Synthesis and Characterization of Photo-Crosslinkable Polyfluorene with Acrylate Side-Chains

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ABSTRACT: A photo-crosslinkable polymer, poly[2,7-(9,9-dioctylfluorene)-*co*-2,7-(9-hexyl-9-(2-acrylate ethyl)-9H-fluorene)] (**P3**), was synthesized and the photo-crosslinkable acrylate groups were introduced into the side-chains of the polyfluorene derivative after its polymerization. This method avoids the possible crosslinkage of the crosslinkable groups on the monomers during polymerization in the traditional synthesis route by the polymerization of the monomers with the crosslinkable side-chains. The soluble and processable polymer **P3** could be crosslinked via the acrylate groups in its side-chains upon exposure to UV light in nitrogen atmosphere. The crosslinking was confirmed by IR spectroscopy: the IR peak of C═C bond at 1635 cm^{-1} decreased and that of the vinyl C—H bond at 742 cm^{-1} disappeared after the UV exposure. The absorption spectra of **P3** remain unchanged after crosslinking, but a longer wavelength emission at 517 nm appeared in the photoluminescent and electroluminescent spectra of the crosslinked **P3**, which could be attributed to the formation of keto defects during the photo crosslinking. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2336–2342, 2006

Key words: light-emitting diodes (LEDs); crosslinking; conjugated polymers

INTRODUCTION

Since the discovery of the electroluminescence (EL) of conjugated polymers in polymer light-emitting diode (PLED) by Burroughes and coworkers, conjugated polymers have attracted much attention because of their potential applications in flat panel displays and lighting technologies.[1,2] In comparison with inorganic and organic small molecule electroluminescent materials, conjugated polymers possess many advantages, such as extended π-conjugation, higher glass transition temperature, excellent film-forming property, and low fabrication cost. These allow them for the fabrication of flexible and large area displays.[3,4]

In the past decades, a variety of opto-electroactive conjugated backbone structures, such as poly(*p*-phenylenevinylene),[5] poly(*p*-phenylene),[6] polythiophene,[7,8] and polyfluorene (PF)[9–11] have been reported. Among these π-conjugated polymers, PFs are being considered as the most promising blue-light-emitting materials because of their high efficient photoluminescence (PL) and EL, chemical and thermal stability, facile functionalization at the C-9 position of fluorene, and good solubility in common organic solvents.[9–11] As we know, the balance in the injection and transportation of electrons and holes into the emissive layer is necessary to obtain highly efficient PLED devices.[12,13] However, it is difficult to synthesize ideal emitting material that meets the request for the balanced charge injection and transportation.[14] Thus, multilayer devices with the addition of an electron transporting layer or a hole transporting layer have been fabricated to achieve the balance of charge injection through the match of the energy levels with the electrodes.

Because of the solubility of the lower layers in the solvents used for casting succeeding layers, the preparation of multilayer PLED by solution casting is difficult. Two approaches can be used to make the lower layers insoluble in this process. One is to select an appropriate solvent. Another is to use physical or chemical methods to make the lower layer crosslinked.[15,16] The introduction of crosslinkable moieties such as styryl group as end capper to suppress excimer emission and to improve the color stability was demonstrated.[17]

The conjugated polymers containing a photo-crosslinkable group, such as diacetylene,[18] acrylate,[19] carbamate,[20] and chalcone[21] groups, could be directly photopatterned when exposing to UV light. The photo-crosslinkable polymers were usually prepared by the polymerization of the monomers with the photo-

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crosslinkable groups.[18–21] However, these photo-crosslinkable groups attached to the monomers were sensitive to light and heat,[17] and could be changed in the processes of polymerization. In this work, we used a novel approach to introduce photo-crosslinkable acrylate group into the side-chains of PF after its polymerization, for the synthesis of the photo-crosslinkable PF derivative. And the polymer was characterized by differential scanning calorimetry (DSC), TGA, UV–vis absorption and PL spectra, and electrochemical analysis.

