

Thermally Stable and Amorphous Polyfluorene

Gwanghoon Kwag, Eunjoo Park, Soo No Lee

Kumho Chemical Laboratories, Korea Kumho Petrochemical Co., P.O. Box 64, Yuseong, Taejeon 305–600, Korea

Received 30 April 2004; accepted 10 October 2004

DOI 10.1002/app.21446

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Two-dimensional ladder-type polyfluorenes, which consist of polystyrene as the polymer backbone and polyfluorene as the light emitting component, were prepared through three synthetic pathways **A**, **B**, and **C**. In path **A**, the precursor polymer **IP1** was obtained from the graft reaction of fluorene to units of poly(vinylbenzyl chloride) and then the ladder-type polymer **P1** was prepared by coupling at the 2,7-position of fluorene with FeCl_3 as an oxidizing agent in chloroform. In path **B**, **IP2** was obtained from the graft reaction of lithiated 2,7-dibromofluorene and units of poly(vinylbenzyl chloride), and then **P2** was prepared by the aryl-coupling of **IP2** with a Ni-catalyst through the reductive polymerization. In path **C**, 4-(fluorenylmethyl)styrene was prepared by the reaction of 4-chloromethylstyrene and lithiated fluorene. Fluorene-attached syndiotactic polystyrene, **IP3**, was obtained in the polymerization of 4-(fluorenylmethyl)styrene with CpTiCl_3 -MAO catalyst, and for

P3 oxidative coupling was further carried out. The polymers exhibited glass transition temperatures (T_g) of 422°C for **P1**, 404°C for **P2**, and 311°C for **P3**, and no melting endotherms were found. Syndiotacticity contributes the high glass temperature of **P3** despite low molecular weight. Thermal decomposition temperatures at 5 wt % loss (T_d) of 475°C for **P1**, 448°C for **P2**, and 365°C for **P3** were observed. The fluorescence peaks of **P1**, **P2**, and **P3** were observed at 401, 416, and 415 nm, respectively. For the emission spectrum of **P3**, no shoulder or peak regarding of aggregation of polyfluorene was observed. Syndiotacticity, due to the alternative configuration of fluorene, prevents a large Stoke's shift of the luminescence spectrum. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1335–1340, 2005

Key words: thermogravimetric analysis (TGA); polystyrene; light-emitting diode (LED)

INTRODUCTION

The polymer-based light-emitting diode (PLED) has been of great interest since the discovery of electroluminescence by a Cambridge group in 1990.¹ Bright large-area display with PLED at a few volts can be made by simple processes such as spin-coating or ink-jetting.^{2,3} One of the limitations that prevents commercialization of PLED is the short life-time of the blue-emitting polymer.^{4–8} Although polyalkylfluorene is outstanding material for blue-emission due to its high photoluminescence yields and oxidative stability, the blue-emitting polymer has a serious problem with the device's lifetime, caused by chain movement.^{9–13} Polymer chains are increasingly moved by heat, generated during device operation, and form domains or aggregations that induce device failures.^{14–18} Thus, it is difficult to expect a long device lifetime of PLED in polymers having low glass transition temperatures (T_g) or poor thermal stability. Some chemical approaches have already been reported for the improvement of high T_g in PLED polymers, such as introducing spiro, one-dimensional ladder-type, or crosslinked structures.^{19–23} Here, in an

effort to increase the thermal stability of polymers for PLED, we have contrived a 2-dimensional ladder-type polyfluorene.

EXPERIMENTAL PROCEDURES

General methods

Anhydrous tetrahydrofuran (THF) was prepared by distillation from Na/benzophenone and degassed by nitrogen. Poly(vinylbenzyl chloride), fluorene, and butyl lithium compounds were purchased from Aldrich. Molecular weight was determined by GPC analysis (Viscotek Co.) using polystyrene standards and THF as solvent at 40°C. JASCO V-570 and Varian Unit Inova 200 (200 MHz) were used to measure UV-visible and ¹H-NMR spectra, respectively. The thermal data of the ladder-polymers were obtained on nitrogen atmosphere at a rate of 20°C/min by using Perkin-Elmer's TGC 7/7. Fluorescence spectra were obtained with the SLM-AMINCO 4800 spectrofluorometer, in which Rhodamin was used as a quantum counter. Mechanics and molecular dynamics calculations were carried out with the Cerius² molecular modeling environment running on SGI Origin3200 (Accelrys Cerius² version 4.7; Accelrys Inc.: www.accelrys.com).

