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Syntheses and photoluminescence properties of UV photocrosslinkable polyesters based on fluorene

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ABSTRACT

Suppression of the green emission for polyfluorene has been widely investigated and various methods have been explored. In the present work, the photocrosslinkable copolyesters based on ferulic acid and 9-hydroxy-9-fluorene-carboxylic acid with different monomer feed molar ratios were synthesized and photocrosslinking reactions were employed to make the copolyesters crosslinked. All the photoluminescence spectra of the polyesters prior to photocrosslinking peaked at 418 nm in chloroform with quantum efficiencies more than 0.65. After crosslinking, copolyester P2 showed better thermo-stability of photoluminescence than the conjugated poly(9,9-dihexylfluorene). This indicated that the crosslinking architecture could suppress the chain aggregation, thus improving the purity of blue emission.

1. Introduction

In the field of polymer light-emitting diodes (PLEDs), polyfluorene and its derivatives (PFs) are very promising candidates for blue-light-emitting materials because of their high photoluminescence and electroluminescence efficiencies [1–3]. However, one drawback that has limited the application of PFs in blue PLEDs is the poor spectral stability, which is associated with the troublesome excimer formation in the solid states. An additional emission band between 500 and 600 nm may appear and become pronounced upon thermal annealing or passage of current [4,5]. Meanwhile, various methods have been explored to solve the aggregation-related problem, such as (a) introducing bulky [6] or oxidant-resistant pendant [7] and ending groups [8], (b) using spiro-linked [9] or crosslinking architecture [10], (c) synthesizing star-like [1,11], ladder-type [12] and even hyper-branched PFs [4,13], (d) designing element-doping polyfluorenes or their nanocomposites [2]. These strategies have to a certain extent increase the structural hindrance of PFs, thus reducing their chain-aggregation tendency in the solid state.

Among the strategies increasing the color stability of fluorene-based materials, designing of crosslinking or networking PFs are interesting. For instance, Cho et al. synthesized thermally stable polyfluorenes containing siloxane bridges, which showed no evidence of aggregation formation and excimers at wavelengths of >500 nm when annealed at 150 °C for 4 h in air [14]. Recently, Tang et al. designed two kinds of hyper-branched crosslinkable polyfluorene with photocrosslinkable groups at C-9 positions [10]. Tang's crosslinked polyfluorenes exhibited stable photoluminescence spectra even after annealing for 3 h at 200 °C in air. Additionally, polyfluorene networks immobilized by boronic acid anhydride linkages or vinyl end-groups were also synthesized to improve the spectral stability [15,16].

As shown above, it is important to prepare polyfluorene derivatives that, even after thermal treatment, could stably emit blue light without an increased level of excimer formation or a spectral tail at long wavelengths. In this study, ferulic acid (FA), an important derivative of cinnamic acid was selected to synthesize crosslinked fluorene-based network. The aliphatic C═C bond in FA unit makes the polymer related with FA easily crosslinked by thermo- or photo-induced initiation. Another bifunctionality comonomer selected was 9-hydroxy-9-fluorene-carboxylic acid (HFCA), which is a blue light-emitting derivative of fluorene. The melt esterification–polycondensation was undertaken and a series of photocrosslinkable poly(FA-*co*-HFCA)esters were synthesized. To the best of our knowledge, such kind of photocrosslinkable fluorene-based polyesters have not been reported in previous literatures. The syntheses, structure characterization and photocrosslinking process of these copolyesters, together with the photoluminescence (PL) properties prior to and after the crosslink, especially the effect of photocrosslinking process on the chain aggregation, were studied in this paper.