EXPERIMENTAL

Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-300 MHz and Bruker-400 MHz instrument using tetramethylsilane as an internal reference. IR spectra were measured with a Bio-rad FTS6000/UMA500 spectrophotometer. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a Waters GPC-410c instrument, using polystyrene as the standard and tetrahydrofuran (THF) as the eluent. Absorption spectra were recorded with a Hitachi (model U-3010) UV–visible spectrophotometer. Fluorescence measurements were carried out with a Hitachi (model F-4500) spectrophotometer. The films on quartz used for PL measurements were prepared by spin-coating with 1% toluene solution. Fluorescence quantum yield (Φ_F) of the samples in trichloromethane was measured by using 9,10-diphenylanthracene (Φ_F = 0.95 in cyclohexane) as standard. DSC of the polymers was performed under a nitrogen atmosphere at a heating rate of 20°C/min using DSC 7A (PerkinElmer Co., USA). Cyclic voltammetry was performed at a potential scan rate of 20 mV/s on ZAHNER IM6e electrochemical workstation. The materials were crosslinked using 365-nm line of mercury arc lamp with a 12 mW/cm^2 power density, under nitrogen atmosphere.

Materials

All reagents were commercial. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**7**) was prepared according to the literature procedure.[11,22]

Preparation of 2-(fluoren-9-yl) ethyl methyl ether (2)

To a solution of fluorene **1** (5 g, 30 mmol) in ether (100 mL) at −78°C was added 12 mL (35 mmol) of *n*-butyllithium (2.89 mol/L in hexane) by syringe. The mixture was kept at −78°C and stirred for 10 min, then warmed to room temperature and kept at room temperature for 5 h, and then cooled again at −78°C for 15 min. 2-Bromoethyl methyl ether was added dropwise to the solution, and the resulting mixture was warmed to room temperature and stirred for 4 h. The mixture was poured into water and extracted with ether. The organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent, the crude product was recrystallized from methanol/ether (20 : 1) to yield white crystals (4.56 g, 20 mmol, 66%). mp: 57–58°C. ^{1}H NMR (400 MHz, $CDCl_3$, δ (ppm)): 7.79 (2H, d, J = 7.42 Hz), 7.56 (2H, d, J = 7.35 Hz), 7.40 (2H, q, J = 7.27 Hz), 7.35 (2H, t, J = 7.37 Hz), 4.14 (1H, t, J = 6.32 Hz), 3.40 (2H, t, J = 6.80 Hz), 3.35 (3H, s), 2.28 (2H, q, J = 6.80 Hz). ^{13}C NMR (300 MHz, $CDCl_3$, δ (ppm)): 145.7, 139.6, 125.7, 125.6, 123.1, 118.5, 68.5, 57.2, 43.1, 31.7. MS: m/z = 224 (M^+). Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19; O, 7.13. Found: C, 85.71; H, 7.23.

Preparation of 2-(9-hexylfluoren-9-yl) ethyl methyl ether (3)

To a solution of 2 (4 g, 17.9 mmol) in ether at −78°C was added 12 mL (35 mmol) *n*-butyllithium (2.89 mol/L in hexane) by syringe. The mixture was stirred at −78°C for 10 min, then warmed to room temperature and kept at room temperature for 2 h, and cooled again at −78°C for 15 min. 1-Bromohexane was added dropwise to the solution, and the resulting mixture was warmed to room temperature and stirred for 6 h. The mixture was poured into water and extracted with ether. The organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent, the crude product was recrystallized from methanol/ether (20 : 1) to yield white crystals (4.1 g, 13 mmol, 66%). mp: 54–55°C. ^{1}H NMR (400 MHz, $CDCl_3$, δ (ppm)): 7.71 (2H, t, J = 7.65 Hz), 7.41–7.31 (6H, m), 3.02 (3H, s), 2.65 (2H, t, J = 5.84 Hz), 2.35 (2H, t, J = 7.7 Hz), 1.99 (2H, t, J = 7.60 Hz), 1.13–1.01 (6H, m), 0.76 (3H, t, J = 6.94 Hz), 0.64–0.60 (2H, m). ^{13}C NMR (300 MHz, $CDCl_3$, δ (ppm)): 148.3, 139.4, 125.8, 125.6, 121.5, 118.3, 67.4, 56.9, 51.5, 39.3, 38.0, 30.0, 28.2, 21.9, 21.1, 19.5, 12.5. MS: m/z = 308 (M^+). Calcd for $C_{22}H_{28}O$: C, 85.66; H, 9.15; O, 5.19. Found: C, 85.67; H, 9.29.

