

Excimer and Aggregate Formations in Poly(fluorene)s

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This paper investigates the absorption and emission changes in poly(di-*n*-hexylfluorene)s. We prepared the poly(di-*n*-hexylfluorene)s end capped with 2-bromofluorene, 2-bromo-9,9-di-*n*-hexylfluorene, and 9-bromoanthracene through Ni (0) mediated polymerization. In addition, we also synthesized a structurally distorted copolymer of 2,7-dibromo-9,9-di-*n*-hexylfluorene and 9,9-bis(4-bromophenyl) fluorene end capped with 2-bromofluorene through the same polymerization method. The absorption and emission changes of these polymers between before and after thermal annealing in a nitrogen atmosphere clarify the role of aggregate/excimer formation in poly(fluorene)s. The large absorption changes must be attributed to aggregate formation (ground state interaction), which causes only a slight red shift of the vibronically structured emission bands. We assign the additional long wavelength emission as an excimer band (excited state interaction), which is preferably formed at chain ends.

I. INTRODUCTION

Conjugated polymers have attracted much research interest in science and technology in the past few decades as semiconductors and electroactive materials for diverse applications. Among their applications, especially electroluminescence has emerged as a promising application of polymeric light emitting diodes (LEDs) in semiconducting polymers. [1], [2]. Poly(alkylfluorene)s are promising new materials for light emitting diodes because of their high photoluminescence (PL) quantum efficiencies and thermal stability [3]-[6]. The fluorene structural unit provides both rigidly planarized biphenyl units within the polymer backbone and the possibility of remote functionalization at C-9, the latter offering the prospect of improving both polymer processability and mediating potential interchain interactions in films [7]-[9].

We have recently reported troublesome long wavelength emission bands in polymer films of poly(di-*n*-hexylfluorene) (DHF) and various copolymers upon thermal annealing or with the passage of current [6], [10], [11]. These reports have also described synthesizing poly(di-*n*-hexylfluorene-co-anthracene)s in an effort to suppress these additional emission bands [10], [11]. The high molecular weight ($M_n > 50,000$) anthracene-containing copolymers display excellent photoluminescence color stability even upon annealing at 200 °C for 3 days in N₂, and stable blue light emission has been observed in operating light emitting devices. The ability of small amounts of anthracene comonomer linked to the poly(fluorene) main chain via the 9,10-positions to completely suppress the broad, structureless long wavelength emission band is quite remarkable. One possible explanation is that the strongly twisted anthracene substituents in the polymer backbone may

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prevent interchain interactions in films.

However, some details of interchain interactions in poly(fluorene)s remain unresolved because this can result in either excited state interactions (excimers) or ground state interactions (aggregates). If there are ground state interactions, absorption and emission spectra changes are observed before and after thermal annealing. On the other hand, for excimers, only emission spectrum changes are expected. We have observed both absorption changes and emission changes in certain poly(fluorene) derivatives after annealing. To clarify the role of aggregates versus excimers, polymers are needed which show only changes in either their absorption or emission spectrum after thermal annealing. In this paper, we clarify these excimer versus aggregate issues by studying the absorption and emission spectra of certain polymers which display only changes in either their absorption or emission spectra after thermal annealing.

