Near-term aging and thermal behavior of polyfluorene in various aggregation states

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Steady-stage photoluminescence and photoabsorption have been used to characterize the impact of aggregation in various poly(di-n-alkylfluorene) thin films. Highly aggregated films exhibit systematic changes in the photoluminescence while aging. These are indicative of a gradual increase in interchain interactions. Nonaggregated films do not exhibit this behavior. However the mesomorphic properties are altered and these films undergo irreversible changes on thermal cycling. All these properties appear to be correlated with changes in the local short-range molecular packing. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1637431]

Conjugated polymers continue to be intensely studied because of their unique properties and the rapidly expanding opportunities for low cost, flexible format electronics applications. Of the many model compounds now available polyfluorenes (PFs) have merit as a blue emitter[1] in organic light emitting diodes (OLEDs). Many PFs exhibit high electroluminescence efficiency in combination with excellent chemical and thermal stability.

An essential prerequisite for OLED applications is control of the physical structure and morphology at molecular length scales and, more importantly, understanding the impact that molecular level ordering has on the photophysics and device properties. The low dimensional nature of polymers in combination with a facile sidechain functionalization leads to diverse structure/property relationships. Studies of the polymer, 2-methoxy-5(2′-ethylhexyloxy-)-p-phenylenevinylene), have demonstrated the great sensitivity of photophysical properties to processing conditions.[2] Changes in solvent, polymer concentration, and/or casting conditions often lead to films with varying degrees of "aggregation" in which a presumed interchain cofacial agglomeration occurs. This process is accompanied by an increase in low energy emission via interchain excited states (e.g., excimers).

Recent PF studies have examined the effects of thermal annealing.[3] Under these conditions many PFs exist in a liquid crystalline polymer (LCP) state[4] and scanning probe spectroscopies[3,5,6] resolve strong variations of film morphology and photophysics. Also reported are effects resulting from the influence of chain structure at shorter length scales.[7,8] Bliznyuk *et al.*[9] observe a systematic reduction in the Franck–Condon type emission in a process denoted as photoinduced aggregation or degradation. Similar behavior is

seen in polyfluorene thin films and working LEDs at ambient temperatures.[10] Aggregation is correlated with large scale reductions the singlet exciton emission and, for OLED devices, is considered disadvantageous. To avoid this effect bulky substituents, spirofluorene,[11] and branched sidechains[12] included, can be introduced although this increases the short-range disorder. Many molecular level attributes still remain incompletely understood.[13]

This letter summarizes steady-state photoabsorption (PA) and photoluminescence (PL) measurements of two di-n-alkyl PFs with radically different levels of aggregation. These range from a state characterized by extensive aggregation to one with virtually none at all. These two "limiting" cases manifest vastly different responses in the observed PL spectra to thermal cycling and to short-term aging. The latter occur at temperatures well below the published glass transition temperatures. In sum, these data demonstrate that local, nanometer length scale structural relaxations are central for determining the photophysics.

The two dimethylphenyl capped PFs (MW $\sim 60\,000$), poly(di-n-hexylfluorene) (PF6) and poly(di-n-octylfluorene) (PF8), used in this study were purchased from American Dye Source and used as received. Generally 1% w/w polymer/solvent solutions were prepared using spectroscopic grade toluene, chlorobenzene (CB), tetrahydrofuran (THF) or heptane (for PF6, toluene only). Grell *et al.*[7] have already shown that solvent casting yields at least two distinctive low temperature backbone conformations characterized by a ~ 100 meV shift in the respective PL spectral features. Designations of α and β are used here to distinguish them. All four solvents used in our study yielded PF8 thin films ($\sim 10 - 20$ nm thick) that incorporated admixtures of these two skeletal conformers. Casting from chlorobenzene generally gave films exhibiting the most aggregation while casting from toluene had the least. The actual results varied and they

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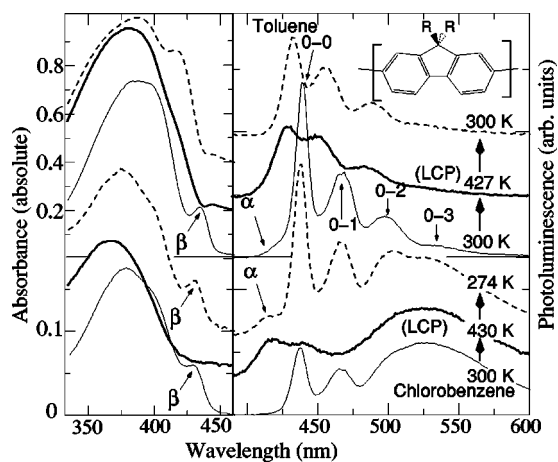[a]Electronic mail: mwinokur@facstaff.wisc.edu

