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Communication

Electroluminescence from novel pyrazole-based polymer systems

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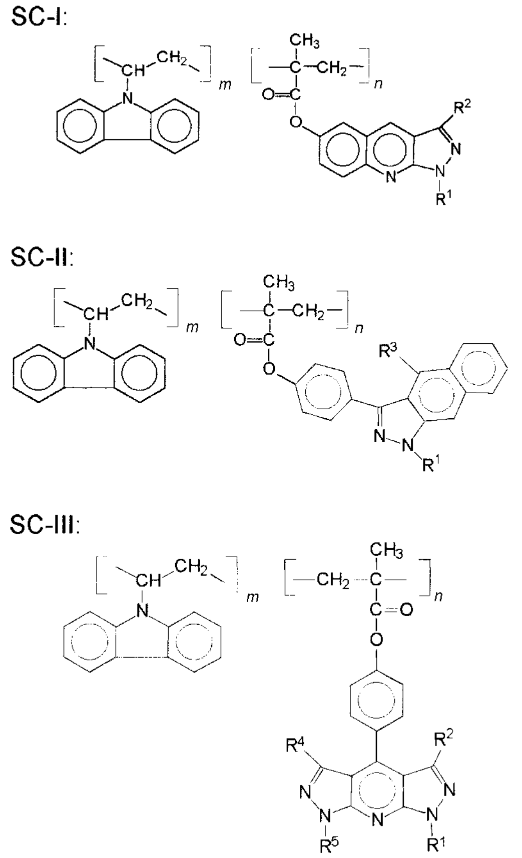
A novel class of electroluminescent pyrazole-based polymers have been synthesised and their electroluminescent properties have been demonstrated. These materials show bright electroluminescence and promising properties for electroluminescent applications.

The success of using organic and/or polymeric materials in electroluminescent devices[1,2] has stimulated considerable interest in the development of new types of organic and polymeric materials and the fabrication of new device structures. Many classes of organic or polymeric materials have been reported to display electroluminescent properties,[3–8] in which the polymers may be conjugated or non-conjugated. The advantages of using organic materials in electroluminescent devices include their high brightness, high efficiency, and potential colour tuning as well as the low cost of fabrication.[9,10] These new technologies have shown a great commercial potential. This subject has attracted much research attention to the development of novel blue light and other wavelength emitting materials and the study of their electroluminescence properties. Many electroluminescent polymers have been reviewed by Kraft *et al.*[11]

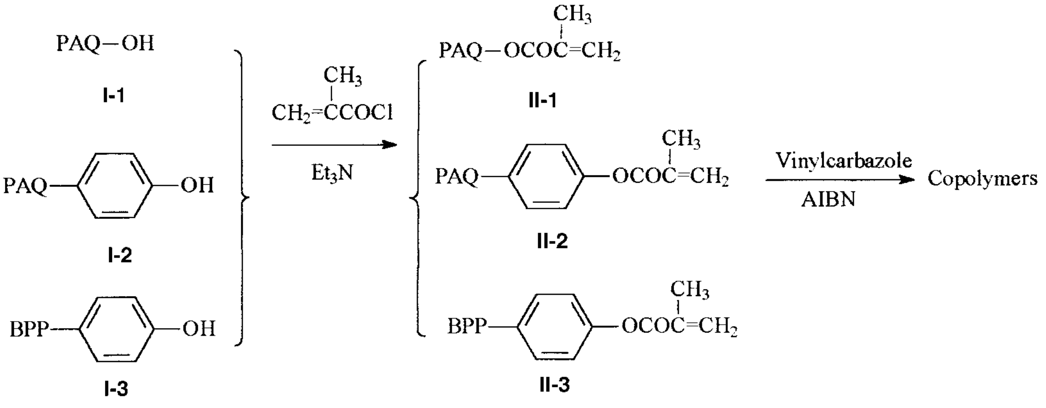
In our previous work, we have reported the use of a novel class of organic pyrazole-based materials, which were physically doped in a polymer matrix, in a blue electroluminescent device[12] and their optical and fluorescent properties.[13] In this communication, we will describe for the first time the preparation of a novel class of pyrazole-based polymers or copolymers, and demonstrate the preliminary electroluminescent properties of these polymers. The pyrazole-based polymers reported here have pyrazole-based chromophores either attached as side groups onto the polymer chains or incorporated directly into the polymer main chains. The pyrazole-based chromophores were selected from a series of novel pyrazoloquinoline (PAQ) and dipyrazolopyridine (BPP) derivatives.

