Synthesis of a Segmented Conjugated Polymer Chain Giving a Blue-shifted Electroluminescence and Improved Efficiency

Paul L. Burn,[a] Andrew B. Holmes,*[a] Arno Kraft,[a] Donal D. C. Bradley,[b] Adam R. Brown[b] and Richard H. Friend*[b]

[a] University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK
[b] Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

Segmented polymers 4 with randomly arranged sequences of saturated and unsaturated units are produced by the thermal treatment of the methoxy leaving group precursor polymer 2 to poly(p-phenylenevinylene) (PPV); these polymers are used as a light-emitting layer in an electroluminescent polymer diode, and the light output is blue-shifted (relative to PPV) and showed a twofold increase in efficiency.

In recent years, major advances in the understanding of the control of the molecular architecture of electroactive polymers have been made as a result of the contributions of synthetic chemistry.[1–5] We have recently reported the use of poly(p-phenylenevinylene) (PPV) as the light-emitting layer

in an electroluminescent polymer device (ELPD).[6] The emission maximum was at 551 nm, which corresponds to a greenish-yellow light, and the efficiency (photons emitted versus electrons injected) was $1 \times 10^{-2}\%$ in a device configuration of aluminium/polymer/indium–tin oxide. Subse-

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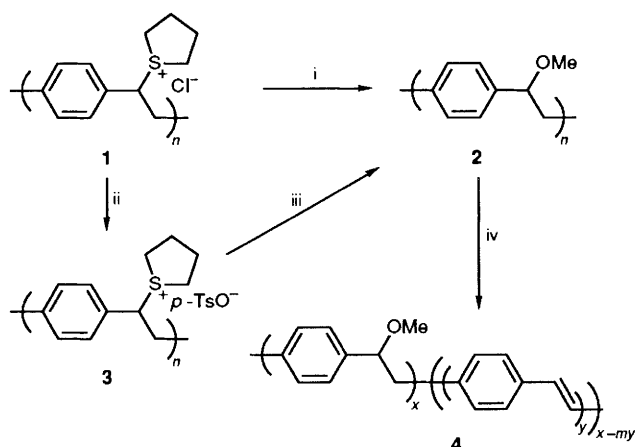
Scheme 1 *Reagents and conditions*: i, MeOH, 52 °C; ii, aqueous NaOTs; iii, MeOH, 52 °C, iv, 300 °C under vacuum
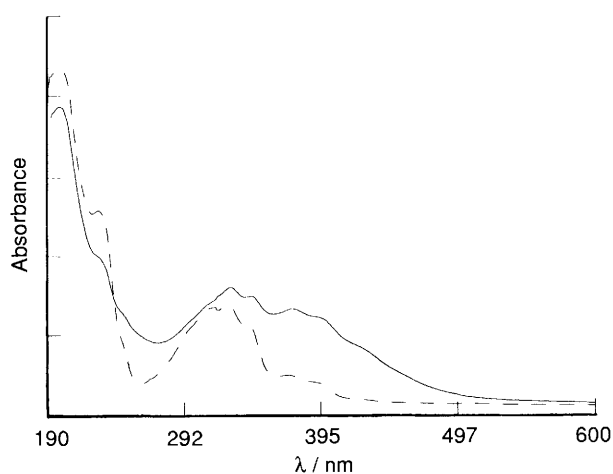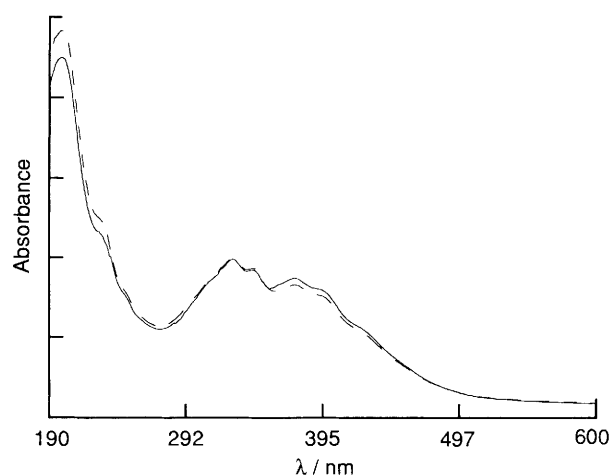

