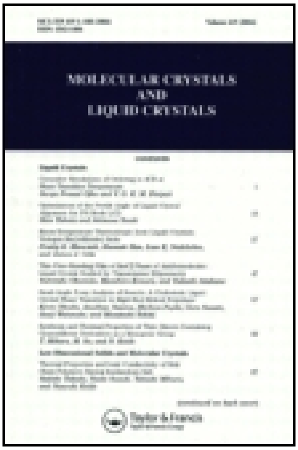

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SYNTHESIS AND CHARACTERIZATION OF FLUORENE-BASED π-CONJUGATED COPOLYMERS CONTAINING PHENYLENEVINYLENE MOIETY

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Random copolymers, PFDEP13 and PFDEP26, were synthesized through Ni(0)-mediated polymerization with 2,7-dibromo-9,9-di-n-hexylfluorene and 1-[2-(2,5-dibromo-4-{2-[4-(2-ethylhexyloxy)phenyl]vinyl}phenyl)vinyl]-4(2-ethylhexyloxy)-benzene (DEP). The resulting polymers are soluble in aprotic polar organic solvents and show good thermal stability up to ca. 400°C. The photoluminescence (PL) emission peaks of the two copolymers are red-shifted with respect to that of common polyfluorene (PF) homopolymer. Both the EL spectra of PFDEP13 and PFDEP26 show maximum emission peaks at 470 nm. In particular, PFDEP26 exhibits a broad emission spectrum in the whole visible region, which suggests the possibility of PFDEP26 as a white-light-emitting polymer.

Keywords: electroluminescence; phenylenevinylene; polyfluorene

INTRODUCTION

Many kinds of conducting polymers and fluorescent dyes have been developed in order to obtain highly efficient electroluminescence (EL), long lifetime, color tuning [1–3] and white color emission [4–7] for the realization of display applications. Polyfluorenes have aroused interest as blue-light-emitting polymers because of their thermal and chemical stability, high quantum yields and good solubility in common organic

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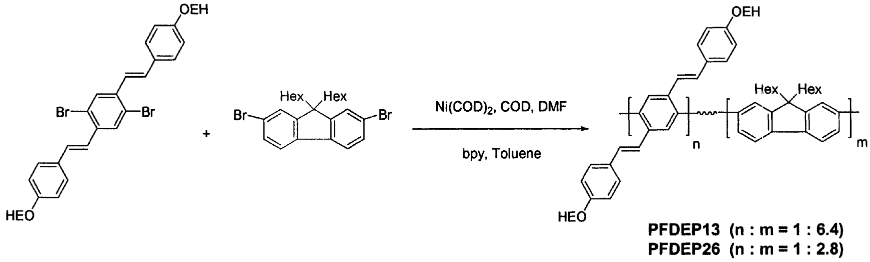
*Corresponding author. Tel.: +82-42-869-2827, Fax: +82-42-869-2810, E-mail: hkshim@mail.kaist.ac.kr solvents [8–10]. Moreover, many research groups have studied various electroluminescent fluorene-based polymers emitting in the region of the three elementary colors of light (red, green, and blue) [11–13]. A small amount of the comonomers was sufficient to change the blue emission of PF to yellow and green emission. The optical and emissive properties of the polymer may be tuned by selection of comonomer structure.

Poly(*p*-phenylenevinylene) (PPV) and its derivatives have attracted much attention because of their optical and physical properties, since its discovery in 1990 [14]. The introduction of various substituents makes PPV derivatives to emit from green to red and orange light. For example, a soluble PPV derivative with alkoxy side groups, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) emits red-shifted wavelength than PPV to give 600 nm (orange light) [15].

It is important to obtain the white-light-emitting diode and color variability in organic light-emitting diodes (OLEDs), because this can permit a multicolor display and facilitate the fabrication process of multicolor displays. In this paper, we report the light-emitting properties of new soluble emissive fluorene-based random copolymers containing modified phenylenevinylene moiety, poly[di-*n*-hexylfluorene-co-2,5-bis{4-(2-ethylhexyloxy)-1-phenylvinyl}-phenylene] (PFDEP13 and PFDEP26). Their thermal, optical and electroluminescent properties are investigated herein.

