Bull. Chem. Soc. Jpn., *72*, *1941—1946 (1999)* 1941

Synthesis and Characterization of a Novel Green Photoluminescent Silicon-Containing Poly(*p*-phenylenevinylene)

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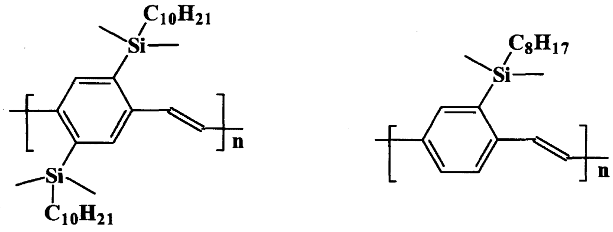
(Received February 1, 1999)

A novel solution processable photoluminescent polymer containing silyl groups has been successfully synthesized through a polycondensation reaction. The polymer was characterized through FT-IR, NMR, UV-vis spectroscopy, photoluminescent spectroscopy (PL), elemental analysis and cyclic voltammetry (CV). A TGA analysis shows that the polymer is stable up to 300 °C both in air and in nitrogen. The UV-vis absorption spectra for both the solution and film samples are very similar. The band gap obtained from the optical spectra is 2.53 eV. The maximum emissions of photoluminescence are at 494 and 507 nm for the solution and film samples, respectively. The UV-vis spectrum of its polymer film also shows a very small temperature dependence. A cyclic voltammogram illustrates that the polymer can be reversibly *n*-doped and dedoped in a negative sweep and irreversibly *p*-doped during a positive sweep. All of the results demonstrate that the obtained polymer is a promising green-light emission material for PLED applications.

Electroluminescent polymers have attracted much attention recently due to their application in light-emitting devices (LEDs) since the first report of poly(*p*-phenylenevinylene) (PPV)-based LEDs by a Cambridge group.[1] A wide range of conjugated polymers, such as PPV and its derivatives,[1—4] poly(*p*-phenylene)s,[5] polythiophenes,[6] pyridyl-containing polymers,[7] and other kinds of polymers,[8—10] have been exploited as emissive layers and/or charge-transporting layers for device fabrication. Currently, the major interest in developing light-emitting polymeric materials is focused on those with high photoluminescent quantum efficiency, good processability and a long operating lifetime.

Among the PPV derivatives, the most commonly utilized materials for polymer LEDs that have been investigated so far, silyl-substituted PPVs are quite attractive due to their extremely high PL efficiencies compared to PPV itself or alkoxy-substituted PPVs. In addition, silicon-containing PPV polymers demonstrate good solubility and uniform film morphology without any crystalline features in the film states.[11] In 1994, Wudl and Heeger's group first introduced a silyl group into PPV, which afforded green-light-emitting poly-(2-cholestanoxy-5-thexylsilyl-1,4-phenylenevinylene) (CS-PPV); an improved quantum efficiency was observed in their device.[12] Further work was performed and reported by the Holmes and Friend group.[11,13] A dimethyloctylsilyl group containing poly(*p*-phenylenevinylene) (DMOS-PPV) was synthesized and single layer as well as multilayer devices with an electron-conducting and hole-blocking (ECHB) material were fabricated. A very high photoluminescence efficiency of 60% for the film sample was observed. Using DMOS-PPV as the emission layer, 0.2% of the external quantum efficiency for indium tin oxide (ITO)/DMOS-PPV/2-(4-biphenylyl)-5-(4-*t*-butylphenyl)-1,3,4-oxadiazole (PBD)/Al was reproducibly obtained. The high EL performance is attributed to a good balance for hole and electron injection into the emissive material when Al was exploited as the negative contact. Their subsequent work concerning silyl-containing copolymers has indicated that polymers show higher PL and EL efficiencies when the ratio of the silyl group in the copolymers is increased.[14]

In this paper we present a very simple and convenient synthesis of a new PPV derivative, poly[2,5-bis(decyldimethylsilyl)-1,4-phenylenevinylene] (BDDMS-PPV), through introducing two silyl groups as substituents on the phenylene ring with the aim of further improving the photoluminescence quantum efficiency and EL performance as well as increasing the solubility over a wide range of organic solvents for the ease of multilayer device fabrication. The structures of BDDMS-PPV and DMOS-PPV are displayed in Scheme 1.



