

# A Study of Light-Emitting Diodes Constructed with Copolymers Having Cyclohexyl Thiophene and Hexyl Thiophene Units

VIBHA SAXENA, V. S. SHIRODKAR

Solid State Electronics Lab, Department of Physics, The Institute of Science, Mumbai 400 032, India

Received 12 July 1999; accepted 8 October 1999

**ABSTRACT:** We report visible light emission from a diode made from copolymers of 3-alkylthiophenes. These chemically synthesized copolymers exhibit improved electroluminescence and quantum efficiencies compared to poly(3-cyclohexylthiophene). Good solubility of copolymers allows the fabrication of the light emitting diodes by spin-cast polymer film. The devices emit greenish-blue light in wavelength region of 550–580 nm, which is easily visible in poorly lighted room. The quantum efficiencies are in the range of 0.002 to 0.01% (photons per electron) at room temperature; which are significantly higher than corresponding values for poly(3-cyclohexylthiophene) based light emitting diodes. The charge carrier mobility in the device is found to be  $5.6 \times 10^{-4} \text{ cm}^2/\text{Vs}$ . © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1051–1055, 2000

**Key words:** polymer; poly(3-alkylthiophene); electroluminescence; light-emitting diode

## INTRODUCTION

The electroluminescence in conjugated polymers is a rapidly expanding field<sup>1,2</sup>, and there is a strong possibility for the commercial utilization of these materials; especially, in the area of display applications. Most common electroluminescent conjugated polymers are poly(*p*-phenylenevinylene), polythiophene, and poly(*para*-phenylene).<sup>3–5</sup> High efficiency, easy processibility, light emission throughout the visible spectrum, and low operating direct current (dc) voltage make polymer light-emitting diodes (LEDs) very attractive for large-area display devices.<sup>6,7</sup> One of the major advantages of using semiconducting polymers, as compared to the inorganic materials, is the control of color in these materials. Visible light emission in entire spectrum range has been reported in these devices.<sup>8–11</sup> This is in contrast

to the inorganic LEDs, in which high-quality emission is restricted from red up to the yellow region, and blue LEDs could not be produced to a satisfactory quality standard to-date. There are different strategies to control the color of conjugated polymers, the band gap of the polymer can be varied by adding different side chains to the main chain or by introducing different leaving groups in the conjugated chain. These substituents may affect the electronic structure, either by denating and/or withdrawing electrons or by introducing steric hindrance to the main chain and, thus, varying the effective conjugation length of the main chain.

Among various polymers, polythiophene is of considerable interest for device fabrication because of its environmental stability, nonlinear optical properties, and electrical conductivity. However, the major drawback of this polymer is insolubility in common organic solvents. The substitution of alkyl chains to thiophene ring at a 3-position not only enhances the solubility of the polymer in organic solvents but also changes its

---

Correspondence to: V. S. Shirodkar.

*Journal of Applied Polymer Science*, Vol. 77, 1051–1055 (2000)  
© 2000 John Wiley & Sons, Inc.

**Table I Feed Ratio of Monomers Used to Synthesize Copolymers**

Polymer	3- <i>n</i> -Hexylthiophene (mL)	3-Cyclohexylthiophene (mL)
Copolymer I	0.1	0.9
Copolymer II	0.4	0.6
Copolymer III	0.5	0.5
Copolymer IV	0.9	0.1

electronic properties and, therefore, make them useful from a practical point of view.<sup>12</sup> Enhanced steric hinderance from side groups leads to the decrease in planarity of the main chain and increasing the band gap, making them good candidates for LEDs. Poly(3-alkylthiophene)s are among important conducting polymers because poly(3-alkylthiophene) was the first soluble and even fusible conducting polymer with novel characteristics such as thermochromism<sup>13</sup> and solvatochromism.<sup>14</sup>

In the present article, we report the characteristics of LEDs constructed with copolymers of 3-*n*-hexylthiophene and 3-cyclohexylthiophene. The copolymers are synthesized with the purpose of enhancing the properties of the individual polymers in solubility, regularity, and functionality. Our purpose is to incorporate the individual properties of the ingredient polymers into one polymer. The device fabrication is simple because of direct casting of the copolymer from the chloroform solution.

