Tunable Electroluminescence from Silicon-Containing Poly(*p*-phenylenevinylene)-Related Copolymers with Well-Defined Structures

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ABSTRACT: A new class of silicon-containing poly(*p*-phenylenevinylene)-related copolymers with a uniform π-conjugated segment regulated by organosilicon units was synthesized by the well-known Wittig reaction between the appropriate diphosphonium salts and the dialdehyde monomer such as terephthaldicarboxaldehyde, 2,5-thiophenedicarboxaldehyde, and *N*-(2-ethylhexyl)-3,6-diformylcarbazole. The resulting polymers were highly soluble in common organic solvents. They could spin cast onto various substrates to give highly transparent homogeneous thin films without heat treatment. Their glass transition temperatures were in the range of 104−119 °C. The UV−visible absorbance of the present polymers shows strong absorption bands at around 347−387 nm, which corresponds to the $\pi-\pi^*$ transition of the conjugated segments. Their maximum photoluminescence wavelengths for SiPPV analogues appeared around 420−480 nm in the blue emission region, except a silicon-containing poly(*p*-phenylenevinylene)-related copolymer having a thiophene unit showed a strong PL peak at 520 nm in the green emission region. In the case of the polymers containing a carbazole unit, their PL spectra show both the highest peak in the PL emissive band at 450 nm and an additional strong emissive band in the green region. The single-layer light-emitting diode of a Al/SiPhPPV or SiPhPVK/ITO glass is fabricated. The threshold voltage is in the range 6−12 V from the $I-V$ curve. The electroluminescence (EL) spectrum of the SiPhPPV gives the highest peak in the EL emissive band at 450 nm, when the operating voltage of 9 V was applied. For the polymer containing a carbazole unit, the EL spectrum of the polymer shows the highest peak in the EL emissive band at 450 nm as well as an additional strong emissive band in the yellow region, when the operating voltage of 10 V was applied. Interestingly, the SiPhPVK gives a strong white emitting light, when the operating voltage of higher than 12 V was applied.

Introduction

Electroluminescent (EL) devices based on polymeric thin layers have attracted much attention because of their academic interests and the potential utility of this technology in a wide variety of applications such as large area flat-panel displays and light-emitting diodes.[1−7] EL polymeric materials offer a number of advantages, such as low operating voltages, three primary R/G/B colors, fast response time, high quality of display, and ease of device processability with semiconductor technologies, compared to inorganic EL materials. They have been considered potential candidates for large area flat-panel displays, due to ease of processability. Since the first report of the polymer light-emitting diodes based on poly(*p*-phenylenevinylene) (PPV) by the Cambridge group,[2] a number of different polymers have been synthesized and extended efforts have been made to obtain high-performance devices from polymeric materials.[5,6] At present, organic EL materials, based on complex types of organic/transition metals, have several problems for LED applications as follows: They easily decompose to moisture in air. They can emit three primary colors by doping the special material (Alq_3) with laser dyes. The device fabrication of multilayered film structures by vacuum deposition techniques is tedious and often causes thermal degradation induced phase separation between organic ELD material and doping dye lasers, leading to poor performance and lifetime of the devices.

The polymeric EL materials confront two important problems: low EL efficiency and short lifetime. The EL efficiency of devices can be affected by the homogeneity of film quality, the injecting efficiency of carriers from electrodes to organic materials, and the material's EL efficiency. The first two can be solved by thin film fabricating processes, but the last can be only achieved by developing materials with high EL efficiency. It should be noted that materials with high EL efficiency should be investigated with main efforts focused on improving the lifetime of the light-emitting diodes.

In recent reports, new processable poly(*p*-phenylenevinylene)s with predictable emission wavelengths were realized by introducing well-defined lumophores to the polymer main chain.[5,8] However, these polymers contained saturated and nonconjugated spacer groups between the lumophores which, although they prevent extended conjugation and contribute to the solubility and film-forming properties of the polymer, act as a barrier to the injection and mobility of the charge carriers, leading to the requirement of materials with high threshold voltages that generally damage the polymeric materials. Therefore it seemed desirable to

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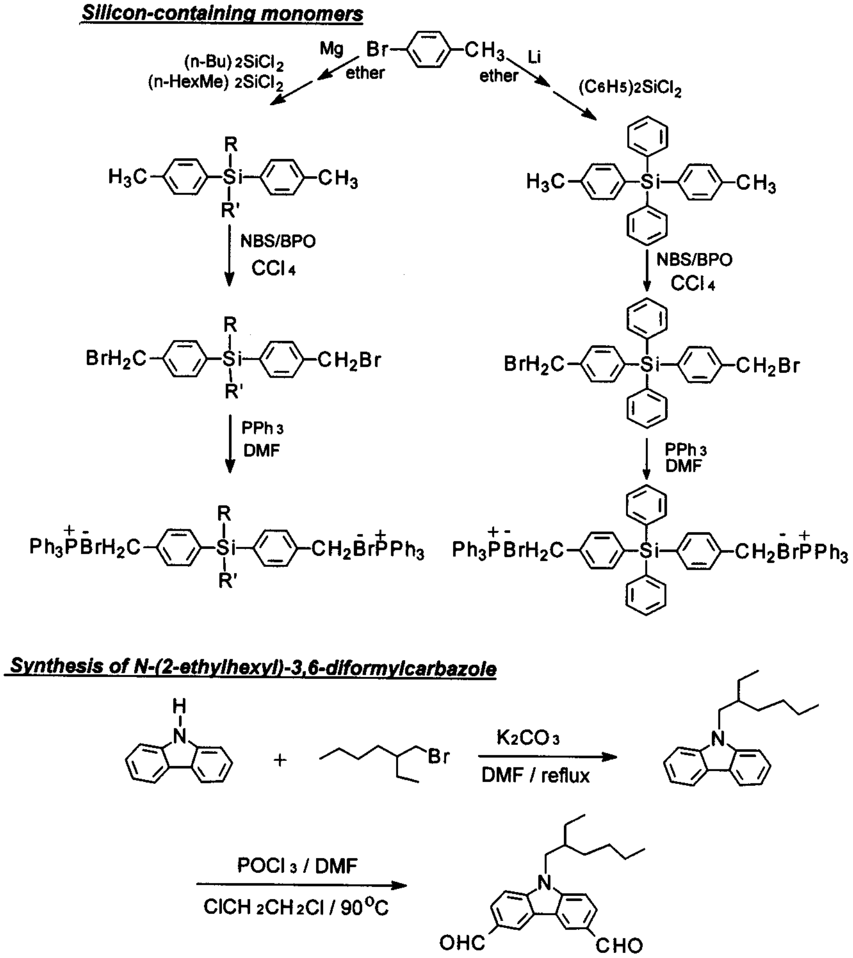
Scheme 1. Synthetic Routes to Bis(*p*-triphenylphosphonium benzylbromide) Organosilanes and N-(2-Ethylhexyl)-3,6-diformylcarbazole



develop new series of polymers requiring low-drive voltages with predictable emission wavelengths. Previously, we reported a type of poly(*p*-phenylenevinylene)-based polymer with a tertiary amine linkage having a well-defined conjugation length in the polymer main chain.[6] These polymers showed a relatively low threshold voltage compared with a block copolymer having similar conjugated units, due to the additional π-electron delocalization between nonpaired electrons in the nitrogen atom and π-electrons in the conjugated units.

