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Living Anionic Polymerization of Styrene Derivatives *para*-Substituted with π-Conjugated Oligo(fluorene) Moieties

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ABSTRACT: The anionic polymerization of styrene monomers *para*-substituted with π-conjugated mono-, di-, and tri(9,9-dihexylfluorene) moieties, **St-Fl**, **St-Fl$_2$**, and **St-Fl$_3$**, was examined under the conditions either in THF at −78 °C or in *tert*-butylbenzene at 20 °C with *sec*-BuLi as an initiator. The polymerization of both **St-F$_l$** and **St-Fl$_2$** was found to proceed in a living manner to quantitatively afford the corresponding polymers with predictable molecular weights and narrow molecular weight distributions ($M_w/M_n < 1.08$). The anionic polymerization of **St-Fl$_3$** was also indicative to proceed in a living manner but with an unpredictable molecular weight. Both AB and BA diblock copolymers with the well-defined and expected structures could be successfully prepared by the sequential addition of **St-Fl** or **St-Fl$_2$** followed by styrene and *vice versa*. The block copolymerization results clearly indicate the living nature of the anionic polymerization of **St-Fl** and **St-Fl$_2$** and the almost same anionic polymerization behaviors of both monomers as styrene in reactivities of monomer(s) and propagating chain-end anion(s). Solubilities, intrinsic viscosities, and glass transition temperatures of the poly(**St-Fl**) and poly(**St-Fl$_2$**) herein prepared were measured. The optical absorption and luminescence spectra of the studied polymer films showed well-resolved vibronic structures and the peak maxima was progressively increased as the fluorene chain length increased. The luminescence spectra also showed reduced aggregation/excimer emission in comparison with that of parent polyfluorene. The present study suggests that living anionic polymerization could be employed to polymerize other styrene derivatives with π-conjugated moieties in a controlled manner and such polymers may exhibit precisely defined physical properties.

Introduction

Conjugated polymers have been widely studied for electronic and optoelectronic applications, including light-emitting diodes (LED), thin film transistors, and photovoltaic devices.[1−13] Among such polymers, poly(fluorene)s have attracted significant scientific interest due to their processability, excellent thermal stabilities, high luminescence yields, and good charge transport properties.[14,15] The photophysical properties of poly(fluorene)s could be tuned through the approaches of copolymer, blend, side chain modification, end-capping, architecture, or different phases (solution, thin film or fiber).[14−18]

Recently, the correlation between the structure of oligo(fluorene)s, including the chain length and donor/acceptor substitution, and their electronic, electrochemical, and optoelectronic properties has been extensively investigated.[19−23] Conjugated chain length is believed to one of the major factors governing the electronic and optoelectronic properties of conjugated polymers. In addition to the main chain oligo(fluorene)s, another approach is to incorporate the fluorene moieties into polymer side chain. Nonconjugated backbone polymers having pendant π-conjugated moieties usually have good solubility to produce uniform films for device applications. Besides, the morphology of the above polymers led to significant difference on the electronic/optoelectronic properties from the main chain conjugated polymers.[24−28] The efficiencies of polymer LED and polymer solar cells could also be significantly enhanced through the architecture or morphology control.[29−33] To the best of our knowledge, however, the synthesis, morphology, and properties of nonconjugated backbone polymers having pendant different π-conjugated fluorene chain lengths have not been enough explored yet. Such polymer could have precisely defined electronic/optoelectronic properties and be used to establish the structure−property relationship. Furthermore, these polymers could be further used to prepare block copolymers and explore the self-assembled morphology and physical properties.[34−37]

Various styrene and methacrylate monomers with pendant π-conjugated moieties have been polymerized by conventional radical (co) polymerization or nitroxide-mediated radical polymerization. The (co)polymers with relatively narrow molecular weight distributions ($M_w/M_n = 1.1-1.5$) and block copolymers were successfully prepared.[21,22,27−29,31] Although a variety of functional monomers can possibly be polymerized by the radical routes, the preparation of high molecular weight polymers ($M_n > 30$ kg/mol) with extremely narrow molecular weight distributions ($M_w/M_n < 1.1$) can not be realized even at the present time by recently developed living/controlled radical polymerization systems.[27,28,33]

We have long been successfully realizing the living anionic polymerization of many styrene derivatives bearing a wide variety of functional groups.[38−42] The resulting living polymers are

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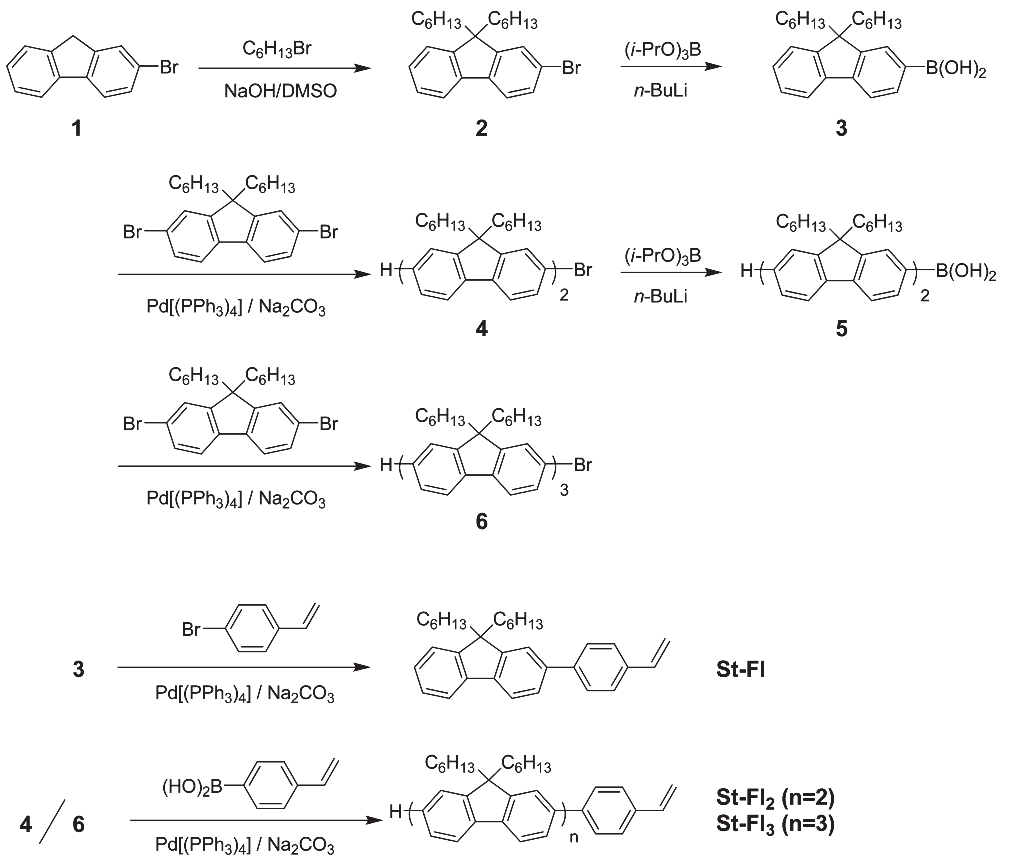
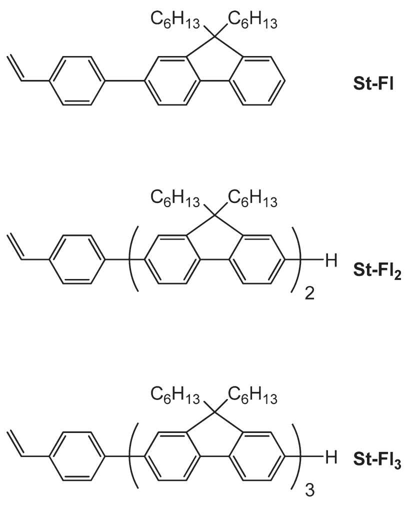
Scheme 1. Synthesis of Monomer: Vinyl−Oligo(fluorene)s with Different Chain Lengths



similar to living anionic polystyrene in precise control of molecular weight and molecular weight distribution as well as synthetic possibility of architectural polymers such as block copolymers, star-branched polymers, and so on. Herein, we report on the synthesis of a new series of three *para*-substituted styrene monomers with π-conjugated mono-, di-, and tri(9,9-dihexylfluorene) moieties, abbreviated as **St-Fl**, **St-Fl$_2$**, **St-Fl$_3$**, and their anionic polymerization behaviors, especially from a viewpoint of living polymerization.

