Rod−Coil Block Copolymers Incorporating Terfluorene Segments for Stable Blue Light Emission

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Spectroscopic studies on a series of rod−coil block copolymers with terfluorene as the rigid segment demonstrate that the main cause of color instability in fluorene oligomers and polymers is aggregate and/or excimer formation and not the presence alone of keto defects (fluorenone formation) along the molecular chain. Keto defects, when present, contribute to the appearance of the undesirable "green" emission band but are not the leading cause of color instability. Thus, the synthesis of materials where aggregation and/or interchain, intersegment interactions are inhibited is the key approach for the production of stable polymeric light-emitting devices (PLED's). The potential of this method is verified by the synthesis of photooxidative stable fluorene/styrene diblock copolymer blue emitters.

1. Introduction

The most challenging topic in the area of polymeric light emitting diodes (PLEDs)[1] is the realization of color stable blue light emission with high efficiency.[2] Polyfluorenes (PFs)[3] have emerged as an attractive class of electroluminescent conjugated polymers for use in blue light emitting diodes, exhibiting high photoluminescence quantum yields in the solid state. Moreover, as a host material, PFs enable the full color range (red, green and blue) via energy transfer to longer wavelength emitters either in blends or in copolymers with perylene dyes and other comonomers.[4] The major disadvantage of PFs is their poor spectral stability under normal operation with the appearance of a low-energy emission band occurring at 520−530 nm.

Several attempts have been made to stabilize the blue color emission using either dendrimers[5] or bulky substituents[6] in the 9-position of the fluorene moiety, copolymerization techniques,[7] oligomers,[8] and purification of the fluorene monomers before polymerization,[9] but the green electroluminescence band was not eliminated. In a more recent study, blends of polyfluorenes with some nonconjugated polymers such as polystyrene or poly-(vinyldiphenylquinoline) minimized the tendency of polyfluorenes to produce green light.[10] Despite the efforts to clarify the nature of this phenomenon, the exact origin of this longer wavelength band remains unclear. Some research groups suggest that the low-energy emission band is attributed to the creation of keto defects in the backbone of polyfluorenes,[3c,11] whereas the formation of aggregates or excimer emission as well as interchain interactions are also believed to contribute to the appearance of this band.[3b,12]

Because high chemical purity and structural uniformity are considered as critical factors for PLED performance, monodisperse conjugated oligomers are used instead of conjugated polymers. However, oligomers are generally more prone to crystallization than polymers, resulting in polycrystalline films that scatter light and limit charge injection and transport. Therefore, one approach to overcome the aforementioned disadvantages is the use of rod−coil block copolymers with a monodispersed conjugated oligomeric unit as the rigid segment and some nonconjugated or hole/electron transporting molecules as the flexible block.[13] Moreover, the resulting block copolymers would combine the advantages of the oligomer approach in molecular electronics such as solubility and well-defined conjugation length with those of polymers such as easy processing, mechanical integrity and absence of crystallization in devices.[14]

From the materials scientist's point of view, polymers containing fullerenes offer opportunities for the production of new optoelectronic materials that can be processed into different objects and thin films due to high solubility in common organic solvents.[15] With this approach, the two major disadvantages of fullerenes (low solubility and poor processability) can be improved. Many efforts have been devoted to the synthesis of polymeric C_{60} derivatives[16] but the easiest method of incorporation the fullerene into a polymer matrix is radical copolymerization.[17] In particular, soluble fullerenes are attractive candidates as electron acceptors for bulk heterojunction plastic solar cells applications.[18]

In this report, we present photostable blue emitters based on diblock copolymers having a well-defined terfluorene unit as the rigid segment and polystyrene as the flexible part, along with the synthesis of soluble polymeric derivatives of fullerene incorporating terfluorene blocks. These materials were synthesized using the atom transfer radical polymerization (ATRP) technique.[19] A combination of FT-IR measurements on thin polymer films after photooxidation treatments with the subsequent collection of the photoluminescence spectra were used to examine the oxidative resistance of these copolymers. The molecular structures of polyfluorene PFH, the terfluorene initiator TFI, the diblock copolymers TFPS(I)−(II) and the TFPSF copolymer are depicted in Chart 1.

