Spectral and Thermal Spectral Stability Study for Fluorene-Based Conjugated Polymers

Gang Zeng,* Wang-Lin Yu, Soo-Jin Chua, and Wei Huang*

Institute of Materials Research and Engineering, National University of Singapore, 3 Research Link, Singapore 117602, Republic of Singapore

Received February 14, 2002; Revised Manuscript Received May 28, 2002

ABSTRACT: We have studied the spectral (UV−vis absorption and fluorescence) and thermally spectral stability of seven fluorene-based blue-light-emitting polymers in film states. These polymers have different side chain and backbone structure. Spiro-functionalization at the C-9 bridge position of fluorene unit could significantly improve the emission spectral quality (narrower spectrum and shorter tail extended to longer wavelength direction) and thermally spectral stability of 9,9-disubstituted polyfluorene derivatives. A glass transition temperature dependence for excimer emission in the polymers was demonstrated, and the improvement of thermally spectral stability by the spiro-functionalization is attributed to the increase of glass transition temperature. The backbone structural modification for 9,9-disubstituted polyfluorenes by alternatively inserting substituted phenylene units could provide blue emission with the spectral quality and thermally spectral stability even better than spiro-functionalized polyfluorenes, and no glass transition temperature dependence for excimer formation was observed in the backbone-modified polymers. The spectral properties of the polymers are dependent on the substitution on the phenylene ring. Thermotropic liquid crystallization was observed in the polymers bearing long alkoxy substituents. The good thermally spectral stability of the polymers is attributed to the poor planar configuration of the backbone and the efficient separation of the side chains on phenylene units for backbones.

Introduction

Light-emitting polymers (LEPs) continue to attract considerate interest because of their potential application in various optoelectronic devices, especially in polymer light-emitting diodes (PLEDs). PLEDs offer many advantages over traditional inorganic LEDs, which include low fabrication cost for large area display, low driving voltage, light weight, and the possibilities of producing displays on flexible substrates.[1-3] Emission over the entire visible spectrum has been demonstrated with impressive efficiency and brightness.[4] Blue-emitting polymers are of special interest because of the need for completing the luminescent spectrum to realize full color displays and its utilization as color converters.[5,6]

Blue emission of LEPs needs large band gaps in the polymers. Poly(*p*-phenylene) (PPP) is suitable structurally for the purpose, in which the phenylene rings are heavily twisted due to its large steric interaction and thus results in the limit for intrinsic conjugation length along the backbone.[7] By functionalizing PPP with bulky side chains, soluble PPP derivatives were developed.[8] Efficient blue PLEDs were successfully fabricated from the soluble PPP derivatives.[9] Motivated by the structural principle of PPP, ladder PPPs and 9,9-substituted polyfluorene derivatives (PFs) were synthesized, and blue emission was demonstrated.[10-14] PFs are more intensively investigated as blue-light-emitting materials in PLEDs because of their high photoluminescence yields, high hole mobility, good photostability and thermal stability, and the emission of polarized blue light.[15-21] One drawback that has limited the application of PFs in blue PLEDs is the poor spectral stability,

which is associated with the troublesome excimer formation in solid states.[15,16,22-26] An additional emission band between 500 and 600 nm may appear and become pronounced upon thermal annealing or passage of current.

To solve the problem of poor spectral stability of PFs in films, Miller et al. introduced a small amount of low-band-gap chromophores, such as anthracene, perylene, or α-cyanostilbene, into the backbone of PF to suppress the excimer emission.[22,27] The suppression to excimer emission is explained as the efficient excitonic energy trapping by the lower-band-gap chromophoric segments upon the excitation of the polyfluorene chromophoric segments.[28] They have also demonstrated that the spectral stability of PFs may be improved by crosslinking the polymers in film states through the end-functionalized styryl groups.[29] The improvement is attributed to the enhancement of amorphous stability of polymer films. Alternatively, we introduced the spirofluorene structure into PF to enhance the amorphous stability of the resulting polymers in film states and demonstrated improved thermally spectral stability.[30] Müllen et al. also demonstrated the stable blue emission by attaching polyphenylene dendron side chains to PFs to prevent aggregation. The prevention is due to the shielding effect provided by different phenylene side groups.[31] Carter et al. reported similar results by using Fréchet-type dendron substituents.[32] In addition, Weinfurtner et al. revealed that the low molecular weight parts in polyfluorene materials are responsible for the excimer emission.[33] Most recently, List et al. explained the excimer-like band in PFs to the formation of fluorenone units.[34] We also noticed that, for a series of polythiophene materials, it is argued that excimer formation may be suppressed if the polymer backbones are completely separated in all three dimensions by attached side chains.[35] It is therefore still an

* Corresponding authors: Tel (65) 6874-8350, Fax (65) 6872-0785, e-mail engp8932@nus.edu.sg (Gang Zeng). Tel (86) 21-6564-3494, Fax (86) 21-6510-2107, e-mail chehw@nus.edu.sg (Wei Huang).
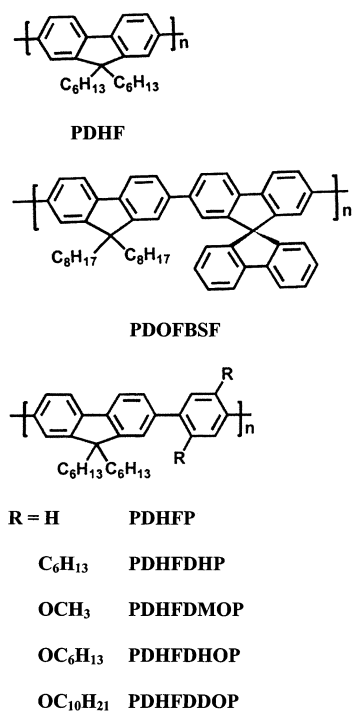
Figure 1. Chemical structures of the polymers used.

issue to understand and solve the troublesome excimer formation in blue-light-emitting polymers and finally to develop stable and efficient blue-light-emitting polymeric materials for the application in PLEDs. In this article, we will present the investigation of spectral stability for a series of fluorene-based blue LEPs with different backbone and side chain structures aiming to understand the factors affecting emission spectral quality and excimer formation.