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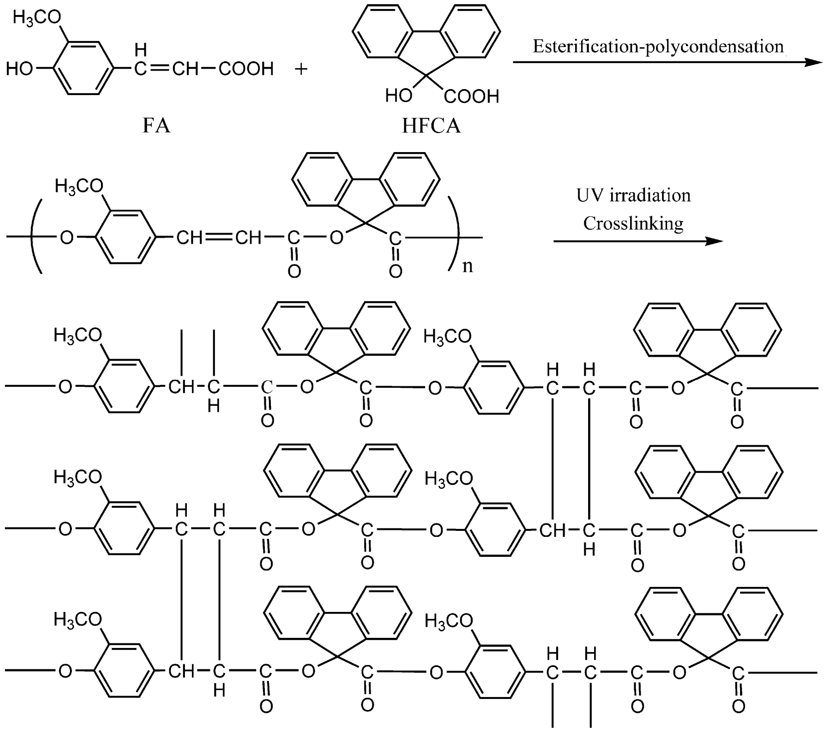

Scheme 1. Syntheses and photocrosslinking of the fluorene-based polyester.

2. Experimental

2.1. General information

9-Hydroxy-9-fluorene-carboxylic acid (HFCA) (99%) was purchased from J&K chemical. Ferulic acid (FA) (99%) was supplied by Shenqiang Co., Ltd. Photoinitiator 1173 (2-hydroxy-2-methyl-1-phenyl-1-propanone, 99%) was obtained from Insigh High Technology Co., Ltd. Poly(9,9-dihexylfluorene) ($\overline{M_n} = 12,000$) used for comparison of UV–vis and PL spectra was purchased from Synwit Technology Co., Ltd. Other reagents and solvents obtained from commercial suppliers were used without further purification.

^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were determined on a Varian mercury-plus 400 at 295 K. Fourier transform infrared (FT-IR) spectra were obtained using an FTS-3000 spectrometer with samples prepared as KBr disk pellets. Elemental analyses were measured on a Vario EL III elemental analyzer. Gel permeation chromatography (GPC) was carried out on a Waters-Breeze GPC 1515 System with chloroform as an eluant. All GPC analyses of polymers were processed at a flow rate of 1 mL/min at 30 °C and the samples were calibrated using polystyrene standards. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate of 10 °C/min using a TA instrument SDT-Q600. The intrinsic viscosities of the polymers were determined on Ubbelohde viscometer at 30 °C. UV–vis absorption and photoluminescence (PL) spectra of polymers were recorded on a Shimadzu UV-1700 and a Hitachi F-4500 fluorescence spectrophotometer, respectively. For the solutions, the polymers were dissolved in chloroform at a concentration of 0.05 wt%. For the preparation of the thin films, samples were first dissolved in

Table 1
Composition, yields and molecular weights of the polyesters.

Sample	FA/HFCA feed ratio	FA/HFCA in copolymers[a]	Yield (%)	T_d[b] (°C)	$\overline{M_n}$ (PDI)	Intrinsic viscosity[c]
P1	75:25	75:21.8	62	254	4200 (1.74)	0.632 dL/g
P2	50:50	50:41.0	60	262	6800 (1.63)	0.949 dL/g
P3	25:75	25:29.4	25	270	–[d]	0.707 dL/g
PF6	–	–	–	400	12,000 (2.3)	–

[a] Molar ratios of FA/HFCA in the copolymers were calculated from the relative integration area of ^{1}H NMR spectra.

[b] T_d was referred as to the temperature at which 5% weight of the samples lost.

[c] The concentration of the chloroform solutions was 0.02 g/dL.

[d] The sample of P3 was only partially soluble in chloroform.

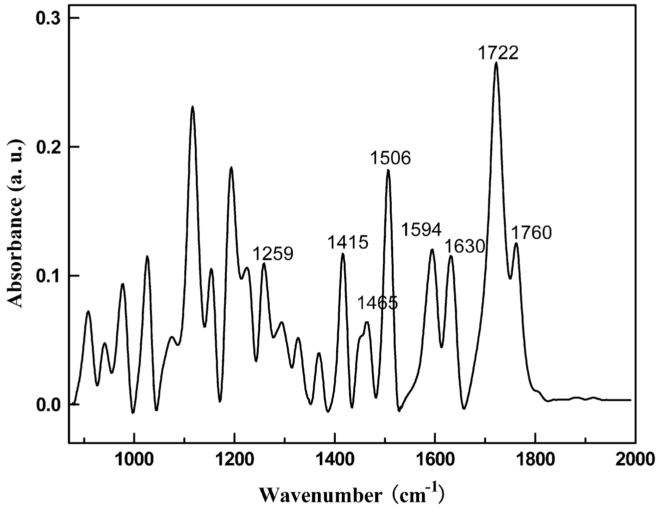

Fig. 1. FT-IR spectrum of P2.

