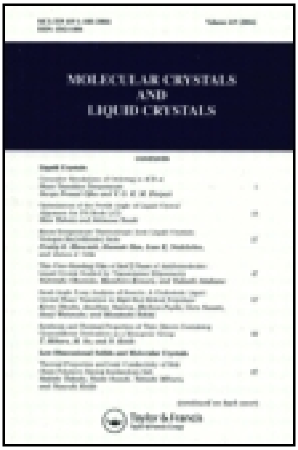

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Optoelectronic Device Physics Based on Conjugated Polymers

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OPTOELECTRONIC DEVICE PHYSICS BASED ON CONJUGATED POLYMERS

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Abstract We have developed means for processing conjugated polymers to allow fabrication of a variety of semiconductor device structures. These polymers include polyacetylene prepared via the Durham precursor route and various poly(arylene vinylenes) prepared via sulphonium precursor polymers. We have shown that these devices exhibit novel electro-optical properties which depend for their operation on the non-linear character of the electronic excitations of the polymer chain. We discuss here the use of poly(phenylene vinylene) and derivatives as the active layers in light-emitting diodes.

INTRODUCTION

Conjugated polymers have been principally studied for their electrical conductivity when oxidised or reduced, either chemically or electrochemically[1]. Recent interest has been directed to the optical and non-linear optical properties of these materials, and there is increased interest in the combination of useful electronic/optical properties and good processing properties that some of these polymers can provide.

Conjugated polymers are not readily processed; they are usually rigid-rod polymers and are thus insoluble in common solvents and infusible below the decomposition temperature of the polymer. Various schemes have been developed to circumvent this problem, of which two have been of use for our work. First, it is possible to find a precursor route in which a non-conjugated "precursor" polymer is processed from solution, e.g. by spin-coating thin films onto appropriate substrates, and which is then converted *in situ* by thermal or chemical elimination of side-groups to form the conjugated polymer. This method was first established for the synthesis of polyacetylene by Feast and co-workers[2] and this method has made possible the fabrication of thin coherent films of this polymer which can be used as the active layers in field-effect semiconductor devices[3]. A second precursor route[4,5] which we have developed for the present work is based on the sulphonium polyelectrolyte precursor to poly(p-phenylene vinylene), PPV. This route was shown to be suitable for the manufacturing of good quality films by several groups, and has been widely developed[4,5]. We return to this later.

An alternative strategy to achieve a processible polymer is to add flexible side groups to the polymer chain, and it has been found that such polymers are soluble when the volume fraction of the side groups is about equal to or greater than that of the backbone. The poly(3-alkyl thienylenes) have been extensively studied[6,7], and again the good film-forming properties allow the fabrication of field-effect devices[8]. Similar strategies have also been used for the poly(arylene vinylenes) and the poly(2,5-dialkoxy phenylene vinylenes) have been shown to be convenient to use[9].

MATERIALS PREPARATION

We have developed a range of precursor routes to PPV[10] which we summarise in figure 1. Among the range of sulphonium salt precursors shown on the top row of the figure, the tetrahydrothiophene material has proved to be particularly good in the elimination step and has been widely used[5]. We restrict discussion here to results obtained with this material. We have found, however, that the methanol-eliminating polymers shown in the lower row can produce better ordered polymer[10]. For the sulphonium salt precursors prepared in aqueous solution we remove the solvent and redissolve the precursor polymer in methanol. We find that this is a good solvent for preparation of thin films of the precursor polymer on suitable substrates by spin-coating. After thermal conversion (typically 250°C or above for 10 hours in vacuo), these films of PPV (typical thickness 100 nm) are homogeneous, dense and uniform.

