JOURNAL OF Materials CHEMISTRY

Photoluminescence study on exciton migration and trapping in a copolymer based on poly(fluorene)

Jeong-Ik Lee,[a] Taehyoung Zyung,[a] Robert D. Miller,[b] Yong Hee Kim,[c] Sae Chae Jeoung[c] and Dongho Kim[c]

[a]*Basic Research Lab., Electronics and Telecommunications Research Institute, Taejon 305-350, Korea. E-mail: jiklee@etri.re.kr*
[b]*IBM Almaden Research Center, San Jose, CA, 95120, USA*
[c]*National Creative Research Initiatives Center for Ultrafast Optical Characteristics Control and Spectroscopy Lab., Korea Research Institute of Standards & Science, Taejon 305-600, Korea*

Received 14th January 2000, Accepted 5th April 2000
Published on the Web 30th May 2000

Steady-state and time-resolved photoluminescence spectra of poly[9,9-bis(2′-ethylhexyl)fluorene-2,7-diyl] and a copolymer of poly[9,9-bis(2′-ethylhexyl)fluorene-2,7-diyl-*co*-α-cyanostilbene-4,4′-diyl] were investigated. In THF, the copolymer exhibits the characteristic blue emission band of the homopolymer together with another emission band arising from chromophoric segments containing comonomer units. A total suppression of the homopolymer emission band in copolymer thin film demonstrates the efficient exciton migration and trapping into the segments containing comonomer units. Exciton migration and trapping in copolymer thin film gives rise to a red-shift in photoluminescence as compared with the homopolymer. Time-resolved photoluminescence results are also consistent with the facile exciton migration from fluorene polymer units to trapping sites composed of cyanostilbene comonomer units. The exciton trapping processes result in a red-shift in the emission spectrum with enhanced color stability in the copolymer relative to the homopolymer.

Introduction

Conjugated polymers have attracted much research interest in the past few decades as electroactive materials for diverse applications such as batteries, molecular electronic devices, and light emitting diodes (LEDs), *etc.*[1–5] Electroluminescence has proven to be an especially promising application in polymeric LEDs of semiconducting polymers.[3–5] Poly(alkylfluorene)s are promising new materials for applications such as light emitting diodes because of their high photoluminescence (PL) quantum efficiencies and thermal stability.[6–11] The fluorene moiety provides a rigidly planarized biphenyl structure within the polymer backbone as well as the possibility of remote functionalization at the C-9 position. The substitution at C-9 offers the prospect of improved polymer processing and mediating potential interchain interactions in films.[12–14]

We have recently discussed the troublesome excimer formation in polymer films of poly(di-*n*-hexylfluorene) (DHF) and various copolymers upon annealing or with the passage of current.[11,15,16] As part of a continuing effort to suppress this excimer emission, we have described the synthesis of poly(di-*n*-hexylfluorene-*co*-anthracene)s.[15,16] The high molecular weight ($M_n > 30\,000$) anthracene-containing copolymers exhibit excellent photoluminescence color stability even upon annealing at 200 °C for three days under N_2. Stable blue light emission has also been observed from light emitting devices employing this copolymer. It is quite remarkable that relatively small amounts of anthracene comonomer linked into the poly(fluorene) main chain *via* the 9,10-positions suppresses completely the excimer formation. One possible explanation is that the strongly twisted anthracene substituents in the polymer backbone prevent the interchain interactions in films.

However, in a poly(di-*n*-hexylfluorene-*co*-anthracene) 85 : 15 statistical copolymer, the concentration of anthracene units is rather dilute; on average there is one anthracene unit for every seven fluorene units. Another possible explanation for the observed color stability is that the emission actually emanates from quasi-electronically isolated anthracene segments populated by a rapid energy transfer. The rapid, efficient exciton migration and trapping could prevent the formation of a main chain excimer by funneling and trapping the excitons into dilute chromophoric sites. The substantial overlap of the anthracene and poly(fluorene) absorption and emission complicates the spectral characterization of the corresponding copolymers. Recently, however, we demonstrated exciton migration and trapping in copolymers containing low band gap comonomers,[17,18] in support of the latter explanation for the emission stability in poly(di-*n*-hexylfluorene-*co*-anthracene). The emission spectra of these copolymers were unchanged upon thermal annealing and upon incorporation into light emitting devices. It seems likely that the exciton migration and trapping play an important role in providing color stability and spectral tuning of light emitting diodes.

