Synthesis and Characterization of Polyfluorene Derivatives for Blue Light Emitting Diode

Virendra Kumar Rai, Ritu Srivastava, Kanchan Saxena, Pankaj Kumar,
Gayatri Chauhan, M. N. Kamalasanan
Polymeric & Soft Material Section, (OLED Lab),
National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi – 110012

Abstract: *Alkyl substituted poly(fluorene) have emerged as a very attractive class of conjugated polymers, which can be utilized as the blue light-emitting active layers in polymer light emitting diodes [PLEDs]. Polyfluorenes are the only class of conjugated polymer that can emit a whole range of visible colors with relatively high quantum efficiency. The fluorene structural unit provides rigidly planarized biphenyl units within the polymer backbone. The facile substitution at 9- position of the monomeric fluorene allows control of polymer properties such as solubility, processability, and morphology. A blue-light-emitting homopolymer derived from fluorene, poly [9,9-(di-hexyl) fluorene] 2,7-diyl [PDHF] was synthesized through Ni (0) – mediated reductive polymerization of 2, 7 dibromo (9,9 dihexyl) fluorene (Yamamoto coupling reaction). The reaction medium consisted of 2,7 dibromo (9, 9 dihexyl) fluorene, Ni (0) catalyst, Zn as a reductant,TPP, bipyridene, toluene and dimethyl formamide as a solvent. The homopolymer was characterized by using NMR spectroscopy, FTIR-spectroscopy, UV-VIS spectroscopy, thermo gravimetric analysis (TGA), and photoluminescence (PL) spectroscopy. This polymer was completely soluble in common organic solvent, such as THF, CH_2Cl_2, $CHCl_3$, and toluene, and they have good thermal stability with onset decomposition temperature (T_d) of 300 °C. The synthesized homopolymer PDHF showed absorption maximum at about 350 nm. The solution of polymer in chloroform shows strong blue photoluminescence (PL) around 440nm.*

Keywords : PLED ; poly(fluorene); Homopolymer; Photoluminescence;

Introduction

The development of new materials displaying proper emission color with high electroluminescence efficiency and stability is essential for the development of a full color displays. Poly(di-alkyl)fluorenes are promising new materials for blue-light-emitting diodes because of their high photoluminescence (PL) quantum efficiencies and thermal stability [1-4]. The high efficiency blue PL emission from the poly fluorene (PF) structure is atrcattive for use in displays [5&6]. Polyfluorene derivatives are interesting since they contain a rigidly planar biphenyl unit and the facile substitution at the remote C-9 site provides the possibility of improving the solubility and processability of polymers without significantly increasing the steric interactions in the polymer backbone [7&8]. The thermal stabilities of the homo polymers are excellent with decomposition temperatures exceeding 400°C [9]. In this paper we are describing the preparation of poly(9,9 dihexyl) fluorene (PDHF), homopolymers with high molecular weight , good solubility in organic solvents such as chloroform, toluene, tetrhydrofuran (THF) dichloromethylene (CH_2Cl_2) high thermal stability by the Nickel(0)-mediated polymerization of 9,9-disubstituted-2,7-dibromofluorene monomers (Yamamoto polymerization) [10, 11] .

Experimental

2,7 dibromo (fluorene), Bromohexane, Benzenetriethylammoniumchloride, Triphenylphosphene and $NiCl_2$ were purchased from Aldrich. All the chemicals were handled in a moisture free atmosphere. Column chromatography was performed using silica gel (Merck, 250-430 mesh).

Using a SDTA851^e Mettler Toledo a equipment thermogravimetric analysis [TGA] of the polymer was carried out. The number and average molecular weights of polymers were determined by gel permeation chromatography [GPC] analysis on a Viscotech GPC-System UK instrument, using tetrahydrofuran (THF) as an eluent and polystyrene as a standard. UV-visible spectra were measured using a Shimadzu UV-VIS 2401 spectrophotometer, photoluminescence were measured using a Fl-3-11 (Jobin yvon – Horiba) spectrofluorometer at room temperature. FTIR Spectroscopy was done by using Nicolet model 5700 spectrometer UK.

