

NOTES

Preparation and Photoluminescence Characteristics of Carbazole-Poly(*p*-phenylenevinylene)s

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Organic conjugated polymers for light-emitting diodes (LEDs) attract much attention for good optical applications. Organic conjugated polymers have been synthesized for development of photoluminescence (PL) properties.^{1–3} Since the discovery of poly(*p*-phenylenevinylene) (PPV) exhibiting photoluminescence a variation of conventional PPV was investigated in which backbone conjugation is partially modified using spacers. In 1993, Karasz *et al.* demonstrated the block copolymer, which has specified units of PPV copolymer with alkyl spacer.⁴ As mentioned in a lots of papers, progress for achievement of blue-emitting organic polymers has been concentrated on the introduction of side group or newly designed backbones by insertion of heterocycles. We recently synthesized PPV copolymers that have shorter backbone conjugations and examined their luminescence.^{5,6} They showed emission spectra in far-blue region and exhibited specific luminescence effect by conjugation length of main chain and methoxy substituents on the phenyl ring. Although hundreds of studies have been conducted using conventional phenylenevinylene-phenylenevinylene-phenylene unit, effective works need variation of backbones to find a blue-emitting polymer showing low turn-on voltage simultaneously.

Recently PPV derivatives containing a carbazole moiety in the backbone or side chain have been reported.^{7–9} In particular, these carbazole-containing PPV copolymers are good materials for making optical and electronic devices due to high hole-transporting capability of carbazole unit.^{10–12} The introduction of new organic polymers based on the carbazole molecule and exploration of applications in the fabrication of organic light-emitting devices will further interest on

carbazole-PPVs for possible optoelectronic applications. So we synthesized three carbazol-PPV derivatives that contain a carbazole unit as a part of main chain and examined luminescence properties. We herein report photoluminescence characteristics and alkoxy substituent effects of carbazole-containing PPV copolymers.

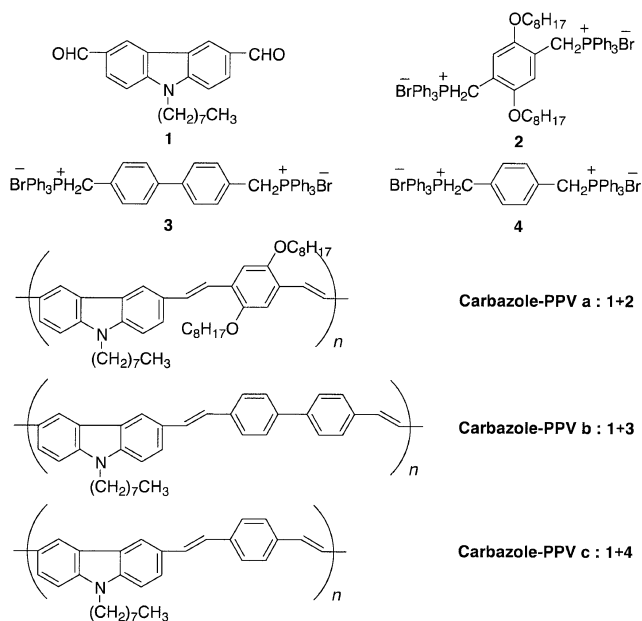
EXPERIMENTAL

All chemicals and solvents were purchased from Aldrich, Junsei, and TCI. Before use, some were purified by normal procedures. All reactions were performed under a nitrogen atmosphere and monitored by thin layer chromatography (TLC). ¹H NMR spectra were recorded on a JEOL-300 (300 MHz) spectrometer, using solvent as internal standard. The samples were dissolved in CDCl₃. FT-IR spectra were measured as KBr pellets on a Perkin-Elmer System 2000 spectrometer. Band positions are expressed in wave number (cm⁻¹). Melting points were determined in capillary tubes using a Mel-Temp II apparatus and uncorrected. UV-Vis spectra were recorded on a Shimadzu UV-3100 UV-Vis spectrometer. Photoluminescence spectra were recorded on a AMINCO-BOWMAN Series 2 luminescence spectrometer. Thermogravimetric analysis was performed on a TA Instrument TGA 2950 thermal analysis system.

3,6-Bisformyl-9-octylcarbazole (I)

1-Bromoheptane (48 g, 270 mmol) was added dropwise to a mixture of carbazole (30 g, 180 mmol) and potassium carbonate (49.8 g, 360 mmol) in 500 mL of DMF followed by refluxing for 14 h. The solution was poured into water and extracted with chloroform

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three times (300 mL \times 3). A black oil was obtained and to which DMF (250 g, 3.4 mol) and POCl₃ (439 g, 2.9 mol) were added. The mixture was heated with stirring for 36 h. The solution was poured into water and the precipitate filtered off. The crude product was recrystallized from ethyl acetate to give a yellow powder (38 g, 62.5%). mp 125–128°C. ¹H NMR (CDCl₃) δ 10.15 (s, 2H), 8.60–7.49 (m, 6H), 4.35 (t, 2H), 1.90 (d, 2H), 1.24–1.38 (m, 8H), 0.84 (d, 3H). IR (KBr pellet, cm⁻¹) 2837, 1675, 1590, 1470.

