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Synthesis and properties of poly(arylenevinylene)s comprising of an electron-donating carbazole unit and an electron-accepting 2,1,3-benzothiadiazole (or fluorenone) unit in the main chain

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Abstract

Two new soluble arylenevinylene-based polymers comprising of an electron-donating carbazole unit and an electron-accepting 2,1,3-benzothiadiazole (or fluorenone) unit in the main chain were synthesized by Heck polycondensation between 3,6-divinylene-9-decyl carbazole and 4,7-dibromo-2,1,3-benzothiadiazole (or 2,7-dibromofluorenone). In the toluene solution, a polymer with benzothiadiazole unit showed strong red photoluminescence, whereas the polymer with fluorenone unit showed white–yellow photoluminescence. The polymers had good thermal stability with 5 wt% loss temperature of more than 430 °C. Electrochemically, the polymers appeared to be reversible under reduction.

Keywords: Arylenevinylene derivatives; Poly(*p*-phenylenevinylene)s; Carbazole derivatives

1. Introduction

Since the first polymeric organic light-emitting diode (PLED) fabricated by poly(phenylene vinylene) (PPV) was reported in 1990 [1], tremendous efforts have been donated to the synthesis of its derivatives and to exploring new electro–optical properties of the obtained derivatives [2–12]. Recently, π-conjugated charge-transfer (CT) type phenylenevinylene derivatives containing an electron-accepting unit and an electron-donating unit have been paid much attention [13–21]. Some examples include introducing an electron-accepting cyanophenylenevinylene unit to substituted polythiophenes for reduction of the energy gap [13], attaching a donor–acceptor unit (e.g. a pyridine–vinylene–thiophene moiety) into different polymer main chains for realization of tunable light-emitting color from blue to red [21] and blending some oligomers containing a cyano–vinylene–thiophene moiety with some engineering plastics for obtaining molecular probes [15]. It is expected that the polymers or oligomers with the CT structure are useful in optic–electronic devices [20–24] such as PLEDs [19,21], frequency doublers and high speed modulators [20], because the conjugated polymers with such CT structure or π-stacked structure usually show good properties [20–24] such as low band gap values [24] and good nonlinear optical properties [20].

We have recently investigated the synthesis and properties of a series of π-conjugated charge-transfer type PPV derivatives processing an electron-accepting fumaronitrile unit and an electron-donating dialkoxybenzene unit [25]. For the further development of the CT type PPV derivatives, studies on the polymers with various electron-accepting units and electron-donating units are helpful for a better understanding of the relationship between the chemical structures and chemical properties of the polymers. Among the electron-accepting units, 2,1,3-benzothiadiazole and fluorenone units are very attractive: the former has low band gap [24,26] and the latter shows good electron-injection ability [27–28]. On the other hand, carbazole is a typical electron-donating unit [2e], combination of carbazole and 2,1,3-benzothiadiazole (or fluorenone) units to a polymer main chain may obtain the polymers with both hole transfer ability and electron injection ability; such polymers may have some special applications in optic–electrical fields. Although there have been many reports about the PPV containing carbazole units [2e] and the reports regarding to the polymers processing 2,1,3-benzothiadiazole [26] (or fluorenone [27]) units, no reports about the CT type

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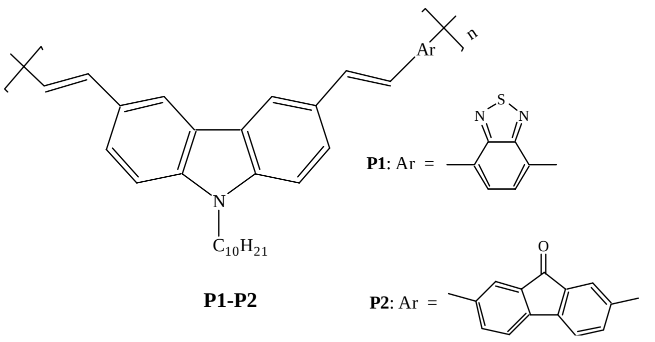


Chart 1. Chemical structure of the new polymers obtained by Heck reaction.

PPV derivatives possessing an electron-donating carbazole unit and an electron-accepting 2,1,3-benzothiadiazole (or fluorenone) unit were found in the literature. Thus, we here report the synthesis and properties of the following CT type polymers (Chart 1).