BDDMS-PPV **DMOS-PPV**

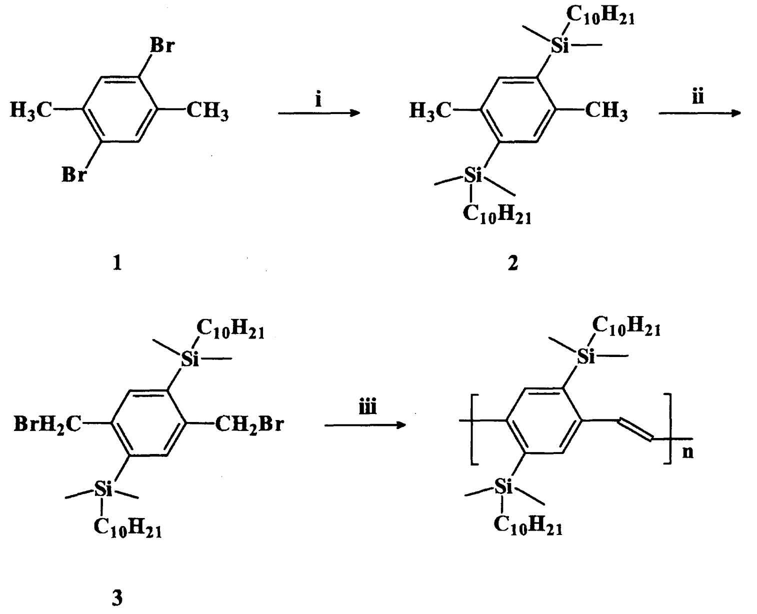
Scheme 1. The chemical structures of BDDMS-PPV and DMOS-PPV.

Results and Discussion

BDDMS-PPV and the corresponding monomer were synthesized according to the route outlined in Scheme 2. A bis(silyl)-substituted compound **2** was obtained through coupling the Grignard reagent derived from **1** with decyldimethylsilyl chloride. Monomer **3** was obtained through the radical bromination of compound **2**, which then underwent dehydrohalogenized polycondensation to afford the polymer BDDMS-PPV.

BDDMS-PPV is a yellow solid which can be completely dissolved in common organic solvents, such as tetrahydrofuran THF, dichloromethane, chloroform, toluene, and xylene. Therefore, a molecular weight measurement can be carried out by GPC. A GPC analysis (polystyrene as the standard for calibration) has revealed the number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the polymer to be 117700 and 239100, respectively, with a polydispersity of 2.03. From the datum of M_n, it can be estimated that the polymer has about 236 repeat units. Such a high molecular weight, but good solubility, can provide a high-quality film and prevent the formation of crystals in the film states.

Thermogravimetric analysis results for BDDMS-PPV in nitrogen and in air (Fig. 1) reveal that the polymer starts to degrade at about 300 and 311 °C, and that the maximum



Scheme 2. Synthetic route for BDDMS-PPV. Reagents and conditions: i) Mg/THF, $Me_2SiC_{10}H_{21}Cl$; ii) NBS/benzene/BPO/*hν*; iii) $KOBu^t$/THF.