To our experience on the living anionic polymerization of functionalized styrene derivatives, the 9,9-dialkyl substituted fluorene moieties are expected to be stable and remain intact under the conditions of living anionic polymerization, resulting in the formation of the stable living anionic polymers with the pendant π-conjugated fluorene moieties. Characteristic features of living anionic polymerization may extend the potential synthesis of well-defined block copolymers. Furthermore, it is of interest to elucidate how the π-conjugation from styrene to fluorine moieties affects on the anionic polymerization behaviors of such monomers.

Chart 1. Vinyl−Oligo(Fluorene) Monomers

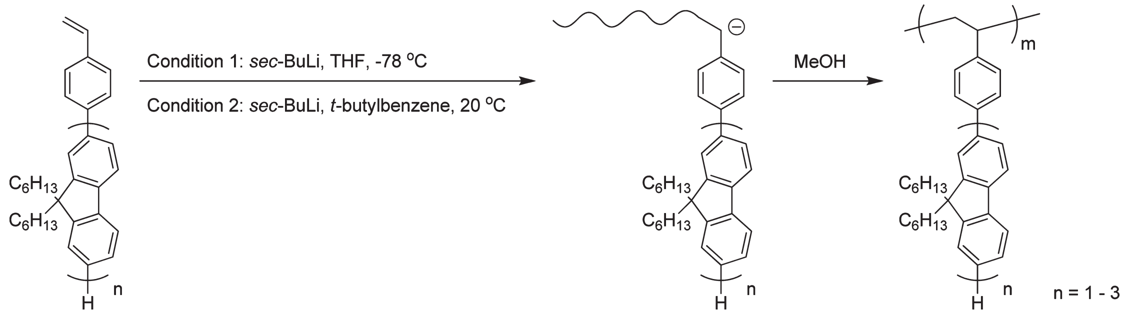


Experimental Section

Materials. All of the reagents were purchased from Aldrich or Acros and used as received, unless otherwise stated. Tetrahydrofuran (THF) was refluxed over sodium wire, distilled over $LiAlH_4$ under nitrogen, and then distilled from its sodium naphthalenide solution under high vacuum conditions (10^{-6} torr). Heptane and *tert*-butylbenzene were washed with concentrated H_2SO_4, water, aqueous $NaHCO_3$, and dried over P_2O_5, and finally distilled in the presence of 1,1-diphenylhexyllithium. Styrene was washed with aqueous NaOH (10 wt %) and water, and dried over $MgSO_4$. After filtration, styrene was distilled twice over CaH_2 under reduced pressures and finally distilled over Bu_2Mg under high vacuum conditions. *sec*-Butyllithium (*sec*-BuLi, 1.2 M in heptane, Aldrich Japan) was diluted with heptane and determined in concentration by the colorimetric titration with standardized octanol in THF solution from colorless end-point of the red-colored solution obtained after the addition of 1,1-diphenylethylene under high vacuum conditions.

The synthetic routes of precursors and monomers will be shown in Scheme 1 later in the part of the results and discussion. 2-Bromofluorene (**1**) was purchased from Acros and used as received. 2-Bromo-9,9-dihexylfluorene (**2**), 9,9-dihexylfluorenyl-2-boronic acid (**3**), 9,9,9′,9′-tetra-*n*-hexyl-2,2′-bifluorenyl-7-boronic acid (**4**), 7-bromo-9,9,9′,9′-tetrahexyl-2,2′-bifluorene (**5**), and 7-bromo-9,9,9′,9′,9″,9″-hexa-*n*-hexyl-2,7′;2′,7″-terfluorene (**6**) were synthesized according to the literature

Scheme 2. Anionic Polymerization of Vinyl−Oligo(fluorene)s



previously reported[17] and detailed in the Supporting Information. Poly(9,9-di-*n*-hexylfluorenyl-2,7-diyl) (**PF**, M_n = 2400, M_w/M_n = 1.70) for the comparison on the photophysical properties was purchased from Aldrich.

9,9-Dihexyl-2-(4-vinylphenyl)-9*H*-fluorene (St-Fl). A mixture of 9,9-dihexylfluorenyl-2-boronic acid (18.0 g, 47.6 mmol), 4-bromostyrene (10.4 g, 57.1 mmol), $Pd(PPh_3)_4$ (1.06 g, 0.95 mmol), Na_2CO_3 (2.0 M aqueous solution, 30.0 mL), and THF (150 mL) was stirred at 90 °C for 2 days. After the reaction mixture was cooled to room temperature, it was poured into a large excess of petroleum ether. The organic portion separated was washed with brine and dried over anhydrous $MgSO_4$. After filtration, followed by removal of the solvents by evaporation, the crude product was purified by column chromatography on silica gel with hexane to afford **St-Fl** as an oily product (5.2 g, 25%). 300 MHz ^1H NMR ($CDCl_3$, ppm): 7.76−7.71 (m, 2H, Ar), 7.65 (d, 2H, Ar), 7.59−7.51 (m, 4H, Ar), 7.36−7.26 (m, 3H, Ar), 6.79−6.75 (m, 1H, CH=), 5.83 and 5.30 (2d, 2H, CH_2=), 2.01−1.99 (m, 4H, $C(CH_2C_5H_{11})_2$), 1.13−1.04 and 0.77−0.64 (m, 22H, $C(CH_2C_5H_{11})_2$) 75 MHz. ^{13}C NMR ($CDCl_3$, ppm): 151.38, 150.95, 141.08, 140.72, 140.50, 139.50 (Ar), 136.45 (CH=), 127.21, 127.02, 126.77, 126.63, 125.77, 122.84, 121.22, 119.92, 119.73 (Ar), 113.7 (CH_2=), 55.12 ($C(C_6H_{13})_2$), 40.41, 31.45, 29.70, 23.75, 22.55 (CH_2), 13.97 (CH_3). Anal. Calcd for $C_{33}H_{40}$: C, 90.77; H, 9.23. Found: C, 90.89; H, 9.11.

9,9-Dihexyl-2-(9,9-dihexyl-2-(4-vinylphenyl)-9*H*-fluoren-7-yl)-9*H*-fluorene ($St\text{-}Fl_2$). A mixture of 7-bromo-9,9,9′,9′-tetrahexyl-2,2′-bifluorene (10.0 g, 13.4 mmol), 4-vinylphenylboronic acid (3.00 g, 20.1 mmol), $Pd(PPh_3)_4$ (300 mg, 0.26 mmol), Na_2CO_3 (2.0 M aqueous solution, 6.7 mL), and THF (100 mL) was stirred at 80 °C for 2 days. After the reaction mixture was cooled to room temperature, it was poured into a large excess of petroleum ether. The organic layer separated was washed with brine and dried over anhydrous $MgSO_4$. After filtration, followed by removal of the solvents by evaporation, the crude product was purified by column chromatography on silica gel with hexane to afford **St-Fl₂** as a semisolid (4.5 g, 43%). 300 MHz ^1H NMR ($CDCl_3$, ppm): 7.80−7.73 (m, 4H, Ar), 7.67−7.52 (m, 10H, Ar), 7.36−7.26 (m, 3H, Ar), 6.80−6.76 (m, 1H, CH=), 5.84 and 5.30 (2d, 2H, CH_2=), 2.07−2.02 (m, 8H, $C(CH_2C_5H_{11})_2$), 1.14−1.08 and 0.78−0.71 (m, 44H, $C(CH_2C_5H_{11})_2$). 75 MHz ^{13}C NMR ($CDCl_3$, ppm): 151.75, 151.46, 151.00, 141.08, 140.79, 140.61, 140.49, 140.34, 140.21, 139.91, 139.51 (Ar), 136.47 (CH=), 127.23, 126.98, 126.79, 126.66, 126.16, 126.04, 125.88, 122.91, 121.46, 121.41, 121.33, 120.00, 119.88, 119.71 (Ar), 113.76 (CH_2=), 55.29, 55.16 ($C(C_6H_{13})_2$), 40.39, 31.46, 29.68, 23.78, 22.55 (CH_2), 13.99 (CH_3). Anal. Calcd for $C_{58}H_{72}$: C, 90.57; H, 9.43. Found: C, 90.73; H, 9.31.