Monomer Preparation (Synthesis of 2'7 dibromo(9,9 di-hexyl) fluorine)

In a three neck 500 ml flask 9.72 gm (0.03 mole) of 2'7- dibromo fluorine was dissolved in 50 ml Dimethyl sulphoxide [DMSO] and degassed for 15 minutes in ultrasonic bath. After degassing 2.5 gm (1.097 mole) of Benzenetiethyl ammonium chloride a phase transfer catalyst in 60 ml of 50 wt % NaOH solution in reaction mixture under nitrogen atmosphere .After vigorous stirring for two hour 27.2 gm (0.165 mole) of n-hexyl bromide was added to the reaction mixture .The reaction was exothermic, temperature reached 80°C within 5 minute after the addition of n-hexyl bromide and dropped down up to 30°C. The mixture was stirred for 12 hrs at 80°C. Color of the reaction mixture changed from deep purple to orange and then finally to yellow. The reaction mixture was allowed to cool to room temperature. 100 ml of deionised water and diethyl ether (125 ml) were added to reaction mixture and stirred for 15 minutes. The etheral layer was separated and washed with water and brine. Bright yellow etheral layer was separated and distilled in high vacuum to remove the DMSO and n-hexylbromide the residue was filtered with a short silica gel column with hexane as eluent. The solvent was evaporated from the filtrate so obtained with the help of vacuum rott-evaporator. The residue was crystallized from ethanol to give white crystal. The crystal was recrystallised twice and then dried over anhydrous $MgSO_4$. The monomer was kept in vacuum for 24 hrs at 40°C and 6.87gm (70.67 %) yield was obtained.

Polymerization (Poly (9, 9 dihexyl fluorene – 2, 7 diyl))

The polymer was prepared according to general procedures for reductive polycondensations of dihaloaromatic compound using $NiCl_2$ bipyridene as coupling agent (Yamamoto coupling) [11]. A dried polymerization reactor is charged with 10 ml dry Dimethylacetamide, Triphenylphosphine (TPP) 1.88 gm (7 mmole), Zinc dust 2,88 gm (44 mmole) and 2,2’ bipyridene 31.2 mg (0.2 mmole) and degassed along with stirring for 15 minutes and the reactor was evacuated and filled with nitrogen. The reaction mixture was continuously stirred for two hours and then Nickel chloride 26 mg (0.2 mmole) was added. The content of the reactor was stirred and heated at 90°C for 30 minutes to generate active Ni(0) catalyst. Degassed solution of 2,7’ dibromo (9,9 dihexyl) fluorene 3.27gm (6.65 mmole) in 10 ml dry dimethyl acetamide is then added to the reaction mixture via a syringe in argon atmosphere. The polymerization is allowed to proceed for 4.5 hours. 10 ml of dry toluene was added to the reaction mixture and stirred and heated continuously at 90°C. 10 ml of toluene was added to the mixture after 6.5 hours and subsequently after 7.3 hours. Heating and stirring are continued for 3.5 hours after addition of the last portion of the toluene .The mixture is poured into 150 ml of chloroform and filtered. The chloroform in the filtrate is removed on a rotary evaporator and the residue stirred with acetone. The large, bright yellow granules obtained are dried for 18 hours in a vacuum oven at 70°C. This crude product was collected and dissolved in chloroform and then reprecipitated. Residual impurities were removed by extraction with chloroform in a soxhlet apparatus, and finally the polymer was dried under vacuum and 1.58gm (70.67 %) yield was obtained.

