



Synthesis and Characterization of New Conjugated Electroluminescent Polyquinoline Derivative

V. M. RAUT, PRATIMA V. DAMRE

Department of Chemistry, Government Vidarbha Institute of Science and Humanities, Amravati

Abstract

The synthesis of new conjugated electroluminescent polyquinoline derivative Poly (2,2-(p-phenyl)-6,6-bis(4-phenylquinoline) [PPPQ], which are soluble in organic solvents and its incorporation in light - emitting diodes as the emissive layer are reported. These electroluminescent devices, containing 1, 1- bis (di-4-tolylaminophenyl) cyclohexane (TAPC) dispersed in polystyrene as the hole-transport layer, emit bright yellow light (λ_{max} = 554 nm) with quantum efficiency of 0.26% photons/electron and a luminance of 280 cd/m² at a current density of 100 mA/cm². Electroluminescence of moderate brightness was achieved with blue-green, green, yellow, orange, and deep red colors depending on the arylene linkage of the copolymer. The thermal, electrochemical, photophysical, and electroluminescent properties of new polyquinolines varied with the arylene linkage, including p-phenylene, 4, 4'-biphenylene, 5, 5'-bithienylene. These results also demonstrate that the new polyquinoline is a good electron transport electroluminescent material. Large enhancement in electroluminescence efficiency and brightness of light-emitting diodes fabricated from binary blends of conjugated polyquinolines was observed compared to devices made from the homopolymers. The polymers have thermal properties with glass transitions temperature of 161-339°C. The electrical properties of the diodes and electric field modulated photoluminescence spectroscopy results confirmed that the enhancement of electroluminescence in the blends originated from spatial confinement of excitons which leads to increased exciton stability and electron hole recombination efficiency. Voltage tunable and composition –tunable multicolor electroluminescence was observed in the polymer blend devices. The observed composition dependent new emission bands and enhanced fluorescence lifetimes in the blends were suggested to originate from exciplex formation and molecular miscibility between the blend components. These results demonstrate new phenomena in the electroluminescence and photophysics of multicomponent conjugated polymers.

Introduction

Poly(quinoline)s were first reported in the 1970s by Stille and coworkers[8–10] in response to increasing demands for thermally stable and mechanically strong polymers. Typically, poly(quinoline)s have high thermal stability with glass-transition temperatures (T_g) above 200°C and onset thermal decomposition temperatures (T_{dec}) above 400°C, high oxidative stability, high electrical conductivity, and outstanding mechanical and optically clear film forming properties.[8 – 10] These characteristics make poly(quinoline)s interesting materials for electronic and/or electro-optical devices. Over the last decade, Jenekhe, Jen, and others have investigated extensively the optical and electronic properties of poly(-quinoline)s including photo-conductivity,[11,12] optical nonlinearity,[3 – 2] photoluminescence,[1–

8] electroluminescence, [2–7] charge-transfer,[38] and electron transporting properties[7–4] for their potential applications in OLEDs,[2–3] organic photovoltaic devices,[12] and selective chemosensors (proton and metal ions).[4 – 5]

Experimental Section

General Procedure for Polymerization

1 equiv of the diacetyl monomer, 1 equiv of 3,3-dinonanoylbenzidine, 6.0 g of diphenyl phosphate, and 3 g of *m*-cresol were added to a cylindrical reaction vessel. The reactor was purged with argon for 20 min. The mixture was mechanically stirred under static argon as the temperature was gradually raised to 140 °C over a period of 12 h. The polymerization mixture was stirred at this temperature for 72 h and then precipitated into 10% triethylamine/ethanol. The precipitate was collected by vacuum filtration and extracted on a Soxhlet apparatus for 72 h with 20% triethylamine/ethanol. The polymer was dissolved in CHCl₃ and precipitated into ethanol, collected by vacuum filtration, and dried at 60 °C in a vacuum for 24 h.

Results and Discussion

Conjugated rigid-rod polyquinolines have excellent thermal stability and high mechanical strength [1, 2]. These *n*-type semiconducting polymers [3] have interesting electronic [2 b], photoconductive [4], and nonlinear optical [5] properties. Recently, some polyquinolines were used as both the electron-transport layer and an emission layer in polyquinoline/poly(*p*-phenylenevinylene) heterojunction light-emitting diodes (LEDs) [6]. The attractive combination of excellent thermal, mechanical, and optoelectronic properties of the conjugated polyquinolines has motivated our synthesis of new derivatives for electroluminescent device applications.

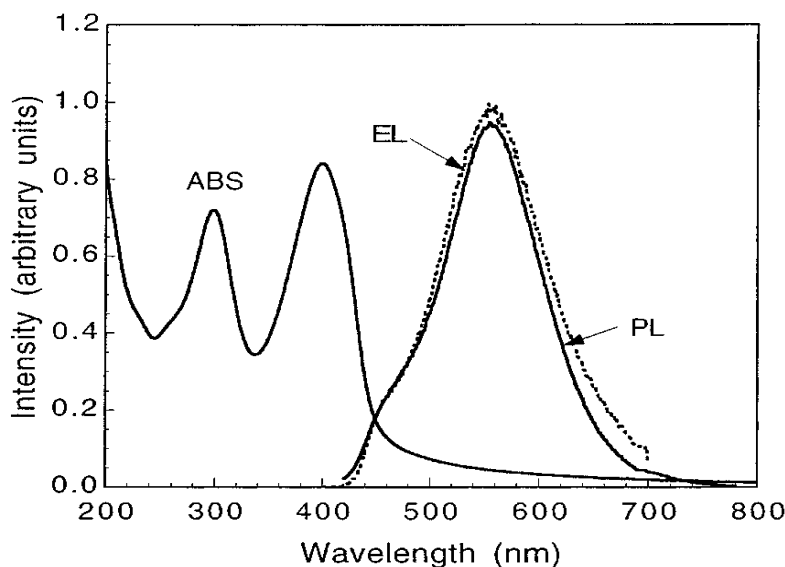


Fig. 1. Optical absorption, photoluminescence (excited at 399 nm) and electroluminescence (8 V) spectra of Bu-PPQ thin films.