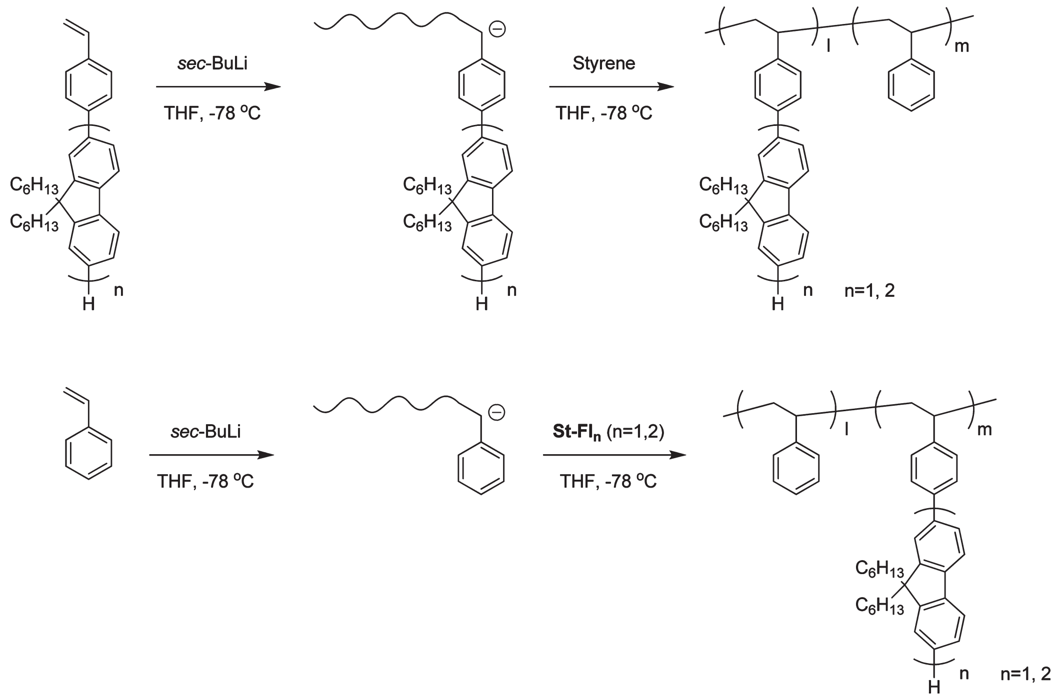
9,9-Dihexyl-2-(9,9-dihexyl-2-(9,9-dihexyl-2-(4-vinylphenyl)-9*H*-fluoren-7-yl)-9*H*-fluoren-7-yl)-9*H*-fluorene ($St\text{-}Fl_3$). A mixture of 7-bromo-9,9,9′,9′,9″,9″-hexa-*n*-hexyl-2,7′;2′,7″-terfluorene (8.0 g, 8.03 mmol), 4-vinylphenylboronic acid (2.37 g, 16.06 mmol), $Pd(PPh_3)_4$ (180 mg, 0.16 mmol), Na_2CO_3 (2.0 M aqueous solution, 4.02 mL), and THF (100 mL) was stirred at 80 °C for 2 days. The same workup as that mentioned above gave **St-Fl₃** as a light yellow semisolid (2.5 g, 28%). 300 MHz ^1H NMR ($CDCl_3$, ppm): 7.83−7.78 (m, 6H, Ar), 7.68−7.62 (m, 12H, Ar), 7.59−7.52 (m, 2H, Ar), 7.44−7.26 (m, 3H, Ar), 6.80−6.76 (m, 1H, CH=), 5.84 and 5.30 (2d, 2H, CH_2=), 2.12−2.02 (m, 12H, $C(CH_2C_5H_{11})_2$), 1.14−1.08 and 0.79−0.69 (m, 66H, $C(CH_2C_5H_{11})_2$). 75 MHz ^{13}C NMR ($CDCl_3$, ppm): 151.9, 151.8, 151.6, 151.1, 140.9, 140.7, 140.6, 140.0 (Ar), 136.6 (CH=), 127.3, 126.9, 126.8, 126.2, 126.1, 123.0, 121.6, 121.5, 120.1, 120.0, 119.9, 119.8 (Ar), 113.9 (CH_2=), 55.4, 55.3 ($C(C_6H_{13})_2$), 40.5, 34.3, 31.5, 30.4, 29.8, 29.8, 29.7, 23.9, 23.8, 22.7 (CH_2), 14.1 (CH_3). Anal. Calcd for $C_{83}H_{104}$: C, 90.49; H, 9.51. Found: C, 90.32; H, 9.57.

Anionic Polymerization. The anionic polymerization was carried out under high vacuum conditions (10^{-6} Torr) in sealed glass reactors with break-seals.[43] The reactors were always prewashed with the initiator solutions after being sealed off from the vacuum line. The polymerization scheme is shown in Scheme 2, which will be introduced later. A typical polymerization experiment was as follows: A THF (11.0 mL) solution of **St-Fl** (1.38 mmol) kept at −78 °C was added instantaneously to *sec*-BuLi (0.0550 mmol) in heptane solution (1.00 mL) through the break-seal with vigorous stirring at −78 °C. The reaction mixture was allowed to stand for additional 3 h at −78 °C and quenched with degassed methanol. The polymer was precipitated in a large excess of methanol, reprecipitated twice from THF to methanol, and freeze-dried from its absolute benzene solution under vacuum for 24 h. A polymer yield was more than 95% isolated yield (100% by ^1H NMR). The polymer was characterized by SEC−RALLS and ^1H and ^{13}C NMR, respectively. 300 MHz ^1H NMR ($CDCl_3$, ppm): 7.8−6.4 (broad, 276H, aromatic), 2.6−1.1 and 1.1−0.3 (broad, 728H, backbone and C_6H_{13}). 75 MHz ^{13}C NMR ($CDCl_3$, ppm) 151.34, 150.96, 140.89, 140.09, 140.50, 135.81, 128.33,.126.81, 125.80, 125.62, 122.91, 120.93, 120.13, 119.80 (Ar), 55.14 ($C(C_6H_{13})_2$), 40.53, 34.31, 31.45, 30.39, 29.74, 23.82, 22.59 (CH_2), 14.07 (CH_3).

The polymerizations of **St-Fl₂** and **St-Fl₃** were similarly carried out under the same conditions. Both **St-Fl** and **St-Fl₂** were also polymerized in *tert*-butylbenzene with *sec*-BuLi by using exactly the same polymerization procedure as that described above except for the temperature of 20 °C. Poly(**St-Fl₂**): 300 MHz ^1H NMR ($CDCl_3$, ppm): 7.9−6.3 (broad, 201H, aromatic), 2.6−1.1 and 1.1−0.3 (broad, 649H, backbone and C_6H_{13}). 75 MHz ^{13}C NMR ($CDCl_3$, ppm) 151.75, 151.49, 151.03, 140.87, 140.56, 140.33, 140.09, 126.84, 126.10, 125.62, 122.98, 121.46, 119.94, 119.79 (Ar), 55.22 ($C(C_6H_{13})_2$), 40.45, 34.30, 31.30, 30.39, 29.75, 23.83, 22.62 (CH_2), 14.09 (CH_3). Poly(**St-Fl₃**): 300 MHz ^1H NMR ($CDCl_3$, ppm): 7.8−6.6 (broad, 154H, aromatic), 2.7−1.5 and 1.2−0.4 (broad, 542H, backbone and C_6H_{13}). 75 MHz ^{13}C NMR ($CDCl_3$, ppm): 151.84, 151.53, 151.06, 140.89, 140.56, 140.38, 140.06 (Ar), 127.05, 126.86, 126.21, 122.99, 121.48, 120.03, 119.79 (Ar), 55.39, 55.23 ($C(C_6H_{13})_2$), 40.45, 31.55, 29.78, 23.85, 22.65 (CH_2), 14.11 (CH_3).

