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Synthesis and Characterization of Polyfluorenes with Light-Emitting Segments

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ABSTRACT: Two new polymers consisting of poly(9-(2′-ethylhexyl)-9-hexylfluorene) (EHH-PF) with a small amount of substituted poly(*p*-phenylenevinylene) (PPV) segments have been synthesized and characterized. The synthetic route was designed to allow the incorporation of only one (or zero) PPV segments per polymer chain. Photoluminescence measurements showed that energy transfer from the PF segments to the more narrow band-gap PPV segments did occur, both in solution and in film. In the solid state, all emissions were detected from the PPV segments with photoluminescence quantum yields up to 68%. One of the polymers has been used as the active material in a microcavity laser device. The threshold for lasing is 2 μJ/cm^2.

Introduction

Although conjugated polymers had been known for a long time, it was not until 1977 it was found that they showed high electrical conductivity.[1] The simplest conjugated polymer, and the first to show high conductivity (in the doped state), is polyacetylene (PA).[1] However, the use of PA has been limited since it is neither processable (fusible or soluble) nor stable in air. By using aromatic rings in the polymer backbone,[2−6] polymers with increased stability against oxidation in air in both the doped and undoped state were found. Fully conjugated polymers without substituents are insoluble and therefore have found limited use. To achieve processability, one can use either soluble nonconjugated prepolymers or conjugated polymers with flexible side chains. In addition to processability, flexible side chains can cause sterical hindrance and thereby provide a means to control the effective conjugation length and thus the color of the emitted light in devices.[7,8] One can also achieve red shift or blue shift of the emitted light by introducing electron-donating[9] or electron-withdrawing[10,11] groups, respectively, on the conjugated backbone.

Since the discovery of electroluminescence (EL) in light-emitting diodes (LEDs) of poly(*p*-phenylenevinylene) (PPV) in 1990,[12] much effort has been devoted to the use of conjugated polymers as the active substances in photonic devices. Today, PPV and its derivatives and polythiophenes (PTs),[13] poly(*p*-phenylenes) (PPPs),[14,15] and polyfluorenes (PFs)[16,17] are the most frequently used conjugated polymers in light-emitting diodes (LEDs). During the past years, new applications using conjugated polymers as the active substance have emerged. Among these are light-emitting electrochemical cells (LECs),[18,19] photovoltaic diodes,[20,21] and microcavity laser devices.[22−24]

Since the discovery of photopumped lasing in conjugated polymers in the solid state in 1996,[22,23] a great number of publications on the same theme have followed. The presence of a Stokes shift in conjugated polymers is an advantage in polymer lasers, as the red-shifted emission will meet little self-absorption. So far, only optically driven polymer lasers are found; electrically driven polymer lasers are yet to be constructed although electrically driven lasers of organic molecular crystals recently have been prepared.[25] To obtain an electrically pumped polymer laser, high EL yield is crucial. Recently, PFs have attracted a lot of interest since they are known to have high photoluminescence (PL) and EL efficiencies.[26−32] One of the important items to make more efficient polymer lasers is the synthesis of suitable conjugated polymers.

Here we report the synthesis and characterization of two polymers with properties suitable for microcavity laser devices. The polymers are based on poly(9-(2′-ethylhexyl)-9-hexylfluorene) (EHH-PF) with a small amount of a low band-gap structure (Scheme 1). The synthetic route was designed to allow the incorporation of only one low band-gap segment per polymer chain. Having the low band-gap segment in a low concentration lowers the probability of interchain exciton diffusion, which should give high PL yield materials. A low concentration of the low band-gap segments also increases the probability that all these segments are in the excited state at the same time. This is necessary for lasing to occur.[33] When excited, most of the light will be absorbed by the EHH-PF segments and then transferred to the more narrow band-gap segments (emitting segments). This will separate the absorption and emission spectra and thus lower the undesirable self-absorption.

