

Synthesis and characterization of polyesters containing fluorescein dye units

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Abstract

Low molecular weight polyesters containing fluorescein units in their backbones were successfully synthesized. These fluorescent polymers showed a high solubility in most of the common organic solvents. The onset degradation temperatures of the polymers were greater than that of fluorescein. The glass transition temperatures were in the range 126–194 °C. The bathochromic fluorescence emissions in organic solutions at high concentrations, which resulted from the aggregation of fluorescein moieties, were prohibited by protecting the OH end groups with benzoyl groups. The polymer powders exhibited a maximum photoluminescence intensity at about 580 nm.

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1. Introduction

The GaN-based high brightness blue and green light emitting diodes (LEDs) are commercially available. These short-wavelength lights can be employed as primary light sources to excite luminescent materials for subsequent emission lights of longer wavelengths. The mixed emissions can produce a white color, in addition to a variety of other colors. The luminescence conversion (LUCO) material can be either an organic or inorganic compound [1]. The representative inorganic LUCO material is a yellow emitting phosphor (YAG:Ce). However, the use of organic LUCO materials, especially fluorescent polymers, seems to be advantageous from the viewpoint of minimal cost, ease of fabrication, and color tuning.

Heeger et al. obtained white light emission from InGaN/conjugated polymer hybrid LEDs, where the InGaN-based LED provided the blue component and simultaneously served as the primary light source to excite the photoluminescence (PL) of the polymer double layer

films [2]. The polymers employed in their research were poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (red-emitting, MEH-PPV) and poly(2-butyl-5-(2'-ethylhexyl)-1,4-phenylene vinylene) (green-emitting, BuEH-PPV). In particular, the color tuning of the hybrid LEDs was readily achieved by choosing the appropriate polymer materials and adjusting the film thickness. Zhang and Heeger also observed pure white light emission from the InGaN LED combined with a single layer of conjugated polymers, or copolymers [3]. Representative examples are poly(2,5-bis(cholestanoxo)-1,4-phenylene vinylene) and poly(MEH-PPV-co-BuEH-PPV), respectively. The operating lifetimes of the hybrid LEDs, where the conjugated polymers were encapsulated, were comparable to those of commercial blue GaN lamps.

The stability of the LUCO materials against photo-oxidation largely depends on their chemical structures. The light emission luminosity of the hybrid LED (or LUCO LED) is limited to the PL quantum efficiencies of the LUCO materials. Thus, various types of organic LUCO materials should be tested in order to fabricate improved LUCO LEDs from the perspective of both light emission luminosity and operating lifetime. However, as far as we know, only poly(phenylene vinylene) derivatives as mentioned above, have been reported as being employed in organic LUCO materials.

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We attempted to synthesize various types of light-emitting polymers for potential applications as LUCO materials to be combined with blue LEDs. In this study, fluorescein dye was selected as a building block for the preparation of LUCO polymers, since its fluorescence quantum efficiency is very high (e.g. 97% in ethanolic KOH solution) [4]. Furthermore, the fluorescein dye has two hydroxyl groups, which can easily form ester linkages by reacting with acid chlorides. In order to improve the thermal stability, aromatic rings were incorporated along with fluorescein units in the polyester backbones, as shown in Fig. 1. This paper describes the synthesis and a few general properties of the fluorescent polymers.

2. Experimental section

2.1. Materials and characterization

Fluorescein, terephthaloyl chloride, benzoyl chloride and bisphenol-A were purchased from Aldrich Chemical Co., and used without purification. All other reagents and solvents of laboratory grades were used as received. The

FT-IR spectra were obtained with a JASCO FT/IR-300E spectrometer, under ambient conditions. The ^1H NMR spectra were recorded using a JEOL FT-NMR (JNM-EX400) spectrometer. The UV-visible spectra were obtained from a Shimadzu UV-2501, spectrophotometer. The fluorescence spectra were obtained from an Aminco-Bowman series-2, luminescence spectrometer. The PL spectra were taken in a He-Ne laser at room temperature with 325 nm for an excitation wavelength. The thermogravimetric analysis (TGA) was performed with a Shimadzu TGA-50, and a heating rate of 20 °C/min under a nitrogen atmosphere. The differential scanning calorimetry (DSC) was performed on a 2910 modulated DSC instrument (TA instruments), at the heating rate of 10 °C/min under a nitrogen atmosphere.