Very recently, the main material efforts have been focused on developing blue light-emitting diodes capable of operating at ambient temperature and low voltages with easy processability and low price.[8-10] We reported the development of blue light-emitting diodes from a new type of processable silicon-containing poly(*p*-phenylenevinylene) derivatives in the polymer main chain.[11] The organosilicon units with an aromatic or flexible aliphatic group improved their processability and limited the π-conjugation length, predicting blue light-emitting diodes. The incorporation of a silicon unit with the flexible alkyl side group into the polymer rigid backbone allowed electroluminescent materials to become processible, and the organosilicon units interrupt the regular π-conjugated chains.[11-13] Furthermore, we introduced a carbazole unit into silicon-containing poly(*p*-phenylenevinylene)-related polymers, yielding poly(*p*-phenylenevinylene)-related copolymers containing both silyl groups and a carbazole unit. Our group and other groups have paid much attention to the development of new carbazole-containing polymers for organic light-emitting diodes, since these polymers have good electro- and photoactive properties due to their high hole-transporting mobility, strong absorption in the ultraviolet region, and blue light emission.[14-16] In this paper, we deal with the synthesis and optical properties of the silicon-containing poly(*p*-phenylenevinylene)-related copolymers in the main chain.

Experimental Section

Materials. Terephthaldicarboxaldehyde, *n*-hexylmethyl dichlorodisilane, 2-ethylhexyl bromide, dibenzoyl peroxide, carbazole, *p*-bromotoluene, *N*-bromosuccinimide, triphenylphosphine, and 2,5-thiophenedicarboxaldehyde were purchased from Aldrich and used without further purification. Di-*n*-butyldichlorosilane, diphenyldichlorosilane, and *n*-hexylmethyldichlorosilane were purchased from Huls, Inc. All of the solvents and other chemicals were used after purification according to conventional methods when required.

Monomer Synthesis. The synthesis of monomers was carried out as follows (see Scheme 1): The difunctional monomers of bis((triphenylphosphonium bromide)-*p*-tolyl)-dibutylsilane (**5**), bis((triphenylphosphonium bromide)-*p*-tolyl)-diphenylsilane (**6**), and bis((triphenylphosphonium bromide)-*p*-tolyl)-*n*-hexylmethylsilane as formated triphenylphosphonium salts were prepared, as described elsewhere.[11,12]

***N*-(2-Ethylhexyl)carbazole.**[5] This compound was synthesized by the reaction of carbazole and 2-ethylhexyl bromide. To the mixture of carbazole (30.0 g, 0.18 mol) and potassium carbonate (49.8 g, 0.36 mol) in DMF (500 mL) was added dropwise a 2-ethylhexyl bromide (52.0 g, 0.27 mol) followed by refluxing for 2 days. The solution was poured into water (700 mL), extracted with chloroform three times (200 mL, each), and dried with anhydrous magnesium sulfate. The solvent was removed, and unreacted 2-ethylhexyl bromide was eliminated under reduced pressure. The residue was purified by using silica gel column chromatography with an eluent of ethyl acetate (1)−*n*-hexane (10). Yield: 85%. IR (KBr pellet, cm^{-1}): 1337 (ν_{C-N}), 748, 723 (ν_{C-H} carbazole ring out of plane). ^{1}H NMR (CDCl$_3$, ppm): 0.81−0.92 (m, 6H. 2CH$_3$), 1.16−1.42 (m, 8H, 4CH$_2$−), 2.05 (m, 1H, −CH−); 4.12 (d, 2H, −NCH$_2$−); 7.16−8.2 (m, 8H, aromatic protons of carbazole).

***N*-(2-Ethylhexyl)-3,6-diformylcarbazole.** To 25.0 g (0.34 mol) of *N*,*N*-dimethylformamide and 20 mL of 1,2-dichloroethane cooled to 0 °C was added dropwise 43.9 g (0.29 mol) of phosphoryl chloride. To the stirred mixture, heated to 35 °C, was added 4.0 g (0.014 mol) of 2-ethylhexyl bromide. After standing for 48 h at 90 °C the mixture was poured into 300 mL of water, extracted with chloroform, and dried with anhydrous magnesium sulfate. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (eluent; ethyl acetate−*n*-hexane = 1:3). Yield: 82%. Mp: 109 °C. IR (KBr pellet, cm^{-1}): 1686 ($\nu_{C=O}$ aromatic aldehyde), 1591, 1479 ($\nu_{C=C}$ aromatic stretching), 810 (ν_{C-H} aromatic ring out of plane). ^{1}H NMR (CDCl$_3$, ppm): 0.81−0.96 (m, 6H, 2CH$_3$); 1.23−1.42 (m, 8H, 4CH$_2$−); 2.04 (m, 1H, −CH−); 4.16 (d, 2H, NCH$_2$−); 7.45−8.56 (m, 6H, aromatic protons of carbazole); 10.09 (s, 2H, 2CHO). ^{13}C NMR (CDCl$_3$, ppm): 191.1, 144.9, 129.4, 127.6, 123.8, 122.8, 109.8, 47.8, 39.2, 30.7, 28.5, 24.1, 22.8, 13.8, 10.7.

Polymerization.[11,12] The syntheses of silicon-containing poly(*p*-phenylenevinylene)-related polymers were carried out using the well-known Wittig reaction between the appropriate diphosphonium salts and the dialdehyde monomers such as terephthaldicarboxaldehyde, 2,5-thiophenedicarboxaldehyde, and *N*-(2-ethylhexyl)-3,6-diformylcarbazole.

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded with the use of Bruker AM 300 spectrometers, and chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. Chloroform (CDCl$_3$) was mainly used as the solvent for recording NMR spectra. Infrared spectra were measured as neat oil or KBr pellets on a Perkin-Elmer spectrometer, where the percentage of transmittance versus the wavenumber (in cm^{-1}) was plotted. Molecular weights and polydispersities of polymers were determined by gel permeation chromatography (GPC) analysis with polystyrene as the standard (Water high-pressure GPC assembly Model M590 pump, μ-Styragel columns of 10^5, 10^4, 10^3, 500, and 100 Å, refractive index detectors, solvent THF). The mobile phase was THF flowing at 1.0 mL/min. The UV−visible absorption spectra were obtained in chloroform on a Shimadzu 3101PC spectrophotometer. The photoluminescence spectra were recorded on a Perkin-Elmer LS-50 fluorometer at room temperature utilizing a lock-in amplifier system with a chopping frequency of 150 Hz.