Other approaches to achieve energy transfer is to use polymer blends or polymers end-capped with low band-gap segments. The drawback with such systems is phase separation with incomplete energy transfer as a consequence and the formation of aggregates which do not give well-defined emitting species. Another way is to use randomly polymerized copolymers with emitting seg-

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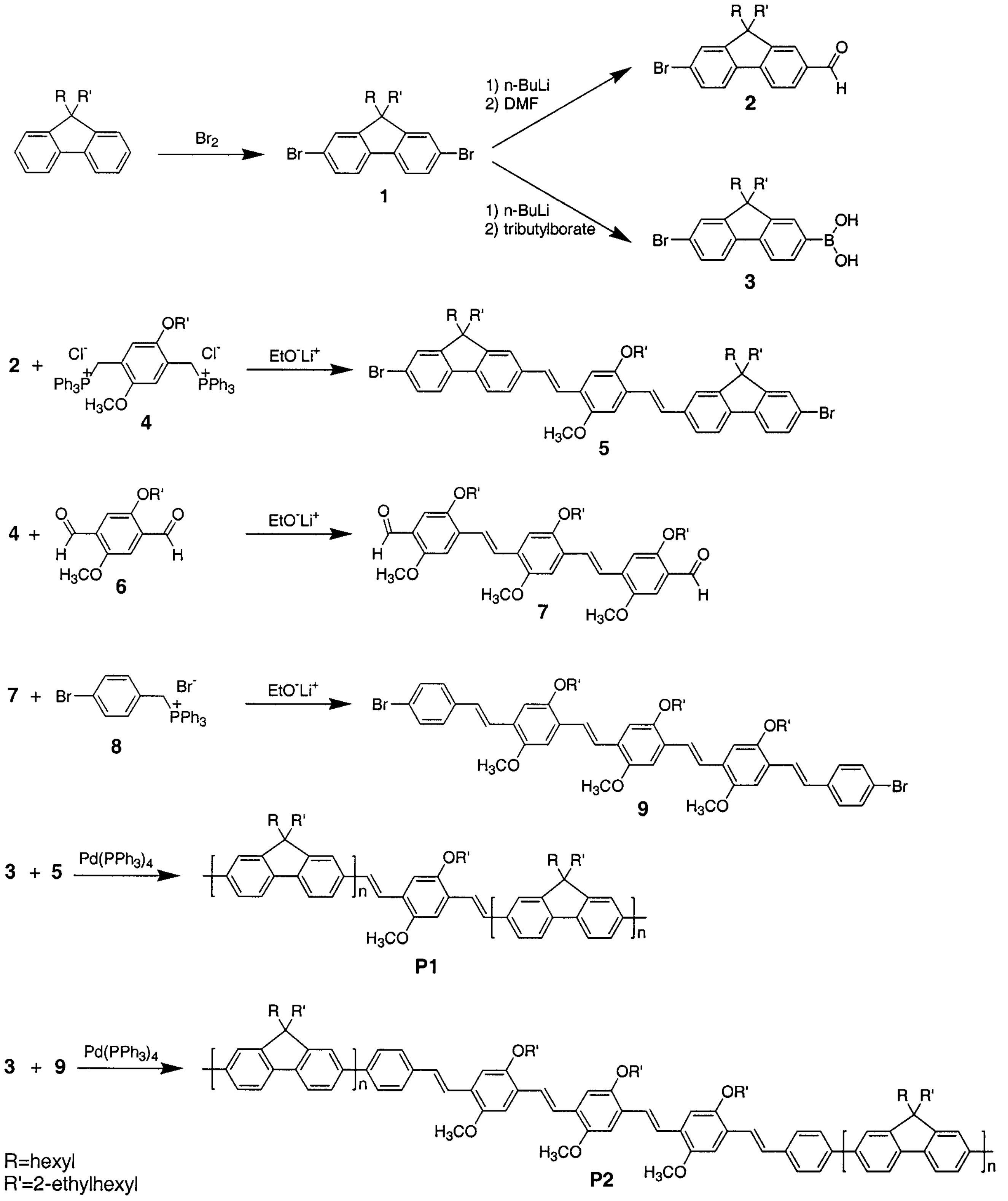
Scheme 1. Synthesis and Chemical Structures of P1 and P2



ments. However, these systems often give regions with more than one emitting segment next to each other which also results in a variation of the band gaps of the emitting segments. Our polymers were designed to have well-defined emitting segments with the lowest possible probability of aggregate formation.

