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# Blue Electroluminescence from Novel Silicon-Containing Poly(Cyanoterephthalylidene) Copolymers

**Ki-Dong Kim, Jin-Sung Park, and Hwan Kyu Kim***

*Optoelectronic Polymer Laboratory, Departments of Macromolecular Science, Hannam University, Taejon 306-791, Korea*

**Tae Bum Lee and Kyoung Tai No**

*Computer Aided Molecular Design Research Center and Department of Chemistry, Soong Sil University, Seoul 156-743, Korea*

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ABSTRACT: A new class of silicon-containing poly(cyanoterephthalylidene) copolymers with a uniform $\pi$-conjugated segment was synthesized using the Knoevenagel reaction between the dialdehyde monomer and the appropriate diacetonitrile. The incorporation of organosilicon units with the flexible alkyl side group into the polymer rigid backbone would afford processable electroluminescent materials and interrupt the regular $\pi$-conjugated chains. The resulting polymers were highly soluble in common organic solvents. The $M_n$ and $M_w$ of the resulting polymers are in the range 3800−4200 and 5400−6000 with a polydispersity index range of 1.38−1.43, respectively. Their glass transition temperature was in the range of 82−87 °C. According to the molecular mechanical calculations for single chain models of SiBuPPV and SiBuCNPPV, trans conformations are more stable than cis conformations. The UV−visible absorbance of present polymers show strong absorption bands around 340−360 nm, since the $\pi$-conjugated system is regulated by organosilicon units. Their photoluminescence spectra appeared around 460−470 nm in the blue region. The threshold voltage of the SiHMCNPPV was about 7 V. Surprisingly, these polymers exhibit blue light-emitting diodes in the EL emissive band at 480 nm in the blue region, instead of red light-emitting diodes, when an operating voltage of higher than 7 V is applied. These copolymers show a relatively low operating voltage compared with a block copolymer having well-defined structures because the incorporation of electron-withdrawing cyano groups into the $\pi$-conjugated system increased the electron affinity of those polymers and decreased the LUMO energy level.

## Introduction

Electroluminescence (EL) devices based on organic thin layers have attracted much attention because of their wide variety of applications such as flat-panel displays, light-emitting diodes, and lasers.[1−8] 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 to obtain high performance devices from polymeric materials.[9,10] In recent reports, the main material efforts have been focused on developing blue light-emitting diodes capable of operating at ambient temperature, low operating voltages and easy processability with low price.[11−13] Previously, processable poly(*p*-phenylenevinylene)s with a short $\pi$-conjugated length were realized by introducing a saturated group or a nonconjugated spacer group to a well-defined lumophores, yielding blue EL polymers. These EL polymers required the materials with high threshold voltages or operating voltages. To reduce the operating voltages, Holmes et al. synthesized a class of poly(cyanoterephthalylidene) derivatives with a relatively high electron affinity cyano group by the Knoevenagel reaction.[4,14] It showed a relatively low threshold voltage and high quantum efficiency compared with PPV because the introduction of a high electron affinity CN group to $\pi$-conjugated polymer system lowers the energy level of LUMO and reduces the energy barrier to the electron injection. However, the electroluminescence (EL) spectrum showed a peak around 710 nm in the red region. Internal quantum efficiencies of over 4% were achieved in a two-layer device, ITO/PPV/CN−PPV/Al.

Very recently 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.[5] The organosilicon units with aromatic or flexible aliphatic group improved their processability and limited the $\pi$-conjugation length, resulting in blue light-emitting diodes.[5,6,15] Surprisingly, silicon-containing copolymers with a relatively short $\pi$-conjugation length exhibited blue light-emitting diodes operating at the low voltages, due to the reduction of the LUMO level in luminescent polymers.[16]

In this paper, we report a new type of processable poly(cyanoterephthalylidene) copolymers containing organosilyl units in the main chain. The incorporation of organosilicon units with the flexible alkyl side group into the polymer rigid backbone would afford processable electroluminescent materials and interrupt the regular $\pi$-conjugated chains. Surprisingly, these polymers exhibit blue light-emitting diodes, instead of red light-emitting diodes.[4,14] Also, they show a relatively low threshold voltage compared to a block copolymer having well-defined structures because the incorporation of electron-withdrawing cyano groups into the $\pi$-conjugated system increased the electron affinity of those polymers and decreased the LUMO energy level. Here, we describe the synthesis and characterization of a new type of processable poly(cyanoterephthalylidene) copolymers containing organosilyl units in the main chain.

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* To whom all correspondence should be addressed.