Block Copolymerization. An AB diblock copolymer of **St-Fl** with styrene was prepared by the sequential addition of **St-Fl** followed by styrene in a manner similar to the homopolymer-

Scheme 3. Block Copolymerization of Vinyl−Oligo(fluorene)s with Styrene



ization, as shown in scheme 3 which will also be introduced later. The first stage polymerization was carried out at −78 °C by mixing **St-Fl** (1.16 mmol) in THF solution (7.50 mL) with *sec*-BuLi (0.107 mmol) in heptane solution (1.80 mL). The reaction mixture was allowed to stand for additional 3 h and then a small portion was sampled to determine the molecular weight and molecular weight distribution. The second block was prepared by adding styrene (8.25 mmol) in THF solution (8.80 mL) to the resulting living poly(**St-Fl**) solution (0.0984 mmol) obtained at the first stage polymerization. After 0.5 h, the reaction mixture was quenched with degassed methanol and the polymer was precipitated in methanol. The polymer was purified by reprecipitation twice from THF to methanol and freeze-dried from its benzene solution. The polymers obtained at the first and second stage polymerizations were characterized by SEC−RALLS and ^{1}H NMR. Poly(**St-Fl**)-*block*-polystyrene: 300 MHz ^{1}H NMR ($CDCl_3$, ppm): 7.5−6.2 (broad, aromatic protons), 2.1−1.0 and 1.0−0.4 (broad, backbone and C_6H_{13}). Another block copolymerization was carried out by adding styrene first and then **St-Fl** under the same conditions. Similarly, the block copolymerization of **St-Fl$_2$** with styrene or *vice versa* was performed under the same conditions. The specific amount of monomers and initiator added in the polymerization were listed in Table 2. Poly(**St-Fl$_2$**)-*block*-polystyrene: 300 MHz ^{1}H NMR ($CDCl_3$, ppm): 7.8−6.2 (broad, aromatic protons), 2.2−1.1 and 1.1−0.5 (broad, backbone, and C_6H_{13}).

Measurements. Size exclusion chromatography (SEC) was performed on an Asahi Techneion AT-2002 equipped with a Viscotek TDA model 302 triple detector array using THF as a carrier solvent at a flow rate of 1.0 mL/min at 30 °C. Three polystyrene gel columns of pore size 650, 200, and 75 Å (bead size 9 μm) were used. Both ^{1}H and ^{13}CNMR spectra were measured on a Bruker DPX300 in $CDCl_3$. Chemical shifts were recorded in ppm downfield relative to $(CH_3)_4Si$ (δ 0) and $CDCl_3$ (δ 77.1) for ^{1}H and ^{13}C NMR as standards, respectively. Glass transition temperature (T_g) was measured by SII NanoTechnology EXSTAR 6000 DSC6220. TG/DTA analysis was performed with SII NanoTechnology EXSTAR 6000 TG/DTA6200. UV−Vis optical absorption and photoluminescence (PL) spectra were obtained using Hitachi U-4100 spectrometer and Fluorolog-3 Spectrofluorometer (Jobin Yvon), respectively.

Results and Discussion

Synthesis of Styrene Monomers *p*-Substituted with Oligo (fluorene)s, St-Fl, St-Fl$_2$, and St-Fl$_3$. As illustrated in Scheme 1, the synthesis of styrene monomers *p*-substituted with fluorene, bifluorene, and trifluorene moieties, **St-Fl**, **St-Fl$_2$**, and **St-Fl$_3$**, was accomplished through the Suzuki coupling reaction of *p*-vinylphenylboronic acid with the corresponding 9,9-dihexyl-2-dibromofluorene derivatives.

Since the fluorene dimer, followed by trimer, had the same terminal bromide as the starting 9,9-dihexyl-2-bromofluorene, the same Suzuki coupling reaction could be repeated to increase stepwise the number of fluorene unit. The resulting styrene monomers were purified by column chromatography and trace amounts of water were removed by azeotropic distillation with absolute benzene several times under reduced pressures and finally dried for 24 − 48 h under high vacuum conditions (10^{-6} torr) in the presence of P_2O_5 placed in another vessel. They are either viscous liquid or semisolid soluble in common organic solvents. Interestingly, however, only **St-Fl** was insoluble in benzene. Therefore, these monomers were dissolved in THF or *tert*-butylbenzene instead of benzene and employed in the anionic polymerization.

Anionic Polymerization of St-Fl. The anionic polymerization of **St-Fl** was first performed in THF at −78 °C for 3 - 24 h using *sec*-BuLi as initiator under high vacuum with break-seals. On addition of **St-Fl** to *sec*-BuLi, a characteristic dark blue color immediately developed as shown in Figure S1, strongly indicating the generation of **St-Fl**-derived propagating chain-end anion. This color remained unchanged during the course of polymerization, but disappeared by adding degassed methanol to quench the polymerization. The yield of polymer was always quantitative. The ^{1}H NMR spectrum of the resulting polymer as shown in Figure 1 revealed the absence of signals for the vinyl protons and the presence of new resonances attributable to the backbone chain protons.

The relative ^{1}H NMR signal intensities of aliphatic protons for both the backbone chain and the hexyl groups to aromatic ones proved that the vinyl polymerization

Table 1. Anionic Polymerization of St-Fl, St-Fl$_2$, and St-Fl$_3$ in THF at −78 °C for 3 - 24 h[a]

run	*sec*-BuLi mmol	monomer (mmol)	M/I	M_n [g/mol] calcd[b]	M_n [g/mol] SEC[c]	M_n [g/mol] obsd[d]	M_w/M_n[d]
St-Fl-1	0.107	**St-Fl**, 1.16	10.9	4810	3550	4990	1.07
St-Fl-2	0.0550	**St-Fl**, 1.38	25.1	11000	6160	11500	1.08
St-Fl-3	0.0363	**St-Fl**, 3.75	103	45200	17800	43500	1.04
St-Fl-4	0.0172 (0.0117[e])	**St-Fl**, 4.73	275 (404[e])	120 000 (177000[e])	72400	177000	1.02
St-Fl-5	0.0565	**St-Fl**, 0.238[f]	42.1	18500	10900	17500	1.08
St-Fl$_2$-1	0.114	**St-Fl$_2$**, 0.869	7.62	5920	5930	6700	1.05
St-Fl$_2$-2	0.0200	**St-Fl$_2$**, 1.14	58.5	45000	21500	54000	1.04
St-Fl$_2$-3	0.0781	**St-Fl$_2$**, 0.923[f]	11.8	9100	9000	10200	1.05
St-Fl$_3$-1	0.0601 (0.0369[e])	**St-Fl$_3$**, 0.402	6.69 (10.9[e])	7 430 (12000[e])	9690	12000	1.12
St-Fl$_3$-2	0.0200	**St-Fl$_3$**, 0.554	27.7	31000		no polymer	

[a] Yields of polymers were always quantitative. [b] M_n(calcd) = $M/I \times$ (molecular weight of monomer). [c] Estimated by SEC with polystyrene standard samples. [d] Determined by RALLS-SEC. dn/dc values of poly(**St-Fl**), poly(**St-Fl$_2$**), and poly(**St-Fl$_3$**) are 0.174, 0.178, and 0.200, respectively. [e] Calculated values based on the colorimetric titration of active chain end with standardized *n*-octanol in absolute THF under vacuum. [f] Polymerization was carried out in *tert*-butylbenzene at 20 °C for 24 h.

Table 2. Block Copolymerization of St-Fl or St-Fl$_2$ with Styrene in THF at −78 °C [a]

run	M_n [g/mol] calcd	M_n [g/mol] obsd[b]	M_w/M_n	composition (**St-Fl$_n$**/styrene, wt/wt) calcd	composition (**St-Fl$_n$**/styrene, wt/wt) obsd[c]
poly(**St-Fl**)-*b*-polystyrene	13000	14000	1.03	0.38/0.62	0.35/0.65
polystyrene-*b*-poly(**St-Fl**)	18300	19500	1.05	0.58/0.42	0.61/0.39
poly(**St-Fl$_2$**)-*b*-polystyrene	17400	18200	1.04	0.39/0.61	0.37/0.63
polystyrene-*b*-poly(**St-Fl$_2$**)	14300	12300	1.02	0.46/0.54	0.42/0.58

[a] Yields of polymers were always quantitative. Polymerization times were taken for 3 and 0.5 h of **St-Fl$_n$** and styrene, respectively. [b] Determined by RALLS-SEC. [c] Determined by ^{1}H NMR.