The polymer films were excited with 351 nm of ultraviolet light from the xenon lamp. Molecular modeling was performed with CS Chem Draw Pro 3.5 Soft Program (Cambridge Soft Corp.). For the measurement of EL, the polymer light-emitting diode was constructed as follows. A glass substrate coated with transparent ITO electrode was cleaned by successive ultrasonic treatment in acetone and isopropyl alcohol, then dried with nitrogen gas, and heated for further drying. The polymer film is prepared by spin casting from 1,2-dichloroethane solution containing 1% polymer by weight. The resulting polymer film has a uniform surface with a thickness around 70 nm. The thickness of the polymer film depends on the concentration of the polymer by weight in 1,2-dichloroethane. Metal contacts (aluminum) are deposited on the top of the polymer films by vacuum evaporation at a pressure below 4×10^{-6} Torr, yielding an active area of 0.2 cm^2. For the measurements of device characteristics, the current−voltage ($I-V$) characteristics were measured using a current/voltage source (Keithley 238) and an optical power meter (Newport 818L). All processing steps and measurements mentioned above were carried out in air atmosphere at room temperature. A DuPont 990 thermal analyzer with a 951 TGA and 910S DSC module attached was used to record thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data, respectively. The glass transition temperatures were taken as the midpoint of the change in slope of the baseline. All samples were recorded under a nitrogen atmosphere at a heating rate of 10 °C/min. Melting point determinations were determined using a Fisher-Johns melting point apparatus.

Results and Discussion

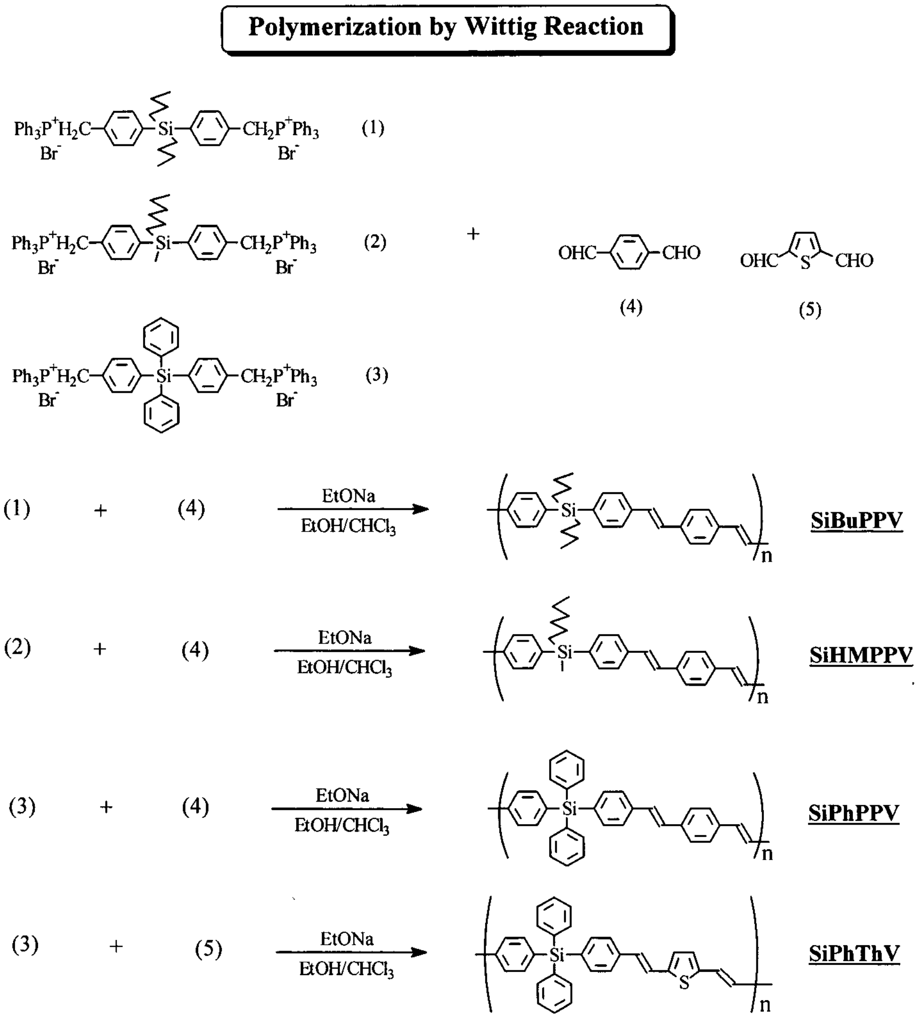
Synthesis and Thermal Properties. The Grignard reaction between *p*-tolylmagnesium bromide and dialkyl/diaryldichlorosilane yields alkyl/aryl-substituted silane synthetic products with high conversion (see Scheme 1).[17] The treatment of di-*p*-tolylsilane derivatives with *N*-bromosuccinimide in the presence of carbon tetrachloride and dibenzoyl peroxide yields brominated intermediates of bis(*p*-(bromomethyl)phenyl)diaryl/dialkylsilanes in a manner of radical chain reaction. The reaction of bis(*p*-(bromomethyl)phenyl)diaryl/dialkylsilanes with triphenylphosphine in dried DMF leads to the salt monomers of bis(*p*-(((triphenylphosphonio)bromo)methyl)phenyl)diaryl/dialkylsilanes. Finally, the monomers of bis(*p*-(((triphenylphosphonio)bromo)methyl)phenyl)di-*n*-butylsilane (**7**), bis(*p*-(((triphenylphosphonio)bromo)methyl)phenyl)-*n*-hexylmethylsilane (**8**), and bis(*p*-(((triphenylphosphonio)bromo)methyl)phenyl)diphenylsilane (**9**) were stored dry in a desiccator before use. The silicon-containing poly(*p*-phenylenevinylene)-related polymers were synthesized by the well-known Wittig reaction of the appropriate diphosphonium salt with the terephthaldicarboxaldehyde, 2,5-thiophenedicarboxaldehyde, or *N*-(2-ethylhexyl)-3,6-diformylcarbazole monomer, as shown in Schemes 2 and 3. The polymerization results of silicon-containing poly(*p*-phenylenevinylene)-related copolymers are summarized in Table 1. The number average molecular weight (M_n) and the weight average molecular weight (M_w) of the polymers, determined by gel permeation chromatography using polystyrene standards, were in the range of 1200−3700 and 3700−30 200 with a polydispersity index of 1.48−8.0, respectively.

Table 2 shows the solubility behavior of silicon-containing PPV-related polymers. All of the synthesized polymers were highly soluble in common organic solvents such as tetrahydrofuran, chloroform, methylene chloride, 1,2-dichloroethane, DMF, etc. This implies that the introduction of silicon atoms in the rigid polymer backbone can reduce the chain stiffness, thus enhancing the solubility of PPVs. They could spin cast onto various substrates to give highly transparent homogeneous thin films without heat treatment.