Correspondence to: G. Kwag (gkwag@mail.kkpc.re.kr).

4-(Fluorenylmethyl)styrene

t-BuLi (1.7M in *n*-pentane, 10.0 mol) was slowly added to a solution of fluorene (10.0 mmol) in THF (20 mL) at -78°C under a nitrogen atmosphere. A reddish-orange color appeared immediately. After 3 h, the fluorenyl lithium was slowly added into a solution of vinylbenzene chloride (10 mmol) in THF (10 mL) at -78°C . The mixture was stirred overnight, and water and ethyl ether were added. The organic layer was extracted and dried, and the yellowish liquid was slowly crystallized in methanol. The solid was filtered with washing *n*-pentane. An ivory and needle-type crystalline was obtained. $^1\text{H-NMR}$ (200 MHz, CDCl_3): δ 7.77 (2H, d, Fu-H), 7.39–7.20 (10H, m, Fu-H, Bn-H), 6.80–6.66 (1H, q, Vy-H), 5.80–5.70 (1H, d, Vy-H), 5.27–5.21 (1H, d, Vy-H), 4.23 (1H, t, Fu-H), 3.10 (1H, d, Bz).

Poly(vinylbenzyl fluorene) (IP1)

Poly(vinylbenzyl chloride) (1.57 g, M_w 55,000) was dissolved in tetrahydrofuran (20 mL) and purged with nitrogen. *n*-Butyl lithium (4 mL, 2.5M in *n*-hexane) was slowly added into a solution of fluorene (1.67 g) in tetrahydrofuran (50 mL) at -78°C . The mixture was slowly added into the poly(vinylbenzyl chloride) solution, stirred for 6 h while the temperature was gradually increased to room temperature, and water (30 mL) and ethyl ether (50 mL) were added. The ethereal solution was washed with water and brine, dried with magnesium sulfate, and evaporated. The product was dried under vacuum. A yellow solid was obtained: M_w 68,160, MWD 2.96, UV-Vis (λ_{max} , THF) 302 nm; $^1\text{H-NMR}$ (200 MHz, CDCl_3): δ 7.76 (d, Fu-H), 7.65 (d, Fu-H), 7.50–7.23 (br, Fu-H), 7.09–6.78 (br, Bn-H), 3.88 (br, Fu-H), 2.70 (br, Bz), 1.80 (br, CH_2 , CH).

Poly(vinylbenzyl dibromofluorene) (IP2)

Poly(vinylbenzyl chloride) (1.57 g, M_w 55,000) was dissolved in tetrahydrofuran (20 mL) and purged with nitrogen. *n*-Butyl lithium (4 mL, 2.5M in *n*-hexane) was added to a 2,7-dibromofluorene (3.24 g) solution in THF (50 mL) at -78°C . The mixture was stirred for 3 h and then slowly added into the poly(vinylbenzyl chloride) solution at -78°C , stirred for 6 h while the temperature was gradually increased to room temperature, quenched with water (30 mL), and extracted with ethyl ether (100 mL). The ethereal solution was washed with water, dried with magnesium sulfate, and evaporated. The product was dried under vacuum. A yellow solid was obtained: M_w 272,900, MWD 5.71, UV-Vis (λ_{max} , THF) 298 nm; $^1\text{H-NMR}$ (200 MHz, CDCl_3): δ 7.76–7.34 (m, Fu-H), 7.0 (br, Bn-H), 3.85 (br, Fu-H), 1.61 (br, CH_2 , CH).

syn-Poly(vinylbenzyl fluorene) (IP3)

Methylaluminoxane (2.43M, 12.1 mmol) under nitrogen atmosphere was slowly added to a solution of 1-vinyl-4-(1-fluorenyl)-methyl benzene (2 mmol, 0.52 g) in toluene (20 mL) at -78°C , and the mixture was stirred for 30 min. Into the mixture, 10 mmol (2.19 mg) of CpTiCl_3 in toluene was slowly added, stirred for 1 h at room temperature, quenched with acidic methanol (200 mL), and filtered. The obtained solid was washed with methanol (200 mL) and dried under vacuum. M_w : 2500. $^1\text{H-NMR}$ (200 MHz, CDCl_3): δ 7.77 (m, Fu-H), 7.39–7.20 (m, Fu-H, Bn-H), 7.20–6.66 (m), 6.60–6.10 (m), 4.25–4.00 (m, Fu-H), 3.10 (1H, d, Bz), 2.0–1.4 (br).