## EXPERIMENTAL

Copolymers having 3-cyclohexylthiophene and 3-*n*-hexylthiophene units were synthesized by the chemical method, described elsewhere.<sup>15</sup> The monomers of different concentrations were taken to produce different copolymers. Table I gives the composition taken for polymerization of different copolymers. The monomers with various concentrations were polymerized with ferric chloride (FeCl<sub>3</sub>) catalyst in chloroform solution under an inert atmosphere.

The solution of anhydrous FeCl<sub>3</sub> (1.23M) in dry chloroform was taken in a round-bottomed flask fitted with a condenser and a dropping funnel. A binary mixture of 3-*n*-hexylthiophene and 3-cyclohexylthiophene in chloroform solution (20 mL) was taken in the funnel, and the contents of the flask were kept in a thermostatic bath, maintained at 0°C. Oxygen-free nitrogen was bubbled

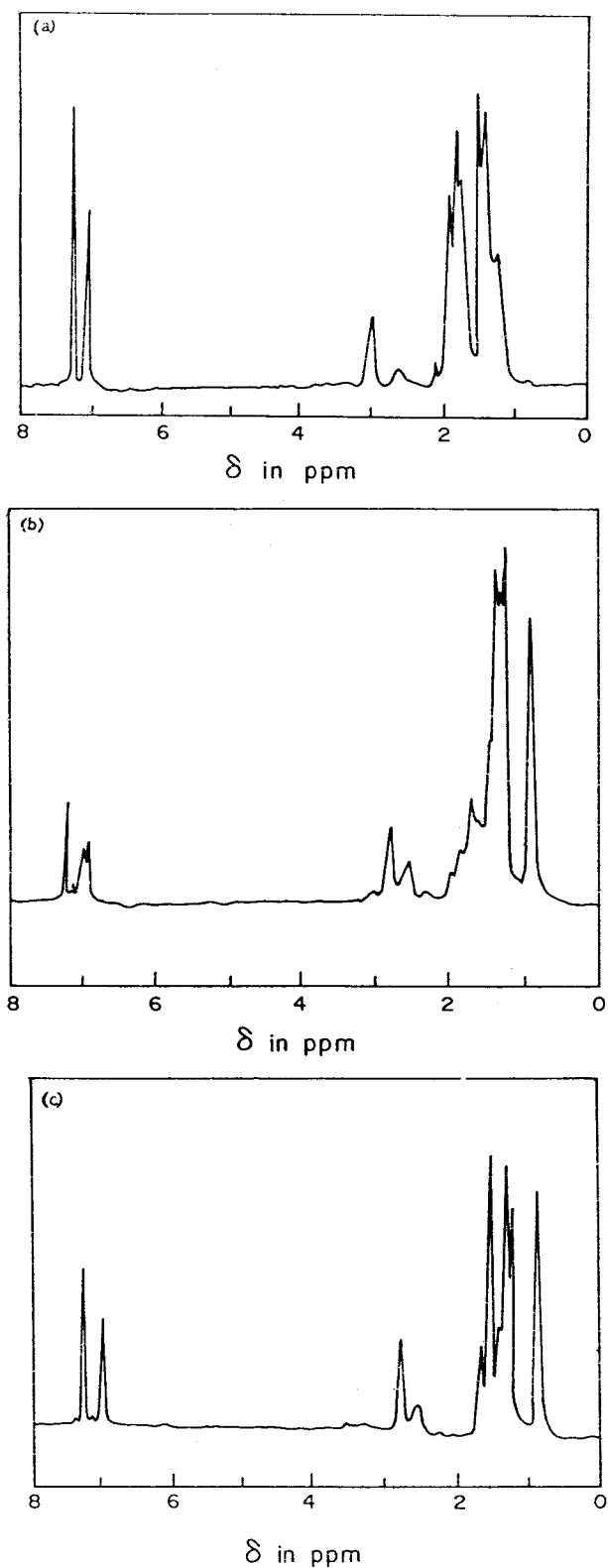
through the solution throughout the reaction. The monomers were added drop by drop for 1 h, and contents were stirred for 21 h. Copolymers were washed with methanol and then extracted with a mixture of acetone and methanol (1 : 1 V/V) using a Soxhlet apparatus. Polymers synthesized in the above manner were dried at 50°C under the reduced pressure.