The pyrazole-based side chain polymers were synthesised from the appropriate vinyl and methacrylate monomers, according to Scheme 1.

The preparation of vinyl and methacrylate monomers and



General structure of the side chain copolymers.

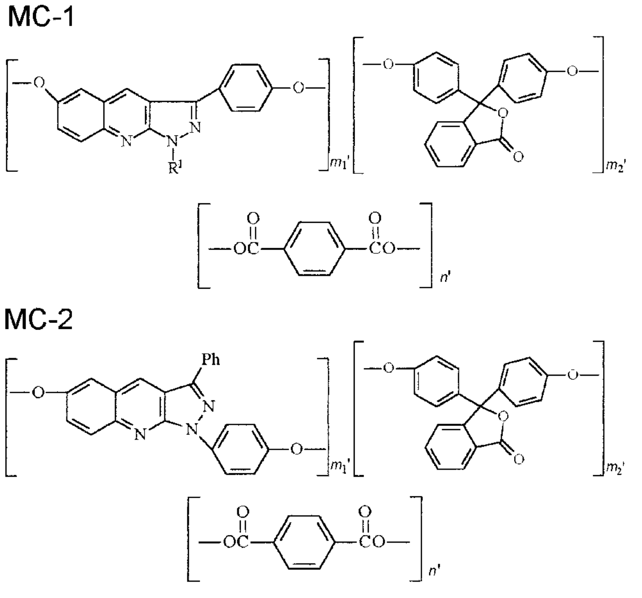


Scheme 1 Reaction schemes for the preparation of the side chain copolymers.

the subsequent polymerisation are described in the Experimental section. A homologous series of the side chain copolymers was prepared. Examples of the copolymers are reported here. These copolymers have the general structures as shown for SC-I, SC-II and SC-III.

The pyrazole-based main chain polymers were synthesised by condensation polymerisation, as shown in Scheme 2.

The preparation of the pyrazole monomers and the consequent polymerisation are also described in the Experimental section. A series of the main chain copolymers was prepared. Two examples are reported here, MC-1 and MC-2, which have the general structures as shown.



General structure of the main chain copolymers.

The copolymers are soluble in many common organic solvents, such as tetrahydrofuran (THF), chloroform, dichloromethane *etc.* They are thermally stable when heated up to 200 °C or higher and are the subject of further investigation. The copolymers have medium average molecular weight (the weight average, $<M_w>$, in the range of $40–160 \times 10^3$). The average molecular weight and the molecular weight distribution of the copolymer were measured by GPC using THF and using polystyrene as a standard. Due to the small proportion of pyrazole groups in the copolymers and the overlapping of peaks, the quantitative determination of the compositions of these polymers was not completed. In particular, the NMR spectra of the side chain copolymers are the same as the spectrum of PVK (polyvinylcarbazole). However, traces of pyrazoloquinoline were observed in NMR spectra for the main chain copolymers and in the IR spectra for the side chain copolymers. The characterisation of the side chain polymers is shown in Table 1.

The electroluminescent properties of these copolymers were examined in a simple device structure, which consisted of ITO as the transparent electrode, a single layer of copolymer, and an aluminium top electrode. The devices constructed in this study have not been optimised. The new polymers have blue light emitting properties and appear to be more stable by comparison with devices fabricated from a dopant–matrix system. The full characterisation of the material properties and optimisation of the device performances are currently being investigated.