Fig. 2 Absorption spectra of **4** after treatment of **2** for 12 h at 300 °C under vacuum (broken) and after 24 h at 300 °C under vacuum (continuous)

Fig. 1 (*a*) Absorption spectrum of **4** (continuous). (*b*) Absorption spectrum of **2** (broken).
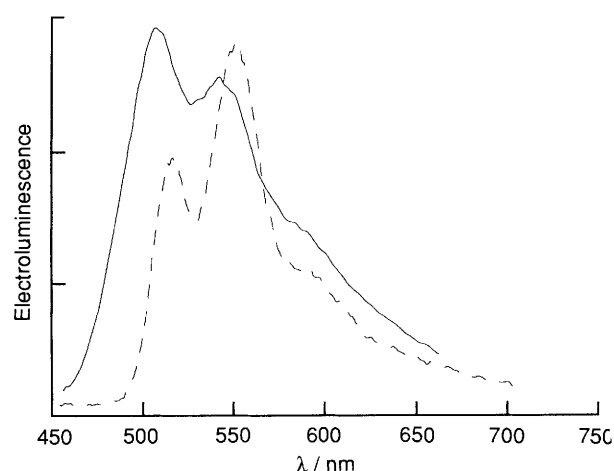

Fig. 3 Electroluminescence spectra of PPV (broken) and **4** (continuous) showing the blue shift

quently, it has been reported that poly[2-(2'-ethylhexyloxy)-5-methoxyphenylenevinylene] can also be used as a polymeric light-emitting layer (emission maximum 591 nm) in an ELPD with a configuration of calcium/polymer/indium–tin oxide.[7]

In this communication, we report the first synthesis of a light-emitting polymer that has conjugated and unconjugated sequences and is derived from a homopolymer precursor. When used as the light-emitting layer in electroluminescent (EL) devices this material exhibits an emission maximum at 508 nm with an efficiency of $2 \times 10^{-2}\%$.

The preparation of light-emitting diodes (LEDs) with blue emission is of particular interest. Some molecular materials emit blue light with high efficiencies in LEDs.[8] However, the stability of the devices is low, as the amorphous molecular films tend to recrystallise, leading to rapid failure of the device. It has previously been reported in photoluminescence (PL) experiments with PPV prepared *via* the sulfonium precursor polymer that light of longer wavelength is emitted, with reduced quantum efficiency, as the conjugation length increases.[9] In view of the fact that PL and EL are thought to have a common origin [*i.e.* annihilation of a polaron exciton, in the first case formed by photoexcitation and, in the second case, by the combination of a negative polaron (radical anion) and a positive polaron (radical cation) on the same chain],[10] it is reasonable to predict that the wavelength and efficiency of the emitted light in an EL experiment may also be determined by the conjugation length. We report here the application of

chemical methods to vary the conjugation length of segments in the conjugated polymer.

We have prepared a precursor polymer **2** to PPV and converted it into partially conjugated material before use in an ELPD. The elimination of tetrahydrothiophene from the sulfonium precursor polymer **1** is difficult to control as the sulfonium group is labile (elimination occurs at room temperature). However, a methoxy leaving group, as in the precursor polymer **2**, offers precisely the right level of control for this operation.[2b] By thermally treating the methoxy leaving group precursor polymer **2** (to PPV) we have been able to produce the polymer **4**, which shows different optical properties from PPV, while retaining the required thermal stability for device work. The methoxy leaving group precursor polymer **2** to PPV can be conveniently prepared by two different methods (Scheme 1). First, exchange of the chloride anion of an aqueous solution of the sulfonium precursor polymer **1** with sodium toluene-*p*-sulfonate (NaOTs) anion produces the polymer **3**, which is soluble in methanol and undergoes substitution with methanol at 52 °C to give **2**.[2b,11] Secondly, direct reaction of a methanol solution of the sulfonium precursor polymer **1**, which had been purified by dialysis against water, resulted in substitution of the sulfonium group by a methoxy group, thus avoiding the separate anion exchange step described above. Films of *ca.* 800 Å thickness for the devices and for UV–VIS absorption characterisation
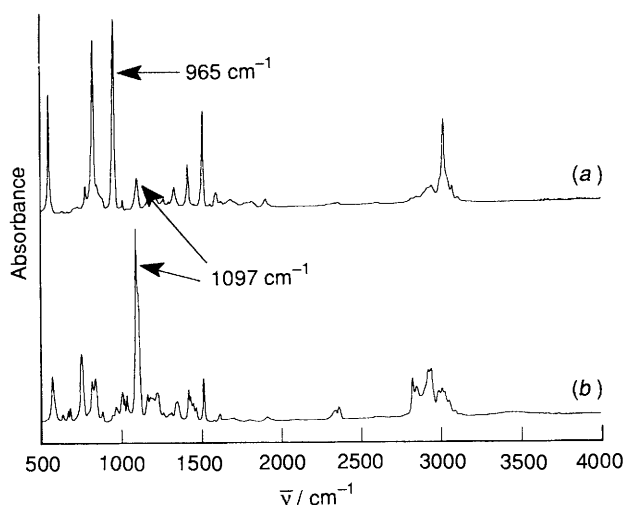
Fig. 4 (a) IR spectrum of 4. (b) IR spectrum of 2.

