Thermally Stable Blue-Light-Emitting Copolymers of Poly(alkylfluorene)

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ABSTRACT: We have prepared a variety of high molecular weight, thermally stable, blue-light-emitting random copolymers of 9,9-di-*n*-hexylfluorene by nickel(0)-mediated polymerization. The copolymers are readily soluble and easily processable from organic solvents. Both the polymer and electronic properties may be tuned by selection of comonomer structure. The electronic properties also vary with composition and film morphology. A blue-light-emitting device has been prepared using ionic salts for electrochemical doping.

Introduction

The earlier work of Partridge[1] and a more recent report by Burroughes et al.[2] have rekindled significant interest in electroluminescent polymers. Polymers offer considerable processing advantages over small molecule systems,[3] particularly for large area applications, since polymer films can be generated by solution deposition techniques and, in general, have higher glass transition temperatures. While electroluminescent organic polymers provide device processing advantages, a major drawback has been operating stability. Recently, however, significant advances have also been realized in this area.[3,4]

Efficient, stable blue-light-emitting materials are needed both to complete the luminescence color spectrum and to serve as energy-transfer donors when used in conjunction with added fluorophores.[5−7] For blue-light emitters, a number of nonconjugated excimers[8−10] as well as conjugated polymer exciplexes[11,12] have also been described, often used in multilayer configurations. The former may be employed either alone or in conjunction with molecular dopants designed to modify both the charge transport and luminescence properties. The development of efficient blue-light-emitting conjugated organic polymers has been hampered because of the normally small band gaps of many fully conjugated polymers. For this reason, poly(*p*-phenylene) (PPP)[13,14] is of interest since ring twisting caused by steric interactions limits the intrinsic conjugation length.[15] The insolubility of the parent polymer, however, causes processing difficulties, and polymeric precursors are often employed.[14,16] The use of bulky substituents in the main chain improves solubility[17,18] but exacerbates the twisting in the main chain, further limiting the conjugation lengths. Recently ladder and stepladder polymeric variants have been studied in an effort to mediate the chain twisting.[19−22] Alternatively, conjugation-interrupting substituents may be employed to limit the effective conjugation lengths in the polymer backbone. Blue-light-emitting poly(*p*-phenylenevinylenes),[23−26] poly(oxadiazoles),[27] and others[28] have been prepared using this technique.

Polymeric derivatives of fluorene present an interesting approach to blue-light-emitting polymers. The facile functionalization at C-9 offers the prospect of controlling both polymer solubility and potential interchain interactions in films.[29−31] These materials contain a rigidly planarized biphenyl structure in the fluorene monomer unit, while the remote substitution at C-9 produces less steric interaction in the conjugated backbone itself. The latter can lead to significant twisting in PPP derivatives, since the substituents used to control solubility are ortho to the aryl chain linkage, as is the case for the monocyclic monomers.[17,18]

Experimental Section

The key starting material, 2,7-dibromo-9,9-di-*n*-hexylfluorene (Br2DHF), was prepared by bromination of 9,9-di-*n*-hexylfluorene using excess bromine in dimethylformamide in the presence of 5% Pd/C. The crude product was purified by chromatography over silica gel followed by recrystallization from petroleum ether−acetone−methanol (90%, mp 156−57 °C). The comonomer dibromides Br2DPF (mp 73 °C) and Br2−6F (mp 82 °C) were prepared from the corresponding commercially available diamines by diazotization (HBr−$NaNO_2$) in the presence of Cu_2Br_2. The other bromides shown in Figure 1 were prepared by literature procedures.[32] The homopolymer poly(9,9-di-*n*-hexylfluorene-2,7-diyl) and the random copolymers[33] were prepared by nickel-mediated coupling of the respective bromides as described by Yamamoto et al.[34] A Schlenk tube containing DMF, bis(1,5-cyclooctadienyl)nickel(0), 2,2′-bipyridyl, and 1,5-cyclooctadiene (molar ratios, 1:1:1) was heated under argon to 80 °C for 0.5 h. The comonomers dissolved in minimal, degassed toluene (molar ratio of dibromide/nickel complex = 0.65) were added under argon to the DMF solution and the polymerization was maintained at 80 °C for 2−3 days in the dark. The polymers were precipitated by addition of the hot solution dropwise to a equivolume mixture of concentrated HCl, methanol, and acetone. The isolated polymers were then dissolved in toluene or methylene chloride and reprecipitated with methanol−acetone (1:1). This procedure was repeated several times, and the copolymers were dried at 80 °C (in a vacuum).