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## Materials and Methods

Terephthaldicarboxaldehyde, dibenzoyl peroxide, *p*-bromotoluene, *N*-bromosuccinimide, and sodium cyanide were purchased from Aldrich and used without further purification. Di-*n*-butyldichlorosilane 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.** Di(*p*-bromomethylphenyl)-di-*n*-butylsilane and di(*p*-bromomethylphenyl)-*n*-hexylmethylsilane were synthesized in a cited reference.[5]

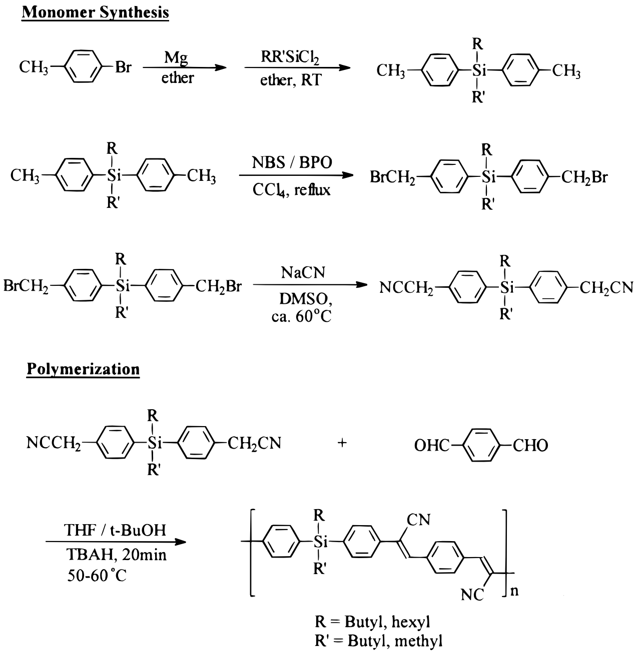
**Di(*p*-cyanomethylphenyl)-di-*n*-butylsilane.** Dry powdered sodium cyanide (0.51 g, 0.0104 mol) in 10 mL of DMSO was heated to 90 °C while being stirred. A solution of di(*p*-bromomethylphenyl)di-*n*-butylsilane (2.0 g, 0.0041 mol) in DMSO (3 mL) was added dropwise to the mixture so that the temperature of the exothermic reaction does not rise above 150 °C. The reaction mixture was stirred until the temperature fell to 50 °C. The reaction mixture was poured into water and extracted with three 300 mL portions of ethyl ether. The ethyl ether layer was washed with saturated sodium chloride and then dried over anhydrous magnesium sulfate. After ethyl ether was evaporated off, the resulting viscous oil was obtained. A dark brown pure product was obtained by silica gel column using eluting solvent (hexane: ethyl acetate = 1:5). The product yield was 73%. IR (KBr pellet, cm$^{-1}$): 1210, 964, 885 (Si−aliphatic); 1105, 750 (Si−Ph); 2250 (Ph-CH$_2$CN). $^1$H NMR (CDCl$_3$, ppm): 0.7−1.2 (m 18H, Si−aliphatic); 3.7 (s, 4H, aryl CH$_2$); 7.0−8.0 (m, 8H, aromatic CH). $^{13}$C NMR (CDCl$_3$, ppm): 13.9, 22.3, 26.6, 28.6 (Si(CH$_2$)$_3$CH$_3$), 25.2 (CH$_2$CN), 127.3, 130.4, 135.5, 136.4 (aromatic carbon). Anal. Calcd for (SiC$_{24}$H$_{30}$N$_2$): Si, 7.50; C, 76.95; H, 8.07; N, 7.48. Found: Si, 7.55; C, 76.75; H, 8.17; N, 7.53. Mass spectra: *m*/*z* 374 [M]$^+$, 348 [M − CN]$^+$, 317 [M − C$_4$H$_9$]$^+$, 258 [M − C$_7$H$_6$N]$^+$.

**Di(*p*-cyanomethylphenyl)-*n*-hexylmethylsilane.** Di(*p*-cyanomethylphenyl)-*n*-hexylmethylsilane was synthesized by a synthetic method similar to that used for di(*p*-cyanomethylphenyl)di-*n*-butylsilane. The product yield was 69%. IR (KBr pellet, cm$^{-1}$): 1210, 964, 885 (Si−aliphatic); 1105, 750 (Si−Ph); 2250(Ph−CH$_2$CN). $^1$H NMR (CDCl$_3$, ppm): 0.7−1.2 (m 18H, Si−aliphatic); 3.7 (s, 4H, aryl CH$_2$); 7.0−8.0 (m, 8H, aromatic CH). $^{13}$C NMR (CDCl$_3$, ppm): 14.1, 15.8, 23.4, 28.1, 32.3, 34.7 (Si(CH$_2$)$_5$CH$_3$), −0.4 (SiCH$_3$), 25.2 (CH$_2$CN), 127.3, 130.4, 135.5, 136.4 (aromatic carbon). Anal. Calcd for (SiC$_{23}$H$_{28}$N$_2$): Si, 7.79; C, 76.61; H, 7.83; N, 7.77. Found: Si, 7.85; C, 76.66; H, 7.95; N, 7.54. Mass spectra: *m*/*z* 360 [M]$^+$, 334 [M − CN]$^+$, 275 [M − C$_6$H$_{13}$]$^+$, 244 [M − C$_7$H$_6$N]$^+$.