2. Experimental

2.1. Materials

The starting chemicals were purchased from Across Co. and used as received unless otherwise stated. $[Bu_4N]BF_4$(Bu = butyl) was purified by recrystallizing three times from ethyl acetate and dried over P_2O_5 under vacuum at room temperature for 3 days.

2.2. Measurements

^{1}H NMR spectra were carried out on a Bruker DRX 400 spectrometer, using $CDCl_3$ as solvent and TMS as internal standard. FT-IR spectra were recorded on a Nicolet spectrometer with KBr pellets. Elemental analysis was taken with a Carlo Erba 1106 elemental analyzer. A Perkin–Elmer Series 200 GPC system was employed to deduce a number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) based on polystyrene as standards. UV–visible absorption spectra were obtained with a Hitachi UV2800 spectrophotometer. Photoluminescence was measured with a Hitachi F-4500 fluorescence spectrophotometer. Thermal stability was determined with a TA 2000 thermogravimetric analyzer at a heating rate 10 °C min^{-1} in nitrogen. Cyclic voltammetry of cast films of the polymers on Pt plates was performed in an acetonitrile solution of $[Bu_4N]BF_4$ (0.10 M, Bu = butyl) under argon using (0.10 M $AgNO_3$)/Ag and platinum wire as reference and counter electrodes, respectively. A CHI 600B analyzer was used for the cyclic voltammetry.

2.3. Synthesis of monomers

2.3.1. 9-Decylcarbazole **1**

1-Bromodecane (31 mL, 150 mmol) was added dropwise to a stirring mixture of carbazole (16.7 g, 100 mmol), sodium *tert*-butoxide (14.4 g, 150 mmol) and THF (280 mL) at refluxing temperature under argon atmosphere. The refluxing temperature was kept constant overnight. After being cooled to room temperature, water (50 mL) was added dropwise to the mixture for quenching the remaining sodium *tert*-butoxide. The solvents were evaporated under vacuum and the residue was extracted with dichloromethane. The organic layer was washed with water and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was recrystallized from methanol to give **1**, as a white solid, 28.96 g, yield, 94.3%.

2.3.2. 3,6-Diformyl-9-decylcarbazole **2**

To a flask containing DMF (14.6 mL) was added dropwise $POCl_3$ (17 mL) over 0.5 h at 0 °C under argon atmosphere, and the obtained deep-red solution was stirred at room temperature for 3 h. A solution of **1** (3.07 g, 10 mmol) in 1,2-dichloroethane (12 mL) was added dropwise to the mixture, and the mixture was allowed to heat to 90 °C and kept at this temperature for 2 days. The dark reaction products were poured into water, stirred at room temperature for overnight, neutralized carefully with powder of sodium bicarbonate, and extracted with dichloromethane. The organic layer was washed with water (3×50 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography on silica by using a mixture of solvents (first a 6:1 mixture of petroleum ether and dichloromethane (v/v) and secondly a 99:1 mixture of dichloromethane and ethyl acetate (v/v)) to give **2**, as a yellow solid, 2.38 g, yield, 66%. MS (*m*/*e*): 363 (M^+). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.14 (s, 2H, CHO), 8.68 (d, 2H), 8.10 (dd, 2H), 7.56 (d, 2H), 4.39 (t, 2H), 1.60 (m, 2H), 1.32 (m, 14H), 0.86 (t, 3H).

2.3.3. 3,6-Divinyl-9-decylcarbazole **M1**

To a stirring mixture of methyl triphenyl phosphonium bromide (4 g, 11.2 mmol) and THF (100 mL), *n*-butyllithium (1.6 M solution in hexanes, 7 mL, 11.2 mmol) was added dropwise at −78 °C under argon atmosphere. The yellow solution was stirred at this temperature for 30 min, followed by dropwise addition of a solution of **2** (1.45 g, 4 mmol) in THF (50 mL). After addition, the mixture was naturally warmed to room temperature and stirred for overnight. The remaining *n*-butyllithium in the mixture was quenched by adding dropwise water. After removing the solvents by evaporation, the residue was resolved in dichloromethane, washed with brine and water, dried over anhydrous Na_2SO_4 and evaporated. The residue was purified twice by column chromatography on SiO_2 using a mixture of petroleum ether and dichloromethane (6:1 v/v) to give **M1**, as a white solid, 1.1 g, yield, 74%. MS-EI: 359 (M^+). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, 2H), 7.63 (dd, 2H), 7.33 (d, 2H), 6.93 (dd, 2H), 5.80 (dd, 2H), 5.22 (dd, 2H), 4.25 (t, 2H), 1.85 (t, 2H), 1.27–1.31 (m, 14H), 0.89 (m, 3H). FT-IR (NaCl pellets, cm^{-1}): 3084, 3046, 2925, 2853, 1626,1601, 1489, 1466, 1030, 987, 882, 808, 747. Anal. Calcd for $C_{26}H_{33}N$, C, 86.85%; H, 9.25%; N, 3.90%. Found: C, 86.92%; H, 9.25%; N, 3.75%.