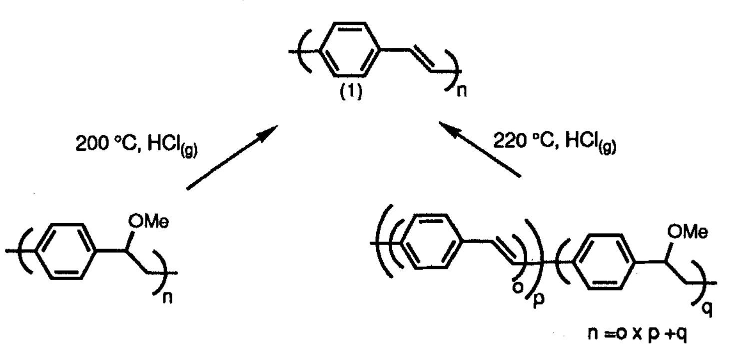

FIGURE 1 Synthetic route to poly(p-phenylene vinylene), PPV

Furthermore, they are robust and intractable[11], stable in air at room temperature, and in vacuo at temperatures in excess of 300°C.

ELECTRONIC STRUCTURE OF PPV

Much of the interest in the electronic structure of conjugated polymers has been directed to the non-linear character of the electronic excitations of the π electron system which couples to the geometry of the chain. There is evidence from the optical absorption spectra of chemically doped polymers that the geometrical relaxation of the chain in response to the excited electronic state is strong, and states are pulled deep into the semiconductor gap[1]. However, rather less attention has been paid to the neutral excited states that can be produced by photoexcitation across the π-π^* gap; singlet excitons can be detected if they decay radiatively, and this process is observed with a reasonably high quantum yield in PPV[12]. The onset for π-π^* interband absorption in PPV is at about 2.5 eV, and the luminescence spectrum, shown in figure 2, appears below this with several vibronic peaks evident. It is characteristic of many molecular semiconductors, with a small Stokes' shift and in this respect it is evident that the extent of geometrical relaxation in the excited state is slight, and very much less than indicated for the charged excitations produced through chemical doping. We have commented previously[12] that this is incompatible with the one-electron models for self-localisation of excited states[13], and we return to this point later in the paper.

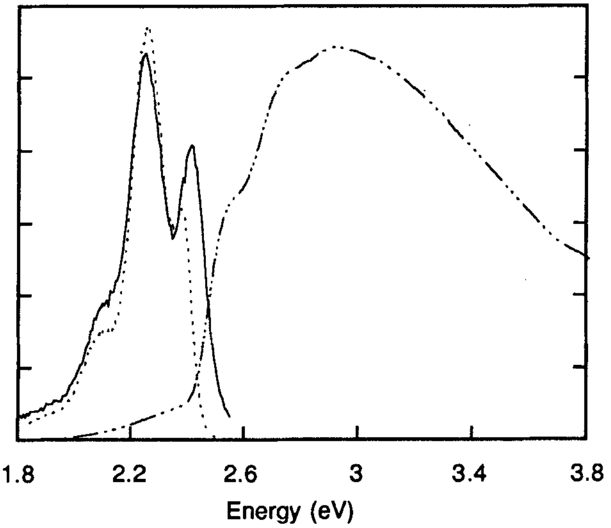

FIGURE 2 Optical absorption (dash-dot), photoluminescence (dot) and electroluminescence (solid) spectra for PPV.

ELECTROLUMINESCENCE

Electroluminescence through charge injection under a high applied field has been known in organic semiconductors for some time. There have been recent reports of high efficiencies for structures built with at least two organic layers, one as the emissive layer, and the others chosen to control electron or hole charge transport[14-19]. These devices are fabricated by vacuum sublimation of the organic layers, and efficiencies and selection of colour of the emission are very good, though there are in general problems associated with the long-term stability of the sublimed organic film against recrystallisation and other structural changes.

We discovered that films of PPV could also be used as the emissive layers in electroluminescent devices[20]. Structures for electroluminescence are fabricated with the PPV film formed on a bottom electrode deposited on a suitable substrate (such as glass), and with the top electrode formed onto the fully-converted PPV film. Electrode materials are chosen with a low work function for use as the negative, electron-injecting contact, and with a high work function as the positive, hole injecting contact. One, at least, of these layers must be semitransparent for light emission normal to the plane of the device, and we have used both indium oxide and thin aluminium (typically 7-15 nm) in this role. We found that forward voltages for devices with PPV film thicknesses of about 100 nm were as low as 10 V with this range of electrode materials. Subsequently Braun and Heeger[21] reported that they had used a soluble derivative of

