

**Femtosecond study of exciton dynamics in 9,9-di-*n*-hexylfluorene/anthracene random copolymers**

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Exciton dynamics of 9,9-di-*n*-hexylfluorene/anthracene (DHF/ANT) statistical copolymers have been measured using femtosecond transient absorption spectroscopy. An investigation of the excitation intensity dependence over the range of 0.1–1.0 mJ/(pulse cm<sup>2</sup>) for solutions and 1.0–17 μJ/(pulse cm<sup>2</sup>) for thin films has been conducted to explore exciton relaxation mechanisms below excitation densities where exciton-exciton interaction is important. Intrachain relaxation of photoexcited singlet excitons is observed in dilute solutions. In contrast, interchain relaxation mechanisms become predominant in thin films. Decay dynamics are independent of excitation intensity for dilute solutions and thin films of DHF/ANT when probed at 790 and 750 nm. In addition, time-resolved measurements for a DHF homopolymer and two copolymer thin films have been carried out as a function of probe wavelength. A stimulated emission (SE) feature and a photoinduced absorption (PA) feature are observed in the visible region. The SE and PA dynamics are similar for the copolymers, suggesting that the same excited state species, the singlet exciton, is responsible for both the SE and PA. There is a significant difference between the SE and PA dynamics for DHF thin films on the 0–3-ps timescale. The SE dynamics show a pulse-width limited rise and a subsequent decay. In contrast, both the 600 and 750 nm PA dynamics show a “double” rise that represents contributions from two separate photophysical processes. These results, in combination with the steady-state photoluminescence spectrum, which indicates excimer emission, lead to the conclusion that interchain species, such as excimers, are formed in <1 ps in DHF homopolymer films following photoexcitation. That the copolymer dynamics show no evidence of excited state species other than the singlet, emissive exciton, is consistent with the interpretation that anthracene substituents in the polymer backbone prevent interchain interactions in films.

**I. INTRODUCTION**

Conjugated organic materials offer several advantages over inorganic materials for light emitting display technology, such as synthetic flexibility, ease of processibility, and relatively low cost. Considerable effort has been directed toward the development of conjugated, organic polymers which emit in the 420–500 nm region of the spectrum. Introduction of efficient and long-lived blue light emitting diodes (LED's) would complete the color spectrum and allow generation of combinations of red, green, and blue, in various percentages, to produce white light.<sup>1</sup>

Recently, a number of materials have been introduced as possible candidates for the emissive layer in blue LED's.<sup>2–5</sup> One of the most promising is polyfluorene and its various derivatives.<sup>6,7</sup> Polyfluorenes exhibit a strong emission centered at approximately 450 nm in solutions.<sup>8,9</sup> However, the emission band shifts toward green in the solid state due to aggregation or localization of excitons to lower energy excimers.<sup>10</sup> Planar conjugation segments, along the rigid polymer backbone in 9,9-di-*n*-hexylfluorene (DHF) homopolymers can interact by stacking together in the solid state. The hexyl groups are not bulky substituents and effective π orbital overlap between adjacent polymer chains occurs. A distinction is made between excited state and ground

state interchain interactions. Interchain interactions that are stable in both the ground and excited states are defined as aggregates.<sup>11</sup> These species have been reported in poly-*para*-phenylene ladder polymers.<sup>12,13</sup> In contrast, an excimer consists of a pair of identical molecules whose interaction is repulsive in the ground state but becomes attractive if one of the molecules is excited.<sup>14,15</sup> Radiative recombination from either excimer or aggregate states leads to a bathochromic shift of the emission spectrum.<sup>16,17</sup>

One approach to decrease interchain interaction is copolymerization. A second molecule, a spacer unit, can be incorporated into the polymer chain that is oriented perpendicular (orthogonal) to the planar 9,9-di-*n*-hexylfluorene unit. At each site along the polymer chain where the second unit resides, there will be a break in the conjugation due to the different directionality of the two units with respect to each other. The conjugation lengths within a single chain can be changed by varying the ratios of the two molecules. A greater amount of spacer molecule results in shorter average conjugation lengths. In addition, the stacking of neighboring chains in the solid state can be minimized so that a true blue emission is observed. Copolymerization of DHF and anthracene (ANT) produces a chain containing conjugation interruptions which result in the polymer being an assembly of oligomers of various lengths. Figure 1 shows a molecular

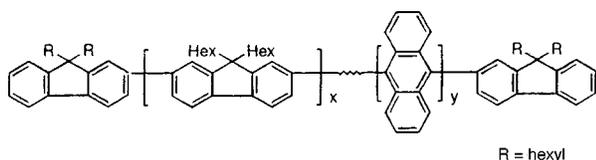


FIG. 1. Molecular structure of a 9,9-di-*n*-hexylfluorene/anthracene copolymer.

structure representative of a copolymer containing DHF and ANT monomer units. Photoabsorption can cause excitation of conjugation segments of all lengths. Energy transfer may occur from a shorter to a longer conjugation segment, or from a polyfluorene conjugation segment to an anthracene molecule, since the energy of the first excited singlet state of anthracene is slightly lower than that of the polyfluorene conjugation segment. In this paper, it is not argued whether energy transfer occurs or if the emissive singlet exciton recombines locally within a dihexylfluorene or anthracene unit.

