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IR and Submillimetre-wave Spectra of Doped Poly(*p*-phenylene vinylene)

Samir El-Atawy† and Keith Davidson*
School of Physics and Materials, Lancaster University, Lancaster, UK LA1 4YA

Poly(*p*-phenylene vinylene) (PPV) films of varying thickness have been prepared using standard precursor routes. A new oxidative doping technique, using degassed concentrated H_2SO_4 under low pressure, was used. Precise levels of doping were achieved, these levels being dependent on the time of exposure and the thickness of the sample. A very wide range of spectral absorption measurements, covering the range 20–4000 cm^{-1}, were carried out on doped and undoped samples and on the precursor polymer. Large variations in absorption peaks throughout the entire range were noticed upon doping. New assignments of the unknown IR peaks together with the observed peaks in the submillimetre range are proposed.

For several years the study of conjugated polymers has been of major interest to chemists, physicists and electronic engineers. A variety of investigations have been done on the semiconducting and conducting properties of intrinsic and doped materials. Conjugated polymers in general are considered to be medium to large bandgap semiconductors with highly anisotropic properties. The relatively weak p_z orbital overlap between chains compared with the potentially delocalised π bonding along the chains gives these materials a quasi-one-dimensional electronic structure that differs strongly from more conventional conductive materials.

Most non-degenerate conjugated polymers are insulators in the ground state. However, creation of self-localised charges, such as polarons, bipolarons and solitons upon doping, results in lattice distortions. These particle-like entities have energy levels much smaller than the intrinsic bandgap between conduction and valence bands. Many attempts have been made to dope conjugated polymers; both p-type and n-type doping can be achieved using chemical, electrochemical or vapour-phase doping.[1–7] Doping of conjugated polymers greatly increases the number of localised polarons and bipolarons (or solitons in doped *trans*-polyacetylene) thereby increasing the rate of inter- and intra-chain transfer causing a large increase in electrical conductivity.[8–11]

The optical properties of conjugated polymers have also been of interest to many workers. First, the non-linear electro-optical properties, such as the dependence of optical transmission on electric field strength, are of potential use in electro-optic modulation devices[12,13] and in active and passive integrated optic wave guides. This has been domonstrated in *trans*-polyacetylene MIS and MISFET device structures where the optical absorption was spectrally resolved as a function of applied electric fields.[12,14]

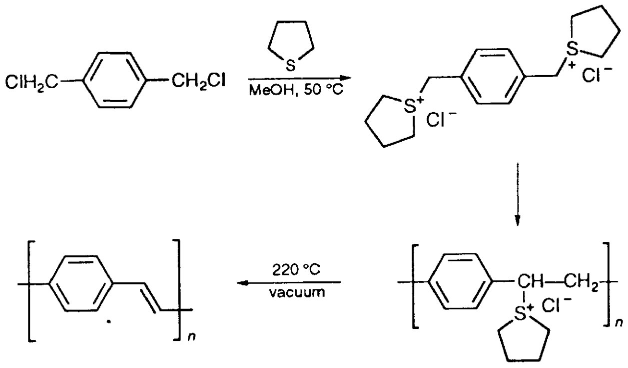
Electro- and photo-luminescence has been extensively studied by a number of researchers. Much of the work has been aimed at developing high-efficiency light-emitting diodes (LEDs) as display devices. Several attempts have been made to increase the efficiency and to control the emission wavelength, and chemical tuning through co-polymerization has been shown to produce a blue shift in the spectral emission of PPV.[15–17]

PPV is amongst the most investigated of conjugated polymers, particularly its potential for use in electro-optical devices.[15–17] Spectral studies in the UV, VIS and IR ranges have been reported for films of PPV and virtually full assignments of absorption peaks have been made down to frequencies as low as 400 cm^{-1} (25 μm wavelength).[5,18,19] A major breakthrough in the study of PPV and other polymers, is the synthetic route, *via* soluble polyelectrolyte precursors, that allows the formation of thin films of the otherwise non-processible PPV. The increase in the processibility provided by this technique is largely responsible for the success of electro-optical and electronic devices based on PPV.[20]

Both oxidative and reductive dopants have been used with PPV. H_2SO_4, AsF_5 and I_2 have been used for p-type doping and sodium naphthalide for n-type doping.[4] Conductivities of 100 and 10 S cm^{-1} have been reported for H_2SO_4 and AsF_5 dopants, respectively.