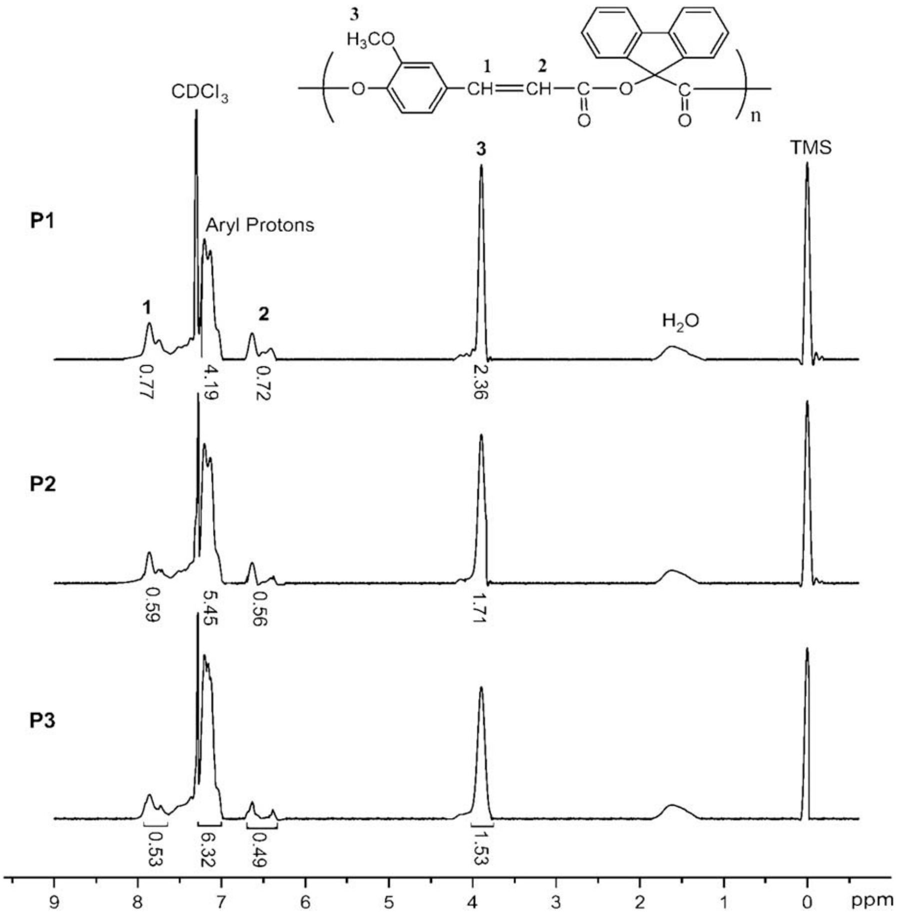

Fig. 2. ^{1}H NMR spectra of P1–3 in $CDCl_3$.

chloroform (0.2 wt%) and then spin cast on quartz substrates for 40 s at 1000 rpm, followed by drying at room temperature for 24 h under vacuum. PL quantum efficiencies (Φ_{PL}) of the samples both in solution and as films were measured by using 9,10-diphenylanthracene ($\Phi_{PL} = 0.91$ in ethanol and $\Phi_{PL} = 0.83$ dispersed in PMMA films with a concentration lower than 1×10^{-3} M) as standards. Values of Φ_{PL} were calculated according to the literature [17] and the final results were averaged from three repeating operations.

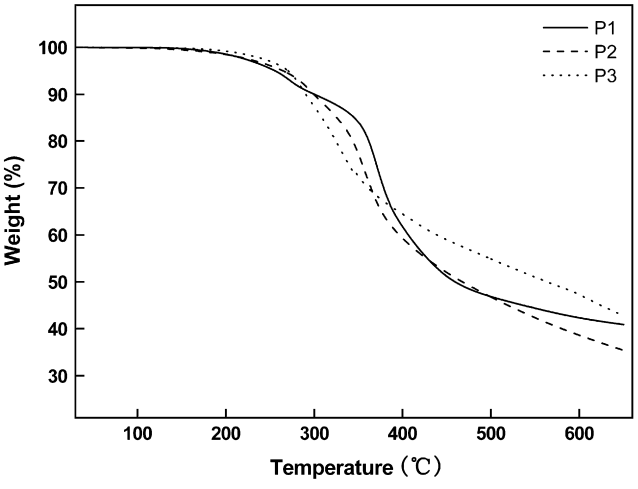

Fig. 3. TGA curves of the polyesters.