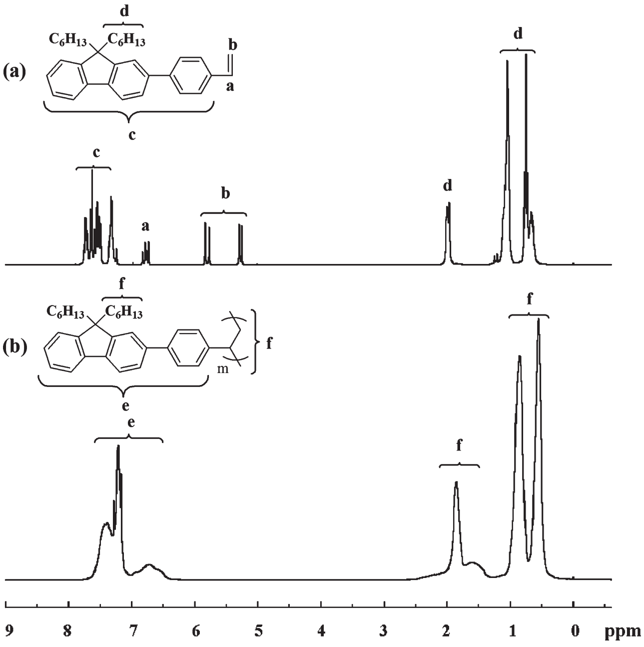


Figure 1. ^{1}H NMR spectra of (a) **St-Fl** and (b) poly(**St-Fl**) in CDCl$_3$.

proceeded exclusively as expected. The same conclusion was obtained by the ^{13}C NMR spectra (Figure S2). The molecular weights and molecular weight distributions of the polymers were measured by SEC−RALLS measurement. The results of the polymerization are given in Table 1.

The polymers possess predictable molecular weights in the range from 5000 to 45000 g/mol (see St-Fl-1−St-Fl-3 in Table 1) that agree well with those theoretically calculated based on the feed ratios of monomer to initiator. The SEC traces of the polymers presented in Figure 2a exhibit very narrow and monomodal distributions in all cases (M_w/M_n < 1.08).

All of the analytical results clearly indicate that the anionic polymerization of **St-Fl** proceeds in a living manner under the conditions in THF at −78 °C where the 9,9-fluorene substituent is stable and remains completely intact as illustrated in Scheme 2.

When a high molecular weight polymer was prepared at a higher molar ratio of monomer to initiator, the molecular weight determined by RALLS (M_n = 177 000 g/mol) was observed to be much higher than the theoretical value (M_n = 120 000 g/mol) as shown in St-Fl-4 of Table 1. On the other hand, the observed molecular weight was in complete agreement with the calculated value using the concentration of the propagating chain-end anion which was obtained by the colorimetric titration from dark blue to colorless end-point under high vacuum conditions. This strongly indicates that some amounts of *sec*-BuLi were deactivated by the impurities in **St-Fl** prior to the polymerization and the residual active *sec*-BuLi initiated the polymerization of **St-Fl** under the conditions.

As shown in Table 1, the M_n values calibrated by SEC with standard polystyrenes are always smaller than the observed values and the deviation becomes more significant with increasing the molecular weight. Therefore, the 9,9-dihexylfluorene substituent may have an influence on the hydrodynamic volume in THF and poly(**St-Fl**) appears to be smaller in hydrodynamic volume than polystyrene with the same molecular weight.

It is well-known that living anionic polystyrene can be prepared not only under the conditions in THF at a low temperature like −78 °C, but also in hydrocarbon solvents at room or even higher temperatures. For this reason, the anionic polymerization of **St-Fl** was carried out in *tert*-butylbenzene with *sec*-BuLi at 20 °C for 24 h. An orange color, but not a dark blue color in THF, immediately developed on mixing **St-Fl** with *sec*-BuLi under such conditions and remained unchanged until quenching with

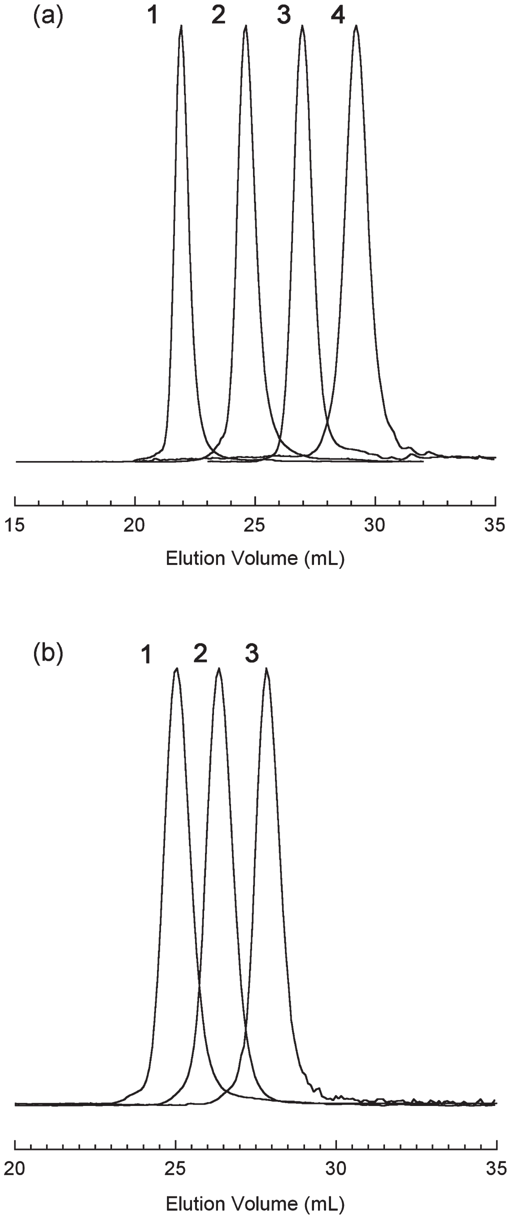


Figure 2. SEC curves: (a) poly(**St-Fl**) with M_n = **1**, 177000; **2**, 43500; **3**, 11500; **4**, 4990 (g/mol); (b) poly(**St-Fl$_2$**) with M_n = **1**, 54000; **2**, 10200; **3**, 6700 (g/mol).

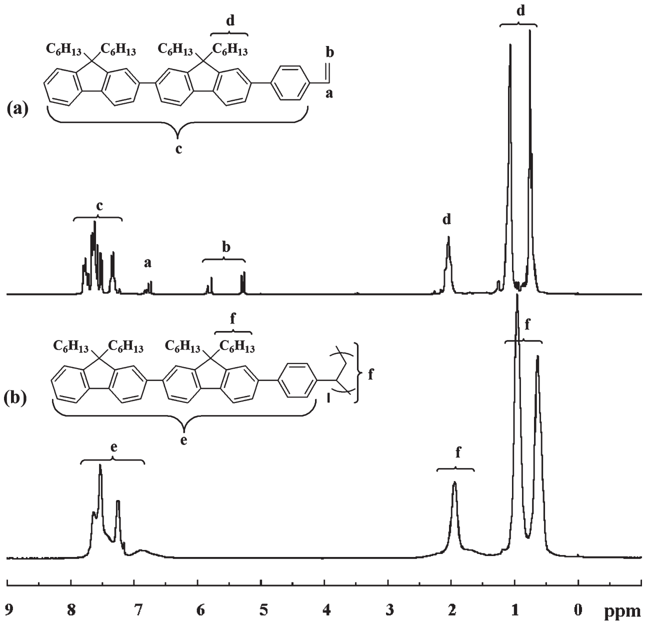


Figure 3. ^{1}H NMR spectra of (a) **St-Fl$_2$** and (b) poly(**St-Fl$_2$**) in CDCl$_3$.

degassed methanol. It should be mentioned that the color developed is very similar to that of polystyryllithium under the same conditions. The polymerization yield was quantitative. Agreement of the M_n values between measured and calculated is satisfactory and a narrow molecular weight distribution is attained as listed in Table 1 (see St-Fl-5). Thus, we have found that the anionic polymerization of **St-Fl** also proceeds in a living manner under the conditions in *tert*-butylbenzene at 20 °C. This is important from an industrial point of view.

Anionic Polymerizations of St-Fl$_2$ and St-Fl$_3$. As mentioned above, the styrene monomer *p*-substituted with 9,9-dihexylfluorene moiety, **St-Fl**, underwent living anionic polymerization without any problem. In this section, the anionic polymerizations of the styrene monomers *p*-substituted with 9,9-dihexylfluorene dimer and trimer, **St-Fl$_2$** and **St-Fl$_3$**, were examined under the same conditions. The anionic polymerization of **St-Fl$_2$** was first carried out in THF with *sec*-BuLi at −78 °C. The polymerization system always colored dark blue, similar to that of **St-Fl**, and remained unchanged during the course of the polymerization. Yields of polymers were quantitative. The ^{1}H and ^{13}C NMR spectra of the resulting polymer revealed that the vinyl polymerization exclusively occurred (Figure 3 and Figure S3). The polymerization results are also given in Table 1 (St-Fl$_2$-1−St-Fl$_2$-3).