Experimental Section

Measurements. NMR spectra were recorded on a Varian 400 MHz spectrometer with tetramethylsilane as internal reference. Mass spectra were recorded using a VG ZabSpec. Unless otherwise stated electron impact was used as the ionization method. When fast atom bombardment (FAB) was used, the compound to be investigated was dissolved in 3-nitrobenzyl alcohol (NBA), and a beam of Cs ions was used to ionize the sample. Molecular weights of the polymers were determined by size-exclusion chromatography (SEC) by a Waters 150 CV using SDVB columns at 25 °C. The calibration was made with a series of monodispersed polystyrene standards in THF. UV−vis spectra were recorded on a Lambda 9 spectrometer. The photoluminescence (PL) spectra were measured by exciting the polymer samples with monochromatic light from a tungsten lamp, and the emission was measured with an Oriel Instaspec IV diode matrix spectrometer. An integrating sphere made by Labsphere was used to measure the PL efficiencies. Solutions used to detect UV−vis spectra and PL spectra were prepared from the polymer dissolved in $CHCl_3$. UV−vis spectra and PL spectra in the solid state were carried out on films spin-coated onto glass slides from chloroform solution. Melting points were determined using a Mettler FP90 instrument with an Olympus BH-2 microscope. Dielectric mirrors were purchased from Melles Griot and were optimized for high reflectivity ($R > 99\%$) at 530 nm. The total polymer thickness in the microcavity was 170 nm (measured with a Sloan-Dektak 3030 profilometer).

Materials. Unless otherwise stated, reagents were purchased from Aldrich and used without further purification. Phosphonium salts **4**[34] and **8**[35] and compound **6**[36] were prepared according to literature procedures. Diethyl ether and THF were distilled over sodium and bensophenone. DMF was dried by azeotropic distillation with benzene, dried over BaO, and finally distilled at reduced pressure.

2,7-Dibromo-9-(2′-ethylhexyl)-9-hexylfluorene (1). To a stirred solution of 9-(2′-ethylhexyl)-9-hexylfluorene (19.5 g, 53.8 mmol) in DMF (200 mL) was added an excess of bromine (approximately 40 g). The solution was kept at room temperature for 30 min, and $Na_2S_2O_5$ (10%) was added to quench the reaction. Diethyl ether and 2 M HCl were added, and the two phases were separated. The water phase was extracted once with diethyl ether. The resulting organic phases were combined and washed with 2 M HCl and water. The organic extracts were dried over Na_2SO_4 and evaporated to yield an oil that was heated to reflux in a mixture of methanol and ethanol (1/1). The resulting precipitate was filtered off and washed with cold ethanol to yield 21.5 g (77%) of 2,7-dibromo-9-(2′-ethylhexyl)-9-hexylfluorene as colorless crystals; mp 65−66 °C. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.53 (t, 6H), 0.68−0.94 (m, 11H), 0.77 (t, 3H), 1.00−1.14 (m, 6H), 1.86−1.96 (m, 4H), 7.43 (d, 1H), 7.44−7.47 (m, 3H), 7.50 (s, 1H), 7.52 (d, 1H). HRMS: Calcd for $C_{27}H_{36}{}^{79}Br_2$: 518.118. Found: 518.111.

