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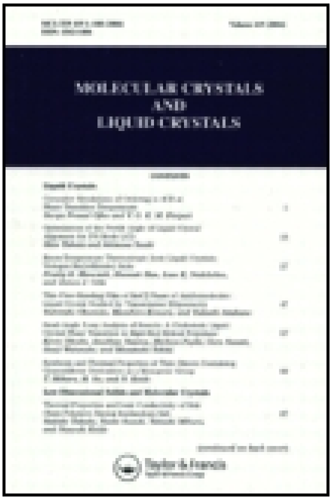

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Synthesis and Luminescent Properties of Novel Silicon-based Electroluminescent Copolymers with Ruthenium(II)-Chelated Complexes

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Synthesis and Luminescent Properties of Novel Silicon-based Electroluminescent Copolymers with Ruthenium(II)-Chelated Complexes

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Abstract A new class of silicon-based alternating copolymers having Ruthenium(II)-chelated complexes was synthesized to use as electroluminescent materials by Heck reaction between organosilicon divinyl monomers and Ru(II)-chelated monomers. The incorporation of organosilicon units with the aromatic or aliphatic groups on the silicon atoms into π-conjugated systems improved their processability and interrupted the π-conjugation length. The maximum absorption wavelength (λ_{max}) of a non-chelated polymer (SiHMPhen) containing a phenanthroline (Phen) unit exhibited one strong bands at 305 nm for Phen units and a moderate peak around 350 nm for π-conjugated backbones. With an excitation wavelength of 360 nm, the PL spectrum of SiHMPhen exhibits a strong band at 420 nm in the blue region. Ru(II)-chelated copolymers showed strong absorption bands around 386~392 nm. Upon a photoexcitation with 400 nm, their PL spectra show a strong band at 430 nm in the blue region. The Ru(II)-chelated copolymers were thermally stable up to 300 °C in air.

Keywords Electroluminescence; Silicon-based copolymers; Heck reaction; Metal-to-ligand charge transfer; Ruthenium(II)-chelated complexes

INTRODUCTION

We have studied the development of a new class of silicon-based copolymers [1] exhibiting a blue emissive color for several years. According to our results,

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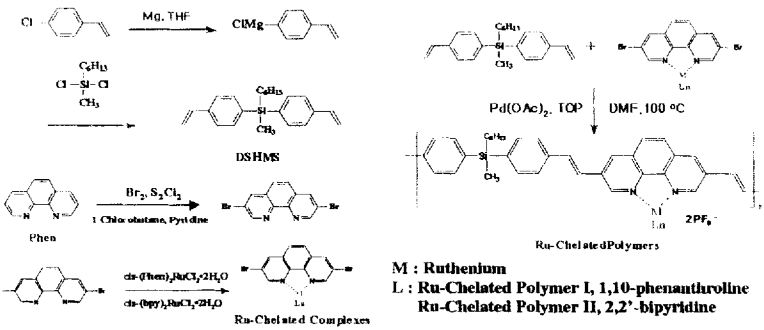
silicon-based copolymers for light-emitting diodes have the main two merits: (1) They have good processability and easy tune of electroluminescent (EL) colors by incorporating organosilicon units into π-conjugated systems; (2) Their EL devices exhibit a blue emissive color at a relatively low operating voltage of less than 10 V, due to the d-orbital participation of silicon atoms and the reducing LUMO level. Very recently, we investigated silicon-based EL copolymers with Ru(II)-chelated complexes. In the past several years, studies on the Ru(II)-chelated complexes have investigated by other research groups [4]. Ru(II)-chelated polymers are very interesting research theme because of their potential use as emitters in electroluminescent device. There were two possible ways to synthesize the target materials. So, we have achieved two synthetic approaches (Method A and B). Method A was first to synthesize the non-chelated polymers with the dibromo-functionalized phenanthroline (Phen) unit by Heck reaction, followed by chelating with Ru(II)-chelated complexes. But the Heck-reaction polymerization occurred very slowly, giving a low molecular weight polymer. It was presumably due to the reduced reactivity of Pd catalyst arising from the chelation of the Pd catalyst used in the Heck reaction with the nitrogens of Phen unit. Method B was first to synthesize the monomer dibromide of Ru(II)-chelated complexes, followed by Heck coupling reaction. This polymerization method was successful to obtain a relatively high molecular weight polymer. In this paper, we describe the synthesis and luminescent properties of non-chelated and metal-chelated polymers.



SCHEME 1 Synthetic routes to the monomers and the silicon-based copolymers with Ru(II)-chelated complexes.

