed in chapter 3. The primary concern was that the matrix was not adequately electronically conductive. Could these problems be overcome by using the LEC design, which relies on high ionic conductivity instead? We sought the answer to this in the lithium ion electrolyte literature. Lithium ion conducting solid electrolytes continue to be an active area of research due to the considerable progress made in the fields of lithium secondary batteries, electrochromic devices and electrochemical sensors. The gel electrolyte and plasticised polymer electrolytes [12-15] have made great progress in increasing the ionic conductivity values to such an extent that they approach those of liquid electrolyte values. There have been three approaches to conducting sol-gel materials: Protonic conductors (aminosils)[16], Rare earth doped sol-gels[17] and incorporation of liquid and solid electrolyte mixtures[18].

A sol-gel solid electrolyte has been fabricated[18] with the properties of a highly conducting lithium solid electrolyte. This high conductivity arises from the presence of a continuous liquid electrolyte encapsulated within the inorganic silica matrix.

Recently, the invention of a new type of light-emitting device has been reported light emitting electrochemical cell (LEC)[19, 20, 21] which combines the novel electrochemical properties of conjugated polymers with the ionic conductivity of polymer electrolytes. When a voltage is applied in excess of the bandgap energy for PPV, *p*- and *n*-doping (i.e. oxidation and reduction) of the regions adjacent to the anode and cathode is initiated. A *p-n* junction is formed within the active layer and positive and negative charge carriers combine with emission of a photon within the compensated *p-n* junction [22]. A two colour LEC based on PPV and MEH-PPV has been made with tuneable emission of red and green simply by changing the applied voltage[23]. In these systems the conjugated polymers are p-doped on the anode side and n-doped on the cathode side and a light emitting p-n junction is formed between the p and n doped regions. These systems use poly(1,4-phenylenevinylene)(PPV) admixed with polymer electrolyte poly(ethyleneoxide) (PEO) which is then doped with lithium trifluoromethanesulphonate (lithium triflate). These devices have the following advantages over polymer LEDs. Low operating voltage <4V, high quantum efficiency, as equal numbers of holes and electrons are automatically injected, high power efficiency as the device has both low operating voltage and high quantum efficiency and air stable electrodes can be used [23].

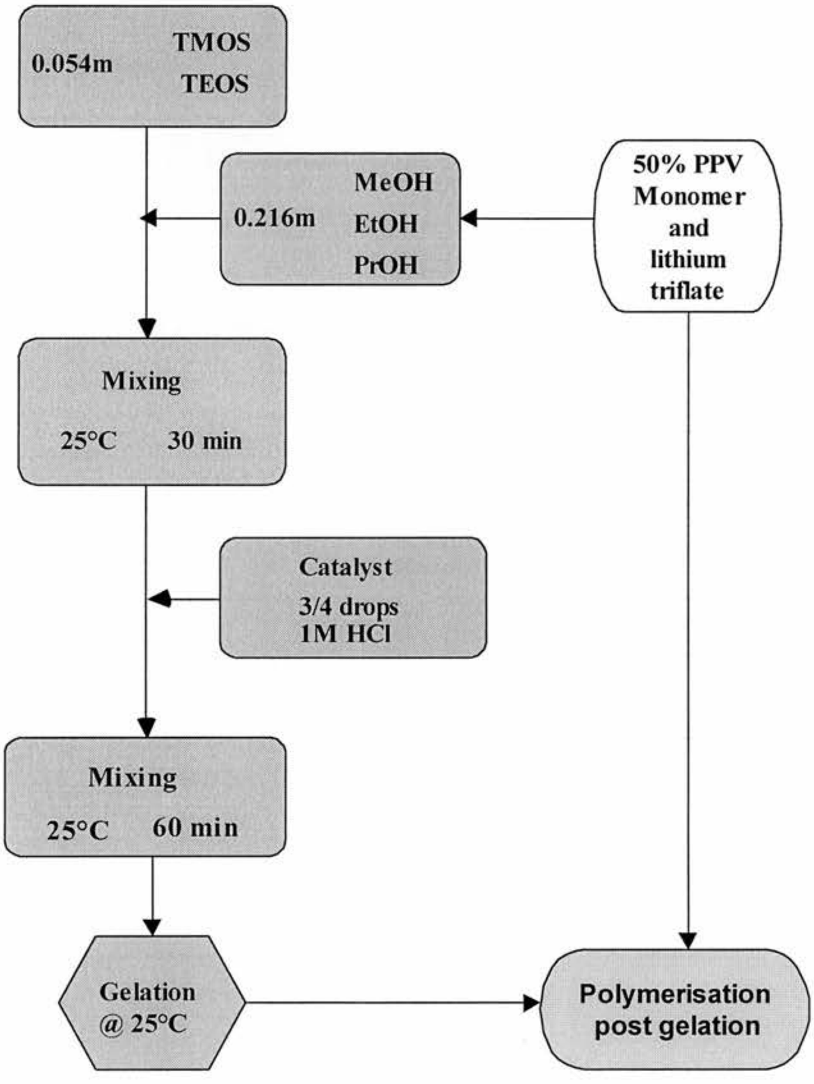


Figure 2 Preparation of Li doped Composite PPV/TEOS gels

Our work uses poly(1,4-phenylenevinylene) (PPV) polymerised (post gelation) within a TEOS matrix which is also doped with lithium triflate the molar ratio of triflate to TEOS was 1:20. The procedure was carried out as shown Figure

2. The lithium triflate was added with the precursor polymer prior to gelation. The monomer was converted to the conjugated PPV by subjecting the monomer in the aged gel to NaOH which resulted in a yellow composite material, with a higher degree of flexibility than TEOS under normal conditions. Figure 3 shows a schematic representation of PPV/TEOS Electrochemical LED. The advantage of this method is that the solubility of the polymer is no longer an issue.

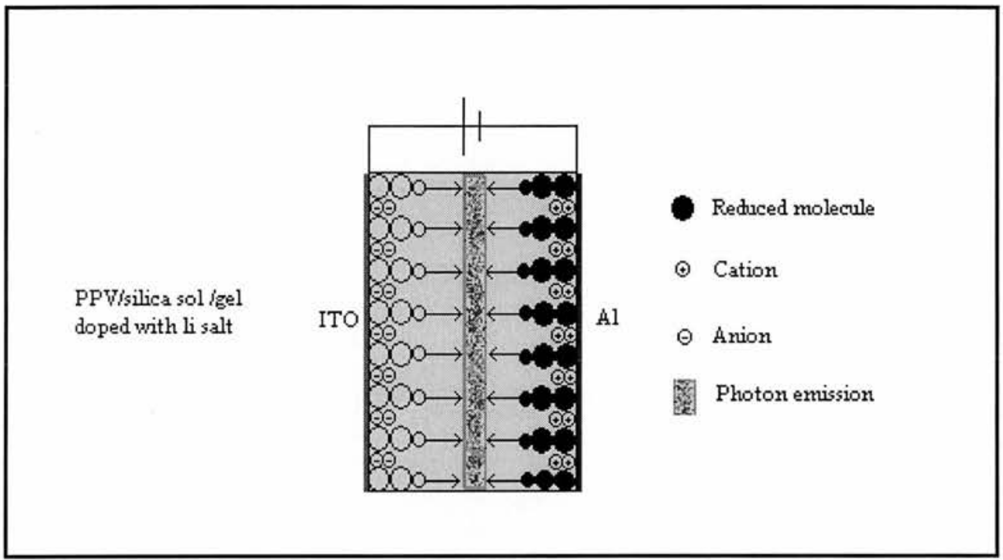


Figure 3

4.2.0 TECHNIQUES USED

The investigative techniques used in this section are photoluminescence A.C impedance, and cyclic voltammetry (CV). These techniques have only been recently used in the study of materials of this type[21]. The photoluminescence spectroscopy apparatus and techniques were discussed in section 2.1.4.