2.2. Synthesis

2.2.1. Poly(fluoresceinyl terephthalate) (PFT)

All reactions were carried out under a nitrogen atmosphere. Fluorescein (3.32 g, 9.99 mmol) was dissolved in DMF (7.5 ml) in the presence of pyridine (4 ml) at room temperature for 15 min to obtain a dark brown solution,

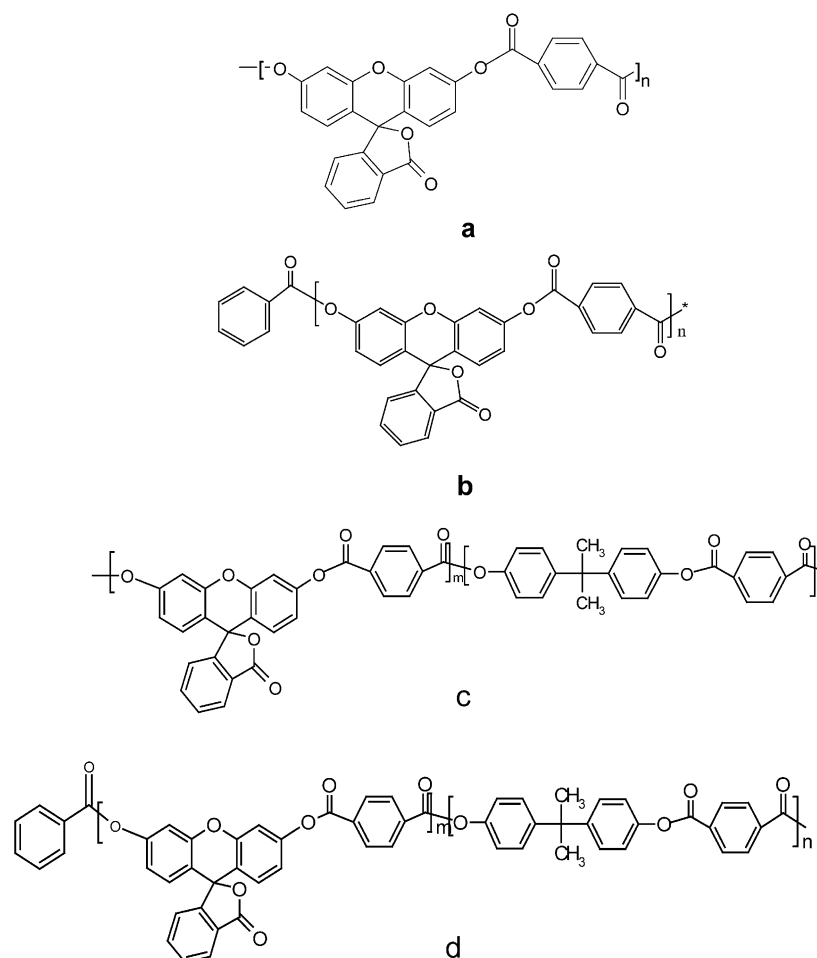


Fig. 1. Chemical structures of (a) PFT, (b) PFT-B, (c) P(FT-co-BT), and (d) P(FT-co-BT)-B.

followed by the slow addition of terephthaloyl chloride (2.28 g, 11.23 mmol) solution in DMF (5 ml) and nitrobenzene (7.5 ml) for 20 min at room temperature. The reaction mixture was stirred for 20 h at room temperature, and the resulting viscous solution was poured into methanol to obtain the polymer as precipitate. The product was purified by repeating the precipitation procedure. The light yellow solid was collected by filtration (isolation yield 75%).

2.2.2. Poly(fluoresceinyl terephthalate-co-bisphenol A terephthalate) (P(FT-co-BT))

Fluorescein (1.16 g, 3.49 mmol) and bisphenol A (1.14 g, 4.99 mmol) were dissolved in DMF (7.5 ml) in the presence of pyridine (4 ml) at room temperature for 15 min to obtain a dark brown solution, followed by the slow addition of a solution of terephthaloyl chloride (2.03 g, 9.99 mmol) in DMF (5 ml) and nitrobenzene (7.5 ml) for 20 min at room temperature. The reaction mixture was stirred for 20 h at room temperature, and the resulting viscous polymer solution was poured into methanol to obtain the polymer as precipitate. The light yellow solid was collected by filtration. The dissolution and precipitation procedure were repeated to obtain the product (isolation yield 70%).