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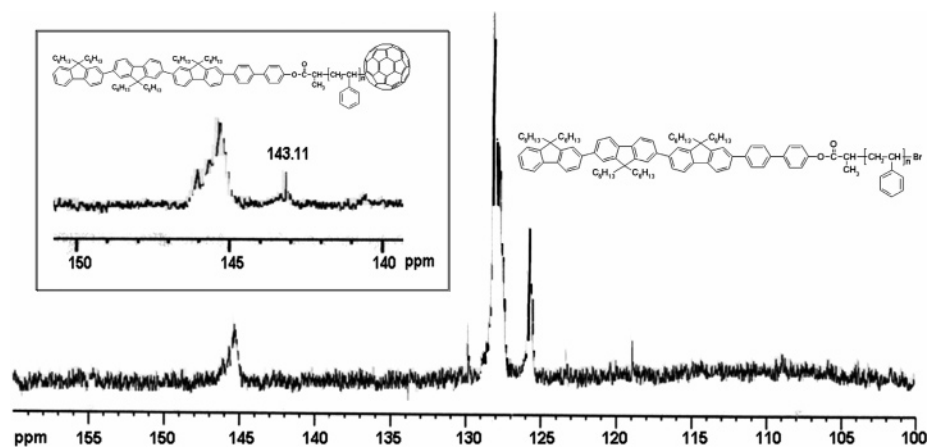‡ University of Patras.

CHART 1: Molecular Structures of the Polyfluorene PFH, the TFI, the Diblock Copolymers TFPS(I)−(II) and the TFPSF Copolymer

2. Experimental Section

Materials. The TFI, the diblock copolymers TFPS(I)−(II),[12b,20] and poly(9,9-dihexylfluorene) (PFH)[21] were synthesized on the basis of published procedures. PFH was synthesized using the Suzuki coupling route and had $M_n = 7200$ and $M_w = 18600$ on the basis of the typical polystyrene equivalent gel permeation chromatography (GPC). Fullerene (C_{60}) was purchased from SES Research, Inc. Houston, TX. Copper(I) bromide CuBr, 2,2′-bipyridine (bpy) and all the other reagents were used as received from Aldrich. o-Dichlorobenzene (ODCB) was purged with argon for 1 h before use.

Measurements. The structures of the synthesized materials were clarified by high-resolution ^{13}C NMR spectroscopy with a Bruker Avance DPX 100 MHz spectrometer. Gel permeation chromatography (GPC) measurements were carried out using a polymer lab chromatographer with two Ultra Styragel linear columns (10^4, 500 A), UV detector polystyrene standards and $CHCl_3$ as eluent, at 25 °C with a flow rate of 1 mL/min. The UV spectra were recorded on a Hewlett-Packard 8452A diode array UV−visible spectrophotometer. Fluorescence was measured on a Perkin-Elmer LS45 spectrofluorometer. FT-IR spectra were recorded with a Nicolet Magna 850 spectrometer equipped with an MCT/A detector. For the photooxidation experiments, the samples were exposed in air and irradiated with UV light at 365 nm (∼1000 mW) from an Efos Ultracure 100SS curing system. For the FT-IR and photoluminescence measurements thin films were spin-coated on barium fluoride (BaF_2) and quartz substrates, respectively.

Synthesis of TFPSF. TFPS(II) (0.05 mmol), CuBr (0.05 mmol), and bpy (0.1 mmol) were placed in a reaction flask, degassed and filled with argon three times. Next, o-dichlorobenzene (3 mL) and fullerene (0.1 mmol) were added in the reaction flask. The reaction mixture was heated at 110 °C for 24 h. Tetrahydrofuran (3 mL) was added in the flask and purification was achieved by passing the reaction solution through a silica column to remove the copper catalyst and unreacted C_{60}. Precipitation into methanol (20-fold excess by volume) gave a crude brownish solid that was redissolved with tetrahydrofuran. Filtration of the solution to remove traces of

C_{60} and reprecipitation from methanol gave TFPSF as brown solids with 81% yield.