In this work, we have further investigated exciton migration and trapping in a copolymer containing a low band gap comonomer, poly[9,9-bis(2′-ethylhexyl)fluorene-2,7-diyl-*co*-α-cyanostilbene-4,4′-diyl] using steady-state and time-resolved photoluminescence techniques. Especially, the time-resolved photoluminescence provided us with an in-depth understanding of the exciton migration and trapping processes in this conjugated copolymer.

Experimental

High molecular weight, readily soluble homopolymer and copolymer derived from 2,7-dibromo-9,9-bis(2′-ethylhexyl)-fluorene and 4,4′-dibromo-α-cyanostilbene were prepared using zero valent nickel.[11,15] The structures of the polymers synthesized are shown in Fig. 1. The monomers were prepared according to literature methods.[19,20] Thin films of polymers were obtained by spin-coating from polymer solutions in 1,1,2,2-tetrachloroethane on fused quartz plates. All the photophysical measurements were performed at room tem-

DOI: 10.1039/b000379o

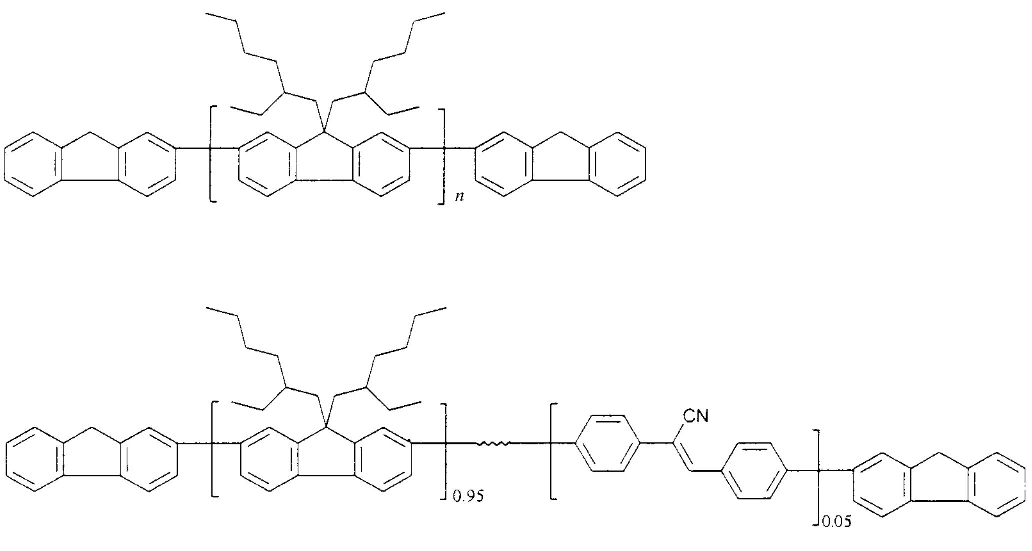

Fig. 1 Structures of BEHF homopolymer and BEHF/CNSt copolymer.

perature. The absorption spectra were measured by a Hewlett Packard diode array spectrophotometer model 8452A. Steady-state photoluminescence spectra were recorded on a Spex FL3-11.

