Synthesis and Fluorescence of Pyridine-*N*-alkyl carbazole Copolymer Prepared by Oxidative-coupling Reaction

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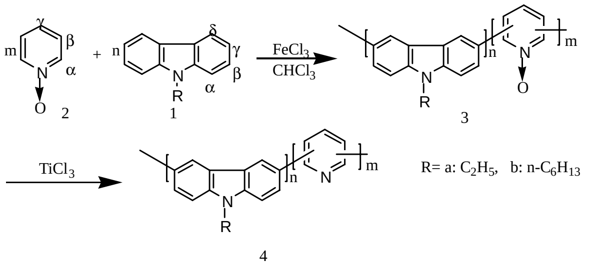
A new kind of copolymers incorporated pyridine and *N*-alkyl carbazole alternatively into main chain has been prepared by oxidative-coupling copolymerization. The polymers are thermostable, highly soluble, and processable. The fluorescence spectra of the polymers display blue light emitting properties.

Over the past decade, polymer light emitting diodes (LEDs) have risen from being a remarkable scientific curiosity to a new core technology in the rapidly expanding display market.[1] Imbalances of minority and majority carrier injection barrier heights and mobilities have been identified as key problems limiting the device performance. Pyridine-based polymers have high electron affinity as compared to phenylene-based analogs, are more resistant to oxidation, and show better electron transport properties. The high electron affinity of pyridine-based polymers enables the use of relatively stable metals such as Al or Au or doped polyaniline as electrodes. Pyridine-containing conjugated polymers have been shown to be promising candidates for light-emitting device,[2] specially used in symmetrically configured alternating current light emitting devices.[3–6] Polypyridine has been successfully used as electron transporting layer and gives much improved performance of LED.[7] The pyridine-containing polymers are highly luminescent.[8] Pyridine-based polymers are sensitive to oxygen and humidity, the optical oxygen sensors used iridium(III) polypyridine complexes as active lays have been investigated.[9]

In this communication, we present a facile method of preparing the copolymers incorporated moieties of *N*-alkyl carbazole and pyridine as main chain by oxidative-coupling copolymerization. As pyridine is of high electron affinity (3.5 ev) and *N*-alkyl carbazole was usually used as hole-transporting material, incorporating the two kinds of fluorophors into polymer main chain may offer an equal injection of both electrons and holes. Whereas pyridine cannot undergo Scholl and related reaction, i.e. oxidative coupling reaction, a facile method of preparing conjugated aromatic polymers, because it's insufficient in electrons on the aromatic rings. In this work, pyridine *N*-oxide was polymerized with *N*-alkyl carbazole easily, then pyridine moieties were incorporated into polymer backbone after reduction. This is the first example of pyridine-based polymer prepared by oxidative-coupling polymerization to our knowledge. The Synthetic route is shown in Scheme 1.

The copolymers of *N*-alkyl carbazole and pyridine *N*-oxide were synthesized in good yield from readily available starting materials by oxidative-coupling copolymerization, showing in Scheme 1. The copolymer **3** was prepared by oxidative-coupling copolymerization of compound **1** (1 mmol) and **2** (2 mmol) in the presence of anhydrous $FeCl_3$, reacting in dry $CHCl_3$ at room temperature under Argon atmosphere for 36 h. Then the reactant was poured into ethanol, the precipitated polymer was collected by filtration and purified by extracting in Soxhlet extractor. The polymer **4** was synthesized by reducing copolymer **3** using 20% aqueous $TiCl_3$ in THF at 0 °C. Ti was removed by washing with NaOH, and the solvent was removed by distillation. The residue was washed with ethanol and collected. The elemental analysis of polymer **4b** (%): C 85.048, H 6.544, N 8.309.



Scheme 1.

The ^1H NMR spectrum of polymer **4a** in $CDCl_3$ displays very sharp and clear signals. The signals positioned at 1.49 ppm(3H) and 4.44 ppm(2H) were attributed to the CH_3 and CH_2 respectively. There are two signals at 7.23 ppm(2H) and 7.83 ppm(2H) assigned to the hydrogen of the α-position and δ-position of the *N*-ethyl carbazole. The signals positioned at 8.21 ppm(1H) and 8.42 ppm(1H) are attributed to the hydrogen of the α-position and γ-position of the pyridine, respectively. The signal at 7.5 ppm(m, 3H) is assigned to the β hydrogen of carbazole and the β hydrogen of pyridine moieties. The results revealed the linking model of the aromatic ring on the copolymer main chains. The areas of the ^1H NMR bands show the moiety ratio of *N*-ethyl carbazole to pyridine is 1 : 1. Considering the strong copolymerizing tendency of the two monomers, we deduce that the copolymers may consist of alternating moieties of carbazole and pyridine.