The chemical structures of the resulting copolymers were identified by FT-IR, ^{1}H NMR, and UV−visible spectrometry. Figure 1 shows the typical FT-IR spectra of the PPV-related polymers. The comparison of the monomer FT-IR spectrum to that of the polymer showed a drastic decrease of the bands at 1686 cm^{-1}, which is expected for the strong aldehyde carbonyl stretching band of the dialdehyde monomer. On the other hand, a weak, sharp absorption peak at 960 cm^{-1}, corresponding to the out-of-plane bending mode of the *trans*-vinylene groups appeared, indicating that the vinylene double bonds newly formed are mainly trans configuration.

Figure 2 shows the ^{1}H NMR spectrum of the poly(*p*-phenylenevinylene) containing a di-*n*-butylsilyl group

Scheme 2. Synthesis of Poly(*p*-phenylenevinylene)-Related Copolymers Containing Silylphenylene Units in the Main Chain



and a carbazole unit (SiBuPVK) in the main chain. As the polymerization proceeded, the aldehyde peak of the monomer present at 10.09 ppm disappeared and new vinylic proton peaks appeared at 6.5 ppm (doublet) and 7.45 ppm along with aromatic protons of a carbazole unit. Also, the broad peak around 0.8−1.3 ppm was assigned to the butyl protons adjacent to a silicon atom and the broad peak around 4.2 ppm was assigned to the α-methylene protons adjacent to a nitrogen atom in a carbazole unit.

The thermal behavior of the silicon-containing PPVs was evaluated by means of DSC and TGA under a nitrogen atmosphere. Also, the thermal properties of polymers are presented in Table 3 and shown in Figure 3. All PPV polymers showed no definite melting points, implying that the silicon-containing PPV-related copolymers could be amorphous. Also, this was identified by the broad pattern of the X-ray diffraction. The PPV polymers have T_g values in the range of 104−119 °C. The T_g of SiPhPPV was higher than that of SiBuPPV, indicating more rigidity of SiPhPPV. Similarly, the T_g of SiPhPVK is a little higher than that of SiBuPVK. These results indicate that the bulky phenyl group in SiPhPPV or SiPhPVK produces a little more rigid structure than the flexible alkyl group due to steric hindrance between the surrounding four phenyl groups on a silicon atom (see Scheme 4). All of the polymers showed good thermal stability up to 220 °C, but a small amount of weight loss began to occur at 300 °C.

Optical and Photoluminescent Properties. Figure 4 shows the UV absorption spectra of the three SiPPV derivatives (SiPhPPV, SiHMPPV, and SiBuPPV) in the chloroform solution. As shown in the absorption spectra, two maximum absorption wavelengths (λ_{max}) of the SiPhPPV absorb at 320 and 375 nm, which are attributed to the π−π^* transition of the π-conjugated segment, while the maximum absorption wavelength (λ_{max}) of SiBuPPV or SiHMPPV absorbs at 347 nm. The maximum absorption wavelength (λ_{max}) of the π-conjugated polymers depends on both the degree of conjugation and the conjugation length. As indicated by the red shift of the absorption maxima bands resulting from the π−π^* transition of the conjugated polymer backbone, the attachment of the phenyl group onto the silane atom forces the π-conjugated segment to be more planar via the bulky phenyl side chain interactions in a dilute solution.[11] This could be explained by the constraint on the free rotation of the Si−C bonds in the main chain via the bulky phenyl side chain interactions (see Scheme 4).

In the case of SiBuPPV, the weak interaction between the flexible alkyl group and phenyl group in the main chain allows the Si−C bond to rotate easily, because the Si−C bond (Si−C = 1.91 Å) is longer than the C−C bond (C−C = 1.53 Å). A similar behavior was also observed

Scheme 3. Synthesis of Poly(*p*-phenylenevinylene)-Related Copolymers Containing a Carbazole Unit and Silylphenylene Units in the Main Chain

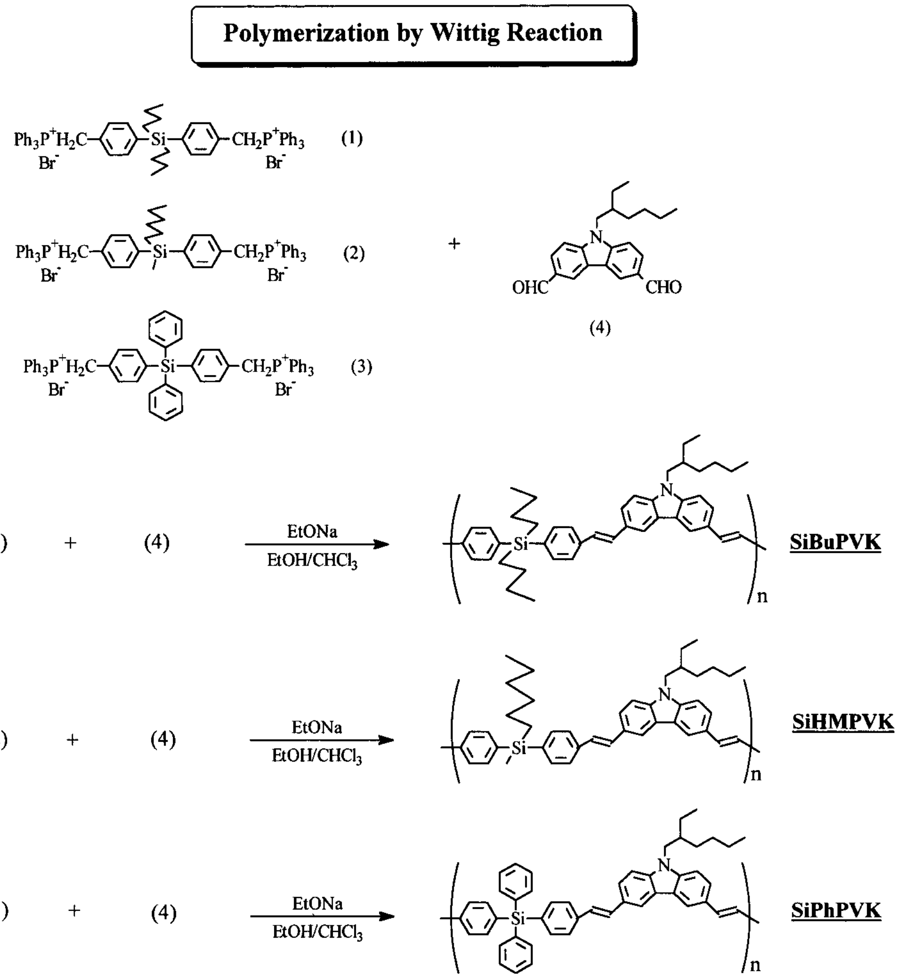


Table 1. Polymerization Results of Silicon-Containing Poly(*p*-phenylenevinylene)-Related Copolymers

polymers	yield (%)	M_n[a]	M_w[a]	PDI
SiBuPPV	21	2500	3700	1.48
SiHMPPV	25	3700	30200	8.0
SiPhPPV	26	2800	4100	1.50
SiBuPVK	27	2100	8300	3.8
SiHMPVK	30	1660	4400	2.6
SiPhPVK	32	1500	4500	3.0
SiPhThV	32	1200	3700	3.0

[a] M_n, M_w, and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards.