Poly(vinylbenzyl)-graft-polyfluorene (P1)

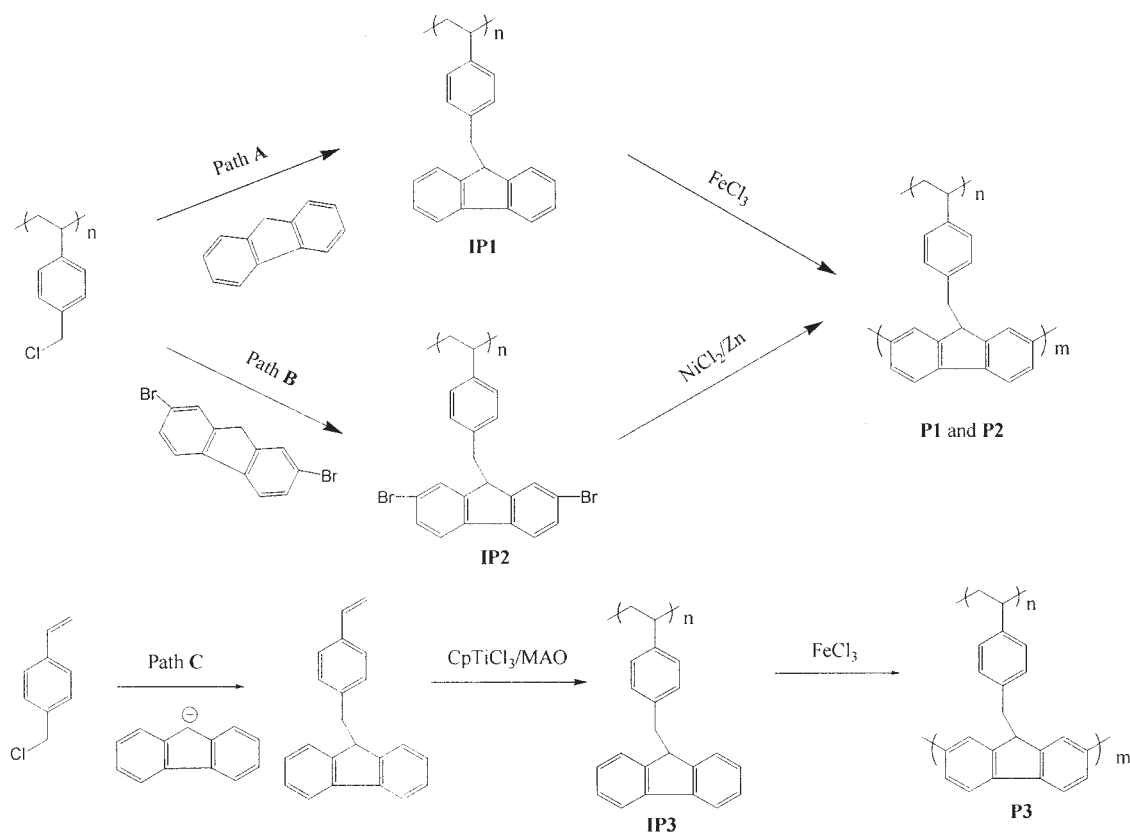
Ferric chloride (5 g) was added to a solution of IP1 and 9,9-dihexylfluorene (3 g) in chloroform (20 mL) under a nitrogen atmosphere. The mixture was stirred at room temperature for 4 h, quenched by methanol, and filtered. The obtained solid was dissolved in tetrahydrofuran. Insoluble solid was removed. The filtrate solution was evaporated and dried under vacuum. A yellow solid was obtained. M_w 79,040, MWD 2.94, UV-Vis; (λ_{max} , THF) 362 nm, PL (λ_{max} , THF) 542 nm, TGA ($\Delta 5\%$) 475°C , T_g 421.8°C ; $^1\text{H-NMR}$ (200 MHz, CDCl_3): δ 7.8–6.2 (br, Fu-H, Bn-H), 3.9 (br, Fu-H), 2.08 (br, H), 1.56 (br, H), 1.22 (br, H), 1.10 (br, H), 0.76 (br, H).