Experimental Section

Materials. The chemical structures of the blue-light-emitting polymers used in the experiments are shown in Figure 1. Poly(9,9-dihexylfluorene-2,7-diyl) (PDHF) was synthesized from 2,7-dibromo-9,9-dihexylfluorene by nickel(0)-mediated polymerization.[15] The synthesis of poly[(9,9-dioctyl-2,7-fluorene)-*alt*-co-(2,7-9,9′-spirobifluorene)] (PDOFBSF) has been reported in our previous publication.[30] Poly[(9,9-dihexylfluorene)-*alt*-co-1,4-phenylene] (PDHFP), poly[(9,9-dihexylfluorene)-*alt*-co-2,5-dihexyl-2,5-phenylene)] (PDHFDHP), poly[(9,9-dihexylfluorene)-*alt*-co-(2,5-dimethoxy-1,4-phenylene)] (PDHFDMOP), poly[(9,9-dihexylfluorene)-*alt*-co-(2,5-dihexyloxy-1,4-phenylene)] (PDHFDHOP), and poly[(9,9-dihexylfluorene)-*alt*-co-(2,5-didecyloxy-1,4-phenylene)] (PDHFDDOP) were prepared from 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) and 1,4-dibromobenzene, 1,4-dibromo-2,5-dihexylbenzene, or the corresponding 1,4-dibromo-2,5-bis(alkoxy)benzenes through Suzuki coupling reaction as described in previous publication.[36] The structures and purity of the polymers were confirmed by ¹H and ¹³C NMR and elemental analysis. For film preparation, PDHF and PDOFBSF both were dissolved in chlorobenzene with the concentration of 30 mg/mL. The solutions of the remaining polymers were prepared in *p*-xylene in the concentration of 30 mg/mL. All polymer films were cast on quartz plates by spin-casting 50 μL polymer solutions at a spin rate of 1200 rpm for 4 min.

Measurements. To investigate the thermally spectral stability of the polymer films, film-coated plates were placed on a surface temperature controlled hot plate and were heated at prescribed temperatures for certain time in air or nitrogen, as specified. Then the polymer films were kept on the hot plate to cool to room temperature and were subjected to spectral measurements. In quenching experiments, the polymer films were heated at 200 °C for 3.5 h and were then immediately put into dry ice–methanol bath. The quenched polymer films were then dried under vacuum at room temperature before spectral measurement. The UV–vis absorption and photoluminescence (PL) spectra were recorded on a Shimadzu UV 3101 spectrophotometer and on a Perkin-Elmer LS 50B luminescence spectrometer, respectively. Differential scanning calorimetry (DSC) was carried out on a NETZSCH DSC 200 thermal analysis system in the atmosphere of nitrogen.

Results

Optical Spectra. All the polymers listed in Figure 1 exhibit structureless absorption spectra in film states without noticeable difference in spectral shape from each other. The absorption maxima and the band gap energies determined from the absorption onset wavelengths of the polymers are summarized in Table 1. PDHF and PDOFBSF have exactly the same absorption peak at 379 nm and the band gap of 2.88 eV. This reveals that the replacement of the two alkyl chains on every other fluorene unit with a spiro-connected fluorene unit does not change the electronic structure of the backbone of the polymers. Modifying the backbone structure of PDHF by alternatively inserting phenylene unit also does not remarkably change the electronic structure of the polymer: PDHFP exhibits the absorption peak at 371 nm with the onset at 425 nm (corresponding to the band gap of 2.92 eV). The substitution on the phenylene ring in PDHFP, however, may induce an obvious substituent-dependent spectral change. The absorption peak of PDHFDHP is blue-shifted to 324 nm with the band gap of 3.25 eV. This could be understood in terms of the steric hindrance of the hexyl chains, which decreases the coplanarity between the adjacent fluorene and phenylene units. When the substituent is changed from hexyl group to alkoxy chains, the absorption spectra of the resulting polymers are close to that obtained from PDHF. PDHFDMOP, PDHFDHOP, and PDHFDDOP all show the absorption maxima around 372 nm and the absorption onsets around 424 nm (corresponding to the band gap of 2.92 eV). The absorption spectra do not exhibit dependence on the length of the alkoxy chains. The spectral red shift of the alkoxy-substituted polymers in relation to that of PDHFDHP is attributed to the stronger electron-donating property and smaller steric hindrance of alkoxy groups compared with alkyl groups.

The PL spectra of the polymers in film states are shown in Figure 2. Except PDHFDHP, which emits in

Table 1. Molecular Weights and Spectral Parameters of the Polymers

polymer	M_n	M_w/M_n	$\lambda_{max,abs}$ (nm)	band gap (eV)	$\lambda_{max,em}$ (nm)	$\lambda_{onset,em}$ (nm)	fwhm (nm)
PDHF	6 400	1.37	379	2.88	452, 420 (480, 520)	610	62
PDOFBSF	>11 600	2.90	379	2.88	451	585	39
PDHFP	11 800	1.70	371	2.92	446, 431	630	62
PDHFDHP	9 400	1.54	324	3.25	409	533	58
PDHFDMOP	27 700	1.78	372	2.92	425 (448)	580	52
PDHFDHOP	50 500	2.00	373	2.91	425 (448)	575	49
PDHFDDOP	41 400	2.08	372	2.92	425	560	46
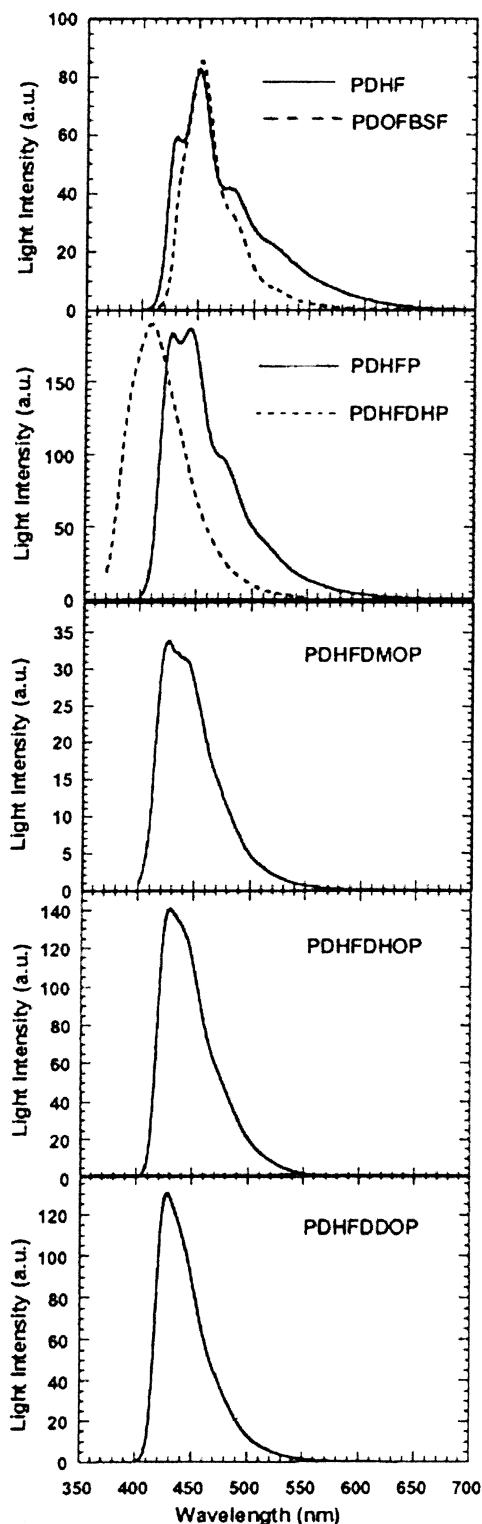
Figure 2. Fluorescence spectra of the polymers in film states at room temperature.