Preparation of 2-(2,7-dibromo-9-hexylfluoren-9-yl)-ethyl methyl ether (4)

To a solution of **3** (3.97 g, 12.8 mmol) in methylene chloride at 0°C were added catalytic amount of iodine and 3 mL of bromine. The solution was warmed to room temperature and stirred for 3 h. An aqueous solution of saturated sodium thiosulfate was added to the solution until the red color disappeared. The mixture was poured into water and extracted with methylene chloride. The organic layer was washed with

brine and dried over anhydrous sodium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel using a mixture of ethyl acetate and petroleum ether (1 : 10) as the eluent, yielding 4.45 g (74.5%) of the pale-yellow solid. mp: 73–75°C. ^{1}H NMR (400 MHz, $CDCl_3$, δ (ppm)): 7.53–7.45 (6H, q), 3.02 (3H, s), 2.64 (2H, t, J = 7.65 Hz), 2.27 (2H, t, J = 7.65 Hz), 1.94 (2H, t, J = 7.71 Hz), 1.13–1.05 (6H, m), 0.77 (3H, t, J = 6.51 Hz), 0.59–0.57 (2H, m). ^{13}C NMR (300 MHz, $CDCl_3$, δ (ppm)): 150.2, 137.3, 129.1, 124.9, 120.2, 119.8, 67.0, 56.9, 52.2, 39.0, 37.7, 30.0, 28.0, 21.9, 21.1, 10.0. HRMS calcd for $C_{22}H_{26}Br_2O$: 466.0330, found: 466.0339.

Preparation of tetrakis(triphenylphosphine) palladium(0) $(PPh_3)_4Pd(0)$

To a mixture of Palladium chloride (100 mg, 0.56 mmol) and triphenylphosphine (0.74 g, 2.83 mmol) was added 8 mL of dimethyl sulfoxide. The system was sealed under nitrogen atmosphere. The mixture was heated at 155°C until total dissolution of the solid material. The heated bath was then taken away, and the solution was allowed to cool for 2 min. Hydrazine hydrate (0.11 mL, 2.26 mmol) was added by syringe over 1 min, and the mixture immediately cooled in a water bath to initiate crystallization. Once the first crystal formed, the mixture was removed away from the water bath. After the mixture reached the room temperature, it was filtered off under nitrogen and the crystals were washed with ethanol and subsequently with ether. The product (0.64 g, 98%) was stored under nitrogen.

Preparation of poly[2,7-(9,9-dioctylfluorene)-*co*-2,7-(9-hexyl-9-(2-methoxy ethyl)-9h-fluorene)] (P1)[23]

Carefully purified 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborlan-2-yl)-9,9-dioctylfluorene(1 g, 1.6 mmol), 2-(2,7-dibromo-9-hexylfluoren-9-yl)ethyl methyl ether (725 mg, 1.6 mmol) were dissolved in a mixture of toluene and aqueous solution of 2 mol/L K_2CO_3. The solvents were degassed in advance. The solution was refluxed with vigorous stirring (20 mL) for 24 h under nitrogen atmosphere. In the end of polymerization, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborlan-2-yl)-9,9-dioctylfluorene was added to remove bromine end groups and bromobenzene was added to remove boronic ester end groups. After the mixture was cooled to room temperature, it was poured into 100 mL of methanol. The precipitated solid was obtained by filtration. After washing for 24 h with Soxhlet apparatus using acetone, the resulting polymer was obtained as a pale-yellow solid (1 g, 1.4 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$, δ (ppm)): 7.96–7.36 (12H, m), 3.22 (3H, s), 2.95 (2H, m), 2.65 (2H, m), 2.27–2.21 (6H, m), 1.35–1.34 (26H, m), 0.91–0.89 (15H, m).

Preparation of poly[2,7-(9,9-dioctylfluorene)-*co*-2,7-(9-hexyl-9-(2-hydroxy ethyl)-9h-fluorene)] (P2)

To a solution of **P1** (800 mg, 1.15 mmol) in methylene chloride at −78°C was added 1.2 mL of boron tribromide (2.12 mol/L solution in methylene chloride). Then the mixture was stirred at room temperature for 24 h. The mixture was poured into water and extracted with methylene chloride. The organic layer was washed with brine and dried over sodium sulfate. After evaporation of the solvent, the crude product was precipitated from methanol/methylene chloride (20:1) to obtain pale-yellow solid (600 mg, 0.88 mmol, 76.5%). ^{1}H NMR (400 MHz, $CDCl_3$, δ (ppm)): 7.87–7.61 (12H, m), 3.20 (O—CH_3, s), 2.80 (2H, m), 2.56–2.55 (2H, m), 2.16 (6H, m), 1.31–1.14 (26H, m), 0.82–0.80 (15H, m).