Purification of Polymer (Removal of Nickel from Polymer)

Liquid extraction with ethylenediamineacetic acid [EDTA] in a 1000 ml flask, 1.0 gm polymer [PDHF] was dissolved in 200 ml of toluene. To this, solution was added 100 ml of 5% EDTA aqueous solution (pH was readjusted to 8-10 with ammonia) and the resulting mixture was vigorously stirred for 4h at 40°C , before transferring to a 1000 ml separation funnel to settle . After the separation of the two layers the toluene layers was collected in a 1000 ml evaporation flask and then concentrated to about 50 ml. The concentrated toluene solution was then slowly poured into a flask containing 100 ml of methanol and stirred. The resulting light yellow precipitate was filtered, washed with methanol and finally dried under vacuum, which gave 0.7 gm of fiber like polymer PDHF.

Result and Discussion

The molecular weight of the polymer was determined by gel permeation chromatography (GPC) analysis in a THF solution calibrated against polystyrene standards. The GPC analysis of the PDHF showed a number-average molecular weight (Mn) of 11620 g mol $^{-1}$ and a weight-average molecular weight (Mw) of 38000 g mol^{-1}.

FTIR Spectroscopy of polymer is shown in Fig (1) the C-H stretching (alkyl chain) at 2868 cm^{-1}, and 2981cm^{-1} and C-H stretching of aromatic ring at 2953 cm^{-1}and aromatic ring breathing vibration at 1456 cm^{-1} is observed.

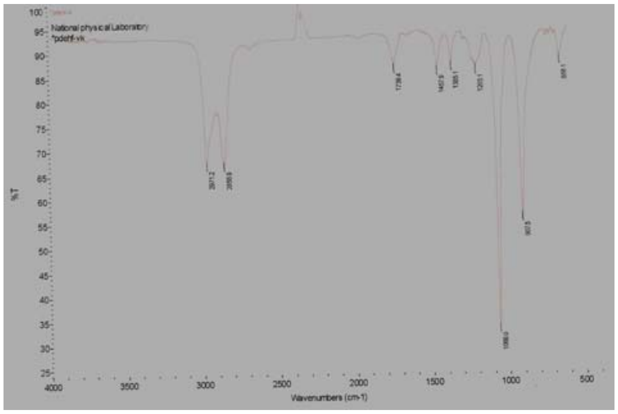

Figure 1. FTIR spectroscopy of PDHF

A thermal property of synthesized PDHF was characterized by TGA (Fig 2), which shows excellent thermal stability. The decomposition temperature of polymer exceeds 300°C.

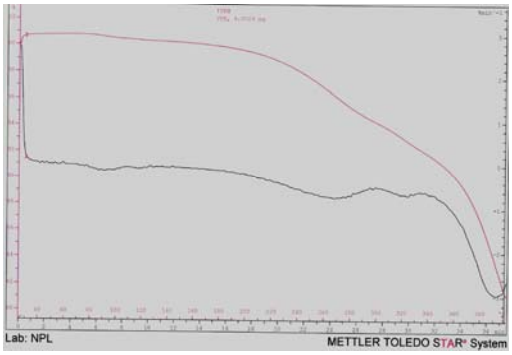

Figure 2. ThermoGravometric Analysis of PDHF.

The optical properties of the polymer are shown in Fig 3. The absorption maximum in solution appeared at 350 nm.

The PL spectrum of PDHF solution is shown in Fig 4. Emission maximum was observed at 440 nm.