Experimental

Free-standing films of PPV were prepared by solution casting of the precursor polyelectrolyte and thermal conversion to conjugated PPV.[12] The materials were prepared following the established synthetic route shown in Scheme 1. *p*-Phenylenedimethylene-1,1-bis(tetrahydrothiophen-1-ium)dichloride was prepared by reacting α,α′-dichloro-*p*-xylene (0.75 mol dm^{-3}) with tetrahydrothiophene (2.2 mol dm^{-3}) in 80 : 20 methanol : water mixture at 50 °C. The product was then precipitated in cold acetone followed by filtration and extensive drying in vacuum. The precursor polymer, poly{*p*-phenylene[1-(tetrahydrothiophen-1-io)ethylene chloride]}, was obtained by reacting the bis-sulfonium salt with an equimolar quantity of NaOH (0.2 mol dm^{-3}) in distilled water at 0 °C for 1 h under a nitrogen atmosphere. This reaction was quenched by slowly adding HCl (1 mol dm^{-3}) until the solution became slightly acidic (pH 6.8). The product was purified by dialysis against distilled water for five days.



Scheme 1

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† Present address: Institute of Graduate Studies and Research, University of Alexandria, Alexandria, Egypt.

The samples examined in this report were obtained by solution casting from methanol and prepared to various thicknesses ranging from 5 to 110 μm. Conversion to PPV was done by heating to 220 °C for 18 h under dynamic vacuum. The resultant homogeneous, dense films were brownish yellow in colour.

A new technique for doping was tried and found to be successful. The samples were immersed in a flask containing concentrated H_2SO_4 that had been degassed by a freeze–thaw process. The pressure inside the flask was then lowered until outgassing of the sample started occur. The sample changes colour very rapidly to deep blue and eventually to almost black. Outgassing occurs at reduced pressure indicating the onset of the ionic transfer interaction of the sulfate group inside the PPV film. The doping level and depth of doping are controlled by immersion time. To stop the process the vacuum is released, the film removed and washed thoroughly with acetone.

IR spectra of the free-standing films were measured in the range 400–4000 cm^{-1} using a Nicolet FT 205 spectrometer. The submillimetre measurements were performed using a millimetre-wave spectrometer and a liquid-helium-cooled composite germanium detector, covering the spectral range 15–600 cm^{-1}. Each submillimetre spectrum is the average of two runs ratioed against three background runs. The detector response was continuously monitored and the post electronics gain adjusted throughout the measurements.

Conductivity was measured using the van der Pauw, four-probe technique.[21] The conductivity was calculated from the following equation:

$$\sigma/\mathrm{S\ cm^{-1}} = \frac{\ln 2}{\pi d}\left(\frac{I}{V}\right)$$

where I is the applied current, V is the measured voltage and d is the sample thickness.

Results and Discussion

High-quality, free-standing films of precursor polymer and fully converted PPV of different thicknesses and dopant content were prepared and their absorption spectra and electrical properties examined.

IR and Submillimetre Absorption Measurements

The IR spectra of films of the precursor polymer and the fully converted PPV are shown in Fig. 1. The spectrum of PPV is identical to the spectra published by other workers[4,5] and virtually all of the absorption features have previously been assigned.[15,19] It has also been shown by the work of Bradley,[18] that all of the assigned peaks are categorised as having a dichroic ratio > 1. That is, the peaks are electric field polarization dependent.[18] The dichroic ratio is $A_{\perp}/A_{\parallel}$, where $A_{\perp}$ and $A_{\parallel}$ are the magnitudes of absorbance of radiation with electric fields polarised perpendicular and parallel to the chain direction. This anisotropy ratio defines whether the absorption mechanism is due to in-plane or out-of-plane bending and stretching modes. The in-plane modes are essentially activated by parallel polarisation, while the out-of-plane modes are due to interchain activation caused by perpendicular fields. Also, for unpolarized fields, the ratio between the in-plane and out-of-plane amplitudes A_{ip}/A_{op} for a specific mechanism and location on the polymer skeleton defines the degree of π electron delocalization caused by the wavefunction overlap along the polymer backbone.