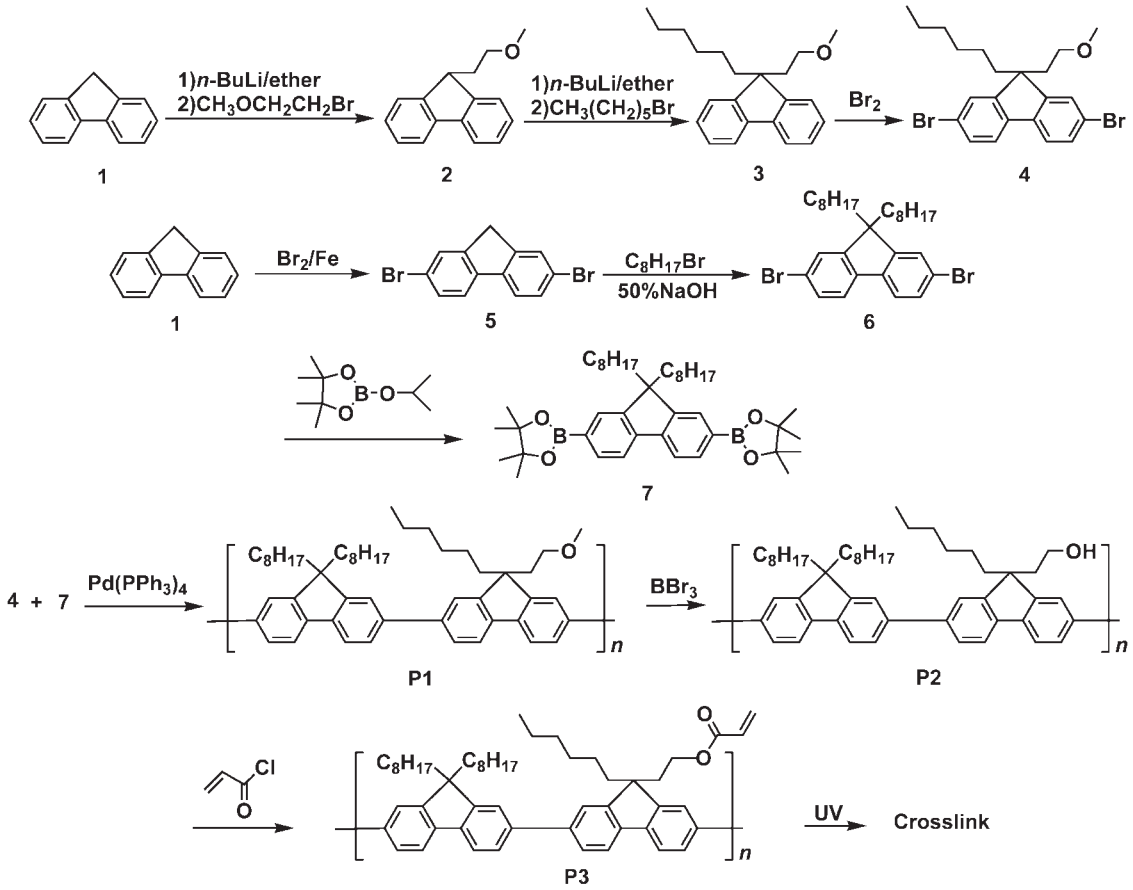
Preparation of poly[2,7-(9,9-dioctylfluorene)-*co*-2,7-(9-hexyl-9-(2-acrylate ethyl)-9h-fluorene)] (P3)