Poly(vinylbenzyl)-graft-polyfluorene (P2)

Poly(vinylbenzyl dibromofluorene) (1.0 g), nickel chloride (0.03 g), 2,2'-dipyridyl (0.03 g), zinc dust (0.8 g), and dimethylformamide (10 mL) were placed in a 100-mL flask, purged with nitrogen, and stirred at 70°C for 48 h, and DMF was removed under vacuum at 65°C . The resultant was extracted with tetrahydrofuran, evaporated, and a yellow solid was obtained. M_w 132,200, MWD 2.07, UV-Vis; (λ_{max} , THF) 362 nm, PL (λ_{max} , THF) 514 nm, TGA ($\Delta 5\%$) 448°C , T_g 404.4°C ; $^1\text{H-NMR}$ (200 MHz, CDCl_3): δ 7.8–7.4 (br, Fu-H), 6.9–6.5 (br, Bn-H), 3.9 (br, Fu-H), 2.9 (br, H), 2.1 (br, H), 1.77 (br, H), 1.41 (br, H), 1.21 (br, H), 0.94 (br, H).

syn-Poly(vinylbenzyl)-graft-polyfluorene (P3)

To a solution of IP3 (50 mg) in CHCl_3 (20 mL) under nitrogen, 2.5 g of FeCl_3 was added, and the mixture was stirred for 4 h. The mixture was quenched with acidic methanol (200 mL) and filtered. The obtained solid was dissolved in tetrahydrofuran (200 mL) and insoluble solid was removed. The filtrate solution was dried under vacuum. M_w : 4,802, MWD 2.42; UV-Vis (λ_{max} , THF): 353 nm, PL (λ_{max} , THF): 460 nm,



Scheme 1 Synthetic paths of ladder-type polyfluorenes **P1**, **P2**, and **P3**.

TGA($\Delta 5\%$) 365°C, T_g 311°C. $^1\text{H-NMR}$ (200 MHz, CDCl_3): δ 7.8–7.5 (br, Fu-H), 7.3–7.2 (br, Fu-H), 7.2–7.0 (br, Fu-H, Bn-H), 6.5 (br, Bn-H), 4.0 (br, Fu-H), 2.9 (br, H), 1.97 (br, H), 1.23 (br, H), 1.10 (br, H), 0.76 (br, H), 0.60 (br, H).

RESULTS AND DISCUSSION

Synthesis

The two-dimensional ladder-type polymers, which consist of polystyrene and polyfluorene, were prepared by the synthetic paths **A**, **B**, and **C** in Scheme 1. Polystyrene was chosen as a polymer backbone, because of its low cost, good solubility, chemical and thermal stability, flexibility in functionalization, and visible transparency.²⁴ Here, poly(vinylbenzyl chloride) was used as polystyrene backbone. In path **A**, the precursor polymer **IP1** was obtained from the graft reaction of fluorene to units of poly(vinylbenzyl chloride) and then the ladder-type polymer **P1** was prepared by coupling at the 2,7-position of fluorene with FeCl_3 as an oxidizing agent in chloroform.²⁵ In path **B**, **IP2** was obtained from the graft reaction of lithiated 2,7-dibromofluorene and units of poly(vinylbenzyl chloride). The molecular weight of **IP2** (M_w 272,900) is higher than that of **IP1** (M_w 68,160), which is due to

the high reactivity of lithiated dibromofluorene in the graft reaction. **P2** was prepared by aryl-coupling of **IP2** with Ni-catalyst through the reductive polymerization in the presence of zinc and the medium of DMF.²⁶ 4-(Fluorenylmethyl)styrene, the monomer of **IP3**, was prepared by the reaction of 4-chloromethylstyrene and lithiated fluorene. The precursor **IP3**, flu-

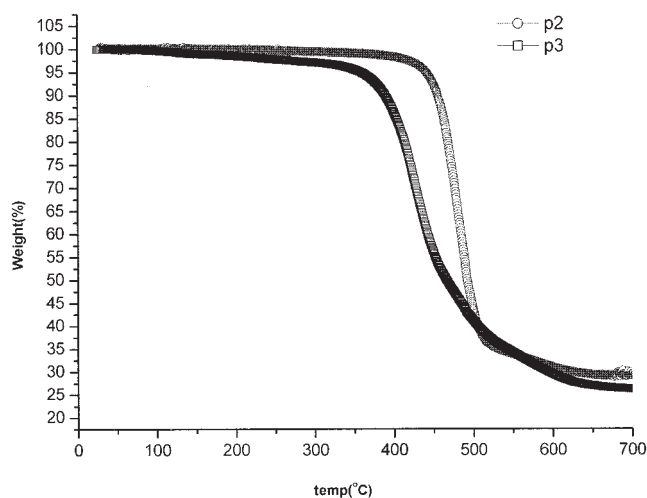


Figure 1 Thermal analysis of **P2** and **P3**.