2.2.3. PFT-B

The phenolic OH end groups of PFT were protected using benzoyl chloride as follows: PFT was synthesized as mentioned above, followed by the addition of an appropriate amount of benzoyl chloride over a period of 30 min. The resulting mixture was continuously stirred for 20 h. The viscous reaction mixture was poured into excess methanol for precipitation. The resulting crude PFT-B was dissolved in chloroform and subsequently precipitated with methanol. The same purification procedure was repeated twice. Finally, pure PFT-B was collected by filtration. FT-IR (KBr, cm^{-1}): 1727 ($-\text{C}=\text{O}$), 1257 ($-\text{C}-\text{O}-$). ^1H NMR (CDCl_3 , ppm): 8.3 (d, 2H), 8.2 (d, 1H), 8.1 (d, 4H), 7.8–7.7 (m, 2H), 7.5 (m, 1H), 7.3 (d, 2H), 7.2 (m, 1H), 6.9 (d, 2H), 6.8 (d, 2H).

2.2.4. P(FT-co-BT)-B

A similar procedure was employed for the protection of polymer P(FT-co-BT) in order to obtain P(FT-co-BT)-B. FT-IR (KBr, cm^{-1}): 1727 ($-\text{C}=\text{O}$); 1257 ($-\text{C}-\text{O}-$). ^1H NMR (CDCl_3 , ppm): 8.3 (d, 2H), 8.2 (d, 1H), 8.1 (d, 4H), 7.8–7.7 (m, 2H), 7.5 (m, 1H), 7.3 (d, 2H), 7.2 (m, 1H), 6.9 (d, 2H), 6.8 (d, 2H).

3. Result and discussion

The synthesized polymers were slightly yellow in color. The solubilities of the four different polymers were tested in various solvents, and the results are listed in Table 1. PFT and P(FT-co-BT) exhibited high solubilities in polar

Table 1
Solubilities of fluorescent polymers in various solvents at room temperature

Solvents	PFT	PFT-B	P(FT-co-BT)	P(FT-co-BT)-B
DMF	++	++	++	++
DMSO	++	+-	++	+-
NMP	++	+-	++	+-
THF	++	++	++	++
Ethyl acetate	+-	++	+-	++
Methylene chloride	+-	++	+-	++
Acetone	+-	++	+-	++
Chloroform	+-	++	+-	++
Methanol	--	--	--	--
Ethanol	--	--	--	--
Toluene	--	--	--	--
Water	--	--	--	--

+, highly soluble; +-, soluble; --, insoluble.

solvents such as DMF, DMSO, NMP, and THF, due to the presence of phenolic OH end groups. Conversely, PFT-B and P(FT-co-BT)-B exhibited lower solubilities in polar solvents, but higher solubilities in less polar solvents, such as ethyl acetate, acetone and chloroform, as compared to PFT and P(FT-co-BT). This result indirectly supports the fact that most OH end groups of PFT and PFT-B were protected.

The FT-IR spectra of fluorescein and polymers containing fluorescein units are shown in Fig. 2. Fluorescein exhibited a very broad and strong peak in the range of 3500–3000 cm^{-1} , due to the phenolic OH groups. However, the strong phenolic OH peak weakened in the IR spectra of PFT and P(FT-co-BT). Instead, strong peaks at around 1750 and 1255 cm^{-1} were clearly observed, due to the ester linkages in the polymer backbones. This observation indicates that most of the phenolic OH groups reacted with the terephthaloyl chloride to form the corresponding polymers