2.2. Syntheses of the poly(FA-co-HFCA)esters and the photocrosslinking reaction

The poly(FA-*co*-HFCA)esters were synthesized basically according to the literature [18] with minor revisions. The synthetic route is shown in Scheme 1. To a 100-mL three-necked flask equipped with a mechanical stirrer, were added FA and HFCA. Then the mixture was dissolved in 20–30 mL of acetic anhydride (as a condensation reagent) in the presence of magnesium acetate (0.1 wt%, as a catalyst). The flask was heated at 150 °C with stirring and at the same time not less than 100 mL/min of nitrogen was blown to remove moisture and residual air, maintained until almost all of the solvent was evaporated. Then the system was raised to 180 °C and reacted under nitrogen for 4 h. Upon completion, the resulting product was removed from the reaction flask, mechanically powdered and washed with acetone for several times. Finally, the brown powder was dried in vacuum at 40 °C overnight. Three kinds of copolyesters named P1–3 with different feed ratios were obtained (Table 1).

FT-IR (KBr, cm^{-1}): P2: 2942 (vs, $-CH_3$), 1760, 1722 (vs, C=O), 1630 (s, C=C), 1594, 1506, 1465, 1415 (s, C=C, Ar), 1259 (m, –C–O–C). P1 and P3 show similar FT-IR spectra as P2 except that the intensities of signals are different due to the different FA/HFCA ratios. ^{1}H NMR (400 MHz, $CDCl_3$): P1: δ (ppm) = 7.71–7.91 (1H, d, Ar-CH=C), 7.08–7.32 (6H, m, Ar-H), 6.38–6.65 (1H, d, –C=C–H), 3.88 (3H, s, $-OCH_3$). P2: 7.71–7.91 (1H, d, Ar-CH=C), 7.09–7.33 (10H, m, Ar-H), 6.36–6.68 (1H, d, –C=C–H), 3.88 (3H, s, $-OCH_3$). P3: 7.69–7.92 (1H, d, Ar-CH=C), 7.08–7.32 (12H, m, Ar-H), 6.35–6.66 (1H, d, –C=C–H), 3.88 (3H, s, $-OCH_3$). Elemental analyses for P1,