FIG. 1. Selected PL and PA spectra from a nonaggregated PF8 thin film (at top from toluene) and from a highly aggregated spin-cast PF8 film (at bottom from chlorobenzene). All spectra have been offset and the PL (only) rescaled for clarity. Bold arrows indicate thermal cycling.
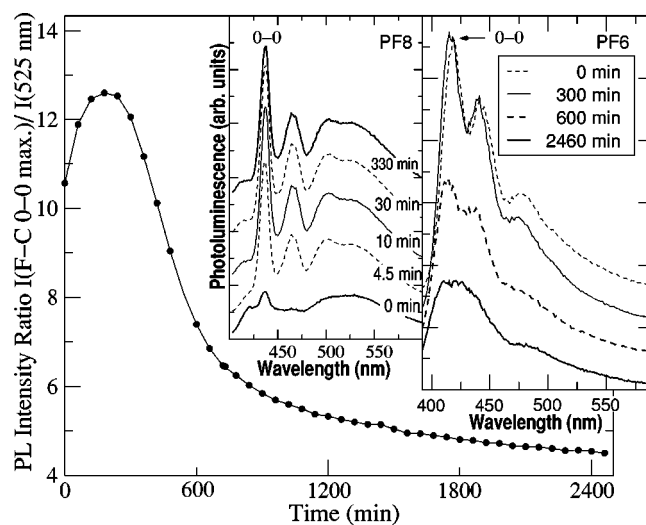

FIG. 2. Near term aging of a spin-cast PF6 film qualitatively showing the loss of FC type photoluminescence. Insets: Representative PL spectra during aging for PF8 (left from CB) and PF6 (right from toluene). PL data are offset for clarity.

were both sample and trial dependent. (Chloroform, which has been shown to inhibit formation of the β "phase," [6] in PF8 was not studied.) All polymer films were typically prepared on 100-μm-thick sapphire substrates by drop casting or spin casting ($\sim$3000 rpm). Thereafter, these films were mounted into a PA/PL/PL-excitation spectrometer described previously.[14] Both the PL (380 nm excitation) and PA were monitored as a function of time and temperature. A fuller analysis will be communicated later.

Figure 1 exhibits representative PF8 spectra and these illustrate the wide ranging levels of aggregation obtained. The toluene nonaggregated (Tol-NA) data seen at the upper right exhibits little or no broad PL emission centered at 525 nm; this is a hallmark feature often associated with excimer type interchain recombinations. The dominant PL features are solely those characteristic of intrachain Franck–Condon (FC) type recombinations. These include the main 0–0 peak and at least three associated vibronic sidebands. The 0–0 band (in the initial 300 K spectra) peaks at 437 nm and this is reflective of β-type chain conformations. The weak shoulder seen near 420 nm is typical of the more disordered α form. The associated PA profile is shown immediately at left and exhibits a distinct long wavelength PA peak. This is consistent with a minority presence of this β conformer.[7] In sharp contrast the CB data, at 300 K ($\sim$100 h after casting) and shown on the lower right, includes a large proportion of the cited broad 525 nm excimer emission. The limited remnants of the intrachain FC PL signal are again dominated by β-type emission.

These differences in photophysical behavior are even more striking when comparing the PL spectra at temperatures reflective of the LCP phase or after thermal cycling. Elevated temperatures, above an order-disorder transition to the LCP phase, eliminate the β conformer and are generally accompanied by a monotonic loss in PL intensity, especially that associated with FC type emission. Although the Tol-NA PF8 PL intensities drift downward there is still no PL signal clearly identified with excimer type emission. There are other differences. Close examination of the FC 0-n peaks in the CB cast film in the LCP state shows them to be blueshifted (in regards to the Tol-NA data). On cooling back to

temperatures at or just below 300 K there are notable changes in both the PA and PL spectra. For the Tol-NA PF8 films there is a significant drop in overall PL intensities while for the CB PF8 data there is initially a large net increase in the relative FC 0-n intensities.

Many other PF8 cast films [i.e., heptane, THF or even toluene (at times)] are intermediate to these two extremes and have temperature dependent properties similar to those in a recent PF8 β phase study.[14] The only PF6 data shown (in the Fig. 2 inset on the right) has PL features identified with high levels of aggregation. In this film the position of the 0–0 PL is centered near 420 nm. Hence no β type conformations are evident. The nominal interchain excimer emission is blueshifted as well and lies centered between 500 and 520 nm. In addition the relative 0–1 and 0–2 intensities are proportionately strongly and indicate a larger Huang–Rhys coupling parameter.