2-Bromo-9-(2′-ethylhexyl)-9-hexylfluorene-7-aldehyde (2). To a stirred solution of **1** (6.0 g, 11.5 mmol) in absolute ether (80 mL) under nitrogen was added *n*-BuLi (7.2 mL, 1.6 M in hexane, 11.5 mmol) at −25 °C. The solution was allowed to warm to room temperature for 1 h. The mixture was then cooled to 0 °C, and DMF (4 mL) was added. The solution was again allowed to warm to room temperature for 1 h before it was treated with 2 M HCl (10 mL). The two phases were separated, and the water phase was extracted twice with diethyl ether. The resulting organic phases were combined and washed with 1 M HCl and water. The organic extracts were dried over Na_2SO_4, evaporated, and purified with column chromatography (silica gel, the byproducts were eluted with pentane and the product was eluted with dichloromethane) to afford 4.85 g (90%) of 2-bromo-9-(2′-ethylhexyl)-9-hexylfluorene-7-aldehyde as a colorless solid; mp 50−52 °C. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.47 (t, 3H), 0.53 (t, 3H), 0.60−0.91 (m, 11H), 0.74 (t, 3H), 0.97−1.12 (m, 6H), 1.9−2.1 (m, 4H), 7.50 (dd, 1H), 7.53 (dd, 1H), 7.63 (d, 1H), 7.80 (d, 1H), 7.85 (d, 1H), 7.87 (d, 1H), 10.05 (s, 1H). HRMS: Calcd for $C_{28}H_{37}{}^{79}BrO$: 468.203. Found: 468.219.

2-Bromo-9-(2′-ethylhexyl)-9-hexylfluorene-7-boronic Acid (3). To a stirred solution of **1** (2.5 g, 4.80 mmol) in absolute ether (25 mL) under nitrogen was added *n*-BuLi (3.0 mL, 1.6 M in hexane, 4.80 mmol) at −25 °C. The reaction mixture was allowed to warm to room temperature for 1 h. The solution was then cooled to −78 °C, and tributyl borate (1.5 mL, 5.56 mmol) was added dropwise. The mixture was allowed to warm to room temperature for 3 h before the reaction was quenched with the addition of water. The two phases were separated, and the water phase was extracted with two portions of diethyl ether. The combined organic extracts were washed successively with three portions of 1 M NaOH and water, dried over Na_2SO_4, and evaporated. The resulting oil was purified with column chromatography (silica gel, the byproducts were eluted with pentane and the product was eluted with diethyl ether) to yield 1.90 g (82%) of 2-bromo-9-(2′-ethylhexyl)-9-hexylfluorene-7-boronic acid as a colorless solid; mp 38−39 °C. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.46−1.14 (m, 25H), 1.52 (m, 1H), 1.90−2.22 (m, 4H), 7.51 (dd, 1H), 7.56 (d, 1H), 7.68 (d, 1H), 7.84 (d, 1H), 8.21 (s, 1H), 8.28 (d, 1H). HRMS: Calcd for $C_{27}H_{38}B^{79}BrO_2$: 484.215. Found: 484.198.

Compound 5. To a stirred solution of **2** (0.150 g, 0.319 mmol) and **4** (0.137 g, 0.160 mmol) in ethanol (10 mL, 99.7%) was added dropwise EtOLi/EtOH (5 mL, 7 mg Li metal/5 mL EtOH) over 30 min. After 19 h at room temperature, the reaction was quenched with the addition of brine and diethyl ether. The two phases were separated, and the water phase was extracted with two portions of diethyl ether. The resulting organic phases were combined and washed with two portions of water. The organic extracts were dried over Na_2SO_4, evaporated, and purified with column chromatography (silica gel, dichloromethane as eluent) to afford 0.134 g (72%) of compound **5** as a bright yellow oil. FABHRMS (NBA/Cs): Calcd for $C_{73}H_{98}{}^{79}Br_2O_2$: 1164.593. Found: 1164.620.

Compound 7. To a stirred solution of **4** (0.400 g, 0.466 mmol) and **6** (0.409 g, 1.40 mmol) in ethanol (40 mL, 99.7%) was added dropwise EtOLi/EtOH (15 mL, 19.9 mg of Li metal/15 mL of EtOH) over 30 min. The solution was kept at room temperature for 21 h. Brine and diethyl ether were added, and the two phases were separated. The water phase was extracted with two portions of diethyl ether. The resulting organic phases were combined and washed with two portions of water. The organic extracts were dried over Na_2SO_4, evaporated, and purified with column chromatography (silica gel, dichloromethane as eluent) to afford 0.160 g (42%) of compound **7** as a red oil. FABHRMS (NBA/Cs): Calcd for $C_{51}H_{72}O_8$: 812.533. Found: 812.539.