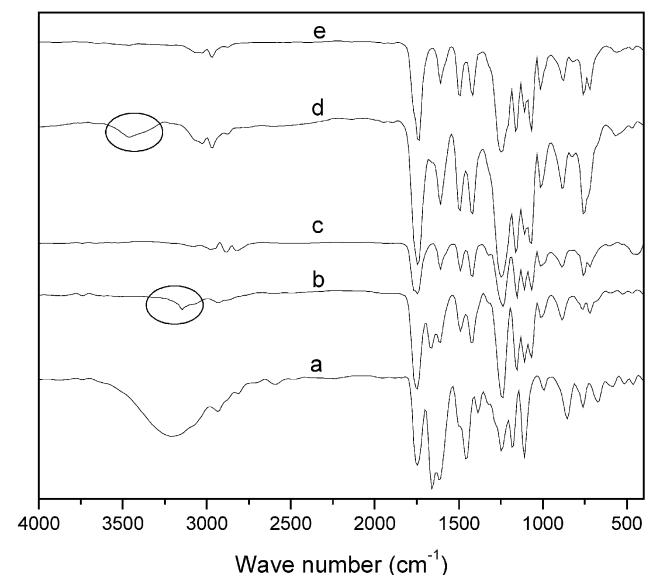


Fig. 2. FT-IR spectra of (a) fluorescein, (b) PFT, (c) PFT-B, (d) P(FT-co-BT), and (e) P(FT-co-BT)-B (KBr pellets).

via ester linkage. The presence of very weak phenolic OH peaks is due to the end groups of polymer chains since the polymer end group should be either methyl ester or phenolic OH. However, the phenolic OH peak was not appreciable in the IR spectra of PFT-B and P(FT-*co*-BT)-B, which indicates that the phenolic OH end groups of PFT and P(FT-*co*-BT) were successfully protected, using benzoyl chloride. The chemical structures of the unprotected polymers PFT and P(FT-*co*-BT) were confirmed by ^1H NMR spectra, as shown in Fig. 3.

According to the gel permeable chromatography (GPC)

data (internal standard; polystyrene in chloroform), the weight-average molecular weights of PFT, PFT-B, P(FT-*co*-BT), and P(FT-*co*-BT)-B were 2100, 4200, 3300, and 7700, respectively. This result suggests that the molecular weights of protected polymers PFT-B and P(FT-*co*-BT)-B may be almost two or three times higher than those of unprotected polymers PFT and P(FT-*co*-BT), respectively. However, the mass spectra obtained from a MALDI-TOF mass spectrometer (Voyager-DE STR, ABI 4700 Proteomics Analyzer) revealed that the molecular weights of PFT and PFT-B were very similar to each other, and ranged up to