the blue to near-UV regions, all the other polymers emit blue light with the emission peak in the range 420–450 nm. The emission peak wavelength, the full width at the half-maximum (fwhm), and the "onset" wavelength at the longer wavelength side of PL spectrum for all the polymers are listed in Table 1. The emission peaks of PDHF are located at 452 nm with two well-identified vibronic structures at around 420 and 480 nm. It is worth noticing that the PL spectrum has a long tail extending to longer wavelength direction (the spectrum "onsets" at 610 nm at the longer wavelength

side) and a shoulder at around 520 nm. This spectral feature is commonly observed in 9,9-disubstituted polyfluorenes and is attributed to interchain excimer formation.[22-25] For blue light emission, one always likes a narrower spectrum in the blue region and less emission component above 500 nm. Otherwise, one will feel whitish or greenish blue but not pure blue color from the emission. In comparison with PDHF, PD-OFBSF exhibits much weaker vibronic structure in the PL spectrum. More interestingly, the PL spectrum of PSOFBSF is obviously narrower than that of PDHF, and the tail of PL spectrum toward the longer wavelength direction is significantly reduced. The results reveal that the quality of emission spectrum of polyfluorene is improved by the spiro-functionalization.

When we compare the PL spectra between PDHF and PDHFP, it could be found that spectral quality is not improved by the structural modification of alternatively inserting phenylene ring into the backbone of polyfluorene. PDHFP shows a heavily structured and broad PL spectrum, which also contains an identifiable shoulder at around 520 nm and a long tail beyond 600 nm. When the phenylene ring in PDHFP is substituted by methoxy group at the 2- and 5-positions, however, the vibronic structures in PL spectrum are remarkably reduced. PDHFDMOP shows emission peak at 425 nm and a vibronic structure at 448 nm. There is no identifiable spectral shoulder above 500 nm observed, and the spectral fwhm is decreased from 62 nm in PDHFP to 52 nm in PDHFDMOP. Moreover, the relative intensity of the vibronic structure at 448 nm, the spectral fwhm, and the "onset" wavelength steadily decrease with the increase of the length of substituted alkoxy chains. Vibronic structure completely disappears in the PL spectrum of PDHFDDOP, and the PL spectrum is characterized by structurelessness and small fwhm (46 nm). When the substituents at the 2- and 5-positions of the phenylene ring in PDHFP are hexyl groups (PDH-FDHP), the PL spectrum also becomes structureless and narrower (fwhm = 58 nm). The spectral quality of PDHFDDOP is even better than that of PDOFBSF. From the results, we can certainly conclude that, while the backbone structure of PDHFP provides similar blue emission features with PDHF, the spectral quality can be improved by attaching long alkoxy groups on phenylene rings.

Thermally Spectral Stability. It has been well-known that the PL spectra of PFs can show an additional broad, featureless band which is red-shifted by some 100 nm from the shortest wavelength peak of the original emission when the polymer films are exposed to heat in air for a long time.[22-24] The additional emission band is normally explained as excimer formation and emission. However, it is also argued that the additional emission band is the result of partial thermooxidative degradation of the polymers under the experimental conditions.[23] To clarify the question, we thermally treated the polymer films in different manners and then studied their absorption and PL spectra.

As shown in Figure 3, after PDHF film was annealed at 150 °C in air for 3.5 h, a pronounced emission peak appeared around 520 nm. When the annealing was conducted in the atmosphere of nitrogen, the additional pronounced emission peak centered at about 520 nm also appeared. For the polymer film, which was annealed at 200 °C in nitrogen for 2 h, the relative intensity of the additional emission is even stronger
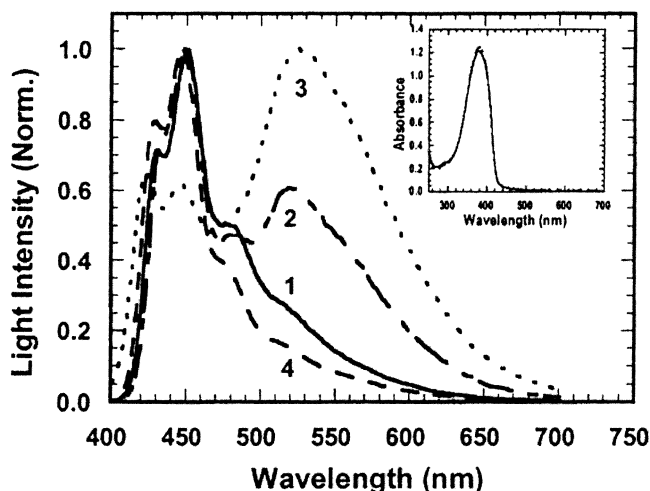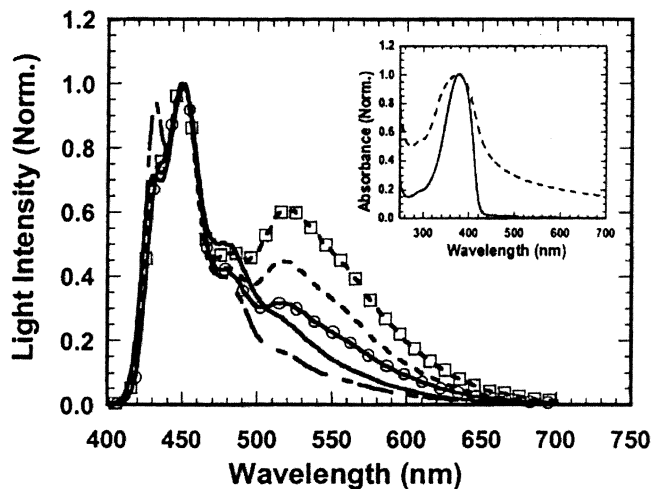
Figure 3. Fluorescence spectra of PDHF as pristine spin-cast film (1) and as films annealed at 150 °C in air (2) and at 200 °C in nitrogen (3). Spectrum 4 was obtained from the film that was first annealed at 200 °C in air for 3.5 h and then quenched in a methanol–dry ice bath. Inset: UV–vis absorption spectra of chlorobenzene solutions of pristine PDHF (solid line) and 150 °C annealed (for 3.5 h) PDHF.