II. EXPERIMENTAL SECTION

1. Instrumentation

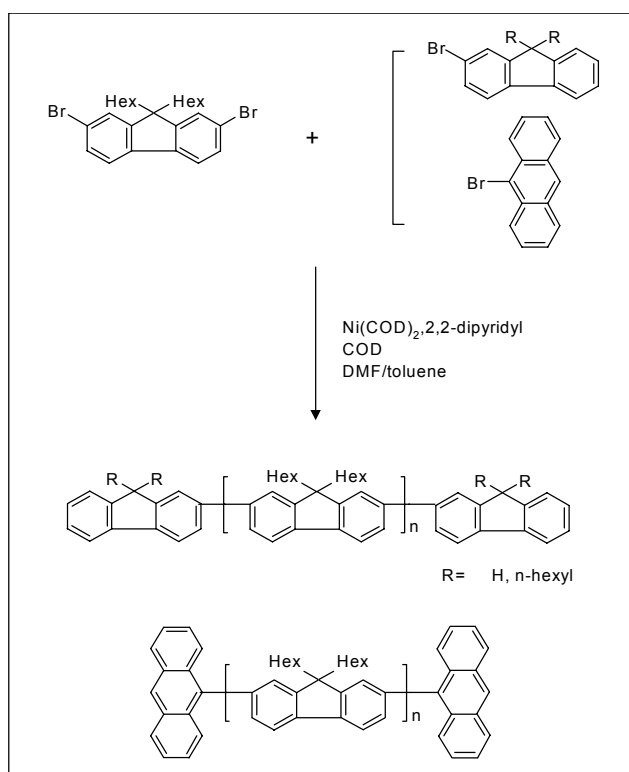
We performed a thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the polymers in a nitrogen atmosphere at a heating rate of 10°C/min using a Perkin Elmer TGS-2 instrument for the TGA and a DuPont 2100 instrument for the DSC. We determined the polymer molecular weights by Waters 150-C Gel Permeation Chromatography (GPC) calibrated with polystyrene standards. The synthesized compounds were identified by their ¹H- and ¹³C-NMR spectra, which were obtained using a Bruker AF250 NMR spectrometer. To investigate the photoluminescence properties, the polymers were spin-coated on fused quartz wafers; the absorption spectra of the polymer films were measured with a Hewlett Packard B452A diode array spectrophotometer and the emission spectra by an SA Instruments FL3-11 fluorimeter.

2. Monomers and End Cappers

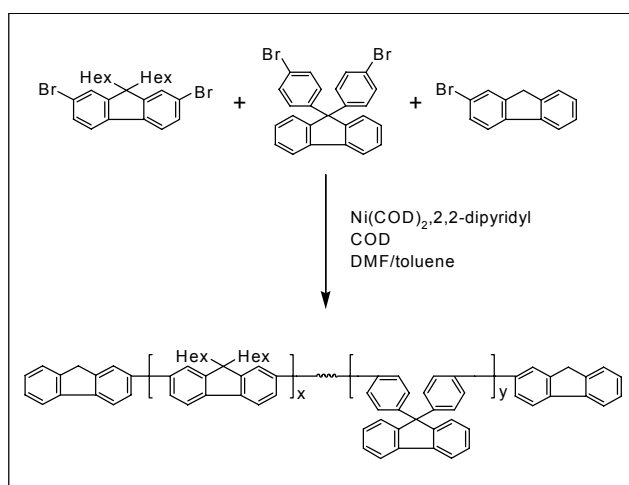
We prepared the monomers, 2,7-dibromo-9,9-di-*n*-hexylfluorene (BR2DHF) and 9,9-bis(4-bromophenyl)fluorene (Br2DPF), according to literature procedures [12]. The comonomer, 9,10-dibromoanthracene (BR2ANT) and the two end capping reagents, 2-bromofluorene (FLUO) and 9-bromoanthracene (ANT), were purchased from Aldrich Chemical Company and used without further purification. We synthesized another end capping reagent, 2-bromo-9,9-di-*n*-hexylfluorene (DHFLUO), from 2-bromofluorene using the same method described for the monomer preparation [13].

3. Polymerization

We synthesized homopolymers with different end groups through nickel (0) mediated polymerization [1], [6], [14]. A Schlenk tube containing 6 mL of toluene, 6 mL of DMF, bis(1,5-cyclooctadienyl) nickel (0), 2,2'-bipyridyl, and 1,5-cyclooctadiene (the latter three in molar ratios 1:1:1) was heated in N₂ to 80 °C for 0.5 hour. The monomer (1.35 mmol) and end



Scheme 1. Synthetic scheme and structures of DHF end capped with FLUO, DHFLUO and ANT.