**Polymerization.**[4] **Synthesis of Poly(di-*n*-butyldiphenylsilylcyanoterephthalylidene) (SiBuCNPPV) and Poly(*n*-hexylmethyldiphenylsilylcyanoterephthalylidene) (SiHMCNPPV).** Under a nitrogen atmosphere, to a stirred solution of equimolar quantities of terephthaldicarboxaldehyde (0.113 g, 0.99 mmol) and di(*p*-cyanomethylphenyl)-di-*n*-butylsilane, tetrahydrofuran, and *tert*-butyl alcohol (1:1) was added dropwise 5 mol % of (C$_4$H$_9$)$_4$NOH (TBAH, 1 M solution in methanol) at 50−60 °C for 20 min. The resulting pastelike polymeric product, which precipitated from the solution during polymerization, was collected and thoroughly washed with methanol to remove ionic species and unreacted compounds. The obtained polymer was dried in a vacuum oven at 40 °C for 2 days to give 23% of a brown polymer, poly(di-*n*-butyldiphenylsilylcyanoterephthalylidene) (SiBuCNPPV). Poly(*n*-hexylmethyldiphenylsilylcyanoterephthalylidene) (SiHMCNPPV) was synthesized by a synthetic method similar to that for poly(di-*n*-butyldiphenylsilylcyanoterephthalylidene).

**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 a solvent for recording NMR spectra. Infrared spectra were measured as neat oil or KBr pellets on a Perkin-Elmer spectrometer. Electron impact mass spectra (EIMS) were recorded on a JEOL JMS-DX 303 mass spectrometer. Samples were dissolved in THF. Elemental analyses were obtained with the use of Fisons Instrument EAGER 200. Molecular weights and polydispersities of polymers were determined by gel permeation chromatography (GPC) analysis with polystyrene standards calibration (Waters high-pressure GPC assembly Model M590 pump; $\mu$-Styragel columns of 10$^5$, 10$^4$, 10$^3$, 500, and 100 Å; a refractive index detector; THF solvent). 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 chopping frequency of 150 Hz, and the polymer films were excited with 350 nm of ultraviolet light from the xenon lamp. The polymer thickness of about 130−150 nm was obtained at a rate of 2500 rpm for 15 s with 5 mol % of solution in 1,2-dichloroethane. A DuPont 990 thermal analyzer attached to 951 TGA and 910S DSC modules was used to record thermal gravimetric analysis and differential scanning calorimetry (DSC), respectively. Melting point determinations were made using a Fisher-Johns melting point apparatus. To calculate the relative stability between cis and trans conformations of the polymers, as well, molecular mechanical calculations were carried out with both SiBuPPV (poly(di-*n*-butyldiphenylsilylphenylenevinylene)) and SiBuCNPPV (poly(di-*n*-butyldiphenylsilylcyanoterephthalylidene)). All the geometrical parameters were optimized during molecular mechanical (MM) calculations. Since the model compounds contain Si atoms, the Dreiding 2.21 force field was used. All the calculations were carried out with Cerius 2.[17]

**Scheme 1. Synthesis of the Silicon-Containing Diacetonitrile Monomers and Their Polymerization**



## Results and Discussion

Scheme 1 shows the synthetic routes to di(*p*-cyanomethylphenyl)alkylsilane monomers and polymerization. The monomer synthesis of di(*p*-cyanomethylphenyl) dialkylsilanes was achieved by the reaction between di(*p*-bromomethylphenyl) dialkylsilane and sodium cyanide in DMSO. The chemical structure of the final monomers was identified by FT-IR and $^1$H and $^{13}$C NMR. The typical FT-IR spectrum of di(*p*-cyanomethylphenyl)hexylmethylsilane shows the sharp absorption peak of a CN stretching band around 2250−2300 cm$^{-1}$ (see Figure 1a). The silicon-containing poly(cyanoterephthalylidene) copolymers were synthesized by using the well-known Knoevenagel reaction between the terephthaldicarboxaldehyde monomer and the appropri-