2.4. Synthesis of the polymers

To a 100 mL three-necked flask, **M1** (360 mg, 1.0 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (294 mg, 1.0 mmol), anhydrous palladium acetate (22 mg, 0.1 mmol) and P(*o*-Tol)$_3$ (152 mg, 0.5 mmol), DMF (20 mL) and triethylamine (8 mL) were charged. The mixture was stirred for 20 min at room temperature under argon atmosphere and was heated to 80 °C. After maintaining this temperature for 24 h under intensive stirring, the mixture was cooled to room temperature and poured into water (300 mL) and extracted with dichlorome thane. The organic layer was washed with brine and water, dried over anhydrous Na_2SO_4 and evaporated. The residue was dissolved in dichloromethane and added dropwise to methanol with stirring. The red precipitate was collected by filtering and drying under vacuum. Polymer **P1** was obtained as a red powder (yield, 64%). Molecular weight (GPC, eluent = chloroform, detector = R. I), M_n, 6000, $M_w/M_n = 2.2$ (PDI). FT-IR (NaCl pellets, cm^{-1}): 3042, 2924, 2852, 1730, 1679, 1619, 1597, 1528, 1490, 1465, 1386, 1350, 963, 890, 806. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.89–8.20 (aromatic and vinylene, 12H), 4.29 (broad, 2H), 1.94 (m, 2H), 1.0–1.8 (m, 17H). Anal. Calcd for Br-$(C_{32}H_{33}N_3S\text{-}0.5H_2O)_{12}$-$C_{24}H_{30}N$, C, 76.35%; H, 6.83%; N, 8.08%; S, 5.99%; Br, 1.25%. Found: C, 76.34; H, 6.57%; N, 8.29%; S, 6.10%; Br, 1.10%.

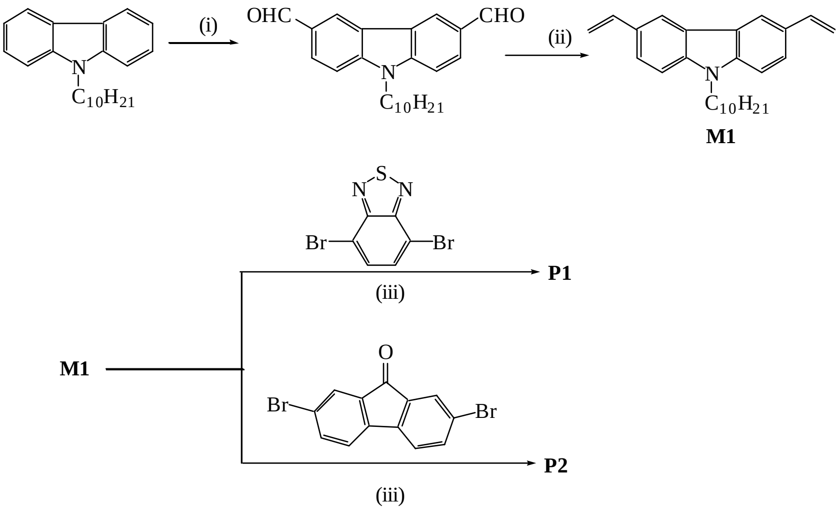
Similarly, **P2** was prepared as a red powder (yield: 34%). Molecular weight (GPC, eluent = chloroform), M_n, 4000, $M_w/M_n = 1.1$ (PDI). FT-IR (NaCl pellets, cm^{-1}): 3028, 2924, 2851, 1715, 1624, 1597, 1488, 1468, 957, 884, 798. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82–8.3 (aromatic and vinylene, 16H), 4.25 (m, 2H), 1.83 (m, 2H), 1.25–1.45 (m, 14H), 0.86 (t, 3H). Anal. Calcd for Br-$(C_{39}H_{37}NO\text{-}0.5H_2O)_7$-$C_{24}H_{30}N$, C, 84.45%; H, 7.01%; N, 2.65%; Br, 1.89%. Found: C, 84.43%; H, 7.32%; N, 2.46%; Br, 1.52%.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic procedure of the monomer, 3,6-divinyl-9-decylcarbazole (**M1**), and that of new polymers **P1** and **P2** are shown in Scheme 1. The starting material, 9-decylcarbazole, was prepared via a somewhat different route from the reported route and the modification method gave the compound in a higher yield (94%) than the previously reported methods (about 60%) [29]. By using the Vilsmeier reaction, 9-decylcarbazole was readily converted into 3,6-diformyl-9-decylcarbazole, a precursor of **M1**, with a yield of 66%. Based on the precursor, monomer **M1** was synthesized with a yield of 74% by a Wittig reaction.