Figure 4. Fluorescence spectra of PDHF as pristine film (solid line), and as films annealed at 80 °C for 3.5 h (broken line), at 100 °C for 3.5 h (circle), and at 150 °C for 1.5 h (dashed line) and 3.5 h (square). Inset: UV–vis absorption spectra of PDHF as pristine film (solid line) and annealed film (dashed line) (150 °C for 3.5 h).

Figure 5. Fluorescence spectra of PDOFBSF as pristine film (1) and as films annealed at 100 (2), 150 (3), and 200 °C (4) in air for 3.5 h. Inset: UV–vis absorption spectra of pristine (solid line) and annealed films (200 °C for 3.5 h) (dashed line).

than those of the original emission peaks. For annealed PDHF film (150 °C in air, 3.5 h), we dissolved the polymer film into chlorobenzene. The chlorobenzene solution of the annealed polymer exhibited the identical UV absorption spectrum with the original PDHF in chlorobenzene (see spectral comparison in the inset in Figure 3). Curve 4 in Figure 3 was recorded from the PDHF film, which was first annealed at 200 °C in air for 3.5 h and then quenched in a dry ice–methanol bath. It can be seen that, with quenching, the additional emission peak at around 520 nm disappears, and the PL spectrum is almost the same as that obtained from the original polymer film. The same experiments were also applied to all other polymers listed in Figure 1, and similar results were obtained. These results evidently demonstrate that the additional emission bands upon annealing in the polymer films discussed here are not the result of thermooxidative degradation but are due to the excimer formation.

The annealing-induced PL spectral change exhibited an annealing temperature and annealing time dependence. As shown in Figure 4, for PDHF, when the polymer film was annealed at 80 °C, we did not observe the spectral change up to 3.5 h of annealing. When the annealing temperature was increased to 100 °C, a clear additional emission peak centered at 520 nm appeared in the PL spectra after a long time (3.5 h) of annealing. At 150 °C, a steady increase of the relative intensity of the additional emission band with prolonging the annealing time was observed. We also noticed that the annealing induced the UV–vis absorption spectrum to broaden (see the inset in Figure 4). The spectral broadening is attributed to polymer aggregation.

In comparison with PDHF, the thermally spectral stability of PDOFBSF is improved. As we can see in Figure 5, annealing at 100 °C does not change the PL spectrum. After being annealed at 150 °C, the polymer gives a weak emission band between 500 and 600 nm, while annealing at 200 °C results in a strong emission band centered at ~525 nm. In contrast to absorption spectral broadening observed in PDHF, the UV–vis spectrum of PDOFBSF did not change after annealing (see the inset in Figure 5), indicating that there is no
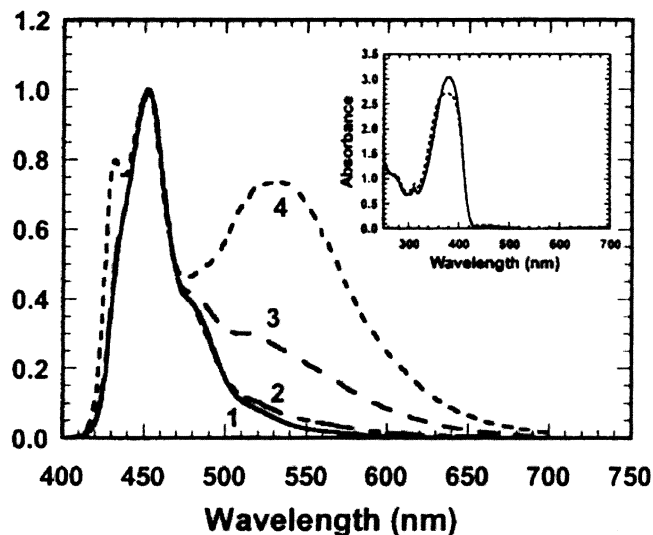
aggregation during annealing.