Results and Discussion

The oxidative polymerization of fluorene itself as well as simple 9-alkyl-substituted derivatives has been reported.[35,36] The polymers produced by this technique are of low molecular weight (DP ∼10),[36] and it is difficult to remove all traces of the oxidant. Despite this, blue-light-emitting devices from these polymers have been described.[37] We now describe the preparation of high molecular weight polymers from 2,7-dibromo-9,9-di-*n*-

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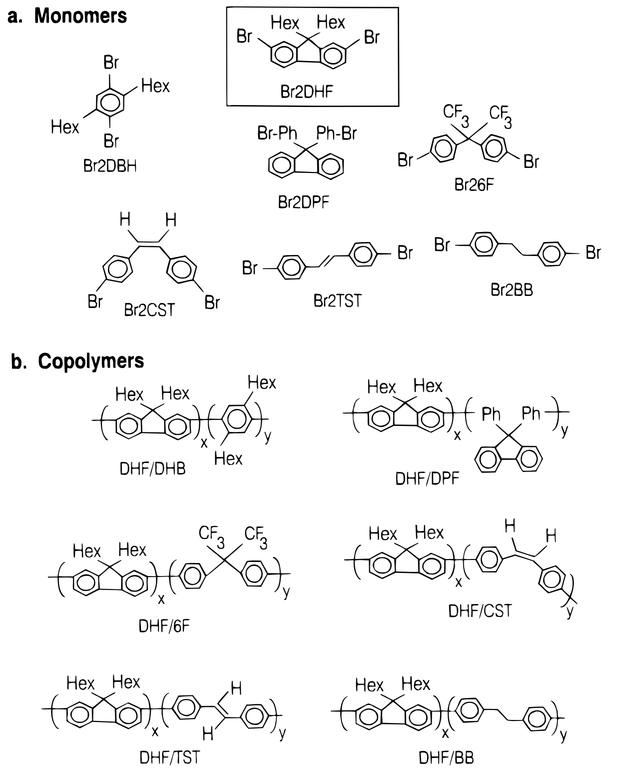

Figure 1. Aryl dibromide monomers and copolymers formed by nickel-mediated coupling.

Table 1. Copolymer Polymer Properties[a]

entry	copolymer composition	yield (%)	M_w[a] ($\times 10^{-3}$)	M_w/M_n	DSC[b] (T_g, °C)	TGA[c] (5%)
1	DHF-100	83	45.0	2.5		430
2a	DHF-15–DHB	94	66.8	2.0	100	435
2b	DHF-25–DHB	88	69.0	2.3	75	420
2c	DHF-50–DHB	71	33.6	2.7	58	425
2d	DHF-50–DHB-A[d]	55	10.0	1.8		430
3a	DHF-15–DPF	92	55.0	2.7	153	450
3b	DHF-25–DPF	88	89.5	2.9	197	440
4a	DHF-15–6F	82	73.5	2.9	125	380
4b	DHF-25–6F	83	206.0	1.9	171	420
5a	DHF-15–CST	82	26.7	3.9	103	450
5b	DHF-25–CST	83	26.5	2.2	125	445
6a	DHF-15–TST	60	46.2	2.8	103	440
6b	DHF-25–TST	35	28.2	3.2	95	420
7a	DHF-15–BB	75	20.2	2.3	71	460
7b	DHF-25–BB	74	24.7	1.9	90	465

[a] Molecular weights determined by GPC analysis using polystyrene standards. [b] Glass transition temperatures as determined by DSC, 10 °C/min. [c] Temperature (°C) for 5% weight loss (TGA, 10 °C/min). [d] 1:1 alternating copolymer generated by Suzuki coupling.