Scheme 2. Synthetic scheme and structures of DHF 80/ DPF 20 end capped with FLUO.

cappers (0.15 mmol) dissolved in 6 mL of degassed toluene (molar ratio of monomers and end capper/nickel complex is 0.57) were added to the above solution and the polymerization was maintained at 80 °C for 24 hours. After the reaction, the polymers were precipitated from an equivolume mixture of concentrated HCl, methanol, and acetone. The isolated polymers were dissolved in chloroform and re-precipitated in methanol. Finally the polymers were dried at 60 °C in a vacuum. The obtained polymers were soluble in various common organic solvents and were characterized by ¹H-NMR, DSC, TGA, and GPC.

III. RESULTS AND DISCUSSION

We used three separate end capping reagents, 2-bromofluorene, 2-bromo-9,9-di-*n*-hexylfluorene, and 9-bromoanthracene to control the molecular weights and to compare the effects of end capping on the spectral properties. To study the effects of structural distortion in the main chain (the incorporation of deliberate tetrahedral conjugation interrupts) on the absorption and emission spectra, we also prepared a copolymer from 2,7-dibromo-9,9-di-*n*-hexylfluorene and 9,9-bis(4-bromophenyl)fluorene end capped with FLUO (Scheme 2). The monomer ratios selected for the preparation of the homopolymers (BR2DHF:end-capper) and the copolymers (BR2DHF:BR2DPF:FLUO) were 90:10 and 70:20:10, respectively. In each case, the overall molar ratio of bifunctional to monofunctional monomers was 90:10, which yields polymers with number average molecular weights (M_n) around 15,000 and a PDI ranging from 2.5 to 2.7. The end capping reagents were present from the onset of the polymerization. The polymers produced were all soluble in common organic solvents such as THF, chloroform, and xylene. For the DHF/DPF copolymer, the composition of the statistical random copolymers, as determined by ¹H-NMR,

tracks the monomer feed ratio, as was reported previously [6], [10], [11]. For the end cappers FLUO and ANT, the presence of end caps in the polymers was confirmed by the ¹H-NMR spectra. In this regard, characteristic signals for ANT were observed at δ 8.0–7.3 while the signals for the protons at C-9 in FLUO appeared at δ 3.9. Based on earlier MALDI-TOF studies on DHF oligomers deliberately capped with fluorene, we assumed that there are two end caps/polymer chains [11]. In general, the thermal stability of the polymers was excellent with observed decomposition temperatures (5% weight loss measured by TGA analysis, 10 °C/min in N₂) in excess of 400 °C. Table 1 shows the polymer properties of the materials used in this study.

Figures 1 and 2 show the absorption and emission spectra of DHF end capped with FLUO and DHFLUO before and after thermal annealing in N₂. In both polymers, significant changes in the absorption occur upon thermal annealing. This is manifested by either the appearance of a new sharp peak at longer wavelengths or a red shift in the absorption edge. Grell et al. recently suggested aggregate formation in poly(di-*n*-octylfluorene) based on absorption and emission studies [15]. In their study, morphological changes resulted in the appearance of an additional absorption band at the absorption edge which was accompanied by a well structured red shifted emission, which they attributed to aggregate absorption. Likewise, we attribute the changes in the absorption spectra of our polymers upon thermal annealing to aggregate formation. In the emission spectra of our materials (Figs. 1 and 2), however, differences between the annealed and nonannealed samples are not apparent. The heated samples show a slight red shift of the first band of the blue emission band but the position of the second band does not change. Therefore, the red shift of the first band should be attributed to self-absorption due to the red-shift at the absorption edge. An additional long wavelength emission band appearing in the emission spectra is particularly

Table 1. Polymer properties.