3. Results and Discussion

3.1. Synthesis. The previously described methodology[12b,20] for the preparation of rod−coil block copolymers using a functionalized terfluorene as the initiator for the ATRP polymerization of styrene was used here for the synthesis of TFPS. Furthermore, the ATRP technique was also used for the synthesis of TFPSF because it is a method that enables the introduction of C_{60} to polymers via controlled radical polymerization to obtain C_{60}-bonded polymers. For the achievement of the monosubstituted fullerene derivative, TFPS(II)/C_{60} (1/2 in molar ratio) in the catalytic system CuBr/bpy with o-dichlorobenzene as the solvent in 110 °C was used on the basis of a known procedure.[22] The synthesized TFPSF copolymer exhibit high solubility in common organic solvents such as tetrahydrofuran (THF), trichloromethane ($CHCl_3$) and o-dichlorobenzene (ODCB). Due to the different solubilities between the C_{60} and the polymer modified with C_{60} and to exclude the presence of unreacted fullerene in the product, the polymeric C_{60} was dissolved in THF and, after filtration, reprecipitated in methanol twice. Even though ^{1}H NMR spectroscopy can be used to confirm the efficient incorporation of the fullerene into TFPS-(II), no significant difference in chemical shift is observed when −CH−Br is converted to −CH−C_{60}. Therefore, ^{13}C NMR spectroscopy is a more useful technique to apply for the characterization of the synthesized TFPSF copolymer. The ^{13}C NMR spectrum of TFPS(II) is depicted in Figure 1. After the introduction of the fullerene in the TFPS(II), a new peak centered at 143.11 ppm is present in TFPSF along with all the other peaks of TFPS(II) (inset of Figure 1). The broad peak at 143.11 ppm is characteristic of the substituted C_{60} in contrast to a narrow peak (single line) observed for pure C_{60}.[23]

3.2. Spectroscopic Characterization. To evaluate the impact of the photooxidation treatment on the chemical structure of the PFH, TFI, TFPSF, and TFPS(I)−(II), thin deposits were studied using FT-IR spectroscopy. The FT-IR spectra of the photooxidative treated PFH, TFI, TFPSF and TFPS(I)−(II) as thin films in the 1850−1650 cm^{-1} region are presented in Figure