Table 2. Copolymer Electronic Properties[a]

entry	copolymer composition	λ_{max} (nm) UV	λ_{max} (nm) emission	Φ_{fl}[a]
1	DHF-	388	420	
2a	DHF-15–DHB	376	417	0.69
2b	DHF-25–DHB	365	417	0.67
2c	DHF-50–DHB	350	414	0.54
2d	DHF-15–DHB-A[b]	325, 308 (sh)	375	0.36
3a	DHF-15–DPF	378	415	0.70
3b	DHF-25–DPF	372	415	0.67
4a	DHF-15–6F	378	422	0.68
4b	DHF-25–6F	374	422	0.79
5a	DHF-15–CST	382	434	0.61
5b	DHF-25–CST	378	432	0.54
6a	DHF-15–TST	390	430	
6b	DHF-25–TST	388	432	
7a	DHF-15–BB	374	419	
7b	DHF-25–BB	368	418	

[a] Solution fluorescence quantum yields measured in methylene chloride relative to 9,10-diphenylanthracene. [b] 1:1 alternating copolymer generated by Suzuki coupling.

hexylfluorene using zerovalent nickel. Both homo- and copolymers can be prepared in high yield using this technique. Very recently Pei and Yang[38] have reported the preparation of homopolymers such as poly[9,9-bis-(3,6-dioxaheptyl)fluorene-2,7-diyl] using a related procedure. In our work, we have prepared a number of dialkylfluorene-containing copolymers where the comonomer is used both to influence polymer solubility and to control the effective conjugation length either by steric interactions or by the deliberate introduction of tetrahedral conjugation interruptions.

Table 1 lists the polymer properties of the representative copolymers. In general, the isolated polymer yields were good and the molecular weights high, sometimes exceptionally so. In the case of the homopolymer (DHF-100), the degree of polymerization was ~54 based on GPC analysis using polystyrene standards. The copolymers were soluble in common organic solvents such as THF, chloroform, xylene, chlorobenzene, etc. The copolymers derived from Br2TST were less soluble when the comonomer composition exceeded 25 mol %. The thermal stability of the homo- and copolymers was excellent with decomposition temperatures (5% weight loss measured by TGA analysis, 10 °C/min) in excess of 400 °C. The effect of copolymer composition on the polymer T_g (DSC analysis, 20 °C/min) depends on the nature of the comonomer. In general, the T_g value of the copolymers increases with increasing comonomer composition, sometimes significantly so (see entries 3–5 and 7, Table 1). The copolymers derived from Br2DHB are anomalous in this regard, since the copolymer T_g steadily decreases with increasing comonomer concentration (Table 1, entry 2). In the case of copolymers derived from Br2TST, the T_g is little affected, at least over the limited compositional range studied. In Table 1, entry 2d describes the 50/50 alternating copolymer derived from the palladium-catalyzed Suzuki polymerization[39] of Br2DHF with 2,5-di-*n*-hexyl-1,4-bis(boronic acid). The polymer and electronic properties of this material were significantly different from those of the 1:1 statistical random copolymer (Table 1, entry 2c). In each of the copolymer examples cited, the monomer composition of the statistical, random copolymers was reflected in the respective monomer feed ratio. This analysis was performed by ^{1}H NMR integration of the C-9 methylene signals from the dihexylfluorene unit ($\delta = 1.8-2.4$) relative to either the olefinic (entries 5 and 6, Table 1) or aromatic signals in the copolymers. In the case of the olefinic comonomers Br2CST and Br2TST, each is incorporated into the copolymers without significant isomerization of the double bond as determined by the ^{1}H NMR chemical shifts of the respective vinyl protons in comparison with model compounds ($\delta = 6.4-6.6$ for cis vs $7.1-7.3$ for the trans isomer). In a number of cases, the copolymer molecular weights seem to peak for comonomer compositions in the range of 25–35%. The stilbene-containing copolymers (Table 1, entries 5 and 6) appear to be somewhat anomalous in this regard.