Polymers **P1** and **P2** are prepared by using Heck polycondensation between **M1** and 4,7-dibromo-2,1,3-benzothiadiazole (or 2,7-dibromofluorenone). The yield of **P1** is higher than 60% and number average molecular weight, M_n, of the polymer determined by GPC vs. a polystyrene standard was 6000 with a PDI (M_w/M_n) of 2.2. According to the M_n, the number of the repeating unit of the polymer is estimated at about 12, which agrees with the results of elemental analysis (cf. Section 2). For polymer **P2**, a low yield (about 35%) and a small M_n (4000, PDI = 1.1) may be attributed to the lower reaction activity of 2,7-dibromofluorenone compared to that of 2,1,3-benzothiadiazole. Structurally, the bromo groups at the 2,7-positions of fluorenone are less influenced by the electro-accepting carbonyl group at the 9-position, a *meta*-position of the bromo groups, whereas the thiadiazole unit greatly promotes leaving of the bromo groups at the 4,7-positions of 2,1,3-enzothiadiazole. According to the M_n of **P2**, the number of the repeating unit of the polymer is about seven; such number also agrees with the results of elemental analysis (cf. Section 2). The low value of M_n for **P2** implies that the polymer seems to be considered as an oligomer, however, casting a chloroform solution of **P2** on glass or platinum plates gives



Scheme 1. The procedure for preparation of the new polymer. Regents and conditions: (i) DMF and $POCl_3$ in 1,2-dichloroethane at 90 °C for 2 days. (ii) Methyl triphenyl phosphonium bromide and *n*-BuLi in THF for 0.5 h at −78 °C, and for 18 h at room temperature. (iii) Anhydrous palladium acetate, P(*o*-Tol)$_3$ in DMF/Et_3N at 80 °C for 24 h.

a smooth film, which is possible to estimate the basic optical and electrochemical properties of the polymer.

P1 and **P2** are easily soluble in common organic solvents such as dichloromethane, toluene and DMF. Under the radiation of a UV lamp with wavelength of 365 nm, a solution of **P1** in toluene emits strong red photoluminescence, whereas the toluene solution of **P2** shows white–yellow photoluminescence, indicating that there is a difference in electronic states between **P1** and **P2** because the chemical structure of **P1** is different from that of **P2**. In the solid state, **P1** exhibits only a weak photoluminescence, presumably due to the quenching of photoluminescence, caused by the intermolecular action; similar phenomena have been observed in some polymers with CT structure [24]. For **P2**, it seems to appear to different color from **P1** in the solid state. However, it also shows very weak photoluminescence (bricklike red). This may be also due to the intermolecular action (donator-carbazole and acceptorfluorenone).