Figure 6 shows the PL spectra of PDHFP, PDHFD-MOP, PDHFDHOP, and PDHFDDOP films, which are annealed at 200 °C for 3.5 h. Compared with PDHF, PDHFP does not reveal any obvious improvement in spectral stability. A strong additional emission band centered at ~510 nm appears in the PL spectrum after the annealing treatment. Note, however, that the spectral stability can be improved by the attachment of alkoxy groups on the phenylene ring, and longer alkoxy chains result in better spectral stability of the resulting polymers. The additional emission band (centered at ~520 nm) is still pronounced in the spectrum of PDH-FDMOP. In the spectra of PDHFDHOP and PDHFD-DOP, the additional emission band has been characterized as a shoulder. It is also worth noticing that PDHFDMOP, PDHFDHOP, and PDHFDDOP, especially the latter two polymers, exhibit much better thermally spectral stability than both PDHF and PD-OFBSF. There is no measurable spectral change ob-
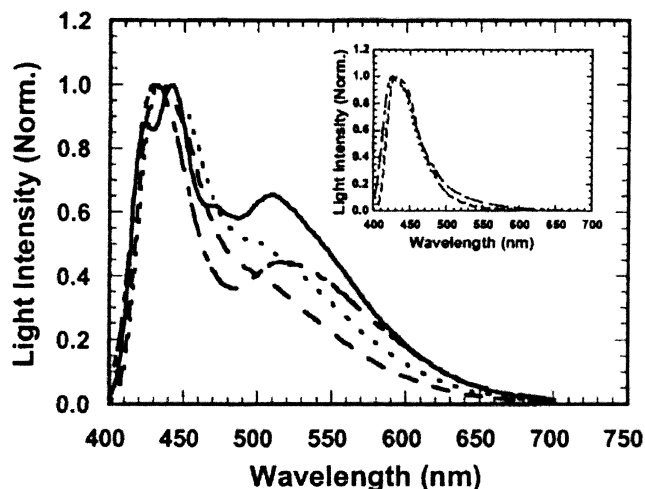
Figure 6. Fluorescence spectra of annealed (200 °C in air for 3.5 h) films of PDHFP (solid line), PDHFDMOP (broken line), PDHFDHOP (dashed line), and PDHFDDOP (dotted line). Inset: fluorescence spectra of PDHFDMOP (broken line), PDHFDHOP (dashed line), and PDHFDDOP (dotted line) films annealed at 150 °C in air for 3.5 h.
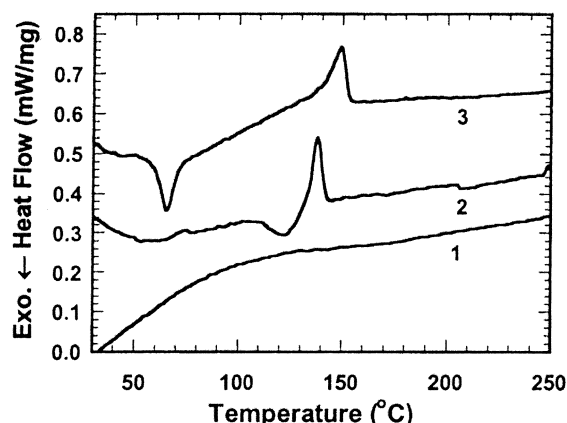

Figure 7. DSC thermograms of PDHFDMOP (1), PDHFD-HOP (2), and PDHFDDOP (3). Heating at 10 °C/min in nitrogen.

served upon the annealing at 150 °C for 3.5 h for all the three polymers (see the inset in Figure 6).

Differential Scanning Calorimetry (DSC) and Crystallization Analysis. The DSC measurements were carried out in nitrogen at a heating rate of 10 °C/min. Before the scans, the polymers were thermally pretreated by equilibrating at 250 °C and then quenching to −50 °C. From the DSC heating scans, the glass transition temperatures (T_g) of PDHF and PDOFBSF were determined to be ~80 and ~105 °C, respectively. In these two polymers, we did not observe any exothermal peak or endothermal peak corresponding to crystallization or melting processes, which are observed in poly(dioctylfluorene).[20]

Both crystallization and melting processes, however, were clearly observed in PDHFDHOP and PDHFDDOP. Figure 7 displays the DSC heating scan traces of PDHFDMOP, PDHFDHOP, and PDHFDDOP. PDHFDMOP (curve 1) shows no phase transition in the heating scan. PDHFDHOP (curve 2) shows, in succession, a glass transition at 74 °C, a crystallization exothermal peak at 123 °C, and a melting endothermal peak at 138 °C. For PDHFDDOP (curve 3), a crystallization exothermal peak appears at 65 °C, and the
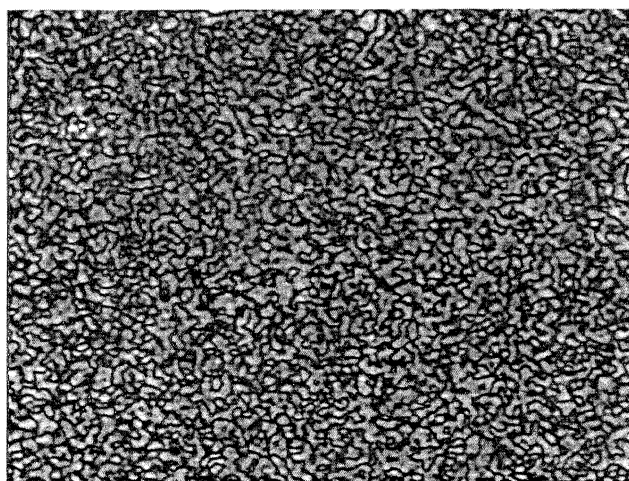
Figure 8. Polarized light microscopy image (magnified 500×) showing characteristic nematic liquid crystalline texture of PDHFDDOP film which was annealed at 200 °C.

melting endothermal peak appears at 148 °C, but the glass transition is not observed.

The only structural difference among PDHFDMOP, PDHFDHOP, and PDHFDDOP is the length of the alkoxy side chains. The DSC results suggest that the crystallization behavior in the polymers is dominated by the alkoxy side chains on the phenylene ring. This suggestion is supported by the following evidence: (1) PDHFDDOP exhibits much lower crystallization temperature (by 58 °C) than PDHFDHOP, while their melting temperatures are close. (2) The enthalpic change of crystallization, as determined by the DSC, in PDHFDDOP (−6.21 J/g) is obviously larger than that in PDHFDHOP (−1.72 J/g), while their melting enthalpic changes are almost the same (~5.3 J/g). The difference in thermal crystallization among the three polymers is also directly observed by polarized light microscopy (PLM). The spin-cast pristine films of all the three polymers are amorphous because of the absence of birefringence under polarized light microscopy, while the annealed (at 200 °C) films of the polymers display different images under polarized light microscopy. PDHFDMOP film is still isotropic without birefringence. A clear birefringence image appears in the annealed film of PDHFDHOP, an indication of the existence of thermotropic liquid crystalline state. In the annealed film of PDHFDDOP, the birefringence image becomes more distinguished. The PLM image of PDHFDDOP is shown in Figure 8. The crystallization of PDHFDHOP and PDHFDDOP was further confirmed by film X-ray diffraction studies. The spin-cast films (on quartz plates) were annealed at 200 °C for 30 min and were then slowly cooled (2−5 °C/min) to room temperature. The films were used for X-ray diffraction measurements. The scans of intensity vs 2θ ($10°−40°$) show clear diffraction peaks at 17.5° for PDHFDHOP and PDHFDDOP but no identifiable diffraction peak for PDHFDMOP. The detailed investigation about liquid crystallization in the polymers is in progress in our lab.