Thin films of polymers were spin-cast on a SnO<sub>2</sub>-coated glass substrate using a chloroform solution containing 3 g/L copolymer to produce 5–6- $\mu$ m thick polymer film. The film was then transferred to the working chamber of a vacuum coater from Edwards Co., UK (model 306). Aluminum was deposited onto the film at a pressure of 10<sup>-6</sup> mbar using the appropriate mask to cover only a part of the film to cover an area of 4 mm<sup>2</sup>. The aluminum electrode served as a hole-injecting contact while the SnO<sub>2</sub> film acted as an electron-injecting contact. The effective device area was kept at 4 mm<sup>2</sup>. This metal–polymer–metal (MPM) configuration was used to record the device characteristics.

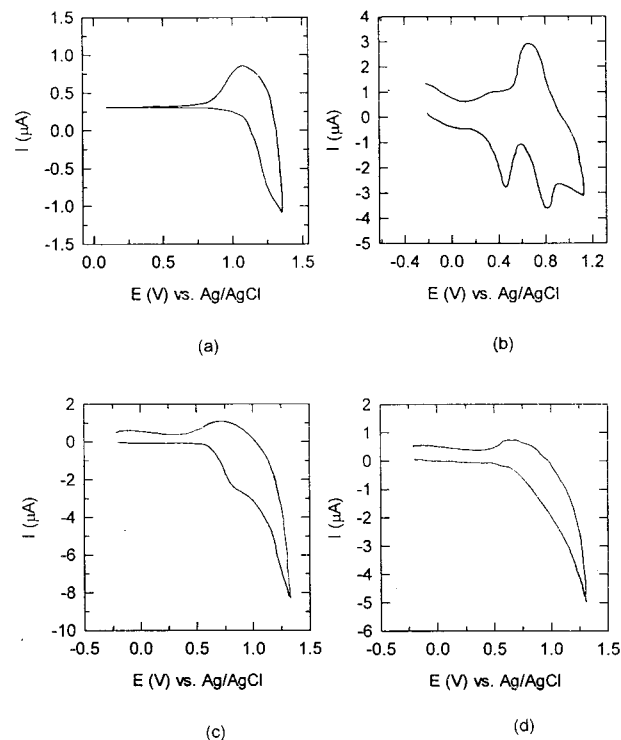
All the measurements were taken in the dark, at room temperature. Dark I–V characteristics and bias-luminescence curves were recorded using a 2000 Houston dual pen recorder, while electrochemical measurements were taken using a PAR 273A Galvanostat/Potentiostat. The emission spectra were taken on Shimadzu-160 spectrophotometer, and nuclear magnetic resonance (NMR) spectra were done on a Bruker AMX-500-MHz NMR.