from the DSC analysis. The maximum absorption wavelength (λ_{max}) of poly((tetraphenylsilyl)thiopheneylidene) (SiPhThV) appears at the longer wavelength of 387 nm, due to the strong delocalization of the π-conjugated thiophene units. Also, Figure 5 shows the UV absorption spectra and the photoluminescence spectra of the two SiPPV copolymer thin films (SiPhPPV and SiBuPPV) coated on a carboglass. The maximum absorption wavelength (λ_{max}) of SiBuPPV and SiHMPPV in a thin film shows a strong absorption band of the $\pi-\pi^*$ transition of the conjugated segment at 347 nm, at which the absorption maxima band of the SiBuPPV and the SiHMPPV solution appears. They also include a shoulder peak at longer wavelengths. In contrast, the maximum absorption wavelength (λ_{max}) of SiPhPPV appears at 340 nm, resulting in a blue shift of 35 nm, compared with that of SiPhPPV in a dilute solution. As indicated by the blue shift of the absorption maxima bands resulting from the $\pi-\pi^*$ transition of the conjugated polymer backbone, the propeller-like phenyl side group interactions, which are caused by the stacking of four bulky phenyl groups attached to silicon atoms in the SiPhPPV thin film sample, could make it flatten the propeller-like phenyl side groups to render a ring-torsional ground state in two different phenyl groups. This flattening force disturbs the coplanarity of the π-conjugated segment (see Scheme 4), reducing the coplanarity of the π-conjugated segment in the thin film. It results in a blue shift. In a dilute solution, however, the attachment of the phenyl group to the silane atom forces the π-conjugated segment to be more planar via the bulky phenyl side chain interactions, leading to a longer maximum absorption wavelength.[11] Similar results were previously reported.[18] Additionally, this observation was proved by adding a polar nonsolvent of methanol into a chloroform polymer solution as follows: The addition of methanol into a chloroform polymer solution shows the blue shift of the SiPhPPV solution in a UV spectrum, since the addition of methanol into a chloroform polymer solution leads to aggregate polymer chains that flatten the propeller-like phenyl side groups, giving thin film behavior.[19]

The PL spectra show shifts similar to those observed in the absorption spectra for the thin film sample (see Figure 4). With an excitation wavelength of 351 nm, the SiBuPPV spectrum shows two emission peaks at 450

Table 2. Solubility Behaviors of Silicon-Containing Poly(*p*-phenylenevinylene)-Related Copolymers

	polymers[a]						
solvent	SiBuPPV	SiHMPPV	SiPhPPV	SiBuPVK	SiHMPVK	SiPhPVK	SiPhThV
n-hexane	−	−	−	−	−	−	−
MeOH	−	−	−	−	−	−	−
acetonitrile	−	−	−	−	−	−	−
acetone	+−	+−	+−	+	+	+	+
$CHCl_3$	+	+	+	+	+	+	+
CH_2Cl_2	+	+	+	+	+	+	+
THF	+	+	+	+	+	+	+
1,4-dioxane	+−	+−	+−	+−	+−	+−	+
1,2-dichloroethane	+	+	+	+	+	+	+
toluene	+	+	+	+	+	+	+
DMSO	−	−	−	−	−	−	−
DMF	+	+	+	+	+	+	+

[a] +, soluble; +−, partially soluble; −, insoluble.

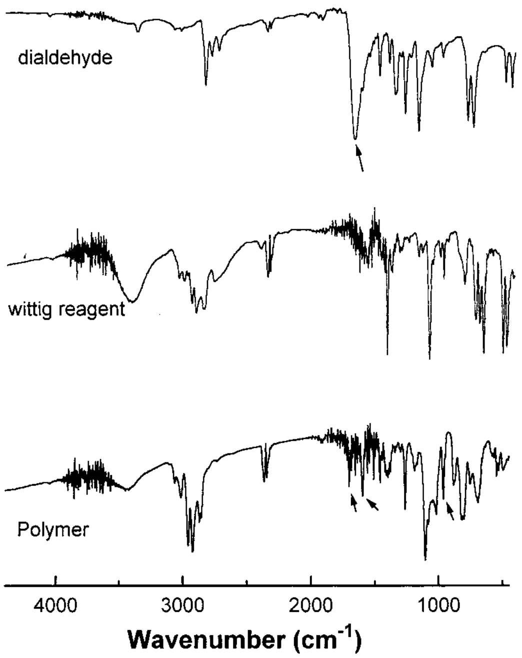


Figure 1. IR spectra of the poly(di-*n*-butyldiphenylsilylterephthalide) (SiBuPPV) and the starting monomers in KBr pellets.

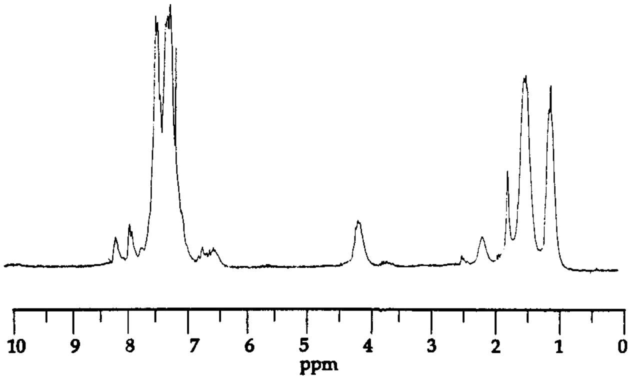


Figure 2. ^{1}H NMR spectrum of the poly(3,6-diformyl-*N*-(2-ethylhexyl)carbazolyl)diphenyldibutylsilylene) (SiBuPVK) in $CDCl_3$.

and 480 nm, indicating a blue emission. Similarly, the SiPhPPV thin film sample exhibits two PL maximum peaks at 410 and 450 nm in the blue region, indicating a blue shift of the PL emission. Also, the PL maximum peaks for both SiHMPPV and SiPhThV can be observed at 470 nm in the blue region and 520 nm in the green region, respectively.

Table 3. Thermal and Optical Property of Silicon-Containing Poly(*p*-phenylenevinylene)-Related Copolymers

polymers	T_{ID}[a] (°C)	char yield[b] (%)	T_g °C	UV λ_{max} (nm)	PL λ_{max} (nm)
SiBuPPV	175	48	105	347	450 & 480
SiHMPPV	187	53	104	348	470
SiPhPPV	250	62	109	320 & 375	410 & 450
SiBuPVK	178	44	108	353 & 314	420
SiHMPVK	192	42	107	352 & 313	430
SiPhPVK	220	60	119	351 & 311	480
SiPhThV	240	64	116	387	520

[a] Temperature at which initial loss of mass was observed. [b] Char yields were obtained at 600 °C.

Interestingly, the present silicon-containing PPV-related polymers have shown strong blue shifts relative to PPV.[20,21] These results indicate that the regular π-conjugated system was effectively interrupted by the organosilicon units, yielding a reduction of π-conjugated length.