Compound 9. To a stirred solution of **7** (75 mg, 92.3 μmol) and **8** (0.133 g, 0.277 mmol) in ethanol (5 mL, 99.7%) was added dropwise EtOLi/EtOH (5 mL, 6.0 mg of Li metal/5 mL of EtOH) over 30 min. The solution was kept at room temperature for 18 h. Brine and diethyl ether were added, and the two phases were separated. The water phase was extracted with two portions of diethyl ether. The resulting organic phases were combined and washed with two portions of water. The organic extracts were dried over Na_2SO_4, evaporated, and purified with column chromatography (silica gel, dichloromethane as eluent) to afford 56 mg (54%) of compound **9** as a red oil. FABHRMS (NBA/Cs): Calcd for $C_{65}H_{82}{}^{79}Br_2O_6$: 1116.448. Found: 1116.451.

Polymer 1 (P1). To a stirred solution of **3** (0.200 g, 0.412 mmol) and **5** (24.0 mg, 20.6 μmol) in absolute THF (5.0 mL) under nitrogen was added $Pd(PPh_3)_4$ (24 mg, 21 μmol) and 1 M $NaHCO_3$ (2.0 mL). After 3 days at reflux, the resulting polymer was precipitated in methanol. The crude polymer was collected, washed with methanol, and dissolved in chloroform. The resulting solution was filtered and stirred successively with ammonia for 1 h (repeated two more times) and water for 1 h. The chloroform solution was added dropwise to methanol to precipitate the polymer. The precipitated polymer was collected, washed with methanol, and dried under high vacuum to yield 128 mg (75%) of polymer **P1**.

Polymer 2 (P2). To a stirred solution of **3** (0.200 g, 0.412 mmol) and **9** (6.5 mg, 5.8 μmol) in absolute THF (5.0 mL) under nitrogen was added $Pd(PPh_3)_4$ (24 mg, 21 μmol) and 1 M $NaHCO_3$ (2.0 mL). After 3 days at reflux, the resulting polymer was precipitated in methanol. The crude polymer was collected, washed with methanol, and dissolved in chloroform. The resulting solution was filtered and stirred successively with ammonia for 1 h (repeated two more times) and water for 1 h. The chloroform solution was added dropwise to methanol to precipitate the polymer. The precipitated polymer was collected, washed with methanol, and dried under high vacuum to yield 132 mg (85%) of polymer **P2**.

Results and Discussion

Synthesis. The polymers were prepared according to Scheme 1. The starting material, 9-(2′-ethylhexyl)-9-

Table 1. Polymerization Yields, Molecular Weights, and Absorption and PL Data for P1 and P2

polymer	yield (%)	M_n/M_w	abs_{max} (nm) $CHCl_3$	PL_{max} (nm) $CHCl_3$	η_{PL} (%) $CHCl_3$	abs_{max} (nm) film	PL_{max} (nm) film	η_{PL} (%) film
P1	75	6700/23300	376	414, 437, 482	75	373	485, 515	68
P2	85	7600/40600	380	414, 437	75	375	528	50

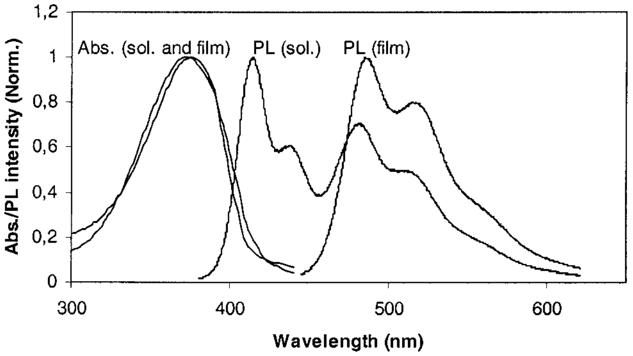


Figure 1. Absorption and PL spectra of **P1** in solution (sol.) and film.