In Fig. 1 the absorbances at 1013 and 837 cm^{-1} have been assigned to in-plane and out-of-plane *p*-phenylene CH bending modes, respectively, and the ratio of these values is: $(A_{ip}/A_{op})_{p\text{-phenylene}} = 0.06$. While for the vinylene CH, the in-plane bending mode at 1267 cm^{-1} and the out-of-plane mode at 965 cm^{-1} gave: $(A_{ip}/A_{op})_{\text{vinylene}} = 0.05$. As these ratios decrease, the π electron delocalization increases, indicating an increase in the uninterrupted conjugation length. Also from the various values of these ratios, it is clear that both mechanisms of the vinylene and *p*-phenylene can express the degree of electron delocalization, in contrast to the disagreement found by Bradley and co-workers[17] about the *trans*-vinylene moiety used by Zerbi *et al.*[22] as a measure for delocalization.

The peaks at 429 and 784 cm^{-1} have not previously been assigned. It is postulated here that both peaks are associated with the *trans*-vinylene moiety. The reason being the absence of these peaks in the precursor polymer spectrum shown in Fig. 1. In that figure, nearly all the large peaks are assigned to the *p*-phenylene ring which is present in both precursor polymer and fully converted PPV (except the broad peak at 3375 cm^{-1} due to the solvent OH-stretch band). For example, peaks at 555, 837, 1423 and 1519 cm^{-1} in Fig. 1 are assigned to *p*-phenylene out-of-plane ring bend, CH out-of-plane bend and semicircular ring stretch (1423 and 1519 cm^{-1}), respectively, and can be clearly identified in the figure. Traces of peaks assigned to the *trans*-vinylene group can be observed in the precursor polymer spectrum; however, these are attributed to PPV formed by partial conversion at room temperature.

Submillimetre transmission spectra of the precursor polymer and fully converted PPV are shown in Fig. 2. A broad band, around 100 cm^{-1}, is seen in the precursor

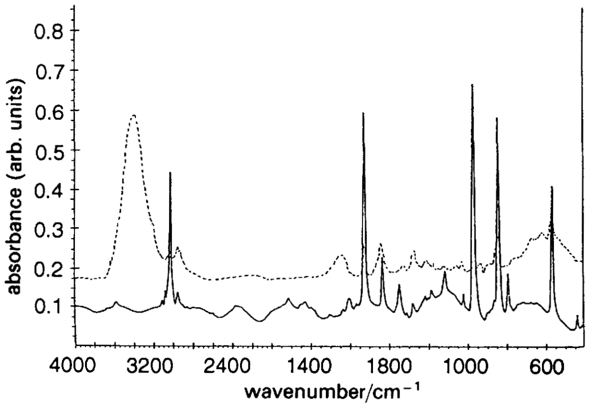


Fig. 1 IR absorbance spectrum of 5 μm thick film of fully converted PPV (——) and precursor polymer (– – –). The latter is shifted upwards for clarity.

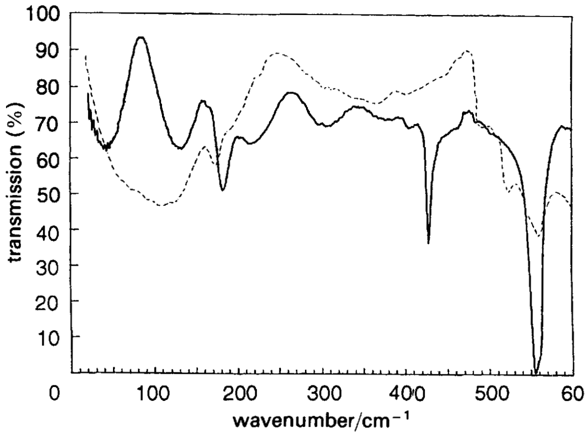


Fig. 2 Submillimetre-wave transmission spectrum of 12 μm thick film of fully converted PPV (———) and precursor polymer (– – –)

polymer spectrum which is not present in that of the PPV. It is believed that both the thiophene ring and trapped solvent contribute to this peak. Note the presence of interference fringes in the PPV spectrum. These confirm the thickness uniformity of the PPV film within the interferometer throughput area of 2 mm^2. The precursor polymer spectrum shown in Fig. 2 exhibits absorption bands at 170, 497, 523 and 555 cm^{-1}. The peak at 555 cm^{-1} has already been assigned whilst the peaks at 497 and 523 cm^{-1} are not observed in the PPV spectrum and are probably associated with the thiophene ring. The peak at 170 cm^{-1} is present in both spectra in Fig. 2 (with a slight shift in the PPV spectrum due to modulation with the dielectric visibility fringes). This suggests that this peak is related to a group frequency characterising the unaltered *p*-phenylene ring. This is also confirmed by the absence of this peak in the spectra of fully doped samples as explained later.