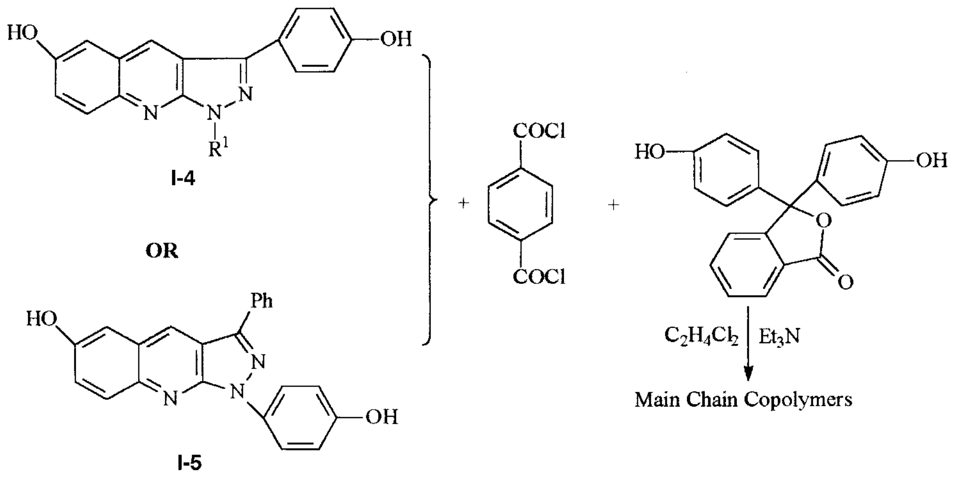
The electroluminescence was observed from a simple device structure comprising only a single polymer layer in between the two electrodes, in a similar fashion to our previous description,[12] which consisted of indium tin oxide (ITO) coated glass as the transparent electrode, a single layer of copolymer, and an aluminium top electrode. This structure was not optimised for device performance and it was only used for comparison of the electroluminescent properties. The devices were also prepared under the same conditions as our previous description,[12] in which the thin polymer layer was spin coated on top of ITO coated glass and the aluminium top electrode was vacuum evaporated on top of the polymer layer. The copolymer layer has a thickness of about 100 nm. The active areas of the device in this study were large with a value of about 15 mm^2. The turn on voltage of the devices was about 8–20 V. Fig. 1 shows the *i*–*v* characteristics of the device and voltage dependence of the light output.

The electroluminescent spectra of these devices lie in the region of the blue or greenish blue spectral range for both the side chain copolymers and displayed a greenish white colour for the main chain copolymers. The electroluminescent spectra appear to be similar to their solid state photoluminescent spectra. The external quantum efficiencies of the current simple structures were estimated at the level of 10^{-3} for side chain copolymers. They are expected to be improved with further development of the device structure. Examples of electroluminescent spectra from two side chain devices and a main chain device are shown in Fig. 2.

Experimental

The preparation of the side chain and main chain copolymers

The preparation of two side chain copolymers and one main chain copolymer are described here. Other polymers were prepared using similar procedures. The side chain polymer was prepared through a free radical polymerisation and the main chain polymer by a condensation polymerisation. Chemicals and solvent are from Merck, Aldrich, or Lancaster



Scheme 2 Reaction schemes for the preparation of the main chain copolymers.

Table 1 The structure and the molecular weight of the copolymers

Structure of the side chain copolymers						Feed stock composition (wt%)			
	R_1	R_2	R_3	R_4	R_5	m	n	$<M_w>$ ($\times 10^4$)	$<M_w>/<M_n>$
PVK-PPQ1	Ph	Ph	H	—^{a}	—^{a}	0.925	0.075	16.2	4.9
PVK-PPQ2	Me	Ph	H	—^{a}	—^{a}	0.95	0.05	6.6	3.7
PVK-PPQ3	Ph	Me	H	—^{a}	—^{a}	0.95	0.05	13.0	3.9
PVK-PPQ4	Ph	—^{a}	Ph	—^{a}	—^{a}	0.95	0.05	4.2	2.9
PVK-PBP1	Ph	Me	—^{a}	Me	Ph	0.95	0.05	6.4	3.9

Structure of the main chain copolymers			Feed stock composition (mole %)			
	R_1	R_2	m_1'	m_2'	$<M_w>$ ($\times 10^4$)	$<M_w>/<M_n>$
MC1	Ph	—^{a}	0.04	0.46	8.1	3.0
MC2	—^{a}	Ph	0.055	0.445	9.0	3.0

^{a}Not valid.

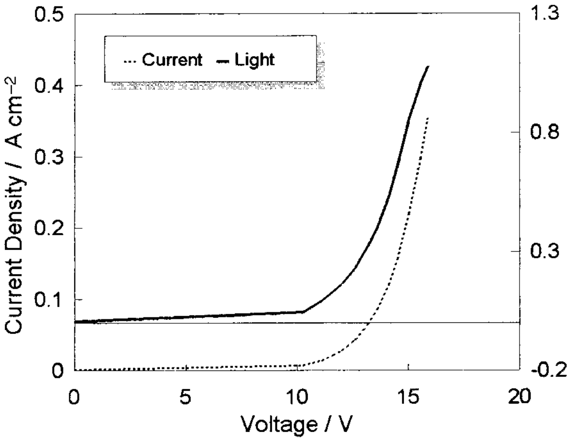


Fig. 1 Current–voltage (dotted line) and light–voltage (solid line) characteristics of an EL device using a side chain copolymer PVK-PPQ2.

