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SILICON-CONTAINING POLY(*p*-ARYLENE VINYLENE)S: SYNTHESIS AND PHOTOPHYSICS*

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Abstract A series of new silicon-containing poly(*p*-arylene vinylene)s (PAVs) with anthracene units in the main chain were synthesized by hydrosilylation reaction. The introduction of organosilicon units improved the solubility of the polymers, and the π-π conjugation of polymeric chains was interrupted. These polymers behaved as blue-green light emitters with their fluorescence maximum at 447–499 nm and quantum yields in the range of 0.28–0.30 in solution.

Keywords: Poly(*p*-arylene vinylene)s (PAVs); Hydrosilylation reaction; Photophysics.

INTRODUCTION

Since the first report of the polymer light-emitting diodes (PLEDs) based on poly(*p*-phenylenevinylene) (PPV) by the Cambridge group[1, 2], PPV and their derivatives have attracted much attention as PLEDs materials due to their film-forming property, thermal stability and high luminescent efficiency[3–8]. However, the strong interactions among the main chains of the PPV derivatives often result in formation of excimers and aggregations, which generally lead to red-shift, broadening of the electroluminescence (EL) spectra and lower EL efficiency of the PLEDs[9, 10]. Much effort has been made to improve the properties of PPVs by modifying the molecular skeletons[11–13]. The incorporation of organosilicon units into the PPVs rigid backbone not only improves processibility but also interrupts the regular π-conjugated chains and thus changes their photophysical properties[14–16]. On the other hand, anthracene derivatives have been utilized as co-monomers in the preparation of conjugated light-emitting polymers because of their electron-rich and fluorescent properties[17–20]. In this paper, we report the synthesis of a series of new PAVs containing anthracene building blocks and organosilicon units in the main chain, and their fundamental photophysical properties were also investigated.

EXPERIMENTAL

Materials and Characterization

Tetrahydrofuran (THF) and toluene were distilled over sodium and benzophenone. 1,4-Di-bromo-2,5-diiodobenzene, 1,4-diethynylbenezene, 1,4-bis(*p*-iodophenyl)benzene, 9,10-bis(ethynyl)anthracene and 9,10-bis(dimethylsilyl)anthracene were prepared according to procedures described in the literatures, respectively[21–25]. All other solvents and reagents were analytical grade and used without further purification.

^{1}H- and ^{13}C-NMR spectra were measured on a Bruker 400 MHz spectrometer. Melting points (mp) were

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measured on an XT 5-2 microscope melting point inspection apparatus. Elemental analyses were obtained with the FLASH EA1112 microanalytical facility. IR spectra were obtained with a Tensor 27 IR spectrometer in the wave number range 4000–400 cm^{-1} using standard procedures. Molecular weights were estimated by gel permeation chromatography (GPC) analysis with polystyrene (PS) standard calibration using a Waters 2690D Separation Module and Waters 2410 refractive index detector equipped with TSK-GEL GMHHR-M and TSK column at 40°C in toluene. UV-Vis absorption and fluorescence spectra were measured at room temperature with a Shimadzu UV-1601PC spectrometer and a Hitachi F-4500 spectrometer, respectively. Thermogravimetric analysis (TGA) was conducted on an EXSTAR6000 TG/DTA 6300 thermogravimetric analyzer at a heating rate of 10 K/min under a nitrogen atmosphere. All experiments were carried out under nitrogen atmosphere unless otherwise noted.