The molecular weights were well controlled in the range from 6000 to 50000 g/mol. Moreover, a poly(**St-Fl$_2$**) with a predictable molecular weight and a narrow molecular weight distribution was quantitatively obtained in *tert*-butylbenzene with *sec*-BuLi at 20 °C for 24 h. As shown in Figure 2b, the polymers all possess narrow monomodal SEC distributions, the M_w/M_n values being less than 1.05.

The anionic polymerization of **St-Fl$_3$** was performed in THF with *sec*-BuLi at −78 °C. Similar to the cases with **St-Fl** and **St-Fl$_2$**, a characteristic dark blue color developed on mixing **St-Fl$_3$** with the initiator. The polymerization yield was quantitative. The SEC profile of the resulting polymer exhibited a narrow monomodal distribution. Although the M_n value measured by SEC−RALLS was somewhat higher than that calculated from monomer to initiator ratio, it became close to the calculated value using the concentration of active chain-end determined by the colorimetric titration in vacuo (St-Fl$_3$-1). This may also possibly be caused by the loss of initiator activity due to impurities in **St-Fl$_3$** as mentioned above (see St-Fl-4). Unfortunately, no polymerization occurred due to the impurities when higher molecular weight poly(**St-Fl$_3$**) (M_n > 30000 g/mol) was prepared (see St-Fl$_3$-2). At the moment, more vigorous purification of **St-Fl$_3$** is essential to examine the anionic polymerization behavior in detail, although the preliminary result strongly indicated occurring of the living anionic polymerization of **St-Fl$_3$**.

Similar to the case of poly(**St-Fl**), the absolute molecular weights of poly(**St-Fl$_2$**) as well as poly(**St-Fl$_3$**) by SEC−RALLS were observed to be always higher than those calculated by SEC using standard polystyrene calibration curve. Again, the presence of the fluorene dimer and trimer as side chains may affect on the hydrodynamic volumes in THF.

Block Copolymerization of St-Fl or St-Fl$_2$ with Styrene. In order to further examine the living nature of the anionic

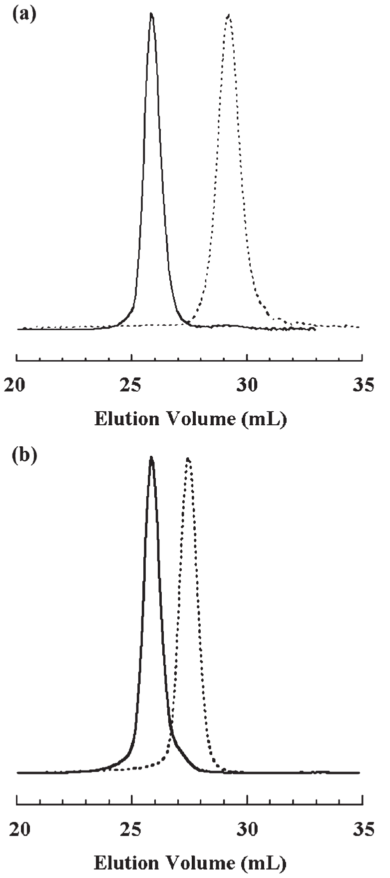


Figure 4. SEC curves of (a) poly(**St-Fl**)-*block*-polystyrene (solid line) and base poly(**St-Fl**), (dash line) (b) polystyrene-*block*-poly(**St-Fl**) (solid line) and base polystyrene (dash line).

polymerization of **St-Fl**, a sequential block copolymerization of **St-Fl** with styrene was performed. The first stage polymerization of **St-Fl** was carried out in THF with *sec*-BuLi at −78 °C for 3 h and an aliquot of the base polymer was sampled to measure the M_n and M_w/M_n values. Then, styrene was added to the reaction mixture to polymerize under the same conditions (Scheme 3).[41]

The SEC profiles of the block copolymerization products are shown in Figure 4a.

As can be seen, the SEC peak of the first stage polymer completely shifts toward a higher molecular weight side and the polymer obtained at the second stage polymerization exhibits a narrow monomodal distribution without the presence of homopolymer of **St-Fl**. The molecular weight and composition measured by RALLS−SEC and ^{1}H NMR as listed in Table 2 agreed well with those calculated from the feed ratios. These analytical results clearly indicate that the living polymer of **St-Fl** is completely stable under the conditions in THF at −78 °C and quantitatively initiates the polymerization of styrene to afford the poly(**St-Fl**)-*block*-polystyrene with well-defined and expected structures.

The block copolymerization with a reverse addition sequence, i. e., styrene followed by **St-Fl**, was also carried out under the same conditions. In this polymerization, the orange red color of the polystyryllithium was immediately changed to the dark blue color characteristic to the propagating chain-end anion derived from **St-Fl**. As is expected, the observed molecular weight and composition of the resulting block copolymer were consistent with the calculated values as listed in Table 2. The block copolymer showed a narrow monomodal SEC distribution without any shoulder and tailing (see Figure 4b). Thus, the expected block copolymer, polystyrene-*block*-poly(**St-Fl**), was also successfully prepared. Based on such block copolymerization results, the anionic polymerization behavior of **St-Fl** is considered to be very similar to that of styrene in reactivities of both monomer and propagating chain-end anion. This is surprising if the π-conjugation through the styrene to fluorene skeletons is present and will be discussed later.

Table 3. Solubility of St-Fl, St-Fl$_2$, St-Fl$_3$, and Polystyrene [a,b]

	poly(**St-Fl**)	poly(**St-Fl$_2$**)	poly(**St-Fl$_3$**)	polystyrene
hexane	S	S	S	I
cyclohexane	S	S	S	S
benzene	S	S	S	S
toluene	S	S	S	S
ether	S	S	S	I
THF	S	S	S	S
chloroform	S	S	S	S
acetone	Sw	I	I	I
DMF	I	I	I	S
DMSO	I	I	I	I
methanol	I	I	I	I
isopropanol	I	I	I	I

[a] M_n of polymers are 11500, 10200, 12000, and 11000 (g/mol) for poly(**St-Fl**), poly(**St-Fl$_2$**), poly(**St-Fl$_3$**), and polystyrene, respectively. [b] S: soluble. I: insoluble. Sw: swelling.

Table 4. Viscosity constants K and α of poly(St-Fl) and Polystyrene [a]

solvent	temperature [°C]	polymer	$K \times 10^3$ [mL/g]	α
toluene	30	poly(**St-Fl**)	26.6	0.55
toluene	30	polystyrene	8.81	0.75
cyclohexane	35	poly(**St-Fl**)	34.1	0.49
cyclohexane	35	polystyrene	86.0	0.50
THF	25	poly(**St-Fl**)	21.8	0.60
THF	25	polystyrene	13.6	0.71

[a] Constants of the Mark−Houwink−Sakurada equation $[\eta] = KM^{\alpha}$.

A sequential block copolymerization of **St-Fl$_2$** with styrene was carried out in THF with *sec*-BuLi at −78 °C. The resulting block polymer was observed to have a narrow monomodal SEC distribution and predictable molecular weight and composition, clearly indicating the formation of poly(**St-Fl$_2$**)-*block*-polystyrene with the expected structures. Similarly, the block copolymerization of styrene first followed by **St-Fl$_2$** gave a well-defined pure diblock copolymer, polystyrene-*block*-poly(**St-Fl$_2$**). These block copolymerization results are also summarized in Table 2. ^{1}H NMR spectra of (a) polystyrene-*block*-poly(**St-Fl**) and (b) polystyrene-*block*-poly(**St-Fl$_2$**) are shown in Figure S4. The successful formation of both AB and BA diblock copolymers strongly indicates that the anionic polymerization of **St-Fl$_2$** is very similar to styrene in reactivities of monomer and propagating chain-end-anion. The living nature of the polymerization of **St-Fl$_2$** was also confirmed by the successful formation of AB diblock copolymer.