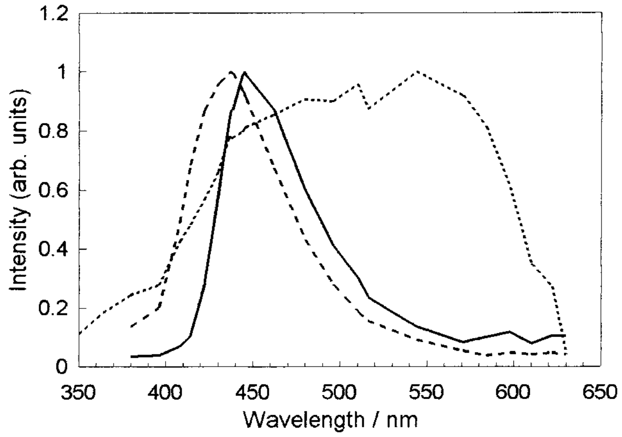


Fig. 2 Electroluminescent spectra from (1) PVK-PPQ2 copolymer (solid line); (2) PVK-PBP1 copolymer (dashed line); and (3) the main chain (MC-1) copolymer (dotted line).

if not specified. Vinylcarbazole (Aldrich) was recrystallized three times before use. The preparation is described as follows.

The preparation of PVK-PPQ2 copolymer: poly(vinylcarbazole-*co*-methacryloyloxypyrazolo[3,4-*b*]quinoline)

(1) The monomer. 6-Methoxy-1-methyl-3-phenylpyrazolo[3,4-*b*]quinoline and 6-hydroxy-1-methyl-3-phenylpyrazolo[3,4-*b*]quinoline were prepared following the procedures described in references 14 and 15 respectively. The monomer, 6-methacryolyloxy-1-methyl-3-phenylpyrazolo[3,4-*b*]quinoline was prepared as follows. 6-Hydroxy-1-methyl-3-phenylpyrazolo[3,4-*b*]quinoline (1.25 g) was suspended in chloroform (15 ml). Triethylamine (0.46 g) and then a solution of methacryolyl chloride (0.47 g) in 15 ml of chloroform were added dropwise to the mixture. The reaction mixture was stirred for 1 hour at room temperature, washed twice with water and dried over Na_2SO_4. A raw product was obtained after evaporation of the solvent. It was then purified by chromatography on silica gel using $CHCl_3$ as a solvent and recrystallised from an acetone–water mixture. Yellow crystals with a melting temperature of 78–80 °C were obtained. (Yield 96%). Calc. for $C_{21}H_{17}N_3O_2$: C 73.45%, H 4.99%, N 12.23%. Found: C 73.36%, H 4.85%, N 12.21%. ^{1}H NMR($CDCl_3$) δ(ppm): 2.15 (s, 3H), 4.48 (s, 3H), 5.35 (s, 1H), 6.45 (s, 1H), 7.50 (t, *J* 7.37 Hz, 1H), 7.59 (t, *J* 7.51 Hz, 2H), 7.98 (s, 1H), 8.01–8.03 (m, 3H), 8.54 (d, *J* 8.99 Hz, 1H), 9.06 (s, 1H). IR(KBr) (cm^{-1}): 1738(C=O), 1635(C=C).

(2) The polymerisation. The PVK-PPQ2 copolymer was prepared as follows: Anhydrous toluene (10 ml) was placed in a 25 ml, three-necked round-bottomed flask, which was fitted with a nitrogen inlet and a reflux condenser. The flask was wrapped with aluminium foil, and a nitrogen flow was continuously passed through for 40 min. *N*-Vinylcarbazole (3.7 g), after recrystallising twice from methanol; 6-methacryloyloxy-1-methyl-3-phenylpyrazolo[3,4-*b*]quinoline (0.3 g); and 10 mg of AIBN were added to the toluene. The mixture was then heated at 75–80 °C for 18 h. The viscous solution was diluted with 10 ml toluene and poured into 200 ml of methanol to precipitate the copolymer. The raw product was a yellow powder. It was further purified by dissolving in chloroform and then by precipitation in methanol two more times to yield the final product. Yield 80% (3.2 g). ^{1}H NMR($CDCl_3$) δ(ppm): 1.0–2.5 (m), 3.0–4.0 (d, broad), 5.0 (s, broad), 6.4 (broad), 7.0 (broad), 7.7 (broad).