The picosecond time-resolved fluorescence experiments were carried out by using the time-correlated single-photon counting (TCSPC) method. The excitation pulses at 400 nm were obtained from a femtosecond Ti : sapphire laser (Coherent, MIRA) with an average power of 600 mW at 800 nm. The pump pulses at desired wavelength were generated by frequency doubling with a β-BBO crystal. The emission was collected at a 45-degree angle with respect to the excitation laser beam by 5- and 25 cm focal length lenses, focused onto a monochromator (Jobin-Yvon HR320), and detected with a microchannel plate photomultiplier tube (Hamamatsu R2809U). The signal was amplified by a wideband amplifier (Philip Scientific), sent to a Quad constant fraction discriminator (Tennelec), a time-to-amplitude converter (Tennelec), a counter (Ortec), and a multichannel analyzer (Tennelec/Nucleus), and stored in a computer.

Results and discussion

The homopolymer, poly[9,9-bis(2′-ethylhexyl)fluorene-2,7-diyl] (BEHF) and the statistically random copolymer, poly[9,9-bis(2′-ethylhexyl)fluorene-2,7-diyl-*co*-α-cyanostilbene-4,4′-diyl] (BEHF/CNSt) were prepared by Ni(0) mediated polymerization as described previously.[11] The branched 2-ethylhexyl substituents were employed to improve the solubility of the resulting copolymer, and the comonomer ratio in the copolymer was 95 : 5 (BEHF : CNSt). The end-capping reagent, 2-bromofluorene, was added at the end of polymerization in order to remove bromine end groups which could lead to stability problems in LED applications (Fig. 1). The number average molecular weight (M_n) and polydispersity index (PDI) of the prepared polymers were 67 000 and 2.3 for BEHF homopolymer and 38 000 and 3.0 for BEHF/CNSt copolymer, respectively. Both polymers were readily soluble in various organic solvents such as chloroform, xylene, methylene chloride, THF, *etc.* The detailed structural analyses of these materials have been reported.[17,18]

Figs. 2 and 3 display the absorption and emission spectra of BEHF/CNSt copolymer and BEHF homopolymer both in THF solution and as thin films. In the absorption spectrum of the BEHF/CNSt copolymer, a slight red-shift in absorption edge was observed as compared with BEHF homopolymer while the absorption maximum was slightly blue-shifted. However, the incorporation of the CNSt comonomer strongly affects the photoluminescence of the copolymer. For the copolymer in THF, two characteristic emission bands were observed as shown in Fig. 2. The high-energy deep blue

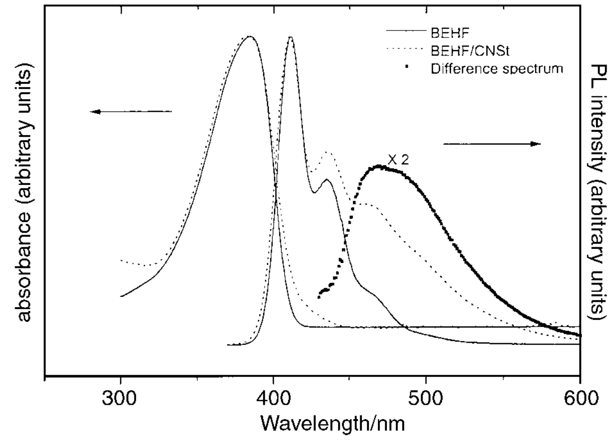

Fig. 2 Absorption and photoluminescence spectra of BEHF homopolymer and BEHF/CNSt copolymer in THF solutions. All PL spectra were recorded with an excitation at 370 nm. The square symbols show the difference spectrum of BEHF homopolymer and BEHF/CNSt copolymer emission spectra.