Discussion

The fluorescent wavelength of a polymer film fundamentally depends on the band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which in turn depends on delocalization of π electrons along the

polymer backbone. The structures or multiple peaks in the emission spectrum arise because an excited electron can relax into one of several vibronic energy levels of the HOMO. Because of the coupling to vibronic modes and the variations in polymer chain configuration, the emission spectra of conjugated polymers are typically broad. On the other hand, the optical spectra of conjugated polymers are also heavily affected by the intermolecular interactions, which are dependent on film morphology and/or molecular chain packaging. Spectral features caused by aggregation,[37-40] exciplexes,[25,41] excimers,[22-25,34,42,43] and energy transfer[5,6,44,45] have been demonstrated in conjugated polymers. Excimer emission is often more intensively considered in conjugated polymers because the materials are easy to configure into potential excimer-forming sandwich-type supramolecular structures, which is due to the relatively planar geometries and very strong intermolecular interactions.[25,46]

The improved PL spectrum of PDOFBSF (narrower spectrum and weaker tail extending to longer wavelength direction) compared to that of PDHF may be understood in terms of the weaker intermolecular interaction in PDOFBSF. PDOFBSF and PDHF have the same backbone structure. The identity of their UV−vis absorption spectra (both in solution and in solid state) indicates that the electronic structure of polymer is not changed by the spiro-functionalization. However, the molecular chain packaging may be affected by the spiro-functionalization. The tetrahedral bonding carbon atom at the spiro center maintains a 90° angle between the two connected fluorene moieties via a σ-bonded network. This structural feature minimizes the close packing between molecular chains. In a series of small molecular materials based on 9,9′-spirobifluorene, it was reported that the solid films of the molecular materials could be completely amorphous.[47] Because of the steric hindrance arised from the spiro structure for molecular chain close packaging, the intermolecular interaction between PDOFBSF molecular chains is thus smaller than the one between PDHF molecular chains. The weaker intermolecular interaction in PDOFBSF film is supported by the fact that polymer aggregation may happen in PDHF film upon annealing but does not happen in PDOFBSF film, as demonstrated by UV−vis absorption spectra (insets in Figures 4 and 5).

The importance of side chain in affecting the intermolecular interaction is also reflected in the blue-light-emitting polymers with the poly(fluorene-*alt*-co-phenylene) backbone. The strong vibronic structures, large width, and long tail extended to longer wavelength direction in the PL spectrum of PDHFP imply a strong intermolecular interaction in PDHFP film. The remarkable decrease in the fwhm of PL spectrum and in the emission intensity above 500 nm in going from PDHFP to PDHFDMOP reveals a significant reduction of intermolecular interaction. The steady decrement of fwhm and onset wavelength at the longer wavelength side in PL spectra from PDHFDMOP to PDHFDDOP implies that longer alkoxy side chains more effectively suppress the intermolecular interaction. This could be interpreted by the more effective separation of longer side chains to the molecular chains in all three dimensions, as demonstrated in other conjugated polymers.[35,48] Also, we think that the different crystallization tendency of the polymers should be considered. The side chain crystallization may fix the conjugated backbone between two crystal layers and prevent the close packaging among backbones. A stronger crystallization enhances such a fixation to polymer backbones. A similar conclusion that the formation of crystal can prevent the formation of excimers was obtained for a substituted polythiophene.[35]

Excimer is a kind of excited-state complex formed by the interaction of an excited chromophore with an unexcited chromophore. The basic supramolecular structure of an excimer is a cofacial sandwich-type configuration. An important condition for excimer formation is that the interplanar distance between the cofacially sandwiched chromophores is between 3 and 4 Å.[25,43,46,49] That means excimer formation is a result of short-distance intermolecular interaction and needs a close packaging of polymer chains. Conjugated polymers are generally stiff chain molecules with relatively planar geometries and have very strong intermolecular interactions.[25] Conjugated polymers, therefore, have a great tendency to cofacial chain packaging in solid states through molecular chain diffusion. These analyses could explain why excimer emission is often observed in solid films of conjugated polymers. Molecular chain diffusion may be enhanced at elevated temperatures. This is why excimer emission exhibits temperature dependence. When we consider the temperature dependence of excimer formation, we have to note a very important property of polymer, glass transition temperature T_g. Molecular chains are frozen and are difficult to diffuse at the temperatures below T_g. Above T_g, molecular chains are softened and become easy to diffuse. Our results evidently demonstrate that the excimer emission enhancement by annealing for PDHF and PDOFBSF is T_g-dependent. When the polymer films are annealed below their glass transition temperatures (80 °C for PDHF and 100 °C for PDOFBSF), their excimer emissions do not increase due to heat treatments. While above their glass transition temperatures, annealing enhances their excimer emissions, and the enhancement becomes more pronounced with increasing annealing temperature. A similar T_g-dependent molecular chain packaging and the subsequent effect on luminescent efficiency were also recently reported for poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEH−PPV) film.[50] The improvement of PDOFBSF over PDHF in thermally spectral stability is thus attributed to the higher T_g of PDOFBSF.

The comparison of absorption spectra before and after annealing for PDHF and PDOFBSF reveals that the spiro-functionalization can prevent the aggregation of polymer chains at ground state. However, the excimer formation or the exciplex formation at excited state is not prevented by the spiro-functionalization. Strong excimer emission is still observed in PDOFBSF film upon annealing above the temperature of T_g, just like what is observed in PDHF film. We proposed that this phenomenon is associated with the structural feature of polyfluorene. The backbone of polyfluorene may be in an all-planar or 2_1 helical conformation, which is structurally very similar to ladder-type poly(*p*-phenylenes) (LPPPs) in which the planarity of the backbone is chemically fixed.[38] Note that LPPPs always exhibit low-energy emission bands apart from their main emission bands.[10,11,37,51] The additional low-energy emission bands are attributed to the aggregate states formed by subunits of different polymer chains. We assume that the relatively high planarity of polyfluorene backbone
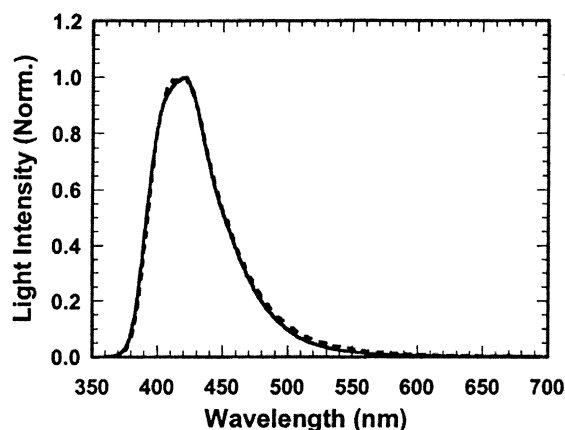
Figure 9. Fluorescence spectra of CN-PPP as spin-cast film (solid line) and as annealed (200 °C in air for 3.5 h) film.