The spectroscopic properties of the homopolymer poly(9,9-dihexylfluorene-2,7-diyl) (DHF-100) and various copolymers are shown in Table 2. The solvent for the

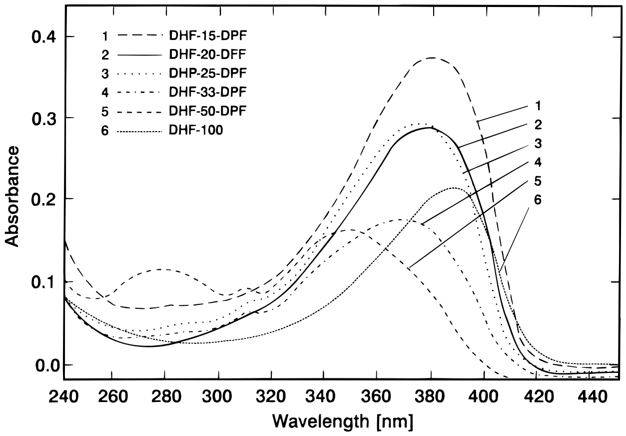

Figure 2. Solution (CH_2Cl_2) UV spectra of copolymers of DHF−DPF.

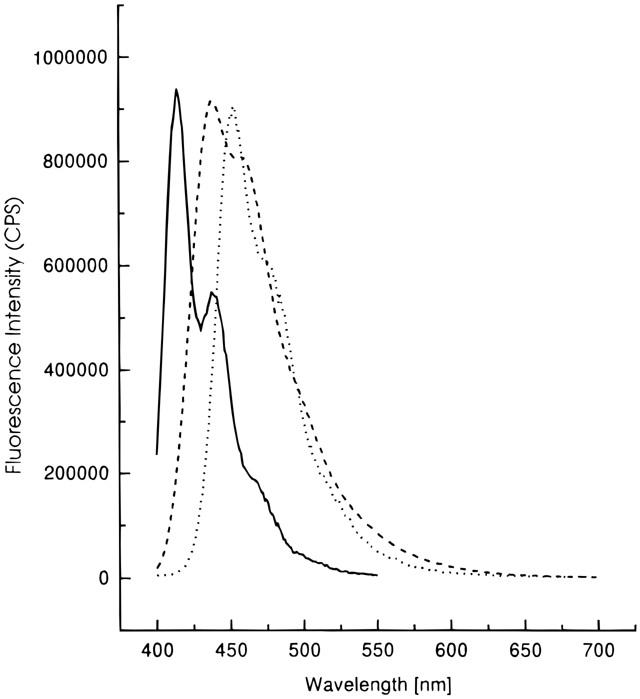

Figure 3. Film emission spectra prior to thermal annealing: (—) poly(di-*n*-hexylfluorene) (PDHF), (- - -) DHF-25−CST, (•••) DHF-25−TST.