4.2.1 ELECTROCHEMICAL TECHNIQUES

Semiconductors can act as both the photoreceptor and the electrode in photoelectrochemical cells. Spectroscopic and electrochemical studies are both very important to the understanding and development of these semiconductors for use as LED's or phosphors. Luminescent properties of semiconductors provide information analogous to that obtained from the molecular systems. The spectral distribution can be used to identify (through interpretation of the electronic structure the states involved in light emission) the efficiency and lifetime of these electrochemical cells and can provide information on the kinetics of the excited state processes. This section will concentrate on elecrochemical techniques.

4.2.2 A.C. Impedance

A.C. impedance measurements analyse a reaction at equilibrium, i.e. at open circuit potential, with no net current flow. The A.C. excitation is generally small (mV) and is varied over a wide range of frequencies. When the A.C. signal is first impressed, a time-dependent diffusion layer is created. As no net current flows, a steady state is set up after a few cycles.[24, 25] Generally, under these conditions, most electrode systems can be represented by an "equivalent circuit"

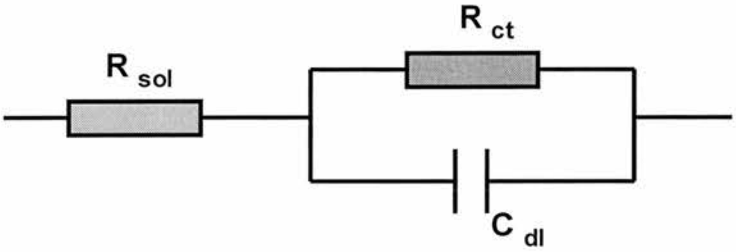


Figure 4

where C_{dl} is the double layer capacitance of the electrode, R_{ct} is the charge transfer resistance due to ionic conductivity and R_{sol} is the solution resistance due to ionic conductivity, that is the solution resistance between the reference electrode and the working electrode. (Figure 4) [24,25]. By Ohms law the current, I, passing through a resistor, R, at an applied voltage, V, is given as:

$$I = VR^{-1}$$ **Equation 1**

Likewise the current through a capacitor, C, is given by:

$$I = i\,\omega CV$$ **Equation 2**

Where ω is the angular frequency ($\omega = 2\pi f$) and $i = \sqrt{-1}$. Thus for a circuit containing both resistance and capacitance, the current may be defined as:

$$I = VZ^{-1}$$ **Equation 3**

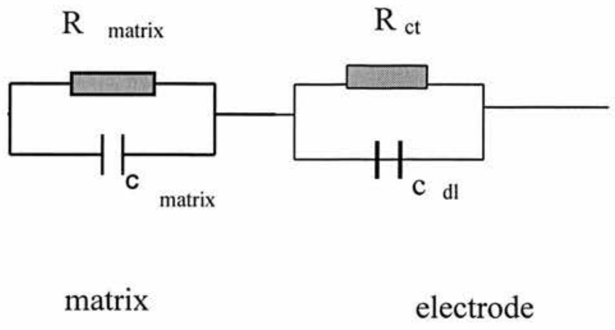
Where Z is the complex impedance of the circuit. The impedance of the capacitance is imaginary due to the 90° difference in phase angle between the sinusoidal current and the voltage. The impedance of the circuit contains both real (Z') and imaginary (Z") terms and is called the complex impedance (Z^*), where:

$$Z^* = Z' - iZ''$$ **Equation 4**

Thus the "equivalent circuit" shown in Figure 4 has a complex impedance of

$$Z^* = R_{sol} + R_{ct}(1+R_{ct}i\omega C_{dl})^{-1}$$ **Equation 5** [25]

Similarly the complex admittance, A^*, of a circuit can be defined as $(Z^*)^{-1}$ and the complex capacitance, C^*, as $(A^*)\omega^{-1}$. Both of these terms have real (Z' and A') and imaginary (Z" and A") components, respectively. Thus complex impedance, admittance and capacitance (Argand plane) plots can be formed uponvarying the applied A. C. voltage frequency. A complex impedance plot for the circuit given in Figure 4 is shown in Figure 5 as a semicircle:



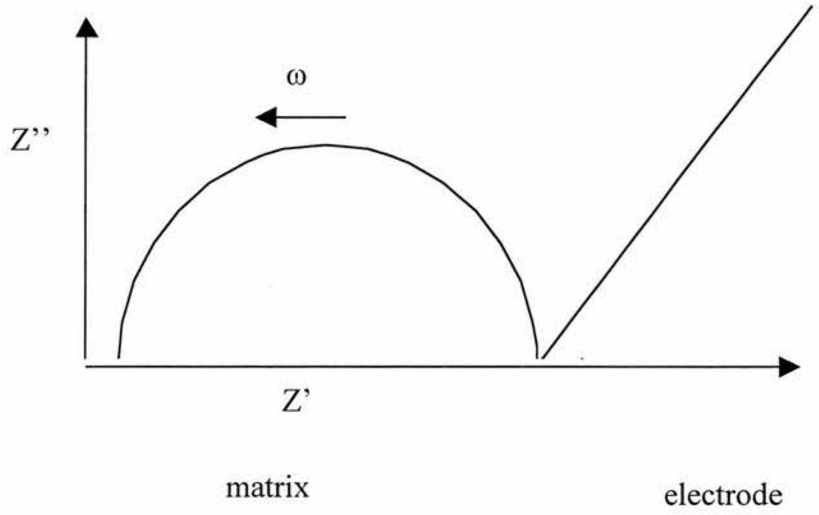


Figure 5

At low frequencies the complex impedance is purely resistive because the reactance of the capacitor is very high, and so $Z^* = R_{sol} + R_{ct}$. As the frequency increases, the capacitor's reactance decreases and it passes increasing current, giving rise to the semicircular plot. At very high frequencies the resistance of the parallel combination (C_{dl} and R_{ct}) decreases to zero and only the series resistance of the solution (R_{sol}) is observed.

4.2.3 CYCLIC VOLTAMMETRY (CV)

Voltammetry refers to the measurement of current that results from the application of potential. Unlike potentiometry measurements, which employ only two electrodes, voltammetric measurements utilise a three-electrode electrochemical cell. The use of the three electrodes (working, auxiliary, and reference) along with the potentiostat instrument, allow accurate application of potential functions, and the measurement of the resultant current. The different voltammetric techniques that are used are distinguished from each other primarily by the potential function that is applied to the working electrode to drive the reaction, and by the material used as the working electrode.

Cyclic voltammetry (CV) is an electrolytic method that uses microelectrodes and an unstirred solution so that the measured current is limited by analyte diffusion at the electrode surface. The electrode potential is ramped linearly to a more negative potential, and then ramped in reverse back to the starting voltage (Figure 6). The forward scan produces a current peak for any analytes that can be reduced through the range of the potential scan. The current will increase as the potential reaches the reduction potential of the analyte, but then falls off as the concentration of the analyte is depleted close to the electrode surface. As the applied potential is reversed, it will reach a potential that will reoxidize the product formed in the first reduction reaction, and produce a current of reverse polarity from the forward scan. This oxidation peak will usually have a similar shape to the reduction peak. The peak current, i_p, is described by the Randles-Sevcik equation:

$$i_p = (2.69\text{x}10^5)\ n^{3/2}\ A\ C\ D^{1/2}\ v^{1/2}$$ **Equation 6**

where n is the number of moles of electrons transferred in the reaction, A is the area of the electrode (cm^2), C is the analyte concentration (in mol/cm^{-3}), D is the diffusion coefficient ($cm^2\ s^{-1}$) , and v is the scan rate ($V\ s^{-1}$) of the applied potential.