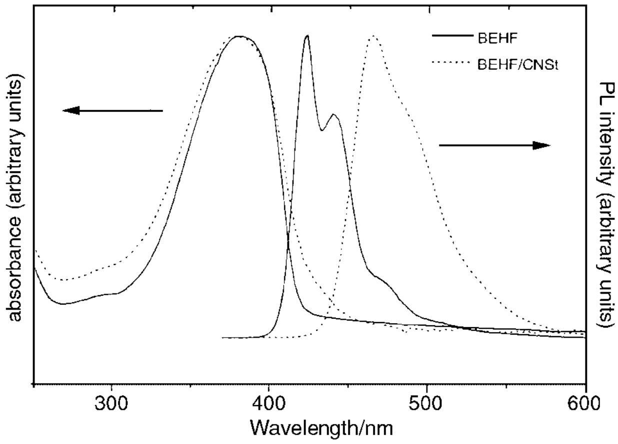

Fig. 3 Absorption and photoluminescence spectra of BEHF homopolymer and BEHF/CNSt copolymer films. All PL spectra were recorded with an excitation at 370 nm.

emission band is considered to be the emission from the isolated fluorenyl chromophoric segments as observed in the PL spectrum of the homopolymer. An additional low-energy emission band appeared in the normalized difference emission spectrum of the homopolymer and the copolymer. The emission maximum in the difference spectrum appears around 470 nm, and seems to arise from the CNSt comonomer units.

In the copolymer film, the emission spectra became dramatically different from that in THF solution. As shown in Fig. 3, the characteristic blue emission from the isolated homopolymer chains disappears in the copolymer film. Instead, BEHF 95/CNSt 5 copolymer film exhibits a single, broad emission band centered at ≈470 nm, which is similar in position and shape to the additional band observed in the solution emission spectrum. The fact that the homopolymer shows similar PL spectra in THF solution and film, implies that the solvent does not affect the PL spectra. Therefore, the lack of blue emission in BEHF 95/CNSt 5 copolymer film suggests a facile exciton migration and trapping process. The excitons produced in BEHF units by direct photoexcitation are likely to migrate readily to the lower energy trapping sites containing CNSt comonomer where emission occurs. It should be noted that in dilute solution only intrachain exciton migration and trapping occurs because of the separation between chains. In the case of the copolymer film, however, a total suppression of the blue emission associated with the BEHF chains demonstrates that the exciton migration and trapping process is more efficient involving both interchain and intrachain interactions. It is quite remarkable that only 5% of CNSt comonomer in the copolymer leads to a complete change in the emission spectrum of the thin film.

In order to study the exciton migration and trapping processes in the copolymer film, we have employed the time-resolved photoluminescence technique to obtain information on the temporal behavior. Figs. 4(a) and (b) show the PL decay profiles of the homopolymer and the copolymer in THF after photoexcitation at ≈400 nm. The homopolymer provides almost the same decay profiles regardless of the monitoring wavelength with lifetimes of about 470 ps. In contrast, in solution the PL decay profile of the copolymer exhibits a wavelength dependence. The PL decay profile monitored at 410 nm with a lifetime of ≈430 ps is similar to that of the homopolymer, implying that these two emissions each originate from the same species. The slightly faster PL decay at 410 nm (≈10%) in the copolymer solution as compared with the homopolymer can be explained in terms of competitive intrachain exciton migration to trapping sites, although this process seems to be not so efficient. As the monitoring wavelength is shifted to the red, the emission arising from the CNSt comonomer containing units becomes dominant. Thus, the slower PL decay observed at longer wavelengths is due to the emission from the CNSt containing units which is longer lived than the emission from the homopolymer (Fig. 4(b)). The measured PL decay at 510 nm was ≈640 ps, a value significantly longer than that observed at 410 nm (≈430 ps).