The chemical structure of the polymers was characterized by FT-IR, ^{1}H NMR spectroscopy and elemental analysis. Fig. 1 gives the IR spectra of the polymers and the corresponding monomer **M1**. Upon comparison of the FT-IR spectrum of **M1** with these of **P1** and **P2**, new peaks at about 970 cm^{-1} corresponding to bending vibration of the out-of-plane of *trans*-vinylene groups appeared, suggesting that *trans* double bond is formed by Heck polycondensation reaction. For **P2**, a characteristic ν(C=O) peak appeared at 1715 cm^{-1}, indicating that the carbonyl group in **P2** is not reduced during the polymerization. Fig. 2 shows ^{1}H NMR spectra of the polymers. As shown in Fig. 2 and in Section 2, the hydrogens in the aryl rings are at δ 6.5–8.3 and the H signals in the alkyl side chains were observed at δ 0.8–4.3. For **P1** and **P2**, the peak area ratios of the H in alkyl side chain to the H in the aryl rings and the –CH=CH– groups were 21/12 and 21/16, respectively, in agreement with the structure of **P1** and **P2**. In some cases, the polymers prepared using Heck reaction contain terminal olefins [30]. In our case, the signals attributed to terminal olefins were also observed in the ^{1}H NMR spectra of **P1**–**P2** (Fig. 2). The ratio of the end vinyl protons vs. –NCH2– protons is found to be 0.11/2 = 1:18 for **P1** and 0.17/2 = 1:12 for **P2**, respectively, on the basis of the integration of the spectra. If it was assumed that only one end of **P1** or **P2** chain is vinyl (the other terminal group would be bromine), the above ^{1}H NMR signals for terminal groups would hint that **P1** and **P2** had average repeating units of nine and six, respectively, which are approximately agree with the results of GPC and the elemental analysis. On the other hand, if **P1** and **P2** had the chain ends with vinyl groups (without bromine), they would have average repeating units of 18 and 12, respectively. However, elemental analysis indicated that the contents of bromine for **P1** and **P2** were 1.10 and 1.52%. Thus, if it is assumed that the polymer chain end is bromo (the other terminal group would be vinyl), **P1** and **P2** would have molecular weights of 80/0.011 = 7300 and 80/0.0152 = 5300, respectively.

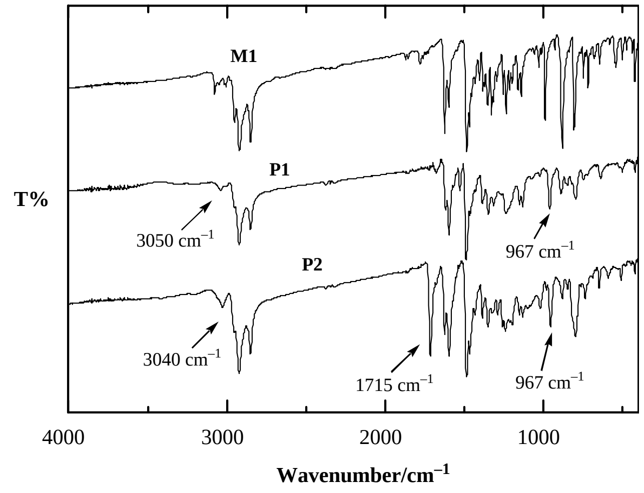


Fig. 1. FT-IR spectra of **P1**–**P2** and monomer **M1**.

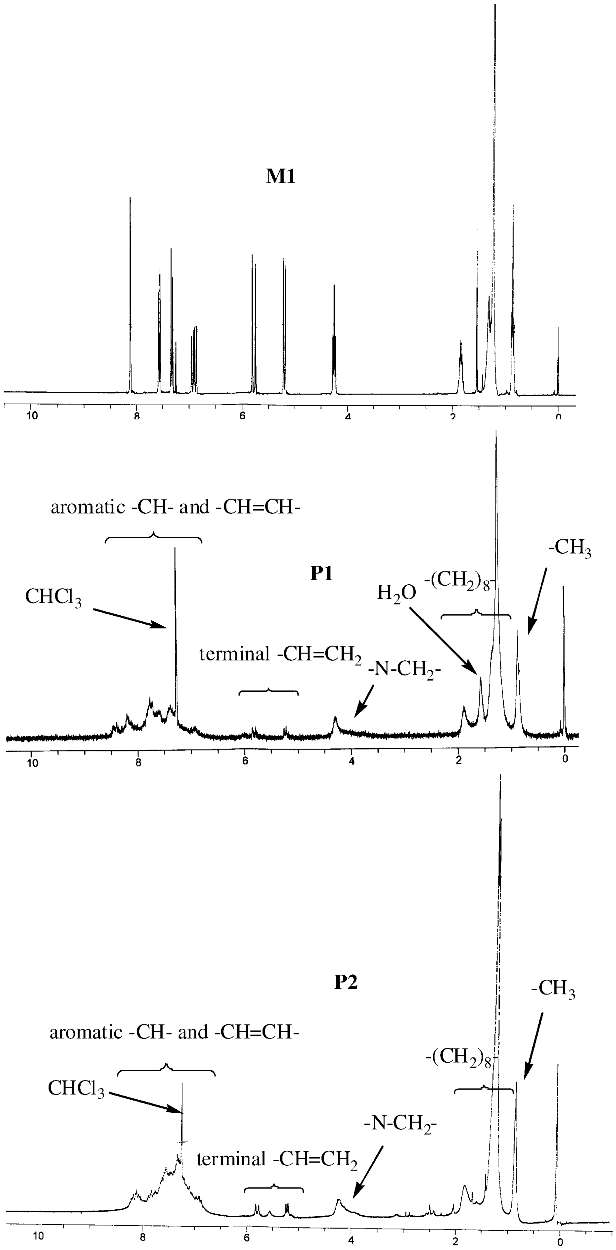


Fig. 2. ^{1}H NMR spectra of **P1**–**P2** and monomer **M1**.