polymers		feed ratio (DHF/ANT/end capper)	M_n ($\times 10^3$) ^a	PDI (M_w/M_n)	DP	T_g (°C)	λ_{max} [nm] ^b absorption	λ_{max} [nm] ^b emission
backbone	end capper						(A/B) ^c	(A/B) ^c
DHF	FLUO		15	2.7	46	94	380/380	427, 445/431, 446
	DHFLUO	90 / 0 / 10	13	2.5	39	96	381/418	426, 449/431, 446
	ANT		14	2.5	41	115	380/414	425, 448/431, 447
DHF 80/DPF 20	FLUO	70 / 20 / 10	10	2.3	32	160	370/370	421/421

a. measured by gel permeation chromatography (GPC) referenced to polystyrene standards

b. measured in thin films on quartz wafers

c. A/B = λ_{max} of before thermal annealing / λ_{max} of after 20 hours thermal annealing in N₂

troublesome since it results in a color change in LED devices. We have already reported several methods [6], [10], [11] to suppress this troublesome emission band, such as copolymerization with 9,10-dibromoanthracene and incorporating low band gap comonomers. There is also an obvious end group dependence on this additional long wavelength emission band. There is relatively less of the long wavelength emission band in the annealed films of DHF end capped with DHFLUO than in those samples end capped with FLUO. From this, we suggest that sterically hindered end groups can suppress the long wavelength emission band which forms upon annealing. While this effect is obvious from the figures, it is not clear whether the broad long wavelength emission band is due to aggregates or excimers.

To clarify this issue, we investigated two additional polymers, DHF end capped with ANT and DHF 80/ DPF 20 end capped with FLUO. Figure 3 shows the absorption and emission spectra of the former before and after thermal annealing. After thermal annealing, there is a significant change in the absorption spectrum as with previous polymers. Consistently we attribute this absorption change to aggregate formation. In the emission spectra of DHF end capped with ANT, we observe a slight red shift in the first peak of the emission spectrum after thermal annealing but no trace of the long wavelength emission band (Fig. 3). These results indicate that aggregate formation in those poly(fluorene)s leads to just a slight red shift of the first peak of the structured blue emission band due to self-absorption. Another important indication from these results is that the sterically twisted chain end group, anthracene, may play an important role in suppressing additional long wavelength emission bands. Therefore, the polymer end capping with either sterically hindered (DHFLUO) or strongly twisted (ANT) groups provides a

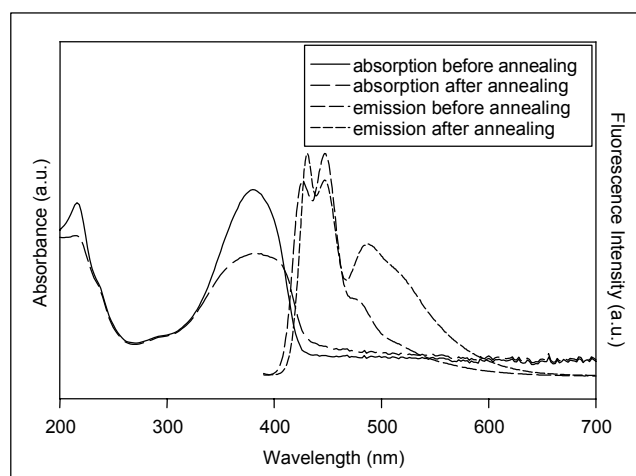


Fig. 1. Absorption and emission spectra of DHF end capped with FLUO before and after thermal annealing for 20 hours in N_2 .

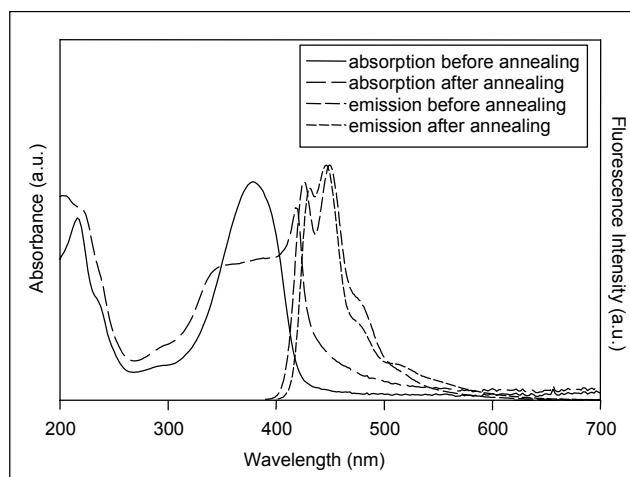


Fig. 2. Absorption and emission spectra of DHF end capped with DHFLUO before and after thermal annealing for 20 hours in N_2 .