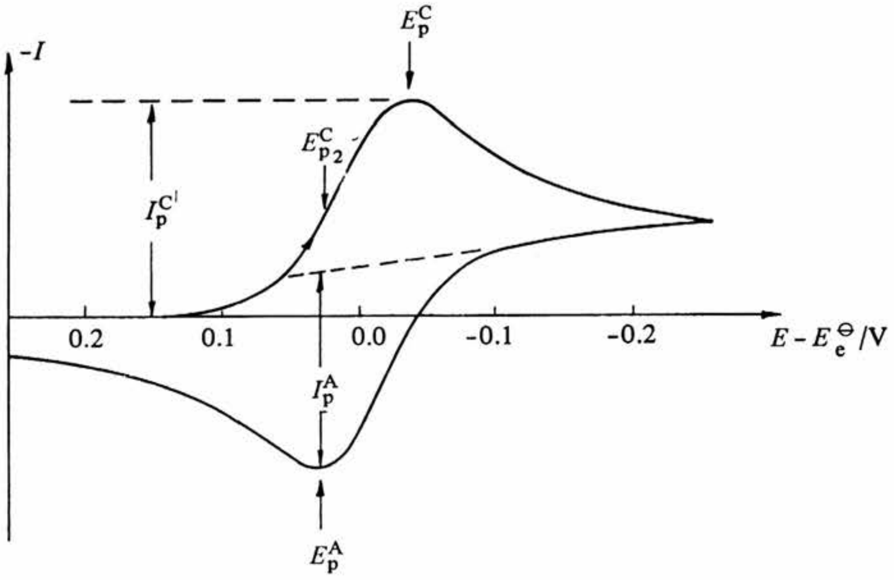


Fig. 6.4 – Cyclic voltammogram for a reversible process, $O + e \rightleftharpoons R$. Initially only O present in solution.

Figure 6 Theoretical CV

The potential difference between the reduction and oxidation peaks is theoretically 59 mV ((E_p^A –E_p^C) /2) for a reversible reaction (Figure 6). In practice, the difference is typically 70-100 mV. Larger differences, or nonsymmetric reduction and oxidation peaks are an indication of a nonreversible reaction. These parameters of cyclic voltammograms make CV most suitable for characterisation and mechanistic studies of redox reactions at electrodes [24].

4.3.0 PREPARATION OF INORGANIC ORGANIC HYBRIDS

Because the sol-gel matrix can cause undesirable quenching of luminescence, we carried out preliminary control experiments in the absence of added electrolyte. Incorporation of inorganic luminescent material into sol gel matrices was attempted. The inorganic complexes were added in the initial stages of mixing, as they were soluble in alcohol. (Figure 7)

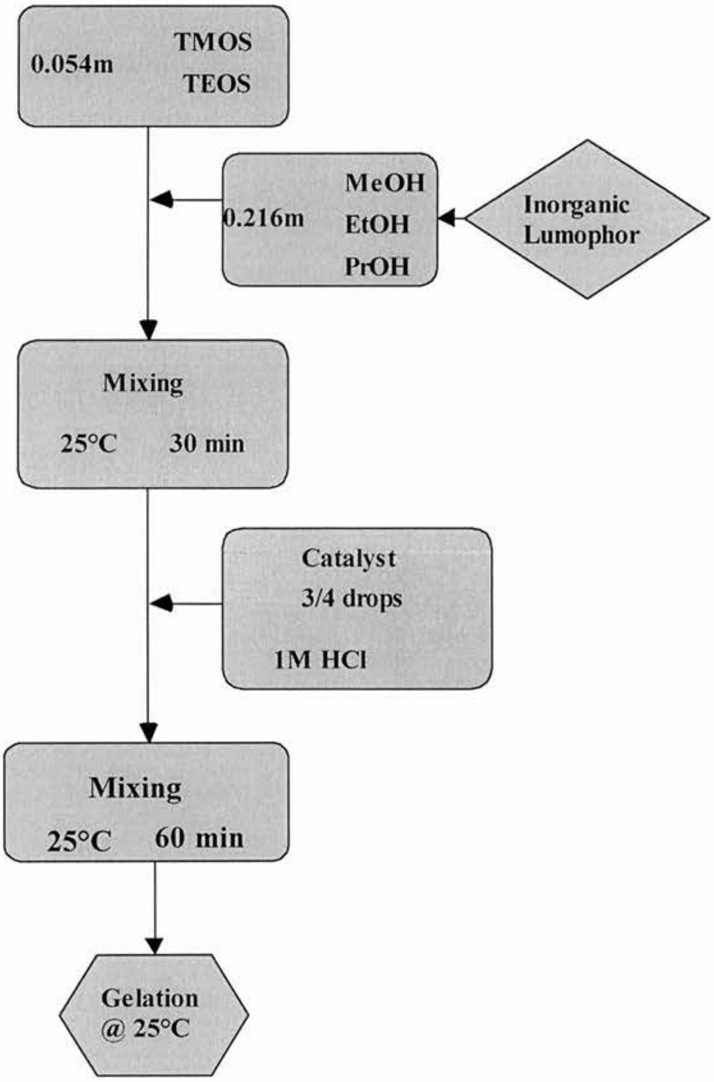


Figure 7

4.3.1 INCORPORATION OF RUTHENIUM BIPYRIDYL

$[Ru(bpy)_3]^{2+}$ is soluble in methanol and was therefore compatible with the sol-gel mixture. On addition to the sol the complex dispersed throught the matrix to yield a homogenous mixture. Gelation time increased according to the doping levels see (table 1).

Doping level	Gelation Time (hours)
1% w/w	38
2% w/w	38
3% w/w	72
4% w/w	96
5% w/w	96

Table 1 Gelation time vs doping level.

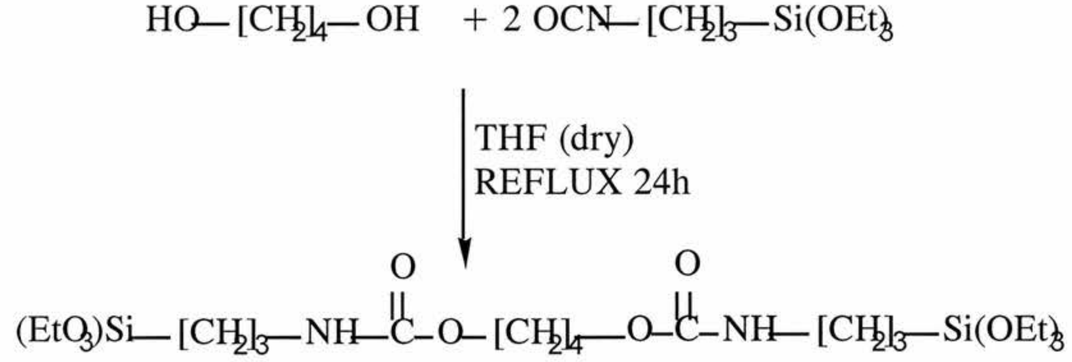
Upon excitation with UV light @365 nm the glass emitted orange light at 600 nm over the whole surface of the material homogeneously. $[Ru(bpy)_3]^{2+}$ was also incorporated into TMOS sols with the same results.

The experiment was also carried out on the aluminium tris(oxime) complex $Al(ox)_3$. Incorporation of this compound also produced a homogeneous material however expected emission of yellow/green light on excitation at 365 nm was quenched when incorporated into the glass matrix.

Coumarin was also incorporated in this manner and formed an homogenous gel which emitted yellow/orange light on excitation at 365nm.

4.3.2 PREPARATION OF LUMINESCENT ORMOSIL FLEXIGELS

This method was adapted from very recent work aimed at preparing free standing polymer/gel composite thin films for ion-selective electrodes (*Anal Chem*).[19] This method employs the sol-gel process to prepare organic/inorganic polymer materials of network structure. These materials are sometimes referred to as ormosils (organically modified silicates).



$$\mathrm{HO{-}[CH_2]_4{-}OH} + 2\,\mathrm{OCN{-}[CH_2]_3{-}Si(OEt)_3} \xrightarrow[\text{REFLUX 24h}]{\text{THF (dry)}} \mathrm{(EtO)_3Si{-}[CH_2]_3{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}[CH_2]_4{-}O{-}\overset{\overset{O}{\|}}{C}{-}NH{-}[CH_2]_3{-}Si(OEt)_3}$$

Figure 8

Flexible organic/inorganic hybrid gels (Figure 8) were formed by preparing a mixture of 1,4-butanediol (3.08 g 34 mmol) and 3-isocyanatopropyl triethoxysilane (16.9 g 68 mmol) which was then refluxed in THF for 24 h under nitrogen. The mixture was cooled and the THF was removed by rotary evaporation. The product was solubilised in approx. 200 cm^3 of DMF and filtered to remove any residual undissolved product. Lithium triflate and $[Ru(bpy)_3]^{2+}$ were added. The gelling mixture was spin-coated onto fluorine-doped ITO glass using a spin speed of 500 rpm. Unfortunately, there was no time for a full conductivity study of these doped flexigels.