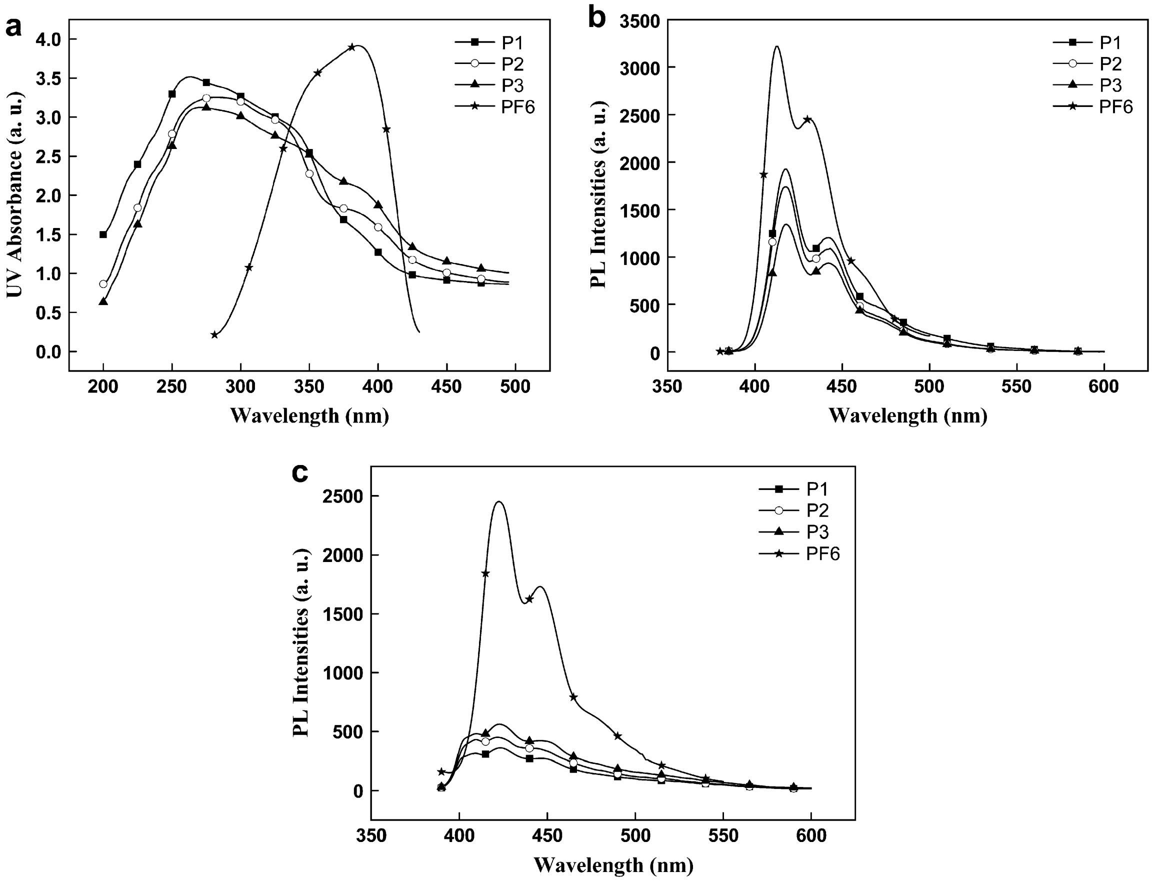

Fig. 4. (a) UV absorptions of the polyesters and PF6 in solution; (b) PL spectra of the polyesters and PF6 in solution; (c) PL spectra of the polyesters and PF6 in films.

found: C, 72.28%; H, 4.51%; for P2, found: C, 76.82%; H, 4.45%; for P3, found: C, 79.87%; H, 4.04%. Molecular weight (GPC, eluent = chloroform), found: for P1: $\overline{M_n}$, 4200; $\overline{M_w}/\overline{M_n}$ (PDI), 1.74. For P2: $\overline{M_n}$, 6800; $\overline{M_w}/\overline{M_n}$, 1.63.

For the photocrosslinking reaction, to a beaker containing chloroform solutions of the copolyesters (50 mL, 0.2 wt%), was added 2.5 mL photoinitiator 1173. Then, the thin films cast from corresponding chloroform solutions of the copolyesters were placed on quartz plates and exposed to UV irradiation from a 400 W high-pressure mercury lamp at various intervals of time.

3. Results and discussion

3.1. Synthetic conditions of the poly(FA-co-HFCA)esters

Melt polycondensation was employed in the syntheses of the copolyesters. The use of acetic anhydride as a condensation reagent could make the polycondensation accelerated. It should be noticed that the reaction temperature was controlled strictly below 180 °C under enough inert atmosphere to protect the C=C bond from being broken. On the other hand, the strong nitrogen current could blow away the vapor produced in polycondensation reaction and make the equilibrium shift to the forward direction. The yields of P1 and P2 were about 60% without other measures of promoting the equilibrium, which indicated that the magnesium acetate catalyst had a high efficiency. The yield of P3 was relatively low (25%), and one possible reason was that the HFCA monomer had a high steric hindrance which was adverse for the condensation when its content increased. P1–3 were hardly soluble in THF, DMSO, and methanol, but showed better solubility in methylene chloride and chloroform. Additionally, the ability of dissolving in these two solvents declined with the increased HFCA feed content.

Table 2
Essential spectral data of the polymers.

Sample	Solution λ_{max} (nm)		Film λ_{max} (nm)		Φ_{PL}	
	Abs.	Em.	Abs.	Em.	Solution	Film
P1	264	418 (442[a])	302	423 (410,[a] 446[b])	0.65	0.13
P2	284	418 (442[a])	302	422 (410,[a] 444[b])	0.68	0.18
P3	269	418 (442[a])	301	423 (410,[a] 447[b])	0.67	0.15
PF6	385	412 (431[a])	395	423 (446[a])	0.61	0.43

[a] The wavelength of the shoulder emission peaks.
[b] The wavelength of the third emission peaks.

