Intermolecular Studies of Polyfluorenes in the Development of Electroluminescent Polymer LEDs

William R. Childs

Literature Seminar

February 8, 2001

The information revolution has made utilization of electronic devices a daily necessity. This interaction requires an interface which usually takes the form of a visual display. Light emitting diodes (LEDs) are currently leading the revolution in visual display technology by providing efficient, high resolution color displays, and through integration into the well-developed field of liquid crystal displays.¹ Unlike their inorganic counterparts, interest in the development of polymer LEDs began recently with Friend et al.'s discovery of a green-emitting polymer in 1990.^{1a, 2} Subsequently, development in the field of polymer LEDs has attracted intense industrial and academic interest due to the commercial application of these devices and the scientific understanding required to develop their potential.³

A fundamental challenge associated with polymer LEDs is understanding the intermolecular interactions which control the polymer's light emitting properties. Polyfluorenes are one of the most promising polymers in this field,^{1a} but, more importantly, they are ideally suited for the systematic study of these intermolecular effects due to their stability and ease of synthetic variability.⁴



Polyfluorenes

In solution and thin films, polyfluorenes have been observed to form aggregates due to poor solubility.^{4,5} These aggregates are problematic as they cause luminescence quenching and the appearance of bathochromically shifted peaks. Another detrimental interaction is the formation of excimers, which occur due to p-stacking when the p-orbital of an excited chain overlaps with the p-orbital of an adjacent molecule in organized thin films. This results is the occurrence of red-shifted peaks and usually a loss of primary luminescence. Excimer formation is dependent upon the length and structure of the polymer's substituents, since they determine the glass transition temperature and the degree of intermolecular communication between the individual chains.⁶ According to these observations, the disorder between chains needs to be maximized by raising the glass transition temperature and increasing insulation while simultaneously retaining solubility.⁷ In addition, the molecular weight of the polymers, which was often overlooked, has been shown to have drastic effect upon fluorescent emission which implies it plays a powerful role in the intermolecular organization of these films.⁸

One of the applications for which polymer LEDs are being developed is the backlighting of liquid crystal displays.⁹ If the anisotropic light emitting properties of these polymers can be harnessed, they will provide polarized light which should greatly improve efficiency in these devices. Since polyfluorenes already possess nematic liquid crystalline properties, researchers have developed alignment techniques which make use of the polymer's inherent intermolecular interactions by pre-aligning the substrate.¹⁰ Subsequent annealing yields an anisotropic monodomain in the resulting thin film. These films have successfully produced linearly polarized electroluminesence as seen in the spectrum below:



In addition, the introduction of enantiomercially pure branched side chains has produced a helical "rigid-rod" structure which produces circularly polarized electroluminesence.¹¹

- (a) Bernius, M.T.; Inbasekaran M.; O'Brien J.; Wu, W. "Progress with Light-Emitting Polymer," Advanced Materials, 2000, 12(23), 1737-1750. (b) Bäuerle, P.; Ullrich, M. "The Electroluminescence of Organic Materials," J. Mater. Chem. 2000, 7, 1471-1507. (c) Holmes, A.B.; Kraft, K.; Grimsdale, A.C. "Electroluminescent Conjugated Polymers-Seeing Polymers in a New Light," Angew. Chem. Int. Ed. 1998, 37, 402-428.
- Friend, R.H.; Gymer, R.W.; Holmes, A.B.; Burroughes, J.H.; Marks, R.N., Taliani, C.; Bradley, D.D.C.; Dos Santos, D.A.; Brédas, J.L., Lögdlund M.; Salaneck, W.R. "Electroluminescence in Conjugated Polymers," *Nature* 1999, 397, 121-128.
- 3. Kim, C.Y.; Kim, D.Y.; Cho, N.H. "Blue Light Emitting Polymers," *Prog. Polym. Sci.* 2000, 25, 1089-1139.

- Vanden Bout, D.A.; Teetsov, J. "Near-Field Scanning Optical Microscopy Studies of Nanoscale Polymer Ordering in Pristine Films of Poly(9,9-dialkylfluorene)," J. Phys. Chem. 2000, 104, 9378-9387.
- Bradley, D.C.C.; Grell, M.; Long, X.; Chamberlain, T.; Inbasekaran, M.; Woo, E.P. "Chain Geometry, Aggregation and Enhanced Dichroism in the Liquid-Crystalline Conjugated Polymer Poly(9,9-Dioctylfluorene)," Acta Polmerica 1998, 49(8), 439-444.
- 6. Teetsov, J.; Fox, M.A. "Photophysical Characterization of Dilute Solutions and Ordered Thin Films," J. Mater. Chem. 1999, 9(9), 2117-2122.
- Huang, W.; Heeger, A.J.; Yu, W.; Pei, J. "Spiro-Functionalized Polyfluorene Derivatives as Blue-Emitting Materials," *Advanced Materials* 2000, 12(11), 828-831.
- Weinfurtner, K.; Fujikawa, H.; Tokito, S.; Taga, Y. "Highly Efficient Pure Blue Electroluminescenece from Polyfluorene: Influence of the Molecular Weight Distribution of the Aggregation Tendency," *Appl. Phys. Lett.* 2000, 76(18), 2502-2504.
- 9. Woo, P.; Wu, W. "Monodomain Alignment of Thermotropic Fluorene Copolymers," *Liquid Crystals* **1999**, 26(9), 1403-1407.
- Whitehead, K.S.; Grell, M.; Bradley, M.; Jandke, M.; Strohriegl, P. "Highly Polarized Blue Electroluminescence from Homogeneously Aligned Films of Poly(9,9-dioctylfluorene)," *Appl. Phys. Lett.* 2000, 76(20), 2946-2948.
- Neher, D.; Scherf, U.; Oda, M.; Nothofer, H.; Lieser, Günter "Circularly Polarized Electroluminescence from Liquid-Crystalline Chiral Polyfluorene," Advanced Materials 2000, 15(5), 362-365.