Synthesis of Monomers

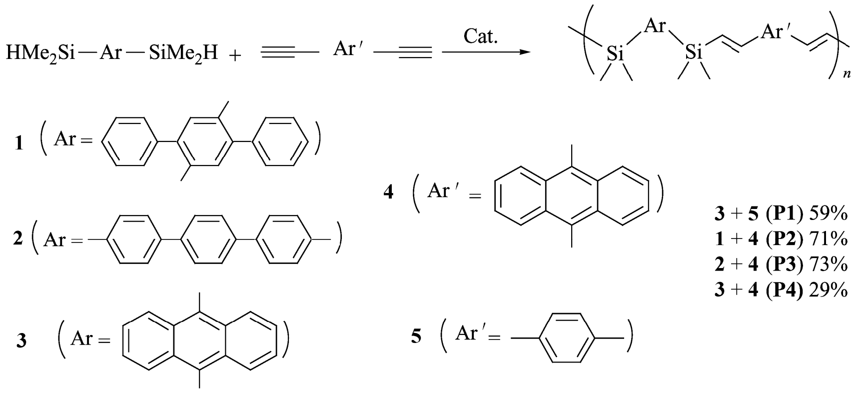
*2,5-Bis(dimethylsilyl)-1,4-diphenylbenzene (**1**)*

The mixture of 1,4-di-bromo-2,5-diiodobenzene (2.00 g, 4.10 mmol), phenylboronic acid (1.25 g, 10.26 mmol), $Pd(PPh_3)_4$ (0.24 g, 0.20 mmol) and K_2CO_3 (2.00 g, 14.76 mmol) in a 3/1 (*V*/*V*) toluene/ethanol mixed solvent (80 mL) containing water (1.0 mL) was stirred for 14 h at 96°C. After removing the solvent by evaporation, the residue was diluted with water and extracted with CH_2Cl_2. The organic layers was combined and dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The mixture was purified by column chromatography (petroleum ether, $R_f = 0.67$) to give 1.32 g (3.40 mmol) of 2,5-bisbromo-1,4-diphenylbenzene in 83% yield as a white solid, which was directly used for next lithium-bromine exchange reaction without further purification (^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.65 (m, 2H), 7.44 (m, 10H)).

To a solution of 2,5-bisbromo-1,4-diphenylbenzene (120 mg, 0.31 mmol) in anhydrous THF (10 mL) was added dropwise a hexane solution of *n*-BuLi (2.5 mol/L, 0.44 mL, 1.08 mmol) at −78°C. After stirring for 1 h, dimethylchlorosilane (118 mg, 1.24 mmol) was added *via* syringe at the same temperature and the mixture was allowed to warm to room temperature and stirred overnight. After quenching with saturated $NaHCO_3$ solution, the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The mixture was passed through a silica gel column with hexane ($R_f = 0.71$) as an eluent, followed by further purification by recrystallization from ethanol to give 98 mg (0.28 mmol) **1** in 91% yield as a white crystal. mp. 118–120°C; ^{1}H-NMR (400 MHz, acetone-d_6, δ): 7.39–7.53 (m, 12H), 4.37 (m, 2H), 0.09 (s, 12H); ^{13}C-NMR (400 MHz, acetone-d_6, δ): 148.07, 144.45, 137.65, 136.55, 130.07, 128.95, 128.15, –2.90.

1,4-Bis(p-dimethylsilylphenyl)benzene (2)

Compound **2** was synthesized essentially in the same manner as described for **1** using 1,4-bis(*p*-iodophenyl) benzene in 67% yield as a colorless solid. mp. 148–150°C; ^{1}H-NMR (400 MHz, acetone-d_6, δ): 7.79 (s, 4H),



Scheme 1 Synthesis of polymers **P1**–**P4**

7.74 (d, $J = 7.8$ Hz, 4H), 7.68 (d, $J = 7.6$ Hz, 4H), 4.47 (m, 2H), 0.39 (s, 12H); ^{13}C-NMR (400 MHz, acetone-d_6, δ): 142.13, 140.81, 137.00, 135.49, 128.28, 127.16, 3.69.

The polymers were synthesized as illustrated in Scheme 1.