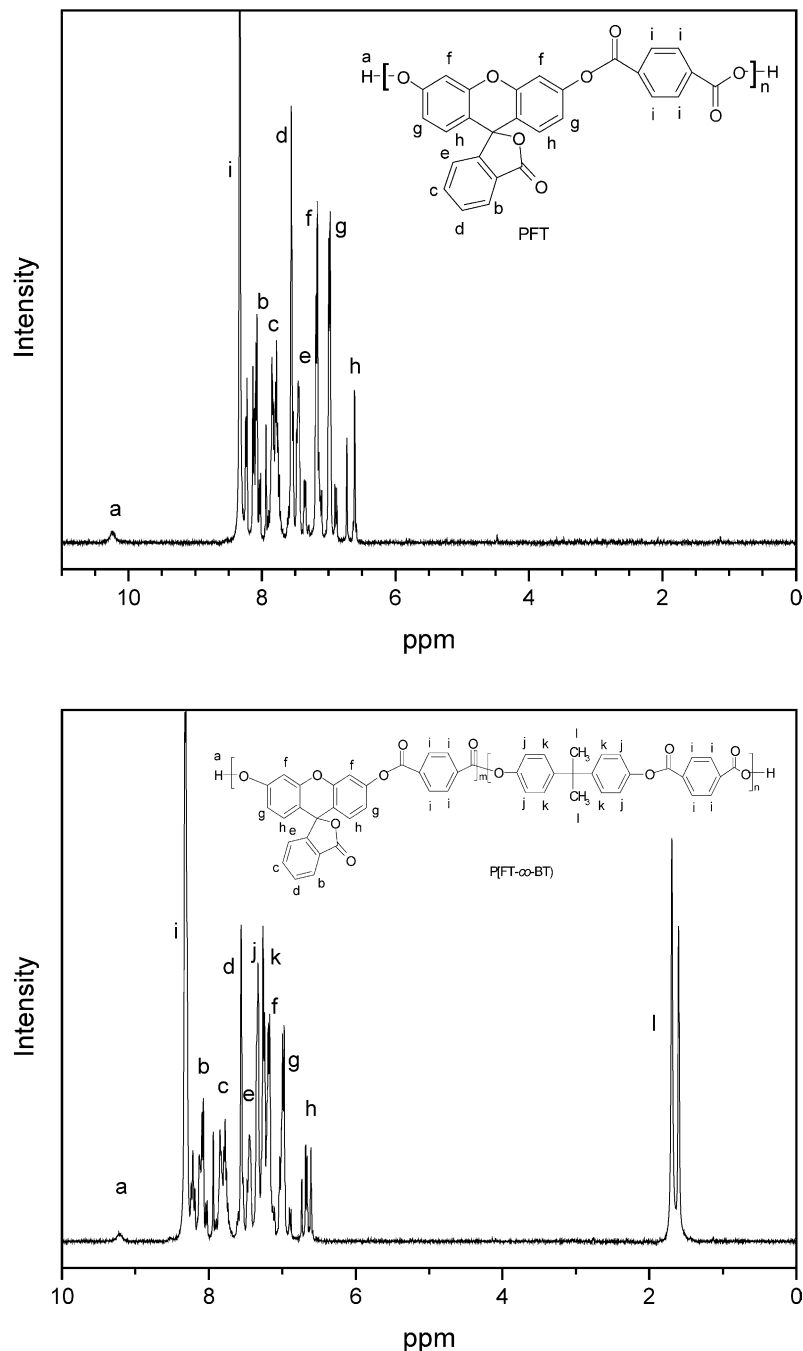


Fig. 3. ^1H NMR spectra of PFT (top) and P(FT-*co*-BT) (bottom).

about 2600. The discrepancy between the GPC and mass data for the protected and unprotected polymers suggests that the conformations of the polymers may be different from each other in the polymer solutions, probably because the protected polymers are more extended due to the presence of the rigid benzoyl end groups.

The TGA thermograms of fluorescein and the polymers are depicted in Fig. 4, and the results are summarized in Table 2. The onset degradation temperatures of the polymers ranged from 383 to 426 °C, while that of fluorescein was 345 °C, indicating that these polymers are thermally more stable than fluorescein, and stable enough to be used in LUCO LEDs [5]. The protected polymers PFT-B and P(FT-*co*-BT)-B exhibited higher thermal stability than the corresponding unprotected polymers, due to the introduction of rigid benzoyl end groups. Interestingly, P(FT-*co*-BT) and P(FT-*co*-BT)-B showed significantly higher thermal stability over PFT and PFT-B. The enhanced thermal stability of these polymers probably resulted from their higher molecular weights. The slight weight loss occurring in the range 100–200 °C results from the evaporation of residual solvent (DMF), which was used in the purification stage for both polymers PFT and P(FT-*co*-BT).

The lifetime of LUCO LED is closely related to the glass transition temperature (T_g) and thermal stability of the polymers, as reported for the organic based LEDs [5,6]. The DSC thermograms of the current fluorescent polymers are shown in Fig. 5. The T_g s of PFT and P(FT-*co*-BT) appeared at 143 and 126 °C, respectively. The relatively lower T_g of P(FT-*co*-BT), as compared to that of PFT, probably resulted from the less closely packed polymer chains, due to the presence of the bulky geminal methyl groups in bisphenol A units. Interestingly, the T_g s of their corresponding protected polymers PFT-B and P(FT-*co*-BT)-B were greatly increased to 194 and 175 °C, respectively. The increase in the T_g s of the protected polymers probably resulted from the benzoyl

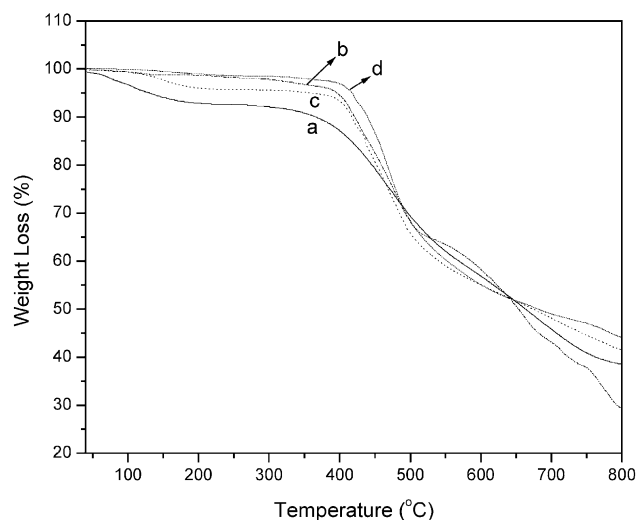


Fig. 4. TGA thermograms of (a) PFT, (b) PFT-B, (c) P(FT-*co*-BT), and (d) P(FT-*co*-BT)-B.

