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Novel Silicon-Containing Poly(*p*-phenylenevinylene)-Related Polymers: Synthesis and Optical Properties

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Electroluminescent (EL) devices based on organic thin layers have attracted much attention because of their academic interest and the potential utility of this technology in a wide variety of applications such as flat-panel displays and light-emitting diodes.[1−7] Since the first report of 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]

Our group and other groups have recently reported new processable poly(*p*-phenylenevinylene)s with predictable emission wavelengths which could be achieved by introducing well-defined lumophores into the polymer main chain.[5,8] However, these polymers inevitably contain 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 materials requiring high threshold voltages which usually damage the polymeric materials. Therefore it seemed desirable to develop a 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 with 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.

Recently, we reported a new class of silicon-containing poly(*p*-phenylenevinylene) derivatives[9] having organosilicon units with aromatic or flexible aliphatic groups in the polymer main chain. These units improve processability and limit the π-conjugation length, predicting blue light-emitting diodes, since the incorporation of the silicon units with flexible alkyl side groups into the polymer rigid backbone affords processable electroluminescent materials and the organosilicon units interrupt the regular π-conjugated chains.[9,10] In this paper, we deal with the synthesis and optical properties of the first silicon-containing poly(*p*-phenylenevinylene)-related polymers in the main chain.

Monomer Synthesis. Di-*p*-tolyldibutylsilane (DTBS) (1).[11] *p*-Bromotoluene (35.3 g, 0.206 mol) in dry ether (18.5 mL) was added with efficient stirring during 3 h into a solution containing magnesium turnings (5.0 g) and dry ethyl ether (43.4 mL) at 10 °C under a nitrogen atmosphere. The reaction was stirred at room temperature for 2 h and cooled to 0 °C, and then a solution of dibutyldichlorosilane (20 g, 0.0938 mol) in dry ether (18 mL) was added dropwise during stirring. After the addition was completed, all solvent and unreacted dimethyldichlorosilane were removed by a vacuum evaporator and the reaction mixture was heated for an additional 18 h at 160 °C. The crude product was poured into cold water to yield the salts, which were removed by filtration on glass wool, and then diluted with ether (150 mL). The two-phase solution was vigorously stirred for 1 h, and the ether layer was washed with water, 5% HCl, 5% NaOH, and water and then dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was distilled under vacuum. The fraction of slightly yellow liquid at 162−164 °C under 0.1 mmHg was collected and the yield was 73%. IR (neat, cm^{-1}): 1210, 964, 885 (Si−aliphatic); 1105, 750 (Si−Ph). ^{1}H-NMR ($CDCl_3$, ppm): 1.2−1.7 (m 18H, Si−aliphatic); 2.7 (s, 6H, aryl CH); 7.5−7.8 (q, 8H, aryl CH).

Di-*p*-tolyldiphenylsilane (DTPS) (2).[11] To a refluxing solution of lithium (4.2 g, 0.6 mol) and dry ethyl ether (60 mL) was slowly added *p*-bromotoluene (51.3 g, 0.3 mol) in dry ether (60 mL) under a nitrogen atmosphere. The reaction was continuously stirred at room temperature for 2 h, and a solution of dichlorodiphenylsilane (38.1 g, 0.15 mol) in dry ether (60 mL) was added dropwise with stirring. After the addition was completed, the reaction mixture was refluxed for 3 h, and 9 mL of hydrochloric acid (10%) was added to remove the excess of lithium. The resulting suspension was filtered, and then the solvent and unreacted dichlorodiphenylsilane were removed. The resulting crude product was recrystallized from ethanol to give 48 g (90%) of **2** as a white powder, mp 118−120 °C. IR (KBr pellet, cm^{-1}): 1425, 1105, 700 (Si−Ph). ^{1}H-NMR (DMSO-d_6, ppm): 2.25 (s, 6H, aryl CH); 7.6−7.2 (m, 18H, aryl CH).