In an LED, electrons are injected at the cathode and holes at the anode, both species subsequently migrate, under the influence of an applied electric field, in the polymer layer to form an exciton. The radiative relaxation of the exciton to the ground state produces light, although the desired emission competes with nonradiative channels.<sup>18</sup> The formation of competing nonradiative species and their subsequent decays on the ultrafast timescale are not well defined. The identity and decay mechanisms of these excited state species, which relax to the ground state nonradiatively have been the subject of intensive investigation.<sup>13,19–22</sup> Studying the nature and lifetimes of these excited states helps to understand the photophysics in conjugated organic polymers and the correlation to their performance in LED applications.

Studies of the photophysics in conjugated polymer thin films are directly related to their applications. In thin films, interchain interactions lead to more complicated photophysics than in solutions. It is constructive to investigate the photophysics in dilute solutions to gain insight into the events that occur on single-polymer chains and to make comparisons to events observed in the solid state. In the solid state, formation of aggregates and excimers are possible, and these species can significantly influence the exciton lifetime and light emission efficiency. Recently, excited state aggregates (excimers) have been reported in poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) solutions and thin films.<sup>23</sup> Rothberg *et al.* reported the quantum yield for excimer formation in (MEH-PPV) thin films to be approximately 45%, and found excimer emission to contribute a negligible amount to the total photoluminescence.<sup>24</sup> Formation of weakly emissive excited states are important to consider when fabricating devices since the efficiency of electroluminescent conjugated polymer LED's is directly related to the ratio of emissive to non-emissive species formed.

In this paper, we compare solution and thin film transient absorption dynamics to explore the difference between intrachain and interchain exciton relaxation mechanisms. In addition, we investigate the time-resolved measurements for a dihexylfluorene homopolymer and two copolymer thin films as a function of both probe wavelength and excitation intensity. We have previously examined the intensity dependent dynamics for similar copolymers in solution and thin films at

excitation intensities exceeding those presented in this paper.<sup>25</sup> Contributions from nonlinear processes, such as exciton-exciton annihilation, were observed in thin films at relatively high excitation intensities. Our motivation for studying the photophysics in thin films at relatively low excitation intensities was to eliminate exciton-exciton interaction and attempt to reproduce the charge carrier density in operating LED's. In the following, the steady state absorption and emission spectra are presented, followed by the transient absorption dynamics, in dilute solution, of a random copolymer containing 85% by weight 9,9-di-*n*-hexylfluorene and 15% by weight anthracene (85 DHF/15 ANT) and of DHF, 85 DHF/15 ANT and 50 DHF/50 ANT thin films. The intensity independent dynamics for 85 DHF/15 ANT in solutions and in thin films are compared. The wavelength independent dynamics for the 50 DHF/50 ANT copolymer thin film are compared to wavelength dependent dynamics of the DHF homopolymer, revealing a significant difference on the (<1 ps time scale, which is attributed to a differing degree of interchain interaction. The exciton is created within the laser pulse (<200 fs). Localization of the exciton may occur as an excited state aggregate, or excimer, if sufficient orbital overlap exists between neighboring conjugation segments on separate chains. Alternatively, the exciton may undergo rapid energy migration from higher energy to lower energy conjugation segments either on the same or adjacent chains. Excimer emission from DHF thin films has been observed in steady-state photoluminescence measurements and we propose that excimer formation occurs in (<1 ps based on transient absorption measurements. The effectiveness of incorporating anthracene into the dihexylfluorene backbone to decrease interchain interactions is discussed.

## II. EXPERIMENT

Synthetic procedures and NMR characterization for 9,9-di-*n*-hexylfluorene/anthracene copolymers have been published.<sup>9,26,27</sup> Dilute solutions of DHF homopolymer, 85 DHF/15 ANT, and 50 DHF/50 ANT (percent by weight) in *p*-xylene were prepared to attain an optical density of approximately 1.0 at 390 nm in a 1-cm pathlength quartz cell. Solutions used for photoluminescence measurements had optical density of 0.1 at 390 nm. Thin films were prepared by mixing 15-30 mg of the respective polymer with 1 ml *p*-xylene, heating at approximately 60-90 C for 60 s to aid dissolution, filtering through a 1 micron syringe filter while hot and spin coating onto clean quartz substrates at 1500 rpm. Thickness measurements were done on an Alpha Step Profilometer. Optical densities of thin films ranged from 0.85–1.3 at 390 nm, with corresponding film thicknesses from 100–200 nm. Static absorption measurements were recorded with a Hewlett-Packard 8452A Diode Array Spectrophotometer with 2-nm resolution. Photoluminescence (PL) measurements were obtained from a Perkin Elmer LS 50B Luminescence Spectrophotometer with 2-nm resolution. PL excitation was 400 nm. Accurate quantum yield measurements for DHF homopolymer, 85 DHF/15 ANT, and 50 DHF/50 ANT in solutions and thin films are in progress.