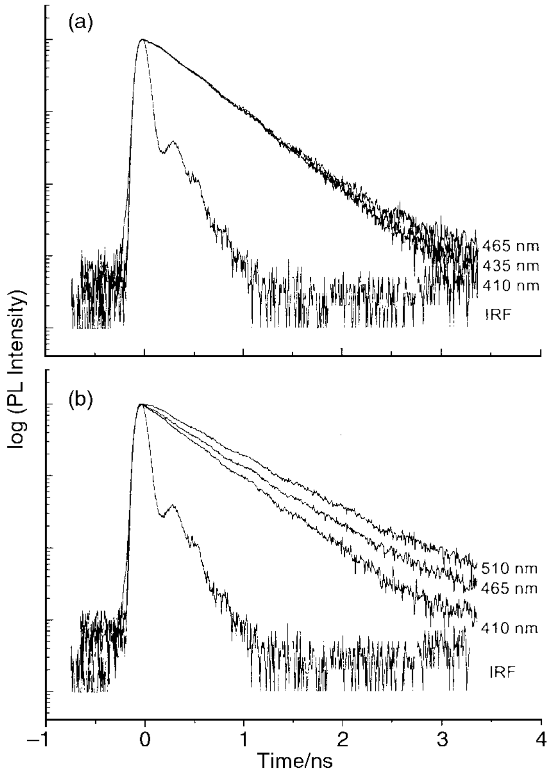

Fig. 4 Time-resolved PL decay profiles of (a) BEHF homopolymer and (b) BEHF/CNSt copolymer in THF solutions observed at various wavelengths. The instrumental response function (IRF) of TCSPC is shown in the short time region.

Figs. 5(a) and (b) display the PL decay profiles of the homopolymer and the copolymer in thin films upon photoexcitation at ≈400 nm. The PL temporal profiles in the homopolymer exhibit much faster and nonexponential decay as compared with the THF solution with an average lifetime of ≈200 ps at 425 nm. In general, π-conjugated polymers exhibit faster PL decay in films than in solution because of various fast nonradiative decay processes such as exciton trapping by defect sites *via* enhanced interchain interactions.[21] The wavelength dependence on PL decay profiles can be accounted for by the random walk of excitations within the DOS (Density of States Distribution).[21–23] This inhomogeneity leads to either fluorescence spectral changes as a function of delay time or increased

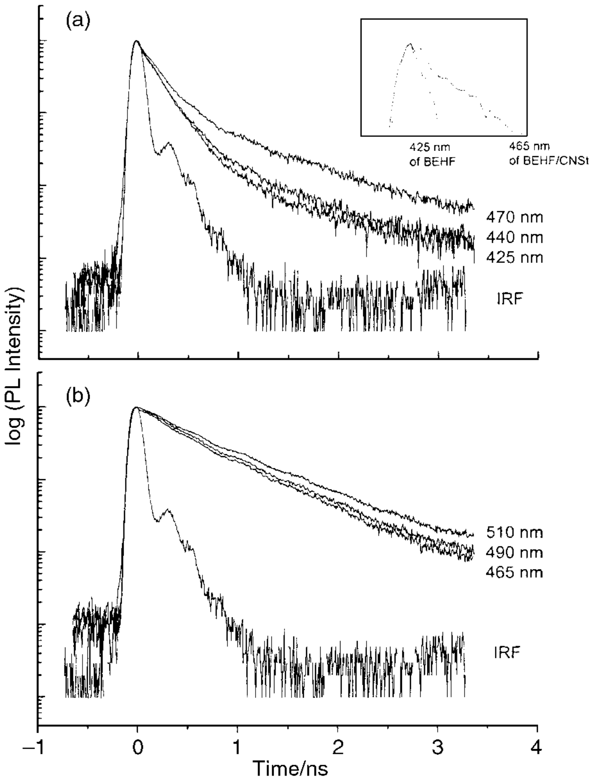

Fig. 5 Time-resolved PL decay profiles of (a) BEHF homopolymer and (b) BEHF/CNSt copolymer films observed at various wavelengths. The instrumental response function (IRF) of TCSPC is shown in the short time region. The inset in (a) shows PL decay profiles of BEHF and BEHF/CNSt observed at 425 and 465 nm, respectively. There is no noticeable rise for the decay profile of BEHF/CNSt copolymer, which reveals that the exciton trapping process is too fast to detect in our measurement limit.

fluorescence decay lifetimes at lower energies. Considering that there is no wavelength dependence on PL decay profiles in homopolymer solution (Fig. 4(a)), the spectral diffusion should occur mainly through interchain interactions.