Bis(*p*-(bromomethyl)phenyl)dibutylsilane (3). Di-*p*-tolyldibutylsilane (10 g, 0.0308 mol), *N*-bromosuccinimide (12.06 g, 0.0678 mol), and benzoyl peroxide (0.056 g) were dissolved in 400 mL of CCl_4 under a nitrogen atmosphere. The mixture was heated at reflux for 48 h. The reaction mixture was cooled to 50 °C and the succinimide was filtered off at 50 °C. After the solvent was evaporated, a viscous oil was obtained. A yellow product was obtained by column chromatography (silica gel, with hexane/ethyl acetate (5/1) as an eluent). The yield was 12 g (74%). IR (neat, cm^{-1}): 1210, 964, 885 (Si−aliphatic); 1105, 750 (Si−Ph); 1410, 1296, 798 (Ph−CH_2Br). ^{1}H-NMR ($CDCl_3$, ppm): 0.8−1.4 (m 18H, Si−aliphatic); 4.5 (s, 4H, aryl CH); 7.4−7.5 (q, 8H, aryl CH).

Bis(*p*-(bromomethyl)phenyl)diphenylsilane (4). To a stirred solution of **2** (3 g, 0.008 mol) in 400 mL of dry carbon tetrachloride were added 0.75 mol % of benzoyl peroxide and *N*-bromosuccinimide (2.9 g, 0.016 mol) at room temperature under a nitrogen atmosphere. The mixture was heated at reflux for 24 h. After the reaction mixture was cooled, the succinimide was filtered off, the solvent was evaporated away, and the crude product was washed with water to remove the residual succinimide. Finally, the resulting solid product was recrystallized twice from carbon tetrachloride to give 1.0 g (30%) of **4**, mp 220 °C. IR (KBr pellet, cm^{-1}): 1425, 1105, 700 (Si−Ph); 1296, 798 (Ph−CH_2-Br). ^{1}H-NMR ($CDCl_3$ ppm): 4.5 (s, 4H, aryl CH); 7.2−7.5 (m, 18H, aryl CH).

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Bis((triphenylphosphoniomethyl)phenyl)dibutylsilane Dibromide (5). A solution of bis(*p*-(bromomethyl)phenyl)dibutylsilane (2.15 g, 0.0045 mol) and triphenylphosphine (2.57 g, 0.0098 mol) in 10 mL of DMF was stirred and heated to reflux for 24 h. The reaction system was cooled to room temperature and poured into 500 mL of dried ethyl acetate. The resulting precipitate was filtered off and dried under high vacuum at 40 °C for 2 days. Yield 55%. IR (KBr pellet, cm^{-1}): 1210, 964, 885 (Si−aliphatic); 1105, 750 (Si−Ph); 1410, 1296, 798 ($\mathrm{Ph{-}CH_2Br}$); 1435, 741, 698 ($\mathrm{PPh_3}$) ^{1}H-NMR ($\mathrm{CDCl_3}$, ppm): 0.7−1.2 (m 18H, Si−aliphatic); 5.1 (d, 4H, aryl CH); 7.0−8.0 (m, 38H, aryl CH).

Bis((triphenylphosphoniomethyl)phenyl)diphenylsilane Dibromide (6). A solution of bis(*p*-(bromomethyl)phenyl)diphenylsilane (1.0 g, 0.002 mol) and triphenylphosphine (1.5 g, 0.005 mol) in 10 mL of DMF was stirred and heated to reflux for 24 h. The reaction system was cooled to room temperature and poured into 300 mL of dried ethyl acetate. The resulting precipitate was filtered off and dried under vacuum at 40 °C for 2 days. Yield 66%, mp 163 °C. IR (KBr pellet, cm^{-1}): 1425, 1105, 700 (Si−Ph); 1296, 798 ($\mathrm{Ph{-}CH_2{-}Br}$); 1435, 750, 685 ($\mathrm{PPh_3}$). ^{1}H-NMR ($\mathrm{CDCl_3}$, ppm): 5.4 (d, 4H, aryl CH); 7.1−7.8 (m, 40H, aryl CH).