favors the formation of aggregate states between subunits. In contrary, in side-chain-substituted poly(*p*-phenylenes) (PPPs), the neighboring phenylene rings are heavily rotated with a twist angle of up to 45°.[52] Such a poor-planar structural feature minimizes the possibility of forming subunit aggregates with cofacial configuration. In fact, there is little report about the excimer emission or any other aggregate-related spectral phenomena for PPPs. We also measured the thermally spectral stability of poly[2-(6′-cyano-6′-methylheptyloxy)-1,4-phenylene)] (CN-PPP), an efficient blue PL and EL PPP derivative material.[9] As we can see in Figure 9, CN-PPP indeed does not exhibit additional low-energy emission even being annealed at 200 °C. We thus proposed a backbone structural modification for polyfluorene with substituted phenylene units.

The structural modification for polyfluorene by alternatively inserting 2,5-dialkoxyl-substituted phenylene units maintains the emission of the resulting polymers still in the blue region. Our experimental results demonstrate a remarkable improvement of thermally spectral stability of the modified polymers (PDHFDMOP, PDHFDHOP, and PDHFDDOP) compared to both PDHF and PDOFBSF. The annealing at 150 °C (3.5 h) does not induce measurable additional emission band for all the three modified polymers. Although we did not get the T_g of PDHFDMOP, both the T_g and the melting temperature of PDHFDHOP were evidently determined. The annealing temperature of 150 °C is much higher than the T_g (74 °C) of PDHFDHOP and is even over the melting temperature (138 °C) of the polymer. We can certainly conclude that the formation of cofacial aggregates between subunits by the diffusion of softened polymer chains is prevented effectively in the modified polymer. When the films of PDHFDHOP and PDHFDDOP were annealed at around their melting temperatures for a long time, or the annealing temperature is higher than the melting temperatures, the additional low-energy emission bands were observed in their PL spectra. Therefore, the formation of cofacial aggregates of subunits is still possible when the polymers are in melted states. According to Figure 6, it seems that longer side chains on the phenylene ring could reduce the aggregation. This may be due to the higher entropy of the polymers with longer side chains at melted states as well as the more effective separation of the longer side chains to the backbones.

Another interesting point is the relationship between crystallization and excimer emission in the modified

polymers (PDHFDMOP, PDHFDHOP, and PDHFD-DOP). In a series of poly(9,9-dialkylfluorenes) with different length of the linear alkyl chains, it is reported that the polymer with the greatest liquid crystalline order produces the greatest excited-state interchain communication or excimer emission.[53] In our experiments, however, the same tendency was not observed. On the contrary, PDHFDMOP, a polymer without crystallization, shows a strongest tendency in forming excimer, while PDHFDHOP and PDHFDDOP, which easily form crystalline states, exhibit better thermally spectral stability than PDHFDMOP. This may be due to the poor planar configuration in these polymers and the enhancement of longer side chains for separating backbones, even at the circumstance of forming crystals.

Conclusions

Spiro-functionalization to poly(9,9-dialkylfluorenes) may narrow down the emission spectrum and reduce the emission spectral tail extended to longer wavelength direction. The improvement of the emission spectral quality is attributed to less molecular close packaging caused by the steric hindrance of the spiro-structure. The spiro-functionalization also improves the thermally spectral stability of the polymers. A T_g dependence for the excimer formation is demonstrated for both the normal polyfluorene polymer (PDHF) and the spiro-functionalized polyfluorene polymer (PDOFBSF). The improvement of thermally spectral stability of PD-OFBSF compared to PDHF is thus attributed to the higher T_g of PDOFBSF. Because of the relatively high planarity of polyfluorene backbone, PDOFBSF also exhibit pronounced excimer emission upon annealing at the temperatures above its T_g.

Backbone structural modification for poly(9,9-dialkylfluorenes) by alternatively inserting substituted phenylene units provides another opportunity to improve the emission spectral quality of fluorene-based blue-light-emitting polymers and to suppress the excimer formation in the polymers. Both the electronic structures and the intermolecular interactions of the modified polymers are dependent on the substituents on the phenylene rings. Blue light emissions, which spectra are close to those of PDHF and PDOFBSF, with improved emission spectral quality (narrower spectra and dramatically reduced tail) are demonstrated with the substituents of alkoxy chains. The polymers show much better thermally spectral stability than PDHF and PDOFBSF, and longer side chains on the phenylene rings can enhance the spectral stability. We attribute the improved spectral stability to the relatively low planarity of the repeat units of the polymers. Relatively low planarity of repeat unit does not favor the formation of close subunit packaging with cofacial sandwich-type configuration, which is necessary for excimer formation. Interestingly, PDHFDHOP and PDHFDDOP easily form thermotropic liquid crystalline states.

References and Notes

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. B.; Marks, R. N.; Mackay, K.; Friend, R. H.; Bum, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539.

(2) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature (London)* **1992**, *357*, 477.

(3) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature (London)* **1999**, *397*, 121.

