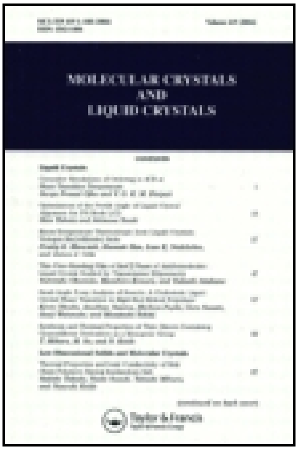

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Pd-Catalyzed Direct Synthesis of Novel Silicon-Based Copolymers for Tunable Light-Emitting Diodes

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Pd-Catalyzed Direct Synthesis of Novel Silicon-Based Copolymers for Tunable Light-Emitting Diodes

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A series of silicon-based copolymers was synthesized by the Pd-catalyzed Heck reaction of the distyrylsilane monomers with various aromatic dibromides. 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 π-conjugated chains. The resulting polymers were highly soluble in common organic solvents. The UV-Visible absorbance of the present polymers shows strong absorption bands at around 365~400 nm. Their maximum photoluminescence (PL) wavelength for SiPPV analogues appeared 470 nm in the blue emission region. The single layer light-emitting diode based on the present copolymer emits the blue emissive light at the operating voltage of 9 V.

Keywords: silicon-based copolymers; Heck reaction; electroluminescence

INTRODUCTION

Electroluminescent (EL) devices based on polymeric thin layers have attracted much attention because of their academic interest and wide variety of applications such as flat-panel displays, light-emitting diodes, and lasers.[1]. 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 materials.

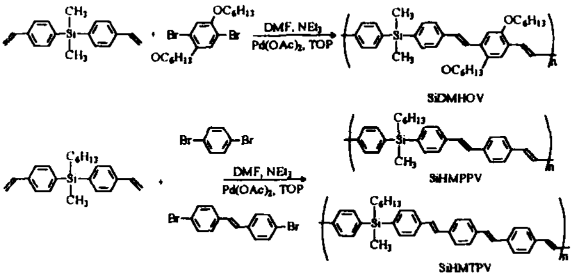
Very recently, the main material efforts have been focused on developing blue light-emitting diodes capable of operating at ambient temperature, low voltages and easy processability with low price[2]. We reported the development of a new type of processable silicon-based copolymers in the polymer main chain by the well-known Wittig reactions for blue light-emitting diodes.[3]. The introduction of organosilicon units with aromatic or flexible aliphatic group into π-conjugated systems improved their processability and limited the π-conjugation length, resulting in blue light-emitting diodes.[4]. Surprisingly, the silicon-based copolymers with a relatively short π-conjugation length exhibited blue light-emitting diodes operated at the low voltages, due to the lowering of the LUMO level in luminescent polymers and the d-orbital participation of silicon atoms[4].

In this paper, we describe the direct synthesis of the silicon-based copolymers by the Pd-catalyzed Heck reaction of the distyrylsilane monomer with various aromatic dibromides.

RESULTS AND DISCUSSION

Scheme 1 shows the synthetic routes to polymerization. The Grignard reaction between p-styrylmagnesiumchloride and dialkyldichlorosilane yields alkyl-substituted silane synthetic products with high conversion. The reaction can be carried out in a one-pot procedure where the formed Grignard reagent reacts immediately with the very active chlorosilane. The silicon-based copolymers were synthesized by the Heck reaction of the distyrylsilane monomers with various aromatic dibromides, including alkoxy-substituted benzene bromide.

The polymerization results are summarized in Table 1. The resulting polymers were highly soluble in common organic solvents such as THF, chloroform, DMF, methylenechloride, etc. The thermal behavior of the silicon-based copolymers was evaluated by mean of DSC and TGA under nitrogen atmosphere



SCHEME 1 Pd-catalyzed direct synthesis of silicon-based copolymers.

TABLE 1 Polymerization results of silicon-based copolymers.

Polymers	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	T_g (°C)	T_{id} (°C)	UV λ_{max} (nm)	PL λ_{max} (nm)
SiDMHOV	9.0	19.3	96	210	400	477
SiHMPPV	4.7	8.5	94	180	365	470
SiHMTPV	1.6	2.7	112	200	386	470

The chemical structure of the resulting copolymers was identified by FT-IR, ^{1}H-NMR, and UV-visible spectroscopy. A sharp absorption peak at 960 cm^{-1}, corresponding to the out-of plane bending mode of the trans-vinylene groups appeared. Figure 1 shows the UV visible and PL spectra of the resulting copolymers in chloroform solution. As shown in the absorption spectra, the maximum absorption wavelength (λ_{max}) of SiHMPPV and SiHMTPV in solution has a strong absorption band of the π-π* transition of the conjugated segment at 365 nm for SiHMPPV and 386 nm for SiHMTPV. These results indicate that the maximum absorption wavelength (λ_{max}) increases with the π-conjugation length.

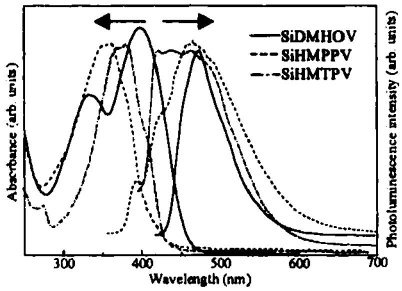


FIGURE 1 UV-visible and PL spectra of silicon-based copolymers.

Also a strong absorption band for the SiDMHOV appears around 400 nm, due to the electron donating effect of the alkoxy group. With an excitation wavelength of 365 nm, the SiHMPPV spectrum give a peak in the emission spectra at 470 nm, indicating a blue emission. Also, the PL maximum peaks for both SiDMHOV and SiHMTPV can be observed at 477 nm for SiDMPPV and 470 nm for SiHMTPV in the blue region, respectively. The current-voltage (I-V) characteristics of the single layer light-emitting diode of a Al/ SiHMPPV/ITO glass shows the threshold voltage of 9 V, which is considerably low compared with the PPV-based block copolymers. The spectra of the SiHMPPV at the operating voltage of 9 V give a peak in the blue EL emissive band at 475 nm.

Acknowledgments

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