## RESULTS AND DISCUSSION

Figure 1 shows a representative <sup>1</sup>H-NMR spectra of copolymer II, together with poly(3-cyclohexylthiophene) and poly(3-*n*-hexylthiophene). The NMR spectra of copolymer shows signals at  $\delta$  3.05,  $\delta$  2.82,  $\delta$  2.59, and  $\delta$  2.29, corresponding to —CH— unit of cyclohexyl substituent and the —CH<sub>2</sub>— unit of hexyl substituent nearest to the



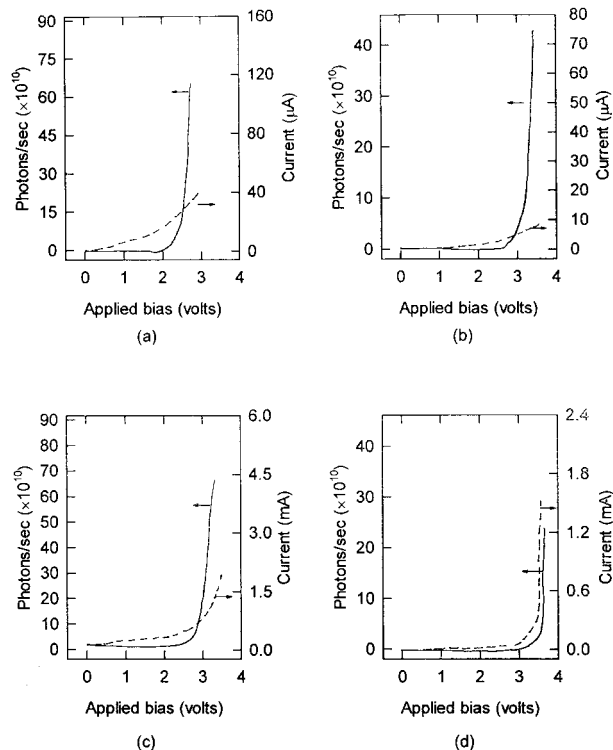
**Figure 1** NMR spectra of (a) poly(3-cyclohexylthiophene) (b) copolymer and (c) poly(3-*n*-hexylthiophene).



**Figure 2** Cyclic voltammograms of (a) copolymer I (b) copolymer II (c) copolymer III and (d) copolymer IV in acetonitrile containing 0.1M TBAP.

thiophene ring in the copolymer. Thus, copolymer contains both 3-cyclohexylthiophene and 3-*n*-hexylthiophene units, as expected.

The cyclic voltammetric curves of copolymer showed shift in peak potentials from the individual monomers. Figure 2 (a–d) shows the cyclic voltammogram of all copolymers in 0.1M tetrabutylammonium perchlorate (TBAP) electrolyte in acetonitrile. The scan rate was kept at 20 MV/s. As clear from Figure 2(a) for copolymer I, a reduction peak at 1.1 V is observed, while the oxidation peak is found to be absent. Figure 2(d) for copolymer IV reveals similar features but with some broad peaks. These characteristics indicate poor oxidizability of copolymers I and IV. In the case of copolymer II [Fig. 2(b)], two sharp anodic peaks at 0.5 and 0.8 V with complementary cathodic peaks are observed. This suggests easier oxidation process (or hole injection) of the copolymer II, as compared to the ingredient polymers, which shows an anodic peak at 1.25 V for 3-cyclohexylthiophene and 1.1 V for 3-*n*-hexylthiophene. Copolymer III [Fig. 2(c)] reveals an anodic peak at 0.9 V and a broad cathodic peak at 0.75V, suggesting good redox property of the polymer.



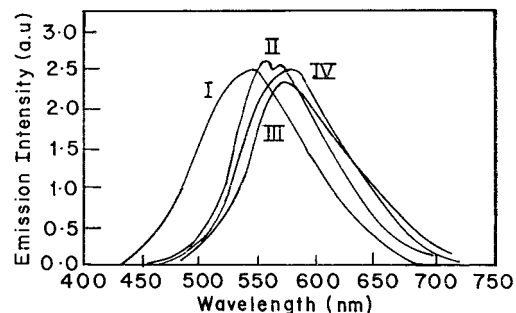
**Figure 3** Luminescence-voltage and current-voltage characteristics of LEDs based on (a) copolymer I (b) copolymer II (c) copolymer III and (d) copolymer IV.