Monomer Synthesis

The three monomers of bis(triphenylphosphinomethyl)-1,4-dioctylbenzene dibromide (**2**), bis(triphenylphosphinomethyl)benzene dibromide (**3**), bis(triphenylphosphinomethyl)biphenyl dibromide (**4**) were prepared as described elsewhere.^{13, 14}

Polymerization^{4, 5}

The synthesis of carbazole-containing poly(*p*-phenylenevinylene) polymers was carried out using the well-known Wittig reaction between an appropriate diphosphonium salt and carbazole dialdehyde monomer.

RESULTS AND DISCUSSION

The synthesis is shown in Scheme 1. Carbazole dialdehyde (**1**) was prepared by *N*-alkylation of the carbazole with 1-bromooctane followed by bisformylation using the Vilsmeier reaction.¹² Phosphonium salts (**2**, **3**, and **4**) were synthesized or commercial available. Phosphonium salt (**2**) was prepared in three

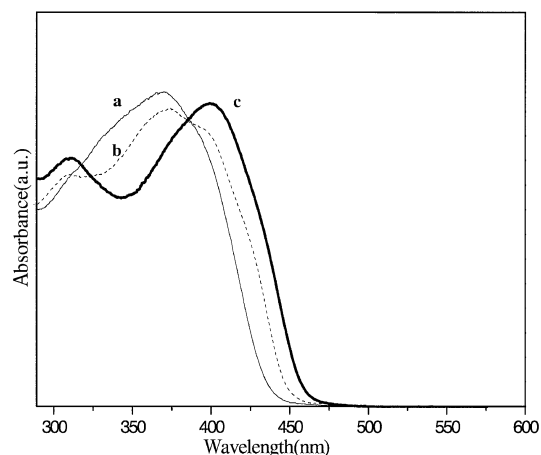
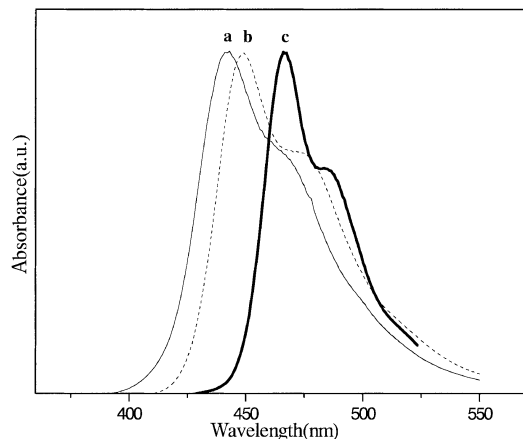


Figure 1. UV-vis absorption spectra of carbazole-PPVs.

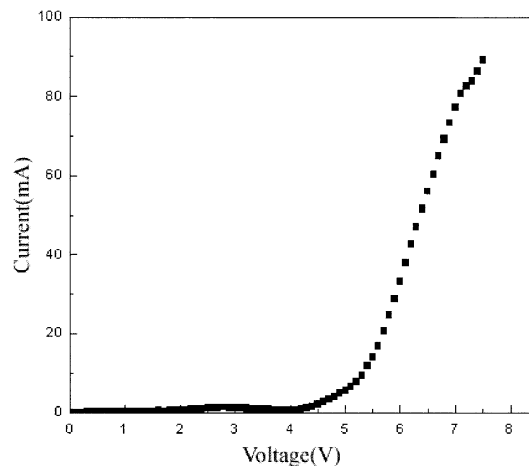
steps as followings. Alkoxy groups were introduced by alkylation of hydroquinone. The resulting 1,4-dioctylbenzene was brominated with paraformaldehyde and hydrobromide in acetic acid to give 1,4-bis(2,5-dialkoxy)benzyl bromide, which was then reacted in dry toluene with triphenylphosphine to give the phosphonium salt. All intermediates were characterized by ¹H NMR and FT-IR. Polymerization was carried out by the Wittig reaction between an appropriate diphosphonium salt and carbazole dialdehyde monomer in mixed solvent (ethanol/chloroform). After recrystallization twice, the carbazole-PPV copolymers (**a**, **b**, and **c**) were obtained. Molecular mass characteristics were analyzed using gel permeation chromatography (referenced to narrow molecular weight polystyrene standards). The molecular weights of copolymer **a** were $M_n = 3284$ and $M_w = 4045$ with polydispersity index of 1.23 (Table I). Those of copolymer **b** and **c** were $M_n = 1528$ and $M_w = 2284$ with polydispersity index of 1.50 and $M_n = 3435$ and $M_w = 10126$ with polydispersity index of 2.95. Only carbazole-PPV **a** containing octoxy substituents was soluble in common organic solvents except alcoholic solvents. Although molecular weights of carbazole copolymers were less than expected, the optical properties of carbazole-PPVs were of primary interest for our purpose. All copolymer samples were investigated for optical absorption and fluorescence properties as solutions. UV-vis absorption spectra of carbazole-PPV copolymers (**a**, **b**, and **c**) in chloroform are shown in Figure 1, with maxima at 369 nm, 375 nm, and 408 nm, respectively and show no much difference with the absorption spectra of conventional phenylene-PPVs. The absorption bands are broad and not well defined. The absorption spectrum of a conjugated polymer depends on molecular conformation due to changing conjugation length of the polymer. These copolymers should thus have different conjugation lengths internally by structures of their backbone.