Synthesis of Polymers

Synthesis of ***P1***

To a solution of 9,10-bis(dimethylsilyl)anthracene (80 mg, 0.27 mmol) and 1,4-diethynylbenezene (35 mg, 0.27 mmol) in toluene (8 mL) was added Karstedt's catalyst (1 mol%). The reaction mixture was gently refluxed for 52 h. After cooling to room temperature, the mixture was concentrated under reduced pressure. The residue was dissolved with a small amount of toluene and poured into a stirred *n*-hexane to form a bright yellow precipitate. The re-precipitation procedure was repeated twice to give 59 mg of polymer **P1** in 59% yield as a bright yellow powder. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.41 (br s, 4H), 6.80–7.67 (m, 8H), 6.03 (d, $J = 19$ Hz, 2H), 5.80 (d, $J = 19$ Hz, 2H), 0.73 (br, 12H). IR (KBr, cm^{-1}): 3072, 2955, 2899, 1599, 1505, 1443, 1381, 1284, 1171, 1073, 987, 847, 817, 692, 647.

Synthesis of ***P2***

This polymer was synthesized in the manner as described for **P1** by the reaction of 2,5-bis(dimethylsilyl)-1,4-diphenylbenzene (**1**) and 9,10-bis(ethynyl)anthracene in 71% yield as a brown powder.

^{1}H-NMR (400 MHz, $CDCl_3$): 8.17 (br s, 4H), 7.87 (br s, 3H), 7.34–7.69 (m, 13H), 6.34 (d, $J = 19$ Hz, 2H), 5.97 (d, $J = 19$ Hz, 2H), 0.29 (br, 12H). IR (KBr, cm^{-1}): 3057, 2955, 2898, 1598, 1465, 1253, 1127, 1020, 940, 837, 815, 763, 702.

Synthesis of ***P3***

This polymer was synthesized in the manner as described for **P1** by the reaction of 1,4-bis(*p*-dimethylsilylphenyl)benzene (**2**) and 9,10-bis(ethynyl)anthracene in 73% yield as a brown powder. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.28 (br s, 4H), 7.98 (br s, 3H), 7.32–7.81 (m, 13H), 6.31 (d, $J = 19$ Hz, 2H), 5.95 (d, $J = 19$ Hz, 2H), 0.29 (br, 12H). IR (KBr, cm^{-1}): 3062, 2955, 2897, 1597, 1484, 1252, 1112, 1034, 940, 823, 804, 774, 701.

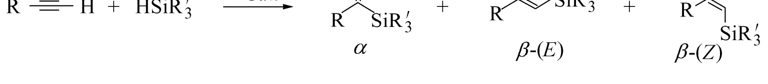
Synthesis of ***P4***

This polymer was synthesized in the manner as described for **P1** by the reaction of 9,10-bis(dimethylsilyl)anthracene and 9,10-bis(ethynyl)anthracene in 29% yield as a reddish-brown powder. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.42–8.32 (m, 16H), 6.64 (d, $J = 19$ Hz, 2H), 6.22 (d, $J = 19$ Hz, 2H), 0.40 (br, 12H). IR (KBr, cm^{-1}): 3046, 2955, 2899, 1596, 1440, 1408, 1379, 1257, 1031, 952, 840, 817, 771, 687.

RESULTS AND DISCUSSION

Synthesis and Characterization

Hydrosilylation of terminal alkynes can result in three isomeric vinyl silanes as illustrated in Scheme 2. In general, the Karstedt's catalyst and the H_2PtCl_6 favor the formation of the β-(*E*)-vinyl silane isomer, the α-vinyl silane is produced in a significant degree (10%–30%), whereas β-(*Z*)-vinyl silanes usually do not appear above the trace level[26–28]. Moreover, the structures of the monomers have an important influence on the hydrosilylation.