Rod−Coil Block Copolymers Incorporating Terfluorene

J. Phys. Chem. B, Vol. 109, No. 18, 2005 **8757**

Figure 1. ^{13}C NMR spectrum of TFPS(II) in the 160−100 ppm region. In the inset is depicted the ^{13}C NMR spectrum of TFPSF in the 150−140 ppm area.
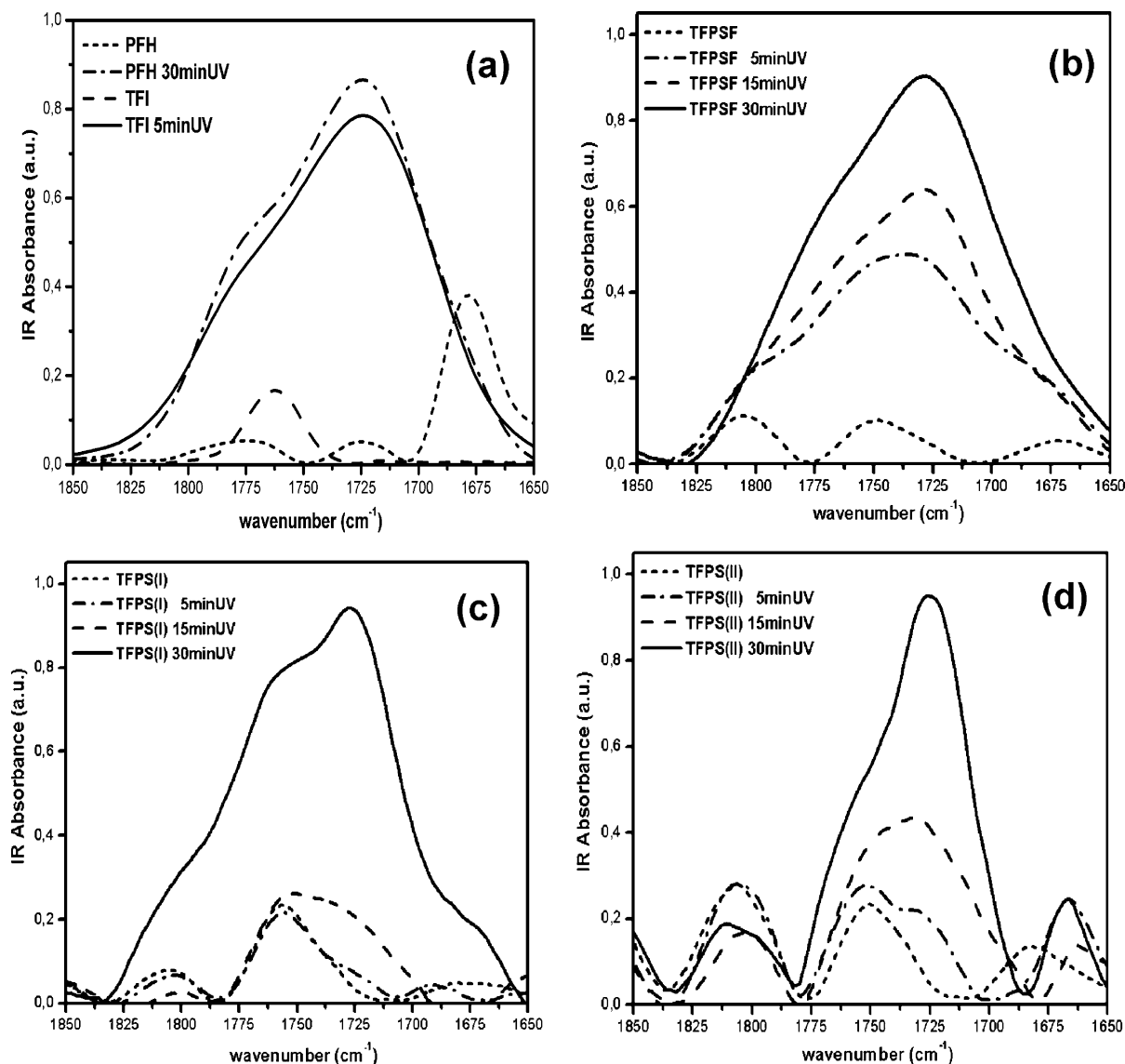

Figure 2. FT-IR spectra of (a) PFH and TFI, (b) TFPSF, (c) TFPS(I), and (d) TFPS(II) as pristine films and after UV treatment in air (exposure for different periods of times between 5 and 30 min).

2. The spectra of all the studied materials are dominated by the appearance of the 1726 cm^{-1} band after 30 min under UV exposure, which is assigned to the carbonyl stretching mode of the fluorenone moiety.[24] In addition, a new band at 1775 cm^{-1} is present as a shoulder and these features suggest that upon

degradation except from the fluorenone moieties, another type of chemical species are also created. In a recent work, the creation of a new type of species was also suggested, but no explanation was given.[25] Moreover, the progressive increase of the 1726 cm^{-1} band under UV treatment in the different time
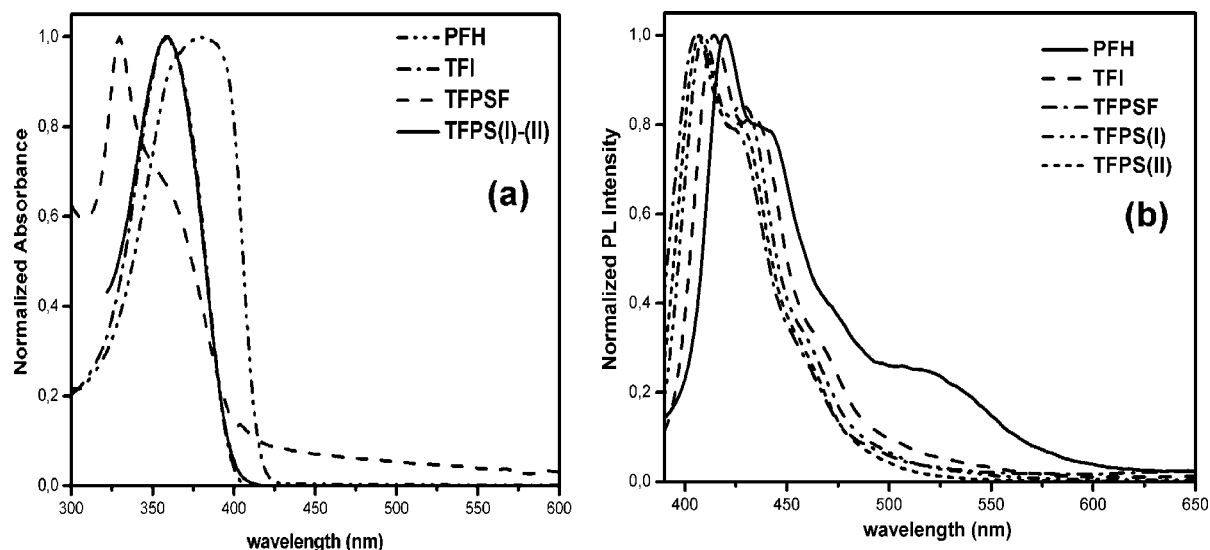
Figure 3. (a) Absorption spectra of the studied materials in chloroform solution and (b) photoluminescence spectra of PFH, TFI, TFPSF, and TFPS(I)−(II) as pristine films. Excitation wavelengths were 360 nm for TFI, TFPSF, and TFPS(I)−(II) and 380 nm for PFH.