The dynamics measurements were carried out with two

different laser systems. The studies of dilute solutions were performed using a pump-probe scheme with a regeneratively amplified, mode-locked femtosecond Ti:Sapphire laser system. The laser system and setup have been described previously.<sup>25</sup> A zero-order half-wave plate and a Glan-Thompson polarizer were placed in the pump and probe beams, respectively. The data were collected with the polarizers set at the magic angle. The energy of relaxation dynamics were measured at 790 nm following excitation at 390 nm. The pump intensity was varied over the range 0.1–1.0 mJ/pulse cm<sup>2</sup>.

The thin film experiments were collected on a separate system, using a regeneratively amplified Ti:Sapphire laser (Clark-MXR CPA-1000) emitting 100 fs pulses of 1 mJ energy at a wavelength of 800 nm and a repetition rate of 1 kHz. The majority (90%) of the fundamental beam was frequency doubled to provide the pump excitation source at 400 nm, with incident energy controlled with a calibrated neutral-density filter wheel. The remainder of the fundamental was attenuated to <2 μJ and focused through a 1-mm sapphire plate to generate a broadband white-light continuum probe pulse with spectral components from 450–110 nm. The details of the instrumentation for fs high sensitivity, broadband chirp-free transient absorption measurements has been described elsewhere.<sup>28</sup> The samples were excited in vacuum at a fixed wavelength of 400 nm (3.1 eV). The pump-photon energy is slightly less than the π-π\* transition for the homopolymer and copolymers, corresponding to a near-resonant band-edge excitation. Thin films mounted in an optical cryostat under high vacuum were systematically adjusted to expose pristine polymer and to avoid effects of photodegradation. As a measure of transmission changes, the differential transmission (DT), defined as follows:

$$DT = (T - T_0)/T_0 = \Delta T/T_0, \quad (1)$$

was used.  $T_0$  and  $T$  are the transmissions in the absence and in the presence of the pump, respectively. The pump-induced absorption change, %ΔA, is proportional to  $\ln(1 + DT)$ .

### III. RESULTS AND DISCUSSION

#### A. Steady-state absorption and emission spectra

The electronic absorption (dotted lines) and photoluminescence (PL) spectra (small-dashed lines) of DHF, 85 DHF/15 ANT, and 50 DHF/50 ANT thin films are shown in Fig. 2. The absorption (solid lines) and emission spectra for dilute solutions (large-dashed lines) are also shown in comparison. The absorption consists of a strong featureless π-π\* transition that peaks at 382 nm for DHF film [Fig. 2(a)] 378 nm for 85 DHF/15 ANT film [Fig. 2(b)], and 380 nm for 50 DHF/50 ANT [Fig. 2(c)] thin films. The absorption spectra of the thin films are similar to those of dilute solution except that the peaks are broader. The pronounced broadening of the DHF thin film absorption spectra can be explained as the homopolymer consisting of an array of oligomers of statistically varying length. This change in absorption spectrum from dilute solution to thin film can be attributed to inhomogeneous broadening and has been previously observed in polyfluorene.<sup>29</sup> The broadening could also be attributed to aggregate formation. The emission spectra show vibronic structure, consistent with the rigidity of the poly-

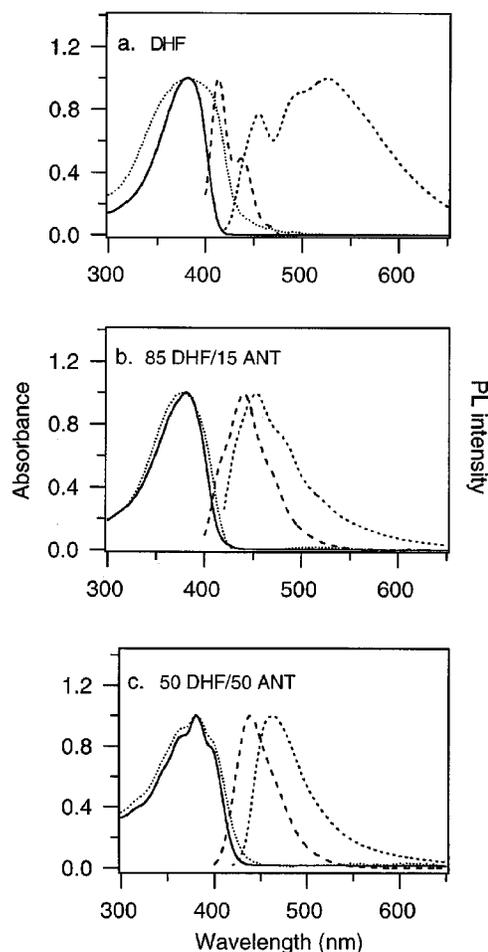


FIG. 2. Electronic absorption and photoluminescence spectra for DHF (a), 85 DHF/15 ANT (b), and 50 DHF/50 ANT (c). Absorption spectra of dilute solutions are indicated by solid lines and thin films by dotted lines. Photoluminescence spectra are represented by large- and small-dashed lines for solution and thin film, respectively (excitation at 400 nm). Peak values have been normalized to unity for all spectra.