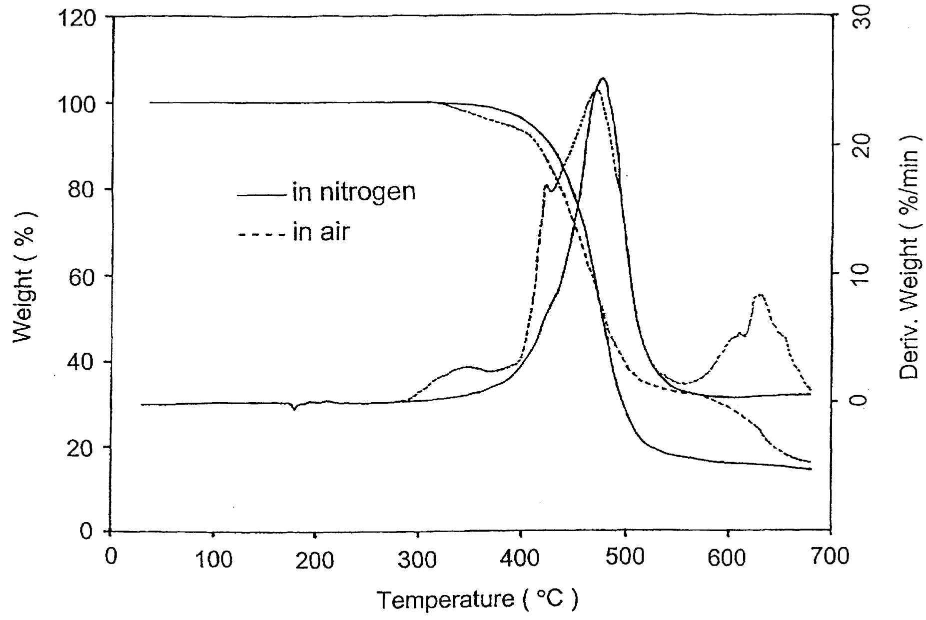


Fig. 1. Thermogravimetric analysis of BDDMS-PPV in nitrogen and in air.

weight loss takes place at 470 and 477 °C, respectively. At 400 °C, the weight loss in nitrogen and in air is just 3 and 7%, respectively. The difference between the two degradation patterns is that there exists two other small weight-loss steps from 300—400 and 500—650 °C besides the main step in air. The first step may be attributed to a partial leaving of the methyl groups attached to the silicon. In air, the silicon and vinylene moiety may be partially oxidized during an earlier stage of the degradation process, which is a possible reason for the slower degradation speed during the later stage compared to that in nitrogen. A second small weight-loss step, which appeared in air from about 500 to 650 °C, should correspond to the oxidized part of the residue. In the degradation pattern, no evidence shows that there is any priority for decomposing the side chain or polymer main chain. These results indicate that this polymer has satisfactory thermal stability.

The UV-vis absorption and photoluminescence (PL) spectra of BDDMS-PPV films and chloroform solution are illustrated in Fig. 2. The maximum UV-vis absorption ($\lambda_{\max}$) takes place at 433 and 423 nm for the solution and film samples, respectively. Both of the absorption edges are at 490 nm, which indicates a band gap of about 2.53 eV. Compared the UV spectra of the film sample to the solution one, it can be found that a 10 nm blue shift takes place, which is contrary to the common observation for conjugated polymers. This result infers that BDDMS-PPV is in an extremely amorphous conformation, even in the film states; further evidence can be obtained from a thermochromic experiment, which will be discussed later. It was reported[11] that a film of DMOS-PPV revealed by AFM was very smooth and without any noticeable crystalline feature when it was examined by TEM and X-ray diffraction analysis. Our AFM observation confirms this result. This feature may be the main reason why there is no evident red shift in the UV-absorption from the solution state to the film state. The position of $\lambda_{\max}$ of film samples is slightly red-shifted compared to that of PPV (420 nm) and DMOS-PPV (410 nm).[13] On the other hand, the absorption edge is blue-shifted by about 40 and 10 nm compared with the above two reference polymers. Therefore, the obtained polymer shows a slightly larger band gap, but a narrower absorption peak, which means that it is more homogenous than the other two reported polymers. The feature of the UV-vis absorption spectra could be ascribed to electron donation and a steric-hindrance effect of the bis-silyl substituents on the phenylene ring. An electron donation from the side chain to the polymer backbone leads to the maximum absorption redshift compared with that of PPV or monosubstituted DMOS-PPV; however, the two bulky substituents on the phenylene ring simultaneously torture the coplanarity of the phenylene ring and the vinylene moiety so as to limit the delocalization of π electrons along the polymer backbone, then leading the whole absorption band to be blue-shifted.

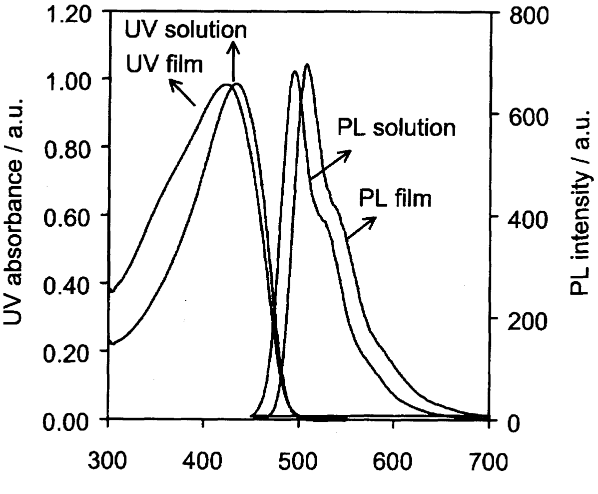


Fig. 2. Spectra of UV-vis absorption (left) and PL (right) of BDDMS-PPV films and solution.