studies were prepared by spin-coating the precursor polymer 2 from chloroform solution. Films for characterisation by IR spectroscopy were free cast (spin-coated films were too thin for standard FTIR techniques) on poly(tetrafluoroethylene) from the same chloroform solutions. All these films were then heated at 300 °C for 12 h under vacuum [10^{-5} Torr (1 Torr = 133.3 Pa)].

Comparison of the UV–VIS absorption spectra (Fig. 1) of both the precursor polymer 2 and the thermally treated polymer 4 with those recorded with synthetic samples of known conjugation length and defined stereochemistry allows determination of the conjugation lengths.[12] The fine structure seen in the absorption spectrum is due to the various vibrational levels that are associated with short conjugated units in a manner analogous to absorption spectra of conjugated organic molecular materials. The absorption spectrum of the precursor polymer 2 [Fig. 1(b)] shows that it already has a significant degree of conjugation, presumably introduced by thermal elimination during the methanol substitution process. This conjugation is mainly due to stilbene units (λ_{max} ca. 327 nm)[13] and a small number of distyrylbenzene units (λ_{max} ca. 413 nm).[12] On thermal treatment (300 °C for 12 h and 10^{-5} Torr) the polymer 2 is converted into the polymer 4, and the intensity of the absorption at 413 nm (corresponding to distyrylbenzene units) increases [Fig. 1(a)].

Films of the polymer 4 formed by this process were thermally stable, unlike those of the analogous sulfonium precursor polymer 1, which had undergone partial elimination. This was confirmed by treating films of 2 for a much longer period (24 h at 300 °C and 10^{-5} Torr), and comparing their UV–VIS spectra (Fig. 2). It can be seen that the two spectra observed after 12 and 24 h are virtually superimposable.

The EL emission spectrum of PPV and the partially converted polymer are illustrated in Fig. 3.‡ This shows the blue shift in the emission of the partially converted polymer 4 compared to that of PPV. By comparison with the PL

behaviour of model molecular compounds we conclude that the EL emission of 4 corresponds primarily with that expected for distyrylbenzene units within the polymer 4.[12,14]

The IR spectra of the thick free cast sample of the polymer 2 before and after thermal (vacuum) treatment were recorded. The disappearance of the band at 1097 cm^{-1} (methoxy leaving group C–O–C asymmetric stretching frequency) and the concomitant increase in the band at 965 cm^{-1} (vinylic out-of-plane C–H deformation) (Fig. 4) indicate that substantial elimination to form conjugated vinylic groups has occurred under these conditions. The possibility of the easier conversion of thick films of the polymer 2 to fully conjugated PPV owing to the presence of adventitious trapped acid has already been noted by us and by other workers.[2b,15b]

In summary, we have successfully produced a stable thin (800 Å) polymer film that has both conjugated and non-conjugated units derived directly from a homopolymer. This polymer has an emission maximum at 508 nm, and an efficiency of $2 \times 10^{-2}\%$ when used in a device configuration of aluminium/polymer/indium–tin oxide.

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‡ The ELPD was fabricated by spin-coating a precursor polymer 2 film on to an indium—tin oxide substrate. The film was thermally converted into the polymer 4. Aluminium top contacts were deposited to a thickness of ca. 1 000 Å at a pressure of 10^{-6} Torr, see ref. 15(a).