Furthermore, we introduced a carbazole unit into silicon-containing poly(*p*-phenylenevinylene)-related polymers, leading to the formation of poly(*p*-phenylenevinylene)-related copolymers containing both silyl groups and a carbazole unit (see Scheme 3); these carbazole-containing polymers have good electro- and photoactive properties due to their high hole-transporting mobility, strong absorption in the ultraviolet region, and blue light emission. The absorption spectra of poly(3,6-diformyl-*N*-(2-ethylhexyl)carbazolyl)diphenyldibutylsilylene (SiBuPVK), poly(3,6-diformyl-*N*-(2-ethylhexyl)-carbazolyl)diphenyl(*n*-hexylmethyl)silylene (SiHMPVK), and poly(3,6-diformyl-*N*-(2-ethylhexyl)carbazolyl)tetraphenylsilylene (SiPhPVK) show two peaks of both a strong absorption band of the $\pi-\pi^*$ transition of the carbazole segments around 311 nm and a strong absorption band of the $\pi-\pi^*$ transition of the π-conjugated segment around 352 nm. Similar results were observed with the absorption maxima bands of SiPPV analogues in the thin film. As shown in the UV absorption spectra and photoluminescence spectra of the present polymer thin films coated on a carboglass, the maximum UV absorption wavelength (λ_{max}) of SiBuPVK has a strong absorption band at 353 nm, while the λ_{max} of SiPhPVK absorbs at 351 nm. Their spectra also include a strong absorption band around 312 nm, corresponding to the $\pi-\pi^*$ transition of the carbazole segments (see Figure 6).

The photoluminescence (PL) of the SiBuPVK polymer thin film coated on a carboglass is also shown in Figure 6. The PL spectra, associated with a blue emission,

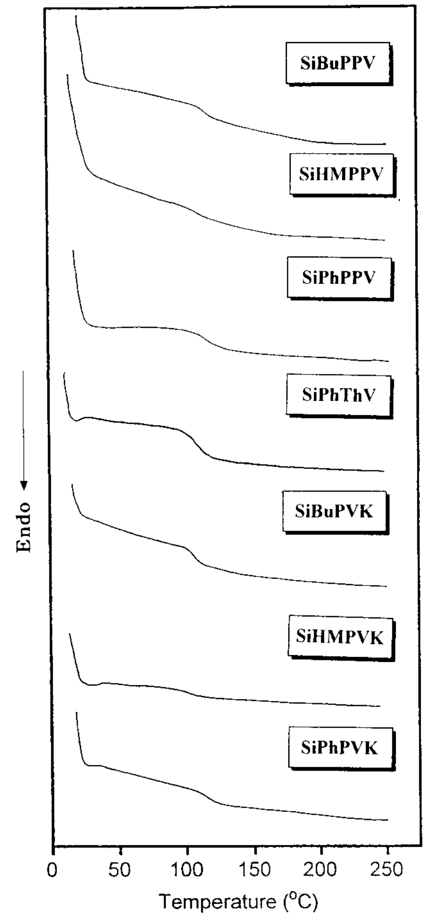
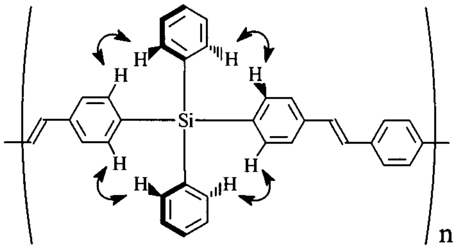


Figure 3. DSC thermograms of SiBuPPV, SiHMPPV, SiPhPPV, SiPhThV, SiBuPVK, SiHMPVK, and SiPhPVK.

Scheme 4. Constraint on the Free Rotation of the Si−C Bonds in the Main Chain via the Bulky Phenyl Side Chain Interactions in a SiPhPPV Thin Film of a Propeller-like Structure



SiPhPPV

show shifts similar to those observed in the absorption spectra. With an excitation wavelength of 351 nm, the PL spectra of SiBuPVK, SiHMPVK, and SiPhPVK give a peak in the blue emissive region at 420, 430, and 480 nm, respectively. Interestingly, these results indicate that the PL maximum peak is strongly dependent on the organic substituents on a silicon atom. This may be ascribed to the dependence of the degree of π-conjugated delocalization on the coplanarity of the main chain affected by the pendent side group interactions. These PL trends are similar to those of SiPPV analogues with different organic substituents on a silicon atom, as discussed above. The PL spectra of all present carbazole-containing polymers show a broad shoulder emissive band in the green range. These peaks can be attributed to the carbazole segment in the main chain, which was reported in previous articles.[14−16]

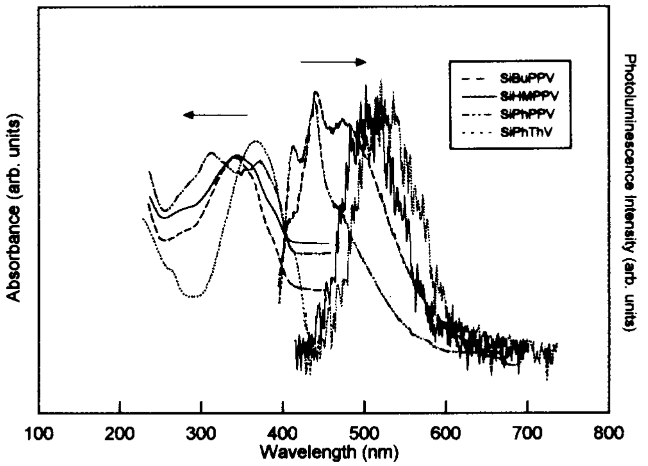


Figure 4. UV−visible spectra of SiBuPPV, SiHMPPV, SiPhPPV, and SiPhThV in $CHCl_3$ as well as PL spectra of SiBuPPV, SiHMPPV, SiPhPPV, and SiPhThV thin films coated on glass slides (excitation = 351 nm/400 nm).

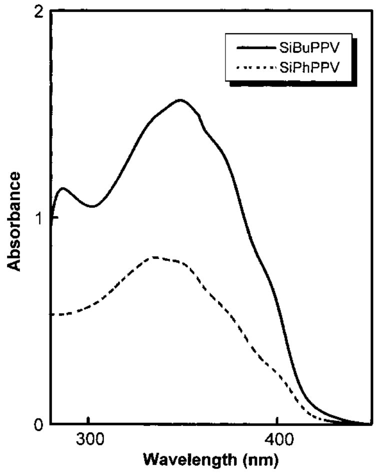


Figure 5. UV−visible spectra of silicon-containing poly(*p*-phenylenevinylene)-related polymer thin films coated on a carboglass: (a) SiBuPPV; (b) SiPhPPV.