The FT-IR spectra of polymer **3a** and **4a** show difference around 1600 cm^{-1} and 1155 cm^{-1} owing to the existing of N–O band or not. Polymer **3a** displays a weak band at 850 cm^{-1} corresponding to the plane bending mode of the N–O band, which disappeared in polymer **4a**. So do the polymer **3b** and **4b**.

The UV-Vis spectra of polymer **4a** and **4b** in THF solution exhibit two absorption bands around 250 nm and 300 nm, and show a little difference due to the different alkyl side chain. In addition, the UV-Vis spectra of the copolymers in thin film were recorded. The absorption spectra in solid state display a strong and sharp band at 312 nm and a very small and smooth band at 214 nm. Upon comparing the absorption spectra in solution, the band at 260 nm is disappear and the second band at 312 nm shows a little red shift and narrower.

The wide-angle X-ray scatting curves of the polymer **4a** and **4b** reveal that the polymers are slightly crystalline. Polymer **4b** has lower crystallinity than polymer **4a** owing to the long alkyl side chain. Completely amorphous copolymers may be obtained by substituting the straight alkyl to branched alkyls.

The solubility of the copolymers was measured. The solubility of copolymer **3b** in chloroform, THF, toluene, and DMF was 3.62, 4.59, 2.58, and 2.50 g/100 mL, respectively. The solubility of copolymer **3a** and **4a** was all in excess of 2 g/100 mL. The solubility results reveal that the copolymers have excellent solubility in common organic solvents.

The good thermal stability of the copolymers was ascertained by thermogravimetric analysis (TGA). The weight loss of polymer **3a** started at 302 °C and got 46.64% at 432.6 °C, while polymer **4a** started at 332.1 °C and got 79.77% at 480.5 °C. The decomposition temperature (Td) of polymer **4a** is higher than polymer **3a** owing to the absence of oxygen atoms.

The fluorescence spectra of the copolymers in THF solution show they are blue light emitting materials (Figure 1). Polymer **4b** displays longer emission wavelength with the maximum at 425 nm, while polymer **4a** with the maximum at 412 nm. The emission bands are sharp and narrow, and display red shift compared to carbazole. Figure 2 depicts the fluorescence spectra of the copolymers in solid state film. Polymer **4a** displays the maximum at 447 nm and polymer **4b** displays a rather wide band with the maximum at 449 nm. The copolymer **4a** and **4b** are blue light emitting materials. The fluorescence spectra of polymer **3a** and **3b** in solid state film were also measured, which also display the polymers are blue light emitting materials.

The fluorescence quantum yield of the copolymers in THF solution were measured relative to quinine sulphate ($\Phi = 0.546$). The quantum yield of polymer **3a** is 0.12, while polymer **4a** is 0.10 respectively.

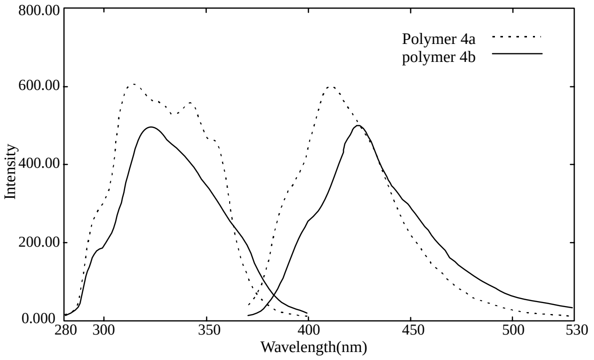


Figure 1. The fluorescence spectra of polymer **4a** and **4b** in THF solution (Slit width: EX: 3 nm, EM: 3 nm; EX Wavelength: Polymer **4a**: 314 nm, **4b**: 320 nm).

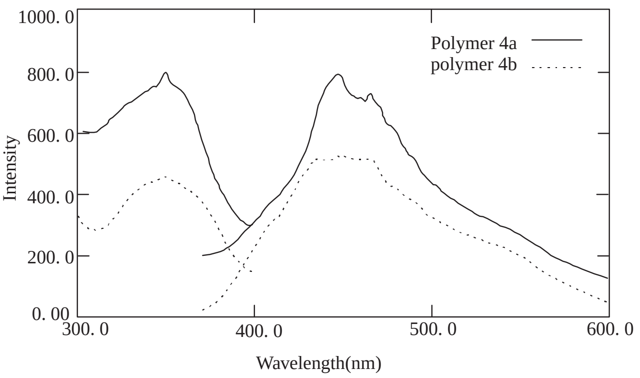


Figure 2. The fluorescence speatra of polymer **4a** and **4b** in solid state film (Slit width: EX: 3 nm, EM: 3 nm; EX Wavelength: Polymer **4a**: 349 nm; **4b**: 351 nm).

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