EXPERIMENTAL

The monomers, DEP [16] and 2,7-dibromo-9,9-di-*n*-hexylfluorene [17], were prepared according to a literature procedure. Random copolymers, PFDEP13 and PFDEP26, were synthesized by Ni(0)-mediated polymerization, as shown in Scheme 1. The numbers, '13' and '26' of PFDEP13 and PFDEP26, mean mole percent of comonomer (DEP) in random copolymers.



SCHEME 1 Synthetic routes for the random copolymers.

The chemical structures of the polymers were well characterized by ^{1}H- and ^{13}C-NMR using a Bruker AM 300 spectrometer. Thermogravimetric analysis (TGA) were performed under nitrogen atmosphere at a heating rate of 10°C/min under nitrogen atmosphere with Dupont 9900 analyzer. The number- and weight-average molecular weights of the polymers were determined by gel permeation chromatography (GPC) instrument on a Waters 2690 model using THF as eluent. UV-visible and photoluminescence (PL) spectra were obtained with Shimadzu UV-3100s and Perkin-Elmer LS-50 Luminescence spectrometer, respectively. Electroluminescence (EL) spectra were measured with a Minolta CS-1000. The current-voltage-luminance characteristics were recorded on a current-voltage source (Keithley 238) and a luminescence detector (Minolta LS-100). All the measurements mentioned above were performed in air and at room temperature.

RESULTS AND DISCUSSION

The synthesized copolymers, PFDEP13 and PFDEP26, were soluble in common organic solvents such as chloroform, THF, and 1,2-dichloroethane. As shown in Figure 1, the copolymers have good thermal stability up to ca. 400°C. The polymerization results are summarized in Table 1.

Figure 2 shows the UV-visible spectra of the spin-coated PFDEP13 and PFDEP26. While PFDEP13 exhibited UV-vis maximum at 380 nm similar

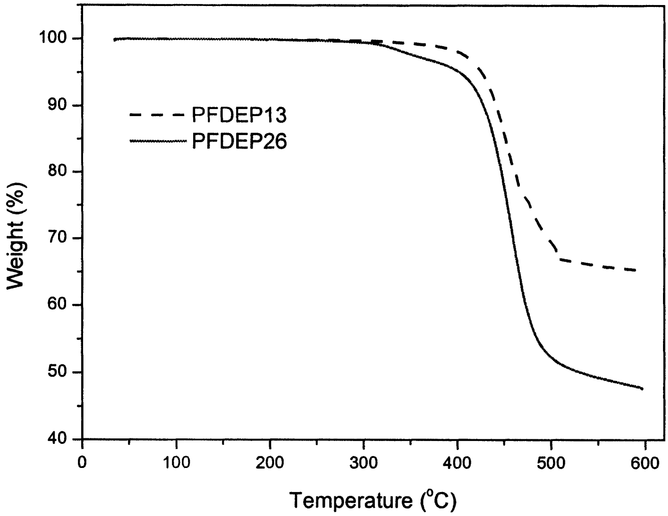


FIGURE 1 TGA thermograms of PFDEP13 and PFDEP26.

TABLE 1 Physical Properties of the Polymers

Polymer	Mn[a]	Mw[a]	PDI	T_{5d} (°C)[b]
PFDEP13	16 900	88 100	5.21	426
PFDEP26	19 000	53 600	2.82	405

[a] Determined by GPC, relative to polystyrene standards.

[b] Temperature resulting in 5% weight loss based on the initial weight measured by TGA analysis.

with PF homopolymers, the maximum absorption peak of PFDEP26 with more DEP moiety was slightly (about 10 nm) blue-shifted to 370 nm. This blue-shifted emission may be resulted from the confinement of succeeded fluorene segments by introduction of DEP moiety [18].

The PL spectra of PFDEP13 and PFDEP26 in THF solution and as film are shown in Figure 3. Both the PL spectra of PFDEP13 and PFDEP26 in THF solution had maximum peaks at 420 nm. The maximum PL peaks of PFDEP13 and PFDEP26 as film were at 477 and 483 nm, respectively. The emission peaks of two polymers were red-shifted with respect to that of PF (430 nm) [19], which could be understood in terms of increasing of DEP momoner, which have the stronger electron-donating property and more extended π-conjugated system than phenylene or fluorene.