To a solution of **P2** (500 mg, 0.74 mmol) in methylene chloride at room temperature was added 0.2 mL of triethylamine. The mixture was stirred for 5 min and 0.09 mL of acryloyl chloride was added to the solution. The resulting mixture was stirred at room temperature for 24 h. Then, the mixture was washed with 1*M* hydrochloric acid, aqueous solution of saturated $NaHCO_3$ and water, and extracted with methylene chloride. The organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent, the crude product was precipitated from methanol/methylene chloride (20:1) to yield pale-yellow solid (434 mg, 80.5%). ^{1}H NMR (400 MHz, $CDCl_3$, δ (ppm)): 7.86–7.50 (12H, m), 6.14–6.08 (1H, d), 5.86–5.77 (1H, d), 5.62–5.59 (1H, d), 3.73 (O—CH_3, s), 3.43 (2H, m), 2.14 (6H, m), 1.26–1.15 (26H, m), 0.82–0.81 (15H, m). ^{13}C NMR (400 MHz, $CDCl_3$, δ (ppm)): 165.90, 151.82, 150.24, 140.81, 140.06, 139.80, 130.27, 128.20, 126.69, 126.19, 121.46, 120.30, 120.02, 55.37, 53.39, 40.39, 31.77, 31.41, 30.03, 29.68, 29.50, 29.23, 23.93, 22.59, 22.51, 14.06, 14.01.

RESULTS AND DISCUSSION

Monomer synthesis

The synthesis route of the photo-crosslinkable polymer **P3** is shown in Scheme 1. The monomer of 2-(fluoren-9-yl)ethyl methyl ether **2** was synthesized using fluorene **1** as starting material, and then 2-(9-hexylfluoren-9-yl)ethyl methyl ether **3** was obtained by alkylation at 9 position of compound **2**. In compounds **2** and **3**, methoxy group acts as a protective group for introducing the photo crosslinkable group into the polymer in a later step. The introduction of hexyl group in compound **3** is for enhancing the solubility of the monomer and preventing the generation of keto



Scheme 1 Synthetic routes to the monomers and polymers.

defect sites at 9 position.[24] Actually, we ever tried several synthesis routes for obtaining compound **3**. Initially, 9-hexylfluorene was synthesized, but as an oil compound, it is difficult to deal with in later reaction. The 9,9-di(2′-methoxyethyl)fluorene was also prepared, however, its solubility is poor in common organic solvents such as chloroform, THF, and toluene. Finally, we utilized the synthesis route shown in Scheme 1.

Polymer synthesis

Polymer **P1** was prepared by Suzuki polycondensation in a biphasic system (toluene/aqueous K_2CO_3) using fresh $Pd(PPh_3)_4$ as a catalyst.[23] The molecular weight determined by GPC against polystyrene standard is listed in Table I. Polymer **P1** displays excellent solubility in common organic solvents such as methylene chloride, THF, and chloroform. With the treatment of boron tribromide, the methoxy group could be easily removed from the polymer in a high yield. The signal of methoxy protons at 4 ppm in ^{1}H NMR spectrum of **P2** decreased largely compared with that of **P1**, which indicates that large amount of methoxy

TABLE I
Physical Properties of the Polymers

Polymer	M_w	M_n	M_w/M_n	T_d (°C)	T_g (°C)
P1	114,593	43,432	2.638	485	108
P2	—	—	—	455	121
P3	—	—	—	410	86

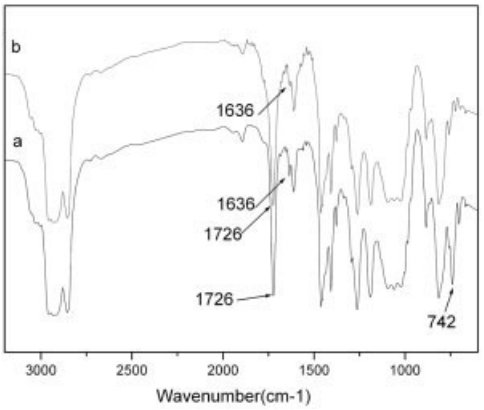


Figure 1 IR spectra of P3: (a) before UV exposure; (b) after UV exposure.