fluorene molecular structure. As the amount of anthracene is increased the vibrational structure becomes less distinct, indicating a more flexible polymer backbone. For the 85 DHF/15 ANT and 50 DHF/50 ANT copolymers, the photoluminescence mirrors the absorption spectra. In contrast, the PL spectra of DHF homopolymer [Fig. 2(a)] has a band shape that does not mirror its absorption spectra. Emission from a dilute solution of DHF has maxima at 413 and 436 nm, assigned to the 0-0 and 0-1 transitions. The DHF thin film spectrum contains an excitonic emission peak, in the same region where the exciton emission is observed for 85 DHF/15 ANT and 50 DHF/50 ANT thin films, plus an additional broad peak centered at 526 nm that dominates the PL spectrum. The blue component in the PL spectrum of DHF thin film is similar to the PL of both the copolymer thin films and therefore this component is assigned to emission from isolated conjugation segments. The 0-0 peak is absent in the DHF thin film PL, possibly due to self absorption. The broad redshifted peak indicates that a significant number of the initial photoexcitations have migrated to lower energy states prior to relaxation to the ground state. This redshifted emission has been previously proposed to be due to excimer or

aggregate emission.<sup>26,27,30,31</sup> Excimer formation is often associated with decreased emission quantum yields.<sup>24,26</sup> Since the electroluminescence and photoluminescence spectra are correlated<sup>26</sup> for devices prepared from these materials, it is important to understand how film morphology affects excimer or aggregate formation. Either excimer formation or aggregate formation could result in the redshifted emission observed in the homopolymer thin film.

It is evident from the photoluminescence spectra of the copolymer thin films that excimer or aggregate formation is reduced by incorporating the anthracene molecule into the DHF backbone. The ANT is oriented approximately perpendicular and is not in the plane of conjugation of the DHF, thereby preventing stacking or aggregation of the fluorene units on adjacent chains. The work described here explores the question of whether anthracene in the chain affects ultrafast dynamics as well as increasing the efficiency of desired blue emission in DHF-based polymers.

### B. Exciton Dynamics of 85 DHF/15 ANT in Dilute Solutions

The exciton dynamics for a dilute solution of 85 DHF/15 ANT in *p*-xylene have been studied as a function of excitation intensity, as shown in Fig. 3. Three panels display low- to high-excitation intensity results on three different time scales with probe wavelength at 790 nm following excitation of 390 nm. The highest intensity used, corresponding to data with the largest amplitude, is about 0.9 mJ/(pulse cm<sup>2</sup>). The lower intensities are approximately 0.46 and 0.12 mJ/(pulse cm<sup>2</sup>), respectively. On the 0-10 ps time scale, the data show a fast rise, limited by the laser pulse width, followed by a fast decay and a relatively slower decay. The single dotted line is the lowest pump fluence data scaled to the same amplitude as the high pump fluence data. The fits shown (solid lines) are generated using a triple exponential function convolved with a Gaussian to represent the pulsewidth [full width at half maximum (FWHM) of 400 fs]. All data shown in Fig. 3 are fit with 2.6(+/-0.8 ps), 15(+/-3 ps), and 220(+/-20 ps) time constants and the corresponding amplitudes scale to the pump intensity. These results are comparable to previous measurements in DHF copolymers,<sup>25</sup> containing 9,9-diphenylfluorene as a spacer, where the intensity independent transient absorption dynamics at 790 nm were fit to a double exponential with time constants of 30(+/-5 ps) and 330(+/-30 ps).

The data were analyzed for qualitative comparison between different data sets. Conventional fitting to a sum of two or three exponentials<sup>32</sup> yields a method for analyzing differences in decay rates. In dilute solutions the primary excitations are confined to individual polymer chains.<sup>33</sup> Photoluminescence quantum yields are high, suggesting that emissive singlet excitons are the primary species formed by photoexcitation. The fastest decay can be assigned to exciton-phonon coupling in the first excited state, or to exciton migration from higher energy to lower energy conjugation segments.<sup>34</sup> The two relatively longer time constants represent a variety of radiative and nonradiative recombination mechanisms. The amplitudes of each of the decay components scale to the excitation intensities at the signal maximum. In dilute solutions the dynamics are independent of the pump power for 790 nm probe wavelength over the excitation intensity range studied. Lack of intensity dependence is