TABLE I
Molecular Weights, UV-vis Absorption, Photoluminescence, Thermal Stability Data of P1, P2, and P3

	M_w	MWD	Absorption (nm)	Emission (nm)	TGA ($\Delta 5\%$, °C)	T_g (°C)
P1	79,000	2.94	315	401	475	422
P2	132,000	2.07	364	416	448	404
P3	4,800	2.42	353	415	365	311

orene-attached syndiotactic polystyrene, was obtained in the polymerization of 4-(fluorenylmethyl)styrene with CpTiCl₃-MAO catalyst in toluene.²⁷ During the preparation of P1 ~ P3, the insoluble solid was separated, and the soluble fraction in THF was obtained. Thus, the lower molecular weight of P2 (M_w 132,200) compared with that of IP2 (M_w 272,900) was obtained. The insoluble polymer resulted from self-crosslinking of polyfluorene.

Thermal analysis

The thermal properties of the ladder-type polymers, P1, P2, and P3, were determined by differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) measurements. The polymers exhibited glass transitions (T_g) of 422°C for P1, 404°C for P2, and 311°C for P3, and no melting endotherms were found. The high T_g values were obtained with the ladder structure irrespective of molecular weight. Syndiotacticity would contribute the high glass temperature of P3 despite the low molecular weight. Thermal decomposition temperatures at 5 wt % loss (T_d) of 475°C for P1, 448°C for P2, and 365°C for P3 were observed as shown in Figure 1. The excellent thermal stability

(high T_d) of P1 and P2 is contributed from both the ladder structure and the high molecular weight.

Optical properties

The electronic absorption data for IP1 ~ IP3 and P1 ~ P3 are summarized in Table I, and the spectra of P1, P2, and P3 are shown in Figures 2 and 3. IP1 shows absorption peaks at 267 and 304 nm, which correspond to the phenyl of polystyrene and the fluorene unit, respectively. The UV absorption at 300 nm corresponds to the fluorene. The λ_{max} peak at 315 nm with five dwarf peaks at 271, 283, 292, 306, and 332 nm was observed in the absorption spectrum of P1. After polymerizing the fluorene unit of IP1, π -conjugation through polyfluorene leads a red shift from 304 to 315 and 332 nm, respectively. The difference in the red shifts is caused by the degree of aryl polymerization. The small peak at 304 nm indicates unreacted fluorene units hanging on the polymer backbone. Three peaks at 267, 292 (with the shoulder peak at 298), and 312 nm were observed in the absorption spectrum of IP2. The peak at 312 nm corresponds to the dibromofluorene attached to polystyrene backbone. The P2 spectrum is different from P1, in which peaks at 364 (λ_{max}), 303,

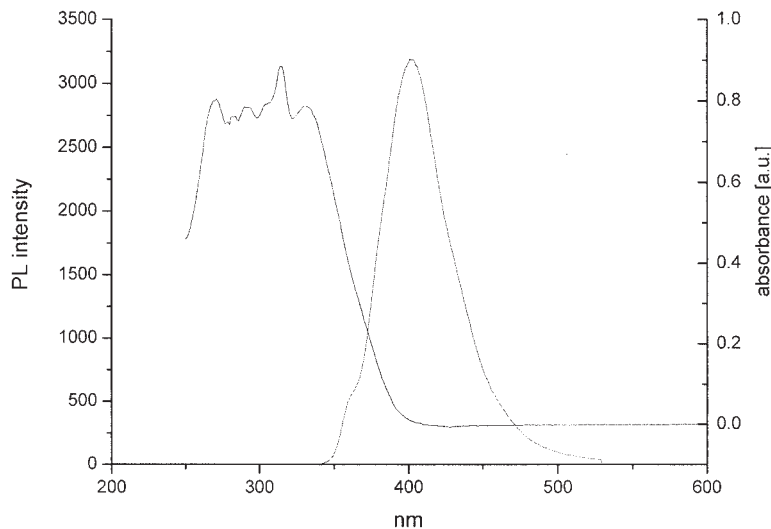


Figure 2 UV-Visible (blue) and emission (red) spectra of P1.

