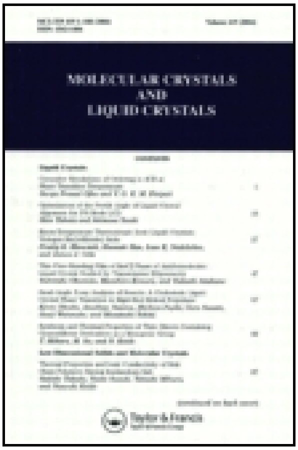

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Blue Electrluminescence from Novel Silicon-Based Copolymers at Low Operating Voltages

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Blue Electroluminescence from Novel Silicon-Based Copolymers at Low Operating Voltages

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Novel silicon-based copolymers show the UV-visible strong absorption bands around 347~387 nm. Their maximum photoluminescence (PL) wavelengths for silicon-based copolymers appeared around 420~480 nm in the blue region. The present copolymers with a relatively short π-conjugation length exhibit blue light-emitting diodes (LED) at the low operating voltages, due to the reduction of the LUMO level in luminescent polymers by introducing silicon atoms in luminescent polymers as well as the d-orbital participation of silicon atoms.

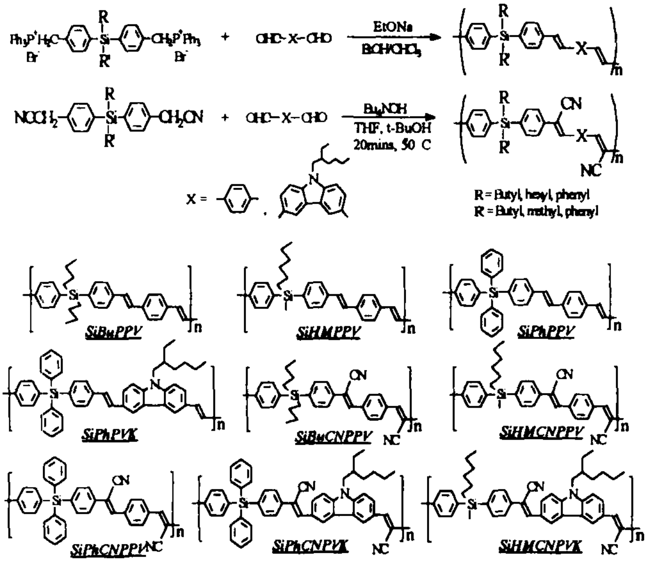
Keywords: silicon-based copolymers; LED; d-orbital participation

INTRODUCTION

Up to now, the main material efforts have been focused on developing blue light-emitting diodes operating at ambient temperature and low voltages and easy processability with low price[1-3]. Recently we have developed a new processable blue light-emitting diode from the silicon-based poly(*p*-phenylenevinylene) (PPV) derivatives in the polymer main chain[2-3]. The incorporation of silicon unit with the flexible alkyl side group into the polymer rigid backbone allowed electroluminescent materials to become processable. The organosilicon units interrupt the regular π-conjugated chains and limit the π-conjugation length, resulting in blue light-emitting diodes. Furthermore, we introduced a carbazole unit into the silicon-containing PPV related polymers, yielding PPV related copolymers containing both silyl groups and the carbazole unit. Many research groups including our group have paid much attention for the development of new carbazole-containing polymers for organic light-emitting diodes, due to its electronic property[3-5]. In this work, we discuss the synthesis and their EL characteristics of the silicon-based copolymers by the Wittig reaction and the Knoevenagel reactions.

RESULTS AND DISCUSSION

Very recently, a new class of silicon-based copolymers with uniform π-conjugated segments was synthesized using the Wittig reaction and the Knoevenagel reaction (see Scheme 1)[2], [6]. The UV-visible absorbance of present copolymers shows strong absorption bands around 320~380 nm. Their photoluminescence (PL) spectra appeared around 420~480 nm in the blue region. In the case of the polymers containing a carbazole unit, their PL spectra show both a strong PL emissive band in the blue region and an additional strong emissive band in the green range. Poly(n-hexylmethyl-diphenylsilylcyanoterephthalylidene) (SiHMCNPPV) and poly(di-n-butyldi-phenyl-silylcyanoterephthalylidene) (SiBuCNPPV) show the UV absorption maximum (λ max) at 345 nm and 356 nm, which is attributed to the π - π^* transition of the π-conjugated segment, respectively. The incorporation of organosilicon units with the flexible alkyl side group into the polymer rigid backbone interrupts the π-conjugated chains, regulating the π-conjugated system. Therefore, these silicon-containing copolymers behave as a block copolymer having a short π-conjugation length.



SCHEME 1. Synthesis of silicon-based copolymers by Wittig and Knoevenagel reactions.