(4) Heeger, J. H. *Solid State Commun.* **1998**, *107*, 673.
(5) McGehee, M. D.; Bergstedt, T.; Zhang, C.; Saab, A. P.; O'Regan, M. B.; Bazan, G. C.; Srdanov, V. I.; Heeger, A. J. *Adv. Mater.* **1999**, *11*, 1349.
(6) Virgi1i, T.; Lidzey, D. G.; Bradley, D. D. C. *Adv. Mater.* **2000**, *12*, 58.
(7) Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36.
(8) Vahlenkamp, T.; Wegner, G. *Macromol. Chem. Phys.* **1994**, *19*, 1933.
(9) Yang, Y.; Pei, Q.; Heeger, A. J. *J. Appl. Phys.* **1996**, *79*, 934.
(10) Chmli, K.; Scherf, U. *Makromol. Chem. Rapid Commun.* **1993**, *14*, 217.
(11) Tasch, S.; Niko, A.; Leising, G.; Scherf, U. *Appl. Phys. Lett.* **1996**, *68*, 1090.
(12) Fukuda, M.; Sawada, K.; Yoshino, K. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2465.
(13) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys., Part 2* **1991**, *30*, L1941.
(14) Fukuda, M.; Sawada, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1989**, *28*, L1433.
(15) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416.
(16) Grice, A. W.; Bradley, D. D. C.; Bemius, M. T.; Inbasekaran, M.; Wu, W. W.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 629.
(17) Janietz, S.; Bradley, D. D. C.; Grell, M.; Giebeler, C.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 2453.
(18) (a) Redecker, M.; Bradley, D. D. C.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 1565. (b) **1999**, *74*, 1400.
(19) Kim, J. S.; Friend, R. H.; Cacialli, F. *Appl. Phys. Lett.* **1999**, *74*, 3084.
(20) Grell, M.; Bradley, D. D. C.; Inbasekaran, M.; Woo, E. P. *Adv. Mater.* **1997**, *9*, 798.
(21) Grell, M.; Knoll, W.; Lupo, D.; Meisel, A.; Miteva, T.; Neher, D.; Nothofer, H.-G.; Scherf, U.; Yasuda, A. *Adv. Mater.* **1999**, *11*, 671.
(22) Kreyenschmidt, M.; Klaemer, G.; Fuhrer, T.; Ashenhurst, J.; Karg, S.; Chen, W. D.; Lee, V. Y.; Scott, J. C.; Miller, R. D. *Macromolecules* **1998**, *31*, 1099.
(23) Bliznyuk, V. N.; Carter, S. A.; Scott, J. C.; Klärmer, G.; Miller, R. D.; Miller, D. C. *Macromolecules* **1999**, *32*, 361.
(24) Lee, J.-I.; Klamer, G.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1083.
(25) Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 765.
(26) Sainova, D.; Miteva, T.; Nothofer, H. G.; Scherf, U.; Glowacki, I.; Ulanski, J.; Fujikawa, H.; Neher, D. *Appl. Phys. Lett.* **2000**, *76*, 1810.
(27) Klärmer, G.; Davey, M. H.; Chen, W. D.; Scott, J. C.; Miller, R. D. *Adv. Mater.* **1998**, *10*, 993.
(28) Klärmer, G.; Davey, M. H.; Lee, J.-I.; Miller, R. D. *Adv. Mater.* **1999**, *11*, 115.
(29) Klärmer, G.; Lee, J.-I.; Lee, V. Y.; Chan, E.; Chen, J.-P.; Nelson, A.; Markiewicz, D.; Siemens, R.; Scott, J. C.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1800.
(30) Yu, W.-L.; Pei, J.; Huang, W.; Heeger, A. J. *Adv. Mater.* **2000**, *12*, 828.
(31) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 946.
(32) Marsitzky, D.; Vestberg, R.; Blainey, P.; Tang, B. T.; Hawker, C. J.; Carter, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 6965.
(33) Weinfurtner, K.-H.; Fujikawa, H.; Tokito, S.; Taga, Y. *Appl. Phys. Lett.* **2000**, *76*, 2502.
(34) List, E. J. W.; Guentner, R.; Freitas, P. S.; Scherf, U. *Adv. Mater.* **2002**, *14*, 374.
(35) (a) Andersson, M. R.; Thomas, O.; Mammo, W.; Svensson, M.; Theander, M.; Inganäs, O. *J. Mater. Chem.* **1999**, *9*, 1933. (b) Theander, M.; Inganäs, O.; Mammo, W.; Olinga, T.; Svensson, M.; Andersson, M. R. *J. Phys. Chem. B* **1999**, *103*, 7771.
(36) Yu, W.-L.; Pei, J.; Cao, Y.; Huang, W.; Heeger, A. J. *Chem. Commun.* **1999**, 1837.
(37) Lemmer, U.; Heun, S.; Mahrt, R. F.; Scherf, U.; Hopmeier, M.; Siegner, U.; Göbel, E. O.; Müllen, K.; Bässler, H. *Chem. Phys. Lett.* **1995**, *240*, 373.
(38) Grell, M.; Bradley, D. D. C.; Ungar, G.; Hill, J.; Whitehead, K. S. *Macromolecules* **1999**, *32*, 5810.
(39) Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Bunz, H. F. *Macromolecules* **1998**, *31*, 8655.
(40) Pschirer, N. G.; Bunz, H. F. *Macromolecules* **2000**, *33*, 3961.
(41) Osaheni, J. A.; Jenekhe, S. A. *Macromolecules* **1994**, *27*, 739.
(42) Samuel, I. D. W.; Rumbles, G.; Collison, C. J. *Phys. Rev. B* **1995**, *52*, Rl1573.
(43) Jenekhe, S. A. *Adv. Mater.* **1995**, *7*, 309.
(44) Gupta, R.; Stevenson, M.; Dogariu, A.; McGehee, M. D.; Park, J Y.; Srdanov, V.; Heeger, A. J.; Wang, H. *Appl. Phys. Lett.* **1998**, *73*, 3492.
(45) Dogariu, A.; Gupta, R.; Heeger, A. J.; Wang, H. *Synth. Met.* **1999**, *100*, 95.
(46) Conwell, E. *TRlP* **1997**, *5*, 218.
(47) Salbeck, J.; Yu, N.; Bauer, J.; Weissörtel, F.; Bestgen, H. *Synth. Met.* **1997**, *91*, 209.
(48) Andesson, M. R.; Yu, G.; Heeger, A. J. *Synth. Met.* **1997**, *85*, 1275.
(49) Winnik, M. A In *Photophysics of Polymers;* Hoyle, C. E., Torkelson, J. M., Eds.; *ACS Symp. Ser.* **1987**, *358*, 8.
(50) Lee, T.-W.; Park, O. O. *Adv. Mater.* **2000**, *12*, 801.
(51) Tasch, S.; Kranzelbinder, G.; Leising, G.; Scherf, U. *Phys. Rev. B* **1997**, *55*, 5079.
(52) Pasco, S. T.; Baker, G. L. *Synth. Met.* **1997**, *84*, 275.
(53) Teetsov, J.; Fox, M. A. *J. Mater. Chem.* **1999**, *9*, 2117.

MA020241M