Figure 3(a–d) shows the luminescence and current of copolymer-based LEDs as a function of bias voltage. It is clear from the figures that onset voltage for the luminescence of the device is different for different polymers, varying from 2.2 V to 3.5 V. The quantum efficiencies of the device constructed with the copolymer are summarized in Table II. As seen from the table that copolymer II is the best candidate for the device, next to which is copolymer III.

Figures 4 and 5 represent the emission and photoluminescence spectra, respectively, of thin films of these copolymers taken in the chloroform

**Table II** Maximum Quantum Efficiencies of Copolymer-Based LEDs

Polymer	Applied Bias (Volts)	Efficiency (%)
Copolymer I	2.80	0.0025
Copolymer II	3.35	0.0163
Copolymer III	3.50	0.0098
Copolymer IV	3.63	0.0031

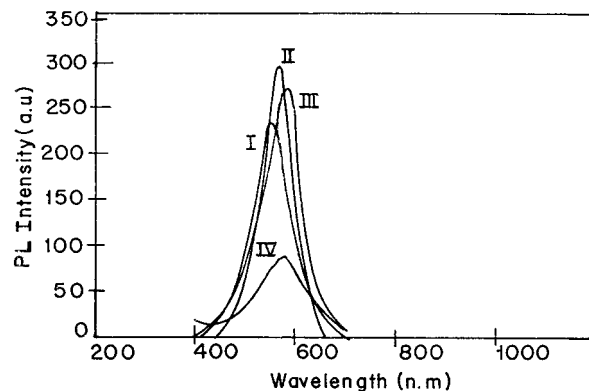


**Figure 4** Emission Spectra of (I) copolymer I (II) copolymer II (III) copolymer III and (IV) copolymer IV, taken in chloroform.

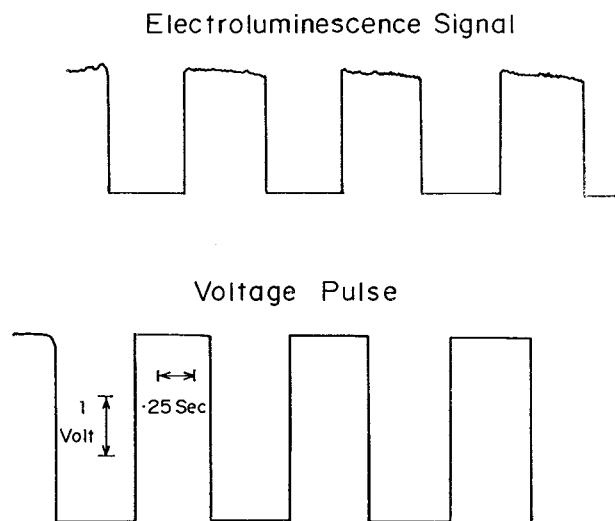
solution. The light emission from different copolymers is in the wavelength region of 550 to 580 nm. The light emission was easily visible in a dark room, and a light variation from yellow to green region could be observed.

Figure 6 shows a typical transient behavior of the device at voltage of 3 V. The shape of the voltage pulse at time duration of 2 s is also shown. The electroluminescence response time was about 0.4 s. The decay of electroluminescence begins as soon as the voltage is turned off. On the other hand, a delay time of electroluminescence after voltage pulse is turned on is observed. This delay gives a measure of the transport of charge carriers, accumulation at the interface, formation of excitons, and their recombination. Therefore, the carrier mobility could be estimated from this transit time.<sup>16</sup> Assuming that the transport of charge carriers constitutes the major part of the time delay  $t_d$ , one can write the following:

$$t_d \approx \frac{d}{(\mu_n + \mu_p)F} \approx \frac{d}{\mu F} \quad (1)$$



**Figure 5** Photoluminescence spectra of (I) copolymer I (II) copolymer II (III) copolymer III and (IV) copolymer IV, taken in chloroform.