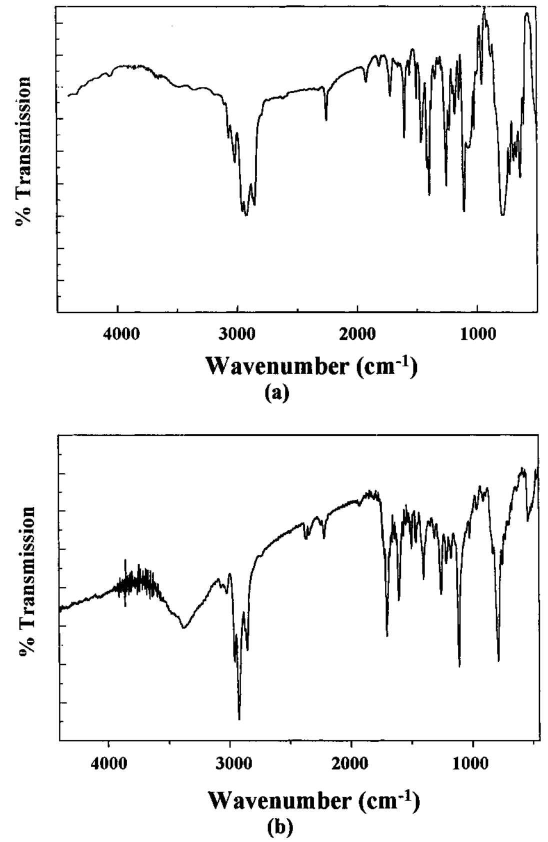


**Figure 1.** FT-IR spectrum of (a) di(*p*-cyanomethylphenyl)-*n*-hexylmethylsilane and (b) poly(*n*-hexylmethyldiphenylsilylcyanoterephthalylidene) (SiHMCNPPV).

**Table 1. Polymerization Results and Thermal and Optical Properties of Silicon-Containing Poly(cyanoterephthalylidene) Copolymers**

| polymers | yield (%) | $M_n$[a] | $M_w$[a] | PDI | $T_g$ (°C) | $\lambda_{max}$ (nm) UV | PL |
|---|---|---|---|---|---|---|---|
| SiBuCNPPV | 23 | 4200 | 6000 | 1.43 | 87 | 356 | 464 |
| SiHMCNPP | 25 | 3800 | 5400 | 1.38 | 82 | 345 | 466 |

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

ate diacetonitrile. The resulting pastelike polymeric product was precipitated from the solution during polymerization, collected, and thoroughly washed with methanol to remove ionic species and unreacted compounds. The polymerization results and thermal and optical properties of silicon-containing 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 3800−4200 and 5400−6000 with a polydispersity index of 1.38−1.43, respectively. All of the synthesized polymers were highly soluble in common organic solvents such as tetrahydrofuran, chloroform, methylenechloride, 1,2-dichloroethane, DMF, etc. (see Table 2). The incorporation of organosilicon units with the flexible alkyl side group into the polymer rigid backbone would afford processable electroluminescent materials. It implies that the introduction of organosilicon units in the rigid polymer backbone can cause chain stiffness to be reduced, enhancing the solubility of poly(cyanoterephthalylidene)s.

**Table 2. Solubility Behavior of Silicon-Containing Poly(cyanoterephthalylidene) Copolymers[a]**

| solvent | polymers SiBuCNPPV | SiHMCNPPV |
|---|---|---|
| *n*-hexane | − | − |
| methanol | − | − |
| acetone | + | + |
| chloroform | + | + |
| methylene chloride | + | + |
| THF | + | + |
| 1,4-dioxane | + | + |
| 1,2-dichloroethane | + | + |
| toluene | + | + |
| DMSO | + | + |
| DMF | + | + |

[a] Key: (−) insoluble; (+) soluble.

FT-IR, $^1$H NMR, and UV−visible spectrometry characterized the chemical structure of the resulting polymer. Figure 1b shows the typical FT-IR spectrum of poly(*n*-hexylmethyldiphenylsilylcyanoterephthalylidene) (SiHMCNPPV). The comparison of the polymer FT-IR spectrum with that of the monomer showed a drastic decrease of the bands at 1686 cm$^{-1}$, which is expected to be present for the strong aldehyde carbonyl stretching band of the dialdehyde monomer. On the other hand, a new sharp absorption peak at 815 cm$^{-1}$, which corresponds to the out-of-plane bending mode of the vinylene groups appeared, indicating that the vinylene double bonds newly formed are mainly of the trans configuration instead of the cis configuration.