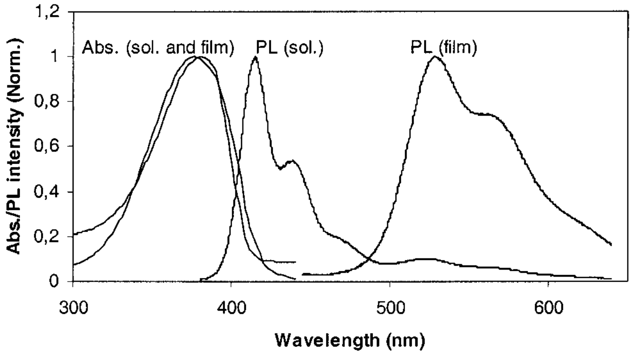


Figure 2. Absorption and PL spectra of **P2** in solution (sol.) and film.

hexylfluorene, was synthesized with a similar procedure as described in the literature.[16,17] Treatment of 9-(2′-ethylhexyl)-9-hexylfluorene with excess bromine gave 2,7-dibromo-9-(2′-ethylhexyl)-9-hexylfluorene. The yield of this reaction (77%) was comparable to a similar reaction described in the literature.[17] The reaction of 2,7-dibromo-9-(2′-ethylhexyl)-9-hexylfluorene with *n*-BuLi[37] followed by addition of DMF or tributyl borate yielded **2** (90%) or **3** (82%), respectively. The Wittig reaction of **2** and **4** with EtO^-Li^+ as base gave the emitting segment **5** in 72% yield. The Wittig reaction of **4** and an excess of **6** with EtO^-Li^+ as base gave **7**, which was further reacted in a second Wittig reaction with 4-bromobenzyltriphenylphosphonium chloride to yield the emitting segment **9** in 23% overall yield. Polymerization of the monomer **3** with the emitting segments **5** or **9** using the Suzuki coupling reaction[37,38] in THF afforded **P1** and **P2**, respectively, in good yields (75–85%) as shown in Table 1. Both polymers were soluble in THF and chloroform at room temperature. The molecular weights of **P1** ($\bar{M}_n$ = 6700, $\bar{M}_w$ = 23 300) and **P2** ($\bar{M}_n$ = 7600, $\bar{M}_w$ = 40 600) correspond to ~18 fluorene units and one emitting segment per polymer chain for both polymers. According to the SEC measurements, it is clear that there are no emitting segments in the polymer materials that have not been incorporated into the polymer backbones.

Since the monomer **3** has two different functional groups and the emitting segments **5** and **9** have two equal functional groups, the incorporation of only one (or zero) emitting segments per polymer chain can occur. Once a segment is incorporated in the growing polymer chain, both chain ends in the polymer have the same functionality, and addition of a second emitting segment is not possible. In Scheme 1, the structures of **7** and **9** are shown exclusively as head-to-tail. The occurrence of head-to-head couplings in the segments cannot be excluded.