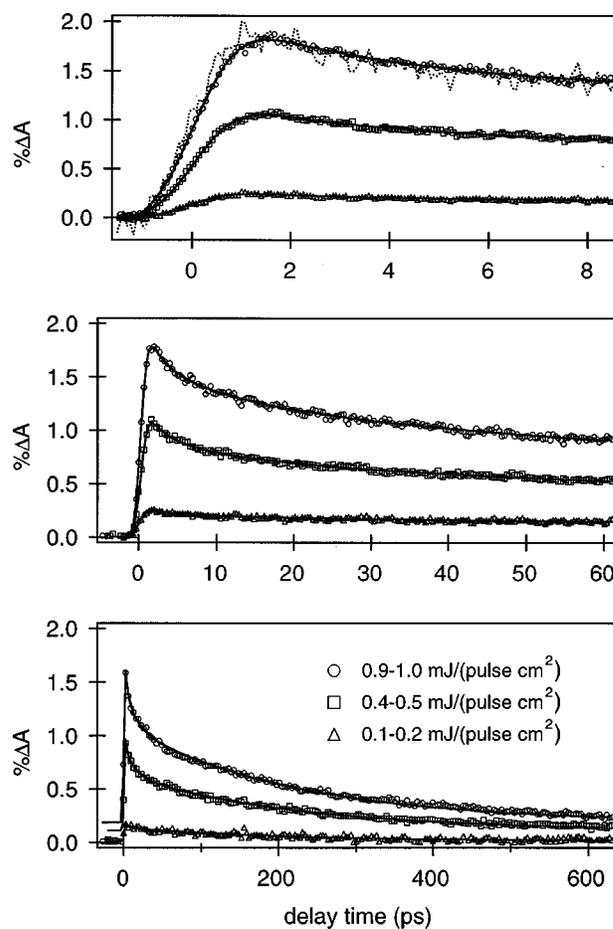


FIG. 3. Energy relaxation profiles for dilute solutions of 85 DHF/15 ANT in *p*-xylene. (O.D.<sub>390</sub>=1.0). The separate panels show intensity independent dynamics on three different timescales. Excitation intensities are 0.1–0.2 mJ/(pulse cm<sup>2</sup>) (open triangles), 0.4–0.5 mJ/(pulse cm<sup>2</sup>) (open squares), and 0.9–1.0 mJ/(pulse cm<sup>2</sup>) (open circles). The single dotted line is the low intensity data scaled to the same amplitude as the high-intensity data for comparison. Pump and probe wavelengths were 390 and 790 nm, respectively, and were oriented at magic angle to each other. The decay dynamics are shown accompanied by a triple exponential fit with time constants of:  $\tau_1=2.6(+/-0.8$  ps),  $\tau_2=15(+/-3$  ps),  $\tau_3=220(+/-20$  ps).

expected where interaction between chains is weak and the dominant excitations at low intensities are noninteracting intrachain singlet excitons.

### C. Exciton Dynamics in Thin Films

Figure 4 shows the chirp-free transient absorption spectra for the DHF homopolymer, and the two copolymer thin films obtained at  $t=0$ , where the maximum transient absorption is measured. These spectra are obtained with excitation at 400 nm, and scanning the probe wavelengths from 450–750 nm and 850–1150 nm, at a fixed time between the pump and probe. Three bands are observed in the  $t=0$  transient absorption spectrum of the DHF homopolymer. The first band with a maximum at 450 nm is a stimulated emission (SE) band, and the second and third bands at 600 nm and approximately 750 nm are due to photoinduced absorption (PA). The PA features are poorly resolved, and the term “band” is used

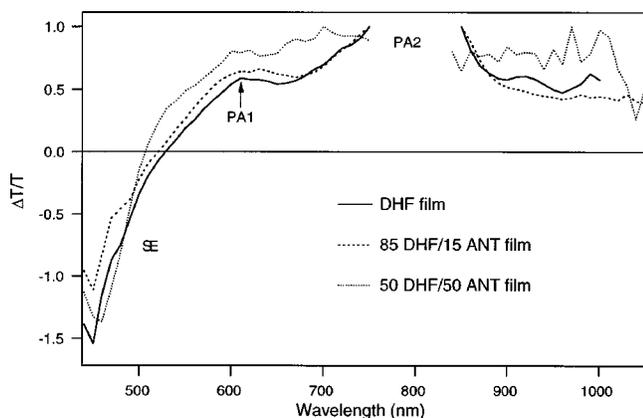


FIG. 4. Transient absorption spectra for DHF homopolymer, 85 DHF/15 ANT, and 50 DHF/50 ANT thin films at 0-ps delay between pump and probe pulses. A stimulated emission (SE) band is observed in the region of steady-state fluorescence. Two photoinduced absorption (PA) bands are observed at approximately 600 and 750 nm. The window around 800 nm is due to saturation of the lock-in amplifier by the laser fundamental.

loosely in this case. The maxima are identified from the transient absorption spectrum. The dynamics at these wavelengths are useful in determining the lifetimes of both radiative and nonradiative excited state species.