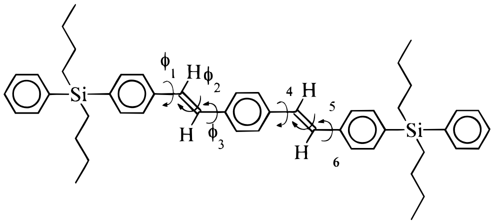
To calculate the relative stability between cis and trans conformations of the polymers, molecular mechanical calculations were carried out with both SiBuPPV and SiBuCNPPV. Since we are interested in only the contributions from the local interaction of functional groups to the stabilization energies of trans and cis conformations, two model compounds were introduced in the calculation (see Schemes 2). All the geometrical parameters were optimized during MM calculations. Since the model compounds contain Si atoms, the Dreiding 2.21 force field was used. All the calculations were carried out with Cerius 2.[17] For each model there are six torsion angles which contribute much to the internal energy. Those angles are designated as $\phi_1$, $\phi_2$, $\phi_3$, $\phi_4$, $\phi_5$, and $\phi_6$ (Chart 1).

Each model compound has three stable minimum energy conformations because the dihedral angles $\phi_2$ and $\phi_5$ have deep energy minima at 0 and 180°. Those conformations correspond to trans−trans, cis−trans, and cis−cis conformations. The energy barriers for the cis to trans isomerization are about 20 and 32 kcal/mol for SiBuPPV and SiBuCNPPV, respectively. In Table 3, the relative stabilization energies and geometrical parameters $\phi_1$ to $\phi_6$ of the conformations of both SiBuPPV and SiBuCNPPV are summarized.

According to the calculated relative stabilization energy, the lowest energy conformations were obtained near to trans−trans conformations in both models. The trans−trans conformation of SiBuPPV is much more stable than cis−trans and cis−cis conformations whereas that of SiBuCNPPV is a little more stable than cis−trans and cis−cis conformations. Since trans−trans conformations have the lowest energy minimum and can maximize the interchain contacts and compact packing between polymer chains, both SiBuPPV and SiBuCN-

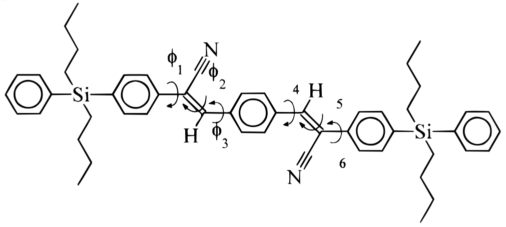
**Chart 1. Model Compounds for the Molecular Mechanical Studies**

**a**



SiBuPPV

**b**



SiBuCNPPV

**Table 3. Minimum Energy Conformation of the Model Compounds and Their Relative Stabilization Energies**

| | $\phi_1$ (deg) | $\phi_2$ (deg) | $\phi_3$ (deg) | $\phi_4$ (deg) | $\phi_5$ (deg) | $\phi_6$ (deg) | $\phi_{ppv}$ (deg) | rel energy (kcal/mol) |
|---|---|---|---|---|---|---|---|---|
| | | | | SiBuPPV | | | | |
| trans–trans | 0.0 | 0.0 | 0.1 | 1.3 | 1.6 | 2.7 | 1.025 | 0 |
| cis–trans | 12.0 | 22.4 | 23.7 | 12.4 | 17.6 | 15.0 | 15.775 | 12.6 |
| cis–cis | 14.5 | 29.7 | 19.2 | 16.6 | 28.5 | 18.5 | 17.2 | 13.4 |
| | | | | SiBuCNPPV | | | | |
| trans–trans | 16.0 | 20.6 | 16.4 | 15.5 | 14.7 | 22.6 | 17.625 | 0 |
| cis–trans | 29.9 | 29.9 | 17.0 | 15.9 | 14.3 | 23.1 | 21.475 | 0.6 |
| cis–cis | 26.2 | 27.2 | 14.0 | 11.1 | 32.0 | 23.6 | 18.725 | 2.1 |

PPV may take trans–trans conformations in solid-state polymers.

For SiBuPPV, the trans–trans conformation is almost planar. However, since the cis–trans and cis–cis conformations deviate much from the plane, the vinyl planes are distorted much. For SiBuCNPPV, all the three conformations greatly deviate from the plane. The dihedral angles $\phi_1$, $\phi_3$, $\phi_4$, and $\phi_6$ are the index of the deviations from the planarity between phenyl and vinyl planes. The averaged values of these four angles, $\phi_{ppv}$, are listed in Table 3. $\phi_{ppv}$ of the trans–trans, cis–trans, and cis–cis for SiBuPPV are 1.0, 15.8, and 17.2°, respectively. $\phi_{ppv}$ of the trans–trans, cis–trans, and cis–cis for SiBuCNPPV are 17.6, 21.5, and 18.8°, respectively, except for trans–trans SiBuPPV, where $\phi_{ppv}$ was obtained between 15 and 22°.

Figure 2 shows the $^1$H NMR spectrum of the poly(cyanoterephthalylidene) containing *n*-hexylmethylsilyl group in the main chain. As the polymerization proceeded, the aldehyde peak of the monomer present at 9.84 ppm disappeared and new vinylic proton peaks appeared at 7.48 ppm along with aromatic protons. Also the broad peak around 0.8–1.3 ppm was assigned to the hexylmethyl protons adjacent to the silicon atom.