The EL spectra of PFDEP13 and PFDEP26 from the device configuration of ITO/polymer/Al are shown in Figure 4. The EL spectra of the

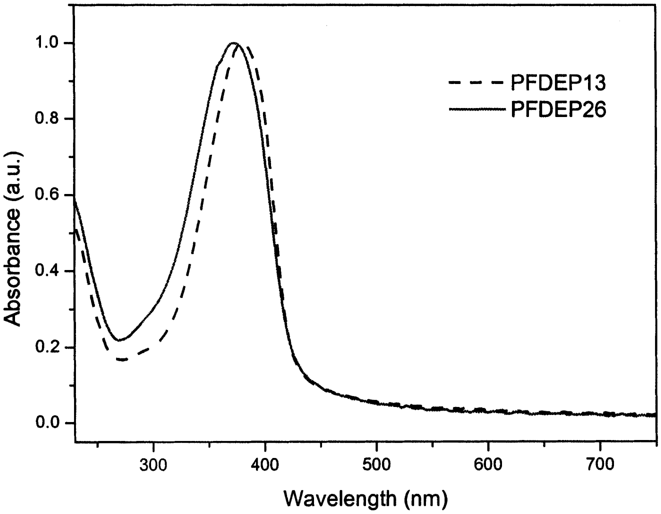


FIGURE 2 UV-visible absorption spectra of PFDEP13 and PFDEP26.

TABLE 2 Optical Properties of the Polymers

	Solution (nm)			Film (nm)			EL (nm)		
	λ_{max}[a]			λ_{max}[a]			λ_{max}[a]		
Polymer	abs	em	fwhm	Abs	em	fwhm	em	fwhm	1931 CIE[b] (x, y)
PFDEP13	381	420 (445)	58	380	477 (427, 455)	112	470	85	(0.215, 0.268)
PFDEP26	373	420 (445)	65	370	483	102	470	190	(0.296, 0.342)

[a] The data in the parentheses are the wavelengths of shoulders and subpeaks.
[b] Determined from the EL spectra (Fig. 4).

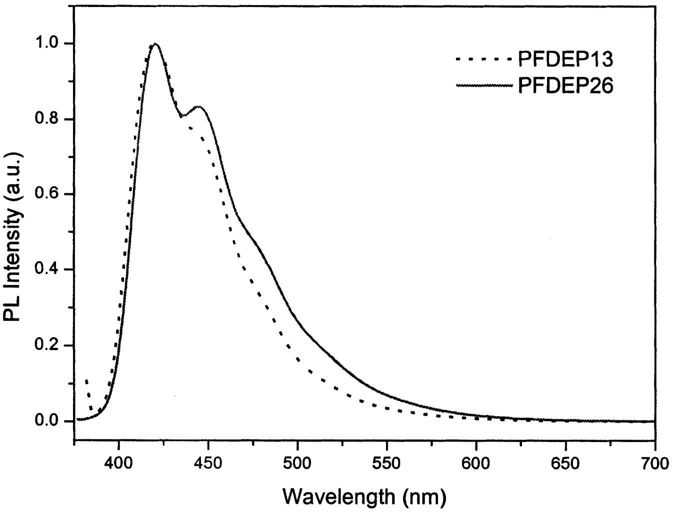


FIGURE 3 Photoluminescence (PL) spectra of PFDEP13 and PFDEP26. (a) In THF solution (b) As film.

copolymers exhibited the same maximum peaks at 470 nm. Similar to PL spectrum as film, the emission peaks of all these copolymers were red-shifted from that of PF homopolymer (452 nm) [19]. Interestingly, it is noticed that PFDEP26 showed a broad EL emission spectrum ranging from 400 to 800 nm with the full width at the half-maximum (fwhm) of 190 nm. While the EL spectrum of PFDEP13 was similar with its PL spectrum, in the EL spectrum of PFDEP26 a new broad shoulder band appeared in the red region. This additional long wavelength emissions in EL may be caused by the red-shifted exciplex formed by two segments in copolymer. Optical properties of these polymers are summarized in Table 2.

Moreover, with increasing ratio of PPV moiety the color of emission from random copolymer gradually approached to white light emission, as pointed out in Figure 5. Namely, compared with blue-light emitting PF homopolymer (0.190, 0.139), the emission color of PFDEP13 and PFDEP26 shifted to the color coordinates (0.215, 0.268) and (0.296, 0.342), respectively. The color coordinates of PFDEP26 are close to those of the standard white (0.310, 0.316) demanded by the National Television System Committee (NTSC) [20,21].