Extensively aggregated films undergo aging and temperature-dependent changes which strongly differ from those of the nonaggregated PF8 sample. The PL line shapes, either from as-cast films or those thermally cycled to the LCP phase, continue to evolve at reduced temperature (in this case at 273 K, PF8 or 300 K, PF6). In aggregated PF8 and PF6 there are slow systemic drops in the relative proportion of the excitonic emission with time. This behavior is exemplified in Fig. 2 by plotting the relative PL intensities at the FC 0–0 maximum and 525 nm. The former wavelength is dominated by intrachain FC exciton emission while the later by excimer recombinations. Also seen in the main figure and two insets is the initial rise in exciton PL soon after cooling from the LCP mesophase. Thus, two distinct relaxation processes are present. The early response is dominated by enhanced emission within more ordered regions of the film. Large scale crystallization is strongly suppressed at these temperatures and so this, the initial intensity increase, is likely associated with local chain relaxations.[14,15] Apparent at longer times is a second short-range response that presumably increases interchain coupling.

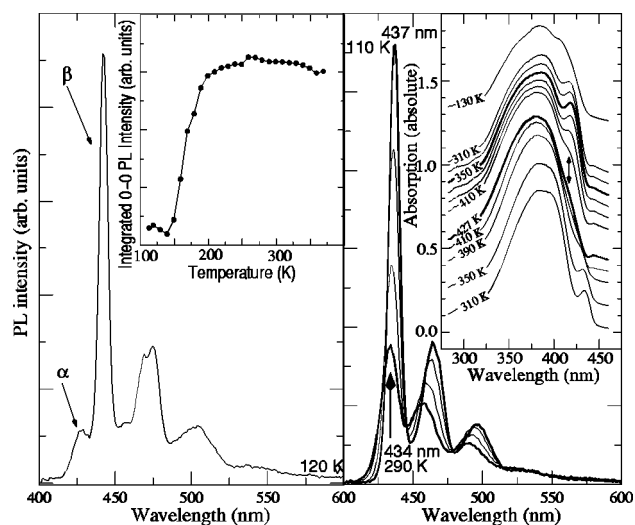The two Fig. 2 insets display selected intermediate time

FIG. 3. Left: Initial low temperature (*T*) PL from Tol-NA PF8 film. The inset shows the 0–0 progression on heating. Right: Low *T* PL from same film after thermal cycling. The inset shows the PA on thermal cycling. Inset data are offset.

PL curves. Individual contributions (i.e., intrachain and interchain) to the PF8 profiles remain relatively fixed in their respective line shapes. In contrast the PF6 data includes significant evolution in the intrachain FC PL lineshape. The 0–0 peak both broadens and shifts to shorter wavelengths. This may reflect the growth in PL intensity by new emitting conformers with decreased effective conjugation length and/or a more twisted chain conformation (rather than evolution at the original emitting sites). This blueshift is quite large and emission is even observed at 380 nm. This process cannot be attributed to chemical degradation because the early time PL is restored by simply cycling to high temperature (~420 K). The extent of aggregation state also impacts the temperature dependent response. Aggregated samples exhibit few irreversible changes in either PA or PL spectra. On the other hand the nonaggregated film undergoes dramatic change. At 120 K the PL, shown at left in Fig. 3, clearly shows emission from *α*- and *β*-type conformers but, on heating the *β* PL intensity rapidly increases and then, at temperatures above 200 K, it levels off and then slightly decreases. The explicit progression is shown in the inset. Comparable behavior has been documented by Ariu *et al.*[16] but it does not universally appear in samples with intermediate levels of aggregation.[14]

Heating of the nonaggregated PF8 produces permanent changes in the optical properties. These have been seen in previous studies as well[7,16] after high temperature annealing.

On cooling back to room temperature there is an apparent irreversible drop in the PL signal but now, at reduced temperature (in Fig. 3 on right), only a monotonic increase in the FC type emission occurs. After thermal cycling the low temperature PL can no longer be associated with a *β*-type conformer because only a single PA band with a peak centered near 420 nm is seen. More significant is the PA progression seen on heating (in the Fig. 3 inset on the right) which shows this conversion does not result from extended annealing but instead becomes thermally activated near 420 K (as denoted by the arrow). This 420 nm PA peak is actually most pronounced at 350 K.

On this basis it appears the *β* conformer is, in reality, a metastable structure and its presence is potentially stabilized by chain aggregation. Some level of aggregation may in itself be desirable for constraining and limiting conjugated polymer phase behavior, especially in mesomorphic materials. Structural evolution takes place at relatively low temperatures and therefore must originate from local short-range physical processes. Control of the molecular level microstructure remains a key issue.

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