We first thought that the fluorene moieties are π-conjugated through the styrene skeletons in both **St-Fl** and **St-Fl$_2$** and therefore the two monomers are more reactive than styrene and their chain-end anions are less reactive than polystyryl anion. However, the block copolymerization results demonstrated that both **St-Fl** and **St-Fl$_2$** behaved almost the same as styrene in anionic polymerization. This indicates that the styrene and fluorene skeletons are not on the same plane possibly due to steric bulkiness and thereby nonconjugated each other. This finding is very important and indicative in the anionic polymerization of the monomers with bulky π-conjugated moieties like **St-Fl** and **St-Fl$_2$**.

Solution and Thermal Properties of Poly(St-Fl) and Poly(St-Fl$_2$). Solubilities of the poly(**St-Fl**) and poly(**St-Fl$_2$**) herein prepared were listed in Table 3.

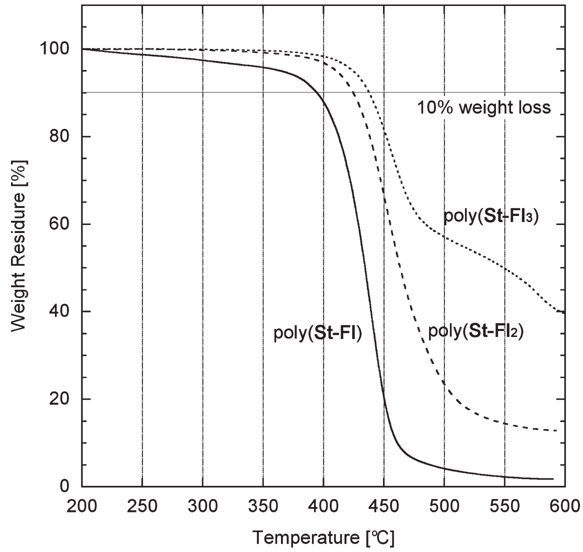


Figure 5. TGA curves of poly(**St-Fl**), poly($\mathbf{St\text{-}Fl_2}$), and poly($\mathbf{St\text{-}Fl_3}$) at a heating rate of 10 °C/min under nitrogen atmosphere.

Table 5. Glass Transition Temperature (T_g) of St-Fl, $\mathbf{St\text{-}Fl_2}$, $\mathbf{St\text{-}Fl_3}$, and Polystyrene

polymer	M_n [g/mol]	T_g [°C]
poly(**St-Fl**)	4990	69.2
poly(**St-Fl**)	11500	74.5
poly(**St-Fl**)	43500	81.2
poly(**St-Fl**)	177000	81.3
poly($\mathbf{St\text{-}Fl_2}$)	6700	78.4
poly($\mathbf{St\text{-}Fl_2}$)	54000	78.6
polystyrene	12000	105.0

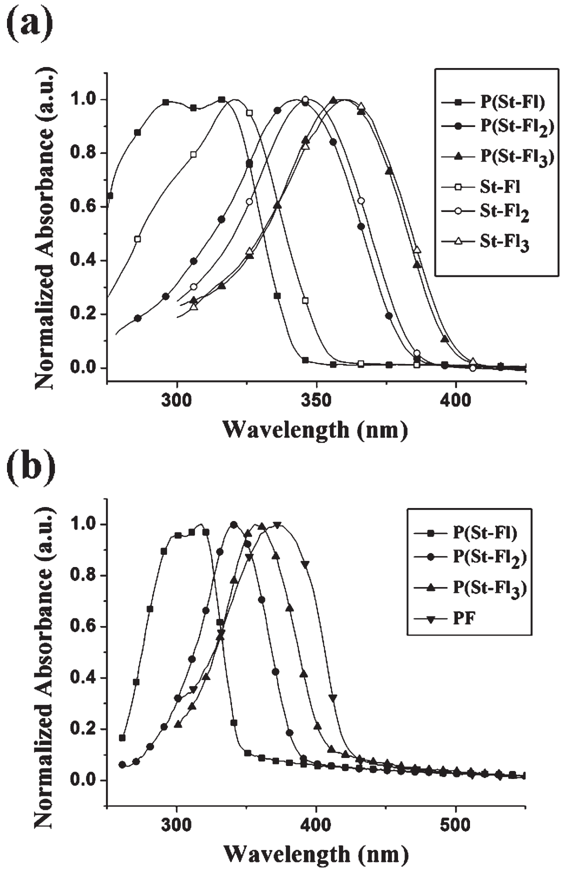


Figure 6. Absorption spectra of (a) chloroform solutions of $\mathbf{St\text{-}Fl_n}$ and poly($\mathbf{St\text{-}Fl_n}$) (n = 1 - 3) and (b) poly($\mathbf{St\text{-}Fl_n}$) films (n = 1 - 3) and PF film.

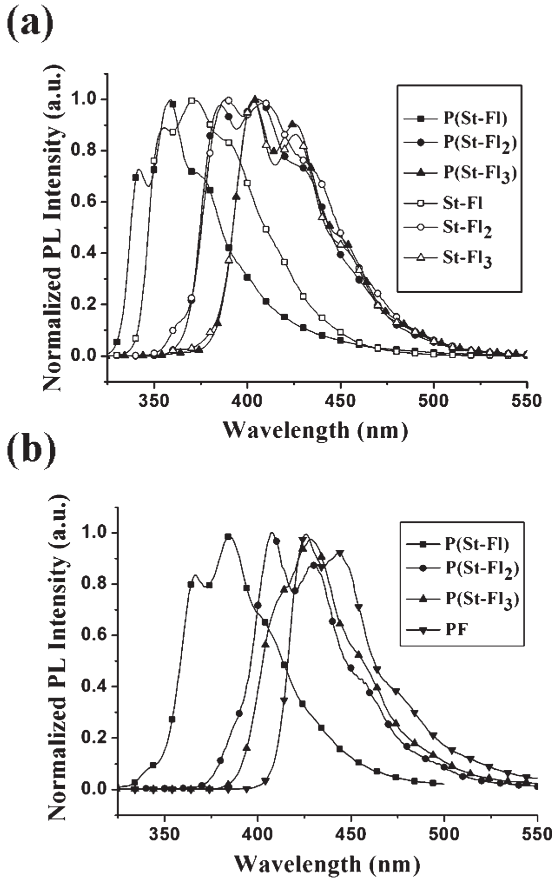


Figure 7. Photoluminescence (PL) spectra of (a) chloroform solutions of $\mathbf{St\text{-}Fl_n}$ and poly($\mathbf{St\text{-}Fl_n}$) (n = 1−3) and (b) poly($\mathbf{St\text{-}Fl_n}$) films (n = 1−3) and PF film.

As a reference, the data for polystyrene were added to this table. Both the polymers are soluble in common aliphatic and aromatic hydrocarbons such as hexane, cyclohexane, benzene, and toluene, diethyl ether, THF, chloroform, but swollen in acetone. On the other hand, they are insoluble in polar solvents like *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), methanol, and ethanol. Dissolving these polymers in hexane and diethyl ether in which polystyrene is insoluble may possibly be attributed to the presence of the two hexyl moieties in fluorene ring.

As mentioned above, the fluorene moieties may have influence on hydrodynamic volumes of the polymers. Since there was significant difference of the molecular weights determined between by SEC−RALLS and by SEC using polystyrene calibration curve and the polymers with a wide molecular weight range were prepared in this study, the intrinsic viscosities and molecular weights (M_w values) of poly(**St-Fl**) were correlated by the Mark−Houwink−Sakurada equation, $[\eta] = KM^{\alpha}$ in toluene at 30 °C, in cyclohexane at 35 °C, and in THF at 25 °C, respectively. Under either of the conditions, good-straight-line plots of log $[\eta]$ versus log $[M_w]$ were obtained using samples of the polymers listed in Table 1. The results are listed in Table 4.