periods (5, 15, and 30 min) for TFPSF and TFPS(I)−(II) is obvious on the basis of the FT-IR spectra in Figure 2b−d.

3.3. Optical Properties. UV−vis absorption spectra of PFH, TFI, TFPSF and TFPS(I)−(II) in chloroform solution are shown in Figure 3a. Strong evidence for the efficient incorporation of TFPS(II) into the fullerene ensue from the corresponding absorption spectra. Although TFPS(II) show an absorption maximum at 360 nm due to the $\pi-\pi*$ transition of the terfluorene segments, no absorption band at 330 nm is present. In contrast, the functionalized TFPSF exhibit the 330 nm absorption band as well as the 360 nm. The band at 330 nm is characteristic of the functionalized fullerenes[26] and at 360 nm of the terfluorene block, respectively. In addition, the appearance of the two well resolved absorption peaks at 330 and 360 nm reveals that the covalently linked fullerene and terfluorene moieties retain the electronic properties of the separated molecules and charge transfer in the ground state does not take place. Moreover, PFH displays a 20 nm red shift of the absorption maximum (380 nm) compared to the materials incorporating the terfluorene units due to the larger conjugation length.

The photoluminescence spectra of the studied materials in the solid state are depicted in Figure 3b. PFH displays a progression of vibronic peaks at 420, 440, and 474 nm, assigned to the 0−0, 0−1, and 0−2 intrachain singlet transitions in the solid state, with the 0−0 transition being the most intense along with an additional broad band at 520 nm. The TFI, TFPS(I)−(II), and TFPSF exhibit a blue shift at the main peaks with no indication for the existence of the green light emission at 520 nm. The emission broad band at 520 nm for the case of PFH has initially been attributed to aggregation and/or excimer formation[3b] but recently has been shown to be due to emission from fluorenone-like defects due to oxidative (photo- or electro-) degradation of the film.[3c,11a,11b,27] In a more recent study,[12c] it was shown the effect of the type of the substituted alkyl chains on the properties of polyfluorenes as thin deposits. Substituted polyfluorenes with linear alkyl groups are made of long fibrils, with lateral dimensions on the order of a few nanometers. This long-range organization that is attributed to the formation of aggregates of well-organized, densely packed molecules is responsible for the red shift and the formation of a broad emission band in the green region of the spectrum. On the contrary, polyfluorenes with branched alkyl chain substituents

typically display a solid-state emission spectrum that is identical with the spectra in dilute solutions.[11c,12c] It appears that branched alkyl as well as aromatic substituents prevent the π-stacking of the polymer chains,[5,6] which results in more homogeneous, featureless films, as previously reported.[12c] Additionally, in a recent work[28] it was suggested that the effect of the dendronization in the 9-position of polyfluorenes is responsible for the appearance of the broad band due to aggregation that takes place at point defects between adjacent chain segments of the first-generation dendronized polymers.