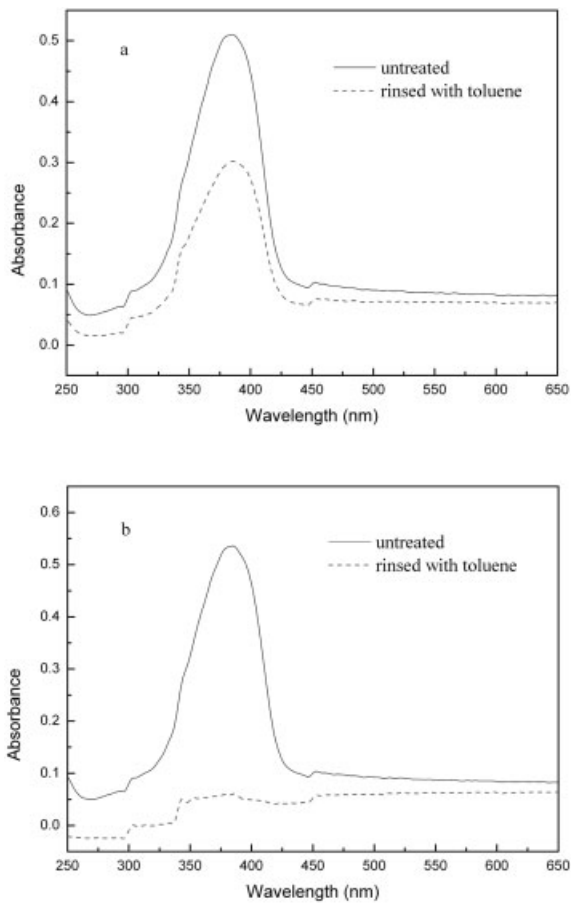


Figure 2 UV–vis absorption spectra of P3 films on quartz: (a) after UV exposure for 15 min; (b) without UV irradiation.

groups in **P1** were de-protected. Then the photo-crosslinkable group of acrylate was introduced into the polymer by a simple acylation reaction to get the target product **P3**. The spectra features associated with the vinyl groups, proton peaks near 6 ppm in the ^{1}H NMR and the carbon peaks near 140 ppm in the ^{13}C NMR spectrum, manifested the successful synthesis of **P3**. In the above reactions, the methoxy group in **P1** was acted as protective group to introduce photo-crosslinkable group and avoid unnecessary side reactions.

Polymer crosslinking

Polymer **P3** was crosslinked upon exposure to UV light.[15,16] After 15-min irradiation of 365-nm UV light, the film of polymer **P3** became insoluble in common organic solvents. To monitor the crosslinking process, IR experiment was carried out on the film of polymer **P3**. Figure 1 shows the IR spectra of **P3** film before and after UV exposure. The intensity of the C═C stretching vibration band at 1636 cm^{-1} decreased after the film was exposed to the UV light for 15 min. Meanwhile, the absorption peak assigned to the vibration of ═C—H at 742 cm^{-1} disappeared. This result suggests that the crosslinked networks were formed via [2 + 2] cycloaddition.

To demonstrate the insolubility of polymer **P3** after UV exposure, the UV–vis absorption spectra of **P3** films on quartz were checked before and after the films were rinsed with toluene. As shown in Figure 2, the **P3** film without UV treatment gave little absorption after washing by toluene, indicating that the film was dissolved in the solvent and was washed away. The absorption intensity of the **P3** film irradiated by UV light and then washed by toluene is still quite strong, although the intensity decreased to some extent. The results verify that the **P3** film after UV exposure was crosslinked and became insoluble in toluene. The decrease of the absorption may be due to the incomplete crosslinking of the polymer.

Absorption and PL properties

The UV–visible absorption and PL properties of the polymers are presented in Table II and Figures 3–5. The maximum absorption wavelengths of **P1**, **P2**, and **P3** in chloroform are 376, 372, and 376 nm, respectively. The PL spectra of **P1**, **P2**, and **P3** in chloroform are entirely the same with two emission peaks at around 420 nm and 440 nm, respectively (see Fig. 3), which is the typical PL spectrum of PF.[25,26] This reveals that the functionalization groups in the side-chain of the PF in the three polymers didn't change the energy gap of the conjugated polymers.

The UV–vis absorption and PL spectra of the polymer films are shown in Figure 4. It can be found that

TABLE II
Optical Properties of the Polymers

Polymer	Λmax (UV abs, nm)[a]		λ (PL, nm)[a]		fwhm[a]		Φ_{PL} (solution)
	Solution	Film	Solution	Film	Solution	Film	
P1	376	379	420,440	426,449	38	42	0.47
P2	372	381	420,440	424,448	38	49	0.55
P3	376	381	420,440	424,448	38	53	0.63
P3 (UV 5 min)	—	381	—	424,446	—	52	—
P3 (UV 15 min)	—	381	—	425,448	—	66	—

[a] The solution data were obtained from the polymer solutions in chloroform.