3.2. Optical and thermal properties of the polymers

UV–vis and PL spectra of **P1**–**P2** are shown in Fig. 3. As can be seen from Fig. 3, **P1** shows a UV–vis absorption peak in toluene at about 504 nm, which is much longer than these of poly(carbazole) (308 nm in chloroform) [31] and poly(benzothiadiazole) (320 and 430 nm in DMSO) [26], suggesting the presence of a charge-transferred (CT) electronic state in **P1** [24b]; such CT action is attributed to the formation of a conjugation system between 2,1,3-benzothiadiazole unit and carbazole unit. For **P2**, although there are an electroaccepting carbonyl group and an electron-donating carbazole unit in the polymer, its UV–vis absorption peak in toluene is at about 388 nm, which is near to that of poly(carbazole-*co*-fluorene)s (about 380 nm, solution) [32a]; such result indicates the absence of CT action in **P2**, suggesting that there is no direct conjugation system between carbazole unit and carbonyl unit of fluorenone. Thus, **P2** mainly shows the similar optical properties to these of poly(carbazole-*co*-fluorene)s [32].

In the solid state, although **P1**–**P2** seem to show the same UV–vis peaks as these of their solutions, the onset positions of the UV–vis absorption band of **P1**–**P2** appear at longer wavelength position than these of **P1**–**P2** in solutions, indicating that there are certain π-stacking structures in the polymers in the solid state.

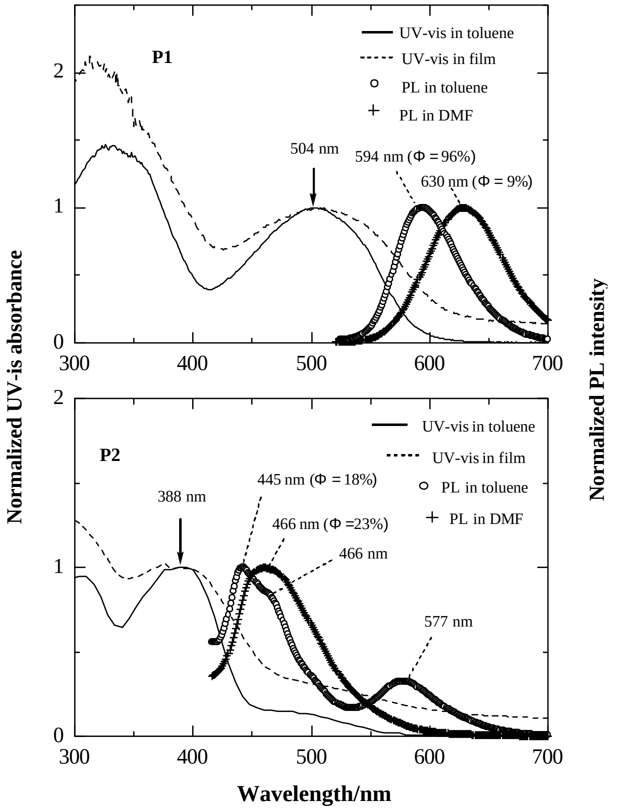


Fig. 3. UV–vis and PL spectra of **P1**–**P2**. For the PL spectra, the exciting wavelengths are UV–vis peaks of **P1**–**P2**. Φ is the quantum yield of PL of **P1**–**P2**. For the measurement of the Φ, a 0.5 M H_2SO_4 solution of quinine (10^{-5} M) was used as a reference for **P2**, and an acetonitrile solution of DCM is employed as a reference for **P1**. Here, DCM is 4-(dicyanomethylene)-2-methyl-6-[*p*-(dimethylamino)styryl]-4H-pyran.