The results of the investigation of the influence of the photooxidation under diffuse UV radiation at ambient atmosphere on the optical properties of the studied materials are presented in Figure 4. The emission spectrum of PFH, which is dominated by the appearance of the "green" emission band after 30 min under UV light, is shown in Figure 4a. In addition, the emission spectra of TFI before and after 5 min of UV exposure are also presented in Figure 4a. The emission spectrum of the untreated TFI after 5 min under UV light is quenched because the fluorenone moieties created due to this UV treatment (Figure 2a) are efficient exciton traps. Furthermore, TFPSF exhibits the typical emission of fluorenes (Figure 4b) but after the application of the UV oxidation the emission intensity of TFPSF subsequently decreases and finally after 30 min the low-energy emission band is clearly present based on the results of the inset of Figure 4b.

The emission spectra of TFPS(I)−(II) after photooxidation in various times were collected and are depicted in Figure 4c,d. It is very interesting to note that TFPS(II), despite the formation of the keto defects on the polymer backbone based in Figure 2d, does not exhibit the low-energy emission band at 520 nm. Thus, the PL spectral characteristics of TFPS(II) remain unchanged in contrast to both TFPSF and TFPS(I), which display the emission broad band at 520 nm after 30 min under UV light. In the case of TFPS(I) the emission band at 520 nm appeared after 30 min and the material shows a lower resistance to color degradation as compared to TFPS(II). The only explanation why the undesirable energy emission band at 520 nm is present in TFPS(I) and not in TFPS(II), as shown in the insets of Figure 4c,d is that although fluorenone moiety is present, it is not the dominant cause for the appearance of the "green" emission band. Sims et al., in a very recently work,[12a] found results similar to ours and suggested that fluorenone is a

Rod−Coil Block Copolymers Incorporating Terfluorene

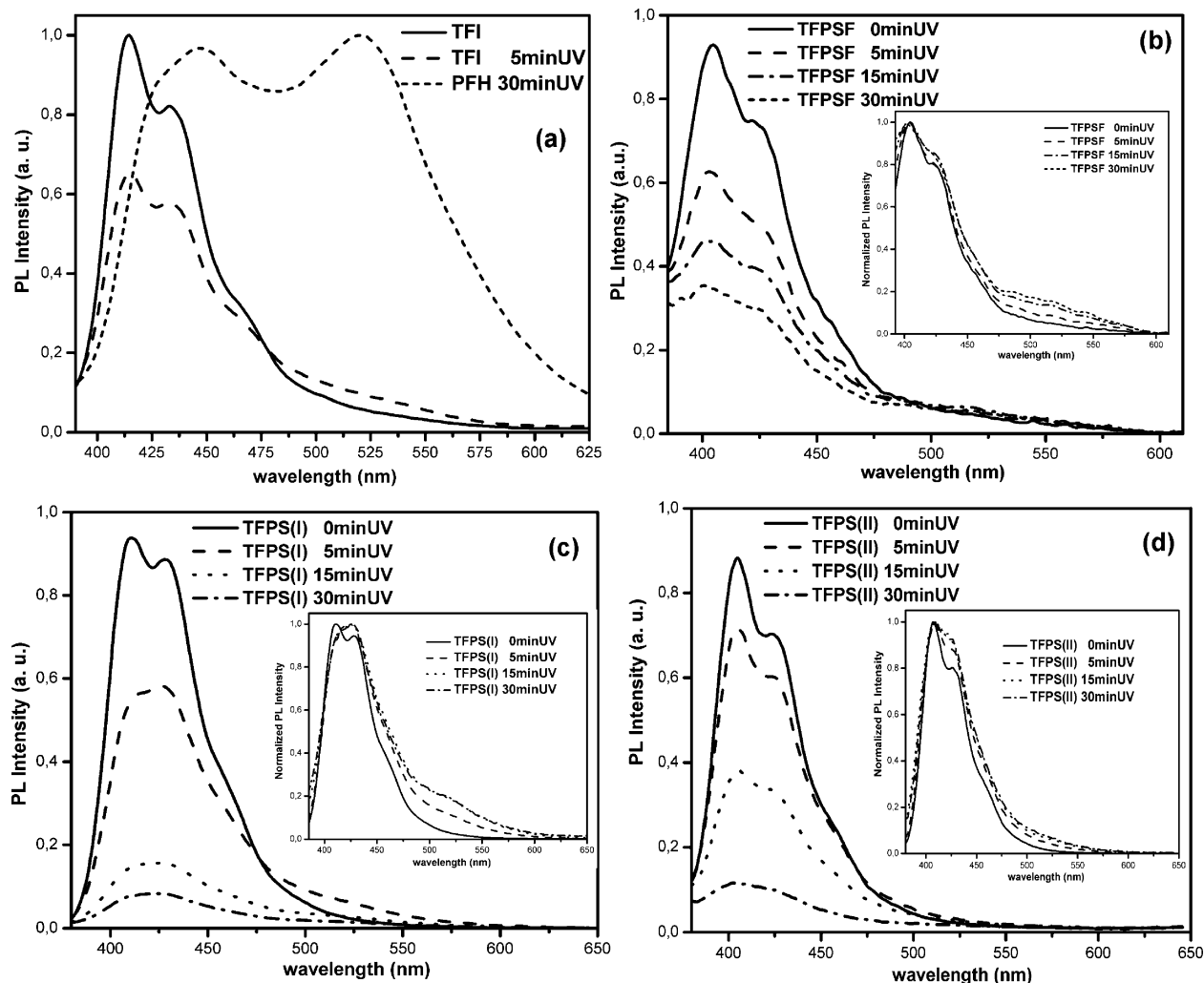*J. Phys. Chem. B, Vol. 109, No. 18, 2005* **8759**