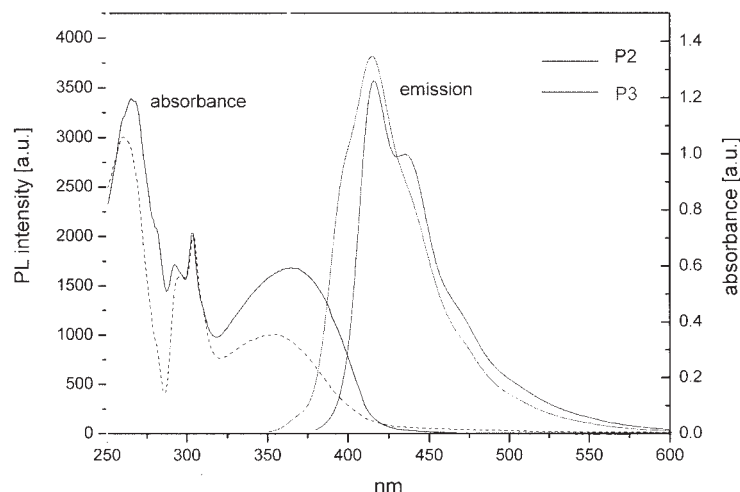


Figure 3 Absorption and emission spectra of P2 and P3 in CH_2Cl_2 .

292, and 265 nm were observed. The λ_{max} at 364 nm indicates a long length of π -conjugation through polyfluorene, which is a similar position to a crosslinkable polyfluorene reported by Klarner et al.²⁸ The fluorescence peak of P1 was observed at 401 nm at the irradiation on 315 nm and that of P2 at 416 nm at the irradiation on 364 nm, which was located at a longer position than that of polyfluorene.²⁹ The emission spectrum of P2 shows the shoulder peak at 437 nm, indicating "aggregations" of interchains. Three peaks at 258, 292, and 303 nm appeared in the absorption spectrum of IP3. A broad peak was observed in the absorption spectrum of P3, and four peaks at 260, 296, 304, and a broad peak at 353 nm were found. The fluorescence peak of P3 at 415 nm appeared at the irradiation on 353 nm. No shoulder or peak with regard to aggregation of polyfluorene was observed.

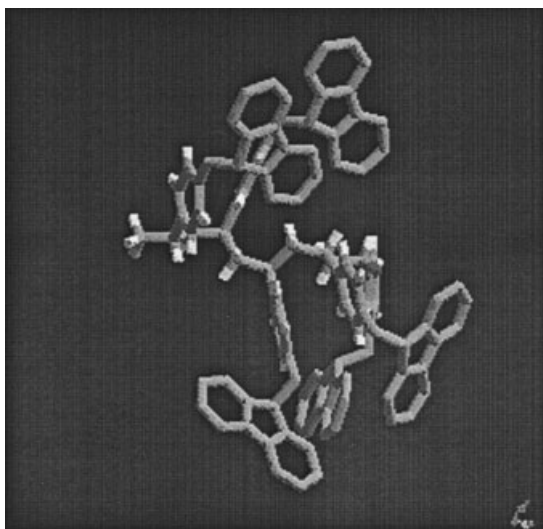


Figure 4 Calculated structure of *syn*-poly(vinyl benzyl fluorene).

Syndiotacticity, due to the alternative configuration of fluorene, prevents a large Stoke's shift of the luminescence spectrum. In Figure 4 the conformation of the optimized structure of *syn*-poly(vinylbenzyl fluorene) is presented. Alternative fluorene units are located, preventing stacking of the aromatic rings.^{30,31}

CONCLUSION

A series of two-dimensional ladder-type polyfluorenes was prepared by introducing atactic or syndiotactic polystyrene as the backbone. The ladder-type polyfluorenes have a high T_g , greater than 400°C, and excellent thermal stability. No remarkable aggregation of interchains was observed in the ladder polyfluorene having syndiotactic polystyrene as the backbone.