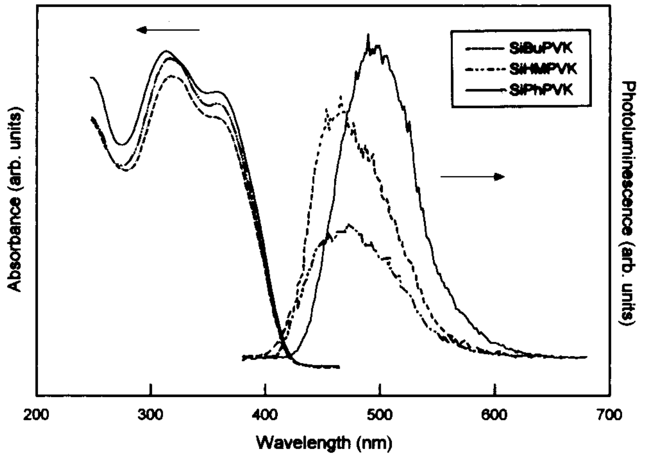
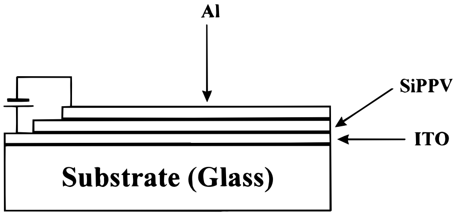


Figure 6. UV−visible spectra of SiBuPVK, SiHMPVK, and SiPhPVK in $CHCl_3$ as well as PL spectra of SiBuPVK, SiHMPVK, and SiPhPVK thin films coated on a carboglass (excitation = 351 nm).

Electroluminescent Property and Current−Voltage (*I*−*V*) Characteristics. Furthermore, the single layer light-emitting diode of a Al/SiPhPPV/ITO glass adopted for this study is shown in Chart 1. The silicon-containing poly(*p*-phenylenevinylene)-related co-

Chart 1. Device Structure of the Single-Layer Light-Emitting Diode of a Al/SiPPV/ITO Glass



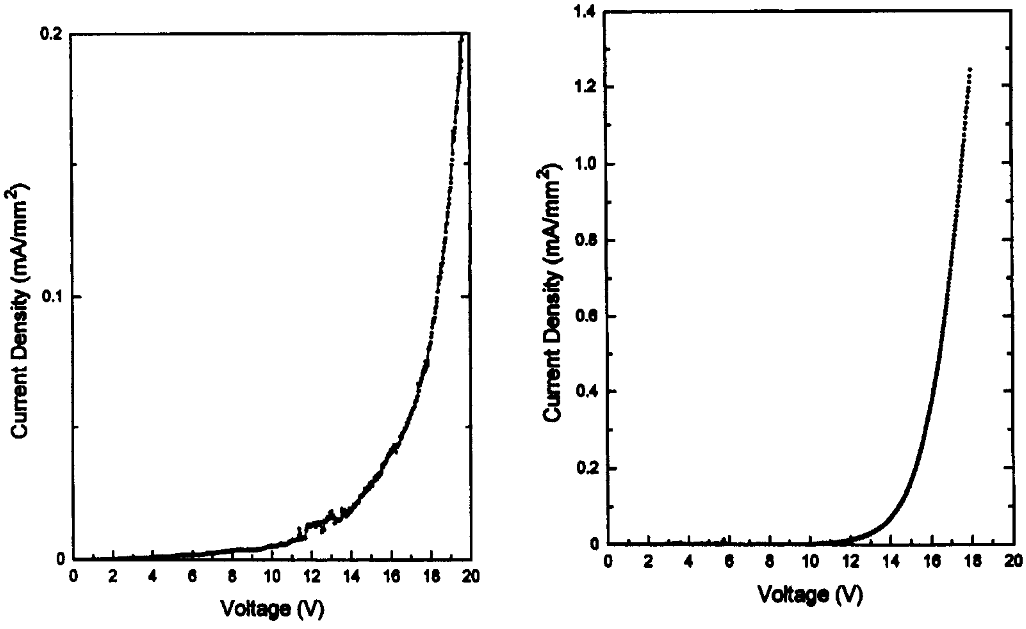
polymers described above were deposited onto indium–tin oxide-covered glass substrates by spin-casting the soluble polymers in 1,2-dichloroethane. The spin-casting technique yielded uniform films with nominal thicknesses of about 70 nm. For the single-layer devices, Al contacts were deposited on top of the spin-cast polymer layer.

Figure 7 shows the current–voltage (*I*–*V*) characteristics of the single-layer light-emitting diode of both a Al/SiPhPPV/ITO glass and a Al/SiPhPVK/ITO glass. The forward bias current is obtained when the ITO electrode is positively biased and the Al electrode negatively. The current increases with increasing forward bias voltage and the reverse bias current remains small, which are typical rectifying characteristics. As can be seen from the *I*–*V* curve, the threshold voltage is in the range of 6–12 V, which is considerably low compared with that of the PPV-based block copolymers.

The electroluminescence (EL) spectra and photoluminescence (PL) excited with 325 nm of ultraviolet light from the Hg–Cd laser for the SiPhPPV and the SiPhPVK polymer films are also shown in Figure 8. A similar PL result excited at 325 nm was obtained from excitation of the SiBuPPV thin film sample with 351 nm of ultraviolet light from the xenon lamp. For the SiPhPVK polymer film, however, the PL spectrum excited at 325 nm of ultraviolet light from the Hg–Cd laser shows a strong PL emissive peak at 425 nm and a weak PL emissive peak in the green region. The former and the latter were attributed to the π-conjugated segment and the carbazole unit, respectively. These results were very different from the PL peaks obtained from excitation of the SiPhPVK thin film sample excited with 351 nm of ultraviolet light from the Xenon lamp. It may be explained by either the energy transfer from the low energy level or the high energy level of carbazole units to the π-conjugated segments or the involvement of several excited states of a carbazole unit[14–16] induced from excitation with 325 nm of ultraviolet light from the Hg–Cd laser. This observation is being studied in more detail by the PL decay dynamics.[22,23]

The spectrum of the SiPhPPV gives a peak in the EL emissive band at 450 nm, at which the PL spectrum also appeared, when the operating voltage of 9 V was applied. This result indicates a blue emission. The EL spectrum of the SiPhPVK film sample shows a peak in the emissive band at 450 nm, when the operating voltage of 10 V was applied. Also, the EL spectrum of the present SiPhPVK polymer shows an additional strong EL emissive band in the yellow region, while the PL spectrum of the present SiPhPVK polymer shows an additional strong emissive band in the green region. This peak can be attributed to the carbazole segment in the main chain. Interestingly, the SiPhPVK gives a strong white emitting light, when an operating voltage of higher than 12 V was applied (see Figure 9). A similar observation was reported in previous articles.[14–16]

In summary, the organosilicon units with an aromatic or flexible aliphatic group improve their processability and limit the π-conjugation length, predicting blue light-emitting diodes, since the incorporation of a silicon unit with a flexible alkyl side group into the polymer rigid backbone would afford processable electroluminescent materials and the organosilicon units interrupt the regular π-conjugated chains.



(a) SiPhPPV (b)SiPhPVK

Figure 7. Current–voltage (*I*–*V*) characteristics of the single-layer light-emitting diode of a Al/SiPhPVK/ITO glass and a Al/SiPhPPV/ITO glass.