Doping of the PPV polymers by H_2SO_4 was achieved by the technique described earlier. Accurate monitoring of the exposure time for successful doping is essential. Overexposure leads to embrittlement of the sample whilst short exposure results only in surface doping of the sample. The exposure time is strongly temperature dependent, being significantly reduced at higher temperatures.

A large number of samples were studied under different doping conditions and the optimum conditions determined. The optimum conditions in this instance are those leading to the maximum level of electrical conductivity with no deterioration in the mechanical properties of the sample. Continuous measurements of the submillimetre-wave spectrum for the doped samples have shown that the optimum doping time is reached when the peak at 170 cm^{-1} disappears. Different thicknesses have been examined and the optimum exposure times recorded. For example, samples of thicknesses 5, 12, 25 and 39 μm required exposure times of 4, 7, 25 and 50 min, respectively. This thickness dependence is shown graphically in Fig. 3.

The submillimetre spectra of three doped PPV samples of different thicknesses are shown in Fig. 4. Two of the samples, of thickness 5 and 12 μm, were doped to optimum conditions, whereas the third sample, of 110 μm thickness, was immersed in the acid for only 30 min, resulting in reduced doping levels. Thus the peak at 170 cm^{-1} can still be observed in the 110 μm sample. All three spectra are dramatically changed from the spectrum of undoped PPV shown in Fig. 2; only the peaks at 429 cm^{-1}, associated with the *trans*-vinylene moiety, and 555 cm^{-1}, associated with the *p*-phenylene group, can be seen in all spectra.

Fig. 5 shows the IR spectrum of a 5 μm thick doped sample with exposure time of 5 min. There are a number of changes in the absorption peaks when compared with the spectrum of the undoped sample shown in Fig. 1. One important difference between the two spectra is the change in the unsymmetrical semicircular ring stretch at 1594 cm^{-1}. It can be seen that this peak increases in intensity after doping, indicating an increase in the loss of centre of symmetry in the phenylene ring. Our observations lead us to propose the following mechanism for the oxidative doping of PPV by concentrated sulfuric acid:

$$2PPV - 2e^- \rightarrow 2PPV^+$$

$$H_2SO_4 + 2e^- \rightarrow H_2 + SO_4^{2-}$$

The bubbles of gas seen when the polymer outgasses are hydrogen (along with small amounts of trapped air). The dopant anions become incorporated into the regimes between the oxidised polymer chains. However, the physical attachment of the sulfate group to the PPV is weak and washing with a proton-containing solvent (such as water) removes the dopant and the polymer returns to its pre-oxidised, non-conducting state. Solvents such as acetone, used in this study for washing the doped samples, have no easily dissociated protons and thus do not lead to undoping of the sample. Although this is a two-electron reduction of sulfuric acid, the electrons could come from widely separated sites on a chain (or even from different chains) leaving individual, positively charged polarons and changing the electronic configuration from the aromatic structure to the conducting quinoid structure, as shown in Scheme 2. The resulting increase of conjugation is responsible for the observed change in colour.