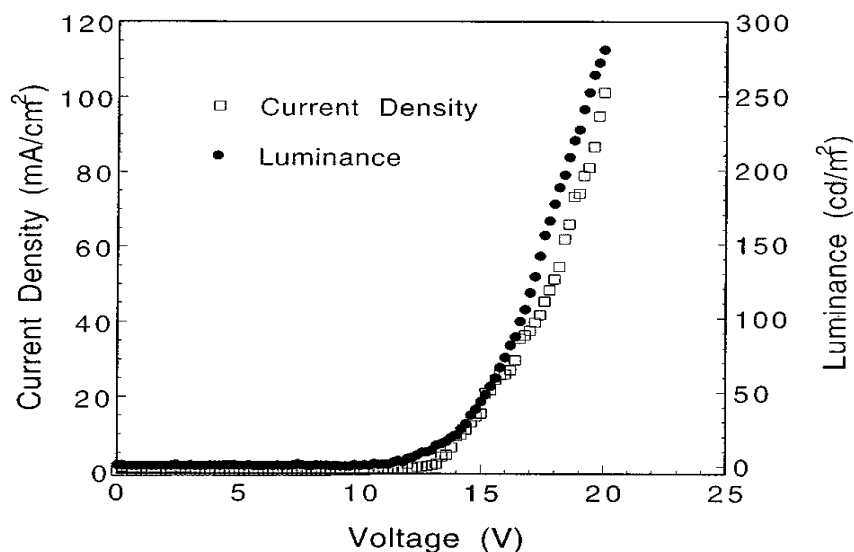


Fig. 2. Current –voltage and voltage –luminance characteristics of the electroluminescent device ITO/TAPC: PS/Bu-PPQ/Al.

Figure 1 shows the optical absorption, steady-state photoluminescence (PL), and electroluminescence (EL)spectra of Bu-PPQ. This polymer shows a strong absorption with a p-p* transition at 399 nm. The optical absorption edge bandgap is 2.78 eV (446 nm). Bu-PPQ thus has absorption peak and bandgap identical to those of PPPQ, which were previously reported [2 b]. This suggests that the ground state electronic structure of PPPQ does not change with the **Introduction** of the *tert*-butyl groups in Bu-PPQ. Also shown in Fig. 1 is the steady-state PL spectrum of Bu-PPQ thin film excited at 399 nm. The PL spectrum shows an emission peak at 554 nm. The yellow emission corresponds to a large Stokes shift of 155 nm (0.87 eV), which is characteristic of excimer emission of the solid film of many conjugated polymers [10]. The PL emission of Bu-PPQ showed a 20 nm blue shift compared to PPPQ(1), which has a PL emission peak at 574 nm. This indicates that the **Introduction** of the *tert*-butyl groups in Bu-PPQ modifies the excited state electronic structure of the parent polymer PPPQ. That chain packing of conjugated polymers should significantly influence their excited state properties more than their ground state electronic properties has been predicted [10].

The EL spectrum of the device ITO/TAPC:PS/Bu-PPQ/Al at a bias voltage of 8 V is shown in Fig. 1. The EL emission peak is at 554 nm. It can be seen that the EL spectrum is identical to the PL spectrum, indicating that the EL emission is from the Bu-PPQ layer only and that the electroluminescence and photoluminescence of Bu-PPQ originate from the same excited states.

Figure 2 shows the current–voltage and luminance–voltage characteristics of the EL device. The turn-on voltage of the ITO/TAPC:PS(50 nm)/Bu-PPQ(50 nm)/Al device was 8 V. It showed bright yellow color emission, which can be clearly seen under room light. The luminance of the device was 280 cd/m² at a



current density of 100 mA/cm². The EL efficiency of the device was estimated to be 0.26% photons/electron. These values were about six times higher than those of PPPQ (1) under the same conditions. For example, the device ITO/TAPC:PS(50 nm)/PPPQ(50 nm)/Al had a luminance of 45 cd/m² at the same current density of 100 mA/cm². The large enhancement of electroluminescence in the *tert*butyl- substituted Bu-PPQ (2) compared to the parent polyquinoline 1 can be understood in terms of reduced concentration quenching of luminescence facilitated by increased interchain packing distances [10, 11]. Observation of efficient electroluminescence in the ITO/TAPC:PS/Bu-PPQ/Al devices implies that the emissive Bu-PPQ layer also exhibits good electron transport (*n*-type) characteristics, in accord with prior findings for other polyquinolines [3, 6].

In summary, a new electroluminescent, yellow lightemitting *n*-type conjugated polymer, Bu-PPQ (2), has been synthesized and characterized. Although the substitution of *tert*-butyl groups in Bu-PPQ did not change the optical absorption properties of the parent PPPQ, a more efficient electroluminescence with an EL quantum efficiency of 0.26% photons/electron and a luminance of 280 cd/m² was observed. The brightness and efficiency of light-emitting diodes from Bu-PPQ (2) were six times higher than those of PPPQ (1) with no *tert*-butyl substitution. These results also demonstrate that thin films of the new polyquinoline exhibit good electron transport (*n*-type) characteristics in EL devices.

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