

Oxidative Stability and Its Effect on the Photoluminescence of Poly(Fluorene) Derivatives: End Group Effects

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Poly(9,9-dialkylfluorene-2,7-diyl) derivatives end-capped with 2-fluorenyl, 9,9-di-*n*-hexyl-2-fluorenyl, and 9-fluorenone-2-yl substituents have been synthesized through Ni(0)-mediated polymerization. Absorption and emission spectra of these polymers were measured after annealing at elevated temperatures in air as a function of annealing time. The fluorescence stability of the polymers end-capped using 2-bromo-9,9-di-*n*-hexylfluorene was much better than for the polymers end-capped with 2-bromofluorene. The exceptional sensitivity of the luminescence of the polymers end-capped with 2-fluorenyl substituents to thermal annealing in air is rationalized by a combination of π -stacking and chemical oxidation of the end groups to fluorenones. The latter was demonstrated by the IR spectra of annealed films and comparison of the results with the absorption, emission, and IR spectra of the polymers deliberately end-capped using 2-bromo-9-fluorenone. This study is directed toward the investigation of color stability of planarized π -systems for light emitting diodes (LEDs).

Introduction

Poly(alkylfluorene)s are promising new polymeric materials for light-emitting diodes¹ because of their high photoluminescence (PL) quantum efficiencies and thermal stability.^{2–7} 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 processibility and mediating potential interchain interactions in films.⁸

We have recently reported troublesome excimer formation upon optical excitation of polymer films of poly(di-*n*-hexylfluorene) (DHF) and various copolymers after annealing or passage of current.^{7,11,12} We have also described the synthesis of poly(di-*n*-hexylfluorene-co-anthracene)s in an effort to suppress this excimer/

aggregate emission.^{11,12} The high molecular weight ($M_n > 50$ K) anthracene-containing copolymers display excellent photoluminescence color stability, even upon annealing at 200 °C for 3 days under N₂, and stable blue light emission has been observed in operating light emitting devices.¹¹ The ability of relatively small amounts of anthracene comonomer (5–15 mol %) linked into the poly(fluorene) main chain via the 9,10-positions to suppress completely excimer formation is quite remarkable. One possible explanation is that the strongly twisted anthracene substituents in the polymer backbone may prevent interchain interactions in films. Alternatively, the anthracene-containing segments may constitute lower band gap chromophores which can serve as dilute excitonic energy traps.

Recently, we have also studied the molecular weight dependence of excimer formation in these copolymers. Controlled end capping with either 2-bromofluorene or 2-bromo-9,9-di-*n*-hexylfluorene allowed the preparation of copolymers with variable molecular weights.^{12,13} The results of this study indicated that lower molecular weight samples always show relatively larger amounts of longer wavelength emission after annealing. This effect was attributed in part to the increased polymer chain mobility expected for the lower molecular weight samples and the increased number of chain ends. Moreover, the nature of the end groups apparently affects the tendency of the fluorene backbones to π -stack; e.g., homo and copolymers terminated with a more sterically hindered end capper such as 9,9-di-*n*-hexylfluorene-2-yl are less prone to excimer formation. From these results, we have proposed that both the number and nature of the end groups also play a critical

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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	
end capper	absorption						emission	
DHF	FLUO	90/0/10	15	2.7	46	94	380	445
	DHFLUO		13	2.5	39	96	381	424
	FLUORENONE		23	2.8	70	100	376	536
85/15 DHF/ANT	FLUO	75/15/10	15	2.0	49	115	376	453
	DHFLUO		14	3.0	45	128	376	446
	FLUORENONE		20	2.6	65	140	384	527

^a Measured by gel permeation chromatography (GPC) referenced to polystyrene standards. ^b Measured in thin films on quartz wafers before annealing.

role in determining the color stability of poly(fluorene) derivatives.

In our original studies on poly(fluorene) oligomers, we introduced end caps using 2-bromofluorene in order to eliminate any residual bromine from the end groups which could quench the emission and lead to stability problems in LED applications. However, the benzylic hydrogens in the 9-position of the fluorene end groups appear to be prone to oxidation. Extended annealing in air at elevated temperatures leads to oxidation of this position. Therefore, it is critical to improve the oxidative resistance of these materials for the development of devices with improved stability. In this paper, we will focus on the oxidative stability of polymer end groups in poly(fluorene)s and the effect on the emission properties.