The single layer light-emitting diode of an Al/silicon-based copolymer/ITO glass was fabricated. The forward bias current is obtained when the ITO electrode is positively biased and the AL electrode negatively. The current increases with forward bias voltage and the reverse bias current remains small, which is the typical rectifying characteristics. The threshold voltage is about 9-12 V for the SiPPV series and 7 V for SiCNPPV series, respectively, which is considerably low compared with the PPV-based block copolymers. Surprisingly, our silicon-based copolymers with a relatively short π-conjugation length exhibit blue light-emitting diodes operated at the voltage of lower than 9 V. It can be explained with our recent results that the lowering of the LUMO level by introducing silicon atoms in luminescent polymers as well as the d-orbital participation of silicon atoms reduces the operating voltages in polymeric light-emitting devices[7].

The SiBuPPV and the SiPhPPV at the operating voltage of 9 V give a peak in the EL emissive band at 460 nm and 450 nm, respectively, indicating a blue emission. At the higher operating voltage, no apparent change was observed in the EL spectra. Interestingly, a single-layered light-emitting device of the Al/SiPhPVK/ITO shows both a strong blue emissive band and an additional strong yellow emissive band. The SiPhPVK film shows an EL emissive band at 450 nm at the operating voltage of 10 V. Also, the EL spectrum of the present SiPhPVK polymer shows an additional strong EL emissive band in the yellow range at the operating voltage of 14 V, while the PL spectrum of the SiPhPVK shows an additional strong emissive band in the green range. As a result, the SiPhPVK gives a strong white emissive light at the operating voltage of over 12 V. This can be explained as follows: Figure 1 (a) shows the PL spectra with photoexcitation at two different steady-state maximum absorption. These two excitation wavelengths at 320 and 400 nm were chosen for selective excitation to carbazole and PPV segments in SiPhPVK, respectively. Two resultant emission spectra exhibit an apparent difference regarding on the excitation wavelengths. In other words, upon photoexcitation to a carbazole unit, the relative PL intensity at 430 nm to that in the longer wavelength region is larger than that in the case of photoexcitation to PPV segments. We have also measured the excitation spectra from 280 nm to 420 nm at the emission wavelengths at 440 and 520 nm, showing the results in Figure 1(b). As expected from PL and UV-Vis absorption spectral data, the two electronic transitions located at 300 and 380 nm are responsible for the PL emission at shorter and longer wavelengths, respectively.

It is quite interesting to compare the experimental observations from PL and EL spectral features. Overall PL spectral feature with a long wavelength excitation is similar to the EL spectra at a low operating voltage, while the PL spectra with the shorter wavelength excitation and and EL spectra at a high operating voltage are similar. These observations led us to conclude that the observed band at shorter wavelengths from either PL or EL spectra do not result from PPV, but from carbazole segments.

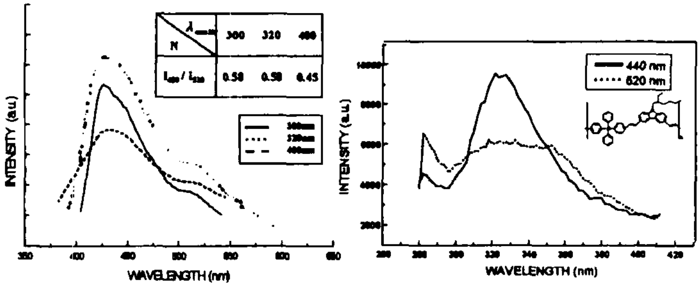


FIGURE 1 (a) The PL spectra of the SiPhPVK at the three different excitation probe wavelengths of 300 nm, 320 nm and 400 nm. The normalized intensity for the maximum band at 430 nm and 510 nm in a box; (b) Two excitation spectra at the wavelengths of 440 nm and 520 nm.

Meanwhile, it is not straightforward to assign the longer wavelength emission band to the PPV segment in the SiPhPVK, because no such a longer wavelength emission is seen in either PL or EL spectra from a SiPhPPV thin film. As mentioned before, the emission peak maximum of SiPhPPV, which does not have a cabazole segments in the main chain, is found to be at the wavelength of 450 nm. Therefore, the longer wavelength emission band in the SiPhPVK may be explained by proposing the involvement of a certain type of excited states, such as either the exciplex between an excited-state carbazole and a PPV segment or the excimer between an excited-state carbazole and a carbazole segment. In fact, the previous emission studies on PVK reveal that the introduction of carbazole unit into a polymeric system is able to form easily the excimer. However, the longer wavelength emission is mainly due to the optical transition of PPV, not due to the optical transition of a carbazole unit, and also the carbazole segement in our SiPhPVK have a branched, bulk alkyl chain, which should reduce the probability of the proposed excimer. So, this is not likely to explain the origin of the emission. The other probable explanation can be drawn from the fact that the effective conjugation length in excited state be remarkably increased due to the presence of carbazole in their π-conjugation, compared to those in ground state. If it is a case, we are able to explain the longer wavelength emission, which is observed not from SiPhPPV, but from SiPhPVK, even if the two silicon-based derivatives have the almost same ground state absorption spectra. Unfortunately, we have no direct evidence to differentiate these proposition on this rather complicated system. This observation is being investigated in more detail by measuring the ultrafast relaxation dynamics upon selective photoexciation at PPV segment.

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