The thermal behavior of the silicon-containing CN–PPVs was evaluated by means of DSC under a nitrogen atmosphere. Also, the thermal properties of polymers are presented in Table 1. All CN–PPV copolymers did not show any melting points. This means that the silicon-containing CN–PPV copolymers are amorphous. This was also confirmed by the broad X-ray diffraction pattern. The CN–PPV copolymers have $T_g$ values in the range 82–87 °C.

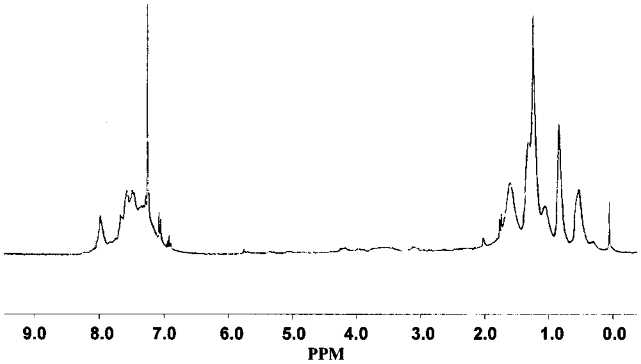


**Figure 2.** $^1$H NMR spectra of poly(*n*-hexylmethyldiphenylsilylcyanoterephthalylidene)(SiHMCNPPV).

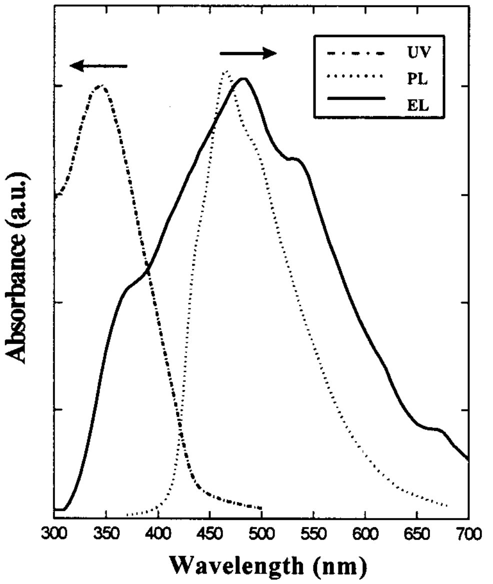


**Figure 3.** UV–visible absorption, photoluminescence (PL) and electroluminescence (EL) spectra of poly(*n*-hexylmethyldiphenylsilylcyanoterephthalylidene) (SiHMCNPPV).

Figure 3 shows the UV–visible, photoluminescence (PL), and electroluminescence (EL) spectra of poly(*n*-hexylmethyldiphenylsilylcyanoterephthalylidene) (SiHMCNPPV). Poly(*n*-hexylmethyldiphenylsilylcyanoterephthalylidene) (SiHMCNPPV) and poly(di-*n*-butyldiphenylsilylcyanoterephthalylidene) (SiBuCNPPV), respectively, show the UV absorption maximum ($\lambda_{max}$) at 345 and 356 nm, which is attributed to the $\pi$–$\pi$* transition of the $\pi$-conjugated segment, respectively. The incorporation of organosilicon units with the flexible alkyl side group into the polymer rigid backbone interrupts the $\pi$-conjugated chains, regulating the $\pi$-conjugated system. Therefore, these silicon-containing copolymers behave as a block copolymer having a short $\pi$-conjugation length. It can be explained as follows: The $\sigma$-electrons in a silicon atom overlap very weakly with the $\pi$-electrons in a $\pi$-conjugation system due to the large difference between their energy levels.[18] Because of the very weak interaction between them, the incorporation of silicon units with the flexible alkyl side group into the polymer rigid backbone interrupts the $\pi$-conjugated chains, resulting in a silicon-containing copolymer with a short $\pi$-conjugation length. Interestingly, the SiBuCNPPV absorbs at a longer wavelength than SiHMCNPPV.