Experimental Section

Instrumentation. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the polymers were performed under a nitrogen atmosphere at a heating rate of 10 °C/min using Perkin-Elmer TGS-2 and DuPont 2100 instruments, respectively. Polymer molecular weights were determined using Waters 150-C gel permeation chromatography instrument calibrated with polystyrene standards. The synthesized compounds were identified by their ¹H- and ¹³C NMR spectra which were obtained using Bruker AF250 NMR spectrometer. To investigate the photoluminescence properties, the polymers were spin-coated on fused quartz wafers and absorption and emission spectra of the polymer films were measured using a Hewlett-Packard 8452A diode array spectrophotometer and SA Instruments FL3-11 fluorimeter, respectively. FT-IR spectra were recorded on a Nicolet Magna IR spectrometer 550.

Monomers and End Cappers. The monomer, 2,7-dibromo-9,9-di-*n*-hexylfluorene, was prepared by reacting 2,7-dibromofluorene with *n*-hexylbromide according to a literature procedure.¹⁴ The comonomer, 9,10-dibromoanthracene, and the two end capping reagents, 2-bromofluorene and 2-bromo-9-fluorenone, were purchased from Aldrich Chemical Co. and were used without further purification. The last end-capping reagent, 2-bromo-9,9-di-*n*-hexylfluorene, was synthesized from 2-bromofluorene using the same method described for the monomer preparation. A 10 g (41 mmol) portion of 2-bromofluorene was reacted with 2.3 equiv of *n*-hexylbromide in a two-phase system composed of 90 mL of toluene and 90 mL of 50 wt % aqueous NaOH using tetra(*n*-butyl)ammonium bromide as the phase transfer catalyst at 60 °C for 4 h. After diluting the reaction mixture with ethyl acetate, the organic layer was washed with water several times to remove excess NaOH. The organic layer was separated and dried with anhydrous MgSO₄. A colorless oil was obtained after column chromatography using *n*-hexane. The yield was 16 g (93%); ¹H NMR (CDCl₃) δ 7.7–7.3 (m, 7H), 2.1–1.9 (m, 4H), 1.3–1.0 (m, 8H), 0.9 (t, 6H), 0.8–0.6 (m, 4H); ¹³C NMR (CDCl₃) δ 150.3,

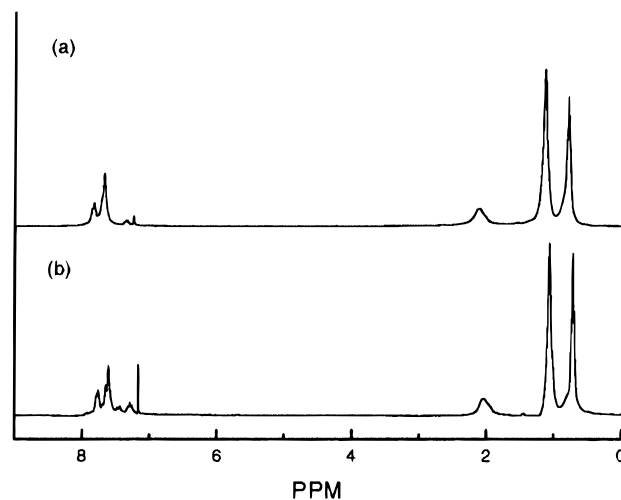


Figure 1. ¹H NMR spectra of DHF ($M_n = 13\ 000$) (a) and 85/15 DHF/ANT ($M_n = 14\ 000$) (b) end capped with DHFLUO.

153.0, 140.2, 140.1, 129.9, 127.5, 127.0, 126.2, 122.9, 121.0, 119.8, 55.4, 40.4, 31.5, 30.9, 29.7, 23.7, 22.6, 14.1.