4.3.3 CONDUCTIVITY MEASUREMENTS

A.C. impedance was used to determine the degree of conductivity in the samples. The conductivity found for the sample 1:20 was in the region of 10^{-7} S cm^{-1}. The conductivity we were aiming for was 10^{-6} S cm^{-1} [22] higher by an order of magnitude. The low conductivity of the gel is probably due to residual organic solvents (DMF used in the preparation of the gel). The presence of aprotic solvents such as DMF or DMSO is known to have the effect of lowering conductivity. A range of materials was prepared differing only in the amount of lithium salt which was incorporated in the matrix i.e. the molar ratios of lithium triflate to the TEOS was 1:20, 1:10, 1:6.7, 1:5. Crystallisation of the lithium salt occurred after three days in the samples with the largest proportion of salt to TEOS 1:6.7 and 1:5. Residual organic solvents were evaporated off under high vacuum and the gels formed were stored in a dessicator prior to conductivity testing.

In turn the dried discs were connected to a platinum wire jig using a compressive force applied by a spring. The jig consisted of a 30 cm rod of alumina with narrow longitudinal holes through it attached to a larger rod of alumina that contained the pellet. Platinum wire was threaded through the inner rod and another platinum wire and a chromel/alumel thermocouple were threaded through the outer rod. The sample end of the jig was placed in a Carbolite horizontal tube furnace, fitted with a Eurotherm temperature controller. The temperature was accurately measured (± 1°C) using the chromel/alumel thermocouple, which was attached to a digital multimeter. Two terminal AC impedance measurements were performed using a Solartron 1260 impedance analyser, which was linked to the computer program Zview. An AC voltage of 100mV was applied, over a frequency range of 10MHz to 100MHz, with ten measurements being made for every decade in frequency. An integration time of 1 second per measurement was used with a delay time of 0.2 seconds between each measurement. Measurements were made, in air, at room temperature. The data were corrected for sample geometry and complex impedance plots allowed conductivities (Sm^{-1}) and capacitance (F) to be calculated.

Table 2: conductivity measured at the high frequency response.

Sol/PPV/Li triflate Molar ratio	**Geometric factor/ cm^{-1}**	**Capacitance/ F**	**Resistance/ Ω cm**	**Conductivity/ $S\ cm^{-1}$**
1:20	0.05	1.36×10^{-11}	1.4686×10^{6}	6.89×10^{-7}
1:10	5.9926	2.2306×10^{-12}	2.83235×10^{5}	3.53×10^{-6}
1:6.7	19.70	1.9×10^{-12}	1.2704×10^{5}	7.87×10^{-6}
1:5	3.648	10^{-12}	4045	2.47×10^{-4}

Table 2

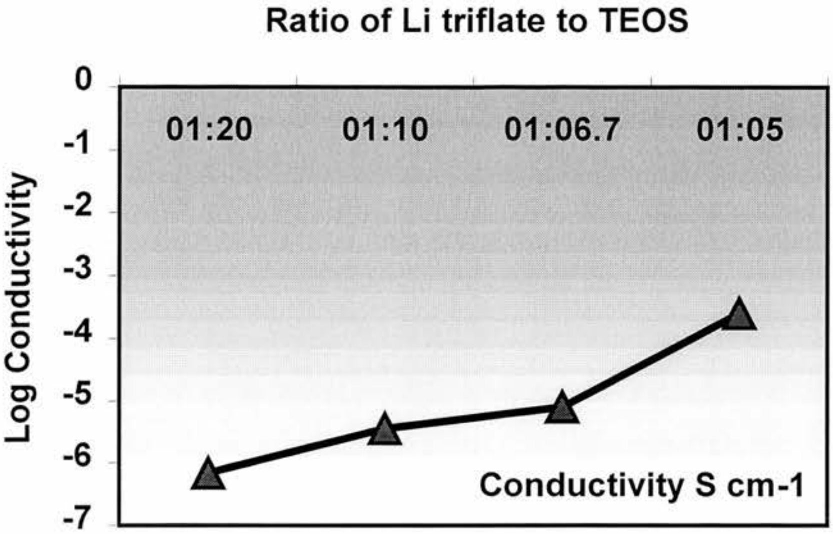


Figure 9

Figures 10-13 show the impedance plots obtained from the samples containing molar ratios of Li to TEOS 1:20, 1:10, 1:6.7, 1:5 respectively.

Although the impedance plots apparently only show one semicircle in accordance with the model in Figure 5, the complex electric modulus ($M^* = j\omega\ C\ Z^*$) [26] reveals a peak corresponding to a further semicircle at high frequency. We assign these semicircles to ionic conduction in the electrolyte (low frequency) and the mixed redox conduction due to the PPV (high frequency). Ionic conductivity values taken from the semicircle due to electrolyte conduction (low frequency) are tabulated (Table 2) and plotted in Figure 9 clearly show a steady increase in conductivity with increased doping level.

These preliminary experiments show exciting results much more work is needed on the characterisation of the conductivity mechanism in these systems. A comparison of these results with those obtained from doped PPV and sol-gels with purely ionic conductors should be made and an investigation into the effect of the post gelation polymerisation has on the conductivity.