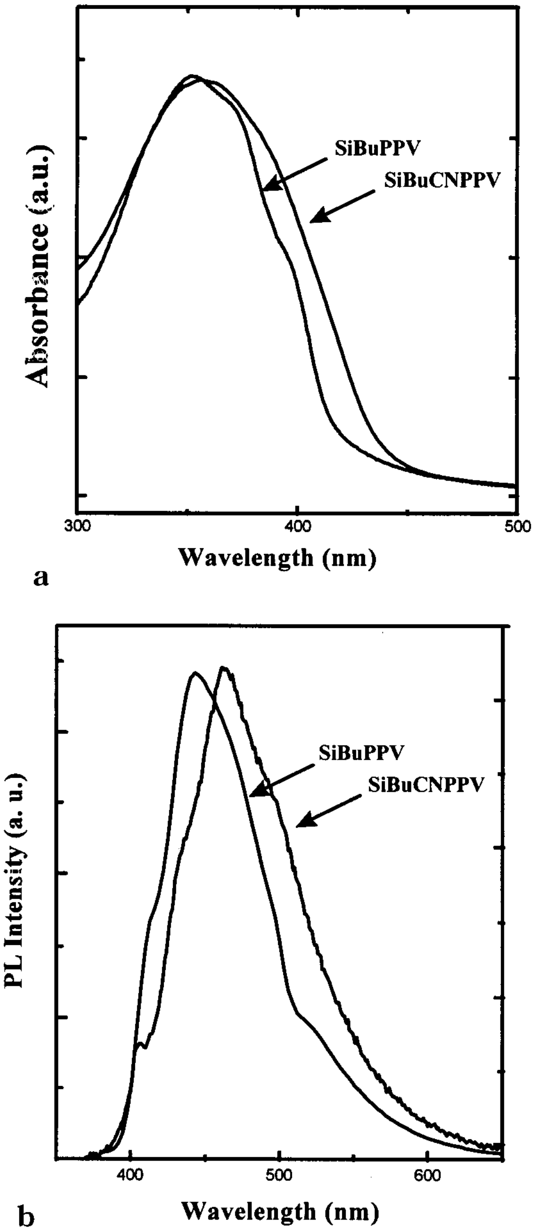


**Figure 4.** Comparison of (a) the UV–visible absorption and (b) PL spectra of SiBuCNPPV with those of SiBuPPV in $CHCl_3$.

Also, we compared the UV absorption band and the PL emission band of the SiBuCNPPV with those of the poly(*p*-phenylenevinylene) containing a dibutylsilyl group (SiBuPPV) (see Figure 4).[5] The SiBuCNPPV absorbs at longer wavelength than SiBuPPV. As indicated by the red-shift for the copolymer with a CN group, the incorporation of electron-withdrawing cyano groups into the $\pi$-conjugated system decreases the LUMO energy level and reduces the band gap between HOMO and LUMO.[4,14] It results in the longer UV wavelength absorption. The PL spectra show shifts similar to those observed in the absorption spectra. The observed emission maximum wavelengths are in the range 460–470 nm. All of the polymers show their emission in the blue region. The PL spectrum shape is similar to that of a PPV parent.[2,19] This was explained by the vibronic features in the main chain.

Furthermore, the single layer light-emitting diode of an Al/SiHMCNPPV/ITO glass was fabricated. The silicon-containing copolymers 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 thickness of about 70 nm. For the single layer devices, Al contacts were deposited on top of the spin-cast polymer layer. Figure 5 shows the current density–applied voltage (*I*–*V*) of the SiHMCNPPV. The threshold voltage of a single layer light-emitting diode of a Al/SiHMCNPPV/ITO glass was about 7 V. Also, the electroluminescence spectrum of the SiHMCNPPV gives the highest peak in the EL emissive band at 480 nm in the blue region, instead of a red color,[4,14] when an operating voltage of higher than 7 V is applied. This result indicates that these silicon-containing copolymers show a relatively low threshold voltage compared with a block copolymer having well-defined structures. The luminescent block polymers, which contain saturated and nonconjugated spacer groups between the lumophores, act as a barrier to the injection and mobility of the charge carriers. This leads to the requirement of materials with high operating voltages.[12,13]

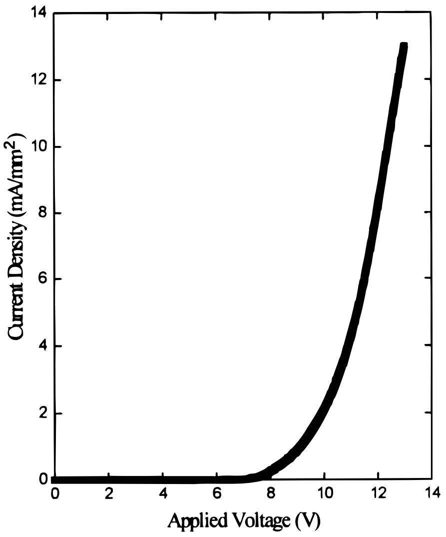


**Figure 5.** Current–voltage (*I*–*V*) characteristics of the single layer light-emitting diode of an Al/SiHMCNPPV/ITO glass.