Polymerization. Homopolymers and the statistical copolymers with 9,10-dibromoanthracene were synthesized by nickel(0)-mediated polymerization.¹⁵ 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 a molar ratio of 1:1:1) was heated under nitrogen to 80 °C for 0.5 h. The monomer (1.35 mmol) and end cappers (0.15 mmol) dissolved in 6 mL of degassed toluene (molar ratio of monomers and end capper/nickel complex = 0.57) were added to the above solution, and the polymerization was maintained at 80 °C for 24 h. After reaction, the polymers were precipitated from an equivolume mixture of concentrated HCl, methanol, and acetone. The isolated polymers were dissolved in chloroform and reprecipitated in methanol. Finally the polymers were dried at 60 °C under vacuum. The obtained polymers were soluble in various common organic solvents and were characterized by ¹H NMR, DSC, TGA, and GPC. These data appear in Table 1 and Figure 1. The C-9 protons for the 2-fluorenyl end caps appear as a broad singlet at δ 3.9 in the ¹H NMR spectra. For those polymers end capped with 9-fluorenone-2-yl substituents, new infrared bands appear at 1720 and 1605 cm⁻¹ which are attributed to the end-capping substituents.

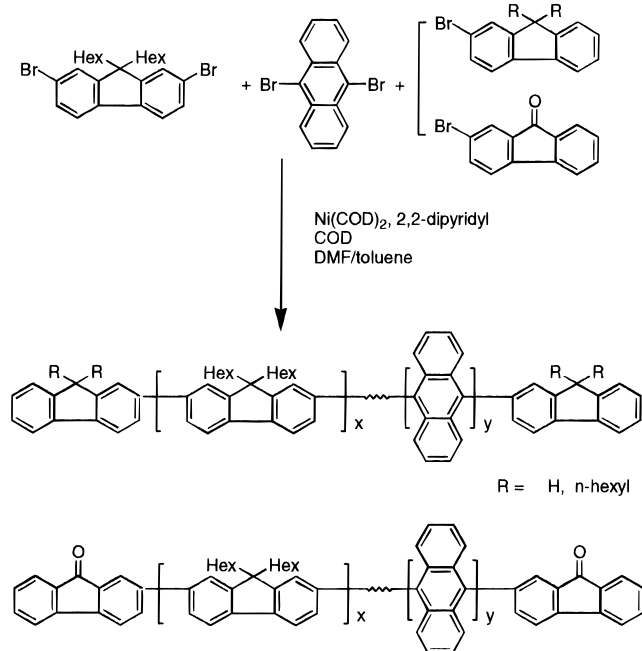
Results and Discussion

Two end-capping reagents, 2-bromofluorene (FLUO) and 2-bromo-9,9-di-*n*-hexylfluorene (DHFLUO), were used to compare the oxidative stabilities of the corresponding end-capped polymers. The homopolymer, poly-(di-*n*-hexylfluorene-2,7-diyl) (DHF), and the copolymer resulting from the statistical incorporation of 9,10-

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Scheme 1. Structures and Synthetic Scheme for Homopolymers and Copolymers with Different End Cappers



dibromoanthracene (ANT), DHF/ANT, each of comparable molecular weights and each containing the different end-capping groups 2-fluorenyl (FLUO) and 9,9-di-*n*-hexyl-2-fluorenyl (DHFLUO), were synthesized using zerovalent nickel (Scheme 1).^{1,6,14} To study the effects of end group oxidation, we also prepared the corresponding polymers end capped with 9-fluorenone-2-yl (FLUORENONE) by adding 2-bromo-9-fluorenone to the polymerization. The monomer ratios employed for the preparation of the homopolymers (DHF:end-capper) and the copolymers (DHF:ANT:end-capper) were 90:10 and 75:15:10, respectively. In all cases, 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. 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, xylene, etc. For each of the copolymers studied, the composition of the statistical, random copolymers tracks the monomer feed ratio, as was reported previously.^{7,11,12} Figure 1 shows the ¹H NMR spectra of the homopolymer and copolymer end capped with 2-bromo-9,9-di-*n*-hexylfluorene. These two spectra are very similar, as expected, and it is difficult to completely resolve the aromatic proton peaks of anthracene from those of the fluorene comonomer. However, we could obtain the anthracene composition in copolymers by comparing the ratios of aromatic protons and alkyl protons in the homopolymers and copolymers, and they are very close to feed ratios in each case. The small peak around δ 7.3 in the homopolymer (Figure 1a) is believed to result from the end-capping groups, since it becomes relatively less intense in higher molecular weight samples. It is assumed that there are two end caps/polymer chain based on MALDI-TOF studies on DHF oligomers capped with fluorene.¹³ In general, the thermal stability of the polymers was excellent, with observed decomposition

temperatures (5% weight loss measured by TGA analysis, 10 °C/min under N₂) in excess of 400 °C. Table 1 shows the polymer properties of the materials used in this study.