Table 2
Thermal stabilities of fluorescent polymers

Sample code	T_d (°C) ^a	T_g (°C)
Fluorescein	345	–
PFT	383	143
PFT-B	397	194
P(FT- <i>co</i> -BT)	401	126
P(FT- <i>co</i> -BT)-B	426	175

^a T_d onset degradation temperature.

protecting groups, which are more rigid and can more efficiently restrict the rotation of the polymer end groups. Overall, the T_g s of the protected polymers were much higher than the well-known light emitting polymers, such as MEH-PPV [7] and polyfluorene [8,9], whose T_g s were reported to be 65 and 75–125 °C, respectively.

Fig. 6 illustrates the absorption and fluorescence spectra of fluorescein dye and PFT in DMF, as well as the PL spectra of their powders. A strong absorption of PFT occurred in the range of 400–525 nm, which corresponds to the characteristic absorption of fluorescein moieties. The maximum absorption wavelength (λ_{max}) of PFT (~460 nm) was very close to that of fluorescein. The three different absorption maxima appeared at 430, 460 and 490 nm for both fluorescein and PFT. The absorption spectra of the four different fluorescent polymers were very similar to each other, except for slightly different absorption edges. Compared to fluorescein, the fluorescent polymers exhibited less intense absorption bands at the same wt% concentrations. This result is not surprising, because the reduction in absorption intensity resulted from the reduced concentrations of fluorescein moieties in the polymer samples, due to the presence of benzoyl and bisphenol A moieties in the polymer backbone.

The maximum fluorescence intensity of the PFT solution

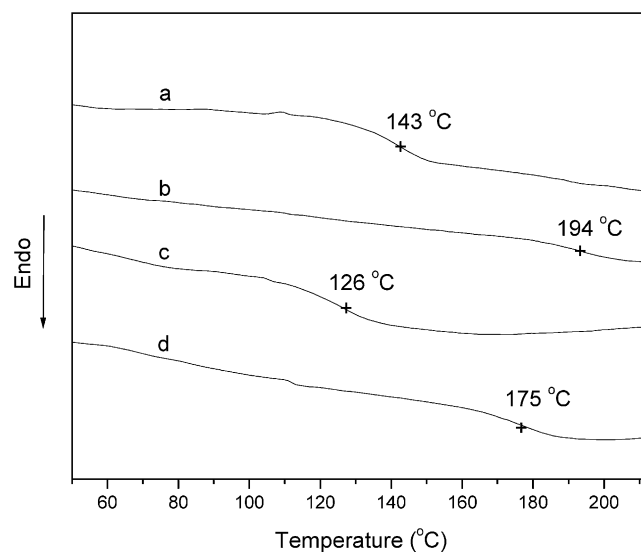


Fig. 5. DSC curves of (a) PFT, (b) PFT-B, (c) P(FT-*co*-BT), and (d) P(FT-*co*-BT)-B.

