The Copolymers of N-alkyl Carbazole and Stilbene Prepared by Oxidative-coupling reaction

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Abstract: A kind of novel electroluminescence polymer has been prepared by oxidative-coupling polymerization of N-alkyl carbazole and trans-stilbene. The structure of the copolymers was characterized by elemental analysis, UV-vis and FTIR spectra. The copolymers have good solubility in chloroform and acetone. Fluorescence spectra showed that these polymers are blue-light emitting materials.

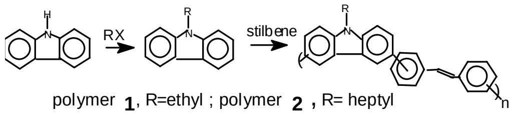
Keywords: Oxidative-coupling polymerization, carbazole-stilbene copolymer, blue light emitting.

Electroluminescence (EL) polymers have attracted extensive investigation in the world. Poly (*p*-phenylene vinylene) (PPV) and its derivatives are well studied due to their applications as active components for light-emitting diode (LED)[1] . Various synthetic methods, such as Witting reaction [2], Heck reaction [3], and Wessling reaction [4] were developed to prepare PPVs. But there are still some drawbacks to need to be improved, such as complicated synthetic routes, low yields, gelation, luminescence quench defects in the individual reaction and material. Meanwhile, many other EL polymers are investigated. Poly (*p*-phenylene) (PPP) and its derivatives also show electro-luminescence properties. Scholl reaction, *i.e.* oxidative-coupling reaction, was improved to prepare soluble PPPs by Mitsuru Ueda *et al* [5]. Qi and Wang *et al* have prepared soluble PPP derivatives and showed they are blue to green light–emitting luminescence polymers [6]. In this communication, we present a facile method to prepare EL polymers, which consist of conjugated aromatic ring and double carbon-carbon bond as main chain, forming analogs of PPV copolymers. The synthetic route is shown in **Scheme 1** and the preparation method, characterization, solubility, as well as fluorescence spectra of the copolymers were investigated.

The co-polymerization was conducted at room temperature, with FeCl3 as catalyst, CHCl3 as solvent. The yields, properties of the copolymers vary with the change of ratio of the monomers and the amount of catalysts used. The results show that the two monomers, stilbene and N-alkylcarbazole are good co-monomer pairs. The former can not be self-polymerized, while the yield of the product was poor for the later. But the co-polymerization of the two monomers generally gets yields above 50%; some could reach 80%. The inherent viscosity measured at 30 oC in acetone is from 0.2 to 0.6 dL.g-1.

FT-TR spectrum exhibits C-H stretch vibration of unsaturated –C=C- bands at 1600 and 1500 cm^{-1}, saturated C-H at 1450 and 1350 cm^{-1} and N-C at 1230 and 1350 cm^{-1}. However, the spectrum does not show multi peaks of mono-substituted benzene ring in region 1700 – 1920 cm^{-1}. A weak, sharp band at 950 cm^{-1}, corresponding to the out-of–plane bending vibration mode of the *trans*-vinylene groups, appeared for both copolymers.

Scheme 1



polymer 1, R=ethyl ; polymer 2, R= heptyl

UV-Vis spectrum shows absorbent maxima at 248, 300 and 350 nm for polymer 1 and 250,302 and 350 nm for polymer 2 respectively. Obviously, the uv spectrum of the two copolymers is very similar but the uv absorption has a slight red shift due to the longer side alkyl chains. For the monomers there only is one band at 300 nm for stilbene and three bands at 240,270 and 300 nm for N-heptyl carbazole. The absorbent bands at 350 nm came from the longer conjugated length and lower transition energy because of polymerization.

The solubility of the copolymers is shown in **Table 1**, which illustrates that the longer side chains led to better solubility in chloroform and toluene but poor solubility in ethanol and acetone.

Table 1 Solubility of the copolymers (g/100mL)

	toluene	ethanol	chloroform	acetone	DMF
polymer 1	0.78	0.34	2.23	1.97	2.70
polymer 2	1.13	0.16	3.70	1.60	4.37

The fluorescence spectra of the polymers with different feed ratio of co-polymerization show that the maximum emitting wavelengths were all in short length, indicating the similar conjugated length and large band gap.

The Photoluminescence emitting wavelength in chloroform and toluene is 448,451 nm for polymer 1; and 467,470 nm for polymer 2 respectively. The red shift of emitting wavelength due to longer side chain is obvious.

In the fluorescence spectrum of solid state film of polymer 2 spin coated on SiO2 glass, the maximum emitting wavelength was at 470 nm. The cut–off emitting wavelength was within 500 nm, indicating a narrow genuine blue emitting.

The quantum yield of the copolymers in different solvents showed that the PL efficiency in chloroform is very poor but quite high in toluene. Especially a very high yield of 0.86 relative to Rhodamine B was obtained from polymer 1. It may be owe to its short side chain and rigid polymer backbone.

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