Polymerization.[8] Copoly(dibutylsilane/phenylene/bis(phenylenevinylene)) (SiBuPPV). To a stirred solution of an equimolar amount of terephthaldicarboxaldehyde (0.113 g, 0.99 mmol) and bis((triphenylphosphoniomethyl)phenyl)dibutylsilane dibromide (1.0 g, 0.99 mmol) in 30 mL of absolute ethanol and 10 mL of chloroform was added dropwise a solution of 0.18 g of sodium methoxide in 10 mL of absolute ethanol at ambient temperature under a nitrogen atmosphere. The mixture was stirred for 12 h after addition. The pastelike product was collected in the wall of the flask. The polymer was filtered and dried in a vacuum drying oven. The crude polymeric product was dissolved in methylene chloride, washed with water, and dried with anhydrous magnesium sulfate ($\mathrm{MgSO_4}$), and the solvent was evaporated. The obtained polymer was dried in a vacuum oven at 40 °C for 2 days, yielding 21% of yellow polymeric product. It was subsequently isomerized to the all-trans configuration by refluxing for 4 h in toluene in the presence of a catalytic amount of iodine. Copoly(diphenylsilane/phenylene/bis(phenylenevinylene)) was similarly prepared.

Results and Discussion. The synthetic routes to the monomers and the silicon-containing poly(*p*-phenylenevinylene)-related polymers are described in Scheme 1. The Grignard reaction between *p*-tolylmagnesium bromide and dialkyldichlorosilane yields alkyl-substituted silane synthetic products with high conversion. Treatment of the di-*p*-tolylsilane derivatives with *N*-bromosuccinimide in the presence of carbon tetrachloride and benzoyl peroxide yields brominated intermediates **3** and **4** in a radical chain manner. Reaction of **3** and **4** with triphenylphosphine in dried DMF leads to the bis((triphenylphosphonomethyl)phenyl)dialkylsilane dibromide salts **5** and **6**. Finally, monomer salts **5** and **6** were stored dry in a desiccator before use.

The silicon-containing poly(*p*-phenylenevinylene) derivatives were synthesized by the well-known Wittig reaction between the dialdehyde monomer and the appropriate diphosphonium salts, as shown in Scheme 1. The polymerization results of silicon-containing PPVs are summarized in Table 1. The number-average molecular weights (M_n) and the polydispersities of the resulting polymers, as determined by gel permeation chromatography using polystyrene standards, were in the range 2500−2800 and 1.46−1.49, respectively. The resulting polymers were highly soluble in common organic solvents such as THF, chloroform, methylene chloride, 1,2-dichloroethane, acetone, DMF, DMSO, and so on. This implies that the introduction of silicon atoms with side organo substituents in the rigid polymer backbone can enhance the solubility of PPVs, due to the reduced crystallinity by side chain interactions. The thermal behavior of the silicon-containing PPVs was evaluated by means of DSC under a nitrogen atmosphere. Also, the thermal properties of the polymers are presented in Table 1. All PPV polymers did not show any melting points. This means that the silicon-containing PPV polymers could be amorphous. The PPV polymers have T_g values in the range 105−109 °C. The T_g of SiPhPPV is a little higher than that of SiBuPPV. This indicates that the bulky phenyl group in SiPhPPV gives a little more rigid structure than the flexible butyl group due to steric hindrance between the

Scheme 1. Synthesis of Bis((triphenylphosphoniomethyl)phenyl)organosilane Dibromides and Silicon-Containing Poly(*p*-phenylenevinylene)-Related Polymers