The photoluminescence emission spectra of BDDMS-PPV in the solution and film states exhibit maximum peaks at 494 and 507 nm, with a shoulder at 530 and 541 nm respectively, which correspond to green-light emission. Compared to PPV and DMOS-PPV, the maximum emission peak is blue-shifted by 44 and 13 nm, respectively. This indicates that the emission spectrum of BDDMS-PPV contains a greener component and a less yellow one than those of PPV and DMOS-PPV. The emission peak is also sharper than that of DMOS-PPV. The full-width-at-half-maximum (FWHM) for BDDMS-PPV and DMOS-PPV are 67 and 76 nm, respectively. Another obvious difference between the PL spectra of BDDMS-PPV and DMOS-PPV is that the spectrum of DMOS-PPV is well resolved. This is because the vibrational coupling with an excitonic transition did not appear in this figure. The quantum yield of BDDMS-PPV in chloroform (ca. 1.0×10^{-6} M, 1 M = 1 mol dm^{-3}) was measured by comparing to quinine sulfate (ca. 1.0×10^{-5} M) in 0.10 M H_2SO_4 as a standard. The relative quantum yield is as high as 133%. The yield is almost the same as that of monosubstituted poly(2-dimethyldodecylsilyl-1,4-phenylene vinylene) (135%), which has a similar structure as DMOS-PPV. However, it is much higher than that of MEH-PPV (25%) measured in the same conditions in our lab. These results indicate that silyl-substituted PPV derivatives can afford intense photoluminescence.

The electrochemical behavior of BDDMS-PPV was investigated in a three-electrode cell. Figure 3 illustrates the cyclic voltammogram (CV) of BDDMS-PPV in 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in acetonitrile. When a cathodic sweep potential is provided, the polymer exhibits a reversible *n*-doping process. The cathodic peak occurs at −1.92 V with a corresponding anodic peak at −1.83 V (vs. SCE), which represents an *n*-doping and dedoping process. Along with the sweeping, the film color first changes from green to purple blue, then after oxidation it changes to brown. The onset for *n*-doping occurs at −1.84 V, which is determined from the intersection of two tangents drawn at the rising current and the baseline charging current of the CV curve. It is noted that BDDMS-PPV also shows a *p*-doping process. The charge-discharging potential is 1.33 V,

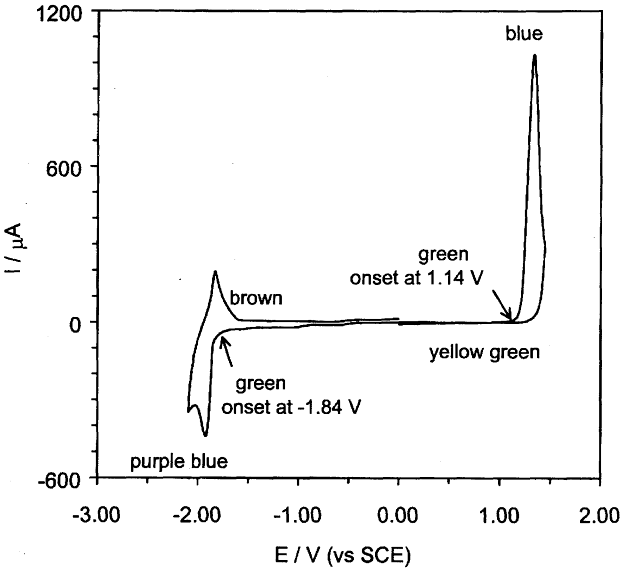


Fig. 3. Cyclic voltammograms recorded in 0.1 M Bu_4NBF_4 of acetonitrile. Working electrode: a platinum plate dipping coated with BDDMS-PPV films; Counter electrode: a platinum wire; Reference electrode: Ag/0.1 M $AgNO_3$ in acetonitrile; Scan rate: $10\ mV\ s^{-1}$.