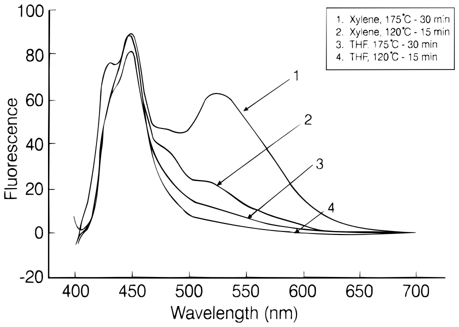

Figure 4. Film emission studies (λ_{exc} = 380 nm) of DHF-15−DPF as a function of casting solvent and annealing temperature.

solution studies was methylene chloride. The fluorescence quantum yields were determined by excitation of the copolymer at λ_{max} and comparison with the solution emission of 9,10-diphenylanthracene ($\Phi_{fl} = 0.83$).[40] In general, the introduction of comonomers with tetrahedral conjugation breaks leads to blue-shifts in the copolymer λ_{max} relative to DHF-100 which increase with increasing comonomer concentration (Table 2, entries 3, 4, and 7). Figure 2 shows this behavior for various compositions of the DHF−DPF copolymer. This effect becomes quite significant for comonomer concentrations exceeding 25%. In the case of copolymers derived from Br2TST (Table 2, entries 6a,b), the absorption maxima are virtually identical with those of the homopolymer DHF-100, although the comonomer concentration range in this case is limited by solubility. The absorption spectra of the copolymer films are generally similar in shape to those in solution, although the absorption maxima are usually blue-shifted by a few nanometers. DHF-25−BB is anomalous in that the absorption spectra of thin films (<150 nm) are unusually broad, while thicker films show an additional maximum on the low-energy side. The thicker films also appear somewhat translucent when spun from xylene, suggesting the formation of microcrystallites or aggregates. No solvent was found which consistently provided good optical quality films from high molecular weight DHF-100.

The emission spectra of both the homo- and copolymers show distinct vibronic fine structure which becomes less pronounced for comonomer concentrations exceeding 30%. In the solid state, the emission maxima are usually red-shifted by a few nanometers relative to those in solution. The shape of the copolymer emission spectra both in solution or as films is quite similar to that of the homopolymer for comonomer compositions less than 30%. These observations suggest that the copolymer emission is occurring primarily from statistical units of PDHF. The emission of the stilbene derivatives (Table 2, entries 5 and 6) is, however, significantly red-shifted from the other homo- and copolymers, and that from DHF−CST is somewhat broadened. Figure 3 shows the emission spectra of DHF-25−TST and DHF-25−CST relative to poly(di-*n*-hexylfluorene) itself. For the copolymer films of DHF−DPF and DHF−6F spun from xylene, an additional weaker broad emission band appears at longer wavelengths (530−540 nm) after drying at 135 °C for 15 min. The strength of this emission is variable, depends on the composition and processing conditions, and grows upon annealing. For films of DHF−DPF (Figure 4), the intensity of this long-wavelength band reaches an intensity comparable to that of the primary emission at 418 nm after annealing for 1 h at 175 °C. Thinner cast films (<100 nm) show much less of the long-wavelength emission after comparable heating. This effect seems to be more dependent on the thickness of the sample rather than the casting solvent. Using THF as a casting solvent, high optical quality films thicker than 100 nm could not be conveniently prepared. However, good optical quality films of DHF-25−6F both thick (~1.0 μm) and thin (~0.07 μm) could be cast from 1,1,2,2-tetrachloroethane. Once again much less excimer was observed for the thin films upon partial annealing at 200 °C for 1 h. This effect, however, appears to be kinetic, since both films which had been annealed for 4 h at 200 °C showed comparable ratios of excimer/monomer emission. A strong excimer band (535 nm) is also observed from the conjugated *cis*- and *trans*-stilbene-containing polymers upon annealing to 130 °C for 12 h under nitrogen. For films cast from xylene, the *absorption* spectra of the DHF−DPF copolymers are unchanged even after heating, suggesting that the emission centered around 540