The EL performances of these copolymers were similar to those of PF homopolymers. Recently, Herguth *et al.* [22] reported that incorporation of comonomer into the polymer backbone can provide an affective mechanism for fine-tuning the charge-transporting properties of the polymers. From adjusting the charge-injecting and charge–transporting properties, high PL

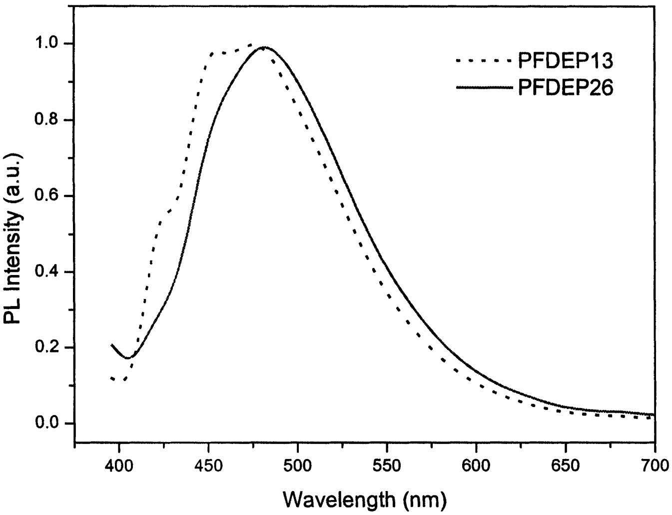


FIGURE 3 (Continued).

quantum efficiencies could be obtained from their copolymers. With similar approach, we can expect that desired efficiencies could be achieved by the incorporation of various comonomers into our polymers. The improvement of EL performance from these copolymerization will be studied further.

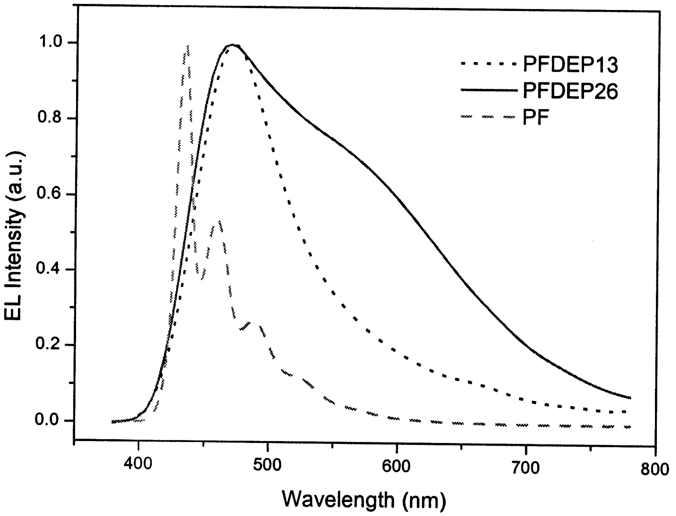


FIGURE 4 Electroluminescence (EL) spectra of PFDEP13 and PFDEP26.

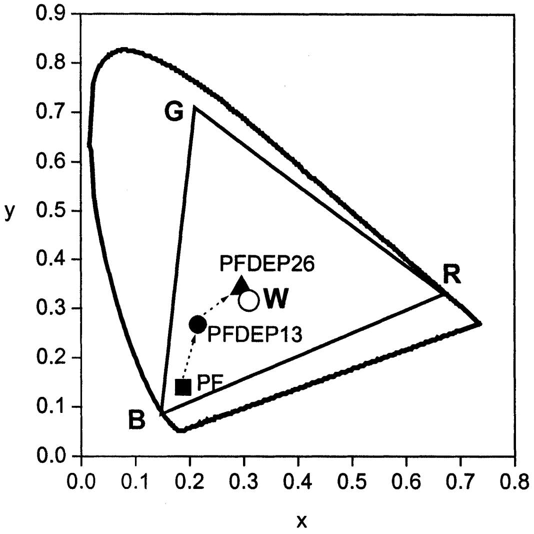


FIGURE 5 CIE chromaticity diagram of the EL device based on PFDEP13 and PFDEP26 in comparison with polyfluorene.

CONCLUSION

We synthesized new emissive fluorene-based π-conjugated copolymers containing phenylenevinylene moiety with bis-styryl group through Ni(0)-mediated polymerization. The copolymer, PFDEP26 showed a broad emission band in the whole visible region. These are expected to be a good candidate as a white-light-emitting polymer.

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