3.2. Characterization of the poly(FA-co-HFCA)esters

The chemical structures of P1–3 were analyzed by FT-IR and ^{1}H NMR. As shown in Fig. 1, a typical FT-IR spectrum of P2 exhibits the characteristic carbonyl stretching band of the ester groups at 1760 and 1722 cm^{-1}, which corresponds to the aliphatic–aromatic ester bonds and the aromatic–aromatic ester bonds, respectively. The sharp absorption peak arising from the ethylene group appears at 1630 cm^{-1}, indicating that the cinnamoyl groups are successfully introduced to polymer backbone. The olefin protons are also confirmed by the ^{1}H NMR spectra (Fig. 2), which exhibit two doublet signals at 6.6 and 7.8 ppm, characteristic for a *trans* cinnamoyl moiety. No matter P1, P2 or P3, the total relative integration

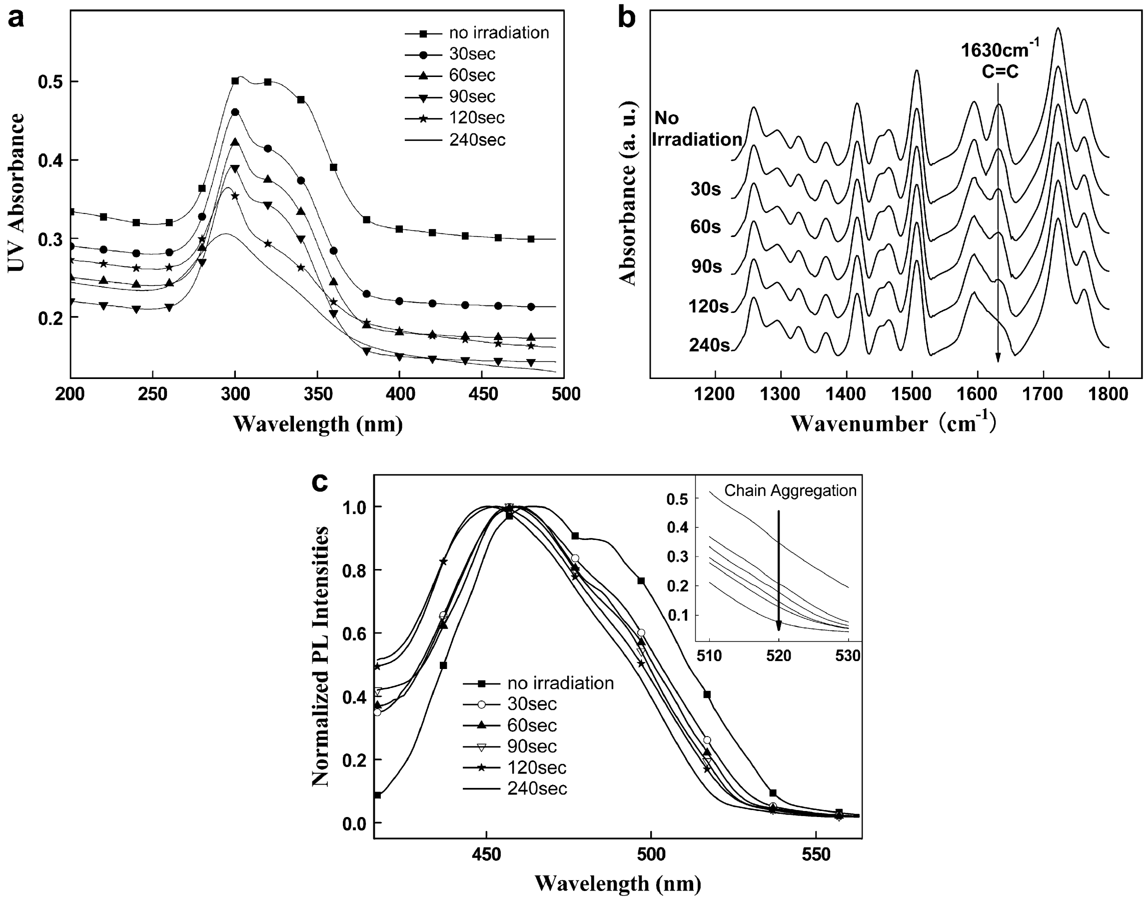

Fig. 5. Change in UV, FT-IR and PL spectra of P2 thin film upon UV irradiation at different times: (a) UV spectra; (b) FT-IR spectra; (c) PL spectra; inset in (c): part enlarged between 510 and 530 nm.

area of olefin protons in the ^{1}H NMR spectra is about two-thirds of the integration area of methoxy protons at 3.90 ppm. Such results corresponds with the ratio of the hydrogen atom numbers in the molecular formula, which could verify that the ethylene groups are hardly destroyed in the melt polycondensation. Additionally, the experimental molar ratios of FA/HFCA in the copolyesters are higher than the theoretical FA/HFCA feed ratios especially for P3. It may indicate that the lower reactivity of HFCA monomer than FA monomer in the polycondensation may be attributed to the rigid structure of HFCA. The $\overline{M_n}$ of P1 and P2 derived from GPC are 4200 and 6800, respectively, and the molecular weight distributions are narrower than PF6. The intrinsic viscosity listed in Table 1 also reveals that P2 had a relative higher molecular weight among P1–3.