The spectra are similar for the DHF homopolymer, 85 DHF/15 ANT, and 50 DHF/50 ANT thin films, this suggests that incorporation of anthracene into the dihexylfluorene, to break the rigidity of the polymer backbone and to interrupt the conjugation length, has a little effect on the features of the transient absorption as a function of wavelength on the 0-ps timescale. The PA features at 600 and 750 nm are separated for the DHF thin film, but are not distinct for the 50 DHF/50 ANT thin film, which suggests a mixing of the two bands.

The intensity independent transient absorption dynamics for an 85 DHF/15 ANT thin film spin cast from *p*-xylene are presented in Figs. 5(a) and 5(b). Thin film measurements were done in vacuum using 400 nm excitation and 750 nm probe wavelengths, on the 0–3 and 0–250 ps timescales. Excitation intensities were 1.0  $\mu\text{J}/(\text{pulse cm}^2)$ , 3.3  $\mu\text{J}/(\text{pulse cm}^2)$ , and 10.6  $\mu\text{J}/(\text{pulse cm}^2)$ . The single dotted line is the low intensity scaled to the high intensity result. The fits shown (solid lines) are generated using a double exponential function convolved with a Gaussian ( $\sim 230$  fs FWHM) to represent the pulsewidth. The data shown are fit with 5( $\pm 1$  ps) and 50( $\pm 5$  ps) time constants with a small ( $\sim 5$ –7%) offset. The amplitudes for both decay components scale linearly to excitation intensity. Similar to the dilute solution dynamics, there is no distinguishable difference between the thin film dynamics over this range of excitation intensities. This lack of intensity dependence suggests that the primary photophysical processes, along the polymer backbone or between adjacent conjugation segments on separate chains, are due to noninteracting, excited state species.<sup>35</sup>

Significant photodegradation was evident above 16.8  $\mu\text{J}/(\text{pulse cm}^2)$  for both of the copolymer thin films in vacuum. The DHF homopolymer was stable up to excitation intensities of 168  $\mu\text{J}/(\text{pulse cm}^2)$ . Electrical and photoinduced deg-

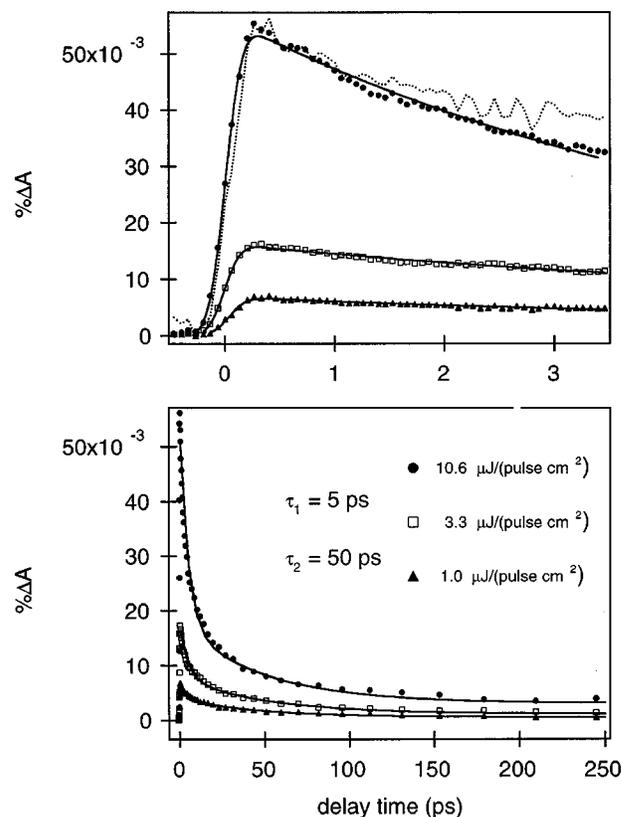


FIG. 5. Transient absorption profiles for an 85 DHF/15 ANT thin film spin cast from *p*-xylene for 0–3 and 0–250 ps. Excitation intensities are 1.0  $\mu\text{J}/(\text{pulse cm}^2)$  (triangles), 3.3  $\mu\text{J}/(\text{pulse cm}^2)$  (squares), and 10.6  $\mu\text{J}/(\text{pulse cm}^2)$  (circles). The single dotted line is the low-intensity scaled to the high-intensity result. 400 nm pump and 750 nm probe wavelengths. The decay dynamics are shown accompanied by a double exponential fit with time constants:  $\tau_1 = 5$  ( $\pm 1$  ps) and  $\tau_2 = 50$  ( $\pm 5$  ps).