To study the oxidative stability of the end groups, photoluminescence spectra of the polymers end-capped with either FLUO or DHFLUO were measured after annealing in air at 200 °C for varying times. Parts a and b of Figure 2 show the emission spectra of DHF homopolymers end-capped with DHFLUO and FLUO, respectively. Although the spectra of the two polymers before annealing are identical, after annealing each shows another emission band located around 500–600 nm which we have attributed to excimer emission. However, the rate of appearance of the long wavelength emission and the shape of the long wavelength emission bands were different for the two samples. In the case of DHF end capped with FLUO, the appearance of the long wavelength emission is very rapid and dominates the emission spectrum after only 25 min heating. At this point the intrinsic blue emission of the isolated chains is barely detectable (Figure 2b). In comparison, the evolution of the long wavelength emission for DHF end capped with DHFLUO is much slower and the blue emission characteristic of the isolated chains is still very much evident after 25 min of annealing (Figure 2a). In this case, the shape of the long wavelength emission is also somewhat unsymmetrical. These results are qualitatively consistent with our previous results (annealing in N₂), which suggest that polymers end capped with sterically less hindered FLUO capping groups are more susceptible to π -stacking.

Similar results were obtained for the various DHF/ANT copolymers (see Figure 2c,d). As mentioned earlier, high molecular weight ($M_n > 50\,000$) 85/15 DHF/ANT copolymers do not show any longer wavelength emission even upon heating. In contrast, the lower molecular weight copolymers ($M_n < 30\,000$) display some excimer emission after annealing, presumably due to enhanced polymer chain mobility and the increased number of chain ends. Again, the rate of formation of the long wavelength emission is much more rapid for the DHF/ANT copolymers end capped with FLUO. As before, the shape of this emission band is also somewhat different than that observed for the DHF/ANT copolymer which had been end capped with DHFLUO.

To study structural changes occurring during thermal annealing in air, we recorded the IR spectra of the polymer samples before and after annealing. As shown in Figure 3, the homopolymers end-capped with FLUO show the appearance of an additional IR peak at 1720 cm⁻¹, while the polymers end-capped with DHFLUO do not. Similar results were obtained for the copolymers. Samples annealed in pure N₂ did not show the appearance of the new band at 1720 cm⁻¹ upon annealing. The position of the new band in the IR (1720 cm⁻¹) is consistent with a fluorenone structure.¹⁶ As the initial structures of these polymers are identical, except for the end groups, we suggest that some of the fluorene end groups are partially converted into fluorenone units after annealing.