Scheme 2 The mechanism of hydrosilylation

The polymers **P1**–**P4** containing anthracene units were synthesized with Karstedt's catalyst and toluene as solvent. All the polymers were characterized by ^{1}H-NMR and FT-IR. In the ^{1}H-NMR spectra, two doublets between chemical shifts of $\delta = 5.80–6.99$ with a large coupling constant ($J \approx 19$ Hz) are characteristic of the β-*trans* isomer. The IR spectra of these polymers exhibited no absorptions around 3300 cm^{-1} ($\upsilon_{\equiv C-H}$) or 2100 cm^{-1} (υ_{Si-H}) that existed in the monomers, but they showed an absorption around 1600 cm^{-1} ($\upsilon_{C=C}$). These results suggest that both hydrosilyl and ethynyl groups in the monomers were consumed after the hydrosilylation reaction. In the ^{1}H-NMR spectra of **P1**–**P4**, the doublet signals around $\delta = 6.24$ and 6.70 are attributed to *trans*-vinyl conformation. The ^{1}H-NMR spectra of **P1**–**P4** revealed a mixture of *trans*-vinyl (two doublets at $\delta = 6.24$ and 6.70, $J \approx 19$ Hz) and α-vinyl (two small singlet peaks at $\delta = 5.48$ and 5.88) isomeric products. The average molecular weights of polymers **P1**–**P4** are listed in Table 1.

Table 1. Average molecular weights and thermal properties of polymers

Polymer	M_n[a]	M_w[a]	M_w/M_n[a]	DP[b]	T_{d5} (°C)[c]	Residue (%)
P1	5500	8800	1.60	13	372	56.9
P2	3600	5800	1.61	6	396	31.9
P3	3500	5300	1.51	6	408	53.5
P4	2700	4500	1.67	5	329	59.8

[a] Estimated by GPC in toluene with polystyrene calibration; [b] Number-average degree of polymerization;
[c] The temperatures at 5% weight loss

Solubility

All of the polymers were soluble in common organic solvents such as THF, methylene chloride, chloroform and toluene. The good solubility in organic solvents should be attributed to the introduction of silicon atoms in the backbone and the methyl substituents on silicon which may increase the chain flexibility.

Thermal Properties

The thermal properties of the synthesized polymers were evaluated by means of TGA under nitrogen atmosphere (Fig. 1). No weight loss was observed up to 250°C, and their temperatures at 5% weight loss (T_{d5}) were higher than 329°C. All of the polymers exhibited good thermal stability due to the introduction of bulky arene units such as *p*-terphenyl unit and anthracene unit to their backbone. Compared with the polymer **P3**, **P2** showed the lower residues because of only one phenyl ring of *p*-terphenyl unit in the main chain.

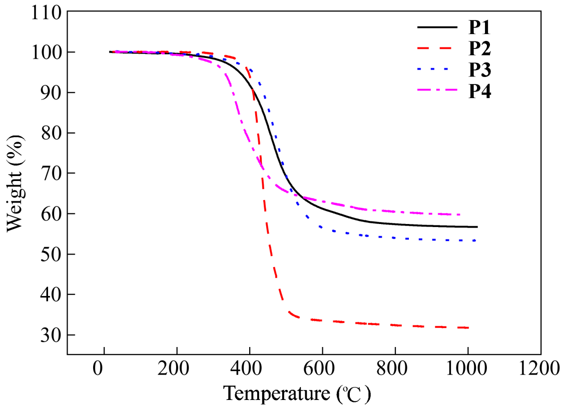


Fig. 1 TGA plots of polymers **P1**–**P4**

Photophysical Properties

The UV-Vis absorption and fluorescence spectra of the polymers in dilute (10^{-5} mol/L) $CHCl_3$ solutions were measured (Fig. 2), and their photophysical data are summarized in Table 2.

Table 2. Photophysical properties of polymers

Polymer	$\lambda_{\mathrm{abs}}^{\mathrm{max}}$ (nm) [a]	lgε	$\lambda_{\mathrm{em}}^{\mathrm{max}}$ (nm) [a, b]	Φ_{F} [a,c]	E_{g} (eV) [d]
P1	266, 408	4.67	447	0.28	2.80
P2	264, 407	4.81	475	0.31	2.82
P3	265, 408	4.90	475	0.30	2.82
P4	261, 410	4.92	499	0.39	2.72

[a] In CHCl$_3$; [b] Excited at 290 nm; [c] Determined with quinine bisulfate as a standard (The Φ_{F} is the average values of repeated measurement within ±5% errors.); [d] Determined from UV-Vis absorption spectra