radation of polyfluorene based films and light-emitting devices, both in the presence of oxygen and in an inert nitrogen atmosphere, have been previously reported.<sup>36</sup> Two primary modes of degradation were identified: oxidation of the polymer matrix with formation of carbonyl groups, that act as fluorescence quenching centers, and a second mechanism, in an inert nitrogen atmosphere, signified by physical aggregation. In the absence of oxygen, changes in photoluminescence are not accompanied by evidence of chemical changes in the polymer.<sup>36</sup> Decreased emission was observed in the experiments carried out under inert nitrogen atmosphere. A mechanism involving physical/structural processes was invoked to explain the enhanced nonradiative recombination of the excited state. In the transient absorption measurements, at excitation intensities exceeding those given above, the amplitude of the observed signal decreased between successive scans, which we attribute to photodegradation. Oxygen was removed from the cryostat prior to our measurements, suggesting a degradation mechanism that does not involve oxygen. Further investigations into the nature of the polymer films after photodegradation were not pursued in the present experiments.

Figure 6 contains the 0–3 ps dynamics at 450, 600, and 750 nm probe wavelengths, for the 50 DHF/50 ANT thin film. Changes in the excited state population were monitored

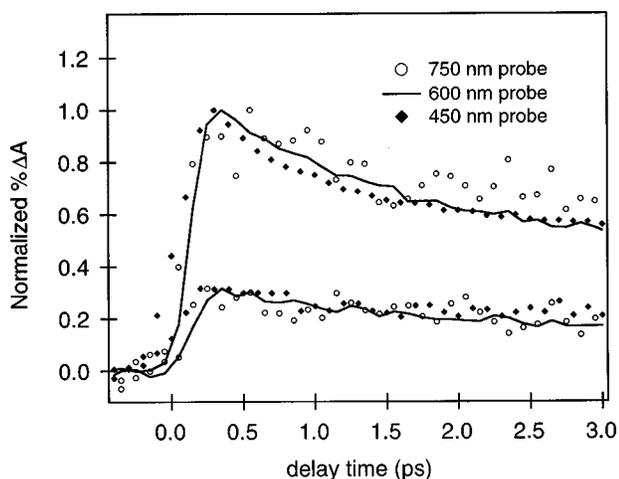


FIG. 6. Transient absorption profile for 50 DHF/50 ANT thin film from 0–3 ps following excitation at 400 nm. Probe wavelengths are 450 (diamonds), 600 (solid line), and 750 nm (circles). Excitation intensities are  $16.8 \mu\text{J}/(\text{pulse cm}^2)$  and  $5.3 \mu\text{J}/(\text{pulse cm}^2)$ . Peak values have been normalized to unity.

at excitation fluences of  $16.8$  and  $5.3 \mu\text{J}/(\text{pulse-cm}^2)$ . The SE data have been multiplied by a factor of negative one for ease of comparison with the PA. In addition, the 450, 660, and 750 nm sets at similar excitation intensities have been normalized. Each data set shows a fast rise, limited by the laser pulse width, followed by a fast decay and a slower decay. On this timescale, the transient absorption dynamics at 450, 600, and 750 nm are comparable within the noise. There is no apparent wavelength dependence in the dynamics for this copolymer at these three wavelengths, suggesting that the transient absorption and stimulated emission are due to the same excited state species in the copolymer. The stimulated emission can be assigned to the singlet exciton and by the similarity between the SE and PA, the PA can also be attributed to singlet exciton decay. The incorporation of anthracene into the polyfluorene backbone has effectively reduced physical aggregation in the ground state and/or excimer formation in the excited state. Anthracene sterically inhibits the electronic conjugation along the chain to suppress interchain  $\pi$  stacking. Similar results were obtained for the 85 DHF/15 ANT copolymer thin film.

Figure 7 shows the dynamics measured for the DHF homopolymer thin film. There are two features in the rise, a fast component which seems to follow the rise of the SE, and a relatively slower component that grows in after a few hundred femtoseconds. This “double rise” feature is absent from the 450 nm, SE data, which is unambiguously assigned to the emissive singlet exciton. In comparison to 50 DHF/50 ANT (Fig. 6), where interchain interaction has been suppressed by incorporation of anthracene into the polymer backbone, there appears to be evidence of contribution from a secondary process on the ultrafast timescale for the DHF thin film, as indicated by this secondary rise in the transient absorption profile. This secondary rise, in combination with the broad red-shifted band in the steady-state photoluminescence spectrum, leads us to propose that energy migration to lower energy, more localized conjugation segments occurs within a few hundred femtoseconds in the DHF homopolymer thin film.