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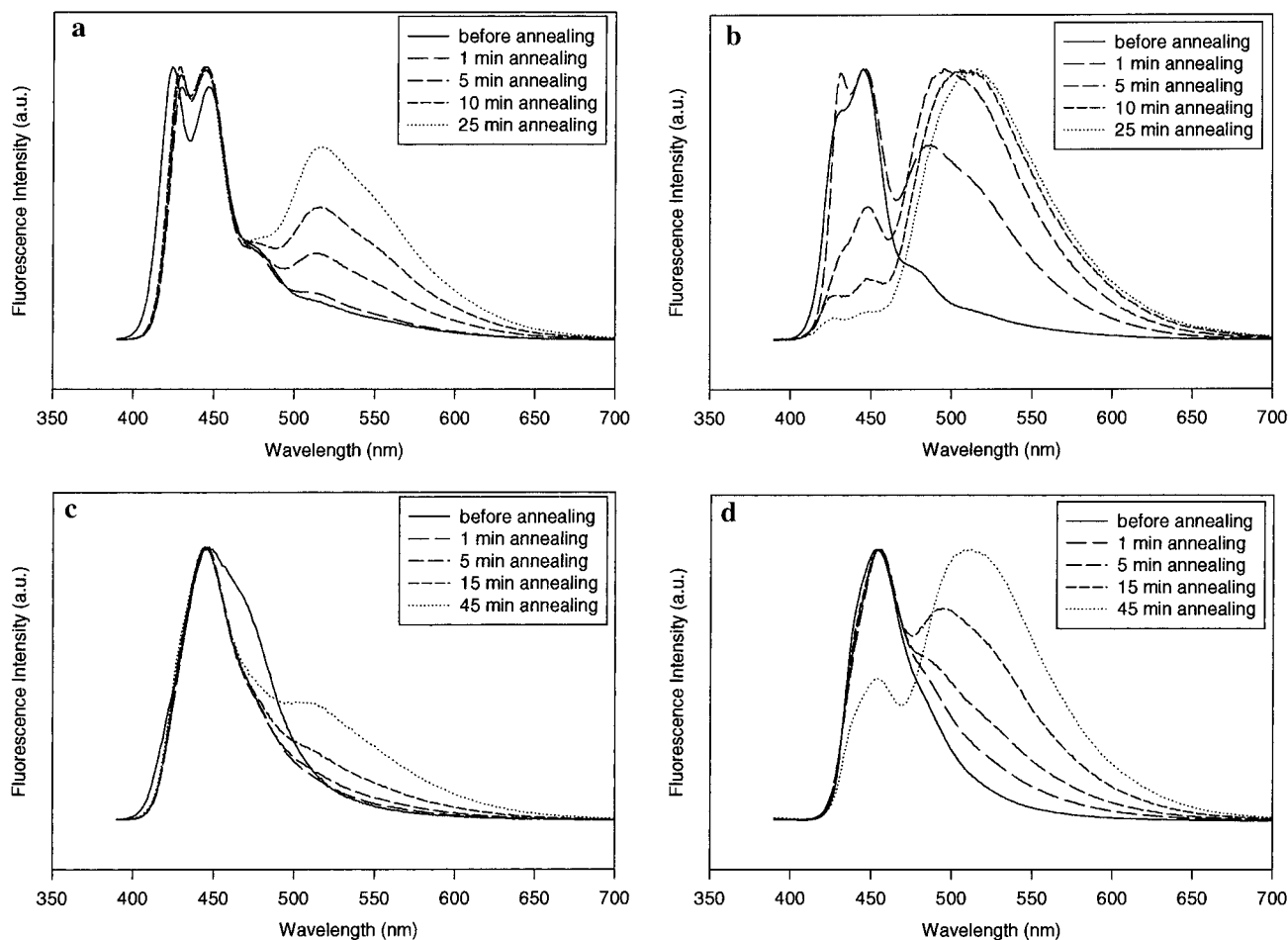


Figure 2. Photoluminescence spectra of DHF end capped with DHFLUO (a) and FLUO (b) and 85/15 DHF/ANT end capped with DHFLUO (c) and FLUO (d) as a function of annealing times at 200 °C in air.

The relative intensity of the carbonyl absorption at 1700 cm^{-1} increases with annealing time. After 24 h at 200 °C, the ratio of this absorption to the polymer backbone absorption at 1453 cm^{-1} approaches that observed in poly(9,9-di-*n*-hexylfluorene) of comparable molecular weight which had been deliberately end capped with 9-fluorenone-2-yl substituents (vide infra, Figure 4).

To verify this structural change, we synthesized model polymers (homopolymer and 85/15 DHF/ANT copolymers) which were deliberately end-capped with 2-bromofluorenone. Consistently, these polymers also showed a carbonyl peak at 1720 cm^{-1} in the infrared, as shown in Figure 4. It seems reasonable, therefore, that the end groups of DHF/FLUO and DHF/ANT/FLUO are at least partially converted to fluorenones upon thermal annealing in air. To investigate the effect of the structural change of the end group on the photoluminescence, we measured emission spectra of the polymers end capped with fluorenone. As shown in Figure 5 a, the PL spectra of the two fluorenone capped polymer films show a long wavelength emission around 480–650 nm together with a barely detectable blue emission characteristic of the isolated chains around 440 nm. Surprisingly, the film emission actually blue shifts slightly upon annealing. The shorter wavelength shoulders in the spectra of the unannealed samples suggest that this component is already present to some degree prior to annealing. The emission spectra of these fluo-

renone-capped polymers in solution in THF are also interesting. As shown in Figure 5b, in solution each sample not only shows the expected blue emission characteristic of the isolated chains but also a longer wavelength band which is located around 500–600 nm. In the case of the DHF/ANT copolymer, this emission is not well-resolved and appears as a long wavelength shoulder on the primary emission. The relative contribution of the long wavelength emission was independent of concentration, which implies that this band does not come from interchain interactions but instead arises from the intrinsic electronic structure of these polymers. In earlier reports, we have described the facile exciton migration and trapping in the poly(fluorene) derivatives.^{17,18} In the solid state, poly(fluorene) derivatives containing small amounts of low band gap comonomers, showed only emission from the low band gap comonomer units because of exciton migration and trapping. In this regard, the polymers end capped with fluorenone appear to show a lower band gap emission uniquely associated with chromophore end group. The position of this emission is similar to that of excimer emission from samples of DHF and DHF/ANT annealed in N_2 , although the shape is more symmetrical.