As can be seen from Fig. 3, a solution of **P1** in toluene shows photoluminescent (PL) emission peak at 594 nm with quantum yield of near 95%, estimated by using an acetonitrile solution of DCM, 4-(dicyanomethylene)-2-methyl-6-[*p*-(dimethylamino)styryl]-4H-pyran, as a reference. However, in DMF with strong polarity, such PL peak shifts to 630 nm and the quantum yield dramatically decreases to about 9%. This solvatochromism observed for the PL indicates that the photoexcited state has a polar structure, which is stabilized by solvation, the similar phenomena were also observed in the small molecules and polymers having CT structures [33,34]. For **P2**, its solution in diluted toluene (10^{-6} mol L^{-1}) shows the emission peaks at 445, 466 and 577 nm, respectively. The emission peaks at 445 and 466 nm (shoulder peak) are attributed to the emission of the carbazole–vinylene–fluorene units in **P2** [32]; such a couple of PL peaks appears for various fluorene polymers [2c,2d,35]. The PL emission at 577 nm in toluene derives from the fluorenone unit [27], whereas such peak disappears in diluted DMF (10^{-7} mol L^{-1}), implying that oxygen-containing DMF likely restrained the emission of fluorenone unit.

Thermal properties of **P1** and **P2** were characterized by DSC and TGA, and the results are listed in Table 1. It is seen that **P1** and **P2** have glass transition temperature, T_g of 127 and 121 °C, respectively. TGA showed that the 5 wt% loss temperature for **P1** and **P2** are 430 and 440 °C, respectively, suggesting that the polymers have good thermal stability.

3.3. Analysis of X-ray diffraction (XRD) data

The powder X-ray diffraction (XRD) patterns of **P1**–**P2** are given in Fig. 4, which indicate that the two polymers are essentially amorphous. π-Conjugated polymers with long side chains often give an XRD peak in a low angle region below $2\theta = 10°$ (Cu Kα), and the *d*-spacing calculated from the peak often corresponds to the distance between the π-conjugated main chains separated by the long side chains [24b]. In our case, no XRD peak in a low angle region below $2\theta = 10°$ (Cu Kα) was observed, revealing that the polymers are not able to form a well packed arrangement.

3.4. Redox properties

The redox behavior of **P1**–**P2** was characterized by cyclic voltammetry (CV) with their films cast on platinum wires. Fig. 5 shows the CV curves of **P1**–**P2**. Electrochemical

Table 1
Thermal properties of **P1**–**P2**

Polymers	T_g (°C)[a]	Weight loss temperature (°C)[b]		
		T_5	T_{10}	T_{30}
P1	127	448	477	519
P2	121	430	460	495

[a] Glass transition temperature, measured from DSC traces of the polymers.
[b] The data were obtained from TGA of the polymers. In all case (DSC and TGA), the data were measured under N_2 atmosphere at a heating rate of 10 °C min^{-1}.

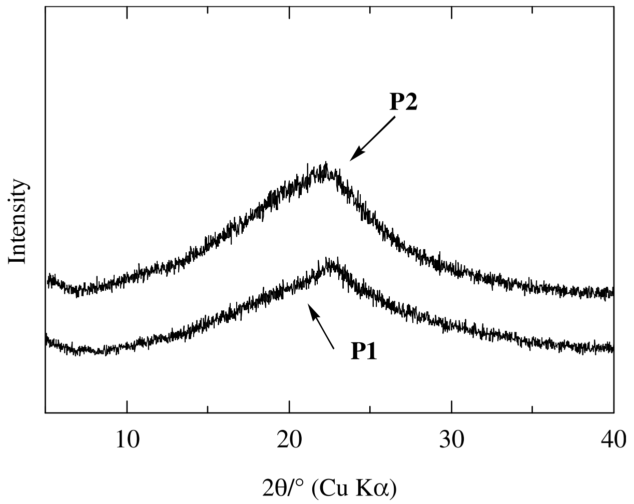


Fig. 4. XRD powder patterns of **P1**–**P2**.

oxidations (or *p*-doping) of **P1** and **P2** start at about 0.42 and 0.50 V vs. Ag^+/Ag, respectively. The polymers show oxidation peaks at 0.67 and 0.78 V, respectively. According to the relationship [36,37] between oxidation onset potential (E_{ox}^{onset}) and HOMO energy, the HOMO values of **P1**–**P2** are estimated as ($E_{ox}^{onset}+4.4$). Thus, the HOMO values of **P1** and **P2** are $-(0.42+4.4)=-4.86$ eV and $-(0.50+4.4)=-4.90$ eV, respectively. These HOMO values are close to that of ITO glass [35], implying that **P1** and **P2** are suitable as the hole-transfer materials for optical devices. As can be seen from Fig. 5, the electrochemical oxidation, attributed to the oxidation of carbazole unit in **P1** and **P2**, are irreversible; such irreversibility is also observed in some carbazole-like polymers with electron-accepting groups [17].