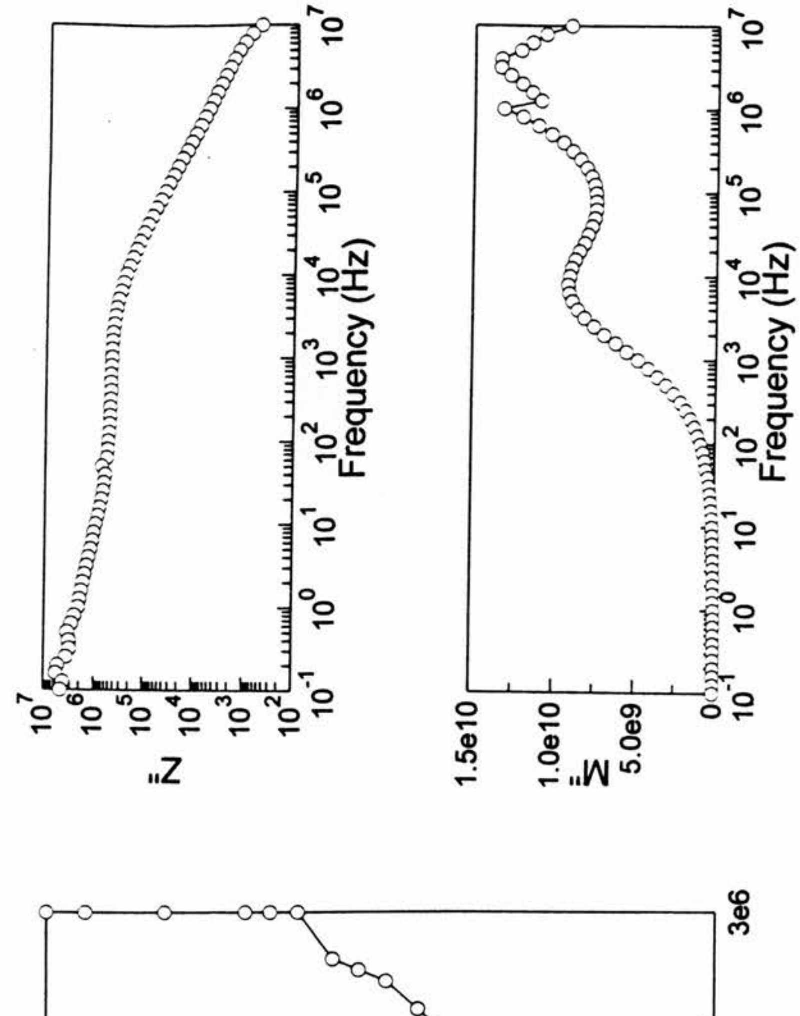


Figure 10 AC inpedence of PCM106

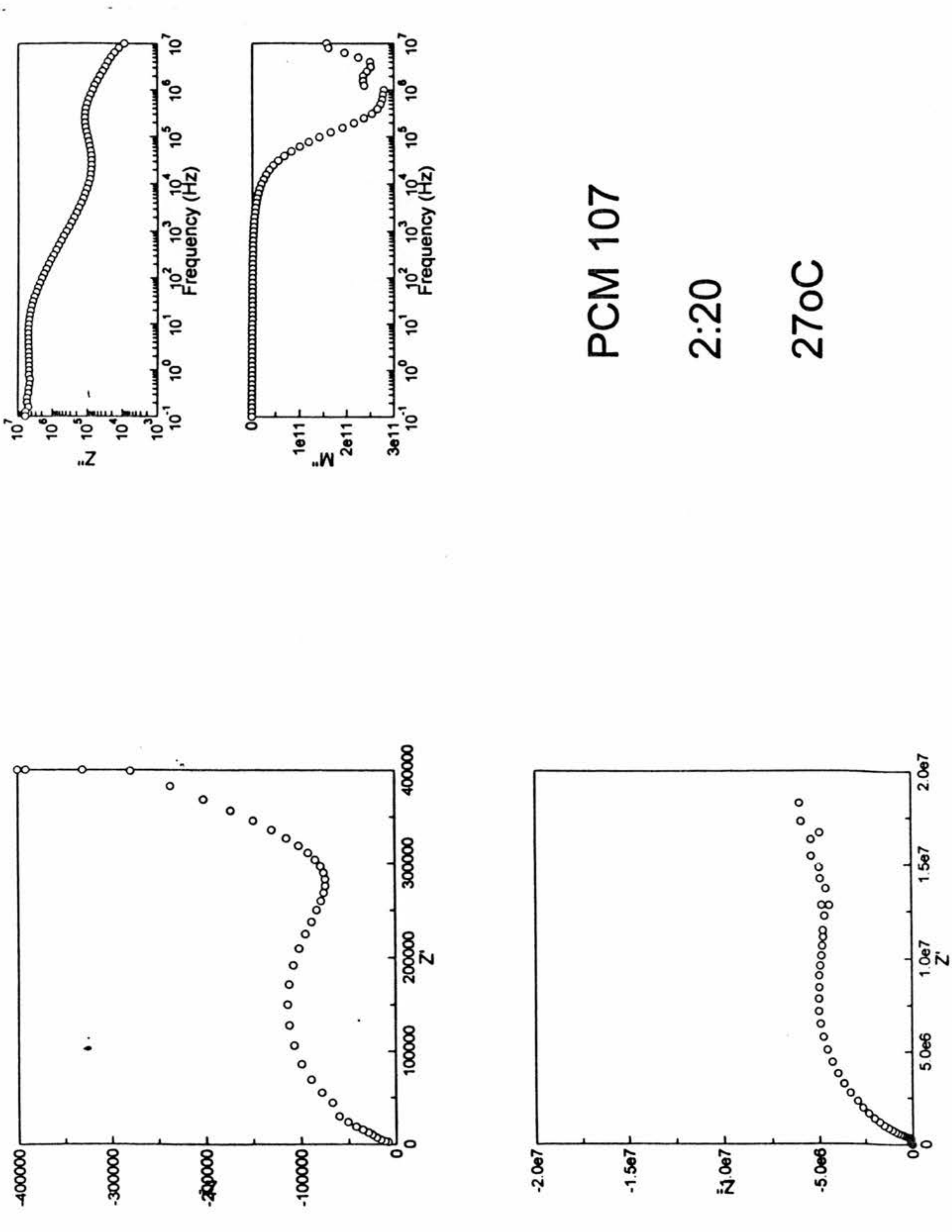


Figure 11 AC Impedance of PCM 107

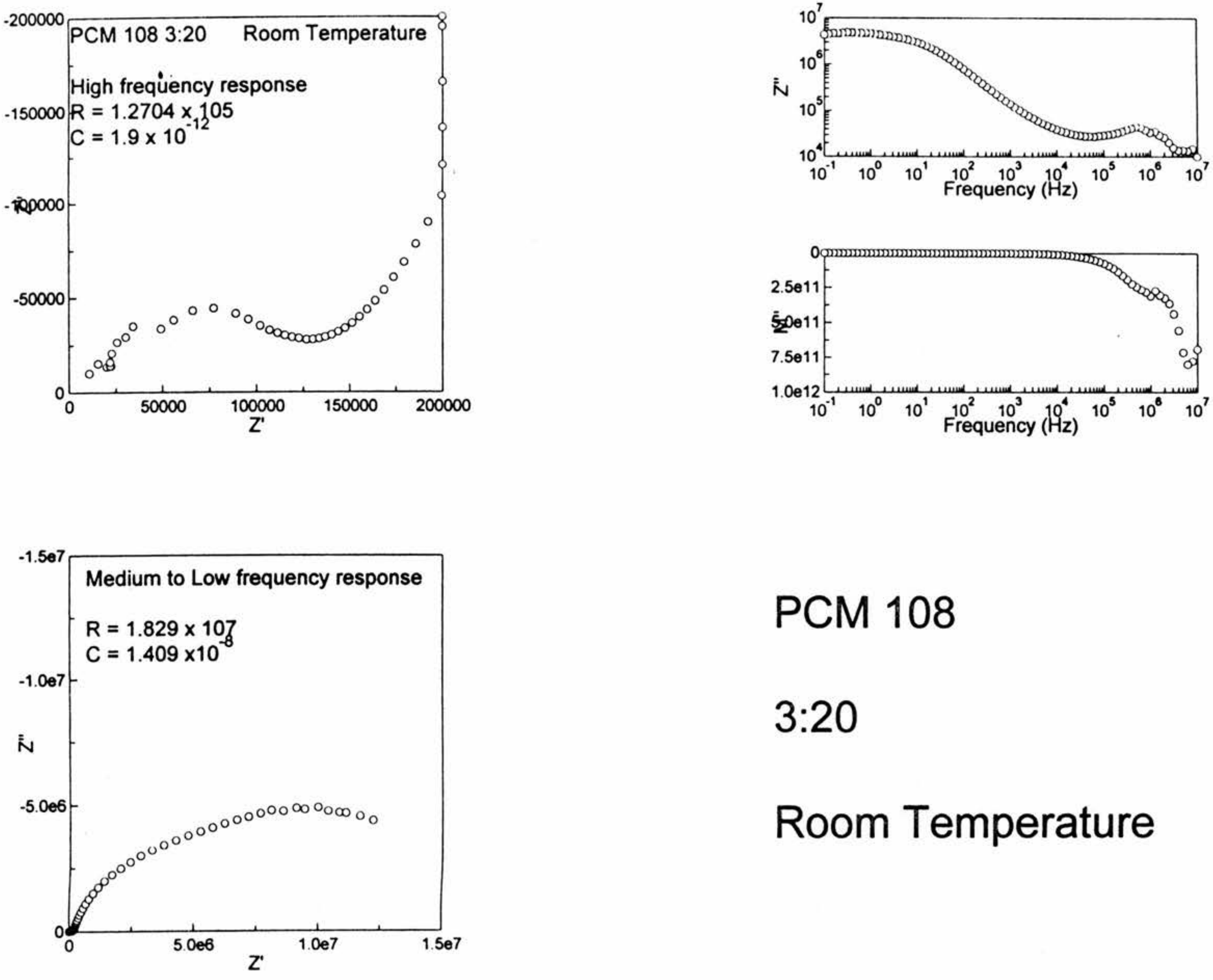


Figure 12 AC Impedance of PCM 108

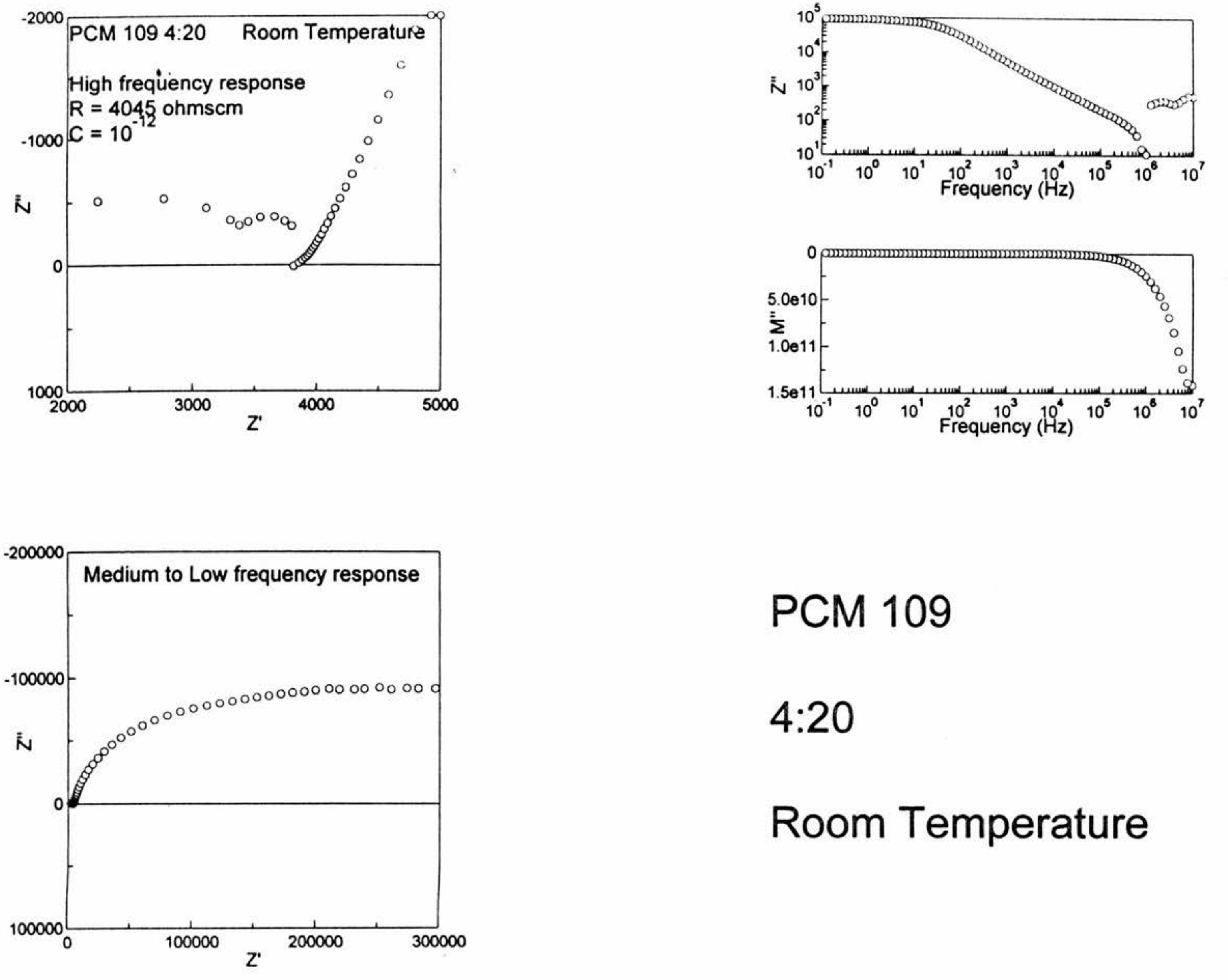


Figure 13 AC Impedance of PCM 10

There is the possibility of a dual mechanism for conductivity in this material, firstly from the gel and secondly from the polymer (Figure 13). From the modulus plots it is unclear whether the conductivity is entirely electronic or ionic. The electronic conductivity if any could be accounted for from the PPV polymer becoming doped by the base used to induce polymerisation .

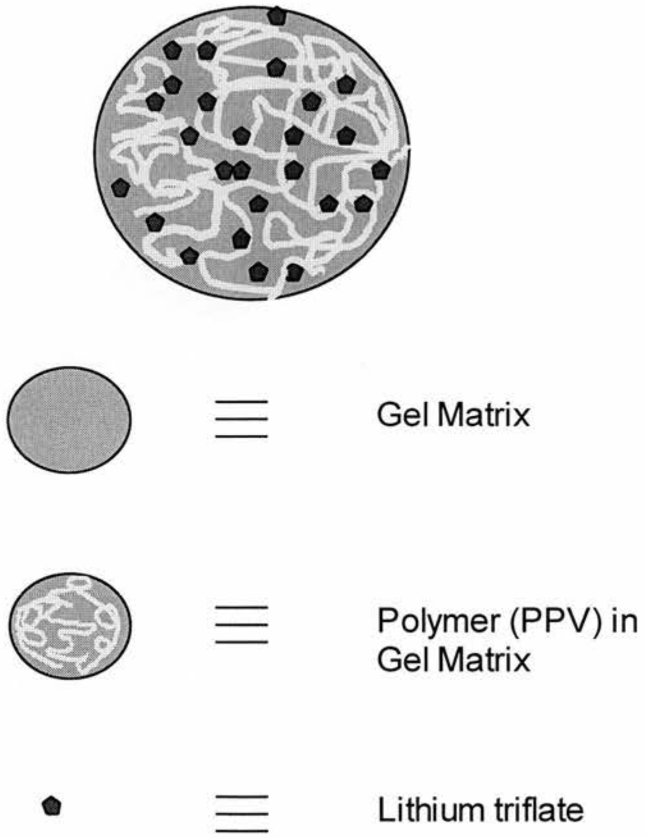


Figure 14

4.3.4 ELECTROCHEMICAL AND SPECTROSCOPIC STUDY OF ELECTROCHEMICAL LED MATERIAL $[Ru(bpy)_3]Cl_3$/SOL-GEL/LITHIUM TRIFLATE