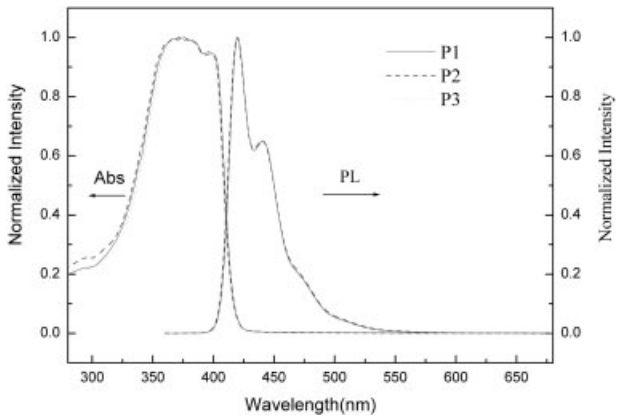


Figure 3 UV–vis absorption and photoluminescence spectra of the polymers P1, P2, and P3 in $CHCl_3$.

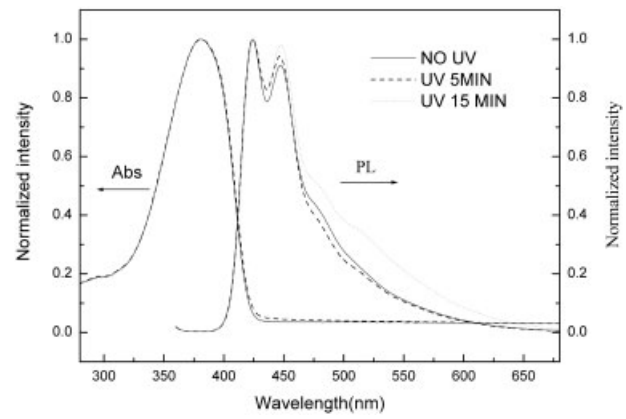


Figure 5 UV–vis absorption and photoluminescence spectra of P3 film before and after UV exposure.

the full width at half-maximum (fwhm) increased slightly and the PL peaks at 480 nm became more intense with the introduction of acrylate group. This is probably attributed to the increase of interchain excimers because of the existence of vinyl in acrylate group. In comparison with dilute solutions, the absorption and emission spectra of the films on quartz substrate show a slightly bathochromic shift.

To investigate the optical properties after photopatterning, the films of **P3** were exposed to UV light under nitrogen atmosphere. Figure 5 shows the absorption and PL spectra of the **P3** films at different exposure times. The maximum absorption wavelengths and spectra patterns of the polymers were not significantly different. However, when the exposure time of the UV light on the **P3** films was prolonged to 15 min, a shoulder emission peak at 517 nm appeared and the fwhm of the PL spectrum increased by 13 nm. This probably resulted from the formation of aggregates, excimers, or keto defects.[24,27–29]

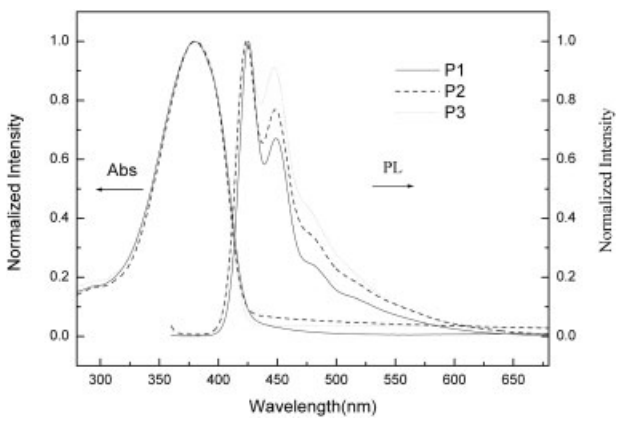


Figure 4 UV–vis absorption and photoluminescence spectra of P1, P2, and P3 films.