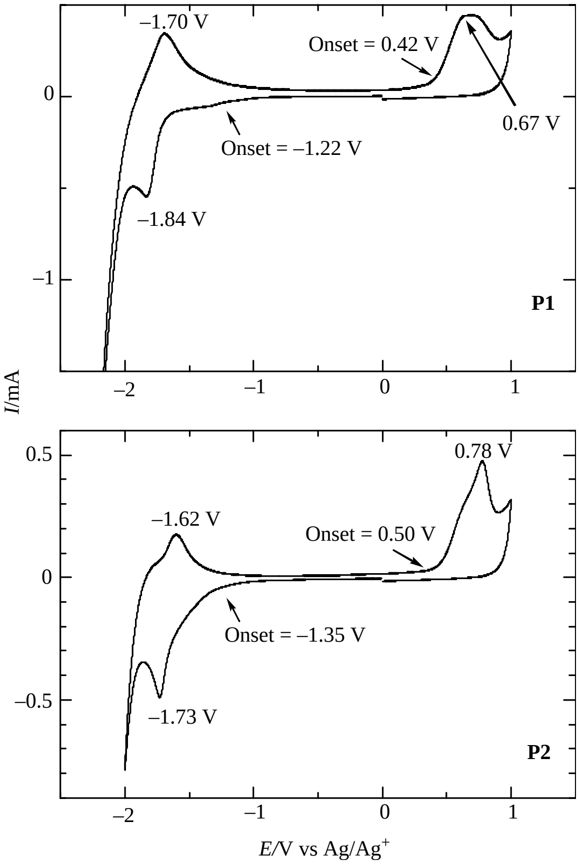


Fig. 5. CV charts of the films of **P1** (solid line) and **P2** (dashed line) on a Pt electrode (wire) in an acetonitrile solution of 0.10 M $[Bu_4N]BF_6$(Bu = butyl) with a sweep rate of 100 mV/s.

The electrochemical reductions (or *n*-doping) of **P1**–**P2** start at about -1.22 and -1.35 V vs. Ag^+/Ag, respectively, which agree with the reported results for poly(2,1,3-benzothiadiazole) [26] and poly(fluorenone) [27]. The reduction potential peaks for **P1** and **P2** are at -1.84 and -1.73 V vs. Ag^+/Ag, respectively. The corresponding *n*-dedoping peaks of **P1**–**P2** appear at -1.70 and -1.62 V, respectively. After repeated scanning of CV, the films of **P1**–**P2** give the same CV curves, suggesting electrochemical stability and reversibility of **P1**–**P2** in a range of the potentials from 0 to -2.5 V. From the reduction onset potentials, the LUMO values of **P1** and **P2** can be estimated [36,37]. For example, these are $-(-1.22+4.4)=-3.18$ eV for **P1** and $-(-1.35+4.4)=-3.05$ eV for **P2**, respectively. These results agree with those reported on poly(benzothiadiazole) [26] and poly(fluorenone) [27].

Based on the above-mentioned electrochemical results, the electrochemical band gaps for **P1** and **P2** are obtained as $(4.86-3.18)=1.68$ and $(4.90-3.05)=1.85$ eV, respectively. The results are much smaller than the optical band gap values of **P1** (about 1.97 eV) and **P2** (about 2.20 eV) (see Fig. 3); such significant difference between optical band gap and electrochemical band gap has been reported [37]. The reason will be further investigated.

4. Conclusion

We have synthesized two new soluble arylenevinylene-based polymers using Heck coupling reaction between 3,6-divinylene-carbazole and 4,7-dibromo-benzothiadiazole (or 2, 7-dibromofluorenone). The UV–vis and photoluminescent (PL) spectra of the polymers showed that the polymer with the benzothiadiazole unit (**P1**) has a charge transfer (CT) system, whereas the polymer with the fluorenone unit (**P2**) has not. The two polymers show good thermal stability and have excellent electrochemical reversibility under reduction. The HOMO and LUMO values estimated from cyclic voltammetry (CV) indicate that the polymers are suitable as both hole transfer and electron transfer materials.

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