TEOS rigid gels and Flexigel containing $[Ru(bpy)_3]Cl_3$ and lithium triflate salt were made with the Li:Si ratio of 4:20 which was previously shown to have the greatest conductivity.

The flexigel/$[Ru(bpy)_3]Cl_3$/Lithium salt gel was spin-coated onto an ITO glass substrate. The film was characterised by UV (Figure 14), which confirmed the presence of the ruthenium complex in the gel thin film by the presence of a broad band typical of that of a molecule in solution, at approximately 460 nm.

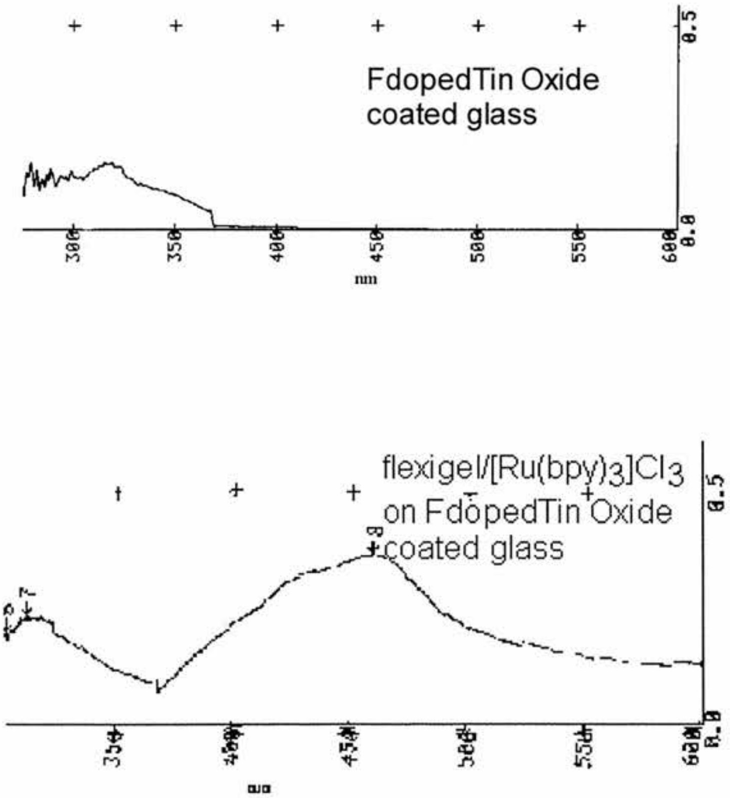


Figure 15 UV Spectra of $[Ru(bpy)_3]Cl_3$/TEOS/lithium thin film

The film behaviour was then studied by cyclic voltammetry. Cyclic voltammetry was carried out using an EG and G PARC 273 A Potentiostat/Galvanostat controlled by version 4.11 of the Electrochemistry Research software package running on a PC.