These results suggest that the interpretation of the emission spectra of DHF homo and copolymers end

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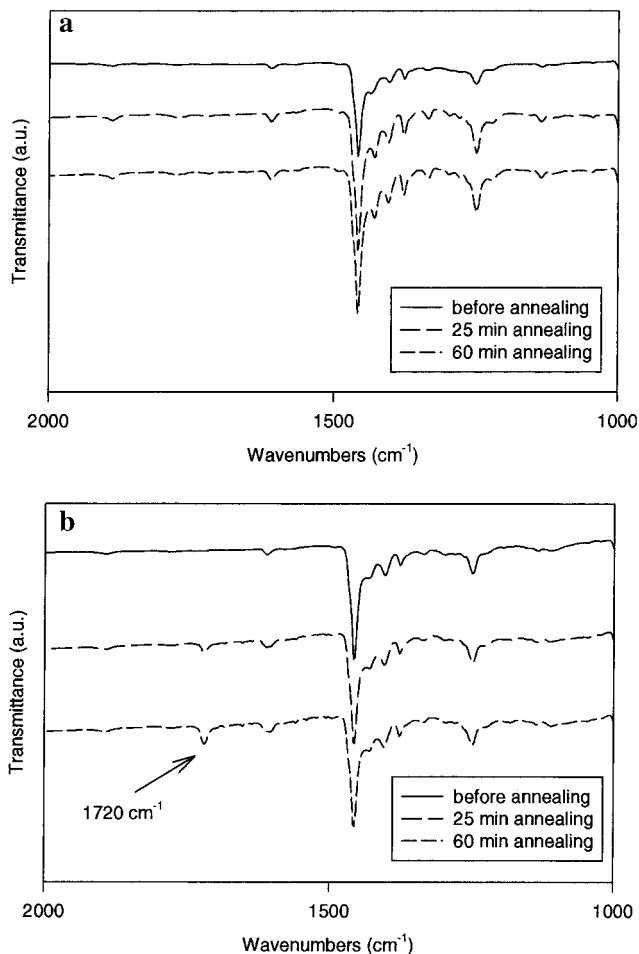


Figure 3. IR spectra of DHF end capped with DHFLUO (a) and FLUO (b) as a function of annealing times at 200 °C in air.

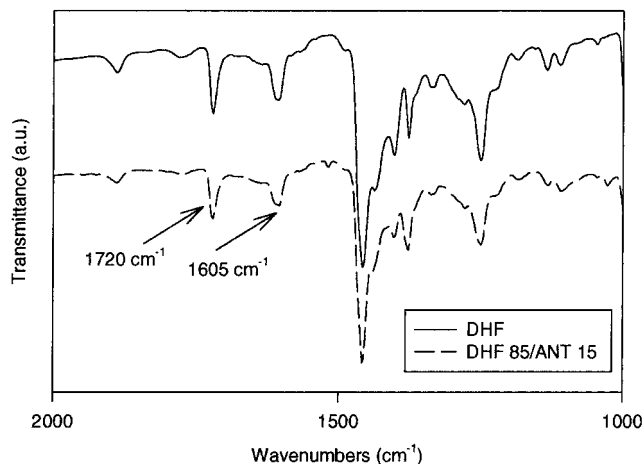


Figure 4. IR spectra of DHF and 85/15 DHF/ANT end capped with FLUORENONE.

capped with fluorene upon thermal annealing in air may be more complicated than simple excimer formation facilitated by morphological changes in the film. Thermal annealing studies of DHF homopolymer and copolymer capped with either DHFLUOR or FLUOR under N₂ show that excimer formation certainly occurs and that its efficiency depends on polymer structure and molecular weight and the nature of the end groups. This is manifested by the appearance of a long wavelength emission band upon annealing. In principle, the pres-