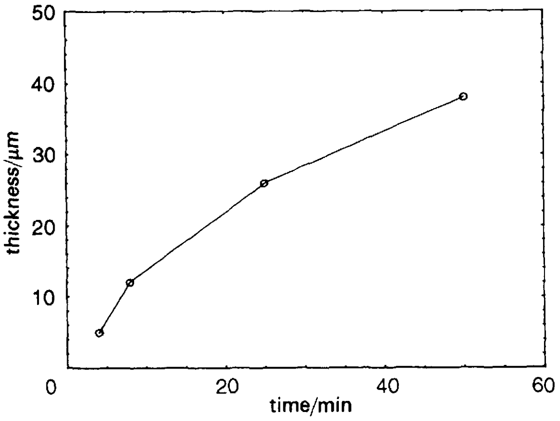


Fig. 3 Thickness dependence *vs.* doping time for optimum doping

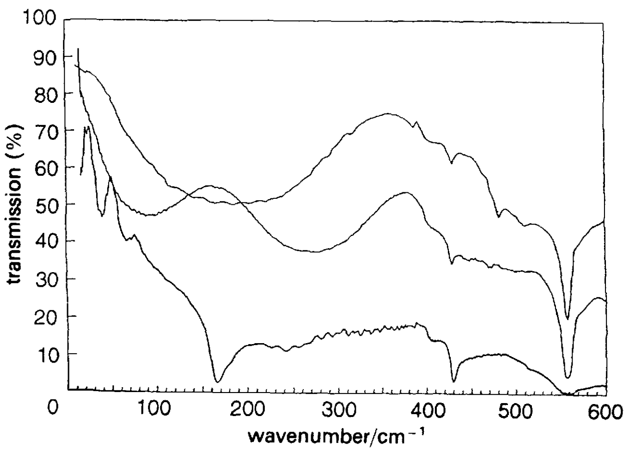


Fig. 4 Submillimetre-wave transmission spectra of three sulfate-doped PPV samples. From top to bottom, 5, 12 and 110 μm thick, respectively. The 110 μm thick film was not allowed to reach optimum doping conditions.

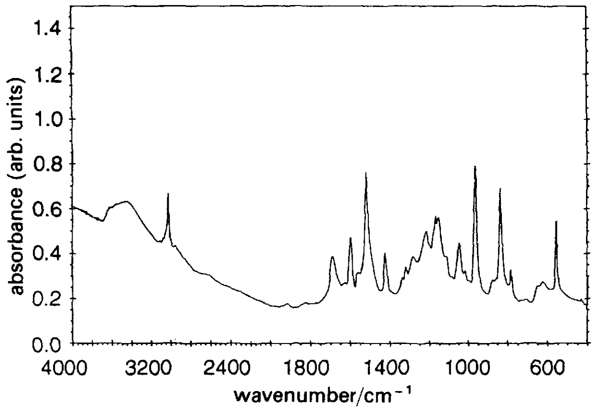
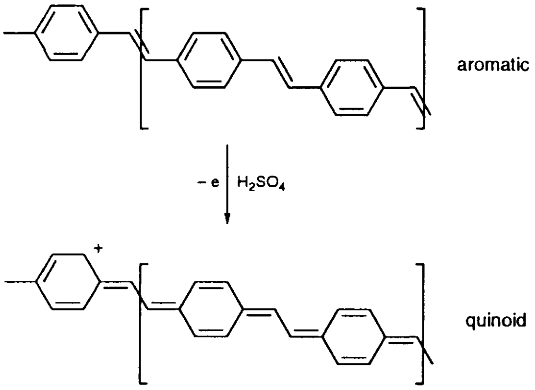


Fig. 5 IR spectrum of a 5 μm thick film of fully converted PPV allowed to reach optimum doping conditions



Scheme 2

This mechanism is in agreement with the observed spectra. That is, the change in the unsymmetrical semicircular ring stretch at 1594 cm^{-1} indicates enhanced loss of centre of symmetry in the phenylene rings after doping.

The loss of mechanical integrity, observed in our experiments, upon excessive doping is due to the production of large numbers of positively charged polaron sites, resulting in electronic rearrangment and the rupture of bonds along the polymer chain.

Conductivity

The maximum conductivity attained using this simple doping technique is 1 S cm^{-1}, when measured soon after doping. This value drops to 0.5 S cm^{-1} after exposure to ambient conditions for one week and remains constant thereafter. This reduction in conductivity is attributed to a redistribution of dopant by diffusion to reach a uniform level thoughout the sample rather than a high concentration near the sample surfaces. Gagnon *et al.*[4] have reported a much higher value for PPV doped by continuous exposure to H_2SO_4 vapour by a cryogenic distillation technique. However, these workers did not comment on the long-term stability and conductivity levels of their sample. The work done in this study suggests that a conductivity value of 100 S cm^{-1} will be achieved only by excessive sulfate oxidation resulting in the degradation of the polymer itself.

Conclusion

In this report a simple and reliable technique was developed for doping fully converted, free-standing PPV films of thicknesses up to 110 μm. Precise control of the doping time results in the production of robust films suitable for practical applications. Optimum doping times can be determined by visual monitoring of the outgassing rate of the immersed sample, something not possible in vapour-phase doping techniques. The conductivity of the samples becomes constant after one week owing to the dopant mobility giving a homogeneous distribution of sulfate throughout the polymer. Excessive doping yields higher conductivities but also results in a large drop in the mechanical properties of the PPV. Assignments have been made for previously unassigned peaks in both the IR and submillimetre absorption spectra.

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