Electrochemical properties

Figure 6 shows the electrochemical cyclic voltammograms of the three polymers in the potential range of 0–1.2 V *versus* Ag/Ag^+. Obviously, the p-doping/dedoping (oxidation/rereduction) processes of the three polymers are reversible, indicating that the introduction of hydroxyl and acrylate groups in the polymer side-chains didn't disturb the reversibility of the p-doping/dedoping processes of the polymer main chains, but the p-doping potential was affected by the functional groups. Introduction of hydroxyl group in **P2** makes the onset oxidation potential decrease by ca. 0.15 V in comparison with that of **P1**, which means that the HOMO energy level of the polymer moves upward by ca. 0.15 eV after introducing the hydroxyl groups in its side-chains. The introduction of acrylate groups in **P3** almost turn the oxidation potential back to that of **P1** (the onset potential of **P3** is only ca. 0.01 V lower than that of **P1**).

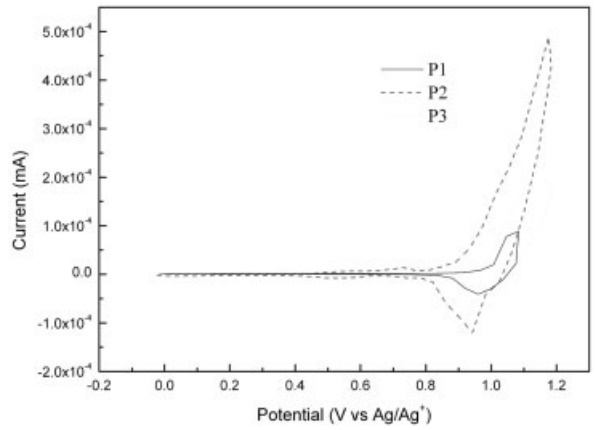


Figure 6 Cyclic voltammograms of P1, P2, and P3 films coated on glassy carbon electrode in 0.1 mol/L Bu_4NPF_6 acetonitrile solution.

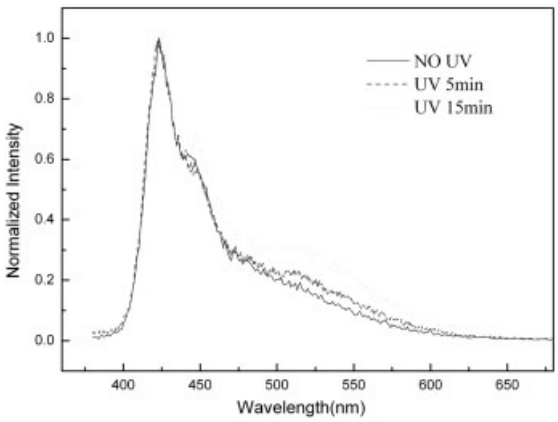


Figure 7 EL spectra of polymer P3 before and after UV exposure.

Electroluminescence properties

PLEDs with the configuration of ITO/PEDOT/**P3**/Ca/Al were fabricated for investigating the electroluminescent properties of **P3**. The EL spectra of the PLED devices are displayed in Figure 7. The EL spectra of **P3** before the UV exposure show the main emission peaks at 422 and 447 nm, which can be attributed to the backbone of fluorene.[30] After the UV irradiation, the EL spectra show slight difference with the appearance of the 517 nm peak as that of the PL spectra. As the time of UV exposure increases, the emission peak at 517 nm enhances. Klärner et al. reported that crosslinking via end groups could inhibit chain mobility and lead to the suppression of intermolecular excited state interactions, while the internal crosslinking could not suppress the longer wavelength emission at 500–600 nm completely.[17] In our experiment, when the crosslinked network formed, emission peak at 500–600 nm appeared. This result could be rationalized by the assumption that the formation of keto defect brought the appearance of the longer wavelength emission.

CONCLUSIONS

A photo-crosslinkable PF derivative with acrylate groups in its side-chains, **P3**, was successfully synthesized via functionalization of the side-chain of PF. Exposure to UV light for 15 min rendered the polymer **P3** crosslinked and insoluble in common organic solvents. There is no effect of the crosslinking on the absorption spectra of the polymer, but a weak longer wavelength emission at 517 nm appeared in the PL and EL spectra of the crosslinked **P3**, which could be attributed to the formation of keto defects during the photo crosslinking.

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