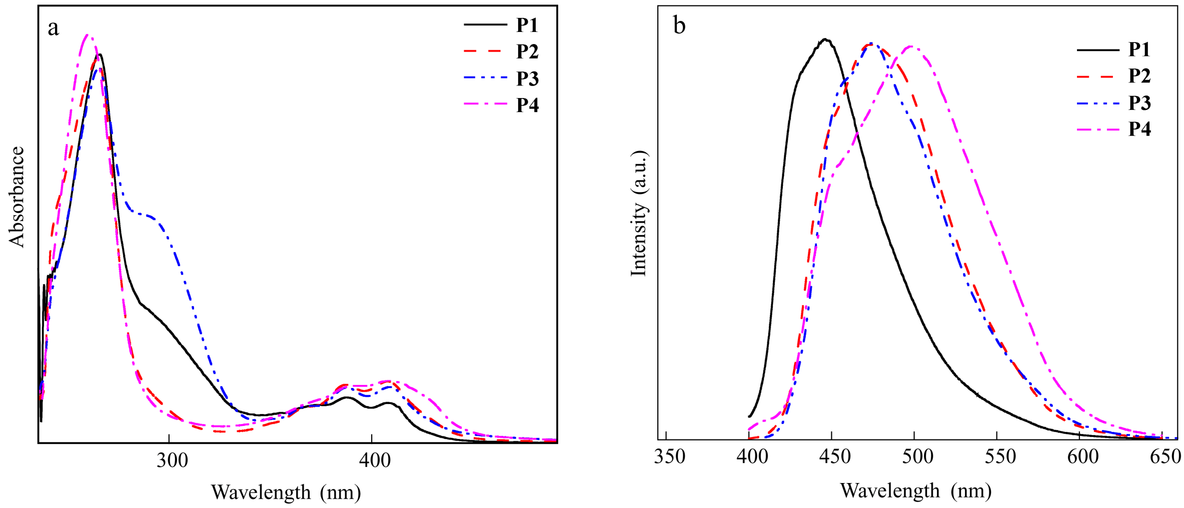


Fig. 2 Normalized (a) UV-Vis absorption and (b) fluorescence spectra of polymers **P1**–**P4** in chloroform

The absorption spectra of the polymers **P1**–**P4** are similar. Besides the main absorption bands, which are around 408 nm, they consist additionally of a hypsochromic peak at $\lambda_{\mathrm{abs}} = 264$ nm which is also attributed to the anthracene units[9]. The chromophore's architecture and the conjugated length influence the emission spectra obviously. The emission maxima of polymers **P1**–**P4** are located at 447, 475, 475 and 499 nm, respectively. Among the four polymers, **P4** has the longest wavelength of emission maximum due to the extended π-conjugation caused by anthracene units. It is known that the PPVs which are interrupted by organosilicon units show blue shifted emission compared with those of the PPV with no organosilicon units in the main chain[29–31]. This is because the regular π-conjugated system was effectively interrupted by the organosilicon units, which results a reduction of π-conjugated length. The same phenomenon also existed for the polymers **P1**–**P4**. Compared with that of fully conjugated polymer poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene-alt-9,10-anthrylene vinylene][30], the analogue of **P1** without organosilicon unit and which has emission maximum around 610 nm, the emission bands of polymers **P1**–**P4** are blue-shifted by more than 100 nm. Also, the introduction of electron-rich anthracene units in the backbone should be responsible for the enhancement of quantum yields of polymers **P1**–**P4**.

CONCLUSIONS

A series of new silicon-containing poly(*p*-arylene vinylene)s (PAVs) containing organosilicon and anthracene units were synthesized by hydrosilylation reaction. All of the polymers display good solubility in common organic solvents due to introduction of organosilicon units. The polymers behaved as blue-green light emitters with their fluorescence maximum in the range 447–499 nm and quantum yields around 0.28–0.30 in solution. Compared with their analogue without organosilicon unit, the emission maxima of the new polymers show dramatic blue shift.

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