The preparation of PVK-PBP1 copolymer: poly(vinylcarbazole-*co*-methacryloyloxydipyrazolo[3,4-*b*:4′,3′-*e*]pyridine)

(1) The monomer. 1,7-Diphenyl-3,5-dimethyl-4-(*p*-methoxyphenyl)dipyrazolo[3,4-*b*:4′,3′-*e*]pyridine, 1,7-diphenyl-3,5-dimethyl-4-(*p*-hydroxyphenyl)dipyrazolopyridine were prepared by following reference 16. The monomer, 1,7-diphenyl-3,5-dimethyl-6-(*p*-methacryloyloxyphenyl)dipyrazolopyridine was prepared using similar procedures to those described above. Pale yellow crystals with a melting temperature of 207–208 °C were obtained. Yield 85%. Calc. for $C_{31}H_{25}N_5O_2$: C 74.27%, H 5.38%, N 13.96%. Found: C 74.12%, H 5.35, N 13.80%. ^1H NMR(CDCl$_3$) δ(ppm): 2.05 (s, 3H), 2.12 (s, 6H), 5.75 (s, 1H), 6.35 (s,1H), 7.07 (d, *J* 6.6 Hz, 2H), 7.25 (m, 2H), 7.36 (d, *J* 6.6 Hz, 2H), 7.50 (m, 4H), 8.35 (d, *J* 8.2 Hz, 4H). IR(KBr) (cm^{-1}): 1735(C=O), 1634(C=C).

(2) The polymerisation. The PVK-PBP1 copolymer was prepared using a similar procedure to the description of PVK-PPQ2 above. ^1H NMR(CDCl$_3$) δ(ppm): 1.0–2.5 (m), 3.0–4.0 (d, broad), 5.0 (s, broad), 6.4 (broad), 7.0 (broad), 7.7 (broad).

The preparation of MC-1 copolymer

(1) The monomer. 6-Methoxy-1-phenyl-3-(*p*-methoxyphenyl)pyrazolo[3,4-*b*]quinoline (mp 159–160 °C) was prepared according to reference 14. The monomer, 6-hydroxy-1-phenyl-3-(*p*-hydroxyphenyl)pyrazolo[3,4-*b*]quinoline was prepared according to reference 15. Yellow crystals with a melting temperature of 250–252 °C were obtained. Yield 90%. Calc. for $C_{22}H_{15}N_3O_2$: C 74.91%, H 4.25%, N 11.82%. Found: C 74.85%, H 4.01%, N 11.76%. ^1H NMR(d_6-DMSO) δ(ppm): 7.05 (d, *J* 8.6 Hz, 2H), 7.35 (t, *J* 7.34 Hz, 1H), 7.4–7.7 (m, 5H), 8.00 (d+s, 2H), 8.12 (d, *J* 8.6 Hz, 2H), 8.55 (d, *J* 7.79 Hz, 2H), 9.2 (s, 1H). IR(KBr) (cm^{-1}): 3200 (broad, OH).

(2) The polymerisation. Phenolphthalein (3 g) and 6-hydroxy-1-phenyl-3-(*p*-hydroxyphenyl)pyrazolo[3,4-*b*]quinoline (0.208 g) were suspended in 25 ml of 1,2-dichloroethane in a three-necked, round bottomed flask. Distilled triethylamine (2.8 ml, 0.02 mol) was added to the mixture with magnetic stirring. Terephthaloyl chloride (2.03 g) in 25 ml of 1,2-dichloroethane was placed in an addition funnel. After stirring the mixture at medium speed for 10 min, the addition of chloride solution began at a rate that produced the total addition in about 40 min. The mixture was then allowed to stand at room temperature for 1 h. It was then diluted with 50 ml of solvent and poured into 250 ml of hexane in a beaker. The resultant polymer was collected on a medium porosity sintered-glass funnel and washed repeatedly with distilled water by stirring vigorously in the blender and filtering. The raw polymer was a yellow powder and was purified by dissolving in THF and precipitation into methanol. Yield 80.6% (4.22 g). ^1H NMR(CDCl$_3$) δ(ppm): 7.25 (d, *J* 8.68 Hz, 4H, *p*-phenylene of phenolphthalein), 7.48 (d, *J* 8.7 Hz, 4H, *p*-phenylene of phenolphthalein), 7.60 (m, 2H, *o*-phenylene of phenolphthalein), 7.65 (t, *J* 7.3 Hz, 1H, *o*-phenylene of phenolphthalein), 7.98 (d, *J* 7.42 Hz, 1H, *o*-phenylene of phenolphthalein), 8.3 (s, 4H, *p*-phenylene of diacid), 8.6 (d, 2H, weak, pyrazoloquinoline group), 8.98 (s, 1H, weak, pyrazoloquinoline group).

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