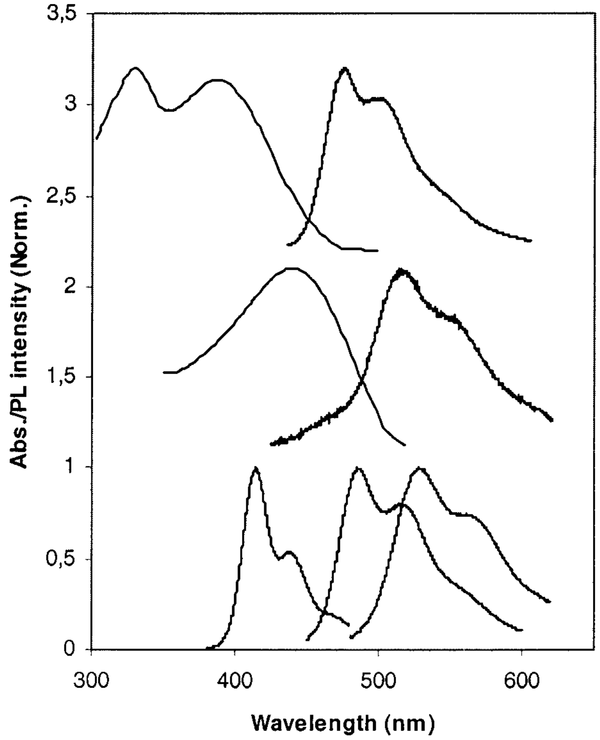


Figure 3. Absorption and PL spectra in solution of the emitting segments **5** (top) and **9** (middle). The bottom spectra show PL spectra in solution (very similar to solid state) of the fluorene part of the polymers (left) and the PL spectra of **P1** and **P2** in film.

Absorption and Photoluminescence Properties. The absorption and emission spectra in film and solution of **P1** and **P2** are shown in Figure 1 and Figure 2, respectively. As shown in the figures and in Table 1 there is almost no difference in absorption maxima for any of the polymers. Since the content of the emitting segments in the monomer feed was very low (5% for **P1** and 1.4% for **P2**), all detected absorption comes from PF part of the polymers. When excited, most of the light will be absorbed by the PF parts, and the created excitons will be transferred to the more narrow band-gap PPV segments. The good overlap of the photoluminescence of the fluorene part of the polymers with the absorption of the emitting segments (Figure 3) indicates that the energy transfer is of Förster type. As shown in Figures 1 and 2, this energy transfer is incomplete in solution. This is most pronounced for **P2**, where almost no emission is detected from the PPV segments. In films, though, all emissions are detected from the more narrow band-gap PPV segments. The fact that only a fraction of the emissions in solution come from the PPV segments can be due to several reasons. The polymers in solution may be twisted in a way that prevents exciton transfer, or the excited states may not be long-lived enough to allow complete exciton diffusion to the PPV segments. The fact that some polymer chains might lack emitting segments also contributes to some extent, since interchain exciton transfer is a much slower process in solution compared to film. As shown in Figure 3, the PL maxima of the polymers are somewhat red-shifted compared to the PL maxima of the emitting segments **5** and **9**. This shows that the actual emitting segments are extended also over the adjacent fluorene units. The photoluminescence efficiencies (η_{PL}) in solution for **5** and **9** are 80% and 50%, respectively. These are rather high values, keeping in mind that the segments contain bromine in both ends.

All emissions show clear vibronic fine structures, which indicates relatively ordered local structures. In films the η_{PL} for **P1** and **P2** are 68% and 50%, respectively, when excited at the polyfluorene maximum. One of the factors that limits the η_{PL} in the solid state of conjugated polymers is the rate of exciton transport to a defect in the polymer film, where nonradiative relaxation to the ground state can occur. It is well-known that excitons live long enough to diffuse a distance before relaxation to the ground state occurs.[7] High PL yield polymers can be achieved by the introduction of appropriate side chains, since separation of the polymer backbones partially can prevent interchain exciton transfer. Too large a separation of the polymer chains must be avoided, since this can cause too low mobility of charge carriers. In an electrically pumped polymer laser this would be adverse since this requires a high electroluminescence yield material. High η_{PL} can also be achieved by exciton confinement in a molecular quantum well. This requires the preparation of polymers with similar structures as for **P1** and **P2**, with segments of high and low band-gap energies. As for **P1** and **P2**, the incorporation of only one segment with lower band gap results in only one local energy minimum, which is advantageous since this lowers the probability of interchain exciton diffusion to an even lower extent. As a result, **P1** proved to have one of the highest photoluminescence quantum yields (68%) measured with an integrating sphere and reported in the literature.

The separation of the absorptions and emissions in the solid state lowers the undesirable self-absorption. Together with the high η_{PL} in films of both **P1** and **P2**, this makes the polymers attractive as the active substances in polymer microcavity lasers.