Table I. Molecular weight, polydispersity, and TGA of synthesized carbazole-PPVs

Carbazole-PPV	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	Polydispersity (M_w/M_n)	TGA (°C)
a	3284	4045	1.23	370
b	1528	2284	1.50	400
c	3435	10126	2.95	370

**Figure 2.** Photoluminescence spectra of carbazole-PPVs.

In contrast, the emission spectra are narrow and well defined in Figure 2. Photoluminescence may thus vary with not only molecular weight characteristics but also structure of backbone. Each peak of emission is at 440–470 nm (440 nm for copolymer **a**, 448 nm for copolymer **b**, and 470 nm for copolymer **c**), with a shoulder at longer wavelength, which may be ascribed to energy transfer prior to emission. The emission peak at short wavelength can be attributed to an excitonic state whereas the shoulder at long wavelength, from aggregates formed between subunits of polymer chains of the excimeric state.¹⁵ PL maxima of copolymers (**a**, **b**, and **c**) showed blue shifts compared to those of conventional PPVs. This can be explained that the introduction of a carbazole moiety in the backbone led to hypsochromic shift in PL emission due to increase in the bandgap. We could not find this consistent trend by substituent effect in Figure 2. But, it is reported that the shape of the emission spectrum is determined by emitting species. It is also expected that the carbazole-containing PPVs, that have similar conjugation backbone lengths compared with PPV copolymers, may show narrow emission bandwidths in the blue region with high intensity. Comparing the PL maximum of copolymer **b** ($\lambda_{\max} = 448$ nm) and **c** ($\lambda_{\max} = 470$ nm) bearing no alkyl groups in phenyl ring with the maximum of **a** ($\lambda_{\max} = 440$ nm) indicated a bathochromic shift of about 8 nm for **b** and 30 nm for **c**. Carbazole-PPV **a** may show red shift compared to copolymer **c** because of the electron-donating effect of alkyl groups. But, as mentioned above, alkyl substituted PPV **a** showed the most blue shifted emission, possibly due to steric influence of the very bulky alkyl substituents, causing

**Figure 3.** Current-voltage characteristics of the ITO/carbazole-PPV **a**/Al organic light-emitting diode. Light-emitting at an operating voltage of 4.5 V was seen.

torsion in the chains.¹⁶ Thus the conjugation length is shortened, leading to blue shift in PL emission. All carbazole-PPV copolymers showed good thermal stability on heating to about 370°C under nitrogen atmosphere in TGA measurement.

We recently synthesized another carbazole-PPV derivative containing hexyl substituents on the phenyl ring and investigated the $I-V$ characteristics (ITO/carbazole-PPV/Al).¹⁷ Light-emitting at an applied voltage of 3.7 V was noted. The turn-on voltage of 3.7 V of single-layer LED is smaller than those of conventional PPV copolymers. So we expect that carbazole moiety in backbone guarantees low turn-on voltage and thermal stability. These three carbazole-PPV copolymers may also show low turn-on voltage. As seen in Figure 3, turn-on voltage of carbazole-PPV **a** was 4.5 V. This suggests that carbazole backbone in organic polymer is important to insure low turn-on voltage below 5 V. Unfortunately carbazole-PPV **b** and **c** showed very poor solubility in most organic solvents. Copolymer **b** and **c** were slightly soluble in NMP (*N*-methyl-2-pyrrolidinone) and DMI (1,3-dimethyl-2-imidazolidinone), respectively. Further studies will include other optical measurement and the enhancement of thermal stability under different reaction conditions.

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