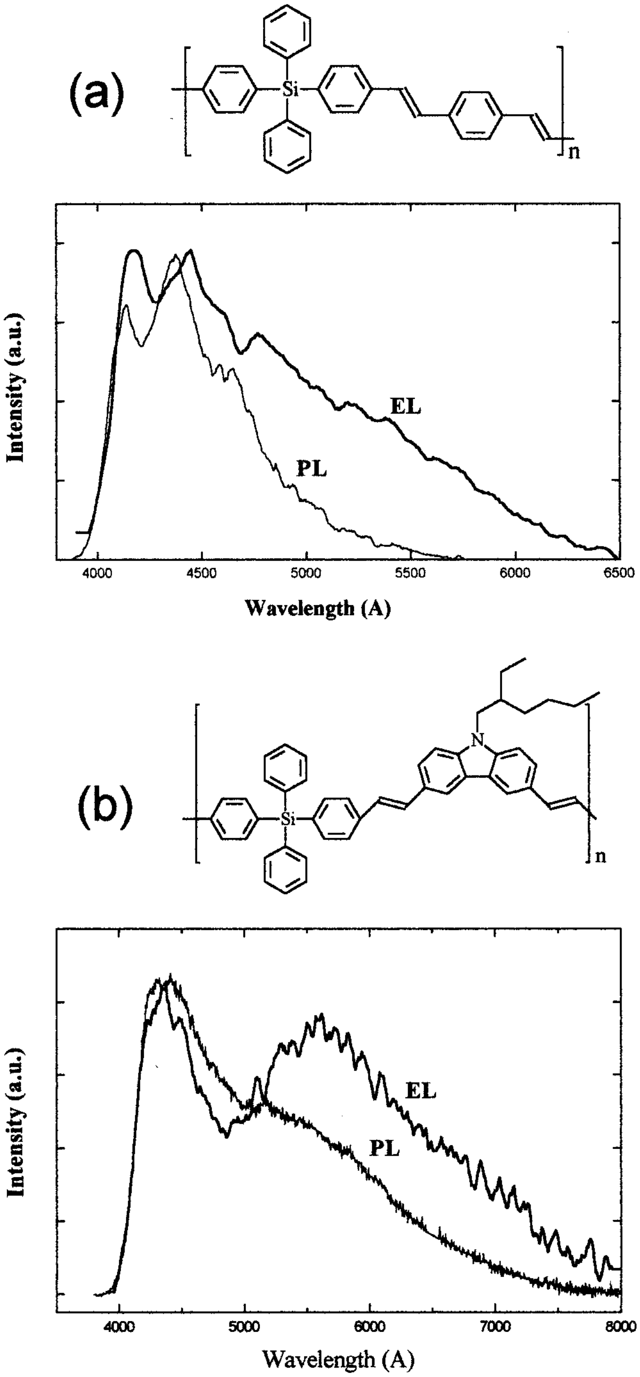


Figure 8. PL spectra excited with 325 nm of ultraviolet light from the Hg−Cd laser and electroluminescence (EL) spectra of the single-layer light-emitting diode of a Al/SiPhPVK/ITO glass and a Al/SiPhPPV/ITO glass.

Summary

A new class of silicon-containing poly(*p*-phenylenevinylene)-related copolymers with a uniform π-conjugated segment regulated by organosilicon units was synthesized by the well-known Wittig reaction between the appropriate diphosphonium salts and the dialdehyde monomers such as terephthaldicarboxaldehyde, 2,5-thiophenedicarboxaldehyde, and *N*-(2-ethylhexyl)-3,6-diformylcarbazole. The resulting polymers were highly soluble in common organic solvents. They could spin cast onto various substrates to give highly transparent homogeneous thin films without heat treatment. Their glass transition temperatures were in the range of 104−119 °C. The UV−visible absorbance of the present polymers shows strong absorption bands around 347−387 nm, which corresponds to the π−π* transition of the conjugated segments. Their maximum photoluminescence wavelengths for SiPPV analogues appeared around 420−480 nm in the blue emission region, except for a silicon-containing poly(*p*-phenylenevinylene)-related copolymer containing a thiophene unit, which showed a strong PL peak at around 520 nm in the green emission region. In the case of the polymers containing a carbazole unit, their PL spectra show both the highest peak in the PL emissive band at 450 nm and an additional strong emissive band in the green region. Single-layer light-emitting diodes of a Al/SiPhPPV or SiPhPVK/ITO glass are fabricated. The threshold voltage is in the range of 6−12 V from the *I*−*V* curve. The electroluminescence (EL) spectrum of SiPhPPV gives the highest peak in the EL emissive band at 450 nm, when the operating voltage of 9 V was applied. For the polymer containing a carbazole unit, the EL spectrum of the polymer shows the highest peak in the EL emissive band at 450 nm as well as an additional strong emissive band in the yellow region, when the operating voltage of 10 V was applied. Interestingly, the SiPhPVK gives a strong white emitting light, when the operating voltage of higher than 12 V was applied.

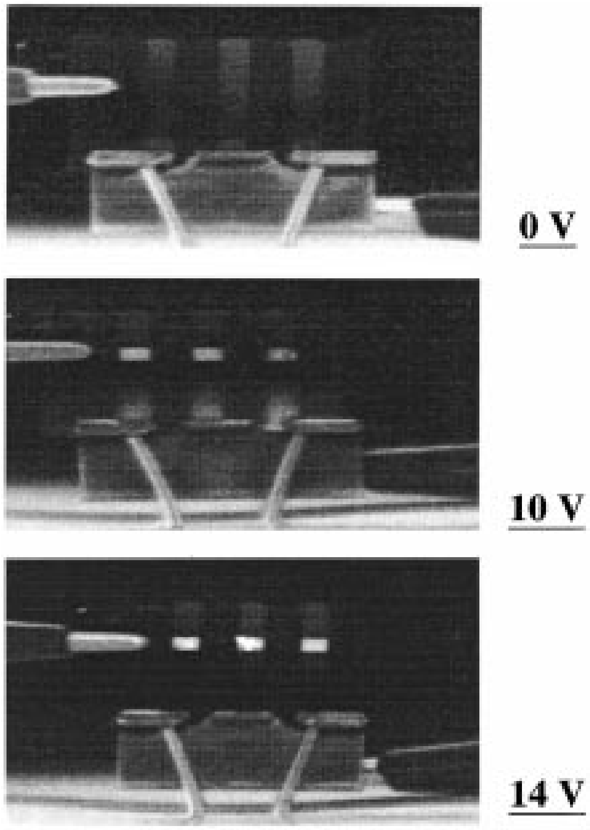


Figure 9. 9. Dependence of electroluminescent color on the applied voltage in the single layer light-emitting diode of a Al/SiPhPVK/ITO glass: no luminescence with 0 V; blue color with 10 V (gray in figure); white color with 14 V. A color version of this figure is available as Supporting Information.

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Supporting Information Available: A color version of Figure 9 (1 page). Ordering and accessing information is given on any current masthead page.

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