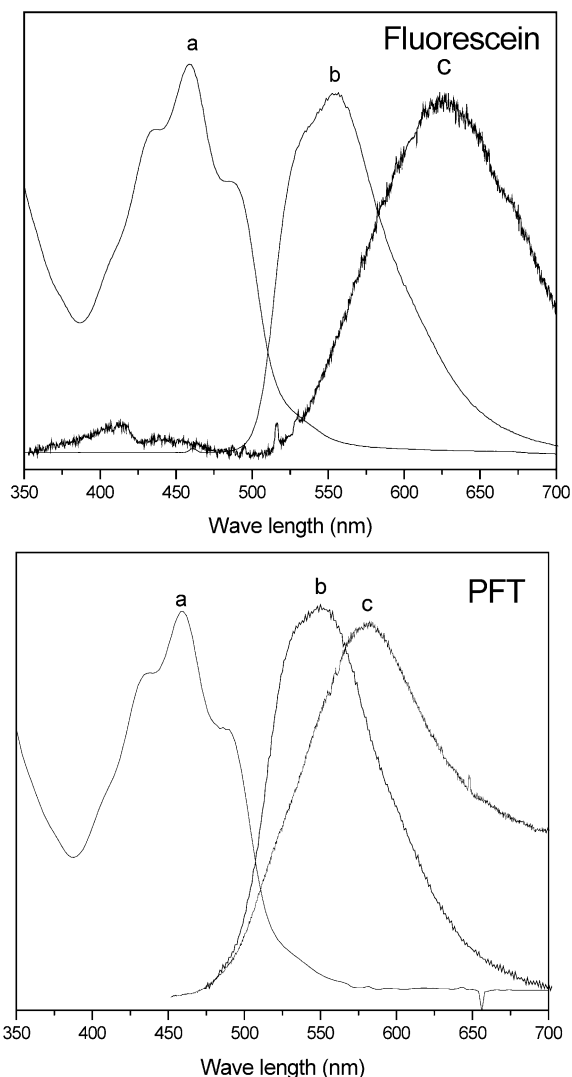


Fig. 6. (a) Absorption, (b) fluorescence spectra in DMF, and (c) PL spectra of powders.

in DMF appeared at 536 nm, which corresponds to the greenish-yellow region, while that of the fluorescein dye solution in DMF was 555 nm. This result indicates that the fluorescence emission of PFT was blue-shifted from that of fluorescein, by almost 20 nm, due to reduced interactions between the chromophores, resulting from non-fluorescent benzoyl moieties in the polymer. The maximum PL intensity of PFT powders was observed at 580 nm, which is perfectly yellow in color. However, the red-shifted PL spectrum of PFT powders, compared to the fluorescence spectrum of the same compound in DMF, is probably due to the stronger interactions between fluorescein units of the polymers in the solid state [10,11]. Similar behaviors were also observed in the protected polymers of PFT-B and P(FT-co-BT)-B. The maximum PL intensity of fluorescein dye powders appeared at about 625 nm, while that of the PFT appeared at 580 nm, as mentioned above. The blue-shifted PL emission of PFT powders, compared to that of

fluorescein powders, probably resulted from the same reason as that for the blue-shift fluorescence emission of PFT solution in DMF, as discussed above. In other words, the blue-shifted emission is due to the non-fluorescent units (benzoyl groups) in the polymer chains, which prohibit any close interaction between the fluorescein moieties.

The fluorescein spectra of PFT solutions in DMF with different concentrations are shown in Fig. 7. The fluorescence intensity increased as the polymer concentration increased up to 5 wt%. However, beyond the particular concentration, it decreased as the concentration increased further. In addition, the second maximum peak of fluorescence emission (~ 556 nm) was more pronounced at higher concentrations (Fig. 7(e) and (f)). The second maximum emission peak probably resulted from the interactions between the fluorescein moieties within each polymer chain and/or in different polymer chains. In order to