References

- Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* 1990, 347, 539.
- Calvert, P. *Chem Mater* 2001, 13, 3299.
- Sarzi Sartori, S.; De Feyter, S.; Hofkens, J.; Van der Auweraer, M.; De Schryver, F.; Brunner, K.; Hofstraat, J. W. *Macromolecules* 2003, 36, 500.
- Tokito, S.; Tanaka, H.; Noda, K.; Okada, A.; Taga, T. *Appl Phys Lett* 1997, 70, 1929.
- Tokito, S.; Tanaka, H.; Okada, A.; Taga, Y. *Appl Phys Lett* 1996, 69, 878.
- Kuwabara, Y.; Ogawa, H.; Inada, H.; Noma, N.; Shirota, Y. *Adv Mater* 1994, 6, 677.
- Itano, K.; Tsuzuki, T.; Ogawa, H.; Appleyard, S.; Willis, M. R.; Shirota, Y. *IEEE Trans Electron Devices* 1997, 44, 1218.
- Berntsen, A.; Croonen, Y.; Liedenbaum, C.; School, H.; Visser, R.-J.; Vlegger, J. *Optical Mater* 1998, 9, 125.
- Pei, Q.; Yang, Y.; *J Am Chem Soc* 1996, 118, 7416.
- Grell, M.; Long, X.; Bradley, D. D. C.; Woo, E. P. *Adv Mater* 1997, 9, 798.
- Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn J Appl Phys* 1991, 30, L1941.

12. Yang, Y.; Pei, Q. *J Appl Phys* 1997, 81, 3294.
13. Yoshida, M.; Fujii, A.; Ohmori, Y.; Yoshino, K. *Appl Phys Lett* 1996, 69, 734.
14. Tang, H.-Z.; Fujiki, M.; Sato, T. *Macromolecules* 2002, 35, 6439.
15. Kim, Y. H.; Shin, D. C.; Kim, S.-H.; Ko, C.-H.; Yu, H.-S.; Chae, Y.-S.; Kwon, S. K. *Adv Mater* 2001, 13, 1692.
16. Steuber, F.; Staudigel, J.; Stossel, M.; Simmerer, J.; Winnacker, A.; Spreitzer, H.; Weissortel, F.; Salbeck, J. *Adv Mater* 2002, 12, 130.
17. Grell, M.; Bradley, D. D. C.; Ungar, G.; Hill, J.; Whitehead, K. S. *Macromolecules* 1999, 32, 5810.
18. Bradley, D. D. C.; Grell, M.; Long, X.; Mellor, H.; Grice, A. *Proc SPIE Int Soc Opt Eng* 1997, 3145, 254.
19. Yu, W.; Pei, J.; Huang, W.; Heeger, A. J. *Adv Mater* 2000, 12, 828.
20. Grem, G.; Paar, C.; Stampfl, J.; Leising, G.; Huber, J.; Scherf, U. *Chem Mater* 1995, 7, 2.
21. Chmil, K.; Scherf, U. *Makromol Chem Rapid Commun* 1993, 14, 217.
22. Su, Y. Z.; Lin, J.; Tao, Y.-T.; Ko, C.-W.; Lin, S.-C.; Sun, S.-S. *Chem Mater* 2002, 14, 1884.
23. Inaoka, S.; Advincula, R. *Macromolecules* 2002, 35, 2426.
24. Koch, M.; Stork, M.; Klapper, M.; Mullen, K.; Gregorius, H. *Macromolecules* 2000, 33, 7713.
25. Fukuda, M.; Sawada, K.; Yoshino, K. *J Polym Sci Part A* 1993, 31, 2465.
26. Kim, D. Y.; Cho, H. N.; Kim, C. Y. *Prog Polym Sci* 2000, 25, 1089.
27. Kim, K. H.; Jo, W. H.; Kwak, S.; Kim, K. U.; Hwang, S. S.; Kim, J. *Macromolecules* 1999, 32, 8703.
28. Klarner, G.; Lee, J.-I.; Lee, V. Y.; Chan, E.; Chen, J.-P.; Nelson, A.; Markiewicz, D.; Siemens, R.; Scott, J. C.; Miller, R. D. *Chem Mater* 1999, 11, 1800.
29. Bernius, M.; Inbasekaran, M.; Woo, E.; Wu, W.; Wujkowski, L. *J Mater Sci Mater Elect* 2000, 11, 111.
30. Gruner, J.; Hamer, P. J.; Friend, R. H.; Huber, H.; Scherf, U.; Holmes, A. B. *Adv Mater* 1994, 6, 748.
31. Gruner, J.; Wittmann, H. F.; Hamer, P. J.; Friend, R. H.; Huber, J.; Scherf, U.; Mullen, K.; Moratti, S. C.; Holmes, A. B. *Synth Met* 1994, 67, 181.