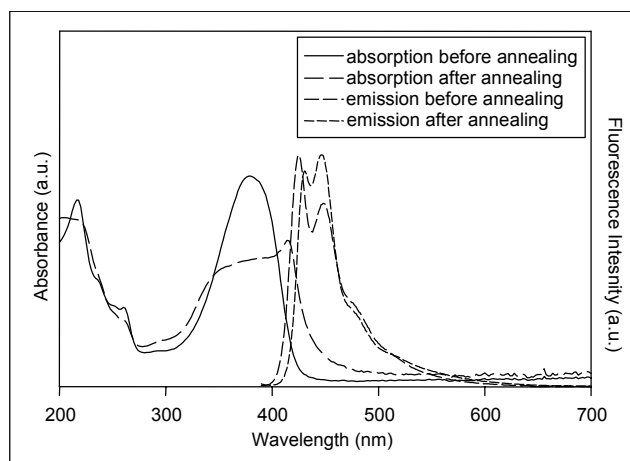


Fig. 3. Absorption and emission spectra of DHF end capped with ANT before and after thermal annealing for 20 hours in N_2 .

viable route to colorfast emitting blue emission from poly(fluorene)s.

The absorption and emission spectra of DHF 80/ DPF 20 copolymer films further clarify the role of aggregate and excimer formation of poly(fluorene)s in absorption and emission spectra changes. As Fig. 4 shows, there is virtually no absorption change in the polymer after thermal annealing. Incorporating a tetrahedral kink in the DHF chain with DPF plays an important role in preventing aggregate formation. However, the appearance of an additional long wavelength emission in DHF/DPF after thermal annealing indicates that this additional long wavelength emission may be attributed to excimer formation, since there is essentially no change in the absorption (or excitation) spectra upon thermal annealing. From the absorption and emission spectra of DHF end capped

with ANT and DHF 80/ DPF 20, we were able to clarify the aggregate and excimer issues in poly(fluorene)s.

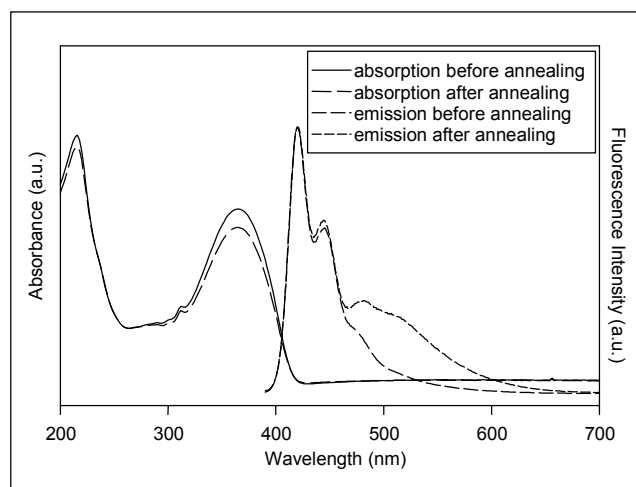


Fig. 4. Absorption and emission spectra of DHF 80/ DPF 20 end capped with FLUO before and after thermal annealing for 20 hours in N_2 .

The results obtained in this experiment clarify the role of aggregate and excimer formation in poly(fluorene)s. Ground state interactions between rigid rod polymer chains occurring upon thermal annealing apparently lead to aggregate formation, which results in additional absorption beyond the original absorption edge but only a slight red shift in the emission spectrum. On the other hand, excited state interactions, which are apparently more prevalent at the chain ends than in the middle of chains, results in the appearance of an additional long wavelength emission band. The end capping poly(fluorene)s with either sterically hindered or strongly twisted groups is another way to suppress excimer formation.

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