Figure 4. Photoluminescence spectra of (a) PFH and TFI, (b) TFPSF, (c) TFPS(I), and (d) TFPS(II) in the solid state before and after UV treatment in air (exposure for different periods of times, 5−30 min) in arbitrary units. In the insets of (b)−(d) the normalized PL spectra of the TFPSF and TFPS(I)−(II) are presented.

necessary but not sufficient condition for the appearance of this undesirable low-energy emission band. Furthermore, the difference between TFPS(I) and TFPS(II) is the percentage of the terfluorene block (13.07% and 7.22%, respectively) or alternatively the molecular weight of the polystyrene content, which appears to play an important role on the final optical properties of the copolymers. In the case of TFPS(II), only quenching from the intrachain emission is displayed without the appearance of the undesirable low-energy emission band after photooxidation and formation of fluorenone moieties (inset of Figure 4d). However, in TFPS(I) except from the efficient quenching of the intrachain emission, the appearance of the "green" emission band is also observed upon UV treatment and the creation of keto defects (inset of Figure 4c). Therefore, we conclude that the low-molecular-weight polystyrene block in TFPS(I) cannot prevent the intersegment interactions between the terfluorene blocks. In contrast, the higher molecular weight polystyrene in TFPS(II) is capable of preventing the intersegment interactions between the terfluorene units despite the formation of the fluorenone moieties upon UV treatment; hence no "green" emission band is observed for this material. Furthermore, because TFPSF was synthesized from the same batch of TFPS-(II) using the ATRP technique, any observed differences in their optical properties after the formation of the same chemical defects can safely be attributed to the incorporation of the

fullerene molecule on TFPS(II) and consequently to the ability of increasing the interchain interactions.

4. Conclusions

The above findings support the idea that the synthesis of materials where aggregation and/or interchain interactions is inhibited is the key step in developing polymeric materials of choice based on polyfluorenes or oligofluorene segments for stable blue light emission. The validity of this argument is demonstrated by the fact that even though the fluorenone moieties are present, the produced blue light is not converted to the undesirable blue-green shade in the case of TFPS(II). In addition, in a recent study it was demonstrated that for a series of fluorene based rod−coil block copolymers having different block lengths the amount of rod−rod stacking is reduced when the rod segment is much shorter than the flexible part.[13c] This result is similar to the one obtained in our study, which clearly shows that the intersegment interactions are minimized when the polystyrene flexible part is at a higher percentage. Finally, we present a block copolymer consisting of terfluorene−polystyrene−fullerene that was synthesized using the ATRP method and exhibits excellent solubility in common organic solvents.

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