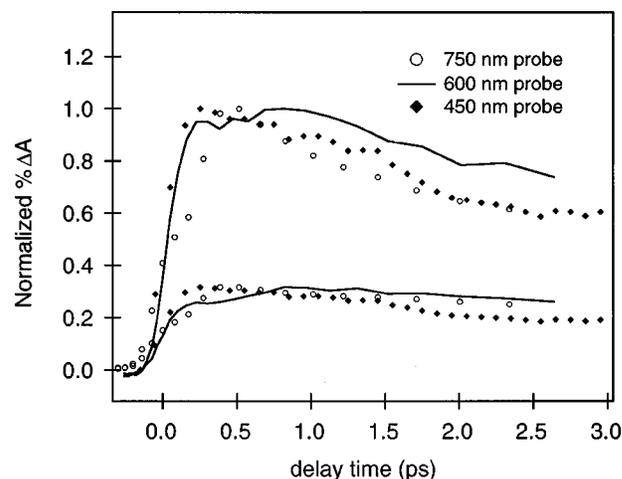


FIG. 7. Transient absorption profile for DHF thin film from 0–3 ps following excitation at 400 nm. Probe wavelengths are 450 (diamonds), 600 (solid line), and 750 nm (circles). Excitation intensities are  $16.8 \mu\text{J}/(\text{pulse cm}^2)$  and  $5.3 \mu\text{J}/(\text{pulse cm}^2)$ . Peak values have been normalized to unity.

The steady-state absorption spectra provides insight as to whether the red-shifted emission is due to excimers or ground-state aggregates. Aggregates are directly accessible in optical absorption and their formation would be signified by a red-shifted absorption in the thin-film relative to the dilute solution. The appearance of an extended low energy tail in the absorption spectrum of ladder-type paraphenylene polymers has been previously observed<sup>12</sup> and was attributed to aggregates. As seen in Figs. 2(b) and 2(c), the absorption spectra of dilute solutions and solid films of 85 DHF/15 ANT and 50 DHF/50 ANT are quite similar. In the ground-state absorption spectra there is no evidence of interactions between polymer chains in the copolymers. The absorption spectrum of the DHF homopolymer thin film is broader than that of the dilute solution. The broadening is symmetric around the wavelength of maximum absorption, and the wavelength of maximum absorption is not red-shifted relative to dilute solution spectrum. Since lower energy aggregate states are directly accessible optically, we would expect red-shifted absorption and photoluminescence excitation spectra if aggregates were formed in the homopolymer thin films. Although broadening of the DHF absorption band was observed, we did not observe an extended low-energy tail in the absorption, indicative of aggregate states. The redshifted emission is thereby assigned to excimers, in agreement with earlier studies.<sup>36</sup> Excimers may form directly following photoexcitation or as a product of exciton-exciton annihilation (at high excitation intensities). Excimers are localized relative to singlet excitons and recombine radiatively from a lower energy state, typically with lower quantum yields.

The PL spectrum for the DHF homopolymer film shows a significant amount of excimer emission. The dependence on probe wavelength of the transient absorption measurements suggests that different species are responsible for the SE and PA signals. Formation of secondary species, in addition to the emissive singlet exciton, is facilitated by the close proximity of conjugation segments on adjacent chains. We propose that the two “separate” rises observed in both the 750 and 600 nm PA are contributions from two different pro-

cesses on slightly different timescales. The “second” process may be associated with secondary excitations. These secondary excitations are not confined to individual polymer chains, and are likely interchain excitons, or excimers.<sup>24,37</sup> The second apparent rise could be direct evidence of excimer formation on the 100-500 fs timescale. In solid state samples, with strong intermolecular interactions, interchain species may be formed in a linear process directly from excitons.<sup>38,39</sup> Interchain excitons formed at the expense of intrachain singlet excitons are less likely to recombine radiatively and are correlated with a decrease in emissive light output.<sup>40</sup>

#### IV. CONCLUSION

In summary, polyfluorene statistical copolymers which emit in the 420-500-nm region have been studied using ultrafast transient absorption spectroscopy to provide insight into the energy dissipation mechanisms. If the polymer chains are sufficiently separated in space such that an excited state species is confined to a single chain, then only the formation and decay of intrachain species will be observed. This is the case for dilute solutions and thin films of di-*n*-hexylfluorene/anthracene copolymers at low excitation intensities. Analysis of the energy relaxation dynamics of photogenerated emissive, singlet excitons reveals that the decay processes are independent of excitation intensity over the range investigated.

In the solid state, individual intrachain photoexcitations are capable of migrating to overlapping conjugation segments on neighboring polymer chains, thereby greatly in-

creasing the complexity of the decay processes. Differences between the decay dynamics for stimulated emission (SE) and those for photoinduced absorption (PA) provide information regarding the nature of the excited state species responsible for the PA bands. That SE dynamics differ significantly from PA dynamics suggests that excited state species other than emissive singlet excitons have formed in DHF thin films. The excimer emission observed in the steady-state PL, in combination with the wavelength dependent transient absorption measurements, lead us to suggest that excimers are forming within a few hundred fs in DHF films. Statistical copolymers designed to prevent formation of interchain species exhibit decay dynamics associated primarily with singlet excitons. In thin films, at low-excitation intensities, the emissive singlet exciton decays via linear processes, which implies exciton-exciton interactions are minimized. Incorporation of anthracene into the chain to break the rigidity of the ladder-type structure of the DHF inhibits excimer formation, thus promoting radiative recombination of singlet excitons.

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