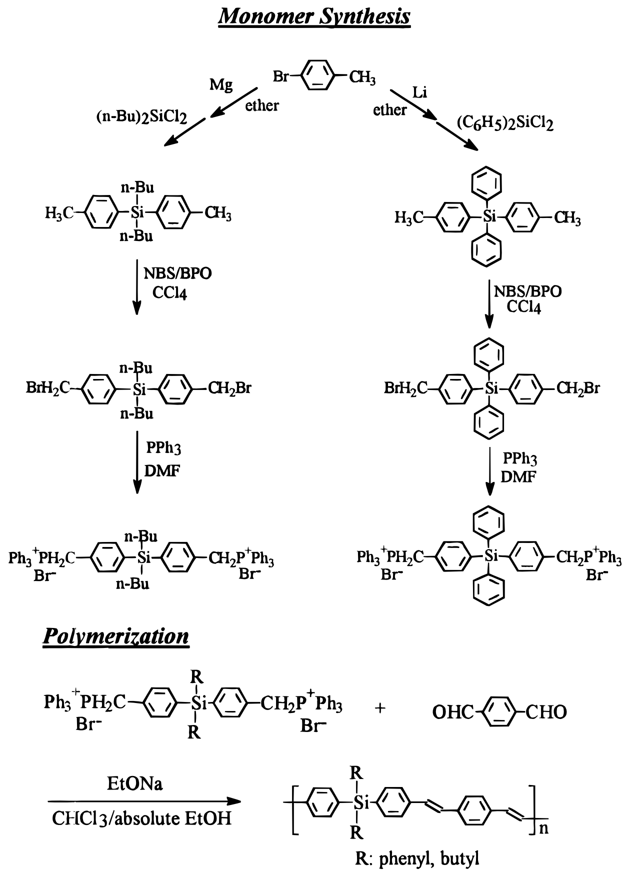

Table 1. Polymerization Results and Thermal and Optical Properties of Silicon-Containing Poly(*p*-phenylenevinylene)-Related Polymers

polymers	yield (%)	M_n[a]	M_w[a]	PD	T_g (°C)	UV λ_{max} (nm)	PL λ_{max} (nm)
SiBuPPV	21	2500	3700	1.48	105	347	440
SiPhPPV	26	2800	4100	1.50	109	375	450, 480

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

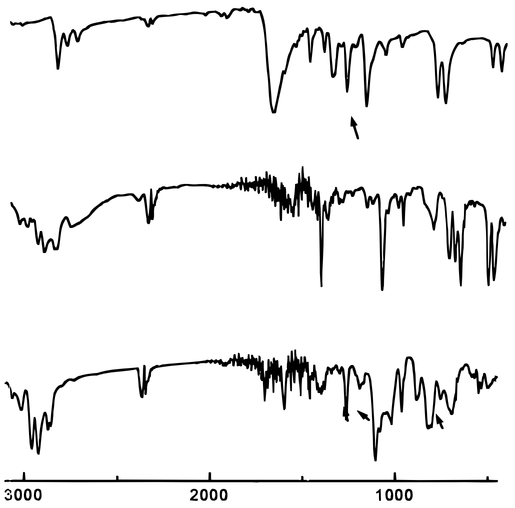

Figure 1. IR spectra of copoly(dibutylsilane/phenylene/bis(phenylenevinylene)) (SiBuPPV) and the starting monomers in KBr pellets.

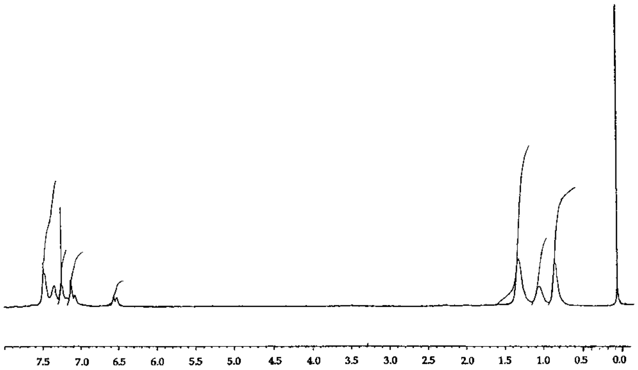

Figure 2. ^{1}H NMR spectrum of copoly(dibutylsilane/phenylene/bis(phenylenevinylene)) (SiBuPPV) in CDCl$_3$.

four surrounding phenyl groups on the silicon atom in SiPhPPV.

The structure of the resulting polymers was identified by FT-IR, ^{1}H-NMR, and UV–visible spectroscopy. Figure 1 shows the typical FT-IR spectra of the PPV containing the dibutylsilyl group (SiBuPPV), dialdehyde, and diphosphonium salt. The comparison of the FT-IR spectrum of the polymer with that of the starting monomers showed drastic decrease of the bands at 1686 cm^{-1}, which is present for the strong aldehyde carbonyl stretching band of the dialdehyde monomer. On the other hand, a weak sharp absorption peak at 960 cm^{-1}, which corresponds to the out-of plane bending mode of the *trans*-vinylene groups appeared, indicating that the newly formed vinylene double bonds are mainly in the trans configuration. Figure 2 shows the ^{1}H-NMR spectrum of the poly(*p*-phenylenevinylene) containing the dibutylsilyl group (SiBuPPV). As the polymerization proceeded, the aldehyde peak of the monomer present at 9.84 ppm disappeared and new vinylic proton peaks appeared at 6.5 (doublet) and 7.45 ppm overlapped with aromatic protons. Also the broad peak around 0.8–1.3 ppm was assigned to the butyl protons adjacent to the silicon atom.