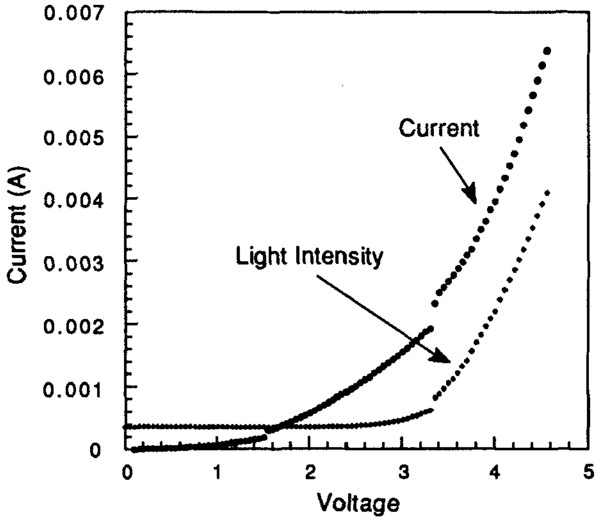

FIGURE 3 Forward voltage current and light output response for an electroluminescent diode fabricated with indium/tin oxide/PPV/calcium.

PPV with alkoxy side groups and had used lower work function metals, particularly calcium, as the electron injecting contact layer. The use of calcium drops the forward voltage to less than 5 V and also increases the efficiency, which can reach 1% (photons per electron injected). We show the characteristics of a device we fabricated with indium/tin oxide, PPV and calcium in figure 3.

The spectrum of the luminescence produced in these devices is essentially the same as that of the photoluminescence, as is shown in figure 2. This indicates that the same excited state is produced by charge injection as by photoexcitation, and we identify this as the singlet exciton[10]. We consider that these devices operate by double charge injection of electrons and holes from negative and positive electrodes, and that these are transported through the polymer layer, combining to form excitons which can then decay by photon emission. There is evidence for the combination of singly-charged excitations to form singlet excitons which decay radiatively in the spin 1/2 response seen in optically-detected magnetic resonance (ODMR) measurements in similar conjugated polymers[22].

We have made mention of the self-localisation of charged excitations to form polarons or bipolarons, and we consider that the injected charges are transported as singly-charged polarons. We note that the localised states of these polarons cannot move further into the gap than those for the exciton that results from combination of oppositely-charged polarons, and are thus very much more weakly self-localised than is the case for the bipolarons taken to be present in chemically-doped polymer[1]. However, there is evidence that charges introduced without an associated chemical dopant do form weakly self-localised polarons. We have measured the optical absorption due to the induced charge layer in metal/insulator/semiconductor field-effect devices fabricated with poly(3-hexyl thienylene) as the semiconductor layer under conditions where charge should be stored in the form of polarons[8]. We find that the separation in energy of the gap states for the polaron is large, 1.8 eV, and close to the energy of the luminescence emission. These findings are consistent with the requirements placed on this model by the observation of electroluminescence.

The efficiency in these electroluminescent devices is determined by a number of factors. First, the quantum yield for luminescence from a singlet exciton is usually well below 100% because there are non-radiative decay mechanisms present. We consider that many of these are extrinsic and require motion of the exciton to a quenching site. This can be limited by reducing the number of quenching sites, or by limiting the mobility of the excitons. We have achieved this by forming copolymers of PPV with the poly(2,5 dimethoxy phenylene vinylene), PDMeOPV, which has a lower band gap (2.1 eV) than PPV. We thus form a polymer chain with a spatially-modulated band gap, and which can trap the excitons in regions of low gap. These copolymers can give greatly enhanced quantum yields for luminescence[23]. Second, the combination of positive and negative charges will give singlets and triplets in the ratio of 1:3. Some of the triplets may decay radiatively, through processes such as triplet-triplet collisions which result in the formation of singlet excitons. There is evidence for such processes following photoexcitation in the spin 1 ODMR response seen by Swanson et al[22]. Third, the requirement for injection of both electrons and holes is best met if the positive and negative electrodes have high and low work functions respectively, and we note that the use of electron and hole transporting layers in the molecular film electroluminescent devices has greatly improved the performance of these structures.

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