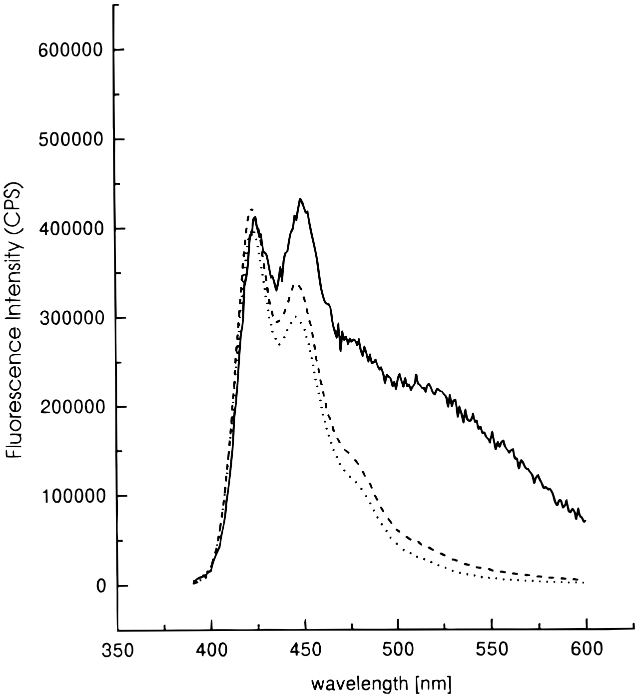

Figure 5. Film emission studies on DHF−DPF: (—) DHF-25−DPF annealed for 30 s at 120 °C, (•••) DHF-50−DPF annealed for 30 s at 120 °C, (- - -) DHF-50−DPF annealed for 3 days at 180 °C.

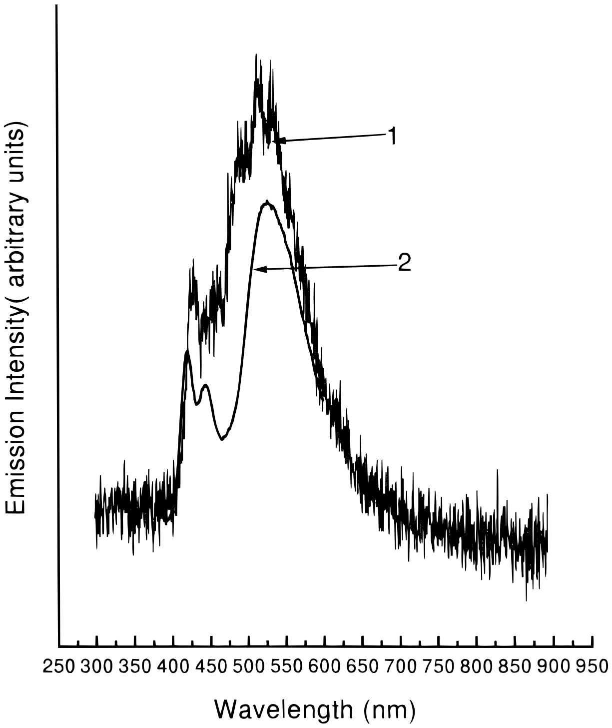

Figure 6. A comparison of the photoluminescence and electroluminescence spectra of DHF-15−DPF: (1) electroluminescence spectrum of DHF-15−DPF; (2) photoluminescence of a DHF-15−PF film annealed at 200 °C for 1 h.

nm is due to excimer emission and that the latter depends on the film morphology. Increasing the comonomer concentration to 50% for the DHF−DPF and DHF−6F copolymers *greatly* decreases the amount of excimer emission upon annealing. This effect is dramatically demonstrated in Figure 5 which shows the emission spectra of annealed films of DHF-50−DPF. These results are shown in comparison with that for a film of DHF-25−DPF which had been briefly heated to 120 °C for 30 s. In the latter case, the onset of excimer emission is already apparent. Although increasing the comonomer concentration in the DHF copolymers always results in less excimer emission upon annealing, even with the 50/50 copolymers the amount of excimer formed depends on comonomer structure. As expected, the long-wavelength emission at 530−550 nm observed in films for entries 3 and 4 was not present in solution in a variety of solvents. The fluorescence quantum yields of the copolymers in solution are quite high and vary only slightly with copolymer composition, at least for comonomer incorporation levels of ≤50%. Preliminary measurements of film fluorescence quantum yields of the copolymers DHF−DPF and DHF−6F yielded values very similar to those reported in solution (Φ_{fl}(film) = 0.66−0.74). The solid-state quantum yields were determined by comparison of the fluorescence intensity of the copolymers with that of a standard sample of 9,10-diphenylanthracene in PMMA (15 wt %). A quantum yield of 0.83 at 366 nm was assumed for the diphenylanthracene-containing film.[41]