On the other hand, the PL decay profiles in the copolymer film did not show a significant decrease in lifetimes as compared with the THF solution (Figs. 4(b) and 5(b)). The PL decay time in the copolymer film is approximately 600 ps. These results indicate that the fast exciton migration to and trapping by CNSt comonomer units in the copolymer film inhibits other nonradiative decay pathways, which reduce PL lifetimes in the homopolymer film. The inset in Fig. 5(a) shows the PL decay profiles of the homopolymer and the copolymer films observed at 425 and 465 nm for comparison. There is no rise component at the early stage of the copolymer PL decay, which implies that there is an ultrafast exciton migration and trapping process in the copolymer film which is beyond our measurement limit.

We have summarized our findings in Fig. 6 by presenting a schematic potential energy diagram for energy relaxation process in the photoexcited copolymer film. Upon photoexcitation of the copolymer, the excited species should relax to BEHF exciton state which emits blue emission (PL1) in the homopolymer. Although there might be excitons formed from the CNSt comonomer units in the copolymer by direct excitation, their population should be negligible because of the low chromophore concentrations. We can also exclude the possibility of direct exciton trapping from the first excited species after photoexcitation to CNSt comonomer units because this process can happen in both solution and in the film leading to similar PL spectra. Instead generated BEHF excitons apparently migrate and are trapped by CNSt comonomer segments, which emit the red-shifted PL2 emission in Fig. 6. This process is fast enough to suppress the characteristic blue emission of the homopolymer (PL1). Ultrafast spectroscopic studies, therefore, might be needed to understand this migration and trapping process in detail. The film studies in comparison with those in solution suggest that the excited species migrate efficiently through interchain interactions rather than intrachain ones. The trapped excitons decay through radiative recombination and then exhibit a red-shifted emission (PL2) in comparison to the emission of the homopolymer.

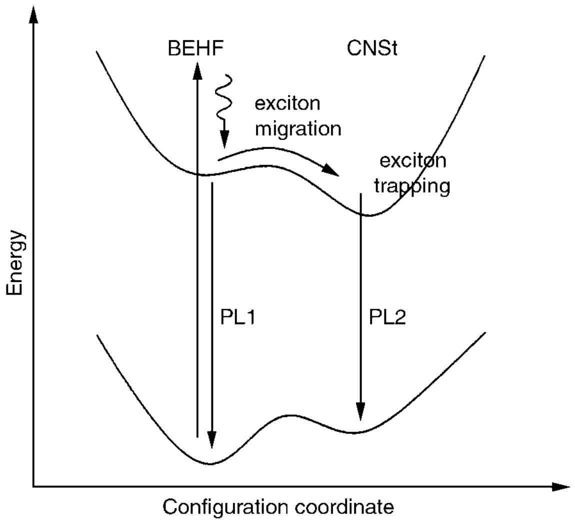

Fig. 6 Schematic potential energy diagram for energy relaxation in photoexcited BEHF/CNSt copolymer film. The excitation wavelength was 370 nm. The trapped excitons at CNSt comonomer units emit PL2, while the isolated BEHF units emit PL1.

In summary, we observed that the fast exciton trapping leads to a red-shift in emission and improved color stability in the copolymer containing CNSt comonomer compared with the polyfluorene homopolymer. The exciton migration and trapping to trapping sites occurs mainly through interchain interactions rather than intrachain ones. The significant interchain interactions in polymer films are important in understanding the exciton dynamics in conjugated polymers. Fast exciton migration and trapping in the copolymer eliminates excimer formation which is ubiquitous in polyfluorene homopolymers. Such processes lead to enhanced performance in LED devices.

Acknowledgements

J.-I. Lee acknowledges support from the Korea Science and Engineering Foundation (KOSEF). R. D. Miller gratefully acknowledges partial support from the NSF Center for Polymeric Interfaces and Macromolecular Assemblies (CPIMA) under cooperative agreement DMR-9400354. The work at KRISS was supported by the National Creative Research Initiatives Program of the Ministry of Science and Technology (MOST) of Korea.

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