accompanied by a color change from green to blue and after reduction to yellow-green. The observation of irreversible *p*-doping could be attributed to instability of the doped state. The onset of oxidation takes place at 1.14 V. All of the processes, either *p*-doping or *n*-doping, can be run up to 5 cycles without any obvious change in the shape of CV. However, the current intensity shows a trend to decrease. From the onset potentials of oxidation and reduction, it can be estimated that the band gap of BDDMS-PPV is 2.98 eV, which is slightly higher than the datum of DMOS-PPV.[14] For DMOS-PPV, the onset potentials for oxidation, reduction, and band gap are about 1.1 V, -1.6 V, and 2.7 eV, respectively. It can be found that BDDMS-PPV shows the same oxidation onset potential as that of DMOS-PPV, but having a slightly negatively higher value for the reduction one, which may be attributed to more silyl-substituents linked to the phenylene ring. The band gap obtained from a cyclic-voltammogram measurement is also higher than that obtained from the UV absorption edge of the film sample. According to the empirical relationship obtained by fitting to the experimental data through the valence-effective Hamiltonian (VEH) technique,[15] the solid-state ionization potential (IP) and electron affinity (EA) of the polymer can be roughly estimated as 5.54 and 2.56 eV, respectively. These data are very useful and essential for EL device consideration. Further work related to device fabrication is in progress.

Figure 4 shows the dependence of the UV-vis absorption of a BDDMS-PPV film on the temperature. When the temperature increases from 25 to 200 °C, no drastic changes in the shape of the absorption curve is observed, except for the maximum absorption position being continuously blue-shifted from 423 to 391 nm. This process is fully reversible; upon cooling, the initial absorption spectrum is recovered.

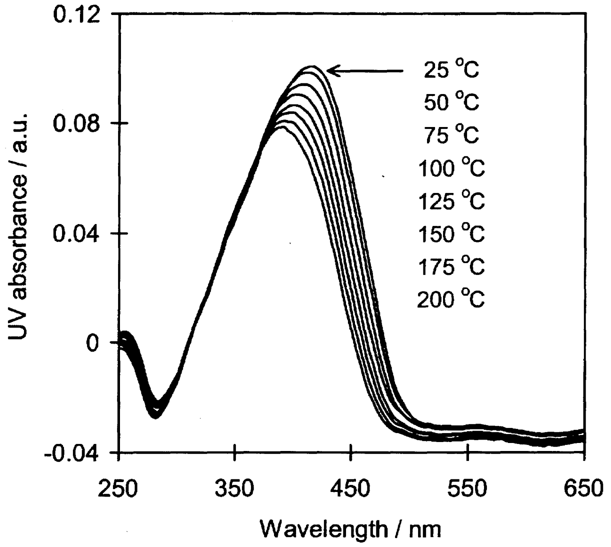


Fig. 4. Temperature-dependent UV-vis absorption spectra of BDDMS-PPV films (heating scan).

With the maximum absorption shift to the higher energy side, the absorption intensity decreases slightly. No isosbestic point has been observed in thermochromic behavior tests, although it is usually the case for those systems of regioregular polythiophene derivatives.[16—18] The isosbestic-point phenomenon is caused by a short range order–disorder transition (interchain and/or intrachain interactions). The ordered structure is associated with a planar and highly conjugated conformation. Upon heating, disordering of the side chains leads to a twisting of the polymer backbone, which decreases the length of conjugation of the π electrons, so as to lead to a strong blue shift of the maximum absorption of the π–π^* transition. In this BDDMS-PPV system, it can not be described as an order–disorder transition of the side chain, but rather only a localized interaction of the backbone without any side-chain cooperative effect. Therefore, it can be inferred that the side-chain crystalline phenomenon found in regioregular polymers does not exist in this PPV derivative, which is similar to a report by the Holmes and Friend group.[11] This feature is critical if emissive polymers are considered for LED applications, because a homogeneous, smooth and amorphous morphology of the emission layer can be expected to give rise to high quantum efficiency and long lifetime of a PLED device. It can also be found that λ_{max} shifts by only about 30 nm, although the temperature is elevated to about 200 °C. Compared to those thermochromic materials with isosbestic points in their temperature-dependent UV-vis absorption spectra, the temperature coefficient for absorption is very small. It is well-known that current-induced heating in polymer-based LED devices is a common phenomenon, and that the temperature in the recombination zone may be increased to 80 °C. Any temperature increase would limit the maximum external and internal quantum efficiencies while leading to an emission color shift.[19] Small-temperature-coefficient materials for absorption and emission have the advantage of the emission color stability in device operation. From this point of view, the optical properties of emissive polymers should show a small-temperature dependence.