The working electrode was fluorine doped ITO glass. The counter electrode was silver. The electrolyte was tetrabutylammonium hexafluorophosphate (0.1M). and acetonitrile was used as the medium

On cycles 1-5 leaching was observed as the decrease in current (Figure 16). Leaching continued on cycles 5-10 (Figure 16). The acetonitrile solution took on the characteristic colour of the $[Ru(bpy)_3]^{2+}$ (red/orange) complex and on removal of the film it became obvious that the complex had leached out as the film had turned clear and colourless but remained intact.

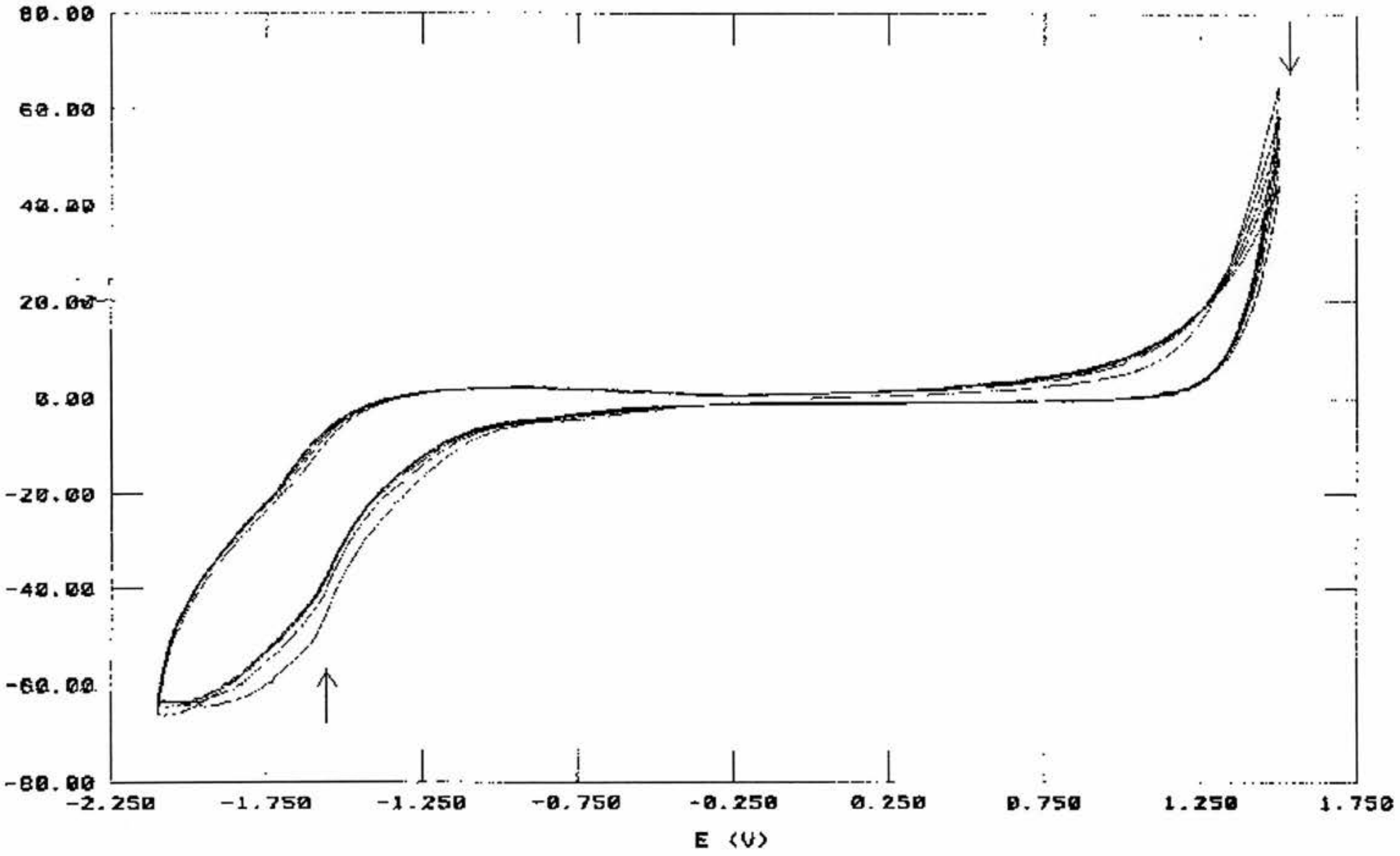


Figure 16 Cycles 1-5 of Rubpy/TEOS/lithium thin film

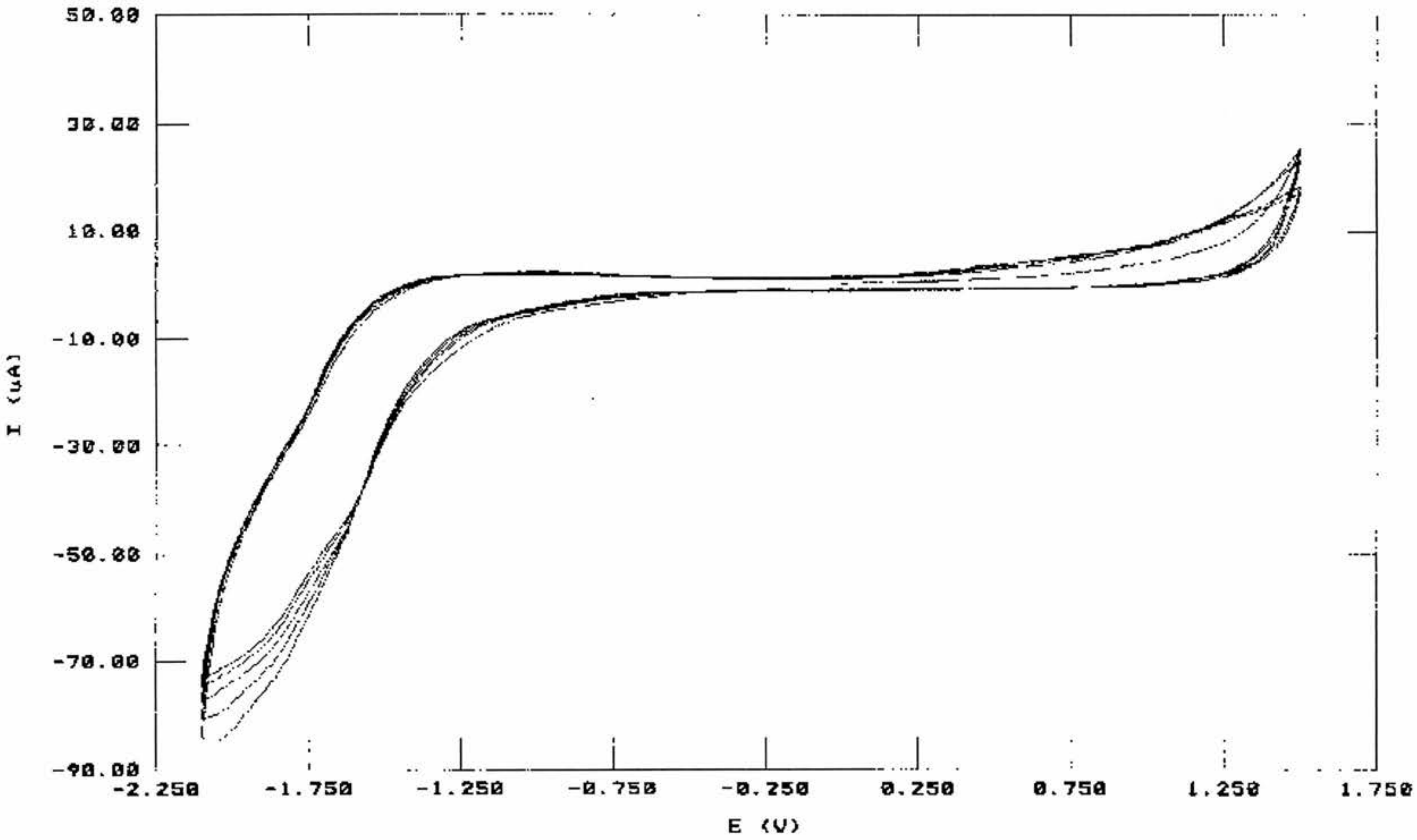


Figure 17 Cycles 5-10 of Rubpy/TEOS/lithium thin film

4.3.5 SUMMARY AND CONCLUSIONS

It has been shown that sol-gel encapsulation using our procedures, including the addition of electrolyte does not have an adverse effect on the luminescence, the only exception being the Al oxime complex. This may be caused by its greater reactivity with the silanol groups. Polymer encapsulation was not possible except in the case of the polymerisation post gelation method, which avoids the necessity for surfactants. Finally we have demonstrated that the high ionic conductivities necessary for LEC device materials may be achieved without the need for added solvent. This latter, surprising finding will be the subject of further study.