Light-emitting diode structures were prepared from the DHF-15−DPF copolymer, first without and then with organic salts for electrochemical doping.[42] Without dopants, the device configuration was ITO/PAni/DPF-15−DHF/Ca/Al, where ITO is indium−tin oxide and PAni is polyaniline-doped metallic with sulfonated polystyrene. ITO was deposited on borosilicate glass substrates by reactive sputtering in Ar/N_2O as described previously.[43,44] PAni was then spin-coated from aqueous solution to a thickness of approximately 100 nm. Earlier studies have shown that PAni forms an efficient hole-injecting anode for polymer light-emitting diodes (PLEDs) fabricated from PPV derivatives.[45,46] The layer of DHF-15−DPF, 130 nm in thickness, was spin-coated from a 3% *p*-xylene solution in a dry nitrogen glovebox and dried in a vacuum at room temperature for at least 12 h. The samples were loaded directly from the glovebox into the vacuum evaporator for the thermal deposition of Ca (25 nm). Finally a protective layer of 25 nm of Al was added.

The electroluminescence (EL) spectrum of an undoped device is shown in Figure 6. This should be compared with the PL spectra of a solid film. The long-wavelength emission in the EL spectra centered around 520 nm may be attributed to the excimer. Emission due to this species is also evident in the PL spectrum of a film which had been annealed at elevated temperatures. The EL spectrum shown in Figure 4 is independent of the drive voltage and does not change significantly with the operating time of the device. Since excimer formation is often associated with substantial decreases in the emission quantum yields, future devices will focus on films of controlled morphology.

Measurements of current−voltage and radiance were carried out in the same dry nitrogen glovebox, using a Keithley Model 238 source-measure unit and an Optronics Laboratories integrating sphere radiometer. The undoped devices first showed detectable emission (2×10^{-10} W/mm^2) at 6 V and a current density of 1 μA/mm^2. The radiance then rose to a value of typically 10^{-7} W/mm^2 (10 Cd/m^2) at 12 V and 0.3 μA/mm^2, corresponding to an external quantum efficiency of approximately 0.01%. Devices made without electrochemical doping showed poorer injection efficiencies and limited stabilities.

Therefore, further device evaluation was carried out on electrochemically doped polymers. This technique, first described by Pei et al.[42] employs an organic salt, the anions and cations of which separate and migrate in an applied electric field to cause electrochemical doping of the conjugated polymer, n-type at the cathode and p-type at the anode. The heavily doped polymer then forms an efficient injecting contact with the metal of the electrode. For example, if 2 wt % of tetraethylammonium tetrafluoroborate is added to DHF-15−DPF during coating, the resulting device turns on at 3.5 V, and gives 10^{-6} W/mm^2 (100 Cd/m^2) at 6 V, with an external quantum efficiency of 0.15%.

In summary, high molecular weight easily processable statistically random copolymers of substituted fluorenes with other aryl moieties can be produced by nickel coupling reactions. The electronic properties of the copolymers are altered somewhat as a function of comonomer structure and composition. The formation of excimers depends on polymer composition and the morphology of the polymer films, the latter of which in turn depends on the processing conditions. Blue-light emission has been observed in devices, although stability was still an issue in the preliminary studies.

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