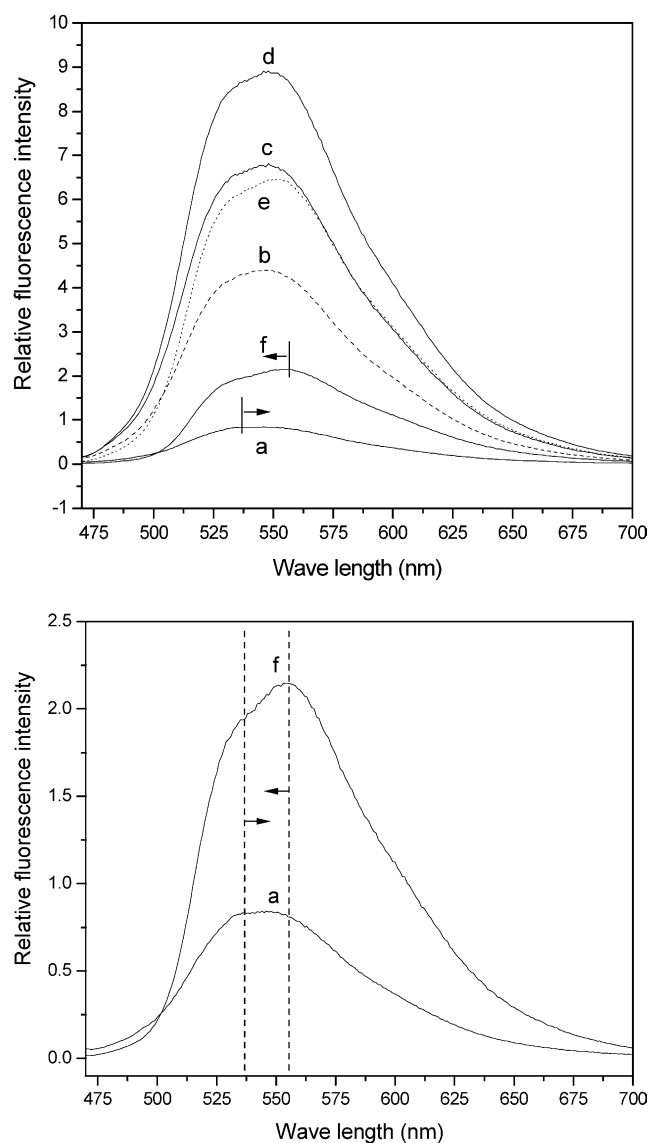


Fig. 7. Fluorescence spectra of PFT in solutions in DMF at different concentrations: (a) 0.05, (b) 0.5, (c) 1.0, (d) 2.5, (e) 5, and (f) 10 wt%.

reduce the interactions between fluorescein moieties, the rigid bisphenol A was incorporated into the polymer chain, to obtain P(FT-*co*-BT). Unexpectedly, the overall fluorescence spectra of P(FT-*co*-BT) were very similar to those of PFT, as shown in Fig. 7. However, the second maximum emission peak appeared at 545 nm in the concentration range 0.5 to 10 wt% in DMF, rather than at \sim 556 nm. This observation indicates that the rigid bisphenol A units in the polymer backbone suppress the chromophore aggregation in solution [12], but not very efficiently.

Interestingly, the protected polymers PFT-B and P(FT-*co*-BT)-B exhibited very high emission intensities even at relatively high concentrations since the emission intensities increased as the polymer concentration increased up to 10 wt%, as shown in Fig. 8. At the same time, no second maximum peak was observed in their emission spectra. It means that molecular aggregation was almost suppressed by protecting the OH end groups. Such an observation indicates that the OH end groups are not available for hydrogen bonding to form molecular aggregation among the polymer chains in the protected polymer system. A similar observation was reported for the hydroxyl-substituted naphthalene carboxylic acids [13]. Based on these results, the formation of the second emission peak is primarily due to intermolecular interactions, rather than intramolecular interactions. The fluorescence quantum yields of these polymers are expected to depend on whether the polymers are in neutral or salt forms in solutions since the lactonoid

moieties of the fluorescein units can be opened in appropriate alkaline conditions [14]. Of course, the quantum yield should also depend on whether the polymers are in solution or solid films. Studies on the fluorescence quantum yields of these polymers are in progress, and will be reported shortly.

4. Conclusions

Low molecular weight fluorescent polyesters, containing fluorescein units, were successfully synthesized. They exhibited a high solubility in most common organic solvents, which varies somewhat, depending on the polarity of the end groups. These polymers were thermally more stable than fluorescein dye, due to the presence of rigid aromatic units in their main chains. The aggregation of the fluorescein units in the polymers could be greatly prohibited in organic solutions by protecting the phenolic OH end groups. These fluorescent polymers seem to be promising LUCO materials for the generation of white light from a blue light source.

Acknowledgements

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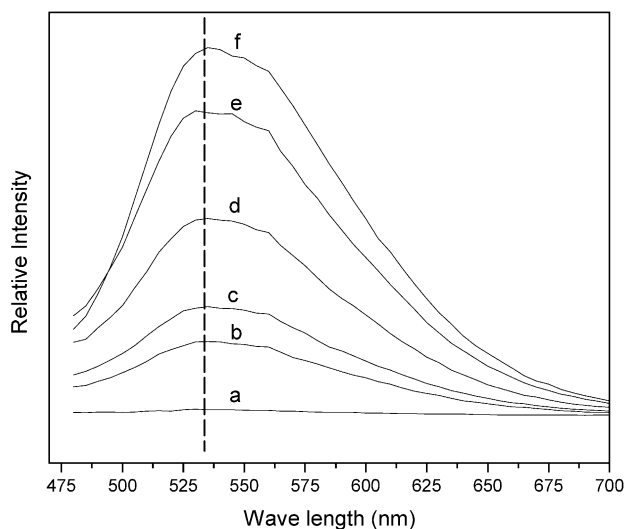


Fig. 8. Fluorescence spectra of P(FT-*co*-BT)-B solutions in DMF at different concentrations: (a) 0.05, (b) 0.5, (c) 1.0, (d) 2.5, (e) 5, and (f) 10 wt%.