Experimental

Proton NMR spectra were recorded on a Bruker AMF-300 spectrometer with chemical shifts being referenced against TMS as the internal standard. Elemental analyses (EA) were performed on a Perkin–Elmer elemental analyzer 2400 for C, H, and N determinations. The halogen content was determined by the oxygen flask method. FT-IR transmission spectra were recorded on a Bio-Rad FTS 165 spectrometer. The solid samples were dispersed in KBr disks. A thermogravimetric analysis (TGA) of a polymer powder was performed under an air or nitrogen atmosphere at a heating rate of 20 °C min^{-1} with a DuPont 9900 thermal analyzer. The polymer number-average molecular weight (M_n) was determined by gel-permeation chromatography (GPC) using Phenogel GPC MXM and MXL (4.6 mm i.d., 300 mm length columns used in series, flow rate at 0.3 ml min^{-1}) using a Waters 410 differential refractometer as detector. The absorption spectra were recorded with a Shimadzu UV-3101PC spectrophotometer. The photoluminescence spectra were obtained with a Perkin–Elmer LS 50B luminescence spectrometer. Film samples for PL spectra were prepared by casting the polymer from its chloroform solution on clean glass substrates. Cyclic voltammograms were recorded at a scan rate of 10 mV s^{-1} and obtained with a potentiostat/galvanostat EG&G model 273A in a dry, degassed acetonitrile solution with 0.10 M of tetrabutylammonium tetrafluoroborate as an electrolyte. An electrochemical investigation was carried out in a three-electrode cell. The working electrode was a 0.5 cm^2 rectangular platinum plate, while Ag/0.1 M $AgNO_3$ in acetonitrile was used as a reference electrode.

Synthesis of 2,5-Dibromo-*p*-xylene (1). Compound **1** was prepared according to a procedure described by Gerns.[20] The product was obtained as white crystals (mp 72.0—73.5 °C (lit, 72—74 °C). ^{1}H NMR ($CDCl_3$) δ = 2.33 (6H, s), 7.39 (2H, s)).

Synthesis of 2,5-Bis(decyldimethylsilyl)-*p*-xylene (2).[21] The Grignard reagent of 2,5-bis(bromomagnesio)-*p*-xylene was prepared by refluxing a mixture of 2,5-dibromo-*p*-xylene (5.28 g, 20.0 mmol) and magnesium turnings (1.04 g, 44.0 mmol) in 40 ml anhydrous THF for 4 h. To this solution, cooled in an ice bath, was added a solution of decyldimethylsilyl chloride (12.2 ml, 45.0 mmol) in 40 ml of THF. The mixture was refluxed for 24 h, and then cooled in an ice bath. After being quenched with a saturated ammonium chloride aqueous solution, THF was evaporated and the residue was extracted three times with 30 ml of hexane. The combined organic layer was washed with water, brine, and then dried over anhydrous magnesium sulfate. After the solvent was evaporated under a reduced pressure, the residue was purified through silicon-gel chromatography eluted with hexane to afford 5.69 g of a colorless liquid (yield 57%, 1.65 g of by-product of 2-decyldimethylsilyl-*p*-xylene was also separated). ^{1}H NMR ($CDCl_3$) δ = 0.29 (12H, s, $-Si(CH_3)_2$), 0.79 (4H, t, $-SiCH_2-$), 0.88 (6H, t, $-CH_3$), 1.25—1.32 (32H, m, $-(CH_2)_8-$), 2.39 (6H, s), 7.19 (2H, s).