The α value was 0.55 in toluene at 30 °C, while 0.72 was reported as the α value of polystyrene under the same conditions. Similarly, the α value of poly(**St-Fl**) was found to be 0.60 in THF at 25 °C, being lower than that of polystyrene (0.75). These results indicate that poly(**St-Fl**) chains are moderately coiled and somewhat compacted than polystyrene both in THF and toluene. As mentioned above, the M_n values of poly(**St-Fl**) estimated by SEC using

Table 6. Photophysical Properties of St-Fl, St-Fl$_2$, St-Fl$_3$, and Their Homopolymers

materials	UV−vis λ_{max}^{abs}, solution (nm)[a]	UV−vis λ_{max}^{abs}, film (nm)	PL λ_{max}^{PL}, solution (nm)	PL λ_{max}^{PL}, film (nm)
St-Fl	320		354, 371	
St-Fl$_2$	346		388, 409	
St-Fl$_3$	360		403, 426	
Poly(**St-Fl**)	296, 313	300, 317	342, 358	365, 384
Poly(**St-Fl$_2$**)	342	343	384, 406	407, 431
Poly(**St-Fl$_3$**)	359	358	403, 425	412, 428

[a] In chloroform dilute solution.

polystyrene calibration were always lower than the absolute values determined by RALLS. The difference between these two values can be reasonably explained in consideration of compact hydrodynamic volume of poly(**St-Fl**) toward polystyrene under the SEC measurement condition. The α value was 0.49 in cyclohexane at 35 °C and hence this condition is possibly a θ condition for poly(**St-Fl**) similar to the case of polystyrene.

The thermal decomposition temperatures (T_d, 10% weight loss temperature) of the studied polymers, poly(**St-Fl**) (M_n = 11500 g/mol), poly(**St-Fl$_2$**) (M_n = 10200 g/mol), and poly(**St-Fl$_3$**) (M_n = 12000 g/mol), under nitrogen atmosphere were found to be 395, 425, and 438 °C, respectively, as shown in Figure 5.

Obviously, the thermal stability was enhanced with increasing the number of fluorene unit in this series of polymers. The T_d values of the block copolymers, poly(**St-Fl**)-*block*-polystyrene and poly(**St-Fl$_2$**)-*block*-polystyrene, are similar to those of the above homopolymers as shown in Figure S5. The glass transition temperatures (T_g) of the poly(**St-Fl**)s and poly(**St-Fl$_2$**)s are listed in Table 5.

In the case of poly(**St-Fl**), the T_g value was increased with increasing the molecular weight and finally reached to around 81 °C. This trend is similar to the case of polystyrene. On the other hand, rather surprisingly, the T_g value of poly(**St-Fl$_2$**) was not affected by the molecular weight and nearly constant to be around 78 °C in the M_n range from 5000 to 50000 g/mol. Both the T_g values are somewhat lower than that (T_g = 105 °C) of polystyrene, possibly due to the two hexyl chains in the fluorene moiety.

Photophysical Properties. Figure 6a and Table 6 show the absorption spectra of the monomers, **St-Fl**, **St-Fl$_2$**, **St-Fl$_3$**, and the corresponding polymers, poly(**St-Fl**) (M_n = 11500 g/mol, St-Fl-2, Table 1), poly(**St-Fl$_2$**) (M_n = 10200 g/mol, St-Fl$_2$-3, Table 1), and poly(**St-Fl$_3$**) (M_n = 12000 g/mol, St-Fl$_3$-1, Table 1) in chloroform, which have peak maxima of 320, 346, 360, 313, 342, and 359 nm, respectively.

The absorption peak is attributed to the $\pi-\pi^*$ transition of the fluorene moiety and progressively red-shifted with increasing the fluorene chain length The slightly blue-shifted peak maximum of the poly(**St-Fl**) in comparison with its monomer **St-Fl** is probably due to the twisted conformation of polymer backbone. However, such a blue-shift is reduced with increasing the fluorene unit. The UV−vis absorption spectra of the studied polymer films, poly(**St-Fl**), poly(**St-Fl$_2$**) and poly(**St-Fl$_3$**), are observed at 317, 343, and 358 nm, respectively, as shown in Figure 6b. The red-shifted spectra with increasing the fluorene chain length suggest the enhancement on the π-conjugation. It would expect that the absorption peak maximum would approach to the parent poly(fluorene) (**PF**, 372 nm in Figure 6b) if the fluorene chain length continues to increase.

The emission peak maxima of **St-Fl**, **St-Fl$_2$**, **St-Fl$_3$** and the corresponding polymers, poly(**St-Fl**), poly(**St-Fl$_2$**) and poly(**St-Fl$_3$**) in chloroform are (354, 371), (388, 409), (403, 426), (342, 358), (384, 406), and (403, 425) nm, respectively, as shown in Figure 7a and Table 6.

The well-resolved fluorescence bands shown in Figure 7 could be considered due to the different energy levels of intra chain singlet transitions.[45−48] Similar to the absorption spectra, the difference on the emission spectra between **St-Fl** and poly(**St-Fl**) is larger than the other two sets, which is probably due to the conformation effect. The progressively red-shift on the emission with increasing the fluorene chain length is similar to that in the optical absorption.

The emission peak maxima of poly(**St-Fl**), poly(**St-Fl$_2$**), poly(**St-Fl$_3$**), and PF films are observed at (365, 384), (407, 431), (412, 428), and (426, 443), respectively, as shown in Figure 7b. As expected, the emission spectrum suggests the well-resolved vibronic structure. The emission peak maximum around 431 or 428 nm is probably due to 0−0 transition, as reported in the literature.[45−48] Although long wavelength emission maxima of poly(**St-Fl$_2$**) and poly(**St-Fl$_3$**) were close to each other, the relative peak intensity of the 428/412 nm (poly(**St-Fl$_3$**)) to 431/407 nm (poly(**St-Fl$_2$**)) was higher. On the other hand, the emission spectrum of **PF** shows the peak maxima at 426 and 443 with a shoulder around 484 nm, which are suggested to be 0−0, 0−1, and 0−2 transition. The shoulder of the **PF** extended to be more than 500 nm and was wider than those of poly(**St-Fl$_2$**) and poly(**St-Fl$_3$**), strongly suggesting that the side-chain polymer with oligo(fluorene) could reduce aggregation. A further study on the morphology and luminescence properties would be carried in the future.

Conclusions

The living anionic polymerization of the styrene monomers *p*-substituted with mono- and di(9,9-dihexylfluorene) moieties, **St-Fl** and **St-Fl$_2$**, was successfully performed to obtain the corresponding polymers with predictable molecular weights and narrow molecular weight distributions (M_w/M_n < 1.08). Well-defined and expected AB and BA block copolymers of **St-Fl** or **St-Fl$_2$** with styrene were also prepared by sequential addition of the corresponding monomers in THF at −78 °C. The successful formation of AB diblock copolymers clearly indicates the living nature of the anionic polymerization of **St-Fl** and **St-Fl$_2$**. These results clearly show that the 9,9-dihexylfluorene moieties are completely stable in the presence of **St-Fl** and **St-Fl$_2$**-derived chain-end carbanions. The anionic polymerization of **St-Fl$_3$** was also indicative to proceed in a living manner but with an unpredictable molecular weight. Thus, the present study demonstrates that styrene derivative with well-defined bulky π-conjugated moieties like oligo(fluorene) could successfully undergo living anionic polymerization. Furthermore, it has been found that the anionic polymerization behavior of **St-Fl** or **St-Fl$_2$** is very similar to that of styrene in reactivities of monomer(s) and propagating chain-end anion(s), indicating that the styrene to fluorine moieties are not π-conjugated. The viscosity behaviors and thermal properties on T_d and T_g of the resulting polymers have been examined. The photophysical properties of the studied polymer films have been observed to be progressively red-shifted as the fluorene chain length increased and exhibited reduced aggregation/excimer emission in comparison with that of parent poly(fluorene).

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Supporting Information Available: Text giving the synthetic details for 2-bromo-9,9-dihexylfluorene (**2**), 9,9-dihexylfluorenyl-2-boronic acid (**3**), 9,9,9′,9′-tetra-*n*-hexyl-2,2’-bifluorenyl-7-boronic acid (**4**), 7-bromo-9,9,9′’,9′-tetrahexyl-2,2′-bifluorene (**5**), and 7-bromo-9,9,9′,9′,9′′,9′′-hexa-*n*-hexyl-2,7′;2′,7′′-terfluorene (**6**) and figures showing the characteristic color of the reaction system observed for **St-Fl** polymerization. ^{13}C NMR spectra of **St-Fl**, poly(**St-Fl**), **St-Fl$_2$**, and poly(**St-Fl$_2$**) in CDCl$_3$. ^{1}H NMR spectra of polystyrene-*block*-poly(**St-Fl**) and polystyrene-*block*-poly(**St-Fl$_2$**) in CDCl$_3$, and TG curves of polystyrene-*block*-poly(**St-Fl**) and polystyrene-*block*-poly(**St-Fl$_2$**). This material is available free of charge via the Internet at http://pubs.acs.org.

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