4.4.0 EXPERIMENTAL

4.4.1 PREPARATION OF LITHIUM ION DOPED/TEOS COMPOSITES

To 0.101g (0.49 mmol.) of tetraethyl orthosilicate was added 0.0624g (1.96 mmol.) methanol at room temperature, 0.135g (0.48mmol) of p-xylene(dimethylsulphonium chloride) and 0.0038g (0.0244m) of lithium trifluoromethanesulphonate (lithium triflate). After 30 min stirring 3 drops of 1M HCl were added as a catalyst. The mixture was stirred for a further 60 min at room temperature 2 drops of DMF was added as a drying control additive. The mixture was covered with Nescofilm and gelation occurred after 3 days. Just prior to gelation the gelling liquid was cast onto a teflon sheet. When the gels formed they were pressed out into circular disks. The gel was soaked in 1N NaOH and the gel turned from clear to bright yellow. As was found in Chapter 3 section 3.5.1. The gel was then washed with distilled water to remove any excess base. This procedure was repeated with varying concentrations of lithium triflate, to afford samples where the molar ratios of lithium triflate to the TEOS were 2:20, 3:20 and 4:20.

4.4.2 TEOS RIGID GELS CONTAINING [RU(BPY)$_3$]CL$_3$ AND LITHIUM TRIFLATE

To 11.24 g (0.54 mol) of tetraethylorthosilicate (TEOS) was added 6.9 g (0.216 mol) of methanol at room temperature. After 30 min stirring 3 drops of 1M

HCl were added as a catalyst. The mixture was stirred for a further 60 min at room temperature. Lithium triflate and $[Ru(bpy)_3]Cl_3$ were added to the sol. The mixture was covered with Nescofilm. A gel formed after 36 h.. On drying and ageing (5 days in ambient conditions) the gel shrank >50% in linear dimensions and became hard and glassy.

4.4.3 PREPARATION OF FLEXIBLE ORGANIC/INORGANIC HYBRID GELS CONTAINING $[RU(BPY)_3]CL_3$ AND LITHIUM TRIFLATE

A mixture of 3.08 g (34 mmol)1,4-butanediol and 3-isocyanatopropyl triethoxysilane 16.9 g (68 mmol) were refluxed together in THF for 24 h under nitrogen. The mixture was cooled and the THF was removed by rotary evaporation. The product was solubilised in approx. 200 cm^3 of DMF and filtered to remove any residual undissolved product. Lithium triflate and $[Ru(bpy)_3]Cl_3$ were added. The gelling mixture was spin-coated onto fluorine doped ITO glass.

4.4.4 ENCAPSULATION OF $[RU(BPY)_3](PF_6)_3$ INTETRAETHYLORTHOSILICATE DERIVED GLASS. (HYDROLYTIC SOL - GEL METHOD).

To 5.62 g (0.027 mol.) of tetraethyl orthosilicate was added 3.45 g (0.108 mol.) of methanol at room temperature. After 30 min stirring 3 drops of 1M HCl were added as a catalyst. The mixture was stirred for a further 60 min at room temperature and divided into 5 batches. Solutions of $[Ru(bpy)_3](PF_6)_3$ were prepared in methanol 0.1%- 0.5% w/w. The solutions were added slowly to each vessel. The mixtures were covered with Nescofilm. Gels formed between 38 and 96 hours. On drying and ageing (5 days in ambient conditions) they shrank 50% in linear dimensions and became hard and glassy.

4.4.5 SYNTHESIS OF ALUMINIUM OXIME

A 2M ammonium acetate solution was slowly added to a 2% solution of 8-hydroxyquinoline in 2 M acetic acid, until a yellow precipitate formed. Then add a further 25 cm^3 of 2 M ammonium acetate was added for each 100 cm^3 of solution in the beaker. The reaction mixture was allowed to stand for 30 mins with frequent stirring for the first 20 mins.

4.4.6 ENCAPSULATION OF ALUMINIUM OXIME IN TETRAETHYLORTHOSILICATE DERIVED GLASS. (HYDROLYTIC SOL - GEL METHOD).

To 5.62 g (0.027 mol) of tetraethyl orthosilicate was added 3.45 g (0.108 mol) of methanol at room temperature. After 30 min stirring 3 drops of 1M HCl were added as a catalyst. The mixture was stirred for a further 60 min at room temperature, and divided into 5 batches. 5 solutions of aluminium oxime were made up in methanol 0.1%- 0.5% w/w. w.r.t. TEOS. The solutions of aluminium oxine in methanol were added slowly to each vessel. The mixtures were covered with Nescofilm. Gels formed after 36 hours. On drying and ageing (5 days in ambient conditions) they shrank >50%in linear dimensions and became hard and glassy.

4.4.7 ENCAPSULATION [RU(BPY)$_3$](PF$_6$)$_3$ IN TETRAMETHYLORTHOSILICATE DERIVED GLASS. (HYDROLYTIC SOL - GEL METHOD).

To 4.10 g (0.027 mol) of tetramethylorthosilicate was added 3.45 g (0.108 mol) of methanol at room temperature. After 30 min stirring 3 drops of 1M HCl were added as a catalyst. The mixture was stirred for a further 60 min at room temperature, and divided into 5 batches. 5 solutions of ruthenium bipyridyl were made up in methanol (0.1%- 0.5% w/w.) and were added slowly to each vessel. The mixtures were covered with Nescofilm. Gels formed after 36 hours. On drying and ageing (5 days in ambient conditions) they shrank >50% in linear dimensions. and became hard and glassy.

4.4.8 ENCAPSULATION [RU(BPY)$_3$](PF$_6$)$_3$ IN (3-ISOCYANATOPROPYL TRIETHOXYSILANE)DERIVED FLEXIGEL. (NON-HYDROLYTIC SOL - GEL METHOD).

A mixture of 1,4-butandiol (3.08 g, (34 mmol) and 3-isocyanopropyl triethoxysilane (16.9 g, 68 mmol) were refluxed together in THF for 24 h under nitrogen. The mixture was cooled and the THF was removed by rotary evaporation. The product was solubilised in approx. 200 cm^3 of DMF and filtered to remove any residual undissolved product. Gelling solution 5 cm^3 was added to 50% w/w [Ru(bpy)$_3$](PF$_6$)$_3$ w.r.t flexigel. The samples were homogeneously mixed. A portion of the mixture was pipetted onto a Teflon sheet which was placed in an oven at 50 °C for 12 h after which time the samples had gelled, and could be peeled off the Teflon sheet.

4.4.9 ENCAPSULATION OF COUMARIN IN TETRAETHYLORTHOSILICATE DERIVED GLASS. (HYDROLYTIC SOL - GEL METHOD).

To tetraethyl orthosilicate (5.62 g, 0.027 mol) was added (3.45 g, 0.108 mol.) of methanol at room temperature. After 30 min stirring 3 drops of 1M HCl were added as a catalyst. The mixture was stirred for a further 60 min at room temperature. A saturated solution of coumarin in 10 cm^3 of methanol was added slowly. The dye changed from fluorescent yellow in methanol to a bright red colour when added to the mildly acidic sol-gel solution. The mixture was covered with Nescofilm. Gels formed after 72 h.

4.5.0 REFERENCES FOR CHAPTER 4

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