3.3. Thermal properties

TGA measurement under a nitrogen atmosphere was performed for the polymer samples in order to investigate their thermal properties. As shown in Fig. 3, TGA analyses reveals that the thermal decomposition temperatures for P1–3 are 254 °C, 262 °C and 270 °C, respectively. This indicates that the copolyesters become more thermo-stable as the HFCA content increases. However, the T_d of the polyesters are lower than the conjugated PF6 (400 °C), because the thermo-stability of the main chains containing ester bonds exists in polyesters is worse than that of the full conjugated main chains of PF6.

3.4. UV absorption and PL properties of the poly(FA-co-HFCA)esters before crosslinking

Fig. 4 shows the UV–vis and PL spectra of the polyesters before crosslinking. In dilute chloroform solution (Fig. 4a), the absorption of P1–3 peaks at 264 nm, 284 nm and 269 nm, respectively. As indicated in the literature, the absorption near 300 nm reflects the existence of cinnamoyl group [18]. Regarding P1–3, the absorption intensities in this wavelength band follows the order: P1 > P2 > P3. Similarly, the absorption intensities around 380 nm reflecting the existence of fluorene ring follows the order of P3 > P2 > P1. These results corresponds with the trend of the increase of monomer feed ratios. Regarding the PL spectra (Fig. 4b and c), the PL intensities no matter in chloroform or as films follows the order: PF6 > P3 > P2 > P1, which just indicates that the fluorene units are major component contributing to the photoluminescence. For the PL spectra of the polyesters in solution (Fig. 4b), the PL main peaks are at 418 nm, which exhibits a 6 nm red shift compared with the main peak of PF6 (412 nm). However, in the film state (Fig. 4c), the PL spectra of P1–3 exhibits new peaks at 410 nm and the intensities of the new peaks exceeds the original shoulder peaks at 446 nm. The PL quantum efficiencies (Φ_{PL}) together with other spectral data of the polyesters and PF6 are listed in Table 2. The quantum efficiencies of the polyesters are higher than PF6 in chloroform solution but lower than PF6 in solid state. All the same, the Φ_{PL} of P2 is the highest among these polyesters no matter in solutions or films.

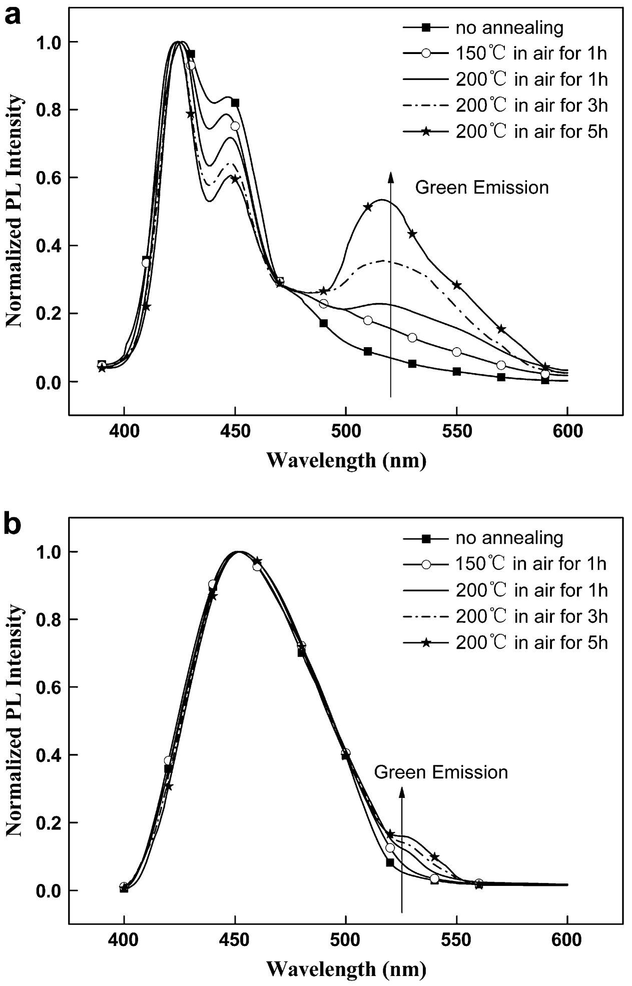

Fig. 6. Annealing spectral stability of PF6 (a) and P2 after UV irradiation of 240 s (b).