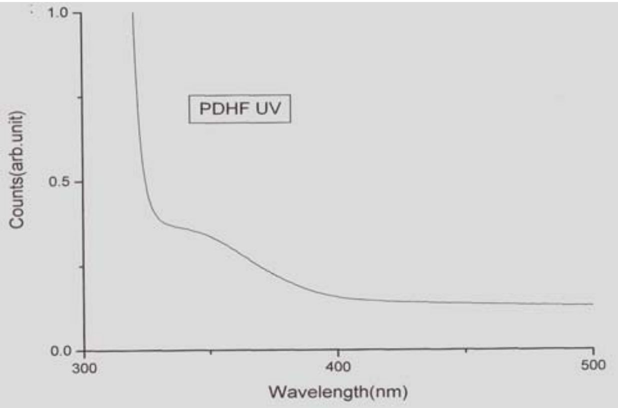

Figure 3. UV- Visible spectrum of PDHF

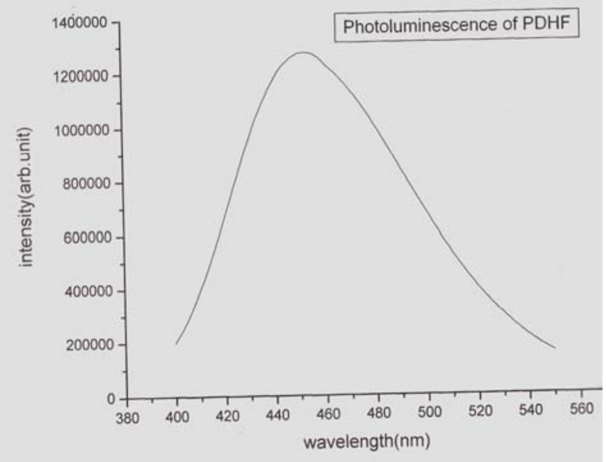

Figure 4. Photoluminescence spectrum of PDHF

Conclusion

We have synthesized and characterized PDHF a derivatives of polydialkylfluorene. This is an important polymer for OLED display and white organic light emitting diode.

Acknowledgements

Authors are thankful to Director, NPL, New Delhi for continuous encouragement. Authors are also thankful to Dr. S. S. Bawa and Dr. S.K. Dhawan for useful suggestion and discussions.

References

1. Kreyenschmidt M., G. Klaerner, T. Fuhrer, J. Ashenhurst, S. Karg, W.D. Chen, V.Y. Lee, J.C. Scott, and R.D. Miller, “Thermally Stable Blue-Light-Emitting Copolymers of Poly(alkylfluorene),” *Macromolecules*, vol. 31, 1998, pp. 1099-1103.

2. Pei Q. and Y. Yang, “Efficient Photoluminescence and Electroluminescence from a Soluble Polyfluorene,” *J. Am. Chem. Soc.*, vol. 118, 1996, pp. 7416-7417

3. Ohmori Y., M. Uchida, K. Muro, and K. Yoshino, “Blue Electroluminescent Diodes Utilizing Poly(alkylfluorene),” *Jpn. J. Appl. Phys.*, vol. 30, no. 11B, Nov. 1991, pp. L1941-3polymer main chain.

4. Jeong –Ik Lee, Hye Yong Chu, Jiyong Oh, Lee i Do,Taehyoung Zyoung, Jaemin Lee and Hong –Ku Shim *ETRI Journal*, Volume 27, Number 2, April 2005

5. Sainova D. , T. Miteva, H. G. Nothofer, and U. Scherf I. Glowacki and J. Ulanski I. Glowacki and J. Ulanski H. FujikawaD. Neher *App ,Phy,Lett* 2000 76 1810]

6. Gong X., P.K. Iyer, D. Moses, G.C. Bazan, A.J. Heeger, S.S. Xiao *Advanced functional materials* 2003 13 no 4 April

7. Lemmer, U., Hein, S.; Mahrt, R. F.; Scherf, U.; Hopmeir, M.; Wiegner, U.; Go¨bel, R. O.; Mu¨llen, K.; Bassler, H. *Chem. Phys. Lett.* 1995, 240, 371.

8. Jenekhe, S. A.; Osaheni, J. A. *Science* 1994, 265, 765

9. Klaerner G. and R. D. Miller *Macromolecules*1998, 31, 2007-2009

10. Dieter Neher *Macromol. Rapid Commun.* 2001, 22, 1365-1385

11. Yamamoto, T.; Hayashi, Y.; Yamamoto, *A. Bull. Chem. Soc. Jpn.* 1978, 51, 209.

12. Yamamoto T., *Pogr Polym.science* 1992 17 1153