Characterization of the Microcavity Device. The idea of having two different side chains on the fluorenes was chosen for two reasons. Two different side chains should decrease the crystallinity in the polymers and reduce the formation of interchain aggregates.[39] It is desirable to have a low concentration of interchain aggregates since they are known to red-shift the emission,[40] which is a drawback when the polymers are to be used as lasing materials. Despite the two different side chains, our attempt to make a microcavity of **P2** failed due to the crystallinity. Once this polymer was introduced in a microcavity, it crystallized and the optical quality of the cavity was poor due to light scattering. The microcavity device structure shown in Figure 4 was made by spin-coating a solution of **P1** (8 mg of polymer/mL of $CHCl_3$) onto each mirror and pressing them together at 150 °C. Letting the device cool rapidly in air while maintaining the pressure, the two polymer films merged together. This formed a 0.5 cm in diameter large spot free from air. Excitation was made by frequency-doubling the output of an amplified Ti:Sa laser system giving 100 fs pulses at 400 nm with 5 kHz repetition rate. Figure 5 shows the PL of the cavity as the excitation energy pulse is increased from 1.2 to 5.9 μJ/cm^2. As a result of the separation of the absorption and emission in the solid state of **P1**, the low self-absorption resulted in a good lasing material with a threshold for lasing of 2 μJ/cm^2. The full width half-maximum (fwhm) of the peak was approximately 1 nm. Because of the liquid crystalline nature of **P1**, alignment of the polymers occurred when assembling the cavity. The most probable explanation is that small shear forces caused the orientation of the polymer when the warm polymer surfaces were pressed together. As a result of the alignment, the cavity showed anisotropy in absorption, refractive index, and emission. Both of the resonance modes, parallel and perpendicular to the polymer orientation, gave rise to lasing but at different thresholds. The anisotropy seen in the cavity could have a useful application in liquid crystal display applications. If the anisotropy could be increased, for instance by prealigned layers, the cavity could be tuned to give linearly polarized light with extremely high anisotropy. A detailed description of the microcavity properties and anisotropy effects is given in ref 41.

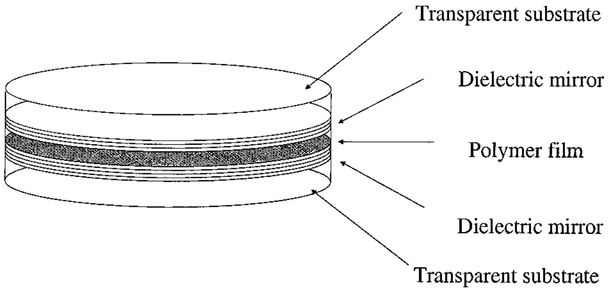


Figure 4. Schematic plot of the microcavity device.

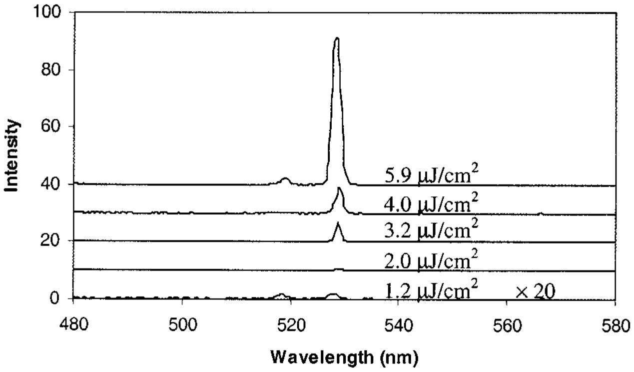


Figure 5. PL of the cavity as the incoming excitation pulse intensity is increased from 1.2 to 5.9 μJ/cm^2.

Conclusions

This study has shown that it is possible to synthesize polyfluorenes with only one (or zero) emitting segments per polymer chain. The investigated polymers showed high PL yields in the solid state, with all emission from the emitting segments. Polymers of this type are excellent lasing materials in microcavity devices due to the separation of the absorption and emission which lowers the undesirable self-absorption.

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