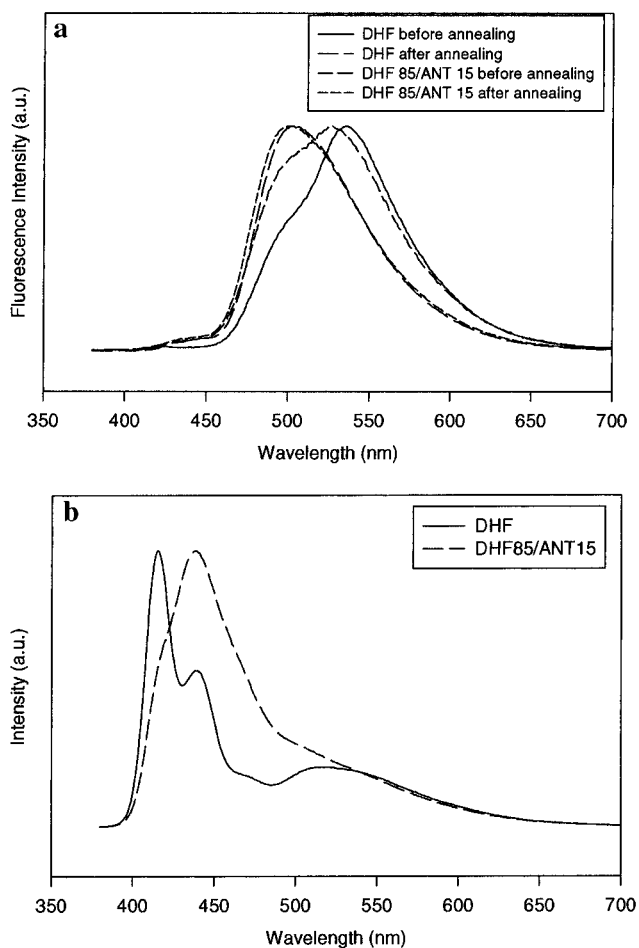


Figure 5. (a) Photoluminescence spectra of DHF and 85/15 DHF/ANT end capped with FLUORENONE before and after 4 h annealing at 200 °C under N₂. (b) Photoluminescence spectra of DHF and 85/15 DHF/ANT end capped with FLUORENONE in THF solution. Solution concentration was 60 μg/mL.

ence of fluorenone end caps could facilitate excimer formation because of reduced steric demands of the end group. However, the presence of fluorenone end groups apparently results in a chromophore with a similar long wavelength emission which is intrinsic even to the isolated polymer chain. Therefore, the long wavelength emission which rapidly appears upon annealing of DHF homo and copolymers capped with fluorene in air may be a composite emission resulting from excimer formation in unoxidized chains and emission from fluorenone containing segments in those chains where end group oxidation has occurred. Time-resolved emission study may clarify these issues.

In summary, the homopolymers of DHF and DHF/ANT copolymers end capped with FLUO, DHFLUO, and FLUORENONE were synthesized through Ni(0)-mediated polymerization. The oxidative stability of chain end group was investigated by studying the IR and photoluminescence spectra after annealing at 200 °C in air as a function of annealing time. Faster and more extensive formation of a long wavelength emission was observed in the polymers end capped with FLUO than in those end capped with DHFLUO. At the same time, carbonyl formation was observed after annealing those polymers end capped with FLUO. The oxidative stability of the polymers which had been end capped with

DHFLUO in air suggests that oxidation occurs at the chain ends for those polymers capped with 2-fluorenyl units. This was supported by spectral comparison with polymers deliberately end capped with fluorenone. These materials show a carbonyl peak for the end group which appears at the same position as in the oxidized polymers. The absorption spectra of these materials in the solid state were similar to those of the polymers end capped with FLUO and DHFLUO. Unexpectedly, films of the polymers deliberately end capped with fluorenone also display a long wavelength emission band that persists even in dilute solution which appears in the same spectral region as that of the excimer emission of poly(fluorene)s (annealed under N₂). Therefore, we propose that the faster and more extensive formation of a longer wavelength emission in the polymers end capped with FLUO and annealed in air may be due to a combination of excimer formation in unoxidized chains

and emission from fluorenone chromophoric segments in those which have been oxidized. In each case exciton migration and trapping appear to be relatively efficient.

To obtain oxidatively stable polymers and suppress long wavelength emissions in poly(fluorene)s, we need high molecular weights as well as sterically hindered and oxidatively stable polymer end groups (e.g., DHFLUO).

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