Figure 3 shows the UV absorption spectra of the two SiPPV derivatives (SiPhPPV and SiBuPPV) in chloroform solution and the photoluminescence spectra of these thin films coated on a carboglass. As shown in the absorption spectra, the wavelength of the maximum absorption ($\lambda_{\max}$) of SiPhPPV has a strong absorption band at 375 nm, which is attributed to the $\pi-\pi^*$ transition of the conjugated segment, while the $\lambda_{\max}$ of SiBuPPV absorbs at 347 nm (see Figure 3a,b). As indicated by the red shift of the absorption maxima bands resulting from the $\pi-\pi^*$ transition of the conjugated polymer backbone, the attachment of the phenyl group into the silane atom forces the π-conjugated segment to be more planar via the bulky phenyl side chain interactions. A similar behavior was observed from the DSC analysis. The photoluminescence (PL) spectra of these polymer films coated on a carboglass are also shown in Figure 3. The PL spectra show similar shifts to those observed in the absorption spectra. With an excitation wavelength of 351 nm, the SiBuPPV spectrum gives a peak in the emission spectrum at 440 nm, indicating a blue emission. In comparison, the PL spectrum of SiPhPPV red-shifted to the emission spectra at two maximum peaks of both 450 and 480 nm in the blue region. Interestingly, the present silicon-containing PPV-related polymers have shown strong blue shifts relative to PPV.[12,13] These results indicate that the regular π-conjugated system was effectively interrupted by the organosilicon units, yielding a blue emission. The electroluminescence and current–voltage characteristics of light-emitting diode structures fabricated with the present polymers and the synthesis of silicon-containing PPV-related polymers with the high electron affinity cyano group or carbazole group are being investigated.

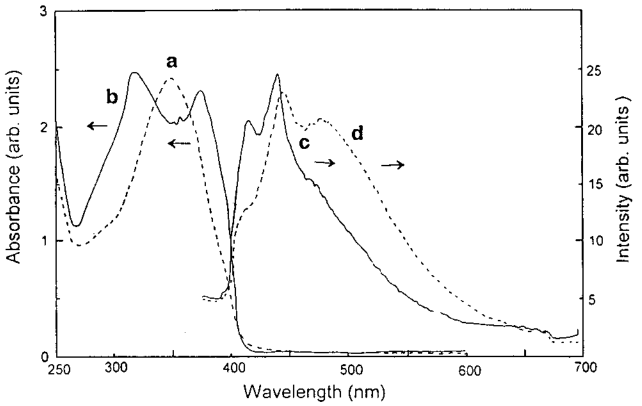

Figure 3. UV–visible absorption specta of silicon-containing poly(*p*-phenylenevinylene)-related polymers: (a) SiBuPPV and (b) SiPhPPV in CHCl$_3$. Photoluminescence spectra of silicon-containing poly(*p*-phenylenevinylene)-related polymer thin films coated on carboglass: (c) SiBuPPV and (d) SiPhPPV.

Summary. A new class of silicon-containing poly(*p*-phenylenevinylene) derivatives were synthesized using the well-known Wittig reaction between the dialdehyde monomer and the appropriate diphosphonium salts. The resulting polymers were highly soluble in common organic solvents. They could be spin cast onto a glass plate to give highly transparent homogeneous thin films. The present polymers have strong absorption bands around 345–375 nm, which corresponds to the $\pi-\pi^*$ transition of the conjugated segments. Their photoluminescence spectra appeared around 440–480 nm, in the blue emission region, since the π-conjugated system is regulated by the organosilicon unit.

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