Synthesis of 2,5-Bis(decyldimethylsilyl)-1,4-bis(bromomethyl)benzene (3). 2,5-Bis(decyldimethylsilyl)-*p*-xylene (2.08 g, 4.0 mmol), 1.42 g (8.0 mmol) of *N*-bromosuccinimide (NBS), catalytic amounts of benzoyl peroxide (BPO) and 120 ml of benzene were charged in a 250 ml flask. The mixture was stirred at ambient temperature under tungsten light for 2 h. The solution was washed with water three times and then with brine. The organic phase was dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated, and the residue was purified through silicon-gel chromatography eluted by hexane to afford 2.41 g of a colorless liquid (yield 46%). ^{1}H NMR ($CDCl_3$) δ = 0.38 (12H, s, $-Si(CH_3)_2$), 0.85—0.87 (10H, m, $-SiCH_2-$, $-CH_3$), 1.24—1.31 (32H, m, $-(CH_2)_8-$), 4.58 (4H, s, $-CH_2Br$), 7.49 (2H, s). ^{13}C NMR ($CDCl_3$) δ = 142.0 140.0, 137.5, 34.1, 33.4, 31.8, 29.6, 29.5, 29.3, 29.2, 23.8, 22.6, 16.3, 14.0, −1.6. Anal. Calcd for $C_{32}H_{60}Br_2Si_2$: C, 58.18; H, 9.09; Br, 24.24%. Found: C, 57.98; H, 9.01; Br, 23.86%.

Synthesis of Poly[2,5-bis(decyldimethylsilyl)-1,4-phenylenevinylene] (BDDMS-PPV).[22] A solution of 0.500 g (0.76 mmol) of 2,5-bis(decyldimethylsilyl)-1,4-bis(bromomethyl)benzene in 25 ml anhydrous THF was charged in a 50 ml flask. To this stirred solution was added dropwise 5 ml of 1.0 M solution of potassium *t*-butoxide (5.0 mmol) in anhydrous THF at room temperature. The mixture was continuously stirred for 24 h. The reaction mixture was then poured into 200 ml of methanol with stirring. The resulting yellow precipitate was washed with deionized water and dried under vacuum. The crude polymer was extracted through a Soxhlet extractor with methanol and acetone for 12 h successively and dried under a vacuum to afford 0.239 g (63% yield) of a yellow polymer. FT-IR 3057, 2926, 2855, 1512, 1470, 1241, 1106, 959, 831, 642, 468 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ = 0.48 (12H, s, $-Si(CH_3)_2$), 0.87—0.90 (10H, m, $-SiCH_2-$, $-CH_3$), 1.26—1.45 (32H, m, $-(CH_2)_8-$), 5.02 (2H, s, $-CH{=}CH-$), 7.00 (2H, s). ^{13}C NMR ($CDCl_3$) δ = 151.4, 135.7, 128.2, 125.4, 34.1, 33.6, 31.8, 29.6, 29.3, 24.1, 22.6, 21.1, 16.7, 14.0, −1.4. Anal. Calcd for $(C_{32}H_{58}Si_2)_n$: C, 77.11; H, 11.65%. Found: C, 76.82; H, 11.39%.

Conclusion

In summary, a novel solution processable polymer, poly[2,5-bis(decyldimethylsilyl)-1,4-phenylenevinylene] (BDDMS-PPV), was successfully synthesized through dehydrohalogenation polycondensation. The as-synthesized polymer is completely soluble in common organic solvents. A thermogravimetric analysis indicates that the polymer is stable both in nitrogen and in air up to 300 °C. Even up to 400 °C, there is only 3 and 7% degradation. The UV-vis absorption spectra for both solution and film samples are very similar. The film spectrum even shows a 10 nm blue shift, which is contrary to the common observation of conjugated polymers. The band gap obtained from the optical spectra is 2.53 eV. The maximum emissions of photoluminescence are at 494 and 507 nm for the solution and film samples, respectively, both with a small shoulder. The UV-vis spectrum of its polymer films also shows a very small temperature dependence. Cyclic voltammograms illustrate that the polymer can be reversibly doped and dedoped in a cationic process. The onset potentials for oxidation and reduction are 1.14 and −1.84 V vs. SCE, respectively, which correspond to 2.98 eV of the band gap. The optical and electronic properties indicate that the obtained polymer is a quite promising green-light emission material for PLED applications.

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