3.5. *The track of photocrosslinking process of copolyester P2 by UV, FT-IR and PL spectroscopies*

P2 was selected as an example for the photocrosslinking reaction. The cinnamoyl group is well known to undergo a [2 + 2] photocycloaddition resulting in the formation of a cyclobutane ring [18]. The photocrosslinking reaction was performed at ambient temperature in a thin film cast from chloroform solution on a quartz plate, by irradiation with a 400 W high-pressure mercury lamp at $\lambda = 365$ nm. Fig. 5a shows the changes in the UV spectroscopic absorption of P2 thin films at different irradiation times. The cinnamoyl absorption near 300 nm decreases gradually with increasing the irradiation time. Additionally, the UV peaks exhibits a blue shift as the irradiation time extends. The same photocrosslinking reactions were conducted under the track by FT-IR spectroscopy. Fig. 5b shows the FT-IR spectra of P2 thin films prior to and after the UV irradiation. After irradiation, the absorption peaks of C=C bond at 1630 cm^{-1} decreases, indicating that the opening of the unsaturated bond leads to the formation of cyclobutane ring. Fig. 5c shows the PL spectra of the P2 thin films at different irradiation times. Under the UV irradiation for the photocrosslinking of P2, the peaks of PL spectra exhibits a total shift about 15 nm to the short wavelength direction. Additionally, the normalized PL intensities at 520–550 nm reflecting an extent of chain aggregation or π–π interaction declines as the irradiation time extends. After completion of the photocrosslinking, the films of P2 were never soluble again in chloroform. These results could reveal that the photocrosslinking reactions surely occur and the crosslinked networks are formed, thus leading to the restriction of molecular mobility and flexibility of polymeric backbones.

Table 3
Normalized green emission intensities of PF6 and crosslinked P2.

Sample	Normalized PL intensities at 520 nm				
	No annealing	150 °C, 1 h	200 °C, 1 h	200 °C, 3 h	200 °C, 5 h
PF6	0.069	0.156	0.225	0.352	0.527
Crosslinked P2	0.082	0.125	0.153	0.160	0.166

3.6. *Thermal stability of P2 thin film in the annealing PL spectra*

It is known that films of polyfluorene containing flexible alkyl chains exhibited poor spectral stability upon exposure to heat [6] as showed in Fig. 6a. To examine the effect of the crosslinking structure on the thermal stability of the copolyesters, the films of PF6 and crosslinked P2 were annealed in air for different times on a hot plate at 150 or 200 °C, respectively. It could be seen from Fig. 6a that the films of PF6 exhibited obvious green emission peaks at 500–550 nm when annealed at 200 °C for 3–5 h. However, the films of P2 after crosslinking only showed inapparent peaks at 520–530 nm when annealed at 200 °C for 1–5 h (Fig. 6b). As listed in Table 3, under different annealing conditions, the normalized PL intensities at 520 nm of the crosslinked P2 are much lower than PF6. Additionally, the annealing process did not affect the positions of the main emission peaks for PF6 and crosslinked P2. The main emission peak for crosslinked P2 was at about 450 nm, which was still in the blue emission band. To sum up, the suppression of green emission under annealing conditions may be contributed to the crosslinked architecture of P2, which successfully suppresses the chain aggregation and improves the heat-resistant properties of the polyester.

4. Conclusion

In conclusion, a series of copolyesters based on ferulic acid and 9-hydroxy-9-fluorene-carboxylic acid were synthesized through melt polycondensation and the photocrosslinking process was undertaken to make the aliphatic carbon double bonds crosslinked. The PL spectra of the polyesters prior to crosslinking peaks at 418 nm in chloroform and 423 nm in films, both of which are similar to the PL spectra of the conjugated PF6. Additionally, the polyesters shows slightly higher quantum efficiencies (0.65–0.68) than PF6 in solution while lower than PF6 in films. The photocrosslinking process of P2 was tracked by UV, FT-IR and PL spectroscopies, and this testified the opening of the unsaturated C=C bond and the crosslinking of the copolyester main chains. After crosslinking, P2 exhibits much better annealing spectral stability than PF6 with much weaker green emission at 520–530 nm. This indicates that the designing of photocrosslinkable copolyesters based on ferulic acid and 9-hydroxy-9-fluorene-carboxylic acid is one of the effective methods for the suppression of green emission.

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