**Figure 6** Transient behavior of the LEDs with an applied voltage of 3 V.

where  $d$  is the thickness of the emitting material,  $\mu_n$  and  $\mu_p$  are the electron and hole mobilities, respectively, at a field  $F$ , and  $\mu$  is the larger of the two mobilities.

From this equation, the carrier mobility in the device was estimated to be  $5.6 \times 10^{-4} \text{ cm}^2/\text{Vs}$ .

## CONCLUSION

In summary, we have constructed light-emitting diodes with chemically synthesized copolymers of 3-alkylthiophene as an electroluminescent layer. Copolymers are synthesized in order to vary the band gap and, hence, the light emission from the device. Good solubility of copolymers allows the fabrication of the light-emitting diodes by the spin-casting technique. The devices emit greenish-blue light in the wavelength region of 550–580 nm. The quantum efficiencies of the device are in the range of 0.002 to 0.01%, which is considerably higher than that of poly(3-cyclohexylthiophene)-based light-emitting diodes.<sup>17</sup> Out of all the copolymers synthesized by us, copolymer II

is best as an emissive material in the fabrication of light-emitting diodes. The charge carrier mobility in the device is found to be  $5.6 \times 10^{-4} \text{ cm}^2/\text{Vs}$ .

## REFERENCES

- Burroughes J. H.; Bradley D. C. C.; Brown A. R.; Marks R. N.; Mackay K.; Friend R. H.; Burn P. L.; Holmes A. B. *Nature* 1990, 347, 539.
- Friend R. H.; Gymer R. W.; Holmes A. B.; Burroughes J. H.; Marks R. N.; Taliani C.; Bradley D. C. C.; Dos Santos D. A.; Bredas J. L.; Logdlund M.; Salaneck W. R. *Nature* 1999, 397, 121.
- Greenham N. C.; Moratii S. C.; Bradley D. C. C.; Friend R. H.; Holmes A. B. *Nature* 1993, 365, 628.
- Andersson M. R.; Berggren M.; Inganas O.; Gustafsson G.; Gustafsson-Carlberg J. C.; Selse D.; Hjertberg T.; Wennerstrom O. *Macromolecules* 1995, 28, 7525.
- Schweitzer B.; Wegmann G.; Hertel D.; Mahrt R. F.; Bassler H.; Uckert F.; Scherf U.; Mullen K. *Phys Rev* 1999, 59, 4112.
- Service R. F. *Science* 1998, 279, 1135.
- Service R. F. *Science* 1998, 282, 2179.
- Hide F.; Diaz-Garcia M.; Schwartz B.; Andersson M.; Pei Q.; Heeger A. *Science* 1996, 273, 1833.
- Yang Y.; Pei Q.; Heeger A. J. *J Appl Phys* 1996, 79, 934.
- Andersson M. R.; Berggren M.; Inganas O.; Gustafsson G.; Gustafsson-Carlberg J. C.; Selse D.; Hjertberg T.; Wennerstorm O. *Macromolecules* 1995, 28, 7525.
- Berggren M.; Inganas O.; Gustafsson G.; Rasmusson J.; Andersson M. R.; Hjertberg T.; Wennerstorm O. *Nature* 1994, 372, 444.
- Sundberg M.; Gustafsson G.; Inganas O. *Appl Phys Lett* 1990, 57, 733.
- Yoshino K.; Nakajima S.; Park D. H.; Sugimoto R. *Jpn J Appl Phys* 1988, 27, L718.
- Yoshino K.; Love P.; Onda M.; Sugimoto R. *Jpn J Appl Phys* 1988, 27, L2388.
- Rani V.; Prakash R.; Santhanam K. S. V.; Somanathan N.; Srivivasan K. S. V.; Ramasami T. *Ind. Pat. No. 288/BOM/97* (in process).
- Okii H.; Ohba Y. *Jpn J Appl Phys* 1987, 26, 1477.
- Berggren M.; Gustafsson G.; Inganas G.; Andersson M. R.; Wennerstorm O.; Hjertberg T. *Adv Mater* 1994, 6, 486.