Surprisingly, our silicon-containing copolymers with a relatively short $\pi$-conjugation length exhibit blue light-emitting diodes at operating voltages of higher than 7 V. This can be explained with our recent results as follows.[16] The ionization potential of the poly(*p*-phenylenevinylene) containing a diphenylsilyl group (co-poly(diphenylsilane/bis(phenylenevinylene), SiPhPPV) measured by a low-energy photoelectron emission analyzer, was found to be 6.45 eV, and the band gap of the SiPhPPV was estimated to be 2.98 eV from its UV absorption spectrum. The conductive band (CB or LUMO) of the SiPhPPV is located 0.2 eV lower than the LUMO of poly(cyanoterephthalylidene) (see Figure 6). The latter polymer contains a high electron affinity group that lowers the energy level of LUMO and reduces the energy barrier to the electron injection. A similar observed result implies that the introduction of silicon units into the main chain in luminescent polymers lowers the LUMO level. Therefore, the lowering of the LUMO level in luminescent polymers reduces the operating voltages in polymeric light-emitting devices, such as poly(cyanoterephthalylidene). Furthermore, the incorporation of the electron-withdrawing cyano groups into the corresponding $\pi$-conjugated system causes the additional decrement of the LUMO energy level result-

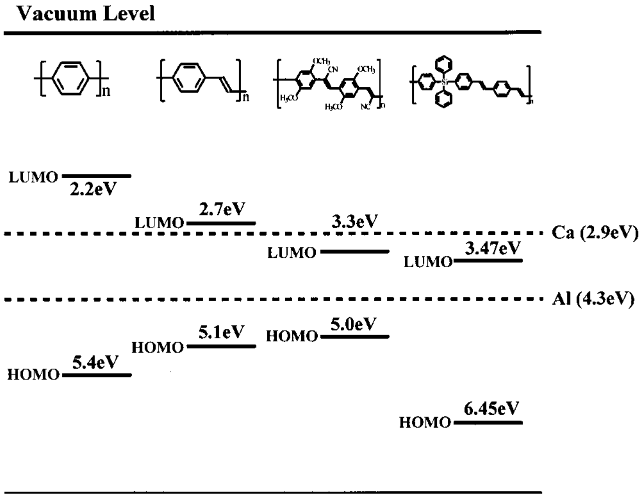


**Figure 6.** Energy diagrams of poly(*p*-phenylenevinylene), poly(cyanoterephthalylidene), poly(*p*-phenylene), and copoly(diphenylsilane/bis(phenylenevinylene) (SiPhPPV).

ing in the reduction of the operating voltages.[19] So, our copolymers with a relatively short $\pi$-conjugation length exhibit blue light-emitting diodes at operating voltages of higher than 7 V. In progress is the synthesis of a series of new silicon-containing poly(cyanoterephthalylidene) derivatives, and the quantum efficiency and brightness of blue light-emitting diodes based on silicon-containing poly(cyanoterephthalylidene) copolymers are also being investigated.

## Summary

A new class of silicon-containing poly(cyanoterephthalylidene) copolymers with a uniform $\pi$-conjugated segment was synthesized using the Knoevenagel reaction between the dialdehyde monomer and the appropriate diacetonitrile. The incorporation of organosilicon units with the flexible alkyl side group into the polymer rigid backbone would afford processable electroluminescent materials and interrupt the regular $\pi$-conjugated chains. The resulting polymers were highly soluble in common organic solvents. The $M_n$ and $M_w$ of the resulting polymers are in the ranges 3800−4200, and 5400−6000 with a polydispersity index range of 1.38−1.43, respectively. Their glass transition temperature is in the range of 82−87 °C. According to the calculated relative stabilization energy, the lowest energy conformations were obtained near to the trans−trans conformation in both models. The trans−trans conformation of SiBuCNPPV is a little more stable than the cis−trans and cis−cis conformations. Since trans−trans conformations have the lowest energy minimum and can maximize interchain contacts and compact packing between polymer chains, SiBuCNPPV may take trans−trans conformations in solid-state polymers. The UV−visible absorbance of present polymers show strong absorption bands around 340−360 nm because the $\pi$-conjugated system is regulated by organosilicon units. SiBuCNPPV absorbs at longer wavelength than SiHMCNPPV due to the interactions between the dibutyl side chain group and the diphenyl main chain group. Their photoluminescence spectra appeared around 460∼470 nm in the blue region. The threshold voltage of SiHMCNPPV was about 7 V. Surprisingly, these polymers exhibit blue light-emitting diodes in the EL emissive band at 480 nm in the blue region, instead of red light-emitting diodes, when the operating voltage of higher than 7 V is applied. These copolymers have a relatively low operating voltage compared to a block copolymer having well-defined structures because the incorporation of electron-withdrawing cyano groups into the $\pi$-conjugated system increased the electron affinity of those polymers and decreased LUMO energy level.

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