RESULTS AND DISCUSSION

Preparation of Monomers and Ruthenium(II)-Chelated Complexes

The synthetic routes to the preparation of monomers (DSHMS) has been

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described previously [2] (see SCHEME 1). The Ru(II)-chelated complexes were synthesized according to a previous procedure described by Meyer et al. [3] The chemical structure of the Ru(II)-chelated complexes were identified by FT-IR, UV-Vis absorption and emission spectroscopies, as shown in FIGURE 1. IR spectra of Ru(II)-chelated complexes showed a very strong band at 840cm^{-1} due to the P-F stretching of the counter anions. UV-visible spectra showed a very intense band at 283~293 nm, which is attributed to the ligand-centered π~π^* transition of the 1,10-phenanthroline (Phen) and 2,2'-bipyridine (bpy) ligand. In addition, the weak bands at 430 nm for a Phen ligand and 442 nm for a bpy ligand were assigned to the metal-to-ligand charge transfer (MLCT) transition. Their emission spectra exhibit a strong band in the red region (FIGURE 1). Those characteristic MLCT bands indicate the formation of the (ligand)$_2$(3,8-dibromo-1,10-phenanthroline) Ru(II) hexafluorophosphate.

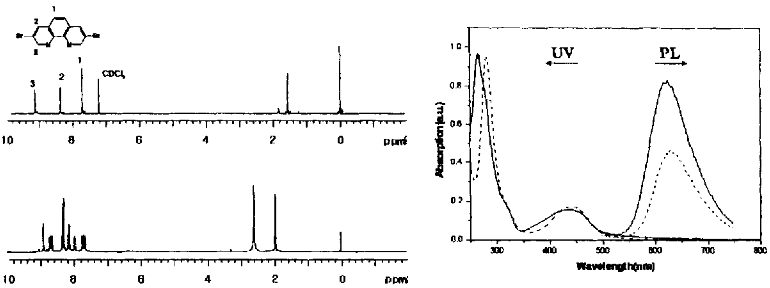

FIGURE 1 ^{1}H-NMR spectra of monomer and Ru(II)-chelated complexes (ligand-Phen), UV-Vis and Emission spectra of Ru(II)-chelated complexes (solid line ; ligand-phenanthroline, dash line ; ligand-2,2'-bipyridine)

Preparation of Copolymers With Ruthenium(II)-Chelated Complexes

As shown in SCHEME 1, Ru(II)-chelated copolymers were synthesized using the Heck reaction between an organosilicon divinyl monomer and the Ru(II)-chelated monomers. The resulting polymers were soluble in common organic solvents, including acetone, NMP, DMAc, DMSO, but insoluble in chloroform. Their IR spectra exhibit a very strong band of the counter anions at 840 cm^{-1}. The maximum absorption wavelength (λ_{max}) of non-chelated polymer containing a Phen unit exhibits one strong band at 305 nm for Phen units and a moderate band around 350 nm for π-conjugated backbones. With an excitation wavelength of 360 nm, its PL spectrum shows a strong band at 420 nm in the blue region. Ru(II)-chelated copolymers show strong absorption bands around 386~392 nm. Upon a photoexcitation with 400 nm, their PL spectra show a strong band at 430 nm in the blue region. Compared to a red emission from the corresponding monomer complexes, the blue emission may be due to the distortion of their copolanarity arising from the rigid-rod structure of π-conjugated copolymers. From thermogravimetric analysis, Ru(II)-chelated polymer I was thermally stable up to 300 °C under air, while Ru(II)-chelated polymer II has a weight loss starting at 250 °C, due to the loss of the bipyridine ligand.

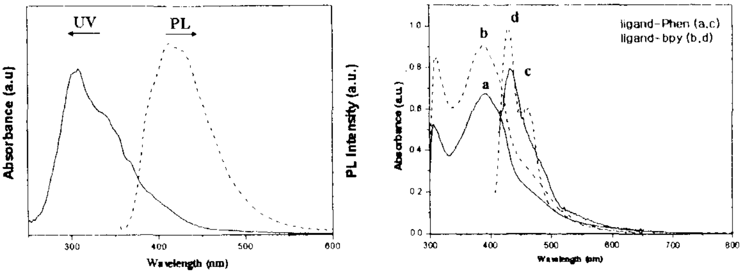

FIGURE 2 UV-Vis (a,b) and emission (c, d) spectra of non-chelated polymer (left) and Ru(II)-chelated copolymers (right) in DMA_C solution.

In conclusion, the non-chelated and metal-chelated polymers were successfully prepared by Heck coupling reaction. The maximum absorption wavelength (λ_{max}) of non-chelated polymer containing a Phen unit exhibits one strong band at 305 nm for Phen units and a moderate band around 350 nm for π-conjugated backbones. With an excitation wavelength of 360 nm, its PL spectrum shows a strong band at 420 nm in the blue region. Ru(II)-chelated copolymers show strong absorption bands around 386~392 nm. Upon a photoexcitation with 400 nm, their PL spectra show a strong band at 430 nm in the blue region. The Ru(II)-chelated polymers were thermally stable up to 300 °C under air.

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